The blast-lamp materials and time will cost thirty cents each, so that it represents quite a saving over the usual burner sold, and it operates perfectly and gives an intensely hot flame. Silica may be blasted to whiteness in one minute easily and ore fusions made with great rapidity. It is admirably adapted for carbon combustions in a platinum crucible giving the bottom of the Shimer crucible an intense heat, so hot indeed that the film of carbonaceous matter can be burnt from the top of the Gooch crucible inclosed.

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REVIEW.

INORGANIC CHEMISTRY.

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IN reviewing the progress of inorganic chemistry during the past year, before running over the field systematically there are two subjects of general import which should be considered. These are solutions and the so-called complex salts. The former of these properly belongs, perhaps, to the division of physical chemistry, and yet its bearing on the department of inorganic chemistry is such that some consideration of it must be regarded as within the scope of this paper. It is, however, only in the work that has been done on non-aqueous solutions that the field of the physical chemist will be trespassed upon.

Franklin has continued his studies of solutions in ammonia (this Journal, **27**, 191, 820), the latter paper containing one of the most notable generalizations recently made in chemistry, in that ammonia solutions are brought into line with water solutions. As water from the standpoint of solution is to be looked upon as a compound of $\overset{+}{H}$ and $\overset{-}{OH}$ ions, so ammonia is a compound of $\overset{+}{H}$ and $\overset{-}{NH_2}$ ions. Acids dissolved in ammonia form, as a matter of course, ammonium salts, but nevertheless they retain true acid properties. Acid amides and imides also are acids in ammonia solution, urea, for example, being ionized into $\overset{+}{H}$ and $H_2\overset{-}{N}CONH$, as well as into $2\overset{+}{H}$ and $CO(\overset{=}{NH})_2$. The metal amides, as $NaNH_2$, act as alkalies, and neutralization reactions in ammonia correspond to those in water. Phenolphthalein can be used as an indicator. Salts hydrolyzed in water are "ammonolyzed" in ammonia; thus, $AsCl_3 + 3H.NH_2 = As(NH_2)_3 + 3HCl$ $(3HCl + 3NH_3 = 3NH_4Cl)$. PCl_3 gives not $P(NH_2)_3$ but $P(NH)NH_2$, and SiS_2 gives $Si(NH)_2$. This ammonolysis need not go to completion, and when it does not we have "ammono-basic" salts, which may be more or less de-ammoniated and hence appear as amines, imines or even as nitriles, that is, nitrides. This treatment of the subject clears up in a very satisfactory way the ammonia compounds of mercury, which have so long been a stumbling block to chemists. They appear as ammono-basic salts, or mixed hydro and ammono-basic salts, occasionally with ammonia of crystallization.

Naumann has added greatly to the experimental side of non-aqueous solutions (*Ber.* **37,** 3600, 4328, 4609), furnishing data as to reactions in solutions of ethyl acetate, acetone and pyridine. Hydrogen sulphide is found by Antomy (*Gazz. chim. ital.* **35,** i, 206) as had also been noticed by Franklin, to act very differently from water as a solvent, and to rather resemble such organic solvents as ether, benzene and carbon bisulphide. Few inorganic salts dissolve; some organic substances as iodoform render the solvent a conductor, while many others dissolve without affecting the conductivity.

Continuing his work on the existence of hydrates in solution, Jones (*Am. Ch. J.* **32,** 308, 338) finds that many organic non-electrolytes form hydrates in solution, and this is especially marked in the case of glycerol. Organic acids show no such tendency. In alcohol solution some salts give evidence of forming alcoholates.

During the past year an increasing amount of work was done upon double and complex salts. Bellucci (*Z. anorg. Chem.* **44,** 168) has studied further the hexaoxyplatinates and finds that the potassium salt, $K_2Pt(OH)_6$, dissociates normally, even in very dilute solutions, and resembles closely the corresponding chloroplatinate. It forms rhombohedral crystals, isomorphous with Marignac's potassium stannate. The formula of this salt is shown (*Atti. Accad. Lincei,* Roma, (5), **13,** ii, 307, 324, 339) to be $K_2Sn(OH)_6$. These stannates are much more stable in solution than the chlorostannates, and stannates of a number of metals have been obtained by double decomposition. They begin to lose water only at temperatures considerably above 100°. By partial hydrolysis of tin tetrachloride and extraction with ether, Pfeiffer (*Ber.* **38,** 2466) obtains $SnCl_3OH$, crystallized with a molecule of water and one of ether, and similarly by alcoholysis the compound $SnCl_3OC_2H_5$ with a molecule of alcohol. These compounds appear to be formed only when the addition products of stannic chloride can split off a molecule of hydrochloric acid.

Quite a series of salts of metachlorantimonic acid have been prepared by Weinland (*Z. anorg. Chem.* **44,** 37) as well as the free acid, $HSbCl_6$, which crystallizes with 4½ molecules of water. Weinland has also (*Ber.* **38,** 1080) further studied the double chlorides of quadrivalent antimony, preparing the (new) rubidium salt, and especially a number of isomorphous crystals with chloroplatinates and chlorostannates. This would seem finally to establish the presence of quadrivalent antimony in these salts.

In a paper upon the chloromolybdates (*Z. anorg. Chem.* **44,** 81) Weinland lays down the rule that in the metal-acids, wherever oxygen can be replaced by sulphur, it can be replaced also by chlorine and bromine, but not necessarily by fluorine. The most important types of chloromolybdates prepared by Weinland are $M'_2MoCl_4O_2$ and $M'MoCl_3O_2.H_2O$.

The compounds of sulphur tetrachloride have been investigated by Ruff and his students (*Ber.* **37,** 4513). They have confirmed the non-existence of the supposed sulphur dichloride, which is merely a solution of the tetrachloride in S_2Cl_2. This solution, formed by leading chlorine into cooled S_2Cl_2, was found satisfactory for most of their experiments. The pure tetrachloride was prepared by sealing the ordinary chloride with liquid chlorine in a tube and leaving it several days. The tetrachloride is hydrolyzed by water almost quantitatively into sulphur dioxide. Fairly stable double compounds were formed with the chlorides of quinquivalent antimony, quadrivalent titanium and tin, and trivalent iron, gold, and iodine. Less stable compounds are formed with zirconium and arsenic trifluoride.

A very thorough investigation of the double chlorides of iron and potassium and caesium has been carried out by Hinrichsen and Sachsel from the standpoint of the phase rule (*Z. physik. Chem.* **50,** 81). Both the crystals and the mother-liquor with which they were in equilibrium were analyzed. Solutions of varying composition and concentration were used, the same temperature being employed in different experiments. At 21° the only potassium salt is $K_2FeCl_5.H_2O$, while caesium forms the two salts, $Cs_2FeCl_5.H_2O$ and $Cs_3FeCl_6.H_2O$. The potassium and the first caesium salt are in accordance with Werner's theory, but the second caesium salt appears not to be.

Work upon the complex molybdates and tungstates has been continued by Smith and his fellow workers (this Journal, **26,** 1474), salts containing aluminum and bismuth, trivalent manganese and nickel, and numerous members of the rare earth group, being added to the already long list of these remarkable compounds.

In connection with Hall and Balke, Smith (*Ibid.* **26,** 1235; **27,** 1140; *Pr. Amer. Phil. Soc.* **44,** 151, 177) has done much to clear up the preparation of columbium and tantalum in a pure form, and has thrown much light upon the perplexing compounds, especially the halides, of these two metals.

Considerable work has been done by Werner (*Ber.* **37,** 4700; **38,** 923, 992, 2009) upon the cobalt bases, especially on the tri- and tetramine compounds in their hydration isomerism. He has also (*Ibid.* **38,** 893) prepared in a pure form the luteohydroxylamine cobalt base, which he finds to be easily made and very stable. A series of new compounds of hydroxylamine with the chlorides of magnesium, calcium, strontium and barium has been prepared by Antonow (*J. Russ. Physik.-Chem. Soc.* **37,** 476). By solution of metallic strontium in ammonia and the evaporation of the excess of solvent, Roederer (*Compt. rend.* **140,** 1252) has obtained a strontium-ammonium, with the formula $Sr(NH_3)_6$, corresponding to barium-ammonium. Caesium-ammonium, $CsNH_3$, has been found by Rengade (*Ibid.* **140,** 1183, 1536) to be very unstable, decomposing slowly into hydrogen and caesium amide, even in ammonia solution. If dry ammonia gas is led over melted metallic caesium at 120°, the amide, $CsNH_2$, is rapidly formed. In the presence of air, caesium-ammonium is very readily oxidized in ammonia solution. By leading oxygen into the solution at —60° there is a gradual oxidation, and by stopping the process at intervals, three different oxides can be isolated in nearly pure condition, Cs_2O_2, Cs_2O_3, and Cs_2O_4. The reactions of sodamide are also attracting attention. Winter (this Journal, **26,** 1484) obtains very complex reactions with phosphorus pentasulphide and with yellow phosphorus. In both cases there are formed insoluble compounds which seem to be amides or oxyamides of phosphorus. Ephraim (*Z. anorg. Chem.* **44,** 185) has investigated the reactions of sodamide with a large number of inorganic compounds and finds that in general it acts as a very powerful reducing agent, all oxygen salts and most oxides and sulphides being reduced. Nitrogen is generally evolved in the reactions, which often resemble, to a considerable degree, those with metallic sodium.

The remainder of the work on inorganic chemistry in this review will be taken up in the order of the periodic system.

Group I.—Those who have had occasion to prepare sodium hydroxide in quantity from metallic sodium will appreciate a new method described by Küster (*Ibid.* **41,** 474). A crystallizing dish about 50 cm. in diameter is filled to the depth of a few centimeters with water and in the middle is placed a low, wide-mouthed flask of platinum, silver or nickel. Above this is a funnel formed out of nickel wire gauze, so supported by a tripod that the tip of the funnel is just over the mouth of the flask. In the funnel are put several hundred grams of sodium, freed from any crust. The whole is then covered with a bell jar of less diameter than the outer dish. This is prevented from reaching the bottom of the dish by a few glass rods, and with the water forms a perfect seal. The sodium begins at once to deliquesce from the moisture present and the oily solution of the hydroxide, about 40 per cent. strong, drips into the flask. The hydrogen escapes under the edge of the bell jar. Any impurity in the sodium remains on the funnel. (The sodium hydroxide is liable to contain nickel but with platinum gauze would be pure.—*Editor.*)

From the work of Treadwell and von Girsewald it appeared that in the solution of a copper salt in potassium cyanide there was present $K_6Cu_2(CN)_8'$, but investigations by Kunschert (*Ibid.* **41,** 359) by conductivity methods seem to indicate that if the potassium cyanide is in excess the anions are $Cu(CN)_4'''$, while if the proportion of potassium cyanide to copper cyanide is less than 2.5 molecules to 1, the copper is in $Cu(CN)_3''$ anions and free potassium cyanide is present. An experiment is described by Caldecott (*Pr. Chem. Soc.* **20,** 199) on the effect of the sunlight on the solubility of gold in 0.5 per cent. potassium cyanide solution. He found that in a flask exposed to the sunlight 43 per cent. more gold was dissolved in five days than in a completely protected flask, although the exposure was only for five and a half hours each day. The temperature in the dark flask was 3.8° higher during the exposure. The cause of the increased solubility is not clear. The action of iodine on gold has been studied by F. Meyer (*Compt. rend.* **139,** 733). At ordinary temperature iodine does not act on gold, and aurous iodide is stable in a vacuum. At 50° iodine begins to act on gold and from this temperature upward the reaction is reversible. In the presence of water the reaction is also reversible and even at ordinary temperatures the gold iodide is decomposed into the elements completely, if the iodine is removed as liberated. It is possible to prepare a crystalline aurous iodide both in the dry and in the wet way.

Group II.—The recently achieved production of metallic calcium in quantity at a reasonable cost has led not merely to a study of the properties of the metal and its alloys, but also to its use in both the inorganic and organic laboratory. Arndt (*Ber.* **37,** 4733; **38,** 1972) finds its specific gravity 1.54 and its melting-point 800°, below which temperature it volatilizes. He has also examined its alloys with aluminum. That of equal parts of each metal is brilliant and stable in the air, but all, except those of high calcium content, are decidedly brittle. A similar brittleness was found by Setlik (*Chem. Ztg.* **29,** 218) to be a characteristic of the alloys with copper, lead, antimony, tin, zinc, and cadmium. Senier (*Chem. News,* **91,** 87) describes the use of calcium in lecture experiments. Calcium is well adapted to show the decomposition of water, since the hydroxide formed is precipitated. One difficulty with this experiment is the slowness with which the hydrogen is evolved, but this can undoubtedly be hastened by heating the calcium beforehand in a current of hydrogen. The calcium absorbs hydrogen, as Setlik has shown, apparently to form a hydride, CaH_2, and this decomposes water with considerable violence. The preparation of the oxide, chloride, sulphide and phosphide of calcium can readily be exhibited by heating the metal in a hard glass tube in a current of oxygen, chlorine, sulphur or phosphorus. Hackspill (*Compt. rend.* **141,** 106), by heating rubidium or caesium chloride in a vacuum with calcium, obtains metallic rubidium or caesium, which distil off and condense in crystals. Lithium cannot be obtained in a similar way, owing to its lesser volatility; it merely forms an alloy with the calcium. Beckmann (*Ber.* **38,** 904) apprehends that metallic calcium will prove a very valuable agent in organic chemistry. He describes several cases of its action as a reducing agent. It seems possible to replace magnesium by calcium in Grignard's reaction. Calcium can further replace aluminum in the reduction of the oxides and sulphides of copper, lead, and manganese, in Goldschmidt's process. In the proceedings of the American Philosophical Society (**43**, 381), Goodwin gives a full account of the preparation of the metal, with especial reference to the economy of the process, and also describes its physical properties.

The study of radium and the other radioactive elements continues to excite an ever-increasing interest. From the wealth of material most must be omitted, but a few of the more important investigations will be noticed. Rudorf (*Z. physik. Chem.* **50**, 100), in a study of the relation between spectrum and atomic weight, discusses the atomic weight of radium. This should be, he holds, 225, as found by Madame Curie, a number which agrees well with the probable decomposition of uranium into radium and helium. If the number proposed by Runge and Precht, 258, were true, Madame Curie's radium must have contained 20 per cent. of $BaCl_2$. Further, this latter number is not reconcilable with the position of radium in the periodic table. Calculations have been made by Liebenow (*Physik. Z.* **5**, 625) regarding the amount of radium in the earth. If uniformly distributed there would be 0.0002 mg. radium per cubic meter. It may be conjectured that the outer portion of the earth contains more radium than the interior. If uniformly distributed on the surface, there would be 0.4 gram radium to each square meter, which would be equivalent to a layer of pitchblende 6 cm. in thickness. At all events there is sufficient radioactive material in the earth to keep the interior at a constant temperature. An examination of the radioactivity of a large number of minerals by Boltwood (*Phil. Mag.* [6] **9**, 599) shows that this is proportional to the uranium present, making it extremely probable that uranium is the source of radium. This ratio—radium : uranium—has been determined by Rutherford and Boltwood (*Am. J. Sci.* [4] **20**, 55) and found to be 7.4×10^{-7}. From this it appears that a ton of pitchblende contains 0.4 gram radium. An attempt to confirm the origin of radium from uranium was carried out by Soddy (*Phil. Mag.* [6] **9**, 768) who freed a kilo of uranium nitrate as perfectly as possible from radium, and sealed it in glass for 500 days. At the expiration of this period the air of the flask was 100 times as radioactive as at the beginning. While the amount found was far less than theory would have called for, Soddy considered it proved that an appreciable amount of radium had been formed from uranium in this period of a year and a half. Similar experiments by Boltwood (*Am. J. Sci.* [4] **20**, 239) gave a different result, 100 grams of purified uranium nitrate showing after 390 days no appreciable increase of activity. Boltwood suggests that the results found by Soddy may have been due to his method of freeing the uranium from every trace of radium, or to his working in a laboratory already full of radioactivity. At all events, even Soddy's results are far smaller than would theoretically be expected. The conclusion drawn is that uranium does not decompose directly into radium, but that there is an intermediate product which decomposes very slowly. In his latest paper Boltwood (*Ibid.* **20**, 253) considers the decomposition products of the radioactive elements, especially as shown by Hillebrand's analyses of different pitchblendes. Without going into detail the following may be taken as decomposition products of radioactive elements: lead, thorium, bismuth, barium, hydrogen, possibly argon. The whole subject of radioactivity is fully discussed by Rutherford (*Arch. Sci. Phys. Nat.* Genève, **19**, 31, 125) in a paper on the actual problems of radioactivity. In this he gives a table of radioactive products, which it may be interesting to reproduce.

Product.	Half decomposed in	Emits	Properties.
Radium	1000 years	α-particles	
↓			
Emanation	4 days	α-particles	Gas of the argon type, boils at −150°.
↓			
Radium A	3 minutes	α-particles	Migrates to negative electrode, soluble in strong acids.
↓			
Radium B	21 minutes	nothing	Volatile at 500°.
↓			
Radium C	28 minutes	α-particles β-particles γ-rays	Volatile at about 1000°.
↓			
Radium D	about 40 years	β-particles γ-rays	Soluble in sulphuric acid.
↓			
Radium E	about 1 year	α-particles	Volatile at 1000°; deposited in solution on bismuth.

Radium E is possibly the active element of Marckwald's radiotellurium and is in Madame Curie's polonium. This and radium D have an atomic weight of about 200. The α-particles are quite possibly nothing other than helium, which is given off as the element breaks up. According to this hypothesis the radium, thorium, and actinium atoms are to be looked on as helium compounds.

By the fractionation of a radium-barium bromide mixture, obtained from 2500 kilos of thorianite, Hahn (*Z. physik. Chem.* **51**, 717; *J. chim. phys.* **3**, 617) has separated a new radioactive element which shows all the properties of the activity of thorium and which has been named by Ramsay radiothorium. The series of decomposition products from thorium are given by Ramsay as follows: 1, inactive thorium → 2, radiothorium → 3, thorium X → 4, thorium emanation → 5, thorium A → 6, thorium B → 7, ? → 8, helium. An effort has been made by Makower (*Phil. Mag.* [6] **9**, 56) to determine the molecular weight of the radium and thorium emanation by the method of diffusion. In the case of radium emanation this was carried out with considerable accuracy, the result being about 97–99. Since the emanation is to be looked on as monatomic, this result would place the element between molybdenum and ruthenium, as the missing next higher member of the manganese series, *i. e.*, eka-manganese. More difficulty was experienced with the thorium emanation, owing to its short existence, but its molecular weight was determined to be approximately slightly higher than that of the radium emanation.

Group III.—The existence of sodium alum has often been called in question. By mixing solutions of aluminum and sodium sulphates, Wadmore (*Pr. Chem. Soc.* **21,** 150) has prepared a compound which crystallizes like alum in octahedra and has the composition of an alum. Its solubility is slightly over one, and its concentrated solution on cooling gives an oily mass which slowly goes over into the crystallized alum. The presence of large, well-defined crystals of sodium chrome alum was reported by Morgan (*Ibid.*) from an oxidizing mixture containing sodium bichromate. It cannot be said, however, that the sodium alum question is yet finally settled.

The colors of the oxides of neodymium have been studied by Waegner (*Z. anorg. Chem.* **42,** 118) using the reflection-spectra. He finds definite spectra characteristic of the blue Nd_4O_7 and of the gray Nd_2O_3, and that the other colors are due to mixtures of oxides, these being always obtained when the heating of neodymium compounds in the air is not continued at very high temperatures for a long time. In this connection attention should be called to an excellent bibliography by R. J. Meyer (*Ibid.* **43,** 416), of the rare earths, which includes the ceria and yttria earths, thorium, and the incandescent light. While not aiming to be exhaustive, it includes practically all papers of importance.

Group IV.—Silicon-fluoroform, $SiHF_3$, and silicon-chloroform, $SiHCl_3$, have been studied by Ruff and Albert (*Ber.* **38,** 53, 2222), the former being prepared for the first time. Most attempts to prepare the fluoroform from the chloroform gave the tetrafluoride, but with stannic or titanic fluoride, chiefly fluoroform is formed. Its boiling-point, —80.2°, is peculiar in being higher than that of the tetrafluoride. Among the reactions of silicon-chloroform of interest is that with ammonia. Owing to the violence of the reaction it must be carried out in an atmosphere well diluted with hydrogen. There is formed a compound, SiNH, which, as far as concerns the elements which it contains, is analogous to HCN. In its properties, however, it bears no resemblance to prussic acid, being a white powder, subliming undecomposed below 300° at 40 mm. pressure, but decomposing readily in water with the evolution of hydrogen. It has strongly reducing properties and reacts with hydrochloric acid to re-form silicon-chloroform.

Stähler has continued his work on titanium (*Ibid.* **38,** 2619), clearing up to a considerable extent the double sulphates and oxalates. He has also (*Ibid.* p. 2611) investigated the ammonia addition products of the halides of zirconium. Both Ruer (*Z. anorg. Chem.* **43,** 267) and Rosenheim (*Ber.* **38,** 812) have also studied zirconium, the former finding the zirconium acids to correspond to those of tin, as regards colloidal and insoluble forms. The latter has succeeded in preparing the pyridine and quinoline chlorozirconates, Pyr_2ZrCl_6, in spite of the great tendency of all salts of quadrivalent zirconium to hydrolyze. The pyridine bromozirconate was also prepared but loses hydrogen bromide in the air.

Two borides of thorium have been prepared by du Jassonneix (*Compt. rend.* **141,** 191) by the action of amorphous boron on thoria in the electric furnace. ThB_4 is a crystalline product, somewhat soluble in acids; ThB_6 is a non-crystalline substance of metallic appearance and of a reddish brown color, and is unacted on by all acids except nitric. Wedekind and Fetzer (*Chem. Ztg.* **29,** 1031) confirm this work and find that when the boron is replaced by crystalline silicon a thorium silicide is formed.

A curious instance of "tin disease" (transformation of the white modification of tin into the gray) is described by Cohen (*Chem. Weekblad,* **2,** 450) as taking place in organ pipes in St. Stephan's church at Nijmegen. These pipes date from 1776, but others only seven years old showed the same disease, indicating infection. Cohen recommends that in such instances all infected pipes should be removed. No connection could be traced between the original quality of the tin and the disease.

To the already long list of metallic peroxides from the Odessa laboratory, Tanatar (*Ber.* **38,** 1184) has added perstannic acid and quite a list of perstannates. The dry perstannic acid has the formula $HSnO_4.2H_2O$, and at 100° the formula $H_2Sn_2O_7.3H_2O$. This seems to be the compound described by Spring in 1899, without, however, its character as a peroxide being recognized.

Group V.—The action of fluorine on the oxides of nitrogen has been studied by Moissan and Lebeau (*Compt. rend.* **140,** 1573, 1621). At ordinary temperature fluorine has no action on the dioxide. No reaction with nitrous oxide occurs even at a red heat, but a reaction is induced by the electric spark, without, however, the formation of any volatile compound. The reaction between fluorine and nitric oxide is violent, but results merely in a decomposition of the oxide into its elements. At the temperature of liquid air, an excess of fluorine acts on nitric oxide with the formation of a white, very volatile solid, which condenses in part to a liquid at —80°. This is nitrofluoride, NO_2F, a very reactive gas, reacting at ordinary temperature with boron, silicon, phosphorus, arsenic, antimony, and iodine, though not with hydrogen, sulphur, selenium, or carbon. It also reacts with organic compounds, both the fluorine and the nitro-group taking part in the reaction.

It has long been known that when vitreous arsenious oxide is dissolved in hydrochloric acid and crystallizes out in octahedra, the crystallization is accompanied by luminescence. This has been investigated by Gernez (*Ibid.* **140,** 1134, 1234, 1337) and Guinchant (*Ibid.* pp. 1101, 1170). The phenomenon is due to friction between the crystals or to their fracture, and hence is a triboluminescence. This luminescence is by no means of as infrequent occurrence as has been supposed. When potassium sulphate crystallizes out of a concentrated solution, if the crystals are touched by a wire a brilliant light is emitted. About a hundred other salts were found which showed the phenomenon, among them potassium selenate and chromate, sodium bromide, iodide, acetate, and arsenate.

One of the notable developments of the past year has been the preparation of metallic tantalum on a considerable scale. Von Bolton describes (*Z. Elektrochem.* **11,** 45, 503, 722) its preparation by electrolysis and also by the action of sodium on fluotantalates. The metal unites great ductility with extreme hardness. The only effect of several days' action of a diamond drill seems to have been to slightly wear down the diamonds. (Since found an error.) It fuses only at about 2250° and gives but little dust in a vacuum on the passage of the electric current. It seems to be particularly suited for the filament of the incandescent light, requiring less than half the usual current per candle-power. The great possibilities of the metal are indicated by the fact that the firm of Siemens & Halske have already taken out 200 patents with about a thousand claims, covering the preparation and uses of the metal.

Group VI.—The interesting studies of Alexander Smith on sulphur have been continued (this Journal, **27,** 797, 979) with especial reference to liquid sulphur. It is found that there are two modifications of liquid sulphur, $S\lambda$ which is light colored and thin, and $S\mu$ which is dark and more viscid. The transition point between the two is at about 160°, and near this temperature the solution of one in the other shows great viscosity. The $S\mu$ modification seems to be the liquid form of amorphous sulphur. The polysulphides have been the subject of investigation by Küster (*Z. anorg. Chem.* **43,** 53; **44,** 431; **46,** 113) who finds that the different sulphides exist in equilibrium with each other in solution. The maximum amount of sulphur dissolved corresponds in the case of sodium to $Na_2S_{5.24}$, thus indicating the presence of a hexasulphide. The hydrolysis decreases with increasing amount of sulphur and is as follows in tenth-normal solutions: Na_2S, 86.4 per cent.; Na_2S_2, 64.6 per cent.; Na_2S_3, 37.6 per cent.; Na_2S_4, 11.8 per cent.; $Na_2S_{5.24}$, 5.7 per cent.; for NaSH, the hydrolysis is only 0.15 per cent. The constitution of the disulphide is probably $Na_2 = S = S$, and that of the higher sulphides $Na_2 = S.S_x$. By using caesium and rubidium, Biltz has prepared (*Ber.* **38,** 123) the pentasulphides of these elements in crystalline form. That of rubidium is deliquescent and very unstable, but that of caesium is not hygroscopic and is soluble in 70 per cent. alcohol. The crystals are not isomorphous with those of the sulphates.

Sulphur dissolves in liquid ammonia without evolution of either nitrogen or hydrogen. The reaction is, according to Ruff (*Ibid.* **38,** 2659), $10S+4NH_3 \rightleftarrows 6SH_2^{\xi}+N_4S_4$. If the concentration of the ammonium sulphide formed is diminished, as by precipitation with silver iodide, then the reaction proceeds to the right. If the ammonium sulphide concentration is increased, as by evaporation, it goes to the left. After evaporation it is possible to recover the nitrogen sulphide, so that this is a new synthesis for this compound. Ruff has also (*Ibid.* p. 549) synthesized thionyl fluoride almost quantitatively by the action of hydrogen fluoride on nitrogen sulphide. During the year a large number of papers have appeared on hydrosulphurous acid and the hydrosulphites, but the constitution of these compounds is far from having been elucidated.

A new preparation of metallic chromium is given by Goldschmidt (*Chem. Ztg.* **29,** 56). A solution of chromium, best one of the crystallized nitrate, is exposed in a vessel of tin or of an alloy of tin to a low temperature. Both amorphous and crystalline chromium are formed in the course of a day. The accompanying precipitated chromium hydroxide can by dissolved in excess of alkali. By the reduction of chromic acid by fuming hydrochloric acid in the presence of pyridine, Weinland and Fridrich (*Ber.* **38,** 3784) have obtained crystals of the formula $CrCl_4(OH)$ Pyr.H_2O, which appear to be derivatives of quinquivalent chromium, corresponding to a similar bromide of molybdenum (*Z. anorg. Chem.* **44,** 115) to which Weinland assigns the formula, $MoBr_4(OH)$Pyr, this being a derivative of quinquivalent molybdenum. The name "chromanate" is proposed for derivatives of the acid $HOCrCl_4$. By the oxidation of chromates in alkaline solution with 30 per cent. hydrogen peroxide, Riesenfeld (*Ber.* **38,** 1885) obtains a series of perchromates having the formula M'_3CrO_8. These are the most highly oxidized perchromates yet prepared, are red, and stable when dry. Working similarly, but in acid solution, a series of blue salts is obtained, having the formula $M'H_2CrO_7$. These seem to be the same as those to which Wiede has assigned the composition $M'CrO_5$.

Many efforts have been made in the past, as by Berzelius, Marignac and Moissan, to prepare a hexafluoride of tungsten, but without result. Ruff has, however, succeeded (*Ibid.* **38,** 742) by the action of liquid hydrogen fluoride on tungsten hexachloride in a copper-lined iron tube, in obtaining the WF_6. It is a heavy, colorless gas, condensing to a solid at low temperature. It volatilizes at about zero. It attacks glass and is rapidly acted on by metals. Considerable work has been done by Giolitti and his students upon uranium (*Atti Accad. Lincei*, Rome, [5]

14, i, 114, 165; *Gazz. chim. ital.* **35**, ii, 145, 151, 162, 170). Giolitti has recommended precipitation with hydrofluoric acid for the determination of uranium. The precipitate he finds to contain two compounds, $UOF_2.2H_2O$, and (perhaps) UF_4. By electrolysis he has prepared $UF_2.2H_2O$ and the above-mentioned oxyfluoride, as well as a double salt of the latter with ammonium fluoride. He has further studied the equilibrium of the hydrates of uranium sulphate, and also the double carbonates of uranium and ammonium.

Group VII.—A number of fluorine compounds of the heavy metals have been described by Böhm (*Z. anorg. Chem.* **43**, 326) and crystallographical measurements made of several of them. The fluorides of mercury, copper, nickel and cobalt were made by heating the oxide with concentrated hydrofluoric acid and evaporation in a vacuum. The crystals all contain water and hydrofluoric acid, the copper salt, for example, having the formula $CuF_2.5H_2O.5HF$. By the action of an excess of (aqueous) ammonia, the mercury salt forms by ammonolysis an amine, $HgFNH_2$; the copper salt a tetrammonium fluoride; cobalt hydroxide in hydrofluoric acid gave an ammonium cobalt fluoride. Several cobaltamine compounds containing fluorine were also obtained, among them luteocobalt fluoride, $Co(NH_3)_6F_3$, and the luteocobalt chlorofluoride, $Co(NH_3)_6Cl_2F$. Moissan (*Compt. rend.* **139**, 711), in connection with his work on fluorine, has prepared pure boron and silicon fluorides for the purpose of examining their constants. The BF_3 melts at —127° and boils at —101°; the SiF_4 volatilizes at —97° without fusion, but at a pressure of two atmospheres melts at —77°. These figures were the same whether the compounds were made by the action of fluorine on boron and on silicon, or by heating fluorspar and sulphuric acid with boron trioxide and with silica.

A contribution to the chemistry of bleaching-powder is added by Tarugi (*Gazz. chim. ital.* **34**, ii, 254) who proceeds from the fact that when fully hydrated lime stands for a time in the air it shows peroxide reactions. He therefore considers that in the making of bleaching-powder the first step is the reaction of chlorine and water with the formation of oxygen and hydrochloric acid. The oxygen immediately changes the calcium hydroxide into the hydrate of the peroxide, upon which in turn the hydrogen chloride acts. Bleaching-powder is hence to be considered as the chloride of calcium peroxide. The quantitative oxidation of mercury to the bichloride by bleaching-powder supports this view. Tarugi suggests the possibility of utilizing this last reaction for the commercial production of the bichloride. He has also investigated (*Ibid.* p. 466) the pink color produced when carbon dioxide is led through a warm solution of bleaching-powder and other hypochlorites. This has ordinarily been attributed to the presence of traces of manganese. He finds that it is due, not to manganese, but to iron, in all probability being caused by the formation of traces of calcium ferrate. Hypochlorite solutions free from iron did not show the reaction, but became pink immediately upon the addition of minute quantities of iron salts.

Mention should be made of an address on the occurrence of manganese in nature, by Bertrand (*Rev. gén. chim.* [7] **8,** 205) which treats the subject in an exhaustive manner, and especially calls attention to the importance of manganese in plant physiology. Its possible importance to animal life is very generally overlooked.

Group VIII.—Work upon the metals of the platinum group has been very meagre during the past year, but a few points deserve mention. Blondel in a long paper (*Ann. chim. phys.* [8] **6,** 81) goes over half a dozen or so classes of platinum compounds, explaining their constitution in accordance with the views of Wyrouboff. Among the compounds included are the hydroxides (oxy-acids), and their salts, sulphates, and oxalates. The views are quite antagonistic to those of Werner. A short rejoinder is made by Bellucci (*Gazz. chim. ital.* **35,** ii, 334) showing that the views of Blondel are wholly inconsistent with his own published work, especially with his physical measurements of the oxy-salts[1] (*Z. anorg. Chem.* **44,** 168). Further work has been done by Rosenheim (*Ibid.* **43,** 34) on the derivatives of phosphorus platinum chloride. A most interesting discovery is the existence of two series of isomers of which the following may serve as an example: $Cl_2.PtP(OC_2H_5)_3.C_6H_5NH_2$ and $Cl.P(OC_2H_5)_3.Pt.Cl.C_6H_5NH_2$. The former *cis* form goes over easily into the latter *trans* form, but the change is not reversible. According to Wilm rhodium possesses far greater power of condensing hydrogen than palladium, and this power varies with the method used in preparation of the rhodium. This has been re-examined by Quennessen (*Compt. rend.* **139,** 795) but not confirmed. He finds that no form of rhodium is as active as palladium, but that it rather resembles platinum in its characteristics. Further he finds no difference in rhodium prepared in different ways. Marino (*Z. anorg. Chem.* **42,** 213) has prepared the alkali series of the iridium alums as well as those of thallium. Curiously the melting-points of all the alkali alums lie between 102° and 110°, caesium and rubidium alums melting at practically the same temperature. That of the ammonium alum is just between those of rubidium and potassium. Considerable has been done by Gutbier (*Ibid.* **45,** 166, 243; **47,** 23; *Ber.* **38,** 2105, 2107, 2385) on palladium and ruthenium. Pallado-chlorides and bromides of a number of organic bases have been prepared as well as the palladosammine salts of the same bases. Meta- and paraphenylenediamine gave in all cases only double salts while the ortho derivative gave amine compounds. A number of ruthenium halides are described as well as the action

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[1] Cf. page 402.

of oxygen on ruthenium. Of the many oxides which have been described, he finds that only RuO_2 and RuO_4 have an actual existence. The work of Wintrebert on osmium has been continued and the nitrites further investigated (*Compt. rend.* **140,** 585). The type is $M'_2Os(NO_2)_5$, and normal salts were prepared of potassium, sodium, ammonium, silver, barium, strontium, calcium, magnesium and zinc. All but the potassium salt contain water of crystallization. The free acid, $H_2Os(NO_2)_5$, was obtained in solution, but decomposed on evaporation, leaving osmium nitrite, $Os(NO_2)_3$.

Upon the inert gases, during the past year comparatively little has been done. Jaquerod and Perrot (*Ibid.* **139,** 789) have experimented with helium thermometers of quartz glass for the measurement of high temperatures. They found that above 900° the pressure in the thermometer gradually sank, owing to the diffusion of the helium through the quartz. Further investigation showed that the velocity of diffusion is proportional to the temperature. In six hours at 1100° six-sevenths of the gas had disappeared. The diffusion is noticeable at 510°, and it was shown to take place very slowly even as low as 220°. The helium thermometer made of quartz is therefore useless for high temperature work. All efforts thus far made to liquefy helium have been unsuccessful, and the same lack of success must be recorded of the latest attempts of Olszewski (*Ann. Phys.* [4] **17,** 994). Helium was compressed to 180 atmospheres at a temperature of —259°, attained by liquid and solid hydrogen. Now on reducing the pressure to a single atmosphere there was no sign of liquefaction, not even a mist. The temperature reached was 1.7° absolute. Olszewski considers it doubtful whether helium will ever be liquefied. The property possessed by wood charcoal of occluding gases very strongly at low temperatures, first utilized by Dewar, has been developed by several experimenters; Valentiner and Schmidt (*Sitzungsber. Akad. Wiss.* Berlin, 1905, p. 816) have, by means of the "fractional distillation" at low temperature of the absorbed gases, prepared from the oxygen- and nitrogen-free residue of the air, neon and helium, and from the last residues of evaporated liquid air, krypton and xenon. Using fractional absorption, Ramsay (*Pr. Roy. Soc.* **76,** A, 111) has calculated the helium and neon content of the atmosphere. There is 1 volume of neon in 80,790 volumes of air, and 1 volume of helium in 245,300 volumes of air. By weight the atmosphere contains 0.0000086 per cent. neon and 0.00000056 per cent. helium. Other experiments have shown that the free hydrogen in the air is less than $^1/_{500}$ of the amount of neon and helium taken together.

The subject of colloids is full of interest, but belongs at present rather in the field of physical chemistry. Attention may, however, be called to a paper on the nature of the colloids by Jordis (*Mon. scient.* [4] **18,** 797), to the work of Gutbier on colloidal metals, especially of the platinum group, and especially to the papers of Whitney and his coworkers, recorded in this Journal.

WASHINGTON AND LEE UNIVERSITY,
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COMPOSITION OF AMERICAN PETROLEUM.[1]

BY CHARLES F. MABERY.

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PETROLEUM may be regarded as one and the same substance with great variations in properties and proportions of constituents, selecting as extremes such light oils as the light colored oil found in Kansas and the extremely thick oils of Wyoming, which are nearly as heavy as water. The series of hydrocarbons that have been identified in petroleum from different fields, in this laboratory, include the following: C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}; doubtless the heavy asphaltic oils contain hydrocarbons even poorer in hydrogen.

The series of hydrocarbons which form the portions of American petroleum distilling below 350° *in vacuo*, corresponding to 475° at atmospheric pressure, are now well understood, and the members of the various series have been identified with respect to their molecular weights. But concerning the structure of these hydrocarbons, except those of the series C_nH_{2n+2} and the lower cyclic hydrocarbons, nothing whatever is known. It is reasonable to assume that the members of the series C_nH_{2n+2}, or the so-called paraffin hydrocarbons, have the open-chain structure which characterizes the lower members of this series. In the earlier literature on petroleum it was generally assumed that the ethylene hydrocarbons, series C_nH_{2n}, formed a considerable proportion of the constituents, and even after the discovery of the cyclic series C_nH_{2n}, the naphthenes, according to the earlier nomenclature of Markownikow, many writers, with no foundation on facts, still insist on the presence of ethylene hydrocarbons. It is now safe to assert that these bodies are present in any petroleum, at most in very small amounts. We have found them apparently in Canadian petroleum, but in very small quantities.

The series C_nH_{2n}, which has been identified in petroleum from many sources, is now well known as the cyclic series. In a paper published in 1902 on the composition of Pennsylvania petroleum, I purposely abstained from naming the hydrocarbons with high boiling-points of this series which we had separated and identified, for although it seemed probable that these bodies were cyclic compounds, I preferred not to suggest names for the several members until more was known concerning their structure. The names suggested

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[1] Presented in abstract at the New Orleans Meeting of the American Chemical Society.