

PART II
REVIEWS OF PROGRESS IN VARIOUS BRANCHES OF
CHEMISTRY IN AMERICA

1876-1926

CHAPTER VI
MINERAL CHEMISTRY

BY EDGAR F. SMITH

Introduction

In preparing this sketch on mineral chemistry, or mineralogical chemistry, if you please, as it has developed in the fifty years of the life of the AMERICAN CHEMICAL SOCIETY, the writer was at once impressed with the fact that many of the earliest independent investigations of American chemists were made in this particular field of chemistry.

For example, as early as 1798 Adam Seybert, a doctor of medicine, laid aside his profession and devoted himself to the study of minerals. His collection was quite unique. In 1814 it became the nucleus of the collections which have grown to splendid proportions in the halls of the Academy of Natural Sciences in Philadelphia. Indeed, for years, Seybert was the master mind in the domain of mineral chemistry in this country. It was this interest, no doubt, which led him to send his only son, Henry, to Paris for scientific training. After graduation from the École des Mines, on his return to his native city, Henry Seybert busied himself with minerals. It was he who first demonstrated the presence of glucinum in the mineral chrysoberyl.

Then, too, in recalling Silliman, the elder, one remembers that in the early years of 1800, which he spent in Philadelphia in the study of chemistry under James Woodhouse, he brought with him, in a candle box, the entire collection of minerals then owned by Yale University, hoping to find someone in the City of Brotherly Love whose knowledge of minerals might enable him to determine his specimens. Such an one he discovered in Adam Seybert, who could with authority tell what the specimens were.

Further, men such as Gerard Troost, William Keating, Lardner Vanuxem, and others were making worthwhile contributions to mineral chemistry in the first third of the nineteenth century and a little beyond.

American chemists should not, therefore, hastily turn aside from mineral chemistry, because it represents a chapter in which their progenitors were leaders and proficient. Again, minerals are definite, distinct chemical bodies. Hence, their constitution is worthy of study; their synthesis is most fascinating. In the field of organic chemistry, for example, the great variety, the beauty, the multiplicity, and, it might be added, the value of the more than 300,000 specimens claim, and have claimed for years, the best thought of chemists who have delighted in determining the constitution of these derivatives of carbon. But the enthusiasm resulting from the unraveling of the constitution of a mineral such as epidote, topaz, or vesuvianite has not been very contagious, the truth being that chemists have not succeeded in determining the constitution of many minerals—true chemical compounds—as has been done, for example, in the case of salicylic acid, indigo, and many other organic products. The problem is a difficult one. It calls for an almost superabundance of patience, for a thorough knowledge of a great list of elements, for the power of analytic generalization, etc. One may purify benzoic acid, oxalic acid, or sugar and be assured that the final product is free from all adventitious foreign material, but the purification of a well-crystallized specimen of garnet or pyroxene is almost heart-rending. Comparatively few chemists have had the courage and patience requisite to search for adequate methods of purification of the material offered by mineral chemistry. Some few methods, falling perhaps within the domain of physical chemistry, have been applied, but there it has ended.

Men of the type and spirit of Berzelius, Wöhler, Friedel, Des Cloizeaux, Wollaston, Marignac, and Haüy are needed. When they arrive, the chapter on mineral chemistry will be emblazoned with glory.

The cobalt bases, discovered by Frederick A. Genth, developed later largely through the efforts of Genth and Wolcott Gibbs, and certain French chemists, e. g., Fremy, seemed to be an enigmatical group, as regards constitution, until the talented, keen Werner of Zurich, reflecting upon methods of approach which had sprung up in the years succeeding the activities of Genth and Gibbs, so brilliantly laid bare that field of interesting derivatives. And was not the chapter on sugars in organic chemistry, often spoken of as a *terra incognita*, marvelously simplified and made to stand forth as one of the most brilliant chapters of organic chemistry by the indefatigable Emil Fischer?

Was it not also this gifted chemist who brought light into the

albumins and other members of the field of animal chemistry, which had long resisted the efforts made to solve their constitution, yielding only when new and modern methods of attack were resorted to by him? These contributions are known to all chemists and gratitude has been expressed by thousands of human beings who were affected in one way or another by the epoch-making endeavors of Fischer. On one occasion, when approached by a young American chemist working in his laboratory, with the question as to what field of chemistry he should devote himself on his return home, whether to the organic field or some other, it was Fischer who promptly replied—"to the inorganic field; the great mineral wealth of your country offers magnificent opportunities for research bound to be of value both from the standpoint of pure science and that of industrial developments."

These preliminary remarks have been prompted by a love for mineral chemistry. All readers may not share it, and some may be disposed to look upon the suggestions as unworthy of consideration. So be it!

Activities of Five Past Presidents

The committee which has in charge the preparation of the present volume proposed that this chapter should deal with activities in the field of mineral chemistry on the part of five distinguished Past Presidents of the SOCIETY who, in the years of the SOCIETY's existence, made worthwhile contributions in that particular domain. Naturally, in fifty years many American chemists have given themselves to the study of mineral bodies. However, it seems wiser that this story should revolve in a general way about these Past Presidents of the SOCIETY, four of whom have passed on, while the fifth continues with us, thinking and working with enthusiasm along the lines which for years he has so well and richly cultivated.

FREDERIC AUGUSTUS GENTH.—To present-day students of chemistry the name of Frederick Augustus Genth (1820–1893) may convey little. Briefly, he was born in 1820 in Germany, was carefully educated and came under the tutelage of such persons as Leopold Gmelin, Bischoff, Blum, Leonhard, Fresenius, Kopp, Liebig, and Bunsen whose chemical assistant he was for three years. In 1848 he came to America, making his home at first in Baltimore and later in Philadelphia. In the latter city, his real research work was done. Passing over the earlier portions, such as the ammonium cobalt bases, to save time and to bring him closer to the period in which our SOCIETY was founded, and of

which he was a corporate member, it will suffice to review cursorily his contributions to mineral chemistry in the seventies, and in later years when he was President of the SOCIETY.

It is with some hesitancy that the writer speaks of this gifted man and chemist, because he may be unduly partial in judgment, as it was in his very early years as a chemist that he enjoyed the privilege of serving as assistant to Genth, and through various experiences came deeply to appreciate him and his comprehensive chemical knowledge. All this happened in the seventies when organic chemistry held sway in the minds of younger chemists about as physical chemistry does now, and as an enthusiast in the former the writer busied himself in his leisure moments with the making of substitution products in the great benzene series and in studying condensation products. Some of these were highly aromatic, and the odors emanating from his little laboratory were not to the joy of his chief, who patiently forebore from remark for awhile but eventually, in very firm words, gave his youthful assistant to understand that further activity with these aromatic benzene bodies must cease. This crushing mandate caused him to work at night when the laboratory was absolutely clear and he could be alone. Upon retiring from this night work, he took the precaution to lower and raise the windows so that by morning the atmosphere of the laboratory might be sweet and free from the "vile stuff."

However, the keen sense of smell of Genth enabled him (at least such was the inference) still to detect aromatic odors. Without comment the writer was invited to a little room until then locked to him. On entering he was surprised to see that everywhere were large glass jars filled with monazite sands. "There," said the Doctor, "is material for your future research." In short, it meant that for the next year or two great quantities of this material were to be studied under the supervision and direction of the Doctor, and together with the many new things in the way of elements, new at least to the writer, there emerged from that research an assistant who was a complete convert to inorganic chemistry. But that is another story. An abundance of zirconium in the form of sulfate was extracted and this particular product, at a certain point, was invariably appropriated by Genth, who would say, with a knowing look as he carried the material away, "Zirconium is not simple; there is another element concealed in it, and when I have leisure I shall endeavor to isolate it."

Very properly the reader may ask—but how about the research work of Genth himself in mineral chemistry? To begin, then,

attention may be directed to his studies of the alterations of corundum. These began early in the seventies and continued for many years. Very few present-day chemists have read the results of that study. Those who have been so fortunate as to have done so will agree that an exceedingly interesting field in mineral chemistry was opened to all who care to consider the constitution of minerals. The first astounding thing is, how did these wonderful transformations of corundum take place? What forces were at work in the change, for example, of corundum to minerals like spinel, diaspore, bauxite, gibbsite, quartz, opal, smaragdite, zoisite, feldspar, tourmaline, fibrolite, cyanite, damourite, and a host of others not necessary to name? The investigation attracted comparatively few chemists. To them these pseudomorphs were enigmatical, and unless in the years which have since gone by earnest efforts have brought to light explanations for their occurrence, of which the writer is ignorant, they continue to be a chapter crying for further consideration and study.

In massive feldspar near Shimersville, Pennsylvania, was found, in 1882, a beautiful black, well-crystallized body. It seemed to be an isolated product but upon presenting it to Genth, he smilingly said, "It is an alteration product of corundum. It is tourmaline." Speculation as to its formation was rife, as were the transformations of corundum into other minerals without the loss of its crystallographic habitus.

On one occasion another distinguished chemist and Past President of our SOCIETY, as well as a close friend of Genth, journeyed from his distant home in the South to discuss with him an alteration of corundum into a substance resembling the mineral damourite. Genth had analyzed this alteration product and was quite certain that it was the mineral which it was supposed to be. Dr. J. Lawrence Smith presented analytical results pointing to the possibility of its being a new member of the family of micas. These eminent chemists were not disposed to enter into a public controversy; hence Smith spent several weeks in Genth's laboratory, the two men working side by side over the material in question. The problem was, perhaps, a minor matter but it beautifully illustrated the care and the accuracy with which Genth studied minerals. These two analysts differed a good deal from each other in the percentage of silica obtained as well as in that of alumina and other components of the supposed damourite. Numerous analyses were made by each. Genth's results were regularly concordant, while those of Smith varied greatly among themselves. Without entering into details, wearisome at best

in this place, the discrepancies in Smith's results were found to be due to incomplete decompositions of the material as well as to indifference in the reduction of the mineral powder to a sufficient degree of fineness. Smith gladly accepted the outcome and the two friends continued to push forward other studies relating to the alteration of corundum. Chemistry students of the present period would probably shrink from the perusal of this classic memoir (*Alterations of Corundum*) in mineral chemistry, but its examination is bound to suggest lines of further investigation which, with all our modern facilities and methods of attack, and unusual exactness in analysis, ought to disclose results of profound theoretical value. One wonders how long it may be until the seeker after truth will turn his attention to some of the problems presented by this fundamental investigation.

It has been said that Genth was almost without a peer as a chemist, especially in analytical work, for he was familiar not only with the reactions and methods of determination and solution of the ordinary elemental and compound ions but, what is more remarkable, with the rarer and less frequently occurring ones as well. Further, all of his scientific work was characterized by a conscientiousness and fidelity to fact which was exceptional. No labor seemed to him too great if by it an added accuracy could be assured. Many personal laboratory experiences confirmed this view of the great exponent of mineral chemistry. Thus, a rare mineral, called "herderite," had been observed at Stoneham, Maine. It was a phosphate of glucinum and calcium. Specimens of the same mineral from a European locality were analyzed by Clemens Winkler, discoverer, a few years later, of the element germanium. In some unaccountable way this distinguished chemist had overlooked, in all his analyses, a fluorine content amounting to about nine per cent. To this omission attention was directed by Genth in several very concordant analyses, followed as might be surmised by an interesting and a bit acrimonious interchange of analytical experiences on the part of the two master chemists. Suffice to add, Genth emerged as the generally accepted victor.

Much attention also was given by Genth to the mineral vanadinite, particularly those specimens which came from New Mexico and which were first observed there by Silliman, the younger. This study brought as an associate to Genth the celebrated Gerhardt von Raht, to whom the crystallography of these interesting bodies fell as his special work. Several communications ensued. Again it was the hope of Genth that he might arrive at some definiteness in the constitution of the mineral, which constitution he finally

announced as a combination of the chloroarsenate of lead with the chlorovanadate of lead. Had he followed the studies of his intimate friend, Wolcott Gibbs, upon the "complex inorganic acids," it is quite possible that he would have pronounced vanadinite to be the salt of a chlorovanado-arsenic acid. The correct interpretation of this particular mineral and allied minerals continues to await solution.

Genth rarely associated anyone with himself in his mineral studies, although in the latter years of his activity the very distinguished mineral chemist, Samuel F. Penfield, participated with him, rarely, however, doing more than such crystallographic research as was possible.

In addition to his more comprehensive papers, Genth was the author of twenty-three minor contributions in mineral chemistry which brought to the attention of the chemical public descriptions of new minerals. In fact, he was the discoverer of twenty-four new mineral species, all of which were so thoroughly individualized, both by chemical and by physical methods, that they took at once a position in the science which they have ever since maintained. To name them would be superfluous. Persons interested in perusing the original documents will be impressed with the astounding skill of the analyst, of which the writer had the most convincing proof, and which disclosed to him the fascinating power of the objects in mineral chemistry, the one regret being that the efforts to unravel constitution appeared so feeble that discouragement on the part of the student was apt to arise. And yet, in the light of the modern spirit of research, the fields opened up by Genth in mineral chemistry must be made intelligible to all who cultivate the science of chemistry.

J. LAWRENCE SMITH.—Reference in a preceding paragraph to Dr. J. Lawrence Smith (1818–1883), devoted member and Past President of our SOCIETY, brings into remembrance his work. In the now priceless photograph of American chemists who, on August 1, 1874, gathered about the last resting place of Joseph Priestley in Northumberland, Pennsylvania, there may be seen the friendly face of this chemist who had come from his distant Kentucky home that he might do homage to the memory of the discoverer of oxygen. There, too, he united with his confrères in the adoption of the motion of the young secretary of the gathering—Dr. J. Persifer Frazer—that an AMERICAN CHEMICAL SOCIETY be constituted. There the matter rested.

The name of Smith has many times been on the lips of chemists, brought there most frequently, perhaps, when the best method

of decomposing silicates, with the object of getting at their alkali content, was the subject of comment. As the writer was favored with many opportunities of observing this celebrated chemist, whom he had often heard characterized as, "a man of great ability and great integrity of character; one who seemed to win all who came within the sunshine of his genial nature," there always comes to mind that Dr. Smith, at eight years of age, was studying algebra, and at thirteen years, calculus, so it was not surprising that before seventeen years of age he might have been discovered at the University of Virginia, busied with such subjects as chemistry, natural philosophy, and civil engineering, including advanced mathematics. His instructor in chemistry was John P. Emmet, under whose stimulus and that of others, including W. B. Rogers, his scientific studies were developed and further confirmed. Whatever attention he may have bestowed upon literary subjects must have been in his preparatory years in the old, aristocratic city of Charleston, South Carolina, where he was born in the year 1818, being, therefore, slightly older than his friend and co-worker, Frederick Genth. After two or three years Smith abandoned scientific pursuits for medicine, receiving his degree in 1840, upon the presentation of a thesis on "The Compound Nature of Nitrogen," soon thereafter journeying to Paris where he diligently attended instruction under Dumas, Orfila, Poulliet, Desprez, Becquerel, Dufrenoy, and Elie de Beaumont.

On one of his summer excursions he found himself at the door of Liebig's laboratory in Giessen, which accidental circumstance turned the whole course of his life to chemistry, from which it was never diverted. Both he and Genth had come under the inspiring influence of Justus Liebig. Hence, they had a somewhat similar training for the work in which they were to engage.

In his student days, Smith had devised a very delicate and most interesting test for the detection of barium, having also determined its quantitative value. This occurred in 1839, and probably there are many whose eyes will rest upon these lines who, like the writer, followed the method with his own students in analysis fifty years later.

As a result of his research upon the monazite sands of North Carolina, the writer was brought on one occasion into a lengthy interview with Smith, who had paid a visit to Genth, but finding him absent, in his friendly and sympathetic way, turned to the young assistant, inquiring as to his work, in which the distinguished scholar apparently took the very deepest interest. On the evening following this particular interview, Dr. Smith de-

livered a verbal communication before the Academy of Natural Sciences (Philadelphia) outlining in considerable detail his work upon samarskite, which he was conducting in Louisville. In his audience there chanced to be an assistant professor, an associate of the writer, who made it his particular business to inform Genth very early the next morning that Smith had evidently trespassed upon the study of his young assistant, the writer. Whereupon, without any further information, Genth reminded his assistant that he should not have made any communication upon this work, which was really his work, not even to Smith—his friend. There was just a bit of human nature, perhaps, in this, which in the end amounted to nothing, because the communication of Smith to the Academy related chiefly to the finding of columbic and tantalic acids in specimens of samarskite. Smith was, however, interested in the writer's work and so expressed himself a little later, because he had been occupied with cerium earths to which, at the time, he was giving a great deal of attention. These studies were discussed with his friend Genth, and it was quite natural that the writer should have heard much of their conversation, particularly the portion relating to the new element, mosandrum, about which Smith had addressed the Academy of Natural Sciences as early as 1877. The details of this remarkable study need not be given, suffice to mention that among his statements he informed Genth that a spectroscopic study of his material by Soret established without question the existence of a new earth and added:

If we take their properties, their spectroscopic properties (meaning the cerium earths) we find didymia at one end of the group, mosandrum in the middle, and terbia at the other end giving absorption bands. In fact, it seems to need these two elements, terbia and mosandrum, to complete the groups.

The writer was filled with awe. He knew little in regard to absorption spectra but was deeply conscious that he was in the presence of one who had discovered a new element. So what harm could an unknown neophyte have done by fully telling the story of his own work! And thus Dr. Genth himself thought; so the writer continued in the good graces of his chief.

It may have escaped the memory of the majority of chemists that during the administration of President James Buchanan, the Turkish government applied to him for a scientist who might develop the agricultural interests of his Empire. Smith was selected for this purpose. During the years of his residence in Turkey he, however, became particularly absorbed in its mineral resources. Emery mines were discovered by him and in working these he came in contact with large deposits of massive corundum,

as well as with the crystallized mineral. His report upon the same was highly regarded by men of science. The occurrence of the corundum claimed more than ordinary attention, and to intimate friends, living in the eastern part of this country, he addressed letters calling attention to the fact that possibly in their localities this mineral would be found, naming its associates as guides in their search for it. His prediction was correct. This observation is made to show that long before Genth and he became intimate, corundum, a pet or favorite study of Genth, was a study which occupied his friend's earnest endeavor. Hence, when in the seventies they were both engaged with an examination of alteration products of the mineral, it was quite natural that they should be occasionally brought into collision but, as has been shown, these differences were amicably adjusted when they worked side by side.

Probably the remarkable studies of Smith upon meteorites will be, for all time, regarded as his *magnum opus*. The collection of these strange bodies and the heroic efforts put forth to ascertain their minutest constituents challenge the admiration of every devotee of mineral chemistry. So ambitious was he in this research that his collection was regarded in its uniqueness and importance as one of the first in this country, if not in the whole world.

For a short period of his life Smith was professor of chemistry in the University of Virginia, in a certain sense his Alma Mater, and there it was that he, together with Professor Brush, afterwards the distinguished professor of mineralogy in Yale University, unceasingly pursued mineral analysis. In one of the earliest editions of Dana's "Mineralogy" their initials "B. & S." appear attached to the analyses of a vast group of minerals. So it is not surprising that the writer, in his personal conversations with Smith in Genth's laboratory, should have conceived for him a very human admiration.

The most important contributions to mineral chemistry made by Smith after the foundation of our SOCIETY were those that related to the minerals in which were present the so-called rare earths; that is, the cerium group of elements and the minerals containing columbic acid, tantallic acid, titanlic acid, tungstic acid, and molybdic acid. In samarskite from North Carolina, for example, he was fortunate in bringing to light new minerals containing columbic and tantallic acids—these were hatchettolite and rogerite. He first called attention to the mineral tantalite, which had been observed in the state of North Carolina. His

interest in the columbates and tantalates was great, and as an introductory to one of his very creditable mineral studies, he made a strong plea for the retention of the name "columbium" discovered in 1801 by Hatchett. He went into great detail of argument against the name "niobium."

Among his associates working along similar lines, he was constantly emphasizing the fact that one of the distinguishing characteristics of the mineral tantalite was its high specific gravity, never falling below 7, and he seems to have made it a habit when minerals of this group were brought to him as being tantalites to dismiss them at once as members of the columbite group if their specific gravity fell below 7. It is very doubtful whether Smith ever succeeded in evolving a complete separation of titanate acid from columbic and tantalate acids, although he made many earnest attempts in this direction. Neither was he any more successful in separating columbic and tantalate acids from each other.

To review all his work would be out of place here, yet the perusal of his experimental efforts in isolating the various components, of what was in those days termed "the cerium earths," made very plain his keenness, his untiring patience, and his ability as an analyst.

There is very little evidence, and that seems to have been of a passing character, that he made any attempt to explain the genesis of the minerals upon which he spent so much time and effort. Thus, he seems to have been quite content with Genth's views in regard to the origin of corundum. To the close of his life he was devoted to mineral chemistry; but, "he set aside the views of Chevreul that spermaceti was a fat, and reached the conclusion that it was a compound *ethal*, and that by its distillation a molecule of ethal hydrate and *celine* was produced. He further demonstrated by the action of potash on cholesterine, that the latter was nearly related to spermaceti." This was a peep into organic chemistry! He loved all chemistry and had joy in its pursuit. His studies command the respect of the entire scientific world.

T. STERRY HUNT.—Among the Past Presidents of the SOCIETY, justly regarded as a chemical philosopher, was T. Sterry Hunt (1826–1892). His scientific interests, strongly developed under Silliman, the elder, extended over a wide range, but in them all he worked from the standpoint of a chemist.

He has been properly credited with having originated the theory of simple water types, and in his earlier papers the germs of the ideas usually attributed to Gerhardt may be found. His re-

searches upon the equivalent volumes of liquids and solids were a very remarkable anticipation of Dumas. In his introduction to "Organic Chemistry" (1852) he first defined that branch of chemistry as the chemistry of carbon and its compounds. To follow him into the field of pure chemistry would require years of steady application. From the fact that he gave himself, at the beginning of his professional life, to geological work, one is not surprised to discover him occupied with experimental work in mineralogy, emphasizing the importance of better analytical work in the field of mineral chemistry, and also the pressing needs of a better understanding and comprehension of the constitution of minerals.

His book entitled, "The New Basis of Chemistry," published in several editions, is a striking work and elicited much discussion. That it was thought to possess value is shown by its appearance in a French and also in a Russian translation. One of his last pieces of literary endeavor was a "Systematic Mineralogy" according to a natural system (1891). Its chapters are thought-arresting. They give evidence of broad training, and show very conclusively how the experiences of his years of experimental work brought to him many original and surprising views. It is impossible to give even an outline of all that he did in mineral chemistry; hence the reader must be content with a concise statement which will indicate his interest in the constitution of minerals—real chemical compounds.

It was Hunt who proposed to regard charcoal, graphite, and diamond as so many "polymeric modifications of elemental carbon." This idea of polymerism clung tenaciously to him, and although the law of progressive and homologous series had at that period been recognized in the hydrocarbon series, only Hunt felt that it might be extended to other compounds, believing it would lead, as it happens to do, to the conclusion that the chemical formulas of many mineral species are very complex and have molecular weights very much higher than those admitted for hydrocarbons and their derivatives. There is no doubt but that this assignment of complex formulas of high molecular weights and of homologous relations to minerals originated with Hunt. To minerals such as pyroxene, amphibole, wollastonite, albite, anorthite and orthoclase, he ascribed very complex formulas.

It will be remembered that the doctrine of progressive series had been enunciated first by James Schiel of St. Louis, Missouri, and later by Charles Gerhardt. Hunt attempted to extend this doctrine to other compounds, maintaining that bodies differing by $(OH_2)_n$, $(OM_2)_n$, and $(SM_2)_n$ might, like those differing by

$(\text{CH}_2)_n$, be homologous, and so he applied the principles of the progressive series of organic bodies to members of the mineral kingdom. While he regarded himself as the first to make such an application, he was yet aware that the doctrine of progressive series in inorganic bodies had been attempted by other chemists. For example, his intimate friend, Wolcott Gibbs, described the polytungstates, in 1877, as a homologous or progressive series. The words of Hunt himself declare that:

The extension of the doctrine of homologous series to minerals serves further to show the importance of small variations in the composition of definite crystalline members since very small portions of different substances may not only occur as necessary elements in such a compound, but may even change essentially its chemical relations. * * * In such compounds partial substitutions and small additions affecting but slightly the centesimal composition of a species may nevertheless be as essential to its chemical composition as the small amounts of silicic and phosphoric acids added to polytungstates. Such substitutions and additions would, however, if found in ordinary analysis of mineral species be disregarded as impurities not essential to the composition. * * * Further and more critical chemical analyses are necessary before we can fully know the constitution of dense, insoluble species, and the great difficulty is to decide how far these small portions of elements are due to impurities and how far they are elements necessary to the constitution of the species, questions which in many cases can only be solved by much care and study. It is well to remember in this connection the effect of minute quantities of various elements in modifying the characters of metals.

The researches of Wolcott Gibbs upon the derivatives of complex inorganic acids, as well as the studies of others who busied themselves with this group of chemical compounds, greatly influenced the thought of Hunt. It had been observed time and time again that 0.10 per cent of some constituents affected the crystalline character and the physical and chemical properties of the products in an astonishing way. Other observations of Wolcott Gibbs also determined the thought of Hunt in regard to the constitution of minerals, particularly that of the silicates. Gibbs called attention to polytungstates in which pentoxides formed very definite compounds with the tungstic acid, and demonstrated that the lower oxides and the pentoxides, such as the trioxide and dioxide, might all combine with the tungstic acid to yield a complex anion which, in turn, united with some one of the many protoxides to form definite derivatives. So in the course of his deliberations Hunt began to query as to whether the alumina in silicates, such as orthoclase, did not function as a part of an acid radical which, with the protoxide of potassium, yielded the mineral. Very definite products had resulted from the union of aluminum oxide with tungstic acid and also with molybdic acid.

Perhaps some readers will recall that among students of mineral chemistry there used to arise the question as to the function of boric acid in tourmalines. It was imagined that this acid or its

oxide had replaced a portion of the aluminum oxide. That was not a very satisfying explanation but in the light of the production of borotungstates, in perfect harmony with the aluminotungstates, the conclusion was that the complex anions in the polytungstates and polymolybdates were quietly existent also in complex silicates. The writer ventures to add that when the constitution of the derivatives of the complex inorganic acids has been made clear the constitution of many complex bodies in mineral chemistry will be rapidly unraveled.

Hunt said, after reflecting upon the results of the brilliant studies on sugars by Emil Fischer, that they were of great significance, and that although such methods of investigation as disclosed the nature of the sugars could not be applied to fixed and insoluble silicates, there was no certainty that in the case of mineral oxides, sulfides, and silicates we are not dealing with bodies which, while physically very similar, have differences in constitution as great as the sugars. When we pass from bodies like the sugars, made up of but three elements united in simple ratios to others far more complex, like the cobaltamines, the polymolybdates, and the polytungstates, we learn that the simplest admissible formulas of these lead to molecular weights of thousands, as in the borotungstate of Klein and in the hydrophosphovanadotungstate of barium first described by Gibbs.

The chemist who, with such facts before him, attempts to calculate, from the results of chemical analysis, formulas for the chlorites, the micas, the epidotes, and the tourmalines, soon finds how inadequate are the principles ordinarily recognized and is led to conclude that did we possess a knowledge as complete for these natural silicates as for the artificial bodies we should find that our present formulas for these silicates are but approximations.

This imperfection must pertain to all our formulas for mineral species except such as calcite, barite, fluorite, and for some metal-line sulfides and arsenides, which for purity and definiteness may be compared with artificially crystallized substances.

Such are some of the generalizations of Hunt as late as the nineties. They indicate that although he was the discoverer of new minerals and a devoted student of geology, a predominating idea with him was the constitution of minerals as definite chemical compounds. He naturally recognized the inefficiency of all then known methods for that purpose. His observations on the elucidation of this problem are set forth in no uncertain language in his "Systematic Mineralogy." His theoretical views

were welcomed. They were supplemental and should have earnest consideration. They are very suggestive. They have been overlooked to a large degree by many students of mineral chemistry. Various reasons are contributory to this omission.

Although born in the United States, Hunt spent many years in teaching science in Canada, where he became a leader in geological and mineralogical circles. The impression made there was a very deep one. He returned to the United States in 1872, accepting the chair of geology in the Massachusetts Institute of Technology made vacant by the resignation of William B. Rogers. Hunt was also present at the memorable gathering of American chemists about the grave of Priestley in Northumberland, Pennsylvania, on August 1, 1874, where he delivered an inspiring address.

This tribute was paid Hunt upon retirement from academic life:

Long an indefatigable experimenter and an extensive observer, Hunt was also an original and philosophical thinker and took an influential part in the establishment of the most matured and scientific theories. He was early in the field of chemical speculation and aided essentially in the revolution of views which has ended in the establishment of a new chemistry.

Refreshing, indeed, is it to know that so brilliant a mind had devoted years to the problems of mineral chemistry.

WILLIAM FRANCIS HILLEBRAND.—It was late in 1878 or early in 1879 when the administration of the newly organized United States Geological Survey advised an inquirer, "that it has just been decided that there would be no opening for a mineral chemist." The modest inquirer was William Francis Hillebrand (1853-1925). In 1880 S. F. Emmons, in charge of the Rocky Mountain Division of the Survey, "asked me (Hillebrand) if I would like to take a position as chemist in his Division of the Survey. Thus was offered me from a clear sky the very position I had sought when applying to Mr. King. Of course the offer was accepted." And so began the career of one of the most distinguished and able Past Presidents of our SOCIETY.

At the close of his preparatory studies in the United States he might have been discovered in 1872 as a matriculant of "Old Heidelberg," pursuing studies under Bunsen, Kirchhoff, Blum, Leonhard, the younger, and Karl Klein.

He has left us so recently that nearly every member of the SOCIETY will recall his face and figure. His modesty and silence generally placed him more particularly among his intimates so that his addresses were not frequently before the public.

His accomplishments in the vast field of mineral chemistry are,

however, fresh in memory. Yet it will be worth while to let pass in review such of his achievements as stamped him a great force in the field of mineral chemistry. Although relinquishing every claim to being an organic chemist, his close friends know that while in the University of Strassburg with Fittig he unfolded the constitution of quinic acid. Genth, J. Lawrence Smith, and Hunt, his predecessors in this group of mineral chemists, also did noteworthy work in the organic domain.

The old Freiberg Mining Academy appealed to Dr. Hillebrand, for there was supplemented "his experience in mineral analysis gained with Bunsen." To return, however, to his contributions to mineral chemistry, analysts universally will declare his "Analysis of Silicate and Carbonate Rocks" a work of paramount importance. The favorable reception given it amply attests this. It was the product of a master mind—of a chemist to whom analysis made a powerful appeal. Many, of course, are indifferent to it. It exasperates them. They would cast it aside. In the words of Wolcott Gibbs, they look upon it "with contempt." But it means everything to those striving to get a better knowledge of the constitution and deportment of minerals which, as we admiringly gaze upon them in their most attractive forms, seem to smile and defy us to pull them apart and reunite their components as has been done for numerous organic derivatives.

Like Genth, Hillebrand was most solicitous as to purity of mineral material, of reagents, of the accuracy of methods pursued, and also as to the determination of the minute quantities of the components which perchance were present, a fact also constantly emphasized by Hunt.

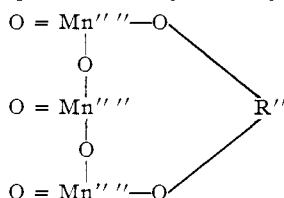
The marvelous patience, the keen discernment, the intelligence manifest in his "System" command the respect and gratitude of every student who wishes for a clearer vision in the domain of mineral chemistry.

His discovery of nitrogen in uraninite was indeed epoch-making! He constantly said that that "gas was well worthy of further examination," and to Sir William Ramsay wrote: "It doubtless has appeared incomprehensible to you in view of the bright argon and other lines noticed by you in the gas from cleveite, that they should have escaped my observation. *They did not.*" Urgent duties of his official position prevented his aggressive pursuit of this point. The modesty and nobility of Hillebrand shine forth in his beautiful letters to Ramsay.

His studies of minerals evince the interest he had in them. What really is their constitution, he must often have asked him-

self. Corroboration of this query is plain in his discussion of the nature of a new mineral which he designated "coronadite."

If this mineral is to be regarded as anhydrous the comparatively simple formula $R''(Mn_3O_7)''$ is quite satisfactory and may be written structurally:



*** Such intricate formulas as this should not cause the least surprise, however unlikely they may at first appear to be. The great number of manganites in varying degrees of saturation observed in nature and prepared artificially, some of them of even greater complexity than the above, are certainly not all mixtures of only a few simply constituted molecules.*** From the known tendency of these bodies to form under laboratory conditions which may very well be repeated in their general character in nature, it is to be expected that a vast number of mineral manganites should exist, and it ought rather to excite surprise than otherwise if two or more are not formed simultaneously from the same solution. This, together with inherent difficulties of analysis, would offer a simple explanation of the fact that so few of the analyses may lead to rational formulas, etc.

His conclusions upon carnotite were also quite convincing—viz., that it was probably a mixture of minerals, the exact nature of which analysis fails to reveal, and he added:

Instead of being the pure uranyl potassium vanadate, it is to a large extent made up of calcium and barium compounds. Intimately mixed with and entirely obscured by it is an amorphous substance—a silicate or mixture of silicates—containing vanadium in the trivalent state probably replacing aluminum.

A great deal more might be written upon his endeavor to gain a fuller insight into minerals.

On assuming the duties of chief chemist in the Bureau of Standards (1908), "his new duties lessened his activity in his favorite field, but did not entirely prevent him from sending out further communications relating to the composition of minerals."

Many will recall his more intimate talks upon the wonderfulness of the constitution of minerals!

FRANK WIGGLESWORTH CLARKE.—Reference to the reports of the United States Geological Survey, to the pages of the *American Journal of Science*, and the various chemical journals in this country, will disclose a vast amount of material submitted by Frank Wigglesworth Clarke (1847-), a former President of the SOCIETY who, throughout his entire career in chemistry, has been an ardent advocate of the study of mineral chemistry. In his numerous addresses and in popular, as well as in scientific

communications, he has steadily held high this most worthy chapter of chemistry. His personal studies confirm these statements and one is really overwhelmed on a careful perusal of what he has effected in the way of elucidating the constitution of various mineral groups.

The value of his material is too extensive for condensation and is also too suggestive and, in many instances, too conclusive to be reviewed except in the most elaborate way; but no further excuse need be made for the conciseness of the statements of the labors of Dr. Clarke in this place.

Clarke emphasized the importance of analysis in mineral chemistry, being as jealous, indeed, of all improvements in this direction as any of his predecessors, but he has published much upon the constitution of mineral bodies. In his own words:

A constitutional formula must fulfil several conditions. It must adequately express the composition of the mineral, covering all its variations; it must be readily applicable to the full discussion of analyses so that the different isomorphous salts which are commingled in a mineral species can be separately identified and given reasonable expressions; finally, it should indicate the relations between a species and the other minerals with which it is allied or into which it commonly alters.

Before the writer lies a beautiful specimen of black tourmaline. According to Clarke the micas seem to be most nearly akin to it, as he declares, "in each group we have to consider comminglings of isomorphous molecules and when tourmaline alters a mica is commonly the product of the reaction." The black tourmaline to which the writer has referred is the common iron tourmaline and from it have come muscovite and biotite.

If space permitted it would be interesting to follow Clarke in his further discussions of tourmaline, which has not yet been synthesized. He says all chemists who of later years have discussed the composition of tourmaline agree in giving the ratio 2:1 between silicon and boron, and offers a number of formulas which he regards as expressing the composition of the tourmalines. In them he assumes that tourmaline is a mixed salt, containing distinct boric and silicic radicals, while he is willing to admit that

future investigations may prove that it is really derived from a complex borosilicic acid as yet unknown, and the same conception may be true of other minerals, such as axinite, datolite, etc.* * * A series of borosilicic acids is theoretically conceivable and until that question has been considered, the constitution of all the minerals mentioned under tourmaline must be regarded as unsettled.

May not the suggestions of Sterry Hunt, Wolcott Gibbs, and others who have occupied themselves with the derivatives of complex inorganic acids be fraught with a great deal of import; which is

to say, that if these bodies which have been built up could be carefully worked out as to constitution, the methods adopted with them would enable the student of mineral chemistry to make decided advances in the deduction of the constitutional formulas of native complex products in the mineral world.

Considerable thought was given by Clarke to another extremely interesting mineral called "roscoelite," which he demonstrated as being essentially a vanadium muscovite. He modestly says:

This constitution seems to be fairly well established. If that view be correct then two-thirds of the aluminum content have been replaced by vanadium and that this replacement is altogether likely is demonstrated by the fact that true vanadium alums have been prepared.

Analcite is another mineral which has undoubtedly attracted thousands of persons interested in mineralogy. Many chemists have queried as to what its true constitution was, as so many different formulas, written in various ways, were said to represent it. It contains one molecule of water which seemed to be a disturbing factor, but in Clarke's hands this difficulty was surmounted and he concluded that its minimum molecular weight was represented by four times its empiric formula. The water in the mineral exists there as water only, not as hydroxyl, for the reason that it was extracted by heat without destroying the crystalline nucleus, the anhydrous salt, hence he adds:

If analcite, instead of being a metasilicate, is really a mixture of ortho- and trisilicate, then all of the analyses are intelligible. In nature analcite may be derived either from albite or from nephelite. * * * Its closest analogue, leucite, has yielded pseudomorphs of orthoclase and laeolite, while leucite and analcite are mutually convertible each into the other.

These examples indicate the problems pressing in from all sides in mineral chemistry. If the student of chemistry be desirous of engaging in the unraveling of profound chemical problems, he will find them in almost inexhaustible stores in that field. The keenness and far-sightedness exhibited by Clarke in the elucidation of this chapter command world-wide respect. Undoubtedly it was his devotion to this problem that led some years after to the preparation of "Data of Geochemistry," now in its fifth edition, a work that certainly is deserving of the study of chemists. It possesses astonishing merit. Whoever reads the chapter on metallic ores will turn from such a perusal with new thoughts on mineral chemistry. The number of syntheses which have been made in various parts of the world impresses one very deeply and cannot fail to inspire enthusiasm for the field of synthetic mineral chemistry. Would that more work of this nature might be done here in America!

Conclusion

But this story must stop. In the very brief and incomplete presentation of the vast achievements of five of the Past Presidents of the SOCIETY in mineral chemistry, during the lifetime of the SOCIETY, there is given a glimpse of the unsolved problems.

These five Past Presidents, Genth, Smith, Hunt, Hillebrand, and Clarke, were all teachers who inspired hosts of younger chemists; and, were the successes of the pupils of these masters combined with those of the latter, it might be truly said, so far as mineral chemistry is concerned, that they

“have placed our Nation's fame among the stars.”