that obtained by the spectroscope, that all the fractions analyzed were of a high degree of purity.

Fraction 4383, which contained all the neodymium which may have accumulated in forty-one series of crystallizations, gives a slightly lower instead of higher figure than the average, while fraction 4368 which contained more cerium than any other fraction gives a result identical with the average. This close similarity is very striking when one considers that a range of sixteen fractions is included in those examined. Fraction 3474, selected at an earlier stage of the fractionation as being very pure, also shows no sign of being different from the other fractions.

The foregoing results leave little opportunity for choice. There seems to be no reason for preferring the value obtained with any one or more fractions to those resulting with the others. Possibly the average of Analyses 5, 6, 9, 10, 16, 24, 25, 30, 31, 38 and 39, 140.913, is more reliable than the average of all, for in these analyses the praseodymium chloride dissolved rapidly and completely at the start, and was probably entirely free from basic salt, but we believe that the final corrected average of all the experiments, 140.92, represents fairly the best material we succeeded in preparing. This result is not far from the value obtained by Brauner in both his researches, but is over three-tenths of a unit higher than the choice of the International Committee upon Atomic Weights.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels, as well as to Dr. H. S. Miner of the Welsbach Light Company for the praseodymium material.

CAMBRIDGE, MASS.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

Received January 25, 1915.

It might seem too soon for publication of chemical research to feel the effects of the war, especially as nearly half of the period that has elapsed since the outbreak of hostilities covered the summer vacation in the continental universities, yet that there has already been a decided influence is apparent in the fact that the *Zentralblatt* from August 9 to December 9 contains only 964 pages as against 1548 pages for the similar dates in 1913. A far more serious diminution of research is to be expected, when we realize that such a large proportion of the students of European and Colonial universities are "with the colors."

There is little that is particularly striking to chronicle in the progress of inorganic chemistry in 1914. The only radical departure from well-established ideas is found in variations in the atomic weight of lead from different sources. The theoretical considerations are discussed by Fajans[1]

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[1] *Physikal. Ztsch.*, **14**, 951, and *Sitzber. Heidelb. Akad. Wiss., Math-naturw. Kl.*, **1914**, 11, *Abh.* 22.

according to which it appears that the end product of decomposition in the uranium-radium series, Ra G, must be lead, but that it would have an atomic weight of 206.0, instead of 207.1, the atomic weight of ordinary lead. Similarly, the end products of the other radioactive series would have atomic weights varying from 206 to 210, that of the end-product of the Ra C_2 series. The first case has been studied by Richards[1] by determining the atomic weight of lead from different sources. While for ordinary lead from commercial acetate and nitrate the figure 207.15 was found, using the same methods of analysis the atomic weight of lead from English pitchblende was found to be 206.86 and from Joachimsthal pitchblende 206.57. Almost this same figure was found for Colorado carnotite, while uraninite from North Carolina gave a still lower value, 206.40. In general, the greater the radioactivity of the mineral, the lower the atomic weight of the contained lead. This variation is also confirmed by Maurice Curie[2] who finds the figure for lead in carnotite 206.36, in pitchblende 206.64, in yttriotantalite 206.54, but that in monazite was 207.08. From these results there would seem little doubt but that in lead there is a variable atomic weight, depending on its origin, and further work along this line will be awaited with interest.

Among the more general papers of the year is one by Kullgren[3] on the hydrolysis of inorganic salts. Using the inversion method, the hydrolysis of a large series of salts, chiefly chlorides and nitrates of bivalent metals, was determined at 85.5° and 100°. In most cases the hydrolysis proceeds according to the equation: $RCl_2 + HOH = R_{Cl}^{OH} + HCl$, the value being the same for chlorides and nitrates, (except $ZnCl_2$). The reaction with aluminum salts appears to be with two molecules of water: $AlCl_3 + 2HOH = Al_{Cl}^{(OH)_2} + 2HCl$. (Lind has found by conductivity methods the hydrolysis of trivalent ruthenium also to be two-thirds.) In these salts with moderate hydrolysis the hydrolysis-constant is seldom a real constant. The hydrolysis of $HgCl_2$ (1.33) and $PbCl_2$ (1.49) is almost independent of dilution, but in the other salts there was some increase of hydrolysis. The degree of hydrolysis is decreased by the presence of neutral salts and this action is independent of the temperature. In a study of organic compounds of tin, Pfeiffer[4] obtained the first hydrolytic product of stannic chloride and of stannic bromide, $SnCl_3(OH).3H_2O$ and $SnBr_3(OH).3H_2O$, by extracting a not too dilute aqueous solution of the halide with ether and recrystallizing the product obtained from water. From his work he draws the conclusion that these hydrates, as well as $SnCl_4.5H_2O$ and $SnBr_4.4H_2O$, are not aquo-salts, but simply addition compounds (Anlagerungsverbindungen). The coördination number of the tin atom is 6, two of the coördination positions being occupied by water. The structure thus becomes $[Cl_4Sn(..OH_2)_2] + 3H_2O$, etc.

Cryoscopic measurements in nonaqueous solutions is a subject of great interest and slow development. Isbekow[5] has worked with $AlBr_3$ as a

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[1] This Journal, **36**, 1329 (1914).

[2] *Compt. rend.*, **158**, 1676.

[3] *Z. physik. Chem.*, **85**, 466.

[4] *Z. anorg. Chem.*, **87**, 235.

[5] *Ibid.*, **84**, 24.

solvent, and finds that in this medium such substances as $AlCl_3$, AlI_3, CBr_4 and S, which give non-conducting solutions, have normal molecular weights. On the other hand $HgBr_2$, $SbBr_3$, $BiBr_3$, $CdBr_2$, PBr_3 and $ZnBr_2$, whose solutions are electrolytes, are polymerized, the first three increasing in polymerization with the concentration. It appears as if in these cases the salt forms a complex ion with the solvent, which decomposes with increasing dilution into the simple undissociated molecule. Olivari[1] has used iodine as a solvent and worked chiefly with organic compounds, which at great dilution show normal molecular weights, but which associate with increasing concentration. The associating tendency is least with hydrocarbons and increases with the presence of hydroxyl groups. In concentrated solutions the molecule of sulfur is S_8, but lower values are obtained on dilution. Selenium gives values between Se and Se_2, the latter only in concentrated solutions. With tellurium, compounds are formed, as is evidenced by the evolution of heat, which seem to have simple molecules of the formula TeI_x. Iodides of the alkalies and organic iodides give abnormal results, the molecular weight increasing with concentration to a maximum value and then decreasing.

The action of ultraviolet light on metals has been investigated by Kimura.[2] He finds that when metals are covered with a layer of water or alcohol and exposed to ultraviolet light they are corroded and the material removed goes into solution in a colloidal form. The colloidal particles seem to consist of both metal and hydroxide. An alloy of 90% cadmium and 10% antimony showed no corrosion in vacuum but was acted on in the air, and much more strongly in pure oxygen. Kimura concludes that the action in air is due to the formation of ozone by the influence of the ultraviolet light. Under water, where the corrosion is much greater, hydrogen peroxide is in part the active agent, but not the exclusive one, as was shown by experiments on the action of hydrogen peroxide on silver.

From experiments at Kilauea in 1912, Brun concluded that in the gases of this volcano there was no water to which a magmatic origin could be attributed. More recent observations by Day and Shepherd[3] indicate the reasons why Brun failed to detect this water, and show its presence. The gases were drawn by Day and Shepherd by means of a metal tube inserted in a narrow lava crack from direct contact with molten lava. Considerable quantities of water were obtained, which could only have been of magmatic origin. The gases, chiefly SO_2 and CO_2, with a little CO, contained nitrogen, but no argon, as would have been the case had any atmospheric gases been present. The water collected was milky from precipitated sulfur, but contained neither chlorine nor titanium. These results are analogous with those of other observers on the gases of Mount Etna, except that here, as well as at Vesuvius, Stromboli and Santorin, large amounts of chlorine are present. It must be concluded that magmatic water plays a large role in volcanic eruptions, as has been generally believed.

The work of Ephraim[4] on "Nebenvalenz," which was described last year, has been extended to the addition compounds of the halides of the

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[1] *Atti accad. Lincei, Rome* [5] **22,** ii, 697; **23,** i, 41.

[2] *Mem. Coll. Sci. Engin., Kyoto,* **5,** 253.

[3] *Compt. rend.,* **157,** 958, 1027.

[4] *Ber.,* **46,** 3742.

bivalent metals with substituted ammonias. Many of the addition compounds formed are analogous to those formed with ammonia, while others differ. The influence of the atomic volume of the central metal upon the affinity of the compound is clear, and in the case of Ni, Co, Fe, and Mn, the expression $\sqrt[3]{\mathrm{v}}.\sqrt[3]{\mathrm{T}}$ (v = atomic volume of the metal, T = dissociation temperature) is nearly a constant, as was found to be the case in the addition products with ammonia. The affinity is also strongly affected both by the anion and also by the neutral portion of the molecule, but the irregularities are so far too great for much generalization. Pfeiffer,[1] working with the stannic halides, finds tin tetrachloride to possess the greatest affinity in the formation of addition products with ethers, esters, and nitriles. The addition compounds of the tetrabromide are far less stable, and no addition compounds were formed with any of the esters tested.. If one chlorine atom in the tetrachloride is replaced by the methyl group, the affinity for esters, etc., almost ceases, while the substituted bromide forms no such addition products. All three tetrahalides form addition products with alkali salts and related compounds, as do the mono- and di-alkyl halides, but this is no longer the case with the stannic halides in which three or four of the halogen atoms are replaced by alkyl groups. The same is true regarding the tendency to unite with pyridine, but with ammonia the trialkyl derivatives, R_3SnX, form addition compounds, though this is not the case with the tetraalkyl compounds. Pfeiffer concludes that the affinity of the "Nebenvalenz" of tin decreases from chloride to bromide, and from bromide to iodide, and also decreases as the halogen atoms are progressively replaced by alkyl or phenyl groups. This is in general accord with the work of Ephraim.

Werner has continued his work[2] with rather striking results, especially in two particulars. First, in his study of the asymmetrical cobalt atom, he has prepared compounds with two cobalt atoms in the nucleus, to each of which are attached two ethylenediamine groups, and which are linked together by a NH_2 and a NO_2 group; these latter groups are held, half by primary and half by secondary valence. Such a compound ought to be capable of existing, like the analogous tartaric acid with two asymmetrical carbon atoms, in four forms, dextro and levo, racemic, and also the meso, or internally compensated inactive form. All of these forms were actually prepared by Werner in the series: $[\mathrm{en_2\,Co} \genfrac{}{}{0pt}{}{.\mathrm{NH_2}.}{.\mathrm{NO_2}.} \mathrm{Co\,en_2}]\mathrm{X_4}$. The inactive forms were resolved into the dextro and levo forms by means of the active bromocamphorsulfonates, and the mixture of these two active forms gave again the inactive racemic form, which could be again resolved into the active forms. On heating with water the active forms become inactive, passing over into the meso forms which cannot be resolved into active isomers by the bromocamphorsulfonate. The meso salts are less soluble than the corresponding racemic salts, 100 parts of water dissolving 1.95 parts of the meso-bromide and 2.31 of the racemic bromide, 2.44 of the meso-iodide and 3.75 of the racemic iodide. From the optical behavior of the salts it appears that here there can be no difference between primary and secondary valence. Further work was done by Werner on similar compounds where the two cobalt atoms in the nucleus are linked together by

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[1] *Z. anorg. Chem.*, 87, 335.

[2] *Ber.*, 46, 3674; 47, 1954, 1961, 2171, 3087.

O_2 instead of NO_2, one of the cobalt atoms being quadrivalent. Here there should be four active forms and two racemic, several of which were obtained. These compounds are characterized by an extraordinary large rotation (in the bromide $[\alpha] = \pm 840°$). Much more striking is the last piece of work which has come from the Zürich laboratory, an optically active substance which contains no carbon, and which has a rotation $[\alpha]_{560} = \pm 4500°$, with a most extraordinary anomalous rotation-dispersion. The value of $[\alpha]$, for example, for wave-length 643.5 = —2100° for 617.0 = 0°, for 560 = +4446°, for 495 = 0°, and for 478 = —858°. This compound belongs to the type $(Co\ en_3)X_n$, the place of ethylene-diamine being taken by $\genfrac{}{}{0pt}{}{HO}{HO}Co(NH_3)_4$, the compound thus being $[Co(\genfrac{}{}{0pt}{}{HO}{HO}Co(NH_3)_4)_3]X_6$, a dodekammine-hexol-tetracobalti-salt. The inactive form has been known for some time, and is prepared from the chloro-aquo-tetrammine-cobalt chloride by the action of dilute ammonia, with fairly good yield. The resolution into the active constituents is accomplished by the bromocamphorsulfonate method. Using the strychnine method Werner has resolved the rhodium oxalates into optical isomers, and here he finds anomalous rotation-dispersion, the potassium salt of the dextro acid having values of $[\alpha]_C = -26.4°$, $[\alpha]_D = 0°$, and $[\alpha]_B = +114.4°$. He also finds that some racemic forms of cobalt compounds can be split into the active forms by crystallization, the solution being inocculated by traces of the active form, and this in some cases at least not necessarily of the same compound.

Both Ramberg[1] and Tschugajew[2] have continued their work on the complex compounds of platinum with the organic thio-compounds, the former using ethyl- and ethylene-thio-glycolic acid and obtaining both *cis*- and *trans*-isomers. In working with the thiobases, Tschugajew found much difficulty in determining the composition of the complex kation, owing to the tendency to form salts of the Magnus type, platinum being thus present in both kation and anion. He has now found that these salts can be resolved by salts of several acids, as nitroprussides, chlororhodates, phosphotungstates, but, best of all, by picrates, and he recommends picric acid as a valuable reagent for complex kations. He has also prepared a number of complex platinum salts with hydrazine and with both hydrazine and ammonia. In these the hydrazine acts like the ammonia and occupies only a single coördination-position. In addition to the large number of complex salts of the metals of the platinum group which he has already described, Gutbier has now studied the bromoplatinates,[3] the bromoaurates,[4] and the chloro- and bromo-tellurates.[5] Large numbers of salts of each of these classes have been prepared, both with inorganic and organic bases, and are fully described. In the balance of this review the order of the periodic table will be followed.

Group II.—K. A. Hofmann[6] has found fused anhydrous magnesium chloride an excellent solvent for many inorganic oxides, and from the melt

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[1] *Ber.*, **46**, 3886; **47**, 730.

[2] *Z. anorg. Chem.*, **86**, 241; *Ber.*, **47**, 2446.

[3] *J. prakt. Chem.*, [2] **88**, 409; *Sitzber. physik.-med. Soz., Erlangen*, **45**, 25.

[4] *Z. anorg. Chem.*, **85**, 353.

[5] *Ibid.*, **86**, 169.

[6] *Ber.*, **47**, 238.

fine crystals are generally obtained. The oxides may be directly dissolved, or other compounds used, especially the sulfates, which undergo decomposition in the melt. The magnesium oxide which is always present in the crystallized mass may be removed by acetic acid or dilute hydrochloric acid. By using iron filings, or dehydrated ferrous sulfate, or Fe_2O_3, and varying the time of fusion, $Mg(FeO_2)_2$, $Fe(FeO_2)_2$, or the intermediate magnesio-ferrites, are obtained. Fine crystals of magnesium borate, $3MgO.B_2O_3$, are formed in the melt of $MgCl_2$ with boric acid, and $3MgO.U_2O_6$ when uranic oxide is used. CeO_2 can be obtained in brilliant crystals of extreme hardness, by the use of cerium sulfate. These crystals are colorless, but if small quantities of rare earth sulfates (Er, Nd, Pr) are added to the fusion beautifully colored crystals are formed. ZrO_2 may be similarly obtained. From the fusion with erbium, neodymium, praseodymium, and samarium-sulfates, the oxychlorides are gotten, ErOCl, NeOCl, PrOCl, SmOCl, and these show in reflected arc light the characteristic spectra of the metals. This method is suggested as a useful one in the investigation of these, and possibly other rare earths. Hedvall[1] has extended his study of Rinman's Green, which proved to be a solid solution of the components, to the red produced by heating magnesium oxide with cobalt compounds. The two oxides were heated directly with a potassium chloride flux, at temperatures from 1100° to 1400°. Crystals were formed which varied under the microscope from colorless to ruby-red, and which were octahedra, often with cube faces. While it was not possible to follow the homogeneity of the crystals through the whole series, for a considerable interval—38–79% CoO—they could be shown to be homogeneous, and it seems probable that a complete miscibility subsists between MgO and CoO in all proportions. The specific volume of the products decreases continuously with increasing content of CoO.

Group III.—The work of Stock on the borides of hydrogen, which was described in the review of last year, has been extended to the reactions of these borides on the alkalies[2] and on the halogens.[3] For action with the alkalies $H_{10}B_4$ was chosen, since H_6B_2 is so sensitive to the presence of moisture. With both the borides, however, the same product is formed and hydrogen is evolved, molecule for molecule. The reaction is: $H_{10}B_4 + 4KOH = 4KOBH_3 + H_2$. The salt formed, potassium hypoborate, is stable in the absence of moisture, and at 0° its solution can be preserved for several hours without decomposition. At ordinary temperature the solution decomposes with evolution of hydrogen and formation of KBO_2: $KOBH_3 + H_2O = KBO_2 + 5H$. The solution gives an alkaline reaction, owing to hydrolysis. It is a powerful reducing agent, resembling in this respect the hypophosphites, which it also resembles in structure. Solutions of aluminum, zinc, manganese, and the alkaline earths are precipitated, hydroxides and borates being formed, while in solutions of silver, bismuth, mercury, arsenic, and antimony, a dark precipitate of the free metal appears at once. In copper solutions copper hydride is formed. The most characteristic reaction is that with nickel solutions, in which black, insoluble nickel boride, Ni_2B, is precipitated; in dry condition this is so easily oxidized that it ignites spontaneously. In a vacuum at 500°

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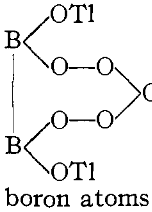
[1] *Z. anorg. Chem.* **86**, 296.

[2] *Ber.*, **47**, 810.

[3] *Ibid.*, 3113, 3115.

potassium hypoborate loses $^2/_5$ of its potassium, which distils off, while hydrogen is also evolved, and a residue with the formula $K_3B_5O_3$ remains, which is probably not a definite compound. In both potassium hypoborate and the nickel boride, the boron is evidently quadrivalent. For reaction with the halogens H_6B_2 was chosen, as being the simplest of the borides of hydrogen. When an excess of chlorine or bromine is used, the resultant product is BCl_3 or BBr_3, but, by using smaller proportions of the halogen, evidence of the formation of intermediate compounds was obtained, and B_2H_5Br was isolated. B_2H_5Cl is probably a spontaneously inflammable gas. It seems also probable that $B_2H_4X_2$ and $B_2H_3X_3$ may exist, but break up into B_2H_6, B_2H_5X, and BX_3. No evidence could be found for the existence of any of the partially halogenated compounds with a monomolecular formula, as BH_2X or BHX_2; nor do any more highly halogenated compounds, such as $B_2H_2X_4$ or B_2HX_5, appear capable of existence. Further, neither BCl_3 nor BBr_3 will take on more of the halogen. While these results which Stock has obtained in boron compounds are altogether unexpected, yet they are not really anomalous. Theoretically, the maximum positive valence of boron is three, and this has not been exceeded in any of these compounds. The maximum negative valence is five, and in the hydrogen borides of Stock it reaches four, and the compounds appear to have similar constitutions to some of the compounds of carbon and hydrogen, as H_6B_2 and $H_{10}B_4$, boroethane and borobutane. In boroethane the hydrogen is replaceable by halogens, as in ethane; when fully replaced, the boron being now positive to the chlorine, or bromine, the B_2Cl_6 spontaneously breaks down into 2 BCl_3.

The compounds of boric acid with thallium have been studied by Buchtala.[1] No compounds with trivalent thallium could be obtained, but the thallous borates are formed by solution or fusion of thallous carbonate or hydroxide with boric acid. The series from $Tl_2O.B_2O_3$ to $Tl_2O.6B_2O_3$, with varying quantities of water, was prepared, and the members resemble the borates of the alkalies except in their water content. All these thallous borates give with hydrogen peroxide a perborate, with formula $Tl_2B_2O_7$, which decomposes explosively on heating, and on warming with water evolves three atoms of oxygen. To this perborate Buchtala assigns the constitution , though it is difficult to see why he should consider the two boron atoms to be linked together.

The fourth paper of R. J. Meyer[2] on scandium presents several points of interest. The most characteristic distinctions between scandium and the other "earths" depend upon its more negative character. From this follows the strong tendency of its salts to hydrolysis, and also to form complex ions. In its hydrolytic tendency scandium resembles aluminum; its chlorides and nitrates in solution are weakly acid, and when heated are partially precipitated by sodium acetate, and completely by sodium

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[1] *J. prakt. Chem.*, [2] **88**, 771.

[2] *Z. anorg. Chem.*, **86**, 257.

thiosulfate. The solution of the sulfate is only incompletely precipitated, owing to the formation of complex salts. In this tendency to form complex ions scandium resembles zirconium and thorium, indeed, in many respects it stands chemically quite close in its properties to thorium. It is distinguished from aluminum by not being amphoteric. Double chlorides of scandium and the alkalies could be realized only in the case of cesium, as seems to be the case also with several of the rare earth metals. Double fluorides are, however, formed, as K_3ScF_6. Scandium sulfate is the scandium salt of a scandium-sulfuric acid, $H_3(Sc(SO_4)_3)$, of which also the alkali salts, as $K_3(Sc(SO_4)_3)$, were prepared. This constitution is confirmed by the work of Wirth,[1] who by dissolving scandium sulfate in sulfuric acid obtains white crystals of the formula $Sc_2(SO_4)_3.3H_2SO_4$, which is in reality the above-mentioned scandium-sulfuric acid. Wirth also finds that when scandium sulfate is heated in dry H_2S the sulfide Sc_2S_3 is formed, which is fairly stable in dry air. Among the other salts investigated by Meyer are the oxalates, and here also, like thorium, scandium forms complex anions. The complex oxalates of the formula $R'Sc(C_2O_4)_2$, are very stable and only slowly decomposed, even by sulfuric acid. These oxalates have also been studied by Wirth, who has prepared salts of the scandium-oxalic acid, $H_3(Sc(C_2O_4)_3)$, and it appears that scandium oxalate itself, $Sc_2(C_2O_4)_3.5H_2O$, is in reality the scandium salt of this acid. Among other recent workers on scandium is Lukens,[2] who has separated it from the residues of Colorado wolframite, and determined its atomic weight from the sulfate-oxide ratio; and Sterba-Böhm,[3] who has purified scandium by the fractionation of the formate. From this work the latter concludes that scandium is a simple element. He has also investigated the rose-colored sulfide supposed by Ogawa to contain a new element, and finds that it consists exclusively of sulfur and copper sulfide.

Group IV.—Lely and Hamburger[4] have prepared metallic titanium, zirconium, thorium and uranium in a state of very considerable purity (uranium 99.5% pure) by the reduction of the chlorides by metallic sodium. The anhydrous chlorides were in general formed by the action of carbon tetrachloride or the chloride of sulfur in a chlorine atmosphere. Metallic titanium is less ductile than the other metals and the pulverulent metal can be formed into coherent masses only with great difficulty. It is also much less resistant to reagents. Zirconium was obtained in large metallic leaflets and easily gave a metallic mirror by rubbing in an agate mortar. While more easily oxidized than titanium, it is much more resistant to acids and alkalies, though readily attacked by hot *aqua regia* or oil of vitriol. Hydrofluoric acid, even when dilute, attacks it rapidly in the cold. Metallic thorium is lead-gray, and very stable in the air, as well as toward alkalies in solution and nitric acid. In hydrochloric acid hydrogen is evolved, but the metal does not dissolve completely. By *aqua regia* thorium is oxidized to ThO_2. Metallic uranium is darker than thorium, but quickly colors brown in the air. It is not attacked by water or alkaline solutions, nor by acetic acid. In dilute hydrochloric acid hy-

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[1] *Z. anorg. Chem.*, **87**, 1, 7, 9.

[2] THIS JOURNAL, **35**, 1470.

[3] *Z. Elektrochem.*, 20, 289.

[4] *Z. anorg. Chem.*, **87**, 209.

drogen is evolved and UCl_4 formed, but in the concentrated acid the metal quickly dissolves to a violet-colored solution of UCl_3, which, however, slowly goes over into green UCl_4. The metal dissolves rapidly in nitric acid with the formation of uranyl nitrate.

Group V.—The question of the existence of an active form of nitrogen has continued to attract the attention of several chemists during the past year. Strutt first called attention to the orange-yellow cloud-like luminescence observed when the electric discharge is passed through nitrogen at pressures from 1 to 10 mm., and ascribed it to an active modification of the nitrogen. In this gas many elements and compounds are acted on with the formation of nitrogen compounds. This was first contested by Comte, who claimed that the luminescence was due to the presence of traces of oxygen, and the compounds to a nitrogen oxide. Tiede and Domcke[1] have repeated a second time Strutt's experiments, using every precaution to free the nitrogen from traces of oxygen and to avoid any possible access of this gas. By adding traces of oxygen the luminescence appeared, by its withdrawal the luminescence was reduced to a minimum. If too much oxygen is added the luminescence disappears. From this the conclusion is drawn that so far from being a proof of the existence of active nitrogen, the luminescence is a sensitive reagent for traces of oxygen in nitrogen. Fischer[2] agrees with Tiede, and ascribes the phenomena to the activation of the traces of oxygen rather than to the nitrogen. These conclusions are disputed by Koenig and Elöd,[3] by Baker and Strutt,[4] by Strutt[5] and by de Kowalski.[6] According to the first, the luminescence is to be looked upon as an accompaniment of active nitrogen, not as proof of its existence. This is proved by its reactions at ordinary temperatures with substances which do not react with nitrogen in its common form. Among many other substances, pentane, carefully purified from all unsaturated hydrocarbons, reacts with active nitrogen, giving amylene, ammonia and a trace of hydrogen cyanide. Not only nitrogen is capable of being thus activated, but pure oxygen gives a modification more active than ozone and this phenomenon is also accompanied with luminescence. Since metallic vapors destroy or inhibit the luminescence of nitrogen, the failure of Tiede to obtain luminescence in his pure nitrogen is attributed to the presence of mercury vapor, or of the metals from the azides which he used to furnish his nitrogen. de Kowalski also obtains the luminescence in nitrogen enclosed in a glass globe in an induced electric field. The work of the others is all confirmatory of the original work of Strutt, but the large volume of exceedingly interesting experimental work must be passed over in this review, which has aimed to touch on only the most salient points.

An apparently successful attempt to solve the problems which surround the conditions of existence of nitrogen sesquioxide has been made by Klinger.[7] He finds that dry N_2O_3 is rapidly and quantitatively absorbed

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[1] *Ber.*, **46**, 4095; **47**, 420.

[2] *Ibid.*, **46**, 4103.

[3] *Ibid.*, **47**, 516, 523.

[4] *Ibid.*, 801, 1049.

[5] *Physik. Ztsch.*, **15**, 274.

[6] *Compt. rend.*, **158**, 625.

[7] *Z. angew. Chem.*, **27**, 7.

by dry caustic potash. Enclosing sticks of dry caustic potash in a measured excess of dry oxygen, in a pipet, he added a measured quantity of NO. The diminution of volume was $^5/_4$ that of the NO added, corresponding to the equation: $4NO + O_2 = 2N_2O_3$. Had NO_2 been formed, the diminution would have been $^3/_2$ corresponding to: $2NO + O_2 = 2NO_2$. From this the conclusion is drawn that oxygen does not unite directly with NO to form NO_2, but that N_2O_3 is formed as an intermediate product. Again, NO_2 is instantly absorbed by caustic potash to a mixture of nitrite and nitrate, while NO does not form any compound instantaneously. A mixture of equal molecules of NO and NO_2 was immediately and completely absorbed by caustic potash with the formation of potassium nitrite, consequently no NO or NO_2, as such, could have been present, or some of the NO would have been left over, and some nitrate formed. It follows that a mixture of NO and NO_2 must be looked on as N_2O_3.[1] Several years ago Raschig described a new oxide of nitrogen formed by leading NO into liquid air, and ascribed to it the formula NO_3. This has been disputed by Müller, and Raschig has repeated and extended his work.[2] The compound is also formed, as noted by Müller, by a high-tension electric flame in liquid air, and is a light green precipitate, becoming a dull gray-blue as the oxygen evaporates. The compound cannot be N_2O_3, as was contended by Müller, since this is deep indigo-blue, both in solid and in liquid form. On the evaporation of the liquid air there is left at —110° a dull blue solid, which breaks up at —100°, and which has the formula NO_2. Since it possesses none of the ordinary properties of NO_2 or N_2O_4, it must be an isomer, and Raschig calls it iso-nitrogen tetroxide. The dull green compound from which the iso-tetroxide is formed, after washing with liquid nitrogen is nitrogen hexoxide, NO_3. Raschig's work is again criticized by Müller,[3] who claims that the supposed NO_3 is merely a mixture of NO_2, N_2O_4, N_2O_3 and NO, and that on washing with liquid nitrogen it loses no oxygen, and no iso-tetroxide is formed. Mention should be made of a very complete investigation of nitrites, their conditions of formation and decomposition, by Oswald,[4] which however, does not admit of useful abstraction. Ball[5] has continued his study of bismuth nitrites, and prepared a large number of new salts, in which the tendency of bismuth to form triple nitrites is very apparent. Of the fifteen possible salts of the formula $X_2YBi(NO_2)_6$, where X = NH_4, K, Rb, Cs, Tl', and Y = Li, Na, Ag, all were prepared. Of triple nitrites with nickel, $K_4NiBi_2(NO_2)_{12}$.aq. and the corresponding thallium salt (anhydrous), were obtained, and also $Rb_7NiBi_3(NO_2)_{18}.4H_2O$ and the corresponding cesium salt with 6 H_2O. There would seem to be still considerable field for investigation among the curious triple nitrites, which, except by Ball, has hardly been touched since the work of Przibylla on the triple nitrites of nickel. In his work upon the compounds of nitric oxide on salts of iron and copper, Manchot[6] has, for the first time, prepared

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[1] The density of the mixture demonstrates that at ordinary temperature N_2O_3 dissociates almost completely into NO and NO_2.—EDITOR.

[2] *Z. anorg. Chem.*, **84**, 115.

[3] *Ibid.*, **86**, 230.

[4] *Ann. chim. phys.*, [9] **1**, 32.

[5] *J. Chem. Soc.*, **103**, 2110.

[6] *Ber.*, **47**, 1601, 1614.

a ferrous-nitric oxide compound of the brown series in a solid crystallized condition. A solution of ferrous chloride in alcohol was saturated with NO and kept in an NO atmosphere. This was precipitated with an alcoholic solution of di-ammonium hydrogen phosphate, a thick oil separating out, which became crystalline at —15°. The compound is (FeNO)-HPO_4, is fairly stable, fuses at +16°, and in it there is present one molecule of NO to each Fe atom. It is oxidized rather slowly in the air or when shaken in water, gradually losing its very dark brown color and becoming white; in concentrated sulfuric acid it dissolves to a deep red solution. Similar salts are obtained with other inorganic acids, but not with organic. Thus, while oxalic acid gives with ferrous solutions an insoluble ferrous oxalate, if the solution is saturated with nitric oxide there is no precipitate, the ferrous-nitric oxide oxalate being very soluble. In these compounds there is present the bivalent kation $(FeNO)^{++}$. The reaction of cupric chloride and bromide with nitric oxide does not seem to be characteristic of bivalent copper in general, since there was found to be no absorption of nitric oxide in solutions of the fluoride, nitrate, acetate, formate, amidoacetate, and other cupric salts in absolute alcohol. The NO in $CuBr_2.NO$ is so sensitive to the presence of water that it would seem that there is a competition between the H_2O and NO molecule for the available addition-position. The action of nitrogen and hydrogen on the alkaline earth metals has been studied by Dafert and Miklauz,[1] the strontium and barium being obtained by distilling a mixture of the oxide with aluminum in a vacuum, and the calcium by redistilling commercial calcium. Metallic calcium begins to react with nitrogen at about 400°, while strontium reacts somewhat lower and barium at 260°. In each case the nitride M_3N_2 is formed. These nitrides begin to absorb hydrogen at 230°–300°,—calcium at the lowest temperature—with the formation of a trimetalamide, $M_3N_2H_4$. In the case of calcium an intermediate product is formed, which is probably tr calciumimide, $Ca_3N_2H_2$, which is especially sensitive to the light. Barium nitride on absorbing hydrogen gives off nitrogen, partly as ammonia. The substance produced is scarcely sensitive to light, and is of interest because at 700–750° it absorbs nitrogen with evolution of hydrogen, and then at 300–400° in a current of hydrogen gives off the nitrogen again, partly as ammonia. These reactions present possibilities of being utilized for the commercial production of ammonia from nitrogen and hydrogen. Calcium reacts with hydrogen at 300°, with strontium the reaction begins at 215°, and with barium at 120°. In each case the hydride, MH_2 is formed. Somewhat below a red heat these hydrides absorb nitrogen, the first two giving the imides CaNH and SrNH, but with barium hydride no imide is formed. At higher temperatures nitrides are obtained. A relatively pure calcium imide, which is very sensitive to light, is formed by heating calcium hydride, or better, calcium nitride to 730–750° in a stream of equal parts hydrogen and nitrogen.

In the course of a paper on the characteristics of the different modifications of phosphorus[2] Stock and Stamm consider the question as to whether the vapors of yellow and red phosphorus are identical. Red phosphorus, distilled from the hot to the cold end of an evacuated tube at 280–400°, condenses always in small part to red phosphorus again,

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[1] *Monatsh. Chem.*, 34, 1685.

[2] *Ber.*, 46, 3497.

while both the yellow phosphorus and the Hittorf modification give colorless distillates. From this and other experiments, it is concluded that in vapor from red phosphorus there are actually present red phosphorus molecules, but that their concentration is exceedingly small. The chief constituent of the vapor of phosphorus of any kind is P_4, which dissociates to a slight extent,—10.5% at 900° and 120 mm.—into P_2. The equilibrium: $P_4 \rightleftharpoons 2P_2$ is displaced by decreasing pressure and increasing temperature in favor of P_2; the equilibrium: $xP_2 + yP_4 \rightleftharpoons P_{2x+4y}$ (red phosphorus vapor) is by decreasing pressure and increasing temperature displaced against the red phosphorus.

Group VI.—An investigation of the polysulfides of sodium was carried out by Rule and Thomas[1] in absolute alcohol. Metallic sodium was dissolved in alcohol and then saturated with H_2S and the excess of gas removed by a stream of hydrogen, while the solution was on a water bath. In this solution of NaSH, aliquot atomic quantities of sulfur were dissolved, and the solid product obtained by evaporation, or cooling, or both. The only pure compound which could be obtained was the tetrasulfide, Na_2S_4. There was evidence of the existence of a higher polysulfide, but none could be isolated. The tetrasulfide is therefore to be looked on as the chief product of the action of sulfur on sodium hydrosulfide in alcoholic solution. By the action of metallic sodium the tetrasulfide is reduced (in alcohol) to the disulfide, Na_2S_2, which is obtained as a microcrystalline powder, while sodium hydrosulfide remains in solution. It has long been a puzzle why nickel and cobalt sulfides, which are not soluble in acids, should not be precipitated from acid solutions by hydrogen sulfides. Two explanations have been offered: (1) The sulfides are insoluble, but their non-precipitation in acid solutions is due to a persistent supersaturation; (2) the sulfides are primarily precipitated in a form soluble in acids, which rapidly passes over into an insoluble form ("by polymerization"). Two other complications offer themselves, in that on long standing hydrogen sulfide does sometimes precipitate nickel sulfide, and the precipitated sulfides are generally, especially when freshly precipitated, far from completely insoluble in hydrochloric acid. The problem in regard to nickel sulfide has been attacked, with seeming success, by Thiel.[2] He finds that nickel sulfide when freshly precipitated is a mixture of three modifications, which he calls α, β, and γ, all of which have the formula NiS. αNiS is rapidly soluble in dilute HCl, but gradually passes over into the β and γ forms on standing, especially with access of air. It is predominatingly precipitated when dilute nickel solutions are slowly added to dilute alkali sulfide solutions in the cold and without access of air. In such cases it may be present in the precipitate to the extent of 85%. It is possible to wash it, dry it with alcohol, warm, and even heat it to red heat without its being completely converted into the other modifications. β NiS is very slightly soluble in cold HCl, but dissolves slowly in hot $2N$ acid. It is converted into γ NiS by boiling several hours with $2N$ acetic acid. It is precipitated free from α NiS and with but little γ NiS by H_2S from a hot solution of nickel acetate with excess of acetic acid. γ NiS in insoluble in cold $2N$ HCl, and its solubility in the hot acid is very slight (0.0013 g. in 100 cc.). It remains as residue when a precipitated NiS

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[1] *J. Chem. Soc.*, 105, 177.

[2] *Sitzber. med.-naturwiss. Ges. Münster*, 1913.

is extracted with hot HCl, in the form precipitated by H_2S after long standing from solutions not too strongly acidified with mineral acids, and into this the other forms are converted by boiling with acetic acid. β and γ forms are obtained when H_2S acts on nickel carbonate or hydroxide, and this explains the action of the air in converting the α modification into these forms; the air oxidizes the α NiS to the hydroxide and this is secondarily converted into the β and γ NiS by an excess of hydrogen sulfide. These changes seem clearly to be polymerization processes.

Several years ago Rosenheim prepared complex molybdenum cyanides with the formula $M_4'Mo(CN)_8$, the only known compound in which eight coördinated groups surround the central atom. In these compounds the molybdenum appeared to be quinquivalent, so that the compound does not seem to accord with the ordinary valence rules. He has now[1] prepared analogous tungsten cyanides which correspond in every way to those of molybdenum, and in which the tungsten, as determined by titration with $KMnO_4$, is also quinquivalent. The $(W(CN)_8)^{iv}$ group is even more stable than the ferrocyanide group, and the free acid can be prepared. Apparently independent of Rosenheim's work, Olsson[2] has prepared these same tungsten octocyanides, but he differs from Rosenheim regarding the valence of the tungsten atom, holding that it is quadrivalent, as would be expected. The results of the permanganate titration he explains by assuming that instead of being oxidized to WO_3, the tungsten forms a complex in which its valence reaches only five. A fuller description is later given[3] by Olsson, and he has succeeded in isolating the complex of quinquivalent tungsten, formed by oxidation with $KMnO_4$, and in preparing the series of salts $M_3'W(CN)_8$, in which the tungsten is quinquivalent.

Group VII.—As a method of preparing anhydrous chlorides, Conduché[4] proposes heating sulfates, which have already been rendered anhydrous, in a current of dry carbon dioxide and chloroform. The reaction with $CuSO_4$ begins at 250°, with $NiSO_4$ and $FeSO_4$ at 300°, and with other sulfates at slightly higher temperatures, $BaSO_4$ and $CaSO_4$ reacting at 500°. At 280–300° by this method $CuCl_2$ is easily obtained in a pure and anhydrous condition. At a higher temperature CuCl is also formed, the reducing action of the chloroform coming also into play. The chloroform acts like a mixture of chlorine and hydrogen chloride and different chlorides of the same metal may be formed at different temperatures. In the case of iron, whether one starts from ferrous or ferric sulfate, both ferrous and ferric chloride are obtained, and can be readily separated by the sublimation of the latter,

Group VIII.—Bellucci and Corelli have continued their efforts[5] to isolate the double cyanide of univalent nickel, described last year. By the reduction of $K_2Ni(CN)_4$ solution with potassium amalgam in a hydrogen atmosphere, they obtain a dark red solution from which alcohol precipitates an exceedingly unstable, dark red, oily substance, which when dissolved in water gives the ratio Ni : 3CN : 2K, and which on titration

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[1] *Ber.*, **47**, 392.

[2] *Ibid.*, 917.

[3] *Z. anorg. Chem.*, **88**, 49.

[4] *Compt. rend.*, **158**, 1180.

[5] *Atti accad. Lincei, Rome* [5] **22**, ii, 485.

with iodine takes up one atom of iodine for each atom of nickel. This establishes the formula, as was expected, as $K_2Ni(CN)_3$, or $2KCN.NiCN$, the complex containing nickel in a univalent condition. Tschugejew and Chlopin[1] have also obtained univalent nickel by the reduction of nickel salts by a concentrated solution of sodium hydrosulfite and nitrite in equimolecular proportion. A violet or blue coloration is produced according to the amount of reagent used. The violet solution contains $HN(NiSO_3)(HSO_3).nH_2O$, which could not, however, be obtained in a completely pure condition. Sodium hydroxide gives a blue precipitate of what is apparently $NiOH$, but which could not be dried without decomposition. This is converted by sodium sulfide into black Ni_2S, which can be isolated only in moist condition. The blue hydrate dissolves in KCN to a red solution, which seems to be identical with that of Bellucci's $K_2Ni(CN)_3$.

Barbieri[2] has entered on a systematic study of resemblances between compounds of elements in different groups of the periodic system, when these elements have the same valence. Thus an element of the eighth group, acting with a valence of three, may be, for practical purposes, considered as an element of the third group. As examples he has prepared Ruthenium acetylacetonate, $Ru(C_5N_7O_2)_3$, and finds it to closely resemble aluminum acetylacetonate, with which it is isomorphous and gives solid solutions. Ammonium rhodio-molybdate, $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$, is in every way similar to the corresponding Al, Fe''', and Cr''' salts, as well as to the Co''' salt of Friedheim and Keller. The isomorphism of palladium acetylacetonate with the corresponding cupric salt was shown by the formation of solid solutions. Delépine[3] has succeeded in preparing the very soluble chloro-iridates and iridites of lithium. Li_2IrCl_6 crystallizes as a hexahydrate, and when crystallized with sodium chloro-iridate does not form any intermediate compound. When reduced by alcohol $Li_3IrCl_6.12H_2O$ is formed and hydrogen chloro-iridite remains in the mother liquor. No intermediate lithium-hydrogen salt is formed. Better results are obtained by reducing the lithium chloro-iridate with lithium oxalate. By mixing with solutions of sodium chloro-iridite, the intermediate compounds, $Na_2LiIrCl_6.12H_2O$ and $Na_{1.1}Li_{1.9}IrCl_6.12H_2O$, were obtained, but when recrystallized from water the sodium salt resulted, containing very small quantities of lithium. Fraenkel has prepared[4] a number of new salts of rhodium and iridium with organic bases. Chloro-iridic acid gave only the familiar type, $M_2'IrCl_6$. With rhodium, however, not only the type $M_3'RhCl_6$ was obtained, but also $M_2'RhCl_5$ (with methylamine), $M_4'RhCl_7$ (with methylamine and tetraethylamine), and $M_3'Rh_2Cl_9$ (with trimethylamine and tetraethylamine).

NOTE.

A Surfacial Burn Produced by an Unknown Radiation.—Woehler,[5] in 1862, heated carbon and an alloy of calcium and zinc together and

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[1] *Compt. rend.*, **159**, 62.

[2] *Atti accad. Lincei, Rome* [5] **23**, i, 334.

[3] *Compt. rend.*, **158**, 1276.

[4] *Monatsh. Chem.*, **35**, 119.

[5] F. Woehler, "Bildung des Acetylens durch Kohlenstoffcalcium," *Ann. Chem. Pharm.*, **124**, 220 (1862).