

REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XVII—DECOMPOSITION OF MIXTURES OF CALCIUM CHROMATE WITH FERRIC OXIDE AND WITH CHROMIC OXIDE

By D S Datta

INTRODUCTION

The formation of mixed basic chromium chromates of definite composition was observed at different stages in the decomposition of the mixtures of calcium chromate with magnesium oxide, with calcium oxide and with sodium carbonate. It was interesting to study the behaviour of the mixtures of calcium chromate with ferric oxide and with chromic oxide at high temperature. The former reaction has a bearing in the manufacture of chromates as a partial replacement of calcium oxide by ferric oxide in $\text{CaO} + \text{Na}_2\text{CO}_3$ + chrome ore mixture has been recommended for use in the chromate furnace. Also as the chrome ore is a ferric chromite, the oxidation of the ore in presence of lime and soda probably occurs with the formation of mixed compounds of iron and calcium or sodium.

EXPERIMENTAL

The apparatus used and the experimental procedure followed was the same as in the previous parts of this series.

Decomposition of mixtures of calcium chromate with ferric oxide—Datta and Jalkar (This Journal 1939, **22A**, 225) have published their results on the decomposition of mixtures of calcium chromate with ferric oxide. Their experiments show the possibility of the formation of the basic chromium chromate of iron. For the investigation is necessary to find out the exact amount of ferric oxide entering into combination with calcium chromate.

A mixture of calcium chromate with ferric oxide (2 : 1 mols) was decomposed in vacuum. The decomposition started at about 250° in agreement with the previous results. The initial pressure of oxygen at 275° was 2.8 mm, which was pumped out to 0.4 mm. The temperature was raised to 331°, when the pressure was 3.16 mm. The gas was slowly absorbed back and the pressure dropped down.

to 2.36 mm in one and half hours and further to 1.76 mm in 3 hours. On cooling only a part of the oxygen was absorbed back. The mixture was heated again slowly, when the pressure of oxygen over the mixture was 1.04 mm at 353° and 2.72 mm at 444°. The pressure at the latter temperature dropped from 2.72 mm to 1.82 mm in two and half hours and remained constant at that value. The temperature was raised when the pressure at 555° was 8.56 mm. On cooling back to the room temperature, only a part of the gas was absorbed, the pressure of the gas unabsorbed being 4.2 mm. On pumping out the gas the pressure values slowly dropped down. The measurements made are shown in fig 1, along with the measurements by Datar and Jatkar at 0% and 25% decomposition stages. The vapour pressures are not reproducible. The pressures depend upon the rate of heating, the higher values being obtained if the system is heated rapidly and the pressures under these conditions drop down at constant temperature until equilibrium is attained. The values for the pressure are low below the temperature, at which the system has been previously evacuated, the original values being attained at higher temperatures.

The decomposition was carried out further and the vapour pressures over the mixture were measured at different stages of decomposition. The pressure values at different stages given in table I and shown in fig 1A and 1B are higher than those obtained by Datar and Jatkar at the 25% decomposition stage and shown in fig 1A and 1B.

TABLE I

% decomposition	Temp °C	Pressure mm
23	835	11.50
25	837	12.40
28.6	849	12.56
33.3	849	11.92
40	849	11.34

The results given above do not show an appreciable drop in the pressure values at the various stages of decomposition. The vapour pressures after the system had reached 50%, 59% and over 60% decomposition have been given in table II and shown in fig 1A and 1B

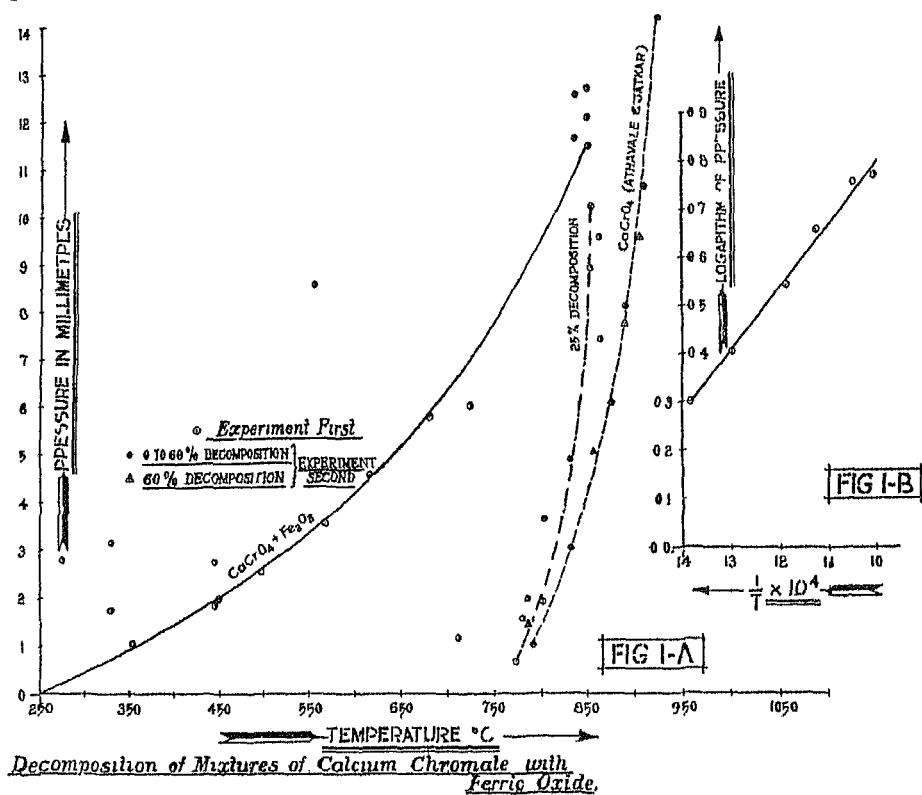
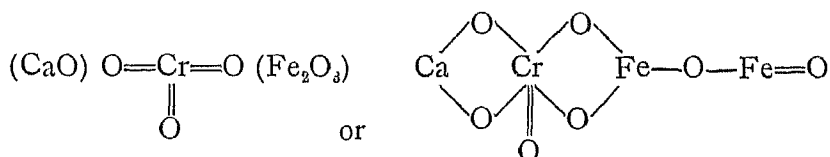


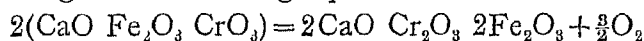
TABLE II

50% decomposition		59% decomposition		OVER 60% decomposition	
Temp °C	Pressure mm	Temp °C	Pressure mm	Temp °C	Pressure mm
711	1.14	778	1.56	785	1.44
803	3.60	785	1.96	887	7.68
862	9.44	863	7.32	905	9.44

The vapour pressures of the system at about 60% decomposition were identical with those in the decomposition of calcium chromate. It is apparent from these results that the decomposition of the basic chromate formed by the combination of a part of the chromate with all the oxide present in the mixture had been complete and the vapour pressures observed at this stage were due to the decomposition of the chromate in excess. The mixture contained 2 mols of calcium chromate and 1 mol of ferric oxide. It appears therefore that half of the total chromate in the mixture had combined with ferric oxide, with the formation of the basic chromate $\text{CaO Fe}_2\text{O}_3\text{CrO}_3$, which can be represented by the structure given below —



This compound decomposed completely and without giving any stages according to the following equation



At high temperatures formation of ferric chromate by the reaction between calcium chromate and ferric oxide takes place as $3\text{CaCrO}_4 + \text{Fe}_2\text{O}_3 = \text{Fe}_2(\text{CrO}_4)_3 + 3\text{CaO}$, which decomposes to ferric chromite as $2(\text{Fe}_2(\text{CrO}_4)_3) = 2\text{Fe}_2\text{O}_3 + 3\text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2$, a large amount of oxygen being given out, which disturbs the equilibrium in the decomposition of the basic chromate $\text{CaO Fe}_2\text{O}_3\text{CrO}_3$. It should be mentioned in this connection that according to Blanc (*Annales De Chimie*, 1926, VI, 182) the chromate of iron, which he represented by the formula $\text{CrO}_3 \cdot 2\text{Fe}_2\text{O}_3$, decomposes at about 500° with evolution of heat. At high temperatures the pressure values obtained for the original mixture were lower than those observed after the subsequent decomposition of the mixture (*cf* fig 1A and 1B). This inconsistency is obviously due to the side decomposition of ferric chromate.

From the above considerations it would appear that a major portion of iron oxide combines with the chromate to form the basic

chromate $\text{CaOFe}_2\text{O}_3\text{Cr}_2\text{O}_3$. The remaining portion of the oxide is utilised in the formation of ferric chromate, the lime liberated in the reaction combining with calcium chromate to form the basic chromate $12\text{CaO} \cdot 8\text{Cr}_2\text{O}_3$. The vapour pressures of calcium chromate are therefore indicated in the decomposition of mixtures of calcium chromate with ferric oxide when the less stable compounds $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ and $\text{Fe}_2(\text{CrO}_4)_3$ are completely decomposed. This stage was indicated in this investigation at 60% decomposition of the total chromate. A simple calculation shows that about 5% of ferric oxide had combined to form ferric chromate. The decompositions of the various compounds occurring at the different stages of the reaction can therefore be represented by the following data (table III)

TABLE III

Compound	Decomposition Total 60.0%	Remarks
$\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	45.0%	Complete decomposition
$\text{Fe}_2(\text{CrO}_4)_3$	15.0%	" "
$12\text{CaO} \cdot 8\text{Cr}_2\text{O}_3$	0%	No decomposition

The final product of decomposition of $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ has been represented as $2\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$. A corresponding compound of calcium, namely $4\text{CaO} \cdot \text{Cr}_2\text{O}_3$ has been obtained by H. Mousson and E. Dufau (*cf.* Mellor, *A treatise on Inorganic and Theoretical Chemistry*, Vol. XI, 199) and also by the author (*cf.* part XV).

Decomposition of mixtures of Calcium Chromate with Chromic Oxide—The addition of ferric oxide accelerates the decomposition of calcium chromate on account of the formation of the basic chromate $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, which decomposes to $2\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ without giving any compounds at the intermediate stages of decomposition. It was therefore interesting to study the decomposition of the corresponding compound $\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, the formation of which is possible in the reaction of calcium chromate with chromic oxide at high temperature.

A mixture of one mol of calcium chromate with one mol of chromic oxide was heated in vacuum. The mixture began to decompose at about 200°, the initial pressures being 0.48 mm at 220°, 2.14 mm at 320° and 2.80 mm at 350°.

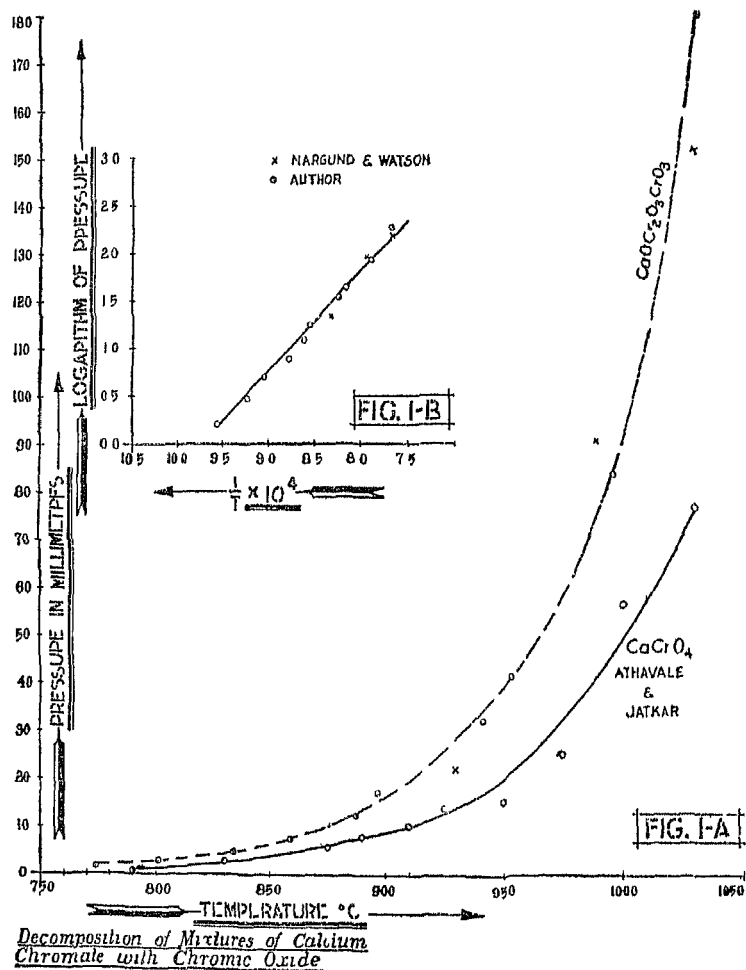
The mixture was heated at 800° for about 3 hours, when it showed a little pressure of oxygen, which was readily and completely absorbed back on cooling the system to room temperature. The decomposition pressures of the mixture at different temperatures are given in table IV and shown in fig. 1A and 1B, p. 280. The decomposition pressures agree with those observed by Nargund and Watson (This Journal 1926, 7, 149) while studying the decomposition of the mixtures of calcium chromate with chromic oxide in different proportions (table IV).

TABLE IV

Author			Nargund and Watson	
Temp °C	Pressure mm	Q Cals	Temp °C	Pressure mm
774	1.60	51.5		
811	3.00	52.1		
834	4.90	52.2		
859	7.68	52.5		
888	12.40	52.8		
897	17.18	52.5	930	22.0
941	31.90	53.1		
953	41.00	53.1		
997	83.00	53.4	990	90.0
1031	178.00	52.9	1030	150.0

On cooling, a portion of oxygen was readily absorbed back the remaining being absorbed very slowly. After pumping out the residual gas, the decomposition pressures were again measured. The higher vapour pressures were observed and the pressure values

at constant temperature slowly increased with approximately a constant rate, viz, 1 mm per hour at 812° and 2.3 mm per hour at 831°. The compound decomposed completely

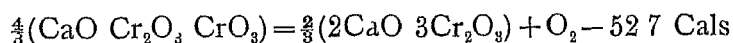


Nargund and Watson believed that the compound formed can be represented by the formula $2\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$. The determination of the exact proportion of the base required to form a compound is, however, a matter of considerable experimental difficulty as side reactions usually occur at high temperatures. It appears now that the assumption of the formula $2\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ for the compound formed in the decomposition of calcium chromate with chromic oxide is not

necessary, as the behaviour of the mixtures can be better explained by assuming the formation of $\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$, the compound corresponding to the general formula $2\text{RO} \cdot \text{CrO}_3$, similar compounds being found to occur in the reactions of chromates with oxides at high temperature

The results observed by Nargund and Watson particularly for the mixtures containing lower proportion of Cr_2O_3 are favourable for the structure $\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ for the compound. The higher decomposition for the mixtures containing 0.5 mol of Cr_2O_3 appears to be due to the side decomposition of calcium chromate. The observation that the vapour pressures at constant temperature increased with a constant rate also supports this conclusion. If the stagewise decomposition of the chromate in different mixtures at 1030° can be assumed to be complete to the 80% stage, the results of Nargund and Watson show that the side decomposition of the chromate is almost absent in the decomposition of the mixtures with lower proportion of chromic oxide.

It is interesting to note that only a portion of oxygen evolved at high temperatures is absorbed back on cooling. As the decomposition pressure measurements are vitiated by the side reactions as well as by the formation of solid solutions, the heat of decomposition of the compound $\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ can be approximately given as 52.7 Cals, the decomposition being represented by the equation



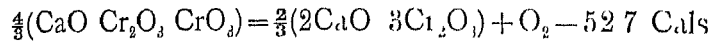
The reactions of calcium chromate with ferric oxide and with chromic oxide are characteristic of the property of weak basic oxides of forming the higher basic chromate $2\text{RO} \cdot \text{CrO}_3$, which decomposes without the formation of compounds at intermediate decomposition.

SUMMARY

It is observed that the addition of ferric oxide accelerates the decomposition of calcium chromate to a great extent. There is no indication of the decomposition in stages. This was due to the formation of basic chromate $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{CrO}_3$ which decomposes

completely without the formation of compounds at the intermediate stages, the final decomposition product being the basic chromate $2\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{Cr}_2\text{O}_3$. The decomposition pressures of the basic chromate could not be measured accurately on account of side reactions

The mixtures of calcium chromate with chromic oxide at high temperatures behave similarly to the mixtures of the chromate with ferric oxide. The basic chromate $\text{CaO}\cdot\text{Cr}_2\text{O}_3\cdot\text{Cr}_2\text{O}_3$, formed by heating calcium chromate with chromic oxide, decomposes without giving additional compounds at the intermediate stages of decomposition, the reaction being represented by the following equation,



Thanks of the author are due to Dr. S. K. K. Jalkar for his keen interest and helpful guidance during the course of this work.

*Department of Pure and Applied Chemistry,
General Chemistry Section,
Indian Institute of Science, Bangalore*

4-7-1941