762. *The Free Energy of Formation of Zinc Ferrite.*

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Determinations are described of the equilibria at high temperatures between hydrogen chloride and (*a*) zinc aluminate and (*b*) zinc ferrite (saturated with respect to ferric oxide). By combining the results with data for zinc aluminate previously determined, there result equations for the free energy of formation of zinc ferrite and for the reaction of zinc oxide and hydrogen chloride.

THE free energy of formation of zinc ferrite

$$ZnO\,(s) + Fe_2O_3\,(s) = ZnFe_2O_4\,(s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{1}$$

cannot conveniently be derived from determinations of hydrogen-reduction equilibria (as previously used for zinc aluminate) because of the high oxygen potential of ferric oxide and the complete miscibility of the ferrite and its first reduction product (*i.e.*, Fe_3O_4) at high temperatures.[1] The method finally adopted was to combine measurements of the equilibria with hydrogen chloride,

$$ZnFe_2O_4\,(s) + 2HCl\,(g) = ZnCl_2\,(g) + H_2O\,(g) + Fe_2O_3\,(s) \quad . \quad . \tag{2}$$

$$ZnAl_2O_3\,(s) + 2HCl\,(g) = ZnCl_2\,(g) + H_2O\,(g) + Al_2O_3\,(s) \quad . \quad . \tag{3}$$

with the data previously obtained for

$$ZnO\,(s) + Al_2O_3\,(s) = ZnAl_2O_4\,(s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{4}$$

The spinel phase in the system ZnO–Fe_2O_3 has a large range of composition;[2] no attempt has been made to investigate the whole range, but only that at the Fe_2O_3 edge as defined by the presence of excess of this oxide.

There are a number of possible side reactions which might interfere with the investigation of reactions (2) and (3). However, preliminary calculations from available thermodynamic and other data showed that they would not interfere under the conditions studied. In particular, the reactions of hydrogen chloride with alumina, with ferric oxide, and with the oxygen derived from its dissociation are negligible in the experimental conditions, and solid oxychlorides of zinc and of iron are not formed.

EXPERIMENTAL

The apparatus is shown in the Figure. Hydrogen chloride was prepared by tilting a controlled amount of concentrated sulphuric acid from tube *A* on to solid ammonium chloride (" AnalaR," previously dried at 110°) in flask *B*, and entered the 5-l. reservoir through a solid carbon dioxide trap. The diluent, cylinder nitrogen, was dried in the same way. Pressures

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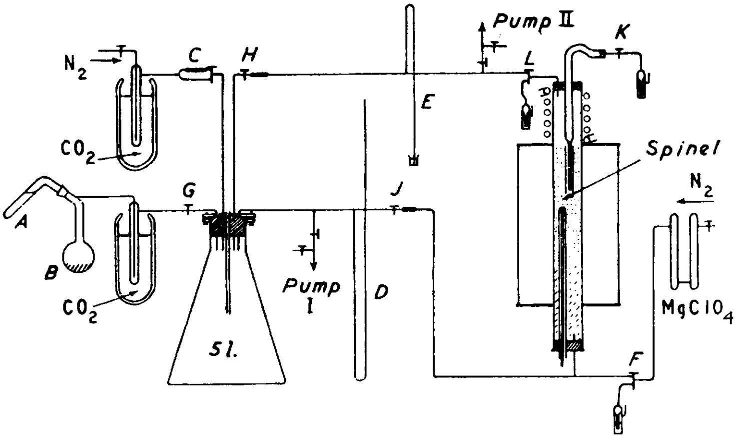
[1] Mason, *Amer. Mineral*, 1947, **32**, 426.

[2] Berger, *Festskr. J. Arvid Hedvall*, 1948, p. 31.

in the reservoir system were measured by manometer *D*, and in the furnace system by manometer *E*. Stopcocks were held in place by wire clips, and the lubricants were first shown to be inappreciably attacked by hydrogen chloride. The volume of the reservoir was obtained by gas dilution from a smaller bulb of directly measured capacity. Zinc aluminate was prepared as in the preceding paper, and zinc ferrite similarly from " AnalaR " zinc oxide and pure iron.

The furnace was brought to a steady temperature, with a stream of dry nitrogen entering through *F*. The reservoir system was evacuated, and a measured pressure of hydrogen chloride introduced, after which nitrogen was allowed to enter through *C* to give a measured excess of pressure of about 1 atm. Temperature corrections were made. The gases were allowed to mix. The condenser was sealed in position with de Khotinsky cement, and the furnace system evacuated. Mixed gas then entered through *H* and *L*, this arrangement eliminating the blank, after which the nitrogen–hydrogen chloride gas stream was switched to enter through *F*, and out through *L*, for time to allow steady conditions to be reached; thereafter the entire flow of a measured pressure of gas was passed through the condenser. To ensure complete deposition of zinc chloride, and also of hydrogen chloride, a tube of moist glass-wool and a silver nitrate bubbler were placed on the outlet side.

HCl *apparatus.*



Chloride and zinc in the dissolved condensate were determined gravimetrically as AgCl and $ZnNH_4PO_4$, respectively.

Results.—The equilibrium constant is

$$K = p_{ZnCl_2} . p_{H_2O} / p_{HCl}{}^2$$

and by the ideal-gas laws,

$$p_{ZnCl_2} = \frac{w(P + p)\mathbf{R}}{65 \cdot 4V(P_1/T_1 - P_2/T_2)}$$

where w (g.) = mass of zinc condensed, V (l.) = volume of reservoir, P = atmospheric pressure, p = the excess of pressure in the furnace, P_1, P_2 are the initial and final pressures in the reservoir, and T_1, T_2 the initial and final temperatures of the reservoir.

By the stoicheiometry of the reaction $p_{ZnCl_2} = p_{H_2O}$.

1. *Zinc aluminate* ($ZnAl_2O_4$). The results for the hydrogen chloride equilibrium are given in Table 1. There is no systematic dependence on flow rate and therefore a true equilibrium had been reached and measured.

TABLE 1.

Temp. (c)	p_{ZnCl_2} (atm. × 10^{-2})	p_{HCl} (initial) (atm.)	$-\log_{10} K$ (atm.)	Mean flow rate (c.c./min.)	Temp. (c)	p_{ZnCl_2} (atm. × 10^{-2})	p_{HCl} (initial) (atm.)	$-\log_{10} K$ (atm.)	Mean flow rate (c.c./min.)
798°	0·912	0·1309	2·184	110	872°	1·138	0·1087	1·756	70
807	0·658	0·0770	1·973	40	952	1·309	0·0903	1·380	50
810	1·268	0·1786	2·164	30	953	0·907	0·0688	1·495	40
846	0·402	0·0447	1·921	60	1034	1·031	0·0596	1·156	30
857	1·316	0·1242	1·744	50	1036	1·306	0·0684	1·021	60
871	1·246	0·1160	1·728	50	1037	1·511	0·0873	1·155	50

By the method of least squares the best straight line through these points is found to be :

$$\log_{10} K \text{ (at 1071—1310° K)} = 3{\cdot}471 - 5992/T\ (\pm 0{\cdot}067).$$

2. *Zinc ferrite* ($ZnFe_2O_4$). The results obtained in the same temperature range were irreproducible, and further investigation showed that chloride was being taken up within the furnace. The cause of this reaction could not be ascertained. Further experiments were made at a range of higher temperatures (for which the original nichrome furnace winding was replaced with one of " Kanthal "). At temperatures of 1100° C and above, it was found that the total chloride entering the furnace equalled that leaving, and concordant results were obtained. Only these higher-temperature results (each being checked by a chloride determination) are given in Table 2. The best straight line through these results is

TABLE 2.

Temp. (K)	p_{ZnCl_2}	p_{HCl}	$-\log_{10} K$	Recovery of Cl^- (%)	Mean flow rate (c.c./min.)
1418°	0·0204	0·0560	0·254	107	30
1424	0·0192	0·0558	0·086	106	30
1367	0·0190	0·0541	0·139	98	40
1367	0·0191	0·0548	0·120	98	30
1484	0·0207	0·0557	0·322	99	45
1481	0·0190	0·0544	0·128	99	60

$$\log_{10} K \text{ (at 1367—1484° K)} = -2000/T + 1{\cdot}58$$

DISCUSSION

The equations for the equilibrium constants yield for the standard free energy of reaction (3) :

$$\Delta G_3° = 27{,}410 - 15{\cdot}88T \text{ cal./mole (at 1071—1310° K)}$$

and for reaction (2) :

$$\Delta G_2° = 9150 - 7{\cdot}23T \text{ cal./mole (at 1367—1484° K)}$$

On combination of these with the earlier value [3] for reaction (4), there results for reaction (1), after averaging because of the uncertainty in the slope :

$$\Delta G_4° = -6490 \text{ cal./mole ZnO (at 1367—1484° K)}$$

This is considered the best representation of the results. The experimental results also yield a direct value for the free energy of the reaction between hydrogen chloride and zinc oxide at high temperatures,

$$ZnO\ (s) + 2HCl\ (g) = ZnCl_2\ (g) + H_2O\ (g) \qquad . \quad . \quad . \quad . \quad (5)$$

by combining the equations for reactions (3) and (4) :

$$\Delta G_5° = +13{,}290 - 14{\cdot}71T \text{ cal./mole (at 1071—1310° K)}$$

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[3] Gilbert and Kitchener, preceding paper.