

# REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

## PART VII. DECOMPOSITION OF BARIUM CHROMATE, AND OF MIXTURES OF BARIUM CHROMATE WITH BARIUM CARBONATE.

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### DECOMPOSITION OF BARIUM CHROMATE.

It was shown in Part V (*This Journal*, 1938, 21A, 159-67) that the decomposition of strontium chromate proceeded stepwise at 50, 66.6 and 75% decomposition, due to the formation of the compounds  $8\text{SrO} \cdot 4\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ ,  $3\text{SrO} \cdot \text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and  $8\text{SrO} \cdot 2\text{CrO}_3 \cdot 3\text{Cr}_2\text{O}_3$  respectively, analogous to the results obtained in the decomposition of calcium chromate. The higher stages of decomposition, namely, at 80% observed in the decomposition of the latter could not be studied owing to experimental difficulties. It was, therefore, considered interesting to find out if the decomposition of barium chromate also occurred in stages. In the present paper we have shown that barium chromate shows a step in the decomposition at 50% forming a compound  $8\text{BaO} \cdot 4\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ , which is stable in vacuum at  $1400^\circ$ . The decomposition of barium chromate has also been studied in mixtures with barium carbonate.

### EXPERIMENTAL.

The apparatus used and the method followed was the same as that described in previous Parts. Barium chromate was prepared by precipitation from a solution of barium acetate by ammonium chromate. The purity of the sample was over 99.5%.

### DISSOCIATION OF BARIUM CHROMATE.

The decomposition pressures of barium chromate are as follows:

Temp. °C.	Pressure mm.
1240	1.0
1260	1.5
1295	2.0
1365	4.0

The heat of decomposition calculated from the above values is 49.6 Cals. per mol. of oxygen evolved.

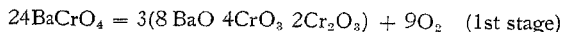
If barium chromate is heated directly to 1400°, it melts with complete decomposition. If, however, oxygen is pumped off from the system at 1265° to a pressure < 0.2 mm. the amount of the gas evolved corresponds to 50% decomposition of the chromate. The decomposed mass does not melt on heating further and does not show any measurable decomposition pressure at 1420°. Unfortunately, the vapour pressures of the 50% compound could not be measured for want of a suitable material of the tube which could stand vacuum at higher temperatures.

The chemical reactions of the compound formed at 50% stage were studied next. Pure barium chromate was decomposed at 1265°, the oxygen being pumped out of the system till there was a sudden fall in pressure to < 0.2 mm. The product was treated with dilute hydrochloric acid and the soluble and insoluble portions were analysed. The gas collected was also analysed and measured. The results are given in the following table:—

TABLE I.

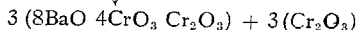
	Observed	Calculated
Per cent. decomposition from oxygen ..	51.3	50.0
„ Chromium as CrO <sub>3</sub> in solution ..	49.9	50.0
„ Barium in solution .. ..	100.0	100.0
„ Total chromium in solution ..	74.8	75.0
„ Barium in the residue.. ..	nil	nil
„ Chromium in the residue ..	25.13	25.0

The acid-insoluble portion was pure chromic oxide Cr<sub>2</sub>O<sub>3</sub>. The analytical data given in the above table are in agreement with the following equation:



(I)

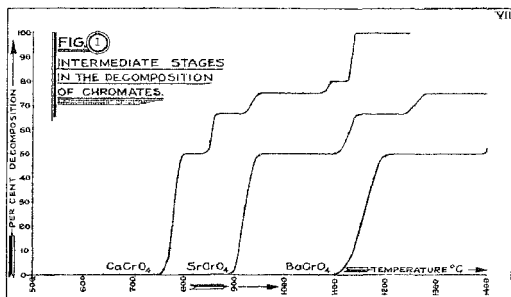
↓ acid



(II)

The compounds formed are (I) barium tetrachromito-quarterchromate, (II) barium dichromito-quarterchromate.

Fig. 1 shows the various stages found in the decomposition of pure chromates of calcium, strontium and barium, and the range of



temperature over which they are stable. The stability of the various compounds increases in the order: calcium, strontium and barium.

The decomposition of calcium chromate occurs in four stages as indicated. The decomposition of strontium chromate could be studied only up to the third stage, and that of barium chromate to the first stage. Further work on the decomposition of strontium and barium chromates is in progress; the decompositions are being studied at both higher and lower pressures using a sensitive gauge.

The products of decomposition formed at various stages yielded acid-soluble portions in which the amount of chromium as  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  was in agreement with the composition of the chromium chromates  $\text{Cr}_5\text{O}_{21}$ ,  $\text{Cr}_6\text{O}_{17.5}$  and  $\text{Cr}_5\text{O}_{12}$  corresponding to 25, 33.3 and 40% decomposition of the chromate. As the vapour pressures of some of the compounds, especially those which are formed at 66.6 and 75% decomposition of the pure chromates, are similar to those of the compounds formed at 33.3 and 40% decomposition of the mixtures of chromates with the corresponding oxides, it appears probable that the intermediate stages formed in the decomposition of the chromates at higher temperatures are mixtures of compounds corresponding to the lower stages, with either chromic oxide or chromite, which may exist as a separate phase, the oxide liberated in the formation of the latter compounds supplying the extra base required for the formation of the former compound.

DECOMPOSITION OF MIXTURES OF BARIUM CHROMATE WITH  
BARIUM CARBONATE.

The results obtained by decomposing the mixtures of the chromates of calcium and strontium with the corresponding carbonates have already been discussed in Parts IV and VI (*This Journal*, 21A, 179-88). In the decomposition of the mixtures of strontium chromate with strontium carbonate, it was observed that the components begin to dissociate at temperatures lower than that required for the decomposition of the constituents of the mixtures separately, and that the dissociation pressures of the mixture were definite functions of temperature and were independent of the concentration of the carbonate. The gas phase was also found to be a mixture of carbon dioxide and oxygen in the ratio of nearly 2:1, which indicated the formation of the compound  $11\text{SrO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  corresponding to 25% decomposition of the chromate.

The experiments on the decomposition of the mixtures of strontium chromate and strontium carbonate also indicated additional stages in the decomposition at 33.3 and 40%, analogous to the results obtained in the decomposition of the mixtures of calcium chromate and calcium carbonate, the formulae of the compounds formed being  $8\text{SrO}$  (and  $9\text{SrO}$ )  $4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and  $17\text{SrO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$  respectively.

In the present paper we have shown that mixtures of barium chromate with barium carbonate were found to decompose much more readily than the corresponding mixtures of strontium compounds. It appears that the intensity of the reaction between the chromates and the carbonates of the alkaline earths increases in order: calcium, strontium and barium. The decomposition curves of the mixtures showed breaks at 25, 33.3 and 40% similar to the behaviour of compounds.

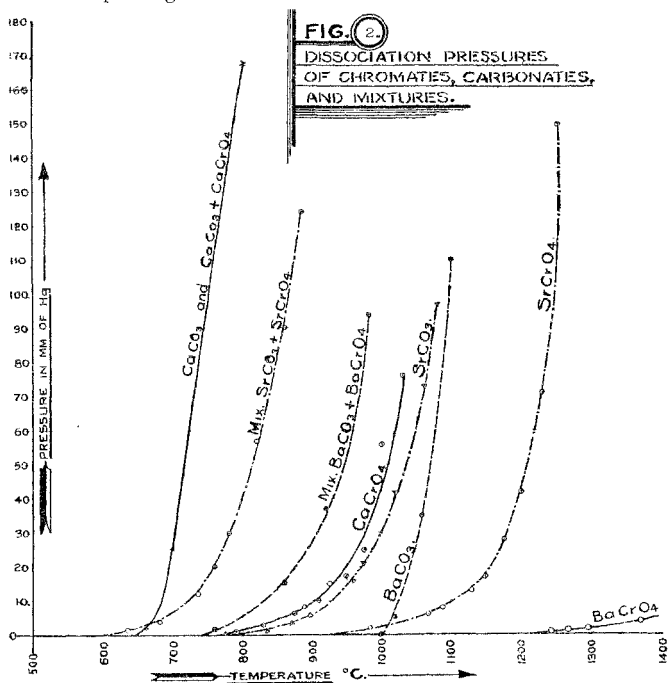
**EXPERIMENTAL.**

The mixtures were prepared by grinding together pure barium chromate and barium carbonate in the required proportions. The temperatures at which barium chromate and pure barium carbonate begin to decompose at low pressures are  $1200^\circ$  and  $1000^\circ$  respectively. It was found, however, that the mixtures began to decompose at  $725^\circ$  and gave the following values for dissociation pressures, which were independent of the concentration of the carbonate in the mixtures as in the case of strontium compounds.

The relation between logarithms of pressure and the reciprocal of absolute temperature was linear and gave 45.1 Cals. as the heat of decomposition.

Temp. °C.	Pressure mm.
760	2.0
860	15.0
920	37.0
980	94.0

Fig. 2 shows graphically the dissociation pressure curves of pure chromates and carbonates of calcium, strontium and barium, and of the corresponding mixtures of the chromates and the carbonates.



While the dissociation pressures of the mixtures of calcium chromate and calcium carbonate are identical with those of the latter, the values for the mixtures of the corresponding strontium and barium compounds are considerably higher.

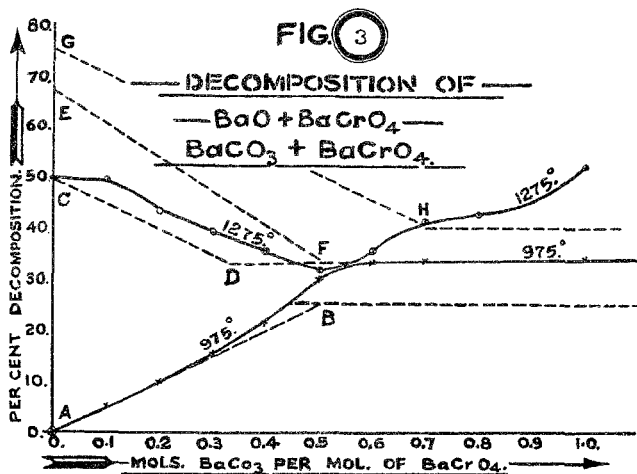
The decomposition of the mixtures was next studied in detail at three temperatures, *viz.*, 975°, 1200° and 1275°.

*Decomposition of Mixtures at 975°.*—The mixtures in different proportions were heated to 975° and the gas was pumped off until the pressures fell to < 0.2 mm. and collected in different tubes which were subsequently analysed for carbon dioxide and oxygen. The results of these experiments are given in Table II and shown in Fig. 3.

TABLE II.

Temp. 975° ; Final pressure < 0.2 mm.

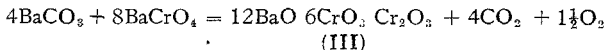
Mols. $\frac{\text{SrCO}_3}{\text{SrCrO}_4}$	I tube		II tube		III tube		% Decomposition
	Volume c.c.	Ratio $\text{CO}_2/\text{O}_2$	Volume c.c.	Ratio $\text{CO}_2/\text{O}_2$	Volume c.c.	Ratio $\text{CO}_2/\text{O}_2$	
0.0	nil	..	nil	..	nil	..	nil
0.1	5.4	2.17	..	..	..	..	5.1
0.2	10.4	2.70	..	..	..	..	10.0
0.3	14.8	2.50	..	..	..	..	15.6
0.4	18.4	2.35	..	..	..	..	21.6
0.5	10.6	2.40	12.9	2.07	..	..	30.0
0.6	12.8	2.37	9.7	2.03	9.3	2.88	33.0
0.7	11.9	2.21	7.7	2.08	14.2	4.26	33.6
0.7	16.3	2.30	16.8	2.05	..	..	..
0.8	12.1	2.27	8.4	2.50	15.3	3.70	35.5
1.0	10.5	2.18	6.8	2.40	15.8	5.30	34.1



Although the chromate by itself does not at all decompose at 975°, measurements of the total oxygen evolved at this temperature show a stage in the decomposition at about 33%, the amount of barium oxide required for its formation being 0.5 mol. per mol. of barium chromate, yielding the compound **barium dichromito-quarter-chromate**,  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ . Reference to the existence of the corresponding compounds for calcium and strontium has been repeatedly made in previous communications on this subject.

Table II shows that the ratio of  $\text{CO}_2/\text{O}_2$  is maximum (2.7), with a mixture having 0.2 mol. of the carbonate.

The relationship between the percentage decomposition and the proportion of carbonate in the mixture is linear (AB in Fig. 3) up to 0.3 mol. of carbonate. The reaction between barium chromate and barium carbonate which would give out carbon dioxide and oxygen in the ratio of 2.7:1 which is observed at about 0.3 mol. is



which, however, requires 0.5 mol. of the carbonate for completion of the reaction as shown by the dotted line, to form the 25% stage. However, owing to the high temperature employed, the decomposition

proceeds along the continuous line on successive addition of the carbonate, to the more stable compound which is formed at the 33% stage. We intend to repeat these experiments at lower temperatures and higher pressures. The decomposition of the mixture along the linear part of the curve appears to be due to the formation of the compound (III) **barium dichromito-sexieschromate** corresponding to a similar calcium compound found by Nargund and Watson in their study of the decomposition of the mixture of lime with calcium chromate at 300 mm. pressure. The corresponding compounds found by us in the case of calcium and strontium compounds are  $10\text{CaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and  $11\text{SrO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ . We have thus got an example of the same chromium chromate combining with 10, 11 and 12 mols. of the base, which will be shown to be structurally possible in a future communication.

All the mixtures which were first decomposed at  $975^\circ$  to 33% stage, were further heated from  $1200^\circ$  to  $1275^\circ$ . The mixture which contained  $< 0.5$  mol. of base, did not show any measurable dissociation pressure up to  $1230^\circ$ , and showed at  $1275^\circ$  a pressure of 1.5–2.0 mm. which is the same as the dissociation pressure of pure barium chromate, the gas phase being pure oxygen. The mixture containing higher proportion of barium carbonate showed a tendency to decompose at  $1200^\circ$  evolving both carbon dioxide and oxygen. The carbonate in the mixtures could be completely decomposed only when the temperature was raised to  $1275^\circ$ . It was observed that the mixtures containing 0.7 mol. and above of the carbonate, were considerably sintered. This fact may account for the remarkable resistance of the carbonate towards decomposition.

*Decomposition of Mixtures at  $1275^\circ$ .*—Experiments were conducted to study the decomposition of the above mixtures at  $1275^\circ$ . The results are given in the following table (III) and shown in Fig. 3.

The curve showing the percentage decomposition on the addition of different amounts of barium oxide, shows that the decomposition first decreases on addition of the base, till a minimum is reached at about 32%, with 0.5 mol. of the barium carbonate.

The products obtained by heating the mixtures A, B and C were partly soluble in acid, while the remaining mixtures were completely soluble in acid. The percentage decomposition in all the experiments was calculated from the amount of oxygen evolved, and checked by the estimation of chromate in solution in the case of mixtures, A and B. The minimum in the value of the decomposition at about 32% on addition of 0.5 mol. of oxide indicates the formation of the same compound which was obtained by heating the mixtures at  $975^\circ$ , namely,  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ . The break in the curve at about



TABLE III.

Temp. 1275°; final pressure &lt; 0.2 mm.

Mols.	BaO BaCrO <sub>4</sub>	Per cent. decomposition from O <sub>2</sub>	Per cent. decomposition from CrO <sub>3</sub>	Calculated
	0.0	51.3	..	50.0
A	0.1	49.5	50.0	(46.7)
B	0.2	43.5	43.1	43.3
C	0.3	39.6	..	40.0
D	0.4	35.8	..	36.6
E	0.5	32.0	..	33.3
F	0.6	35.8	..	..
G	0.7	41.8	..	..
H	0.8	42.9	..	..
I	1.0	52.2	..	..

0.7 mol. of the carbonate and at about 40% decomposition indicates the formation of a compound **barium tetrachromito-sexieschromate**— $17\text{BaO } 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ .

The decomposition of the mixture of barium chromate and barium carbonate containing higher proportion of the carbonate is quite different from that observed in the corresponding mixture of calcium and strontium. While the latter shows a region of constant decomposition with increasing amount of the base, in the case of the barium compounds we get increased decomposition showing greater affinity between barium chromate and barium carbonate. Further decomposition is also due to the fact that all the barium carbonate is not decomposed owing to the formation of a fused mass. The increase observed in the decomposition at 1275° with addition of the base is in line with the results obtained at 975° with smaller quantities of the base. At the latter temperature although pure chromate is quite stable, decomposition takes place readily with the addition of carbonate.

The values of the per cent. decomposition given in the last column of Table III for concentrations below 0.5:1, are calculated on

the basis that the amount of the oxide added, goes to form the compound  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ , while the rest of the chromate decomposes to the 50% stage according to its own vapour pressure at this temperature. The observed and calculated values show fair agreement.

Referring to Fig. 3, the decomposition curve at  $975^\circ$  for different mixtures shows that the amount of the base required for 25% decomposition is about 0.44 mol. instead of 0.5 mol. theoretically required to form the compound  $12\text{BaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ . Owing to the higher vapour pressure of this compound, the decomposition goes to the higher stage, namely, 33.3%, when actually 0.5 mol. of the base are added. With a lower proportion of the base the decomposition goes to 25% stage at  $975^\circ$ . On raising the temperature to  $1275^\circ$  a portion of the compound decomposes to 33% stage in combination with the extra base required for its formation and stability, and the rest of the chromate goes to form the 50% stage.

The composition of the acid-soluble product formed by the decomposition of the pure chromate at 50% stage is  $8\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ . From analogy with the results obtained with calcium and strontium chromates, a break in the curve ought to have occurred at 33.3% decomposition with the addition of 0.33 mol. of barium carbonate (curve CD, Fig. 3). The experimental results, however, show a break on addition of 0.5 mol., indicating the formation of the compound  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ , as observed in the case of strontium chromate.

The dotted lines EF and GH in Fig. 3 are theoretical curves, which have been drawn on the assumption that the products formed at 66 and 75% stages of the pure chromate contain the compounds which are formed at 33.3 and 40% decomposition of the mixtures of the chromate with the corresponding base.

The curve showing the decomposition at  $1275^\circ$ , (which is intermediate between the two curves CD and EF in Fig. 3), indicates that the compounds which are formed with the addition of lower proportions of the base, are mixtures of  $8\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ ,  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . This fact and the remarkably low decomposition pressure of the compound  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  are exactly analogous to the results obtained in the case of the corresponding strontium compounds.

The dotted line GH given in Fig. 3 indicates that the compound  $17\text{BaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$  which is formed at the 40% decomposition might be the same as the decomposition product, less chromite, which should be formed when pure barium chromate decomposes to 75%.

Further work is in progress.

**SUMMARY.**

The dissociation pressure of pure barium chromate has been measured up to  $1400^{\circ}$  and the heat of decomposition calculated.

A stage of 50% decomposition was observed as in the case of calcium and strontium chromates. The compound formed at this stage is  $8\text{BaO} \cdot 4\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ , which has practically no dissociation pressure at  $1420^{\circ}$  and which yields an acid-soluble product of the composition  $8\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ .

The decomposition of mixtures of barium chromate and barium carbonate was more energetic than that observed in the corresponding experiments with calcium and strontium compounds. Stages were found in the decomposition of the chromate in the mixtures, at 25%, 33.3% and 40% due to the formation of the compounds  $12\text{BaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ ,  $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$  and  $17\text{BaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$  respectively.

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