REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

Part X. Decomposition of mixtures of calcium chromate with sodium carbonate and with ferric oxide.

by

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INTRODUCTION.

A study of the decomposition of the chromates of calcium, strontium and barium when mixed with varying amounts of the corresponding base, indicated a definite stage corresponding to 25% decomposition of the chromate, due to the formation of a compound 12RO 6CrO$_3$ Cr$_2$O$_3$, which was apparently preceded by the formation of the basic chromate 3RO 2CrO$_3$. The decomposition pressures of the compounds formed in each case were measured and the heats of decomposition calculated (This Journal, 1939, **22A**, 111).

In the present paper we have reported the results of experiments on the decomposition of calcium chromate when mixed with sodium carbonate and with iron oxide. The present investigation was undertaken in order to find out whether stages similar to those obtained in the decomposition of calcium chromate with lime, were also shown when mixed with soda, and to measure the decomposition pressures of the compounds formed. A knowledge of the stability of these compounds, is of fundamental importance in operating the chromate furnace. The results indicated that the mixed basic chromate of calcium and sodium was far more stable than the corresponding basic chromates of the alkaline earths, and that the 25% decomposition of the former, gave a compound which was also far more stable than those obtained at 33% and 40% decomposition. The significance of the results obtained, in the mechanism of the reactions in the chromate furnace, will be discussed in a future communication.
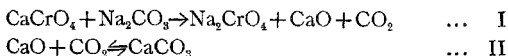
EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as described in Part VIII of this series (This Journal, 1939, **22A**, 111). The oxygen evolved gave the % decomposition.

Decomposition of a mixture of calcium chromate with sodium carbonate.

A mixture of 1 mol of calcium chromate with 0.5 mol of sodium carbonate was heated in vacuum. The decomposition started at about 350°. On heating the mixture to 380°, the pressure of carbon dioxide was 6.8 mm. The gas was however slowly absorbed back, giving a pressure of 1.5 mm. after 2 hrs. The temperature was then raised to 522°, when the pressure rose to 2.8 mm. and dropped to 2.2 mm. in 30 minutes. At 685°, the pressure of carbon dioxide over the mixture was 37 mm. which corresponds to the equilibrium decomposition pressure of calcium carbonate at that temperature. The decomposition of the mixture was further carried on at 755° by evacuation of the carbon dioxide evolved. When 92% decomposition occurred the rate of decomposition was very slow. The temperature was therefore raised and the carbonate was completely decomposed at 780°.

The reaction is not a decomposition of *sodium carbonate* as the decomposition pressures do not correspond to those of *sodium carbonate.* The pressure at 685° is identical with the equilibrium pressure in the decomposition of calcium carbonate at this temperature, and at lower temperatures the gas initially evolved is slowly absorbed back. The reaction is represented by the following equations :

$$CaCrO_4 + Na_2CO_3 \rightarrow Na_2CrO_4 + CaO + CO_2 \qquad \ldots \quad I$$
$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \ldots \quad II$$

The decomposition of $CaCO_3$ commences at about 640°. At temperatures below 640°, the mixture initially shows a pressure of carbon dioxide in accordance with the equation (I). The gas is absorbed back on keeping the system at that temperature (equation II).

After complete decomposition of the carbonate, the decomposition pressures of the system were measured (Table 1) :—

TABLE I.

Temperature °C	Pressure mm.
798	3.00
809	3.52
831	4.30
852	5.20
933	7.55
1010	9.26

The results are plotted in Fig. I A in which the decomposition pressure is shown as a function of temperature, and in Fig. I B the logarithm of the pressure is plotted against the reciprocal of absolute temperature. The results show that the basic chromate is stable at the temperature at which the carbonate was completely decomposed. The intermediate basic chromates of calcium, strontium and barium (cf. Part VIII) decomposed along with the corresponding carbonate. The formula of the new basic chromate is $8CaO\ 4Na_2O\ 8CrO_3$, and the heat of decomposition of the basic chromate to the 25% stage is 14.9 Cals. per oxygen molecule evolved.

25% stage.—When the basic chromate was decomposed by evacuation at 1052° the decomposition reached 26.5%. The product was cooled and the decomposition pressures were measured in the usual way. The results are shown graphically in Fig. I and given in Table 2.

TABLE 2.

Temperature °C	Pressure mm.
907	0.24
945	0.52
961	0.88
985	1.41
1018	3.00
1066	6.92

The heat of decomposition of the 25% stage is 43.6 Cals. and the formula of the compound formed is $8CaO\ 4Na_2O\ 6CrO_3\ Cr_2O_3$.

33.3% stage.—Further decomposition of the above compound was carried out at 1025°, at which the pressure of oxygen was 3.30 mm., which was regained on consecutive evacuations. There was a sudden rise in the pressure from 3.30 to 4.83 mm. when the decomposition reached 33.9%. The system was cooled down to the room temperature and the decomposition pressures of the compound formed at 33.3% stage were measured, which are given in Table 3 and shown graphically in Fig. I A and B.

TABLE 3.

Temperature	Pressure
°C	mm.
889	0.90
922	1.30
965	2.26
992	3.94
1025	4.83

The heat of decomposition of the compound $6CaO\ 3Na_2O\ 4CrO_3\ Cr_2O_3$, which is formed at 33.3% stage of decomposition, is 24.4 Cals.

40% stage.—The above compound was heated at 996°. On continuously pumping out the gas from the apparatus at this temperature, a drop in the pressure from 3.96 to 2.32 mm. was observed when the decomposition reached 41.5%. The measurements of the decomposition pressures for this stage are shown in Fig. I and given in Table 4.
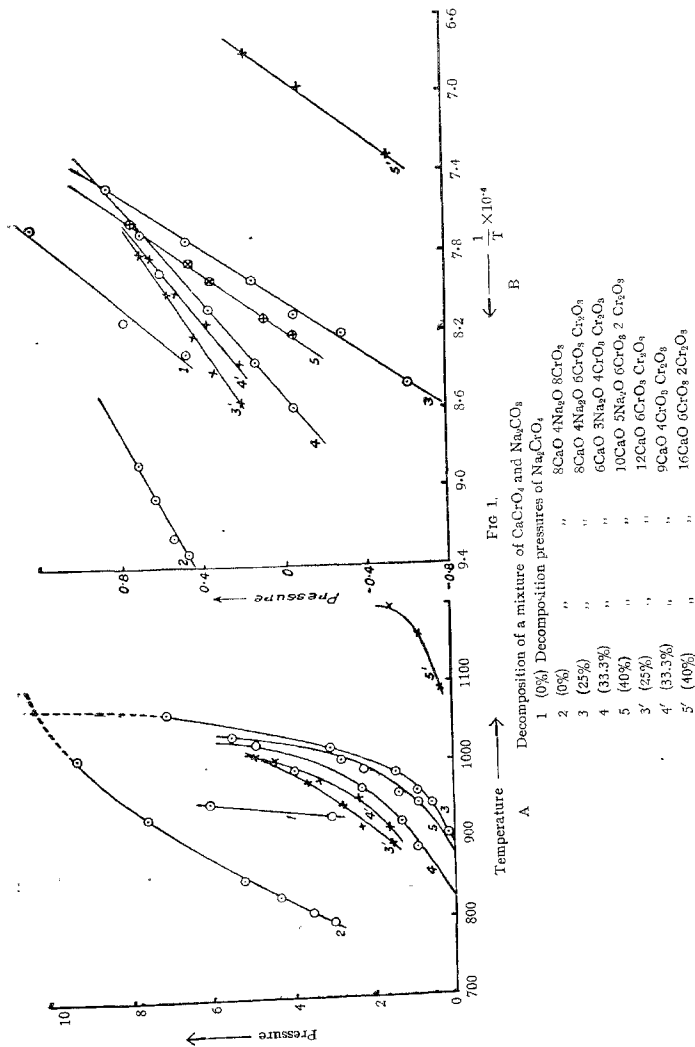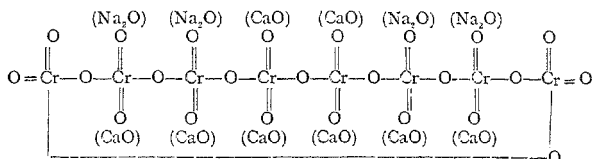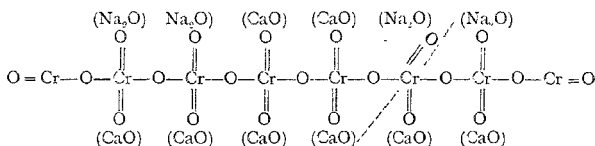
Fig. 1.

Decomposition of a mixture of $CaCrO_4$ and Na_2CO_3

A

B

1 (0%) Decomposition pressures of Na_2CrO_4
2 (0%) ,,   ,, $8CaO \cdot 4Na_2O \cdot 8CrO_3$
3 (25%) ,,   ,, $8CaO \cdot 4Na_2O \cdot 6CrO_3 \cdot Cr_2O_3$
4 (33.3%) ,,   ,, $6CaO \cdot 3Na_2O \cdot 4CrO_3 \cdot Cr_2O_3$
5 (40%) ,,   ,, $10CaO \cdot 5Na_2O \cdot 6CrO_3 \cdot 2 Cr_2O_3$
3' (25%) ,,   ,, $12CaO \cdot 6CrO_3 \cdot Cr_2O_3$
4' (33.3%) ,,   ,, $9CaO \cdot 4CrO_3 \cdot Cr_2O_3$
5' (40%) ,,   ,, $16CaO \cdot 6CrO_3 \cdot 2Cr_2O_3$

TABLE 4.

Temperature	Pressure
°C	mm.
945	0.88
957	1.24
987	2.22
1001	2.76
1034	5.46

The heat of decomposition of the compound $10CaO\ 5Na_2O\ 6CrO_3,$ $2Cr_2O_3$ formed at this stage is 37.4 Cals. per mol of oxygen.

The various formulae for the compounds obtained at the different stages of decomposition of the chromate have been arrived at on the basis of the formulae suggested for the corresponding compounds in the decomposition of mixtures of the chromate of calcium with the corresponding carbonate, by partially replacing calcium by sodium. In all the compounds obtained by us, the molecular proportion of Ca : Na : Cr is 1 : 1 : 1. The possibility of the formation of several compounds in which sodium replaces calcium in varying proportions is being investigated.

The higher decomposition stages are usually more stable than the compounds formed at lower stages. The compound formed at the 25% decomposition stage is, however, more stable than those formed at 33.3% and 40% stages. Further the stability of the basic chromate is comparatively greater above 1050° than that of the further decomposition products. These results explain why, at the high temperatures used in the chromate furnace, addition of excess of base is recommended.

The formation of the basic chromate and the structure of the various intermediate compounds, according to the scheme to be outlined by us in the next part, is given below :—

(I) Basic Chromate $4Na_2O$ $8CaO$ $8CrO_3$:

```
        (Na₂O)  (Na₂O)  (CaO)   (CaO)   (Na₂O)  (Na₂O)
     O     O     O     O     O     O     O            O
     ‖     ‖     ‖     ‖     ‖     ‖     ‖            ‖
O = Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr = O
     |     ‖     ‖     ‖     ‖     ‖     ‖            |
     |     O     O     O     O     O     O            |
     |    (CaO)  (CaO)  (CaO)  (CaO)  (CaO)  (CaO)     |
     |_____O
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(II) 25% decomposition : $4Na_2O$ $8CaO$ $6CrO_3$ Cr_2O_3

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        (Na₂O)  Na₂O)   (CaO)   (CaO)   (Na₂O)    (Na₂O)
          O     O     O     O           O        O
          ‖     ‖     ‖     ‖         O ⁄        ‖
O = Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr = O
          ‖     ‖     ‖     ‖      ⁄    ‖        ‖
          O     O     O     O   ⁄      O        O
        (CaO)  (CaO)  (CaO)  (CaO)⁄   (CaO)   (CaO)
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(III) 33.3% decomposition $3Na_2O$ $6CaO$ $4CrO_3$ Cr_2O_3:

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        (Na₂O)  (Na₂O)  (CaO)   (CaO)
          O     O     O     O
          ‖     ‖     ‖     ‖
O = Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr = O (Na₂O)
          ‖     ‖     ‖     ‖
          O     O     O     O
        (CaO)  (CaO)  (CaO)  (CaO)
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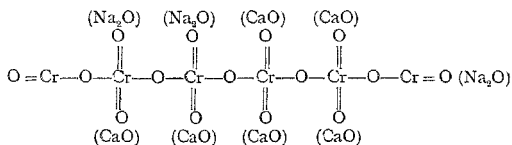
(IV) 40% decomposition $5Na_2O$ $10CaO$ $6CrO_3$ $2Cr_2O_3$:

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(Na₂O) (CaO)   (CaO)   (Na₂O)                  (Na₂O) (CaO)   (CaO)   (Na₂O)
  O     O     O     O                           O     O     O     O
  ‖     ‖     ‖     ‖                           ‖     ‖     ‖     ‖
  Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr—O—Cr
  ‖     ‖     ‖     ‖     ‖     ‖     ‖     ‖     ‖
  O     O     O     O     O     O     O     O
(CaO)  (CaO)  (CaO)   Na     Na   (CaO)  (CaO)  (CaO)
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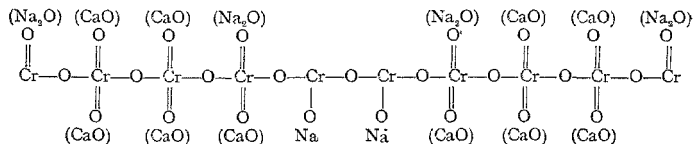
The vapour pressure of the compound (1), which is represented by structure I, is given in Table 1 and shown graphically in Fig. I, curve 2, the corresponding basic chromate of the alkaline earths $12RO \cdot 8CrO_3$ being unstable.

On decomposition, compound (I) shows a stage at 25%, yielding the compound (II) $4Na_2O$ $8CaO$ $6CrO_3$ Cr_2O_3. The decomposition

pressures of the latter are given in Table 2 and shown by curve 3, Fig. I, which shows the increased stability of this compound as compared with the corresponding calcium chromium chromate, the decomposition pressures of which are shown by curve 3′.

On further decomposition 33.3% stage is reached forming the compound (III) $3Na_2O\ 6CaO\ 4CrO_3\ Cr_2O_3$. The formation of the compound (III) from (II) takes place according to the following equation:

$$3(4Na_2O\ 8CaO\ 6CrO_3\ Cr_2O_3) = 4(3Na_2O\ 6CaO\ 4CrO_3\ Cr_2O_3) + \tfrac{3}{2}O_2$$
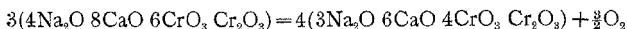
the compound breaking along the dotted line shown in the structure. The vapour pressure of compound (III) is shown by curve 4, Fig. I, which is less stable than the corresponding calcium chromium chromate, the decomposition of which is shown by curve 4′.

The 40% stage in the decomposition of the mixed basic chromium chromate is formed by the reaction of two molecules of the compound (III), and is represented by structure (IV). The decomposition pressures of this compound $(5Na_2O\ 10CaO\ 6CrO_3\ 2Cr_2O_3)$ are shown by curve 5, Fig. I, which when compared with that of the corresponding calcium chromium chromate $15CaO\ 6CrO_3\ 2Cr_2O_3$, brings out the decreased stability of the compounds formed at higher stages of decomposition when a portion of lime is replaced by a corresponding amount of alkali.

It will be interesting to study the decomposition of sodium chromate with lime in order to find the stability range of the other possible compounds $8Na_2O\ 4CaO\ 8CrO_3$ (I), $8Na_2O\ 4CaO\ 6CrO_3\ Cr_2O_3$ (II), $6Na_2O\ 3CaO\ 4CrO_3\ Cr_2O_3$ (III) and $10Na_2O\ 5CaO\ 6CrO_3\ 2Cr_2O_3$ (IV). Work on these lines is already in progress.

Decomposition of a mixture of calcium chromate with ferric oxide.—A mixture of 1 mol of calcium chromate with 0.5 mol of ferric oxide was used. The mixture began to decompose at about 250°. The decomposition pressures of the mixtures are given in Table 5 and shown graphically in Fig. 2.
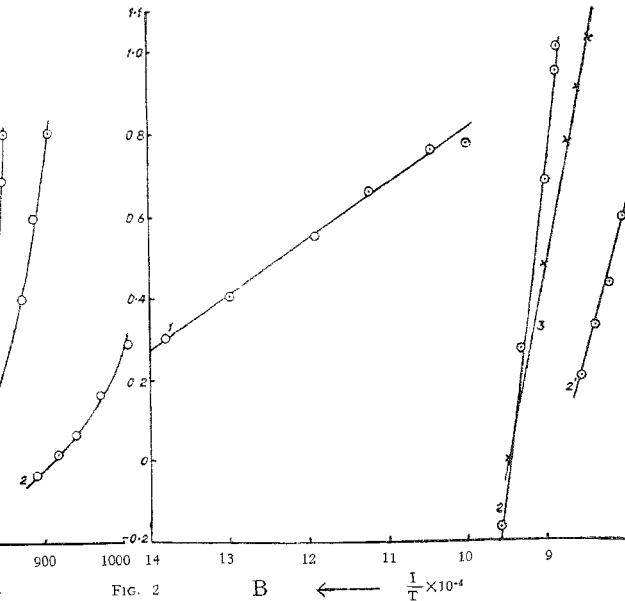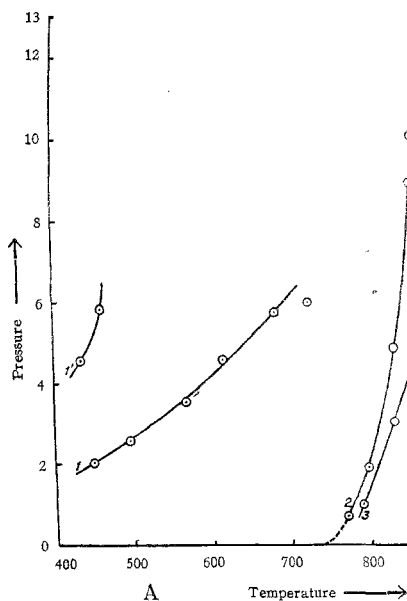
FIG. 2

A   Temperature ⟶   B   ⟵ $\frac{1}{T} \times 10^{-4}$

DECOMPOSITION OF A MIXTURE OF CALCIUM CHROMATE AND FERRIC OXIDE

1   Decomposition pressures of Basic iron calcium chromate
2   „   „   25%   „   „
3   „   „ $CaCrO_4$
2'   „   „ $12\ CaO\ 6CrO_8\ Cr_2O_8$
·' $CaCrO_4 + CaO$

TABLE 5.

Temperature	Pressure
°C	mm.
450	2.00
497	2.55
567	3.52
615	4.56
682	5.74
725	5.96

The mixture gives characteristic pressures, which are different from that of the chromate, obviously due to the formation of a basic chromate. The heat of decomposition of the basic chromate is 38.6 Cals. per mol of oxygen.

The pressures did not however regain on decomposition of the mixture by pumping out the gas evolved. The decomposition was carried on at about 750° until 25% decomposition was attained. The decomposition pressures of the compound have been given in Table 6 and shown graphically in Fig. II.

TABLE 6.

Temperature	Pressure
°C	mm.
772	0.68
799	1.89
830	4.82
853	8.80
854	10.08

The heat of decomposition is 50 Cals.

The above experiments show the possibility of the formation of basic chromium chromates with iron. Further experiments are in progress in order to find out the amount of iron oxide required to form the compound.

From the results described in the foregoing pages, it seems likely that the oxidation of chromite ore in presence of sodium carbonate and calcium carbonate takes place with the formation of the complex compounds, corresponding to those described in this paper and that the final product of oxidation is a complex basic chromate of the general formula 12RO 8CrO$_3$, in which R represents Na$_2$ + Ca + Fe in different proportions.

The reactions between the solids are rarely quantitative. When due allowance is made for this fact, the results obtained in the investigations in this series show the remarkable property of the chromium chromates in forming highly stable mixed basic chromates with characteristic vapour pressures, when the decomposition of the chromate reaches 25, 33.3 and 40%.

Further work is in progress.

SUMMARY.

A mixture of calcium chromate with sodium carbonate in the ratio of 2 : 1 when heated decomposes with evolution of carbon dioxide to form the basic chromate 4Na$_2$O 8CaO 8CrO$_3$ (1), which on heating further, decomposes in stages corresponding to 25%, 33% and 40% decomposition of the chromate to form the compounds 4Na$_2$O 8CaO 6CrO$_3$ Cr$_2$O$_3$ (II), 3Na$_2$O 6CaO 4CrO$_3$ Cr$_2$O$_3$ (III) and 5Na$_2$O 10CaO 6CrO$_3$ 2Cr$_2$O$_3$ (IV). The characteristic decomposition pressures of the various mixed basic chromium chromates have been measured and the corresponding heats of decomposition are 14.9, 43.6, 24.4 and 37.4 cals. respectively per mol of oxygen.

The formation of a basic chromium chromate of iron is also indicated at the 25% decomposition stage.

It has been shown that the basic chromate 4Na$_2$O 8CaO 8CrO$_3$ is remarkably stable. The compound 4Na$_2$O 8CaO 6CrO$_3$ Cr$_2$O$_3$ is also far more stable than the corresponding calcium chromium chromate. The compound obtained by further decomposition, viz., 3Na$_2$O 6CaO

$4CrO_3 Cr_2O_3$, is however less stable than the corresponding calcium chromium chromate. In the same way, the compound obtained by decomposition to 40% stage is less stable than the corresponding calcium compound $15CaO 6CrO_3 2Cr_2O_3$.

The formation and the structures of the various mixed basic chromates, based on the ordinary valencies of chromium, have been given.

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