## THE HEATS OF COMBUSTION OF ALUMINIUM, CALCIUM, AND MAGNESIUM.

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The values given by various experimenters for the heats of formation of  $Al_2O_3$ , CaO, and MgO differ very considerably, as is shown in the following table :—

Ι.	Mg + O:	= MgO-		
	Heat E	volution.		Authority.
	148,000 calories			Dr. Strauss, Minet, Production of Al, p. 209.
	143,300	,,	•••	Beketoff.
	143,400	>>		Electrochemical and Metallurgical Industry, 6–8.
II	. Ca + O	= CaO-		
	151,900 (	calories	•••	A. Guntz and H. Bassett, jun., C. R., 1905, 140, 863,864.
	131,500	,,	•••	Thomsen (see L. and B.).
	145,000	,,	•••	Moissan.
	131,648	,,	•••	Dr. Strauss, Minet, Production of Al, p. 209.
	130,900	,,		Thomsen,

Guntz used pure Ca and formed pure compounds, from which he determined the heats of solution; this, of course, introduces complications, leading to various corrections. Forcrand, using pure CaO from Ca(OH)<sub>2</sub> and determining heats of solution, obtained the same value as Guntz (C. R., 1908, 146, 217-220). Thomsen used CaO prepared from calcium nitrate, and Forcrand (C. R., 146, 217-220) points out that the low value obtained was probably due to impurities; consequently all values based on Thomsen's results will be low (see also  $\mathcal{F}$ . C. S., Abst. II., 155, 1908).

Moissan's result was obtained by direct determination of the heat of combustion, and therefore is less liable to error than those results obtained by indirect means.

III.  $2 \text{ Al} + 3 \text{ O} = \text{Al}_2 \text{O}_3 -$ 

386,988 calories	•••	Dr. Strauss, Minet, Production of Al, p. 209.					
380,200 ,,		Thomsen (see L. and B.).					
392,610 ,,		Richards, Electrochemical and Metallurgica					
		Industry, 6–8.					

Calculating these results for 1 gram-atom of O, they become 128,996, 126,733, and 130,870 respectively.

On account of the great divergence in the above numbers, experiments were carried out with a view of ascertaining as far as possible which element has the greatest heat of combustion by examining the reducibility of the oxides of aluminium, calcium, and magnesium by the metals Al, Ca, and Mg respectively.

## THE HEATS OF COMBUSTION

From the foregoing tables it will be seen that the average value of the heat of combustion of Mg is 145,000 calories, that of Ca is 137,000 calories, and that of Al is 129,000 calories; hence from the theory of greatest heat development Mg should reduce CaO and  $Al_2O_3$ , Ca should reduce  $Al_2O_3$  and not MgO, and Al should not reduce CaO or MgO.

Now Goldschmidt (*Minet, Production of Al*, p. 213) has already shown that Al can reduce CaO, and Dr. F. M. Perkin has succeeded in reducing  $Al_2O_3$  by Ca; but it was thought advisable to repeat these experiments in order that a complete comparison could be made between the various reductions when carried out under the same conditions.

#### EXPERIMENTAL.

#### Series I. The Action of Al Powder upon Al<sub>2</sub>O<sub>3</sub>, MgO, and CaO respectively.

The Al powder was the same as that used by the authors in their previous work (see *Trans. Far. Soc.*, vol. iv., **1**, 1908). The  $Al_2O_3$  was prepared by ignition of pure ammonia alum. The MgO was made by ignition of precipitated magnesium carbonate, and was heated for some hours in a muffle at 1,000° C. and was in an extremely fine state of division. The CaO was obtained by ignition of marble, finely powdered, passed through a 40,000-meshed sieve, and the resulting powder again heated at 1,000° C. for one hour.

I.  $Al_2O_3 + 4Al$ . This experiment was first carried out by Duboin (C. R., cxxxii., No. 13). The mixture readily reacts with a fuse, forming a blackishgrey product which dissolves in HCl with the evolution of H; it contains, probably, a suboxide of aluminium, but very little nitride.

2. 2 Al + 3 CaO. The mixture, contained in a Hessian crucible, would not react in the cold, even when a fairly large fuse was used; when heated over a bunsen burner for two hours (the bottom of the crucible was at a dull red heat), a fuse again brought about no reaction. The crucible was then placed in the muffle at its hottest part; after two minutes, the crucible then being bright red, action started at the surface and then very rapidly spread throughout the whole mass, giving a somewhat violent reaction. The reaction consisted first of the oxidation of the surface Al by the air, and the heat produced by this reaction, together with the heat supplied by the furnace, brought about the reduction of the CaO by the Al; this reaction appears to us to be endothermic, since it was only possible to bring about the reaction under the conditions stated. The product of the reaction consisted of a hard, black, fused mass, and contained free Ca, calcium aluminate, free Al (and possibly some Al<sub>2</sub>O), Al<sub>2</sub>O<sub>3</sub>, and CaO; it also contained a small amount of nitride and carbide.

Estimation of Free Ca and Al.—The finely powdered substance was treated with cold water and the gas evolved collected and analysed. From volume of H evolved the percentage of free Ca was calculated; a small quantity of  $C_2H_2$  and  $CH_4$  was found present. After treatment with water, HCl was added and the process repeated.

> Per cent. free Ca = 8.3", ", free Al = 6.1", ", nitrogen = 0.375(as nitride)

Hence it is evident that Al powder can reduce CaO at high temperatures, and it is probable that the reaction  $2 \text{ Al} + 3 \text{ CaO} \rightleftharpoons 3 \text{ Ca} + \text{Al}_2\text{O}_3$  is a reversible one and that a stage of equilibrium is reached under the above conditions.

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3. 2 Al + 3 MgO. The reduction could not be brought about even at the highest temperature attainable (*e.g.*, about 1,100° C.); the only change obtained was a superficial oxidation of the Al; the contents of the crucible were otherwise unacted upon.

Hence it appears that the heat of formation of MgO is greater than that of CaO.

### Series II.

1.  $_3$  Ca + Al<sub>2</sub>O<sub>3</sub>. The calcium was first converted into fine shavings in a lathe, and these were then crushed as small as possible in an iron mortar, and that portion which passed through a 120-meshed sieve was used.

The mixture, in a Hessian crucible, would not react in the cold even when a moderately large fuse was used, but on heating with a bunsen burner until the bottom of the crucible was at a dull red heat, a violent reaction took place and the larger portion of the contents of the crucible was ejected. From the way in which the reaction took place it is fair to assume that if calcium powder in a sufficiently fine state of division were employed the reduction would take place readily in the cold, and if air were excluded and sufficiently large quantities of mixture employed, fused Al could be obtained (see also Dr. Perkin, T. F. S., iii., 3, 184). In this reaction the Al produced probably volatilised, and consequently oxidised under the very high temperature obtained, and this may account for the small percentage of Al found and also for Dr. Perkin's failure to obtain globules of metallic Al. The authors intend repeating this experiment under such conditions as to avoid loss, &c.

The presence of free Al was shown by treating the finely powdered product with water until no more gas was evolved, even on heating, and then adding HCl; a rapid effervescence of H took place, and Al was found in the solution. The product contained about 8 per cent. of free Al.

2. Ca + MgO. The mixture, placed in a Hessian crucible, was found to react slowly when the surface was heated with a bunsen burner; the surface Ca ignited, and the incandescence *slowly* spread throughout the mass from the top downwards. On cooling the contents of the crucible were found to be white at the top to a depth of about  $\frac{1}{8}$  inch, and then of a deep yellow.

It was thought at first the action was due to reaction of the Ca with the atmosphere forming a small amount of lime and a large amount of calcium nitride. That this was not so was evident from (1) the analysis of the resulting mixture; (2) that the calcium when heated in a crucible by itself under the same conditions only burnt on the surface and remained unchanged below; and (3) a mixture of CaO and Ca when treated in the same manner or even when strongly heated by a Bunsen flame only reacted at the surface.

Analysis of the product gave—

N as	nitride	=	5.29	per	cent.
Free	Ca	=	4.10	,,	,,
,,	Mg	=	0.28	,,	,,

It was not possible to decide whether the nitride was calcium nitride or magnesium nitride or a mixture of both. But from the large percentage of nitride (about 30 per cent. if calcium nitride) it appears that the atmospheric N plays a great part in the reaction observed.

#### Series III.

r. Mg + CaO. That Mg will readily reduce CaO in the cold is, of course well known, this reaction serving for the preparation of argon from the air. A mixture made in the proportion Mg + CaO can easily be fired by a lighted

match, the reaction proceeding steadily throughout the mass. The resulting product is of a bright yellow colour, and consists chiefly of calcium nitride.

Analysis of product gave-

$$Ca_3N_2 = 33.65 \text{ per cent.}$$
  
Free Ca = 1.29 ,, ,,  
,, Mg = 0.47 ,, ,,

In this reaction, in order to obtain a yield of Ca, air would have to be excluded.

2.  $3 \text{ Mg} + \text{Al}_2O_3$ . This mixture, in a Hessian crucible, easily reacted with a fuse; the reaction was somewhat violent, the mass swelling up considerably. The resulting product was quite black.

Analysis of product gave-

N as nitride = 7'43 per cent. Free Al = 0'71 , , , , Mg = 3'87 , ,

In this reaction, as in the case of Ca and  $Al_2O_3$ , it is probable that most of the Al liberated is converted into nitride and some re-oxidised to  $Al_2O_3$ .

Although in these experiments, which were only carried out on a small scale (20 to 50 grams), complications arise partly from the interaction of the various hot metals with the air and with the oxides, it is quite evident that both Mg and Ca reduce  $Al_2O_3$  in the cold and also that Mg easily reduces CaO with the formation of the free metal.

It is thus evident that the heat of combustion of Mg is greater than that of Ca, since MgO is not reduced by Al, whilst CaO is at a very high temperature; however, the heat of combustion of Mg is not much greater than that of Ca, since it is possible to cause Ca to interact with MgO; also the heats of combustion of Mg and Ca are much higher than that of Al.

The partial reductions of CaO by Al and of MgO by Ca—probably endothermic reactions—are analogous to the reduction of  $B_2O_3$  by K and Na respectively. Gay-Lussac prepared B by heating  $B_2O_3$  with K to a red heat in an iron tube. Now, the heat of combustion of B to  $B_2O_3$  is given as 317,200 (Troost and Hautefeuille-Watts, *Dictionary*), 314,821 by Roscoe and Schorlemner; whilst the heat of combustion of K to  $K_2O$  is given by Beketoff as 97,100 (L. and B.), 86,800 by Rengarde ( $\mathcal{F}$ . C. S., Abs. II., 156, 1908), and 84,800 (*ibid.*).

Hence  $B_2O_3 + 6K = 3K_2O + B_2$  becomes thermally (using average values)

$$-[(316,000) - 3(89,500)]$$
  
*i.e.* = -47,500;

*i.e.*, heat must be supplied ; a similar reaction occurs with Na.

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