CHAPTER VIII

INORGANIC CHEMISTRY

BY JAMES LEWIS HOWE

Introduction

The close of the third quarter of the nineteenth century found inorganic chemistry at its lowest ebb. Under the leadership of Hofmann, organic chemistry had well-nigh preëmpted the whole field of chemistry. Wöhler was the last living representative of those who had devoted their lives largely to the development of inorganic chemistry, and he was an old man, no longer active in the laboratory. In truth, inorganic chemistry had progressed about as far as it could with the tools at hand. The good behavior of the carbon atom, holding the atoms steady in the molecule in the position in which they had been placed, with its four stable valences—not too many for easy handling, yet sufficient to afford a reasonable variety—and, above all, its willingness "to combine with itself indefinitely without affecting the stability of the molecule," all these contributed to hold the attention of chemists, enabling them to prepare a multiplicity of definite new compounds. The organic compounds and reactions were systematized and made the basis of chemical theory, and many of the compounds found application in the dyestuff and other industries.

In this country there had been a few workers along inorganic lines, such as Charles Upham Shepard, who had done much to develop the phosphate beds of South Carolina; T. Sterry Hunt, who had extended the work of Gerhardt, but whose views were often erratic; J. Lawrence Smith, whose particular interest was in minerals and meteorites and their analysis, and who perfected many analytical procedures; Josiah Parsons Cooke, who had been one of the first to grasp the whole trend of what was then modern chemistry. But these men had none who could properly be called their successors, nor was there incentive or training for the development of inorganic chemists.

A half-century ago there was practically no graduate work done in chemistry in this country. There were good teachers and good students, but the chemistry of that day was "made in Germany," and thither went the American students, largely to Göttingen for the sake of its old reputation under Wöhler, or Berlin to work with Hofmann, or Bonn with Kekulé, or Würzburg for analytical work with Fresenius, or Heidelberg, perhaps for a good time, for Bunsen's work was practically over. With the exception of those at Würzburg, by far the largest number of theses were in organic chemistry, and little interest was paid to inorganic research. As a result, few American chemists of the period worked on inorganic problems. A decade later and the scene had changed, but not directly to the advantage of inorganic chemistry. Kolbe had been succeeded at Leipzig by Ostwald, and a new field of chemistry opened—that of physical chemistry. From now on research problems were offered in abundance, and the then younger generation of American chemists was not slow to take them up. Johns Hopkins University had been founded, other well-equipped graduate departments in chemistry were established, and in them all research in physical chemistry was dominant, in spite of the hold organic chemistry had on the older teachers.

But if physical chemistry was opening a field of its own, it was also furnishing a most valuable tool to the inorganic chemist, and it was soon recognized that practically all of the older work in inorganic chemistry must be repeated in the light of the newer theories. Furthermore, the periodic system of the elements, as set forth by Mendeléef and Lothar Meyer, was gradually becoming recognized as a foundation principle, and it was seen that from this standpoint the rarest and least investigated of the elements was as important as the best known, or even as carbon with its myriad compounds. It was soon realized that inorganic chemistry offered a limitless field of problems, and the most that a single worker or group of workers could hope to accomplish seemed insignificant when viewed in comparison with all that must be done before any far-reaching generalizations could be gained.

For this reason, there have been few systematic researches along purely inorganic lines; it has been a bit here and a bit there, but in the aggregate making no small contribution to our knowledge of inorganic chemistry. There have been three lines of work, however, in which American chemists have done much to advance our whole knowledge of chemistry, though the work has been done almost wholly in the inorganic field.

Double and Complex Salts

The first of these lines concerns double and complex salts. The first worker in this field was Wolcott Gibbs who, before the period we are considering, had done much work on the compounds of tungstic and molybdic acids. He early recognized the complexity of the problem, which had, indeed, been suggested long before by Berzelius and later by Marignac, and found it necessary at the start to go into a long and detailed study of the tungstates and molybdates of the alkalies and other bases. Regarding the alkaline tungstates, he states in his opening paper some of his difficulties: they are numerous and unusually complex; salts of essentially different formulas approach so closely in percentage composition that the differences lie very near the unavoidable errors of analysis; almost all are markedly efflorescent, and the salts of different series often agree closely in chemical properties; many are decomposed by hot water, yielding two or more different salts in solution. Of course these difficulties are a commonplace to workers in this field today, but must have been well-nigh overpowering to a pioneer. It was rather the custom of that day to solve a problem if the solution was easily reached, but if it proved difficult, to lay it aside and take another; there were plenty of problems easy of solution. It is to Dr. Gibbs' credit that he kept at his problem and vastly widened our knowledge of complex salts, even if many of the conclusions he reached are not valid in the light of modern methods. From the simple tungstates and molybdates he was led to the phospho- and arseno-tungstates and molybdates, and then to others, till in his final paper he sets forth no less than thirty-five series of complex salts in addition to the seven which had been earlier described by Struve and Parmentier, all containing MoO_3 or WO_3, together with some of the following oxides: P_2O_5, As_2O_5, V_2O_5, Sb_2O_5; VO_2, SnO_2; P_2O_3, (H_3PO_2), (HPO_3), As_2O_3, Sb_2O_3. He also points out the possibility of further classes of salts in which the group $PtCl_2$ takes the place of O, or $(2PtCl_3)'''$ the place of 3O. Of these, $(HO)_3P(PtCl_2)$ is the simplest member. The Cl of the $PtCl_2$ may be replaced by Br, and his experiments showed that similar compounds are formed with all the platinum metals except rhodium, which he was unable to test as he could get no rhodium. Among the salts of these series prepared by Gibbs were $5(NH_4)_2O.As_2O_3.3(As_2O_3.2PtO).7H_2O$ and $K_2O.(As_2O_3.2PtCl_2).2H_2O$. This work opens up an enormous field which no one has entered, and of which Gibbs only skirted the edge; it would offer today great possibilities to the chemist equipped with X-ray spectroscopy.

The investigations of Gibbs on the complex tungstates and molybdates were followed by the work of Edgar F. Smith, alone and with Allen Rogers. They much enlarged the field, bringing in many new oxides, such as tantalic and columbic acids, as well as the oxides of the rare earths. While Gibbs never had more than three different acids acting as a complex anion, they prepared many compounds with four. An example of the complexity of some of these salts is shown by the formula $82(NH_4)_2O.12P_2O_5.3As_2O_5.5V_2O_5.201WO_3.567H_2O$, a salt crystallizing in regular octahedra. These compounds certainly offer an interesting field for X-ray analysis.

Meanwhile Ira Remsen had been taking up the subject of the double halides, of which some, such as the chloroplatinates and fluosilicates, were very familiar salts. He discussed them from a theoretical standpoint, bringing out his theory of the double halide atom and thereby seeking to clear up the valence difficulty. Under the old view, these double halides were "molecular" compounds; K_2PtCl_6 was a "molecular" compound between two potassium chloride molecules and one of platinum chloride. In the case of many of the double salts this was fairly satisfactory, since the double salts were resolved into their simpler components in solution, but in others, such as those mentioned, the groups $PtCl_6$ and SiF_6 were far too stable for chemists to be content with any of the earlier explanations. The same, of course, was true of "water of crystallization." According to Remsen's view, the halogen atoms are in part in pairs, these pairs functioning like oxygen as a bivalent element. In many cases the halogen double salts were wholly analogous to the corresponding oxygen salts. Although this conception has been largely superseded, it was an important generalization, and led to much advancement in our knowledge of this class of compounds. While quite a number of contributions to the subject were made by the pupils of Remsen, the most important developments on double halides were made by H. L. Wells, assisted on the crystallographical side by S. L. Penfield. Wells collected the literature of the subject and prepared a systematic arrangement of all known double halides, thereby furnishing a starting point for all future investigators. He and his students also prepared large numbers of new salts, among them the chloroantimonates, in which the antimony is quadrivalent. The work of Remsen, and more particularly that of Wells, laid the foundations and furnishes no inconsiderable portion of the material used by Werner in developing his coördination theory, while the work of Gibbs led to that of A. Rosenheim in the application of Werner's theory to the tungstic and molybdic acid complexes.

Since that time further work on double and complex salts has been carried on by H. W. Foote and others. One interesting phase, which dates from an earlier period, is in connection with mixed haloplatinates. One of the first papers of importance in THE JOURNAL was that of Lucius Pitkin, who prepared the whole series of mixed potassium chlorobromoplatinates, from K_2PtCl_5Br to $K_2PtClBr_5$. With the development of the methods of physical chemistry, it appeared that this series was in reality made up of solid solutions, and possibly none of the members was a chemical individual. Charles H. Herty, however, later showed that certain mixed haloplatinates could be prepared as definite compounds. In the light of modern methods it has been shown that a great many inorganic compounds described in the earlier chemical literature are not valid, and a repetition of much of this work has revealed that it needs to be again gone over from a modern standpoint.

Liquid Ammonia Solutions

A second line of work, largely if not wholly American in its development, is that of E. C. Franklin on liquid ammonia solutions. Although not so extensive as that on double salts, it is more far-reaching in its implications. Until this work by Franklin, practically all chemistry and chemical theory, except that at high temperatures, had been confined to elements and compounds in relation to oxygen and water. This was inevitable when one considers the extreme difficulty of completely removing water from any sphere of reaction. Starting with reactions in liquid ammonia as a solvent, Franklin has gradually unfolded the conception of a chemistry in which nitrogen plays the familiar part of oxygen or, more accurately, ammonia the part of water, the amino group, NH_2, that of the hydroxyl, and the imino group, NH, that of oxygen. In this chemistry appear ammono acids, ammono bases, and ammono salts, and many of the reactions are wholly analogous to those of our ordinary oxy acids, bases, and salts. Of course this is a low-temperature chemistry, since liquid ammonia is the solvent, and this has entailed manipulative difficulties which would have completely deterred many experimenters; but Franklin has surmounted them, often most ingeniously, and has opened a new field, of which the surface has as yet hardly been scratched. The present state of the work is much like that of general inorganic chemistry a hundred years ago. For the most part only relatively simple compounds have been prepared, but there is evidence of complexity, possibly as great as that in water chemistry. But the story does not stop here, as Franklin has shown in his recent presidential address before the AMERICAN CHEMICAL SOCIETY. The possibilities of a sulfur or thio chemistry open up. We have already knowledge of a considerable number of thio acids, bases, and salts, but these include only such compounds as are relatively stable toward water. Replacing water by liquid hydrogen sulfide, the new field appears. Toward many of our familiar compounds, especially salts, liquid hydrogen sulfide is not an ionizing agent, but it may have a chemistry of its own, as is more than hinted at in the recent and very promising work of J. A. Wilkinson. A halo chemistry has already been recognized, but here, too, only in relation to water; liquid hydrogen chloride is also not an ionizing agent, but perhaps only because we have not found the proper conditions. Franklin suggests that there may even be a carbon chemistry, very different from our present conceptions of organic chemistry, and independent of oxygen. From this standpoint alone it may be that inorganic chemistry, as we know it, is only in its infancy.

All this is somewhat connected with the use of liquids other than water as solvents and ionizing agents. Victor Lenher has worked with selenyl chloride, SeO_2Cl_2, as a solvent; H. B. North with sulfuryl chloride, SO_2Cl_2, as well as with thionyl chloride, $SOCl_2$; F. E. Brown with vanadyl chloride, $VOCl_3$. H. A. Curtis has used isoamyl alcohol; and Davidson absolute sulfuric acid. The work of H. S. Fry and A. W. Browne, and C. A. Kraus should also be noted. Browne has used liquid hydrazine as a solvent, while Kraus is working with metals, as well as with organic compounds, in liquid ammonia. All this shows what a field stands before the inorganic chemist, waiting for exploration.

Solvates

The third line of work by American chemists leading to important generalizations is that of Harry C. Jones on solvates. While the work of Jones would probably be claimed by the physical chemists, the conclusions drawn belong in the field of inorganic chemistry. At a time when the physical chemists were busying themselves with dilute solutions, progressing as nearly as conditions would allow to ideal solutions, that is, solutions of infinite dilution, Jones began his attack on actual solutions, such as those in which our ordinary chemical reactions are carried out, approaching the saturated solution as a goal. It quickly appeared that such solutions were far from obeying any of the theoretical laws of solution, and Jones set himself the task of finding out why. One factor soon appeared, that the water of his solutions was disappearing as solvent water in an unaccountable way; the solutions were acting as if more concentrated than they really were. Further experimentation showed a relation between this missing water and the "water of crystallization" of the salt. It required prolonged research to prove, as Jones and his pupils did, from many different standpoints, that both salts and ions exist as hydrates in solution; indeed, that in a saturated solution of a hydrate, the solid phase is actually in equilibrium with a saturated solution of the hydrate itself, rather than with some of its constituents. An analogous condition applies to solvents other than water, and the term "solvate" has been well coined to apply to the condition of many solutes which exist in solution already combined with more or less of the solvent. This has furnished an important contribution to our knowledge of solutions, and has yet an important part to play in assisting X-ray spectroscopy in the study of crystal formation from solution.

Early Miscellaneous Investigations

Turning back to the earlier part of the half-century under review, we find that most of the contributions to inorganic chemistry were of the nature of pieces of work which a busy college professor could find time to carry out with his own hands, possibly with the aid of some assistant; the period of graduate students had not yet arrived, and the limitations on research were great.

PHOTOCHEMISTRY.—M. Carey Lea accomplished a notable piece of work on the photochemistry of silver salts and on colloidal silver, and, with the work of Romeyn Hitchcock and of Spencer B. Newbury, the way was paved for the later marvelous developments of photography. These were the pioneers.

ATOMIC WEIGHTS.—Frank W. Clarke, who had just begun his career by studying the iodates and selenocyanates, a number of other double salts, and the action of phosphorus on platinum and iridium, was soon attracted by atomic weight calculations and the molecular structure of the silicates. It is with these last two we always associate him. The subject of atomic weights will also be thought of in connection with the name of Theodore Richards, not to omit J. W. Mallet, E. W. Morley, W. A. Noyes, Edgar F. Smith, and G. P. Baxter, but this belongs to the field of analytical chemistry.

GEOCHEMISTRY.—In his work upon the silicates, Clarke undertook to carry over the ideas of structural chemistry, on which organic chemistry had been built, into the realm of inorganic chemistry, and particularly to apply these ideas of structure to the silicates. This brought out unexpected relations between minerals and enabled a systematization, otherwise impossible, of these compounds. Although structural formulas mean less and less to us today in inorganic compounds, they served an indispensable purpose in the development of our theories, while waiting for the revelations of X-ray spectroscopy. In this development the work of Clarke had a most important part. Of more permanent value has been his geochemical work, which is wholly in the field of the inorganic; especially in his calculations of the relative abundance of the elements on the earth and the gross make-up of its outer portion. Another contribution of Clarke to inorganic chemistry—one unmentioned in the books—is his habit of throwing out pregnant suggestions to those in close contact with him. I suspect that many a piece of work with which the name of Clarke is never associated was in reality inspired by him.

WATER OF CRYSTALLIZATION.—In these pre-Wernerian days there was naturally much speculation as to water of crystallization, and how it could be reconciled with the then current valence theories. Even in this period it was recognized that oxygen might possibly be quadrivalent—incidentally one of the facts that chemists have had most difficulty in swallowing—and A. S. Cushman suggested a structure for the hydrated chlorides, in which the chlorine might be directly attached to the metal, or to the oxygen of the water, which itself, in turn, was attached to the metal or to the oxygen of another water molecule. This accounted very neatly for the fact that only a part of the water was lost at lower temperatures, but F. A. Gooch and D. A. Kreider, working on the loss of water in atmospheres of hydrochloric acid gas, came near applying the methods of modern physical chemistry, and rendered Cushman's ideas improbable. Nevertheless, this work was a contribution to the development of modern theories, and incidentally had a rather direct bearing on the problem of obtaining anhydrous chlorides, especially of aluminum and magnesium. The dehydration of crystalline salts was also studied in this period by T. W. Richards, and by J. W. Mallet.

Although much of Mallet's work was taken up with the chemistry of minerals, he also worked on the dehydration of alums and on nitrogen iodide. This last was a precursor of the later work of W. A. Noyes on the chloride of nitrogen and its reactions. A. R. Leeds was interesting himself largely with the mechanism of oxidation, which included studies of ozone and hydrogen peroxide, and what Leeds called "the atomation of oxygen." One of his papers, as well as an early paper by Remsen, was on the oxidation of carbon monoxide, a topic which was later to come to the front in connection with masks for poison gases, and on which much has recently been done by W. C. Bray and by A. F. Berton in connection with various catalysts.

THE WORK OF EDGAR F. SMITH.—Of those who were beginning activities at this period none was more versatile than Edgar F. Smith, to whose work on the salts of complex acids allusion has already been made. Although his attention was early devoted to analytical chemistry and especially drawn to the possibilities of electrolytic analysis, the development of which will doubtless be considered his *magnum opus*, his studies of many of the less common elements greatly enlarged our knowledge. This was particularly the case in his work on tantalum and columbium. His studies of the action of hydrogen chloride on such salts as selenates, tellurates, and phosphates, and of the chloride of sulfur on substances, led to important developments in the analysis of numerous minerals, and this, in turn, to many valuable atomic weight determinations. Much of his work in pure inorganic research has, in the hands of others, led to important applications in other fields. It is interesting that in recent years Smith has devoted himself to historical chemistry, and has brought to light so much of worth accomplished by early American chemists. Not the least valuable of Smith's work is the stimulus given to those working under and with him. Of these, none has done more to contribute to our knowledge of inorganic chemistry than Victor Lenher. Beginning nearly three decades ago with the study of selenium and tellurium, he is continuing this work at the present time. Of particular interest is his work on selenyl chloride, SeO_2Cl_2, which not only shows peculiar reactions as a solvent, but is apparently a useful reagent for the separation of molybdenum from tungsten and columbium from tantalum, and may possibly be capable of industrial applications. This latest work is on selenium monochloride, which shows itself to be a typical acid chloride and a strong chlorinating agent.

Hydrated Silica

Along quite a different line Lenher has made a valuable contribution to inorganic chemistry in the study of hydrated silica. It has long been a question how far hydroxides are to be considered as chemical individuals and how far as merely hydrated oxides. In the case of the silicates, we have derivatives of a great number of silicic acids, but do any of these acids actually exist? Thirty years ago T. H. Norton prepared a hydrated silica having the formula of orthosilicic acid, H_4SiO_4. This was obtained by squeezing the water out of a silica gel, and drying under constant conditions. More recently Lenher has followed the same procedure, but used far greater pressures. While Norton used perhaps 100 kilos per square inch, Lenher carried his pressures to considerably over 100 tons per square inch. Under these conditions far more water is removed, but there still remains water corresponding to about $H_2O.2SiO_2$. A portion of this water is removable in the presence of phosphorus pentoxide. The amount of water in the gel appears to be a function of the pressure, and it would seem extremely doubtful that any definite hydrate of silica exists. It is a natural inference that the same is true of other gelatinous hydrates. The silica gel has also been studied by W. A. Patrick, both as to its heat of wetting and also as to the possibility of displacing the water by organic liquids, as alcohol and benzene. He has found, contrary to earlier observations, that not all the water can be displaced, and the nature of this small amount of residual water, so difficult to drive off at any but high temperatures, still remains to be determined. All of this has also a very important practical and industrial application in the adsorptive power of the dry silica gel for gases, on which much work has been done by Patrick. Lenher has also thrown light, not only on the solubility of water in silica, but on the solubility of silica in water. It is well known that practically all natural waters contain silica in solution, at least to the extent of a few parts per million. By grinding quartz, as well as other minerals, in a ball mill it was found possible to carry notable quantities of silica into solution, and this solution is colloidal. It would thus seem that fine grinding is responsible for the silica content of natural waters. This recalls the earlier work of Cushman on the formation of plastic clays by ball-mill grinding of silicates and even of glass. Lenher also found that the solubility of silica increased rapidly with the temperature. Here would seem to open a large field for investigation in geochemistry.

The Rare Earths

A subject that has attracted the attention of many workers abroad also owes much to American chemists in its development, the subject of the rare earths. More than forty years ago J. Lawrence Smith proposed the oxalates as suitable salts for effecting the separation of these elements, a problem which is by far the most difficult of its type in the whole range of chemistry. At about the same period T. H. Norton did considerable work on cerium. It was reserved for the development of the Welsbach mantle to furnish an abundance of what had been rare raw material. Thanks to the interest of Waldron Shapleigh and later of H. S. Miner in rare earth research, the great mass of by-product earths from which the thorium had been extracted became available to chemists. It is nearly a score of years since Charles James began his work; at about the same time Lenher, and shortly after L. M. Dennis, tackled the intricate problems associated with the separation of these elements which resemble each other so closely. James has continued his researches down to the present time and has made large contributions to our knowledge of the subject. His first success was in the use of the bromates for separation, and for the first time thulium was prepared in a pure condition and in considerable quantities. James later, in addition to the more commonly used salts, called the sebacates and cacodylates to his aid. In addition to preparing the earths in pure form, he has studied their properties and in a large number of cases determined the atomic weight. Lenher studied especially the yttrium earths and has used the succinates and the stearates for separation. Dennis made use of the picrates and also studied the electrolytic separation of the earths. Somewhat later, work on the rare earths was taken up by C. W. Balke and by B. S. Hopkins, who have studied particularly dysprosium and holmium, and very recently Hopkins, armed with the methods of X-ray analysis, has announced the discovery of the lines of "61," the missing element for which many chemists abroad and L. F. Yntema in this country had been diligently searching. This element, called "illinium" from the university and state in which it was discovered, is the second to be associated by name with America. May its fortune be better than that of the first, columbium, which long masquerading under the name "niobium" nearly lost its patriotic birthright! The story of the hunt for "61" is most interestingly told in the June number of THE JOURNAL,[1] and is a fine illustration of modern scientific methods of research.

Other Rare Elements

Two other elements will always be associated with American chemists, zirconium, to the knowledge of which F. P. Venable has contributed so much, and beryllium, to which C. L. Parsons devoted his time until called to develop the AMERICAN CHEMICAL SOCIETY. To Parsons also belongs the credit of fastening the name

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[1] *J. Am. Chem. Soc.*, **48**, 1594 (1926).

"beryllium" to the element, earlier and more commonly known as glucinum. While the association of the name of Venable with zirconium is known to all chemists, it is not so generally known that to Venable belongs the credit of the discovery of calcium carbide in electric-furnace products and the production of acetylene by its action on water. It was while the poles of a large dynamo at Spray, North Carolina, were being stuck into every conceivable mixture, that in one of the fused masses Venable discovered a brown crystalline substance which gave him a combustible gas on dropping into water. Simple enough in the retrospect, but in that day not every one, not even every chemist, would have had the knowledge to follow up the phenomenon. Although the work of the electric furnace belongs in another field, this review of inorganic chemistry would be incomplete without at least a mention of the early work of E. H. and A. H. Cowles and C. F. Mabery on the reduction of the oxides of boron and silicon, aluminum and other metals, by carbon in the electric furnace, and the work of G. De Chalmot on silicides and carbides.

We have already alluded to the work of L. M. Dennis on the rare earths. His earliest research was on the chlorides and hydroxides of cerium and the resolution of didymium, but his attention was soon attracted by the newly discovered hydrazoic acid, HN_3, the nature and reactions of which he and his students have done so much to elucidate. This has been extended by Dennis and A. W. Browne and J. W. Turrentine to the study of hydrazine and its oxidation, and by Browne to azido (N_3) derivatives of thiocarbonic acid, which promise further very interesting results. Some ten years ago Dennis took up the investigation of gallium, and to him, as well as to P. E. Browning, we owe a much fuller knowledge of this rather rare element. More recently Dennis was fortunate enough to find germanium present in certain zinc-ore residues, they running at times as high as 0.25 per cent germanium oxide, and he has been able to work with quantities of the metal hardly dreamed of by Winkler. Up to this time germanium had been the rarest of the metals, our knowledge of it being confined to the work of its discoverer, Clemens Winkler, on a small amount obtained from Freiberg argyrodite, and to some non-chemical work of Viktor Goldschmidt on quite a considerable quantity of argyrodite from Bolivia, which had been received by the Oslo University as "Fahlerz." Dennis extracted the element in quantity and has been enabled to make a much more complete study of its properties and compounds than had Winkler with his small amount of material. The most interesting part of his work is now in progress and concerns the hydrogen compounds of germanium, in which germanium shows a striking analogy to carbon. Monogermane (GeH_4), digermane, and trigermane have already been prepared and the end is not yet. Work on germanium has also been carried on by J. H. Müller (Is there any rare element that has not been studied in the laboratories of Edgar F. Smith?) on the allotropy of germanium dioxide and on the recognition of germanium by Marsh's arsenic test, in which germane functions as arsine. He has also found that fluorgermanic acid is not precipitated by hydrogen sulfide, which enables the purification of germanium from arsenic—a difficult problem. Dennis has further made some interesting experiments with germanium glasses. Mention should also be made of Dennis' unsuccessful search for eka-cesium, in which chlorides of the alkalies of pollucite were submitted to an exhaustive fractionation; but the end fractions showed no spectroscopic evidence of a new element.

Allusion has been made to the studies of W. A. Noyes on the chlorides of nitrogen. The composition of the very explosive iodide of nitrogen had long been a matter of discussion but was practically cleared up by the work of H. P. Cady and of F. D. Chattaway nearly thirty years ago. The chloride of nitrogen is far more unstable, but has been successfully worked on by Noyes for many years, especially in connection with its organic derivatives Some of these chloramines have acquired great importance as antiseptics. Considering from its oxidizing power that the chlorine in NCl_3 is positive and the nitrogen is negative, Noyes has tried to prepare an isomer in which the nitrogen is positive and the chlorine negative, but has not thus far succeeded. Mention of Dr. Cady recalls his work in 1907 on the analysis of the natural gas from Kansas wells. In one of these, the Dexter well in southern Kansas, quite an appreciable amount of helium was found. This led to an examination of other wells from the helium standpoint, and it was found that helium was present, at least in very small amounts, in practically all the wells of Kansas, though the quantity was variable. There was so much geographical regularity in its occurrence that Cady prepared an isohelium map for the state. No one could have then foreseen that little more than a decade later this work would have led to the use of helium in balloons. A chance remark of Sir William Ramsay that helium would be an ideal gas for the inflation of military balloons; a still hunt, based on Cady's work, for helium-richer wells; cylinders of compressed helium ready for shipment to the front; and had the Armistice been a few weeks delayed it would have been a surprised enemy at the failure of incendiary bullets to ignite the observation balloons—and all as the result of pure inorganic research.

Catalysis

Another line of research in which pure science and practical application are closely tied together is the work on the catalytic oxidation of carbon monoxide, already touched on in connection with the early work of Leeds. The more modern chapter originated in the effort to make gas masks which would absorb carbon monoxide, but it was soon recognized that from an industrial standpoint it was even more important that there should be some way in which to remove the last traces of carbon monoxide from the gases used in the Haber process of making synthetic ammonia from a mixture of hydrogen and nitrogen. The source of the hydrogen is generally water gas, and whereas the carbon dioxide and most of the carbon monoxide are readily removed, a minute trace of this latter gas is very poisonous to the catalyst. As there appears to be no selective absorbent for carbon monoxide, the problem is to find a catalyst by which the carbon monoxide will be oxidized in the presence of hydrogen. The solution of this problem has occasioned much research on the larger problem of the oxidation of carbon monoxide in general and under the influence of various catalysts. With this research are connected especially the names of J. C. W. Frazer and W. A. Patrick, W. C. Bray, A. F. Berton, and A. B. Lamb. While the subject of the fixation of nitrogen belongs to industrial research, the work of C. S. Bradley and F. W. Lovejoy ought to be mentioned as pioneer work, as well as the researches of J. E. Bucher, and the more recent work of E. W. Guernsey and M. S. Sherman on the fixation of nitrogen as sodium cyanide, in which they have studied the equilibria involved in the successive formation, from Na_2CO_3, Na_2O, Na, Na_2C_2, to NaCN. Nor should, for the sake of old times, a paper by A. A. Breneman be overlooked, which was published in an early issue of THE JOURNAL, giving a review of the subject of fixation of nitrogen as it then appeared, a valuable paper for its time, and possibly foreshadowing some of the more recent work.

The Platinum Metals

Looking back once more to the latter portion of the last century, we find in W. L. Dudley one who did much work in inorganic chemistry, little of which found its way into print. He was particularly interested in the platinum metals (from his association with John Holland, in whose laboratory he for a time was employed), and devised a method for melting iridium by adding a small amount of phosphorus. This alloy of iridium with iridium phosphide was brittle and could be broken up, and much of the phosphorus roasted out. These fragments found an important use in tipping gold pen points in place of the natural iridosmium flakes. This reminds us of Achard's process of fusing platinum by adding arsenic, and it was this first method of getting malleable platinum that may have suggested to Dudley the idea of using phosphorus with iridium. Dudley also found that platinum could be dissolved in hydrochloric acid if air is present, a method later developed for the preparation of chloroplatinic acid by the use of hydrogen peroxide as an oxidizing agent, thereby avoiding the nitro compound formed when nitric acid is used. Dudley's most important work was his study of the action of sodium peroxide on metals, especially on those of the platinum group, most of which are attacked by this reagent. Dudley was also one of those who was interested in the anomalous position of tellurium in the periodic table, and published a paper reviewing what had been done to resolve the difficulty. It was the ordinarily received view that tellurium was really a mixture with a homolog of higher atomic weight, and many were the efforts to separate the supposed mixture into its constituents. Dudley examined specimens variously fractioned with the spectroscope but found no evidence of complexity. W. R. Flint had at first effected a seeming separation by hydrolysis of the chloride, but J. F. Norris and Henry Fay, by fractionation of potassium bromotellurate, failed to find any sign of complexity. The work of W. C. Morgan, also on the hydrolysis of the chloride, seemed to settle the question in favor of ordinary tellurium being a simple element, and this view obtains today. The anomalous results of Flint, and of Flint and P. E. Browning remain to be explained. Browning has greatly extended our knowledge of many of the rarer elements, and his work should be mentioned here, though much of it has been with a view to analytical separations. The work of J. F. Norris on the isomorphism of selenium and tellurium should be noted in connection with the place of tellurium in the periodic table.

Reaction Products of Phosphorus Oxychloride

An important research in the last decade of the last century was that of H. N. Stokes on the reaction products of phosphorus oxychloride, $POCl_3$. His first work was with the silicic acid esters, which led to the production of a chloride of silico-pyrophosphoric acid. This was followed by papers on the reaction of phosphorus oxychloride with ammonia, which led to very interesting results, this reaction giving several series of amino and imino phosphoric acids. While Stokes made for the time a very full investigation of the subject, he left much that might be done, and pointed the way to the possibilities of similar amino and imino compounds with other less familiar acids. Of course this work ties on to Franklin's ammono compounds, but represents mixed ammono and hydro compounds.

Sulfur Problems

A number of problems connected with sulfur have been studied by American chemists in this half-century, an early research being that of L. W. McKay on the reaction between hydrogen sulfide and arsenic acid. It had been handed down from early literature that the action of hydrogen sulfide was to reduce the arsenic to arsenious acid, and that only arsenious sulfide and free sulfur are precipitated. McKay showed that here, as in so many other cases, everything depends on the conditions, and that it is quite possible to precipitate the pentasulfide. He also discovered the trithioarsenic acid, which is involved in the reaction. This work was all later confirmed in the light of modern methods by William Foster.

The problem of the preparation and composition of the hydrogen polysulfides is an old one, and many chemists have worked on it with various results. Quite recently J. H. Walton has again attacked the problem and from the oily liquid obtained by running a solution of the sodium polysulfides into cold hydrochloric acid, which produces a mixture of the polysulfides of hydrogen, he has isolated the disulfide and trisulfide, H_2S_2 and H_2S_3, in a state of great purity. These persulfides dissolve sulfur very readily and evidence was obtained of the existence of the hexasulfide, H_2S_6, which begins to decompose a little below zero.

The action of sulfur on alkalies has also furnished a perennial problem, which has in recent years become a very practical one, owing to the extensive use of the lime-sulfur wash as a fungicide, and the chemists of several government experiment stations have busied themselves with it. Much of this wash is purchased by farmers and much is homemade, and in both cases rule-of-thumb methods have been largely used in its manufacture. Hence the importance of the investigation of a very intricate reaction, very variable under varying conditions. H. V. Tartar finds that with hot caustic potash, K_2S_3 is formed, together with $K_2S_2O_3$, and with more sulfur, K_2S_5, while with lime and sulfur, CaS_4 is formed, also taking on more sulfur to form the pentasulfide.

With metallic sodium and excess of sulfur in boiling toluene the trisulfide is formed, while under like conditions with metallic potassium the product is the pentasulfide. It would not be venturesome to predict that the last word on the action of sulfur on alkalies has not been said. With the introduction of lead arsenate as an insecticide, and later of calcium arsenate, it was necessary to work over old material in the light of newer chemistry, and C. C. McDonnell and H. V. Tartar have pretty well cleared up the lead arsenates; C. M. Smith has done the same for the lime-arsenic acid equilibrium, while Story and Anderson have studied the arsenites. The work of these chemists has revealed how much there is yet to be learned of the chemistry of old and familiar things.

Radiochemistry

So much of the field of radiochemistry is really inorganic that at least allusion must be made to the work of B. B. Boltwood and of S. C. Lind on radium, Boltwood's discovery of ionium, and Lind's work on the chemical reactions produced by the alpha particle. Similarly, Irving Langmuir's work on chemical reactions at infinitesimally low pressures belongs in another field and must be passed over with a mere mention.

Recent Miscellaneous Investigations

So, too, must be omitted numerous other pieces of work which it would be worth while to dwell on did the limitations of this chapter permit. Such are, for instance, the work of W. F. Hillebrand on the isomorphism of thorium and uranium; of Edward Hart on glucinum; of T. W. Richards and of D. W. Horn on the cuprammonium compounds and of W. D. Harkins on the cobaltamines by physicochemical methods; of Allen Rogers on molybdenum and F. C. Mathers on indium; of A. B. Lamb on periodic acid and of Maxwell Adams on hydroxylamine; of E. E. Reid on perchromic acid and of H. H. Willard and of F. C. Mathers on the preparation of perchloric acid; of H. R. Carveth on the electrolytic deposition of chromium, now twenty years later being put into practical application, thus fulfiling his prediction that as the plated metal is very hard, it is capable of industrial use; of L. J. Curtman on double arsenates and phosphates; and of H. I. Schlesinger on the double fluorides of the platinum group; of E. G. Mahin and of William Blum on the constitution of the aluminates; and finally F. W. Bridgman's discovery of two new modifications of phosphorus and Leonard Hasche's discovery of a new oxide of nitrogen, N_3O_4.

Conclusion

As was stated at the opening of this chapter, conditions can hardly have been considered favorable for research in pure inorganic chemistry in America, and if it *is* pure inorganic chemistry it must today largely pass over into the realm of physical chemistry. On the other hand, using the methods of physical chemistry, the field of inorganic chemistry is enlarging at a rapid rate; we are realizing how every step taken in what was the large field of inorganic chemistry a century ago is today merely a starting point for new research. On still another hand, the applications of chemistry to industry are increasing by leaps and bounds, in both inorganic and organic realms, and problems of volume production and efficiency are largely depending on the physicochemical study of inorganic and organic compounds and reactions; general chemistry it all is.