REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

PART VIII. THE 25 % STAGE IN THE DECOMPOSITION OF THE CHROMATES OF CALCIUM, STRONTIUM AND BARIUM

By

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INTRODUCTION.

In a comprehensive study (Parts III to VII of this series, This Journal, **20A,** 55–56, **21A**, 119–129, 159–169, 179–188 and 273–283) Athavale and Jatkar reported the formation of various intermediate stages in the decomposition of the chromates of calcium, strontium and barium, and of the mixtures of the chromates with the corresponding oxides. The latter gave indications of the stages at 25 %, 33.3 % and 40 %, while the pure chromates decomposed in stages corresponding to 50 %, 66.6 %, 75 % and 80 %. The higher stages could not be obtained in the case of barium chromate owing to the high temperature required. The composition and the chemical properties of the compounds formed at various stages were established and their individuality proved by their characteristic decomposition pressures (except in the case of the 25% stage), on the basis of the several corresponding chromium chromates reported in literature. The experiments were carried out at comparatively high temperatures and low pressures, under which conditions the compounds formed at the 25 % stage, were not probably stable.

There were, however, several indications for the formation of the 25 % stage: (1) The acid soluble portion of the 50 % stage in the decomposition of calcium chromate corresponded to the formula $10CaO$ $6CrO_3$ Cr_2O_3 (This Journal, 1937, **20A,** 61). (2) The ratio of CO_2: O_2 in the gas phase in the decomposition of mixtures of strontium chromate and strontium carbonate (This Journal, 1938, **21A**, 182), was 2: 1, and indicated the formation of a compound 11SrO $6CrO_3$ Cr_2O_3. (3) The decomposition of mixtures of barium chromate and barium carbonate indicated the possibility of the formation of the compound 12BaO $6CrO_3$ Cr_2O_3. (This Journal, 1938, **21A**, 279). (4) There is a chromium chromate Cr_8O_{21} reported in literature corresponding to approximately 25 % decomposition, by Ryss and Seljanskaja (Acta Physica Chemica 1938, **8**, 623), the existence of which has been confirmed in our laboratory. The results of this investigation will be reported in the next part of this series. The conclusions from the previous study of the decomposition of the mixtures of chromates and carbonates led to the possibility of the formation of compounds of the chromium chromates 6 CrO_3 Cr_2O_3 with 10, 11 or 12 mols of the base.

The object of the present investigation was to decide the exact amount of the base required to form the stable chromium chromate of this composition, and to determine the decomposition pressures and the corresponding heats of decomposition of the compounds formed. The reverse reaction, namely, the oxidation of the chromite, occurs through the formation of the intermediate compounds, in presence of excess of the base, at comparatively high temperatures in the chromate furnace. A complete knowledge of the vapour pressure of the first stage of the decomposition of the chromates is therefore of fundamental importance in the manufacture of chromates.

EXPERIMENTAL

The apparatus used and the experimental procedure followed was the same as described in the previous parts of this series.

The purity of the compounds used was better than 99.5%. The various mixtures were prepared by thorough grinding in an agate mortar. The temperature was measured and controlled within 1° by a Micromax recorder and controller. Owing to the comparatively low stability of the compounds, it was essential to work at lower temperatures. As the vapour pressures were also very low, the measurements were made on a cathatometer reading to hundredth of a mm.

I. Decomposition of mixtures of calcium chromate and calcium carbonate :

The mixture of calcium chromate and calcium carbonate in the ratio of 1 : 0.5 mol, was heated in the vacuum. The decomposition pressures of the mixtures did not agree with the observations of Athavale and Jatkar. The results are given below:

Temp. °C	Pressure mm.
435	4.56
462	5.86
533	14.32

The gas was pumped out at 670° when the decomposition of the chromate was 13% and that of the carbonate 89%. At 875°, the decomposition of the chromate was 25% and that of the carbonate 100%. The substance was then cooled to lower temperatures and the vapour pressures at different temperatures were measured in the usual way. The results are given below :

Temp. °C	Pressure mm.
894	1.61
917	2-15
943	2.74
975	3.63
1009	4.88

On evacuating at 900°, the 33.3% stage was obtained. The vapour pressures of this substance are given below :

Temp. °C	Pressure mm.
885	0.99
925	1.62
952	2.38
978	3.35
1005	4.45
1028	6.12

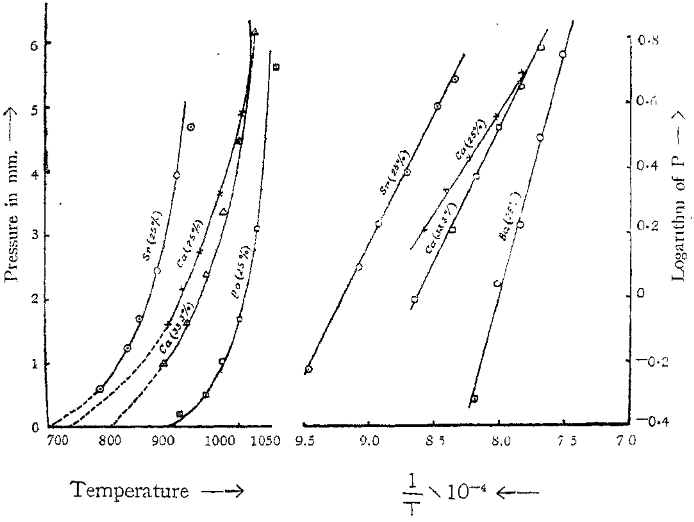

Fig. 1 (a).

Fig. 1 (b).

Decomposition of mixtures of chromates and oxides of calcium, strontium and barium.

The results are plotted in Fig. 1 (a), in which the vapour pressures are shown as a function of temperature, and in Fig. 1 (b) the logarithm of the pressure is plotted against the reciprocal of absolute temperature. The heat of decomposition of the 25 % stage to 33.3 % stage is 26.9 Calories. There was no indication of the formation of the 25 % stage with lower additions of the base corresponding to the formation of the compound with 10 or 11 mols of the base. It is therefore probable that these compounds are not stable under the conditions of the experiment. The decomposition of the mixtures started with the evolution of pure carbon dioxide, which indicated the formation of a stable basic chromate.

II. Decomposition of mixtures of strontium chromate and strontium carbonate :

(a) 1 gm. of the mixture containing 0.5 mol of carbonate to 1 mol of strontium chromate, was heated from 742° to 850°, in stages. At 742° the decomposition of the chromate and the carbonate reached 17.5% and 71% respectively, in vacuum. The temperature was raised to 816°, at which the corresponding decomposition was 24.3 and 96.2 %. The carbonate decomposed completely at 852° at which the decomposition of the chromate was 25.3 %. The product was cooled and the vapour pressures were measured in the usual way. The results are given below and shown graphically in Fig. 1.

Temp. °C	Pressure mm.
786	0.60
830	1.25
849	1.69
877	2.45
908	3.93
930	4.68

In Fig. 1, (a) shows the relationship between temperature and pressures and (b) shows the relationship between logarithm of pressure and the reciprocal of absolute temperature. The heat of decomposition of the compound formed at 25 % stage is 38.4 cals. per mole of oxygen.

(b) The decomposition of a mixture containing 0.375 mol of strontium carbonate to 1 mol of strontium chromate was studied at 740 and 785° The decomposition of the chromate was 10.7 and 19.8 % and that of the carbonate was 53.1 and 100 % respectively. On further heating the mixture to 1050°, the decomposition of the chromate proceeded up to 23 % only, showing that the amount of the base was not sufficient to form the 25% stage. The decomposition pressures were also not steady or reproducible.

(c) The mixture containing 0.25 mol of strontium chromate to 1 mol of strontium carbonate was heated at 825° and 1020° at which the decomposition of the chromate was 15 and 17.8 % respectively, the carbonate having been completely decomposed at 825°. The vapour pressures were not reproducible and the results indicated the incomplete formation of the 25 % compound. The values of the decomposition pressure for the mixtures of carbonate and chromate at different temperatures agreed with the previous results of Athavale and Jatkar (This Journal, 1938, **21A**, 118). The decomposition of the mixtures commenced at about 600° with evolution of carbon dioxide and oxygen.

III. Decomposition of mixtures of barium chromate and barium carbonate .

The previous experiments with calcium and strontium chromates have shown that a 25% decomposition is obtained when the compound contains 12 mols of the base. In the case of the decomposition of barium chromate, the previous results of Athavale and Jatkar were in agreement with the formation of the compound $12BaO\ 6CrO_3\ Cr_2O_3$. Experiments were therefore made with a mixture of barium chromate and barium carbonate in the ratio of 1 : 0.5. The mixture was heated in vacuum at 948°, when the decomposition of the chromate was 23% and that of the carbonate was 80 %. At 1050° the decomposition reached 27.5% and that of the carbonate 100 %. The decomposition pressures of the compound formed at 1050° were measured. The results are given below and shown graphically in Fig. 1 (a) and (b).

Temp. °C	Pressure mm.
907	0.20
948	0.48
975	1.04
1005	1.68
1031	3.10
1060	5.60

The heat of decomposition is 62.3 Calories. The barium carbonate is more stable towards heat, while the basic chromate and the compounds formed at the 25 % stage are less stable than the corresponding calcium and strontium compounds. It was on this account that the chromate decomposed to 27.5 % instead of 25 %, when the decomposition of the carbonate reached 100 %.

It therefore appears that the base obtained by the decomposition of the carbonate forms an intermediate basic chromate, which subsequently decomposes and forms the 25 % stage. The assumption of the formation of the intermediate basic chromate is also supported by the work of Nargund and Watson, (This Journal 1926, **9**, 149), who obtained the basic chromate $CrO_3\ \frac{3}{2}CaO$. The ratio of carbon dioxide : oxygen in the gas phase, shows the relationship between the rate of decomposition of the carbonate and of the unstable basic chromate. According to the equation

$$4RCO_3 + 8RCrO_4 = 12RO\ 6CrO_3\ Cr_2O_3 + 4CO_2 + \frac{3}{2}\ O_2$$

the ratio of carbon dioxide to oxygen will be 2.66 : 1, if the basic chromate completely decomposes as fast as it forms. At higher temperatures, the 25% compound is further decomposed, and the ratio of carbon dioxide : oxygen becomes 2 : 1. The analysis of the gas phase from the various experiments was in agreement with these assumptions. The 25% stage was not obtained with the addition of 10 or 11 moles of the base. The assumption of the formation of the basic chromate also explains the formation of the 25% compound with 12 mols of the base according to the following equation :

$$4(3RO\ 2CrO_3) = 12RO\ 6CrO_3\ Cr_2O_3 + \frac{3}{2}\ O_2.$$

SUMMARY.

The decomposition of the mixtures of calcium, strontium and barium chromates with the corresponding carbonates in different proportions has been studied at comparatively lower temperatures, special attention being paid to allow the reactions between the solids to reach equilibrium. The results show a 25% decomposition of the chromate due to the formation of the compound $12RO\ 6CrO_3\ Cr_2O_3$, which is preceded by the formation of the basic chromate $3RO\ 2CrO_3$.

The decomposition pressures of the above compounds have been measured and the calculated heats of decomposition of the compounds of calcium, strontium and barium are, 26.9, 38.4 and 62.3 calories, respectively.

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