

# REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

## PART V. DECOMPOSITION OF STRONTIUM CHROMATE.

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### INTRODUCTION.

In Part III (*This Journal*, 1937, 20A, 55-66) we have shown that the decomposition of pure calcium chromate occurs in four stages corresponding to 50, 66.6, 75 and 80% of the complete decomposition, while the mixtures of calcium chromate with lime (Part IV, *This Journal*, 1938, 21A, 119-129) indicated two additional stages in the decomposition at 33.3 and 40%, due to formation of compounds similar in composition to the soluble products obtained by treating the 50 and 66.6% stages in the decomposition of plain chromate, with acids.

Although there are numerous papers on the decomposition of calcium chromate and the complex nature of the systems  $\text{CaO-Cr}_2\text{O}_3\text{-O}_2$  and  $\text{Cr}_2\text{O}_3\text{-O}_2$  was pointed out by Nargund and Watson (*This Journal*, 1926, 9, 149), there has been so far no attempt made to study the decomposition of strontium chromate.

The object of the present investigation was to find out if the decomposition of strontium chromate also occurred in stages similar to that of calcium chromate and to measure the dissociation pressure at each stage.

### EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as described in Part III (*loc. cit.*). Strontium chromate was prepared by precipitating the salt from a solution of strontium chloride by potassium chromate. The purity of the sample was above 99.5%.

*Dissociation of strontium chromate.*—Strontium chromate begins to dissociate in vacuum at about 900°. The dissociation pressures are given in Table I and shown in Fig. 1, which also shows the relation between the log of pressure and the reciprocal of the absolute temperature.

TABLE I.

Temperature °C.	Pressure in mm.	Temperature °C.	Pressure in mm.	Temperature °C.	Pressure in mm.
985	2.0	1175	28.5	1265	300.0
1070	6.0	1200	42.0	1275	450.0
1090	8.5	1230	81.0	1310	580.0
1130	13.5	1250	150.0	1425	> 750.0
1150	17.0				

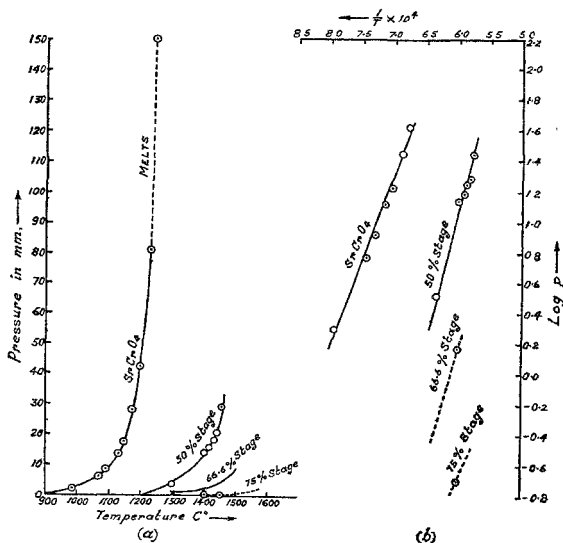


FIG. 1.

Dissociation of Strontium Chromate and of the Intermediate Stages of Decomposition.

The curve obtained by plotting  $\log P$  against  $\frac{1}{T}$  [Fig. 1 (b)] shows that the curve deviates above  $1200^\circ$  from linearity (not shown

in figure) due to strontium chromate melting with decomposition into strontium chromite. The heat of dissociation of strontium chromate is 51.5 cal. per mol of oxygen.

*Dissociation of the first stage.*—If, instead of heating strontium chromate directly to a temperature above 1200°, the gas is pumped off at 1060° until there is a sudden fall in pressure (<0.2 mm.), the amount of oxygen evolved corresponds to 50% decomposition and the new compound formed does not melt at 1200°. The dissociation pressures of this compound are given in Table II and are shown graphically in Fig. 1 (a) and Fig. 1 (b).

TABLE II.

First stage 50%		Second stage 66.6%		Third stage 75%	
Temp. °C.	Pressure in mm.	Temp. °C.	Pressure in mm.	Temp. °C.	Pressure in mm.
1300	3.5	1300	< 0.2	1390	< 0.2
1400	14.0	1390	1.5		
1415	15.5				
1430	18.0				
1440	20.5				
1455	29.0				

The heat of dissociation of the first stage is 57.9 cal. per mol of oxygen.

The dissociation pressures could not be measured above 1455° as the 'Pythagoras' tube used in our experiments collapsed at higher temperatures.

While the furnace was being cooled the dissociation pressures were measured at various temperatures. The results indicated that the dissociation pressures on cooling the system were much higher than the dissociation pressures of the first stage of decomposition as given in Table II. The pressures first decreased from 30.0 mm. at

1465° to 21.0 mm. at 1380° but suddenly began to rise at this temperature. When the temperature was lowered below 1380° this abnormal rise in pressure stopped but continued again on raising the temperature to 1380° above which the product melted with complete decomposition.

It appears from these results that the absorption of oxygen takes place in such a manner as to form, instead of the 50% stage, some other compound which lowers the fusion temperature of the whole mass resulting in the complete decomposition of the chromate.

*Dissociation of the second stage.*—If the oxygen is pumped off to a pressure  $< 0.2$  mm. at 1300° a second stage in the decomposition corresponding to 66.6% is obtained. The dissociation pressure of this compound is 1.5 mm. at 1390° (Table II).

Evacuation of the system to a sudden drop in pressure  $< 0.2$  mm. at 1390° indicated a *third stage* in the decomposition at 75%.

The range of temperatures over which the various intermediate stages are stable are 930–1200°, 1225–1300° and 1325–1450°. The properties and chemical composition of the products formed at various stages of decomposition were next investigated.

*First stage.*—Strontium chromate was heated in vacuum at 1070° and the oxygen was pumped off till the pressure suddenly dropped to  $< 0.2$  mm. The results of analysis of the products formed are given in Table III.

TABLE III.

Weight of SrCrO <sub>4</sub> in grams	Per cent. decomposition from O <sub>2</sub>	Acid-soluble			Acid-insoluble	
		% Cr as CrO <sub>3</sub>	% Sr	% Total Cr	% Sr	% Cr
(A) 0.50 ..	50.6	..	..	..	..	..
(B) 1.75 ..	50.7	48.5	100	70.0	nil	26.2
(C) 1.75 ..	51.0	49.1	97	65.7	..	33.5
(D) 1.75 ..	50.2	49.5	100	73.2	nil	26.6

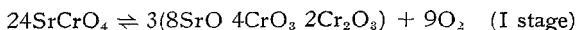
The quantity of the chromate in experiment (A) was 0.5 grams, and 1.75 grams in the other three experiments. The percentage

decomposition calculated from the amount of oxygen evolved gave concordant results in all the experiments and indicated a stage in the decomposition at 50%, which was also confirmed by the estimation of the chromate in the decomposed product.

The decomposed chromate, which was black in colour, was partly soluble in both hydrochloric and acetic acids. The extraction was not, however, complete with cold hydrochloric acid, while warm hydrochloric acid could not be used because the chromate was reduced. In experiments (B) and (D) the product was treated with warm acetic acid and in experiment (C) with cold hydrochloric acid.

The acid-soluble and insoluble portions were analysed for the chromate, total chromium and strontium. The insoluble residue did not contain any strontium but contained about 26–27% of the total chromium. The composition of the insoluble residue was very near to that of chromic oxide  $\text{Cr}_2\text{O}_3$ . The higher percentage of chromium in the residue and lower percentage of strontium in solution in experiment (C) was due to the incomplete extraction of the soluble portion from the decomposed product with cold hydrochloric acid.

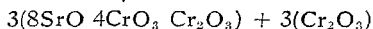
From the analytical data presented in Table III, it is probable that the following reactions take place, starting from strontium chromate:—



(I)



warm acetic acid



(II)

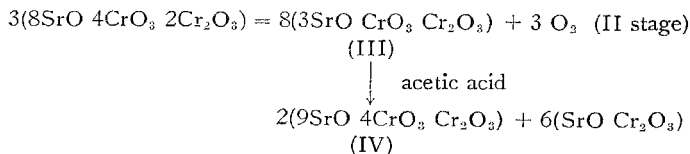
Compound (I), **strontium tetrachromito-quarterchromate**, corresponds to the first stage of decomposition obtained in the decomposition of calcium chromate (Part III, *loc. cit.*). The reaction of the compounds formed in the two cases is, however, considerably different when treated with acids. The **calcium tetrachromito-quarterchromate** gives on treatment with cold hydrochloric acid,  $10\text{CaO } 6\text{CrO}_3 \text{ } \text{Cr}_2\text{O}_3$  as the acid-soluble portion which corresponds to 25% decomposition of the chromate, and calcium chromite as an insoluble residue, while the corresponding strontium compound yields on treatment with an acid, a soluble compound (II) **strontium dichromito-quarterchromate** corresponding to 33.3% decomposition and chromic oxide as an insoluble residue.

*Second stage.*—Strontium chromate cannot be heated directly to a temperature above 1200°. The second stage in the decomposition was therefore obtained by first decomposing the chromate to the 50% stage at 1100° and then evacuating the system further at 1285° until the pressure fell sharply to <0.2 mm. The results of analysis of the product are given in Table IV.

TABLE IV.

	Observed	Calculated
% Decomposition from oxygen ..	68.2	66.6
% Chromium as CrO <sub>3</sub> in solution ..	33.1	33.3
% Total chromium in solution ..	48.3	50.0
% Strontium in solution ..	75.5	75.0
% Residue insoluble in acid ..	32.0	31.4
% Chromium in the residue ..	49.6	50.0
% Strontium in the residue (by difference) ..	24.5	25.0

The second stage in the decomposition of strontium chromate occurs at 66.6% similar to the reaction observed in the case of calcium chromate (Part III, *loc. cit.*). From the analytical data given in Table IV, the reactions can be represented in the following manner, starting with the first stage in the decomposition:



Compound III, **strontium dichromito-chromate**, corresponds to the chromium chromate, **chromium-trita-hexaoxide**, reported by several workers (*cf.* Part III, this series). The compound IV, **strontium dichromito-quarterchromate**, is the salt of the same chromium chromate 4CrO<sub>3</sub>·Cr<sub>2</sub>O<sub>3</sub> as that of compound (II) obtained by treating the 50% stage with acid but containing one mol of

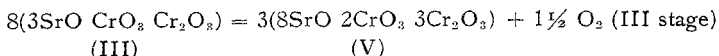
strontium oxide more. A calcium compound corresponding to compound (IV) has been reported by us in Parts III and IV (*loc. cit.*). The behaviour of the 66.6% stages towards acid in the case of both the strontium and calcium chromate is the same.

*Third stage.*—The third stage in the decomposition of strontium chromate was obtained by first decomposing the chromate to 50% stage at 1100° and then pumping off further quantities of oxygen to a pressure <0.2 mm. in one experiment at 1350°, and in the other at 1375°. The following results were obtained:

	1350° C.	1375° C.	
Weight of chromate in grams . . . . .	1.5	1.0	1.5
% Decomposition from oxygen . . . . .	74.6	77.2	75.3

Analysis of the decomposed chromate could not be carried out. The decomposed product did not dissolve in warm acetic acid even in 36 hours, while it dissolved in warm hydrochloric acid but the chromate was all reduced. Extraction with sulphuric acid was not possible.

Owing to the difficulties encountered in the estimation of the chromate the percentage decomposition was determined by the volume of oxygen evolved. The results show a stage at 75% decomposition similar to the 75% stage obtained in the decomposition of calcium chromate. Starting from the second stage in the decomposition the reaction can be represented as follows:



Compound V, **strontium hexachromito-dichromate**, is analogous to the corresponding calcium compound obtained by Nargund and Watson and also by the authors. It is doubtful whether both of these compounds of calcium and strontium are pure substances or are mixtures of  $17\text{RO } 6\text{CrO}_3 \text{ } 2\text{Cr}_2\text{O}_3$  and the chromite as pointed out in Part IV. This point will be further discussed in Part VI. According to the results given in Part III for the 75% stage for calcium chromate, it was expected that compound V on treatment with an acid would yield acid-soluble portion corresponding to  $17\text{SrO } 6\text{CrO}_3 \text{ } 2\text{Cr}_2\text{O}_3$  in composition.

The dissociation pressure of the 75% stage was low even at 1450° and it was not possible to investigate whether any more stages in the decomposition above 75% exist, because no suitable material to stand the vacuum above 1450° was available. Experiments are on hand for carrying out further decomposition at lower temperatures and pressures using a diffusion pump and Pirani gauge.

### SUMMARY.

The experiments on the decomposition of strontium chromate confirm the results obtained in the decomposition of calcium chromate given in Part III and indicate stages in the decomposition corresponding to 50, 66.6 and 75% decomposition, the range of temperatures over which these are stable being 930–1200°, 1225–1300° and 1325–1450° C. respectively at 0.2 mm. pressure.

The stages in the decomposition corresponding to 80% and complete decomposition could not be obtained for want of suitable materials to carry out experiments in vacuum above 1450° C.

The vapour pressures of the intermediate stages have been measured and the heats of dissociation calculated therefrom. The products corresponding to 50 and 66.6% stages, which resisted further decomposition in vacuum, partly dissolved in warm acetic acid leaving an insoluble residue, which was identified as chromic oxide in the former case and strontium chromite in the latter.

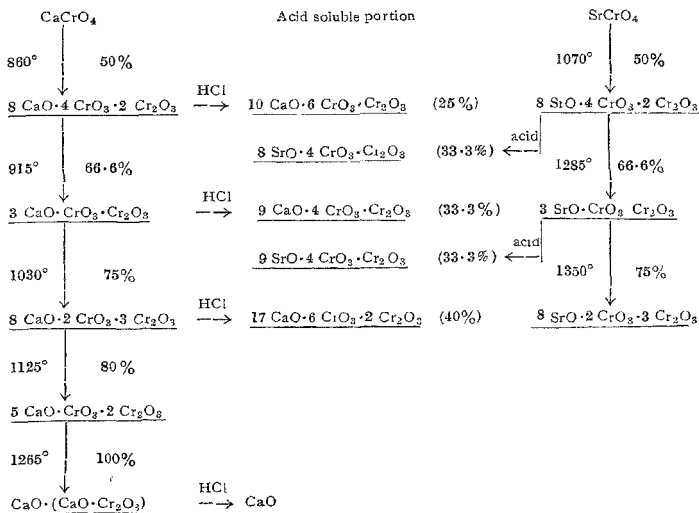
The steps observed in the decomposition of strontium chromate are due to the formation of the following compounds:

(1)  $8\text{SrO} \cdot 4\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ , (2)  $8\text{SrO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ , (3)  $9\text{SrO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ , (4)  $3\text{SrO} \cdot \text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and (5)  $8\text{SrO} \cdot 2\text{CrO}_3 \cdot 3\text{Cr}_2\text{O}_3$ . Compounds (2) and (3) are the strontium salts of the same chromium chromate  $4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  but differ in the amounts of strontium oxide required for the formation of the compounds. Compound (2) was not obtained in the study of the decomposition of calcium chromate.

Strontium chromate melts at 1200° and decomposes completely above this temperature.

The scheme given below shows a comparative picture of the reactions observed in the decomposition of calcium and strontium chromates.





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