

of an initial 'hydroxylation' that I still regard it as the best interpretation of the known facts.

Moreover, when in due course the details are published of the further experiments recently carried out here (1) by Dr. D. M. Newitt and Mr. A. E. Haffner on the pressure-oxidation of methane and (2) by Mr. R. E. Allum on the kinetics of its slow combustion at atmospheric pressure, I think there will remain but little room for doubt about methyl alcohol being the initial product, unaccompanied by any vestige of a hypothetical 'peroxide'.

If, however, Dr. Mardles can adduce satisfactory experimental proof of his supposed initial formation of 'methyl-hydrogen-peroxide' during the slow combustion of methane, by actually isolating and identifying it among the products, there will be grounds for reconsidering the matter, but otherwise not.

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<sup>1</sup> NATURE, July 18, p. 116.

<sup>2</sup> Proc. Roy. Soc., A, 129, p. 424.

### Unusual Lightning.

ON the night of July 12 we witnessed a display of atmospheric electricity which was sufficiently unusual to merit description.

The display was confined to one cloud, low on the horizon in the direction north by west, and apparently at a considerable distance. To one of us, observing from 10.15 P.M. to 10.30 P.M., the phenomena appeared as flame-coloured discharges which recurred in the cloud with considerable regularity at intervals of about a minute and were remarkable for their duration, which was sometimes as great as one second. No thunder was audible.

To the other, observing independently from 10.30 P.M. to 11.30 P.M., the discharges seemed to have their origin in the upper part of the cloud, for each one showed the dark upper edge of the cloud in strong relief: glows of flame-coloured light shone upward and illuminated higher clouds. Sometimes the glow would extend over the whole cloud, sometimes only over a portion of it, and occasionally would start at one end of the cloud and move to the other before being extinguished. The discharges occurred at intervals of one to one and a half minutes, and frequently lasted for a second, in marked contrast to the apparent instantaneity of forked lightning.

Dr. Simpson has suggested that the description tallies well with that of *Flachenblitz*, which appears to be a silent discharge over the surface of a cloud. In his Robert Boyle Lecture (1930) he states that very little is known about this form of discharge and that it is probably due to a kind of St. Elmo's Fire over the whole surface of a cloud.

There is no mention of this form of lightning in the "Encyclopædia Britannica".

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### Valency and Diamagnetism of Titanium in the Tetrachloride.

TITANIUM (atomic number 22) is known to be paramagnetic. It shows anomaly in that its paramagnetism after decreasing from  $1.6 \times 10^{-6}$  at  $-170^\circ$  to  $1.25 \times 10^{-6}$  at  $-80^\circ$  becomes constant. All its compounds so far studied are also known to be paramagnetic;  $TiO_2$ ,  $Ti_3O_5$ ,  $TiS_2$ , and  $Ti_2S_3$  having values

0.066, 8.1, 0.56, and 0.91 ( $\times 10^{-6}$ ) respectively, for the specific susceptibility (Int. Crit. Tables).

In a recent paper, Weir<sup>1</sup> has found by electron diffraction that titanium tetrachloride has tetrahedral symmetry with the titanium atom in the centre and the Ti-Cl bonds, being equally and symmetrically directed towards the corners of a tetrahedron. In this case, the titanium central atom has 18 electrons forming a completed group and the four valency electrons symmetrically distributed with respect to the centre, and titanium chloride must be expected to show diamagnetism as contrasted with other compounds of titanium.

An accurate investigation of titanium chloride (a strongly fuming liquid) was made with a sensitive Curie balance, with quartz suspension and retorsion head. The liquid was contained in thin sealed capsules, correction being applied for the latter. The liquid was found to be diamagnetic with a value ( $-0.287 \times 10^{-6}$ ) for the specific susceptibility at  $35^\circ C$ .

This suggests that the paramagnetism of the element titanium is due to the two pairs of valency electrons being in different orbits and giving rise to a resultant paramagnetism, and similarly in the compounds of titanium, the paramagnetism in the compounds is due to the unsymmetrical nature of the valency links. When all the valency links are symmetrically distributed as in titanium tetrachloride, the paramagnetism disappears.

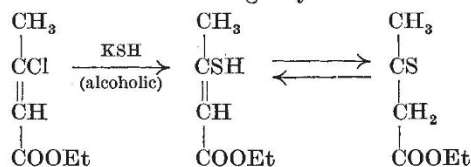
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<sup>1</sup> Ann. der Phys., vol. 8, ser. 5; 1931.

### Synthesis of Ethyl Thio-aceto-acetate.

WITH the view of investigating the negative character of the methylene group due to the proximity of :C : S group, Mr. E. K. Mitra, Sir T. N. Palit research scholar, working in my laboratory, has succeeded in effecting the long-looked-for synthesis of ethyl thio-aceto-acetate in the following way:



The mercaptan at the moment of its formation tautomerises as indicated above.

The so-called thio-ester described in the text-books is really diacetoacetic ester sulphide, as is evident from the mode of its preparation and reactions. The new ester behaves exactly like ethylacetoacetate in its reactions towards hydrazines, hydroxylamine, aromatic amines, etc., with the formation of heterocyclic ring compounds. It undergoes Grignard's, Reformatsky's, and Michael's reactions, resulting in a vast series of interesting compounds. In Knoevenagel's reaction, however, the course taken up is a novel one, giving rise to the formation of thio-aldehydes, hitherto almost unknown in a very good yield. The characteristic behaviour of these true thio-aldehydes and their relationship with ordinary aldehydes are also being closely studied. A detailed account of the investigation will in due course appear in the *Journal of the Indian Chemical Society*.

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University College of Science and  
Technology,  
Calcutta, June 6.