REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

PART III. THE DECOMPOSITION OF CALCIUM CHROMATE.

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INTRODUCTION.

One of the paradoxes of the reactions in the chromate furnace is the fact that under the conditions recommended for obtaining a good yield of chromate, the chromate itself is not stable.

The method consists of roasting, in an oxidising flame, the powdered mineral mixed with lime in the ratio 1:1.6–1.9 for chromium to calcium, a higher ratio being used if the furnace is to be operated above 1100°C. Calcium chromate actually decomposes under these conditions.

Nayer, Watson and Sudborough (This *Journal*, 1924, 7, 53, Part I of this series) found that calcium chromate decomposed more readily on addition of lime, a 33% decomposition being observed at 800°C.

A systematic work on the decomposition of calcium chromate alone and in admixture with lime was carried out by Nargund and Watson (This *Journal*, 1926, 9, 149, Part II of this series), who pointed out the complex nature of the system $CaO\text{-}Cr_2O_3\text{-}O_2$ and tentatively suggested the existence of a large number of compounds of calcium oxide, chromic oxide and chromium trioxide in various proportions:

(1) $CrO_3.CaO$ (Calcium chromate): dissociation pressure 15 mm. at 950°; 44 mm. at 1000°; decomposes to (6).

(2) $CrO_3.3/2\ CaO$: quantity of CaO somewhat uncertain; dissociation pressure 188 mm. at 835°; 358 mm. at 855°; decomposes to (3).

(3) $1/6\ Cr_2O_3.CrO_3.2\ CaO$ formed by heating (2): dissociation pressure at 910° about 270 mm. below which it decomposes to (4).

(4) $1/4\ Cr_2O_3.CrO_3.9|4\ CaO$ or possibly 2CaO formed from (3) or by heating CaO and $CaCrO_4$ in air. Black substance soluble in dilute acids. Dissociation pressure 22 mm. at 920° and 45 mm. at 1000°, the compound (5) being formed.

(5) $1/3\ Cr_2O_3.CrO_3.2CaO$ formed from (4) or by supplying oxygen at a pressure less than 20 mm. to a mixture of Cr_2O_3 with more than one mol. of CaO. Soluble in acid. Dissociation pressure not measurable at 1030°.

(6) $Cr_2O_3.CrO_3.3CaO$ (formula somewhat doubtful), the first decomposition product of pure calcium chromate. Also formed on supplying oxygen under pressure less than 20 mm. to a mixture of Cr_2O_3 with two mols. of CaO at 1030°.

(7) 3/2 $Cr_2O_3.CrO_3.4CaO$: decomposes at about 2 mm. at 1030° to give (8).

(8) 2 $Cr_2O_3.CrO_3.5CaO$: the final decomposition product of calcium chromate with no appreciable dissociation pressure at 1030°.

(9) ½ $Cr_2O_3.CrO_3.CaO$: (quantity of Cr_2O_3 uncertain) formed by heating calcium chromate with Cr_2O_3. Dissociation pressure 22 mm. at 930°, 90 mm. at 990° and 150 mm. at 1030°, yielding compound (9).

(10) $Cr_2O_3.2CaO$: the simplest chromite obtained by heating compound (9) *in vacuo.*

(11) 2 $Cr_2O_3.2CaO$: obtained when mixtures of CaO and Cr_2O_3 are heated *in vacuo.* One mol. of CaO is soluble in acid yielding compound (12). The quantity of CaO is not quite definite.

(12) 2 $Cr_2O_3.CaO$: obtained from (11) on treatment with acid.

It is remarkable that although the experiments described by Nargund and Watson were tentative, their results appear plausible on the basis of the existence of a number of intermediate chromium oxides (Mellor, *Inorganic & Theoretical Chemistry,* XI, 206) which may be regarded as chromium chromates. Thus chromium trioxide when heated passes through a number of intermediate stages before decomposing to chromium sequioxide (*cf.* K. Honda, *Science Rep., Tohoku Univ.,* 1915, **4**, 97; K. Honda and T. Sono, *ibid.,* 1914, **3**, 223; A. Simon and T. Schmidt, *Zeit. anorg. Chem.,* 1926, **153**, 191–218). Mellor has given the nomenclature for the intermediate chromic oxides reported by different authors and also for the various calcium compounds reported by Nargund and Watson, which we have adopted in the present paper.

As the existing data on the subject of decomposition of calcium chromate is not satisfactory, the authors have undertaken the systematic study of the thermal decompositions of this substance and extended the research to the decomposition of strontium and barium chromates for which no data are available. The present paper describes the results obtained with pure calcium chromate which was only partially studied by Nargund and Watson (*loc. cit.*). As the oxidation of chromite occurs necessarily through the formation of the intermediate compound, a knowledge of the vapour pressures, heats of decomposition and the nature of the products formed at various stages is of great importance in the study of the reactions in the chromate furnace.

EXPERIMENTAL.

Construction of a Molybdenum Wire Wound Furnace.—Experiments below 1000° could be carried out in a furnace wound with nichrome wire. For temperatures above 1000° a molybdenum wire-wound furnace (Fig. 2) was employed. The molybdenum was protected from oxidation by passing a mixture of nitrogen and hydrogen obtained from ammonia which was cracked over a platinum gauze heated to 1000° (Fig. 1), over the windings. The inner tube (A) of 'Pythagoras' 30 cm. long and 2.0 cm. internal diameter and closed at one end is wound with molybdenum wire No. 24, leaving open space of 4 cm. at both ends. This tube is fixed in another Pythagoras tube (B) 35 cm. long, 4 cm. internal diameter also closed at one end. This tube has two small holes, one at each end, to which are cemented thin clay tubes which serve as the inlet and outlet for the gas. The electrical lead near the outlet was kept cool by clamping two nickel plates (N).

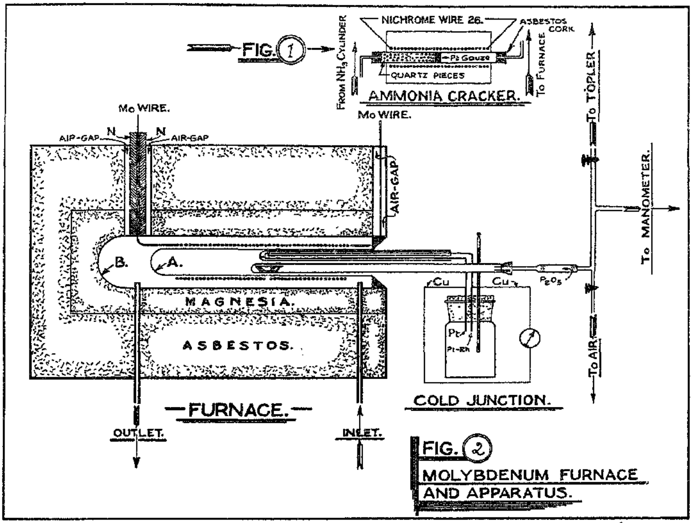


FIG. 2
MOLYBDENUM FURNACE AND APPARATUS.

A furnace of the simple design given above has been in continuous use for over a hundred experiments within a temperature range of 1000°–1500°.

The temperatures were measured by a platinum rhodium thermocouple on a galvanometer calibrated up to 1000° against a platinum resistance thermometer and occasionally checked by E. M. F. measurements. The extrapolated curve was checked for higher range against an optical pyrometer of the disappearing filament type. The difference at 1450° was less than 10°.

A platinum boat containing the substance was heated in a Pythagoras tube (50 cm. × 1.5 cm.) which was put in the furnace in such a way that the boat came in the centre of the furnace. The tube was joined to the rest of the apparatus by a rubber cork covered with sealing wax. The rest of the apparatus consists of a manometer to note the pressures, a Töpler pump to evacuate the apparatus whenever necessary and two phosphorus pentoxide tubes to dry the gas evolved (see Fig. 2).

Calcium chromate was prepared by evaporating to dryness an equivalent mixture of calcium oxide and chromic acid. The calcium oxide itself was prepared by heating analytically pure calcium carbonate in air at 1000°.

Nomenclature used to indicate various stages in the decomposition.—The term "% decomposition" has all along been used to indicate the extent of the decomposition of the original chromate, present either alone or in a mixture. The intermediate stages have been always referred to the corresponding percentage decomposition. Thus the 50% stage or compound means the stage in which 50% of the original chromate is decomposed according to the equation

$$2\,CaCrO_4 \rightleftharpoons 2(CaO)\ Cr_2O_3 + 3/2\ O_2.$$

Dissociation of Calcium Chromate.—Calcium chromate begins to decompose in vacuum at about 780°. The dissociation pressures are given in Table I.

TABLE I.

Temperature C.°	Pressure in mm.		Temperature C.°	Pressure in mm.	
	N. & W.	Authors		N. & W.	Authors
790	..	1·0	925	11·5	14·0
830	..	3·0	950	15·0	15·5
875	..	6·0	975	25·5	25·0
890	5·0	8·0	1000	44·0	56·0
910	8·0	10·5	1030	70·0	76·0

Although the dissociation pressures below and above 950° differed from those obtained by Nargund and Watson (*loc. cit.*), the gas was given out in several stages in agreement with their observations. The difference in pressures will be accounted for by a change of 10° in temperature.

At 1000° calcium chromate has a decomposition pressure of 56 mm. If the gas is pumped off, the pressure is regained till 50 per cent. of the chromate is decomposed when the pressure suddenly falls to 27 mm. and remains at this value on successive evacuation. 27 mms. is therefore the dissociation pressure of the 50 per cent. compound. This value was confirmed by pumping off the gas at 1000° till there was a sudden fall in the pressure readings. The furnace was then cooled to 850° when most of the gas is absorbed back. The residual gas was pumped off. The temperature was then raised and the dissociation pressures for the successive stages of decomposition were determined.

Table II gives the dissociation pressures of the three stages of decomposition observed in the case of calcium chromate. Values marked with an asterisk (*) were confirmed by both the methods.

TABLE II.

First stage		Second stage		Third stage	
Temperature C.°	Pressure in mm.	Temperature C.°	Pressure in mm.	Temperature C.°	Pressure in mm.
885	2·0	950	1·0	1125	0·9
905	4·0	*1000	2·0	1200	1·7
*930	7·5	*1030	4·0	1265	2·5
*950	12·0	1090	8·0		
975	19·0	1120	12·0		
985	21·0	1180	22·5		
*1000	27·0	1210	31·0		
*1030	48·0	1230	38·0		

There is a fourth stage at 80 per cent. decomposition reported by Nargund and Watson which will be discussed later.

Fig. 3 (*a*) shows graphically the vapour pressures of calcium chromate and of the various intermediate compounds formed at different stages. The ranges of temperature over which the various compounds are stable at low pressures are 0–780°; 800°–850°; 850°–920°; 920°–1080°.

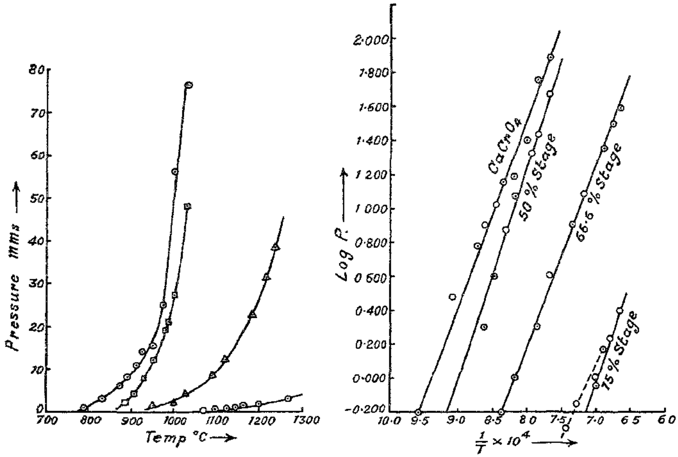


Fig. 3 (*a*)

Fig. 3 (*b*)

Dissociation Pressures of $CaCrO_4$

Fig. 3 (*b*) shows the plot of logarithm of pressures against the reciprocal of absolute temperature from which the heats of formation of each of the stages from the preceding stage are 48.4, 60.3, 47.5 and 58.0 Calories per mol. of oxygen respectively.

Having known the range of temperature within which the various stages are stable, the composition and properties of these stages were next determined.

First Stage.—Calcium chromate was decomposed at 860° and the oxygen pumped off till the pressure fell down to 0.5. The product was cooled and analysed (A). Another experiment (B) was carried out at 920°. The gas was pumped off at this temperature till the pressure fell down suddenly from 12 mm. to 6 mm. The measurement of oxygen showed 52.7 per cent. decomposition. On cooling, the oxygen remaining over the apparatus was completely absorbed.

TABLE III.

	860° (A)	920° (B)
% Decomposition from oxygen ..	51·0	52·7
% Chromium as CrO_3, in solution ..	52·5	50·7
% Chromium in insoluble residue ..	33·4	34·8
% Calcium in insoluble residue ..	15·0	16·85

Table III shows that the first stage of decomposition is at about 50% which was missed by Nargund and Watson because of the small range of temperature 800°–850° over which it is stable. The reaction in both the series (A) and (B) occurs according to the equation $8CaCrO_4 = 8(CaO)\ 4(CrO_3)\ 2(Cr_2O_3) + 3O_2$.

A part of the product dissolves in dilute hydrochloric acid, which is represented by the formula, $10CaO\ 6CrO_3\ Cr_2O_3$, while the residue is pure calcium chromite. Nargund and Watson obtained a compound **calcium dichromitosexieschromate** $12CaO\ Cr_2O_3\ 6CrO_3$ by decomposing a mixture of calcium chromate and lime.

The compound $8CaO\ 4CrO_3\ 2Cr_2O_3$ corresponds to the **chromium tetra-nonoxide** $Cr_2O_3\ 2CrO_3$ which was described by Schukoff (*Journ. Russ. Phys. Chem. Soc.*, 1909, **41**, 302) and was also obtained by Nargund and Watson (*loc. cit.*) in the decomposition of chromium trioxide. The latter authors obtained the corresponding **calcium dichromito-bis-chromate** by heating calcium chromate with chromic oxide, but the compound contained calcium oxide the amount of which was half that given in the above equation.

Second Stage.—A stage corresponding to 66.6 per cent. decomposition was obtained by Nargund and Watson by evacuating the apparatus at 1030° till the pressure fell down sharply from 70 mm. to 5 mm.

We carried out the decomposition of the chromate at 915°. The evacuation was stopped when the pressure suddenly fell to 0.5 mm.

Analysis of the vacuum cooled product gave the following results.

TABLE IV.

	Observed	Calculated
% Decomposition from oxygen ..	67·9	66·6
% Chromium as CrO_3 in solution ..	35·2	33·3
% Chromium in residue ..	47·1	50·0
% Calcium in residue	23·3	25·0

The analytical data given in Table IV are in agreement with the following reaction starting from calcium chromate:

$$\begin{array}{lcr} 24\,CaCrO_4 = 3(8CaO\ 4CrO_3\ 2Cr_2O_3) + 9\ O_2 & & \text{(1st stage)} \\ & \text{(I)} & \\ & \downarrow\uparrow & \\ = 8(3CaO\ CrO_3\ Cr_2O_3) + 12\ O_2 & & \text{(2nd stage)} \\ & \text{(II)} & \\ & \downarrow + \text{acid} & \\ 2(9CaO\ 4CrO_3\ Cr_2O_3) + 6(CaO\ Cr_2O_3) & & \\ & \text{(III)} & \end{array}$$

Both the compounds (II) **calcium dichromitochromate** and (III) **calcium dichromitoquarterchromate** were reported by Nargund and Watson who were, however, doubtful about the exact composition.

The reaction of (II) with dilute hydrochloric acid gives rise to insoluble calcium chromate and the soluble portion corresponds to compound (III), the formulæ of which is established in Part IV of this series to follow.

The oxide corresponding to (II) is **chromium-tritahexo-oxide** $Cr_2O_3CrO_3$ which was obtained by H. Blanc [*Ann. Chim. Phys.*, 1926, (**10**), **6**, 182], and several others.

A chromium chromate, **chromuim hexitapentadecoxide** Cr_6O_{15}, corresponding to the compound (III) was found by Honda and coworkers (*loc. cit.*) during the decomposition of chromium trioxide. Simon and Scmidt (*loc. cit.*), however, could not obtain this compound.

Third Stage.—Nargund and Watson observed that the decomposition was 75 per cent. at 1030° on evacuating the system until the pressure fell down to 2 mm.

We carried out experiments at 950°, 1000° and 1030° the results of which are given in Table V.

TABLE V.

	Observed			Calculated
	950°	1000°	1030°	
% Decomposition from oxygen ..	77·5	78·1	77·5	75·0
% Chromium as CrO_3 in solution ..	25·5	24·2	24·0	25·0
% Residue insoluble in acid ..	41·7	41·7	41·8	44·0
% Chromium in the insoluble residue	54·9	..	..	58·2
% Calcium in the insoluble residue ..	27·7	..	..	29·1

The analysis of the product in all the three experiments showed that 75% of the original chromate was decomposed.

The fall in pressure on consecutive evacuations at all the three temperatures occurred in stages of 50, 66.6 and 75% approximately of the decomposition as calculated from the volumes of oxygen collected separately at each drop in the vapour pressure (see Tables I and II).

Starting from the second stage the third stage of decomposition occurs according to the equation

$8(3CaO.CrO_3Cr_2O_3)$ (II stage)

II $\downarrow\uparrow$

$3(8CaO.2CrO_33Cr_2O_3) + 1\frac{1}{2}\ O_2$ (III stage)

IV $\downarrow$ + Acid

$17\ CaO.6CrO_32Cr_2O_3 + 7(CaOCr_2O_3)$

V

The oxide corresponding to the compound IV **calcium tetrachromitochromate** is **chromium octitapentadecoxide**, Cr_8O_{15} reported by M. Traube (*Liebig's Ann.*, 1848, 66, 87). This calcium compound was also obtained by Nargund and Watson (*loc. cit.*).

The compound (V) corresponds to **chromium pentadodecoxide** Cr_5O_{12} found by Simon and Schmidt (*loc. cit.*). Nargund and Watson obtained a compound **calcium-dichrmito-tris-chromate** $6CaO\ Cr_2O_3\ 3CrO_3$ or $12CaO\ 2Cr_2O_3\ 6CrO_3$, on the basis of their study of the decomposition of mixtures of calcium chromate and lime, taking into account only .2 mols. of calcium oxide as taking part in the reaction although .33 mols. were indicated by experiment. The significance of these results will be discussed in a later communication.

Fourth Stage.—A compound $5CaO.CrO_3.2Cr_2O_3$ corresponding to 80% decomposition was obtained by Nargund and Watson by pumping off oxygen completely at 1030°. As has been pointed out already in this paper the decomposition proceeds only to 75% under these conditions. The results of Nargund and Watson, therefore, are not confirmed. It is interesting to note, however, that there is a compound **chromium pentitenneaoxide**, Cr_5O_9, in support of the existence of such a calcium compound, **calcium tetrachromitochromate.** An attempt was therefore made to settle this point by a study of the vapour pressure of the product corresponding to 75% decomposition at higher temperatures.

The 75% stage was first obtained by pumping off oxygen at 1030° and the temperature was raised. Table VI gives the decomposition pressures observed in two independant sets of experiments (A) and (B).

TABLE VI.

A		B	
Temperature C.°	Pressure	Temperature C.°	Pressure
1070	0·5 mm.	1150	1·0 mm.
1100	0·7 mm.	1170	1·5 mm.
1125	0·9 mm.	1200	1·7 mm.

On plotting the results of vapour pressures given in Tables II and VI a break is shown at 1125°, which is more markedly shown in Fig. 3(*b*) showing the plot of logarithm of pressure against reciprocal of absolute temperature. The gas obtained by evacuating the system at this temperature showed 81% decomposition.

It appears therefore that there is an 80% stage in the decomposition of chromate stable up to 1125° at low pressures. The formula of the compound formed under these conditions is more likely to be $3CaO\ 2Cr_2O_3\ CrO_3$ on structural grounds as will be shown in a subsequent paper in this series. The excess of lime in the compound given by Nargund and Watson may exist as a separate phase.

In a similar experiment (B) carried out at 1200°, 85% of the decomposition occurred. Experiments were carried out with 0.2 gram of the chromate which was one-fifth of the quantity used in all previous experiments. The gas was pumped off and the temperature gradually raised to 1160°. The vapour pressures observed were the same as given in Table VI. The gas is pumped off and the substance was found to be completely decomposed.

It appears therefore that the apparent stage present at 85% was due to the large quantity of the substance taken which offered less surface for decomposition.

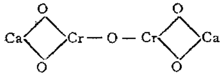
Final Decomposition of the Chromate.—When the chromate was decomposed in vacuum at 1265° the analysis of the product showed that 50% of the calcium was soluble in dilute hydrochloric acid. The following are the results:—

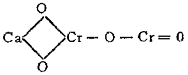
	Observed	Calculated
(*a*) % Decomposition from oxygen	102.0	100.0
(*b*) % Chromium as CrO_3 in solution	nil	nil
(*c*) % Calcium in the residue	51.1	50.0

These values are in agreement with the following equations:

$$2CaCrO_4 = 2CaO.Cr_2O_3 + 3/2\ O_2$$
$$2CaO.Cr_2O_3 = \underset{\text{soluble}}{CaO} + \underset{\text{insoluble}}{CaO.Cr_2O_3}.$$

Both the compounds $2CaO.Cr_2O_3$ and $CaO.Cr_2O_3$ are structurally possible and may be represented thus





In conclusion, we wish to express our best thanks to Dr. H. E. Watson for advice and assistance during the course of the work.

SUMMARY.

A simple design of a molybdenum wire wound furnace has been described.

Calcium chromate passes through four stages corresponding 50; 66.6; 75 and 80% of the complete decomposition, the range of temperatures over which these are stable being 800°–850°; 850°–920°;

920°–1080° and 1080°–1125° respectively. Calcium chromate decomposes completely above this temperature at low pressures. The vapour pressures of these intermediate stages have been measured and the heats of decomposition calculated. The products corresponding to these stages which resisted further decomposition *in vacuo,* partly dissolved in acids leaving an insoluble residue which was identified as calcium chromite.

Considerations based upon the acid-soluble chromium trioxide and sequioxide in the product, taken along with the formula of the corresponding chromium chromates, show that the steps observed during the decomposition of the calcium chromate are due to the formation of the following compounds—(1) $8CaO\ 4CrO_3\ 2Cr_2O_3$, (2) $9CaO\ 4CrO_3\ Cr_2O_3$, (3) $17CaO\ 6CrO_3\ 2Cr_2O_3$, (4) $3CaO\ CrO_3\ Cr_2O_3$, (5) $3CaO\ CrO_3\ 2Cr_2O_3$, (6) $8CaO\ 2CrO_3\ 3Cr_2O_3$ and (7) $10CaO\ 6CrO_3\ Cr_2O_3$.

The stability of chromates in the chromate furnace is due to the formation of these intermediate compounds during the reaction, which are far more stable than pure chromate itself.

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