The Development of Chemistry in the Nineteenth Century

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Lecture delivered at the annual festival of the Royal Veterinary and Agricultural College of Copenhagen on the 8th of March 1922 Translated from Naturens Verden 6 (1922) 145-154

It is an interesting coincidence that the beginning and end of the nineteenth century open and close a clear cut epoch in the evolution of chemistry. Lavoisier's famous text-book of 1789 may be said to introduce this period. Here for the first time we find in a text-book of chemistry a table of chemical elements closely resembling our present table, and for the first time we see the chemical compounds arranged according to the elements from which they are built instead of place of occurrence or properties. Throughout the nineteenth century order is introduced into chemistry by application of Lavoisier's new system based upon the conception of indestructible elements, and the period comes to a natural close, when Rutherford in 1903 demonstrated the transitoriness of radioactive elements and their transmutation into other elements with changed chemical properties. The task of reviewing the chemistry of this period is an attractive one, for the achievement of the nineteenth century chemists is magnificent. On the other hand one may well hesitate before the task of covering this field in a single lecture, for practically the whole of present day chemistry was developed in this period. However I shall try to give an outline.

Lavoisier's system set chemists the problem of determining the chemical elements in all matter from the plant, mineral and animal kingdoms. In the first decades of the 19th century this was the central problem. *Chemical analysis* dominated the field. It may be said that the century solved the problem of determining the qualitative and quantitative composition of all kinds of bodies. This included determinations of even the sun's and the fixed stars' compositions by the aid of spectral analysis. About the middle of the century the preparation of old and new compounds, *chemical synthesis* came into the foreground. Chemists have now synthesized, analyzed and described several hundred thousands of compounds.

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Towards the close of the century the interest in preparing new compounds ebbed away, except such as had special economic or scientific interest. On the other hand great efforts were now made to lay down laws for chemical phenomena, to express them in numbers and set them to equations. After analysis and synthesis followed the "mathematization" of chemistry. Theoretical or physical chemistry has already done important work in this field, but has undoubtedly left plenty for posterity to do. In the chemical laboratory of our college things have developed along the same line. Professor C. T. Barfoed, founder of the laboratory, cultivated analysis and wrote his classical text-books of analytical chemistry. His successor in the chair of chemistry Professor Odin T. Christensen was a synthetist and prepared a large number of new compounds of manganese and chromium. To-day we try in this same laboratory to make chemistry accessible to mathematical treatment. This is for instance our intention in work on the various factors which determine the acidity of soil.

The splendid achievements of the nineteenth century in analysis and synthesis would have been unthinkable had not the atomic theory made it possible to interpret the experimental material and to reduce it to order as it appeared. The nineteenth century can justly be called the age of atomic chemistry. Albeit the conception of matter as built of minute indestructible and indivisible atoms is an old one; but it was the famous work of Dalton in the first decade of the nineteenth century which transformed the atomic theory into a scientific hypothesis and made it valuable for chemistry. Dalton assumed that all atoms of an element are alike, and that chemical compounds are built of small identical assemblies of atoms, molecules he called them. From these assumptions he deduced the important laws which govern the quantitative composition of chemical compounds, and he taught us from the results of a chemical analysis to compute the composition of the molecule in terms of atoms. The chemical formula of the atomic theory in the hands of Berzelius proved to be the means to make oneself at home in the mass of results in quantitative analysis which gradually accumulated.

To day any keen first-year student can calculate the nitrogen content of salpeter and ammonium sulphate and he can compute, without special tables, the lime content of a sample of marl from the loss of weight when treated with hydrochloric acid. This is solely due to Daltons atomic theory.

But the atomic theory is very far from being limited to use in cases like those mentioned. It has been an indispensable guide in synthetic work. Chemistry has set up structural formulae in terms of atomic theory and through such formulae has obtained a comprehensive view of the reactions of compounds. Structural formulae show how the atoms are linked together in molecules. To the molecule of acetic acid we ascribe the following structural formula:

$$\begin{array}{ccc}
H & O \\
 & | & || \\
H - C - C - O - H \\
 & | \\
H
\end{array}$$

where H denotes a hydrogen atom, C a carbon atom and O an oxygen atom. The structural formulae are based on experimental knowledge of the behaviour of the compounds when they react chemically. Hence it is possible from the structural formula of a compound to deduce how it will behave when given the chance of reacting. When the reactions take place certain links in the molecule break, after which the fragments combine with molecules of another compound or perhaps with fragments of other molecules. When *bases* or *alcohols* act upon acetic acid the bond between oxygen and hydrogen (O and H) in the molecule is disrupted. *Chlorides of phosphorus* break the bond between carbon and the oxygen atom linked to a hydrogen atom. When acetic acid is heated with *lime* the bond between carbon and carbon is broken, and when *chlorine* reacts with acetic acid the hydrogen atoms linked to carbon are removed.

The system of structural formulae was created in the eighteen fifties. They summarize — in a very compact form — chemistry's knowledge of the creation and destruction of compounds. Nowhere in science has a shorthand notation been developed which summarizes such an abundance of exact knowledge in so small a space. Guided by these formulae chemists have not been content with synthesizing most of the compounds previously isolated from plants and animals. They have conjured up an immense multitude of new substances, drugs more curative and less poisonous than plant drugs, dyes faster and more brilliant than any previously known.

There are still species of vegetable and animal matter such as starch, cellulose and proteins, which have not been produced by the new magic of synthetic chemistry, but one feels sure that the achievement of their synthesis is only a question of time. Preliminary work on the elucidation of their structural formulae has been done, and when the structural formula of a compound has been established it is seldom long before its synthesis has been accomplished.

In the mathematization of chemistry the atomic theory has so far been of less use than one might have expected. In one respect it even proved a total failure. It has not contributed to our understanding of *chemical affinity*. But even if the nineteenth century has been compelled to leave the development of a complete theory of chemical affinity to the future, a preliminary system for the affinity phenomena based on energetics has been constructed. Julius Thomsen in 1852 put forward the hypothesis that the liberation of energy accompanying a chemical process was a measure of the chemical force of the process. This hypothesis has

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proved to contain a grain of truth, but as put forward the statement is only approximately true. In the years around 1880 it was shown that in order to obtain a true measure of the chemical force we must not take all the energy liberated in the process but only that part of the energy which is available as mechanical work. The chemical force of combustion of petrol is not its entire heat of combustion but the maximum work which can be performed by its combustion in an ideal explosion motor. The failure of the atomic theory when applied to chemical affinity made a group of chemists, led by Ostwald, think that the application of atomic conceptions as realities in chemistry was unwarranted. They sought to remove the symbols and conceptions of atomic theory from chemistry and took great pains to replace them by those of energetics. They did not speak of atomic weights and molecular weights but of equivalent weights and volume weights. They preferred the solid descriptions of energetics to the hypothetical conceptions of atomic theory and did not see that what they gained in confidence they lost in initiative. Because of the brilliance with which the school of energetics advocated its views it came to play a not unimportant rôle for a number of years. Our national adaptability both to good and to evil made its recruiting of proselytes here a matter of course. When I was a student it was fashionable to doubt the existence of atoms, even though such doubt was distressing. The advent of the electronic theory, the discovery of radium and investigations in the Brownian movement in the first years of the 20th century added a series of direct proofs of the existence of atoms to the circumstantial evidence previously amassed by chemists. Effects of processes taking place in single atoms were observed and atoms were counted. In 1908 even Ostwald himself had to admit the existence of atoms and the superiority of the atomic theory.

The vast amount of chemical facts and chemical theories which the nineteenth century produced could not fail to have effects in most of the provinces of human life. *The engineer* builds his structures from materials produced and often analyzed by chemistry. *The physician* diagnoses by methods of chemical analysis and cures with the products of chemical industry. *The physiologist* builds his science on chemistry and from the synthesis of organic chemistry he has learned to dispense with special vital forces as explanations. The *physicist* has taken over the atomic theory from chemistry and has been taught to work with pure substances.

The world war has revealed to us the military importance of industrial production of fertilizers and munitions.

To agriculture the development of chemistry has been of paramount importance. In 1840 Liebig developed from a chemical basis the main principles of a nutrition theory for plants and animals which still holds. His work was the foundation of a rational *science of plant fertilizers*. Chemical analyses were used to estimate the fertility of soils and the proper market value of fertilizers and feeding stuffs. The middle of the century was a time when it appeared as if chemistry could solve all problems of plant growth and animal husbandry. In the official report of the commission of 1855 concerning the erection of a Royal Veterinary and Agricultural College in Denmark, chemistry is dealt with in the following words: "It is unquestionably to this science that rural economy mainly owes the advances it has made in the last decades and from which we may expect essential improvements in agriculture in the future".

owes the advances it has made in the last decades and from which we may expect essential improvements in agriculture in the future". In the following years chemistry had however difficulties in living up to these intense expectations. Liebig's rationally composed mixed fertilizers did not have the expected effects and soil analyses did not yield adequate estimations of the fertility of soils. Only by degrees it was understood why chemical theories appar-ently failed, and it was slowly realized that chemistry was not to blame. The explanation of the results of soil analysis is that only such fractions of the plant nutrients in soil have fertilizing value as are sufficiently soluble to be absorbed by the plants. Efforts to estimate the *available* plant nutrients in soil by leaching with a suitable solvent proved futile for a long time but have lately given promising results after having been redirected by improved theoretical chemistry. Chemical analysis, however, is not the only branch of chemistry which has played a rôle in agriculture. The development of synthetic chemistry has also been important. Chemical factories have given to agriculture a series of excellent artificial ferti-lizers and remedies against plant diseases. But the development of synthetic chemistry has been detrimental as well as beneficial for agriculture. In several fields the synthetic products of chemical industry have entered into successful competition with products of agricultural plant growth. In the years before 1870 the beautiful red dye, with which for instance the red bunting of our Danish flag is dyed, came from madder roots grown in France. The cultivation of the madder plant brought to France an annual revenue amounting to 60 million Danish crowns. In 1869 Graebe and Liebermann found a method for making this red dye from anthracene present in coal tar, and within a few years German this red dye from anthracene present in coal tar, and within a few years German factories had destroyed the lucrative cultivation of madder in France. In 1897 the same story was repeated, this time with the indigo dye. Artificial indigo from German factories in few years ruined the indigo cultivation of India which had occupied one million acres of land and brought in an annual revenue equivalent to 70 million Danish crowns.

Over-imaginative writers have depicted a future in which the main products of agriculture, the starch- fat- and protein- containing foodstuffs had been replaced by synthetic products from chemical factories. It can however be said with confidence that in this field the 19th century chemistry will be unable to compete. It is, if I may say so, too clumsy. The 19th century chemists can synthesize organic compounds, but they work with much less agility than the living cells. They are unable to make artifical products which can bring about or accelerate chemical processes as easily as can the enzymes of the living cell. The 19th century has failed in its efforts to lift the veil from the secrets of enzymatic action. The running expenses of chemical factories are therefore high. Only those compounds present in very small percentages in the tissue of cultivated plants such as dyes, drugs, scents and stimulants whose agricultural production is very expensive, can at the present be produced more cheaply in factories than on farms or plantations.

A suitable problem for the chemistry of the nineteenth century is the production of a synthetic coffee extract. A German factory has devoted much work to the production of such an extract. The synthesis of coffein, the stimulating alkaloid in coffee, has been accomplished but, as far as we know, the problem of making the substance which is of paramount importance for the sale of the product, I mean the aromatic component, is still unsolved.

Another problem which most likely can be solved by 19th century chemical methods is the synthesis of the aromatic substance in butter. It is not a problem I would recommend to Danish chemists. If chemists could provide margarine factories with butter aroma as well as butter colour, the Danish production of butter would be seriously endangered, and if chemists also succeeded in synthesizing the vitamin of butter, the production would undoubtedly be doomed. So far, however, no work of that kind is known to me.

Time forbids going in detail into the deeply interesting subject of the effect of chemistry upon the pattern of culture, because I wish to say a few words of the general methods by which chemistry in the 19th century has obtained such striking results.

Characteristic of 19th century chemistry as of the culture of the 19th century in general is a strong critical sense. Experimental work as well as hypotheses have benefited from this criticism. In the preface to one of his text-books of analytical chemistry Professor Barfoed writes that he has himself tried out all specifications given in his text-books because "a written account too easily becomes marred by mistakes and inaccuracies if it does not arise from recent personal experience". Probably not many writers on chemistry have been as critical as that. At times the criticism of new hypotheses has been over-severe and clogging in its zeal for making chemistry a purely descriptive science free from assumptions. But the damage inflicted was small in comparison with the benefit, for it was criticism which made chemistry reliable.

In the excellent book on the philosophy of the nineteenth century just published by Professor Høffding, he sets forth the thesis that the most characteristic feature of the century consists in its being a time of realization and empirical

confirmation more than a time of creation. To me it appears that Høffding's thesis contains an underestimation of the original thoughts of chemistry (and physics) in the nineteenth century. Lavoisier's conceptions, his new system, mean a new departure for chemistry, and Daltons atomic theory is not a mere realization of thoughts from classical antiquity. It is a new-born theory; its elements are new and fundamental thoughts. Of course Lavoisier and Dalton built upon previous work. Everybody, even the greatest genius builds more or less upon previous work. New thoughts have in the nineteenth century infused new life into old conceptions. At no time in the history of chemistry has an explosive development started comparable to that of the early nineteenth century. In addition to calling the nineteenth century a time of realization Høffding speaks of it as a time of empirical confirmation. As for the second characterization I would prefer to call it an age of empirical decision. The century has not merely confirmed earlier views, but it has empirically found decisions where past centuries had stood at a loss. The age has for science been a manhood in which the vague and hazy dreams of childhood become achievements. From weak and tottering thoughts strong and general principles have been created. New thoughts have been conceived from which the twentieth century now is creating a new physics and chemistry.

The nineteenth century chemistry is not completely characterized by its critical sense and its faculty for infusing new life into old conceptions. It is also remarkable for perfect coordination in at least three distinct fields. Coordination of active work and contemplation has been remarkable. Never before has experiment and hypothesis been so happily united as in science in the nineteenth century. Science was not allowed to degenerate into "uninspired research" or into futile speculation devoid of reality.

Secondly the coordination of research and scientific education has been a fine achievement, highly advantageous for both. It was Liebig who created the type of laboratory in which the education of youth is coupled with original scientific research. It was the laboratories created by Liebig and his followers which moved the foci of chemical research from Sweden, England, and France to Germany and made the German universities centres of education for all the world's chemists.

Last but not least the coordination of science and technology, of theory and practice must be mentioned. This concerted action has developed in a capital way. New results obtained by chemistry have promptly been converted in industry into capital values. Industry and governments have therefore found it profitable to subsidize chemistry in order to facilitate its progress. As a consequence the number of chemists has multiplied and their facilities been increased. Technology has perhaps aided chemistry even more in an indirect way by supplying the necessary chemicals and apparatus. To-day industry supplies che-

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micals and apparatus better and cheaper than those made by the chemists themselves. Technology has provided chemical research with gas, water and electricity, efficient ventilation and drains, facilities the importance of which can hardly be overestimated. New and improved apparatus and accessories have appeared in such rapid succession, that for purely economic reasons it has been impossible for the laboratories to keep their technique up to date. The laboratories of Europe to-day are behind those of the United States of America. They must seek consolation and hope in remembering that progress in scientific work, in spite of all time-saving gadgets, largely springs from the underlying spiritual force and mental discipline.

Finally I would like to say a few words of the chemistry of the twentieth century and its relation to that of the preceding century. The new chemistry, which was born when Rutherford in 1903 showed us that our chemical elements are not indestructible, builds upon the chemistry of the nineteenth century. The new chemistry supplements the old chemistry, but it does not supersede it. The structure and constitution of atoms had been discussed in the nineteenth century but the new chemistry made it a burning question. Work by J. J. Thomson, Rutherford and our fellow-countryman Niels Bohr has with amazing speed substantiated a theory of atomic structure, according to which atoms are built of two kinds of "electrons": negative electrical particles with a mass equal to one two-thousandth of the mass of a hydrogen atom, and positive electrical particles with a mass equal to that of a hydrogen atom. The problem which the twentieth century now faces is that of reducing the properties of all substances to the properties of these two species of electrons and the laws of their interaction.

According to the views of Bohr it is possible, but extremely difficult and as yet far from realized, to calculate all the chemical and physical properties of an element from one characteristic whole number, the so-called atomic number of the element. When the goal is reached the properties of the elements will simply be mathematical functions of whole numbers from 1 to 92. In the views of Bohr a complete mathematization of chemistry is possible, but even when this has become accomplished, the chemistry of the nineteenth century will be indispensable. Let us remember that we go on adding and subtracting figures long after higher mathematics has developed new methods of calculation. We may be convinced that when the electronic theory has reached perfection the chemical formulae of the nineteenth century will still continue to be the ideal instrument of stating the composition of substances and of understanding their interactions.