Mr. Cock is in error, consequently, when he assumes the abnormal behavior of water to be due to the fact that the solution is too concentrated with respect to water, as he will see by reference to either of the above mentioned works. J. LIVINGSTON R. MORGAN.

COLUMBIA UNIVERSITY, December 14, 1908.

REVIEW.

REVIEW OF INORGANIC CHEMISTRY, 1908.

JAS. LEWIS HOWE.

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In his inaugural address as rector of the Technical High School at Graz, Emich[1] discussed the present tendencies of pure chemistry. While it is not impossible that were the views of Wald and Ostwald to be followed out to their logical conclusions, we might gain as clear a conception of matter as is given us by the atomic theory, as far as regards economy of thought, the atomic theory cannot be equaled, nor is any reform of view demanded from the standpoint of either chemist or physicist. Among problems immediately before us are the connection between chemical structure and crystalline form, and between chemical structure and color. These problems are particularly important in organic chemistry. The development of physical chemistry enables us to forecast, to a considerable degree, the phenomena which are taking place in gases and solutions. In such predictions, valence, of such dominating importance in organic chemistry, has its value only in connection with Faraday's law. Werner's conceptions utilize both view-points. Since the radium emanation possesses the character of the inactive gases, further developments along this line are to be looked for, and the speculations of Mendeléeff regarding the nature of ether are unnecessary. Since these transformations of the elements are unaffected by the temperature, they stand in sharp contrast to chemical changes. Both electric and radioactive investigations point to the complex nature of the atom, so that we may consider ordinary chemistry as the chemistry of the molecule, while radioactive chemistry is that of the atom. Since the free existence of atoms of negative electricity is known, while free positive electrons have not been isolated, we may conclude, according to Ramsay[2], that positive electricity is merely the absence of negative electricity. Compounds between the negative electron and material atoms, *i. e.*, ions, exist not only in the gaseous condition and in solution but also in solid form, as is rendered probable from the many analogies between solid and dissolved salts. It is probable, for example, that the metal sodium is really a compound of some, now unknown, electron-free substance and the electron. So Thomson has shown that zinc loses its electrons more readily than platinum. Fluorescence and tautomerism in organic compounds are probably due to the oscillation of the electrons, the vibration showing itself, at least, in ultraviolet rays.

The experiments of Ramsay, a year ago, which seemed to indicate a

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[1] *Oester. Chem.-Ztg.* [2], 11, 105.

[2] *Ibid.*, p. 111.

possible degradation of copper into lithium and sodium by the action of radium emanation, have been very carefully repeated by Madame Curie and Mlle. Gleditsch,[1] using platinum vessels exclusively and the purest reagents. After exposing the copper sulphate solution to the action of the emanation and then removing the copper by hydrogen sulphide, the amount of residue was much less than that obtained by Ramsay, and in it no trace of lithium could be found. They suggest the probability that Ramsay's lithium may have come from his glass and quartz vessels, for they find that lithium is present in all glass and even in quartz. Both transparent and opaque quartz vessels were tested and lithium found in considerable quantity in both, and especially in the transparent quartz. In a paper read by Hartley before the British Association meeting at Dublin,[2] exception is taken to Ramsay's statement that sodium and potassium are more widely distributed than lithium, and that lithium is an unlikely constituent of dust, glass, copper, etc. In a series of experiments, Hartley finds lithium in almost everything tested and concludes that it is one of the most widely distributed elements in nature. Incidentally, it was found that rubidium was present in all preparations of potassium salts, unless specially prepared, showing that this element, too, is more nearly ubiquitous than had been supposed. Further, Hartley finds no connection between the occurrence of lithium and the radioactive elements. Experiments by Engler[3] bring in question the ordinarily received view that radioactive transformations are independent of the temperature. He finds that at 1300° in an electrically heated quartz vacuum tube, the decomposition of radium is more rapid than at ordinary temperatures but, on cooling, the radium resumes its normal activity. His experiments also seem to show that fresh radium emanation is not a simple gas, but is accompanied by another slowly decomposing substance.

NEW ELEMENTS.—In the fall of 1907, the discovery was announced by Boltwood[4] of a new radioactive element in carnotite, to which the name of ionium was given. This has been further studied by Boltwood[5] and it seems well established that ionium is the direct parent of radium. Ionium sends out α-rays for a distance of 2.8 cm. and possibly also β-rays, which are more readily absorbed than the β-rays from uranium X. From its properties, ionium seems to resemble thorium and will probably have about the same atomic weight.

In November, 1907, Urbain published a paper in the *Comptes rendus* (**145**, 759), describing the decomposition of ytterbium by fractional crystallization from nitric acid into two elements, neo-ytterbium with an atomic weight of about 170 and a new element, which he called lutecium with an atomic weight of slightly over 174. In December of the same year, v. Welsbach read a paper before the Vienna Academy[6] in which he describes the fractionating of ytterbium by use of the double ammonium oxalate into two elements, one of which with an atomic weight

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[1] *Compt. rend.*, **147**, 345.

[2] *Chem. News*, **98**, 151.

[3] *Ann. Physik* [4], **26**, 483.

[4] *Amer. J. Sci.* [4], **24**, 370.

[5] *Ibid.*, **25**, 269, 365; *Physik. Z.*, **9**, 502.

[6] *Monatsh.*, **29**, 181.

of 172.90 he calls aldebaranium (Ad), and the other with atomic weight of 174.23 cassiopeium (Cp). According to Urbain,[1] aldebaranium is identical with lutecium and cassiopeium with neo-ytterbium, and he claims priority for his nomenclature.

In a volume of papers contributed by his pupils to the jubilee of Professor Sakurai, on completion of his twenty-fifth year as professor in Tokyo University,[2] Ogawa gives preliminary notes on two new elements, one from thorianite and the other from molybdenite. The former was first met with in study under Ramsay on thorianite, and is also found in reinite and molybdenite. The element is precipitated with aluminum by ammonia as a yellowish white hydroxide, soluble in alkalies, and by ignition converted into a dark brown oxide, insoluble in acids. The solution of the hydroxide in hydrochloric acid is yellowish green and the precipitate with ammonium sulphide, greenish-black and insoluble in excess. Fusion with soda and saltpeter gives a green melt, decomposed by carbon dioxide after solution in water, with formation of a brown precipitate. The anhydrous chloride is difficultly volatile and gives a characteristic spectrum. The combining weight is about 50 and indicates that the new element is a higher member of the manganese group, possibly eka-manganese, with an atomic weight of 100. The name given to the new element is one suggested by Ramsay, nipponium (Np). The new element from molybdenite was in the supposedly ammonium vanadate residues, and is closely allied to molybdenum, but its oxide dissolves in concentrated hydrochloric acid on prolonged boiling. If the element is sexivalent like molybdenum, its atomic weight would be about 100, so that it, too, may belong to the manganese group. Further investigation will be awaited with interest.

Some years ago, Bayer announced the discovery of a new element in French bauxite which he named bauxium. This material has been studied by Greiner and Urbain,[3] and bauxium appears to be a mixture of vanadium and tungsten, with traces of molybdenum, copper, bismuth, lead, calcium and sodium. They attribute Bayer's error to too much confidence in ammonium vanadate as a means of separating vanadium, and too much dependence on the insolubility of tungstic acid.

The earlier work of Landolt on the possible change of weight in chemical reactions has been gone over again by him.[4] The previous work seemed to show that in certain reactions there is a small but constant loss of weight. Further investigation has shown that the heat of the reaction causes a slight change of volume which affects the weight and does not disappear for some time. After a few days there is apparently a constant weight, but actually the original volume is not reached for several weeks. Subsequent to this time, the weight after the reaction is the same as before within experimental error, so that Landolt's conclusion is that in the fifteen reactions studied there is no change of weight which can be experimentally determined.

Several papers on the theory of valence have appeared during the year, and among them one by Viroubov[5] who draws a distinction between

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[1] *Compt. rend.*, **146**, 406.

[2] *Jour. Col. Sci.*, Tokyo, **25**, 15, 16.

[3] *Bull. soc. chim.* [4], **1**, 1158.

[4] *Sitzungsber. Akad. Sci. Berlin*, **1908**, 354.

[5] *Ann. chim. phys.* [8], **13**, 523.

atom-valence, or atomicity as he calls it, and molecular valence. He would keep the conceptions of valence and chemical energy entirely distinct. After atoms have united in a molecule according to their atomicity, the compounds still possess chemical energy, of variable nature (positive or negative), according to which they unite. The valence of the molecule is independent of the atomicity of the component atoms. Thus in the place of the equation $M(OH)_n + nHCl = MCl_n + nH_2O$, he would write $M(OH)_n + nHCl = M(OH)_n.nHCl$. Salts are thus formed from bases and acids simply by addition and are characterized by being electrolytes, and capable of double decomposition. The amount of water in a salt is thus determined by the atomicity of the two molecules which compose the salt. When anhydrous salts are dissolved in water, they pass from the condition of anhydrides into that of true salts. In some cases, however, as $PbCl_2$ and $HgCl_2$, they remain when dissolved very largely in the state of anhydrides, and are poor electrolytes. The theory is illustrated by a study of the chlorides of platinum and the oxalates and sulphates of chromium. Peters[1] has continued his work on the increase of valence at low temperatures by a study of the increase in valence towards ammonia in the cold. In a few salts such as silver chloride and bromide, and their double salts with platinum, there is a well-defined molecular increase in the amount of ammonia held at low temperatures, while other salts, such as potassium gold thiocyanate and silver thiocyanate, absorb ammonia when the temperature is lowered, without regard to molecular ratio. In general, salts of the same metal take up more ammonia when they are in their state of higher valence; gold and platinum salts take up more than those of silver and mercury, going to show that the more positive a metal is, the less secondary valence its salts have. The relation toward ammonia is much the same as to water.

Krafft, who has recommended the use of a vacuum for the determination of the water of crystallization of salts, has studied[2] the effect of exceedingly high vacua, in order to determine the irregularities, long ago noticed by Graham. Krafft finds that while such vacua are effective in ultimately removing all the water of crystallization, in many cases, as with the vitriols, the same difference is found in the tenacity with which the last molecule of water is held as when high temperatures are used. Thus at room temperature, zinc and magnesium vitriols are reduced to monohydrates in 15 hours, iron, cobalt and nickel vitriols in 45 hours, while copper vitriol required 60 hours. The last molecule is given off at somewhat above 200° in a vacuum in an hour or two. Gypsum loses 1½ molecules of water in two hours at 100° and the remainder in two hours further heating at 150°. Alums rapidly lose all their water in a vacuum. Most other salts lose their water completely in a day's standing in vacuum over BaO. Sulphuric acid cannot be used in a vacuum, owing to its own vapor pressure. High vacua can be conveniently used for the determination of water of crystallization.

An apparently new line of investigation has been proposed by Emich,[3] in the use of fused salts as solvents. He has experimented with a solution

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[1] *Ber.*, **41**, 3175.

[2] *Ibid.*, **40**, 4770.

[3] *Phys. Chem. Centralbl.*, **5**, 641.

of barium chloride in fused sodium chloride, using as precipitants solutions of sodium carbonate, sulphate, silicate, ortho-, pyro- and metaphosphates, tungstate and borate in the same solvent. The orthophosphate and orthosilicate alone gave precipitates, which consisted of crystalline $Ba_3(PO_4)_2$ and $BaSiO_3$. The latter of these salts is much less soluble than the former. This would seem to open up an interesting line of research.

A noteworthy event of the year was the liquefaction of helium, which was accomplished by Onnes during the past summer.[1] The helium was compressed before entering the apparatus to 100 atmospheres, and cooled by liquid hydrogen to 15° abs. Liquid helium is colorless, has a density of 0.154 and a boiling point of 4.5° abs. Its critical temperature is about 5° abs. and its critical pressure about 2.3 atmospheres. Solid helium was not obtained. The capillarity of helium is extraordinarily small and its cohesion force 0.00005.

GROUP I.—In view of the great demand for potash in the fertilizer industry, the possibility of the economical extraction of potash from feldspar has been for some time an object of study on the part of many chemists. An important contribution to the problem has been made by Cushman and Hubbard.[2] The various suggested methods and new methods have been studied both from a chemical standpoint and from the possibility of economical application on a large scale. The conclusions drawn are that a portion of the potash is made available by fine grinding with water and that the presence of ammonium salts, lime and gypsum increases the effect, but the action being confined to the surface of the particles, soon ceases and hence is a function of the fineness of the grinding; that by an electrolytic method it is possible to extract all the potash with or without the addition of hydrofluoric acid, but that this would be uneconomical commercially; that the potash can be completely extracted by fusion methods, but that the cost would be great, fusion with potash, however, offering possibilities of economic enrichment; that by hydrofluoric acid the potash can be recovered and that there may be economic possibilities in this method. Altogether, the work done thus far offers encouragement for further investigation of an important problem.

GROUP II.—The chemical properties of metallic calcium have been more fully investigated by Erdmann and van der Smissen.[3] While calcium reacts readily with most substances, it is very stable toward oxygen, if the gas is dry. The hydride, CaH_2, while decomposing water with great violence, is without action on anhydrous reagents. If perfectly dry, calcium amalgamates with mercury, but if a trace of moisture is present no amalgamation takes place until the temperature is raised above 100°, to drive off the water. The amalgam itself is only slowly oxidized in a current of oxygen at 400° to 500°. The nitride, Ca_3N_2, is most readily formed by fusing lumps of calcium in a crucible into which a rapid stream of nitrogen is being led. The nitride gives no trace of ammonia when heated in hydrogen between 500° and 800°, nor does the hydride yield ammonia when heated in nitrogen under

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[1] *Compt. rend.*, **147**, 421.

[2] THIS JOURNAL, **30**, 779; Office of Public Roads, U. S. Dep't Agric., *Bull.* 28.

[3] *Ann.*, **361**, 32.

the same circumstances. At 0°, calcium filings absorb ammonia with the formation of $Ca(NH_3)_4$, to which Erdmann gives a cyclic formula. It burns brilliantly in the air. In organic amines, calcium generally replaces the amine hydrogen. With hydrocarbons there is little reaction. Calcium hydride does not react with sulphur dioxide, nor with acetylene or carbon dioxide, contrary to the statements of Moissan.

GROUP III.—The so-called "crystallized boron" of Kühne, and its preparation have been carefully investigated by Biltz,[1] who finds that the best mixture is equal parts of boron trioxide with 2.2 parts aluminum. From 250 grams of boron trioxide, 27 grams of the black crystals of "crystallized boron" were obtained. In smaller quantities, the yield is somewhat better. These crystals seem to be the same product long ago described by Wöhler, Deville and others. The crystals are rarely over two millimeters across, are black and opaque except in very thin sections, when they transmit red light. They are generally tabular, but occasionally resemble octahedra. They appear to be rhombic. Analyses, in which both boron and aluminum were directly determined, show them to have the composition AlB_{12}, which had already been assigned to them by Hampe. A crystalline form of pure boron remains to be prepared.

Great difficulty has been experienced in obtaining material free from silica, which would withstand high temperatures and at the same time not be porous. Heinecke[2] finds that if alumina is mixed with magnesia which has already been submitted to a high heat, and the mass formed with a little organic binding material and burned at a very high temperature, a porcelain-like, translucent mass is obtained which is very resistant. It fuses only at Seger cone 37, that is, above the fusing point of platinum, and has greater resistance to alkalies than silicate mixtures. Heinecke considers that a spinel compound is formed which acts as binder to the infusible alumina and magnesia.

Since the discovery of scandium by Nilson in 1879, and the work done upon it the following year by Nilson and Cleve, it has received but few notices in literature and has been accounted perhaps the rarest of the elements. Its sole occurrence appeared to be associated with the rare earths in gadolinite and euxenite, and even here it was present to the extent of only a minute fraction of a per cent. During the past year, new light has been thrown on its occurrence and three notable papers have appeared, by Crookes,[3] Eberhard[4] and R. J. Meyer.[5] Led by the fact that the strongest lines of the scandium spectrum are found in the spectra of stars of the most different stages of development, Eberhard concluded that it must be a widely distributed element. Examination of 366 minerals and rocks showed that its arc spectrum was rarely absent, and that instead of being one of the rarest, scandium was, as he had expected, one of the most widely distributed of the elements. It is found in greatest frequency in zirconium minerals, in beryl, in titanates and columbates of the rare earths, and especially in wolframite

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[1] *Ber.*, **41**, 2634.

[2] *Z. angew. Chem.*, **21**, 587.

[3] *Proc. Roy. Soc.*, **80A**, 516.

[4] *Sitzungsber. Akad. Sci. Berlin*, **1908**, 851.

[5] *Z. anorg. Chem.*, **60**, 134.

and cassiterite, and is markedly abundant in the latter minerals from certain localities, as Saxony and Bohemia. The Zinnwald wolframite contains more than 0.1 per cent. scandia, and the crude oxides from the commercial manufacture of tungsten contain as high as 0.3 per cent. scandia, being its most convenient source. Crookes found that many of the rare earth minerals, such as cerite, orthite, pyrochlore, thorite and thorianite contain more than 0.01 per cent. scandium, while the newly discovered mineral from Finnland, called wiikite, which contains tantalic, columbic and silicic acids with titanium, zirconium, iron and the rare earths, has more than 1 per cent. of scandia. This is the richest source yet found of scandium. Attempts to separate scandia from the tungsten residues by the oxalate method were only partially successful, and the same was true of the hydrofluoric acid method, but by the use of fluosilicic acid it was easily possible to obtain oxides running over 95 per cent. of scandia. It is particularly difficult to separate scandium from ytterbium, but this was accomplished by the thiosulphate method, leaving only thorium as an impurity, and this present to the extent of nearly 1 per cent. Scandium, indeed, seems chemically to be far less allied to the rare earths than to aluminum and glucinum, and to thorium. No satisfactory way has yet been found to separate it from the latter, but certain of its properties are so distinct that Meyer hopes soon to discover some simple method. In view of its properties, Brauner well called scandium "an extrapolation" in the series of rare earths. In its strong tendency to hydrolysis and to the formation of complexes, scandium has much resemblance to glucinum. Many of its salts of organic acids, prepared by Crookes, are basic. Crookes did not obtain an alum, but the double sulphate has the formula $3K_2SO_4.Sc_2(SO_4)_3$.

A number of new salts of indium have been prepared by Mathers and Schluederberg,[1] among them the perchlorate, iodate and selenate, and the cesium indium selenate alum. The latter appears to crystallize in well-formed tetragonal octahedra, which effloresce in the air.

GROUP IV.—Two preparations of graphite for lubrication have recently come into the market under the name of oildag and aquadag. They are described by Acheson in the *Journal of the Franklin Institute* (**164**, 375). Going out from the well-known effect of tannic acid on the plasticity of clay, the effect of tannic acid on graphite was investigated by grinding graphite to a very fine condition with three to six per cent. of its weight of tannin. The graphite (artificial or natural) was thus obtained in a "deflocculated" or seemingly colloidal state, remaining for months in suspension and passing through the finest filters. On the addition of hydrochloric acid, the graphite is coagulated, and can be settled or filtered, drying to a hard mass which is free from all grit, and the best form of graphite for lubrication. The percarbonates have been more fully studied by Wolffenstein and Peltner.[2] When a rapid stream of carbon dioxide is led into water in which barium peroxide is suspended, barium carbonate is formed and hydrogen peroxide remains in solution. The reaction, however, takes place in two stages, and if the amount of water is definite, the carbon dioxide passed in slowly, and the reacting substances kept cold, the barium percarbonate, $BaCO_4$, formed in the

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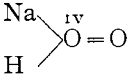
[1] THIS JOURNAL, 30, 211.

[2] *Ber.*, **41**, 275, 280.

first stage, is precipitated and can be washed with alcohol and ether, and dried in a vacuum. This percarbonate, or barium dioxide carbonate according to the name preferred by the authors, is a light yellow powder and very easily decomposed on standing in the air. It is slowly decomposed by cold water and instantly by acids, with the formation of hydrogen peroxide. It appears to be a true percarbonate and not a substance containing hydrogen peroxide of crystallization. By a similar action of carbon dioxide on sodium dioxide and trioxide, several percarbonates were formed, Na_2CO_4, $Na_2C_2O_6$, Na_2CO_5 and $NaHCO_4$. The authors consider that the free percarbonic acid obtained by Bach in ethereal solution was not a true percarbonate but a solution of hydrogen peroxide and carbon dioxide, since the CO_2 could be expelled by air, leaving the hydrogen peroxide in solution. They also consider that the hydrate of sodium trioxide exists in two forms: one described by Tafel by the action of sodium peroxide on alcohol has the formula $O = Na'''OH$, and the other, formed by the action of hydrogen peroxide on sodium alcoholate, is NaO—OH. The formula



$\begin{matrix}Na\\H\end{matrix}\!\!>\overset{\text{IV}}{O}=O$

may also be suggested.

An important reaction from a practical standpoint has been taken up by Hüttner[1] at the Physico-Technical Reichsanstalt at Charlottenburg. It has been noticed that phosphoric acid attacks quartz vessels when heated above 300°, and also that phosphoric acid attacks glass and porcelain. Hüttner finds that there is formed in this reaction a compound, $SiO_2.P_2O_5$, which has previously been prepared by Hautefeuille and Margottet. This silicyl metaphosphate seems to have the formula $SiO=(PO_3)_2$, and to be analogous to boryl phosphate. It may easily be prepared by heating finely powdered silicic acid with an excess of metaphosphoric acid in a quartz tube. At first there is a clear solution, but soon a fine white crystalline precipitate appears. It is also formed in the reaction between silicon tetrachloride and phosphoric acid. Silicyl metaphosphate is decomposed in the oxy-hydrogen flame and to a slight extent even in the bunsen flame with evolution of P_2O_5, the substance thus becoming amorphous and easily decomposable by water. It is stable in water and in all acids except hydrofluoric. Phosphoric acid dissolves powdered sodium metasilicate with the formation of silicyl phosphate and sodium metaphosphate, and sodium metaphosphate dissolves finely pulverized sodium metasilicate to a clear glass, and it also dissolves silica when in the same condition. This will perhaps account for the fact that under certain circumstances the microcosmic bead does not give the usual reaction for silica.

Continuing the work under Franklin, on the ammono-compounds of zinc, Fitzgerald[2] has prepared an analogous compound with tin, the potassium ammono-stannate. This was made by the action of an excess of potassium amide upon tin tetraiodide in liquid ammonia. The compound has the formula $Sn(NK)_2.4NH_3$, which the author suggests may be written $(NH_2)_2=Sn=(NHK)_2.2NH_3$ (this would be the analogue of $(HO)_2Sn(OK)_2.2H_2O$), or $(KHN)_2=Sn=(NHNH_4)_2$ (the analogue of

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[1] *Z. anorg. Chem.*, **59**, 216.

[2] THIS JOURNAL, **29**, 1693.

$(KO)_2Sn(ONH_4)_2$), or $Sn(NH_2)_4.2KNH_2$ (the analogue of $Sn(OH)_4.2KOH$). Inasmuch as Bellucci has shown that the ordinary trihydrate of potassium metastannate is really to be considered as the potassium salt of the hexahydroxystannic acid, $H_2Sn(OH)_6$, it would seem that Fitzgerald's compound is the ammono-analog of the ordinary potassium metastannate, and its formula should be written $K_2Sn(NH_2)_6$. It is noteworthy that this ammono salt should correspond so exactly to the oxygen salt. (If this were written in the common nomenclature, it would be $K_2Sn(NH)_3.3NH_3$ corresponding to $K_2SnO_3.3H_2O$.) The salt is not explosive but decomposes rapidly with flame when heated. In a vacuum at 145°, it loses three molecules of ammonia, leaving a red powder, $K_2Sn(NH)_3$, potassium ammono-metastannate, an analogous reaction to that of the metastannate. At 175° it loses further, half a molecule of ammonia and then remains constant, the rest of the ammonia not being lost even at 316°. The red powder is slowly changed by water vapor into a white powder with loss of ammonia, but in direct contact with water there is partial reduction and a portion of the tin is deposited in mirror form.

GROUP V.—In a study of the absorptive power of metals for nitrogen, Shukov[1] finds that at 1200°, vanadium, iron, copper and tungsten do not absorb nitrogen, and molybdenum has very little absorptive power. On the other hand, it is rapidly absorbed by magnesium, calcium, aluminum, titanium, chromium and manganese, absorption beginning at about 800°. The first three give definite compounds, Mg_3N_2, Ca_3N_2 and AlN. Although the others absorb a large amount of nitrogen (titanium takes up 21 per cent., while the amount required theoretically for TiN is 22.5 per cent.) it does not seem to unite chemically, but rather to be in a state of solid solution, inasmuch as no constant dissociation tension is shown. The magnetic properties which nitrogen imparts to these metals are very marked, the manganese-nitrogen solution being only surpassed by iron.

Ramsay has shown that nitrogen trioxide exists in the green liquid obtained by the condensation of the gas evolved by the action of arsenious oxide on nitric acid. On the other hand, the gas before condensation is a mixture of NO, NO_2 and N_2O_4. The discovery some years ago by Baker that traces of moisture are necessary for the dissociation of ammonium chloride has led him to determine the vapor density of nitrogen trioxide when dried by phosphorus pentoxide.[2] Densities were found, varying from 38.1 (the density of undissociated N_2O_3 is 38) to 62.2, showing that not only does N_2O_3 exist as a gas, but that it is accompanied by a polymer, probably N_4O_6. Efforts to obtain this latter in a pure state were not successful, but are being continued. The density of the vapor from the slightly moist liquid N_2O_3 was also taken and found to be almost exactly the theoretical density demanded by its complete dissociation into NO, NO_2 and N_2O_4. Freezing point determinations of the dried liquid in benzene gave results showing that the molecular weight corresponds to N_2O_3, with but little association into its higher polymer. At ordinary temperature, liquid N_2O_3 is green, but below —2° it becomes deep indigo-blue. It does not solidify at —81° but in liquid air forms very deep blue crystals.

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[1] *J. Russ. Phys. Chem. Soc.*, 40, 457.

[2] *J. Chem. Soc.*, 91, 1862.

In a paper on the phosphorescence of phosphorus and its compounds[1] Scharff concludes that the ordinary phosphorescence of yellow phosphorus is due to the phosphorus trioxide which is present. A carefully prepared sample of the trioxide gives no phosphorescence in dry oxygen, but in moist oxygen shows at 15° a maximum at 310 mm., the pressure for maximum phosphorescence increasing with the temperature, just as the author has found to be the case with yellow phosphorus. The trioxide also shows the same phenomenon of intermittent phosphorescence with change of pressure as yellow phosphorus, and is inhibited by the same gases and vapors. The phosphorus sulphide, P_4S_3, shows similar phosphorescence phenomena as the trioxide. An investigation has been begun by Prideaux[2] on the atomic volumes of elements compared with their atomic volumes in binary compounds. The first instalment consists of a determination of the specific volumes of phosphorus and phosphorus pentachloride, and the comparison of their atomic volumes and those of chlorine and of phosphorus trichloride, already accurately determined. Taking the molecular volumes of the two chlorides (PCl_5, 128.9; PCl_3, 93.34) and subtracting the atomic volumes of chlorine (Cl, 22.76), the value for the atomic volume of P''' is found to be 25.06 and that of P^v to be 15.10. The mean of these values, 20.08, is almost identical with that found for elementary phosphorus, 20.04. From this it might appear as if elementary phosphorus consisted of a compound between trivalent and quinquivalent phosphorus atoms. This would not, however, be a safe generalization for at least two reasons. First, from the known tendency of chlorine to have a much smaller atomic volume in compounds than in elementary condition, it is more probable that the volume of the phosphorus atom would vary less in compounds than that of chlorine, hence if one calculates this in PCl_3 and PCl_5 as the same as in elementary condition, one finds the atomic volume of chlorine in PCl_3 as 24.43 and in PCl_5 as 21.772. This may be accounted for by either a different contraction of the chlorine atom in these two compounds, or more possibly by merely spatial relations. Second, these molecular volumes are all calculated at the boiling point. This has certain advantages, but it is hardly probable that a safe comparison can be made, using the atomic volume of elementary chlorine at —33.6° and of chlorine in PCl_5 at 160°, and that of elementary phosphorus at 290°. That valuable results as to the character of the atom will be gained by the study of atomic volumes cannot be doubted, but at present the many unknown factors in the problem render generalizations dangerous. Such work as that of Prideaux is very welcome as affording valuable data for further study.

An interesting reaction, confirmatory of the generally accepted asymmetrical formula for phosphorous acid, has been carried out by Palazzo and Maggiacomo.[3] By the action of diazoethane in ethereal solution on phosphorous acid, the ethyl ester is formed in theoretical quantity. In every case it is the diethyl ester which results from the reaction, even when the diazo compound is used in large excess. A smooth and quantitative reaction like this would seem to leave little room to doubt that

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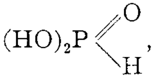
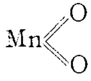
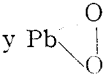
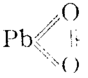
[1] *Z. physik. Chem.*, 62, 179.

[2] *J. Chem. Soc.*, 91, 1171.

[3] *Atti Accad. Lincei* [5], 17 i, 432.

the constitution of phosphorous acid must be expressed by the formula  $(HO)_2P\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix}$, and that the tautomeric form $(HO)_3P$ does not exist even at —5°, the temperature at which the above reaction was carried out. Similar experiments with the action of diazoethane on selenious acid give the diethyl ester, thus indicating the probability of the symmetrical formula $(HO)_2SeO$, for selenious acid. Diazoethane appears to offer a very useful means of determining hydroxyl groups in inorganic compounds.

A series of new gold phosphorus compounds is described by Levi-Malvano.[1] Gold trichloride is reduced at once in ether solution by phosphorus trichloride, with the formation of the compound $(AuPCl_3)Cl$, which was previously obtained by Lindet by the direct action of PCl_3 on AuCl. On addition of methyl alcohol, the auromethyl phosphite chloride, $(AuP(OCH_3)_3)Cl$, is formed, which is soluble in water without decomposition and forms a normal chlorplatinate. Triethyl phosphine gives with $AuCl_3$ a similar chloride, $(AuP(C_2H_5)_3)Cl$, which is only slightly soluble in water, but soluble in both concentrated hydrochloric acid and in potassium hydroxide. In a similar manner, from triphenyl phosphine, the corresponding triphenyl compound is formed, which is insoluble in water, but even more stable than the ethyl compound. Both are soluble in organic solvents. The aurotriphenylphosphine forms a chlorplatinate and also a sulphate. Both the ethyl phosphine and the methylphosphite compound take up two molecules of ammonia, giving $AuP(OCH_3)_3(NH_3)_2Cl$ and $AuP(C_2H_5)_3(NH_3)_2Cl$. The triphenyl compound does not take up ammonia.

GROUP VI.—It is ordinarily recognized that barium dioxide belongs to a different type from lead and manganese dioxides, since with acids it yields hydrogen peroxide. Since MnO_2 and PbO_2 both give, with hydrochloric acid, chlorides in which the metal has a higher valence than two, it is usually considered that the metal is quadrivalent. In view of the difference in behavior of these two dioxides with SO_2 Marino[2] considers that they belong to different types, although the metal in both is quadrivalent. With SO_2, MnO_2 gives a dithionate, no oxygen being thereby rendered free. Here we are dealing with an addition product and the corresponding formula for the dioxide is  $Mn\begin{smallmatrix}\nearrow\!\!\!\!\nearrow O\\ \searrow\!\!\!\!\searrow O\end{smallmatrix}$. When, on the other hand, SO_2 acts on PbO_2, a sulphite is formed, and one atom of oxygen freed, which oxidizes a molecule of sulphurous acid to sulphuric, which, in turn, decomposes the lead sulphite, so that the end product of the reaction is lead sulphate. It is evident then, according to Marino, that PbO_2 has a different constitution from MnO_2, which may be expressed by  $Pb\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\!\!\Big|$ or  $Pb\begin{smallmatrix}\nearrow\!\!\!\!\nearrow O\\ \searrow\!\!\!\!\searrow O\end{smallmatrix}\!\!\Big\|$. The former is considered by Marino more probable, since the sulphite formed by the action of SO_2 has an asymmetrical formula: the reaction in its first stage would be:

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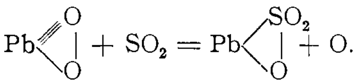
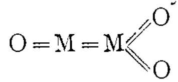
[1] *Atti Accad. Lincei* [5], **17** i, 847.

[2] *Z. anorg. Chem.*, **56**, 233.



$$\mathrm{Pb}\left<\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right. + \mathrm{SO_2} = \mathrm{Pb}\left<\begin{matrix}\mathrm{SO_2}\\ |\\ \mathrm{O}\end{matrix}\right. + \mathrm{O}.$$

Since the sesquioxides of iron, cobalt and nickel also give dithionates on treatment with sulphur dioxide, they also must contain the MO_2 group, and their constitution should be written



$$\mathrm{O{=}M{=}M}\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right.$$

A paper by F. Fischer and Ringe[1] on the formation of hydrogen peroxide gives some interesting experimental confirmations of theoretical deductions. Hydrogen peroxide is formed from its components at a high temperature in an analogous manner to ozone. Since, however, the amount of hydrogen peroxide in equilibrium with its components at such temperatures is very small and its decomposition velocity very great, the mixture must be cooled very rapidly or all the hydrogen peroxide will be destroyed. This was accomplished by the authors in several ways. When a gentle current of steam was blown from a small slit against a glowing Nernst pencil (110 volts, 0.25 ampere) and the vapor immediately condensed, it was possible to get a solution containing 1/200 per cent. of hydrogen peroxide. In another experiment, steam and oxygen were blown through a thin magnesia tube 0.6 mm. in diameter. The middle of the tube was heated with a Bunsen burner and the end with a protected oxy-gas burner. The vapor was condensed by being blown against a tin cooler and a solution containing 0.0045 per cent. of hydrogen peroxide was obtained. If the magnesia tube was heated in the middle to a white heat, instead of at the end, only a trace of H_2O_2 was obtained, owing to its decomposition, by slower cooling. In a similar way, H_2O_2 was obtained by blowing a current of steam through a hydrogen flame into a tin cooler, and it was further possible to replace the hydrogen flame by a Bunsen flame or even by one of alcohol. Hydrogen peroxide is also formed when steam and oxygen are blown through the electric arc into a cooler.

The composition of the yellow oil obtained when a solution of an alkali persulphide is poured into cold dilute hydrochloric acid has attracted the attention of a number of experimenters during the past year. Bloch and Höhn[2] prepared large quantities of the oil, and by means of an ingeniously devised vacuum distilling apparatus, fractioned off the more volatile portion, working with small amounts at a time (15 cc.) without interrupting the vacuum. By this means they obtained two fractions in a pure state, the more volatile being H_2S_2 and the less volatile H_2S_3. Both have an exceedingly offensive and irritating odor, between the chloride of sulphur and camphor. Both are fairly stable at low temperatures but are decomposed by heat, the H_2S_2 being the less stable. Alkalies decompose them quickly, but they are quite stable in the presence of hydrochloric acid; indeed it is necessary to have all the apparatus washed out with acid to avoid the effect of the alkali of the glass. They are unstable in the presence of water but mix with carbon bisulphide, benzene or ether in all proportions without decomposition. On the other hand, if free sulphur, which they dissolve, is present, it is precipitated when

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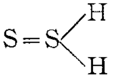
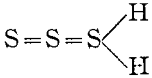
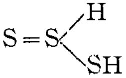
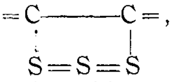
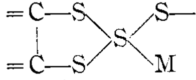
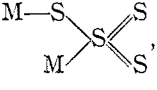
[1] *Ber.*, **41**, 945.

[2] *Ibid.*, **41**, 1961, 1971, 1975, 1980.

they are poured into these solvents. Thus a method is at hand to determine whether they are contaminated by dissolved sulphur. It may be noted that the original yellow oil, if freshly made, does not give a precipitate when poured into these solvents, indicating that it is composed of hydrogen compounds and does not contain any free sulphur. In considering the many formulas which have been proposed for polysulphides, the authors incline to the opinion that in the cases of H_2S_2 and H_2S_3, we are dealing with tautomers. In the former we have  $S{=}S\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$ $\rightleftarrows$ $H{-}S\overset{\cdots}{\underset{\cdot\cdot}{-}}S{-}H$, and in the latter case  $S{=}S{=}S\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$ $\rightleftarrows$  $S{=}S\begin{matrix}\diagup H\\ \diagdown SH\end{matrix}$ $\rightleftarrows$ $H{-}S{-}S{-}S{-}H$. At low temperatures the chain formula may predominate, while at higher temperatures, where the color darkens, the more condensed molecule is probable. The fact that Bloch and Höhn have not yet investigated the other constituents of the yellow oil and that their H_2S_2 and H_2S_3 may have originated from the decomposition of more highly sulphuretted compounds, serves probably to explain the very different results obtained by Bruni and Borgo.[1] They heated potassium sulphide with varying molecular quantities of sulphur in closed tubes to obtain definite polysulphides, and poured these into acids. Analysis of the oils obtained showed that when the polysulphide contained from three to six atoms of sulphur, the oil had an approximate composition of H_2S_6, but by using more sulphur and by letting the oil stand, higher sulphides were formed. They consider that H_2S_5, H_2S_6 and H_2S_7, and possibly H_2S_9, are definite chemical individuals, basing their results both on analyses and on cryoscopic determinations. Independently of Bloch and Höhn, Schenck and Falcke[2] reach the conclusion that the distillate in vacuum of the yellow oil contains H_2S_3.

In Liebig's *Annalen* (**362**, 133) Erdmann deduces from a number of reactions, especially with organic compounds, the existence of a new form of sulphur, S_3, which he calls thiozone, and the constitution of which is $S{=}S{=}S$. This form of sulphur is present in highly heated sulphur, in largest quantity at 160°, and reacts more readily than any other variety of sulphur. When many unsaturated organic substances are heated with sulphur at 160°, they unite with three atoms of sulphur forming thiozonides, which contain the group  $\begin{matrix}{=}C & — & C{=}\\ | & & |\\ S & {=}S{=} & S\end{matrix}$, and these in turn unite with alkaline sulphides to form thiozonidates, which have conjecturally the formula  $\begin{matrix}{=}C{-}S & & & S{-}M\\ | & \diagdown & S & \\ {=}C{-}S & \diagup & & \diagdown M\end{matrix}$. The thiozonidate ions give characteristic precipitates with many metals. The various sulphur dyestuffs, formed by heating organic compounds with sulphur and sodium sulphide, are thiozonides. All well-characterized inorganic polysulphides are thiozonates and have the constitution  $\begin{matrix}M{-}S & & & S\\ & \diagdown & S & \\ M & \diagup & & \diagdown S\end{matrix}$, being thus thio-

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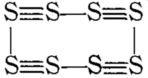
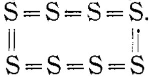
[1] *Atti Accad. Lincei* [5], **16** ii, 745.

[2] *Ber.*, **41**, 2600.

sulphites, and may be considered as direct addition products of thiozone with metallic monosulphides. Ultramarine is a thiozonate and not a thiozonide. In addition to thiozone, fused sulphur at 160° contains amorphous sulphur, which is a viscous polymer of S_8. Rhombic sulphur is  and monoclinic sulphur is . When the eight-atom ring breaks up, thiozone is one of the products and the rest of the molecule polymerizes to amorphous sulphur. The transformation is reversible and when highly heated sulphur is cooled to 160°, one has in addition to the mixture of S_3 and $(S_8)_x$, a layer of almost pure light yellow S_8. Vulcanized sulphur is a semi-solid solution of polymerized S_8 in a mixture of polymerized $C_{10}H_{16}$ and its thiozonide, while vulcanite is a poly-thiozonide. Erdmann further conjectures that oxygen also exists in a form expressed by an octatomic ring, O_8.

Derivatives of nitrogen sulphide, N_4S_4, have been studied by Wölbling.[1] With the higher chlorides of titanium, antimony and tin, N_4S_4 unites to form addition products. $N_4S_4.TiCl_4$ is unstable and easily decomposed into its constituents, while $N_4S_4.SbCl_5$ and $(N_4S_4)_2.SnCl_4$ are much more stable, and their constituents cannot be recovered unchanged. The last decomposes in dry air, giving off SO_2. With S_2Cl_2, N_4S_4 gives a thio-trithiazyl chloride, N_3S_4Cl, and also the addition product $N_4S_4.SCl_2$. N_4S_4 is regenerated from N_3S_4Cl by the action of ammonia. N_4S_4 seems to unite with hydrogen sulphide, but the product formed decomposes with formation of ammonium polysulphides, but on treatment with stannous chloride, N_4S_4 gives a crystalline compound, whose formula corresponds approximately to $(NSH)_x$. This seems to be a reduction product of the nitrogen sulphide, and is decomposed by alkalies with evolution of nitrogen, and by concentrated hydrochloric acid with formation of sulphur dioxide. Its constitution is as yet problematical.

The work begun by Stock three years ago on the sulphides of phosphorus has been continued the past year.[2] P_2S_5, P_4S_7 and P_4S_3 have been found to be definite chemical individuals. The first cannot be formed in a pure condition by mixing solutions of the elements in carbon bisulphide in the presence of iodine, contrary to text-book statements, nor is the commercial phosphorus pentasulphide a uniform compound. If, however, phosphorus is heated with 10 per cent. more sulphur than theoretically called for, and the resulting mixture extracted with carbon bisulphide, the pure compound is obtained. It can be vaporized at not much above its melting point (276°) though its boiling point is about 520°, and its vapor density shows that it is little dissociated when boiled under atmospheric pressure, but much more when heated in a vacuum or in a stream of carbon dioxide. The other two sulphides can be distilled unchanged in an atmosphere of carbon dioxide, but like the pentasulphide decompose at higher temperatures. They are prepared by heating red phosphorus and sulphur in closed tubes. When the proportion is 4P and 3S, P_4S_3 is formed, but when 2P and 3S is used, in the effort to prepare P_2S_3, not this, but P_4S_7 is formed, showing the tendency on the part of phosphorus to form the P_4 group.

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[1] *Z. anorg. Chem.*, **57**, 281.

[2] *Ber.*, **41**, 558, 657.

Ditte[1] has completed a long investigation of the metallic sulphides, especially with reference to the thio salts of the alkalies. The double sulphides of mercury, tin, antimony, bismuth, copper, silver and gold were prepared and the double selenides and thio-selenides of quadrivalent tin. Most of the thio salts are hydrated, the amount of water varying from two molecules in the silver salts to 20 molecules in a sodium thioaurate; the thio-cuprite, $K_2S.4Cu_2S$, and a thio-antimonite, $2K_2S.Sb_2S_3$, were the only anhydrous salts found. The only salts which could be looked on as basic were the double sulphide of bismuth, $4K_2S.Bi_2S_3.4H_2O$, and one of gold, $2Na_2S.Au_2S.20H_2O$. Quite a series of tin salts were formed, the thio-metastannate type, $M_2S.SnS_2$, predominating, though one orthostannate was made, $2CaS.SnS_2$. The ammonium-tin salts were more acidic, as $(NH_4)_2S.3SnS_2$ and $(NH_4)_2S.3SnSe_2$. Mercury and gold formed normal salts, but mercury a more acidic one, $K_2S.5HgS$, while antimony, silver and copper formed acidic salts exclusively. No double salts of univalent mercury, bivalent copper or trivalent gold could be made. The conditions of formation of artificial cinnabar were found and as well as a form of antimony sulphide resembling stibnite. By fusion at a high temperature of the metal with sulphur and alkali, Italio and Lilio Bellucci[2] have prepared $K_2S.3NiS$ and $BaS.4NiS$, the former corresponding to palladium and platinum salts of similar composition. With cobalt, no double salt could be prepared, but the fusion gave Co_2S_3; nor could sulphides of trivalent or quadrivalent nickel be formed. This corresponds to the decreasing stability of the quadrivalent form in the series, platinum-palladium-nickel. Jaeger[3] calls attention to the influence of light on the conductivity of natural stibnite. This was more than trebled by the light from a 110-volt incandescent light at 16 cm. distance, and it was more than doubled in green light, which had the least effect. When removed from the light, the conductivity decreased, at first rapidly and then slowly till its original value was reached in twenty minutes. Heat was found to have little effect upon conductivity. If the stibnite was fused and then allowed to crystallize, the specific resistance decreased several thousandfold, and was not affected by light. Powdering did not change the conductivity appreciably, but entirely destroyed the sensitiveness to light. Jaeger considers the phenomena due to the macrocrystalline structure. In a paper[4] on the oxidation of sulphur and sulphides Pollacci shows that moist sulphur, when finely divided, is rapidly oxidized in the air at 25°-30° and slowly below 20°. If moistened flowers of sulphur are exposed to the air and sunlight in warm weather, the presence of sulphuric acid is recognizable in a few hours. If the air in contact with the sulphur is previously heated, no oxidation takes place, and the author attributes the oxidation to the ozone of the air. Precipitated sulphides as well as hydrogen sulphide are rapidly oxidized when moist, but it is the metal or the hydrogen which is oxidized, sulphur being liberated. Secondarily the sulphur is itself oxidized and the sulphuric acid formed may then react with the oxide and give sulphates. Some sulphides, such as those of iron, manganese and co-

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[1] *Ann. chim. phys.* [8], **12**, 229.

[2] *Atti Accad. Lincei* [5], **17** i, 18.

[3] *Z. Kryst.*, **44**, 45.

[4] *Mon. Sci.* [4], **221**, 373.

balt, are very rapidly oxidized, others like those of arsenic, cadmium, and barium, more slowly, while zinc and copper sulphides oxidize quite slowly. Pollacci calls attention to the inaccuracy of estimating sulphides such as those of cadmium and arsenic by drying at 100° and weighing. He also proposes sulphur recovery from natural sulphur waters, by allowing the water to run through masses of ocher, exposing the iron sulphide formed to the air, and then extracting the precipitated sulphur by distillation or by the use of carbon bisulphide.

The non-existence of a compound of sulphur and iodine is shown by Smith and Carson,[1] the eutectic point of the sulphur-iodine mixture being 65.6° with a composition of 51 per cent. sulphur. At this point the whole mass solidifies, forming neither compound nor solid solution. Ephraim[2] comes to the same conclusion and also shows that the molecular weight determination indicates that the common solution of sulphur and iodine in carbon bisulphide contains the molecules of both elements in an unchanged state. Pellini and Pedrina[3] have examined the supposed compounds of selenium and iodine, and find that here, too, no compound exists, but that at the eutectic point, 58°, the ratio is very close to a composition of Se_2I_2, and hence the earlier error in supposing that this mixture was really a compound.

Lenher, in continuing his work on tellurium,[4] notes the action of many anhydrous chlorides on tellurium and tellurium dioxide, with the formation of $TeCl_4$, and in some cases $TeCl_2$. With antimony chloride and phosphorus oxychloride, double compounds are formed. Lenher utilizes this reaction to fractionate tellurium and finds no evidence of any of the fractions being anything other than the ordinary tellurium.

Since the restrictions placed upon the use of Paris green on account of its poisonous character, Guignet's green has been the best substitute as regards brilliancy of color. This is formed technically by fusing together borax and potassium bichromate, and grinding the glass formed with water until most of the boric acid is removed. It has been assumed that a chromium borate was formed by the fusion, which was then hydrolyzed by water, and that the green pigment was a form of hydrated oxide. This has been investigated by Wöhler and Becker[5] and found to be essentially the fact. By using ammonium bichromate and boric acid, and dissolving out the excess of boric acid with anhydrous ether, they obtained a chromium borate of the formula $Cr_4O_3(B_4O_7)_3$, that is, a basic chromium tetraborate. By long-continued boiling with water, this salt is completely hydrolyzed, giving the chromium hydroxide, $Cr_4O_3(OH)_6$, which is Guignet's green. This hydroxide has a higher water-vapor pressure than the ordinary greenish violet hydroxide formed by precipitation, and unlike the latter, is, even when in moist condition, insoluble in acids. The transition from the violet hydroxide into its brilliant green isomeric form can be accomplished by heating under water to 250°. The change indeed takes place at a somewhat lower temperature, but the transition point could not be determined, while the reverse

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[1] *Z. phys. Chem.*, **61**, 200.

[2] *Z. anorg. Chem.*, **58**, 338.

[3] *Atti Accad. Lincei* [5], **17** ii, 78.

[4] THIS JOURNAL, **30**, 737, 741.

[5] *Z. angew. Chem.*, **21**, 1600.

reaction of the change from the Guignet's green to the violet modification could not be accomplished by continued heating in water at 180° or 150°, nor by days of standing at 90°. The violet modification appears to be the metastable form, which passes into the less hydrated stable green modification at temperatures somewhat above 100°, the velocity of the reverse change being infinitesimal at this temperature. It is possible that technical use can be made of this reaction in the preparation of Guignet's green.

A new class of complex chromium salts has been prepared by Weinland[1] by the action of glacial acetic acid on chromic acid in the heat. When two parts of acetic acid to one of chromic acid are used, the whole solidifies to a brownish green crystalline mass of the aceto-bichromate of the aceto-chromium base, whose composition is $[Cr_3(Ac)_6.H_2O]$. By various reactions many other double and basic salts of the base were obtained. In many of the salts one molecule of water seems to be a part of the coördinated group, but in the basic salts it is uncertain whether the hydroxide group belongs within or without this group. By the action of glacial acetic acid on chromyl chloride, salts of the base $[Cr_4(Ac)_9]$ were obtained. Iron, and possibly aluminum also, appears to form salts of a similar base.

Miolati[2] has entered on a study of the complex salts of molybdenum and tungsten from a physico-chemical standpoint. He has determined the effect upon conductivity of the successive additions of molybdic acid to solutions of phosphoric, arsenic, and other acids. The curve thus obtained gives an insight into the constitution of the acids present. Thus the solution of phospho-duodecamolybdic acid appears in reality to contain phospho-decamolybdic acid and two molecules of free molybdic acid. Phosphomolybdic and phosphotungstic acid, instead of being tribasic, as ordinarily accepted, are in reality hexabasic, as is shown both by conductivity and by neutralization against methyl orange. Inasmuch as the complex anions of these salts show a great tendency to contain a multiple of six simple molecules, they may be explained along the lines of Werner's views as (XO_4) and (XO_6) anions, with a valence depending on the valence of X, in which the oxygen is replaced by other bivalent acid radicals. Thus he would look on the complex acids which contain 12 molecules of MoO_3 or WO_3 as derivatives of acids of the type $(XO_6)H_{n}$, in which all the coördinated oxygen atoms are replaced by the bivalent anions $(Mo_2O_7)''$ or $(W_2O_7)''$. In the acids with less than 12 molecules of MoO_3 or WO_3, this replacement has only partially taken place. The number of MoO_3 molecules which can be added to an acid appears to be dependent on the number of hydroxyl groups which are present in the anion. Every hydroxyl group makes the addition of two molecules of MoO_3 possible. Thus dichlorplatinic acid, $(PtCl_2(OH)_4)H_2$, forms two molybdo acids, one with two and the other with eight molecules of MoO_3. Maas and Sand[3] and Rosenheim[4] have continued their work on the complex salts of molybdenum, dealing especially with the thiocyanates, and Mazzucchelli[5] his work on the complex salts of

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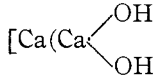
[1] *Ber.*, **41**, 3236.

[2] *J. prakt. Chem.* [2], **77**, 417.

[3] *Ber.*, **40**, 4504; **41**, 1500, 1861, 3367.

[4] *Ibid.*, p. 2386.

[5] *Atti Accad. Lincei* [5], **16** ii, 576; **17** ii, 30.

tungsten and uranium, dealing especially with the oxalates and other organic acids, but it is impossible to give a brief abstract of their work, which has as yet not gone far enough to be systematized. In this connection note should be made of the large amount of work by Pfeiffer[1] and Werner[2] in continuation of their study of complex salts, the former dealing chiefly with chromium, and the latter at present with cobalt. Light is gradually being thrown on these interesting compounds, and Werner's views are at least a good working hypothesis, where the valence theory is completely inadequate. In discussing basic salts, Werner suggests that metallic hydroxides may take the same place in the coördinated group as ammonia, water, acid radicals, and other molecules and atoms. Thus he would write the basic calcium chloride, $CaCl_2.3CaO.16H_2O$, as  $[Ca(Ca\langle{}^{OH}_{OH})_3]Cl_2 + 13H_2O$, and other basic salts similarly. The conception of a metallic hydroxide as a constituent of the coördinated group appears to be new, but follows logically from the conception of the water molecule as a constituent, as the hydroxide is a substituted water, just as the amines are substituted ammonias, and can replace them within the coördinated group.

Group VII.—The great difficulty in preparing anhydrous iodides, owing to the instability they often exhibit in air, has been obviated by Guichard[3] in a new method of preparation. He seals iodine and the other element in different parts of an evacuated tube, and heats the portion containing the iodine to 180° and that containing the other element to 500°, while the remainder of the tube can be kept cold, if the iodide formed is volatile at higher temperatures. In this way ferrous iodide was readily formed, as well as nickel iodide and the iodides of silicon and aluminum. On treating uranium in this manner uranium tetraiodide, a new compound, was obtained. This is a black crystalline mass, fusing at 500° and volatilizing to some extent at this temperature. It decomposes readily in moist air and even in dry air slowly changes to the oxide, becoming covered with minute crystals of iodine. It dissolves in water to a green, strongly acid solution, which gives the reactions of a uranous salt.

Group VIII.—Several articles on the rusting of iron have appeared during the year and there is a complete confirmation of the results of the work of Walker and of Cushman that carbon dioxide is not a necessary factor in the rusting of iron, though the rusting may be accelerated by its presence, and that even in the absence of oxygen iron is acted on by pure water. By the work of Cushman it has been shown that the rusting is primarily an electrolytic action, due to hydrogen ions, which are furnished by the electrolytic dissociation of the water and that the ferrous hydroxide formed is oxidized to 'rust' by oxygen. Certain agents, as alkalies, by reducing the concentration of the hydrogen ions inhibit rusting, and certain substances, such as bichromates, by rendering the iron 'passive,' possibly owing to the deposition of a minute trace of oxygen, have the same effect. Heyn and Bauer[4] hold that while carbon

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[1] *Z. anorg. Chem.*, **56**, 261, 279; **58**, 228, 272, 297, 317.

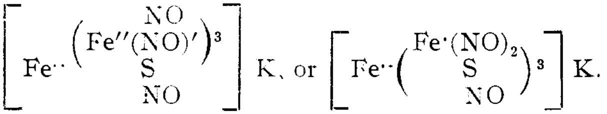
[2] *Ber.*, **40**, 4426, 4434, 4441, 4605, 4817, 4834; **41**, 3007, 3447.

[3] *Compt. rend.*, **145**, 807, 921.

[4] *Mitt. Materialprüfgs. Amt. Gross-Lichterfelde West*, **26**, 1.

dioxide is not necessary for the rusting of iron, free oxygen is. Oil on water or on the iron does not prevent rusting, since oil is pervious to oxygen, but it renders the action slower. Contact of iron with other metals increases the action, provided the metals are more positive, and when different kinds of iron are in contact, one is rusted more strongly than the other. Contrary to Cushman's results, they hold that manganese, between 0.46 and 3.08 per cent., has relatively very little effect on rapidity of rusting and the same is true of phosphorus up to 3.38 per cent. Tilden[1] concludes that the rusting of iron is an electrolytic phenomenon, which is ordinarily caused by the presence of carbon dioxide and the impurities of commercial iron, although he recognizes that carbon dioxide is not absolutely necessary. Dudley[2] attributes the corrosion of wrought iron pipe buried in the earth, to the chlorine present in the ground, and thinks that this corrosion is furthered by the presence of nitrates. The action is often inhibited by the presence of coal gas.

During the past year a number of articles by Bellucci (Rome) and by Cambi (Bologna) have appeared[3] on the constitution of the nitrososulphides of iron (Roussin's salt). Molecular weight determinations by conductivity, freezing point, and boiling point methods, all point to the conclusion that the heptanitrososulphide has the simple formula $Na(Fe_4(NO)_7S_3)$, and is strongly electrolytically dissociated in dilute solution into sodium and nitrososulphide ions. The latter ion possesses a considerable degree of stability. The sulphur is given off as hydrogen sulphide with mineral acids, but not by acetic acid, and in the former case little or no free sulphur is obtained. This points to the sulphur being directly combined with the iron, which is, at least for the most part, in the ferrous condition, as other experiments show. Bellucci proposes for the constitution of the salt, either the formula



$$\left[Fe^{\cdot\cdot}\left(\begin{array}{c}NO\\ Fe''(NO)'\\ S\\ NO\end{array}\right)^3\right]K,\ \text{or}\ \left[Fe^{\cdot\cdot}\left(\begin{array}{c}Fe^{\cdot}(NO)_2\\ S\\ NO\end{array}\right)^3\right]K.$$

The tetranitroso salt gives off hydrogen sulphide when treated with acetic acid, so that in it the sulphur is probably directly connected with the alkali.

During the past year comparatively little has been published on the platinum metals. In the course of an interesting address on platinum at the centennial of the Wetterauische Gesellschaft für die gesamte Naturkunde, Geibel calls attention to the fact that some 2000 kilos of platinum, or one-third of the whole output, is annually used for pins for artificial teeth. Of all the platinum used in industry, only about one-third is recovered, and the remainder is practically lost. A study of the explosive condition of the platinum metals, which has long been familiar to workers with these metals, by Cohen and Strengers[4] does much to clear up this remarkable phenomenon. Bunsen and Debray and others have attributed this explosive condition to the existence of an unstable allotropic form of the metals. The authors show that by heating the

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[1] *J. Chem. Soc.*, **93,** 1356.

[2] THIS JOURNAL, **30,** 247.

[3] *Atti Accad. Lincei* [5], **16 ii,** 542, 584, 658, 740; **17 i,** 202, 424, 545, 720.

[4] *Z. physik. Chem.*, **61,** 698.

metals (after dissolving the zinc of the zinc-platinum metal regulus in hydrochloric acid) for a long time at 100° the explosive character is not lost, but if the temperature used is 200–300° and the heat very carefully applied, the metals gradually but completely lose their explosiveness. When explosive rhodium was heated to explosion, in every case considerable quantities of water were formed (contrary to the observations of Bunsen) and a calorimetric test showed that well up toward theoretical values were obtained, on the assumption that the explosive character of the metal was due to the presence of occluded hydrogen and oxygen. This was confirmed by the fact that when the zinc was dissolved from the regulus in the absence of air and the rhodium then dried in a current of nitrogen completely free from oxygen, the rhodium was not explosive. When zinc is dissolved from the regulus by nitric acid, the explosion appears to be due to the occlusion of hydrogen and nitrogen oxides. When rhodium, dried in the absence of oxygen and hence not explosive, is exposed to the air it becomes explosive. Similar results were obtained with the other platinum metals, except ruthenium. Here other unknown influences are present, for the metal is explosive, even when extracted from the regulus and dried in the absence of oxygen. Previous observations of a difference in solubility between explosive rhodium and that which has been exploded, are incorrect, and due to the fact that when rhodium is treated with nitric acid it assumes a passive condition, and is then insoluble in aqua regia, but if the hydrochloric acid is added first, the rhodium, in this finely divided condition, goes into solution in aqua regia.

Martin and Wöhler[1] have prepared a sesquioxide of palladium by the anodic oxidation of palladous nitrate. When this sesquioxide, which loses oxygen slowly even at ordinary temperature, is dissolved in hydrochloric acid at a very low temperature, the sesquichloride is formed, which is also very unstable. The caesium and rubidium double salts, Cs_2PdCl_5 and Rb_2PdCl_5, are more stable, the former giving a dark green powder, and the latter gray-green regular crystals. It is also possible to prepare these salts from the chloropalladites by cautious treatment with chlorine at low temperature, care being used not to add chlorine enough to oxidize up to chloropalladates. Chloropalladic acid is reduced by long boiling to some extent to the trivalent stage, but the chloropalladates are not changed under similar circumstances. By boiling chloroiridates with a small amount of oxalic acid, Delepine[2] finds that they are reduced to chloroiridites, which should more properly be considered as aquopentachloroiridates, since they contain one molecule of water, which is not removed until the salt is heated above 150°. The formula of these salts is $M_3Ir(H_2O)Cl_5$, and they are analogous to the aquopentachlororuthenates, $M_2Ru(H_2O)Cl_5$. which they resemble in properties. Vèzes used a similar method of reduction with oxalic acid some years ago, both for chloroplatinates and chloroiridates, and since then it has been in use technically as by far the best method for the preparation of the chloroplatinites. A series of complex oxalates of iridium has been prepared by Gialdini.[3] These are formed by boiling iridium

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[1] *Z. anorg. Chem.*, **57**, 398.

[2] *Bull. soc. chim.* [4], **3**, 901.

[3] *Atti Accad. Lincei* [5], 16 ii, 551, 648.

dioxide with oxalic acid, the first action being the reduction of the oxide by the oxalic acid with evolution of carbon dioxide, and then the formation of the complex salt, which has the formula $M_3IrOx_3.nAq$. The oxaloiridite is a fairly stable ion, and all its salts are hydrated, but the amount of water is variable.

LEXINGTON, VA.

[CONTRIBUTION FROM THE INSTITUTE OF ANIMAL NUTRITION OF THE PENNSYLVANIA STATE COLLEGE.]

THE DETERMINATION OF CARBON BY MEANS OF THE BOMB CALORIMETER.

BY J. A. FRIES.

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In the investigations carried on by this institute, the problems of animal nutrition are being studied from the standpoint of energetics and hence the heats of combustion of numerous samples of feed, excreta and other materials are determined by means of a bomb calorimeter. Having, therefore, the charges of these samples completely oxidized in the bomb calorimeter at the time of the heat determinations, the idea naturally suggests itself to try to determine the CO_2 pent up in the bomb. The writer made an attempt several years ago to determine carbon by means of the ordinary Atwater-Hempel bomb, but the results were unsatisfactory. This was due, in part, to the fact that the construction of the bomb used was not well adapted to this particular purpose, and in part to the quality of the oxygen supply which was then in use. The work was, therefore, dropped until a more suitable bomb could be obtained. During the past summer, the work of determining carbon has been taken up again with a new Atwater-Hempel bomb, which has the top modified according to the suggestions of Dr. H. P. Armsby and the writer. This time it has been satisfactorily demonstrated that the carbon in organic compounds can be determined accurately, in less time, and with less expense, by means of the bomb than by the ordinary copper oxide method.

While this method for carbon is especially to be recommended to those who desire to determine both energy and carbon in the same material, it can also be recommended for carbon alone. Where the bomb calorimeter is in use already, a new top suitable for this work would, undoubtedly, in many instances prove to be a good investment. The top which we have used has two separate openings and valves, an inlet terminating on the under side of the cover, and an outlet extending by means of a fine platinum tube to within about 5/8 inch of the bottom of the bomb.

The figure shows the arrangement of the two valves, and the general construction of the top, as well as of the other parts of the bomb. For