

KEKULÉ MEMORIAL LECTURE *

(DELIVERED ON DECEMBER 15th, 1897.)

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THE great chemist whose life and work I shall endeavour to pass in brief review before you this evening, was not one of the popular heroes of science. Whatever may have been his qualifications for playing such a part—and surely, great natural eloquence, unfailing lucidity, and a humour that enlivened the discussion of even the driest subjects, are to be thus regarded—he apparently disdained to put them to so ignoble a use as the achievement of mere popular fame. He brought an intellect of incomparable power and subtlety to bear on problems so abstruse, so remote from the everyday thoughts and interests of mankind, that the vast majority even of educated persons have never heard either of the problems, or of the man who did so much to solve them. The greater, then, is the need that we, who realise both the direct scientific value of Kekulé's work and the furthering influence which, in spite of its apparent remoteness, it has exercised indirectly on the welfare of mankind, should place on record our sense of his high deserts.

Friedrich August Kekulé—he made use of only the second of his Christian names—was born at Darmstadt on September 7th, 1829.† His father was a Hessian *Oberkriegsrath*. Even as a boy, Kekulé displayed remarkable powers; at the Gymnasium of his native town he distinguished himself in mathematics and in drawing; whilst outside the school curriculum his instincts as an observer found congenial scope in the study of the flora and butterflies of the district. After passing the leaving examination at the Gymnasium in 1847, he determined, in accordance with his father's wish, to become an architect, and for this purpose entered as *studiosus architecturæ* at the University of Giessen. Kekulé, in later life, by no means regarded the time thus spent as wasted; he always laid stress on the turn which the study of architecture had given to his thoughts; on the necessity which he ever afterwards felt of having before him, if possible, an actual picture of any problem he was dealing with. He was doubtless right. After

* Chemical Society's Memorial Lectures, No. VII.

† For the facts of Kekulé's life I am indebted partly to two obituary notices: one by Wallach (*Naturwissenschaftliche Rundschau*, 1896, **13**, 437) and the other by Königs (*Münchener Medicinische Wochenschrift*, 1896, **39**, 920); and partly to Kekulé's well known address delivered before the German Chemical Society in 1890 on the occasion of the *Kekuléfeier*.

all, he remained an architect to the last: only it was the architecture of molecules, instead of that of buildings, with which it was his lot to concern himself.

In any case, chemists may feel thankful that Kekulé's architectural studies led him to the University, instead of into an architect's office. Liebig was then at Giessen; Kekulé attended his lectures on chemistry; and such was the fascination both of the lecturer and of the subject, that the young student resolved to abandon architecture and devote himself entirely to chemistry. His relatives insisted that he should take sufficient time to consider his decision; and he therefore returned to his native town, where he spent a semester studying at the Polytechnic School. At the end of that time he returned to Giessen and entered the University Laboratory as a pupil of Liebig and Will. His first research, carried out under Will's guidance, was an investigation of amylsulphuric acid and its salts, published in 1850. About this time, Liebig offered Kekulé an assistantship, which, however, he declined, as he was enabled, through the generosity of a stepbrother, a merchant in London, to study for a year in Paris. Here he remained from 1851 to 1852, attended Dumas' lectures, and made the acquaintance of Wurtz, Cahours, Regnault and others. Of most influence on the formation of Kekulé's views, however, was the friendship which he formed with Gerhardt, the originator of the type theory, whose great *Traité de Chimie Organique*, then just ready for the press, he was allowed to read in manuscript. On returning to Germany, he graduated as Doctor of Philosophy at Giessen in 1852. He then obtained his first appointment, that of private assistant to Baron von Planta, at whose beautifully situated château, Reichenau, near Coire, in Switzerland, he spent a year and a half. He published, jointly with von Planta, two papers on the action of ethylic iodide on nicotine and coniine, and some elaborate analyses of Swiss mineral waters; the latter work can hardly have been very congenial to Kekulé, who, as he afterwards said, was employing the leisure and freedom from distractions which his post afforded, in elaborating the ideas which he had found in Gerhardt's unpublished manuscript. In January, 1854, he exchanged his assistantship with von Planta for a similar post with Stenhouse in London. Here he became intimate with Williamson and Odling, both of whom, but especially the former, exercised great influence on the development of his ideas. He says:

"If in Paris I had an opportunity of acquainting myself with Gerhardt's unpublished views, I had now the good fortune to enter into active friendly intercourse with Williamson and to familiarise myself with the modes of thought of this philosophical intellect.

"Originally a pupil of Liebig, I had become a pupil of Dumas, Gerhardt, and Williamson: I no longer belonged to any school."

The training which Kekule received during these *Wanderjahre* was undoubtedly the best he could possibly have had for the task he was destined to perform. Suppose that, instead of going to Paris, he had been shortsighted enough to accept the assistantship which Liebig offered him. In that case he might have shared the fate of many promising students who have been promoted to be the assistants of their teachers; he might have gone on producing research work cut to a single pattern; he might have become a *Privatdocent* in the institution in which he was trained; and so on to the end of the chapter. Not that a man of Kekule's originality and strength of intellect could ever have been satisfied to play the part of a mere scientific hodman; but had he been hampered by a one-sided training, it might have been much longer before he discovered where his strength as a reformer lay: in fact he might not have discovered it at all until the brief period—the too brief period—during which the great creative geniuses of science really create, was in his case past. A Kekule trained solely in Liebig's laboratory would never have adopted the masterful attitude of the actual Kekule towards the doctrines of the school of Berzelius; and although he might have excited the ire of some of his opponents less, organic chemistry would have moved more slowly.

Kekule always emphasised the necessity for getting rid of preconceptions due to early training. "Free yourselves from the spirit of the school," he said; "you will then be capable of doing something of your own. Remember that it was Mephisto who gave the Scholar the advice:

Am besten ist's auch hier, wenn Ihr nur Einen hort
Und auf des Meisters Worte schwort."

A few months after his arrival in London Kekule published his well-known "Note on a new Series of Organic Acids containing Sulphur" (*Annalen*, 1854, 90, 309; *Proc. Roy. Soc.*, 1856, 7, 37—received April 5, 1854). This paper is noteworthy as the first published work of Kekule's which exhibits his distinctive modes of thought. Various passages contained in it clearly show that, although only briefly indicated, at least the germ of his later system, the linking of atoms in terms of their valency, was present to his mind. I will illustrate this more fully later on when I come to deal with Kekule's theoretical views. Meanwhile, in the present merely historical connection, the interesting passage from his speech delivered before the German Chemical Society (*Ber.*, 1890, 23, 1306) on the occasion of celebrations held in his honour, in which he describes the origin of the idea of the linking of atoms, may be quoted. The local colour should commend it to a London audience.

"During my stay in London I resided for a considerable time in Clapham Road in the neighbourhood of the Common. I frequently, however, spent my evenings with my friend Hugo Muller at Islington, at the opposite end of the giant town. We talked of many things, but oftenest of our beloved chemistry. One fine summer evening I was returning by the last omnibus, 'outside,' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie (*Träumerei*), and lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain, dragging the smaller ones after them, but only at the ends of the chain. I saw what our Past Master, Kopp, my highly honoured teacher and friend, has depicted with such charm in his 'Molekularwelt'; but I saw it long before him. The cry of the conductor: 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream forms. This was the origin of the *Strukturtheorie*."

Then he relates a similar experience of how the idea of the benzene theory occurred to him. This refers to a later period, when Kekulé was professor in Ghent, but may be quoted here in connection with the previous passage. He describes how he was at work one evening:

"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen," adds Kekulé, "then perhaps we shall find the truth . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding."

After his return from England, Kekule went to Heidelberg, where on February 29th, 1856, he obtained the *venia legendi* in Chemistry at the University. The young *Privatdocent* fitted up a modest laboratory consisting of a room with a kitchen adjoining it. Among the few students whom he could accommodate was Adolf Baeyer, who there carried out his well-known work on the organo-arsenic compounds. Kekulé himself prepared the experiments and most of the specimens for his lectures on organic chemistry. Generally the last item of his

hard day's work was the sweeping out of the class room against next morning's lecture.

The various investigations which Kekulé published about this time, excellent as they were from an experimental point of view, were still more remarkable for the theoretical conceptions which they embodied; indeed, in the latter respect, as every chemist knows, they inaugurated a new era in organic chemistry. The two papers on the constitution of mercuric fulminate (1857 and 1858); that on the so-called conjugated compounds and the theory of polyatomic radicles (1857), which contains a complete system of multiple types and mixed types based on this theory; those on the conversion of acetic acid into glycolic acid and on chloralide (1858) and finally, the celebrated paper "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon" (*Annalen*, 1858, 106, 293), which contained a full statement of Kekulé's views on the linking of atoms—the foundation on which our modern system of constitutional formulæ rests—attracted the attention of chemists throughout the world, with the result that, in 1858, Kekulé, on Stas's recommendation, was called as ordinary professor of chemistry to the University of Ghent.

It might have seemed that the inspiring influence of a great chemist and teacher had thus been lost to Kekulé's fatherland. But this was not the case. Thanks to the fact that in Germany a student need not have studied at the university at which he graduates, German students are attracted to teachers rather than to institutions; in fact, in their peregrinations from one university to another, they resemble the wandering scholars of former days. Many young Germans thus made the pilgrimage to Ghent to study under Kekulé: among their number Baeyer, Glaser, Hübner, Körner, Ladenburg, Linnemann and Wichelhaus.* Later on, these disciples, as teachers in the German universities, were instrumental in disseminating Kekulé's doctrines.

The nine years which Kekulé spent in Ghent were years of great productivity. In the theoretical papers which he had up to that time published, he had laid down the lines of his future work—nay, of the future work of the organic chemists of his generation. That work would consist in experimentally verifying the innumerable predictions, and in considering the further logical consequences, of his theory.

Of the investigations belonging to this period may be mentioned: those on organic acids, their basicity and hydricity (atomicity); on the relations between succinic, malic, and tartaric acids; on the isomeric unsaturated dibasic acids—fumaric and maleic acids on the one hand, and mesaconic, citraconic and itaconic acids on the other—a marvellous piece of experimental work, in which, however, Kekulé was less for-

* Among English chemists, Dewar and G. Carey Foster studied under Kekulé in Ghent.

tunate than usual in the interpretation of his results, although, considering the complexity of the problem, this was not to be wondered at; the conversion of hydroxy-acids into bromo-acids; the electrolysis of dibasic acids; the synthesis of acids of the benzene series by the replacement of bromine in bromobenzenes by carboxyl; the elucidation of the constitution of azo- and diazo-compounds, and the transformation of diazo- into azo-compounds. The theoretical work is of course for the most part involved in the practical and cannot be discussed apart from it. One piece of theoretical work must, however, be specially mentioned. It is Kekulé's benzene theory—the crowning achievement of the doctrine of the linking of atoms. Of this, more will be said later on.

A new system of chemistry is not a proposition in Euclid, to be proved in a few words; its proofs are cumulative, and its truth or error—or to speak more accurately, its expediency or in expediency—can be tested only by applying it to the whole body of the science. This is why so many of the great originators in our science have bent their minds to the task of writing a text-book. The text-books of Lavoisier, Berzelius, Gerhardt, Kolbe and Kekulé are cases in point.

The publication of Kekulé's *Lehrbuch der organischen Chemie* falls for the most part within the Ghent period. The first instalment appeared in 1859. The effect produced by the book was enormous. The facts of organic chemistry appeared to group themselves spontaneously under the new system. Whatever might be its ultimate fate, here was a method of exposition immeasurably superior to any that had preceded it; and as a result, every text-book of organic chemistry that has since appeared has shown more or less distinctly the influence of this remarkable work. Even Kolbe's accusation that the method owed its success to the fact that it saved chemists the trouble of thinking, may be regarded as indirect praise.

Kekulé's *Lehrbuch* was never finished. The first instalment of the third volume appeared in 1867—the year in which Kekulé left Ghent—after which further publication ceased for thirteen years. On one occasion, Kekulé received from his students an amusing reminder that they desired to see the continuation of the work. It was at a *Commerz* held at Bonn in the early seventies. For the benefit of those who may be unfamiliar with German academic customs, I may explain that the *Commerz* is a students' festivity in which the beer of the country plays an important part. Professors are frequently present by invitation, and just as, at the ancient *saturnalia*, the position of master and servant was reversed, so, at these mild modern *saturnalia*, there is a certain relaxation of the attitude of strict respect which the German student otherwise maintains towards his professor. Thus a professor may hear his work, or some literary or

other controversy in which he is engaged, playfully discussed in a set of occasional verses, or made the theme of a humorous dramatic interlude enacted by the students. On the occasion referred to, Kekulé, on taking his seat, found on the table in front of him what purported to be a complete, bound copy of the only partially existent third volume of his *Lehrbuch*. On closer examination it proved to be a box, in book form, containing writing materials. Kekulé enjoyed the joke, but declined to take the hint, at least for the time being. Later on, in 1880, with the collaboration of Anschütz and Schultz, he returned to the work; but with the conclusion of the third volume this second attempt also collapsed.

In 1867 Kekulé was appointed to the Professorship of Chemistry in the University of Bonn. Here he found himself at the head of a palatial laboratory, built shortly before from Hofmann's designs. During the first part of the time which he spent at Bonn his scientific activity continued, and he published various important researches, chiefly in collaboration with pupils. Among the numerous chemists who studied under Kekulé at Bonn may be mentioned: Anschütz, Bedson, Bernthsen, Carnelley, Claisen, Dittmar, Franchimont, van't Hoff, Klinger, Königs, G. Schultz, Thorpe, Wallach, and Zincke. The research work belonging to this period deals with the following subjects, amongst others: phenylmercaptan and phenylic sulphide (investigated jointly with Szuch); ethylbenzoic acid (with Thorpe); the formation of hydroxyazobenzene by the action of diazobenzene chloride on sodium phenoxide (with Hidegh); an aromatic glycolic acid—hydroxymethylbenzoic acid—(with Dittmar); the condensation products and polymeric modifications of aldehyde (with Zincke); the action of phosphorus pentachloride on sulphonic acids (with Gibertini and Barbaglia); on triphenylmethane (with Franchimont); the formation of cymene and cymyl hydrosulphide by the action of phosphorus pentasulphide on camphor (with Pott and Flesch), and of cymene by the action of iodine on oil of turpentine (with Bruylants); the constitution of the allyl compounds and of crotonic acid (with Rinne); and the well-known speculations on the constitution of isatin and isatic acid, which led, later on, to the synthesis of these compounds by Claisen and Shadwell. About the year 1876, however, Kekulé's physical powers began to show signs of failure, and for the rest of his life he practically never again enjoyed a continuance of good health. He aged prematurely and rapidly. Increasing deafness exercised a depressing effect upon him, and led him to shun the society even of his more intimate friends. Under these circumstances it is not surprising that the time which he devoted to his laboratory was greatly curtailed. There was still, however, an

occasional but unfailing incentive to research ; namely, the publication, by other chemists, of results which clashed with his theoretical views. In such cases, Kekulé's suspicions of the accuracy of the observations were at once aroused ; the work was carefully repeated and shown to be vitiated by some blunder ; in fact, the effect of the corrected work was generally to establish Kekulé's views more securely than ever. Cases in point are the re-investigation of Tanatar's "bioxyfumaric acid" and "trioxymaleic acid," which proved to be racemic acid and mesotartaric acid respectively, published jointly with Anschütz in 1880—81 ; of Gruber and Barth's "carboxytartronic" (dihydroxytartaric) acid in 1883 ; and of Carius' "trichlorphenomalic" (trichlor- β -acetylacrylic) acid, jointly with Strecker, in 1884. The whole of this work, both experimental and theoretical, is masterly, finished in all its details, worthy of Kekulé at his best. How the supposed "carboxytartronic" acid, up to that time regarded as a pillar of Ladenburg's prism formula for benzene, was shown to be dihydroxytartaric acid and to furnish fresh evidence in favour of Kekulé's hexagon ; how "trichlorphenomalic" acid, first discovered by Carius and furnished by him with a wrong formula and various self-contradictory reactions, then apparently abolished by Krafft, was finally rehabilitated, explained, and summoned as a fresh witness on behalf of the hexagon : these narratives are, to those capable of following them, of absolutely dramatic interest. Of this dramatic interest none was more conscious than Kekulé himself ; he calls the story of "trichlorphenomalic" acid a "Comedy of Errors."

Kekulé's premature physical decay was, therefore, entirely unaccompanied by any corresponding failure of his mental powers. These remained fresh to the last. Even up to a few months before his death, he would, when his strength permitted, discuss with his assistants problems connected with the recent progress of chemical science.

There is no doubt that Kekulé had presumed too much on a naturally strong constitution and had undermined it by excessive study in early life. In the speech already referred to, he admits as much. I will quote the passage and also that immediately following it, which contains much excellent advice to young students :

"I have faithfully followed the counsel which my old master, Liebig, gave me when I was a young beginner. 'If you want to be a chemist,' Liebig said to me when I was working in his laboratory, 'you will have to ruin your health ; no one who does not ruin his health with study will ever do anything in chemistry nowadays.' That was forty years ago. Is it still true ? I faithfully followed the advice. During many years I managed to do with four and even three hours' sleep. A single night spent over my books did not count ; it was only when two or three came in succession that I thought I had done

anything meritorious. At that time I had acquired such a fund of knowledge as to make my friends think that I was more trustworthy than the *Jahresbericht*.

"Those good days are long past. Of the various mental powers, imagination is the first to go; memory follows—fortunately, slowly; the longest to remain is the critical faculty, but this may still do good service, provided that it rests on the broad foundation of solid knowledge acquired by thorough industry. May I draw a moral? I would recommend my young fellow-chemists to be diligent during youth.

"One cannot explore new countries in express trains, nor will the study of even the best text-books qualify a man to become a discoverer. Whoever is content to follow well-laid promenades until he reaches some pleasant eminence frequented by tourists, may, by striking into the thickets, gather some forgotten flower; or, if cryptogams, mosses, and lichens satisfy him, may even bring home a well-filled vasculum; but anything essentially new he will not find. Whoever wishes to train himself as an investigator must study the travellers' original works; and that, too, so thoroughly that he is able to read between the lines—to divine the author's unexpressed thought. He must follow the paths of the Pathfinders; he must note every footprint, every bent twig, every fallen leaf. Then, standing at the extreme point reached by his predecessors, it will be easy for him to perceive where the foot of a further pioneer may find solid ground."

These words were spoken on the occasion of what, I believe, was Kekulé's last appearance before a public audience. The German Chemical Society had resolved to celebrate the twenty-fifth anniversary of the publication of Kekulé's benzene theory. To this end they held, in his honour, on March 11th, 1890, a festival of a magnificence perhaps unparalleled in the history of science. Chemical Societies in all parts of the world—our own, as the oldest, heading the list—united in sending delegates with addresses of congratulation. A portrait of Kekulé had been painted by H. von Angeli at the instance of the German coal tar colour manufacturers, who had adopted this means of testifying to their sense of the influence which Kekulé's theoretical views had exercised in furthering their branch of chemical industry; this portrait, which is now in the National Gallery in Berlin, was unveiled on that occasion. The President of the Society, A. W. von Hofmann, delivered one of these felicitous addresses of which I fear that the secret, so far as chemists are concerned, has died with him: in it he sketched the history of benzene from the time of its discovery as "bicarburetted hydrogen" by Faraday up to the point when Kekulé appeared, to "pluck the heart out of its mystery." Then

cavil, the culminating point of the day's proceedings, striking as these had been. It was the personal utterance of a man whose utterances had hitherto been confined mainly to the exposition of the impersonal facts and theories of his science. It was modestly autobiographical; it traced the growth and training of the speaker's powers; it afforded a glimpse into his intellectual workshop. Needless to say that it produced a profound impression. I have already given copious extracts from this speech; I only wish that time permitted me to quote the whole. It should be read by every one who desires to understand Kekulé's character and influence.

On the day preceding these celebrations, Kekulé communicated verbally* to the German Chemical Society, at the ordinary meeting of March 10th, 1890, the results of the last scientific investigation on which he was ever engaged. It was an experimental proof of the absence of a para-bond in pyridine, and was doubtless intended to have an indirect bearing on his benzene formula.

A chill which Kekulé received in April, 1896, on a journey to Cassel, told on his already weakened system. The state of his health began to occasion the gravest fears. At the same time symptoms of heart disease manifested themselves. However, his health again improved; but just when the immediate danger appeared to have passed over, he succumbed to failure of the heart's action on July 13th, 1896.

Kekulé's merits never lacked recognition. He was a member of most of the European academies and other learned societies. He was elected a Foreign Member of our own Society in 1862, and of the Royal Society in 1875. He received the Copley Medal in 1885, and the Prussian *Ordre pour le Mérite* in 1895. The present German Emperor, who, during his period of study at Bonn, was a pupil of Kekulé, revived an old title of nobility which Kekulé's family had formerly borne; and during his later years the great chemist signed himself Kekule† von Stradonitz. Posterity, however, will probably prefer to know him by the name under which the work of his life was published.

Great as were Kekulé's powers as a thinker and an investigator, it is no exaggeration to say that he was equally distinguished as a teacher, whether in the lecture room or in the laboratory. His speech was of extraordinary ease and precision. His lectures, which were delivered, so far as my recollection goes, without notes, might have been published in the form in which they were spoken. His

* The memoir does not appear to have ever been written; at all events it was not published in the *Berichte*. A statement of the interesting results obtained, privately communicated by Kekulé himself, is, however, to be found in Anschütz's edition of Richter's *Organische Chemie*, 2, 1896, pp. 518—520.

† The acute accent on the final *e* is dropped.

ideas were always ready at his call ; thus when, in directing the work of research students, the chances of an investigation brought him upon some subject which he could not possibly have been previously considering, his exposition was as sure and as logical as in his set lectures, and save that he naturally made much freer use of colloquialisms, might, like the lectures, have been written down as it stood. The effect of his discourse was heightened by a natural play of humour, of a somewhat dry and caustic type, for the exercise of which the opinions of scientific opponents and the blunders of students equally afforded scope. He was invariably fresh and stimulating ; one detected no trace of that listlessness which is so frequently the bane of speakers who are compelled to lecture year after year on the same theme to what is practically the same audience of average students. He had, moreover, the advantage of a striking personal appearance ; and his face, ordinarily of a grave and reflective cast, lighted up when he spoke. His laboratory teaching, in which, during his later years at all events, he devoted himself almost exclusively to directing the work of research students, was remarkable for the way in which he endeavoured to awaken independent thought in the student ; thus he did not dictate a particular course to be carried out blindly by the student, and resent any suggestion as an impertinence—a method of teaching not unknown in some laboratories where the output of research work is possibly in excess of its educational value ; on the contrary, he was never better pleased than when a student was full of suggestions, which he would spend much time in patiently listening to and criticising. The one thing which he never pardoned in a student was want of interest in his work ; such a student was, for the future, quietly ignored.

If one compares Kekulé's published experimental work with that of many other eminent chemists among his fellow-countrymen—with that, for example, of Liebig, or Wöhler, or Hofmann—one is struck by its much smaller volume. His ill-health affords only a partial explanation. Although no one acquainted with Kekulé's extraordinary powers of work would dream of taxing him with indolence, yet the whole of his career unmistakably showed that with him work was a means and not an end. He began by formulating certain important theoretical conceptions, and he then, for a time, exerted himself to verify them experimentally. But when he saw that his ideas had taken root, and that hundreds of willing disciples were engaged in this task of verification ; when he realised that only by such general co-operation could the work be brought to a successful issue ; he contented himself, for the most part, with looking on and criticising. As he said, the critical faculty was, of the various mental powers, that which survived longest. His criticism, as we have seen, frequently took the

useful form of the correction of inaccurate observations. Again, with a view to disseminating his doctrines, he began to write his text-book. But long ere the text-book was finished, it had done its work; the doctrines were almost universally received; and the text-book remained a noble fragment.

After all, Kekulé's supreme merit lies in his contributions to theoretical chemistry. There is, here as elsewhere, a necessary division of labour, and it is irrational to complain that the intellectual gifts of a Kekulé do not include those of a Hofmann—that a Lavoisier is not also a Scheele.

It now remains to consider, somewhat more fully than has been possible in the course of the foregoing brief sketch of Kekulé's life, the main features of his theoretical work. But here a two-fold difficulty arises.

Kekulé's greatest achievements in theoretical chemistry are: the doctrine of the linking of atoms in terms of their valency, and, growing out of this, the theory of the structure of organic molecules, both in open-chain and in closed-chain compounds. Even the youngest branch of these theories—that dealing with the structure of closed-chain or cyclic compounds—has been before the world more than thirty years. Moreover, they are not recondite theories, hidden away in the depths of the science; on the contrary, they are organic chemistry itself, and our students learn them on their first introduction to the subject. In addressing an audience, therefore, of expert chemists, what new thing can be said on these well-worn themes?

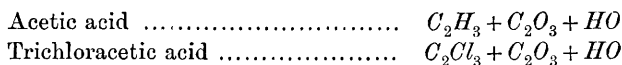
The only admissible course is to take up the question of origins. Here the second difficulty presents itself.

Great theoretical conceptions are not created out of nothing. Not only is, in most cases, the substratum of experimental or observational fact on which they rest previously on record; but later historical research generally discloses the presence, scattered throughout the literature of the subject, of anticipatory germs of the theories themselves. This commonplace in the history of science finds expression in the saying that "the theory was in the air." Hence arise the innumerable claims to priority, with some of which I fear I must deal on the present occasion.

As a preliminary to the discussion of the theoretical conceptions which we owe to Kekulé, it will be necessary to consider briefly the state of organic chemistry at the time when he came upon the scene.

The dualistic electro-chemical theory elaborated by Berzelius, which for many years had dominated the entire field of chemistry, had, so far as organic chemistry was concerned, fallen before the attacks of

Dumas, Laurent, and the other supporters of the doctrine of substitution. In 1842, Melsens showed that trichloroacetic acid could be reconverted into acetic acid; and Berzelius, compelled at length to admit that the two compounds belonged to the same class, made a noteworthy concession to the doctrine of substitution. Unable to accept without qualification the view that elements so widely separated in the electro-chemical scale as hydrogen and chlorine could mutually replace one another in compounds without materially changing the properties of the latter, he devised the doctrine of conjugated compounds, and limited the operation of this process of substitution to the conjuncts. Thus acetic acid and trichloroacetic acid were conjugated oxalic acids in which the respective conjuncts were C_2H_3 and C_2Cl_3 ;



According to Berzelius, the replacement of hydrogen by chlorine, as long as it was confined to the conjunct, did not materially change the properties of the compound.

This limitation of the action of substitution to the conjuncts, and indeed the entire theory of conjugated compounds, has generally been looked upon as an unconscious subterfuge, adopted by Berzelius to cover his retreat. I think, however, that, regarded even from the standpoint of our modern electro-chemical theories, the limitation appears a perfectly legitimate one. The error in Berzelius' original system was an error of excess: it had arisen from applying conceptions drawn from the behaviour of electrolytes, or ionisable compounds, to non-electrolytes, or non-ionisable compounds. In making the limitation just referred to, Berzelius merely withdrew the previous undue extension of his system, whilst retaining the portions which still held good. It is precisely when a halogen atom replaces hydrogen of the conjunct—that is, of the hydrocarbon radicle of a compound—that it is not ionisable; and it is only when the substituents are non-ionisable that the Dumas-Laurent statement of the law of substitution is valid. I mention this, because it appears to me that, in this matter, Berzelius hardly received justice from his opponents. Kekulé, for example, ridiculing Berzelius' change of front, says (*Lehrbuch*, 1, 74—75): "That which had been absurd as long as it was regarded without any hypothesis, became 'surprisingly clear and simple' when seen through the medium of the hypothesis of the conjuncts . . . In his joy over the conjuncts, he [Berzelius] had forgotten that his object was to combat the theory of substitution."

The chief point, however, is that Berzelius and his school were thus compelled to abandon their doctrine of the unchangeable nature of compound radicles.

Kolbe, the great continuator of Berzelius' system, adopted and extended this doctrine of the conjuncts. At the same time he introduced the conception of more complex radicles (*nähere Radicale*) which were built up from simpler radicles (*entferntere Radicale*). Thus, according to Kolbe, acetic acid contains a conjugated radicle, $C_2H_3\text{---}C_2$ (called by Kolbe "acetyl") consisting of carbon conjugated with methyl; this unites with oxygen to form $C_2H_3\text{---}C_2O_3$, acetoxyl; and the latter in turn combines with water to form acetic acid, $C_2H_3\text{---}C_2O_3.HO$. This view of the constitution of acetic acid is, as will be seen, not far removed from that now held; it clearly indicates that one half of the carbon in the molecule is present as methyl, whilst the other half serves to satisfy the affinity of oxygen.

Kolbe's extraordinary power of expressing chemical reactions in terms of chemical constitution was unfortunately coupled with an almost complete inability to realise the force of arguments drawn from physical laws. One result was that until 1870 he continued to use Gmelin's equivalents instead of our present atomic weights. There can be little doubt that this both hampered his efficiency as an investigator and prevented his theoretical views from being received at their full value. Kolbe, however, afterwards contended that his mistaken adherence to the old equivalents had facilitated his discovery of the constitution of acids, aldehydes, and ketones, and his prognosis of secondary and tertiary alcohols.

Thanks mainly to the conceptions of chemical structure which we owe to Kekulé, we can, looking back on the disputes which raged round the radicle theory, perceive where truth lay, and where error; nay, we can often see that, of two competing rational formulæ, both were right, each affording a partial glimpse of a truth which afterwards found its fuller expression in the structural formula of the compound. But Kekulé's predecessors were not in this position, and it is not surprising that the manifold hypotheses, and the contradictions, real or apparent, of the radicle theory led many to regard the problem of the constitution of chemical compounds, at least in the sense in which the supporters of this theory understood it, as insoluble.

Gerhardt was one of those who held this view, and in his earlier exposition of his "unitary system" (1848) he employed empirical formulæ only. His chief efforts were at that time directed to representing the various chemical compounds by comparable quantities—their molecular weights—and for this purpose he selected as his unit the molecular weight of water, the formula of which he wrote H_2O . He employed our present atomic weights for carbon, oxygen, sulphur and their analogues; but somewhat misleadingly called these atomic weights "equivalents."

The difficulty of dealing with organic compounds by means of empirical formulæ alone, led Gerhardt to extend his original system, and to introduce into the formulæ certain atomic groups which he termed "residues." When two compounds interact, eliminating jointly the elements of water or of some simple inorganic compound, the two residues of the original compounds combine. Thus, in the formation of nitrobenzene from benzene and nitric acid, water is eliminated, and the "benzene residue," C_6H_5 , unites with the "nitric acid residue," NO_2 . The so-called residues were thus in many cases identical with the old radicles (leaving out of account the fact that Gerhardt used the new atomic weights), and the system was an attempt to secure the benefits of the radicle theory whilst avoiding its more or less hypothetical basis. The way was thus paved for the union of the radicle theory with Dumas' type theory, the outcome of which union was Gerhardt's type theory.

As regards the latter theory, the idea of the ammonia type was furnished by the researches of Wurtz and Hofmann (1849-50) on the substituted ammonias, in which 1, or 2, or 3 hydrogen atoms of the original ammonia molecule were replaced by alcohol radicles. Williamson (1850) showed that alcohol and ether might in like manner be derived from 1 mol. of water by the replacement of either 1 or 2 hydrogen atoms by such radicles; and in the following year (1851) he adopted a similar view in the case of the acids; thus, he regarded acetic acid as 1 mol. of water in which a hydrogen atom is replaced by acetyl, C_2H_3O . Shortly afterwards (1852), Gerhardt, applying to the monobasic acids a method analogous to that by which Williamson had effected the synthesis of ether, obtained acetic anhydride and its analogues, which were thus shown to stand in the same relation to the monobasic acids as the ethers to the alcohols.

When once it had been recognised that organic compounds might be derived by substitution (double decomposition) from simple inorganic compounds like water and ammonia, and might therefore be formulated on the *type* or pattern of these, the process of finding other simple inorganic compounds which should serve a similar purpose and so complete the type theory, was a tolerably obvious one. Gerhardt selected, as his four types, hydrogen (free hydrogen was, according to the Laurent-Gerhardt view, a compound, H_2), hydrochloric acid, water, and ammonia. The typical formulæ were not intended to indicate the constitution of the compounds as the term was understood by the adherents of the radicle theory. If two compounds belonged to the same type it meant merely that they had in common certain functions and certain modes of formation and decomposition.

The idea of valency, both of elements and of compound radicles, had already been propounded. In his well-known paper "On the

Constitution of Salts" (1851*), Williamson points out that certain compound radicles, such as C_2H_3O and NO_2 , can replace 1 atom of hydrogen in 1 mol. of water, giving rise to monobasic acids; whilst others, like CO , C_2O_2 , and SO_2 , can replace 2 atoms of hydrogen in 2 mols. of water, yielding dibasic acids. That the linking function of these dyad groups was clearly present to his mind is shown by the following passage (this Journal, 1852, 4, 353) in which, speaking of Wurtz's decomposition of ethylic isocyanate by potassium hydroxide, he says: "One atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, *holds together* the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\begin{smallmatrix} (CO) \\ K_2 \end{smallmatrix} O_2$, carbonate of potash." This important passage contains the earliest statement of the fact that a double type (here the double water type) is possible only when the compound contains a dyad radicle. Later on, in 1854, Williamson (*Proc. Roy. Soc.*, 7, 11) showed that, by the action of phosphorus pentachloride on sulphuric acid, sulphuryl chlorhydrate and sulphuryl dichloride could successively be obtained, thus proving sulphuric acid to have the formula $SO_2(OH)_2$ which he had previously assigned to it, but which had been called in question by Gerhardt. In the same year he prepared, jointly with his pupil Kay (*loc. cit.*, p. 135), the tribasic formic ether (ethylic orthoformate), $CH(OC_2H_5)_3$ by the action of chloroform on sodium ethoxide, and pointed out that it was "a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform." About the same time, Odling (this Journal, 1855, 7, 1) extended Williamson's views on the constitution of salts and assumed the presence of a triad radicle PO''' in the acids of phosphorus: thus orthophosphoric acid was formulated on the triple water type as $\begin{smallmatrix} PO''' \\ 3H' \end{smallmatrix} \} O_3$. And just as Williamson had shown that the dyad group SO_2 could unite two water residues to form sulphuric acid—a double water type—so Odling employed this same group to unite together a water residue and a sulphuretted hydrogen residue to form thiosulphuric acid—a mixed type; he formulated sodium thiosulphate $\begin{smallmatrix} SO_2'' \\ 2Na' \end{smallmatrix} \} O'' + S'$. He thus laid down the conditions under which a mixed type might exist: namely, when the molecule contains a polyad radicle capable of holding together the various residues.† In the same

* First published in the *Chemical Gazette* for 1851; afterwards reprinted in full in the *Journ. Chem. Soc.*, 1852, 4, 350.

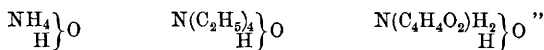
† Ladenburg (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 232) credits Gerhardt and Chiozza with having, in 1854, derived succinamic acid from the mixed type $NH_3 + H_2O$ in which the two residues were united by the dyad radicle succinyl. In that case these chemists would have anticipated Odling in showing how mixed types

year, Berthelot showed that glycerol formed ethereal salts containing 1, 2 and 3 radicles of a monobasic acid, a result which Wurtz correctly interpreted as proving that glycerol was a trihydric alcohol $\left. \begin{smallmatrix} \text{C}_3\text{H}_5''' \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_3$, formulating it on the triple water type. From this Wurtz was led to foresee the existence of a class of dihydric alcohols, the first member of which, glycol, $\left. \begin{smallmatrix} \text{C}_2\text{H}_4'' \\ \text{H}_2 \end{smallmatrix} \right\} \text{O}_2$, he prepared in the following year (1856). Chemists were thus beginning to familiarise themselves with the idea of polyvalent compound radicles of different hydrogen-replacing power.

In the memoir just quoted, Odling employs his well-known valency marks to indicate the valency not only of compound radicles, but also of elements. The conception of a valency of the elementary atoms was introduced into chemistry by E. Frankland in 1852. As Frankland's claims in this respect have been called in question by at least one member of the Kekulé school and were never openly acknowledged by Kekulé himself, I will quote the original passage more fully than would otherwise have been necessary. It occurs at the end of a paper "On a New Series of Organic Bodies containing Metals" (*Phil. Trans.*, 1852, 417). Frankland, who up to that time had been a follower of Kolbe, now criticises unfavourably Kolbe's doctrine of conjugated compounds. After referring to Kolbe's view that cacodyl is "arsenic conjugated with two atoms of methyl, $(\text{C}_2\text{H}_3)_2\text{As}$ " (Frankland uses Gmelin's equivalents in this paper), and pointing out that the various organo-metallic compounds obviously belong to the same class as cacodyl, he proceeds (*loc. cit.*, p. 439):

"It is generally admitted that when a body becomes conjugated, its essential chemical character is not altered by the presence of the conjunct: thus for instance, the series of acids $\text{C}_n\text{H}_n\text{O}_4$, formed by the conjunction of the

should be formulated. What they really say, however, is: "Succinamic acid represents the hydrate of an ammonium in which 2 atoms of hydrogen are replaced by their equivalent of succinyl:



(*Compt. rend.*, 1854, **38**, 458), which is a very different matter. Ammonium hydrate is here formulated on the water type, and succinyl replaces two atoms of hydrogen in ammonium: it does not link two residues together. Bearing in mind that, in Part 4, vol. 4 of the *Traité*, Gerhardt formulates the ammonium compounds with pentad nitrogen, it would seem that Ladenburg has read into Gerhardt and Chiozza's formulæ a meaning that was not present to the minds of the authors.

Gerhardt had not grasped Williamson's principle that polyvalent radicles are necessary to link together the residues in multiple types, and in Part 4, vol. 4 of the *Traité* he frequently writes formulæ that are quite at variance with it: thus $\left. \begin{smallmatrix} \text{C}_3\text{H}_5\text{O} \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_2$ for glycerol; $\left. \begin{smallmatrix} \text{C}_7\text{H}_5 \\ \text{H}_3 \end{smallmatrix} \right\} \text{N}_2$ for hydrobenzamide.

radicals $C_nH_{(n+1)}$ with oxalic acid, have the same neutralising power as the original oxalic acid ; and, therefore, if we assume the organo-metallic bodies above mentioned to be metals conjugated with various hydrocarbons, we might reasonably expect, that the chemical relations of the metal to oxygen, chlorine, sulphur, &c., would remain unchanged ; a glance at the formulæ of these compounds will, however, suffice to show us that this is far from being the case : it is true that cacodyl forms protoxide of cacodyl and cacodylic acid, corresponding to a somewhat hypothetical protoxide of arsenic, which, if it exist, does not possess any well-defined basic character, and the other to arsenious acid ; but no known compound corresponding to arsenic acid can be formed, and yet it cannot be urged that cacodylic acid is decomposed by the powerful reagents requisite to procure further oxidation, for concentrated nitric acid may be distilled from cacodylic acid without decomposition or oxidation in the slightest degree ; the same anomaly presents itself even more strikingly in the case of stanethylum, which, if we are to regard it as a conjugate radical, ought to combine with oxygen in two proportions at least, to form compounds corresponding to protoxide and peroxide of tin ; now stanethylum rapidly oxidises when exposed to the air, and is converted into pure protoxide ; but this compound exhibits none of that powerful tendency to combine with an additional equivalent of oxygen, which is so characteristic of protoxide of tin ; nay, it may even be boiled with dilute nitric acid without evincing any signs of oxidation : I have been quite unable to form any higher oxide than that described ; it is only when the group is entirely broken up and the ethyl separated, that the tin can be induced to unite with another equivalent of oxygen. Stibethyl also refuses to unite with more or less than two equivalents of oxygen, sulphur, iodine, &c., and thus forms compounds which are not represented amongst the combinations of the simple metal antimony.

"When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction ; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied ; thus in the ternary group we have NO_3 , NH_3 , NI_3 , NS_3 , PO_3 , PH_3 , PCl_3 , SbO_3 , SbH_3 , $SbCl_3$, AsO_3 , AsH_3 , $AsCl_3$, &c. ; and in the five-atom group NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, *no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.* It was probably a glimpse of the operation of this law among the more complex organic groups, which led Laurent and Dumas to the enunciation of the theory of types ; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts—had they not assumed that the properties of an organic compound are dependent upon the position, and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done ; such an assumption could only have

been made at a time when the data upon which it was founded were few and imperfect, and, as the study of the phenomena of substitution progressed, it gradually became untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable; for, whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its single atoms, and not merely upon the relative position of those atoms. . . .

"Taking this view of the so-called conjugate organic radicals, and regarding the oxygen, sulphur, or chlorine compounds of each metal as the true molecular type of the organo-metallic bodies derived from it by the substitution of an organic group for oxygen, sulphur, &c., the anomalies above mentioned entirely disappear, and we have the following inorganic types and organo-metallic derivatives:—

Inorganic types.	Organo-metallic derivatives.
$As \begin{Bmatrix} S \\ S \end{Bmatrix}$	$As \begin{Bmatrix} C_2H_3 \\ C_2H_3 \end{Bmatrix}$ Cacodyl.
$As \begin{Bmatrix} O \\ O \end{Bmatrix}$	$As \begin{Bmatrix} C_2H_3 \\ O \end{Bmatrix}$ Oxide of Cacodyl.
$As \begin{Bmatrix} O \\ O \\ O \\ O \end{Bmatrix}$	$As \begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ O \\ O \end{Bmatrix}$ Cacodylic acid.
$Zn \ O$	$Zn \ (C_2H_3)$ Zincmethylum.
$Zn \begin{Bmatrix} O \\ O_x \end{Bmatrix}$	$Zn \begin{Bmatrix} C_2H_3 \\ O_x \end{Bmatrix}$ Oxide of Zincmethylum.
$Sb \begin{Bmatrix} O \\ O \\ O \end{Bmatrix}$	$Sb \begin{Bmatrix} C_3H_5 \\ C_3H_5 \\ C_3H_5 \end{Bmatrix}$ Stibethine.
$Sb \begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix}$	$Sb \begin{Bmatrix} C_3H_5 \\ C_3H_5 \\ C_3H_5 \\ O \\ O \end{Bmatrix}$ Bin oxide of Stibethine.
$Sb \begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix}$	$Sb \begin{Bmatrix} C_3H_5 \\ C_3H_5 \\ C_3H_5 \\ C_4H_5 \\ O \end{Bmatrix}$ Oxide of Stibethylum.
$Sn \ O$	$Sn \ (C_4H_5)$ Stannethylum.
$Sn \begin{Bmatrix} O \\ O \end{Bmatrix}$	$Sn \begin{Bmatrix} C_4H_5 \\ O \end{Bmatrix}$ Oxide of Stannethylum.
$Hg \begin{Bmatrix} I \\ I \end{Bmatrix}$	$Hg \begin{Bmatrix} C_2H_3 \\ I \end{Bmatrix}$ Iodide of Hydrargyromethylum."

The foregoing extract from Frankland's paper contains a complete statement, in terms of Gmelin's equivalents, of the valency of the various elementary substances employed as "grouping elements" (to make use of a term introduced later by Frankland) in the formulæ given. In the case of the perissads—nitrogen, phosphorus, arsenic, and antimony—the valencies are 3 and 5, being thus identical with those now assigned to these elements. Arsenic appears in cacodyl as a dyad—a pseudo-dyad, as Frankland would have called it later. In the case of the artiads, zinc and tin, the atomic weight is twice the equivalent; hence the valency given by Frankland must be doubled. Mercury has been taken with the atomic weight 200, and its valency is correctly given.

Another important point is, that Frankland rejects the conception of conjugated compounds and writes typical formulæ explicitly based on the valency of the elements.

One result of Frankland's employing Gmelin's equivalents was that his statement of the law of valency did not impress the adherents of the type theory so much as it might otherwise have done. Kekulé, who in the introduction to his *Lehrbuch* fully acknowledges his obligations to "Williamson and Odling, Hofmann and Wurtz," does not mention Frankland; and a similar omission occurs in Wurtz's *Atomic Theory*. Kekulé, as already mentioned, never expressed himself, at all events in his published writings, on the subject of Frankland's claims; but, if we have not Kekulé's "official" opinion on the subject, we have an opinion, put forward in a paper published by Baeyer in 1858, when the latter was a student in Kekulé's laboratory, which must, I think, be regarded as "semi-official." Baeyer gives a list of compounds formed by the union of monads alone (methyl and chlorine) with the elements of the nitrogen group, in which the latter exhibit either triadic or pentadic character—belonging, as Baeyer expresses it, either to the ammonia type, or to the ammonium chloride type—and adds (*Annalen*, 1858, 105, 274):—

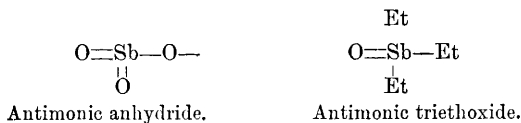
"I would here remind the reader of the series of compounds which Frankland gave in his investigations on zinc-ethyl, in which he drew a parallel between the compounds of the metals with oxygen and those with the alcohol radicles, whilst the latter are analogous to hydrogen and not to oxygen. The view which is thus gained is purely superficial; it vanishes immediately when the proper atomic weight of oxygen is adopted, and the formulæ which contain an odd number of atoms of that element are doubled."

With regard to the foregoing passage, I think we may lay it down as a safe general principle, to be adopted in dealing with this interesting period of chemical history, that a discovery, made by an adherent of the radicle theory and correctly formulated by him in terms of the

old equivalents, does not become the property of the first adherent of the type theory who happens to translate it into the new atomic weights.

Baeyer's criticism has been replied to by Frankland in the introduction to the series of papers on organo-metallic compounds reprinted in his *Experimental Researches* (p. 153). As some chemists may not have seen the passage, I will quote it :—

"Exception has been taken, I think somewhat unfairly [here Baeyer's criticism is given as a footnote], to the analogies upon which, in the following papers, I have founded the doctrine of atomicity. It has been stated, for instance, that there is no real analogy between antimonie anhydride and antimonie triethoxide, if the dyadic atom of oxygen be used in the formula of the first—that the real analogy is between antimonie chloride and antimonie triethoxide, &c. But even in the light of our most recent conceptions of the constitution of chemical compounds, the analogies which I pointed out are strictly correct ; for in antimonie anhydride each atom of antimony has five bonds satisfied by oxygen, whilst in the organo-metallic analogue, antimonie triethoxide, the oxygen of three of these bonds has been replaced by ethyl :



"At the time when the second paper of this chapter was written, I employed, in common with nearly all chemists, what is known as the small atom of oxygen ($\text{O}=8$). With this atomic weight oxygen was monadic ; and as it formed the only pentadic inorganic compound of arsenic, it lent itself, on the whole, better to the expression of my analogies than either chlorine, bromine, or iodine ; but (and it is on this ground that I complain of the unfairness of my critic) I distinctly stated * that I regarded 'the oxygen, sulphur, or *chlorine* compounds of each metal as the true molecular types of the organo-metallic bodies derived from them by the substitution of an organic group for oxygen, sulphur, &c.,' and I actually used, in the table of analogous compounds, HgI_2 as the type of HgMeI ."

If Kekulé did not express himself regarding Frankland's claims, he went further than this, for he claimed to have been himself the first propounder of the doctrine of the valency or, as he termed it, the atomicity, of the elements. In a note "On the Atomicity of the Elements" (*Compt. rend.*, 1864, 58, 510), published in reply to views put forward by Naquet and others, he says : "I consider that it is all the more my duty to intervene in this discussion, seeing that, if I am not mistaken, it was I who first introduced into chemistry the conception of the atomicity of the elements." (It should be mentioned that the first occasion on which Kekulé refers to valency is in his paper on thiactic acid, published in 1854, two years later than Frankland's

* See the extract from Frankland's paper already given.

paper.) He then proceeds to combat the doctrine of varying valency: the equivalent of an element may vary; but its valency is as invariable as its atomic weight. Neither is valency to be regarded as identical with maximum capacity for saturation: thus, in reply to Naquet, who regarded iodine as triadic and the elements of the sulphur group, including oxygen, as tetradic, he points out that if iodine is a triad in ICl_3 , tellurium must be dodecadic in TeI_4 —a supposed *reductio ad absurdum* which Kekulé's opponents might justly regard as a travesty of their views. He then defines the conditions which, he considers, alone render the determination of the valency of an element possible: the element in question must be combined solely with monads, and the resulting compound must be volatile without decomposition. Such a compound he regards as *atomic*. Two or more atomic molecules may unite to form a *molecular* compound; such a compound may be distinguished by the fact that, when volatilised, it dissociates; it is not available for the purpose of determining the valency of the elements which it contains. Thus ICl , PCl_3 , and NH_3 , are atomic compounds, and their formulæ show iodine to be monadic, and phosphorus and nitrogen to be triadic. Iodine trichloride, phosphorus pentachloride, and ammonium chloride are represented as molecular compounds, ICl_3 , PCl_5 ; NH_4Cl . (At that time the existence of phosphorus pentafluoride, a compound of pentadic phosphorus gaseous at ordinary temperatures, and the fact that dry ammonium chloride may be vaporised without dissociation, were, of course, unknown.) Again, referring to his doctrine of fixed valency, he speaks (*loc. cit.*, p. 512) of "the reasoning which has made me remain faithful to my original manner of viewing the subject, and which, I venture to hope, will end by carrying the day against the modifications which have been proposed since." Surely, Frankland's doctrine of varying valency was earlier in the field!

Of all the doctrines which we owe to Kekulé that of fixed valency is probably the one which has met with least acceptance, even among chemists of his own school. At the present day it is, so far as I am aware, without supporters. Yet Kekulé held it to the last.

Whilst we must thus admit that it was with Frankland and not with Kekulé that the idea of the valency of elementary substances originated, we are in a position, I think, to explain how it was that Kekulé came to ignore Frankland's work and to claim the theory for himself. To Kekulé, varying valency and, moreover, varying valency referred to equivalents instead of to atoms, was not valency at all, as he understood it. We must bear in mind the attitude of the two opposed schools in questions of chemical theory: how each seemed to labour under an absolute inability to place itself in the mental position of the other. I have no doubt that Kekulé paid very little atten-

tion to Frankland's theoretical views ; that he evolved the doctrine of valency in part independently and in part from the indications which he found in the writings of Williamson, Odling, and Wurtz ; and that afterwards, perceiving that Frankland had put forward similar ideas, he came to the conclusion that they had not been deduced by a legitimate process and were not correctly stated.

These considerations, which may have appeared important at the time, need not weigh with us at the present day. The battle between the radicle theory and the type theory is long past. The victory was not entirely with either, for the theory of chemical structure, based on the doctrine of valency, absorbed and assimilated both. Frankland correctly perceived that the views which he was advocating promised "to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable." But the theory of chemical structure which effected this fusion is imperishably associated with the name of Kekulé, and, therefore, if he did not originate the doctrine of valency, no other chemist used it to so good purpose. Frankland, speaking of valency, says (*Experimental Researches*, p. 154): "I do not forget how much, in its present developments, this law owes to the labours of other chemists, especially to those of Kekulé and Cannizzaro. Indeed, until the latter had placed the atomic weights of the metallic elements on their present consistent basis, the satisfactory development of the doctrine was impossible."

In his later years, Kekulé looked back upon those troublous times with a more tolerant eye. I again quote from his Berlin address :

"No science has developed so steadily as chemistry, although during one period of its development which fell partly within my own experience, the very opposite seemed for a time to be the case. Fifty years ago, the stream of chemical progress had divided into two branches. The one flowed, chiefly on French soil through luxuriant flower-decked plains ; and those who followed it, with Laurent and Dumas at their head, could reap, during the whole voyage, almost without effort, an abundant harvest. The other followed the course indicated by an old and approved guide-post set up by the great Swedish chemist, Berzelius ; it led for the most part through broken boulders, and only later on did it again reach fertile country. At length, as the two branches had again approached much nearer to one another, they were separated by a thick growth of misunderstandings, so that those who were sailing along on the one side neither saw those on the other, nor understood their speech. Suddenly a loud shout of triumph resounded from the host of the adherents of the type theory. The others had arrived—Frankland at their head. Both sides saw that they had been striving towards the same goal, although by different routes. They exchanged experiences ; each side profited by the conquests of the other ; and with united forces they sailed onward on the reunited stream. One or two held themselves apart and sulked ; they thought

that they alone had held the true course—the right fair-way—but they followed the stream.

“Our present opinions do not, as has frequently been asserted, stand on the ruins of earlier theories. None of the earlier theories has been recognised by later generations as entirely false; all, when stripped of certain ill-proportioned, meaningless excrescences, could be utilised in the later structure, and form with it one harmonious whole.

“Here and there a seed may have lain in the ground without germinating; but everything that grew came from seed that had been previously sown. My views also have grown out of those of my predecessors and are based on them. There is no such thing as absolute novelty in the matter.”

I have allowed the protagonists to speak for themselves, and so great is their agreement, at least in their later utterances, that it seems almost superfluous to call in the aid of an umpire. For the sake of completeness, however, I venture to do so. Ladenburg, although a pupil of Kekulé and thoroughly imbued with his master's teaching, has displayed, in his well-known historical treatise, a most praiseworthy spirit of impartiality in dealing with the various questions at issue between the adherents of the radicle and the type theories. Referring to Frankland's enunciation of the doctrine of valency already quoted, he says (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 251):—

“With this memoir of Frankland's the first step was taken towards a reconciliation of the hitherto opposed schools—the means was furnished for a mutual understanding. This means was destined to lead to a fusion of the different opinions, and out of the fusion the theory of valency developed. It was a gain for the adherents of the type theory to have secured Frankland's adhesion to their principles; for he brought with him ideas foreign to their modes of thought and capable of being turned to excellent account. I will not assert that the former school could not have taken the final great step—the differentiation of the atoms in terms of their valency—independently; but, having regard to the course which the development actually followed, the influence of Kolbe, and especially of Frankland, on the representatives of the Gerhardt-Williamson school (Wurtz, Kekulé and Odling) can hardly be mistaken. The efforts of both schools were necessary to impart to formulæ the significance which they afterwards acquired.”

I have treated this question of the authorship of the doctrine of valency at considerable length; but the subject seemed to me by its importance to justify this, especially in the present connection, seeing that the whole of Kekulé's work is based on this doctrine.

We must now pass on to consider the use which Kekulé made of the ideas which he found scattered throughout the writings of his predecessors; how he added to them; and how he welded the whole

into the coherent system which forms our present theory of the structure of organic compounds.

Kekulé's first published work of theoretical importance was, as has already been mentioned, his "Note on a New Series of Organic Acids containing Sulphur" (*Annalen*, 1854, 90, 309). He treats various organic compounds of the water type, such as acetic acid and acetic anhydride, with the sulphides of phosphorus, and in this way replaces the typical oxygen by sulphur. He compares the action with that of the chlorides of phosphorus and significantly remarks: "One sees, indeed, that the decomposition is essentially the same; only, when the chlorides of phosphorus are employed, the product breaks up into chloride of ethyl [acetylic chloride] and hydrochloric acid, or into two atoms of chloride of ethyl, as the case may be; whereas, on employing the sulphur compounds of phosphorus, both groups remain united, *because the quantity of sulphur equivalent to 2 atoms of chlorine is not divisible.*" Elsewhere, in the same paper, he refers this difference to "the *dibasic* nature of sulphur." He then proceeds to defend Gerhardt's new atomic weights, and declares the formulæ written with these to be a better expression of the facts than the prevailing formulæ. He says: "It is not merely a difference in the mode of writing, it is an actual fact, that 1 atom of water contains 2 atoms of hydrogen and only 1 atom of oxygen; and that the quantity of chlorine equivalent to *one* atom of oxygen is divisible by 2, whereas sulphur, like oxygen itself is *dibasic*, so that 1 atom is equivalent to 2 atoms of chlorine."

We thus see that the theory of the linking of atoms and groups by means of polyad radicles was already present to Kekulé's mind. Moreover, as was always the case with him, the thought is expressed with such precision and emphasis, as to render it impossible for even the least attentive reader to overlook his meaning.*

After this apparently unconditional acceptance of Gerhardt's atomic weights, it may surprise us to find Kekulé returning in his next published work to the use of Gmelin's equivalents. The same concession to the prevailing usage was, however, made by other members of the Gerhardt-Williamson school whenever they were merely stating experimental results, or explaining theories for the understanding of which the new atomic weights were not required. Later on, in adopting the new atomic weights, the adherents of this school used, as is well known, crossed symbols for the artiads, thus: $\text{C} = 12$, $\text{O} = 16$, as proposed by Williamson, partly in order to indicate

* Kolbe's well-known hostile criticisms on Kekulé's literary style deal almost exclusively with verbal points; they seldom touch the meaning, which indeed Kolbe's own preconceptions prevented him from grasping. This, it need hardly be said, is written in no spirit of detraction of Kolbe's own work and influence.

that the atom was in these cases equal to twice the equivalent, and partly to avoid confusion with the uncrossed symbols which were employed by the opposed school to denote the old equivalents. Kekulé continued to use these crossed symbols until 1867. How liable to misinterpretation these concessions to the prejudices of opponents were, and how little gratitude they evoked, may be seen from the accusations which Kolbe (*J. pr. Chem.*, 1881, [ii], 24, 398) brings against Kekulé: firstly, of having until 1857 held the view that the old equivalents were identical with the true atomic weights, whereas we have seen that as early as 1854 Kekulé had perfectly clear views to the contrary, although he for some time continued to use the equivalent formulæ for purposes of exposition; and secondly, of afterwards, "until 1867, attributing the atomic weight 16, not, strictly speaking, to the single oxygen atom, but to the double oxygen atom Θ ." Kolbe goes on to state that he himself adopted the new atomic weights in 1870, and draws the comforting conclusion that Kekulé anticipated him in this course by only three years!

The first of these papers in which Kekulé reverts to the use of the old equivalents is entitled "On the Constitution of Fulminic Acid" (*Annalen*, 1857, 101, 200), and was followed a year later by a second paper on the same subject. The experimental work was difficult and dangerous. The conclusion at which Kekulé arrived, namely, that fulminic acid is nitroacetonitrile is no longer held by chemists; but the work is of great interest. Perhaps the most important point in the paper is a tabular arrangement of compounds of the marsh gas type: the earliest enunciation of the tetravalency of carbon. After ascribing to mercuric fulminate the formula $C_2(NO_4)(C_2N)Hg_2$, Kekulé adds (*loc. cit.*, p. 204):

"This formula shows at the first glance that mercuric fulminate exhibits in its composition the closest analogy with a large number of known compounds, to which, for example, chloroform, $C_2 H Cl Cl Cl$, belongs. We might regard it as nitrated chloroform in which the chlorine is replaced partly by cyanogen and partly by mercury.

"The following compounds may be referred to the same type:

C_2	H	H	H	H	Marsh gas.
C_2	H	H	H	Cl	Methylic chloride, &c.
C_2	H	Cl	Cl	Cl	Chloroform, &c.
C_2	(NO_4)	Cl	Cl	Cl	Chloropicrin.
C_2	(NO_4)	(NO_4)	Cl	Cl	Marignac's oil.
C_2	(NO_4)	Br	Br	Br	Bromopicrin.
C_2	H	H	H	(C_2N)	Acetonitrile.
C_2	Cl	Cl	Cl	(C_2N)	Trichloroacetonitrile.
C_2	(NO_4)	Hg	Hg	(C_2N)	Mercuric fulminate.
C_2	(NO_4)	H	H	(C_2N)	Hypothetical fulminic acid,

“ . . . In assigning these compounds to the same type, I do not use the word in the sense which it bears in Gerhardt's unitary theory, but in that in which it was first employed by Dumas on the occasion of his fruitful investigations on the subject of types. I wish essentially to indicate the relations in which the said compounds stand to one another; that the one, under the influence of appropriate agents, can be produced from, or transformed into, the other.”

I have quoted this passage somewhat fully because Kolbe (*J. pr. Chem.*, 1881, [ii], 23, 374, footnote) has denied that Kekulé here refers mercuric fulminate to the marsh gas type and, indeed, that the passage affords any justification for ascribing to Kekulé the enunciation of the marsh gas type and of the tetravalency of carbon. He bases this denial on Kekulé's statement that he uses the word “type” in Dumas' sense (“mechanical type”) and not in Gerhardt's sense (“chemical type”). Why this statement should deprive Kekulé of all right to the theory which he so clearly expresses in his formulæ, Kolbe does not explain, unless, indeed, the explanation is to be found in a reference which he makes a little further on (*loc. cit.*, p. 375) to Kekulé's paper “On the So-called Conjugated Compounds,” and in which, speaking of Kekulé's direct statement that carbon can be shown to be “tetrabasic or tetratomic,” he says: “He nevertheless feels so uncertain of his ground, that he still hesitates to add the type ‘marsh gas’ to Gerhardt's three types.”

The meaning of Kekulé's remark about types, which Kolbe has, it seems to me, entirely mistaken, is perfectly clear if we view it by the light of the various statements on the subject of types to be found in Kekulé's writings. Kekulé's types (compare *Annalen*, 1857, 104, 132; *Lehrbuch*, 1, 116—117), even when outwardly identical with Gerhardt's “chemical types,” were in reality “mechanical types”: that is, they were based solely on the valency of the constituent elements. Thus, whereas Gerhardt classed the hydrogen type, HH , and the hydrochloric acid type, HCl , as distinct *chemical* types, Kekulé, looking upon them as *mechanical* types, regarded the latter as merely a special case of the former. Applying this to the matter under consideration, it is evident, that, if Kekulé had employed Gerhardt's types, he could not have tabulated the foregoing compounds in the way he did, as they would not have belonged to the same type. Thus, if he had followed Gerhardt, marsh gas would have belonged to the hydrogen type, methylic chloride to the hydrochloric acid type, and so on; and the parallelism which Kekulé wished to indicate would have been completely hidden. It was, therefore, necessary for him not merely to tabulate the compounds on the marsh gas type, but, seeing that he had used the word “type,” to obviate any possible misunderstanding by stating that he did not mean Gerhardt's types.*

* Kolbe also argues (*loc. cit.*) that, in the passage just quoted, Kekulé refers marsh gas to the chloroform type, not chloroform to the marsh gas type. To

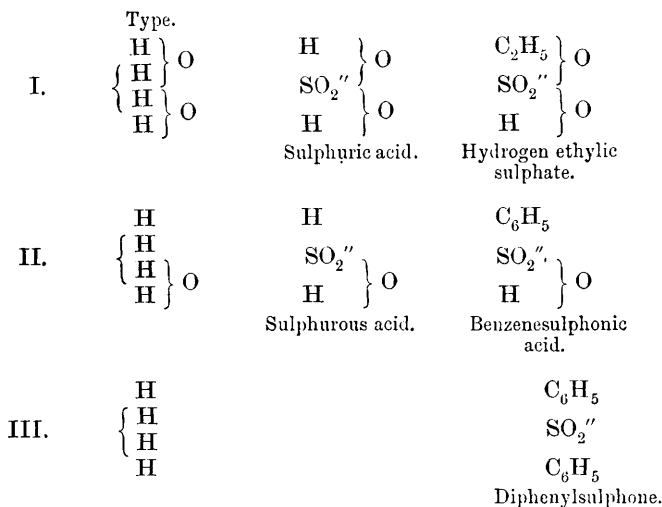
The foregoing demonstration of the tetravalency of the double equivalent of carbon, C_2 (which, as we have seen, meant for Kekulé the atom $C=12$), is obviously incomplete, as it holds good only for the limited class of compounds derivable from methane by the replacement of the hydrogen atoms by the same number of monad radicles. It contains no suggestion of the law of mutual linking of carbon atoms and can at most be regarded as the germ of Kekulé's later theory.

In the same year, Kekulé published an important theoretical paper: "On the So-called Conjugated Compounds and the Theory of Polyatomic Radicles" (*Annalen*, 1857, 104, 129). As the question is entirely one of valency and there are no experimental results to state, he uses Gerhardt's atomic weights, although in three experimental papers published the following year he again reverts, for the last time, however, to the old equivalents. In the introduction to the paper he states that the views which he advocates have, in great part at least, no claim to originality: they are an extension of ideas incidentally put forward by Williamson and forming what might be termed his "theory of polyatomic radicles"; ideas which had already been extended by Odling in his paper "On the Constitution of Acids and Salts," and which had been adopted, although not in a strict form, by Gerhardt in the fourth volume of his *Traité*. Kekulé divides the elements into monobasic or monatomic, dibasic or diatomic, and tribasic or triatomic, and points out that the three principal types—hydrogen, water and ammonia—follow from this classification. In a footnote he adds (*loc. cit.*, p. 133): "Carbon is, as may easily be shown, and as I shall explain in detail on a later occasion, tetrabasic or tetratomic: that is, 1 atom of carbon $C=12$ is equivalent to 4 atoms of H." He shows that, as regards the so-called conjugated compounds, there is no need to refer these to a separate class: their constitution may be expressed in terms of the valency of the radicles, simple and compound, which they contain. We have already seen, however, that this view of the nature of conjugated compounds had been clearly stated by

disprove this it is only necessary to point out that in the table of compounds which "may be referred to the same type," the formula of chloroform is given *under* that of marsh gas. Kolbe apparently understands the words "referred to the same type" to mean "referred to the same type as chloroform," whereas the sense is: "may all be referred to one and the same type," namely the type that heads the list. This is clearly shown both by the context and by the way in which the words "same type" are again used after the table of compounds.

Kolbe put himself completely out of court in any discussion involving a knowledge of Kekulé's writings, by the statement that he did not consider them worthy of serious attention. In his historical study: *Meine Betheiligung an der Entwicklung der theoretischen Chemie* (*J. pr. Chem.*, 1881, [ii], 23, 377) he says: "In this connection I have had occasion for the first time to read attentively Kekulé's *Lehrbuch*, especially the historical and theoretical chapters. Until then, I had only glanced hastily through it, as I perceived that I could learn nothing useful from it."

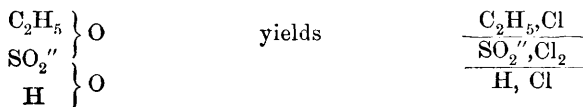
Frankland in 1852. Kekulé, starting, as he premises, with the theory of multiple types and mixed types containing polyvalent radicles, as expounded by Williamson and Odling, develops it into a complete system, laying special stress on the fact that these classes of types are possible only when such polyvalent radicles are present. Thus, of compounds containing the divalent radicle SO_2 , he gives :



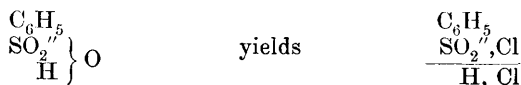
"Compound radicle" is understood in Gerhardt's sense of "a residue left unattacked in any particular reaction," and the "basicity" (valency) of these radicles is deduced from the number of atoms, greatly differing from the radicles themselves in chemical character, with which they combine.

This introduction of the radicles into the types, which must at the time have appeared to place the type theory on a firm basis, was destined to render that theory unnecessary.

Another point worthy of note is the way in which Kekulé uses the action of the chlorides of phosphorus to distinguish between the water type and the hydrogen type. Developing an idea to be found in his memoir on thiactic acid, he points out, that, in the case of the water type, two atoms of chlorine replace one atom of typical oxygen, causing the compound to break up into two atomic groups, whereas the hydrogen type is not acted upon and remains intact. Thus



whereas



In the foregoing paper, Kekulé accepts the radicles (residues) in the form in which he received them from his predecessors and empirically deduces their valency from a study of their compounds. In his great theoretical paper, published the following year (*Annalen*, 1858, 106, 129), "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon"—a paper which is the foundation of our present theories of organic chemistry—he goes to the root of the matter. He says:—

"I regard it as necessary and, in the present state of chemical knowledge, as, in many cases, possible, to explain the properties of chemical compounds by going back to the elements themselves which compose these compounds. I no longer regard it as the chief problem of the time, to prove the presence of atomic groups which, on the strength of certain properties, may be regarded as radicles; and in this way to refer compounds to a few types, which can hardly have any significance beyond that of mere pattern formulæ. On the contrary I hold that we must extend our investigation to the constitution of the radicles themselves; that we must ascertain the relation of the radicles to one another and, from the nature of the elements, deduce both the nature of the radicles and that of their compounds."

He then points out how the conception of the valency of the different elements may be utilised for this purpose. In this connection he further develops his ideas on the tetravalency of carbon, and gives the list of compounds: CH_4 , CCl_4 , CH_3Cl , CHCl_3 , COCl_2 , CO_2 , CS_2 , CNH , pointing out that "the sum of the chemical units combined with one atom of carbon is 4. This leads to the view that carbon is *tetratomic* (or *tetrabasic*). At this point he introduces (*loc. cit.*, p. 153, footnote) a passing reference to the advantage of referring compounds to the marsh gas type: "If carbon is introduced as a *tetratomic radicle* among the types, several already known compounds may be formulated in a relatively simple manner."

He next proceeds to discuss the question of the linking of carbon atoms with one another:

"In the case of substances which contain several atoms of carbon, one must assume that some at least of the atoms are held in the compound in the same way [as in the cases already quoted] by the affinity of the carbon, and that the carbon atoms themselves are attached together, whereby a portion of the affinity of the one carbon atom is of course held in combination by an equal portion of the affinity of the other.

"The simplest and therefore most probable case of this union of two carbon atoms is that in which one unit of affinity of the one carbon atom is combined

with one unit of affinity of the other. Of the 2×4 units of affinity of the two carbon atoms, two are used up in holding the two atoms together; there therefore remain six which may be held in combination by atoms of other elements. In other words the group C_2 is hexatomic.

"If more than two carbon atoms unite in the same way, the basicity of the carbon group will be increased by two units for each fresh carbon atom. Thus the number of hydrogen atoms (chemical units) which may be combined with n carbon atoms is expressed by

$$n(4 - 2) + 2 = 2n + 2.$$

". . . . Up to this point we have assumed that all the atoms attaching themselves to carbon are held by the affinity of the carbon. It is equally conceivable, however, that in the case of polyatomic elements (O, N &c.) only a part of the affinity of these—for example, only one of the two units of affinity of the oxygen, or only one of the three units of the nitrogen—is attached to carbon; so that one of the two units of affinity of the oxygen, and two of the three units of affinity of the nitrogen, remain over and may be united with other elements. These other elements are therefore only in indirect union with the carbon, a fact which is indicated by the typical mode of writing the formulæ :



"In like manner the carbon groups are held together by the oxygen or the nitrogen."*

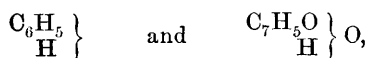
He points out that a great many organic compounds may be formulated on the basis of the "simplest" attachment of carbon to carbon, but that, in others which contain more carbon in proportion the "next simplest" attachment may be assumed, involving a closer union of the carbon atoms. He does not, however, go into details regarding the principles to be adopted in formulating such unsaturated compounds.

It is to be noted that at that time Kekulé still held Gerhardt's view that rational formulæ were merely an expression of chemical reactions. The idea that it was possible to express the relative positions of the atoms within the molecule was of later growth.

Kekulé had by his interpretation of the types in terms of the law of valency, and by his dissection of the compound radicles in accordance with the same law, superseded both the type theory and the radicle

* As a further example of how little Kolbe thought it necessary to master the details of theories he set himself to criticise, the following passage may be quoted, in which, after making merry over the expression "carbon skeleton," used by Kekulé in the foregoing paper, he says (*J. pr. Chem.*, 1881, [ii], **24**, 407): "If I am not mistaken, it is assumed that *all* organic compounds which contain more than one atom of carbon possess such carbon skeletons. Where, then are we to place the cacodyl compounds, trimethylamine, trimethylsulphine iodide and other organic substances?"

theory, except so far as they might be useful for purposes of exposition. Nevertheless, partly as a concession to the prevailing usage of his school, and partly, doubtless, from force of habit, he continued for a long time to write typical formulæ. This led to a somewhat mechanical mode of formulation, occasionally attended with misleading results. Thus, in the paper just quoted (pp. 145—146), we find benzene formulated on the hydrogen type and benzoic acid on the water type,



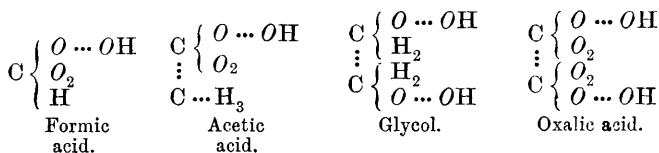
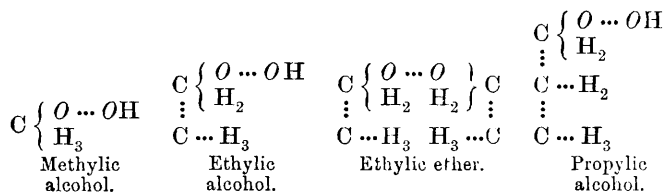
which leads him to state that, in the sulphonation of benzene, it is the typical hydrogen, but, in that of benzoic acid, hydrogen of the radicle, which is replaced, and to assign these reactions to two distinct categories. Again the hydroxy-acids are formulated on the double water type; thus lactic acid is $\left. \begin{array}{c} \text{C}_3\text{H}_4\text{O}'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$; a mode of representing these substances which obliterates the distinction between the acidic and the alcoholic hydrogen atoms, and was responsible for the errors into which Wurtz fell in the earlier part of his well-known controversy with Kolbe. Kekulé himself is perfectly clear about the difference between these two typical hydrogen atoms and explains its cause with all possible precision (*Lehrbuch*, 1, 731); nevertheless he quotes the formula $\left. \begin{array}{c} \text{C}_3\text{H}_4(\text{HO})\text{O} \\ \text{H} \end{array} \right\} \text{O}$ for lactic acid (first put forward in the old equivalents by Kolbe) only to reject it with the remark (*loc. cit.*, p. 736): "Such formulæ offer no advantages over the typical formulæ; on the contrary they conceal a great number of analogies and, in other cases, cause analogies to be suspected where none exist." I venture to think that I have just shown that the typical formulæ are not quite free from these defects. As regards the particular case of the formula of lactic acid, there is no doubt that the reluctance which Kekulé and his school at that time displayed to make use of the hydroxyl group in formulating compounds was an effect of Laurent's supposed burlesque proof of the existence of the radicle *eurhyzene*, that is, hydroxyl (see Laurent's *Chemical Method*, Odling's translation, p. 293). I say "supposed burlesque," because, at the present day, there is probably no chemist who has occasion to refer to "the hydroxyl-group"—which, in chemical compounds, is an abstraction and, in certain electrolytic dissociations, an entity—but would willingly subscribe, in all seriousness, the words which Laurent wrote in jest.*

* When, however, Kekulé (*Lehrbuch*, 1, 736, footnote) quotes Laurent's *eurhyzene* as a proof that Kolbe's view of the constitution of the acids of the lactic series as hydroxy-derivatives of the acids of the acetic series, is not original, one can only surmise that he was infected by Laurent's spirit of elaborate pleasantry.

This adherence to the outward form of the typical formulæ was, however, a minor defect, especially as Kekulé showed in his *Lehrbuch* how, by means of his graphic formulæ, the relations of the different atoms to one another within the molecule might be clearly exhibited. The graphic symbols were, however, as Kekulé himself pointed out, too cumbrous for ordinary use; they shared the fate of Dalton's atomic symbols and had to yield to the superior simplicity of those of Berzelius, which, with a few additions in the shape of bonds and valency marks, were found to satisfy all requirements. Even the circles with which Crum Brown, in his system of graphic formulæ, at first surrounded the symbols, were soon discarded.

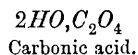
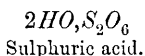
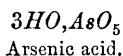
Kekulé's models of atoms, on the other hand, to which reference will be made later, had a brilliant future before them.

It must be mentioned that, shortly after the publication of Kekulé's paper on the constitution of chemical compounds, analogous views were put forward independently by Couper (*Ann. Chim. Phys.*, 1858, [iii], 53, 469; *Phil. Mag.*, 1858, [iv.], 16, 104). The two investigators followed different paths, and their results were in some respects different. Kekulé accepted the type theory and furnished it with a philosophical basis by explaining the existence of the pattern formulæ, or types—simple, multiple, and mixed—by means of the valency of the constituent elements; Couper, on the other hand, rejected the type theory altogether, and, starting with the idea of the valency of the elements, proceeded to construct constitutional formulæ for various compounds. Couper held peculiar views on the subject of the atomic weights: thus, whilst carbon was $C = 12$, oxygen was only $O = 8$. Carbon was tetradic; and the small oxygen atoms were dyadic, but were supposed always to occur linked together in pairs, so that the resulting group, $O \dots O$, as Couper wrote it, was also dyadic, and was therefore, to all intents and purposes, identical with the dyadic $O = 16$. The following formulæ will illustrate his system:

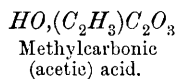
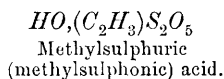
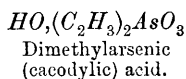


Couper's formulæ are thus, in spite of the peculiarity in the mode of writing oxygen, nearer to our present formulæ than those used by Kekulé at that period, and from the manner in which he discusses them it is evident that he intends them to be constitutional formulæ and not mere "formulæ of double decomposition" such as were employed by Gerhardt's school. The constitution assigned to the foregoing compounds is, however, identical with that previously proposed by Kolbe, with a difference, however, in the mode of writing the formulæ.

Kolbe (*J. pr. Chem.*, 1881, [ii], 23, 366) and Frankland (*Proc. Roy. Soc.*, 1865, 14, 198) claim to have anticipated Kekulé's enunciation of the tetravalency of carbon in a paper which they * published in 1857 (*Annalen*, 1857, 101, 262 *seq.*). This claim, however, cannot be sustained, unless we ignore the list of compounds formulated on the marsh gas type, which Kekulé drew up in his paper on mercuric fulminate published a short time previously. Kolbe, indeed, gave what he considered to be reasons for ignoring this list; but I believe I have shown (p. 123) that these supposed reasons are based on a misunderstanding of Kekulé's meaning. Kolbe and Frankland's paper appeared so soon after Kekulé's that there can be no doubt of their having arrived at their conclusions quite independently of Kekulé, the more so as these conclusions are drawn entirely from their own work. Moreover, as the whole paper deals with the application of the law of valency, discovered by Frankland, to the interpretation of the constitution of organic compounds, it is clear that the authors had the tetravalency of carbon, or rather the tetravalency of the double equivalent, C_2 , in their minds, although they did not mention it in so many words. Frankland had already shown (*v. supra*) how cacodylic acid might be derived from arsenic acid, or, strictly speaking, how the hypothetical cacodylic anhydride might be derived from arsenic anhydride, by replacing two equivalents of oxygen by two of methyl. Kolbe and Frankland now apply this view to the hydrated acids: thus from

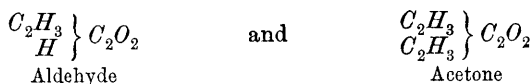


they deduce



* Through inadvertence this paper appeared under Kolbe's name only (compare Frankland's *Experimental Researches*, p. 148). Except in the opening sentences, in which Kolbe is referring to previous work of his own, the pronoun "we" is used throughout as denoting the joint authors.

They point out that, for each atom (equivalent) of oxygen which is replaced by methyl, one equivalent of water HO is simultaneously removed, so that for each introduction of a methyl group the basicity of the acid is reduced by 1. By replacing a further atom (equivalent) of oxygen in acetic acid by hydrogen or by methyl and again simultaneously removing HO , they obtain



which are no longer acids at all. Further on, in the same paper, they point out that carbonic acid may be formulated $2HO, (C_2O_2)O_2$, and that it is the two "extra-radical" oxygen atoms which are replaced by methyl, each carrying with it an equivalent of water.

If we translate this into modern atomic weights, each "extra-radical" equivalent of oxygen, plus an equivalent of water, represents a hydroxyl group: $O + HO(O=8)=OH(O=16)$; so that the above formula for carbonic acid is identical with $CO(OH)_2$. It is thus hydroxyl of the hypothetical carbonic acid, and not, as the authors suppose, oxygen of carbonic anhydride, which is replaced by methyl or hydrogen in the foregoing mode of deducing acetic acid, aldehyde, and acetone from carbonic acid.

The tetravalency of the double equivalent of carbon, C_2 , is certainly implied in Kolbe and Frankland's paper; but, as already mentioned, it is nowhere expressly stated, and one may be permitted to doubt whether many chemists could at that period have disentangled the doctrine from the very complicated hypothesis in which the use of the old equivalents had compelled the authors to involve it. Those who profited most by the work were those who could translate it into Gerhardt's atomic weights, and probably Kekulé and his school were more indebted to it than they were at that time conscious of. It is clear, however, that the paper contains no hint of the linking of carbon atoms, as this conception could not be developed in terms of Gmelin's equivalents. Indeed, so far as Kolbe was concerned, even after he had accepted the new atomic weights, he continued, to the end of his life, to cast ridicule on this conception (compare *J. pr. Chem.*, 1881, [ii], 24, 414).

That Kolbe and Frankland's work on the tetravalency of carbon did not, therefore, exercise a direct and immediate influence in any degree comparable with that produced by Kekulé's great paper on the same subject, is to be ascribed to the fact that their conclusions were stated in terms of an inconsistent scheme of atomic weights. We must not forget, however, that the same principle, namely, that of the

derivation of organic acids, aldehydes and ketones from carbonic acid, led Kolbe, later on, to the prognosis of secondary and tertiary alcohols, of which triumph of theoretical foresight the germ is contained in the concluding paragraph of Kolbe and Frankland's paper (compare *Annalen*, 1857, 101, 265).

I have already referred to Kekulé's models of atoms. The conception which he introduced in these, as to the distribution of the four affinities of the carbon atom, has led to most important results. He begins by referring (*Zeitschr. f. Chem.*, 1867, *N.F.*, 3, 217) to the imperfections of his original system of graphic formulæ and of the models based upon them, and further points out that models constructed on the basis of Crum Brown's graphic formulæ and consisting of spheres with rods radiating from them in one plane, do not really express more than the graphic formulæ themselves, inasmuch as the representation which they afford of a space formula is only apparent, the atoms being all in the same plane; and that, unless the rods are bent or arbitrarily displaced, certain combinations, *e.g.* triple bonds between carbon atoms, cannot be represented by them at all. He then proceeds to describe a model of the carbon atom which he has devised and which avoids these difficulties: "The four units of affinity of the carbon atom, instead of being placed in one plane, radiate from the sphere representing the atom in the direction of hexahedral axes, so that they end in the faces of a tetrahedron. . . . A model of this description permits of the union of 1, 2 and 3 units of affinity, and, it seems to me, does all that a model can do."

Even while making this apparently sweeping statement, Kekulé can hardly have realised the part that this model was destined to play in the development of theoretical chemistry; how in van't Hoff's hands it was to be the means of tracing the subtle asymmetry which Pasteur had deduced from the optical behaviour and the crystalline form of certain organic compounds, back to the asymmetric structure of the molecule itself; of explaining the mysterious isomerism of fumaric and maleic acid, which had baffled Kekulé's own acumen; and of laying down the space conditions of existence or non-existence of the closed-chain compounds of which Kekulé himself had introduced the conception into chemistry in his benzene theory.

I have already referred to Kekulé's benzene theory as the crowning achievement of the doctrine of the linking of atoms. To give a complete account of this theory and of the criticisms to which it has been subjected, would far exceed the scope of the present lecture; whilst to treat it briefly may seem superfluous, as the theory, in its main outlines, is familiar to every one with even the most elementary knowledge of organic chemistry.

This theory was first published in 1865 in the *Bulletin de la Soc. Chimique* (1, 98). I quote, however, from the fuller account published a year later in Liebig's *Annalen* (1866, 137, 129).

In this paper, "On the Constitution of the Aromatic Compounds," Kekulé begins by stating that none of the chemists who have dealt with the subject of benzene and its derivatives, have attempted to deduce the constitution of these compounds from the tetravalency of carbon and that some have gone so far as to state that this cannot be done. He then enumerates various distinguishing characteristics of the benzene compounds: amongst others, that there is no benzene compound containing fewer than six carbon atoms. After pointing out that six carbon atoms might be linked together by alternate single and double bonds, he says:

"If one assumes that six carbon atoms are attached to one another according to this law of symmetry, one obtains a group which, regarded as an *open chain*, contains *eight* unsaturated units of affinity. By making the further assumption that the two carbon atoms at the ends of the chain are linked together by one unit of affinity each, a *closed chain* (a symmetrical ring) is obtained, which still contains *six* unsaturated units of affinity.*

"From this *closed chain* all the substances usually designated as 'aromatic compounds' are derived. . . .

"In all aromatic substances a common nucleus may be assumed: it is the closed chain C_6A_6 (in which A denotes an unsaturated affinity).

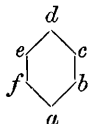
"The six affinities of this nucleus may be satisfied by six monatomic elements. They may also, wholly or at least in part, be satisfied by one affinity of polyatomic elements, the latter necessarily bringing with them other atoms into the compound, thus producing one or more *side chains*, which in their turn may be lengthened by the addition of other atoms.

"The satisfying of two affinities of the nucleus by one atom of a diatomic element, or of three affinities by one atom of a triatomic element, is, according to the theory, impossible. Compounds of the molecular formulæ, C_6H_4O , C_6H_4S , C_6H_3N , are, therefore, unthinkable."

Here we meet for the first time (if we except Kekulé's preliminary note on the same subject) with the now familiar expressions "closed chain," "nucleus," and "side chain," without which it would, at the present day, be impossible to discuss the problem of the constitution of the benzene compounds. The last paragraph quoted is worthy of note: it contains a very positive statement on a point which does not appear to follow with absolute necessity from the formulæ which Kekulé uses. It involves conceptions regarding the actual distribution of the atoms in space; and the conclusion at which Kekulé arrives suggests that he was already using the space-models of atoms which he described two years later.

* In the original paper these atomic groups are represented by means of Kekulé's graphic formulæ.

He points out that the foregoing constitution of the benzene nucleus involves the equivalence of the six unsatisfied affinities and proceeds to deduce the number of possible substitution derivatives of benzene, containing 1, 2, 3, &c., identical substituents, the isomerism depending on the relative positions of the substituents towards one another. Amongst other things he points out that whereas there are only three substitution derivatives possible of the general formula $C_6H_3X_3$, there are six of the formula $C_6H_3X_2Y$. In stating this conclusion he makes use of a hexagon lettered as follows



and says: "For dibromnitrobenzene, for example, there would be the following forms:

- "(1) For abc : $C_6H_3BrBr(NO_2)$
 $C_6H_3Br(NO_2)Br$
 (2) For abd : $C_6H_2(NO_2)HBr_2$
 $C_6H_2BrH(NO_2)Br$
 $C_6H_2BrHBr(NO_2)$
 (3) For ace : $C_6HBrHBr(NO_2)$."

It was this series of compounds that Körner used later (*Gazzetta*, 1874, 4, 305) in his well-known method for the orientation of the bromine atoms in the dibromobenzenes.

The homologues of benzene are discussed. "The homology may depend either upon an increase in the number of the side chains, or on the lengthening of side chains the number of which remains the same." Thus there ought to be three dimethylbenzenes (only one was at that time known) and, isomeric with these, the synthetical ethylbenzene of Fittig and Tollens.

The law of oxidation of the homologues of benzene is laid down: namely, that each hydrocarbon side chain, no matter how many carbon atoms it may contain, is oxidised away, with the exception of the carbon atom attached to the nucleus, which remains in the shape of a carboxyl-group. The resulting acids thus contain as many carboxyl-groups as there were hydrocarbon side chains in the original compound. By more moderate oxidation intermediate products are obtained: thus, xylene and cymene both yield toluic acid. Moreover, the possibility is foreseen, in the case of side chains containing more than one carbon atom, of oxidising only a portion of the chain, and thus obtaining an acid in which the carboxyl is not directly attached to the nucleus.

The question of substitution in the nucleus and substitution in the

side chain is also gone into, and the difference in the character of the resulting derivatives is pointed out.

At the end of the theoretical portion of the memoir, Kekulé says, referring to different possible formulæ for benzene :

"A problem of this kind might at first sight appear quite insoluble ; but I nevertheless believe that experiment will furnish a solution. It is only necessary to prepare, by methods as varied as can be devised, as great a number of substitution products of benzene as possible ; to compare them very carefully with regard to isomerism ; to count the observed modifications ; and especially, to endeavour to trace the cause of their difference to their mode of formation. When all this is done we shall be in a position to solve the problem."

Could the course of subsequent investigation in this field have been more accurately laid down in advance ?

Kekulé's memoir on the benzene theory is the most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. What Kekulé wrote in 1865 has since been verified in every essential particular. Not only have the various substitution derivatives been discovered, in the number and with the properties required by the theory, but various observations which appeared to contradict this theory have been proved erroneous. Moreover, the theory has shown itself capable of boundless development. There seems to be no limit to the fruitfulness of Kekulé's conception of closed chains or cycloids. The extensions of the idea, of which extensions Erlenmeyer's naphthalene formula and Dewar's formulæ for pyridine and quinoline were amongst the earliest instances, have gone on increasing in a rapid geometrical ratio, until, at the present day, the literature dealing with cycloids, although of so recent growth, is more than twice as voluminous as that of the paraffinoids. To quote the words of the address which our Society presented to Kekulé on the occasion of the *Benzolfeier* : "This theory found the chemistry of even the immediate derivatives of benzene an almost untilled field ; it has transformed it into a fertile province, to which have been annexed regions the very existence of which was unknown."

But even in the undeveloped state of the subject prior to Kekulé's theory, the facts were apparently so intricate and so unconnected that few chemists could claim to have mastered them. The theory appeared ; the previously unmarshalled facts fell into their proper places ; and not only this, but it was possible to say whether, in any given section of the subject, the facts were complete or only fragmentary. The increased ease in dealing with this branch of chemistry, the fascination of the numerous scientific problems which Kekulé's theory suggested, and lastly the economic importance of many of the benzene compounds and of other allied cycloids, attracted to this field

a crowd of workers, whose numbers, if they have not of late years actually increased, at least show no signs of diminishing. The debt which both chemical science and chemical industry owe to Kekulé's benzene theory is incalculable. As regards the former, three-fourths of modern organic chemistry is, directly or indirectly, the product of this theory; and as to the latter, the industries of the coal-tar colours and the artificial therapeutic agents, in their present form and extension, would be inconceivable without the inspiration and guidance which they have received and still receive from Kekulé's fertile idea.

Various points in Kekulé's theory which were at first either fundamental assumptions, or deductions from these fundamental assumptions, have since been experimentally proved: thus the equivalence of the six hydrogen atoms in benzene by Ladenburg, and the fact that there is, relatively to every hydrogen atom, a symmetrically situated ortho-pair and a symmetrically situated meta-pair, by Hübner and Petermann, Wroblewsky, and others.

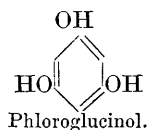
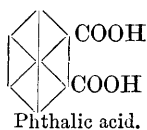
The orientation of the substituents in the derivatives of benzene, merely indicated by Kekulé, has been successfully carried out by von Baeyer, Graebe, Ladenburg, Griess, and, above all, Körner. The concordant results obtained by the most diverse methods have placed this part of the subject on a sure foundation.

The non-identity of the two ortho-positions 1 : 2 and 1 : 6 in Kekulé's formula containing alternate double and single bonds, which is in contradiction to the proved identity of the two ortho-products and which would necessitate the existence of four isomeric disubstitution derivatives instead of three, has called forth much criticism. Kekulé sought to meet the difficulty by means of his well-known oscillation formula, in which the double and single bonds continually exchange places. This is virtually a return to the simple hexagon, given as an alternative formula by Kekulé in his original paper: the distribution of the unsaturated affinities is ignored.

Of the various formulæ which have been proposed in place of Kekulé's, I will mention Ladenburg's prism formula, Claus's diagonal formula, and Armstrong and von Baeyer's central formula. All of these agree with Kekulé's formula in connecting together six CH-groups by single bonds so as to form a closed chain; the disposal of the remaining six affinities is the point wherein they differ. Ladenburg's formula is seldom discussed at the present day. It represents the ortho-carbon atoms as not directly connected, thus ignoring the analogy between the ortho-position in benzene compounds and the α -position in paraffinoid compounds, and rendering the formulation of compounds like naphthalene and phenanthrene impossible, at least in accordance with the prevailing views. Moreover, the substitution of any two dissimilar groups for hydrogen would render carbon atoms of

the nucleus asymmetric, so that every compound of the general formula C_6H_4XY ought to exist in two enantiomorphous forms, whereas all efforts to isolate such forms have hitherto proved fruitless, benzene derivatives being optically inactive unless there is an asymmetric carbon atom in a side chain. Claus's diagonal formula was formerly objected to on the ground that the ortho- and para-positions were identical and that it therefore required the existence of only two di-substitution products. This difficulty has been got over by introducing spatial considerations and assuming that the greater distance between the para-carbon atoms, as compared with the ortho-, constitutes a difference. It is necessary, however, further to assume that the carbon and hydrogen atoms lie in one plane, otherwise asymmetric substitution derivatives would exist; and this assumption, taken in conjunction with that of para-bonds, would appear to demand the placing of the four affinities of carbon in one plane; in other words, it would involve the abandonment of van't Hoff's tetrahedron. The central formula is difficult to criticise; the mode of disposing of the central bonds is entirely without analogy and does not appear to be accessible to the test of experiment. In its application and predictions, the central formula is identical with Kekulé's simple hexagon.

The question of the disposal of these unsaturated affinities is, indeed, a very difficult one. Thus von Baeyer, who formerly opposed Claus's formula, has now, with certain limitations, adopted it (*Annalen*, 1892, 269, 177). According to him, it is impossible to devise a benzene formula which shall be applicable to all derivatives of benzene. He regards (*loc. cit.* p. 188) phthalic acid as derived from a benzene of Claus's formula and phloroglucinol from one of Kekulé's formula with alternate double and single bonds:



Possibly the solution of this difficulty will be found when we possess a space formula capable of representing these various modes of distributing the unsaturated affinities as different desmotropic oscillation-phases of a ring of 6 CH-groups (compare Collie, *Trans.*, 1897, 71, 1013). Of such a formula Kekulé's oscillation formula is a partial anticipation. Meanwhile chemists will doubtless continue to employ Kekulé's simple hexagon, without alternate double and single bonds, as a statical representation of the symmetry of the benzene molecule.

Various other important theoretical questions discussed by Kekulé might be mentioned here; but time does not permit.

If, in conclusion, we ask ourselves what is the characteristic note of Kekulé's theoretical creation, the chemistry of structure, I think we may reply that it is the treatment of the problem of isomerism—the problem which first necessitated the use of constitutional formulæ—as one of geometrical symmetry. Kekulé's formulæ, stripped of the fetters of the type theory with which he at first encumbered them, were, from one point of view, merely more or less symmetrical geometrical figures. In order to predict the number of substitution compounds, it was only necessary to consider the degree of dissymmetry of the parent compound: the less the symmetry, the greater the number of isomeric substitution compounds. The extraordinary fertility of this conception is shown by the development which it has undergone at the hands of van't Hoff, J. Wislicenus, von Baeyer, and others.

Kekulé's structural formulæ cleared away at one stroke the entire brood of pseudo-constitutional formulæ. If organic chemists no longer waste their time in wrangling over the question whether, for example, methylamine is methane in which one atom of hydrogen is replaced by the amido-group, or ammonia in which one atom of hydrogen is replaced by methyl, the merit is Kekulé's.

The accuracy of Kekulé's predictions has done more to inspire a belief in the utility of legitimate hypotheses in chemistry, and has therefore done more for the deductive side of the science, than that of almost any other investigator. His work stands pre-eminent as an example of the power of ideas. A formula, consisting of a few chemical symbols jotted down on paper and joined together by lines, has, as we have just seen, supplied work and inspiration for scientific organic chemists during an entire generation, and affords guidance to the most complex industry the world has yet seen.

Although much research remains to be done on the lines laid down by Kekulé, yet other problems are clamouring for solution, and other methods of investigation have been called into existence to solve them. The younger generation of chemists are, fortunately, labouring diligently in the field of physico-chemical research, which the organic chemists, occupied with questions of chemical structure, had perhaps unduly neglected. One problem, however, which, in many points at least, still awaits the physical chemist, is the correlation of his results with those of the structural chemist. When this is fully accomplished, there will be a debt of gratitude on both sides; but no one will be entitled to more gratitude than August Kekulé.
