

tries makes for the advancement of science and art. But time has changed this somewhat, and I think it will change it more.

With regard to all the sciences a large number of misstatements are made regarding their commercial value. Probably Astronomy has been of as much benefit to mankind as any. Every ocean passenger owes to it his safe and rapid passage. Through its help the carriage of every ton of freight is made cheaper. It would be difficult to calculate the money value it has been to the world.

The conception which most people have of the nature of the questions to be solved in Astronomy is a false one. They look on them as text-book problems in mathematics which are arranged to come out nicely. They suppose such questions can be solved definitely and exactly, once for all. They do not know that instruments are imperfect and that observers have personal errors, nor that it is possible to be sure only to a certain limit, personal opinion founded on experience carrying us a little farther, and the rest being uncertain, though methods and instruments and mathematical conceptions may, after a while, be improved. So that in any actual question in practical or theoretical Astronomy it is necessary to deal with facts as they are in nature, and obtain the best possible solution, though perhaps not the one which is exactly true.

Many people, too, and well educated ones, have very curious ideas as to the amount of labor involved in the solution of questions in Astronomy, and as to the progress of the science. An intelligent doctor, who knows that the science of medicine, as far as it is a science, is something of slow growth, who experiments for a year or two on some fairly simple question, cannot understand the same thing in Astronomy, and thinks that it was really founded and developed by some one whom he happens to know about.

In the case of the small observatories, where teaching is expected of the astronomer, the question of economy of time is a difficult one. At Harvard and Johns Hopkins, for instance, six hours of lectures per week would be expected to occupy half of a teacher's time, while in a small establishment one cannot give that proportion and make and reduce observations. At the smaller observatories, too, there is difficulty in requiring proper preparation and in enforcing a high standard of scholarship. Men who believe that the training in law, medicine or engineering should be thorough and severe, because they think the students will be better off commercially, cannot understand that students in Astronomy ought to have the same thorough discipline.

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*THE EIGHTH GROUP OF THE PERIODIC SYSTEM AND SOME OF ITS PROBLEMS.*

II.

We have seen that nearly half a century ago, it was clear to Claus that iron, ruthenium, and osmium belonged in a group together. It was later easily recognized that cobalt, rhodium, and iridium furnished a second triad, while nickel, palladium, and platinum must also be grouped together. The analogies between the three metals of each of these groups is too patent to require discussion, though incidentally we shall have occasion to recur to it. When the elements were arranged in the first periodic tables, these metals did not fall into orderly arrangement; as late as 1878 the atomic weight of osmium was considered greater than that of iridium, platinum, or even gold, while gold was given a weight less than that of iridium or platinum. Cobalt and nickel on one hand and iridium and platinum on the other were considered to have an identical atomic weight. The seeming impossibility of reconciling these nine metals with the periodic law is undoubtedly the reason why they were thrown

out in a single group; dumped into a chemical Gehenna as it were, while the rest of the elements were reduced to orderly arrangement. Lothar Meyer, however, saw that there was a possibility that these elements also might be amenable to system, and under his direction Carl Seubert began the revision of the atomic weight of iridium.\* This he found to be more than four units less than the figure formerly used, and now the order of these elements appeared to be iridium, gold, platinum, osmium. Three years later Seubert † revised the atomic weight of platinum, finding it lower than that of gold, and this work was confirmed by Halberstadt, ‡ and by Dittmar and McArthur. § The only anomaly in these four metals now was in osmium and this also was resolved by Seubert, || who found that the old value of Berzelius and Frémy was about eight units too high, and that so far from having an atomic weight greater than that of gold, osmium in reality has the lowest atomic weight of the four metals. This revision was justly accounted a great triumph for the periodic law.

As with the other metals, so also much doubt existed as to the atomic weights of rhodium and ruthenium, but the work of Seubert and of Joly, while changing somewhat the older figures, confirmed the order given in Meyer's table. Much work has been done on palladium by Keiser and by Keller and Smith in this country, by Bailey and Lamb and by Joly and Leidié abroad. The figures for platinum and palladium represent a much greater degree of accuracy than those for the other four platinum metals. Indeed it must be said that little accuracy can be claimed for the present figures of rhodium and iridium, and certainly those

of ruthenium and osmium cannot be depended on more closely than half a unit.

In the case of the three other metals of this group, the atomic weight of iron has been well determined, but is now being subjected to a most careful examination in the laboratory of Professor Theodore Richards. As was supposed a few years ago to be the case with iridium and platinum, so cobalt and nickel were thought to have the same atomic weight. Then Lothar Meyer showed that, judged by their properties, nickel should follow cobalt in the periodic system and hence have the higher atomic weight. Revisions of these metals followed, but the more accurate the work the more probable it appeared that the atomic weight of nickel is below that of cobalt. It was suggested that nickel was quite probably a mixture and efforts were made to resolve it into its constituents. In this connection will be recalled the efforts of Gerhardt Kruss to decompose nickel, in which for some time he thought he had been successful and christened the new metal gnomium. But like so many other aspirants for chemists' favor, gnomium proved to be but a mixture. The latest work on these metals by Richards and Cushman and Baxter, far surpassing all that has previously been done, confirms the higher atomic weight of cobalt, and lends no support to the view that nickel is anything but a simple element.

Here we meet apparently one of those chemical mysteries, which seem to baffle our attempts at solution. We are not permitted to doubt the correctness of the general principles of the periodic system, and yet here, and the case is perhaps not unique, two elements seem to have exchanged places. When we know *why* the properties of an element are a function of its atomic weight, we shall perhaps come to understand why the atomic weight of nickel is not greater than that of cobalt.

\* Inaug. Diss., Tübingen, 1879.

† *Ber. d. Chem. Ges.*, 14, 865 (1881).

‡ *Ibid.*, 17 (1884), 2962.

§ *J. Soc. Chem. Ind.*, 6, 799 (1887).

|| *Ber. de Chem. Ges.*, 21, 1839 (1888).

If the chemical study of these metals supports the conception of their elementary nature, an examination of the spectrum of nickel and of cobalt, and particularly of iron, forces upon us the thought of the complexity of the atom. If each line of the spectrum, representing the vibration of a certain wave length, is occasioned by a corresponding vibration of the atom, it becomes difficult for us to conceive of so many hundred simultaneous vibrations of a simple atom, a great share of which stand in no apparent harmonic relation to each other. It has been suggested that it is by a study of the spectroscopic portrayal of atomic vibration we may hope to gain the most complete knowledge of the dynamical character of the atom, but it must be remembered that with the spectroscope we study the motion of the atom at a high temperature, when vibration apparently overcomes in most instances chemical affinity; a knowledge of the atom at this temperature may give us no hint whatever as to the nature of the atom at lower temperatures, even as the spectrum of the same element may change with varying temperature. While we might thus conjecture that perhaps by some process of careful and refined fractionation, it might be possible to resolve iron into a series of meta-elements with nearly the same atomic weight, we are met by the fact that complex though it is, we find not only the same spectrum for iron whatever its terrestrial source, but that the spectrum of sidereal iron, from meteorite, from sun, from star, gives us no evidence of any variation in the composition of iron. We are, I think justified in concluding that the nine metals of the eighth group fulfill every definition of an element, and that they are just as much to be looked upon as simple elementary substances as any of those substances which we call elements; and further that while refined determinations may change, to a slight extent, the atomic weight of some of

these elements, especially those of ruthenium and osmium, we may expect the weight of these elements relative to each other, and hence their position in the periodic system to remain unchanged. This, of course, carries with it the conclusion that in the periodic table an element may have an atomic weight slightly lower than that of the element which precedes it. I have discussed this possibility briefly elsewhere,\* and will only add that seeming exceptions to accepted laws, instead of overthrowing the law, often serve to broaden our conception of the law itself.

Before considering some of the compounds of the metals of the eighth group, attention must be called to the phenomenon exhibited by several of these metals, and particularly by palladium, of condensing hydrogen and other gases upon their surface. The first observation in this connection seems to have been that of Sir Humphrey Davy†, who in 1817 showed the Royal Society how a warm platinum wire, plunged into the vapor of alcohol or ether or certain other inflammable gases, became incandescent, and continued to glow as long as kept in the vapor, causing an oxidation of the gas and in some mixtures even an explosion. This phenomenon attracted great attention on the part of chemists and many were the discussions over this lamp 'without a flame' or Davy's 'aphlogistic lamp' as it was called. It was soon after noticed by Edmund Davy‡ that the platinum reduced from solution, now called platinum black, but then platinum suboxid, is especially active and can oxidize alcohol to acetic acid. In 1823 Döbereiner announced§ that platinum black and platinum sponge, when held in a stream of hydrogen, ignite the gas and that the hydrogen is absorbed

\* *Chem. News*, 80, 74 (1899).

† *Phil. Trans.*, 107, 77 (1817).

‡ *Ibid.*, 110, 108 (1820).

§ *J. für. Chem.* (Schweigger), 38, 321 (1823).

by the platinum. This was the origin of Döbereiner's hydrogen lamp, regarding which he writes under date of August 5, 1823: "You have doubtless guessed before this that I have already utilized this new observation (of the heating effect of the condensation of hydrogen) for the preparation of a new Feuerzeug and a new lamp, and that I shall put it to many other important uses."\* The interest which attached to this discovery of Döbereiner's can be judged from the fact that in the literature of the decade following are found over fifty references to the subject. Little attention was, however, paid to the similar action of palladium upon combustible gases, although the phenomenon had been noticed, until in 1868, half a century subsequent to Davy's first observation on platinum, Graham presented to the Royal Society his remarkable paper on the occlusion of hydrogen by metals,† followed the next year by his papers on the relation of hydrogen to palladium,‡ and additional observations on hydrogenium.§

Graham's view that the hydrogen is present in solid form as a metal and that the palladium saturated with hydrogen must be looked upon as an alloy, was received with considerable dissent. The work of Troost and Hautefeuille|| tended to the view that the substance is a definite compound, Pd<sub>2</sub>H. Against this is the fact that the conductivity of palladium is but slightly reduced by the occlusion of hydrogen. Calculations of the specific gravity of Graham's hydrogenium by Dewar gave the number 0.62 and the same figure is obtained for the hydrogen in hydrides of sodium and potassium, studied by Troost and Hautefeuille. The recent determinations of the specific

gravity of liquid hydrogen by Dewar, however, show a figure only about one-ninth of the density of occluded hydrogen, so that the question as to the nature of the hydrogen condensed by the palladium and platinum remains still unsettled. The other metals of the group possess this property to some considerable degree, but much less than is the case with palladium and platinum. In this connection it is interesting to note that one of the earliest papers of Dewar was on the motion of a palladium plate, during the formation of Graham's hydrogenium.\*

Reference has been made to the natural grouping of the elements of the eighth group into three triplets, iron, ruthenium, osmium; cobalt, rhodium, iridium; and nickel, palladium, platinum. That this is a natural grouping is attested by a comparison of the compounds of these metals. However, in considering now some of these compounds the evidence of this grouping is only incidentally presented; I desire chiefly to call attention to some of the more unusual of these compounds, especially with reference to problems which this group presents, and to problems of other groups, suggested by the chemistry of this group.

The position of an element in the periodic system is, to a very considerable extent, determined by its oxids, and that too by its highest oxids, excluding the peroxids of the hydrogen peroxid type; a considerable number of these last have been studied especially by Melikoff and Pissarjewsky of Odessa, but their character still presents many points of obscurity and cannot be used with reference to the periodic law. The triplet iron, ruthenium, osmium presents the highest oxids of the eighth group, and, as is the case with other divisions of this group, an increasing stability of the higher oxids with increasing molecular weight. The type of salts of the acid-forming oxids FeO<sub>3</sub>, RuO<sub>3</sub>, OsO<sub>3</sub>, occurs in this group, as in the posi-

\* Loc. cit.

† *Proc. Roy. Soc.*, 16, 422 (1868).

‡ *Ibid.*, 17, 212 (1869).

§ *Ibid.*, 17, 300 (1869).

|| *Compt. rend.*, 78, 686, 968 (1874) 80, 788 (1875).

\* *Proc. Roy. Soc. Edinb.* 6, 504 (1869).

tive series of the elements of the sixth and seventh groups; viz,  $\text{CrO}_3$ ,  $\text{MnO}_3$ ,  $\text{WO}_3$ ,  $\text{UO}_3$ ,  $\text{MnO}_3$ . This type is not represented in the second or third triplet of group eight. Potassium ferrate,  $\text{K}_2\text{FeO}_4$ , exists only in solution and is very unstable; potassium ruthenate,  $\text{K}_2\text{RuO}_4$  is stable when dry but slowly decomposes when in solution; potassium osmate,  $\text{K}_2\text{OsO}_4$ , on the other hand, has a very considerable degree of stability. Of the lower base-forming oxids, iron has not only the sesquioxid,  $\text{Fe}_2\text{O}_3$ , and monoxid,  $\text{FeO}$ , but also several intermediate oxids which may be looked upon as merely compounds of these two—such is magnetite. In the case of ruthenium, the sesquioxid,  $\text{Ru}_2\text{O}_3$ , seems to be what one might call the normal base-forming oxid. The different conditions which occasion the formation of the lower oxids of osmium are ill known, though several different oxids seem to exist, as  $\text{OsO}$ ,  $\text{Os}_2\text{O}_3$ , and  $\text{OsO}_2$ . Much more interest, however, attaches to the tetroxids of ruthenium and of osmium,  $\text{RuO}_4$  and  $\text{OsO}_4$ , which are the highest volatile oxids of any known element. The almost intolerable odor of osmium tetroxid incited Tennant, in 1803, to give its name to this element, while ruthenium tetroxid, first noticed by Claus, has, if not too concentrated, a rather fresh pleasant odor, with just a suspicion of the smell of ozone, due probably to the formation of ozone in the decomposition of the oxid. As far as physical properties go, these oxids, while solid at ordinary temperature, melt easily and can be distilled. Ruthenium tetroxid is, however, far less stable than the corresponding osmium oxid, for it decomposes slowly at ordinary temperature, and explodes with great violence if heated much above  $105^\circ$ . On one occasion Deville and Debray\* attempted to distil a hundred and fifty grams of ruthenium tetroxid, and when the temperature reached a little above  $100^\circ$ , the whole mass

\* *Ann. Chim. Phys.* [5], 4, 537 (1875).

exploded with terrific violence, filling the laboratory with a dense sooty smoke. In a recent similar explosion in my own laboratory, occasioned by the contact of a little alcohol with ruthenium tetroxid, but happily on a much smaller scale than that of Deville and Debray, this black soot was found to be readily soluble in hydrochloric acid. This is unexpected, as all the anhydrous lower oxids of ruthenium are insoluble in acids, and from its methods of formation the black substance could hardly be anything other than an anhydrous oxid or the metal itself. Osmium tetroxid is commonly known as osmic acid, but as a fact these tetroxids are neither acid-forming oxids nor are they peroxids in the ordinary acceptance of the term. When treated with an alkali, we have a gradual reduction with formation of perruthenate and ruthenate, or of osmate.

Turning to the third triplet, we have the monoxid of nickel well characterized, and it is, we may say, the only well-characterized oxid of the metal, for though higher hydrated oxids of nickel exist, and perhaps anhydrous oxids also, their composition is not definitely known. With palladium and platinum also, monoxids seem to exist and dioxids as well ( $\text{PdO}_2$  and  $\text{PtO}_2$ ). Platinum dioxid may be looked upon as being perhaps a very weak acid-forming acid. While nickel forms practically only the monoxid  $\text{NiO}$ , and iron forms from choice, as we might say, the sesquioxid,  $\text{Fe}_2\text{O}_3$ , the intermediate metal cobalt, while forming most generally the monoxid, is easily oxidized to the sesquioxid,  $\text{Co}_2\text{O}_3$ , and thus cobalt may be considered in its relations to oxygen, as intermediate between nickel and iron. Similarly in the case of rhodium and iridium, there is a strong tendency to form the sesquioxid, so that this middle triplet is intermediate between the other two triplets of the group. As a whole, there is a large field at hand in a revision of the

oxids of this group, especially those of the first triplet.

The same may be said even more emphatically of the sulfids. Those of iron, cobalt and nickel are fairly well investigated, but of the remainder comparatively little is known except the somewhat exhaustive work of Schneider on the thioplatinates and thiopalladates. After a very considerable amount of work upon the sulfids of ruthenium, I have come to distrust nearly all that has been published and to have nothing definite to add myself. The precipitates with hydrogen sulfid from ruthenium solutions ( $\text{RuCl}_3$ ) contain apparently a considerable amount of free sulfur, but oxidize very rapidly with formation of sulfuric acid on drying, making their composition very difficult of determination. From ruthenate solutions a sulfid is precipitated which seems to have the formula  $\text{RuS}_3$ , but there is no assurance that a part of the sulfur may not be free and not combined.

Of all the compounds of the metals of the eighth group, by far the best investigated are those with the halogens, and upon our knowledge of these rests the greater part of our chemical knowledge of the platinum metals. Yet here again our knowledge is wholly inadequate. If we except the work done under Wöhler's direction by Oppler and Birnbaum on the bromids and iodids of iridium, that by Topsöe on the bromids and iodids of platinum, we may say that very little is known of any halids of this group except the chlorids. In some instances, as with ruthenium, even the chlorids are very unsatisfactorily known. Of nickel we know only the bichlorid  $\text{NiCl}_2$ ; of cobalt the only stable chlorid is the bichlorid,  $\text{CoCl}_2$ , but the trichlorid,  $\text{CoCl}_3$ , seems capable of existence in solution; of iron, the ferric chloride,  $\text{FeCl}_3$ , is the stable compound, into which the ferrous chloride,  $\text{FeCl}_2$ , is readily oxidized. Here

again the intermediate position of cobalt is apparent. There is a strong tendency on the part of all these chlorids to form double salts, of which we have examples in  $\text{K}_4\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_4\text{FeCl}_6$ , and  $\text{Rb}_3\text{FeCl}_6$ . These salts seem to be broken up in solution and the chlorine can be precipitated by silver nitrate. Turning to the halogen compounds of the platinum metals, we find double salts of a very different character. The common types for platinum and palladium, for example, are  $\text{K}_2\text{PtCl}_4$  and  $\text{K}_2\text{PtCl}_6$ . This latter type seems also to be known for all platinum metals except rhodium. Osmium, iridium, and rhodium present also the type  $\text{K}_3\text{OsCl}_6$ , while ruthenium and rhodium also form salts of the type  $\text{K}_2\text{RuCl}_6$ . The most important features of these salts is that they are not decomposed when dissolved in water, silver nitrate precipitating not silver chlorid alone, but the double chlorid of the metal and silver; that is, for example, when  $\text{K}_2\text{PtCl}_6$  is dissolved in water, it is electrolytically dissociated, K being the positive ion, while the negative ion is the group  $\text{PtCl}_6$ . The platinum metal then in these salts is a part of the negative ion. Double salts of this class are, of course, well known, but nowhere are they developed to the same extent as in the eighth group, indeed double salts of several acids are found among no other metals. The question may be fairly raised among the platinum metals as to whether there is any salt which is electrolytically dissociated giving the platinum metal as the positive ion.

The chlorids of ruthenium furnish an instructive illustration of the difficulties which may arise in getting complete knowledge of chemical facts as to what would naturally be considered simple substances. As we have seen, Claus discovered ruthenium in 1844. He obtained two chlorids or rather double chlorids, the one  $\text{K}_2\text{RuCl}_5$  and the

other  $K_2RuCl_6$ , the former corresponding to the type found in osmium and rhodium, the latter to that found in platinum and palladium as well as in iridium and osmium. In describing this latter salt, Claus shows that it was in the hands of Berzelius and probably in a pretty pure state, but that great chemist thought it to be an iridium salt, Berzelius was not convinced, and in the 'Handwörterbuch der reinen und angewandten Chemie,' edited by Liebig, Pogendorff and Wöhler, the work of both Berzelius and Claus is given. This was naturally somewhat irritating to Claus and he writes: \* "Even if reverence for the great authority of the great chemist (Berzelius) should seem to justify such a course, regard for the truth of science should not have permitted it." The subject was now dropped and for a third of a century no one had worked upon this chlorid, when Professor A. Joly, of the l'École Normale, began his study of the platinum metals, and much of the work of Claus upon ruthenium was revised. Now it appears that not only Berzelius, but also Claus himself was mistaken, and what he had taken for a chlor-ruthenate,  $K_2RuCl_6$ , was in a reality a *nitroso chlorruthenate*,  $K_2RuCl_5NO$ . My own work of a little later date upon the chlorids of ruthenium abundantly confirmed this. Many efforts were made to prepare a tetrachlorid of ruthenium but it proved elusive. It may be noted in this connection that the cesium and rubidium nitrosochlorids exist in an anhydrous as well as in a hydrated form and while the very easily soluble hydrated salts lose their water on warming the solution, the very slightly soluble anhydrous salt being precipitated, the reverse change is seemingly impossible, as the anhydrous salt will not take up water and pass back into the hydrated form.

The history of the higher chlorid of ruthenium is not yet completed. Within

\* *Bull. Akad. St. Petersb.* (2), 108; 1 (1860).

the past year Professor Ubaldo Antony and A. Lucchesi, of the University of Pisa, have described \* the preparation of the real tetrachlorid,  $K_2RuCl_6$ , which like the corresponding salts of platinum and the other metals of the group, crystallizes in octahedra. I have more recently by methods similar to those of Antony, prepared the cesium salt,  $Cs_2RuCl_6$ , which also crystallizes in octahedra and corresponds to Antony's salt; and I have also been fortunate enough to obtain a new salt of a rare type, lying intermediate between the tetroxide and the tetrachlorid,  $Cs_2RuO_2Cl_4$  ( $2CsCl, RuO_2Cl_2$ ). Now a question may arise here as to whether Claus was after all, wrong in believing he had the tetrachlorid. As the salt was commonly made by Claus, by the action of nitric acid, it was, without question, a nitrosochlorid, and his description corresponds completely; but Claus adds in a footnote † that it is also possible to prepare the salt by heating the trichlorid with potassium chlorate and hydrochloric acid. This could not give the nitrosochlorid, but while under these conditions the tetroxid is usually formed, it is possible that the tetrachlorid may also have been formed. In another place he speaks of making it by action of hydrochloric acid on potassium ruthenate, but in the presence of saltpeter. Except for this latter salt, this is the method of Antony, but usually at least it gives the trichloride. The salt which Claus generally describes is the nitrosochlorid, but in one place ‡ he says the salt seems to be dimorphous, for after crystallizing out the common prismatic crystals (of the nitrosochlorid) he, on one occasion, obtained large regular octahedra, isomorphous with tetrachlorids of the other platinum metals. As the molecular weight of the nitrosochlorid is almost the same as that of the

\* *Gazz. chim. ital.*, 29 i (1899).

† *J. prakt. Chem.*, 39, 96 (1846).

‡ *Bull. Akad. St. Petersb.* (2), 1, 105 (1860).

tetrachlorid, and as the chlorin seems to have been generally estimated by loss, analysis would reveal no discrepancy, but in one case at least, the chlorin was directly determined, and these figures can be accounted for only on the supposition that in this case it was a tetrachlorid which was analyzed; so that it would seem possible that Claus actually formed the tetrachlorid, although he did not distinguish it from the nitrosochlorid. Even now the conditions of formation of the tetrachlorid are obscure, and not less so is the cause of a phenomenon, noticed first by Claus, and since his day used as a test for the detection of ruthenium, and which is familiar to all of you who have experimented at all with this metal. I refer to the beautiful indigo-blue color assumed by the solutions of ruthenium trichlorid when hydrogen sulfid is led into them. Since, at the same time, sulphur is precipitated, and since the trichlorid also assumes a blue color on treatment with metallic zinc,\* it was assumed by Claus that reduction takes place and hence that the solution contains ruthenium bichlorid,  $\text{RuCl}_2$ . When ruthenium is heated in a current of mixed chlorin and carbon monoxid, it increases many times in volume and there is formed an anhydrous trichlorid. This is insoluble in water and in strong alcohol, but dissolves with considerable readiness in dilute alcohol to a similar deep blue solution. Joly succeeded in distilling off the alcohol and water from this solution, in a vacuum, and obtained a blue deliquescent substance which he considered to be an oxychlorid,  $\text{RuOHCl}_2$ . I have also formed this blue solution by electrolytic action, and while it seems to be formed by a reducing action, this is not perfectly clear. Considerable work upon this solution, however, leads me to agree with Claus that it is

\* It has already been mentioned that Vauquelin had noticed this blue color, but not knowing of ruthenium had attributed it to osmium.

probably a lower chlorid of ruthenium, but it has not been proved. I have dwelt perhaps unduly upon these compounds for the purpose of showing the obscurity in which even such seemingly simple points are enveloped, for it well illustrates how much work must yet be done before we acquire any adequate knowledge of the nature of even the commoner compounds and reactions of these elements.

Of the simple salts of oxy-acids few are known of any metals of this group except the lower series, iron, cobalt and nickel; a single sulfate of rhodium, one of palladium, and perhaps a double sulfate of platinum, a chromate of iridium, a basic carbonate of palladium, two or three nitrates, a phosphate of rhodium, and a hypophosphite of platinum; such is practically the whole list. The platinum metals have little tendency to form crystalline salts with oxy-acids, and many such salts are unquestionably incapable of existence, but in many cases at least the difficulty is our ignorance of the condition of formation of such salts. And herein, I may say, is one of the most marked differences between investigation in organic and in inorganic chemistry. In the former the field has been so thoroughly studied that the conditions of reaction are often well known and the course of a reaction can be foretold with considerable certainty; in inorganic chemistry the work is like exploration in an almost wholly unknown land. We know neither the possibility of existence of conjectured compounds, nor the conditions under which alone such formation or existence is possible. For this reason inorganic research is slower and far more apt to be fruitless. No better example of this can be cited than the fact already referred to that Professor Joly, as well as myself, exhausted every method which occurred to us for the formation of the tetrachlorid of ruthenium, and failed in our efforts by missing just the proper con-

ditions, which happily Professor Antony has hit upon.

But while the platinum metals seem to form few simple salts, few or none show such a decided tendency to form double and complex salts, and this property is, to some extent, shared by the three light metals of the group.

Best known and best developed of these compounds are the cyanids, which are especially familiar to us in the prussiates of iron. In nickel we have the ordinary cyanid,  $K_2Ni(CN)_4$  or  $2KCN, Ni(CN)_2$ , formed by the solution of nickel cyanid in potassium cyanid. As electrolytically dissociated, the nickel is a positive ion, and the double salt is at once broken up by acids with the precipitation of nickel cyanid. The double cyanid of palladium,  $K_2Pd(CN)_4$  is similar but less easily decomposed. The corresponding double cyanid of platinum,  $K_2Pt(CN)_4$  is clearly a salt of the complex platinocyanic (or cyanoplatinous) acid,  $H_2Pt(CN)_4$ , which is formed on treating the salt with a strong acid, can be separated in a pure condition, and is an acid strong enough to expel hydrochloric acid from sal ammoniac. The platinum atom is here a constituent of the negative ion,  $Pt(CN)_4$ .

If we proceed from nickel along the horizontal series, we find that while a double cobalt cyanid,  $K_4Co(CN)_6$  or  $4 KCN, Co(CN)_2$ , can be formed, it is very unstable, and belongs to the same easily decomposable class as the double nickel cyanids. This cobalt cyanid has, however, a great tendency to oxidize and form potassium cobalticyanid,  $K_3Co(CN)_6$ , which is stable and a salt of the cobalticyanic acid, which can be obtained in a free state. In passing we note a very interesting point, that under the influence of such reducing agents as potassium cyanid, potassium nitrite, and potassium sulphite, cobalt shows a great tendency to become oxidized from its biva-

lent condition to the very stable complex compounds in which it is trivalent; under other circumstances, simple compounds in which cobalt is trivalent are formed with great difficulty and are of decided instability. This seeming anomalous property still demands an explanation.

Turning to the iron cyanids we find both types,  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ , ferrocyanid and ferricyanid, well developed and extremely stable. From each, the corresponding acid can be obtained in a free state, and is a strong acid. Of the remaining metals, the double cyanids of rhodium and iridium resemble the cobalticyanid, while of iridium the iridocyanid,  $K_4Ir(CN)_6$  is also known, and is stable, thus completing the analogy found in the nickel group. Potassium ruthenocyanid,  $K_4Ru(CN)_6$  and osmocyanid,  $K_4Os(CN)_6$  resemble the ferrocyanid, the free acids being easily separable from the salts. Outside of the eighth group, the stable complex cyanids are known only in the case of manganese and chromium.

Regarding the constitution of the double cyanids, you are all familiar with the various suggestions that have been made from time to time, which involve the polymerization, probably by threes, of the cyanogen group. To this there have been raised two objections: an explanation which is satisfactory for the double cyanids should also be available for the double chlorids, as  $K_2PtCl_6$  which are also salts of complex acids, and where polymerization by threes is at least improbable; and second it is possible to replace a single cyanogen group or chlorine atom, without changing essentially the nature of the molecule, as in sodium nitroprussid,  $Na_2Fe(CN)_5NO$ , and potassium nitrosochlorruthenate,  $K_2RuCl_5NO$ . There is a large field for study in these cyanids from the standpoint of the newer physical chemistry.

Closely connected with the chemistry of the cyanids is that of the thiocyanates, but

it has been very meagerly worked out for the eighth group. In the case of platinum both potassium platino- and platithiocyanatés,  $K_2Pt(SCN)_4$  and  $K_2Pt(SCN)_6$ , are known, and are salts of the platino- and platithiocyanic acids. These are complex acids and may be separated out, but in the free state are very unstable. The double ferric thiocyanates may be formed but there is no corresponding complex acid, that is, they are ordinary double salts. The ferrous, cobaltous, and nickel thiocyanates are known, but form no double salts. It is extremely probable that the other metals of this group would show a full series of thiocyanates.

Another interesting class of complex salts is that of the double nitrites, first studied in the case of platinum by Nilson, but for the other platinum metals by Wolcott Gibbs, who bases upon these his method of separating the metals. More recently these nitrites have been investigated by Joly, Vèzes, and Leidié. The most familiar double nitrite is the potassium cobaltinitrite, which has long served for the separation of cobalt from nickel, and which is also used as a pigment under the name of aureolin or cobalt-yellow. These nitrites resemble, to a considerable degree, the double cyanids, and in the case of iridium the free complex iridonic acid has been obtained. In the case of iron, cobalt, and nickel, we have also representatives of a large class of very staple triple nitrites, first noted by Künzel and Lang and studied by Erdmann.\* More recently these have been investigated by Przibilla† who, after great difficulty, succeeded in preparing the triple iron potassium nitrites with lead, barium, strontium, and calcium; this is the first nitrite of iron to be prepared and leaves osmium as the

only metal of the eighth group of which no nitrite is known.

In the case of all platinum metals double sulfites are known, which are salts of complex metallo-sulfurous acid. In these metals the presence of the sulfurous acid radical cannot be detected by ordinary reagents. In the case of cobalt, a full series of cobaltisulfites is known, which are stable salts, while the cobaltosulfites are very unstable. Little is known of iron and nickel sulfites, and there is much room for further investigation in the case of the sulfites of the other elements of this group. There is at the same time reason to believe that a study of the thiosulfates and possibly the dithionates of this group would not be without interest.

Another acid which is capable of forming complex salts is oxalic. The platinoxalates are the only ones which have been carefully studied, though some work has been done upon the rhodoxalates. Several iron oxalates and double oxalates are known, but aside from this the field is unworked but promising. In this connection it may be added that while oxalic acid is the only organic acid which has been investigated to any considerable extent in complex salts, it by no means follows that it is the only acid which is capable of entering into such combinations. Some of my students have made preliminary tests with a large series of acids and found that several among them enter combination with chromium with the formation of complex salts, and it is quite possible that similar compounds may be formed with the eighth-group metals. Mention should also be made that Gibbs has introduced platinum into his complex salts, forming platinumolybdates and platinitungstates.

Since complex salts of hydrocyanic, nitrous, sulfurous, oxalic, and other analogous acids are best developed generally with the metals of this group, it is in the study

\* *J. prakt. Chem.* 97, 385 (1866).

† *Ztschr. anorg. Chem.*, 15, 419 (1897).

of these and other compounds of this group that we may hope to gain an insight into the constitution of these interesting compounds of which so little is known, and further extend our knowledge regarding valence, for it is just at this point that the generally accepted theory of valence begins to break down.

Before alluding to the ammonia bases, which are so well developed in this group, and would naturally follow these complex salts we have just considered, a brief digression may be made to refer to three classes of anomalous compounds, which should not be passed without reference. The first of these is the nitroso compounds. It is only recently that, largely through the efforts of Joly, the nature of the so-called nitro-prussids was discovered,—double cyanids in which one cyanogen group is replaced by one nitroso group, NO. Joly then found that the old osmium acid of Fritzsche and Struve is also to be considered as a nitroso compound, and that the supposed tetrachlorid of ruthenium is, in reality, a nitroso-chlorid. But while there appear to be no representatives of the nitroso compounds in the cobalt or the nickel groups, several other compounds of iron are known which contain this group, as the potassium iron tetra- and heptanitrosulfonates,  $K_2Fe_2(NO)_4S_2$  and  $KFe_4(NO)_7S_3$ , and the iron nitroso-thiocarbonate and thioantimonate of Löw. There seems also to be a nitroso-cyanid of ruthenium, corresponding to the nitroprussids, but it has not been isolated. In none of these cases has the interesting question been brought out as to whether the nitroso group remains attached to the metal when in solution, or whether it is electrolytically dissociated and acts the part of an acid radical.

In some respects yet more remarkable are the compounds formed with carbon monoxid and with phosphorus trichlorid. The best known compound of this class is

the nickel carbonyl,  $Ni(CO)_4$  of Ludwig Mond. The nature of this volatile liquid is yet unknown, but it is by no means unique. Immediately after its discovery it was found that iron formed similar compounds,  $Fe(CO)_5$  and  $Fe_2(CO)_7$ . That a volatile compound of iron exists had been very apparent on the lime of the Drummond light, when water gas, compressed in iron cylinders, was used instead of hydrogen, and also in the clogging of gas burner tips with an oxid of iron, especially when a carburetted water gas is used as an illuminant. The volatile iron carbonyl seems to be formed at ordinary temperatures by the passage of carbon monoxid through iron pipes. But it is not alone with metals that carbon monoxid combines to form volatile compounds. As early as 1868 Schützenberger\* discovered that platinous chlorid  $PtCl_2$  would combine directly with carbon monoxid, with the formation of three distinct compounds, containing respectively one, two and three molecules of CO to one of  $PtCl_2$ . A compound is also known in which one CO group replaces one cyanogen group in potassium ferricyanid, that is  $K_3Fe(CN)_5CO$ . This reminds us naturally of the nitroso-ferricyanid, the so-called nitroprussid. Again in 1870 Cahours and Gal† discovered a series of compounds containing platinous chlorid united with phosphorus trichlorid, and also with some of the organic phosphines. These compounds are not of the nature of double chlorids, for they can be hydrolyzed with the formation of chlorplatophosphorous acid. An analogous class of compounds of iridium has been made by Geisenheimer,‡ which are also capable of hydrolysis, giving chloriridophosphorous acid. Geisenheimer has formed similar compounds con-

\* *Compt. rend.*, 66, 666, 747 (1868).

† *Comp. rend.*, 70, 897, 1380 (1870); 71, 208 (1870).

‡ *Comp. rend.*, 110, 1004 (1890).

taining bromin\* in the place of chlorin, and also others containing arsenic† in the place of phosphorus. How far compounds of this nature can be extended is only conjectural, but there is evidence of the existence of something of the kind with iron.

Of binary compounds with the less negative elements, such as the phosphids and carbids of iron, little is known. Like iron, nickel and also platinum and iridium form phosphids. Iridium phosphid possesses an economic importance in that it enables the metal to be fused in a furnace. Up to the discovery of this process in 1882 by Dr. Wm. L. Dudley, the native grains of iridosmium were alone available for tipping gold pens, stylographs, and the like. It was, however, found that when iridium was heated to a high temperature in a crucible, on introducing a piece of white phosphorus, the whole mass immediately melted, and could be cast into plates, afterward to be worked up into desired form. This reminds one of the early method of working platinum by alloying it with arsenic and then roasting the arsenic off in a muffle.

There remains a single class of compounds to be noticed, the ammonia bases, whose greatest development is found in this group. The first member of this class was the compound now known from its discoverer as the green salt of Magnus, which was first made in 1828.‡ Then came the work of Gros, of Reiset, and of Peyrone. Among the many chemists who have cultivated this field are Cleve, Jörgensen, who has given us most of our knowledge of the rhodium bases; Gibbs, Palmaer, who has developed the iridium bases, and Joly, who has revised the bases of ruthenium; while the theory of these bases has been discussed especially by Claus, Blomstrand, Jörgensen, and Werner. In connection with these bases appear

what must, with our present knowledge, be considered anomalies. The greatest development of these bases is found with platinum, where nearly or quite a dozen distinct classes of bases are known, and where we find several groups of isomers, which Werner seeks to explain as stereo-isomers, while Jörgensen strenuously combats the view. In type, the palladium bases resemble those of platinum, but as far as yet studied are much less well developed. Nickel, on the other hand, forms no true bases, though many ammonia compounds. The cobalt, rhodium, and iridium bases are all formed on the same general types, but by far the greatest development is found in cobalt, which almost rivals platinum in the number of classes; but few of these are developed with iridium, and fewer still with rhodium. In the iron group no bases are formed by iron, and only two or three ammonia compounds; ruthenium and osmium form fewer bases as far as yet investigated, than any of the other platinum metals. It is interesting to note, however, that one of these ruthenium bases, discovered by Joly, and which possesses intense tinctorial power, resembles very strongly an organic dye, both on fabrics and as a stain in microscopy. The constitution of the ammonia bases is to-day, as it has been for half a century, one of the greatest problems of inorganic chemistry, and it is apparently no nearer solution. In accordance with the valence theory, it becomes necessary with Jörgensen to assume the existence of chains of at least four  $\text{NH}_3$  groups in a molecule, stable enough to be unaffected by aqua regia and also that these ammonia groups are replaceable by water molecules. We must also assume that while in ordinary salts, as for example chlorids, the chlorin atoms, which are directly united with the metal, are dissociated in aqueous solution, in these bases the chlorin which is directly united with the metal is not dissociated, but

\* *Ibid.*, 111, 40 (1890).

† *Ibid.*, 110, 1336 (1890).

‡ *Ann. der Phys.* (Pogg.), 14, 239 (1828).

that which is united with the metal through the medium of one to four ammonia groups is dissociated. Led by a consideration of these seeming inconsistencies, Werner has proposed his theory of co-ordinated groups within the molecules; a theory which seems to possess at least elements of truth, even if not expressing the whole truth. It is possible, too, that Werner's theory may explain some of the difficulties of the theory of electrolytic dissociation, and harmonize it with the hydrate theory of solution.

The constitution is, however, not the only problem of these bases. To my mind their connection or rather lack of connection with the periodic system is one of the most inexplicable facts in chemistry. It makes it apparent that while the periodic law expresses a truth without doubt the greatest generalization of modern chemistry, yet even this is in its present statement not the whole truth. We find a marvelously full development of these bases in connection with cobalt, platinum, and

chromium. Manganese and iron which lie between chromium and cobalt form no bases. The higher members of the chromium group, that is, molybdenum, tungsten, and uranium, form no bases, while the higher members of the iron series, that is, ruthenium and osmium do. Of nickel, which stands next to cobalt and resembles it so closely, no bases are known, and yet it is the lowest member of the series which contains platinum. It is true that bivalent cobalt forms perhaps like nickel, no bases, but as trivalent cobalt forms so many bases, trivalent iron would seem likely to form many, instead of none. If indeed manganese and iron are capable of forming these bases, it seems strange that no one has yet happened upon the proper conditions. It is the consideration of a subject like that of these inorganic bases, which forces upon us a realization of how much there is after all which we do not know about chemistry.

We turn now to a short consideration of the eighth group from a theoretical stand-

PERIODIC TABLE BY F. P. VENABLE—MODIFIED.

H												He			
Li		G1		B		C		N		O		F		Ne	
Na		Mg		Al		Si		P		S		Cl		Ar	
K		Ca		Sc		Ti		V		Cr		Mn		Fe	
Cu		Zn		Ga		Ge		As		Se		Br		Co	
Rb		Sr		Y		Zr		Cb		Mo		—		Ni	
Ag		Cd		In		Sn		Sb		Te		I		[8,2] [8,4]	
Cs		Ba		La		Ce		*		*		*		Ru	
?		†		†		†		†		†		†		Rh	
*		*		*		*		Ta		W		*		Pd	
Au		Hg		Tl		Pb		Bi		†		†		?	
+		+		+		Th		*		U		+		Os	
Series		-		-		-		-		-		-		Ir	
Series		-		-		-		-		-		-		Pt	

\* Possible + Series elements.

† Possible — series elements.

— Eka-manganese.

point. Following Dr. Venable\* we may assume that each of the first seven groups consists of a group element, as in group one, lithium, a type element as sodium, and two series, one of more positive elements as potassium, rubidium and cesium, and the other more negative, as copper, silver and gold. Further, the more positive the type metal, the more closely will the metals of the positive series resemble it; the more negative the type metal, the more closely will the negative series resemble it. Thus in the first group, the positive series potassium, rubidium and cesium closely resembles the type element sodium; in the seventh group the negative series, bromine and iodine, resembles the type element chlorine. Now the eighth group differs materially from the other seven in that it contains three series, with no group or type element. These three series are transitional from the least positive among the seven positive series, manganese, to the least negative among the negative series, copper, silver and gold. The properties of the metals of group eight show this transition as from a chemical standpoint, iron, cobalt and nickel form a direct gradation between manganese and copper. Now comes a further question as to possible transition elements between the most negative series, fluorine, chlorine, bromine, iodine, and the most positive series sodium, potassium, rubidium and cesium. From a theoretical standpoint such transition elements should be neither positive nor negative, and should have a valence of zero. A few years ago the realization of such a conclusion would have seemed impossible, yet since the discovery of argon and its congeners, it seems almost probable that these places have been filled in accordance with theory. If we take the most generally accepted atomic weights, we find helium preceding lithium, neon following lithium and preceding sodium, and argon,

\* See periodic table.

really between chlorine and potassium, but with an atomic weight apparently slightly greater than that of potassium which follows it, resembling in this respect cobalt and nickel of this same group, and also tellurium and iodine. There would, in addition, be expected from the analogies of group eight, one, two, or three transitional elements between bromine and rubidium, of atomic weight, 80 to 85, and Ramsay has suggested that krypton may belong in this place—so also an element or elements of similar character might be expected between iodine and cesium, with atomic weight of about 130. The recently published work of Ladenburg and Kruegel on krypton give it an atomic weight of about 59. This would, as Professor Ladenburg suggests, make it immediately precede copper, but unless we change very materially our ideas of the periodic law, it is difficult to conceive of an element with the properties of krypton lying between nickel and copper. If these inert gases belong in the eighth group it may seem strange that iron and the other familiar metals which belong here should be so unlike such a type element as argon or neon; it must, however, be borne in mind that this is only an expected exaggeration of the departures found in the first and seventh groups, where copper departs from its type element sodium, and manganese from its type element chlorine. As to whether three elements are to be expected of atomic weight 150 between the light and the heavy platinum metals we have little data upon which to theorize. As a matter of fact, there is very little definite knowledge of the elements between cerium and tantalum. The inter-Jovian planet proved to be an indefinitely large number of asteroids; Sir William Crookes' study of the rare earths leads him to the conception of a group of asteroidal meta-elements in this vacant space in the periodic table. We must await further knowledge be-

fore these problems can be satisfactorily solved.

In conclusion one word as to a very practical problem connected with this group. It is but a few years past a century since the use of platinum was introduced into the chemical laboratory. For a few decades the supply exceeded the demand, but the applications of platinum have steadily increased, and never so rapidly as in the last two decades. For many purposes no substitute for platinum has been found. At the same time the supply of platinum is not keeping pace with the demand, and as a result the price of platinum has very materially advanced. While platinum is very widely distributed, there are few places where it occurs in workable quantities. It is possible, however, that it has been often overlooked, as in placer mining for gold, and efforts have been made to attract miners' attention to more careful search for platinum deposits. At the present outlook it will, within a few years, be imperatively necessary either to materially increase the platinum supply of the world or to replace it for many purposes by some other substance. How this problem will be solved cannot now be foreseen.

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SCIENTIFIC BOOKS.

*The Elements of Physics for Use in High Schools.*

By HENRY CREW, Ph.D., Professor of Physics in Northwestern University. New York, The Macmillan Company. 1899. Pp. 347.

One of the most striking indications of the steadily increasing demand for instruction in science as a part of elementary education, is found in the periodic recurrence of new books on a market that would seem to have become already overcrowded. If the new competitor is written by one who manifests his possession of the teacher's instinct in addition to the scholar's knowledge, its reason for existence is

quickly established. The author of the present volume plainly shows himself to be the possessor of both, though as a teacher he may have had little experience in the grade of schools for which his book is intended. In the preface he expresses his obligations to one friend, a high school teacher, 'for many important excisions in the MS.,' and his readiness to have others 'point out sins either of omission or of commission.'

In criticising such a book it is a pleasure to find so little to condemn, even if a few more excisions may seem advisable. Physics is essentially applied mathematics, even when no attempt is made to introduce openly the ideas of calculus or even of trigonometry. It is most natural therefore that a physicist, who is not himself a high school teacher, should overestimate the ability of the average high school pupil to grasp mathematical conceptions that are not usually introduced in the work of the secondary school.

In the introductory chapter on motion a brief and clear exposition of vectors and scalars is given, and a subsequent application is made in the discussion of uniform motion in a circle, where the position vector and velocity vector are contrasted, and the nature of the path deduced, along with the formula for acceleration in terms of radius, angular velocity, and periodic time. There is no theoretic objection to this, but it is probably safe to predict that many secondary pupils will agree in thinking the discussion much too abstract for them. Indeed it would not be hard to find college juniors of literary bent, who would be sympathetic with their friends in the preparatory school, and who would congratulate themselves on the absence of problems, necessary as these may be to bring home a difficult subject. There are fashions in educational method as well as in dress. Whether the vector analysis fashion can be maintained in elementary schools may be doubted. To immature students the method is certainly not so easily grasped as are some other methods that have hitherto been satisfactory to many.

In the discussion of angular motion much stress is laid upon the distinction between speed and velocity, the former being a scalar and the latter a vector quantity. This distinction has