THERMIC REACTIONS IN VACUO.

PART III.

REDUCTION BY MAGNESIUM POWDER OF SILICIC ANHYDRIDE

By H. RUSSELL ELLIS, B.Sc., and FRANK E. WESTON, B.Sc.

Magnesium powder readily reduces silicic anhydride in presence of air without external heating during the reaction; the products consist of free silicon, one or more of the silicides of magnesium, magnesium oxide, and possibly silicon monoxide.

It has been shown previously that in similar actions the air plays an important part, more especially in the initial stages of the reduction. In the experiments now described the interaction has been studied in absence of air, and mixtures containing the following varying quantities of the constituents have been made to react *in vacuo* and the products examined.

- (a) Equal weights of each.
- (b) In proportions Mg + SiO₂.
- (c) In proportions 2Mg + SiO₂.
- (d) In proportions 4Mg + SiO₂.

The magnesium powder was supplied by Kahlbaum, and was found to contain a small amount of MgCO₃, which caused an evolution of gas during the reduction.

The silica used was precipitated, and before use was strongly ignited.

The fuse used to start the reaction consisted of a mixture of Al powder and Na₂O₂ in proportion 4Al to 3Na₂O₂.

The apparatus used was the large bottle of about three litres capacity, fitted up as shown in diagram 3, Part I.

Analysis of the Mixture resulting from the Reaction.

It was thought that by using excess of Mg it would be possible to use up the whole of the SiO₂, and by subsequent treatment of the residue with acids to obtain pure silicon. A mixture was therefore made consisting of equal parts of SiO₂ and Mg; for the reaction demanded by the equation—

48.7 parts Mg are required to 60 parts of SiO₂.

Twelve reductions were carried out, each time 20 to 30 grams of the mixture being used; the contents of the crucible from each reaction were powdered, mixed, and analysed. The products consisted of free Mg, unreduced SiO₂, two or more silicides of Mg, free Si, MgO, and possibly some silicon monoxide.

The complete quantitative analysis of the mixture has not yet been successfully carried out, owing to the difficulties met with.

The authors are carrying out experiments to throw light on the formation of "monox," and to find certain reliable tests for this substance. Owing to lack of reliable information with regard to magnesium silicides, no complete estimation of these bodies has yet been made

1. *Examination and Estimation of Silicides.*—On treatment with strong HCl a large amount of spontaneously inflammable gas was evolved, and on washing and drying the residue at 100° C. and then treating with HF more inflammable gas was evolved. It was found impossible to completely decompose the silicides with HCl; this was either due to (a) a protective layer of SiO₂ formed in the reduction, (b) to a film of SiO₂ deposited during the action of the acid, (c) to different silicides being present which are unattacked by HCl.

The decomposition by HCl was carried out in an atmosphere of hydrogen or CO₂ and also *in vacuo*, and in each case a large amount of undecomposed silicide remained.

2. *Decomposition in CO₂ or H.*—The weighed powder was placed in the middle flask and just covered with water; H or CO₂ suitably washed was passed through the apparatus until the whole of the air was expelled; by adjusting the taps shown a very slow stream of gas was then driven through the apparatus during the experiment. Strong HCl was added very slowly,

FIG. 4.

and a vigorous reaction took place, the evolved gases passing through the three test-tubes, which contained AgNO₃ solution.

The AgNO₃ solution in the first tube became black immediately, while if the operation was carefully carried out the solution in the last tube remained clear.

The flask was warmed when the reaction had become slow, and H or CO₂ passed until the whole of the SiH₄ was driven over. The deposited silver was dissolved in HNO₃ after filtering and washing, and estimated by standard NH₄CNS.

The mixture in the flask still contained undecomposed silicides.

If the reactions are—

then 108 grams Ag $\equiv$ to 19 grams Mg₂Si.

In two estimations—

1 gram mixture used and 5.9 c.c. of .098 N. NH₄CNS.

1 gram mixture used and 6.35 c.c. of .098 N. NH₄CNS.

corresponding to about 1.2 per cent. Mg₂Si.

The estimation in this manner was abandoned after many attempts.

3. *Reaction between HCl and the Mixture in Vacuo.*—The gas was generated by adding concentrated HCl very slowly and carefully to the mixture after exhausting the apparatus (see Fig. 5); the gas evolved was finally driven over into a mercury gas holder by means of freshly boiled distilled water, and was stored out of contact with water.

The gas when first made was spontaneously inflammable, but after storing for some time it lost this power and consisted of almost pure hydrogen, giving no deposit of SiO_2 when burnt. (The mixture, after keeping for some time and decomposed *in vacuo* gave no spontaneously inflammable gas with HCl, although with HF this was given off rapidly.) The gas evolved was estimated as shown later.

The residue in the flask, although it showed no reaction on warming with HCl, readily evolved spontaneously inflammable gas with HF.

FIG. 5.

The authors were not able to estimate the total silicides by this method but consider that at least two silicides were present.

Method of Analysing the Gas.

A small volume of about 10 c.c. of the gas was transferred very slowly into an explosion pipette containing a known volume of pure oxygen.

As soon as a bubble of the gas came into the oxygen a sharp explosion took place and a cloud of SiO_2 was produced. This continued until the whole of the gas was transferred. A slight black deposit formed on the bulb, probably due to a small amount of the gas being decomposed by the high temperature of the explosion.

The diminution in volume was observed and the residual gas sparked, the volume again noted, and finally the gas was mixed with electrolytic gas and again sparked.

Knowing the volume of gas used and the contraction after explosion, and assuming that the gas consisted of SiH_4 and H_2 only, the amount of each can be calculated.

To illustrate the method of calculation an experiment is given fully.

2 grams mixture used.

247.3 c.c. gas at 19°C . and 760 mm.

THERMIC REACTIONS IN VACUO

Analysis of gas : 14.5 c.c. of gas used and passed into 49.9 c.c. of oxygen.

Contraction after mixing = 20 c.c.

Further loss on mixing with electrolytic gas = 1.7.

Total loss of oxygen = 7.4 c.c.

Equation representing reaction between the gases and oxygen is—

where x and y are volumes of SiH_4 and H_2 .

$$\therefore x + y = 14.5$$

$$\text{and } \left(2x + \frac{y}{2} \right) = 7.4$$

$$\therefore x = 0.1$$

$$\text{and } y = 14.4$$

The total loss on explosion was 21.7 c.c.

For above composition should be 21.9 c.c.

A large number of analyses gave the same result, showing the gas to consist of almost pure H mixed with a very small quantity of hydride of silicon, and that, moreover, a very small quantity of this gas is sufficient to inflame the hydrogen when mixed with air or oxygen.

This analysis enables the percentage of free Mg to be found ; this was 12.27.

The action of the gas on KOH was examined, but the changes in volume were too small to be measured, showing the existence of traces only of gases other than hydrogen.

Estimation of Total Silicon in the Mixture.

It was thought possible to estimate the Si and SiO_2 by (a) dissolving in boiling HCl and weighing the residue left ; (b) dissolving the Si in KOH and weighing the SiO_2 left ; (c) fusing with KOH and estimating the total silica.

Concordant results could not be obtained, and it was found that the finely divided SiO_2 dissolved freely in both HCl and KOH, and that any treatment to render SiO_2 insoluble would also convert some of the Si into SiO_2 .

The total silicon was found correctly by fusing with KOH, &c. ; it was always necessary to evaporate HCl solutions to dryness and ignite, as the finely divided silica readily dissolved.

$$\text{Percentage Si found} = 22.124.$$

Estimation of Free Si.

The mixture was first heated with concentrated HCl and then with HF for several days. The residue obtained completely combined with Cl gas, forming SiCl_4 . The percentages of Si found by this method were concordant and equalled 12.75.

Result of Analyses.

1. Percentage of free Mg = 12.27
2. Percentage of free Si = 12.75
3. Percentage of total Si = 22.124

Hence $(22.124 - 12.75) = 9.374$ per cent. of Si is combined as SiO_2 , SiO, and silicides.

CHEMICAL DEPARTMENT, THE POLYTECHNIC,
REGENT STREET, W.