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From September 15th to 17th of this year the "Kekulé Symposium on Theoretical Organic Chemistry" is to be held in London. It is therefore appropriate to devote a few words to Kekulé and his work in this journal and to explain why the symposium has been organized precisely this year and in London. I gladly undertake this task, but I shall necessarily have to be brief. About Kekulé a great deal has already been written, and in an eminent way, too. I would mention the very detailed biography by Anschütz[1] and the fine Kekulé Memorial Lecture by Japp[2].

Friedrich August Kekulé was born at Darmstadt (Grand Duchy of Hesse) on September 7th, 1829. He came of a distinguished Hessian family of officials; his father held high military rank in the Grand Duchy. As a pupil of the grammar school of his native town he showed great interest in science, but he attracted attention especially by his extraordinary ability at drawing. Thus it was not surprising that in 1847 he took up the study of architecture at the University of Giessen.

At Giessen, Liebig was professor of chemistry. Attendance at his lectures made Kekulé a follower of this branch of science. "Nicht die chemische Arbeit war es, die ihn in erster Linie anzog, sondern die Philosophie der Chemie", Anschütz writes very properly; strictly speaking, this remained true—I shall revert to this presently —throughout his life.

After a transition period at the "Höhere Gewerbeschule", the later "Technische Hochschule", at Darmstadt, where he engaged in practical work in the field of analytical chemistry, Kekulé started to study chemistry in real earnest at Giessen in 1848. Liebig naturally was his chief teacher; Kekulé gained his friendship and assisted him in his researches. On June 25th, 1852, the student took his doctor's degree on the basis of an investigation about "Amyloxydschwefelsäure" (pentyl hydrogen sulphate), which actually dated from 1850.

Kekulé had a stepbrother on the father's side, who had made a fortune as a merchant in London and who, in 1851, helped him to go

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abroad for a year. This was the first benefit, though still a very indirect one, which England conferred on him. Liebig advised him to go to Paris; "da erweitern Sie Ihren Gesichtskreis, da lernen Sie eine neue Sprache, da lernen Sie das Leben einer Groszstadt kennen, aber Chemie lernen Sie dort nicht." On the latter point Liebig was wrong. In Paris Kekulé became acquainted with, among others, Dumas, Cahours, Wurtz and Regnault and also with Gerhardt. The ideas of the father of the theory of types exercised a great and even decisive influence on him; numerous long conversations helped him to gain a survey of the whole of organic chemistry of that time and a key to a way through the maze of theoretical views pertaining to this part of science. Kekulé read Gerhardt's famous book, the "Traité de Chimie organique", while it was still in manuscript.

In December, 1854, after staying for about a year and a half at the castle of Reichenau near Chur in Switzerland as the private assistant of the owner, Dr von Planta, with whom he studied vegetable bases and analysed Swiss mineral waters, Kekulé left for England, to act—again on Liebig's recommendation—as assistant to Stenhouse at St. Bartholomew's Hospital, London. From his collaboration with Stenhouse, Kekulé derived very little benefit. His intercourse with Odling, and especially with Williamson, on the other hand, became of the utmost importance for him. As he himself later remarked, "Williamson drang auf klare Formeln, ohne Kommata und Kolbe'sche Schnallen oder Gerhardt'sche Klammern. Das war eine vorzügliche Schulung, die den Geist unabhängig machte". It may be said that in London Kekulé's mind matured fully. It was here that, in a way to be dealt with later, there came to him the ideas which were developed in particular in the first of the two papers that pre-eminently made for Kekulé's fame; *i.e.* here Kekulé's valency theory and his new views on the constitution of organic compounds were born.

In the autumn of 1855, after an unsuccessful bid for the chair of general chemistry at the recently instituted Zürich "Polytechnicum", Kekulé returned to Germany. Early in 1856 he qualified as an unsalaried lecturer ("Privatdozent") on organic chemistry at the University of Heidelberg. The place was well chosen; Bunsen as "ordinary professor" was, on the one hand, attracting many German and foreign chemists to Heidelberg, but on the other had turned away entirely from organic chemistry and plunged into problems of analytical, inorganic, and physical chemistry. A teacher of organic chemistry was therefore needed. But the latter had to perform his task in a laboratory rented and equipped by himself;

here again Kekulé's stepbrother in London supported him financially. The Heidelberg period, which lasted till 1858, was characterized by the development of the ideas brought from Paris and London, culminating in the paper referred to above, entitled "Ueber die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs". This most famous of Kekulé's papers was dated March 16th, 1858, and appeared in the issue of Liebig's *Annalen der Chemie*[3], published on May 19th, 1858. It is in order to celebrate the centenary of this paper that the Kekulé Symposium on Theoretical Organic Chemistry has been organized.

In 1858, through the intermediary of Stas, Kekulé became professor of chemistry at the University of Ghent (Belgium), where he stayed till 1867. He married there, but his wife died within a year, in giving birth to a son, Stephan, of whom Kekulé took care in a touching way. In scientific respects his period at Ghent was characterized in particular by the appearance of numerous instalments of the "Lehrbuch der organischen Chemie oder der Chemie der Kohlenstoffverbindungen", which contained theoretical views that were extremely advanced at the time (and for which a good deal of preliminary work had already been done at Heidelberg), and by the creation of the benzene theory; the second of the two papers which pre-eminently contributed to Kekulé's fame, entitled "Sur la constitution des substances aromatiques", appeared in 1865 in the *Bulletin de la Société chimique*[4]. As Anschütz has testified, "keine andere Abhandlung Kekulé's hat so grosses Aufsehen bei seinen Fachgenossen erregt, keine hat so unmittelbar die Entwicklung der organischen Chemie wissenschaftlich und technisch gefördert". It was soon followed by a long paper in Liebig's *Annalen*[5], which contained also experimental work in support of the new theory.

The last phase of Kekulé's life, and a long one, was formed by his professorship at the University of Bonn (Prussia). He took this post in 1867 and died at Bonn in 1896. Shortly before his death the genealogical investigations of his son, Stephan, had revealed that the Kekulés were descended of an old Bohemian noble family and they were received into the Prussian nobility under the name of Kekule von Stradonitz, the accent on the last "e" now being dropped. It was one of the numerous marks of honour of various kinds which Kekulé received. He himself preferred people to keep to the old name. "Lassen Sie's beim alten Pseudonym", he is reported to have said on one occasion. The family of Kekule von Stradonitz died out with the above-mentioned Stephan.

In the quantitative respect Kekulé's work cannot be called very

voluminous, especially if it is borne in mind that in his day editors of professional journals were not at all accustomed to press for briefness. This applies in particular to his period at Bonn, accordingly to almost the whole of the second half of his life. Other duties, ill-health, and domestic troubles due to his second marriage in 1876 undoubtedly contributed to his small productivity in this period. But the real cause of it lay deeper, and was to some extent hinted at by Kekulé himself during his address[6] at the "Benzol-Fest" of 1890: "Die schönen Tage sind längst vorüber. Von den verschiedenen Fähigkeiten des Geistes erlischt die Phantasie am ersten; ihr folgt bald, aber glücklicherweise langsam, das Gedächtniss; am längsten erhält sich die Kritik; . . . Ich könnte den jüngeren Fachgenossen nur rathen, in der Jugend fleissig zu sein". In his Heidelberg period already, *i.e.* before he was thirty, Kekulé shone like a star of the first magnitude in the chemical firmament. But long before middle age little was left of his genius, his imagination and his creative powers. It is significant that even his textbook, at which he had worked with such enthusiasm, was not continued at Bonn; the third volume, which appeared only in 1882, was written entirely by Anschütz and Schultz. The former states: "(Kekulé) behielt sich anfangs vor, die Köpfe der Hauptkapitel zu verfassen, überliess aber später auch diese Tätigkeit uns". On the basis of the results of Wilhelm Ostwald's studies on the biology of genius[7] it may be said that Kekulé was in a marked degree a scholar of the romantic and by no means of the classical type.

Kekulé was a theoretician, a philosopher rather than an experimenter. This appears already, for example, from the way in which, by his own testimony, he spent his days during his stay in Paris—endless conversations with Gerhardt formed the main item—or mapped out his days at Ghent. It is also clear from statements by Lothar Meyer and Adolf von Baeyer, both of whom were among Kekulé's first pupils, about their work in his laboratory at Heidelberg. "Kekulé . . . wirkte unter uns eifrig als Apostel der Typenlehre. Noch sehr lebhaft erinnere ich mich der damals Stunden und Tage lange geführten Debatten, in denen er Schritt für Schritt Boden gewann", the former has declared. Further this becomes quite evident when one examines the content of Kekulé's papers of an experimental nature; this is—especially in comparison with the theoretical papers, of which only a few of the most famous have been mentioned above—certainly not spectacular. There are, for example, groups of papers about carboxylic acids, about sulphonic acids, about benzene derivatives, and about piperidine and pyridine; it is, however, unnecessary to discuss this work in this short

essay. It is striking and significant that Kekulé did not achieve more in the experimental field, though especially at Bonn his fame might undoubtedly have attracted a host of collaborators.

Kekulé was above all things a thinker of great originality, whose interest and attention, in consequence of his natural gifts and initial studies, went out to speculations on the architecture of the molecules. The results of his speculative activity have been of inestimable value for the development of organic chemistry and, what is more, they have preserved their importance for this branch of science to the full down to the present day. It is therefore perfectly justifiable that the Symposium in London, with which is associated the name of Kekulé, is to be devoted to theoretical organic chemistry.

It is easy enough to describe Kekulé's enormous services to organic chemistry on the theoretical side in a few words quite generally. They consist in an extremely important share in the transformation of Gerhardt's type-formulæ into the planar structural formulæ which are still used so widely and successfully at the present day. The significance of this "revolution" in organic chemistry need not be demonstrated at length. The recognition of the true way of combination of the atoms in the molecule naturally led to a better understanding of the course of chemical reactions and to an improved possibility of predicting reactions. A powerful development of organic chemistry, and also of organic chemical industry, formed the logical and immediate consequence.

The main points in this "revolution" were a consistent use of the atomic weights C = 12, O = 16, S = 32, *etc.*, development of the valency theory, a good definition of the radical concept ("nichts weiter als die bei einer bestimmten Zersetzung gerade unangegriffen bleibenden Reste"), understanding of the nature of the varying "Basizität", *i.e.* the valency of the radicals, the conception of the quadrivalency of the element carbon, the introduction of the type ("Haupttypus") CH_4 by the side of the hitherto assumed types NH_3, H_2O and H_2, and the conception of the formation of chains of carbon atoms. It is the three last-mentioned points which are dealt with in the famous paper of 1858, the centenary of which is to be celebrated in London. They led to the assumption of double and triple bonds between carbon atoms and of rings of carbon atoms, and they led later to speculations about the structure of the aromatic compounds, to the benzene theory, *i.e.* to the conception of benzene as *cyclo*hexa-1:3:5-triene, which forms the subject matter of Kekulé's other famous paper published in 1865.

It is much more difficult, and within the compass of this short essay quite impossible, to separate Kekulé's share in this powerful

theoretical development of organic chemistry in an objective, *i.e.* scientifically correct, way from that of his predecessors and contemporaries. A few brief remarks will have to suffice here.

In the first place it should be stressed that Kekulé himself by no means invariably claimed complete originality for his ideas. He repeatedly mentioned others—in particular Gerhardt, Williamson and Odling—whose theoretical conceptions he acknowledged and praised, and used as the basis of his own ideas.

It should also be recorded that in 1855 the Englishman Odling had already recognized the type CH_4, on which he based discussions about radicals similar to those of Kekulé. According to Anschütz, Kekulé did not know the paper in question[8], which was not readily accessible; there is not the slightest reason to doubt this. However, in any case the priority has to be assigned to Odling.

Here the adage cited by Kekulé during the "Benzol-Fest" in 1890 in another connection was thus applicable: "Zu gewissen Zeiten liegen gewisse Ideen in der Luft". The truth of this adage also appears from the fact that, very shortly after the appearance of Kekulé's famous paper of 1858 and quite independently, the Scotsman Couper, working in Wurtz's laboratory in Paris, published a paper[9] in which analogous ideas about the quadrivalency of carbon and about the formation of chains of carbon atoms were proclaimed; Couper was the first to designate the bonds between atoms in the formulæ by dashes. Kekulé at once joined issue with Couper in order to defend his priority. It is curious to remember that, had Wurtz been less careless, Couper's paper would have appeared before that of Kekulé.

However, no one worked so comprehensively and with such great originality as Kekulé at the development of the *structure theory*—the term was introduced by Butlerow in 1861. No one else was able to propagate the new ideas with equal authority. Here Kekulé's didactic gifts, his talents as an author, a teacher and an orator, and his excellent and fascinating textbook played a considerable part.

The progress made in the course of about fifteen years was incredible. At the beginning of this period we find Gerhardt, who was firmly convinced that it would never be possible to know the structure of the molecules and considered his type-formulæ merely as reaction formulæ; the number of type-formulæ that could be assigned to a given compound was equal to that of the reactions by which it could be formed. A few years later a virtually complete structure theory was available, even though it still required an extension in the steric sense, and much later one on an electronic

basis, before arriving at the present structural formulæ, which are confirmed with the aid of modern physicochemical methods.

Of recent years it has been very persistently contended from the Russian side that it is not Kekulé or Couper, but the Russian chemist Butlerow, who has to be considered as the founder of the structure theory. This view is altogether mistaken, as appears, for example, from an interesting Dutch paper[10]. It will suffice to quote Butlerow himself; he wrote in 1859, in reviewing a paper by Couper: "Die von Couper erwähnte Vieratomigkeit des Kohlenstoffmolecüls ist schon von Kekulé angenommen worden; diesem letzteren Chemiker gehört auch die Priorität der Betrachtung der freibleibenden Affinitätseinheiten, wenn ein Theil derselben für die Bildung eines zusammengesetzten Molecüls verbraucht worden ist. . . ."[11] Butlerow, however, is undoubtedly to be given credit for having consistently applied and propagated the new ideas of Kekulé and Couper. "Ihm und Erlenmeyer verdankt man manche notwendige begriffliche Klärung und damit einen nicht unwesentlichen Anteil am Sieg der neuen Lehre", Richter[12] has rightly observed.

Finally, a few words have to be said about the mystical way in which the fundamental conceptions came to Kekulé. He himself made some statements about this in his address during the "Benzol-Fest" in 1890. A part of this may be quoted here in the original text*:

"Während meines Aufenthaltes in London wohnte ich längere Zeit in Clapham Road in der Nähe des Common. Die Abende aber verbrachte ich vielfach bei meinem Freund Hugo Müller in Islington, dem entgegengesetzten Ende der Riesenstadt . . . An einem schönen Sommertage fuhr ich wieder einmal mit dem letzten Omnibus durch die zu dieser Zeit öden Strassen der sonst so belebten Weltstadt; 'outside', auf dem Dach des Omnibus, wie immer. Ich versank in Träumereien. Da gaukelten vor meinen Augen die Atome. Ich hatte sie immer in Bewegung gesehen, jene kleine Wesen, aber es war mir nie gelungen, die Art ihrer Bewegung zu erlauschen. Heute sah ich, wie vielfach zwei kleinere sich zu Pärchen zusammenfügten; wie grössere zwei kleine umfassten, noch grössere drei und selbst vier der kleinen festhielten, und wie sich Alles in wirbelndem Reigen drehte. Ich sah, wie grössere eine Reihe bildeten und nur an den Enden der Kette noch kleinere mitschleppten. . . . Der Ruf des Conducteurs: 'Clapham Road' erweckte mich aus meinen Träumereien, aber ich verbrachte einen Theil der Nacht, um wenigstens Skizzen jener Traumgebilde zu Papier zu bringen. So entstand die Strukturtheorie".

*A translation of this and the following quotation is to be found in F. R. Japp's obituary notice, reference 2.

The insight he had gained in this way was committed to writing by Kekulé at the beginning of his residence at Heidelberg. He showed the paper to two of his friends: "Beide schüttelten bedenklich den Kopf. Ich dachte, eines von beiden ist noch nicht reif, entweder meine Theorie oder die Zeit, und legte das Manuscript in die Schublade". More than a year afterwards a paper by Limpricht induced him to rewrite and publish the paper, dated March 16th, 1858, in the issue of Liebig's *Annalen der Chemie*, which appeared on May 19th, 1858. It is perfectly natural to celebrate the centenary of this paper in London, for it was there that the foundations of it were laid in 1855.

A similar event led to the birth of the benzene theory. Again according to Kekulé himself, one night in 1865 the following happened at Ghent:

"Da sass ich und schrieb an meinem Lehrbuch, aber es ging nicht recht; mein Geist war bei anderen Dingen. Ich drehte den Stuhl nach dem Kamin und versank in Halbschlaf. Wieder gaukelten die Atome vor meinen Augen. Kleinere Gruppen hielten sich diesmal bescheiden in Hintergrund. Mein geistiges Auge, durch wiederholte Gesichte ähnlicher Art geschärft, unterschied jetzt grössere Gebilde von mannigfacher Gestaltung. Lange Reihen, vielfach dichter zusammengefügt; Alles in Bewegung, schlangenartig sich windend und drehend. Und siehe, was war das? Eine der Schlangen erfasste den eigenen Schwanz und höhnisch wirbelte das Gebilde vor meinen Augen. Wie durch einen Blitzstrahl erwachte ich; auch diesmal verbrachte ich den Rest der Nacht um die Consequenzen der Hypothese auszuarbeiten."

Obviously we have no right to doubt the truth of these statements, but the familiar saying, "se non è vero, è ben trovato", is bound to occur to many people.

On the other hand, it is to be noted that the snake biting its own tail had also played a part early in Kekulé's life. In 1847 he appeared as a witness in a trial for the murder of Countess Görlitz, who lived next door to his father at Darmstadt; this murder was coupled with a theft of jewellery, including a ring that consisted of two intertwined metal snakes biting their own tails. The incident in question made a deep impression on Kekulé and may have led to the famous dream.

It should not be forgotten that Kekulé was above all things a thinker, a dreamer, an artist, and as such was highly impressionable. Organic chemistry has every cause to be grateful for this; it has derived ample benefit from Kekulé's great talents.

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CONTENTS

KEKULÉ AND THE CHEMICAL BOND

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One hundred years ago Kekulé published a paper of great significance to chemistry. The concept of valence had been suggested by Frankland[1] in 1852. Five years later Kekulé[2] and Kolbe[3] extended the concept to carbon and said that carbon usually has the valence 4. Then in 1858 Kekulé suggested[4] that carbon atoms can unite with other carbon atoms to form chains. In the same year Couper independently discussed the quadrivalence of carbon and the ability of carbon atoms to form chains[5]. Couper's chemical formulas were much like the modern ones; he was the first chemist to use a line between symbols to represent the valence bond.

The term "chemical structure" was used for the first time in 1861, by Butlerow[6], who stated that it is essential to express the structure by a single formula, which should show how each atom is linked to other atoms in the molecule of the substance. He stated clearly that all properties of a substance are determined by its molecular structure, and suggested that it should be possible to find the correct structural formula of a substance by studying the ways in which it can be synthesized.

The simple ideas about valence and the chemical bond that were proposed one hundred years ago have been of inestimable value to science and to mankind. They grew, slowly but steadily, into the present chemical structure theory, which may be described as one of the most inclusive and powerful generalizations ever made by man about the nature of the universe.

We have become so accustomed to the power of chemical structure theory that it comes as a surprise (although it should not, because of the simplicity of the fundamental concepts and the difficulty of predicting the extent of their usefulness) that Kekulé presented his ideas with diffidence. He concluded his 1858 paper with the statement: "Finally I have to mention that I myself lay only small value on considerations of this sort . . . but these ideas seem to me to give a simple and rather general expression of recent discoveries, and perhaps their use will help in finding some new facts."

The picture of the chemical bond that was developed in greater

and greater detail from the consideration of the facts of chemistry during the period of sixty or seventy years after its discovery is an excellent one. It has been somewhat refined during the past forty years by the precise knowledge of molecular structure gained through the use of new physical methods of experimentation and through quantum mechanical calculations, but it has not been changed in any revolutionary way nor been replaced to any great extent by significantly different concepts.

There may be chemists who would contend that one innovation of great significance has been made (other than the use of two or more valence-bond structures to represent the state of a molecule; I consider this to be a significant innovation in chemical structure theory, rather than in the theory of the chemical bond)—the introduction of the σ,π description of the double bond and the triple bond and of conjugated systems, in place of the bent-bond description. I contend that the σ,π description is less satisfactory than the bent-bond description, that this innovation is only ephemeral, and that the use of the σ,π description will die out before long. Arguments supporting this contention will constitute the remainder of my address today.

It is likely that all of the important properties of the single bond have now been discovered. The last one to be discovered[7], the restriction of rotation about the bond, has been known for twenty-one years. A satisfactory theory of the potential barriers for single bonds has been delayed; only one year ago Wilson pointed out that none of the proposed theories could be said to be in satisfactory agreement with the experimental values[8]. An attractive idea is that bond orbitals are not cylindrically symmetrical, but are scalloped, with a trefoil cross-section for methyl carbon, and that maximum overlap and hence maximum bond energy correspond to the orientation that matches the trefoils. But this orientation gives the eclipsed configuration for ethane, which is known to be the unstable one; and, moreover, the theory of hybridization of bond orbitals leads to the conclusion that the best bond orbitals for unstrained single bonds are cylindrically symmetrical about the bond axis.

It now appears that the barrier is due to the exchange interactions (repulsions) of electrons involved in the other bonds (adjacent bonds) formed by the two atoms connected by the bond under consideration. This idea was suggested rather vaguely by Kistiakowsky, Lacher and Ranson[9] and more precisely by Pitzer[10], and has recently been given a detailed discussion[11].

If the bond orbitals of the carbon atom in ethane were sp^3 hybrids