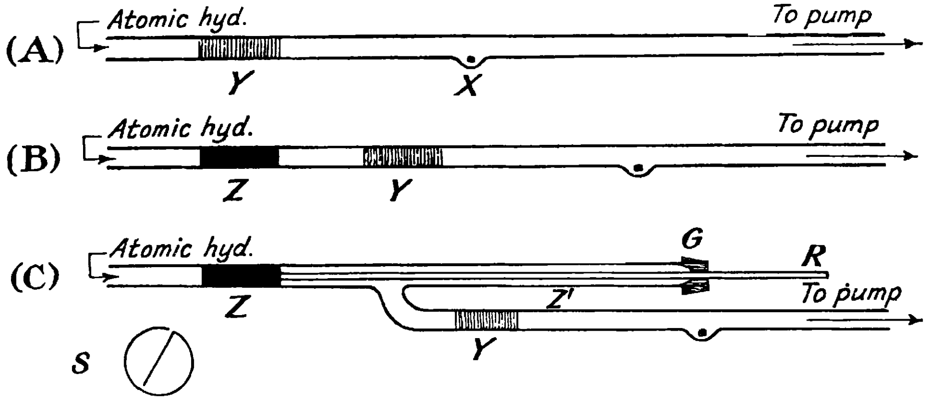
2. *The Formation of Alkali-metal Hydrides by Atomic Hydrogen.*

By Edna Ferrell, Thomas G. Pearson, and Percy L. Robinson.

The reactions of atomic hydrogen with a number of elements have recently been described (*Proc. Roy. Soc.*, 1933, *A*, **142**, 275). Those elements were comparatively insensitive to moisture and gave rise usually to volatile hydrides. The technique has been somewhat modified in studying the behaviour of lithium, sodium, and potassium, which have been shown to combine readily at the ordinary temperature with atomic hydrogen to form their respective hydrides, the presence of which was evident not only from visible changes in the metals but also from specific chemical tests.

Fig. 1.



In the earlier experiments, films of metal condensed on the walls of the reaction tube were used, and sodium and potassium could be readily volatilised in a vacuum to form such mirrors. Lithium, however, is known, when liquefied, to fracture the glass at the point of contact; this difficulty was overcome by supporting the metal in a small porcelain boat, for although this invariably cracked, the reaction tube was left intact.

The apparatus used consisted of a discharge tube, similar to that previously described (*loc. cit.*), in which hydrogen at 0·2—2·0 mm. could be excited with a current of 0·5 amp. at about 5000 volts, to which was attached a working tube (Fig. 1; A, B, C) by means of a picëin-sealed joint, whence the gas was removed by a pump system with its protective condensing vessels. The arrangements enabled a stream of hydrogen rich in atomic species to be drawn through the working tube at a velocity of about 10 m./sec.

In the first experiments, with a tube of type A, sodium was volatilised in a black vacuum from the point X to form a metallic mirror at Y. Such a mirror was unaffected by molecular hydrogen which had been dried over potassium hydroxide pellets and fused calcium chloride and had subsequently passed through the unexcited discharge tube. When, however, the gas was subjected to the discharge, the mirror at once began to lose its grey metallic appearance at the end nearest the discharge tube, and was rapidly converted throughout its entire length into a white film. The reaction began spontaneously and was accompanied by the evolution of heat; but apparently started and continued at the ordinary temperature, since effective cooling of the tube did not lessen the speed of conversion. The conversion of thicker deposits of metal was arrested by the protective coat of hydride formed, but could be carried to completion by the simple expedient of evacuating the apparatus, driving the unchanged metal to the surface by gentle heat, and there treating it with a further quantity of atomic hydrogen. When the conversion was complete, as shown by the fact that metal could no longer be evaporated from the material if appropriately heated in a black vacuum, the following tests were performed. The portion of the tube carrying the deposit was cut out and the product was shown to effervesce with water; this phenomenon, in the absence of free metal, was attributed to the liberation of hydrogen from the hydride. The apparatus was filled with carbon dioxide with the product *in situ*, and then heated; the product, when dissolved in water, gave positive tests for a formate with ammoniacal silver nitrate and neutral ferric chloride.

Mirrors of the alkali metals were known to us to be extremely sensitive to moisture; *e.g.*, they are practically instantaneously converted into hydroxide by the moisture present in ordinary air, and the possibility remained that some, perhaps most, of the change observed was due to moisture, either expelled from the discharge tube or its electrodes by the heating effect of the current, or arising from the influence of the discharge on traces of oxygen present in the hydrogen. With these possibilities in mind, a mirror was prepared at Y in a working tube (Fig. 1B), which was provided with a lining of silver foil Z about 3 in. long, sufficient to catalyse the complete recombination of all the atomic hydrogen present in the gas stream but offering no interference to the passage of moisture or oxygen. Under these conditions the conversion of a similar mirror was incomparably slower, being incomplete in 3 hours. For a crucial demonstration of this point, a tube of the form C was employed. It was constructed in Pyrex glass and was provided with a 3-in. cylinder of silver foil (twisted as shown in section S) attached to the glass rod R which passed through the air-tight rubber gland G, movement being facilitated by lubrication with glycerol. By this means the silver could be moved from position Z to position Z′, where it was out of the direct gas stream. At X the alkali metal was vaporised in a vacuum and gave a mirror at Y. After a stream of hydrogen of appropriate velocity had been started, the discharge was switched on with the silver foil at Z, the tube surrounding the silver being kept cold by pads of wet cotton-wool. After the passage of atomic hydrogen for 45 minutes the alkali-metal mirror was quite unaffected, but the instant the silver foil was removed to position Z′ attack began and proceeded quickly over the whole area of metal. The attack was not quite so rapid as in the straight tube, which is readily explained by the less direct path taken by the atomic gas and the fact that some of it would diffuse towards Z′.

Lithium.—The hydride formed a white powdery deposit. Carbon dioxide, dried over calcium chloride and phosphoric oxide, was passed over the heated material, which remained white, and when the product was dissolved in water and treated with ammoniacal silver nitrate, metallic silver was deposited on boiling. The same solution, made neutral and treated with neutral ferric chloride, gave a reddish coloration which disappeared on acidification with hydrochloric acid. Simultaneous blank tests were negative, and it was concluded that the formate had arisen from the hydride: $LiH + CO_2 \longrightarrow H{\cdot}CO_2Li$. In thicker layers the hydride was faintly blue. The material appears to be identical with that obtained by Troost and Hautefeuille (*Ann. Chim.*, 1874, **2**, 279) from the combination of the elements at 500°; Dafert and Miklanz (*Monatsh.*, 1912, **33**, 63) mention a bluish colour.

Sodium.—The white compound formed gave the above tests for hydride, and appeared similar to the material obtained by Moissan (*Compt. rend.*, 1902, **134**, 71) and by Ephraim and Michel (*Helv. Chim. Acta*, 1921, **4**, 762) when the metal is heated to 360° in hydrogen. It was formed as readily as the corresponding lithium compound.

Potassium.—The material was white, gave all the tests for hydride, and was of the same nature as the hydride of Ephraim and Michel (*loc. cit.*), who found that the combination of potassium was promoted by traces of calcium. No promoter was needed with atomic hydrogen, reaction being instantaneous.

Acknowledgment is made to the Research Committee of this College for a grant.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

[*Received, October 25th,* 1933.]