Whenever the ash has been burned at too high a temperature it is necessary therefore to determine the phosphoric acid in the ash by means of the Neumann method (digestion with 5–10 cc. of a mixture of equal parts concentrated sulphuric and nitric acids).

These results show that neither phosphoric acid nor ash is appreciably volatilized on high ignition, but that to recover the converted phosphoric acid from the ash, the Neumann or an equally efficient method must be used.

RESULTS.

	Ash.		Phosphoric acid.			
Sample.	Low redness. (1)	Bright redness. (2)	Hot nitric acid. (1)	Hot nitric acid. (2)	Boiled 1 hr. Nitric acid. (2)	Neumann method. (2)
A	2.11	2.08	1.10	0.42	0.99	1.09
B	2.18	2.16	1.16	0.48	1.07	1.16

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REVIEWS.

REVIEW OF INORGANIC CHEMISTRY FOR 1907.

BY JAS. LEWIS HOWE.

Received January 13, 1908.

The most important paper which has appeared in inorganic chemistry during 1907 is the lecture which was delivered before the German Chemical Society by Werner, on "The Problems of the Constitution and Configuration of Inorganic Compounds" (*Ber.*, 40, 15). The subject was treated under five heads, *viz.*: constitution of the metal-ammonia salts; constitutional relations between the metal-ammonia salts and complex salts; relations between the metal-ammonia salts and the hydrates; the special relations of complex inorganic radicals; polynuclear metal-ammonia salts. The paper, which unfortunately does not admit of abstraction within the limits of this review, gives the latest and most comprehensive views of the author, which are winning general acceptation, as offering the only rational theory of the constitution of complex inorganic compounds. The application of Werner's view to many classes of compounds is as yet far from clear or satisfactory, but an important beginning has been made which bids fair to be second only in importance to the doctrine of valence itself.

Two other important papers from a theoretical standpoint have been by Pfeiffer and by Werner on the theory of hydrolysis and the theory of bases (*Ber.*, 40, 4036, 4133). According to the ideas of these chemists hydroxo-compounds, that is, those containing the undissociated hydroxide group, when treated with acids give salts, not by substitution as generally assumed, but by addition, and the salt formed is primarily an 'aquo' salt, though it may secondarily go over into an anhydrous salt by the loss of water. Applying this idea in its simplest form we would have for the neutralization of cuprous hydroxide the following: $CuOH + H^+.Cl^- = Cu(OH_2)^+ + Cl^-$. Applying this to the theory of hydrolysis, we have the reaction, $Me(OH_2)X = MeOH + HX$, or $Me(OH_2)^+ \rightleftarrows MeOH + H^+$, in which hydrolysis is conditioned by the tendency of the aquo-metal ion to break up into a hydroxo-compound and the hydrogen ion. According to the theory of Arrhenius, on the other hand, we have the hydrolytic reaction: $MeX + H_2O = MeOH + HX$, or $Me^+ + H_2O = MeOH + H^+$. Here the dissociation of water is the determining factor in hydrolysis, while in the theory of Pfeiffer, it is of little influence. This may be, however, taken account of in the reaction which conditions the basic nature of the hydroxo-compound: $MeOH + H_2O \rightleftarrows Me(OH_2)^+ + OH^-$. Here the water molecule is dissociated in the formation of the aquo-metal ion, the hydroxyl ion being left and imparting the basic reaction to the solution. The strength of the basic character of the hydroxo-compound is thus conditioned upon the tendency of the metal to form aquo-metal ions, and upon the dissociation of water. According to Arrhenius the basic character is independent of the dissociation of water and only dependent upon the dissociation tendency of the metal hydroxide. In Pfeiffer's theory hydrolysis is practically a measure of the tendency of the aquo-metal ion to break up, and of the hydroxo-compound to unite with the hydrogen ion. The application to amphoteric hydroxides is best seen by an example, as of zinc hydroxide:

$Zn(OH)_2$ (base) $+ 2H^+ = Zn(OH_2)_2^{++}$, and

$Zn(OH)_2$ (acid) $+ (OH^-) = Zn(OH)_3^-$.

In his paper on the theory of bases this idea is further developed by Werner and bases are divided into two classes: the anhydro bases which unite with water to form a hydrate which is dissociated in aqueous solution into a complex cation and a hydroxyl anion; and aquo-bases, which comprehend all products formed by the addition of water which dissociate in water giving hydroxyl anions. A number of different classes of anhydro bases exist, as oxygen, nitrogen, phosphorus bases, etc. While the theories of Pfeiffer and Werner have been worked out chiefly in the effort to explain the metal-ammonia bases, they bid fair to throw much light on the more general reactions of inorganic chemistry. The above is but a bare outline and the original papers will well repay a careful perusal.

That which may prove to be the most important inorganic research of the year is one which has been presented as yet only in two preliminary papers by Sir William Ramsay and Cameron (*J. Chem. Soc.*, 91, 1266, 1593). By the action of a large quantity of radium (87.7 mg.) as bromide and sulphate on water, a mixture of hydrogen and oxygen was obtained. On explosion, a small quantity of hydrogen and emanation remained. An important characteristic of this emanation is its rapid decrease in volume, which seems to point to a chemical change, perhaps into a diatomic gas. A calculation of the life of radium points to a period of only 236 years, a lower value than that found by Rutherford and others. The attempt to account for the excess of hydrogen led to most remarkable results. With the thought that if the emanation acted on the salt of a heavy metal, this would be liberated instead of hydrogen, a solution of copper sulphate was submitted to the action of radium. No copper was deposited, but on removal of the copper, lithium was recognized in the solution by the spectroscope. Numerous experiments were carried out, with every possible precaution against error, but each time with similar results. A small quantity of sodium seems also to be formed. When lead nitrate is used in the place of copper sulphate, only sodium seems to be present. An examination of the evolved gases showed that from the emanation alone helium is formed, in the presence of pure water, neon, while in the presence of copper sulphate the gaseous product is argon, with no trace of either helium or neon. The suggested explanation of these remarkable phenomena is that the α-particles are, contrary to the view of Rutherford, not identical with helium, but when they collide with the atoms of the emanation, if nothing but the emanation is present, helium results. If, however, the emanation is mingled with the heavier water molecules, the decomposition does not go so far, and neon is the result. In the presence of the still heavier copper atoms, the decomposition remains at argon. By the action of the α-particles atoms seem to be decomposed into other atoms of the same group, thus copper is broken up into sodium and lithium. The authors also find that a solution of thorium nitrate produces continuously minute but clearly detectable quantities of carbon dioxide. The importance of these experiments in opening up new lines of research can hardly be overestimated. In this connection may be noted the work of Boltwood (*Am. J. Sci.* (4), **22**, 537; **24**, 370) on the relation of radium to uranium in carnotite. From the fact that the amount of radium obtained in a given time from uranium is less than theoretically would be formed if radium is an immediate product of uranium, the formation of an intermediate product seemed probable. This was found in carnotite, and at first supposed to be identical with actinium, but further investigation showed that it could be separated from actinium, and that it differs from it in several important particulars. It seems without doubt to be a decomposition product of uranium and the progenitor of radium. Boltwood proposes for it the name *ionium*.

It has been suggested by Coblentz (*Jahrb. Radioaktiv. u. Elektronik*, **3**, 397) that it should be possible to determine whether water is present in crystallized compounds as water of crystallization or as so-called water of constitution, by the presence or absence of the absorption bands of water in the infra-red spectrum. The results obtained from a number of minerals and compounds gave results quite in accordance with the ordinarily received ideas on the subject, but there were also results which were anomalous, such as the presence of water of crystallization in cane sugar, though not in *d*-fructose and *d*-raffinose. Similarly absorption bands for the hydroxyl group were found in talc but not in serpentine. The method seems to offer possibilities of throwing light upon molecular structure, but needs much further investigation.

The subject of isomorphism continues to attract some attention, especially in its connection with molecular volume. Gossner (*Z. Kryst.*, **43**, 130) concludes that isomorphous substances, while in general not possessing the same molecular volume, do not differ to any considerable extent. If there is much difference in molecular volume, the series of mixed crystals will not be continuous. In another paper (*Ber.*, **40**, 2373) he compares the members of the series of double alkali sulphates of nickel, cobalt, copper and zinc, and also the fluosilicates of the same metals. In the latter case the nickel and zinc salts have nearly the same molecular volume and form a continuous series of mixed crystals, while the cobalt and copper salts differ considerably in molecular volume and there is a break in the series of mixed crystals from 10–30 per cent. of the cobalt salt. In considering the isomorphism of the elements, Tammann (*Z. anorg. Chem.*, **53**, 446) holds that Mitscherlich's rule that similarly constituted compounds are isomorphous cannot apply, because we know nothing regarding the constitution of the elementary molecule, and he concludes that those elements which are chemically analogous are isomorphous. In general, elements of the same group in the periodic system form mixed crystals and not compounds, but occasionally elements of different groups form a much more marked series of mixed crystals than those of the same group. This is particularly apt to be the case when the elements in question are chemically similar and have high melting points. Indeed, the temperature of crystallization seems to be even more important in determining the power of elements to form mixed crystals than is chemical analogy. As a rule, elements of high melting point separate out as mixed crystals, while those of low melting point crystallize as the pure metal. If the melting point of both the metals in a binary mixture is high, a complete series of mixed crystals may be expected to separate.

Fused salt mixtures have been largely studied from a thermometric standpoint, but Shemchushny (*J. Russ Phys. Chem. Ges.*, **38**, 1135) has recently begun an investigation of the microscopic structure of fused salt mixtures, by etching with an appropriate solvent the polished surface of the solid melt. From the study of several series of binary mixtures, such as those of potassium chloride-potassium chromate, he concludes that the micro-structure of salt mixtures differs little from that of metallic alloys.

An interesting case of the action of light, which seems to be recognized for the first time, is described by Alefeld (*Z. wiss. Phot.*, **4**, 364; *Chem.-Ztg.*, **30**, 1087, 1127). In his earlier experiments, a solution of colophonium was spread thinly on a glass plate and dried for fifteen minutes at 100°. The plate was then exposed under a photographic negative for half an hour to direct sunlight. On heating the negative more highly, a clear positive appears on the plate. This action was strongest on exposure to blue light, and careful experiments showed that it was not due to the action of heat. The experiments were later extended and it was found that practically any solution could be used, those giving the best results which leave the most highly colored ash. The solutions may be dried sufficiently before exposure to the light to have the negative placed directly against the plate, but if dried too hard, no change is effected by the light. The action seems to be due to the migration of the molecules from the shaded portions of the plate to those exposed to the light. The best results are obtained by the use of such varnishes as are used as menstrua in porcelain painting. Forty-five different elements were tested and found to be susceptible to this action of light. It is thought that practical application of this phenomenon can be made in the transference of photographs and other designs to porcelain and glass.

That manganese is perhaps the best excitant in luminous paint has long been known. It now appears from the investigations of Karl (*Compt. rend.*, 144, 841) to play a similar part as regards triboluminescence. If zinc sulphide is heated in an electric furnace with one-sixth its weight of manganese nitrate to 1200°, the resulting crystalline mass, after powdering and washing, shows a remarkably strong triboluminescence, visible even in the daylight. The mass, however, does not exhibit the phenomenon of phosphorescence at all. The manganese nitrate can be replaced by other manganese salts, and even by the oxides of tin, silicon, zirconium, titanium, etc., and triboluminescence ensues, but it does not seem possible to replace the zinc sulphide by even zinc oxide.

Quite an extensive paper by von Hasslinger on the nature of metallic and electrolytic conductivity has appeared in the *Monatshefte* (28, 173). Considering the criteria by which metallic elements are distinguished from the non-metallic, he notes that increase in metallic properties accompanies increase in atomic weight, and it also accompanies an increase in temperature. Thus, sulphur becomes almost black and far less transparent at high temperatures, and those forms of carbon which are most like metals are formed at high temperatures. It may be assumed as probable that all the elements could be brought to the same degree of metallic character by properly choosing the temperature for each. At absolute zero, on the other hand. all substances would become non-metallic, and non-conductors of electricity. The distinction between metallic and electrolytic conductors is rendered more difficult from the fact that decomposition products cannot always be detected in the latter case, nor can the conductors be distinguished by their temperature coefficients. If, however, a metal is in contact with a substance in which its ions can exist, it will show a solution-tension which is recognizable by the development of an electromotive force. Conversely, in such a case the presence of an electromotive force indicates that the conductivity is electrolytic, while no electromotive force is developed if the conductivity is metallic. From this standpoint we must conclude that iodine, and even sulphur are electrolytic conductors. Some substances, as for example, silver sulphide, are electrolytic conductors at ordinary temperatures, and metallic conductors at lower temperatures, and since no abrupt change from one form of conductor to the other can be observed, it follows that both kinds of conductivity may exist side by side. This transition from one form of conductivity to the other is exhibited in carbon, where the conductivity increases with the temperature up to a certain point, and then on further heating decreases. Developing the subject further, the author concludes that there is a practical similarity in the two kinds of conductivity, the number of ions in metallic conduction being very great, and their motion very rapid.

In order to determine the degree of dissociation of fused electrolytes, Arndt (*Ber.*, 40, 2937, 3612) has used fused boric oxide as a solvent. The conductivity of this at 900° is very small ($k=0.000,021$). When sodium metaphosphate is dissolved in this solvent, the equivalent conductivity is found to decrease with decreasing concentration. Taking into account the increasing viscosity with decreasing concentration, it appears that the equivalent conductivity is independent of the concentration. This is most simply explained by assuming that the fused sodium metaphosphate is completely dissociated, so that there is no further dissociation on further dilution with boric oxide. Arndt believes the same to be the case with all fused electrolytes which are made up of univalent ions.

A clear and comprehensive review of the whole subject of non-aqueous solutions is given by Carrara in the *Gazzetta* (**37**, 1, 525), which is fully abstracted in the *Chem. Zentralbl.* (**1907**, 2, 1576). It is the conclusion of the author that between aqueous and non-aqueous solutions a great similarity exists, but in non-aqueous solutions the phenomena are attended by many and most diverse complications. In the meantime the accumulation of data regarding these solutions must be carried on before generalizations are possible.

Beckmann and his pupils continue (*Z. anorg. Chem.*, **51**, 236; **55**, 371) their work on the accumulation of these valuable data. Using quinoline as a solvent the boiling point method gives normal molecular weights for the halide compounds of zinc and cadmium, while the values for cuprous chloride show increasing association toward Cu_2Cl_2 with increasing concentration, but indicate the simple formula at infinite dilution. Cobalt and nickel chloride and bromide show little tendency toward association even in concentrated solutions, and their compounds with quinoline give normal molecular weights. Phosgene, giving double molecules for acetic and benzoic acids, belongs to the class of weakly dissociating solvents. In it iodine (I_2), iodine trichloride, arsenic and antimony trichlorides, antimony pentachloride and S_2Cl_2 give normal molecules. The S_2Cl_2 molecule is also normal in a solution of ethyl chloride and in liquid sulphur dioxide. In all three of these solvents sulphur dichloride shows abnormality. In the first two its molecular weight is respectively 147 and 130, while that of SCl_2 would be 103. In liquid sulphur dioxide the molecular weight of sulphur dichloride is 226, greater than that required for the molecule S_2Cl_4 (206). In this last solvent potassium iodide was found to have the doubled formula, as previously determined by Walden.

Group I.—A very full investigation of the oxides of the alkali metals has been given by Rengade in *Compt. rend.* (**143**, 592, 1152; **144**, 753, 920; **145**, 236), and summarized with additions in *Ann. chim. phys.* ((8), **11**, 348). When the metals of the alkalies are heated in the air they burn to higher oxides, but if insufficient oxygen is furnished to burn the metal completely to the normal oxide, this seems to dissolve in the excess of metal. By heating in a vacuum this excess may be distilled off, leaving the normal oxide in a crystalline condition, often, as in the case of rubidium oxide, in comparatively large octahedra. Sodium oxide, Na_2O, is white and hardly changes its color on heating; potassium oxide, white when cold, becomes clear yellow at 200°; rubidium oxide is pale yellow when cold and golden yellow when heated, while caesium oxide is orange-yellow cold and darkens on heating to carmine-red, purple-red, and at 150° black. The oxides are somewhat volatile on heating and above 400° melt and decompose into the metal and the dioxide. They are similarly decomposed in liquid ammonia, the sodium oxide least readily, and the compound of the metal with ammonia reacts in turn with the dioxide forming the amide and the hydroxide. By hydrogen the oxides are converted into an equimolecular mixture of hydroxide and hydride, and on heating to 300° in a vacuum the latter is decomposed. The halogen elements react with the oxides only when warmed. The reaction then becomes violent. The same is true of many other reagents such as sulphur and sulphur dioxide, while hydrogen sulphide reacts violently in the cold. Boron and carbon react only above 400°. Dry carbon dioxide is absorbed at about 300°. Caesium and rubidium oxides absorb the vapor of their metals at ordinary temperature in a vacuum, but the metal distils off on heating to 60° or 80°. Potassium oxide absorbs potassium vapor less readily and sodium is not absorbed by its oxide. On warming in the air, higher oxides are formed, giving in the case of rubidium and caesium the dioxides, trioxides and tetroxides, all of which were prepared and are described. As regards the heat of formation, they vary from 82.4 cal. for Rb_2O to 97.7 cal. for Na_2O. The heat of formation thus does not increase regularly with the molecular weight. The work of Rengade fills an important gap in the chemistry of the alkali metals. With this should be mentioned the work of de Forcrand on lithium oxide (*Compt. rend.*, **144**, 1321, 1402). This oxide was prepared by heating the pure hydroxide in a current of hydrogen at 780°. It can also be prepared by using lithium carbonate in the place of the hydroxide. At this temperature lithium oxide has a very low vapor pressure, but at higher temperatures it volatilizes appreciably.

There are numerous references in chemical literature to the formation of a copper peroxide by different methods. These and other methods have been investigated by Moser (*Z. anorg. Chem.*, **54**, 121) with the result that the only instance in which the peroxide is formed is when a 30 per cent. hydrogen peroxide solution is added to a fairly concentrated (2*N*) copper sulphate solution. There is an immediate precipitation of a yellowish green copper peroxide, which seems to have the formula $CuO_2.H_2O$. To avoid the presence of the acid formed in the reaction, Moser found it best to use instead of copper sulphate a suspension of finely divided copper hydroxide. In this case the peroxide is brown, seems to be crystalline, and may be washed clean by ice water. The product is decomposed by boiling water, and more violently by alkalies, and dissolves easily in acids with decomposition. It also breaks up when in a moist condition, but more slowly when dry. Its rapid decomposition by alkalies explains why Moser could not obtain it by oxidation of copper in alkaline solution or suspension with chlorine, and also why it cannot be prepared by the action of sodium peroxide. However, Müller in reviewing Moser's work (*Ibid.*, 417) finds that if a copper solution is treated with very strong (13*N*) sodium hydroxide solution and allowed to stand for several months, a small amount of copper goes into solution, and that if chlorine then be led into the solution the peroxide is formed, but begins to decompose as soon as the current of chlorine is stopped, the original blue color of the solution being restored. The peroxide is also formed when a concentrated alkaline solution of chlorine acts on metallic copper. The method of Moser, however, seems to be the only way to prepare the peroxide, which must be considered as a very unstable compound. Müller also calls attention to the fact (*Z. Elektrochem.*, **13**, 25) that on the electrolysis of a very strongly alkaline (12–14*N*) solution of copper hydroxide there is formed at the anode a dirty yellow copper peroxide which seems to have the formula Cu_2O_3. This may be also formed on a copper anode as an orange-red or yellow coating by the electrolysis of concentrated sodium hydroxide.

Group II.—According to Glassmann (*Ber.*, **40**, 3059) the only compound in which the bivalence of glucinum is above question is the acetylacetonate. Glassmann has now prepared glucinum picrate by the neutralization of picric acid in aqueous solution with glucinum carbonate. The normal salt is formed which is soluble in numerous organic solvents. The determination of its molecular weight by the cryoscopic method in acetophenone confirms the bivalence of glucinum, which only among French chemists seems to be seriously doubted. By the action of water, glucinum picrate is converted into a basic salt.

Lohnstein (*Z. Elektrochem.*, **13**, 613) has described a passive state of metallic magnesium. The metal, which is rapidly soluble in dilute acetic acid, as in most acid and even neutral solutions, if immersed in acetic acid to which a sufficient quantity of potassium bichromate has been added, is not attacked at all, but seems to be in a 'passive' condition. Solution and evolution of gas begin immediately if the metal is made the anode of a cell in which the electrolyte is an acetic acid solution of the bichromate. The stronger the acetic acid, the more potassium bichromate is needed to induce the passive state, although small quantities reduce the action of the acid on the metal. The passive state disappears with the addition of chlorides and sulphates to the solution, and the metal dissolves in proportion to the amount of these salts which has been added. Lohnstein thinks that these phenomena are due to catalytic processes.

In a paper before the British Association (*Chem. News*, **96**, 100) at the Leicester meeting, the properties of calcium, especially in its relations to other metals, were discussed by Pratt. Owing to its large atomic volume, calcium has, even in small quantities, a marked influence upon the physical properties of other metals. The chemical activity of those metals which are easily attacked by reagents is much increased by alloying with calcium, and in many cases the alloy is more active than either of its components. The action of calcium upon metals of large atomic volume is greater. than upon those of lesser volume. This may be a general principle, and not merely applicable to calcium alloys. Calcium alloys do not give promise of much industrial application, except as far as possibly small quantities of the metal may be used for purposes of hardening, but calcium bids fair to have an extended industrial value in the metallurgical purification of other metals.

Two compounds containing three metals, $NaKHg_2$ and NaCdHg, have been prepared by Jänecke (*Z. physik. Chem.*, **57**, 507), the first of the kind. These compounds were discovered by a study of the melting and solidification points of different mixtures of the metals. The compounds have higher melting points than any of the binary alloys which come near them in composition, the former melting at 188° and the latter at 325°. Jänecke has also (*Ibid.*, **58**, 245) confirmed the work of Kurnakow on the compounds of potassium with mercury, and finds the melting point of KHg to be 178° and that of KHg_2 279°. The three compounds whose formulas were not definitely determined by Kurnakow, Jänecke finds to be K_3Hg_9, melting point 204°; K_2Hg_9, 173°; and KHg_9, 70°. Kurnakow (*Z. anorg. Chem.*, **52**, 416) has extended his observations to the amalgams of rubidium and caesium, and finds here also as characteristic the mercurides corresponding to $NaHg_2$ and KHg_2. In addition to $CsHg_2$ (melting point 208.2°) $CsHg_4$ and $CsHg_6$ were found, with melting points 163.5° and 157.7°. As far as examined the rubidium curve resembled that of caesium. Kurnakow calls attention to the fact that the formulas $M'R_2$, $M'R_4$ and $M'R_6$ seem to be characteristic for mercurides and cadmides.

Although appearing in THIS JOURNAL (**29**, 844) the work of G. McP. Smith on ammonium amalgam should not be omitted from this review. After examining the three views of the constitution of this much-studied substance; that of Berzelius, supported by LeBlanc, that it is a compound of mercury with the metallic radical NH_4; that of Moissan that it is an ammonia compound of mercury and hydrogen; and that of Rich and Travers that it consists of free ammonium NH_4, dissolved in mercury, Smith shows conclusively that it must be considered exactly analogous to the amalgams of the other alkali metals, the radical NH_4 acting as an alkali metal. The work of Coehn, indeed, where copper, cobalt and zinc salts were precipitated by ammonium amalgam, would be sufficient to establish this view, were there not a possibility that this precipitation might be due to nascent hydrogen, formed in the decomposition of the amalgam. Barium and potassium are not precipitated by nascent hydrogen, but Smith, on treating ammonium amalgam with barium and potassium salts, effected an exchange between the ammonium of the amalgam and the barium and potassium ions. The amalgam is thus a solution of a very unstable compound, $(NH_4)Hg_m$, in mercury and is properly called ammonium amalgam. At about zero it begins to break up into mercury, ammonia and hydrogen, and the entangling of these gases in the mass causes the familiar frothing, which is not a property of the compound but a phenomenon of its decomposition.

Early in the year there was published a posthumous paper (*Compt. rend.* **144**, 593) by Moissan regarding a property of platinum amalgam. When the amalgam is shaken with water there is formed a semi-solid, buttery mass, which exceeds the original volume of the amalgam several times. This emulsion, for such it seems to be, is stable at 100° and at —80°. Platinum amalgam forms a similar emulsion with sulphuric acid, ammonia, salt solution, glycerol, acetone and many other organic liquids, but not with benzene. The simplest method of preparing this emulsion is to shake 2 cc. of mercury with 12 cc. of water to which a few drops of a 10 per cent. solution of chlorplatinic acid have been added. Lebeau (*Ibid.*, 843) gives further particulars received from Moissan regarding the amalgam. The amount of platinum necessary to produce the emulsion phenomena is very small. It is quite noticeable when a 0.038 per cent. amalgam is used, and the best results are obtained when about one-half of 1 per cent. platinum is present. The amalgams of the other metals of the platinum group show no tendency to form similar emulsions. The presence of amalgams of other metals, such as zinc, tin, lead or calcium, destroys the emulsifying power. The emulsion with a 5 per cent. gelatin solution shows under the microscope a structure similar to that of a soap foam, in which the air is replaced by the liquid. It was noticed that in forming an emulsion with platinum amalgam and ether, if the tube in which the amalgam was shaken was closed by the finger, no emulsion was formed, but if a clean, dry cork stopper, or better a rubber stopper was used, the emulsion was readily formed.

Group III.—No inconsiderable amount of work has been done upon the rare earths, but little of this work calls for notice here. Barbieri (*Atti. accad. Lincei Roma* (5), **16**, 1, 399) has studied the properties of several of the rare earths as catalytic agents, using as tests the reaction between nitric acid and oxalic acid, and that between potassium permanganate and oxalic acid. In the former reaction ceric salts act much like those of manganese as catalyzers, lying in this respect between manganese and iron. Incidentally it was found that cobalt salts lie between those of iron and nickel. Salts of lanthanum, praseodymium, neodymium, and yttrium have no influence upon the reaction. By measuring the time of reduction of potassium permanganate in sulphuric acid solution of oxalic acid, the order of catalytic action was found to be manganese, cerium, cobalt, praseodymium, neodymium, lanthanum and nickel. Here again cerium lies close to manganese, which reminds the author of the observation of Mendeléeff that in the rare earths one seems to see analogues of the members of the iron group, especially as cerium in many respects resembles manganese. This seems a rather remarkable prediction in the light of the chemical knowledge at the time it was written. By the fractional crystallization of ytterbium nitrate from nitric acid, Urbain (*Compt. rend.*, **144**, 759) has succeeded in decomposing it into neoytterbium with atomic weight close to 170, and a small quantity of a new earth, for which Urbain proposes the name lutecium, Lu, derived from the old name of Paris. The atomic weight of lutecium is not much above 174.

Electric furnace products. Du Jassonneix has continued his researches upon the borides, adding quite a number to those already prepared (*Compt. rend.*, **143**, 897, 1149; **145**, 121, 240; *Ber.*, 40, 3193). In his work with chromium he finds that chromium oxide can be reduced by boron only in the electric furnace, and that while two definite compounds exist, Cr_3B_2 and CrB, they can be isolated only when one starts out with an almost homogeneous melt of nearly the desired composition. Boiling acids attack these compounds with ease, and the second one is acted on in the cold. By using the thermite process, Wedekind (*Ber.*, 40, 297) has also prepared a boride of chromium which has a composition near CrB, but has a lower specific gravity and decidedly greater resistance to acids than the boride prepared by du Jassonneix. The oxides of manganese are readily reduced by boron in the electric furnace, the products being MnB_2 and MnB. The latter only is magnetic, contrary to the opinion of Wedekind, and is easily attacked by acids. It has been supposed that the green flame with which the evolved hydrogen burns when borides are attacked by acids, is due to the presence of an unisolated hydrogen boride, but du Jassonneix considers that it is merely due to the presence of traces of boric acid, or in cases to boron chloride. In addition to the iron boride, FeB, prepared by Moissan, du Jassonneix has prepared both Fe_2B and FeB_2; they are formed by the direct union of reduced iron and boron, the former either in the electric furnace or in a gas furnace, the latter in the electric furnace only. FeB_2 is very resistant. The only borides of cobalt and nickel that could be prepared are Co_2B, Ni_2B, CoB_2 and NiB_2. These can be formed by heating a mixture of the elements in a current of hydrogen at 1100–1200°. Wedekind's researches (*Ibid.*, 40, 1259) were chiefly with reference to the magnetic properties of the borides. He found the pulverulent manganese boride, MnB, to be half as strongly magnetic as powdered iron, while in compact form it was about one-fourth as magnetic as iron. Manganese antimonide, MnSb, is more magnetic than the boride, and the phosphide, Mn_3P_2, is also magnetic. The boride of manganese is recommended by Hoffmann (*Z. angew. Chem.*, **19**, 2133) as superior to the boride of iron for the preparation of boron sulphide. The manganese boride is heated in a current of hydrogen sulphide to about the melting point of antimony. The boron sulphide, when heated in hydrogen sulphide, fuses and on cooling gives a vitreous modification, different from either the crystalline or amorphous. This vitreous modification is more stable in the air than the others but like them is decomposed very rapidly by water into boric acid and hydrogen sulphide.

In the preparation of zirconium carbide, Moissan used the pure oxide and sugar carbon, and found the reduction difficult with a current of 1000 amperes. Wedekind finds (*Chem.-Ztg.*, **31**, 654) that by using the natural oxide and pure coal, zirconium carbide is readily formed by prolonged heating at 600 amperes. The fused or sintered mass is very resistant to water, air and hydrochloric acid, but not to concentrated nitric or sulphuric acid. It thus fully resembles Moissan's carbide. This zirconium carbide, ZrC, is an excellent conductor of electricity and Wedekind suggests its use as electrodes. On heating in nitrogen, the nitride is formed, but no cyanide.

In order to determine whether it were possible to prepare a silicide of copper, richer in silicon than Cu_4Si, Vigouroux (*Compt. rend.*, **144**, 917) heated a mixture of copper and excess of silicon in the presence of lead, bismuth and antimony, in a current of hydrogen for three hours at 1200°. The copper silicide formed distributed itself differently in the different metals, but in every case the limit was reached with 10 per cent. of silicon, corresponding to Cu_2Si. Another method of investigation of these silicides was that of Rudolfi (*Z. anorg. Chem.*, **53**, 216), who fused together copper and commercial silicon and studied the product as an alloy. Account was taken of the iron present in the silicon as Fe_2Si, and in preparing the richer silicon alloys, an alloy with low silicon content was used, in the place of pure copper. The quantities were so chosen as to give the same volume (5 cc.) of alloy in each case, and the temperatures used were the melting points of antimony, gold and nickel (630.6°, 1064°, 1451°). Two distinct compounds were found, Cu_3Si and $Cu_{19}Si_4$. Up to 5 per cent. silicon the alloys are ductile, but the higher the content of silicon, the more frequently is annealing necessary. Under 5 per cent., the alloys are about as hard as copper, but from 5–10 per cent. silicon, they increase in hardness very rapidly. Above this the hardness increases very slowly until 60 per cent. is reached; the alloys with above this amount of silicon are of approximately the same hardness as pure silicon. The hardness is not appreciably increased by chilling. The red color of copper is very materially lightened by even traces of silicon, the 1 per cent. alloy being brass yellow, while the 6–10 per cent. alloys are silver white. With more silicon the steel-gray color of silicon is gradually approached.

$MoSi_2$ and WSi_2 have been prepared by Defacqz (*Compt. rend.*, **144**, 848,

1424) by fusing copper silicide with metallic molybdenum or tungsten in the electric furnace. These silicides are very stable when heated in the air and very resistant to all acids except to the hydrofluoric-nitric acid mixture, and also to fused acid potassium sulphate, but they are easily attacked by hot chlorine and fused alkalies. The WSi_2 may also be prepared by the reduction of a mixture of silica and tungstic acid with aluminum. Hönigschmid has also prepared (*Monatsh.*, **28,** 1017) $MoSi_2$ and WSi_2 by this method, as well as $TaSi_2$, which resembles the others except that it is somewhat soluble in hydrofluoric acid. Quite similar but less resistant is manganese silicide, Mn_3Si_2, prepared by Gin by the reduction of rhodonite in the electric furnace. Lebeau, however (*Compt. rend.*, **143,** 1229; **144,** 85) thinks Gin's product is not pure Mn_3Si_2 but an impure Mn_2Si. Wedekind calls attention to the fact that the silicide of manganese is never magnetic (*Ber. physik. Ges.*, **4,** 412) while manganese forms magnetic compounds with most of the other moderately negative elements. Thus manganese carbide when prepared in the electric furnace is magnetic and the same is true of the nitride when it has been very highly heated. At a high temperature the unmagnetic MnAs changes into the magnetic Mn_2As; some of the numerous manganese phosphides are magnetic, others not; the bismuthide (MnBi?) is strongly magnetic although bismuth is typically diamagnetic. Wedekind considers that these facts, together with the fact that numerous compounds of chromium, cobalt and nickel, as well as those of iron are magnetic, prove that magnetism is not merely an atomic property, but also a property of molecules. The only other new silicides prepared during the year are PtSi, made independently by Lebeau (*Compt. rend.*, **145,** 241) and Vigouroux (*Ibid.*, 376) by fusion of the constituents in the electric furnace, and the double silicide, Cu_2PtSi, prepared by the latter by fusing platinum with copper silicide.

The preparation of nitrides possesses an industrial importance from the fact that they yield ammonia on hydrolysis, and hence numerous patents have been taken out along this line. It has long been noticed that nitrogen is much more rapidly absorbed by calcium carbide when in the presence of calcium chloride, and this idea is covered by patents. Going out from the fact that calcium chloride is hygroscopic and its presence may give rise to the formation of acetylene and thus occasion dangerous explosions, Carlson proposes (*Chem.-Ztg.*, **30,** 1261) to replace the chloride by fluorspar, which he claims gives equally good results. Bredig has taken up the investigation of this catalytic action of calcium chloride (*Z. Elektrochem.*, **13,** 69, 605), and finds that at the temperature of 800° the absorption of nitrogen is very much increased by the presence of 10 per cent. of the chloride, and that the other chlorides of alkalies and alkaline earths also have an accelerating action, but much less marked than that of calcium chloride. While the fluorides, oxides, phosphates and sulphates have some accelerating action, it is also far less than that of the chlorides. From the fact that the free metals, calcium, magnesium and sodium, have little catalytic action, Bredig concludes that the hypothesis that the action is primarily an absorption of nitrogen by the free metal, cannot be true. The fact that the absorption is so little increased by the presence of the easily fusible chlorides, such as those of lithium and potassium, seems to show that the increased action is not due merely to a lowering of the melting point. It is unquestionably dependent upon the specific nature of the added substance. The results of Bredig are in the main confirmed by those of Foerster and Jacoby (*Ibid.*, 101), except that they find that calcium fluoride has a much more marked action than was found by Bredig, but this action does not become manifest to an appreciable extent until the temperature of 900° is reached. They recommend the use of fluorspar, but a somewhat higher temperature is necessary than when the chloride is used. Fischer (*Ber.*, **40,** 1110) suggests the use of the calcium carbide-chloride mixture in the preparation of argon from the atmosphere, oxygen being absorbed with the formation of oxide and carbon, the nitrogen with the formation of calcium cyanamide and carbon. By circulating air over the mass at 800° crude argon is rapidly obtained. Fichter (*Z. anorg. Chem.*, **54,** 322) would make use of crude aluminum nitride for the preparation of ammonia. The nitride is made by heating aluminum bronze and a small quantity of carbon in the form of soot, in a current of air. To obtain a pure aluminum nitride nitrogen and not air must be used. The nitride is decomposed very slowly by the moisture of the air, but rapidly by heating with an alkaline solution. Serpek has taken out German patents (Kl. 12.181991–2) for the preparation of aluminum for the manufacture of ammonia, by heating a mixture of aluminum carbide and a small amount of carbon in the air. The nitride obtained readily gives off almost all its nitrogen as ammonia with boiling water. In his second patent Serpek recommends the addition of a very small quantity of hydrochloric acid gas or sulphur dioxide to the nitrogen, for the purpose of accelerating its absorption by the calcium carbide.

Group IV.—Some preliminary experiments have been described by Parsons (*Proc. Roy. Soc.* (*A*), **79,** 532) on the effect of high temperature and pressure on carbon. Coal was subjected to a pressure of 30 tons to the square inch and a current varying from 6000 to 50,000 amperes at two volts. In spite of cooling, the steel walls were somewhat fused. The carbon was in every case changed to soft graphite and no trace of diamonds was found. In the effort to prevent erosion of the walls of the cylinder the carbon was packed in magnesia, but this was quickly converted into magnesium carbide. Even at a pressure of 100 tons and a current of 12 volts and 100 kilowatts no diamonds could be found. When carbon was heated with carbon dioxide, the monoxide was almost exclusively formed. Incidentally it was found that at a pressure of 30 tons to the square inch, liquid carbon dioxide is compressed to one-fifth of its volume.

The investigation of complex carbonates, which was begun several years ago by Reynolds, has been extended by Wood and Jones (*Proc. Cambridge Phil. Soc.*, **14,** 171) to many new metals. The precipitate formed by potassium carbonate with solutions of most metals is soluble in excess, but this solution is decomposed on boiling. If, however, potassium bicarbonate is added, the solution is stable. In many cases, as with cobalt, copper, nickel, ferrous manganese, uranium, zinc, cadmium, bismuth, calcium, silver and magnesium salts, a crystallized double salt is deposited on standing. The general formula of these salts of the bivalent metals is $K_2M''(CO_3)_2.4H_2O$, but no copper salt of this formula was obtained, although it has been described by Reynolds. The copper salts prepared were the anhydrous salt and the monohydrate, and the equilibrium of both of these with their solutions was worked out. While ammonium sulphide and potassium ferrocyanide precipitate copper from the solutions of the double carbonate, and potassium cyanide decolorizes the solution, potassium iodide has no effect upon it, and from its electrolytic behavior it appears that it is dissociated into potassium cations and $Cu(CO_3)_2$ anions, and the latter are further somewhat dissociated into copper cations and carbonate anions. From a cobalt solution treated with potassium carbonate the potassium cobaltocarbonate crystallizes out as the normal tetrahydrate. The cobalt solution is similar to that of copper but more stable. On heating it is blue but on cooling becomes a deep red-violet as at first. The $Co(CO_3)_2$ ion thus seems to be red, which is perhaps noteworthy, since some of the blue cobalt solutions are attributed to the presence of the $CoCl_4$ ions, which also contain quadrivalent cobalt.

For the investigation of fused silicates there are decided disadvantages connected with the use of platinum vessels, but Tammann has suggested the use of test tubes of carbon, rendered non-absorbent by an especially dense layer on the surface. These can be heated in the electric furnace easily as high as 2100°, and permit the study of fusions of silica with various oxides to be carried out with great facility. Using these tubes, Stein (*Z. anorg. Chem.*, **55**, 159) has investigated the preparation of a large number of silicates, formed by fusing the oxides together. He also finds that pure silica, which is viscous at 1600°, becomes at 1750° thin fluid, and sublimes. The sublimate, which forms several rings, is tridymite above, and just below a broad ring of vitreous silica. Even by slow cooling the fused silica could not be made to crystallize. Heating quartz revealed by discontinuous expansion the existence of a transition point at 552°, while chalcedony showed one at 173° and flint none between 100° and 600°.

An easy preparation of titanium tetrachloride has been described by Ellis (*Chem. News*, **95**, 122). Rutile is easily powdered after having been heated to 1000° and chilled in water. The powder is then mixed with half its weight of aluminum powder in a Hessian crucible at 500°, and the mixture ignited by burning magnesium. The product is broken up when cold and heated to a red heat in a current of dry chlorine. Titanium tetrachloride distils over and can be separated from the silicon tetrachloride formed at the same time by fractional distillation. The fact that some of the latter product is formed shows that free silicon must have been formed in the reaction with the aluminum, but inasmuch as silica is with difficulty reduced by aluminum alone, the cause of the reduction must be the great heat generated in the reduction of the titanium oxide by the aluminum.

An important piece of work is being carried out by Rosenheim in going over the chemistry of zirconium to see how much of the work of the past can stand, in the advances of inorganic chemistry of recent years. It is needless to say, that here, as practically everywhere else that this test is applied to inorganic chemistry, much of the earlier work becomes null and void. Rosenheim's second and third papers (*Ber.*, 40, 803, 810) deal with salts of some of the more common acids. Two strong tendencies appear in zirconium salts, which have been long recognized, *viz.*, the formation of basic (zirconyl) salts, and the formation of complex acid-zirconates, in which the zirconium is in the anion. The former tendency is illustrated by the great difficulty of preparing normal zirconium salts. Even from a concentrated hydrochloric acid solution the zirconyl chloride and not the zirconium tetrachloride crystallizes out, and the presence of hydrobromic or nitric acid does not overcome the hydrolytic tendency. By evaporating a solution with excess of nitric acid at 15° over phosphorus pentoxide the hydrated normal nitrate is obtained, but even here there appears to be considerable ground for supposing that the compound is really a complex zirconyl-nitric acid (nitrato-zirconic acid), $H_2ZrO(NO_3)_4.4H_2O$. The normal zirconium acetate may be prepared by the action of anhydrous acetic acid on the anhydrous chloride. Quite a series of new compounds have been prepared by Rosenheim by this reaction with the anhydrous zirconium chloride and organic acids, aldehydes and esters. In general, two of the chlorine atoms of the chloride are replaced, and if any moisture is present, these two atoms are replaced by oxygen by hydrolysis. The compounds with salicylic ester and aldehyde, $ZrCl_2(O.C_6H_4.CO_2CH_3)_2$ and $ZrCl_2(O.C_6H_4.CHO)_2$, will serve as examples of these compounds. The zirconium tetracetate undergoes partial hydrolysis in the presence of moisture, forming zirconyl acetate, but in aqueous solution is rapidly and completely hydrolyzed; indeed, this is suggested as an excellent method of preparing a solution of colloidal zirconium hydroxide. The normal sulphato-zirconic acid, $H_4Zr(SO_4)_4$, has not been prepared by Rosenheim, nor by Hauser, who has been studying the sulphates of this metal chiefly from the standpoint of physical chemistry (*Z. anorg. Chem.*, **54**, 196); but the potassium salt of this acid has been long known (so-called double sulphate of zirconium and potassium), and Rosenheim prepared the analogous sodium salt. The ordinary 'zirconyl sulphuric acid' has the formula $H_2ZrO(SO_4)_2.3H_2O$, or possibly $H_2Zr(OH)_2(SO_4)_2.2H_2O$. In more concentrated sulphuric acid solutions Hauser obtained an 'acid sulphate' of the formula $Zr(SO_4)_2.H_2SO_4.3H_2O$, which should more probably be considered as one-fourth hydrolyzed normal sulphato-zirconic acid, $H_3Zr(OH)(SO_4)_3.2H_2O$. The corresponding oxalic acid compound, $H_3Zr(OH)(C_2O_4)_3.7H_2O$, was prepared by Rosenheim, as well as the potassium salt of the normal oxalo-zirconic acid, $K_4Zr(C_2O_4)_4.5H_2O$, and the half hydrolyzed acid, $H_2ZrO(C_2O_4)_2.3H_2O$. The latter is the ordinary zirconyl oxalate. The only salt of a complex tartrate that was obtained was the potassium salt of the half hydrolyzed tartrato-zirconate, $K_2ZrO(C_4H_4O_6)_2.3H_2O$. Hauser (*Ibid.*, **53**, 74), by heating the sulphate, which had been previously dried at 400°, in a current of hydrogen sulphide at a moderate red heat, obtained an oxysulphide, $ZrOS$. If this is exposed to the air before it has become completely cold, it ignites spontaneously. The oxysulphide of thorium was obtained in a similar way and was somewhat more stable. Matignon (*Ann. chim. phys.* (8), **10**, 130) finds that thorium dioxide is slowly converted into thorium tetrachloride by heating in a porcelain tube in a current of dry carbonyl chloride, but the conversion is more satisfactorily brought about by heating in a current of carbon tetrachloride at a temperature not quite high enough to sublime the thorium chloride. If the operation is interrupted before the oxide is converted completely into the chloride, and the product rubbed up with absolute alcohol, the crystallized oxychloride, $ThOCl_2$, is obtained, which is insoluble in alcohol but soluble in water. Pure metallic thorium cannot be prepared by the action of sodium on the chloride, as the oxide will always be present. The hydride of thorium dissociates very easily, its dissociation pressure reaching 760 mm. below 400°. It is, however, not immediately acted on by chlorine at ordinary temperature. Attention should also be called to a paper by Schenck and Rassbach (*Ber.*, 40, 2185) on the chemical equilibria between lead sulphide and its oxidation products. It does not admit of brief abstraction but is an example of the application of the study of conditions of equilibrium to an important metallurgical problem.

Group V.—But three or four papers have appeared the past year on the combustion of nitrogen in the electric flame, and these do not indicate much progress in the study of the reaction, although it is claimed that considerable advances have been made from a practical standpoint. When one takes into account the enormous industrial importance and possibilities connected with the manufacture of nitric acid and nitrates from the air, and on the other hand the great differences in output with the slightest variations in conditions, it will be realized that few processes offer more opportunities for investigation.

An interesting addition to the compounds of nitrogen is that of monochloramine, NH_2Cl, which has been prepared by Raschig (*Chem.-Ztg.*, **31**, 926). Starting with the well-known blue coloration produced when aniline is oxidized in aqueous solution by hypochlorites and the fact that no color is produced if the hypochlorite has been previously treated with ammonia, Raschig found that when one molecule of ammonia is added to one molecule of sodium hypochlorite, monochloramine and sodium hydroxide are formed quantitatively. The solution can be distilled in a vacuum at low temperature and a pure solution of the new compound obtained, indeed, by using concentrated solutions and a high vacuum it was found possible to obtain it in pale yellow, oily drops, floating on the distillate. Monochloramine is very volatile, with a very irritating odor, resembling that of nitrogen chloride, and is very unstable. With potassium iodide it reacts giving a dark brown solution of what is possibly moniodamine, but which soon decomposes into ordinary iodide of nitrogen. The chloramine reacts with ammonia, with the production of either nitrogen or hydrazine, according to circumstances. Traces of iron, cobalt and other metals act as catalytic agents accelerating the decomposition into nitrogen, especially in the presence of substances, such as acetone, which decrease the viscosity of the solution. On the other hand, boiling the solution, especially in the presence of such substances as increase the viscosity, and of an excess of ammonia, tends to promote the formation of hydrazine. By the use of albumen, casein and gelatin it was found possible to obtain from 60–80 per cent. of the theoretical yield of hydrazine, and the possibility is suggested of using the method in the commercial production of hydrazine.

By dissolving nitric anhydride in freshly distilled sulphuric anhydride, Pictet and Karl (*Compt. rend.*, **145**, 238) obtain a product which distils at about 218° and solidifies to a hard, white crystalline mass which melts at 124°. The same compound is formed by mixing solutions of each anhydride in carbon tetrachloride. The substance has the formula $(SO_3)_4N_2O_5$, and seems to be anhydride of nitric and tetrasulphuric acids. It is very hygroscopic and dissolves in water with the regeneration of the two acids.

It has a powerful action on most organic substances, frequently both nitrating and sulphonating them, while if warmed both oxidation and carbonization may take place. No satisfactory solvent for the anhydride has been found. Potassium pernitrate, KNO_4, has been prepared by Alvarez (*Chem. News*, **94**, 269; from *Ann. chim. anal. appl.*, **11**, 401) by the action of sodium peroxide upon an alcoholic solution of potassium nitrate at a low temperature. On evaporating the solution the pernitrate is obtained in good crystals, which are neutral in reaction and give characteristic, but very unstable precipitates with solutions of metallic salts. The pernitrates of the alkaline earths are white crystalline precipitates. In a similar manner Alvarez has prepared perphosphates, perarsenates and pertungstates, $NaPO_4$, $NaAsO_4$ and $NaWO_4$. The pernitrate is recommended as a powerful oxidizing agent for combustions, and it is suggested that the perphosphates can perhaps be used in medicine. An interesting series of double compounds with nitrogen sulphide has been prepared by Davis (*J. Chem. Soc.*, **89**, 1575) by direct addition in chloroform solution. $SnCl_4.2N_4S_4$, $SbCl_5.N_4S_4$ and $MoCl_5.N_4S_4$ were thus prepared. Tungsten hexachloride and titanium tetrachloride were both first reduced and then gave the compounds $WCl_4.N_4S_4$ and $2TiCl_3.N_4S_4$. No compounds could be obtained with ferric chloride or the trichlorides of antimony and arsenic. All of the addition products were very unstable in moist air.

A useful lecture experiment to show the conversion of yellow into red phosphorus and at the same time illustrate the action of a catalytic agent is described by Zecchini (*Gaz. chim. ital.*, **37**, i, 422). Into a glass tube 30 cm. long and 7 or 8 mm. diameter and closed at one end, is put sufficient dry yellow phosphorus to fill the tube one-third full when melted. The tube is then heated to about 180° in a concentrated sulphuric acid bath. A fragment of iodine is then dropped onto the surface of the fused phosphorus, and the conversion of the yellow phosphorus into the red proceeds rapidly. According to Wolter (*Chem.-Ztg.*, **31**, 640) when phosphorus 'sesquisulphide,' P_4S_3, is shaken with a solution of iodine in carbon bisulphide, the color of the iodine disappears, and becomes golden yellow, and on cooling or on the addition of a little benzene or petroleum ether, characteristic orange leaflets of the di-iodide, $P_4S_3I_2$, are formed. Since none of the other sulphides of phosphorus give characteristic compounds with iodine, this reaction can serve to detect the presence of the 'sesquisulphide' in matches and other easily inflammable masses.

A number of salts of sulphato-arsenious acids have been prepared by Kühl (*Arch. der Pharm.*. **245**, 377), by heating together arsenious oxide and a sulphate in concentrated sulphuric acid solution, and evaporating off the acid. These salts are all somewhat basic, if one may use that term toward the arsenious acid, but should perhaps be better called oxy-salts. Such are $K_4As_2O(SO_4)_4$, $CaAs_2O(SO_4)_3$ and $PbAs_2O_2(SO_4)_2$. Somewhat similar salts of antimony (*Z. anorg. Chem.*, **54**, 256) are derived from a meta-sulphato-antimonious acid, as $AgSb(SO_4)_2$ and $Ca(Sb(SO_4)_2)_2.6H_2O$. Corresponding salts of tin, prepared by Weinland and Kühl (*Ibid.*, 244) are derived generally from the meta-sulphato-stannic acid, as $K_2Sn(SO_4)_3$ and $CaSn(SO_4)_3.3H_2O$. Some are, however, derived from the ortho-acid, as $ThSn(SO_4)_4.2H_2O$ and $CeHSn(SO_4)_4$. The titanium salts (*Ibid.*, 253) are derived generally from meta-sulphato-titanic acid, as $CaTi(SO_4)_3$. With molybdic acid also double sulphates are formed (*Ibid.*, 259), one type being a pyro-sulphato-molybdate, $K_2Mo_2O_4(SO_4)_3.6H_2O$, and another having only one oxygen of a pyromolybdate replaced by the sulphate group, as $K_2Mo_2O_6(SO_4).6H_2O$. All of these compounds are looked upon by Weinland and Kühl as being arsenites, antimonites, stannates, titanates and molybdates, in which the oxygen atoms are more or less completely replaced by sulphate groups.

In quite an extended study of vanadium, Rutter (*Ibid.*, **52**, 368) has prepared salts of bivalent vanadium by the electrolytic reduction of vanadic acid in the presence of sulphur dioxide, using a tile diaphragm and mercury cathode with low temperature. While it was not possible to prepare crystals of vanadous sulphate, crystals of the double ammonium sulphate were easily obtained, $(NH_4)_2V(SO_4)_2.6H_2O$. Vanadous sulphate oxidizes so readily that in the absence of oxygen a dilute solution decomposes with evolution of hydrogen, while if the solution is concentrated hydrogen sulphide is given off. When solutions of bivalent vanadium are mixed with vanadium solutions of other valences, equilibria are at once attained. Bivalent and quadrivalent give trivalent vanadium as a green solution, while vanadic acid with bivalent vanadium gives first a quadrivalent and then a trivalent solution. A study of the accelerating action of vanadium pentoxide on oxidation processes has been made by Naumann and his pupils (*Jour. pr. Chem.* [2], **75**, 146). Small traces of the pentoxide accelerate very markedly the oxidation of sugar to oxalic acid by nitric acid, and the reaction can be easily studied by precipitating the oxalic acid formed and titrating with permanganate solution. If the temperature is allowed to reach 70°, the oxalic acid is further oxidized to carbon dioxide. When a mixture of air and alcohol vapor is led over a layer of asbestos which has been saturated with vanadium pentoxide, the alcohol is oxidized to aldehyde with some acetic acid, while the vanadium asbestos becomes red-hot. The oxidation of stannous salts to stannic by nitric acid or by potassium chlorate and hydrochloric acid is greatly accelerated by the presence of vanadic acid, but on the other hand, the oxidation of ferrous and manganous salts seems scarcely affected. The accelerating action of vanadium pentoxide is attributed by Naumann to the readiness with which it gives up one atom of oxygen, becoming the tetroxide, which in turn is quickly re-oxidized by whatever oxidizing agent happens to be present. Thus if to a slightly warmed, acid solution of the pentoxide is added a sugar solution, the blue color of the tetroxide at once appears, only to give place to the yellow color of the pentoxide as soon as a few drops of nitric acid are added.

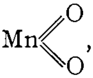
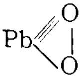
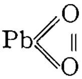
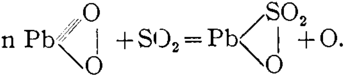
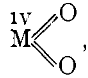
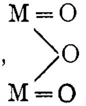
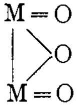
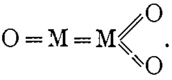
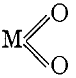
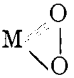
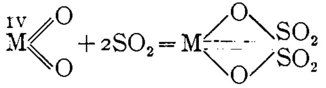
The interest connected with the use of tantalum in the incandescent light has naturally begun to stir up chemists to the further investigation of this puzzling element and its neighbor, columbium. While no inconsiderable number of chemists have worked with these metals, it is probably true that less is known of their chemistry than of any other two elements, if we except those that show radioactivity. Werner von Bolton (*Z. Elektrochem.*, **13**, 145) has, probably for the first time, prepared pure columbium, previous workers apparently having had in their hands only a lower oxide or a carbide. Bolton mixes columbium pentoxide with paraffin and makes it into fibers that are reduced to the tetroxide by heating in charcoal powder. The tetroxide as thus obtained is a conductor and is reduced to the metal by heating highly with the alternating current in a vacuum. If the direct current is used, only a lower oxide is obtained, which is, however, a good conductor of electricity. Columbium was also prepared by the Goldschmidt reaction. It is a bright light gray metal unacted upon by acids. It is about as hard as wrought iron, malleable and ductile, and can be welded at a red heat. It is so passive as an anode that it may find industrial application. Although it fuses only at 1950°, it 'dusts' so badly at high temperatures that its use in incandescent lights is precluded. When heated in hydrogen the hydride, CbH, is formed, which is readily oxidized, while the metal itself is only slowly acted on by oxygen at even a red heat. With nitrogen it forms a nitride. At a red heat in chlorine the pentachloride is produced, and it is also attacked by fused alkalies, by sulphur and selenium. It forms no amalgam with mercury but alloys with iron in all proportions. The chlor- and bromcolumbates and tantalates have been studied by Weinland (*Z. anorg. Chem.*, **54,** 223) and for the most part are formed according to the type M'_2CbOCl_5 (or $CbOCl_3.2M'Cl$). The chlorcolumbates of the alkalies crystallize in octahedra, seemingly belonging to the type of chlorplatinates in which one atom of chlorine is replaced by one atom of oxygen. Weinland has also found (*Ber.*, **39,** 4042) that the oxychloride of 'quinquivalent chromium' prepared by him last year, forms double salts with the alkali chlorides, having the formula $M_2'CrOCl_5$ ($CrOCl_3.2M'Cl$). These crystals also have the octahedral habit, although only the caesium and rubidium salts belong to the regular system. A similar case is that of the monoxychlorosmates discovered by Wintrebert, and another the dioxychlorruthenates and dioxychlorosmates. With organic bases other types of chlorcolumbates appear, but all are compounds of the oxychloride, $CbOCl_3$, and the same is true regarding the chlorotantalates. The bichloride of tantalum has been prepared as a dihydrate, $TaCl_2.2H_2O$, by Chabrié (*Compt. rend.*, **144,** 804) by the reduction of the pentachloride with sodium amalgam at a red heat, and crystallization from concentrated hydrochloric acid in a vacuum. The green color of this chloride is seen when tantalum solutions are reduced by various agents, but it very readily becomes oxidized. The properties of both these metals have also been examined by Muthmann (*Ann.*, **355,** 58), with essentially the same results as found by von Bolton. A moderate red heat is required to oxidize columbium, the tetroxide, Cb_2O_4, being formed, while tantalum burns at a lower temperature to the pentoxide, Ta_2O_5.

Group VI.—In a recent paper (*Z. anorg. Chem.*, **56,** 233) Marino argues in favor of a new class of dioxides. When manganese dioxide is treated with sulphur dioxide, manganese dithionate is the principal product, though there is some sulphite formed. With lead dioxide, sulphur dioxide gives at first lead sulphite and oxygen, which latter immediately oxidizes the sulphurous acid to sulphuric. The course of the reactions, as followed by Marino, is:

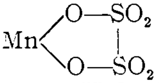
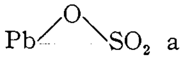
I. $PbO_2 + SO_2 = PbSO_3 + O$
II. $SO_2 + O + H_2O = H_2SO_4$
III. $PbSO_3 + H_2SO_4 = PbSO_4 + H_2SO_3$.

With true peroxides, the reaction is:

$$\text{I. } BaO_2 + H_2SO_3 = BaSO_3 + H_2O_2$$
$$\text{II. } SO_2 + H_2O_2 = H_2SO_4$$
$$\text{III. } BaSO_3 + H_2O_2 = BaSO_4 + H_2O$$

In neither of these cases is any trace of dithionate formed. From the reactions with hydrochloric acid, it may be assumed that in lead and manganese dioxide the oxygen is united solely to the metal and that the metal is quadrivalent, while in barium dioxide the barium is bivalent and the atoms of oxygen are united together, as shown by the hydrogen peroxide formation. From the dithionate reaction it is probable that the formula of manganese dioxide is  $Mn{<}^{O}_{O}$, but from the fact that lead dioxide forms only the sulphite, it must have some other formula. The only two which conform to the conditions are  $Pb{<}^{O}_{O}{\mid}$ and  $Pb{<}^{O}_{O}{\parallel}$. The former of these is the more probable since the sulphite formed from it has the asymmetrical formula, as was experimentally shown by its reaction with dimethyl sulphate. Its reaction with sulphur dioxide is then  $Pb{<}^{O}_{O}{\mid} + SO_2 = Pb{<}^{SO_2}_{O}{\mid} + O$. Lead dioxide may thus be considered to belong to a hitherto undescribed type of dioxides. Since the formation of a dithionate is conditioned upon the group  $\overset{IV}{M}{<}^{O}_{O}$, and since a dithionate is formed when sulphur dioxide reacts with the sesquioxides of iron, cobalt and nickel, it follows that the constitution of these sesquioxides is not, as generally assumed,  $\begin{matrix} M=O \\ M=O \end{matrix}{>}O$ or  $\begin{matrix} M=O \\ \mid \\ M=O \end{matrix}{>}O$, but  $O=M=M{<}^{O}_{O}$. In the opinion of the reviewer the conclusions of Marino do not seem to be well justified. Aside from the question as to whether there is any real difference between the two constitutions  $M{<}^{O}_{O}$ and  $M{<}^{O}_{O}{\mid}$ (which is extremely doubtful), the constitution proposed for the sesquioxides is improbable. There is no other evidence to indicate that all of the metal in these compounds is not uniformly trivalent (or $[M_2]^{VI}$). Further, the fact that MnO_2 gives dithionate, and PbO_2 primarily sulphite, does not necessitate a difference in constitution of the dioxides. The difference in solubility of lead and manganese compounds is quite sufficient to account for the breaking down of the primarily formed quadrivalent sulphites along different lines. The primary reaction would be  $\overset{IV}{M}{<}^{O}_{O} + 2SO_2 = M{<}^{O-SO_2}_{O-SO_2}$

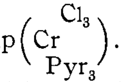
In the case of manganese the reduction in valence of the metal is to

 $Mn\left\langle\begin{matrix}O-SO_2\\ |\\ O-SO_2\end{matrix}\right.$ and in the case of lead to the insoluble  $Pb\overset{O}{\diagup\diagdown}SO_2$ and $(SO_3 + H_2O =)H_2SO_4$, as found by Marino.

The old problem of the constitution of the thiosulphates has been attacked by Julius Meyer (*Ber.*, 40, 1351) from the standpoint of the double thiosulphates, but no very definite results have been obtained. The double thiosulphates are in general quite unstable, but a pretty full series of the lead, silver and copper thiosulphates with the alkalies was prepared. $Cs_2S_2O_3.PbS_2O_3.2H_2O$ is a salt of a type which frequently occurs, though quite a number of other types exist, sometimes more than one with the same two metals, as for example the rubidium-copper thiosulphates, of which three distinct salts were prepared. In the case of some of the ammoniacal double thiosulphates of silver both white and yellow salts were obtained, which Meyer thinks may possibly point to a difference in constitution, the silver in the one case being attached to oxygen and in the other to sulphur. The difference in color may, however, be due to other causes, as the salts have not the same formula. In the case of the double rubidium salts, the white salt is $Rb_2S_2O_3.Ag_2S_2O_3.NH_3$, and the yellow salt $3Rb_2S_2O_3.4Ag_2S_2O_3.NH_3$.

In reviewing the sixth group, the work of Norris, published in THIS JOURNAL (28, 1675), on the elementary nature of tellurium should not be passed over. There seems to be little doubt but that tellurium is rightly placed as a member of the sixth group of the periodic system, but the most careful determinations of its atomic weight agree in placing it above iodine. Mendeléeff and others have plausibly conjectured that the discrepancies are due to the presence of some element, such as Mendeléeff's dvitellurium, in our ordinary tellurium, and special efforts have been made by several chemists to separate out such an element. In earlier work with Fay and Edgerly, Norris purified potassium bromotellurate by fractional crystallization, Brauner sublimed the tetrabromide of tellurium, and Köthner distilled tellurium itself fractionally. Since the boiling points of both the bromides of selenium and tellurium, and of the elements themselves, are not far apart, it is probable that a higher element of the same group would not differ greatly in its own boiling-point or in that of its bromide. Consequently it might be difficult to separate such an element if it were present in tellurium. On the other hand, there is a great difference between the boiling points of the dioxides of sulphur, selenium and tellurium, and it is probable that the dioxide of a heavier element of the sulphur group could be readily separated from the other members by sublimation. Norris therefore purified tellurium by the sublimation of the dioxide, but no difference in the atomic weights of the different fractions could be detected. In order to purify tellurium from any element of any other group, the reaction of sodium thiosulphate with tellurium dioxide to form the tellurium analogue of the pentathionate, $Na_2S_4TeO_6$, was utilized. This breaks up by alkalies into the tetrathionate and tellurium. It is hardly possible that any element of another group could replace sulphur in the pentathionate, so the precipitated tellurium from this compound may be considered free from any element except sulphur (and possibly selenium). On further purification this tellurium shows the same atomic weight as that purified in other ways.

This work of Norris's presents further strong confirmation of the elementary nature of what we now know as tellurium, and the solution of the problem of its anomalous position in the periodic table must be sought in some other direction. A paper has just appeared by Marckwald (*Ber.*, 40, 4730) on the atomic weight of tellurium which seems to bring out a new phase of the subject. Marckwald admits that the work of Norris and others has conclusively demonstrated the absence of any other element in their tellurium, which could affect its atomic weight, but he claims that most of the atomic weight determinations thus far made are defective. He has carried out a number of determinations based on heating H_6TeO_6 and weighing the TeO_2 formed, and gets fairly concordant results, with an average of 126.85 ± 0.02. As this is below the accepted atomic weight of iodine, it puts a new face on the whole matter, and the criticisms and results of the other workers in this field may prove interesting.

In the light of Werner's theory of the constitution of inorganic compounds, the question of the constitution of the product formed when chromium chloride is dissolved in pyridine and the solution precipitated by water, is of interest. The product has the empiric formula, $CrCl_3(Pyr)_3$. According to Werner's theory none of the chlorine atoms should be ionizable, but the insolubility of the compound in water precludes the possibility of determining this directly. Pfeiffer (*Z. anorg. Chem.*, **55**, 97) finds that the compound can be easily dissolved in concentrated nitric acid to a deep green solution, from which water precipitates the original compound in crystalline form. From this he argues that the chlorine cannot be ionizable, since if it were, some of the chlorine would be replaced by the nitrate group. Furthermore, the compound, while insoluble in water, is soluble in pyridine, chloroform, methyl alcohol and other organic solvents, which renders it probable that it has nothing of the character of a salt. The compound must hence be looked on as the coördinated group  $\left(\mathrm{Cr}\begin{matrix}\mathrm{Cl}_3\\ \mathrm{Pyr}_3\end{matrix}\right)$. Several papers have appeared during the year on the conditions which pertain in solutions of chromates and bichromates, but the problem still seems far from a final solution, and must be passed over here. Gröger has continued to work upon the double chromates (*Ibid.*, **51**, 348; **54**, 185), and finds that two quite general types of double chromates prevail. The type which is found in most of the double alkali sulphates of the bivalent metals, $M'_2M''(SO_4)_2.6H_2O$, is also found among the chromates, but hardly with the same frequency. It is found, for example, in the double alkali chromates of nickel and cobalt. On the other hand, a commoner type is $M'_2M''(CrO_4)_2.2H_2O$. This is found not only in the double chromates of cadmium, zinc and magnesium with potassium, but also in the potassium calcium chromate. Other types are also found, the double chromates of lead and univalent mercury with potassium being anhydrous. The large number of complex molybdates prepared by Hall have already been described in THIS JOURNAL (**29**, 692). Rosenheim has confirmed the formula of the potassium molybdi-octacyanide ($K_4Mo(CN)_8.2H_2O$) described by Chilesotti. It appears from titration experiments with potassium permanganate that this peculiar compound is a derivative of quinquivalent molybdenum. This only serves to increase the anomalous character of this salt, which represents the unique case of a stable anion, soluble in water, which contains eight coördinated groups about one atom. Quite a number of salts of this anion were prepared by Rosenheim, and they are comparable in stability with the ferrocyanides. A quite complete investigation of the compounds of quadrivalent uranium has been published by Colani (*Ann. chim. phys.* [8], **12**, 59). The anhydrous chloride was prepared by the action of chlorine and chloride of sulphur on the dioxide, the product containing other chlorides if any other oxides are present. The tetrabromide was readily formed but the anhydrous tetraiodide could not be prepared. The sulphide, selenide, nitride, phosphide and arsenide were all found to be normal in their formulas. A large series of phosphates and double phosphates was prepared, the latter giving generally rather simple types.

Group VII.—During the past year considerable work has been published from the University of Danzig by Ruff and his pupils on fluorine and its compounds (*Ber.*, **39**, 4310; **40**, 2926; *Z. anorg. Chem.*, **52**, 256; *Z. angew. Chem.*, **20**, 1217). The pentafluoride of antimony was prepared by the action anhydrous hydrogen fluoride upon antimony pentachloride at zero, the temperature being gradually raised and the hydrogen chloride and hydrogen fluoride being successively distilled off. It was not found possible to prepare the pentafluoride by the action of hydrofluoric acid upon antimony pentoxide. With a small quantity of water the pentafluoride forms a dihydrate, but dissolves in more water to a stable solution, in which no precipitate is formed in the cold with either hydrogen sulphide or potassium iodide. While dry metals have little action upon the pentafluoride, several of the elements form addition products. Such are SbF_5I, $(SbF_5)_2I$ and SbF_5S. At about 250° an equilibrium seems to be attained with a formula $(SbF_5)_{1.4}I$, and this whether the mixture heated contained an excess of the pentafluoride or of iodine. With liquid ammonia a compound is formed with the formula $(SbF_4)_2(NH_3)_3$, which according to Ruff is probably a difluohydrate of diaminodiantimonotrifluoramide, which may be formulated $HF.NH_2.SbF_3.NH.SbF_3.NH_2.HF$. With tungsten hexachloride, tungsten hexafluoride is formed, but a better method of preparing the latter is the action of anhydrous hydrogen fluoride upon tungsten hexachloride. Arsenic trifluoride can also be used. Tungsten hexafluoride is the first fluoride of a metal which is a gas at ordinary temperature. At 19.5° it is condensed to a liquid which freezes at 2.5°. It fumes strongly in the air and is very sensitive to moisture. The oxytetrafluoride, WOF_4 was prepared, and a mixture containing this and the dioxydifluoride, WO_2F_2, but the latter could not be obtained pure. While efforts to prepare the hexachloride of molybdenum have not proved successful, and the hexafluoride could not be obtained by the action of hydrogen fluoride or any of the other fluorides, in some cases fluorine compounds of hexavalent molybdenum were obtained, but they were generally the oxytetrafluoride or the dioxydifluoride, corresponding to the tungsten oxyfluorides mentioned above. The molybdenum hexafluoride was finally prepared by the direct action of fluorine upon metallic molybdenum, obtained by the Goldschmidt process. MoF_6 fuses at 17° and boils at 35° and is a very reactive substance. Another interesting compound prepared by Ruff is the acid potassium compound of lead tetrafluoride, $PbF_4.3KF.HF$. This may also be looked upon as the tripotassium salt of fluo-orthoplumbic acid, K_3HPbF_8. This is readily prepared in quantity and when heated gives off a part of its fluorine, hence it is proposed by Brauner to use it in the preparation of fluorine. It is probably the most stable known halide compound of quadrivalent lead. Bismuth pentafluoride was also prepared, hydrofluoric acid being used to dissolve the product obtained by the action of chlorine upon an alkaline suspension of bismuth. Lebeau has also been engaged in work upon fluorine and has prepared (*Compt. rend.*, **144,** 1042, 1347; **145,** 190) selenium tetrafluoride by the direct action of fluorine upon selenium. It boils somewhat above 100°. With an excess of fluorine no higher fluoride could be obtained. This is, however, contrary to the work of Prideaux, who obtained a hexafluoride, the vapor density of which, as determined by Ramsay, corresponded to the hexafluoride. In his later papers Lebeau seems to admit the formation of the hexafluoride. The subject of the basicity of hydrofluoric acid has been further studied by Kremann (*Monatsh.*, **28,** 917) and Pellini and Pegoraro (*Z. Elektrochem.*, **13,** 621). The former studied the conductivity of the solutions, using as a vessel a hollow block of paraffin. On the basis of Ostwald's dilution law, the acid has the formula H_2F_2. Pellini studied the conductivity on neutralizing hydrofluoric acid with alkalies, and from this concludes that the acid acts as if it were bibasic and consisted of a combination of two monobasic acids, one of which is strong and the other weak. The free acid and the neutral salts thus act as binary electrolytes, while the hydrogen fluorides and the neutralization phenomena correspond to a bibasic acid.

Recent work by Schwarz (*Z. angew. Chem.*, **20,** 138) on bleaching powder confirms the hypothesis that the underlying reaction of its formation is $Cl_2 + HOH \rightleftarrows HCl + HOCl$. This explains why the presence of water is necessary to the reaction. So long as the lime is present in excess the reaction is merely a neutralization of the acids according to the above equation. As soon, however, as the lime has all been used up, the excess of hydrochloric acid liberates hypochlorous acid from the bleaching powder and this, with the hypochlorous acid formed in the above reaction, oxidizes undecomposed hypochlorite to chlorate. The excess of chloride which is always found in commercial bleaching powder may be due, according to Schwarz, to the loss of oxygen from the hypochlorite, or to hydrochloric acid present in the chlorine used. If the amount of water present in making bleaching powder is too great, the same effect is produced as with an excess of chlorine, since the hypochlorite is very easily hydrolyzed. The fact that the synthetic bleaching powder (prepared by the action of chlorine monoxide on calcium oxide in the presence of moisture) gives up much less chlorine when treated with carbon dioxide, is probably to be explained by considering it merely a mixture of calcium chloride and calcium hypochlorite, while that prepared in the ordinary commercial method is a true double salt, $CaCl(OCl)$. Bleaching powder from strontia resembles very closely in preparation and properties, that from lime. Two new salts of some little interest are hydrazine chlorate and perchlorate, prepared by Salvadori (*Gaz. chim. ital.*, **37,** ii, 32) by the neutralization of a solution of hydrazine hydroxide with the free acids, and evaporation in a vacuum. The chlorate is exceedingly hygroscopic and has three times as great explosive force as fulminate of mercury.

Alcohol is rapidly oxidized by its solution even in the cold to aldehyde and acetic acid. Hydrazine perchlorate is, on the other hand, far more stable and can be fused at 131° on platinum foil, and burned quietly at a higher temperature. It is, however, exploded by a blow. It can be boiled in solution, even in the presence of alcohol, without decomposition. A specimen of the perchlorate was preserved for two years unchanged over calcium chloride.

Several years ago the method of preparing anhydrous chlorides by heating the oxides in a current of chlorine and chloride of sulphur was introduced. Bourion (*Compt. rend.*, **145**, 243) now finds that this reaction is equally applicable to the preparation of bromides, and he has obtained a number of new bromides of the metals by heating their oxides in a current of bromine containing a small amount of the chloride of sulphur. The amount of the latter reagent necessary for good results varies in different cases.

A new suggestion regarding the place of manganese in the periodic table has been made by Reynolds (*Chem News*, **96**, 260). Recognizing the slight resemblance between manganese and the other elements of the seventh group and the fact that no other elements of higher atomic weight have been found to take the vacant places in the second series of group seven, he transfers manganese to the first period of the eighth group, making this series, Mn, Ru, Os. The second series becomes Fe, Rh, Ir, and the third series, Ni, Pd, Pt. One advantage of this arrangement is that nickel precedes cobalt in position as it should with its undoubtedly lower atomic weight. It may be questioned, however, whether this arrangement has actually come as near the natural arrangement as the ordinary table. Cobalt would here stand alone as a single member of a fourth series of group eight. It is true that group seven with only one series would correspond to the so-called group zero with the inert gases, which has only one series, but as a matter of fact the halogen group seven corresponds rather to the alkali group one, and the compounds of manganese are no more unlike those of the halogens than are those of copper, silver and gold unlike the alkalies. According to Reynolds's arrangement, the iron-platinum metal group represents a transition from the sixth group to the first, while the inert gases would be the transition from group seven to group one. If the iron-platinum metals and the inert gases represent the two divergent series of group eight, then the iron-platinum metals are a natural transition from the positive series of group seven to the negative series of group one, while the inert gases form the transition from the negative series of the seventh group to the positive series of group one. Mention ought to be made here of the fact that Holmes (THIS JOURNAL, **29**, 1277) has succeeded in preparing the long sought for tetrachloride of manganese, by the action of dry hydrogen chloride upon freshly precipitated manganese dioxide, suspended in carbon tetrachloride. It is hydrolyzed in the presence of even a trace of water and loses chlorine on heating. This work of Holmes renders probable what has long been surmised, that the first product of the action of hydrochloric acid on manganese dioxide is the tetrachloride, and the reason that this has eluded so many investigators is not so much the inherent instability of quadrivalent manganese compounds (a thing in itself improbable) as the great tendency of the compounds of quadrivalent manganese to hydrolyze.

Group VIII.—That in the action of iron on water the temperature and the surface are the two determining factors has of course long been recognized, but few have realized how extensive the influence of increasing the surface by using finely divided iron might become. Birnie (*Chem. Weekbl.*, **4**, 291) has studied this reaction using *ferrum reductum* and the vapor of water at different temperatures. When 10–20 grams of this iron are heated in a current of steam with an ordinary gas jet, 100 cc. of hydrogen can be collected in a few moments. It is even possible to obtain a rapid evolution of hydrogen by the use of 'florists' wire,' if a sufficiently high heat is used. At a temperature of 15° with 500 grams of *ferrum reductum* little hydrogen was obtained the first day, but after that from 100–500 cc. every 24 hours. A decided evolution of hydrogen is apparent when two kilos of florists' wire is boiled with distilled water. The color of iron alum (and incidentally of other ferric salts) has long been an unsolved puzzle. It has been described as colorless, as yellow, as violet, as blue, but it has often been conjectured that the ordinary amethyst color is due to manganese, since the salts of trivalent manganese vary from amethyst to red according to concentration. Christensen (*Danske Vid. Selsk. Förh.*, **1906**, 4, 173) has experimented with the fractional crystallization of iron alum and of pure iron alum to which a trace of manganic sulphate (manganic acetate in sulphuric acid) has been added. It was found that crystals could be obtained varying from colorless to garnet red, depending on the content of manganese. In the more deeply colored crystals, it is safe to say mixed alum crystals are present, but in those which are amethyst the color is possibly due to a ferric-manganic sulphate, such as has been prepared by Étard. While this salt is green, its addition to a colorless iron ammonium alum gave violet crystals. Pure iron alum is colorless but colorless iron alum is not necessarily pure, for on fractioning such an alum a mother-liquor was obtained from which violet crystals were obtained. Bellucci and his pupils have continued the work (*Atti accad. Lincei, Roma* (5), **15**, ii, 467; **16**, i, 654) begun several years ago on the nitrososulphides of iron (nitroprussides). By action upon the sodium salt, $NaFe_4(NO)_7S_3.2H_2O$, with the hydrochloride of hydrazine in slight excess, the hydrazine nitroprusside was obtained. The hydroxylamine salt was similarly formed but required rather longer heating to complete the reaction. The potassium, thallium, rubidium and caesium salts were readily formed by treating the hydrazine salt with the corresponding chloride, and the salts obtained in this way were all anhydrous, while when otherwise prepared they are hydrated. Nitroprussides were also prepared of a number of organic bases, such as phenylhydrazine, pyridine, tetra-alkyl ammoniums, phenylenediamine and semicarbazine. Cobalt hexamine (luteo salt) also forms a crystalline compound.

An article has lately appeared by Gross (*Elektrochem. Z.*, **14**, 146) claiming the decomposition of platinum by the alternating current. Potassium carbonate was heated to a yellow heat in a platinum crucible and subjected for several hours to an alternating current of 120 volts and 35 amperes, with 50 alternations per second. A small amount of potassium nitrate was added to the melt. The platinum was strongly attacked and in and over the melt graphite-like crystals were formed. After treatment with water a brown substance remained which was soluble in water but after heating to a red heat could be dissolved only in aqua regia. Its solution gave a dark brown precipitate with hydrogen sulphide. On evaporation of the filtrate from the melt a red powder was obtained which was free from platinum but on solution in hydrochloric acid showed the same properties as the brown substance. The above-mentioned needles, on solution in aqua regia showed also similar properties. The total amount of new substance was 15 per cent. less than the loss of the platinum crucible and the electrodes. Gross considers that the red powder is a hydrate and the brown material the new substance itself, obtained by the decomposition of platinum. The same results were obtained when potassium hydroxide or a mixture of nitric and sulphuric acids was used as an electrolyte. Further information is to be looked for, as the data given are insufficient to form a conjecture as to the meaning of the published results, and especially as to whether the other metals which are present in all commercial platinum may not be responsible for the results obtained by Gross.

Gutbier has continued his work upon the halopalladites and palladates of organic bases as well as the pallado-amines of the same bases (*Ber.*, 39, 4134). Pyridine, picoline, quinoline and a number of primary alkylamines were used and the results obtained are similar to those which have been previously described. The halopalladites are formed by direct union of the components in hydrochloric acid solution and can generally be recrystallized from hydrochloric acid, but on treatment with water they are decomposed with the formation of the palladamines. Gutbier has also (*Ibid.*, 40, 690) prepared a large number of hexachlor- and bromruthenates of organic bases. His method is to saturate a solution of ruthenium trichloride with the halogen and then add the solution of the hydrochloride of the base, or to mix the trichloride with the base and then saturate the solution with chlorine or bromine. Since earlier investigations have shown that the true trichloride or rather pentachlorruthenic acid, H_2RuCl_5, and its salts are not converted into the hexachlorides directly by the addition of chlorine, but only after they have been converted into the aquochlorides, it must have been the latter, $M'_2Ru(H_2O)Cl_5$, with which Gutbier worked. The acid solution of the trichloride is readily converted into the aquochloride by heating its solution with alcohol and other organic substances, so that this change may well have occurred in the presence of the organic substances with which Gutbier was working. The properties of Gutbier's hexahaloruthenates agree with those of the corresponding hexahaloruthenates of the alkali metals. A very useful piece of work has been carried on by Paal and Amberger (*Ibid.*, 40, 1378) on the quantitative determination of osmium. When a compound of osmium can be heated in a hydrogen current and reduced to the metal, this can be very satisfactorily handled on a Gooch filter, as has been well worked out by Wintrebert; but where the osmium is in solution the problem is difficult. Paal and Amberger have gone critically over the whole ground of the quantitative precipitation of osmium, testing no less than ten proposed methods, generally with very unsatisfactory results. When the osmium is in the form of osmium tetroxide ('osmic acid') it can be completely precipitated by alcohol on long standing, though the precipitate is a hydrogel and hard to wash. Other compounds of osmium, as the osmates, are also precipitated by alcohol but here again the precipitate is difficult to free from alkalies, if they are present. No method, which can be considered thoroughly satisfactory, is known by which osmium can be quantitatively precipitated. The same is even more true of ruthenium, for no method is yet known by which this metal can be completely precipitated from solution.

WASHINGTON & LEE UNIVERSITY,
LEXINGTON, VA.
January 1, 1908.

ON THE NON-EQUIVALENCE OF THE FOUR VALENCES OF THE CARBON ATOM.[1]

BY J. U. NEF.

Received January 8, 1908.

Three assumptions are made with reference to the carbon atom in our present system of organic chemistry: first, that the valence of this atom is invariably four; second, that the four valences are equivalent; and third, that they are distributed in three dimensions and act in the direction of the axes of a tetrahedron.

If we believe, as many at present are inclined to do, that the chemical forces are analogous to or identical with the electrical forms of energy, it at once becomes improbable that the four valences of the carbon atom can be equivalent. Had Berzelius, for example, realized that the molecules of hydrogen and oxygen were each composed of two atoms he would have developed his electrochemical theory from a different standpoint; he would have concluded, as have Clausius, Schönbein, and many others in more recent times, that the forces holding the two atoms of oxygen or hydrogen together in these molecules must be alternately positive and negative.

Let us first analyze critically, however, the evidence which has led us, for some fifty years past, to assume that the four valences of a carbon atom are equivalent. In the last analysis the fact that up to the present moment every one of the great number of monosubstitution products of methane has been found to exist in one modification only is all we have to justify our assumption. There is but one acetic acid, one nitromethane, one aniline, one acetaldehyde, etc., etc. It is evident that we are here drawing positive conclusions from negative evidence—always an unreliable and dangerous process of reasoning. How can we ever be certain when we have a monosubstitution product before us that it is not always one and the same hydrogen atom of marsh gas which has been replaced?

A Belgian chemist, Henry,[2] has spent a number of years in trying to prove by experiment that any one of the four hydrogen atoms of methane, *a*, *b*, *c* or *d*, may be replaced by the carboxyl or nitro group and yet give thus one and the same acetic acid or nitromethane respectively. Such experiments can not conceivably be decisive, for they necessitate the unjustifiable assumption that the various atoms or radicals bound to the

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[1] See THIS JOURNAL, 26, 1549–1577. Read at the Chicago meeting of the American Chemical Society.

[2] Bull. acad. royal de Belgigue (3), 12, 644; 15, 333.