was used as the reducing agent in eight experiments of the series; in Experiments 9, 10, and 11, hydrazine hydrate served this purpose. The mean result by each method is practically the same. This is strong evidence that there is little error connected with the removal of the mercury from mercuric bromide. The results are slightly but uniformly lower, however, in the cases where hydrazine hydrate was used. This would indicate that all the bromine from mercuric bromide had not been measured when hydrogen peroxide was used or, on the other hand, that foreign matter was weighed in the other series. The latter assumption would seem to be the more probable, if either carries any weight, for hydrazine hydrate, if any remained after the treatment with hydrogen peroxide, might reduce the silver nitrate and thus give an apparently large amount of silver bromide. This seems unlikely, however, for the solution was purposely made more strongly acid in this case than where the peroxide was used in order to counteract such a tendency. The effect is certainly small and should be connected with the accuracy of the second, rather than the first decimal place.

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RECENT WORK IN INORGANIC CHEMISTRY.

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The past year has witnessed no startling discoveries in the field of inorganic chemistry, yet there has been great activity along every line, especially in working over old material in the light of new theories. Such work is often difficult and painfully slow, attracts little attention and adds little to reputation, but is vitally necessary if we are to broaden our generalizations. But one new element has been added to the list, Urbain's keltium (Ct) from the gadolinite earths, unless we are to believe the newspaper statements of a new platinum metal from the northwest, and while Ramsay has given radium emanation standing as niton, doubt has been thrown on Flint's companion to tellurium.

No attempt will be made to review the whole field, but rather to consider some of the most important papers which have appeared the past year. The order followed will be that of the periodic table.

Group III.—Further work has appeared from Biltz (*Z. anorg. Chem.*, **71**, 182, 427) on the sulfides of this group. Al_2S_3 is prepared by fusing together the metal and sulfur in a crucible and then igniting the mass by magnesium ribbon. The material is then sublimed, best in a vacuum. The felted product consists of fine needles, which are quite possibly isomorphous with corundum, and this is the more probable since the solidifying curve with alumina indicates the formation of mixed crystals ("Mischkrystalle"), though the intersolubility is not unlimited. Al_2S_3 is readily attacked by moisture, and seems to form one or more compounds with the Al_2O_3 formed. The product obtained by Regelsberger from alumina and sulfur in the electric furnace is a complex mixture, but one of its constituents is the monosulfide, AlS, which is more difficultly volatil than Al_2S_3. The latter fuses at 1100°. A sulfide of lanthanum is formed by heating the sulfate in a stream of hydrogen sulfide, which gives hydrogen persulfide with acids and has the formula La_2S_3S. It loses sulfur above 600° giving La_2S_3, which shows no sign of fusion or sublimation at 1000–1250° in a vacuum, but which is hydrolyzed very actively by water. When praseodymium sulfate is heated in hydrogen sulfide only an oxysulfide is formed, Pr_2SO_2, but if cerium is present, even in minute quantity, as an "inductor," $PrS_2(Pr_2S_3S)$ is formed, and this loses sulfur in a stream of hydrogen sulfide at 600–700°, with the formation of the sesquisulfide, Pr_2S_3. This reaction is delicate enough to detect the presence of cerium in praseodymium compounds, and corresponds to the superoxidation of praseodymium in the presence of cerium.

By the use of his bromate method James (THIS JOURNAL, **33**, 1332) has prepared pure thulium and describes a number of its salts. All attempts to resolve it by fractional crystallization failed, no change in its absorption spectrum appearing after about 15,000 operations.

In the *Journal of Industrial and Engineering Chemistry*, (**3**, 299), Weintraub describes the preparation and properties of pure boron. It may be prepared by the action of magnesium on the oxide; the suboxide, B_6O, as well as other impurities are removed by heating to 2000°, at which temperature they dissociate. A second method of preparation is by heating BCl_3 (from the action of chlorine on the carbide) with hydrogen. Pure boron is black, amorphous, and exceedingly hard, only being surpassed by the diamond. It shows traces of volatilization at 1200° but fuses only above 2000°. Its most remarkable property is the increase of its electrical conductivity with the temperature. In the cold it is a poor conductor, its specific resistance being 10^{12} times that of copper. At 400° its specific resistance has decreased in the proportion $2 \times 10^6 : 1$. Weintraub suggests that this property may give it important industrial applications.

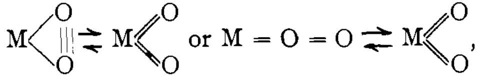
Group IV.—A very suggestive attempt to study the association of silicate minerals from the standpoint of heterogeneous equilibrium is made by Sosman (*J. Wash. Acad. Sci.*, **1**, 54), who treats the mixture of the metasilicates of Mg, Ca, and Fe as a three-component system, plotting the analyses of the various minerals and rocks made up of these constituents (by triangular coördinates). He finds a boundary line between the mineral analyses and rock analyses, which he considers to represent the boundary between magma compositions that will form homogeneous solid solutions and those that will separate into two different solid solutions between which is a eutectic. The rock analyses lie in the "eutectic field," the minerals outside of it. The two types of minerals of which these rocks are made up are in each case the two solid solutions which appear on opposite sides of the "eutectic field." A much broader generalization is attempted by Goldschmidt (*Z. anorg. Chem.*, **71**, 313) who treats mineral association from the standpoint of the phase rule. He uses the following form of the rule "the maximum number n of solid minerals which can exist together in stable form is equal to the number n of components which the minerals contain." This is true for any arbitrary temperature and any arbitrary pressure. At a definite "singular" temperature (transition-temperature), or pressure, $n + 1$ minerals can coexist. He discusses numerous illustrations, SiO_2 as a one-component system, $Al_2O_3.SiO_2$ as a two-component system, $CaO.TiO_2.SiO_2$ as one of three components, and cites instances of the practical value of study from this standpoint. Last year Cambi described a monosulfide of silicon formed by the action of sulfur on ferro-silicon in the electric furnace. This existed in two forms, one black and compact, and the other a yellow powder, formed from it by sublimation. He now presents (*Atti accad. Lincei, Rome,* [5] **20,** i, 433) a more extended study of these compounds. The yellow sulfide is acted on violently by water with the evolution of hydrogen, but by care the white hydrolytic product can be obtained without decomposition and proves to be the anhydride of silico-formic acid, $(HSiO)_2O$. This has strong reducing powers and at 400° decomposes into hydrogen and SiO_2 (with some free Si). The $Si(OH)_2$, evidently first formed on the hydrolysis of SiS, passes by tautomeric change into silico-formic acid, analogous to the tautomerism of $Ge(OH)_2 \rightleftharpoons HGeO.OH$ described by Hantzsch. By the action of dry HCl on the yellow SiS, silico-chloroform is formed: $SiS + 3HCl = H_2S + SiHCl_3$. The hydrolysis of the black silicon monosulfide is very different from that of the yellow, giving among other products SiO_2, and Cambi concludes that it is the product of a decomposition of the yellow sulfide, $2SiS = Si + SiS_2$, the transition temperature being slightly below 1000°, the sublimation point of SiS, and above which temperature only it is the stable form. In this connection note may be made that Besson and Fournier (*Compt. rend.,* **151,** 1055) have found that the product when dry HBr is led over amorphous silicon at a red heat is chiefly $SiBr_4$, but that $SiHBr_3$ is also formed, with a trace of SiH_2Br_2 and possibly SiH_3Br. By the action of the silent discharge silico-bromoform is converted into silico-methane homologues, Si_2Br_6, Si_3Br_8 and Si_4Br_{10} having been isolated.

Attention is called by Werner von Bolton (*Z. Elektrochem.,* **17,** 816) to an interesting biological action of metallic thorium. It was noticed that in distilled water, in which metallic thorium (prepared by the action of Na on $ThCl_4$) was kept, bacterial-like growths appeared, which was not the case in the presence of other metals. In further experimentation the amphioxus was kept in North Sea water to which metallic thorium and thorium oxide had been added. The animals remained alive much longer than in the absence of thorium, and the preservative action seemed to be proportional to the amount of thorium present and to depend but slightly on the oxide. On the other hand the metal appeared to be injurious to vegetable life, so that possibilities are suggested of destroying bacterial growths on animal life by thorium.

Group V.—In his Baker lecture before the Royal Society, Strutt (*Proc. Roy. Soc. London,* [*A*], **85,** 219) describes a chemically active modification of nitrogen, formed when pure nitrogen is submitted to the electric spark. This modification is characterized by a luminescence which persists for a short time after the discharge has ceased. The luminescence is decreased by heat and increased by cold. This form of nitrogen attacks many elements, forming an explosive compound with mercury. It unites with yellow phosphorus, much red phosphorus being formed at the same time. With iodine a beautiful light blue flame appears, which gives a spectrum with broad bands. With nitric oxide the dioxide is formed, and with acetylene and with organic halides cyanogen is formed, which was recognizable by its spectrum and also by chemical tests. Whether this modification is to be looked upon as atomic nitrogen or as a molecule of the ozone type does not yet appear. The constitution of the nitroso compounds of ferrous iron and of copper has been further studied by Kohnschütter (*Ber.*, **44,** 1423) and the conclusion reached that the brown color which appears when nitric oxide is led into ferrous solutions is due to the direct addition of NO to the ferrous ion. This is confirmed by the electrolytic migration of the color toward the cathode. The reaction $Fe^{++} + NO \rightleftharpoons Fe(NO)^{++}$ is reversible and the NO absorbed never reaches the proportion of one molecule to each ferrous atom. The capacity of ferrous solutions for nitric oxide increases markedly in the presence of strong acids and here the color changes. In this case the color migrates toward the anode and indicates the formation of a complex anion containing both iron and NO. These complex anions are somewhat more stable than the nitroso-ferrous cations. Blue cupric solutions do not absorb nitric oxide, but those which are green or brown, such as solutions of cupric chloride or bromide in alcohol, acetone, or concentrated solutions in water, form with NO complex anions similar to those with iron. Nitroso-cupric cations are unknown. The author holds that there is no relation between these nitroso compounds and nitroso-sulfuric acid, H_2SO_5N, which has been suggested by some chemists.

The composition of solid hydrogen arsenide has been investigated by Reckleben and Scheiber (*Z. anorg. Chem.*, **70,** 255, 275), by determining the amount of arsenic acid and reduced silver after the action of ammoniacal solution of silver on the arsenide and the metallic arsenic which invariably accompanies it. In using this method it is not necessary to isolate the arsenide, hence all risk of oxidation is avoided. The conclusion is drawn that the formula H_2As_2, best satisfies the results obtained. They also find that when arsenic is sublimed in hydrogen no solid arsenide is formed and no considerable quantity of arsine, H_3As, a result to be expected, but not in accordance with the statements of Retgers. They also find that no solid arsenide is present in the black spot produced by cooling the arsine flame, even when an excess of hydrogen is present. It appears that the yellow modification of arsenic has often been mistaken for the solid arsenide. Incidentally the authors note that arsine does *not* have the garlic odor commonly attributed to it, but that this odor is due to the suboxide. An investigation of stibine shows no evidence of the existence of any solid antimonide of hydrogen.

Reference should be made to the exhaustive work of Ruff (*Ber.*, **44,** 506, 2534, 2539) on the halides of vanadium, in which the methods of preparation and the properties of the chlorides, bromides and fluorides are studied, but the articles do not admit of a brief abstract. The solubility of hydrogen in tantalum has been studied by Sieverts and Bergner (*Ibid.*, p. 2394) and it is found that while at 500° the gas-free metal is inactive toward hydrogen, if it has been saturated at higher temperatures it continues to absorb when the temperature is lowered. For a given temperature the solubility is proportional to the square-root of the pressure, and not directly to the pressure, as would be the case if the solubility followed Henry's law. The absorption is endothermic and decreases with the temperature. In most of these respects palladium is the only metal which resembles tantalum, and the solubility of hydrogen in tantalum is of much the same magnitude as its solubility in palladium. In both cases the solubility is due to some combination of the metal with hydrogen, the nature of which is unknown. After absorption of hydrogen, tantalum wire becomes brittle. The hydrogen can be removed by heating to a red heat in a vacuum, but the wire remains brittle. The reaction between the metal and hydrogen is thus reversible, but the structure change of the metal is not. The original properties of the metal are slowly restored by heating to a high white heat.

Group VI.—The suggestion is made by Ebler and Krause (*Z. anorg. Chem.*, **71**, 150) that the name *peroxydate* ("peroxydat") should be used for derivatives of hydrogen peroxide, in order to avoid confusion with peroxides in which the metal has a higher valence; that is, in tautomeric compounds,  $\mathrm{M}\Big\langle{}^{\mathrm{O}}_{\mathrm{O}} \rightleftharpoons \mathrm{M}\Big\langle{}^{\mathrm{O}}_{\mathrm{O}}$ or $\mathrm{M} = \mathrm{O} = \mathrm{O} \rightleftharpoons \mathrm{M}\Big\langle{}^{\mathrm{O}}_{\mathrm{O}}$, the former would be a peroxydate and the latter a peroxide. It would seem to the reviewer better to confine the term peroxide to the former and to denominate the latter simply as a dioxide. The term peroxide would then be used only for those compounds which on treatment with acids give the reaction for hydrogen peroxide, from which they may be considered as derived. Ebler gives two general methods for the preparation of peroxides, one by the action of metal alkyles on hydrogen peroxide in dry ether solution, and the other the action of metal amides on the same solution. By these methods all secondary hydrolytic reactions are avoided. In this way Ebler has prepared zinc peroxide, which has the formula $ZnO_2.{}^1/_2H_2O$. This is a fairly stable compound which is very slowly hydrolyzed in cold water, and with acids gives the reactions for H_2O_2.

The reaction between SO_2 and NH_3, to which already so much attention has been given by Divers, Ogawa, and others, has been further studied by Ephraim (*Ber.*, **44**, 379, 386, 395), who finds three distinct products: by excess of SO_2, aminosulfinic acid, $NH_2.SO_2H$, is formed; by excess of NH_3, either white ammonium aminosulfite, $NH_2.SO_2NH_4$, or a red compound with the formula $2SO_2.4NH_3$. Since three of the nitrogen atoms differ from the fourth and since a silver salt with three atoms of silver can be formed from it, the red compound must be the tri-ammonium salt of imino-disulfinic acid, $NH_4.N(SO_2NH_4)_2$. This compound is also formed by the reaction between thionyl chloride and liquid ammonia. By the action of thionyl chloride and hydrazine, an analogous compound is formed, hydrazine-disulfinic acid, $HO_2S.NH.NH.SO_2H$, in which all the hydrogen is replaceable, as by Ba. In the reaction between thionyl chloride and hydrazine a portion of the thionyl chloride is reduced to sulfur which dissolves in the hydrazine with the formation of sulfohydrazinium, which is analogous to sulfammonium, for which Ruff has found the formulas $(S(NH_3)_6)_2$ and $(S(NH_3)_3)_2$ (*Z. anorg. Chem.*, **70**, 49). In this connection Ephraim also prepared sulfohydrazide, $SO_2(NH.NH_2)_2$, and nitrosulfamide, $NH_2.SO_2.NH.NO_2$, the first representatives of hydrazides of inorganic acids and of inorganic nitramides. In this connection may be noted the first of a series of compounds in which sulfaminic acid takes the place of ammonia in the metal-ammines. By the action of sulfaminic acid on potassium chloroplatinite Kirmreuther (*Ber.*, **44**, 3115) has formed two salts of the formula $(Cl_2Pt(NH_2.SO_3)_2)K_2$, one being a dihydrate but not converted into the other by loss of water of crystallization. These two salts prove to be stereoisomers, the hydrated salt being the *cis*-form. Both salts are neutral but the *trans*-form is converted by caustic potash into a tetra-potassium salt, which apparently has the formula $(Cl_2Pt(NH.SO_3K)_2)K_2$, a derivative of an isomeric di-potassium salt, $(Cl_2Pt(NH.SO_3H)_2)K_2$, which has not been prepared. In discussing the formula of the lead chamber crystals, Jurish (*Chem. Ztg.*, **34,** 1065) holds that it is neither a nitro- or a nitrosyl-sulfuric acid, but that the formula must be doubled, as indeed Weber, from whom the acid is often named, suggested. The formula $SO_2(OH)_2$, which is ordinarily given for sulfuric acid, should be discarded since the acid contains neither SO_2 nor hydroxyl groups, but is rather a compound, after Werner, of SO_3 with H_2O. In the union of SO_3 with H_2O in the lead chamber, when insufficient water is present, instead of forming (double formula) $H_2O.SO_3.SO_3.H_2O$, one H_2O is replaced by N_2O_3, giving $H_2O.SO_3.SO_3.N_2O_3$, which is the formula of the chamber crystals.

Harcourt and Brereton Baker (*J. Chem. Soc.*, **99,** 1311) have repeated the work of Flint on the fractional hydrolysis of tellurium tetrachloride but, contrary to Flint, find no evidence of a fraction with a lower atomic weight for tellurium. They suggest that Flint's results might have been occasioned by the presence of the trioxide. In the course of his extensive work on salts of the type $M''_2M^{IV}Hal_6$, Gutbier has described (*J. prakt. Chem.*, [2] **83,** 145) a large number of chloro- and bromo-tellurates of organic bases, and these have also been crystallographically examined by Lenk. These salts, while soluble without decomposition in very little water, even if warmed, are rapidly hydrolyzed by the slightest excess, and cannot be recrystallized from pure water. They are, however, readily recrystallized from dilute HCl or HBr. In acid solution they act toward reagents in every respect like solutions of TeO_2 in the acid. By passing an electric arc between tellurium electrodes under strongly cooled CS_2, Stock (*Ber.*, **44,** 1832) has obtained carbon ditelluride, CTe_2, in dilute solution. The compound could not be isolated, but its analysis was determined by its decomposition products. It is exceedingly unstable; its solution is golden-yellow, and when its concentrated solution is cooled to —100° it deposits minute brown crystals. Even in a 0.1% solution its odor is intolerably suffocating. It resembles in many respects the little known CSe_2.

The "complex" acids containing molybdic, tungstic, and other acids have long interested chemists and many unsuccessful efforts have been made to account for these compounds on valence theories. The application of Werner's theories proved no less elusive until Miolati suggested the resemblance of these acids to salts of the familiar type, $(M^nX'_6)^{n-6}$, (such as $PtCl_6$), where the valence of the ion depends upon the valence of the central atom, being the difference between the valence of this atom and that of the atoms or groups which surround it. We would thus have the ions $(TeO_6)^{VI}$, $(IO_6)^{V}$, $(PtO_6)^{VIII}$, etc. The difficulty of applying this to the complex acids is the same as presents itself in applying it to many of these simpler acids, that frequently the end-form is not developed. Thus in the telluric and periodic acids, the commoner salts are derived from H_2TeO_4 and HIO_4. Salts of the normal acids, as Ag_6TeO_6 have, however, been prepared. Again, in platinic acid six of the hydrogen atoms migrate within the nucleus and its salts are those of the acid $(Pt(OH)_6)^{II}$. The beginnings of Miolati have been followed up in the work of Rosenheim (*Z. anorg. Chem.*, **69,** 247, 261; **70,** 73, 248; *Z. Elektrochem.*, **17,** 694), and he has been remarkably successful in preparing salts of the end-forms of the different types, thus substantiating the predictions of the theory. In the application of this theory to the complex acids, in the types noted above the oxygen is replaced by bivalent groups, such as MoO_4 and WO_4, or Mo_2O_7 and W_2O_7, and we would have as complex acids such as the following:

from $H_5(IO_6)$	$H_7(PO_6)$	$H_8(SiO_6)$
$H_5(I(MoO_4)_6)$	$H_7(P(Mo_2O_7)_6)$	$H_8(Si(Mo_2O_7)_6)$
$H_5(I(WO_4)_6)$	$H_7(P(W_2O_7)_6)$	$H_8(Si(W_2O_7)_6)$, etc.

Now while many of these acids are evidently tribasic, as the familiar phosphomolybdic acid, Miolati had already found by physico-chemical methods that the free acid gave evidence of a higher basicity, and Rosenheim has now prepared the guanidinium salts of phosphomolybdic and of arsenomolybdic acids, in which the acids are actually septi-basic, and yet the salts by conductivity determinations prove to be neutral salts, a remarkable confirmation of theory. In the oxalo-tellurates, telluric acid, of formula H_6TeO_6 (not TeO_3), is actually present in the anion. Metatungstic acid he finds to be an aquo-acid with formula $H_2(WO^{(WO_4)_3}_{(H_2O)_3})+aq.$, and this is confirmed by the fact that the silver, thallium and guanidinium salts all contain three molecules of water. It may, however, be noted that this is contrary to the views of Copaux regarding the water (*Ibid.*, **70**, 297). For those "complexes" made up of the same acid anhydrides, Rosenheim proposes the name *isopolyacids*, as polymolybdic acid, while for those which contain different anhydrides *heteropolyacids* is used, as for phosphomolybdic or arsenotungstic acids. This beginning of the systematization of the complex acids will be welcomed by all who have worked on these interesting but perplexing compounds.

Group VII.—The method of preparation of anhydrous chlorides recently developed by Bourion, heating the oxide in chlorine and the chloride of sulfur, has been extended in various directions. Chauvenet (*Compt. rend.*, **152**, 87, 1250) finds that by heating in a current of $COCl_2$ many different oxides are converted into chlorides. The temperatures necessary to induce the reaction vary from 350° for Fe_2O_3 to 650° for ThO_2. WO_3 forms at 350° the oxychloride WO_2Cl_2, but in all other cases the chloride was formed. Carbonyl chloride reacts also similarly with sulfides, carbonyl sulfide being the by-product. This reaction is capable of many applications, as in the decomposition of sulfide ores, and their analysis, and also in the preparation of carbonyl sulfide. Michael and Murphy (*Am. Chem. J.*, **44**, 365) have studied the reaction between chlorine in carbon tetrachloride solution on many oxides, especially with a view to the positions of the metals in the periodic system, as well as to the relation of unsaturated oxides to chlorine. Thus in the case of FeO, MnO, NiO and CoO, the general reaction is $3MO + Cl_2 = M_2O_3 + MCl_2$. With FeO the reaction takes place actively at —18°, while that with MnO is not quite as active. NiO reacts at ordinary temperature, but the reaction is completed only after some time, while with CoO heating in a closed tube to 100° is necessary for the completion of the reaction. In some cases oxychlorides are formed at lower temperatures and chlorides when more highly heated. The action of the Cl–CCl_4 solution on MoO_3, and WO_3 would appear to be the best method of preparing $MoCl_5$, $WOCl_4$, and WCl_6. In some cases, as with Ag_2O and CrO_3 the solvent takes part in the reaction, the CCl_4 being oxidized to $COCl_2$. The authors call attention to the fact that since chlorine is soluble in CCl_4 to the extent of

10% of its weight at ordinary temperature and 25% at 0°, this solution affords a convenient means of using chlorine in a fairly concentrated condition. Darzens (*Compt. rend.*, **153**, 270) has studied the action of thionyl chloride on oxides, and finds that in general its action is similar to that of the Cl–S_2Cl_2 mixture. In some cases, however, as with WO_3 and with gadolinium oxide, it was found impossible to complete the chlorination, the oxychloride being formed, even at high temperatures and with excess of the reagent. Thionyl chloride offers in no case any advantage over the Cl–S_2Cl_2 mixture for converting oxides into chlorides, while it is much more difficult to prepare and especially to obtain free from phosphorus. The action of $POCl_3$ on metallic oxides is the subject of a paper by Bassett and Taylor (*J. Chem. Soc.*, **99**, 1402). In some cases, as with the oxides of cadmium, cobalt, copper, mercury, iron and aluminum, the anhydrous chloride of the metal was at least the chief product. In other cases what appear to be addition products were formed, such as $CaO.2POCl_3$ at 110° and $CaO.3POCl_3$ at ordinary temperature, and analogous compounds with MgO, MnO, and ZnO. The fact that these compounds give up their $POCl_3$ content to petroleum ether would seem to relegate them to the class of addition products, still it is possible that they may be looked on as phosphates in which hydroxyl groups are replaced by chlorine, and their constitution may have a bearing on that of apatite and wagnerite. When the reaction between phosphoryl chloride and oxides was carried out in a solution of acetone or of esters, the solvent took part in the reaction and complex compounds were formed containing the solvent, $P_2O_3Cl_4$, and the metallic oxide. An interesting case of isomerism is noted by Costachescu (*Ann. Scient. Univ. Jassy*, **7**, 5) in his study of metallic fluorides. When freshly prepared cobalt hydroxide is dissolved in HF and evaporated in vacuum over H_2SO_4, large garnet-red crystals are obtained of the formula $CoF_2(H_2O)_4$, while, if the original solution is precipitated by alcohol, small rose crystals of the same composition are obtained, but which lose much more water at 60° and which unite directly with pyridine in the cold, while the dark red modification reacts only when heated on the water bath. The isomerism seems to be attributable to the fluorine in the first more stable form being on opposite angles of an octahedron, while in the latter, less stable form, they are on neighboring angles. Both give the same pyridine compound, $((H_2O)_2CoPyr_4).F_2 + H_2O$. With nickel the modification corresponding to the less stable form only was obtained, and this forms with pyridine a compound analogous to that with cobalt. Attention should be called to a paper by Herrmann (*Z. anorg. Chem.*, **71**, 257) from the Göttingen physico-chemical laboratory, which opens up a little worked field. It is entitled "The Combining Power of the Chlorides of Copper, Lead, Iron, Tin and Bismuth, and of the Chlorides, Bromides and Iodides of Copper and Cadmium," and is a study of these compounds from a similar standpoint to that of metallography. Where not prevented by the "alloy" being too hygroscopic, microscopic studies were also made. In some cases compounds were found and two eutectics; in others only a single eutectic; in some cases mixed crystals with complete or with limited solid solubility. The paper does not admit of abstraction here, especially as it is quite fully treated in *Chemical Abstracts*, **5**, 3545, but it may be noted that no parallel is found between the combining power of metals and of their salts. Further developments along this line cannot fail to bring out much of interest. Bleaching-powder has been again the subject of investigation, this time by Taylor (*J. Chem. Soc.*, **97**, 2541), who finds that when CO_2 is led over bleaching-powder only chlorine is evolved and no hypochlorous acid. The same is true when CO_2 is led into a solution of NaCl and NaOCl. Thus CO_2 acts in this respect like other acids. That HCl is set free by CO_2 may be made evident by leading CO_2 into a solution of NaCl or $CaCl_2$ containing methyl orange, when the indicator is turned red. If air free from CO_2 is led into a bleaching-powder solution, the evolved gas, which is given off very slowly in the cold but more rapidly when warmed, is almost exclusively HOCl, but with ordinary air which has not been freed from CO_2, the HOCl is accompanied by chlorine. It is suggested in explanation of these reactions that in bleaching-powder there exists the equilibrium:

$$2Ca(OH)_2 + 2Cl_2 \rightleftharpoons CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

The action of CO_2 would then consist in neutralizing the $Ca(OH)_2$, and thus displacing the equilibrium to the left. Similarly, in bleaching as the chlorine is used up, more is freed and the reaction goes on to the left to completion. This equation would explain why the action of bleaching-powder is more intense in the presence of $CaCl_2$ in excess, increasing its concentration, and why electrolytic bleach is more active than a mere solution of hypochlorite.

What seems to be a salt of quadrivalent manganese with an oxy-acid has been prepared by Marino (*Atti accad. Lincei, Rome*, [5], **20**, i, 447). Analogous with the action of SO_2, when MnO_2 is treated with SeO_2, a compound is formed which has the formula $MnSe_2O_6$. This is a yellow crystalline powder, insoluble in water and in dilute HNO_3 and H_2SO_4, but it possesses none of the properties which would be expected of an analog of a dithionate. In concentrated HCl it dissolves with evolution of chlorine, and liberates iodine from an acetic acid-KI solution. With alkali hydroxides and carbonates, MnO_2 is formed, and oxalic acid is oxidized to CO_2. Numerous other reactions show that it is an oxidizing agent of considerable strength. It thus seems quite certain that quadrivalent manganese is present. Selenous acid is recovered by the action of alkalies, so that the salt is to be looked on as a selenite of quadrivalent manganese, $Mn(SeO_3)_2$. By heat it is converted by loss of SeO_2 into manganese selenate, $MnSeO_4$, which on further heating is decomposed into SeO_2 and Mn_3O_4 (and O).

Group VIII.—Two papers have appeared on the relation of FeO and Fe_3O_4 to water at moderately high temperatures, the one by Friend, Hull and Brown (*J. Chem. Soc.*, **99**, 969), who have studied the action of water vapor on iron, and the other by Hilpert and Beyer (*Ber.*, **44**, 1608), who use the reaction between hydrogen saturated with water vapor on ferric oxide. According to the former, the velocity of the reaction between Fe and H_2O, as measured by the increase in weight of the iron, is at 500° practically zero. At 820° and at higher temperatures the iron is completely oxidized to Fe_3O_4. Between these temperatures the curve of oxygen absorption finally becomes parallel to the time axis, which according to the authors is explicable if it is assumed that at lower temperatures (350°) the dissociation pressure of water is but little greater than that of FeO, but less than that of Fe_3O_4. Only at 820° does the dissociation pressure of water reach that of Fe_3O_4. Then we can conceive that at the lower temperature FeO is first formed, and from there to 820° a mixture of FeO and Fe_3O_4, the dissociation pressure of the oxides being in equilibrium with that of water for each particular temperature. At 820°, the dissociation pressure of water reaching that of Fe_3O_4, this oxide only will be formed. The authors were unable to bring any direct proof of this view, since they could not reduce Fe_3O_4 in a current of steam. Starting out from the fact that it is impossible to obtain the lower oxides of iron by reduction of Fe_2O_3 in hydrogen or CO, since owing to the removal of the oxidation products the partial pressure of the oxygen remains at zero and hence less than that of the oxide, Hilpert and Beyer inhibit this reduction of the oxygen pressure by carrying on the reduction by a mixture of hydrogen and water vapor. At a red heat the dissociation pressure of the oxygen of water is certainly greater than that of Fe_3O_4, since the latter is formed by heating the metal in steam. Thus by mixing hydrogen and steam the dissociation of the latter is inhibited to any desired degree, and hence one can prepare mixtures of these gases in which the partial pressure of the oxygen shall correspond to any desired value, between that of the metal and Fe_3O_4. Experimentally the authors prepared their mixtures by leading hydrogen through water at fixed temperatures; their oxide was pure Fe_2O_3 prepared from the oxalate, and heating and cooling was carried on in a stream of nitrogen. The composition of the resulting products was determined by loss of weight, and by titration of the ferrous iron and of the total iron. Some 150 experiments were carried out from 300–1100°. Between 300° and 400° by using less than 4% of water vapor, all possible stages of reduction of the metal were obtained. When the amount of water vapor passed this limit pure Fe_3O_4 was obtained. In no case was FeO obtained as a definit phase. It is thus possible to prepare pure Fe_3O_4 by heating ferric oxide to 400° in a stream of hydrogen which has been passed through a wash bottle of water heated to 30–50° At 500° a mixed oxide with 50% FeO was obtained, and by using higher temperatures the mixed oxides contained larger proportions of FeO. At 700° the limit is 85% FeO, the limiting proportion of water in the vapor being 38%. Even at 1100° the oxide still contained a minimum of 1.5% Fe_2O_3, nor does it appear possible by reduction to obtain pure FeO. By starting with pure iron instead of ferric oxide the iron was but slowly attacked by the hydrogen-water vapor mixture, and oxides of indeterminate composition were formed, nor was it found possible by pure water vapor to convert the iron completely into Fe_3O_4, even after many hours. The magnetic character of the resultant oxides was also examined. This diminishes with increasing amounts of FeO and when between 80 and 90% FeO is present the magnetic quality has well nigh disappeared. Since Fe_2O_3 is paramagnetic it appears that the marked magnetic quality of Fe_3O_4 is due to a compound of the two oxides. The conditions necessary for the formation of iron pyrites are very fully discussed by Feld (*Z. angew. Chem.*, **24**, 97, 290), the working of a method for the purification of illuminating gas from H_2S and NH_3 by means of certain iron compounds having led to the discovery of the ready formation of FeS_2 in aqueous solution. If a solution containing iron thiosulfate and iron polythionates is boiled with FeS and sulfur, FeS_2 is formed. It is also rapidly formed when FeS is heated in neutral or weakly acid solutions with excess of sulfur or substances which can readily part with the sulfur which they contain. The presence of basic substances even as weakly basic as magnesia, hinders the formation of FeS_2, while the presence of reducing substances promotes the union of FeS and S to FeS_2. The author suggests that precipitated iron sulfide is actually Fe(OH)(SH), and that this unites with sulfur, water being split off and FeS_2 formed. Bases or oxidizing substances would antagonize the precipitation of the Fe(OH)(SH). The following proposition, a modification of that of Bischoff (*Lehrbuch d. chem. u. physik. Geologie*, 1, 917), is laid down: Where-ever iron-carrying waters come into contact with reducing substances which can give up sulfur and are not basic, and wherever rocks which contain iron and are not basic come into contact with waters which contain reducing substances and substances which can give up sulfur, there FeS_2 will be formed. This then is the condition of pyrites formation in nature. Rosenberg has concluded his investigations of the nitroprussides by a long paper (*Arkiv. Kem. Min. Geol.*, **4**, Nr. 3, 1), in which he considers the mother substance of the nitroprussides to be nitroso-iron-trisulfide, $(NO)_2FeS_3$. This is prepared by leading nitric oxide into a solution of ferrous chloride at —2° and then partially precipitating by the addition of a very dilute solution of sodium trisulfide, though other alkali sulfides will answer. The precipitate is filtered off and nitric oxide and the sulfide again added until the iron has been completely precipitated. Rosenberg considers that a nitrosochloride, $(NO)_2FeCl_2$, is at first formed, but in view of the fact that ferrous iron will unite with only one nitroso group this may be doubted. The nitroso-iron trisulfide is very stable towards acids but is attacked by alkalies. In sodium sulfide it dissolves with the separation of sulfur and the formation of the red, unstable, nitroprusside. The reaction is: $2(NO)_2FeS_3 + Na_2S = (NO)_4Fe_2S_2Na_2 + 5S$. By the action of dilute acids, even carbonic, or better by the action of the nitroso-iron trisulfide, the red salt goes over into the stable black nitroprusside: $2(NO)_4Fe_2S_2Na_2 + 2H^+ = (NO)_7Fe_4S_3Na + 2Na^+ + NaS + H_2 + NO$. Both salts contain the sexivalent (Fe_2) group, the constitution of the black salt being $(NO)_3Fe_2(SFe(NO)_2)_2.SNa$. This indicates why the black salt should be formed by the action of the nitroso-iron sulfide on the red salt. By the action of alkalies the black salt is changed into the red.

The recent work of Werner (*Ber.*, **44**, 873, 1887, 2445, 3132) on isomerism in cobalt and chromium bases is hardly surpassed in brilliancy by the classic work on the asymmetrical carbon atom. From the standpoint of Werner's valence theory numerous isomers should be possible among the metallo-bases, though none were known when he suggested his theory. By persistent work these gaps have gradually been filled, giving thereby the strongest substantiation to his theory. In the simple cobalt bases the six atoms or groups surrounding the cobalt atom in the coördinated group are conceived of as situated at the six corners of an octahedron. This group has best lent itself to detection of isomerism when four of the corners are occupied by two molecules of ethylenediamine. In the group X_2CoEn_2 (En is used as the symbol of ethylenediamine) the two groups X may be on contiguous or on opposite corners. Thus we may have the *cis*-form $\left[\begin{matrix}(1)X\\(2)X\end{matrix}\text{Co En}_2\right]$ and the *trans*-form $\left[\begin{matrix}(1)X\\(6)X\end{matrix}\text{Co En}_2\right]$. This isomerism has been realized in numerous cases. In case $X = NO_2$ another form of isomerism is possible according to whether NO_2 represents the nitro or the nitrito group. Both of these possibilities are realized experimentally.

A third realized form of isomerism is called by Werner ionization-metamerism, as is found in two forms such as $\left[\begin{matrix}O_2N\\O_2N\end{matrix}Co\ En_2\right].X$ and $\left[\begin{matrix}O_2N\\X\end{matrix}Co\ En_2\right].NO_2$, where X = Cl, Br, SCN, etc. Again in coördination-polymerism we have the nitrito-cobaltites of two different bases, $(Co\ En_3).Co(NO_2)_6$, and $\left[\begin{matrix}O_2N\\O_2N\end{matrix}Co\ En_2\right]_3.Co(NO_2)_6$, which are polymers. But yet more remarkable is the possibility of a fifth kind of isomerism. If the formula of the coördinated group $\left[\begin{matrix}(1)O_2N\\(2)O_2N\end{matrix}Co\ En_2\right]$ is really represented by the figure of an octahedron, it follows that there should be two forms which should be mirror images of each other, and from the analogy of compounds with an asymmetrical carbon compound, these should be optically active. This compound, as well as several others of similar type, have been prepared and have proved to be racemic compounds. They have been split into their active components by a method familiar in organic chemistry, namely, obtaining their campho-sulfonates or bromo-campho-sulfonates. The optical isomers show themselves to be actually optically active, and the two isomers have approximately the same but opposite rotation. What is true of cobalt bases, if representing a general principle, should be true of other similar bases, and therefore Werner attempted to apply it to the chromium ethylenediamine bases. Here he found in chromium dichloro-ethylenediamine chloride, $(Cl_2Cr\ En_2)Cl$, (chromium violeochloride) a racemic compound, which was broken up into its optically active components by bromo-campho-sulfonate, showing itself in every way analogous to the cobalt racemates. The chromium compounds have a smaller rotation than the corresponding compounds of cobalt. This brief summary will suffice to show the far-reaching character of Werner's recent work. If full justification for the old valence theory is found in the development which through it organic chemistry was enabled to make, certainly Werner's theory is well justified by the order it has already brought into the field of the complex compounds of inorganic chemistry. In this connection mention should be made of the work of Rosenheim (*Ibid.*, p. 1865) on the nitrito-cobaltites (cobalti-nitrites). Some time since, Hofmann and Buchner prepared a salt with the anion $Co(OH)_3(NO_2)_3$, which should show stereoisomerism, according as to whether three similar groups are at the three corners of one face of the octahedron or not. By treating $Na_3Co(NO_2)_6$ with guanidinium carbonate, there crystallize out at ordinary temperature large garnet-red crystals of $(CN_3H_6)_3.(Co(OH)_3(NO_2)_3)$. From the mother liquor are obtained dark brick-red needles of the same composition, but which differ in solubility and in various precipitation reactions. In all probability they are the two stereoisomers called for by theory. Numerous other salts of the trihydroxy-trinitrito series were prepared, as well as the strontium salt of the dihydroxy-tetranitrito series. By the action of metal acetylacetonates on the hexanitrito salt a series of diacetylacetonodinitrito compounds was formed, where the coördinated group contains four negative groups, $Co(C_5H_7O_2)_2(NO_2)_2$.

In his investigations upon platinum Wöhler (*Z. Chem. Ind. Kolloide*, 7, 243) has found the most sensitive reagent for platinum to be $SnCl_2$, which gives a red coloration to the solution unless very dilute, in which case the color is yellow. In this way it is possible to detect 10^{-7} grams platinum in 1 cc. solution. This coloration is due to colloidal platinum, which is held in this condition by the presence of protective colloids resulting from the hydrolysis of $SnCl_2$. It can also be produced by other reducing agents, as with ethereal phosphorus, in the presence of gelatin as protective colloid. On standing it goes over into a coarse brown colloid. The chocolate-brown precipitate in the red solution by the presence of the hydrolytic products of the $SnCl_4$ formed in the reaction is not a compound, but a mixture of platinum metal with stannic acid, analogous to the gold purple of Cassius. It is soluble (as appears to be the case with purple of Cassius) in acetic ester and in ether. With the bromides of platinum, stannous bromide causes a similar reaction. Wöhler also finds that the red coloration formed when stannous nitrate is added to silver nitrate (Ditte's reaction) is due to the formation of an analogous silver "purple."

In connection with the work of Gutbier, already mentioned, he has prepared a large number hexachloroplatinates, ruthenates and osmates, and hexabromoplatinates, of organic bases, both of the aliphatic and aromatic series (*Ber.*, **43**, 3228, 3234; **44**, 306, 308). The hexachlororuthenates are not formed by double decomposition from the alkali salts, as is the case with compounds of this type from the other platinum metals, but are formed by the interaction of the organic base, the pentachlororuthenite (M'_2RuCl_5) and chlorine. On the other hand the alkali salts of the hexachlororuthenate (M'_2RuCl_6) cannot be formed directly from the pentachlororuthenite by the action of chlorine or any other oxidizing agent. The explanation of this anomaly appears to the writer to rest in the fact that in the presence of organic substances the pentachlororuthenites are converted into the aquopentachlororuthenates, $M'_2Ru(H_2O)Cl_5$, and that by the action of chlorine the water in these last salts is exchanged for Cl, giving the normal hexa-salts. This explains why the earlier workers on these salts, especially Claus and Joly, failed to prepare the hexachlororuthenates. Gutbier's success in preparing the hexachlororuthenates, so many of which he has described, is due to the fact that in the presence of the organic bases with which he worked, the penta-salt was converted into the aquopenta-salt, which readily unites with chlorine, giving the hexa-salts. Several additional papers have appeared from Delépine (*Compt. rend.*, **151**, 878; **152**, 1390, 1589; **153**, 60; *Bull. soc. chim.*, [4] **9**, 710, 771) on irido-disulfates, especially in connection with the action of pyridine. Unlike the stronger bases, pyridine seems to have no action on the iridodisulfates, but on standing, or more rapidly by heating, there takes place an externally almost unnoticeable change, resulting in the formation of a salt of pyridino-iridodisulfuric acid, $((SO_4)_2.Ir.(C_5H_5N)OH).H_2$. This forms crystalline salts with many inorganic bases; in these salts not all the cationic hydrogen is replaced, as is also the case with the original irido-disulfuric acid. Pyridine is found further to react with the aquopentachloroiridates, $M'_2Ir(H_2O)Cl_5$, the water being replaced by pyridine, giving pyridinochloroiridates, $M'_2Ir(C_5H_5N)Cl_5$. With the hexachloroiridites, M'_3IrCl_6, the same compound is formed, in this case one chlorine atom being replaced and the valence of the coördinated group reduced from three to two. If the solution obtained by the action of chlorine on ammonium hexachloroiridate, $(NH_4)_2IrCl_6$, is evaporated, a black deliquescent crystalline mass is obtained, $H_2IrCl_6 + 6H_2O$. On slow heating this loses both water and HCl, but it was not found possible to obtain either $IrCl_4$ or $IrCl_3$. Further work on iridium has been done by Duffour (*Compt. rend.*, **152**, 1393, 1591). By treating sodium hexachloroiridate with sodium oxalate, the oxalato-tetrachloroiridite, $Na_3.IrCl_4(C_2O_4)$, is formed. On treating the silver salt with HCl, the free acid is obtained. On heating, this decomposes into tetrachloroiridous acid, $H.IrCl_4$, of which several salts were formed. From the silver salt of tri-oxalatoiridous acid by HCl the free acid is formed, which gradually, by reversible reaction, goes over into diaquo-dioxalatoiridous acid, $H_3.Ir(C_2O_4)_3 + 2H_2O \rightleftharpoons H.Ir(H_2O)_2\cdot(C_2O_4)_2 + H_2C_2O_4$. From the potassium salt by the action of KOH there is formed a hydroxy-aquo salt, $K_2.Ir(OH)(H_2O)(C_2O_4)_2$. On half neutralizing the free acid from this salt by KOH there is obtained an acid salt, $KH.Ir(OH)(H_2O)(C_2O_4)_2$, which is an isomer of the potassium salt of the (monobasic) diaquo salt, $K.Ir(H_2O)_2(C_2O_4)_2$, above.

The fact that the best determinations of the atomic weight of argon place it above that of potassium instead of below, as seems to be required by the periodic system, has led many to believe that ordinary argon contains similar elements of higher atomic weight. Fischer and Froboese (*Ber.*, **44**, 92) have tried to solve the problem by the fractional crystallization of argon, using liquid air of different compositions as cooling agent, and an apparatus of their own devising for separating the crystals from the mother liquor. They find, however, no sign of resolution of argon into components, all fractions having the same density, representing the atomic weight of 39.9.

No attempt can be made here to review the work that has been done the past year on the radioactive elements, except to note that radium emanation, under the name of niton (Nt), has taken its place with some definiteness in Group VIII as the highest member of the He, Ne, Ar, Kr, Xe series, with an atomic weight of 223, and to call attention to two cases of the influence of niton, the one on atomic and the other on molecular reaction. In 1909 Ramsay announced that by the action of radium emanation on a solution of thorium, carbon dioxide appeared to be formed and that it seemed possible that under this influence carbon was a decomposition product of thorium. This was called in question by Herschfinkel (*Compt. rend.*, **153**, 255), who on repeating Ramsay's experiments failed to get the same results, and attributed the carbon dioxide to the presence of oxalic acid in Ramsay's thorium. The latter has again described his work (*Ibid.*, p. 373) and the precautions taken. No oxalic acid could have been present; thorium nitrate without niton gave no CO_2, nor did bismuth, mercury or silver nitrate under the same conditions give with niton any CO_2. It seems probable therefore that the carbon actually arose from the decomposition of thorium under the influence of niton. The other case is a study by Lind (*Le Radium*, **8**, 289) of the influence of radium upon the equilibrium $H_2 + Br_2 \rightleftharpoons 2HBr$. No decomposition of hydrogen bromide could be detected in 37 days, but in the system H_2,Br_2, in 14 days 2.6% of HBr had been formed. It is obviously impossible, starting from a definit amount of niton, to reach an equilibrium, since the decomposition of the niton has a higher velocity than that of the chemical reaction. No acceleration of the reaction due to the niton could be detected at higher temperatures. The decomposition of anhydrous liquid HBr, on the other hand, was decidedly hastened.

Aqueous solutions, both of the acid and of its salts, were rapidly decomposed by the emanation, the concentrated more rapidly than the dilute, but the increased velocity was not proportional to the concentration and is clearly influenced by secondary reactions.

In conclusion, allusion should be made to three new attempts to prepare periodic tables which shall prove more satisfactory than that of Mendeléeff, or others now in use. These are respectively by Schmidt (*Z. physik. Chem.*, **75**, 651), Emerson (*Am. Chem. J.*, **45**, 160) who proposes a "Helix chemica," and Van den Broek (*Physik. Ztschr.*, **12**, 490), in whose table each group has three series instead of two, and which is based on "ideal" atomic weights, which often differ to the extent of several units from those which have been experimentally determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]

THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS.

BY JOHN B. EKELEY AND PAUL M. DEAN.

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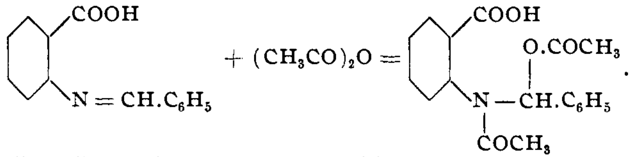
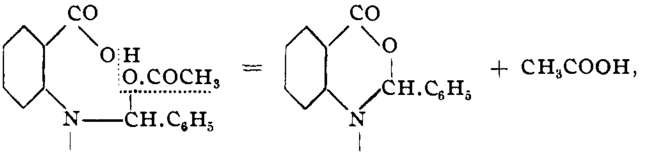
Anthranilic acid reacts with aromatic aldehydes with the formation of benzylidene derivatives. These derivatives react with acetic anhydride, giving a series of oxazines. The reaction probably passes through an intermediate stage in which a molecule of the benzylidene derivative adds a molecule of acetic anhydride thus:



Heating splits off a molecule of acetic acid thus,



giving an acetketodihydrobenzmetoxazine.[1]

The reaction seems to be general, since in the cases thus far studied with aromatic aldehydes, the condensation takes place with ease. This paper will deal with the oxazines obtained from benzylidene, metanitrobenzylidene, paranitrobenzylidene, paraoxybenzylidene, salicylidene, and vanillylidene anthranilic acids. These oxazines are colorless,

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[1] The Badische Anilin und Soda Fabrik has patented a process for making a series of compounds containing the metoxazine ring, abstracts of which are given in the *Chem. Zentralblatt*, 1910, I, 308, 309, 1564; 1911, I, 853.