REACTIONS OF CHROMATES AT HIGH TEMPERATURES

Part XVIII—Decomposition of Mixtures of Strontium Chromate with Calcium Oxide and of Calcium Chromate with Strontium Oxide

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Introduction

In the previous parts it has been shown that calcium chromate possesses the property of combining with calcium oxide, ferric oxide and chromic oxide to form the basic chromates of the general formula $2RO\ CrO_3$, which decompose to $4RO\ Cr_2O_3$, without the formation of intermediate compounds It was intended to study the decomposition of mixtures of strontium chromate with calcium oxide and of calcium chromate with strontium oxide

Experimental

The apparatus used and the experimental procedure employed was the same as described previously Calcium oxide was prepared by heating calcium carbonate at 775° for 5 hours and strontium oxide by heating strontium carbonate at 980° for 5 hours The oxides were cooled and preserved in a soda lime desiccator

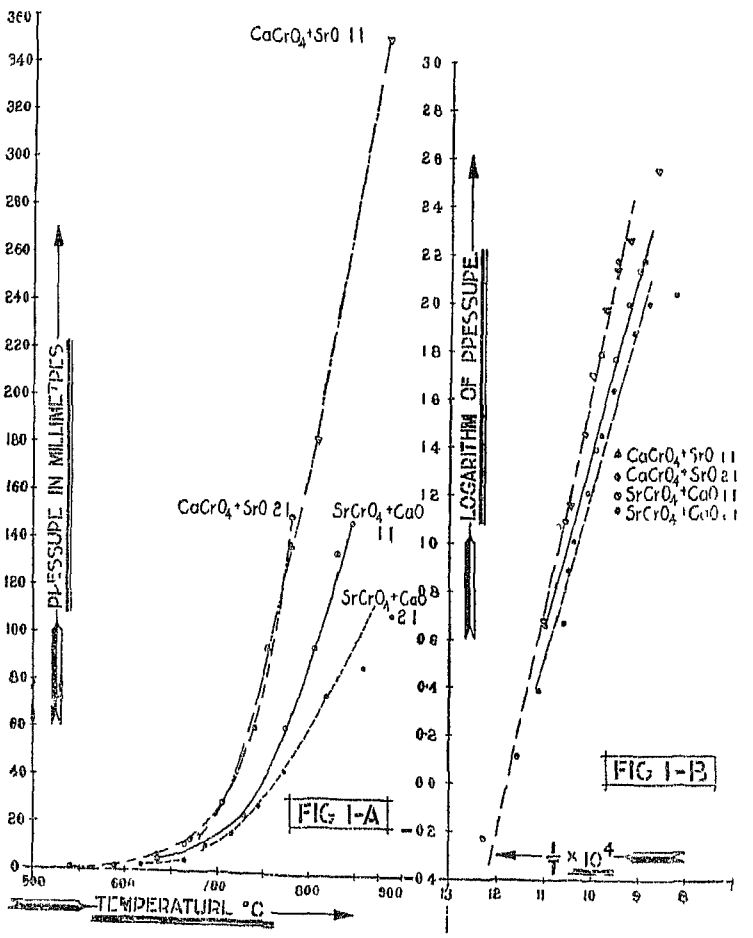
Decomposition of a mixture of 2 mols of strontium chromate with 1 mol of calcium oxide—A mixture of 2 mols of strontium chromate with 1 mol of calcium oxide was heated in vacuum The reaction started at about 200° due to the decomposition of the carbonate, which was present in traces in the mixture The carbonate was completely decomposed below 300° and the decomposition pressures of the mixture were measured The results of the measurement at several temperatures are given in table I and graphically shown in fig 1A and 1B The vapour pressures were reversible and the gas was completely absorbed back on cooling

The vapour pressures dropped down on decomposition at constant temperature When the decomposition of the chromate was about 43 2%, the vapour pressures of strontium chromate were observed in the decomposition. The results show that about 75% of the

TABLE I

Strontium chromate + Calcium oxide (2 1 mols)

Temp °C	Pressure mm	Temp °C	Pressure mm
617	2 42	744	28 02
664	4 60	772	43 00
675	7 64	817	75 00
687	10 24	858	87 00
716	16 26	887	109 00



base takes part in the formation of the basic chromate CaO SrO CrO_3 which decomposes completely The remaining oxide probably enters into combination with the chromate to form the basic chromate 8SrO 4CaO $8CrO_3$, which decomposes in stages the corresponding compounds having a higher stability than strontium chromate The decomposition pressures of strontium chromate are therefore observed when the basic chromate CaO SrO CrO_3 is completely decomposed and the basic chromate 8SrO 4CaO $8CrO_3$ to the 25% decomposition stage

Decomposition of a mixture of 1 mol of strontium chromate with 1 mol of calcium oxide—A mixture of 1 mol of strontium chromate with 1 mol of calcium oxide was heated in vacuum The decomposition pressures of the mixture are given in table II and graphically shown in fig 1A & 1B

TABLE II

Strontium chromate + calcium oxide (1 1 mols)

Temp °C.	Pressure mm	Temp °C	Pressure mm
634	4·58	806	95 00
666	11 72	831	135 00
730	24 14	845	147 00
776	61 50		

On lowering the temperature from 845° to 775° the gas was absorbed back and the pressure dropped down to 84 mm in 30 mins and to its equilibrium value in about 3 hours The vapour pressures were completely reproducible On decomposition, a gradual drop in the pressure values was observed The vapour pressures at the various stages of the decomposition are given in table III

When the decomposition exceeded 50%, the reaction was very slow and further decomposition was extremely difficult On complete evacuation at 1025°, the decomposition of the chromate was about 66% It is obvious that the decomposition of CaO SrO CrO_3 is complete

TABLE III

% decomposition	Temp °C	Pressure mm	% decomposition	Temp °C	Pressure mm
10	723	20 64	50	717	1 28
	781	62 0		776	3 88
25	787	52 0		811	7 68
33 3	681	7 72		836	11 76
	748	22 76			
	787	47 00			

at this stage The stability of the system at the higher stages of decomposition is presumably due to the existence of exceedingly stable mixed basic chromium chromates of calcium and strontium

The decomposition pressures of the mixture of strontium chromate with calcium oxide (1 1 mols) are higher than those obtained for the mixture of strontium chromate with calcium oxide (2 1 mols) [fig 1] It is probable that in both the reactions the amount of the basic chromate formed is inadequate to produce the characteristic vapour pressures in the decomposition It is evident that the amount of the basic chromate formed is greater and the decomposition pressures higher as the proportion of the base in the mixture is increased

Decomposition of a mixture of calcium chromate with strontium oxide (2 1 mols)—A mixture of 2 mols. of calcium chromate with 1 mol of strontium oxide was heated in vacuum The carbonate present in the mixture was completely decomposed below 500° The decomposition pressures of the mixture are given in table IV and graphically shown in fig 1

On decomposition the vapour pressures dropped down until the decomposition of the total chromate was about 51 7%, when the decomposition pressures of calcium chromate were observed in the reaction The decomposition pressures given in table IV are obvi-

TABLE IV

Calcium chromate + strontium oxide (2 1 mols)

Temp °C	Pressure mm	Temp °C	Pressure °C
540	0 60	706	28 52
588	1 30	741	61 00
633	4 80	779	150 00
668	12 40		

ously due to the decomposition of CaO SrO CrO_3 to 2CaO 2SrO Cr_2O_3 It is interesting to note that the formation of the stable basic chromate 8CaO 4SrO 8CrO_3 is not indicated in the reaction

Decomposition of a mixture of calcium chromate with strontium oxide 1 1 mols)—The decomposition pressures of a mixture of 1 mol of calcium chromate with 1 mol. of strontium oxide are given in table V and graphically shown in fig 1A and 1B

TABLE V

Calcium chromate + Strontium oxide (1 1 mols)

Temp. °C	Pressure mm	Q Cals	Temp °C	Pressure mm	Q Cals
679	14 5	42 4	780	138 0	42 5
728	50 0	42 2	807	182 0	43 1
754	95 0	42 0	883	350 0	(44 9)

The mixture decomposed completely The decomposition pressures of the mixture are higher than those of the mixture of 1 mol of strontium chromate with 1 mol of calcium oxide, the equilibrium decomposition pressures of the mixture tending to equalise at higher temperatures It will be seen that an increase of the proportion of strontium oxide in the mixtures of the oxide with calcium chromate does not alter the decomposition pressures of the mixture to

a very great extent, indicating the formation of CaO SiO CrO_3 in both the reactions in adequate quantity to produce the decomposition pressures

The heat of decomposition of SiO CaO CrO_3 has been calculated from the vapour pressures of the compound obtained in the reaction between calcium chromate and strontium oxide (1 1 mols) by Nernst's approximation formula The decomposition occurs according to the following equation

$$\tfrac{4}{3}(SrO\ CaO\ CrO_3) = \tfrac{2}{3}(2SrO\ 2CaO\ Cr_2O_3) + O_2 - 42\,5\ Cals$$

Decomposition of a mixture of calcium chromate with strontium carbonate —It has been shown that both the basic chromates 8SiO 4CaO $8CrO_3$ and CaO SrO Cr_2O_3 are produced in the reactions between strontium chromate and calcium oxide Although the mixtures of calcium chromate with strontium oxide combine to form the basic chromate CaO SrO CrO_3, no indication for the formation of 8CaO 4SiO $8CrO_3$ is given in then decomposition The stable basic chromate can be prepared by substituting the oxide in the mixture by the corresponding carbonate

A mixture of 2 mols of calcium chromate with 1 mol of strontium carbonate was heated in vacuum The decomposition of the mixture started at about 200° Carbon dioxide initially evolved was removed and the decomposition pressures were measured The decomposition pressures given in table VI correspond to the vapour pressures of calcium carbonate, which is produced in the reaction by the double decomposition of strontium carbonate and calcium chromate

TABLE VI

Temp °C	Pressure mm	Temp °C	Pressure mm
554	3 30	706	48 0
643	11 24	718	58 0
688	32 0	757	91 5

The pressures dropped down on decomposition at constant temperature and the carbonate could be completely decomposed only by raising the temperature, when carbon dioxide and oxygen were simultaneously evolved The vapour pressures of the system after complete decomposition of the carbonate and 25% decomposition of the chromate are given in table VII

TABLE VII

Decomposition pressures of $8CaO\ 4SiO\ 6CrO_3\ Cr_2O_3$

Temp °C	Pressure mm	Q Cals	Temp °C	Pressure mm	Q Cals
1008	1 0	(65 3)	1051	1 34	66 7
1019	1 16	(65 3)	1056	1 76	66 3
1046	1 24	66·6			

The composition of the system indicates the formation of $8CaO\ 4SrO\ 6CrO_3Cr_2O_3$ at the 25% stage The compound was completely soluble in HCl (0 1N), a long time (about 40 hours) being required for solution The decomposition pressures dropped continuously on progressive decomposition A value for the heat absorbed during the decomposition of this compound is given by the equation

$$2(8CaO\ 4SiO\ 6CrO_3\ Cr_2O_3) = \tfrac{8}{3}(6CaO\ 3SiO\ 4CrO_3\ Cr_2O_3) + O_2 - 66\ 5\ \text{Cals}$$

Several mixed basic chromium chromates have so far been prepared and the results show the possibility of the formation of basic chromates of the general formula $R_1O\ R_2O\ R_3O \qquad R_{12}O\ 8CrO_3$

An isomerism depending upon the position of the oxides is also possible The vast possibility of the complex chromium compounds will form a subject for further investigation

SUMMARY

The mixtures of strontium chromate with calcium oxide and of calcium chromate with strontium oxide decompose with the formation of $CaO\ SiO\ CrO_3$ The results indicate variations in the de-

composition pressures owing to the incomplete formation of the basic chromate, and also to the existence of stable mixed basic chromium chromates of calcium and strontium The mixture of calcium chromate with strontium oxide however do not give any indication for the formation of mixed basic chromium chromates, the formation of the stable basic chromium chromates in this case being possible if strontium carbonate substitutes strontium oxide The thermochemical data obtained in this investigation may be represented by the following equations

$$\tfrac{4}{3}(CaO\ SrO\ Cr_2O_3) = \tfrac{2}{3}(2CaO\ 2SrO\ Cr_2O_3) + O_2 - 42\ 5\ Cals \qquad (I)$$

$$2(8CaO\ 4SiO\ 6Cr_2O_3Cr_2O_3) = \tfrac{8}{3}(6CaO\ 3SrO\ 4CrO_3\ Cr_2O_3) + O_2 - 66\ 5\ Cals \qquad (II)$$

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