REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

PART VI. DECOMPOSITION OF MIXTURES OF STRONTIUM CHROMATE AND STRONTIUM CARBONATE.

By V. T. Athavale and S. K. K. Jatkar.

INTRODUCTION.

It has been shown in Part V (*This Journal,* 1938, **21A**, 159) that the decomposition of strontium chromate indicated intermediate stages at 50, 66.6 and 75% decomposition in conformity with our observations on the decomposition of calcium chromate (*This Journal,* 1937, **20A**, 55–56). The stages corresponding to 80 and 100% decomposition could not be obtained in this case because of the lack of a suitable tube material which would stand temperatures above 1450° in vacuum.

While studying the decomposition of the mixtures of lime with calcium chromate (*This Journal,* **21A**, 119) two additional stages in the decomposition corresponding to 33.3 and 40% decomposition were obtained, the composition of each stage being, respectively, identical with the acid-soluble portions from 66.6 and 75% stages for plain chromate. The composition of the acid-soluble portion is thus an indication of the composition of the intermediate stages obtained in the decomposition of the chromate when mixed with the corresponding oxide.

The difference in the behaviour of the compounds formed at the 50% stages for calcium and strontium chromates towards acid has already been pointed out in Part V of this series. We thus get from 50% stage for strontium chromate, an acid-soluble compound $8SrO\ 4CrO_3\ Cr_2O_3$ corresponding to 33.3% decomposition, which though obtained otherwise in the decomposition of calcium chromate and its mixtures with lime, contained one mol of SrO less, while the corresponding stage in the decomposition of calcium chromate yields an acid-soluble portion $10CaO\ 6CrO_3\ Cr_2O_3$ A strontium compound corresponding to 33.3% stage was also obtained by treating the 66.6% stage with acid, the composition of which was $9SrO\ 4CrO_3\ Cr_2O_3$. Thus, we have here a case in which the same chromium chromate $4CrO_3\ Cr_2O_3$ combines with different quantities of the base, The question now arises whether the products formed at 50 and 66.6% stages in the decomposition of pure chromates are single compounds or are mixtures of the products formed at lower stages of decomposition with those of higher stages or complete decomposition. A study of the decomposition pressure of the various products would throw light on the problem. The object of the present investigation was to study the decomposition of mixtures of strontium chromate *with strontium carbonate* and compare the decomposition pressures of the products obtained at various stages with those obtained in the decomposition of the pure chromate.

The study of the decomposition of the mixtures of strontium chromate with strontium carbonate was also important from a practical standpoint, because the use for strontium oxide and also of barium oxide is recommended for the manufacture of chromates from chrome iron ore, in preference to calcium oxide.

EXPERIMENTAL.

The apparatus used was the same as described in Part III. Mixtures were prepared by mixing pure samples of strontium chromate and strontium carbonate thoroughly in an agate mortar.

Reaction between $SrCrO_4$ *and* $SrCO_3$.—The dissociation pressure of strontium carbonate at 850° is 2.5 mm. and the chromate has practically no dissociation pressure at this temperature. It should have been, therefore, possible to decompose the carbonate independently at 850°. The mixtures started decomposing at about 600° and gave reproducible dissociation pressures which are given in Table I.

TABLE I.

Temp. °C.	Pressures for mixtures : $SrCO_3/SrCrO_4$						Pressure in mm. (mean)
	0·175	0·2	0·33	0·4	0·5 (A)	0·5 (B)	
615	(1·5)	(5·5)	..	..	(5·0)	..	..
635	(2·0)	(6·0)	1·5	(6·0)	(5·5)	1·5	1·5
680	4·0	(7·0)	4·0	(8·0)	(7·0)	4·0	4·0
735	(9·0)	(11·0)	12·0	12·0	12·0	12·0	12·0
760	(15·0)	17·5	20·0	17·5	18·5	20·0	18·6
780	(20·0)	20·0	28·0	28·0	33·3	31·0	29·2
820	(35·0)	56·0	58·0	58·0	..	..	57·0
855	..	..	..	102·0	..	..	102·0

In experiments with the ratio of strontium carbonate: strontium chromate, as 0.175, 0.33 and 0.5 (B), the gas was first pumped off (<0.2 mm.) at 600° before heating to higher temperatures. The gas was not pumped off in experiments with mixtures containing 0.2, 0.4 and 0.5 (A) mols of SrO, which therefore gave higher pressures up to 680°. The dissociation pressures above 735° are practically the same in all the experiments.

The mean values of the dissociation pressures are given in the last column and the logarithms of these if plotted against the reciprocal of the absolute temperature, yield a straight line. With mixtures containing fairly high concentrations of the carbonate, the pressures are regained when the gas is pumped off and the gas is absorbed back readily when the temperatures are lowered.

In the course of these experiments it was noticed that the gas phase was a mixture of carbon dioxide and oxygen. Experiments were therefore carried out to find out whether there was any definite relationship between the amounts of the two gases evolved during the dissociation.

Mixtures with different concentrations of the carbonate were heated and the gas was first pumped off at 825° (except in one experiment with 0.175 mols of $SrCO_3$) and subsequently at 1070° till the pressure fell down to <0.2 mm., and collected in separate tubes 1, 2 and 3 successively. The results are given in Table II.

TABLE II.

Mols $\frac{SrCO_3}{SrCrO_4}$	825° C Ratio CO_2/O_2	1070° Ratio CO_2/O_2	
	Tube 1	Tube 2	Tube 3
0·175	2·26	O_2	O_2
0·2	2·10	O_2	O_2
0·4	2·03	1·97	1·97
0·4	..	1·99	1·82
0·5	2·09	2·00	1·90
0·5	2·09	2·00	1·95

The results show a fairly constant ratio between the carbon dioxide and oxygen evolved, indicating a definite reaction between the carbonate and the chromate.

It will be shown subsequently in this paper that if the gas is pumped to a pressure <0.2 mm. at 1070°, a stage in the decomposition corresponding to 33.3% is indicated.

In the experiment with the mixture containing 0.175 mol of $SrCO_3$ per mol of $SrCrO_4$ it was found that when the gas was pumped off at 825° to a pressure < 0.2 mm., the carbonate had all decomposed and the amount of oxygen given out along with carbon dioxide corresponded with only about 10% decomposition of the chromate. It appears, therefore, that there exists a stage in the decomposition below 33.3%, probably at 25%, which can be obtained by pumping off the gas at 825° to a low pressure, taking mixtures with different concentrations of the carbonate. Experiments in this direction are in progress.

Nargund and Watson report a compound $12CaO.6CrO_3.Cr_2O_3$ in their study of the mixtures of lime with calcium chromate while we have obtained (*cf.* Part III) a compound $10CaO.6CrO_3.Cr_2O_3$ by treating the 50% decomposition product of calcium chromate with an acid. Russ and Seljanskaja in a paper very recently published (*Acta Physica Chemica,* 1938, **8**, 623) have confirmed the earlier observations of Simon and Schmidt and shown a stage in the decomposition of hydrated chromium oxides at 25%, corresponding to the above calcium chromium chromate. If the dissociation pressures of the mixtures of strontium carbonate and the chromate as given in Table I are due to the formation of the 25% stage, the reaction

$$3SrCO_3 + 8SrCrO_4 = 11SrO\ 6CrO_3\ Cr_2O_3 + \tfrac{3}{2}O_2 + 3CO_2$$

will take place, giving a ratio of 2: 1 for CO_2: O_2 in the gas phase as observed (*cf.* Table II).

It will be shown in a later communication that the structural formula of the oxide $6CrO_3\ Cr_2O_3$ is in harmony with the formation of compounds having 10, 11 or 12 mols of the base.

It follows from the above discussion that the dissociation pressures of the mixtures as given in Table I are due to a stage in the decomposition of the mixtures at 25%.

Decomposition at 1070° in vacuum.—Mixtures of strontium chromate and strontium carbonate in various proportions were heated to 1070° and the gas was pumped off to a pressure <0.2 mm. the carbonate having been first decomposed completely below 1000° C.

The decomposed mixtures were cooled in vacuum, treated with acid and the chromate in the product was estimated. The gas was analysed for carbon dioxide, oxygen and any admixed air, by treating with potassium hydroxide and phosphorus in succession. The results are given in Table III and shown in Fig. 1.

TABLE III.

Mols $\frac{SrCO_3}{SrCrO_4}$	Per cent. decomposition from			
	Oxygen	CrO_3	Mean	Calculated
1. 0·175	49·8	49·2	49·5	48·9
2. 0·20	43·8	43·3	43·5	44·6
3. 0·30	35·9	37·0	36·5	35·5
4. 0·33	34·8	35·2	35·0	33·3
5. 0·40	32·5	33·6	33·0	33·3
6. 0·50 .. .	32·5	33·2	32·7	33·3
7. 0·60	33·2	..	33·2	33·3

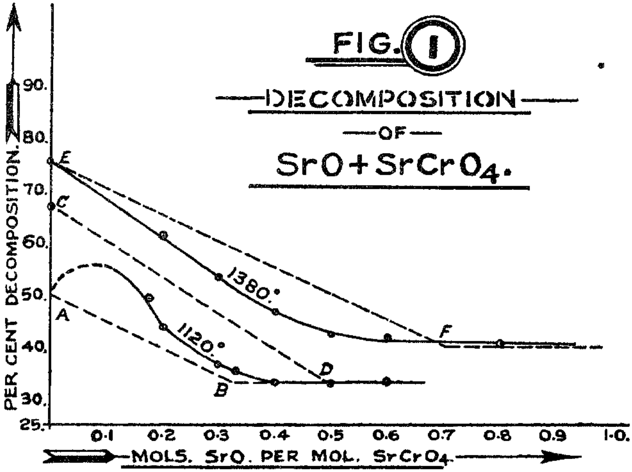


FIG. ①
DECOMPOSITION
OF
$SrO+SrCrO_4$.

Mixtures with 0.33 mol of carbonate and above were completely soluble in dilute acetic and sulphuric acids. However, as the concentration of SrO increased the product obtained could be dissolved with some difficulty. The first three mixtures leave an acid insoluble residue of 12.4, 5.8 and 3.0% of the original chromate respectively.

The results show clearly a stage in the decomposition at 33.3% the amount of SrO necessary for its formation being 0.33 mols per mol of $SrCrO_4$. The calculated results given in Table III are on the basis that, 0.33 mol of SrO per mol of the chromate, decompose the chromate to the 33.3% stage, the excess of the chromate, if any, decomposing independently to the 66.6% stage. The calculated and observed decompositions show fair agreement. The formation of the intermediate compound obtained by decomposing the mixtures in vacuum at 1070° is therefore $8SrO\ 4CrO_3\ Cr_2O_3$, **strontium dichromito-quarterchromate.**

It has already been shown (*cf.* Part V) that the products formed at the 50% and 66.6% stages in the decomposition of the pure strontium chromate yield $8SrO\ 4CrO_3\ Cr_2O_3$ and $9SrO\ 4CrO_3\ Cr_2O_3$ as the acid-soluble portions respectively, the corresponding acid insoluble portions being Cr_2O_3 and $SrO\ Cr_2O_3$. The results of the decomposition of the mixtures of strontium oxide and strontium chromate given in Table III show a 33.3% stage decomposition and were obtained under conditions when pure strontium chromate itself decomposes to 50% stage.

Fig. 2 shows the vapour pressures of the mixtures of strontium oxide and strontium chromate at different temperatures. The mixtures were initially heated at 1120° and the system was evacuated until there was a sudden fall in pressure to <0.2 mm. From the figure it will be evident that the product obtained with 0.3 mols of strontium oxide has got nearly the same vapour pressure as that of the products obtained at the 50% stage for pure strontium chromate, indicating that the compounds formed in the two cases may be the same, namely, $8SrO\ 4CrO_3\ Cr_2O_3$.

When the same system was further evacuated at 1380°, oxygen was given out at a nearly steady pressure of 1.5 mm., which is approximately the same as the dissociation pressure of the 66.6% stage for pure chromate. Fig. 2 shows that the latter pressure is in agreement with the vapour pressure of the product formed by the addition of 0.5 mols of strontium oxide to strontium chromate, thus indicating the formation of the same compound $9SrO\ 4CrO_3\ Cr_2O_3$.

As in the case of the results obtained with calcium chromate a stage at 33.3% is observed on addition of 0.5 mol of strontium oxide per mol of strontium chromate. The composition of the compound formed is $8SrO\ 4CrO_3\ Cr_2O_3$ which corresponds to the acid-soluble portion from the 50% stage, and when the amount of strontium oxide is less than 0.33 mol, the percentage decomposition does

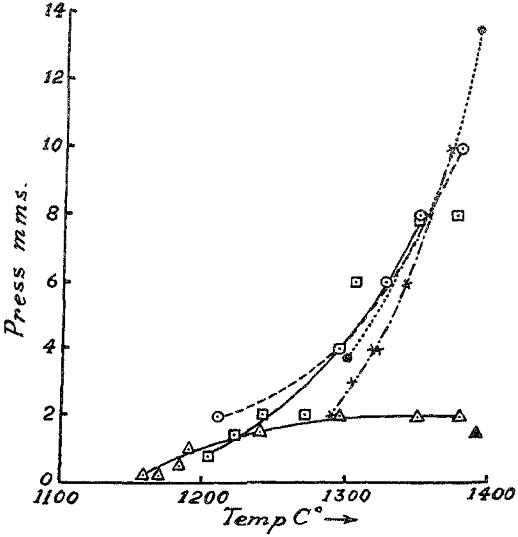


Fig. 2.

Dissociation pressures of mixtures of SrO with $SrCrO_4$ decomposed in vacuum at 1070° to the 33·3% stage.

×--× 0·2.1 SrO : $SrCrO_4$
⊙---⊙ 0·3 : 1 ,, ,,
△—△ 0·5 : 1 ,, ,,
⊡—⊡ 0·6.1 ,, ,,
●-----● 50% stage $SrCrO_4$
▲ ▲ 66·6% stage $SrCrO_4$

not vary between 50% and 33.3% (Curve AB, Fig. 1) but proceeds to 66.6% stage. As the acid-soluble portion from the latter stage is $9SrO\ 4CrO_3\ Cr_2O_3$, a break in the curve showing the relationship between the amount of base added and the percentage decomposition ought to have occurred at 0.5 mols of strontium oxide instead of 0.33 mols observed (Curve CD, Fig. 1).

It appears, therefore, that the products obtained by decomposing strontium chromate when mixed with varying quantities of strontium carbonate in vacuum at 1070°, contained mixtures of two compounds $8SrO\ 4CrO_3\ Cr_2O_3$ and $9SrO\ 4CrO_3\ Cr_2O_3$ which exist in the products formed by the 50 and 66.6% decomposition of pure chromate, the balance of chromite remaining as a separate phase.

The dissociation pressures of the two compounds 8SrO $4CrO_3$ Cr_2O_3 and 9SrO $4CrO_3$ Cr_2O_3 are 10 mm. and 1.5 mm. respectively at 1380°. If the above findings are correct, the structures of these two compounds should be entirely different, though both of them are the compounds of the same chromium chromate, $4CrO_3$ Cr_2O_3, or the combination with extra base makes the compound more stable. Probably the latter is the case.

Decomposition of the mixtures in vacuum at 1380°.—The dissociation pressures of the 33.3% stage have already been discussed. The mixtures first decomposed in vacuum at 1100° were decomposed further by evacuating at 1380° till the pressure fell down sharply to <0.2 mm., which is nearly the same as that of the products formed when 75% of the pure chromate is decomposed. The results are given in Table IV and shown in Fig. 1.

TABLE IV.

Mols $\frac{SrO}{SrCrO_4}$	Per cent. decomposition	
	from oxygen	from chromate
1. 0·2	61·3	..
2. 0·3 ..	53·2	..
3. 0·4	46·5	..
4. 0·5	42·1	..
5. 0·6	41·6	42·3
6. 0·8	40·5	..

The decomposed products in experiments 1–3 were insoluble in acids and therefore the amount of the chromium as CrO_3 could not be estimated. Mixture 4 dissolved partly in cold hydrochloric acid leaving a small amount of insoluble residue. Mixtures 5 and 6 were completely soluble in cold hydrochloric acid and the estimation of chromium as CrO_3 in solution in experiment 5 agrees with the decomposition calculated from the oxygen.

The results indicate the formation of the compound 17SrO $6CrO_3$ $2Cr_2O_3$, **strontium tetrachromito-hexieschromate**, on the basis of 40% decomposition and 0.7 mol of SrO per mol of $SrCrO_4$ as taking part in the reaction, in agreement with the results obtained with mixtures of calcium chromate with lime (*cf.* Parts III and IV).

As shown in Part IV, the composition of the acid-soluble portion from the products obtained at the 66.6% stage in the decomposition of the calcium chromate, was similar to the composition of the 33.3% stage observed in the decomposition of the mixtures of lime with calcium chromate. The dissociation pressures of the compounds formed at these two stages were different. It was therefore thought that we were dealing with two different compounds. The dissociation pressures of the products formed at the 75% stage in the decomposition of the calcium chromate were, however, nearly identical with those of the 40% stage observed in the case of mixtures of lime and calcium chromate and the composition of the acid-soluble portion from the 75% stage was identical with that of the 40% stage. It appears, therefore, that the compounds formed in the two cases are identical, the balance of the chromite at the 75% stage behaving as a separate phase.

The vapour pressure of the products formed at the 75% stage in the decomposition of the pure strontium chromate is very low (<0.2 mm.) at 1400° and is very nearly the same as that of the 40% stage observed in the decomposition of the mixtures of strontium chromate and strontium oxide. The compounds formed in both the cases, therefore, appear to be identical as in the case of calcium compounds. Further experiments are in progress.

The above findings are in harmony with the fact that the two chromium chromates formed by 33.3 and 40% decomposition of chromium trioxide have been well established, while the individuality of the intermediate stages assumed in explaining the compounds formed at 50, 66.6 and 75% stages in the decomposition of the pure chromates of the alkaline earths, have not been confirmed by recent workers, although a stage in the 50% decomposition of chromium trioxide has been shown to exist by Nargund and Watson.

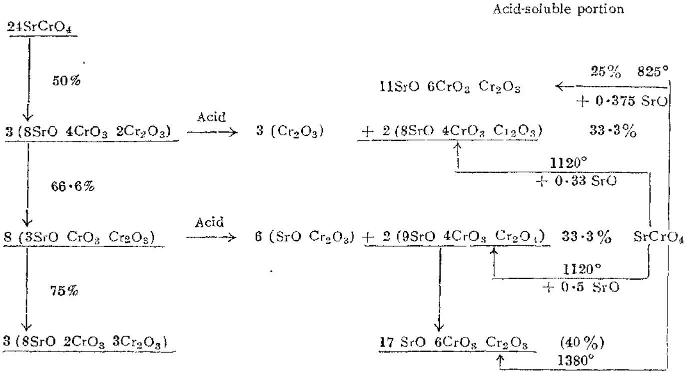
SUMMARY.

The decomposition of mixtures of strontium carbonate and strontium chromate, confirm the previous results obtained with mixtures of calcium carbonate and lime and indicate additional stages in the decomposition at 33.3 and 40% which were not obtained in the decomposition of pure strontium chromate. A stage in the decomposition at 25% is also indicated. Experiments are in progress to isolate this stage and to study its decomposition pressure.

The dissociation of the mixtures of strontium carbonate and strontium chromate starts with the evolution of carbon dioxide and oxygen simultaneously and at a much lower temperature than that required for the dissociation of either of the components independently, the ratio of CO_2/O_2 in the gas-phase being 2 : 1.

The formulæ of the compounds corresponding to 33.3 and 40% decomposition, are, 8Sro (and 9SrO) $4CrO_3$ Cr_2O_3 and 17SrO $6CrO_3$ $2Cr_2O_3$ respectively. The former was also represented by the acid-soluble portion of the 50 and 66.6% stages observed in the decomposition of strontium chromate and showed remarkably increased stability in combination with the extra base.

The results of the decomposition of strontium chromate and of the mixtures of strontium chromate with strontium oxide may be summarised as follows:—



The decomposition pressures of the various stages indicate that the products formed at 50 and 66.6, and at 75% decomposition of pure strontium chromate are probably mixtures of the compounds formed at 33.3 and 40% stages respectively, which were observed in the case of decomposition of mixtures of strontium chromate with strontium oxide, with chromium oxide or chromite.

The reaction between the strontium chromate and strontium carbonate was found to be more intense than between calcium carbonate and calcium chromate and this explains why strontium carbonate is preferred to calcium carbonate in the manufacture of chromates.

Department of General Chemistry,
Indian Institute of Science,
Bangalore (India).

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