

season. The experience gained suggested new departures, and next season United Whalers co-operated with Electrohval in two catchers fitted with different guns supplied respectively by Messrs. Westley Richards, Ltd., and the Kongsberg Gun Factory. Sir Vyvyan Board, of United Whalers, Ltd., took part in this voyage. Last summer a further trial with the Westley Richards gun was made off Sao Thomé in the Gulf of Guinea.

In this post-war research, both Electrohval and the British workers have made progress in the difficult matter of electrifying forerunners and whale-ropes. The fact that electrocuted whales do not always float is sufficient to banish the optimistic suggestion that whale-lines need not be used in electric whaling. The main needs have been to overcome breakage due to differential stretch of forerunner and conductor, to reduce the weight of electrified ropes (for a heavy forerunner impedes the harpoon in flight), and to overcome the unlaying of the conductor by differential centrifugal forces acting when the forerunner flies out from its coil. Manilla, hemp, nylon and terylene have been tried. Nylon ropes, lighter and stronger than manilla, and less affected by extreme cold, are now favourites among post-war gunners, so it is important for the future acceptance of electrical methods that the Pirelli-General Cable Works, Ltd., have devised an extensible conductor which can remain intact during the 40 per cent or so stretch of nylon under strain.

In guns and harpoons two approaches are discernible. The more conservative development of Electrohval and the Kongsberg Gun Factory has been to retain the standard gun, but to modify the electric version of the Svend Foyn harpoon. Especially with the smaller fin and humpback whales, the harpoon may completely pierce the animal, causing (as already mentioned) a heavy current leakage from the barbs. To remedy this, Weber had introduced a hinged tip as a stop to slew the harpoon round after penetration⁴. But the cumbersome harpoon-shaft or 'leg', when partially withdrawn from the blubber on a taut line, was still a source of current leakage, requiring heavy insulation. Electrohval have therefore developed the 'detachable leg' harpoon where the shaft falls away after the barbed electric head with attached forerunner has fastened itself in the whale. The approach of United Whalers, Ltd., and associated firms has been to deviate from Electrohval in experimenting with a new gun, firing a new light-weight harpoon which has a flatter trajectory and longer range than the conventional harpoon weighing around 150 lb. The experimental gun, built by Messrs. Westley Richards, Ltd., fires on the spigot principle. One difficulty is to prevent, in the cramping tension of electrocuted muscle, the snapping of the new harpoon, which has to be made of high-tensile steel in order to combine strength with lightness.

Research and development continue. Other techniques are in the air, including carbon dioxide shells, and even rockets for possible helicopter whaling. But the electric harpoon undoubtedly combines humane killing with better preservation of whale products. It also shows real promise in reducing the time of hunting, and so shortening the season and reducing the enormous overhead costs in financing a modern expedition to the Antarctic grounds. Moreover, a shorter season could allow increased oil production within the International Whaling Convention's present limit of 16,000 blue whale units, since

baleen whaling could start later and so take whales which have fattened through an Antarctic summer. Actually there is a limit to the late start because of deteriorating weather in late summer, and because there are indications of an influx of immature whales from lower latitudes at this time¹⁰.

Whether electric whaling will find general adoption must ultimately depend upon the attitude of the whale-gunners. Until they are completely satisfied that the electric harpoon is superior, they are not likely to relinquish Svend Foyn's grenade, which has served them well for more than half a century of modern whaling.

¹ Brown, J. T., in Goode, G. B., *et al.*, Rep. U.S. Comm. Fish. Sect. V, 2, 218 (1887).

² Spears, J. R., "The Story of the New England Whalers" (New York, 1908).

³ Johnsen, A. O., *Norsk Hvalfangsttid.*, No. 8, 222 (1940).

⁴ Peters, N., "Der neue deutsche Walfang" (Hamburg, 1938).

⁵ Schubert, K., *Fischereiwelt*, 1, 35 (1949).

⁶ Reichert, W., *Fischereiwelt*, 1, 36 (1949).

⁷ Schjold, E., *Norsk Hvalfangsttid.*, No. 1, 8 (1936).

⁸ Hirata, M., Sci. Rep. Whales Res. Inst. Tokyo, No. 6, 199 (1951).

⁹ Lillie, H. R., *Canad. Geog. J.*, 28, 105 (1949).

¹⁰ Mackintosh, N. A., "Discovery" Rep., 22, 197 (1942).

RECENT SOVIET PRONOUNCEMENTS ON MOLECULAR STRUCTURE

THE resolution adopted at the Moscow Conference on the Theory of Chemical Structure in Organic Chemistry, a translation of which appeared recently in *Nature*¹, while giving some insight into Soviet methods of treating scientific questions, gives little indication of the precise nature of the views endorsed by the Conference. A more complete picture can be formed by an examination of other Soviet publications, namely, a paper on the theory of the chemical bond by N. D. Sokolov², the report of a committee set up by the Institute of Organic Chemistry of the U.S.S.R. Academy of Sciences to consider the present state of the theory of molecular structure³, a paper on the theory of organic chemistry by O. A. Reutov⁴ (the foregoing papers appeared prior to the Conference), and also reports of the Conference by Reutov⁵ and Sokolov⁶. Some relevant information derived from these publications is given below.

The proceedings at the Conference were based on the report of a second committee, set up by the Chemical Sciences Section of the Academy of Sciences under the chairmanship of A. N. Terenin; it had two members in common with the other committee of the Academy. Its report (though not available to me) is discussed and summarized in some of the papers cited^{1,5,6}, and it appears to be very similar to the first report, though covering a wider field.

There were two main topics at the Conference: the significance of the work of Butlerov, a Russian contemporary of Kekulé, and the unsound nature of the theory of resonance or mesomerism.

With regard to Butlerov, the following is quoted from Sokolov's summary⁶ of the Terenin report:

"The basic principles of the theory of chemical structure, which is the foundation of chemistry, were developed by the Russian genius of chemistry, Aleksandr Mikhaylovich Butlerov. . . .

"These principles are:

"(1) the molecule has a quite definite structure (spacial configuration of atoms, bond orders, and bond sequence);

"(2) the chemical properties of substances are directly related to the chemical structures of their molecules, and these structures may be ascertained by chemical methods;

"(3) the mutual effects of atoms within the molecule are of supreme importance for the chemical behaviour and properties of the molecule, and we may distinguish interactions between atoms that are directly united and also between atoms that are not directly united. . . .

"Shortly after Butlerov's formulation of the basic principles of structural theory, this theory began to gain more and more support from chemists, while at the same time the name of Butlerov began to be mentioned less and less. Non-appreciation, imperfect understanding, and perversion of the Butlerov theory of structure and suppression of the name of Butlerov became characteristic of bourgeois chemists.

"There is at present a very obvious tendency to pervert the true sense of the Butlerov structural theory, and there is a tendentious falsification of historical facts amounting to a disparagement of the significance of Russian science".

Butlerov first published his views on structure in 1861⁷. His ideas contrast with those of Kekulé, as expressed in the latter's "Lehrbuch der organischen Chemie", published also in 1861: "Which of the different rational formulæ to use in particular cases is essentially a question of expediency. The basis for accepting different rational formulæ for one given substance cannot be disputed on present-day views. It must, of course, be remembered that *rational formulæ are only formulæ for expressing chemical changes, and are not structural formulæ* [the emphasis is Kekulé's]; they serve merely for the expression of the transformations of bodies and can in no sense express their structures, that is, the disposition of the atoms". Butlerov discussed the phenomena of isomerism, including tautomerism (1862)⁸. These, of course, are in no way inconsistent with a theory that postulates a *single* structure for an organic substance. It is considered that the Butlerov theory is the true line along which modern quantum-mechanical electron theory must proceed, but that resonance theory (mesomerism), in the form in which it is universally applied, is inconsistent with the theory, since it implies the existence in the molecule of a single substance of *several* distinct structures, differing qualitatively in the distribution of valency bonds.

In the discussions on resonance there is a notable absence of reference to specific experimental facts, such as thermochemical or bond-length data. In fact, the theory is rejected not on the grounds of its inadequacy to account for experimental facts, but on methodological and philosophical grounds. The objections may be grouped under three headings: idealism, arbitrariness, and mechanisticism.

As regards idealism, it is stated³ that "the fundamental error in bourgeois theoretical thought of the twentieth century is 'physical' idealism and, in particular, mathematical fetishism. . . . As an example of the appearance of 'physical' idealism in theoretical chemistry we have the theory of resonance developed by Pauling, Wheland, and some of their followers. In this theory, on the basis of a formal interpretation of one of the approximate methods of calculating the state of a molecule, a concept has been formed of a physical phenomenon that is supposed to have

a real existence—the quantum-mechanical resonance of structures—and this has been widely applied to 'explain' actual facts and relationships. This is done by ascribing the sense of a definite chemical structure to each member of a summation that is an approximate representation of the wave function describing the state of the molecule. It is asserted that the 'resonance' of these 'structures' determines the actual state of the molecule. These structures are supposed to exist or, as it is expressed in resonance theory, 'to be in superposition' in every molecule. All the properties of the molecule and the very fact of its existence are determined by the nature of these resonance structures and of their superposition. Thus, 'resonance structures' and their resonance form the principal 'discovery' of resonance theory".

Reutov⁴ states that the non-validity of the basic principle underlying resonance theory can be summarized as follows, the example taken being benzene: "the functions f_1, f_2 , etc., in the equation $\psi_0(x) = a_1f_1 + a_2f_2 + \dots$, which is applied in the linear variant of the variation method, define the state of an unperturbed system of six carbon atoms that are at infinite distances from each other. When the carbon atoms approach to distances close to or equal to the lengths of covalent bonds, the separate members of $\psi_0(x)$ (f_1, f_2 , etc.) no longer define real states of the perturbed system, that is, of the real chemical molecule. Hence, there are no theoretical or experimental grounds for the identification of 'resonance structures' with any of the real states of the molecule. A resonance structure is not a physical phenomenon. The concept has arisen as a result of an incorrect treatment of one of the approximate quantum-mechanical methods of calculating the state of a molecule. When the calculation is done, for example, by the molecular-orbital method, no such concept emerges. In fact, resonance theory has no basis in quantum mechanics".

It is noted²⁻⁶ that authors of works on resonance theory indicate quite clearly in their preliminary discussions that 'resonance structures' and 'resonance energy' are abstract notions derived from a particular method of mathematical analysis; but it is asserted that they proceed, in fact, to treat these concepts as objective realities. This idealistic treatment is illustrated by quotations from Pauling⁹, Wheland¹⁰, Syrkin and Dyatkina¹¹, and Volkenshteyn¹². In these quotations a formal interpretation of the author's words supports the allegation. For example³, the following statements of Volkenshteyn are placed in juxtaposition: (1) "Actually, of course, there is no resonance: electrons in molecules are in certain quite definite states, and, in principle, these can be established without our being concerned with the states of the free atoms or with the purely speculative states ψ_i and ψ_n and the corresponding energies ϵ_i and ϵ_n ". (2) "The actual state of the molecule is a superposition of the separate structures, just as the state of an individual bond is a superposition of a homopolar and an ionic bond."

Particular attention is directed^{3,4} to the following quotation from Pauling: "The difficulty for benzene and for other molecules showing electronic resonance is to devise an experimental test which could be carried out quickly enough and which would distinguish among the structures under discussion" (p. 429 of ref. 9); an examination of the context of this quotation indicates that Pauling does not identify the "structures under discussion" as "resonance structures".

It should be noted that, throughout the discussions, the terms 'resonance', 'resonance structure', 'resonance energy', etc., are used almost entirely to indicate the objective concepts to which exception is taken. Thus, at the Conference, the mathematical physicist E. I. Adirovich said⁶: "The Heitler-London method, since it reflects an objective reality, cannot be regarded as idealistic. It is not on quantum mechanics or on quantum-mechanical calculations that idealism in physics and chemistry rests, but on scientific and philosophical perversions of these. The theory of resonance may be taken as an example".

The view was expressed that the adoption of the idealistic theory of resonance has led to the replacement of investigation into real factors determining molecular structure and properties by fruitless investigation into separate 'resonance structures', none of which has any physical reality; it is considered, therefore, that the theory has impeded the progress of chemical science.

The second objection to resonance theory is that of arbitrariness, and it is asserted that exponents of the theory attempt to justify the arbitrary element by recourse to the 'principle of convenience'. It is alleged^{4,5}, in fact, that the 'principle of convenience' forms the methodological basis of resonance theory.

In support of this allegation, quotations are made from Pauling and others. For example, "The convenience and value of the concept of resonance in discussing the problems of chemistry are so great as to make the disadvantage of the element of arbitrariness of little significance"⁹; "[resonance] does not correspond to any intrinsic property of the molecule itself, but instead it is only a mathematical device, deliberately invented by the physicist or chemist for his own convenience"¹⁰. It is argued that the 'principle of convenience' does not constitute a sound basis for any theory.

The arbitrary nature of the choice of resonance structures is examined in some detail by Sokolov²: "Resonance energy' is a simple *mathematical* consequence of the variation principle, according to which the energy of a system of electrons, calculated by the aid of a linear combination of a definite number of arbitrary functions, will always be less (that is, more in absolute magnitude) than when calculated using a smaller number of these same functions. Using the variation method, it would be possible to substitute any function f (even the most absurd function, so long as it is antisymmetrical, continuous, finite, and becomes zero at infinity) for one of the functions representing 'resonance structures', and the value obtained for the energy of the system would necessarily be less than that obtained without taking f into consideration".

However, Sokolov and others^{2,3} approve the method, borrowed from resonance theory, of representing a molecule by reference to an assembly of different structures. Sokolov states that this method is the sole contribution of value that has come to chemistry from resonance theory, and considers it to be a valuable alternative to the 'English' method of representing a molecule by means of a classical valency formula supplemented by straight and curved arrows (the Academy committee³ pays a tribute to Ingold and Robinson for the part they played in the development of electronic theory in organic chemistry).

Finally, it is objected that the theory of resonance is mechanistic. It has attempted to reduce chemical phenomena to the mechanics of the electron, and

this violates the principle, developed, for example, by Engels, that a higher form of movement cannot be reduced to a lower form of movement. It is here that a parallel is drawn between resonance theory and Mendelian theories in biology. The manner in which this principle is applied will be clear from the following passage⁷:

"It is quite obvious that the laws of quantum mechanics do not cover all the laws to which the chemical form of movement of matter is subject. When we speak of the chemical form of movement, we mean the processes of converting some substances into others, which occur as a result of the redistribution of the bonds of atoms and changes in the electron clouds of atoms and molecules. At the basis of the chemical form of movement lies the quantum laws to which electrons, atoms, and molecules are subject. However, the specific nature of the chemical form of movement is determined not so much by these laws, as by the laws that are associated with the presence of complex forms of interaction among large numbers of particles (electrons, atoms, molecules), and it is not covered by quantum mechanics. Such questions as the reactivity of substances, that is, the mechanism and kinetics of their chemical transformations, cannot be studied by quantum mechanics alone, but require also the application of statistical theory for their treatment. It is obvious that the theory of chemical processes must rest, in the first place, on the study of the processes themselves; in other words, the basis for the study of the chemical form of movement of matter must always be chemical investigational methods".

Turning now to other aspects of the proceedings: In the publications that preceded the Conference, the authors named in the Resolution and other Soviet workers were criticized for their views on structural theory. I have found no reference to papers in which any one of these workers defended his position; most of them came forward at the Conference and recanted their views.

A notable exception was G. V. Chelintsev, who was criticized for his 'New Structural Theory', which states that an electron orbit cannot be associated with more than two atoms, that is, that there are no 'non-localized' bonds. At the Conference, Chelintsev was adamant in support of his theory and strongly criticized the Terenin report. He accused the organizers of the Conference of being "former direct supporters of the pseudoscientific theories of Ingold and Pauling", and said that under their guidance there was "little hope of extricating chemical theory from the blind alley into which it has been brought by idealistically thinking bourgeois physicists and chemists". Chelintsev continued: "As the Conference aims at deciding questions of methodology in chemical science, the working report should have presented in clear contrast the two existing, mutually exclusive solutions of the most important problem of chemistry—the structural problem. The Report does not do this, and it is therefore absolutely worthless". The "two . . . solutions" are Chelintsev's own theory and the quantum-mechanical treatment of molecular structure presented in the report.

The ideas of Chelintsev are related to those of M. I. Batuev, who was criticized at the Conference for his views, as expressed in a recent paper. Batuev, however, vigorously defended his position and accused the compilers of the report of not fully exposing resonance theory. He said that the report treats existing quantum-mechanical methods of

calculating the structure of a molecule as valid, whereas they are, in fact, Machist in nature. In effect, Batuev denied the possibility of applying quantum mechanics in chemistry.

Chelintsev and Batuev received no support and were very strongly criticized, though it was recognized that Chelintsev's continual pronouncements in criticism of resonance theory had been of service by directing general attention to the principles upon which the theory rested. The presence of non-localized bonds in organic molecules was considered to be an established fact and to have received valuable support from quantum-mechanical methods of treatment, such as the molecular-orbital method.

It is notable that great emphasis is placed, in all the Soviet publications, on the value of quantum-mechanical methods. Thus³, "In spite of the approximate nature of calculations made by its aid, quantum mechanics has shown that the concept of non-localized bonds in aromatic and conjugated systems, which was developed previously by chemists on the basis of experiment, is in agreement with the basic principles of modern physics. Note also the basis of the theory of the transition state (the activated complex) in chemical reactions (the absolute reaction rate theory), qualitative deductions from which have found applications in organic chemistry. It must be emphasized that most of the approximate calculations of the structures of organic molecules, made by one or other valid quantum-mechanical method, characterize the structure quantitatively, taking mutual effects of atoms into account. In spite of the approximate nature of these calculations, they can play a positive part in theoretical organic chemistry". Again, in the Terenin report⁴: "Quantum-mechanical calculations done by the 'electron-pair' and 'molecular-orbital' methods on polyatomic molecules are extremely approximate and can be regarded as only semi-empirical. Quantitative results obtained by their aid cannot be treated as trustworthy without further investigation. However, these calculations often permit general qualitative conclusions, which may be sufficiently valid so long as they are not bound up with the particular nature of the assumptions that lie at the basis of the method of calculation used. These general qualitative deductions enable us to interpret a number of peculiarities of complex molecules. Thus, such calculations have shown that the concept developed by chemists of mutual effects between atoms that are transmitted through a chain of bonds by means of a redistribution of electron densities is in full accord with the quantum properties of electrons. Quantum chemistry has enabled the specific laws of this redistribution to be discovered, for example, the reduction in the interaction between neighbouring parts of a molecule when there is a departure from parallelism between the axes of the π -clouds of two directly united atoms. This prediction of quantum chemistry has been confirmed experimentally. For molecules with a conjugated system of double bonds, a very simple model has been proposed in which all the π -electrons move in a potential box along the length of the conjugated chain. It is able to explain regularities among the spectra of groups of similar molecules and to confirm the fact, well known to chemists, that in a conjugated chain, mutual effects are transmitted for long distances without being appreciably damped out. Hence, thanks to the successful application of quantum mechanics to the solution of problems relating to the chemical bond and the structure of

the molecule, many concepts in chemical structural theory have been given a physical basis, and new concepts have been created that are taking an important role in the development of chemical structural theory". The general view of the Conference, as summarized by Reutov⁵, was that "the use of existing quantum-mechanical methods of calculation for molecules is valid and necessary. But an unrelenting struggle must be waged against all forms of idealistic interpretation of the results of these methods; this struggle is being waged successfully by Soviet chemists and physicists, armed with the dialectical-materialism world-view".

General optimism was expressed regarding the possibility of further progress in quantum chemistry, and Syrkin and Volkenshteyn were criticized by a number of the participants for the pessimistic attitude they displayed. For example, Syrkin⁶, after admitting his errors and acknowledging that he bore a great share of the guilt for the acceptance of resonance concepts by other Soviet authors, said that he rated future prospects of quantum chemistry "rather pessimistically". "There is at present," he continued, "no way of approaching a solution that would give a sufficiently close approximation, and it is doubtful whether one will be found in the near future." Adirovich commented: "The speeches of Syrkin and Volkenshteyn are permeated by an extremely unpleasant pessimism: in their opinion, there is no hope for the progressive development of quantum mechanics in its application to chemistry. The impression is given, that if we reject the theory of resonance, then quantum mechanics has nothing to give to chemistry. This is an erroneous and harmful conclusion. Chelintsev's and Batuev's speeches practically amount to the same: quantum mechanics must be rejected from chemistry". Prof. Adirovich remarked further that he did not share the pessimistic belief that the problem of the polyatomic molecule was in general insoluble.

The above account of the relevant Soviet publications is not exhaustive; but it covers the principal topics discussed, apart from the question of the formulation of a qualitative theory of the reactivity of organic substances. Much discussion³⁻⁶ was given to this matter, for, in Reutov's words⁴, "With the exposure of the speculative nature of resonance theory, it becomes essential to make a wide review of theoretical concepts of organic chemistry, in order to eliminate speculative hypotheses introduced by resonance theory. At the same time, it is very important to mark out and preserve the rational part of the achievements of the last few decades in the theory of organic chemistry". The interpretations given of the reactivity of an organic molecule in terms of induction, conjugation, and radical effects, etc., are on lines that will be familiar and generally acceptable to Western organic chemists.

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¹ *Nature*, **169**, 92 (1952).

² Sokolov, N. D., *Uspekhi khimii*, **18**, 697 (1949).

³ Kursanov, D. N., et al., *Uspekhi khimii*, **19**, 529 (1950).

⁴ Reutov, O. A., *J. Gen. Chem. U.S.S.R.*, **21**, 186 (1951).

⁵ Reutov, O. A., *Voprosy filosofii*, No. 4, 167 (1951).

⁶ Sokolov, N. D., *Uspekhi fizicheskikh nauk*, **45**, 277 (1951).

⁷ Butlerow, A. M., *Z. Chem. u. Pharm.*, 549 (1861).

⁸ Butlerow, A. M., *Z. Chem. u. Pharm.*, 482 (1862).

⁹ Pauling, L., "The Nature of the Chemical Bond", 2nd edit.

¹⁰ Wheland, G. W., "The Theory of Resonance" (1944).

¹¹ Syrkin, Ya. K., and Dyatkina, M. E., "The Chemical Bond and Molecular Structure" (in Russian. Goskhimizdat, 1946. English translation: Butterworths Scientific Publications, Ltd., 1950).

¹² Volkenshteyn, M. V., "The Structure of Molecules" (in Russian. U.S.S.R. Acad. of Sciences, 1947).