Vol. XXVIII. [February, 1906.] No. 2.

THE JOURNAL

OF THE

American Chemical Society

## CHEMICAL RESEARCH IN AMERICA.[1]

BY FRANCIS P. VENABLE.

AT THE last meeting of the American Chemical Society, held in June at Buffalo, the secretary called for reports from various educational institutions as to the investigations then in progress in their laboratories. I was much struck by three things connected with these reports. The large number of institutions reporting, the wide field covered, analytical, inorganic, organic, physical, physiological, technical, and the high grade of the work. These reports promise to be one of the most interesting features of future meetings, and the thought how meagre such details would have been a decade or so ago has led me to devote this presidential address to a discussion of the progress in chemical research in America.

It is to be expected that a people, thinly scattered over a vast area of new and unbroken country, confronted with the problems and difficulties of a nation just emerging from its birth throes, would have little time to give to the arts and sciences, and yet the impetus from the wonderful discoveries of Priestley, Scheele and Cavendish and the splendid work of Lavoisier with his revolutionary deductions crossed the ocean and found its echoes in our wilderness. That Priestley, one of the greatest of these heroes of chemistry, should have been forced to flee from his native land and find refuge on these shores, and should have

[1] Presidential address delivered at the New Orleans meeting of the American Chemical Society, December 30, 1905.

continued his work here for a time, brought the great movement nearer home to us. It is a pleasure to note the appreciation of his work shown by the offer of the chair of chemistry in the University of Pennsylvania, the first institution in this country to show an active interest in the development of chemical science, and the first one to have a distinct professor of chemistry in the person of the celebrated Dr. Benjamin Rush, whose appointment dated from 1769.

This interest took active shape in the formation of the earliest known chemical societies. The Chemical Society of Philadelphia was "instituted" in 1792, forty-nine years before the founding of the London Chemical Society, the first one to be established in Europe. Its first president was Dr. James Woodhouse, professor of chemistry in the University of Pennsylvania, and Priestley was one of the members. Probably the most important paper brought before it was one by Robert Hare on the "Discovery of Means by which a Greater Concentration of Heat Might Be Obtained for Chemical Purposes." In this he announced his invention of the oxy-hydrogen blowpipe—called by him the "hydrostatic blowpipe." Hare was then only twenty years of age. Later he became professor of chemistry in the medical school of the University of Pennsylvania and had a distinguished career as an author and chemist.

In 1811 there was founded by "a number of persons desirous of cultivating chemical science and promoting the state of philosophical inquiry" the Columbian Chemical Society of Philadelphia. The patron was Thomas Jefferson, the president was James Cutbush, professor of natural philosophy, chemistry and mineralogy in St. Johns College, and the membership seems to have been drawn from a wider area, as we find among them Archibald Bruer, professor of mineralogy in Columbia College, New York; Thomas Cooper, afterwards professor of chemistry and president of South Carolina College; Edward Cutbush, professor of chemistry in Columbian University, Washington; de Butts, of the College of Maryland; Jackson, of Athens College, Ohio; Maclean, of Princeton; Silliman, of Yale; Troost, of Nashville; etc., truly a national society and the first national society with a distinguished roll of foreign members.

The Delaware Chemical and Geological Society was organized in 1821. It was much more local in character and soon died for lack of support.

The papers presented before these societies are largely discussions of the discoveries or views of European chemists or are of a speculative character. Analyses are reported and methods of analysis devised but synthetical research is lacking. Dr. Bolton, to whom I am indebted for the foregoing facts concerning the early America nchemical societies,[1] suggests various reasons for the absence of research, but it seems to me that there is sufficient explanation in the necessity for devoting thought and. strength to the development and building up of a new country and the small incentive to the search after truth for the truth's sake.

During the first quarter of the nineteenth century while European chemists were busied with atomic weight determinations, the testing of the law of multiple proportions, the extension of the list of elements and the multiplication of new compounds, the few American chemists who had access to laboratories were busied with the analysis of minerals and natural waters. It must be borne in mind that at this time there were no public laboratories either in this country or abroad to which students could readily find access. Universities did not provide laboratories for their students. Certain great teachers abroad, as Berzelius and Gay-Lussac, had private laboratories but it was extremely difficult for a young worker to secure admission. The available equipment in this country must have been meagre indeed. Even the illustration of chemical lectures by experiments was a rare thing. Liebig, in his autobiographic fragment, writes of the lectures which he heard in Paris in 1822. "The experiments were a real delight to me, for they spoke to me in a language which I understood and they united with the lectures in giving a definite connection to the mass of shapeless facts which lay mixed up in my head, without order and without arrangement." It was Liebig himself who a few years later at the University of Giessen opened to students the first public laboratory for research in chemistry.

In this country during the second and third quarters of the nineteenth century the American Journal of Science furnished an excellent medium for the publication of scientific papers. Established in 1816 by Benjamin Silliman at Yale University,

[1] This Journal, 19, 1717.

it stood for fifty years almost alone for the upbuilding of scientific investigation in America and can boast ninety years of great usefulness. Without some such journal there is little encouragement for research. The scientific man finds a keen delight in the search after truth, but he also loves to impart his discoveries to others and to win the commendation of those who can understand and appreciate his work, and there must be some arena upon which controversies can be fought out and truth winnowed from the chaff. The chemical contributions to the American Journal of Science have dealt largely with the analysis of minerals, meteorites and waters. This was especially true of the first few decades.

Schiffot Sentini[1] mentions as the first work in pure chemistry in America the formation of a compound of arsenious acid with potassium iodide. This was described in the year 1830 by J. P. Emmett. He obtained the compound in the form of a white crystalline powder by adding potassium iodide to a very dilute solution of arsenious acid, or potassium arsenite exactly neutralized with acetic acid. Emmett was professor of chemistry in the University of Virginia from its foundation in 1825 to 1842, one of the band of brilliant men brought over from England by Mr. Jefferson to aid in the upbuilding of his pet institution. With the exception of a few investigations by Robert Hare and the elder Silliman, which pertained rather to analytical, technical and mineralogical subjects, the communication of Emmett belongs to the earliest period of chemistry in North America.

It will scarcely repay us to linger over the years from 1830 to 1870. These were largely barren years. Not that chemical research was altogether lacking, but it was rather a dim and uncertain light beside the shining of such bright, particular stars as Dumas, Thénard and Marignac in France, Graham in England, Stas in Belgium, and Wöhler, Liebig and Kekulé in Germany.

One name stands out prominently during this period, conspicuous not merely because of the paucity of the work done by others but because of the sterling character of his own work. This is the name of J. Lawrence Smith. According to the elder Silliman the first piece of elaborate work or research in organic chemistry by an American was done by J. Lawrence Smith in 1842. Smith was a student of Emmett at the University of

[1] Ann. 228, 72.

Virginia, and a visit to Liebig's laboratory at Giessen formed the turning point in his life. His first organic research was entitled "The Composition of Products of Distillation of Spermaceti." In this he first made known the composition of spermaceti and set aside the views of Chevreul.

Smith was later professor of chemistry in the University of Louisiana, then in the University of Virginia and lastly in the University of Louisville where he furnished his private laboratory and did most of his work. He was an untiring worker and while much of his time was given to analyses of mineral and meteorites he was also a brilliant investigator. In analytical work we find him suggesting the use of potassium chromate for the separation of barium and strontium, and methods for the decomposition of silicates, especially the well-known method for the determination of alkalies. Only once or twice did he touch again upon organic chemistry, the subject of his first research. He contributed some sixty or seventy papers up to 1870 and his total contributions number one hundred and forty-five.

Besides the work of Lawrence Smith during this period some excellent work was done by Mallet at the University of Alabama, where he was professor of chemistry and chemist to the Geological Survey of Alabama. Here he made his first of that long and brilliant line of investigations upon the atomic weights—the first atomic weight work done in America. Following up the master work of Berzelius upon these constants, Dumas, Marignac and many others in Europe were busily engaged in making new determinations of them with all the accuracy possible from their improved apparatus and new methods. In his scantily furnished laboratory Mallet, a pupil of Wöhler, gave himself, so far as his many other duties permitted, to this exacting work, completing in 1856 his determination of the atomic weight of lithium from the chloride, and in 1859 the determination from the sulphate.

While not coming strictly under the head of researches it may be mentioned that some interesting speculations as to chemical theories were proposed by Cooke, of Harvard, and Lea, of Philadelphia, in the fifties, and we have Hinrichs' remarkable deduction of the fundamental principle of the periodic system that the properties of the chemical elements are functions of their atomic weights, drawn from the consideration of their spectra. The synoptical table of Gibbs, of Charleston, falls just beyond this period, but is interesting to all Americans as so closely paralleling the practically cotemporaneous work of Meyer and evidently independent of it.

In this diagram, prepared for his classes in 1872, he made use of the spiral very much as was done by de Chancourtois, Meyer and Mendeléeff, anticipating in a measure the work of Spring, Reynolds and Crookes. Further he anticipated some of the geometrical work of Haughton, observing that no linear equation can be constructed to give more than rude approximations of the atomic weights, and that to construct curves, two points of inflection or contrary curvature must be given. These are the serpentine cubics afterwards worked out by Haughton.

It is not a sufficient explanation of the barrenness of this period to say that laboratories and other facilities were poor. The absence of proper facilities had not proved a bar in the way of some of the greatest chemists of the century. The spirit of investigation was lacking in our colleges and few of the teachers had the necessary training for it. Very few indeed were those who had received an inspiration by coming in contact with the great masters of the science.

A few years after the close of the great civil war American students began flocking in large numbers to the German universities. A great many of them studied chemistry under the masters of the science such as Wöhler, Liebig, Fresenius, Kekulé, and Hofmann. The best laboratories and the most enthusiastic teachers were then to be found in Germany. The marvelous development of organic chemistry offered a most attractive field of research. Very little attention was given to this branch of chemistry in America before 1875, and the facilities for investigations in organic chemistry were very limited. Such work as was done was still chiefly in the line of mineral analyses or simpler investigations among the inorganic salts. The most important work was the determination of atomic weights, and Americans may well be proud of their contributions to the knowledge of these constants which can be worthily compared with those of any nation. Cooke, Mallet, Clarke, Richards, Morley, Edgar F. Smith and others have been the leaders in this work, to which some of the best laboratories were largely given up during the last quarter of the nineteenth century.

The hundreds of young chemists, trained in the best methods of the Germans and inspired by their contact with vigorous original thinkers, returning home, brought with them an enthusiasm and an impetus which has since placed American research well to the front. Those who had this training in the first half of the nineteenth century were comparatively few in number but they were practically the only ones who engaged in important investigations. Cooke, Mallet, Lawrence Smith and Wolcott Gibbs all studied in German laboratories.

Aside from occasional scattered papers by a student here and there the first institution to send out annual reports of researches undertaken in its laboratory was the University of Virginia. These were regularly reported by Mallet in the London Chemical News beginning with the year 1872, and have continued for thirty-three years. In 1877 the Johns Hopkins University began its work and scientific research became an essential function of every true university. From that year we may date the building up of the graduate departments of our larger, wealthier institutions and the setting into motion that immense force which is giving America its proper place among the learned nations of the world—a force which has made Germany what it is to-day. Looking back over the work accomplished it seems scarcely possible that this truly great event took place only a little more than twenty-five years ago.

In 1879 this University gave to the growing body of American chemists the first suitable journal for the publication of their researches. It is true the American Chemist, published by the Chandlers in New York, had made its appearance in 1871, but it had failed to secure the adherence and support of more than a small body of chemists and had too technical a tendency for general support. It had already passed out of existence two years before the American Chemical Journal appeared. From the beginning the distinguished editor of the latter Journal, our former president, Ira Remsen, President of Johns Hopkins University, and fully worthy of all honors which he has received, set a high standard, and for twenty-six years has maintained its excellence.

It is difficult to overestimate the influence of such a journal upon the development of research. At first the regular contributions came from a few laboratories only, notably the Johns Hopkins, Yale, Harvard, Pennsylvania, Virginia and Cincinnati.

Speedily the number grew until all parts of the country were represented and the valuable researches published placed the Journal on a plane with the best in the old world. It has thus done more to secure recognition for American research than any other one factor.

There was a crying need, however, for a strong well-organized chemical society. The memory of those early Philadelphia societies had faded out. The only common meeting ground for chemists was furnished by the sub-section of chemistry of the American Association for the Advancement of Science which did not rise, however, to the dignity of a section until 1881. It is true that this became one of the largest and most active sections of that association, gathering in annual meeting a hundred or more chemists. It is also true that certain local chemical societies were formed, but a national society was needed on the lines of the English or German or French societies. The social need for such a society for receiving and entertaining distinguished guests was especially felt during the centennial year, and so in 1876 the American Chemical Society was established in New York City. Though it failed to receive hearty support at first and the Journal appeared with discouraging irregularity and a woful paucity of pages, it grew surely and the need for it was increasingly felt. When the happy idea of local sections was evolved many of the difficulties arising from the vast territory covered by the Society disappeared, and a rapid growth ensued which has placed us in the forefront of national societies. The Journal of the Society in 1889 contained 158 pages. In 1904 the total number of pages exceeded 2300, nearly 1700 of these being taken up with original articles. The number of members of the Society is rapidly nearing the 3000 mark.

Besides the Journal of the Society and the American Chemical Journal other specialized journals have arisen and worthily represent American research. Among those may be mentioned the Journal of Physical Chemistry, the Transactions of the Electro-Chemical Society, the Chemical Engineer and others. The government scientific departments at Washington have contributed largely to the sum total of American research, and a vast amount of investigation in agricultural chemistry has been done in the laboratories of the agricultural colleges and experiment stations established in every state.

Some years ago it was humiliating to see how the work of American chemists was almost completely ignored by foreign investigators and writers. It is a source of pride to-day that we are pressing forward in every branch of pure and applied chemistry and hold a worthy place among those who are adding to the world's store of knowledge and extending the bounds of science. A distinguished European authority has lately testified to the growing strength of American research and the way in which this country is forging to the front. But the fact remains that in these hundred years and more America has produced no great chemist, no Lavoisier to develop a new chemistry, no Wöhler to break down old barriers and add a new realm to the science, no Liebig to revolutionize the agriculture and industries of a world.

In conclusion, let me plead for the encouragement of research among American chemists. I sometimes fear that the immense industrial development of the country will call away our strongest and most promising chemists to fields in which the material rewards are greater. And yet for the success of our chemical industries it is imperatively necessary that a large army of quiet workers should be busied in investigation, in the simple search after truths without a dream of the practical utilization of the results obtained. These are the men who patiently and laboriously forge the chain, link by link, that leads to some of the greatest economic changes, often changing the industries of a whole nation. It is chiefly in the laboratories of our colleges and universities that these investigators must be found. There alone can the necessary freedom of purpose, of view and of action be preserved. There alone is the truth all important and the money value unconsidered. No truth is insignificant, no fact is too trifling to warrant observation and careful accounting. It was in the laboratory of the University of Giessen that Liebig did his quiet work that made agriculture a science and made possible much of the comfort and luxury of the present day. It was Graebe and his discovery of synthetic alizarin in the laboratory of the University of Berlin which revealed the value of the almost useless coal tar and laid the foundations of Germany's great commercial growth. And many lesser cases might be cited. The governments of Europe vie with one another in fostering chemical research, Germany most wisely doing this in her universities. We as a nation cannot long afford to be behind them in this matter. In the close competition of the near future we must depend upon these toilers of the laboratories for our supremacy in the world's markets. But to my mind a far stronger plea for investigation lies in the inspiration which comes from such work, the broadening horizon and the fuller life.

What are the conditions necessary for chemical research and can we meet these conditions in most or all of our educational institutions? As the spirit of research seems to have developed with the increase in wealth of our larger institutions, many have come to regard research as a prerogative of these institutions and expensive equipment as a prerequisite to it. The idea is totally false and calculated to do much harm. It is accepted by many who hold positions in the smaller colleges as an excuse for their quietly sinking into a dull round of routine and unproductive drudgery. I do not believe that any teacher of science can keep fresh and enthusiastic and have a touch of inspiration about him unless he keeps in touch with nature through personal investigation of her facts and laws. And unless a teacher has these qualities he is not worth his salt and should not have the opportunity for dulling the originality of others. It too often happens that our young chemists, having completed their researches at some of the larger institutions, published their dissertations, won their doctorates and secured professorships in minor colleges, stifle their consciences with the excuse that they lack equipment or leisure, give up all idea of original work, settle down to a humdrum teaching of text-books and limit their ambition to drawing their meagre salaries and grumbling at their poor opportunities.

Let me tell you that which is no secret but is open to every one who has studied the history of the science, neither fine laboratory nor costly outfit nor abundant leisure are essentials for the search after nature's secrets. These are good and helpful things but the one essential is the earnest investigating mind, enthusiastic, determined and plucky in surmounting obstacles. A quiet corner, a little apparatus, some spare time snatched from a multitude of other duties, these will suffice to give any one the opportunity to show what is in him. If he fails to avail himself of it, it is a tacit confession to his lack of energy, or originality, or pluck. He need not grumble at his meagre salary. He is getting more than he is worth.

I do not mean to be unjust or harsh but when I think of the thousands of young men who year after year are subjected to deadening, uninspiring, humdrum teaching of science and are thus lost to the ranks of our workers, and of the possible brilliant, elect spirits among that number, I must cry out at the terrible waste. The field of knowledge is vast and growing vaster with the ever-widening horizon. The harvest is plentiful and the call for laborers is ever more insistent. It is necessary to impress this great truth that the true teacher must be a learner also, drawing constantly fresh inspiration from the fountain head.

---

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 8.]

## CONCERNING SILVER OXIDE AND SILVER SUBOXIDE.

BY GILBERT NEWTON LEWIS.

Received December 18, 1905.

ON account of the uncertainty as to the correctness of the value at present accepted for the electrolytic potential of oxygen, I have attempted to calculate this extremely important quantity by an indirect method. One of the important data needed in this calculation is the decomposition pressure of silver oxide at 25°. The determination of this pressure is the subject of the present paper. Incidentally it will be necessary to consider the question of the existence of the silver suboxide, which has been described by certain chemists.

LeChatelier[1] was the first to show the reversibility of the reaction,

$$2Ag_2O = 4Ag + O_2.$$

By the decomposition of silver oxide in a closed tube at 300° he obtained a pressure of 10 atmospheres. On the other hand, by heating silver at the same temperature in oxygen at 15 atmospheres he observed the oxidation of the silver. He therefore placed the decomposition pressure of silver oxide between 10 and 15 atmospheres.

Knowing this pressure for one temperature, and the heat of decomposition, it should be possible to calculate with the aid of the van't Hoff equation, the pressure at another temperature. Such a calculation, however, must be made with great caution.

[1] Z. physik. Chem. 1, 516 (1887).