EXPERIMENTS WITH ATOMIC HYDROGEN: A SEARCH FOR HIGHER HYDRIDES OF NITROGEN, PHOSPHORUS AND SULPHUR.

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Elements in Groups VB, VIB and VIIB of the Periodic Table show a lower valency towards hydrogen than towards the halogens. Phosphorus and sulphur, for example, form the fluorides PF_5 and SF_6 whilst the highest known hydrides are PH_3 and H_2S. As no explanation of this behaviour seems to have been given, it was decided to attempt the preparation of the hypothetical hydrides PH_5 and SH_6. For this purpose, PH_3 and H_2S were brought into contact with atomic hydrogen.

The first short period forms an exception to the above remarks. From Group IV to Group VII the valency, towards both hydrogen and the halogens, follows the sequence 4, 3, 2, 1, and the reason for this, of course, is that the number of electrons in the corresponding electron group is limited to eight. A hydride of nitrogen, for example, higher than NH_3 would not be expected and the existence of NH_4 in the so-called ammonium amalgam is unlikely. It seemed worth while, however, to investigate the reaction of atomic hydrogen with NH_3.

The behaviour of both NH_3 and H_2S with atomic hydrogen has been described by Boehm and Bonhoeffer.[1] NH_3 was unchanged,

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[1] Boehm and Bonhoeffer, *Z. physik. Chem.*, 1926, **119**, 385.

whilst H_2S caused the hydrogen atoms to re-combine with separation of sulphur. The experimental method, however, was not one which would have allowed these authors to have detected small amounts of higher hydrides.

In the present work the reaction products were condensed in liquid air and were then analysed. This was carried out by thermal decomposition at constant volume. If the reactant gases had remained unchanged, the analyses would have been according to the equations :—

$$2NH_3 = N_2 + 3H_2$$
$$2PH_3 = 2P + 3H_2$$
$$H_2S = S + H_2.$$
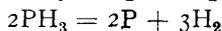
The measured pressure increases would then have been 100 %, 50 %, and nil respectively. If any higher hydrides had been formed, greater pressure increases would have been observed.

Experimental.

Moist hydrogen was drawn through the capillary A, of the diagram, at 20-30 c.c./min. and its pressure was maintained at about 0·3 mm. by
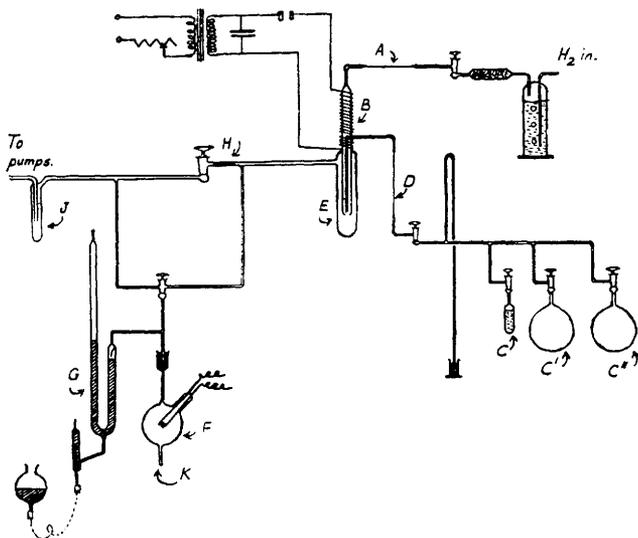
means of a mercury vapour pump and a Hyvac. It was dissociated at B by means of an electrodeless discharge. The other reactant gases were withdrawn from the storage vessels C, C', and C'' and were passed through a second capillary D to meet the atomic hydrogen at a nozzle in the vessel E, cooled in liquid air. The flow rate of these gases was about a tenth of the hydrogen rate. Samples of the condensed products were subsequently volatilised into the bulb F, connected to a constant volume manometer G. Decomposition was effected by means of a heated platinum filament, or, in the case of the phosphine experiment, by heating the bulb itself. It was continued to a steady pressure, as observed on a cathetometer. Constant temperature was attained by means of a water bath.

A platinum spiral was inserted in the pumping tube at H to prevent atomic hydrogen reaching the tap grease. Normally it glowed brightly but occasionally it became inactive. That this inactivity was not due

to the absence of hydrogen atoms was proved by inserting a fresh piece of platinum. Poisoning in the catalysis of hydrogen atom recombination does not seem to have been reported previously.

The glowing platinum was not completely effective in removing hydrogen atoms, for a blue-green luminescence was sometimes observed in the mercury vapour pump and was probably the chemiluminescence attributed [2] to the formation of HgH. It even appeared with the trap J immersed in liquid air.

As a check on their purity, samples of the NH_3, PH_3 and H_2S were analysed by thermal decomposition. In all cases, the observed pressure changes were within 0·4 % of theoretical. In another check on the experimental method, an examination was made of the reaction product which was condensed when moist hydrogen alone was passed through the apparatus, with the discharge taking place. Its vapour pressure was that of water and it gave no volume change when its vapour was examined in the decomposition bulb. It was satisfactory that no SiH_4 was formed.

In experiments *without* liquid air under the reaction vessel, NH_3, PH_3 and H_2S were all found to cause the recombination of hydrogen atoms, as shown by the quenching of the glow at the platinum spiral. H_2S also gave a deposit of sulphur and PH_3 gave a brilliant yellow mirror on the glass. This was not yellow phosphorus but was probably the substance known as the solid lower hydride. Both deposits disappeared under the influence of the atomic hydrogen alone.

With the reaction vessel immersed in liquid air, the condensed products were all white, except in the case of phosphine where the material was yellowish, probably again due to the presence of lower hydrides. The products were analysed in a number of fractions according to volatility. In order to correct the observed pressure changes for the presence of water vapour, especially in the least volatile fractions, this vapour was condensed out in the tube K by means of liquid air after decomposition was complete. Non-condensible gas was then pumped out of the bulb and the partial pressure of water vapour was measured on the manometer.

The measured pressure changes were all within 0·5 % of theoretical, indicating no detectable formation of higher hydrides. The following results on H_2S are typical :—

	Most Volatile Fraction.	Middle Fraction.	Least Volatile Fraction.
Pressure before decomposition .	35.8_2 mm.	32.6_1 mm.	76.0_5 mm.
Pressure after decomposition .	35.6_9 mm.	32.5_6 mm.	76.0_6 mm.

In the case of the product obtained with PH_3, only the most volatile part was examined, for the presence of lower hydrides in the remainder would have interfered with the detection of PH_5. If the latter had been formed, it would, however, have been expected to be present in the most volatile fraction and this was found not to be the case.

The analyses were, of course, carried out at room temperature and it might have been possible for a higher hydride to have existed at liquid air temperature but decomposing into the normal hydride and hydrogen during the warming up. It was found, however, that the various reaction products, after volatilisation, could again be recondensed completely, *i.e.* no appreciable quantity of hydrogen had been formed. This test was not carried out in the case of the hydrogen sulphide experiment.

[2] Bonhoeffer, *Z. physik. Chem.*, 1925, **116**, 391.

Concluding Remarks.

The non-existence of hydrides of elements in Groups VB, VIB and VIIB corresponding to the highest halides is surprising, for these elements might be expected to form as many bonds with hydrogen atoms as with halogens. Pauling [3] considers that in a fluoride such as PF_5 the completely covalent structure, with a decet of shared electrons, is probably of minor importance since it would involve the unstable $3d$ orbitals. Instead, it is believed that this molecule has an ionic structure in which a negative fluorine ion resonates amongst the five positions and the phosphorus atom has a normal octet and a positive charge.

If this view be correct, it may account for the non-existence of PH_5, since in this the hydrogen atoms would be *more* electropositive than the phosphorus atom and an ionic structure of the above type is therefore unlikely.

Another possibility is that the highest known hydrides may show a lack of tendency to add on extra hydrogen for the same reason as that which accounts for the inertness of the rare gases. Thus PH_3, H_2S and HCl all possess exactly the same total number of electrons as argon : AsH_3, SeH_2 and HBr possess the same number as krypton and so on. The extranuclear structure of these hydrides may therefore bear some resemblance to those of the rare gases. In the hydrides, of course, protons are embedded in the electron cloud and are bound to modify the structure in spite of the equal number of electrons. But the case is very different with the corresponding lower fluorides, PF_3, etc., for here the *total* number of electrons is not the same as in a rare gas and the fluorine nuclei have a much higher charge than the protons of the hydrides.

Some support for this view is given by the steady and systematic falling off in the valency towards hydrogen in the sequence 4, 3, 2, 1 for elements in Groups IV to VII.

Summary.

Ammonia, phosphine and hydrogen sulphide were brought into contact with atomic hydrogen in an attempt to prepare higher hydrides. All three gases caused hydrogen atoms to recombine and the two latter were also decomposed. The reaction products were analysed but there was no evidence of higher hydride formation.

Possible reasons for the non-existence of hydrides corresponding to PF_5 and SF_6 have been briefly considered.

A case of poisoning of platinum in the catalysis of hydrogen atom recombination is also reported.

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[3] Pauling, *The Nature of the Chemical Bond*, 1939, p. 90.