REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

PART IV. DECOMPOSITION OF MIXTURES OF CALCIUM CHROMATE WITH CALCIUM CARBONATE.

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In Part III (*This Journal,* 1937, **20A**, 55–66) we confirmed the observations of Nargund and Watson (*This Journal,* Part II, 1926, **9**, 149) that calcium chromate, when heated, passes through a number of intermediate stages of decomposition. We also reported a stage at 50% decomposition which was missed by these authors owing to the comparatively small range of temperature over which the intermediate compound formed is stable, and the decomposition pressures of the various stages.

Attention has already been drawn to the remarkable property of the decomposition products in yielding acid-soluble chromate and chromite in combination with lime. Thus the composition of the acid-soluble portion from the 66.6% stage of decomposition of chromate was $9CaO\ 4CrO_3\ Cr_2O_3$. The corresponding chromium chromate Cr_6O_{15} having been reported by Honda (*Science Rep.. Tohoku Univ.*, 1915, **4**, 97; K. Honda and T. Sone, *ibid.*, 1914, **3**, 223), it should be possible to confirm the existence of the calcium compound by an arrest at 33.3% in the decomposition of the chromate when mixed with lime. Similarly, the acid-soluble portion from 75% stage is represented by a compound $17CaO\ 6CrO_3\ 2Cr_2O_3$. This compound should be formed as the result of 40% decomposition of the chromate in presence of lime, the corresponding oxide Cr_5O_{12} having been shown to exist by Simon and Schmidt (*Zeit. Anorg. Chem.,* 1926, **153**, 191–218).

In this paper we have brought forth further evidence in support of these two earlier stages of decomposition at 33.3 and 40% decomposition. Although Nargund and Watson missed the 50% stage in the decomposition of plain chromate, they discovered additional stages at 25%, 33.3% and 40% in the study of decomposition of mixtures of lime with calcium chromate. There is a chromium chromate reported in literature corresponding to 25% stage by Simon and Schmidt (*Z. Anorg. Chem.*, 1926, **153**, 191), the formula of which, *viz.*, $Cr_2O_3\ 6CrO_3$ is structurally possible. We failed to obtain the 25% stage owing to the low temperature required at the low pressures used in our experiments and of the consequent small reaction velocity between solids and to the fact that we employed calcium

carbonate instead of calcium oxide which was used by Nargund and Watson, which had to be decomposed first by heating to moderately high temperature. We, however, believe that there is a tendency to form a compound of the type, because the 50% stage in the decomposition of calcium chromate, when treated with hydrochloric acid, yields an acid-soluble portion having the composition $10CaO\ 6CrO_3\ Cr_2O_3$ which corresponds to 25% decomposition of the chromate. We intend to take up the study of the vapour pressure of this compound in the near future.

Nargund and Watson (*loc. cit.*) found that if mixtures of lime and calcium chromate were heated *in air* at 920° and 1030° there was a break in the curve showing relationship between the amount of lime added and the % decomposition, at 33.3%. There was gradual increase in decomposition with increasing proportion of lime up to 0.2–0.5 mol., the exact amount of lime taking part in the reaction being somewhat uncertain. 0.5 mol. of calcium oxide was assumed to be the reactive amount for the 33.3% stage. The formula of the intermediate compound was $9/4CaO\ CrO_3\ \frac{1}{4}Cr_2O_3$. But as the amount of CaO is very nearly 2, Nargund and Watson thought that the most probable formula was $2CaO\ CrO_3\ \frac{1}{4}Cr_2O_3$. It is interesting to note that the results obtained by supplying oxygen to the mixtures of CaO and Cr_2O_3 were, however, in favour of the first compound. This compound is reported to be soluble in acid. It has been pointed out by us previously that the 66.6% stage in the decomposition of calcium chromate yields on treatment with an acid a soluble portion, the composition of which is also $9CaO\ 4CrO_3\ Cr_2O_3$ in agreement with the first compound. Decomposition of the mixtures at 1030° in vacuum (< 0.2 mm.) indicated a stage at about 42% decomposition. The break in the curve occurred at about 0.25 mols. of lime. The decomposition was between 41–42% even in those experiments where a large excess of lime was added. The formula of the compound was, however, derived on the basis of 40% decomposition and the amount of the calcium oxide taking part in the reaction as 0.2 mol. per mol. of calcium chromate.

We have already referred to the close similarity between the composition of the acid-soluble portions from the decomposition products of plain chromates and the compounds obtained by Nargund and Watson by decomposing mixtures of the chromates with the oxide. Thus our results show that the composition of the acid-soluble portion from the 75% stage for calcium chromate is $17CaO\ 6CrO_3\ 2Cr_2O_3$ from which it is obvious that the amount of calcium oxide required for the formation of 40% stage is 0.7 mol. of calcium oxide per mol. of calcium chromate and not 0.2 as given by Nargund and Watson.

The problem thus becomes interesting, because, either the chromium chromate corresponding to 40% decomposition must be capable of combining with different quantities of the basic oxide. or the break in the curve as reported by Nargund and Watson may not be at 0.2 mol. of calcium oxide but at a higher concentration of the oxide.

In view, therefore, of the great affinity of lime in forming stable chromium chromates and particularly with the object of deciding the exact amount of lime necessary for the formation of the intermediate stages, it was thought worthwhile to investigate the decomposition of mixtures of calcium chromate and calcium carbonate.

EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as described in Part III. The carbonate was mixed with the chromate in the required proportion and the carbonate was decomposed completely by pumping off the gas at 730°. The chromate, however, does not remain absolutely inert, for a very small quantity of oxygen is also given out at this temperature.

25% Stage.—Nargund and Watson showed the existence of a stage at 25% decomposition by heating a 1 : 1 mixture of lime and calcium chromate at 900° and pumping off the gas to a *pressure of 300 mm.* The dissociation pressures of mixtures in the proportion of 0.5 and 1.0 mol. of lime to one of calcium chromate were 188 mm. at 835° and 358 mm. at 855°.

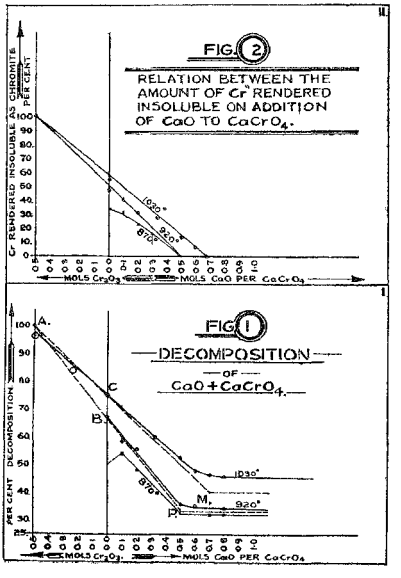
We decomposed the mixtures of lime and calcium chromate in different proportions *in vacuum* (0.2 mm.) at 870° C., the carbonate having been first decomposed completely at 730°. The oxygen was given off extremely slowly and no equilibrium was observed at 25% decomposition. The dissociation pressure of the mixtures was 43 mm. at 860° much higher than that of pure calcium chromate at the same temperature which was about 5 mm. However, the dissociation pressures of these mixtures as given by Nargund and Watson are considerably different from our value.

33.3% Stage.—This stage was obtained by Nargund and Watson by decomposing the mixture *in air* at 920° and 1030° and also by evacuating the system to a pressure of 22 mm. at 920°. It is interesting to note that Nayer, Watson and Sudborough (*This Journal,* 1924, 7, Part IV, 53) obtained 33.3% decomposition, when mixtures of calcium chromate and lime, and chromic oxide and lime in the ratios of 1 : 1.87 and 1 : 2 for Cr : Ca respectively were heated from 700° to 1000° *in air.*

We carried out two sets of experiments *in vacuum* at 870° and 920°, the results of which are given in Table I and shown graphically in Figs. 1 and 2.

TABLE I.

Temp. 870°C. Pressure < 0·2 mm.			Temp. 920°C. Pressure < 0·5 mm.		
Mol. $CaO/CaCrO_4$	% Decomposition from O_2	% Cr rendered insoluble	Mol. $CaO/CaCrO_4$	% Decomposition from O_2	% Cr rendered insoluble
0·0	51·7	33·4	0·0	67·1	47·4
0·1	54·0	—	0·1	58·2	40·5
0·2	48·0	23·2	0·2	55·5	31·5
0·3	44·8	16·2	0·5	35·1	nil
0·5	32·6	nil	0·6	35·0	nil
0·7	31·9	nil	0·8	34·2	nil
0·8	32·0	nil			



At 870° the decomposition first increases to 54% on adding 0.1 mol. of lime and then decreases with further addition of lime, to 32%. At 920° the decomposition of mixtures with a large excess of lime is 34.2%. The 33.3% line meets the line joining A (Fig. 1, complete decomposition with 0.5 mol. of Cr_2O_3) and B (decomposition of plain chromate) at P which occurs at 0.5 mols. P, therefore, represents the amount of the oxide taking part in the reaction. The mean of the two results at 870° and 920° indicate a stage at 33.3% decomposition. The amount of lime necessary for the formation of this stage is 0.5 mol. per mol. of calcium chromate which gives the formula of the intermediate compound as $9CaO\ 4CrO_3Cr_2O_3$. This compound, **calcium dichromito-quarter chromate,** was reported by Nargund and Watson, who were, however, doubtful about the exact amount of lime necessary for its formation, and was also obtained by us by treating the 66.6% stage for pure chromate with an acid (*cf.* Part III, *loc. cit.*).

There is another method of finding out the amount of lime required for the formation of the compound, which depends on the determination of the percentage of chromium which remains as an insoluble residue when the decomposed products are treated with an acid. The relation between the amount of lime added to calcium chromate and the corresponding percentage of chromium rendered insoluble is shown in Fig. 2. The variation, which is linear, indicates that there should be no chromium insoluble in acid when 0.5 mols. of lime is added to the chromate which is confirmed from the results given in Table I.

Although the formula of the intermediate stage is $9CaO\ 4CrO_3\ Cr_2O_3$ and there are no experimental grounds for approximating it to $8CaO\ 4CrO_3\ Cr_2O_3$, compounds of the latter type are represented by the composition of the acid-soluble portion of the products of decomposition of strontium and barium chromates.

40% Stage.—Calcium chromate was mixed with various quantities of calcium carbonate and heated at 1030° at 0.2 mm. pressure. The results are given in Table II. The decomposition values were obtained from the estimation of the chromate in the decomposed mixture. The decomposed mixtures (2), (3) and (4) when treated with acid, leave a green residue of calcium chromite.

TABLE II.

Temp. 1030° C. Final Pressure < 0.2 mm.

Mol $CaO/CaCrO_4$	% Decomposition	% Cr rendered insoluble
(1) 0·0 ..	75·0	54·9
(2) 0·33 ..	59·9	27·2
(3) 0·50 ..	52·5	13·2
(4) 0·60 ..	47·7	6·0
(5) 0·70 ..	46·5	nil
(6) 0·80 ..	45·5	nil

From the results given by Nargund and Watson for the decomposition of these mixtures at 1030° in vacuum and also as judged according to our experiments (*cf.* Part III, *loc. cit.*) on the composition of the acid-soluble portion from 75% for chromate, a stage in the decomposition was expected at 40% and not at 45% as found in Table II. Moreover, there is no chromium chromate reported in literature corresponding to 45% decomposition. Further, the results of the decomposition of mixtures of strontium and barium chromates with the corresponding oxides (which will be described in a subsequent communication) indicate a stage at 40% and not at 45% decomposition of the chromate.

The higher decomposition in our experiments which is not due to the vapour pressure of the compound can be explained on the assumption that a small portion of the chromate does not enter into combination with lime, but decomposes directly to the higher stage of decomposition just like pure calcium chromate. This assumption is also supported by the results of Nargund and Watson in an indirect way. The addition of lime to the chromate decreases the percentage decomposition, while an addition of chromic oxide increases the decomposition of the chromate. Theoretically an addition of 0.5 mols. of Cr_2O_3 should suffice to convert all the calcium to calcium chromite and decompose the chromate completely (AB and AC in Fig. 1). Nargund and Watson, however, found that the decomposition of a mixture containing 0.5 mol. of chromic oxide in vacuum at 1030°

was only 95–96% (*cf.* Fig. 1). This is most probably due to a small amount of chromate decomposing independently.

Calculations show that the decomposition of the mixtures of calcium chromate and lime will proceed from 40% to 45% even if 0.025 mol. out of one mol. of calcium chromate decomposes independently.

As regards the amount of lime taking part in the reaction, a break in the curve (Fig. 1) occurs at about 0.68 mols. of lime. This result is in good agreement with the above suggestion that a small portion of chromate decomposes directly to chromite yielding the necessary oxide. But for this side reaction, the break would have occurred at 0.7 mols. of added lime (M, Fig 1).

The relation between the amount of lime added to the chromate and the percentage of chromium rendered insoluble is shown in Fig. 2 and Table II. The relation is linear and shows that a completely soluble product has to be obtained when about 0.7 mols. of lime are added to the chromate. The product obtained under these conditions is identical with the composition of the acid-soluble portion from 75% stage for chromate, *viz.*, $17CaO\ 6CrO_3\ 2Cr_2O_3$.

Thus the study of the decomposition of mixtures of lime and calcium chromate in vacuum at 1030° indicates the formation of the compound $17CaO\ 6CrO_3\ 2Cr_2O_3$, **calcium tetrachromitosexieschromate**, and not of $12CaO\ 6CrO_3\ 2Cr_2O_3$ as reported by Nargund and Watson. It is, however, interesting to add that the latter compound is also structurally possible being the calcium salt of the same chromium chromate with less amount of lime.

The mixtures first decomposed at 1030° to a pressure < 0.2 mm. were heated to 1200°. The vapour pressure is very low and the gas is given out extremely slowly. Experiments were carried out with small quantities of mixtures containing 0.33 and 0.8 mols. of lime per mol. of calcium chromate, which showed complete decomposition of the chromate at 1200° in vacuum. No intermediate stage in the decomposition therefore exists above the 40% stage when calcium chromate mixed with lime is heated to high temperature at low pressures.

The dissociation pressures of the mixtures and of the intermediate stages formed in the decomposition are given in Table III and are shown in Fig. 3, which also shows the relationship between log of pressure against reciprocal of absolute temperature for the various stages. The heats of formation of each of the stages from the preceding stage are 42.1, 50.9 and 61.0 cals. per mol. of oxygen respectively.

TABLE III.

Dissociation pressures of	Temp. °C	Pressure in mm.		Remarks
		N. and W.	Authors	
$CaCO_3$ ..	730	..	40·0	The carbonate decomposed completely in vacuum at 730°
Mixtures $CaO + CaCrO_4$	810	..	18·0	Mixtures decomposed in vacuum at 860° and 920° to a pressure < 0·5 mm. Decomposition stage at 33·3% (I stage)
	825	..	24·5	
	835	188	..	
	855	358	..	
	860	..	43·0	
I stage .. (33·3%)	920	22·0	< 0·5	Mixtures decomposed in vacuum at 1030° to a pressure < 0·2 mm. Decomposition stage at about 40% (II stage)
	955	..	1·7	
	990	..	3·0	
	1000	45·0	..	
	1005	..	4·0	
	1022	..	5·0	
	1030	..	6·0	
II stage .. (40%)	1030	< 0·2	< 0·2	Mixtures decomposed completely in vacuum at 1195°
	1090	..	0·3	
	1160	..	0·8	
	1195	..	1·5	

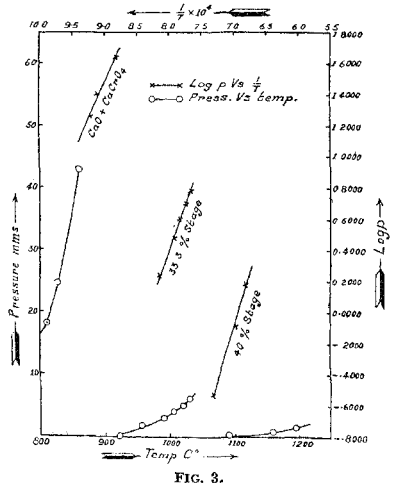


FIG. 3.
Dissociation pressure of mixtures of $CaCrO_4$ + CaO

The dissociation pressures of the mixtures of lime with calcium chromate measured by Nargund and Watson given in the third column are considerably higher than the values obtained by us. Nargund and Watson prepared the mixtures by first calcining the carbonate in air and then mixing the oxide with the requisite amount of the chromate. As the dissociation pressures given by these authors are very close to the dissociation pressures of pure calcium carbonate (Johnston, *Mellor's Inorganic Chemistry*, 3, 655), *viz.*, 166 mm. at 800° and 373 mm. at 850°, it is probable that the mixtures used by Nargund and Watson were contaminated with a fairly large quantity of calcium carbonate.

From the results shown in Fig. 2, it will be noticed that the amount of the acid-insoluble portion, *i.e.*, calcium chromite from the decomposed product, decreases linearly with an increase in the amount of lime added, while the amount of the acid-soluble portion correspondingly increases, its composition being fixed. When the amount of lime added is sufficient to convert all the chromium into the intermediate compound, no acid-insoluble residue is left.

The dissociation pressures of the mixture of CaO and $CaCrO_4$ and of the 33.3% stage obtained in the decomposition of these mixtures are different from the dissociation pressures of pure calcium chromate or its products of decomposition (Part III, *loc. cit.*). The dissociation pressures of the 40% stage in the decomposition of mixtures are, however, very near to those of the 75% stage of decomposition of pure chromate. However, as the dissociation pressures measured are very low, it cannot be said with certainty that these are the same in the two cases. As the composition of the acid-soluble portion of the 75% decomposition stage of pure chromate is the same as that of the 40% stage obtained in the decomposition of mixtures, the 75% stage in the decomposition of chromate may be a mixture of the above 40% stage and calcium chromite.

It may be interesting to point out the bearing of the results given in this paper on the reactions in the chromate furnace. Popoff (*Continental Met. Chem. Engg.*, 1927, 1, 143; *Jour. Russ. Chem. Ind.*, 1926, 2, 465) found that while the theoretical quantity of sodium carbonate is added, the amount of lime added is always in excess, the ratio of Cr : Ca in the mixture bearing 1 : 1.5 to 1.9 depending on the quality of the ore, the higher ratio being used at temperatures above 1100°. In the light of the results we have presented in this paper, the formation of sodium chromate takes place through the formation of the intermediate calcium compound corresponding to 33.3% stage, the amount of lime required for the formation of the latter being 0.5 mol. per mol. of calcium chromate. At

temperatures above 1100° the 40% compound, *viz.*, $17CaO.6CrO_3.2Cr_2O_3$ is formed, the amount of lime necessary for its formation being 0.7 mol. of lime per mol. of calcium chromate. The maximum conversion of the chromite in the two cases is 66 and 60% respectively *in presence of only lime*, as is found to be the case. Further discussion regarding the reactions in the chromate furnace will be given in a subsequent communication.

Most of the experiments recorded were carried out at low pressures and comparatively high temperatures. As the reactions occurred in solid phase one could hardly expect quantitative results. When allowance is made for this fact, the results are fairly concordant and the formulæ of the compounds suggested are supported by the existence of the corresponding chromium chromates.

The results of experiments recorded in this Part as well as Part III of this series have been further borne out by analogous experiments on the decomposition of strontium and barium chromates, and the decomposition of the mixtures of these chromates with the corresponding carbonates. These results and the general discussion of the properties and structural formulæ of the various chromium chromates will be published in the subsequent Parts of this series.

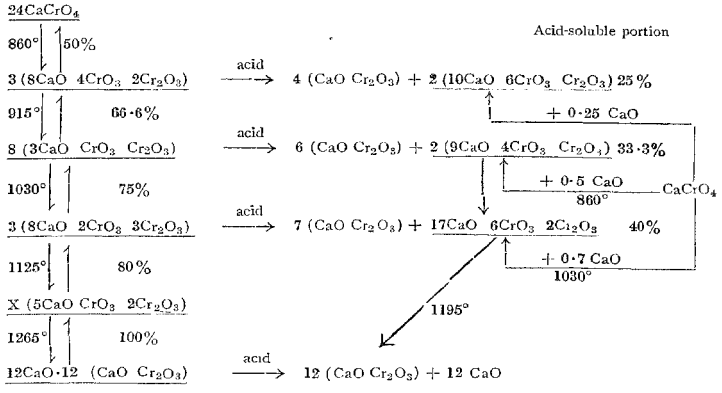
Our thanks are due to Dr. H. E. Watson for his keen interest in this investigation.

SUMMARY.

The decomposition of mixtures of calcium chromate and lime in vacuum indicate two additional stages corresponding to 33.3 and 40% decomposition. The formulæ of the two compounds formed are $9CaO\ 4CrO_3\ Cr_2O_3$ and $17CaO\ 6CrO_3\ 2Cr_2O$ respectively and agree with the composition of the acid-soluble portions from the 66.6 and 75% stages for the decomposition of pure calcium chromate. The vapour pressures of these compounds have been measured and the heats of decomposition calculated.

The intermediate stages formed in the decomposition of pure calcium chromates may not all be mixtures of the above compounds with calcium chromite as they are characterised by definite vapour pressure and heats of decomposition, the values of which are quite distinctly different, although the dissociation pressures of the 75% stage for pure chromate and of the 40% stage for mixtures are very low and nearly identical and may indicate that the compounds formed in both the cases are the same.

The results of the decomposition of calcium chromate and of its mixtures with lime at low pressures (< 0.2 mm.) may be summarised as follows:



In the chromate furnace, the oxidation of chromite necessarily occurs through the formation of the intermediate stages. The addition of lime in the ratio of 1 : 1.6 to 1.9 for the ratio of Cr : Ca is recommended when the furnace is to be operated above 1100°, because the compound $17CaO\ 6CrO_3\ 2Cr_2O_3$ has comparatively low decomposition pressure. The maximum conversion of the chromite under these conditions is 60%.

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