

Nature of the Covalent Binding

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Surface Tension of Micelle-Forming Solutions

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August 26, 1942

THE recent communication by Cassel¹ on this much-discussed topic agrees, on the whole, with the conclusions arrived at by the present author in a note of last year,² and since amplified into a more detailed and general form.³

In these publications the earlier views of other authors⁴ were examined and rejected, and a quite general treatment, still based upon that of Gibbs, was shown to be in accord with experiment. The vanishing of $d\gamma/dC$ (as at the minimum of surface tension), was very simply explicable on the basis of micellar aggregation.

While in general agreement with Cassel, the writer would disagree somewhat with his last paragraph, in which a crystalline or liquid-crystalline structure is assigned to the adsorbed surface films, and a superposition of surface tension and surface stress is suggested as possibly responsible for time effects before the minimum surface tension is reached.

In a recent paper on the structure of the surfaces of solutions,⁵ it was pointed out that the adsorbed films are most certainly of the compressed gaseous type, and that the area occupied by each molecule at the minimum surface tension is of the order of 50 percent greater than that possible on the basis of close-packed hydrocarbon chains. Thus the adsorbed films definitely cannot be classed as crystalline, nor even as liquid-crystalline save insofar as all highly compressed gaseous films possess a considerable degree of molecular orientation.

With regard to the time effects occurring before the minimum surface tension is reached, the explanation suggested some time ago,⁶ admittedly a tentative one but in terms of a definite molecular mechanism, seems preferable to a rather vague phrase such as that quoted above.

¹ H. M. Cassel, *J. Chem. Phys.* **10**, 246 (1942).

² A. E. Alexander, *Nature* **148**, 752 (1941).

³ A. E. Alexander, *Trans. Faraday Soc.* **38**, 248 (1942).

⁴ R. F. Nickerson, *J. Phys. Chem.* **40**, 277 (1936); N. K. Adam, *Physics and Chemistry of Surfaces* (O. U. Press) third edition, p. 408; J. W. McBain and G. F. Mills, *Reports on Progress in Physics* **5**, 30 (1939); F. A. Long and G. C. Nutting, *J. Am. Chem. Soc.* **63**, 625 (1941).

⁵ A. E. Alexander, *Trans. Faraday Soc.* **38**, 54 (1942).

⁶ A. E. Alexander, *Trans. Faraday Soc.* **37**, 15 (1941).

Nature of the Covalent Binding

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October 14, 1942

IT has been found advantageous to consider the binding within di- and polyatomic covalent particles as due to the interaction of electrons and charged atomic cores rather than to an interaction between neutral atoms.¹

This emphasis on the electric interaction throws additional light on the binding within H_2^+ and H_2 , already so successfully clarified by wave mechanics.²

For comparison, we apply to H_2^+ the assumptions used in Niels Bohr's³ treatment of the hydrogen molecule. 1. Coulomb forces are the only source of the molecular potential energy. 2. Classical mechanics applies to the motion of the electron considered as permanently symmetrical to both protons; speed v , radius of the circular orbit a . 3. $mva = nh/2\pi$.

On this basis, $E = -11.9$ ev ($n = 1$) results for the binding energy $2H^+ + e^- = H_2^+$. The experimental value is -16.3 ev, with which the wave mechanical value is in full agreement. It should be emphasized that in the wave mechanical treatment the potential energy is also purely Coulombic. However, contrary to assumption 2, the density of negative electricity proves to be distributed symmetrically with respect to both protons only on the time average, which gives rise to a temporary dipole moment of H_2^+ .

This temporary asymmetry makes the potential energy V of H_2^+ with respect to $2H^+ + e^-$ lower than it would be in the permanently symmetrical Bohr model. For the latter: $V = -23.8$ ev, the kinetic energy $E_k = 11.9$ ev. Calculations on the basis of wave mechanical variation functions of H. M. James or of V. Guillemin and C. Zener⁴ give the average potential energy $V = -32.6$ ev, the average $E_k = 16.3$ ev.

In the case of the binding energy of the hydrogen molecule ($2H^+ + 2e^- = H_2$), the situation is qualitatively the same. When both electrons would move permanently symmetrically to both protons, $E = -29.9$ ev. The corresponding experimental value is $E = -31.8$ ev. The binding energy is again larger, but only by 6.4 percent, while in the case of H_2^+ the difference between 11.9 and 16.3 is 37 percent. Obviously, the temporary deviations from the average symmetrical position are smaller for H_2 , with its two electrons and internuclear distance $r = 0.74$ Å, than for the single electron of H_2^+ and $r = 1.06$ Å.

The above considerations prove to be useful when applied to Li_2 . The binding energy ($2Li^+ + 2e^- = Li_2$) is $E = -11.9$ ev, the internuclear distance $r = 2.67$ Å. The difference between H_2 and Li_2 is due to the fact that Li^+ has an electronic shell. The electron distribution curve for Li^+ indicates that at the internuclear distance of H_2 (0.74 Å), the electronic systems of the two Li^+ would considerably overlap, and the repulsion between the excess charges would be increased by that of the electronic shells. At the distance 2.67 Å, the latter can be neglected. Based on Bohr's model, treating Li^+ as a point charge, the large difference in r and E of H_2 and Li_2 could be due only to a different value of n in assumption 3. Putting $n = 2$; $r = 2.33$ Å and $E = -7.5$ ev.

By analogy with H_2^+ and H_2 , the large relative difference between 7.5 and 11.9 eV can be interpreted as due to the asymmetry of the motion of the electrons of Li_2 , enhanced by the large internuclear distance 2.67 Å.

Hence, to the above emphasis that the binding in the covalent molecules H_2^+ , H_2 , Li_2 , which do not have a permanent dipole moment, is caused by Coulombic forces, one has to add that part of the potential energy is due to the temporary polarity of the molecules. The Bohr model represents the idealized permanently unpolar binding. While the idealized binding between rigid ions is an electrostatic phenomenon, the idealized and the real covalent bindings are electrokinetic in nature.

*Horace H. Rackham Predoctoral Fellow, 1941-1942 and 1942-1943.

¹ See abstracts of our papers presented at the Buffalo Meeting of the American Chemical Society on September 10, 1942. The detailed publication will follow soon.

² H_2^+ : O. Burrau, *Kgl. Danske Vid. Sels. Math-Fys. Medd.* 7, 1 (1927); E. A. Hylleraas, 1931; G. Jaffé, 1934. H_2 : H. M. James and A. S. Coolidge, *J. Chem. Phys.* 1, 825 (1933).

³ N. Bohr, *Phil. Mag.* 26, 857 (1913).

⁴ See L. Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, New York, 1935), pp. 332-333.

On the Structure of a Metal During Deformation

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August 21, 1942

THE cold working of a metal must produce extreme disarrangement of the orderly atomic array known to exist in metals. Even a short time after as violent a distortion as 90 percent rolling a metal consists of crystallites—each of which contains several million atoms in a quite orderly pattern¹—although practically every atom must have changed at least some of its neighbors. However, the mechanism by which the originally crystalline metal passed through the deforming process, to become, finally, crystalline again, is still in question.

In order to study the structure of a metal during deformation, the following simple experiment was performed: A hardened steel edge was clamped in the center of a cylindrical x-ray diffraction camera so that the edge could serve as a powder specimen. A copper ribbon was bent around this edge and pulled so that it traveled over the edge continuously. During the motion of the copper ribbon, the edge could be irradiated with x-rays and the diffraction pattern recorded on a photographic film in the usual way. This apparatus is diagrammed in Fig. 1. A piece of carefully annealed copper ribbon 0.1 mm thick was made very hard and springy by one pass over the edge, so that considerable

work hardening and, therefore, distortion must have been given the metal during this process. Two kinds of diffraction pattern were made: one with the copper ribbon bent around the edge, but not moving; the other with the copper ribbon traveling over the edge at about four centimeters a second. The two kinds of pictures turned out to

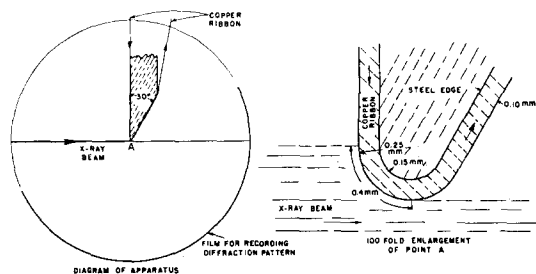


FIG. 1.

be indistinguishable—both showed only the lines of cold-worked copper with the same positions, intensities, and widths.

W. L. Bragg² has a picture of the behavior of metals during deformation from which my result could have been predicted. According to this picture, crystallites will grow very rapidly from an amorphous mass of metal until they reach a certain minimum size. My result insures that not more than one-tenth of the copper irradiated was non-crystalline, and also that the crystalline material present was of about the same particle size and state of strain, whether the copper ribbon had been deformed one one-hundredth of a second or several minutes previously. Crudely, one could say that, according to this experiment, a metal recrystallizes as fast as it is deformed.

The possibility of finite thicknesses of amorphous, or "vitreous," metal seems very faint indeed, in view of the results just described.

¹ W. A. Wood, *Proc. Phys. Soc.* 52, 111 (1940).

² W. L. Bragg, *Proc. Phys. Soc.* 52, 108 (1940).

Erratum: The Diffraction of X-Rays by Liquid Oxygen

(*J. Chem. Phys.* 10, 504 (1942))

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Temperatures in Figs. 2a and b are incorrect. They should read: Fig. 2a, 89°K in place of 62°, and 62° in place of 85°; Fig. 2b, 89°K in place of 85°.