brown iron ore, 2.0; total, 100. The analysis is certainly far from satisfactory. The second analysis is by Carnot[1] who gives 96.70 per cent. Bi_2O_3 with the remainder distributed over eight compounds, including 0.95 per cent. H_2O, also SO_3, HCl, CO_2, etc. While indicating the probable presence of Bi_2O_3, the existence of the simple oxide can hardly be considered as established by the analysis of Carnot. As the first natural crystals of bismite described do not agree[2] with those artificially prepared, it seems doubtful whether Bi_2O_3 actually occurs in nature. The apparent identity of the natural crystals described by Rogers[3] with the artificial crystals of Bi_2O_3 is rendered somewhat questionable by the lack of chemical data on his crystals and by the evidence of the composition of the San Diego County ochers, as shown in this paper.

Summary.—The chief points brought out in this paper may be briefly summarized as follows:

(1) The existence of natural Bi_2O_3 has not been established.

(2) Natural bismite or bismuth ocher, when pure, is more probably a bismuth hydroxide.

(3) The bismuth ochers from San Diego County, California, are either a bismuth hydroxide or bismuth vanadate, pucherite, or mixtures of these two.

(4) Pucherite has been found noncrystallin and determined for the first time in the United States.

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RECENT WORK IN INORGANIC CHEMISTRY.

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Received December 10, 1910.

The problem of chemical formulas and nomenclature of inorganic compounds, with especial reference to indexing, is discussed by M. K. Hoffmann,[4] and the system used in his recently published *Lexicon der anorganischen Verbindungen* is described. Without attempting changes which can be considered radical, a logical and unambiguous system is worked out, which deserves general consideration.

The solubility of gases in metals has been studied by Sieverts.[5] Nitrogen dissolves in no metals, but reacts with several, forming nitrides. Carbon monoxide dissolves in both solid and fused nickel and also in cobalt, but not in copper. Sulfur dioxide is soluble in fused copper but insoluble in solid copper. Oxygen is soluble in silver but not in gold. Hydrogen is the most generally soluble of gases, but is not soluble in silver, gold, tin, and many other metals. Its solubility in copper is in-

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[1] See Hintze's Handb., *loc. cit.*, for references.

[2] W. T. Schaller and F. L. Ransome, "Bismite," *Am. J. Sci.*, [4] 29, 173 (1910).

[3] *Loc. cit.*

[4] *Chem.-Ztg.*, 34, 73.

[5] *Z. physik. Chem.*, 68, 115; 74, 277. *Ber.*, 43, 893. *Z. Elektrochem.*, 16, 707.

creased by the addition of nickel and platinum in which it is soluble, and decreased by tin and aluminium in which it is insoluble. In the occlusion of gases by metals adsorption plays very little part, as the phenomenon is independent of surface area, and its true solubility. This solubility varies with the square root of the pressure. Greenwood[1] has determined the boiling points of several metals, using a resistance furnace and graphite, or magnesia-lined crucibles. The following figures were obtained:

Magnesium	1120°	Lead	1525°	Chromium	2200°
Bismuth	1420°	Aluminium	1800°	Tin	2270°
Antimony	1440°	Manganese	1900°	Copper	2310°
		Silver	1955°	Iron	2450°

Some two years ago Hasslinger announced a new form of "tin pest" which has been since investigated by Cohen, who finds that it has nothing in common with the ordinary "disease" of tin, but is due to mechanical stress, and to it he gives the name of stress-sickness (Forcierkrankheit). He now finds[2] that this condition is not peculiar to tin, but that all metals assume a metastable condition by being worked, and that this condition can be transmitted by contact infection. In his experiment with tin, he etches a smoothed surface of rolled tin by a moment's action of $KClO_3$-HCl mixture and presses on the carefully cleaned surface a clean piece of tinfoil. On heating to 184°, the etched surface of the tin is reproduced on the foil. The phenomenon was repeated with lead, zinc brass and bismuth.

The experiments of Naumann on reactions in non-aqueous solutions have been continued[3] by the investigation of the action of ammonia and hydrogen sulfide on the metals of the second (analytical) group in ethyl acetate solution. The most marked departure from aqueous solutions is that hydrogen sulfide generally precipitates the sulfide only in the presence of ammonia, though stannous sulfide is precipitated from stannous chloride solution by hydrogen sulfide alone. Ammonia generally precipitates ammines, which are insoluble in ethyl acetate.

Group I.—By heating various elements and compounds with dry sodium formate in intimate mixture, Vournasos[4] finds the nascent hydrogen is given off much more reactive than ordinary hydrogen. Red phosphorus gives phosphine, sulfur gives hydrogen sulfide, free or combined arsenic, arsine; sodium antimonite gives but little stibine, and silicon does not react, though both the sulfide and chloride of silicon give hydrogen silicide. Nitrides give ammonia, cyanides, hydrocyanic acid, and carbides of the alkalies give acetylene. With boron nitride and also with a mixture of boron oxide, sodium formate and metallic sodium, a small amount of hydrogen boride was obtained, which was, however, not isolated.

In 1863, Rose described a suboxide of copper, Cu_4O, which has since retained its place in text books. Moser[5] has repeated the work of Rose in the light of modern methods and finds no evidence of the existence of this oxide, Rose's compound being a variable mixture of cuprous

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[1] *Proc. Roy. Soc. London*, (*A*) **82**, 396.

[2] *Chem. Weekblad*, **6**, 625, 881.

[3] *Ber.*, **43**, 313.

[4] *Compt. rend.*, **150**, 464, 922.

[5] *Z. anorg. Chem.*, **64**, 200.

oxide and copper. On the other hand the work of Etard and of Rogojski on cuprous sulfites has been largely confirmed by Ramberg.[1] When a current of sulfur dioxide is led into a copper acetate solution, cuprous acetate is first formed and then crystallin $Cu_2SO_3.1/2H_2O$ (colorless). By the action of aqueous sulfurous acid on this hemihydrate, the red monohydrate of Rogojski, $Cu_2SO_3.H_2O$, is formed. If sulfur dioxide is led into an ammoniacal solution of copper sulfate, the colorless anhydrous double sulfite, $(NH_4)_2Cu_2(SO_3)_2$, crystallizes out. In all these preparations care must be taken to exclude all air.

According to Turner when flakes of gold are heated on glass they become transparent. Chapman and Porter[2] find that when heated alone they show no transparency, but that at about 320° the flakes splinter, owing to a contraction, and that it is this splintering into minute particles which, when it takes place on glass, seems to render the gold transparent. On the other hand the finest gold wire shows no sign of contraction, even when heated up to 500°. Grünwald[3] finds that the purple of Cassius consists of a hydrogel of stannic acid colored by colloidal metallic gold.

Group II.—Levi-Malvano[4] has prepared glucinum sulfate hexahydrate in crystals large enough for crystallographical measurement by using a solution of potassium sulfate as solvent. The crystals show no relation to the crystals of the other hexahydrated sulfates of the magnesium series. Parsons and Sargent[5] have reviewed the subject of glucinum compounds with organic acids. Solutions of the normal salts dissolve large amounts of glucinum hydroxide or carbonate, which separates out on dilution. On evaporation, gelatinous or glassy masses are obtained which have no definit composition. The salt with trichloroacetic acid alone crystallizes out as a normal salt (dihydrate) and can be recrystallized from water acidified with trichloroacetic acid.

In a study of Sorel cements, Kallauner[6] finds that in all cases the magnesium chloride can be extracted completely by cold water, and, unless the water in the cement is below 40 per cent., by absolute alcohol. In any case, the alcohol removes a large quantity of the magnesium chloride. The magnesium oxide is only partially converted into the carbonate by carbon dioxide. Kallauner concludes that these cements are to be looked on as solid solutions of magnesium hydroxide and magnesium chloride.

The subject of chemical phosphorescence and luminescence is discussed by Vanino and Zumbusch.[7] The phosphorescence of the alkaline earth sulfides is attributed to the presence of small quantities of polysulfides, the best results being obtained by heating lime with a minimum of sulfur, while the reduction of the sulfate with carbon does not give a phosphorescent mass. The addition of minute traces of heavy metals, as manganese, increases the phosphorescence, but bismuth is far more active in this respect than any metals which have previously been used. Luminescence is often brought out by treatment with hot liquids.

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[1] *Z. physik. Chem.*, 69, 512.

[2] *Proc. Roy. Soc. London*, (A) 83, 65.

[3] *Sprechsaal*, 43, 419.

[4] *Gazz. chim. ital.*, 39, ii, 438.

[5] THIS JOURNAL, 31, 1202.

[6] *Chem.-Ztg.*, 33, 871.

[7] *J. prakt. Chem.*, [2] 80, 69.

After many unsuccessful attempts, which are fully described,[1] Glascock has succeeded in preparing metallic strontium in quantity, and its properties are described.

Attempts to prepare metallic radium have apparently met with success in two directions. Madame Curie[2] has electrolyzed a solution of radium chloride, using a mercury cathode. The radium amalgam is very unstable and decomposes water. On distilling it in a current of dry hydrogen most of the mercury distilled at 270°. At 400°, the amalgam was solid and at 700° all the mercury had passed off, and the radium, which fuses at this temperature, began to volatilize. Its vapors attacked the quartz tube very strongly. The metal is silver white, becoming black immediately in the air, owing to the formation of the nitride. It blackens paper, decomposes water energetically and goes into nearly complete solution. As it is much more volatil than barium, sublimation in a vacuum is proposed for its purification. Ebler[3] prepared an azide of barium and radium, $Ra(N_3)_2$, and heated it in a vacuum several hours at 180–250°, obtaining the radium as a metallic mirror. Stock[4], in an investigation of the volatility of the bromides of the alkaline earths in a vacuum, finds that this property is a function of the atomic weight. Thus calcium bromide, $CaBr_2$, sublimes at 720°, strontium bromide at 770° and barium bromide at 820°. Radium bromide seems to require a temperature of about 900°, and this method of separation, or at least enrichment of the barium-radium bromide mixture, is proposed. Working with 0.3942 g. radium bromide, Gray and Ramsay[5] have made a study of the radium emanation. The liquid emanation is colorless and, in glass, phosphorescent. The solid emanation is opaque, fuses at —71°, and shows intense luminosity, varying in color with the temperature. From theoretical considerations its atomic weight would seem to be 176, corresponding to a higher member of the argon group. This would require that radium should also give, on breaking up, a non-active substance of atomic weight 46, or 42 on the supposition that two helium atoms are formed. Using a modification of Bunsen's method, Debierne[6] finds the molecular weight of the emanation to be 220, which is in agreement with the theory that radium breaks up into one atom of helium and one atom of emanation. There is also a place for an element of this atomic weight in the argon group. Later, Ramsay and Gray[7] determined the density of the emanation by actually weighing less than 0.1 cm. on a balance of fused quartz, and as a mean of five experiments find the molecular weight 220, in agreement with Debierne's results. They propose the name of *Niton* for the element. The supposed radioactivity of the alkali salts has continued to attract some attention, but little that is definit has resulted. Henriot[8] decides that potassium gives out β-rays, and that rubidium is twice as active, while lithium, sodium, cesium, and thal-

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[1] THIS JOURNAL, 22, 1222.

[2] *Compt. rend.*, 151, 523.

[3] *Ber.*, 43, 2613.

[4] *Ibid.*, 42, 4088.

[5] *J. Chem. Soc.*, 95, 1073.

[6] *Compt. rend.*, 150, 1740.

[7] *Ibid.*, 151, 126.

[8] *Radium*, 7, 40.

lium show no activity. Elster and Geitel,[1] after efforts to separate some active impurity, conclude that potassium itself is radioactive, as well as rubidium. Büchner,[2] working with the photographic plate, finds an undoubted blackening in the presence of rubidium salts, but none with any of the other alkalies. The rubidium activity passes through aluminium foil, but is greatly weakened. After working up several tons of pitchblende, Madame Curie and Debierne[3] have obtained the polonium present concentrated in 2 mg. of substance, which contain about 0.1 mg. of actual polonium. Its spectrum and some of its properties have been studied. Among the gases given off from its solution, helium was found in nearly theoretical quantity.

If a test tube is partly filled with barium amalgam and closed with a rubber stopper, in the course of time the under edge of the stopper shows a black ring, which proves to be carbon. As other amalgams show the same phenomenon, von Bolton[4] ascribes it to the vapors of mercury. Other carbon compounds, such as $CHCl_3$, CS_2, and CO_2, are similarly decomposed with the deposition of carbon. In the case of caoutchouc the carbon showed minute crystals, which appear to be diamond. von Bolton suggests that the formation of (inorganic) graphite and diamond in nature may be due to the action of metallic vapors on CO_2.

Group III.—In the attempted preparation of crystallized boron by the Goldschmidt process, using boric oxide, aluminium filings and sulfur, in addition to the black crystals of AlB_{12}, the lighter colored transparent crystals first described by Wöhler were in no case obtained by Biltz.[5] These crystals, to which Hampe assigned the formula $C_2Al_3B_{48}$, were readily obtained when carbon or aluminium carbide was added to the mixture, and were separated from the slightly lighter black crystals by floating in methylene iodide-benzene solution. This quadratic boron, called by Wöhler "diamond boron," is not attacked by concentrated sulfuric acid with chromic acid, but is slowly acted on by boiling concentrated nitric acid. The formula is $C_2Al_3B_{44}$, but in spite of the constancy of the carbon-aluminium ratio it is very doubtful if the crystals are a definit chemical compound.

Verneuil[6] has prepared sapphires in the oxyhydrogen blowpipe by adding iron oxide and titanic acid to the alumina. The best color was obtained when 1.5 per cent. Fe_3O_4 and 0.5 per cent. TiO_2 were used. Crystallographically true sapphire was formed, although Deville and Caron attribute the color of natural sapphires to the presence of a lower oxide of chromium.

In continuing his work on scandium, Crookes[7] has prepared a large number of new salts, many of them with organic acids. A considerable number of these are basic. Meyer and Winter[8] have also continued their

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[1] *Physik. Z.*, 11, 2750.

[2] *K. Akad. Wetenschappen*, 18, 91.

[3] *Radium*, 7, 38.

[4] *Z. Elektrochem.*, 16, 667.

[5] *Ber.*, 43, 297.

[6] *Compt. rend.*, 150, 185.

[7] *Proc. Roy. Soc. London*, (*A*) 84, 79.

[8] *Z. anorg. Chem.*, 67, 398.

work on scandium, and their paper deals with its preparation and purification. It is readily separated from all the earths except thorium. The nearly insoluble scandium iodate offers a satisfactory means of separation, but boiling with a saturated solution of sodium carbonate is even better, a nearly insoluble double carbonate, $4Na_2CO_3.Sc_2(CO_3)_3.6H_2O$, being precipitated. Further spectroscopic examination of rocks and minerals by Eberhard[1] confirms the exceedingly wide distribution of the element. All the minerals in which it can be detected chemically, however, have their origin in granits and pegmatites.

In continuing his work upon the bromates of the rare earths, James (and Langelier)[2] describe the properties of the bromates of lanthanum, cerium, praseodymium, neodymium, and yttrium, which are best prepared by action of the sulfates on barium bromate, and which have the formula $M_2(BrO_3)_6.18H_2O$. James and Pratt[3] have studied the system $Y_2O_3.N_2O_5.H_2O$, and find one definit basic yttrium nitrate, $3Y_2O_3.4N_2O_5.20H_2O$. The priority contest regarding the splitting of ytterbium continues to call forth articles, but the names given by Urbain, lutecium and neoytterbium, seem to receive more favor than the aldebaranium and cassiopeium of Auer von Welsbach. Thiele has continued his researches on indium.[4] He finds In_2O_3 stable up to about 1000° but above this it is slowly decomposed, and in one experiment he obtaineed In_3O_4, in regular crystals, possibly corresponding to magnetite. InI_3 and InI were prepared synthetically, and evidence of the existence of InI_2 was obtained from the fusing-point curve of their mixture. The three sulfides, In_2S, InS and In_2S_3, all exist as well as In_2Se_3 and InTe.

Group IV.—The action of carbon tetrachloride on metallic oxides has been studied by Camboulives,[5] both with reference to the compound formed and the temperature at which the reaction begins. Fe_2O_3 is attacked as low as 245° while WO_3 requires 560°. In general the chloride is formed but tungsten gives the oxychloride and columbium and thorium, mixtures of the chloride and oxychloride. The chloride formed generally corresponds in valence to the oxide, but V_2O_5 gives VCl_4, MoO_3 gives $MoCl_5$, and UO_3 a mixture of UCl_4 and UCl_5. For Cr, Ni, V, Ti, Zr, Gl and especially for the rare earths the method is an excellent one for the preparation of the chlorides. Some minerals, as corundum and beryl, are but little acted on, and silica is not attacked. The method is available for quantitative separation of SiO_2, since this is not affected. Thus the aluminium silicate in clay is volatilized as $AlCl_3$ and $SiCl_4$, while the free silica and sand are not acted on. Work on metallic carbonyls, upon which Ludwig Mond was engaged at the time of his death, has been published by his son.[6] Carbonyls of nickel, cobalt, iron, molybdenum and ruthenium have been made, except in the case of nickel, by the use of high pressures. The $Co(CO)_4$ consists of orange crystals with a very low vapor pressure. At 50°–60°, it decomposes into $Co(CO)_3$ and CO. $Fe(CO)_5$, a yellow liquid with considerable vapor pressure, is decomposed in the

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[1] *Sitzb. kg. preuss. Akad. Wiss.*, 1910, 404.

[2] THIS JOURNAL, 31, 913.

[3] *Ibid.*, 32, 873.

[4] *Z. anorg. Chem.*, 66, 288.

[5] *Compt. rend.*, 150, 175, 221.

[6] *J. Chem. Soc.*, 97, 798.

light, $Fe_2(CO)_9$ being formed, and this when heated in solution to 95° becomes $Fe(CO)_4$. $Mo(CO)_6$ consists of white crystals. A carbonyl of ruthenium was formed as an orange-red deposit in very small quantity when the metal was heated to 300° at 350–450 atmospheres. No carbonyls of chromium, manganese, tungsten, palladium or rhodium were obtained, even at extreme pressures. No evidence of any carbonyl of nickel other than $Ni(CO)_4$ was found. As regards constitution, direct combination of the carbonyl groups with the metal seems contradictory to our ideas of valence, and there seems to be no probability that the carbon atoms form a ring, especially since the cobalt carbonyl has the formula $Co_2(CO)_8$ in solution while the formula of nickel carbonyl is $Ni(CO)_4$, nor can the nonacarbonyl of iron be brought into line from the standpoint of a carbon ring. It seems probable that these compounds have a "molecular" composition, the carbonyl group being somewhat similar to water of crystallization or hydration, though on this hypothesis it is difficult to explain the normal gas density of several.

Hönigschmid has investigated the silicides of the alkaline earths.[1] Technical calcium silicide with 30 per cent. calcium contains $CaSi_2$, with free silicon and some iron silicide. The 60 per cent. silicide contains some $CaSi_2$, but consists chiefly of Ca_3Si_2, and approaches metallic calcium in its properties. The technical magnesium silicide consists of Mg_2Si and free silicon. When free silicon is present the color is bright blue. On decomposition with fuming hydrochloric acid, $CaSi_2$ gives a silicone of composition $Si_3H_3O_2$, which was discovered by Wöhler. This is dark yellow, but instantly becomes white on exposure to sunlight, through oxidation. On heating in a vacuum it leaves a residue which is probably Si_3O_2. The white silicone, Wöhler's leucone, on similar heating leaves a brownish-yellow residue, apparently a new oxide, Si_3O_4. Kolb,[2] by fusing together in hydrogen calcium and pure silicon, obtains two silicides to which he assigns the formulas Ca_6Si_{10} and $Ca_{12}Si_{10}$. From each of these a silicone is obtained. Both silicides absorb nitrogen readily, the former giving a mixture of $CaSi_2N_3$ and $Ca_2Si_3N_4$, and the latter giving $Ca_{11}Si_{10}N_{10}$.

Attempts to obtain metallic titanium by the reduction of the fluorotitanates were found by Hunter[3] to give a product containing at best 73 per cent. of the metal. The reduction of TiO_2 by carbon in a vacuum likewise gave an impure product. The reduction of pure $TiCl_4$ by metallic sodium in a steel cylinder proved more successful, the product being partly a powder, but with some completely fused material which was pure titanium. The metal looks like polished steel, and is hard and brittle, but can be worked at a dark red heat. It burns in the air at 1200°, and fuses at 1800°–1850°. Its specific gravity is 4.50. Weiss and Kaiser[4] also have studied metallic titanium, using the fluorotitanate method to prepare it. Their product seems to have been less pure than that of Hunter.

Two investigations on metallic zirconium have appeared, one by Weiss[5]

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[1] *Monatsh.*, 30, 497. 509.

[2] *Z. anorg. Chem.*, 64, 342.

[3] THIS JOURNAL, 32. 330.

[4] *Z. anorg. Chem.*, 65, 345.

[5] *Ibid.*, 65, 178, 248.

and the other by Wedekind[1]. Weiss' source of zirconia was a Brazilian dioxide "Zircon-Favas," which, though microcrystallin, seems to be isomorphous with rutile and cassiterite. The metallic zirconium was obtained by the reduction of the fluo-zirconate by sodium, and also by aluminium, the aluminium being finally removed by volatilization in an electric vacuum furnace. Wedekind used the former method, but did not get so pure a zirconium. That of Weiss was obtained in fused globules. The density of the pure metal is 6.4, its melting point 2350°. Zirconium hydride, ZrH_2, is formed when powdered zirconium is heated in hydrogen. When the hydride is heated in oxygen it burns, forming a new greenish-white oxide, Zr_2O_3, which is very stable and is but slowly oxidized to ZrO_2 by heating in the air.

Group V.—In the course of attempts to prepare compounds of argon (later referred to), Fischer and Schröter[2] have obtained nitrides of most of the metals, many of them never before described, as those of Na, K, Rb, Cd, In, Tl, Pb, As, Sb, Te. By heating the element in an atmosphere of nitrogen in the electric arc and cooling the products by a mixture of liquid argon and nitrogen, it was possible to prepare nitrides of all the metals of the second series of each periodic group, even the very unstable nitrides such as those of mercury, thallium, lead and bismuth. All were found to be derivatives of NH_3, no trace of derivatives of N_2H_4 or any other N-H compounds being found. The nitrides of elements of high atomic weight, as mercury, lead, and bismuth, explode on being allowed to come to ordinary temperature, while the others decompose more quietly. Only the elements of the first series of each periodic group form nitrides which are stable at ordinary temperature. The authors suggest the hypothesis that when the atmosphere of the earth was at a temperature of several thousand degrees, at least a part of the nitrogen was present in the form of these endothermic nitrides, which have been gradually decomposed as the earth has cooled. Wolk[3] finds the most favorable temperature for the formation of aluminium nitride, AlN, by heating finely divided aluminium in nitrogen, is 820–850°. Below 700° no action takes place, while at higher temperatures the product sinters together and has no longer a uniform composition. The lower the temperature of formation the more readily does the nitride decompose in water. The nitrogen compounds with silicon have been studied by Weiss.[4] The silicon was heated in a current of nitrogen. The absorption of nitrogen was slow, the most favorable temperature being 1240°–1300°. According to different treatments of the resultant mass, the silicides SiN, Si_3N_4, and Si_2N_3 were obtained. All are white amorphous solids, very resistant to chemical action. When silicon is heated in the presence of carbon, nitrogen is absorbed and a carbonitride, Si_3C_3N, formed. This is probably identical with the similar product to which Schützenberger assigned the formula Si_2C_2N.

Zinc hydrazide has been prepared by Ebler and Krause[5] by the action of dry hydrazine on zinc ethide in dry ether and in a nitrogen atmos-

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[1] *Ann.*, 371, 366.

[2] *Ber.*, 43, 1465.

[3] *Compt. rend.*, 151, 318.

[4] *Z. anorg. Chem.*, 65, 38.

[5] *Ber.*, 43, 1690.

phere, and also by the action of hydrazine on zinc amide. The hydrazide takes fire spontaneously in the air. Hydrazides of other metals can be prepared by a similar reaction. The dry hydrazine was prepared by Ebler by the prolonged action of barium hydroxide on hydrazine hydrate, while Raschig[1] advises the use of caustic soda.

A complete summary of his work on the metal-ammonia bases, containing more than one atom of the metal in the nucleus, is given by Werner,[2] together with the bearing of the work on his theory of the constitution of these bases. The metal atoms (Co) in the nucleus may be united not only by an oxygen atom, but also by NH_2, NH, OH, OH_2, O_2, and further by certain acid radicals such as NO_2, SO_4, and $OCO.CH_3$. Altogether 23 different complex nuclei have been recognized, which are fully described and discussed in the paper. Werner has further, partially in conjunction with Riesenfeld,[3] described a number of new aquochromiumtriammine salts, which show many correspondences with the cobalt salts of similar constitution. They are all derived from the chromium triammine tetraoxide, which is readily prepared by the action of concentrated ammonia on pyridine perchromate, the latter being formed from chromic acid, pyridine and hydrogen peroxide. The aberrant results obtained in the determination of hydroxylamine with copper sulfate, according to concentration and temperature, have been investigated by Adams and Overman,[4] who find the existence of several intermediate compounds, which have been isolated. These are $CuSO_4.NH_2OH$, $CuSO_4.2NH_2OH$, $CuSO_4.3NH_2OH$ and $Cu_2O.SO_4.2NH_2OH$. When heated with excess of hydroxylamine in the presence of NaOH the reduction to metallic copper is complete. The reaction between ammonium chloride and potassium dichromate has been found by Frankforter, Roehrich and Manuel[5] to be very complex, the evolved gas containing not merely nitrogen as assumed by Ramon de Luna, but also nitric oxide and even nitrogen dioxide. In one case as much as 45 per cent. NO was obtained. The composition of the residue also depends upon the composition of the original mixture. The complexity of the reaction is attributed to the fact that the ammonium chloride dissociates into ammonia and hydrogen chloride, and the former diffuses out of the mixture more rapidly than the latter.

Hayhurst and Pring[6] have examined the atmosphere at different elevations for the presence of nitrogen oxides and ozone, by passing the air through a perfectly neutral solution of potassium iodide, and determining the liberated iodine, the free alkali and the iodate formed. They find that at low and at moderate elevations the amount of nitrogen oxides is very variable and that the amount of ozone is not sufficient to determin, at all events less than 0.003 mg. per 10 cu. m. At the height of 10 miles small amounts of ozone are found, 0.04 mg. in from 0.1 to 0.3 cu. m. The amount of nitrogen oxides is here less than the amount of ozone. Adwentowski[7] has studied nitric oxide at low temperatures,

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[1] *Ber.*, **43**, 1927.

[2] *Ann.*, **375**, 1.

[3] *Ber.*, **42**, 4222; **43**, 2286.

[4] THIS JOURNAL, **31**, 637.

[5] *Ibid.*, **32**, 178.

[6] *J. Chem. Soc.*, **97**, 868.

[7] *Anz. Akad. Wiss. Krakau*, **1909**, 742.

and from the vapor-pressure curve concludes that at high pressures the gas is somewhat polymerized. It is, however, completely dissociated at atmospheric pressure. The melting point of the solid NO is —160.6° with a pressure of 168 mm. The boiling point at 760 mm. is —150.2°, the critical temperature —92.9° and the critical pressure 49,095 mm. The bluish color of the solid and liquid is attributed to the presence of a little N_2O_3, which it is impossible to remove. Numerous articles by Haber and his colleagues have appeared in Vol. 16 of the *Z. Elektrochem.* on the formation of the oxides of nitrogen from the atmosphere in the electric arc under various conditions, and Guye has reviewed the whole subject critically in the *Bull. soc. chim.*, [4] **5**, No. 20. The papers are of great interest in connection with the rapidly developing synthetic nitrate industry, but do not admit of abstraction. Guntz and Martin[1] have prepared the anhydrous nitrates of manganese, nickel, cobalt and copper by the use of N_2O_5 in a vacuum for the removal of the last of the water of crystallization. By the action of metals on $AgNO_3$ in non-aqueous solvents, the nitrates of the above metals are obtained, combined with the solvent, as $5Cu(NO_3)_2.4CH_3COCH_3$ and $2Mn(NO_3)_2.C_6H_5CN$. In liquid ammonia, $Mn(NO_3)_2.9NH_3$ was obtained and analogous compounds of nickel and cobalt. With copper, $Cu(NO_3)_2.7NH_3$ was formed, which in a vacuum became $Cu(NO_3)_2.4NH_3$.

Several papers on elementary phosphorus have appeared during the past year, whose results are not in complete agreement. Gernez[2] has examined the coating which appears on ordinary yellow phosphorus when kept under water. This coating is white when formed in the dark but yellow to red when exposed to the light. In both cases, however, it is composed of ordinary yellow phosphorus. Phosphorus oxidizes slightly under water and the oxide formed dissolves in the water leaving the surface covered with phosphorus in minute flakes which causes the opaque appearance. According to Jolibois[3] the red phosphorus of commerce can be separated into larger dark violet and smaller yellowish red particles, but the violet are changed into the yellowish red by rubbing and are not a distinct modification. If the violet particles are heated out of access of air to 400° they pass slowly into a new modification, which Jolibois calls red pyromorphic phosphorus. The change takes place rapidly at 600°, and it is also accelerated by the presence of iodine. This modification has a density of 2.37 and is a definit allotropic form. On the other hand, Cohen[4] finds only two modifications of phosphorus, the ordinary yellow and the "metallic" or Hittorf's phosphorus. The red or amorphous phosphorus of trade is a solid solution of yellow phosphorus in metallic phosphorus. The composition of this solid solution is a function of the temperature. The so-called constants of red phosphorus found in its literature have no value. Stock[5] has made a very complete study of the metallic phosphorus, which also according to him is the only modification of phosphorus except the ordinary yellow form. The metallic phosphorus is best prepared by dissolving phosphorus in metallic lead

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[1] *Bull. soc. chim.*, [4] **5**, 1004; **7**, 313.

[2] *Ann. chim. phys.*, [8] **21**, 5.

[3] *Compt. rend.*, **149**, 287.

[4] *Z. physik. Chem.*, **71**, 1.

[5] *Ber.*, **42**, 4510.

and separating the lead by anodic solution in an acetic acid solution of lead acetate. By using 100 grams lead and 1.5 grams of phosphorus, about 0.5 gram metallic phosphorus can be obtained. Bismuth can be substituted for lead, and while better crystals are obtained the output is smaller. It can also be prepared with difficulty by sublimation. Under the microscope the metallic phosphorus is seen to consist of yellow to brown, more or less transparent tables, with some acicular crystals. They contain small quantities of lead (or bismuth), apparently in solid solution. While ordinary yellow phosphorus unites slowly with sulfur to form phosphorus sulfide, the metallic phosphorus hardly reacts with sulfur. It oxidizes slowly in the air, and that formed by sublimation oxidizes as soon as the tube in which it was formed is opened. [The nomenclature of phosphorus is much in need of revision. We now have "common," "white" or "yellow" phosphorus; "red "or "amorphous;" and "metallic," "crystallin," "violet," or "Hittorf's" phosphorus; and not one of these names is wholly satisfactory.—REVIEWER.] Gernez[1] has also examined the so-called "black" phosphorus discovered by Thénard in 1812. When mercury is dissolved in phosphorus the solution is colorless and if saturated or supersaturated, it remains colorless. When it crystallizes the mercury separates out and colors the mass intense black. The mercury is then so finely divided that, on warming, the fused phosphorus immediately redissolves the mercury again to a colorless solution. Stock[2] has continued his work on the sulfides of phosphorus, completing his description of the properties of P_4S_7, and also of P_4S_{10}, which has not before been obtained in a pure condition. The latter boils at 513°–515° with some decomposition, and at 600° its density corresponds to the formula P_2S_5. It is interesting to note that as regards color, specific gravity, melting and boiling points, solubility and stability, P_4S_7, so far from standing intermediate between P_4S_3 and P_4S_{10}, lies entirely outside the other two. This much simplifies the problem which Stock has before him of investigating other sulfides of phosphorus, which he feels certain exist. By submitting a mixture of phosphorus trichloride and hydrogen to the action of an electric discharge, Besson and Fournier[3] obtained the dichloride, P_2Cl_4, a colorless oil, solidifying at low temperatures to a white mass, which fuses at —28°. In the presence of an indifferent gas it boils at 180° with slight decomposition. The compound is rather unstable and gives decomposition products which have not yet been investigated. Zhemchuzhnuii and Shepelev,[4] prepare metallic phosphides by mixing the finely divided metal with red phosphorus and throwing the mixture in small lumps into a hot crucible. Some of the phosphorus burns while the rest unites with the metal. The melt is covered with a protecting layer of barium chloride and the temperature raised. Red phosphorus is then added in asbestos capsules, and more metal and phosphorus as desired. The mass is then investigated as an alloy. In this way but a single phosphide of cobalt is found to exist, Co_2P, which, however, is found in two distinct modifications.

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[1] *Compt. rend.*, 151, 12.

[2] *Ber.*, 43, 414, 1223.

[3] *Compt. rend.*, 150, 102.

[4] *Z. anorg. Chem.*, 64, 245.

The action of phosphorous and hypophosphorous acids on metallic salts has been studied by Sieverts,[1] who finds that cupric salts alone are reduced to a hydride by hypophosphorous acid. The oxidation of the acid to phosphorous acid corresponds to the accepted formula, CuH. Phosphorous acid reduces copper sulfate to metallic copper. Cupric chloride is reduced by both acids to cuprous chloride. Gold and silver salts are reduced by both acids to the metal and the same is true of palladium, while platinum chloride is not affected, nor are the salts of nickel and cobalt. More work has been done on hypophosphoric acid by Cornec,[2] who proposes as a better method of preparation, placing sticks of phosphorus between glass rods on the corrugated bottom of a developing tray, and partly covering with water. The tray is covered with a glass plate, and by putting ice on this the temperature can be controlled, if necessary. From cryoscopic determinations of the acid and its salts, Cornec inclines to the formula $H_4P_2O_6$, though the esters seem to have the simpler formula. Rosenheim[3] prepares hypophosphoric acid by a modification of a process proposed by Cornec, allowing yellow phosphorus to react with a solution of copper nitrate containing considerable nitric acid. The copper nitrate can be replaced by silver nitrate, but not by the nitrates of other metals, since the catalytic action of the copper or silver seems to be necessary. Good results were also obtained by the anodic oxidation of copper phosphide, while iron phosphide gave only phosphoric acid. The hypophosphoric acid is separated as the acid sodium salt, $NaHPO_3.2H_2O$, which is but slightly soluble. Guanidine carbonate is the best reagent for the detection of hypophosphates, forming a very slightly soluble salt, $(CN_3H_5)_4.H_2PO_3.5H_2O$. By this means it may be detected in mixtures of other phosphorous acids. The boiling point determinations of benzylhypophosphate in ether confirmed the results previously obtained with the methyl and ethyl esters and indicate the simpler formula as correct. The same was true of conductivity determinations of the acid. Rosenheim concludes that while the formula of the acid is H_2PO_3, it has a strong tendency to association in aqueous solutions, which accounts for the results obtained which seem to point to the formula $H_4P_2O_6$. Schmidlin and Massini[4] have prepared by the action of phosphorus pentoxide on hydrogen peroxide a phosphorus "monoper acid" analogous to the Caro acid, and possessing similar properties. Its formula is H_3PO_5. If sirupy pyrophosphoric acid in large excess acts on hydrogen peroxide, a perphosphoric acid is formed which from analogy has the formula $H_4P_2O_8$. Several hundred crystals of struvite are recorded by Böggild as having[5] been found in a well 10 to 35 meters deep, on Limfjord. The deposit contained many shells of mollusks and vegetable remains. The crystals were from 1 to 5 cm. in diameter and 1 to 5 mm. in thickness. Ephraim[6] has prepared barium and magnesium mono-oxy-trithiophosphates and barium dioxydithiophosphate ($Ba_3(PS_3O)_2.20H_2O$ and $Ba_3(PS_2O_2)_2.18H_2O$) by the restrained

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[1] *Z. anorg. Chem.*, 64, 29.

[2] *Bull. soc. chim.*, [4] 5, 1058, 1081, 1121.

[3] *Ber.*, 43, 2003.

[4] *Ibid.*, 43, 1162.

[5] *Neues Jahrb. Min. Geol.*, 1910, i, 335.

[6] *Ber.*, 43, 285.

action of barium (or magnesium) sulfide on sodium (tetra) thiophosphate. He has also prepared[1] a number of oxy-selenophosphates, but apparently the mono-oxytriseleno- and dioxydiselenophosphates form isomorphous mixtures. It was not found possible to prepare the tetraselenophosphates in solid form.

Steel describes[2] a deposit of feathery plates of pearly white luster of $As_2O_3.SO_3$ found in the iron sight tubes of a sulfur burner at Clyde, New South Wales. The burners used Japanese sulfur with a content of about 0.005 per cent. arsenic. The crystals were very hygroscopic and instantly decomposed by water. Ephraim has repeated[3] the work of Gibbs on the arseno-molybdates and fails to obtain any of the compounds made by Gibbs which had 3 : 5 : 12 : 24 and 3 : 2 : 8 : 13 ratios, but has prepared salts of potassium with 3 : 1 : 5 : 3 and 3 : 1 : 8 : 18 ratios, and sodium salts with 1 : 1 : 2 : 6 and 2 : 1 : 4 : 13 ratios, as well as ammonium barium and ammonium copper salts.

A new type of compounds is described by Ruff,[4] containing SbF_5 and $SbCl_5$ in the ratios 3 : 1, 2 : 1, 1 : 1, 2 : 3, 1 : 2, and 1 : 3. These are formed by direct mixture or by the action of chlorine on a mixture of SbF_3 and $SbCl_5$. They seem to be definit compounds, and the two constituents of the compounds are considered by Ruff as acting as elements, the affinity of SbF_5 lying between that of fluorine and chlorine while that of $SbCl_5$ is as strong as that of bromine. The affinity between the two constituents may be therefore considered as equal to that existing between fluorine and bromine, or between chlorine and iodine. He likens these compounds to such as $AgI.AgNO_3$ and $CaF_2.CaCl_2$. Ephraim[5] has made a study of the double halides of quadrivalent antimony, and concludes that the equilibrium $SbCl_3 + SbCl_5 \rightleftarrows 2SbCl_4$ is to a great extent dependent on the temperature and the possibility of ionization. He has also prepared triple salts containing $FeCl_3$ with quadrivalent antimony, and a number of salts of the alkylammonium halides, with trivalent and with quinquivalent antimony.

The solubility of bismuth sulfide in alkali sulfides and bismuth oxide in the alkalies has been re-investigated by Knox,[6] who finds that the sulfide is somewhat soluble in K_2S and Na_2S, the solubility increasing nearly proportionally to the third power of the concentration. This is accounted for by assuming the existence of a thio-bismuthic anion. The sulfide is insoluble in the hydrosulfides and in the higher polysulfides. In the disulfide it is only one-third as soluble as in the monosulfide. In ammonium sulfides it is practically insoluble. A slight solubility was found for bismuth oxide in sodium hydroxide. These results correspond to the position of bismuth in the periodic table.

Prandtl and Bleyer[7] have tried to prepare pure metallic vanadium by reduction of the pentoxide with aluminium or calcium-aluminium by the Goldschmidt process. The best results are obtained by using a

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[1] *Ber.*, **43**, 277.

[2] *J. Soc. Chem. Ind.*, **29**, 1142.

[3] *Z. anorg. Chem.*, **66**, 53.

[4] *Ber.*, **42**, 4021.

[5] *Ibid.*, 4447.

[6] *J. Chem. Soc.*, **95**, 1760.

[7] *Z. anorg. Chem.*, **64**, 217. *Ber.*, **43**, 2602.

fluorspar lining for the crucible or by adding fluorspar to the mixture, but in no case was a vanadium more than 95 per cent. pure obtained. As the ordinary impurities were absent, the result can only be accounted for by the presence of a lower oxide of vanadium, which alloys itself with an excess of the metal and so is protected from the action of the reducing agent.

A long paper by Weiss and Landecker[1] has appeared on the preparation and separation of columbic and tantalic acids, in which they describe critically the action of many reagents and methods of separation. To separate the metals they prefer to fuse with sodium carbonate and a minimum of saltpeter. The columbate melt is easily soluble in water and not precipitated by CO_2, while the tantalate melt is far less soluble and is precipitated by CO_2. Hence they warm the melt with very little water and wash the tantalate residue with sodium bicarbonate solution. Any columbate that goes into solution is precipitated by CO_2 and brief boiling. The tantalate residue is free from columbic acid, and is dissolved in sulfuric acid with the addition of hydrogen peroxide, from which the tantalum is precipitated by SO_2. If care is used as to temperatures and quantities of reagents, they claim that the separation is practically complete. The investigation of the halides of tantalum at the University of Pennsylvania laboratory has been continued.[2] Chapin applied the process by which Chabrié obtained the dichloride, $TaCl_2.2H_2O$, to the bromide, heating the pentabromide with sodium amalgam in a vacuum. The bromide obtained has the formula $Ta_6Br_{14}.7H_2O$. While the dichloride is green, this bromide is black, but gives a dark green powder in a mortar. Its solution is almost opaque. Only two atoms of bromine are precipitated by silver nitrate, and these may be replaced by other negative radicals, so that Ta_6Br_{12} proves to act as a bivalent base. A re-investigation of Chabrié's chloride shows that it also has a complex formula, being really $Ta_6Cl_{12}.Cl_2.2H_2O$, analogous to that of the bromide. Van Haagen finds that $TaBr_5$ is readily formed by heating the oxide with carbon in a current of dry bromine, fuses at 240° and boils at 320°. It dissolves in absolute methyl and ethyl alcohols with which it seems to form esters. Lower bromides, except the one described above, could not be prepared. The pentaiodide was made by distilling the bromide repeatedly in a current of hydrogen iodide. No oxy-iodide was found. Biltz[3] has prepared the sulfide of tantalum, which has the formula TaS_2, by heating the oxide in a stream of H_2S saturated with carbon disulfide. The reaction begins at 650° but is not complete at 900°. The sulfide is stable up to at least 1300°, but is hygroscopic and decomposes in warm, moist air. Biltz conjectures that the formula for the sulfide of columbium should also be CbS_2.

Group VI.—In connection with his work on the conditions of existence of matter,[4] von Veimarn describes the preparation of colloidal ice[5] by the sudden cooling in liquid air of saturated solutions of numerous salts, such as various thiocyanates, calcium chloride, aluminium sulfate, ferric

[1] *Z. anorg. Chem.*, 64, 65.

[2] THIS JOURNAL, 32, 323, 729.

[3] *Ber.*, 43, 1636.

[4] *Z. Chem. Ind. Kolloide*, 3, 282.

[5] *J. Russ. Phys. Chem. Soc.*, 42, 65, 69.

chloride, etc. In this way are formed completely transparent and stable glasses which contain solid solutions of ice. By adding small quantities of water to liquid air the water assumes in part a semi-solid condition, while by adding drops of liquid air to water the drops become covered with an elastic ice membrane. Wolfgang Ostwald[1] discusses the subject fully and describes colloidal ice solutions obtained by cooling dilute solutions of water in organic solvents such as toluene, xylene, etc. These solutions may be made more stable by the addition of protective colloids as mastic, or the aluminium salts of the fatty acids. They have a yellowish blue fluorescence and pass unchanged through the finest filter paper.

Jones has continued his work on hydrates in solution,[2] with especial reference to the temperature coefficient of conductivity, and finds further confirmation of the theory that the change in conductivity with the temperature is largely due to the decrease in complexity of the hydrates. The water of crystallization of many salts has been studied by Masson[3] by mixing with calcium carbide, and collecting the evolved acetylene over mercury. $ZnSO_4.7H_2O$, for example, loses five molecules of water in the cold, and one further molecule at 100°. Ammonium iron alum goes over in the cold into the trihydrate and at 145° into the monohydrate. Ammonium aluminium alum and common alum lose 10.5 molecules of water at 130°–160°, etc.

By pouring liquid sulfur at 400° into liquid air, von Veimarn[4] obtains threads of sulfur which are hard and brittle but which when the temperature rises become remarkably elastic. At ordinary temperature they pass rapidly into common plastic sulfur. He regards sulfur as presenting an especially good example of the tendency of those substances which can exist in numerous modifications to give most readily colloidal forms. Gardner and Hodgson[5] have investigated the tendency of wool, dyed with sulfur blacks, to deteriorate, especially in warm climates. They find that by boiling with ether it is possible to extract considerable quantities of sulfur from the dyes, alone, or on the fiber, and it is the ready oxidation of this finely divided sulfur that weakens the wool. No dyeing procedure obviates this difficulty, which proceeds from the decomposition of the dyestuff itself, in which the sulfur seems to be loosely combined. They find also that from "pure" antimony sulfide of commerce upwards of 35 per cent. of sulfur can be extracted by ether in 24 hours. This is quite in line with investigations of Jordis[6] on sulfides, in which he finds that sulfur can be more or less readily extracted, and this, whether working on sulfides formed by precipitation or by fusion. The conclusion is that sulfides, while definit in composition, nevertheless have their sulfur somewhat loosely combined, and it is given up to solvents more or less easily. Precipitated sulfides are, however, often if not generally, of indefinit composition. The ready formation of sulfuric acid in precipitated sulfides is not due solely to free sulfur which may be present, but to sulfur liberated from the sulfides.

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[1] *Z. Chem. Ind. Kolloide*, 6, 183.

[2] *Am. Chem. J.*, 43, 187.

[3] *J. Chem. Soc.*, 97, 851.

[4] *Z. Chem. Ind. Kolloide*, 6, 250.

[5] *J. Soc. Chem. Ind.*, 29, 672.

[6] *Z. angew. Chem.*, 23, 577.

The stability and decomposition products of silver sulfite have been studied by Baubigny.[1] Contrary to the ordinarily accepted view that in boiling water the sulfite decomposes into silver sulfate and metallic silver, he finds that silver dithionate is the principal product of the decomposition. Only at higher temperatures, as 200°, are any considerable quantities of sulfate and SO_2 formed, and these come from the decomposition of the dithionate. The same is true even when the alkali sulfite is in large excess. Precipitated silver sulfite has the normal formula Ag_2SO_3, and is scarcely soluble in water (less than 1 : 20,000). In the dark the precipitate is stable, but gradually darkens in the light. To determin the dithionic acid the evaporated solution is heated with sodium carbonate and saltpeter, since neither aqua regia nor bromine oxidize it completely to the sulfate. This decomposition confirms the formula $H_2S_2O_6$ (and not HSO_3 as held by Kolbe). It also furnishes a new argument for the asymmetrical formula, $H.SO_2.OH$, since in the silver salt the two silver atoms act differently. It agrees also with the asymmetrical formula for thiosulfuric acid, $HS.SO_2.OH$. According to this view, dithionic acid is to be looked on as disulfonic acid, $HO_3S.SO_3H$, sulfurous acid as hydrogen monosulfonic acid, $H.SO_3H$, thiosulfuric acid as the monosulfonic acid of hydrogen sulfide, $HS.SO_3H$, and benzene sulfonic acid as the monosulfonic acid of phenyl, $C_6H_5.SO_3H$. The last is monobasic, while sulfurous and thiosulfuric acids are dibasic, since in these latter there is retained a typical hydrogen atom of the original H_2 and H_2S molecule. The reaction between sulfuryl chloride and ammonia, first studied by Traube and Hantzsch, has been further investigated by Ephraim and Michel.[2] Instead of the expected sulfamide, $SO_2(NH_2)_2$, a series of much more complicated imides is formed whose formulas can be expressed by $NH_2.(SO_2.NH)_x.SO_2.NH_2$. These compounds give silver salts in which the hydrogen is partly or completely replaced by silver. In other efforts to prepare sulfamide, the chloroamide of sulfuric acid, $ClSO_2.NH_2$, and the ammonium salt of chlorosulfuric acid, $ClSO_2.ONH_4$, were formed, both hitherto undescribed. The best results in the preparation of sulfamide were obtained by the method proposed by Ruff, where sulfuryl chloride is slowly dropped into liquid ammonia. A mixture of the ammonium salt of imidosulfamide, $NH.(SO_2.NH_2)_2$, and ammonium chloride is first obtained, which after acidification is gently evaporated to dryness. The ammonium imidosulfamide is converted by hydrolysis into amino sulfuric acid and sulfamide, the latter being extracted by dry acetic ester, from which it crystallizes in great purity.

Pellini[3] finds but one compound of mercury and selenium, HgSe, which is formed slowly and in an impure condition by rubbing the elements together in a mortar, but better by heating molecular quantities under pressure to 550°–600°, or by heating mercury with an excess of selenium at ordinary pressure. By rubbing together mercury and tellurium, the telluride, HgTe, is formed more readily than the selenide, but the compound is less stable and decomposes in a vacuum at 370°. According to Olivari[4] the molecule of selenium in fused $HgCl_2$ solution varies from

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[1] *Compt. rend.*, **149**, 735, 858; **150**, 973. *Bull. soc. chim.*, [4] **7**, 4, 51.

[2] *Ber.*, **42**, 3833; **43**, 138.

[3] *Atti accad. Lincei, Rome*, [5] **18**, ii, 211.

[4] *Ibid.*, 94.

Se_2 to Se_4 when the solution is dilute, but in more concentrated solutions tends toward Se_8. In similar solution the S_8 molecule shows greater stability. Tellurium, when heated with mercuric chloride, reacts, with the formation of HgCl and $TeCl_2$. Investigation by Beckmann[1] renders the existence of $SeCl_2$ highly improbable, the only two chlorides of selenium being Se_2Cl_2 and $SeCl_4$. Unlike the case with sulfur, $SeCl_4$ is by far the most stable. With bromine and selenium are formed mixtures of Se_2Br_2 and $SeBr_4$ but no $SeBr_2$. While boiling point determinations show the molecule of sulfur in bromine is S_2, selenium has under the same conditions a monoatomic molecule. When aqueous solutions of KSeCN and $HgCl_2$ react in the proportion of 2 : 1, Rosenheim and Pritze[2] find that $Hg(SeCN)_2$ is precipitated in white needles, which are decomposed by hot water with the separation of selenium. If the proportion is 1 : 1, Hg(SeCN)Cl is precipitated in yellow needles, soluble in absolute alcohol. If the proportion is 3 : 1, $KHg(SeCN)_3$ crystallizes out as yellow needles, somewhat soluble in water, while if the proportion is 4 : 1, $K_2Hg(SeCN)_4$ is formed, easily soluble in water and alcohol, crystallizing from absolute alcohol in amber plates. Crystallin $CoHg(SeCN)_4$ and $ZnHg(SeCN)_4$ were formed by double decomposition from the potassium salt, showing the existence of the complex anion $Hg(SeCN)_4^{--}$, and thus indicating the relation of the selenocyanates to the thiocyanates. No complex salts containing cobalt (bivalent) or trivalent iron or chromium could be formed. From a solution of mercuric nitrate, sodium selenite precipitates the mercury salt, $HgSeO_3$, as a white crystallin powder, which is very soluble in a solution of sodium selenite, with formation of $Na_2Hg(SeO_3)_2$. Conductivity determinations showed unmistakable evidence of the existence of mercuriselenite anions, which are, however, largely hydrolyzed in dilute solution. $NaSeO_3.HgCl.2H_2O$ was also formed by the action of one molecule of $HgCl_2$ on one molecule of Na_2SeO_3.

The investigations of Flint on the complexity of tellurium have been continued.[3] Working on a kilogram of crude dioxide by fractionating the chloride by precipitation with water, the tenth fraction, which consisted of 23 grams, showed an atomic weight of 124.3, while the original material gave the accepted atomic weight of 127.5. Fractionating by solution in nitric acid gave the atomic weight of the less soluble portion as 126.51. Work with the less hydrolyzed portion in the first fractionation revealed some difference in properties from pure tellurium, and this portion is now being investigated. Tibbals[4] has prepared sodium telluride by fusing sodium and tellurium in a hydrogen atmosphere and recrystallizing from water with careful exclusion of air. Na_2Te crystallizes in colorless crystals which contain much water of crystallization. The solution dissolves metallic tellurium up to the composition Na_4Te_3. By double decomposition a number of metallic tellurides were prepared in the wet way for the first time, and the following are described: $ZnTe.H_2O$, $Ni_2Te_3.4H_2O$, which by heating goes into NiTe, $Co_2Te_3.4H_2O$, $Pb_2Te_3.4H_2O$, Ag_2Te, CuTe, Cu_2Te_3. A telluride of arsenic goes into solution in excess, indicating a telluro-arsenite. Gold and platinum are precipitated as metals from chloride solution, $TeCl_4$ being formed.

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[1] *Z. physik. Chem.*, 70, II. *Arrhenius Festband*, 1.

[2] *Z. anorg. Chem.*, 63, 275.

[3] *Ibid.*, 68, 251.

[4] THIS JOURNAL, 31, 902.

The influence of a second solute on crystallization is shown by work of Hauser and Herzfeld[1] on potassium dichromate. When to a hot, three-fourths saturated solution of the ordinary triclinic salt is added an equal quantity of a saturated solution of potassium thiocyanate, and the whole allowed to cool, the potassium dichromate crystallizes out in monoclinic prismatic plates of yellowish brown color with a bronze luster. The specific gravity of these crystals is 2.10, while that of the ordinary form is 2.67. These crystals are metastable and probably isomorphous with ammonium dichromate. By heating the carbonates with chromic acid in a closed tube, Briggs[2] has obtained cobalt chromate both anhydrous and as dihydrate, and also nickel chromate, $NiCrO_4$. The latter is stable in water and hardly attacked by nitric acid. By evaporating solutions of the carbonates with chromic acid in excess, Gröger[3] has prepared the dichromates of zinc, cadmium, copper and cobalt, all as hydrated salts. These dichromates have a great tendency to decompose into the normal chromate and higher chromates. By using the proper proportion of the constituents and evaporating in a vacuum over sulfuric acid, cadmium trichromate, $CdCr_3O_{10}.H_2O$, and copper tetrachromate, $CuCr_4O_{13}.2H_2O$, were obtained. The work of Weinland on hexa-acetato-trichromium bases has been continued.[4] Numerous salts of the tribasic cation $(Cr_3(CH_3.COO)_6(OH_2)_2)^{+++}$ are described, as well as of the cations $(Cr_3(CH_3.COO)_6(OH_2)(OH))^{++}$ and $(Cr_3(CH_3.COO)_6(OH)_2)^{+}$. Similar cations are formed with iron in the place of chromium, and also with Cr_2Fe and $CrFe_2$. Both chromium and iron cations have also been obtained with pyridine in the place of the water in the cation, and in the case of the chromium cation with NH_3 in the place of the water. Weinland calls attention to the fact[5] that in the official ferric acetate solution, the deep red color is due to the presence of the $(Fe_3(CH_3.COO)_3(OH)_2)^{+}$ cation. This base also lies at the foundation of the ordinary acetic acid reaction with ferric chloride. Bjerrum[6] has studied the conductivity and the transition velocity of the chlorochromisulfates, and has also prepared analogous sulfates in which the hexahydrated chromium atom of $(CrCl_2(OH_2)_4)(Cr(OH_2)_6)^{++++}$ is replaced by aluminium, by iron and by vanadium, and he has also prepared the corresponding bromosulfates.

In his investigations of molybdenum, Rosenheim[7] has prepared the so-called dichloride of Blomstrand and confirms the latter's trimolecular formula, Mo_3Cl_6. It crystallizes from hydrochloric acid with one molecule of acid and four of water. The loss of water and acid on heating show its constitution to be $(Mo_3Cl_6.H_2O)HCl.3H_2O$. With alkalies it gives $Mo_3Cl_4(OH)_2$ and with ammonia $(NH_4)Mo_3Cl_7(NH_3)$. The amount of its reduction of ammoniacal silver confirms the bivalence of the molybdenum., Rosenheim[8] has also further studied the double cyanides, which

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[1] *Z. physik. Chem.*, 68, 175.

[2] *Z. anorg. Chem.*, 63, 325.

[3] *Ibid.*, 66, 7.

[4] *Ber.*, 42, 2997, 3881; 43, 2144. *Z. anorg. Chem.*, 67, 167, 250.

[5] *Arch. Pharm.*, 248, 337.

[6] *Z. anorg. Chem.*, 63, 140, 151.

[7] *Ibid.*, 66, 1.

[8] *Ibid.*, 65, 166.

contain the $Mo(CN)_8^{----}$ anion, and in which the oxidation with potassium permanganate and also with ammoniacal silver shows the molybdenum atom to be quinquivalent. The free acid $H_4Mo(CN)_8.6H_2O$ was prepared. The only suggestion regarding the valence is that the complex may be really $Mo_2(CN)_{16}^{''''''}$, and the two molybdenum atoms united with each other; of this, however, there is no experimental evidence. Salts of the anion $MoO_2(CN)_4^{----}$ were also prepared, the constitution being more probably $Mo(OH)_4(CN)_4^{----}$. Ephraim[1] in his studies of the molybdates has prepared lithium, rubidium and cesium molybdates of numerous different ratios, as well as numerous phospho- and arsenomolybdates of these three alkalies, while Miolati[2] has prepared telluromolybdates and formomolybdates, and Mazzucchelli,[3] oxalo-permolybdates.

A very full investigation of the methods for preparing metallic tungsten is described by Weiss.[4] Reduction by metallic aluminium from wolframite gives a regulus containing about 80 per cent. tungsten, and reduction of the amount of aluminium gave no better results, for while less iron and manganese were reduced, the same was true of the tungsten, as only 2/3 of the tungstic acid present was recovered as metal. This method can possibly serve to prepare a carbon-free alloy of tungsten with some iron and manganese for use in steel-making. Wolframite is completely resolved by fusion with sodium carbonate or caustic soda, and also with lime. In the last case, though its outward appearance seems unchanged, it is rendered largely soluble in hydrochloric acid. Fusion with calcium carbonate and salt is a method which may be of technical value. Tungstic acid can be reduced by zinc powder to a crystallin regulus containing at least 99.8 per cent. tungsten. No satisfactory method was found for the direct preparation of tungsten from scheelite, nor from the sulfide. By the use of a vacuum electric furnace tungsten can be satisfactorily fused, and the metal obtained is very resistant.

A number of uranium compounds have been studied by Wyroubow,[5] chiefly from a crystallographical standpoint. $U(SO_4)_2$ exists as octo- and nonohydrate, isomorphous with thorium sulfate. Four distinct types of uranyl oxalates of the alkalies were obtained.

Group VII.—A new form of apparatus for preparation of fluorine is described by Gallo,[6] and the result of experiments to prepare a compound of fluorine with oxygen. The mixed dry gases were passed through an ozone apparatus, and after a few moments a strong explosion occurred, shattering the apparatus. Gallo thinks it probable that there had been formed an exceedingly unstable endothermic compound of oxygen and fluorine. A series of double fluorides of thallium has been prepared by Ephraim,[7] including those of manganese, antimony, vanadium, tantalum, and tungsten.

The work of Richards on atomic compressibility has been continued,[8]

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[1] *Z. anorg. Chem.*, 64, 258, 263; 65, 233, 237.

[2] *Z. physik. Chem.*, 70, II. *Arrhenius Festband*, 330.

[3] *Atti accad. Lincei, Rome*, [5] 18, ii, 259.

[4] *Z. anorg. Chem.*, 65, 279.

[5] *Bull. soc. franç. min.*, 32, 340.

[6] *Atti accad. Lincei, Rome*, [5] 19, i, 206, 295, 753.

[7] *Ber.*, 42, 4456.

[8] *Z. physik. Chem.*, 71, 152.

comparing the compressibility of the halides of potassium, sodium, thallium and silver, with that of the constituent elements. While the molecular compressibility is in every case less than that of the constituents, there is a marked difference in the amount of this lessening. For example, thallium is hardly one-tenth as compressible as sodium, yet its halides are more compressible than those of sodium. The facts indicate that the specific volume of compounds is strikingly dependent upon the chemical affinities of the constituents.

Bourion[1] has further developed his work on the preparation of anhydrous chlorides by heating the oxide in a current of chlorine saturated with chloride of sulfur. The chlorides of the rare earths are readily formed by this method and a large number of them are described, as well as methods of determining tungsten and the quantitative separation of cerium, thorium and glucinum. In his work on double halides, Ephraim[2] finds that manganese has little tendency to form double bromides, $CaMnBr_4.4H_2O$ being the only one he could prepare. Two calcium-zinc chlorides were found, $CaZnCl_4.5.5H_2O$ and $Ca_2ZnCl_6.6H_2O$, but only one of each of the other alkaline earths, $SrZnCl_4.4H_2O$ and $BaZnCl_4.2.5H_2O$. The sodium and ammonium zinc iodides are constituted after the type $NaZnI_3$, while the potassium salt is K_2ZnI_4, and the double iodides of the alkaline earths are of the same type. All the double iodides are hydrated. A number of chlorates and perchlorates of ammonia bases are described by Salvadori,[3] who suggests a strongly ammoniacal solution of ammonium perchlorate for the separation of cadmium from copper. $Cd(NH_3)_4(ClO_4)_2$ is insoluble and immediately precipitated, while the copper salt is precipitated only slowly, even from concentrated solutions. A weakness of the separation consists in the fact that the cadmium precipitate carries copper, if present, down with it, though the method serves excellently to detect cadmium in the presence of copper. The resistance of chlorates, perchlorates, iodates, periodates and bromates to reduction is discussed by Vitali,[4] and he finds that chlorates are reduced by aluminium in dilute sulfuric acid while perchlorates are not. No distinction was found between iodates and periodates, and both these and bromates resemble chlorates in showing less resistance to reducing agents than the perchlorates. The so-called hypoiodic acid is considered by Skrabal and Buchta[5] to be really a base, I.OH, which is relatively stable in very dilute solutions. In the presence of hydrochloric acid ICl is formed, which by great HCl concentration is exceedingly stable. In sulfuric acid solution the base is unstable owing to hydrolysis, but its stability is much increased by the presence of free halogens, in which case ICl_2OH and I_3OH are formed. Free iodine hydroxide decomposes, according to the acidity of the solution, into iodine and iodic acid.

Group VIII.—The relation of iron solutions to nitric oxide has been studied by Manchot,[6] who finds the absorption of NO is less in ferrous sulfate solutions containing dilute sulfuric acid than in those of pure

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[1] *Ann. chim. phys.*, [8] 20, 547.

[2] *Z. anorg. Chem.*, **67**, 376, 379.

[3] *Gazz. chim. ital.*, **40**, ii, 9, 19.

[4] *Giorn. farm. chim.*, **59**, 18.

[5] *Chem.-Ztg.*, **33**, 1184.

[6] *Ann.*, **372**, 153, 179.

water, but that in solutions containing concentrated sulfuric acid (82 per cent.) a maximum of one molecule of NO to one molecule of $FeSO_4$ is reached. The same limit is attained in a 34 per cent. HCl solution. Many other solvents and additions to the solutions were tested, but in no case was the maximum of 1 : 1 passed. On the other hand, while nitric oxide is not absorbed by aqueous solutions of ferric sulfate, in the presence of concentrated sulfuric acid (90.6–97.6 per cent.) a maximum absorption of two molecules NO to each iron atom was attained, and the compound formed may be considered as $Fe_2(SO_4)_3.4NO$. From this it seems to follow that since in hemoglobin the absorption of nitric oxide is in the proportion of two molecules for each atom of iron, the iron of the blood is in the ferric condition. The compound $2FeSO_4.NO.13H_2O$ was isolated, which Manchot considers to be $FeSO_4.NO$ crystallized with $FeSO_4$. Le Chatelier[1] and also Konstantinov[2] have investigated the phosphides of iron, the latter with especial reference to the metallurgy of the metal, a diagram of the iron-phosphorus system being given. Out of the nine different phosphides which have been described by different workers, Le Chatelier finds the following only to be chemical individuals: Fe_3P, Fe_2P, FeP and Fe_2P_3. The preparation and properties of each are described.

Ephraim[3] shows that the NH_3 of $CoC_2O_4.4NH_3$ is progressively replaced by H_2O by standing in the air, $CoC_2O_4.4H_2O$ being ultimately formed. The latter salt can be directly prepared from aqueous solution. Each member of the series was isolated. Of the double cobalt oxalates both $(NH_4)_2CoOx_2.6H_2O$ and $(NH_4)_4CoOx_3.6H_2O$ were prepared. Three of the nitrite groups in sodium cobaltinitrite (sodium nitritocobaltiate) can be replaced according to Hofmann and Buchner[4] by the hydroxyl group by the action of guanidine carbonate, guanidine or sodium-guanidine salts of the trihydroxy-trinitrito-cobaltiate, $Co(NO_2)_3(OH)_3^{---}$, being formed. From certain differences between the guanidine and the sodium-guanidine salts, it is conjectured that the anion may exist in two isomeric forms.

In preparing osmium for atomic weight determination, Gutbier and Maisch[5] put it into solution by repeated heating with salt in chlorine, and from the sodium hexachloro-osmate, which could not be obtained in a pure condition, prepared the other alkali chlorides by double decomposition. The chloro-osmates decompose slowly on standing in aqueous solution. The rubidium and cesium salts are almost insoluble in water. Ruff[6] has also studied the chlorides as well as the oxides of osmium. To prepare osmium tetroxide he distils with concentrated sulfuric acid and chromic acid, instead of nitric acid. Reduction in acid solution with alcohol, formaldehyde, or hydrazine gives the dioxide, but in a colloidal condition which is difficult to filter. It may be precipitated by barium sulfate. It is better, however, to precipitate with alcoholic potash, heat on a water bath, and exactly neutralize with sulfuric acid. The

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[1] *Compt. rend.*, 149, 709.

[2] *J. Russ. Phys. Chem., Soc.* 41, 1220.

[3] *Ber.*, 42, 1624.

[4] *Ibid.*, 3389.

[5] *Ibid.*, 4239.

[6] *Z. anorg. Chem.*, 65, 429.

dioxide is then precipitated completely and settles well. If filtered at once it decomposes explosively when dried at 100°–150°, but if heated for several hours on the water bath before filtering, it may be gradually heated in a carbon dioxide atmosphere to 250° and weighed. The use of titration with potassium permanganate for the estimation of osmium is possible with certain precautions, but presents few advantages. When osmium is heated in chlorine, the product obtained depends upon the temperature and the rapidity of cooling. If rapidly cooled, the chief product is $OsCl_3$, which heated in a vacuum to 560°–600° decomposes into the volatil $OsCl_4$ and leaves the non-volatil $OsCl_2$. By slow cooling $OsCl_4$ is obtained. It is insoluble in water and other solvents except the strong oxidizing acids. $OsCl_2$ is also but slightly soluble. On the other hand, $OsCl_3$, even in anhydrous condition, is soluble in water, unlike the anhydrous trichlorides of the other platinum metals.

A large number of hexachloro-iridates and hexabromo-iridates of organic bases have been prepared by Gutbier.[1] Iridium tetrachloride was made by passing chlorine over iridium mixed with KCl or NaCl, at a low red heat, from this preparing the ammonium salt by precipitation with NH_4Cl, decomposing the ammonium in this by chlorine, and finally distilling the water and HCl off at 40° in a moderate vacuum. The organic salts were formed by precipitating hexachloro-iridic acid with solutions of the chlorides of the bases. When bromides of the bases were used, the precipitated salts were still *chloro*-iridates, but on boiling these with hydrobromic acid, they were changed over into the hexabromo-iridates. Bromine does not act directly on iridium, nor on a mixture of iridium with sodium bromide to more than a very slight extent, but the chloride is converted into the bromide by boiling with excess of hydrobromic acid. In general the bromo-salts are more soluble than the corresponding chloro-salts. Vèzes and Dufour[2] have made an extended study of the complex derivatives of iridium containing oxalic cid. By heating chloro-iridates or iridites with potassium oxalate, derivatives of dichloro-dioxalato-iridous acid are formed, several of which are described. The free acid, $H_3IrCl_2(C_2O_4)_2.4H_2O$, was also obtained. By boiling the salts of this acid with a concentrated solution of a nitrite, one-half the oxalate group is exchanged for nitrite groups, and a series of dichloro-dinitrito-oxalato-iridites was obtained. Work on iridium sulfates has been continued by Delépine,[3] who finds two series of salts, one derived from $(Ir(SO_4)_2(OH)_2)^{---}$, and the other from $(Ir(SO_4)_2(OH_2)OH)^{--}$. The change from one anion into the other seems to present a case of inorganic tautomerism. Delépine has also prepared silver chloro-iridate, which is unstable and goes over on standing into the iridite, and also the ammonia-silver iridite, $Ag_3(NH_3)_6.IrCl_6$, which was supposed by Claus to be merely another form of silver chloro-iridite. Thallium chloro-iridite and chloro-iridate were also prepared.

Compounds of platinum with a valence of three and with a valence of six have been discovered by Wöhler and Martin.[4] By anodic oxidation of a solution of hydrated platinum dioxide in caustic potash at low tem-

[1] *Z. physiks. Chem.*, **69**, 304. *Ber.*, **42**, 3905, 4770.

[2] *Bull. soc. chim.*, [4] 5, 869, 872; **7**, 507, 512.

[3] *Compt. rend.*, **149**, 785, 1072. *Bull. soc. chim.*, [4] **5**, 1084.

[4] *Z. Elektrochem.*, **15**, 769, 791. *Ber.*, **42**, 3326, 3958, 4100.

perature, thin gold-like scales are obtained which are probably $K_2O.3PtO_3$. The potassium is removed by dilute acid and the trioxide, PtO_3, is obtained, which is extremely unstable. By the careful chlorination of $PtCl_2$, or dechlorination of $PtCl_4$ at 390°, $PtCl_3$ was obtained as a greenish black powder, which is slightly soluble in cold water, and which dissolves rapidly in boiling water with the formation of the acid H_2PtCl_3O, some hydrolysis also taking place. By precipitation with sodium carbonate pure platinum sesquioxide hydrate was obtained, but the sesquioxide could not be prepared. The hydrate dissolves in hydrochloric acid but the solution immediately decomposes into a mixture of chloroplatinous and chloroplatinic acids. If, on the other hand, cesium chloroplatinite in dilute solution is treated with chlorine water a dark green precipitate of the "sesquichloride," or pentachloride, Cs_2PtCl_5, is obtained, which has a strong tendency to decompose into the chloroplatinite and chloroplatinate. According to Werner's nomenclature, the platinum acids would receive the following names: H_2PtCl_4, tetrachloro-plat*o*-acid; H_2PtCl_5, pentachloro-plat*i*-acid; H_2PtCl_6, hexachloro-plat*e*-acid; H_2PtO_4, plat*on*-acid. In addition to the iridium salts spoken of above, Gutbier[1] has prepared similarly a large number of salts of bromoplatinic acid with organic bases. His bromoplatinic acid was prepared by evaporating chloroplatinic acid several times on the water bath with hydrobromic acid, the last time with the addition of bromine. The free acid, $H_2PtBr_6.9H_2O$, was obtained by evaporation over lime. The two isomers of the compounds of platinum dichloride with organic sulfides are accounted for by Werner by stereoisomerism. The third modification of the methyl sulfide salt, it has been suggested, may be constituted after the type of the green salt of Magnus. This, Chugaev and Subbotin[2] now show to be the case, its constitution being, in fact, $(Pt.4(CH_3)_2S)PtCl_4$. Further, it is found that other organic sulfides can form platinum salts after this same type. By the action of formaldehyde on a solution of potassium chloroplatinate and selenium dioxide in an excess of caustic potash, Minozzi[3] has obtained platinum triselenide, $PtSe_3$, which on heating to a low red heat in carbon dioxide gives the diselenide, $PtSe_2$. Both are stable compounds, little acted on by acids.

The experiments of Fischer and Schröter on argon have been extended[4] and 45 metals examined in the electric arc in liquid argon. In no case could argon compounds be obtained, nor was there any evidence of the formation of any such even transitionally.

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NOTES.

The Efficiency of the Borax Bead Tests for Nickel and Cobalt.— In order to determine the reliability of the borax bead tests for nickel and cobalt (in the presence of each other), a few simple tests were carried out. As the object of these experiments was to ascertain the efficiency

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[1] *Ber.*, 42, 4243.

[2] *Ibid.*, 43, 1200.

[3] *Atti accad. Lincei, Rome,* [5] 18, ii, 150.

[4] *Ber.*, 43, 1435, 1442, 1454, 1465.