761. *The Free Energy of Formation of Zinc Aluminate.*

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The equilibrium

$$ZnAl_2O_4\ (s) + H_2\ (g) = Zn\ (g) + H_2O\ (g) + Al_2O_3\ (s)$$

has been investigated over the range 771—1044° C, and the results used to calculate the free energy of formation of zinc aluminate from the oxides. The forms of alumina involved have been studied and are discussed.

IN a previous paper [1] determination of the equilibrium constants of the reactions

$$ZnO\ (s) + H_2\ (g) = Zn\ (g) + H_2O\ (g) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$Zn_2SiO_4\ (s) + H_2\ (g) = 2Zn\ (g) + H_2O\ (g) + SiO_2\ (s) \quad . \quad . \quad . \quad (2)$$

was described, and hence the free energy of formation of zinc silicate from zinc oxide and silica was derived. In the present paper similar equilibrium measurements are reported for the reaction

$$ZnAl_2O_4\ (s) + H_2\ (g) = Zn\ (g) + H_2O\ (g) + Al_2O_3\ (s) \quad . \quad . \quad . \quad (3)$$

These results are combined with the data already obtained for reaction (1) to obtain the free energy of formation of zinc aluminate.

In order to define the composition of the solid phase (which might conceivably be non-stoicheiometric) the equilibrium was established in the presence of excess of α-aluminium oxide.

EXPERIMENTAL

The furnace, measurement of temperature, and technique were similar to those described previously,[1] except that the furnace contained a closely fitting alumina tube to eliminate silica from the reaction zone.

Zinc aluminate was prepared by ignition of the co-precipitated zinc hydroxide and (excess of) aluminium hydroxide at 1100° C for several hours. *X*-Ray powder diagrams of the product showed the presence of alumina and zinc aluminate only. Preparations at 1050° C (the experimental maximum) of nominal composition from 33% to 72% of Al_2O_3 had the same lattice parameter to within about 1 part in 8000 parts, indicating the absence of appreciable non-stoicheiometry.

Two gas streams were used in these experiments: one of "oxygen-free" nitrogen and one of cylinder "forming-gas" (H_2 25%, N_2 75%), freed from oxygen by passage over heated palladized asbestos. Both gases were dried by anhydrous magnesium perchlorate.

The hydrogen–nitrogen mixture was analysed by burning a measured volume over heated copper oxide and collecting and weighing the water produced in anhydrous magnesium perchlorate. The cylinder of gas used contained 0·2592 ± 0·0015 mole of hydrogen per mole of mixture. The volume of gas passed through the condenser was measured with a wet gas meter.[2]

Temp. (C)	p_{Zn} (10^{-3} atm.)	$-\log_{10} K$ (atm.)	Flow rate (c.c./min.)
771°	0·517	5·985	56
787	0·656	5·774	68
791	0·716	5·700	110
792	0·771	5·634	60
873	2·16	4·733	48
874	2·13	4·746	78
874	2·24	4·701	64
905	3·31	4·362	62
906	3·56	4·299	67
969	7·51	3·656	31
970	7·71	3·632	52
973	7·85	3·615	68
1041	16·17	2·969	55
1044	16·34	2·959	76
1044	16·71	2·940	92

The zinc condensed was determined gravimetrically as zinc ammonium phosphate.

The experimental procedure was similar to that previously described,[2] a stream of nitrogen

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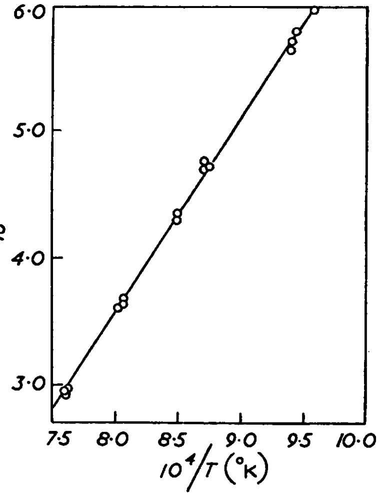
[1] Kitchener and Ignatowicz, *Trans. Faraday Soc.*, 1951, **47**, 1278.

[2] Gilbert and Kitchener, preceding paper.

being used in the preparatory period, followed by one of a hydrogen–nitrogen mixture. A correction was found by a separate experiment. In no example was this more than a few units %, and at the lower temperatures it was negligible.

Results.—The method of calculation was similar to that used in the example of zinc silicate.[1] The results are given in the Table. The graph of log K against $1/T$ is accurately linear (see Figure), and there is no systematic dependence on flow rate; this shows that errors due to failure to saturate the entraining gas and thermal diffusion have been eliminated.

$$ZnAl_2O_4\,(s) + H_2\,(g) = Zn\,(g) + H_2O\,(g) + Al_2O_3\,(s).$$



The best straight line representing the results was found by the method of least squares to be :

$$\log_{10} K \text{ (atm.)} = 8{\cdot}622 - 15{,}253/T$$

DISCUSSION

The standard Gibbs free energy of reaction (3) follows from the equation above :

$$\Delta G^\circ \text{ (at 1060—1317° K) } (\pm 70^\circ) = 69{,}760\ (\pm 1600) - 39{\cdot}44\ (\pm 1{\cdot}3)T \text{ cal./mole.}$$

On combination with the corresponding equation for (1), there follows for

$$ZnO\,(s) + Al_2O_2\,(s) = ZnAl_2O_4\,(s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\Delta G^\circ \text{ (at 1060—1317° K) } (\pm 80^\circ) = -14{,}120\ (\pm 1700) + 1{\cdot}17\ (\pm 1{\cdot}3)T$$

There is some uncertainty regarding the allotropic form of the alumina which enters into reactions (3) and (4). On the one hand, the products of almost complete reduction of zinc aluminate, as found in separate experiments, consist of γ- and θ-alumina, depending on the temperature. Fricke and Weitbrecht[3] found γ-aluminas as a product of complete reduction of nickel aluminate in a similar temperature range. The particle size in this example was small enough to influence the free energy, but Richardson and Jeffes[4] have suggested that this is due to the simultaneous formation of two solid products which mutually interfere with crystal growth.

On the other hand, the technique used in the present work employs a large amount of reactant relative to the amount of reduction, and consequently small amounts of " active " alumina would probably dissolve in the spinel saturated by the stable form, and would have little influence on the free energy of the phases. In agreement with this, only α-alumina could be detected by X-ray analysis of the material after the equilibrium

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[3] Fricke and Weitbrecht, *Z. Elektrochem.*, 1942, **48**, 86.
[4] Richardson and Jeffes, *J. Iron Steel Inst.*, 1948, **160**, 261.

experiments, and no deviations from linearity, corresponding to phase changes γ-$Al_2O_3 \longrightarrow \theta$-$Al_2O_3 \longrightarrow \alpha$-$Al_2O_3$, are apparent in the graph. The thermodynamic properties of the various forms of alumina are as yet little elucidated.[5]

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[5] Fricke, *Koll. Z.*, 1934, **69**, 312; Stumpf, Russell, Newsome, and Tucker, *Ind. Eng. Chem.*, 1950, **42**, 1398; von Wartenberg, *Z. anorg. Chem.*, 1952, **269**, 76; Schneider and Gattow, *ibid.*, 1954, **277**, 41.