

method of visual tuning has been incorporated in the receiver. The great advance that has taken place in this year's sets, however, is the extension of the tuning arrangements to cover the short wave broadcasting bands. The title 'all-wave' tuning is generally applied to such receivers, but in only one or two cases can the set be tuned continuously from a wave-length in the region of 10-15 metres up to nearly 600 metres. The majority of the 'all-wave' receivers cover the short wave broadcasting bands only, there being gaps in the wave-length scale, where, at present, there are no transmissions of interest to the broadcast listener. Even with this restriction, however, it is necessary to provide the receiver with four separate wave-length bands, selected by an extension of the usual wave-change switch.

The production on a manufacturing scale of such a set in which the tuning on each band is controlled by the same knob, with a pointer reading on scales calibrated directly in wave-lengths, is a technical achievement of considerable merit. It is evident that, following upon the use of short-waves for Empire and other long-distance broadcasting, the reception of such short-wave programmes has now successfully passed beyond the experimental stage.

The other great feature of the exhibition was the demonstration of the present stage of television with the aid of the special test transmissions from the B.B.C. experimental station at Alexandra Palace. At this station separate television transmitters have been installed by the Baird Television Co. Ltd. and the Marconi E.M.I. Television Co. Ltd., and during the course of the radio exhibition these installations were used on alternate days for broadcasting a television programme. The accompanying sound was radiated from a separate transmitter installed by the B.B.C. The wave-lengths in use are 6.67 metres (frequency 45 megacycles per second) for the vision and 7.23 metres (41.5 megacycles per second) for the sound.

The daily programmes were received at the exhibition and demonstrated to the public on a number of receiving sets, the makers of which were not stated. Although naturally the interest displayed by large numbers of visitors precluded the study of the results for more than a short period, the demonstration was sufficient to indicate that the successful reproduction of a television programme broadcast from a station ten miles away is a present-day achievement. For the first time, the public has been enabled to see, as well as hear, the announcer in the studio and a well-known broadcasting singer. The majority of the programme comprised the transmission of sound-films, either constructed specially for this demonstration or extracted from standard news and entertainment films.

In the exhibition hall itself several firms displayed sets suitable for receiving these transmissions, although these were unpriced and were not in operation. The output on the vision side of these sets operates a cathode ray tube of unusually generous dimensions, the largest having a bulb of 22 inches diameter, the luminescent screen providing a picture area of $17\frac{1}{2}$ in. \times $13\frac{1}{2}$ in. In most cases it is claimed that these receivers will give satisfactory results on the transmissions from the Alexandra Palace at distances up to 40 miles. In accordance with the recommendations of the Television Advisory Committee, all such receivers are arranged to reproduce the vision programme whether this be emitted on the Marconi E.M.I., or the Baird system.

It would thus appear that the time is ripe for the carrying out of practical and widespread tests of the possibilities of radio-television in Great Britain, although it is natural that some time must elapse before the technique has been simplified and the manufacturing costs reduced to such a point as to make television reception in the home available to the majority of the general public. R. L. S.-R.

Valency and Molecular Structure

By Prof. R. F. Hunter and Prof. R. Samuel

THE connexion between the numerical valency exhibited by an atom and the number of its outside electrons, which prevailed in certain pre-wave mechanical theories of valency and in the theory of Heitler and London, appears to us of fundamental importance to the problem. It cannot be fortuitous that iodine, for example, which possesses two *s*- and five *p*-electrons, exhibits odd covalencies of 1, 3, 5 and 7. Nevertheless, this relationship appears to have been lost sight of in the chemical theories of Lowry, Sidgwick, and others on account of the conception of co-ordinate covalency, in which only electrons belonging to one of the atoms concerned are made responsible for chemical combination. This conception appears to connect these theories with the theory of molecular orbitals (Herzberg, Lennard-Jones, Mulliken) in that chemical linkage is ascribed to the bonding power of single independent electrons, while the formation of pairs is an essential feature of the theory of Heitler and London.

Since valency is an ambiguous term, it is necessary

to distinguish clearly between energetical questions and numerical chemical valency. While bond energy may vary from molecule to molecule, the valency number indicates the possibilities for chemical reaction and is a property of the free atom or radical. The maximal valency of the halogens is 7, but since this necessitates the fission of the s^2 group, considerable energy, which decreases with rise in atomic number, is required, so that heptavalency obtains with oxygen in Cl_2O_7 , and with fluorine in IF_7 . Although we are here mainly concerned with experimental facts, it is necessary to make brief reference to the wave mechanical interpretation of bonding power.

*Wave Mechanical Considerations*¹.—It is true that in the exchange integral (in formula 11 of Heitler and London's original paper),

$$E_{12} = \int \left(\frac{2\varepsilon^2}{r_{12}} + \frac{2\varepsilon^2}{R} - \frac{\varepsilon^2}{r_{a1}} - \frac{\varepsilon^2}{r_{a2}} - \frac{\varepsilon^2}{r_{b1}} - \frac{\varepsilon^2}{r_b} \right) \frac{\psi_1\psi_1\psi_2\psi_2}{2} dr_1 dr_2,$$

the attraction (negative sign) is produced by those terms which are caused by the terms of the potential representing interaction between one nucleus and one electron. The pure interaction between the electrons themselves (ϵ^2/r_{12}) gives an effect of opposite sign, and is antibonding. This, however, cannot be interpreted as proof of the bonding power of the single electron. That the whole expression E_{12} is called the exchange integral is not due to this term containing r_{12} representing the interaction of the electrons between themselves, but to the fact that the mere existence of the quantity E_{12} is connected with the use not of the wave function $\psi_{1\varphi_2}$, but of the wave function $\psi_{1\varphi_2} \pm \psi_2\varphi_1$. This, in its turn, is the direct consequence of the degeneracy produced by the identity of the electrons.

Thus, the relation of the electron pair bond theory to the single electron bond theory in the method of molecular orbitals becomes quite clear. In the latter, the same terms appear even without the repulsion term with r_{12} , but the appearance of the double product $\psi_1\varphi_1$ is produced here not by the use of the function ψ_1 but of the function $\psi_1 \pm \varphi_1$. In other words, it is introduced by the identity of the nuclear fields.

From the point of view of a theory of valency, this is of course purely incidental. Chemical linkage is not confined to atoms of the same element, and attempts have therefore been made to explain this by means of a pseudo degeneracy of unequal nuclei, if the interaction is of the order $E_\psi - E_\varphi$, meaning that the valency of an atom not only as regards bond energy, but also in the numerical sense, should depend on the partner, and the greater the difference in the nuclear fields the smaller must be the distance between them to bring about this bonding effect.

The latter point is certainly empirically untrue as seen, for example, from the known diameters of oxides of the first short period. Regarding the first point, since we are not concerned here with the development of a perturbation method of calculation but with a theory of valency, it seems obvious that the valency number of an atom cannot depend on the partner with which it combines, other than in the energetical sense. Indeed the method of molecular orbitals gives incorrect results with regard to the products of dissociation of a molecule, due to neglect of the wave mechanical interaction of the electrons.

Since dissociation is the converse of molecule formation, this confirms our view that the method of molecular orbitals describes the electronic configuration and term system of the completed molecule but is not a theory of valency. Actually, it is unable to distinguish in itself between terms of attraction (molecule formation) and terms of repulsion (elastic collisions), and only becomes a theory of valency by the introduction of a postulate which identifies non-promoted with bonding electrons and promoted ones with anti-bonding. From new spectroscopical data it becomes increasingly evident, however, that this postulate can no longer be maintained.

Spectroscopical Evidence.²—The number of molecules in which it is possible to correlate the molecular terms with those of the separated atoms has increased considerably of late. Particular interest is attached to the halides and oxides of the second group, in which it has been shown that the ground level of the molecule is correlated, not to an unexcited halogen

or oxygen atom plus an unexcited metallic atom with the configuration $s^2 {}^1S$, but to an excited metal atom with the configuration $sp {}^3P$. This now receives confirmation from some ten examples, the most striking of which are those in which the metal possesses high excitation energy. Whenever an excited molecular term appears in which the bond energy is higher than in the ground level, it is correlated to the so-called anomalous terms of the metal atom, in which both the original s -electrons have been simultaneously excited, showing that whenever a second linkage is formed (as in BeO and MgO), it occurs only in the presence of two p -electrons. Whenever an odd-electron molecule is formed (BeF and CaF), the partial removal of the odd electron increases the bond energy, showing that the unpaired electron is always disturbing.

Both these points receive confirmation from molecules of other types. NO, PO, and AsO, and also SiF and SnCl, all show the disturbing influence of the unpaired electron. On the other hand, molecules such as AlO and GaO are formed by the combination of oxygen with unexcited metal atoms of the configuration $s^2p {}^2P$, but the molecular term, of which the bond energy is much higher than in the ground level, is formed by the combination of oxygen with metal atoms of the configuration $sp^2 {}^4P$; the second linkage again occurring only after fission of the s^2 group. These results are incompatible with the theory of the co-ordinate link and show the anti-bonding character of the closed helium-like s^2 group, which constitutes the 'lone pair' in the majority of cases. While the pair bond conception of valency gives a straightforward and consistent interpretation of these results, the theory of molecular orbitals, on account of its promotion postulate, would predict that molecules such as BeO and BeF would be formed by unexcited metal atoms because they possess an excess of non-promoted (and therefore bonding) electrons.

The difference between an electron pair bond theory of valency and that of molecular orbitals finally finds its expression between localized and non-localized electrons in polyatomic molecules. The first experimental evidence in this connexion has been obtained from a complete vibrational analysis of the band spectra of SO_2 and SeO_2 . These results show that the harmonic vibrations, for example, of SeO in its unexcited and excited states, agree closely with two symmetrical valence vibrations of unexcited and excited SeO_2 ; the energy of electronic excitation being almost identical in the two molecules and the factor of anharmonicity of the ground states, which could not be accurately determined for SeO_2 , appears at least to be of the same order. Furthermore, the heat of dissociation of SeO_2 into gaseous atoms is about twice that of SeO. The molecular constants of SO_2 bear the same relationship to those of SO, and the continuous absorption spectra of halides and oxyhalides of sulphur show that the bond energies of the S-Cl, S=O, and S=S bonds are approximately of the same order in widely differing molecules such as SO, SCl_2 , SOCl_2 , S_2Cl_2 , and SO_2 .

Each of the bonds in polyatomic molecules of this type appears to be localized between two atoms, in accordance with the older structural formulæ of chemistry. It is characteristic that there is one atom which may be regarded as the central atom, and for such cases the Heitler-London theory indicates strong localization of bonds.

*Chemical Evidence*³.—It has been shown that the conception of the lone pair of electrons as an agent for true chemical linkage is in direct contradiction to the results of band spectroscopy. In our opinion, the spectroscopical evidence is of the greatest importance for the following reasons. The difference between two non-electrostatic links (normal and co-ordinate covalency) involves a difference of the role played by individual electrons. Physico-chemical measurements such as the parachor, dipole moment, etc., are concerned with the whole electronic cloud of valency electrons, and *a priori* cannot give information as to the part played by a particular electron. This can only be obtained from spectroscopical experiments. It is therefore always possible to interpret the mechanism of chemical linkage from the results of physico-chemical experiments in alternative ways, as has already been indicated in cases of the parachor, optical activity (for example, toluene-sulphonic esters and beryllium benzoylpyruvate), and crystal structure (SiF_6^{--}).

Similarly, the increase in dipole moment accompanying the formation of certain molecular associations in solution observed by Earp and Glasstone⁴ is no proof of the presence of a co-ordinate link. The dipole moments of such associations sometimes decrease and sometimes increase, depending on the geometrical position of the constituent molecules as to whether there is a cancelling out, or an increase through induction⁵. The energies of dissociation of such complexes, determined by these and other authors, vary between 1 and 10 k.cal./mol., which is about 1/100 to 1/10 of that associated with a true chemical bond. This, in our opinion, proves conclusively that the complexes are loose associations held together by van der Waals forces.

With regard to the resonance linkage suggested, for example, for the NO_2 group, it is possible that a co-ordinate link would oscillate between the oxygen atoms if it existed, but no experimental proof has so far been advanced for its existence. These arguments therefore in no way invalidate our earlier conclusion that chemical and physico-chemical evidence fail to provide any proof for the existence of a second form of non-electrostatic linkage in molecules of the first order.

It is true that an atom possessing a lone pair of electrons is frequently associated with chemical reactivity in carbon chains and the formation of complex associations in inorganic chemistry. Since band spectroscopy excludes a mechanism of the 'donor' and 'acceptor' type, something else must be responsible for such phenomena. As a tentative suggestion, it may be pointed out that the molecular refractivity indicates that the polarizability is always high in such atoms so long as the electrons of the lone pair are not involved in chemical linkage, and that the large dipole moment induced on approach of a reagent molecule might be responsible for such phenomena.

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¹ See Hunter and Samuel, *J. Chem. Soc.*, 1180 (1934); Lessheim and Samuel, *Proc. Ind. Acad. Sci. (Bangalore)*, 1, 623 (1935), and the literature mentioned in these papers.

² Lessheim and Samuel, *Phil. Mag.*, 21, 41 (1936); Asundi and Samuel, *Proc. Phys. Soc.*, 48, 27 (1936); *Proc. Ind. Acad. Sci. (Bangalore)*, 2, 30 (1935); 3, 466 (1936); Asundi, Jan Khan, and Samuel, *Proc. Roy. Soc.*, in press, and literature mentioned there.

³ Hunter and Samuel, *Chem. and Ind.*, 54, 31, 467, 635 (1935); *Rec. trav. chim.*, 54, 114 (1935), and literature mentioned there.

⁴ *J. Chem. Soc.*, 1709 (1935).

⁵ cf. Stuart, "Molekülstruktur," p. 114 (1934).

Science News a Century Ago

Death of John Pond, F.R.S.

ON September 7, 1836, John Pond, the sixth Astronomer Royal, died at Blackheath at the age of sixty-nine years, and a few days later was buried in the tomb of Halley in Lee churchyard. Pond was born in London in 1767. After attending schools at Hadleigh and Maidstone, at the age of sixteen years he entered Trinity College, Cambridge, and attended the mathematical lectures of Vince. Ill-health led him to travel, and during visits to Portugal, Malta, Turkey and Egypt he made many astronomical observations. From 1798 until 1807 he lived at Westbury, near Bristol, where by his observations on the declination of some of the principal stars he showed conclusively that Bird's quadrant at Greenwich had altered its form.

Pond was elected a fellow of the Royal Society in 1807. He married and removing to London in 1811 was chosen to succeed Maskelyne at the Royal Observatory. In 1812 he mounted a six-foot mural circle by Troughton, in 1816 a transit instrument of 5-in. aperture, in 1821 substituted the mercury horizon for the plumb-line and spirit-level, and in 1825 introduced the system of observing the same object by direct and reflected vision. A sound practical astronomer, he published catalogues of stars, translated Laplace's "Système du Monde" and wrote many articles for Rees' "Encyclopædia". In 1817 he was awarded the Lalande Medal and in 1823 the Copley Medal. He was succeeded at Greenwich by Airy, who, writing to Henry Warburton, M.P., to support an application for a pension for Mrs. Pond, said that Pond's claims to the gratitude of astronomers were due first to the accuracy which he introduced into all the principal observations, secondly, to the attention he bestowed on those points (chiefly of sidereal astronomy) which he regarded as fundamental, and thirdly his regularity of observation. "Since the commencement of Mr. Pond's residence at Greenwich," said Airy, "Astronomy considered as an accurate representation of the heavens in the most material points has acquired a certainty and an extent which it never had before."

Discovery of Fossils on the Continent

IN its column of Miscellanea, the *Athenæum* for September 10, 1836, said: "Dr. Klippstein, a German savant, who has been long devoted to geology, and who directs the researches in the environs of Alzei (a little town of the Rhine Hesse) has lately made a discovery. On digging twenty-eight feet under the soil, near Eppelsheim, and a league from Alzei, his workmen found a head of a *Dinotherium giganteum*, in perfect preservation. This is probably the most colossal of all antediluvian animals, and the existence of which was first pointed out by the learned zoologist, Dr. Caup. This head is six feet long and three feet and a half broad. Near the head was also found a shoulder bone of which remains have not been met with elsewhere. Also at one thousand feet below the surface, in the mines of Anzin, an entire fossil palm tree has been found in an upright position. Its roots pierced the soil to a depth of several feet, and it is to be brought to the Museum of Natural History in the Jardin des Plants."

The neighbourhood of Mainz and Alzey early attracted the attention of geologists on account of its wealth of fossils. Von Zittel said: "The discovery