THERMAL ANALYSIS OF CHROMIUM(III) AND CHROMIUM(VI) SYSTEMS WITH SILICA AND SODIUM SILICATE

D. H. BROWN and D. A. FERGUSON

Department of Pure and Applied Chemistry, University of Strathclyde,
Glasgow G1 1XL, U. K.

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Sodium silicate, or a mixture of silica and sodium carbonate, reacts with chromium(III) oxide in the presence of oxygen to give sodium chromate, within the approximate temperature range 300-900°. Above 900° the reaction is reversed and chromium(III) oxide regenerated.

It has been long known in the chrome chemical industry that an ore with a high silica content produces a low yield of chromium(VI). Yet it is also known that sodium silicate, a product of the reaction between sodium carbonate and silica, will produce a considerable degree of oxidation of chromium(III) when heated in air with chrome ore. This paper describes some experiments designed to clarify these apparently contradicting results.

Experimental

Thermoanalytical results were measured using a Stanton thermobalance fitted with a differential thermal analysis attachment. Anhydrous sodium silicate was prepared from the pentahydrate by heating to 600°. Precipitated amorphous silica was prepared and dried at 600°. Laboratory grade chromium(III) oxide, "AnalaR" sodium chromate and sodium carbonate were used. Chrome ore was supplied by Albright and Wilson Ltd.

Results

The DTA curve of sodium silicate exhibited only one feature — a reversible endotherm at 1082° due to fusion. A 1 : 1 mixture of chromium(III) oxide and silica gave no reaction up to 1100°. Sodium chromate showed two reversible endotherms — the first at 414° due to a polymorphic transition and the second at 785° resulting from fusion. Addition of sodium silicate (1 : 1) to sodium chromate did not affect these results. (The National Bureau of Standards Circular 500 quotes 413° and 792° for the two sodium chromate values.) The reaction of sodium carbonate and silica

\[ \text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2 \]

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began (from DTA results) at 300° and ended at 860°. Throughout its course it was weakly endothermic with a sharp fusion peak at 854°.

The DTA of a 1 : 2 chromium(III) oxide and sodium silicate sample showed a weak endotherm beginning at 550° and finishing at 850° with a fusion peak at 778°. TG showed a steady increase in weight over the same temperature range, corresponding to the reaction

\[ \text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{SiO}_3 + 1\frac{1}{2}\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4 + 2\text{SiO}_2 \]

At 850°, the weight change corresponded to 35% oxidation — confirmed by subsequent analysis for chromium(VI). Above 1000° the sample lost weight slowly.

The DTA/TG of the system \( \text{Cr}_2\text{O}_3-\text{Na}_2\text{CO}_3-\text{SiO}_2 \) 2 : 1 : 1 is given in Fig. 1. This shows that the sample began to lose weight (\( \text{CO}_2 \) evolution) at 280° when the DTA curve became endothermic. An endothermic region stretches from 280 to 730°. This was due to the evolution of \( \text{CO}_2 \) both in the reaction of sodium carbonate with silica and with chromium(III) oxide and the slow oxidation of the latter either by \( \text{Na}_2\text{CO}_3 \), or by \( \text{Na}_2\text{SiO}_3 \) and oxygen. The 730—860° region of the curve is taken up by an exotherm caused by the increasingly dominant oxidation reaction as carbon dioxide evolution ceased. This exotherm is split by a sharp reversible endotherm at 785° caused by the liquidus of the system (\( \text{Na}_2\text{CrO}_4 \) fusion). The sample weight continued to decrease between 730° and the liquidus temperature and then increased up to 800° when the oxidation reaction ended. On further heating the sample lost weight around 1000° with a corresponding weak endotherm appearing on the DTA curve. Both this weight change and thermal effect were reversible although on repeated cycling a slow decrease in the amount of chromium(VI) present was observed. This was repeated using a 1 : 1 : 1 instead of a 2 : 1 : 1 ratio and the results obtained were similar. Comparable runs were made but with no silica present, and stopping at a temperature of 850°. On analysis the samples with silica contained about 10% more chromium(VI).

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