

Ammonolatroly: The Life Element*

By Prof. Henry E. Armstrong, F.R.S.

(To a muted, musical undercurrent reminiscent of Aïda, in face of a moving, desert panorama with camels.)

FOR several months, while I have been confined to my room, I have had before me two unusual and remarkable books which are of special interest to me, at a time when we have to admit that far more consideration must be given to the manner in which chemists are trained. The books are E. C. Franklin's "Nitrogen System of Compounds" and N. V. Sidgwick's "Organic Chemistry of Nitrogen", in both of which I have particular reason to be interested.

About thirty years ago, soon after the great San Francisco earthquake (1906), I visited Leland Stanford University at Palo Alto. The founder was doing penance: he had been tossed from his pedestal and was standing upside down, with his head through the stone pavement: I believe he was ultimately restored to righteousness without a feature injured. Chemistry was well on its feet. The professor, Edward Curtis Franklin, was at an early stage in the inquiry, now so associated with his name and school, into the properties of liquid ammonia in comparison with those of water, especially as an electrolytic solvent: though boiling at -33.35° , it comes close to water in activity. Liquid ammonia was being brought into use at that time as a refrigerating agent, and Franklin had command of the technical product.

It may be mentioned here in parenthesis that Gore in his earlier work on the subject (1872-73) was forced to prepare the liquid separately for each experiment, by heating ammoniated calcium chloride in the tube containing the substance to be tested. He tested the solubility of more than five hundred substances. He had great difficulty in securing support for his work—in those prehistoric days it was considered to be of little interest. He made a similar study of liquid hydrogen fluoride, and all but isolated fluorine. Few are left to remember his persistent pioneering efforts in advocacy of pure research, for which he made a great personal sacrifice: unfortunately, he was not original. I had the privilege of being made his confidant and always regretted that he

* The proof of this article was corrected by Prof. Armstrong only a week before his death on July 13. The article represents, therefore, the final expression of the frank and critical views which he held upon the training of chemists and subjects of research. Whatever significance may be attached to these views, the fact that, while on his dying bed, he desired to make the two volumes mentioned in the article the subject of a contribution to NATURE, is a remarkable tribute to the active attention he gave to scientific subjects right unto the last. Prof. Sidgwick's book to which Prof. Armstrong refers was reviewed in NATURE of July 3—The Editor.

had so little encouragement. We were then near to the renaissance period, but so low was the ebb of curiosity that Frankland, Vernon Harcourt and others were suggesting that a list of subjects for research should be prepared. Actually the main cause of activity was not Kekulé's benzene formula but the discovery by Kolbe and others, after the 1870 war, that research work could be made of commercial value. The poor professor disappeared but academic training began to lose its value; now, after a second war, in Germany, freedom of thought is gone. She may have gained much commercially but she has sold her scientific soul. Our task is to make the same change impossible here: it is already set in, largely through the influence of commercialism.

Franklin's reason for entering on the inquiry is stated by him as follows:

"In the autumn of 1896, Hamilton P. Cady, then an undergraduate was working at the regulation course in quantitative analysis. Observing after a time that the young man was becoming bored with the task, the writer, at the time giving instruction in analytical chemistry, proposed to him that he prepare several of the cobaltamine salts and confirm the composition of one or two of them by analysis. Some days later, with a beautifully crystallised specimen of one of these interesting salts in his hand, Cady stated that the ammonia in these and other salts containing ammonia must function in a manner very similar to that of water in salts with water of crystallisation. He suggested furthermore that liquid ammonia would probably be found to resemble water in its physical and chemical properties. As a direct consequence of Cady's suggestion has followed all the work done in this country on liquid ammonia."

Franklin died on February 13, 1937. We have to lament the loss of a colleague who could still regard chemistry as a practical subject but take notice of theory in general. His work on ammonia, already of no slight value, may some day rank high when the great problem of electrolytic conductivity is discussed with knowledge and without prejudice: as yet, it never has been. Franklin makes close comparison, compound by compound, of corresponding members of the oxygen and nitrogen systems. The ammonia work, however, is far from sufficiently described in his book. I had hoped the original papers would have been largely reproduced in readable form. If his friends were to provide a reprint it would be a pious act and a great boon to students. None the less, it is a most valuable conspectus.

Sidgwick's "Organic Chemistry of Nitrogen" is a book of very different type. Franklin would

take us back to the worship of Jupiter Ammon, begun in the dry distillation of camel's dung. Sidgwick would have us 'resonate' to the latest doctrine of electro-valency. The first edition of his book was published in 1910; it was a positive thriller. Sidgwick gave me a copy, which I have always prized; this has rested on a shelf near to my elbow and has often been taken down; my hope that the new edition would have similar attraction is disappointed. Two Oxford fellows, T. W. J. Taylor and Wilson Baker, seem to have been mainly responsible for the new edition, but the names of a host of other helpers are given. Sidgwick only contributes seven pages of introduction and a page or two on *Chelate Orthonitrophenol derivatives*, which show that he is now devoted to the fashionable morganatic game of crab catching, an appropriate exercise, for the Upper reaches of the Thames.

The plan remains what it was. The intention is said to have been to give an account of the simpler organic compounds and to discuss some of the interesting problems which these properties present, giving so far as possible adequate explanation of the necessary physical background. The authors have not the practical experience and critical judgment necessary to carry out their task in a way to make the book of practical value to students who would train to be chemists—of whom there are very few at Oxford. It is not a beginners' book and makes high demands upon previous knowledge, without explanation plunging the reader forthwith into technicalities known only to the specialist and impossible for the ordinary reader to understand. Though highly discursive and scrappy at times, necessarily a book written at such length contains much that is interesting, but no training in judicial method is to be gained from its use.

At least half of what is regarded as the most intellectual of our youth is attracted to the University of Oxford; this element is all but absolutely classical in its outlook. Oxford needs medicine of a very different order from that represented in Sidgwick's book: medicine that will make it a school of practice in chemistry, not one of elocution. The University is receiving large funds but its traditions are such that it does not attempt to train men to be efficient and effective laboratory workers. It has grown up upon words and lives upon them. The Oxford way is to enforce knowledge of what is done as a preliminary to doing work—but you cannot learn a subject like chemistry without *doing* from the beginning and all the time. The book will suit Oxford youth able to memorize the purple patches and offer them up on the examination altar, hoping on leaving the Examination Schools to find an

emissary of I.C.I. awaiting their return with the prized admission card to an assured haven of research. They, however, will have had little or no effective training in chemistry but only parrot instruction in structural formulæ.

In the first line of the brief introduction to the book the author at once plunges into the valency problem with full measure of 'noughts and crosses', mainly dealing with *Resonance*, blankly asserting that:

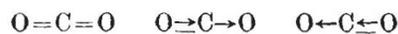
"The conception is the most important development which structural chemistry has had since it was extended to three dimensions by van 't Hoff in 1874. It is a result of the application of wave mechanics and could not have been deduced from classical dynamics; but its essential conclusions can be stated very simply. If a molecule can have two or more different structures in the ordinary organic sense of the term, then under certain conditions its actual state is neither one nor the other but something intermediate between the two, which partakes to some extent of the properties of both but cannot be expressed in the usual structural symbols. The molecule is then said to exhibit resonance and to be a resonance-hybrid of the two or more structures.

This is a declaration which I hesitate to endorse. In his recently delivered presidential address to the Chemical Society (*J. Chem. Soc.*, April), our would-be trumpeter of nitrogen speaks with even greater modesty and exceptional clearness. We are there told that it was a product of the obscure doctrine of wave mechanism.

"The general conclusions of the theory of resonance are of great practical importance, especially to the organic chemist. But it is not to be expected that more than a very few organic chemists will have either the time or the ability to master these mathematical operations. It is therefore obviously our duty to express—or to induce the wave-mechanicians to express—the results in the simplest terms that are possible and this can really be done quite easily. The use of the technical language of wave mechanics for this purpose is quite unnecessary and in fact misleading, for it makes the non-mathematical reader think that as he can't understand the language he can't understand the conclusions either, which is quite untrue; and not uncommonly, I think, it leads the non-mathematical writer to believe that if he knows the technical terms he must understand their meaning, which is by no means always the case."

I have known strange things said in chemistry but have never before been quite so stood upon my head.

Passing to the examples given, with carbon dioxide we have the three formulæ:



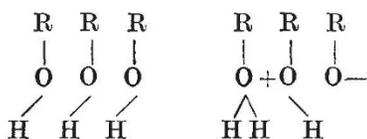
"According to the theory of resonance, since all these formulæ represent linear molecules and should have about the same stability or heat of formation, resonance must occur and the actual state of the molecule will be something intermediate between

them which we call a resonance hybrid, which will have a greater stability and heat of formation and a rather smaller distance between the atoms, than correspond to any one of the formulæ. Experiment shows that this is so. Further, since the last two formulæ are really the same, they must be represented to the same extent in the actual state of the hybrid, which therefore should be non-polar, as it is found to be."

According to this, resonance would seem to be a state of suspended animation in a molecular system with a shortened waist. Is not this "Much Ado about Nothing"? In what way it is an advance upon van 't Hoff is not clear. Kolbe was angered that van 't Hoff should introduce metaphysics into chemistry—what he would have said to Sidgwick passes expression. I am open to the retort, I know, that van 't Hoff was justified, but he had a solid model to build upon.

One of the more important applications of the conception of resonance is to the explanation of the power of hydrogen to serve as a bivalent link. There is no doubt, says Sidgwick, that a hydrogen atom is able to hold two oxygen atoms together. To me the evidence is entirely inadequate, nor is his present argument impressive.

"The crystallographers," he says, "have actually measured the length of this O-H O link (about 2.5 Å) which they call the hydrogen link but the idea which formerly prevailed that this link, like co-ordinate links in general, was due to the hydrogen taking up two more shared electrons (so that it had four in all) is now known to be impossible, since a hydrogen atom cannot hold four electrons with sufficient firmness. The only alternative explanation is that we have resonance between the ordinary form and one in which there is an oxonium cation and an R-O anion:"



Truly a soul-saving set of symbols. Faint praise ; scarcely hanging evidence. The nonchalance with which the inability to carry more electrons is treated and a new hypothesis at once found is amusing. Still better follows :

"The most extensive group of organic substances whose behaviour is determined by resonance is that of the aromatic compounds. It was recognised from the beginning that the two difficulties in the way of Kekulé's formula for benzene are, first, that we should expect two ortho di-derivatives ; secondly, that benzene should have the reactivity of an ethylene derivative, whereas in fact it behaves almost always as a saturated compound. The conception of resonance removes both of these objections at once : the first because we assume the state of the ortho-compound to be permanently half-way between the two formulæ and the second on account of the in-

creased stability which the resonance must produce. The last point can be determined experimentally from the heats of formation."

Such a statement cannot be taken seriously and it suggests insufficient historical and practical knowledge of the subject. I was one of the earliest workers with benzene, beginning in 1868. We never treated Kekulé's formulæ seriously—except for the purpose of registering the assumed disposal of substituent affinities : apart from the few who 'hammered' the idea for their own purposes, we thought of the two forms as present, if at all, in balanced proportions. The benzene symbol was used, not as a structural expression but as a convention in expressing interactions. We soon learnt that benzene had not the reactivity of an ethylene derivative. This led me to introduce the Centric formula.

The X-ray workers in course of time may help us out of our difficulty, but they are very slow. What are the forms of carbon : what of the form of that in benzene ? The paraffins are the only hydrocarbons containing diamond carbon. We know scarcely anything of paraffinoids generally. Edgar's work with heptanes shows that isomerides differ greatly, presumably owing to shape and difficulty of packing. Rumour goes that a paraffin has been made which won't pack and therefore declines to solidify—too resonant, I suppose.

Benzene, we know, contains a second form of carbon, which I would call *ethenoid*. The centres of the atoms are in a plane, not zigzagged, the distance between them less than in diamond carbon. What is hexamethylene—benzene with six "electronic" pits filled in ? It is little but a copy of benzene in appearance and properties.

During my lifetime the theory of valency has been developed from remarkably simple beginnings. When I began with Frankland in 1865, I heard his first course of lectures at the Royal College of Chemistry, published in his well-known book. He adopted Crum Brown's Graphite formulæ, behind which lay the tetrahedral conception. Carbon was a wooden ball with four holes in it. He had assimilated Kekulé's formulæ. I hold a paged proof of the later edition of his book in which he has written in all these. The original struggle between Kekulé and Frankland was over a fixed maximum of valency, that need not all be exercised but partly in abeyance. Kekulé as a joke copied Munchausen's method of shooting ducks on a ramrod.

Graphite is the puzzle—it seems to combine the two forms of carbon. This comes out very clearly in the model (Fig. 1).

The crystal is shown to consist of flat phenoid rings in parallel planes, 3-4 Å. apart, more than double the distance between two atoms in the

plane ring. When oxidized, oxygen atoms seem to penetrate directly into the wide space between layers and this plane is porous to other agents also. I seem to see the atoms as a bird-like structure, with unequal wings, one paraffinoid about double the length of the other one : the other, the shorter, ethenoid as in benzene.

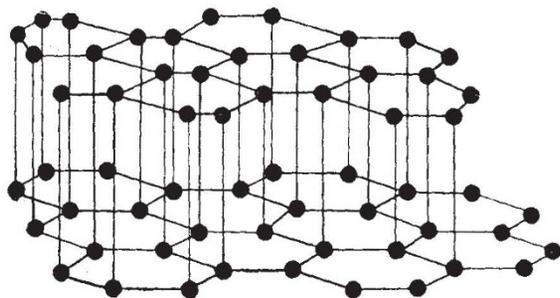
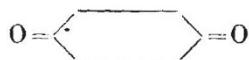


Fig. 1.

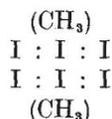
MODEL OF GRAPHITE. FROM *Chemistry and Industry*, AUG. 14, 1936.

Two forms of valency ultimately emerged—which acquired precision only when one was seen to be fixed by the *Electronic Charge*; the other being that which Pickering and I termed *Residual Affinity*. I discussed this very fully in March 1886 in the *Proceedings of the Royal Society* in a paper on electrolytic conduction in relation to molecular composition, valency and the nature of chemical change. In the previous year (March 1885) I dealt fully with the conditions of chemical change, a subject entirely left out of account in modern times. Then in 1888 I discussed the origin of colour and formulated the explanation since known as the Quinonoid Hypothesis (*Chem. Soc. Proc.*, March 1888).

I postulated a triple unsymmetrical absorbing system, such as that in quinone.



I soon discarded mere material absorption and taking iodoform as type, assumed that the residual affinities of the iodine atoms came into play as absorbent centres.



In fact, I became dotty at an early stage in my career. I was specially fascinated at the time by fluorescent compounds and triphenyl methane derivatives. My colour hypothesis is applicable to all ethenoid properties, and what I set out to explain fifty years ago is little short of what Sidwick would now explain. I doubt if there be much difference between us, but having read

the classics early, I have always been held up by the caution :

What's the use of Mercators
Tropics, Zones and Equators.
They are merely conventional signs.

Kekulé wrote an imperishable sign upon the fair face of our science when he introduced the simple hexagon. This expresses the one fact that is established—that six carbon atoms form a symmetrical complex, providing a convention which permits us to register and discuss isomerism in particular.

The colour of meta-compounds, I early asserted, was merely a case of the absorbent centres being in part formed between contiguous molecules—that is to say, extramolecular; whilst in para- and ortho-quinones it is within the molecule, intramolecular.

Whatever resonance hybrids may be, do or suffer, they have little practical significance. To take up time in indoctrinating students at the university with such vagaries is not justifiable. At the moment we are in sorest need of chemists—it were time that the University Grants Committee or similar body intervened to secure rational, practical training for those few who will give serious attention to the several subjects to be studied.

Students have to be taught according to their dispositions. The biological type is very rare; no greater perversion of the type exists than the ordinary biochemist, who is so-called because he works with material of living origin. The flag can be carried by very few. Mathematics beyond more than a very elementary stage is also without appeal to the chemist proper: the mathematician is a machine—prepared to let it be granted and act accordingly. The chemist should be inspired with feeling and only ask for truth and substance; he should go straight to Nature. Of course, the majority who inflict themselves upon the natural sciences are just machines. The only teacher is experience.

The fact is, we forget how much that is taught as chemistry is mere convention. The hands-across, down-the-middle, business of "The Lancers". The "bridged-ring" is just Huck Finn, let-on stuff, yet the majority swallow it whole. Kekulé so demoralized chemists by his Ring that they have no hesitation even in giving it a handle, a bridge. Benzene must be a solid block of atoms—in so far as atoms made of electrons can be solid.

For a book on the chemistry of nitrogen, the most wonderful of all the elements in forming character—the determining element of life—to be of outstanding value, it must make manifest the sympathy which only long experience in the laboratory begets and inculcate habits of scientific

thought that will be of service to the student who desires to be a working chemist or to teach the subject in our schools. It is possible to reach the standard of knowledge required for a 'first' without acquiring these habits; this would not matter were it not that Firsts go into schools and stagnate. The failure of Firsts in the schools is the out-

standing calamity of the costly attempt to introduce scientific training into education made during the past seventy years.

Chemistry at present is a sick man—"mostly conventional signs". Something less Snarkian is needed than "to measure the value of an idea in terms of incomprehensibility."

Darwin in Uruguay

By Dr. J. D. Falconer

H. M.S. *BEAGLE*, under the command of Capt. Fitzroy, sailed from Rio de Janeiro on July 5, 1832, for the Plata and anchored at Montevideo on July 26. For more than a year the ship was employed in surveying the extreme southern and eastern coasts of South America. The Plata was used as a base and to it from time to time the *Beagle* returned. Thus Charles Darwin, the naturalist aboard, had several opportunities of making closer acquaintance with the northern shores of the estuary and more particularly with the natural history and geology of the Banda Oriental, by which name the Republic of Uruguay, to the east of the Río Uruguay, was at that time known.

During the nineteenth century, Maldonado Bay at the mouth of the estuary was a favourite anchorage for ocean vessels. A strip of sand lined the margin of the bay and provided a playground for the men of the sea. In 1832 Darwin spent ten weeks at Maldonado and procured "a nearly perfect collection of the animals, birds, and reptiles" of the vicinity. He described Maldonado as "a most quiet, forlorn, little town: . . . separated from the river by a band of sand hillocks about a mile broad: it is surrounded on all other sides by an open slightly undulating country, covered by one uniform layer of fine green turf, on which countless herds of cattle, sheep, and horses graze. . . . The scenery is very uninteresting; there is scarcely a house, an enclosed piece of ground, or even a tree, to give it an air of cheerfulness"¹. To this day Maldonado retains its secluded aspect, being overshadowed by the modern resort of Punta del Este on the eastern horn of the bay. The sands, however, are now grassed and treed over, the pastures fenced and decorated with plantations, rail and road communications developed and frequented, and the landscape dotted with houses and gardens and cultivated fields.

It was at Maldonado that Darwin's attention was directed to the occurrence of vitrified siliceous

tubes (fulgurites) in the sand dunes, similar to, but shorter than, those described from Drigg in Cumberland in 1814². These tubes, believed to be formed by lightning, are still found at Maldonado but less frequently than before, on account of the cover of vegetation.

Between Maldonado and Montevideo along the northern bank of the Plata, Darwin again remarked upon the absence of trees and the uninteresting character of the grassy plains, decorated only by occasional hummocks of granitic rock. He concluded somewhat hastily that in spite of abundant rain and a favourable climate "herbaceous plants, instead of trees, were created to occupy that wide area"³. However this may be, within the last hundred years there has been much successful afforestation, and along the shores of the estuary and in many parts of the interior the aspect of the country has been completely changed.

In November 1833, Darwin made an excursion into the south-western corner of Uruguay, from Montevideo to Colonia Sacramento, and thence to Mercedes on the Río Negro. By this time, after some experience of the pampas of Argentina, his opinions of the scenery and amenities of the Banda Oriental had undergone a change. He wrote: "I find that I look at this province with very different eyes, from what I did upon my first arrival. I recollect I then thought it singularly level; but now, after galloping over the Pampas, my only surprise is, what could have induced me ever to have called it level. The country is a series of undulations, in themselves perhaps not absolutely great, but as compared to the plains of St. Fe, real mountains. From these inequalities there is an abundance of rivulets, and the turf is green and luxuriant"⁴.

On this expedition, Darwin visited the Arroyo de las Vivoras and Punta Gorda on the left bank of the Río Uruguay. From Mercedes he rode to the Sierra del Pedro Flaco, 20 miles up the Río Negro, and examined the natural sections in the