ceptacle, diameter (internal) and depth (internal), each 9.5 cm.; thickness of wall, 1 cm.; the small cylinder support, length, 3.5 cm.; diameter (adjusted to the size of burner in which it is to rest), in our case, 5.2 cm. outside, and 3.5 cm. inside.

These muffles may, of course, be used with any common Bunsen burner by placing them on a tripod.

The accompanying cut shows the parts of the battery of muffles: 1 is the gas-supply pipe, 2.5 cm. in diameter; 4 is a smaller pipe, provided with an air-hole and gas-cock, which feeds the Argand burner above; 2 shows the muffle in position and without asbestos covering; at 3 is a small hole through which the gas is lighted, and through which the flame may be seen and regulated; 5 gives an inside view of the muffle; 6 shows the under part of a muffle; 7 shows the top side of a graphite lid, the central vent-hole of which is hidden by its handle; and 8 and 9 are top and bottom views of the asbestos-aluminum-platinum lids.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

By Jas. Lewis Howe.

Few notable papers have appeared during the past year on theoretical inorganic chemistry. Perhaps the most important is one by Abegg[1] on a new theory of valence. The author assumes the existence of two kinds of valence, with opposite polarity, in each atom. These he calls normal valence and contra-valence. The sum of the valences of an atom is eight. Thus chlorine has a negative normal valence of one and a positive contra-valence of seven. Negative contra-valences are much weaker than positive, since positive electrons are much more firmly attached to matter than the negative. The inert gases have a normal valence of zero and an (unexercised) contra-valence of eight. In his paper, Abegg applies these conceptions to the so-called molecular compounds.

In two papers,[2] Werner has developed his theory of primary and secondary valences with reference to the constitution of the ammonium and the oxonium compounds. Locke[3] has again attacked the theory of electro-affinity of Abegg and Bodländer, and holds that while the electro-affinity of the elements bears a close and interesting relation to the properties of many salts, it does not furnish a rational principle for chemical classification.

Erdmann claims[4] that the distinction enunciated by him in

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[1] *Vid. Skrift.* I, 1902, No. 12.

[2] *Ann. Chem.* (Liebig), **322**, 261, 296.

[3] *Am. Chem. J.*, **28**, 403.

[4] *Ztschr. anorg. Chem.*, **32**, 404.

1892, between metals and non-metals, *viz.*, that metals are those elements whose molecules consist of single atoms, while non-metals are those whose molecules contain several atoms, has been confirmed by all the more recent work along this line. On the other hand, Martin,[1] reasoning from the fact that in the same group the metallic characteristics of an element increase with the atomic weight and that among the non-metals the metallic character increases with the temperature, draws the conclusion that the metallic and non-metallic conditions are merely phases which each element can assume. At higher temperatures non-metals become metallic, their electrical conductivity increasing rapidly; in the vicinity of absolute zero, metals become non-conducting metalloids.

In the consideration of the periodic table, Brauner[2] suggests that the difficulty of accounting for the place of the rare earths will be minimized if we put them as a group in the place usually assigned to cerium. Thus, in this place we shall have *Ce, etc., 140-178*, followed immediately in the next space by *Ta 184*. In this way the vacant ninth period of Mendeléeff's table disappears. Brauner begins his table with Group 0, which is made up of the inert gases.

The study of double salts continues to attract increasing attention, though no satisfactory theory of their constitution has yet appeared. An important contribution to the chemistry of the double halides is the *Habilitationsschrift* of P. Pfeiffer.[3] Following up the systematic treatment of the double chlorides by Werner, he takes up the bromides and iodides from the same standpoint, and after a theoretical discussion of these salts, he gives a systematic survey of the whole field, with references to the literature. In connection with his study of vanadium salts, in which many new double halide compounds have been prepared, Ephraim[4] discusses these salts from a theoretical standpoint, holding that their constitution is largely dependent upon the atomic volume of the constituent elements. In particular, he formulates the law that the number of halogen alkali molecules which can unite to the halide of the heavy metal acting as a central nucleus, decreases with the increasing atomic weight of the positive metal. Grossmann[5] denies that the facts accord with this law. In a number of cases, such as $PbBr_2,4CsBr$, the highest value is reached with the cesium salt. Rubidium and ammonium salts often show a strong analogy which may be conditioned by the fact that they possess a similar atomic volume. Nor do the double cyanides, which are, according to Werner, of the same character as the halides, follow Ephraim's law. Grossmann's conclusion is that

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[1] *Chem. News*, **86**, 295.

[2] *Ztschr. anorg. Chem.*, **32**, 1.

[3] Partially republished in *Ztschr. anorg. Chem.*, **31**, 191.

[4] *Ber. d. chem. Ges.*, **36**, 1177.

[5] *Ibid.*, **36**, 1600.

no comprehensive rule can be, at present, laid down regarding the composition of double salts. The discussion is being continued by Ephraim,[1] who has also prepared a series of new antimony double salts, and by Grossmann,[2] while Pfeiffer[3] and Jordis[4] both fail to find an experimental foundation for Ephraim's law. The probability is that there is a considerable sub-stratum of truth in the so-called law, but that it represents only a part of the truth. At all events, it is encouraging to find an increasing number of keen minds attacking this important problem of the double salts. Mention should be made, in this connection, of the interesting class of triple thiocyanates under investigation by Wells,[5] and the double periodates and manganese studied in the same laboratory by Price.[6]

In an address before the Fifth International Congress of Applied Chemistry at Berlin, Moissan gave a review of his work on the metallic hydrides. The alkali and alkali-earth hydrides are definite crystalline compounds and have nothing of the nature of hydrogen alloys. They are strong reducing agents, decomposing water with the evolution of hydrogen, forming formates with carbon dioxide and hydrosulphites with sulphur dioxide. With acetylene they form double compounds, of which $K_2C_2.H_2C_2$ is a type; on heating the latter, acetylene is evolved and the metallic carbide left.

A new preparation of nitrides has been discovered by Guntz.[7] When lithium nitride acts upon metallic chlorides, much heat is evolved and the corresponding nitride formed. This appears to be a method of general application. Lithium hydride seems to give a similar reaction, but it is so violent that it has not yet been possible to isolate the hydride, which is formed.

Moissan continues to enlarge our knowledge of the silicides. While it has been found very difficult to prepare the potassium and sodium silicides corresponding to silicon-ethane, Si_2H_6, the lithium compound, Li_6Si_2, is prepared by direct union of the elements in a vacuum. It is naturally a very active substance, decomposing water and acids generally with evolution of hydrogen, but when very concentrated hydrochloric acid is used the silicon-ethane is obtained, which is collected as a liquid by the use of liquid air.[8] Moissan has also prepared two silicides of vanadium, V_2Si and VSi_2. Lebeau has studied the silicides of cobalt, manganese and chromium. In the case of the last two metals, he has investigated, from a physical standpoint, the equi-

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[1] *Ber. d. chem. Ges.*, **36**, 1815, 1912.

[2] *Ibid.*, **36**, 2499.

[3] *Ibid.*, **36**, 2519.

[4] *Ibid.*, **36**, 2539.

[5] *Am. Chem. J.*, **28**, 245; **29**, 474; **30**, 184.

[6] *Ibid.*, **30**, 182.

[7] *Compt. Rend.*, **135**, 738.

[8] *Ibid.*, **134**, 1083, 1549; **135**, 1284.

librium which exists between copper, silicon and manganese, and copper, silicon and chromium. This has enabled him to prepare several new silicides.[1]

Muthmann and Kraft[2] have prepared the hydrides and nitrides of cerium and lanthanum by burning the metals in hydrogen or nitrogen. In hydrogen, cerium ignites at 250°, while in pure oxygen its kindling temperature is little above 150°. In nitrogen, cerium does not ignite until 850° is reached. The kindling temperature of lanthanum is, in each case, somewhat higher than that of cerium. The hydrides and nitrides of these metals are stable in dry air, but are quickly decomposed by water or in the presence of moisture.

Several articles have appeared from the laboratory at Odessa, continuing the work of Pissarjewski on the compounds of inorganic salts and acids with hydrogen peroxide. The carbonates, arsenates, tungstates, uranates, vanadates, and the rare earths are included in this list. There is a very decided question as to whether many of these compounds are to be considered as true peroxides, or whether some of them, which have been designated as pseudo-peroxides, should not rather be considered as compounds in which the hydrogen peroxide is present in the form of a so-called peroxide of crystallization. This is discussed by Tanatar in a recent paper,[3] and by Willstätter.[4] A new class of peruranates has also been described by Alloy,[5] having the formula M_2UO_5. In a lecture at the meeting of the Verein of the German chemists at Düsseldorff, Staedel illustrated the preparation of pure hydrogen peroxide. A 95 per cent. solution was solidified by the ether-carbon dioxide mixture. When, to a new portion of the 95 per cent. solution, at a temperature of —10°, a little of the solid is added, crystals of pure hydrogen peroxide begin to form. On recrystallization, these consist of 100 per cent. hydrogen peroxide, and this is suggested as the safest method of preparing the anhydrous compound. The crystals are fairly stable, but are exploded at once by contact with platinum black or pyrolusite. With the monohydrate of sulphuric acid, ozone is at once formed. Some interesting notes on ozone are contributed to the *Berichte* (**35**, 2902) by Arnold and Mentzel. Tetramethyl-*p*-*p*'-diaminodiphenylmethane (tetra-base for short) is proposed as the best reagent for gaseous ozone, to differentiate it in the presence of other gases which have action upon starch-iodide paper. Ursol D, which had been suggested by Chlopin for a similar purpose, is shown to be useless, as its supposed characteristic reaction is caused by the impurities present and not by ozone.

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[1] *Compt. Rend.*, **136**, 231, 1329.

[2] *Ann. Chem.* (Liebig), **325**, 261.

[3] *Ber. d. chem. Ges.*, **36**, 1893.

[4] *Ibid.*, **36**, 1828.

[5] *Bull. Soc. Chim.* (3), **29**, 292.

Dudley[1] has studied the action of sodium peroxide on several more metals. With nickel, $Ni_3O_4,2H_2O$ is formed, which loses water at 240°. It is unlike Daubigny's Ni_3O_4 in its properties. Iron gives Fe_3O_4,H_2O in tabular, magnetic crystals. Gold is rapidly attacked, but the oxide formed is immediately decomposed, giving spongy gold. Silver is also rapidly acted upon with the formation of gray crystals, which seem to be a lower oxide. Spongy platinum burns with the peroxide like tinder, giving, after washing, $Pt_2O_3,2H_2O$. On heating, the sesquioxide is left, which is a new oxide of platinum.

Moissan has continued his studies on fluorine, examining, in conjunction with Dewar, the action of the element at low temperatures.[2] The melting-point of solid fluorine was found to be — 223°. The solid fluorine reacted with liquid hydrogen at — 252.5° (20.5° absolute) with explosive violence. At — 187°, the reactions of various compounds and elements with liquid fluorine are hardly less violent than at higher temperatures, its affinity being little in abeyance even at this low temperature. Iodine pentafluoride has been prepared by Moissan[3] and proves to be so stable that it can be distilled in hydrogen without decomposition.

Starting from the fact that chlorine is liberated from hydrochloric acid by Caro's reagent, Wedekind[4] has attempted the use of the analogous reaction for the preparation of fluorine. Caro's reagent, however, had no action upon hydrofluoric acid, neither fluorine being evolved directly, nor any trace of ozone, which might indicate that it had been temporarily formed.

By using a modification of the Goldschmidt process, the magnesium, aluminum, and oxides being taken in such proportions as to give the composition of the natural matrix of the diamond, von Hasslinger[5] has succeeded in converting finely divided graphite into clear, octahedral diamonds of 0.5 mm. diameter. The interesting point about this synthesis is that the diamonds are formed by slow cooling in the absence of any considerable pressure.

A new variety of phosphorus has been prepared by Schenck,[6] by heating white phosphorus to boiling in PBr_3 for ten hours. It is light red, resembling, in appearance, the ordinary red modification, and, like it, being physiologically inert, but, on the other hand, it is very active chemically, often more so than white phosphorus.

For the preparation of phosphine, Bodroux[7] uses a crude aluminum or magnesium phosphide, made by igniting a mixture

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[1] *Am. Chem. J.*, **28**, 59.

[2] *Compt. Rend.*, **136**, 641, 785.

[3] *Ibid.*, **135**, 563.

[4] *Ber. d. chem. Ges.*, **35**, 2267.

[5] *Monatsh. Chem.*, **23**, 817.

[6] *Ber. d. chem. Ges.*, **30**, 9 9.

[7] *Bull. Soc. Chim.* (3), **27**, 568.

of 2 parts aluminum (or magnesium) and 1 part red phosphorus. The resulting mass gives off pure phosphine slowly on treatment with cold water, and more rapidly when the water is warm. Above 50° the phosphine is contaminated with hydrogen, as is the case when acids are used.

Stock and Hoffmann,[1] by the action of ammonia on phosphorus pentasulphide, have prepared a series of amino- and imino-thiophosphoric acids, and by the successive elimination of ammonia and hydrogen sulphide obtain at last phosphorus nitride, P_3N_5. This interesting compound proves to be a white, insoluble, odorless and tasteless body, stable up to a low red heat. Although outside of the strict range of inorganic chemistry, it should be noted here that Michaelis and his pupils have developed much further the organic compounds containing both phosphorus and nitrogen, forming several hundred compounds.[2]

The metaphosphates have been subjected to a somewhat extended investigation by Warschauer,[3] who finds that Fleitmann's dimetaphosphate is in reality a tetrametaphosphate. This result is confirmed both by the Ostwald-Walden valence law, and by the transference number of the sodium salt. When lead oxide is heated with phosphoric acid, if the temperature is kept below 400°, the tetrametaphosphate is formed, while above that temperature a different modification, Fleitmann's 'tetrametaphosphate,' appears, which is, in all probability, the hexametaphosphate. He also finds that the solutions of the hexametaphosphate decompose directly into the orthophosphate, but a small amount of the pyrophosphate is formed at the same time.

Erdmann and Unruh[4] have made a study of the yellow modification of arsenic, first described by Linck in 1899. It is prepared by the rapid cooling of arsenic vapor, and must be immediately dissolved in carbon bisulphide or benzene to prevent its almost instant conversion into the ordinary metallic arsenic. Erdmann prepared a large quantity by collecting the vapor directly in carbon bisulphide. It may be obtained in solid form by cooling a saturated solution to — 70°, but is exceedingly unstable. By the gradual action of light on the solution, a new red-brown modification of arsenic is obtained. The molecular weight of the yellow modification corresponds to the molecule As_4. From the fact that vitreous arsenious oxide is formed by rapid cooling, Erdmann concludes that it contains a ring of four arsenic atoms, and he has succeeded in obtaining a small quantity of yellow arsenic by the reduction of this form of the oxide.

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[1] *Ber. d. chem. Ges.*, **36**, 314.

[2] *Ann. Chem.* (Liebig), **326**, 129, 171, 220.

[3] *Ztschr. anorg. Chem.*, **36**, 137.

[4] *Ibid.*, **32**, 437.

The pentachloride of arsenic has been obtained by Baskerville and Bennett[1] by the action of chlorine on the trichloride at very low temperatures.

Our knowledge of the halide double salts of quinquivalent antimony has been very materially enlarged by Weinland and Feige,[2] who have prepared a series of double chloro- and bromo-antimonates. Most of these are derived from metachloro-antimonic acid, $HSbCl_6$, and the corresponding bromo-acid. A second salt of quadrivalent antimony, Rb_2SbBr_6, was also found.

After a study of sundry alloys of antimony, Stock and Doht[3] find that the alloy of antimony with 2 parts magnesium is best suited for the preparation of stibine. This alloy is treated with hydrochloric acid, the gas is carefully dried and condensed by the use of liquid air. The fusing-point of stibine is —88°, its boiling-point —17°. When pure, it is fairly stable for a few hours, but is immediately decomposed at 150°.

By an examination of the composition of the vapor of a mixture of S_2Cl_2 and chlorine, Ruff[4] finds that the supposed compound SCl_2 has no existence. The same is true of SBr_2 and SBr_4,[5] while Boulouch[6] has, by the use of the dilatometer, proved that none of the supposed compounds of sulphur and iodine have any claim to recognition. Russel and Smith[7] have failed to find any evidence for the existence of Deninger's carbon monosulphide, but Thomsen later shows that it is really formed by the action of hot copper upon a mixture of carbon bisulphide and nitrogen, but it has not proved possible to isolate it.[8]

Contrary to the views of Ringer and Muthmann, that the supposed compounds of sulphur and selenium are isomorphous mixtures of the elements, Rathke[9] considers that in this mixture there are present not less than two distinct compounds of sulphur and selenium. He suggests that it is possible that in the sulphur molecule, S_8, a larger or smaller number of the sulphur atoms may be replaced by selenium. Rathke also considers that the characteristic decayed horseradish odor, when selenium is heated on charcoal, is due to carbon selenide, which, even in the most extreme dilution, has the same odor.

In his *Habilitationsschrift* (Breslau, 1903), Meyer shows that P_4Se_3 and P_2Se_5 are to be looked upon as distinct chemical compounds, but that P_4Se and P_2Se do not exist.

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[1] This Journal, **24**, 1070.

[2] *Ber. d. chem. Ges.*, **36**, 244.

[3] *Ibid.*, **35**, 2207.

[4] *Ibid.*, **36**, 418.

[5] *Ibid.*, **36**, 2437.

[6] *Compt. Rend.*, **136**, 1551.

[7] *Proc. Chem. Soc.*, **18**, 197.

[8] *Ztschr. anorg. Chem.*, **34**, 187.

[9] *Ber. d. chem. Ges.*, **36**, 594.

Several interesting classes of double salts of selenates with iodates, phosphates and arsenates have been prepared by Weinland and Barttlingck.[1] The complex iodates are of the formulas

$$I_2O_5,2SeO_3,2R_2O,H_2O$$

and

$$3I_2O_5,2SeO_3,2R_2O,5H_2O;$$

the phosphates and arsenates follow the types

$$P_2O_5(As_2O_5),2SeO_3,2R_2O,3H_2O$$

and

$$P_2O_5(As_2O_5),5SeO_3,3.5K_2O,5.5H_2O.$$

All these salts crystallize well.

Some considerable work has been done along the line of improvements in the electrolytic preparation of calcium. Borchers and Stockem[2] use fused calcium chloride as the electrolyte, starting the current through a thin carbon rod. Their calcium is spongy, but may be pretty thoroughly freed from calcium chloride by squeezing when fused. They prepare strontium by the same method, and find it is as soft as lead. Arndt[3] modifies this method by using the electric arc, and obtains a calcium 99 per cent. pure. Ruff and Plato[4] discuss the subject very fully, and describe their process for producing the metal, either on a small or on a large scale. The most important point in their process is the use of a mixture of calcium salts as an electrolyte. The best mixture they find to be about 1 part of fluor-spar to 6 of calcium chloride. Their calcium is pure white, somewhat harder than lead.

Goodwin and Smith[5] describe an apparatus for the preparation of calcium by the electrolysis of calcium chloride.

The difficulties attending the electrolytic preparation of barium are shown by Guntz[6] to be due to the formation of a 'basic' chloride, BaCl, which he has prepared in a pure state. This chloride forms double salts with the alkali chlorides, which are also formed when barium chloride is heated with metallic sodium or potassium.

Attention is called by Granger[7] to the fact that at 600° aluminum becomes granular and exceedingly brittle. At a somewhat higher temperature it is very soft as well as granular, and is easily pulverized in small quantities. In the *Comptes Rendus* (**135**, 791), Verneuil discusses, at some length, the conditions necessary for the production of artificial rubies. It appears, among other conditions, that the temperature must be but little above the point of fusion of alumina, else the melted mass will

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[1] *Ber. d. chem. Ges.*, **36**, 1397.

[2] *Ztschr. Elektrochem.*, **8**, 757.

[3] *Ibid.*, **8**, 861.

[4] *Ber. d. chem. Ges.*, **35**, 3612.

[5] This Journal, **25**, 873.

[6] *Compt. Rend.*, **136**, 749; *Bull. Soc. Chim.* (3), **29**, 490.

[7] *Bull. Soc. Chim.* (3), **27**, 789.

become opaque on cooling. In less than two hours, Verneuil prepared a ruby of nearly 3 grams weight, which could not be distinguished from the natural stone. The utmost accuracy in conforming to the necessary conditions is demanded to attain such a result.

During the past year a considerable amount of work has been done upon thallium. Especially has there been an effort to obtain thallium alums, in which thallium is the trivalent metal. Numbers of double sulphates have been obtained by Marshall,[1] and Meyer and Goldschmidt,[2] but in no case an alum. The nearest approach to a solution of the problem is by Piccini and Fortini,[3] who have prepared mixed crystals of ammonium alum in which a portion of the aluminum is replaced by thallium. They have not succeeded, however, in preparing the pure thallium alum. The thallium oxalates have also interested Meyer and Goldschmidt,[4] as well as Rabe and Steinmetz,[5] particularly in the effort to form complex thallium salts. While their efforts in this direction were not attended with success, numerous new, double oxalates were discovered. Meyer and Goldschmidt also prepared double salts of thallic acetate and of thallic nitrate, both rather rare classes of salts.

Investigations upon the rare earths have not been neglected during the past year, though few new ideas have been brought out. Drossbach[6] splits didymium into its components by the use of a concentrated potash solution, and the recrystallization of the double magnesium nitrate. From a potash solution containing cerium, lanthanum and didymium, he precipitates pure cerium quantitatively by a current of chlorine. Meyer and Koss[7] have studied the iodimetry of cerium dioxide and the didymium oxides, perfecting a method for the estimation of the former. Following up his work upon the preparation of the anhydrous chlorides of neo- and praseodymium, Martignon[8] has studied the effect of heat upon the chlorides of samarium, yttrium and ytterbium in a current of dry hydrogen chloride. $SmCl_3,6H_2O$ loses 5 molecules of water at 110° and the last at 150°. Anhydrous samarium chloride is a yellow powder darkening with heat and fusing to a dark brown liquid at about 1000°, but regaining its original color on cooling. It is very deliquescent and evolves much heat on solution in water. The anhydrous chlorides of yttrium and ytterbium are very similar to that of samarium.

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[1] *Proc. Roy. Soc.* (Edin.) **24**, iii, 305.

[2] *Ber. d. chem Ges.*, **36**, 238.

[3] *Ztschr. anorg. Chem.*, **31**, 451.

[4] *Loc. cit.*

[5] *Ber. d. chem. Ges.*, **35**, 4447.

[6] *Ibid.*, **35**, 2826.

[7] *Ibid.*, **35**, 3740.

[8] *Compt. Rend.*, **134**, 1308.

Starting with a mixture of the yellow oxides obtained in the preparation of didymium from monazite by the chromic acid method and fractioning with ammonia and then with oxalic acid, Marc,[1] while failing to isolate terbia, has thrown light upon the subject. He concludes that the so-called terbia is a mixture of yttria and another heavier earth, probably ytterbia, colored with a small amount of the real terbia. Terbium has two oxides, the lower white and the higher colored. It probably has an absorption spectrum in which the principal band is $\lambda = 464\text{-}461$. Its atomic weight should be about 157. Cleve's thulia he considers to be an yttria-ytterbia mixture with a little holmia and terbia, and Cleve's decipia a gadolina-yttria mixture colored with praseodymia. Cleve has separated out a very pure ytterbia and described a long list of its salts.[2] Ytterbium is always trivalent and resembles most closely yttrium and erbium. Rosenheim[3] has described a large number of new thorium salts, some of them with organic acids. He also finds thorium chloride to form compounds with many organic oxygen compounds such as alcohol, aldehyde, acetone, and benzaldehyde.

According to Elba, by the electrolysis of hydrochloric acid with a lead anode $PbCl_2$ is formed, but with two anodes, one of lead and one of carbon, the $PbCl_2$ formed is oxidized by the chlorine at the carbon anode to $PbCl_4$. The double chloroplumbates can be prepared in this way, and the slightly soluble quinoline salt can be used to determine the production of the tetrachloride quantitatively.[4] Seyewetz and Trawitz[5] prepare the ammonium chloroplumbate by adding a moist lead dioxide in small portions to an excess of concentrated hydrochloric acid at 0°, and also[6] by the action of ammonium persulphate on lead dichloride. The chloroplumbate is used by them as a very effective agent for chlorination in organic chemistry.

Titanium trichloride and other compounds of trivalent titanium have been found by Knecht[7] to be excellent reducing agents, far more powerful than stannous chloride. Among other instances, nitro compounds are instantly reduced to amines.

By electrolytic reduction Piccini and Marino[8] have prepared a number of salts of bivalent vanadium. The sulphates belong to the ferrous-iron type, crystallizing alone with 7 molecules of water, and as alkali double salts with 6 molecules. Isomorphous, crystal mixtures were formed of vanadium-magnesium, and of vanadium-ferrous sulphates. Quadrivalent vanadium is being

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[1] *Ber. d. chem. Ges.*, **35**, 2382.
[2] *Ztschr. anorg. Chem.*, **32**, 129.
[3] *Ibid.*, **35**, 424.
[4] *Ztschr. Elektrochem.*, 8, 512.
[5] *Bull. Soc. Chim.* (3), **29**, 455.
[6] *Compt. Rend.*, **136**, 686.
[7] *Ber. d. chem. Ges.*, **36**, 166.
[8] *Ztschr. anorg. Chem.*, **32**, 55.

investigated by Koppel and Behrendt.[1] In their first communication they described a series of simple and double vanadyl sulphates, and another of sulphites.

An extended investigation of chromium salts has been begun by Wyrouboff,[2] with especial reference to the constitution of the violet and green modifications. He considers that the violet salts always contain the group $Cr_2(OH)_6$. to which the acid is added. Thus the hydrated violet sulphate has the formula

$$Cr_2(OH)_6,3H_2SO_4,10H_2O,$$

while the anhydrous form is

$$Cr_2(OH)_6,3H_2SO_4.$$

On the other hand, the green salts contain the radical

$$Cr_2(OH)_2(OH)_4,$$

in which two hydroxyls are acid and four basic. Thus we have the green salts

$$Cr_2(OH)_2(OH)_4,2H_2SO_4$$

and

$$Cr_2(OH)_2,2KOH,(OH)_4.$$

The formation from the violet salt is not merely a loss of water, but often a loss of acid. The chromosulphuric acids exist in several modifications, the first member of the series having the formula

$$[Cr_2O(OH)_2(OH)_2(SO_2)_4]O(OH)_4(OH)_2,$$

the last two hydroxyls being acid in their nature. Wyrouboff holds that many of the seemingly simple inorganic compounds are in reality very complex and must be likened in their constitution to the compounds of organic chemistry. By the action of hot concentrated hydrochloric acid, Recoura[3] finds that chromium sulphate is converted into a chlorosulphate,

$$CrSO_4Cl,6H_2O,$$

in which the chlorine is not immediately precipitable by silver nitrate, while the sulphate group is immediately precipitated by barium chloride. On heating this compound to 85°, it gradually loses 1 molecule of water, the sulphate group is no longer affected by the barium chloride, and its aqueous solution is a non-electrolyte. Aluminum forms a similar chlorosulphate, but iron does not.

The question of the existence of bichromates of any metals except those of the alkalies has been settled by Autenrieth,[4] who prepares silver bichromate, $Ag_2Cr_2O_7$, by double decomposition in the presence of nitric acid, and also by the action of silver nitrate on chromium trioxide. Barium bichromate was also obtained, but not lead bichromate. He further clears up the reac-

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[1] *Ztschr.. anorg. Chem.*, **35**, 154.

[2] *Bull. Soc. Chim.* (3), **27**, 666, 719.

[3] *Compt. Rend.*, **135**, 163.

[4] *Ber. d. chem. Ges.*, **35**, 2057.

tion for the preparation of chromyl chloride, by finding that while a 20 per cent. hydrochloric acid gives, with chromium trioxide, only chlorine, if the acid is 35 per cent. to 40 per cent. strong, a large amount of the chromyl chloride is obtained. A double chromate has been at last prepared by Briggs,[1] who, by the action of ammonium chromate on nickel sulphate, has obtained the ammonium nickel sulphate

$$(NH_4)_2Ni(SO_4)_2,6H_2O.$$

The pure potassium salt was not made, but an isomorphous mixture of the potassium-nickel sulphate and chromate was obtained.

Doering[2] has made an extended study of a chromium, 97 per cent. to 98 per cent. pure, prepared by the Goldschmidt process. The metal is rapidly dissolved by hydrochloric acid, $CrCl_2$ being first formed, but the whole being eventually converted into $CrCl_3$. Since in a hydrogen atmosphere the bichloride is rapidly converted into the trichloride only in the presence of catalytic agents, such must be present in this solution of chromium. This agent was found to be Geuther's oxide of silicon, $Si_3H_2O_5$, formed from the silicon present as an impurity in the chromium. The fusing-point of a similar chromium, 99 per cent. pure, was found by Lewis[3] to be 1515°.

Several pieces of valuable work on tungstates have been carried out in the laboratory of the University of Pennsylvania under the direction of Dr. Edgar F. Smith, and published in this Journal.[4] The so-called para- and metatungstates have been investigated by Taylor, who finds all the known ammonium salts to have a complex formula. He assumes that in all these salts the group $2NH_4OH,4WO_3$ is present as a nucleus, the side chains containing varying proportions of NH_4OH,WO_3 and H_2O. A new class of complex tungstates, containing vanadium and phosphorus, or arsenic, in different stages of oxidation, has been described by Smith and Exner, and further developed by Rogers.

$$13(NH_4)_2O,2P_2O_5,8V_2O_5,34WO_3,86H_2O$$

may be cited as an example of one of these salts. Friedheim and Henderson[5] have described a somewhat similar class of tungstates containing vanadic and silicic acids.

Interest in the subject of colloids has greatly increased among chemists since Bredig's work upon colloidal platinum and several new methods of preparing metallic and other colloids have been recently described. By means of hydrazine hydrate, hydroxylamine hydrochloride, or hypophosphorous acid, Gutbier[6] obtains hydrosols of gold, silver, platinum, mercury, and copper, as well

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[1] *J. Chem. Soc.*, **83**, 401.

[2] *J. prakt. Chem.* (2), **66**, 65.

[3] *Chem. News*, **86**, 13.

[4] This Journal, **24**, 573, 629 ; **25**, 298.

[5] *Ber. d chem. Ges.*, **35**, 3242.

[6] *Ztschr. anorg. Chem.*, **31**, 448 ; **32**, 292, 347.

as of selenium and tellurium. The gold hydrosol prepared by the action of hydrazine on a dilute neutral solution of gold chloride, is blue and resembles that obtained by Bredig electrolytically. It is very stable in the cold, but on warming is immediately converted into the hydrogel. Gutbier also obtains hydrosols of tellurium disulphide and trisulphide, and of selenium disulphide. Kuespert uses formaldehyde as his reducing agent[1] in the presence of water-glass. He prepares a hydrosol of copper acetylide by adding a trace of copper and ammonia to water, which has been shaken up with acetylene. Henrich's reducing agents[2] are the photographic developers, of which he finds pyrogallol the best for the production of colloidal metals. By varying his solvents, he gets organosols of gold with ether, acetone, and alcohol. He calls attention to the fact that in the electric current the metal of a hydrosol moves toward the positive pole. While the method of Bredig failed to give colloidal mercury, this has been prepared electrolytically by Billitzer[3] by the electrolysis of a very dilute solution of mercurous nitrate with a current of 220 volts at 0.2 to 0.3 amperes. An interesting colloid of silver (and mercury) oxide, under the name of collargol, is prepared by Paal[4] by adding caustic soda to a solution of silver nitrate and sodium protalbinate, or lysalbinate. On warming the solution, colloidal silver is formed, and colloidal gold may be prepared in a similar way. Within the past few months there has been some little discussion as to whether or not the silver in collargol is in chemical combination. The colloidal hydroxides have been studied by Biltz,[5] who prepares them by the dialysis through parchment paper of a dilute solution of the nitrates, the reaction being hydrolytic. Nitrates are chosen from the fact of their lesser influence in promoting the formation of a hydrogel, since some of the acid remains present after dialysis, in the form of a basic nitrate. By a similar method, Melikoff[6] obtains from potassium percolumbate, colloidal percolumbic acid, from which oxygen is evolved on standing, or more rapidly by the addition of concentrated sulphuric acid. This indicates that percolumbic acid is not to be looked upon as a compound of hydrogen peroxide.

But little work has been done upon the inert gases of the atmosphere. By working on a large mass of air (191.1 kg.). Ramsay[7] has studied more completely krypton and xenon, the boiling-points of which are respectively —151.7° and —109.1°. The amount of krypton in the atmosphere is estimated as 1 volume in 20,000,000, and that of xenon as 1 volume in

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[1] *Ztschr. anorg. Chem.*, **34**, 453; *Ber. d. chem. Ges.*, **35**, 2815, 4066.

[2] *Ber. d. chem. Ges.*, **36**, 609.

[3] *Ibid.*, **35**, 1929.

[4] *Ibid.*, **35**, 2206, 2219, 2224.

[5] *Ibid.*, **35**, 4431.

[6] *J. Russ. Phys.-Chem. Soc.*, **35**, 457.

[7] *Chem. News*, **87**, 159.

170,000,000. By a comparison of the spectra, Liveing[1] concludes that the presence of the inert gases in the sun is exceedingly probable. The spectra of these gases have been more thoroughly studied by Baly,[2] and from the spectra of krypton and xenon it seems probable that some unknown element of higher atomic weight is present.

That subject which has attracted more attention than any other during the past year has, undoubtedly, been radio-activity. Even a brief outline of the work done would require much space, and there may be a question as to how far this subject belongs to chemistry. Two points of interest may, however, be noted. It was recently currently reported that Huggins had found the spectrum of radium to be, in part, identical with that of helium, but this has since proved to be a mistake. It appears, however, that Ramsay has actually obtained helium in the emanations from radium. It also seems, from the most recent reports, that Curie finds the energy of radium to be given off more actively at extremely low temperatures than at higher.

Some little has been done upon the metal-ammonias and metal-ammonium bases. Barium-ammonia has been carefully investigated by Guntz and Mentrel.[3] At temperatures not above 28°, barium unites directly with ammonia, forming the compound $Ba(NH_3)_6$. Below —23° this compound is stable, but above that begins to decompose, forming barium amide, $Ba(NH_2)_2$, which is also formed by the action of ammonia on barium at 280°. At 650° the amide is decomposed into barium nitride, Ba_3N_2. The action is reversible, and below 680° barium nitride unites with ammonium to form the amide. It is worthy of note that by the action of carbon monoxide upon barium-ammonia, barium carbonyl, $Ba(CO)_2$, is formed, a yellow body, fairly stable, but decomposing in the air or moisture. Sodium and lithium form compounds much similar to those of barium. The cesium and rubidium-ammonia have been prepared by Moissan,[4] and have the formula $CsNH_3$ and $RbNH_3$.

The copper-ammonium bases have been the subject of continued investigation by Bouzat.[5] He suggests for the constitution of the three cupri-ammonium bases the following:

$$Cu(NH_3)_2,2HCl;$$

$$Cu(NH,NH_4)_2,2HCl;$$

and

$$Cu(N(NH_4)_2),2HCl,$$

formulae which seem rather a step backward toward the old Blomstrand theory. Several of the metal-ammonium bases have been studied from the standpoint of physical chemistry by Euler[1]

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[1] *Proc. Cambr. Phil. Soc.*, **12**, II, 87.

[2] *Proc. Roy. Soc.*, **72**, 84.

[3] *Bull. Soc. Chim.* (3) **29**, 585.

[4] *Compt. Rend.*, **136**, 1177.

[5] *Ann. chim. phys.* (7), **26**, 479; **29**, 305.

[6] *Ber. d. chem. Ges.*, **36**, 1854.

and Bonsdorff.[1] The complex cathions are all strong bases, $Ag(NH_3)_2$ being comparable with the alkalies, its hydroxide being more strongly dissociated than barium hydroxide. The cadmium cathion is $Cd(NH_3)_4$, and that of zinc $Zn(NH_3)_3$. In this connection it may be noted that Bonsdorff obtained argento-cyanic acid, $HAg(CN)_2$, by solution of silver cyanide in HCN and it proves to be a very strongly dissociated acid. Apropos of the Werner hypothesis, Kremann[2] has described an interesting experiment in which the colored complex ions of the luteo-, purpureo- and praseo-cobalt bases migrate to the cathode, while the colored ions of potassium diamino-cobaltonitrite migrate to the anode, as is demanded by the theory. Werner and Goslings[3] discuss the carbonato-cobalt amines, showing that the CO_3 group can enter the co-ordinated nucleus of a molecule, occupying a single co-ordinated position. They, however, seem to assume that it is linked by one unit of combining power to one of the ammonium groups. Several new carbonato-pentamine salts are described by them.

There appears to be a renewed interest of late in those fields which lie in both inorganic and organic chemistry, the organic compounds of inorganic elements. Wyrouboff[4] has examined the didymium and double glucinum oxalates; Guerbet,[5] the lactates of mercury; Buroni,[6] the mercurous and halo-mercurous salicylates; Biilmann,[7] the mercury salts of many other organic acids; Howe and Smiley,[8] chrom-malonic acid and some of its salts; Pictet,[9] acetyl-nitric and acetyl-chromic acids, as well as[10] boro-acetates, boro-butyric acid, etc.; and Pope and Peachy,[11] halo-derivatives of stanni-methane.

In conclusion may be noticed a paper read by Dewar before the Royal Society,[12] giving the density and the coëfficient of expansion of ice, carbon dioxide, hydrated salts, and many other compounds, at low temepratures, generally at about — 188°. The interesting point is brought out that the density of ice never becomes as great as the least density of liquid water, or, as expressed by Dewar, the ice molecules can never approach so near each other by thermic contraction as are the molecules of liquid water.

[1] *Ber. d. chem. Ges.*, **36**, 2322.

[2] *Ztschr. anorg. Chem.*, **33**, 87.

[3] *Ber. d. chem. Ges.*, **36**, 2378.

[4] *Bull. Soc. Franc. Min.*, **25**, 66, 71.

[5] *J. Pharm. Chim.* (6), **16**, 5.

[6] *Gazz. chim. ital.*, **32**, II, 305.

[7] *Ber. d. chem. Ges.*, **35**, 2571.

[8] This Journal, **25**, 444.

[9] *Arch. Sci. Geneve*, **15**, 589; *Ber. d. chem. Ges.*, **35**, 2526; **36**, 2215.

[10] *Ber. d. chem. Ges.*, **36**, 2219.

[11] *Proc. Roy. Soc.*, **72**, 7.

[12] *Chem. News*, **85**, 277, 289.