REACTIONS OF CHROMATES AT HIGH TEMPERATURE

Part XVI—Decomposition of Mixtures of Strontium Chromate with Strontium Oxide and with Strontium Carbonate

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Introduction

It has been shown in Part XV that calcium oxide possesses tl property of combining with calcium chromate to form the bas chromates $1.5CaO.CrO_3$ and $2CaO.CrO_3$. The higher basic chroma is obtained by heating calcium chromate with calcium oxide, while t formation of $1.5CaO.CrO_3$ is shown in the decomposition of mixtur of calcium chromate with calcium carbonate. The results also in cate that the latter reaction is accompanied to some extent by t formation and decomposition of the other basic chromate. It is p posed to extend the investigation to the reactions of strontium chrom with strontium oxide.

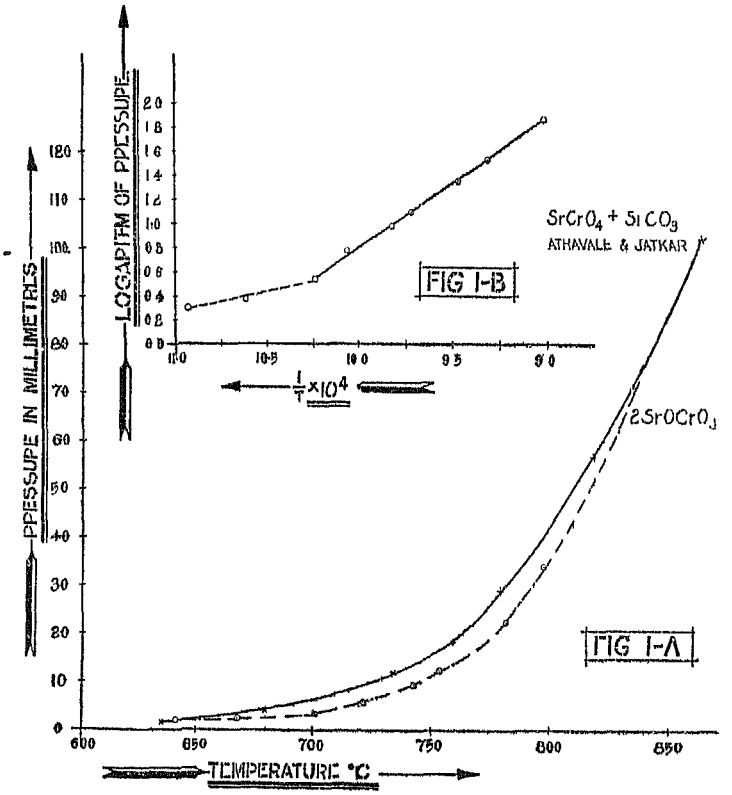
Experimental

The apparatus used and the experimental procedure follow was the same as employed previously. Strontium oxide was p pared by heating strontium carbonate at 980° for 5 hours. The ox was contaminated with the carbonate to the extent of 2.7%.

A mixture of 2 mols of strontium chromate with 1 n of strontium oxide was heated in vacuum. The mixture be to decompose at about 600°. The carbonate was comple decomposed below 650° and the vapour pressures at sev temperatures were then measured. The measurements are give table I and graphically shown in fig. 1A. In fig. 1B, the logarithn pressure has been plotted against the reciprocal of temperat which shows a linear relationship at higher temperatures. values for the decomposition pressures at lower temperatures de tion of the curves, probably indicates the incomplete formation of basic chromate.

TABLE I

$2SrO\ CrO_3$			$SiCrO_4 + SiCO_3$	
Temp °C	Pressure mm	Q Cals	Temp °C	Pressure mm
641	2 00	(44 1)	635	1 5
668	2 32	(45 3)	680	4 0
701	3 46	46 17	735	12 0
722	6 00	46 14	760	18 6
743	9 52	46 26	780	29 2
754	12 40	46 16	820	57 0
782	22 40	46 36	855	102 0
798	34 24	46 16		
836	72 00	46 52		



On cooling the gas was absorbed back The residual gas was pumped out and the decomposition pressures were measured again The results showed that the pressures were completely reproducible In the initial stages of decomposition the vapour pressures regained on evacuation On further decomposition at constant temperature, the pressures dropped down gradually When the decomposition of the chromate reached about 52%, the vapour pressures of strontium chromate appeared in the decomposition, indicating thereby that the basic chromate $2SrOCrO_3$, produced by the combination of whole of the base with half of the chromate decomposed, the decomposition pressures of the chromate in excess being observed at this stage The formation and the decomposition of the basic chromate takes place according to the equations given below

$$SrOCrO_3 + SrO = 2SrOCrO_3 \qquad I$$

$$\tfrac{4}{3}(2SrO\ CrO_3) = \tfrac{2}{3}(4SrOCr_2O_3) + O_2 - 46\ 2\ Cals \qquad II$$

The heat of decomposition of the basic chromate is 46 2 Cals per mol of oxygen

After consideration of the results of Athavale and Jatkar (This Journal, 1938, **21A,** 179) and Datar, Athavale and Jatkar (*Ibid*, 1939, **22A,** 111), Datar and Jatkar (*Ibid*, 1939, **22A,** 287) have shown that basic chromate $12SrO\ 8CrO_3$ decomposes into $12SrO\ 6CrO_3Cr_2O_3$, $9SrO4CrO_3Cr_2O_3$ and $15SrO6CrO_32Cr_2O_3$ corresponding to the stages at 25%, 33 3% and 40% decomposition

Athavale and Jatkar have shown that the decomposition pressures of the mixtures of strontium chromate with strontium carbonate in different proportions are the same irrespective of the composition of the mixtures Their results have been reproduced in table I and fig 1 The pressure of carbon dioxide and oxygen evolved in the decomposition of the mixtures of the chromate with the carbonate is nearly the same as the pressure of oxygen alone over $2SrO\ CrO_3$ It therefore, follows that the decomposition pressures of the mixtures represent the reaction involving the formation of a basic chromate having a higher stability than $2SrO\ CrO_3$

They have also observed that the vapour pressures of the mixtures of strontium chromate with strontium carbonate are regained when the gas is pumped out and the gas is absorbed back readily when the temperature is lowered and also that a definite relationship exists between the amount of carbon dioxide and oxygen evolved during the dissociation This observation would show that at any stage of this equilibrium reaction, only a part of the carbonate is decomposed, the whole of the oxide produced entering into combination with the chromate and that at no stage an excess of the oxide is present in the reaction On the other hand, in the decomposition of the chromate with the oxide, a large amount of free oxide is present along with the basic chromate produced in the reaction The absence of any indication for the existence of the basic chromate $1\,5SrO\ CrO_3$ in the reactions of the chromate with the oxide is obviously due to the reaction mainly proceeding with the formation of the higher basic chromate when larger amounts of oxide are available for the reaction

A confirmation of the above conclusions was obtained by studying the decomposition of strontium chromate with strontium carbonate at 920° in air The decomposition pressure of $12SrO\ 6CrO_3Cr_2O_3$ at the 25% stage is very low 920° (*Ibid*, 1939, **22A,** 111) The partial pressure of oxygen over the mixtures of strontium chromate with strontium carbonate at the same temperature is also definitely less than the partial pressure of oxygen at Bangalore, i e, about 140 mm (*cf* table I) About 1 8 gms of a mixture (2 1 mols) when heated in air at 917° for 12 hours, however, showed complete decomposition of the carbonate and 29 3% decomposition of the chromate As the carbonate is completely decomposed at this temperature, the oxide produced reacts with strontium chromate and the conditions are favourable for the formation of $2SrOCrO_3$

The decomposition of mixtures of strontium chromate with strontium oxide and with strontium carbonate, confirm the previous results obtained with mixtures of calcium chromate with calcium oxide and with calcium carbonate

SUMMARY

On heating strontium chromate with strontium oxide, the basic chromate $2SrOCrO_4$ is formed, which decomposes completely without the formation of intermediate compounds The mixtures of the chromate with the carbonate decompose in vacuum in stages with the formation of the compounds $12SrO\ 6CrO_4,\ Cr_2O_3$, $9SrO\ 4CrO_4,\ Cr_2O_3$ and $15SrO\ 6CrO_4,\ 2Cr_2O_3$ The essential feature of the latter reactions is the availability of a limited amount of oxide for the reaction with the chromate at the various stages of the decomposition The reaction proceeds with the formation of $2SrOCrO_3$, when the oxide phase is present in the system The heat absorbed in the decomposition of $2SrOCrO_4$ is 46 2 Cals per mol of oxygen, the decomposition being represented by

$$\tfrac{4}{3}(2SrO\ CrO_3) = \tfrac{2}{3}(4SrO\ Cr_2O_3) + O_2 - 46\ 2\ \text{Cals}$$

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