REACTIONS OF CHROMATES AT HIGH TEMPERATURES

Part XIV—Decomposition of Mixtures of Strontium Chromate with Magnesium Oxide

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Introduction

A mixture of calcium chromate with magnesium oxide (2 1 mols) decomposes with initial formation of the basic chromate 8CaO 4MgO $8CrO_3$ in successive stages at 25%, 33 3%, 40% and 50% decomposition with the formation of the compounds 4MgO 8CaO $6CrO_3$ Cr_2O_3 (25%), 3MgO 6CaO $4CrO_3$ Cr_2O_3 (33 3%), 5MgO 10CaO $6CrO_3$ $2Cr_2O_3$ (40%) and 2MgO 4CaO $2CrO_3$ Cr_2O_3 (50%) The mixtures with the lower or the higher proportion of the base, however, decompose giving pressures of calcium chromate It was proposed to extend the investigations to the study of the decomposition of strontium chromate with magnesium oxide

Experimental

The apparatus used and the experimental procedure was the same as already described in part XIII of this series

A mixture of 2 mols of strontium chromate with 1 mol of magnesium oxide was heated in vacuum The carbonate which was present to the extent of 0 25% was completely decomposed at 300° The mixture was heated up to 843° when the pressure of the gas over the mixture was 14 44 mm The gas was pumped out and the heating was continued for about 3 hours The system was cooled to the room temperature and the residual gas pumped out The initial pressures of oxygen over the mixture were probably due to the decomposition of magnesium chromate (about 5%) formed by the reaction of strontium chromate with magnesium oxide The characteristic vapour pressures of the basic chromate 8SrO 4MgO $8CrO_3$ have been given in table I and graphically shown in fig 1a and 1b

TABLE I

Temp °C	Pressure mm	Q Cals	Temp °C	Pressure mm.	Q Cals
917	1 36	59 4	996	4 41	60 7
941	1 84	60 2	999	4 60	60 8
964	2 70	60 3	1019	6 60	60 8
975	2 96	60 6	1032	9 00	60 7

The gas was completely absorbed back on cooling and the vapour pressures were reproducible The heat of decomposition of the

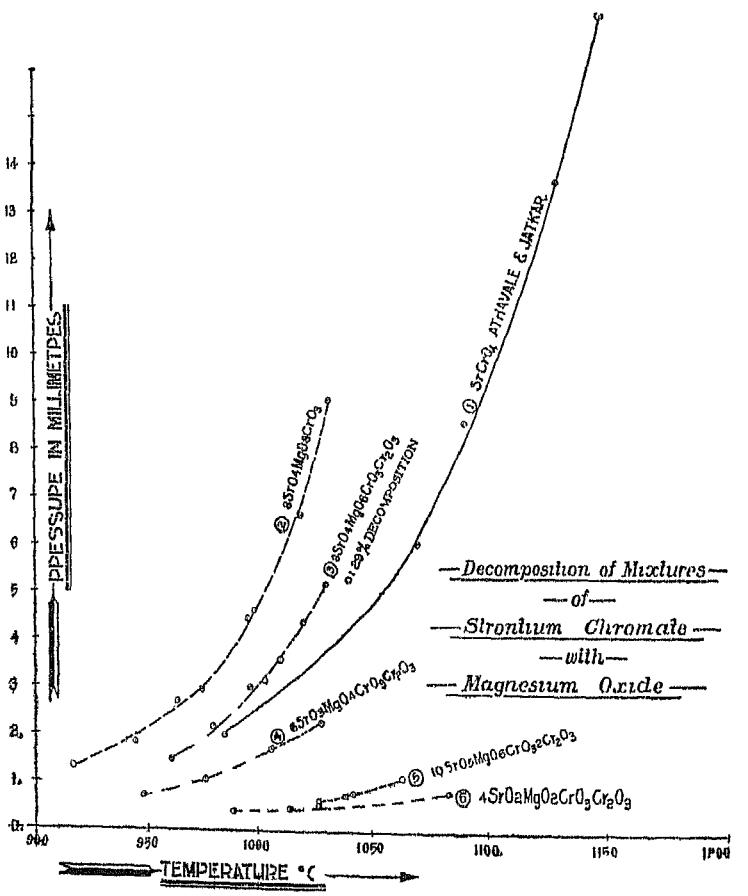

FIG 1a

basic chromate is 60 7 Cals (*cf* part XIII) The decomposition takes place according to the equation

$\frac{2}{3}(8SrO\ 4MgO\ 8CrO_3) = \frac{2}{3}(8SrO\ 4MgO\ 6CrO_3\ Cr_2O_3) + O_2 - 60\ 7$ Cals

25% stage—The basic chromate was decomposed by evacuating at 997° until a drop in pressure from 4 5 mm to 3 0 mm was observed when the decomposition was 25%. The decomposition pressures of the compound at this stage have been given in fig 1a and 1b and table II

TABLE II

Temp °C	Pressure mm	Q Cals
961	1 48	61 6
997	3 00	61 7
1020	4 34	62 0
1030	5 16	62 0

TABLE III

Temp °C	Pressure mm	Q Cals
980	2 18	61 7
1004	3 12	62 0
1010	3 60	62 0

The gas was pumped out until the decomposition reached 29% The decomposition pressures at this stage given in table II and shown in fig 1a and 1b are identical with those of the compound 8SrO 4MgO $6CrO_3$ Cr_2O_3 at the 25% stage

The heat of decomposition of the compound 8SrO 4MgO $6CrO_3$ Cr_2O_3 to the next stage is 61 9 Cals, the reaction being represented by

$2(8SrO\ 4MgO\ 6CrO_3\ Cr_2O_3) = \frac{8}{3}(6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3) + O_2 - 61\ 9$ Cals

33 3% stage—On further decomposition at 1037° the pressure value suddenly dropped down, the total decomposition at this stage being 33 4% The decomposition pressures of the compound 6SrO 3MgO $4CrO_3$ Cr_2O_3 are given in table IV and graphically shown in fig 1a and 1b.

TABLE IV

Temp °C	Pressure mm	Q Cals.
948	0 72	62 7
976	1·08	63 2
1006	1·72	63 6
1028	2·24	64 1

TABLE V

Temp °C	Pressure mm	Q Cals
1027	0 64	67 3
1039	0 76	67 5
1042	0·80	67 5
1063	1 12	68 0

TABLE VI

Temp °C	Pressure mm	Q Cals
989	0·10	66 4
1014	0 48	67 3
1027	0 56	67 6
1083	0 82	69 7

The heat of decomposition of the compound is 63 4 Cals per mol of oxygen, the reaction taking place according to the equation

$$\tfrac{10}{3}(6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3) = 2(10SrO\ 5MgO\ 6CrO_3\ 2Cr_2O_3) + O_2 - 63\ 4\ Cals$$

40% stage—The compound 6SrO 3MgO $4CrO_3$ Cr_2O_3 was decomposed at 1028°. A drop in pressure from 2 24 mm to 0 64mm. was observed, the corresponding decomposition being 40% The product was cooled down to room temperature and the decomposition pressures at various temperatures were measured (table V and fig 1a and 1b)

The heat of decomposition of this compound to the next stage is 67 5 Cals, the reaction proceeding according to the following equation

$$\tfrac{4}{3}(10SrO\ 5MgO\ 6CrO_3\ 2Cr_2O_3) = \tfrac{10}{3}(4SrO\ 2MgO\ 2CrO_3\ Cr_2O_3) + O_2 - 67\ 5\ Cals$$

50% stage.—The decomposition was carried on further to the 50% stage and the decomposition pressures were measured (table VI and fig 1a and 1b)

The heat of decomposition of this compound is 67 6 Cals per mol of oxygen

The pressures did not regain on further decomposition by evacuation This observation points out to the possibility of the decomposition of the compound 4SrO 2MgO $2CrO_3$ Cr_2O_3 at the 50% stage into a mixture of compounds, having different compositions, producing a series of solid solutions.

The results of this investigation confirm the observations of the

experiments on the reactions of calcium chromate with magnesium oxide at high temperatures The basic chromium chromates obtained in the decomposition of strontium chromate with magnesium oxide are all stable, the stability increasing with the decomposition

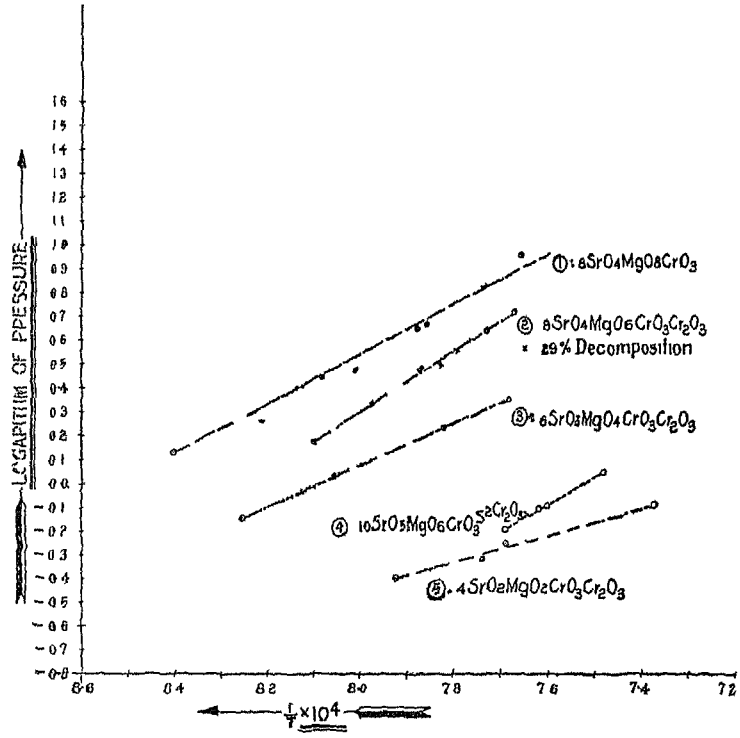

FIG 1b

It was observed in the reactions of calcium chromate with magnesium oxide that the formation of the intermediate compounds was not possible, when extra quantity of magnesium oxide was present in the mixture The results of a similar experiment on the reactions of strontium chromate in presence of excess of magnesium oxide are described below

A mixture of strontium chromate with magnesium oxide (1 0 6 mols) was heated in vacuum The initial pressures were due to the decomposition of magnesium chromate produced in the reaction of strontium chromate with magnesium oxide The decomposition pressures given in table VII show that the pressures at the initial

stages are approximately the same as those of the basic chromate $8SrO\ 4MgO\ 8CrO_3$

TABLE VII

% decomposition	Temperature °C	Pressure mm	% decomposition	Temperature °C	Pressure mm
7	957	2 32	50	976	2 46
	997	4 56		1017	2 84
	1022	7 60	54	948	1 44
25	948	2 20		981	2 12
	996	4 90		1020	2 40
	1023	7 86	56	1023	3 50
33 3	957	2 70	58	954	1 58
	1013	7 28		967	2 16
40	1013	7 08		1014	3 92
			60	1017	1 96
			61	1005	2 50

The comparison of the decomposition pressures with those of the intermediate stages in decomposition of the basic chromate $8SrO\ 4MgO\ 8CrO_3$ indicate the existence of the corresponding compounds during the course of the decomposition There are indications also for the assumption that strontium chromate decomposes to a certain extent independently

The vapour pressure of the system at the 40% decomposition at 1013° was initially very low and attained the value for the basic chromate in about 6 hours The vapour pressures at about 60% decomposition indicated the existence of $10SiO\ 5MgO\ 6CrO_3\ 2Cr_2O_3$ If we assume that the basic chromate completely decomposed at about 45% decomposition and that the further decomposition was due to the decomposition of $8SiO\ 4MgO\ 6CrO_3\ Cr_2O_3$ to $6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3$, the calculations show that about 55% of the total basic chromate decomposes in stages. It must be noted that owing to the

presence of several products in the reactions the vapour pressures at the various stages are not exact to draw any definite conclusions

Summary

A mixture of strontium chromate with magnesium oxide (2 1 mols) decomposes with the initial formation of $8SrO\ 4MgO\ 8CrO_3$, in successive stages at 25%, 33 3%, 40% and 50% decomposition of the chromate, with the formation of the compounds $8SrO\ 4MgO\ 6CrO_3\ Cr_2O_3$, $6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3$, $10SrO\ 5MgO\ 6CrO_3\ 2Cr_2O_3$ and $4SrO\ 2MgO\ 2CrO_3\ Cr_2O_3$

A mixture of strontium chromate with magnesium oxide (1 0 6 mols) containing excess of the base, decomposes with the vapour pressures of the basic chromate $8SrO\ 4MgO\ 6CrO_3\ Cr_2O_3$ decomposes to $6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3$ and to $10SrO\ 5MgO\ 6CrO_3\ Cr_2O_3$ The remaining strontium chromate decomposes independently

The results confirm the remarkable property of magnesium in forming highly stable mixed basic chromium chromates

The heats of decomposition calculated by Nernst's equation from the characteristic decomposition pressures of the basic chromium chromates are given by the thermochemical equations

$\frac{2}{3}(8SrO\ 4MgO\ 8CrO_3) = \frac{2}{3}(8SrO\ 4MgO\ 6CrO_3Cr_2O_3) + O_2 - 60\ 7$ Cals I

$2(8SrO\ 4MgO\ 6CrO_3Cr_2O_3) = \frac{8}{3}(6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3) + O_2 - 61\ 9$ Cals II

$\frac{1}{3}^0(6SrO\ 3MgO\ 4CrO_3\ Cr_2O_3) = 2(10SrO\ 5MgO\ 6CrO_3\ 2Cr_2O_3) + O_2 - 63\ 4$ Cals III

$\frac{4}{3}(10SrO\ 5MgO\ 6CrO_3\ 2Cr_2O_3) = \frac{1}{3}^0(4SrO\ 2MgO\ 2CrO_3Cr_2O_3) + O_2 - 67\ 5$ Cals IV

$X(4SrO\ 2MgO\ 2CrO_3\ Cr_2O_3) =$ mixtures of several compounds $+ O_2 - 67\ 6$ Cals V

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