

## REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

### Part II.—The System $\text{CaO}-\text{Cr}_2\text{O}_3-\text{O}_2$ .

By K. S. Nargund and H. E. Watson.

It has been shown in Part I (*This Journal*, 1924, 7, 53) that pure calcium chromate decomposes very slightly on heating to  $1000^\circ$  in air but that the amount of decomposition is greatly increased by the addition of calcium oxide. Complete decomposition of this mixture could not be effected by heating to  $1300^\circ$ . The present investigation was undertaken with the object of ascertaining more accurately the conditions under which decomposition takes place and indicating the existence of possible intermediate compounds.

### EXPERIMENTAL.

The materials used were similar to those described in Part I. Calcium oxide from ignited carbonate and specially purified chromic acid were used for preparing the sample of calcium chromate employed in the majority of the experiments. This sample contained 3.8 per cent. of water and 0.25 per cent. of calcium carbonate; the molecular ratio of calcium to chromium was 1.005 : 1. Two other samples were prepared by neutralising calcium hydroxide solution with chromic acid and evaporating to dryness in a platinum dish.

The furnace was one used in the previous experiments and temperatures were measured with a nickel-nichrome couple; this was compared with a Hoskin's couple and checked at (a) the boiling point of sulphur and (b) the melting point of silver in air, the latter value being taken as  $995^\circ$ .

The substance under investigation was placed in a platinum boat which was not appreciably attacked at the highest temperatures reached, and was contained in a quartz tube of 13 mm. diameter and 90 cm. length which passed through the furnace. The ends were water-cooled and glass tubes passing through rubber stoppers were fitted into them, the joints being made perfectly gas tight with a beeswax-resin mixture. The rest of the apparatus consisted of a manometer, a gas burette and a pump suitably connected so that measured volumes of gas could be introduced into the apparatus and any gas evolved could be removed and measured. Soda-lime and phosphorus pentoxide tubes were inserted between the quartz tube and the manometer and a phosphorus pentoxide tube was attached to the pump, so that all gases were measured dry.

In Part I, the method adopted for determining the amount of decomposition was to withdraw the boat containing the substance from the furnace and allow it to cool rapidly. After cooling, the product was analysed. It was pointed out that in certain cases the speed of the reaction was such that great accuracy in the results could not be expected. In the present experiments it was impossible to remove the boat from the quartz tube without seriously disturbing the equilibrium, and gas measurements were therefore practised. In some cases the total amount of gas in the tube and dead space was estimated; in others, some or all of the gas was pumped out and measured. The estimation of the total quantity of gas could not be made with any great degree of accuracy owing to the appreciable volume (100 c.c.) of the quartz tube and its uneven temperature. It was found however, that the temperature gradient was approximately constant after maintaining the temperature in the centre constant for about an hour, so that it was possible to calibrate the apparatus by admitting known volumes of gas at different temperatures and measuring the pressures produced. The results thus obtained were sufficiently accurate for the required purpose.

#### THE DISSOCIATION PRESSURE OF CALCIUM CHROMATE.

About 1 gm. of calcium chromate was introduced into the quartz tube, heated to 400° and the whole apparatus evacuated. The temperature was then raised to 900° and kept constant at that temperature until the pressure observed in the manometer became constant. This required about half an hour. The process was repeated at different temperatures. When 1030° was reached the tube was allowed to cool and a set of readings taken at decreasing temperatures, each temperature being maintained for 30 minutes. The results are shown in Table I.

TABLE I.

#### *Dissociation Pressure of Calcium Chromate.*

| Temperature° C. | Pressure, mm. (rising) |     |     |     |      | Pressure, mm. (falling) |
|-----------------|------------------------|-----|-----|-----|------|-------------------------|
|                 | 1                      | 2   | 3   | 4   | Mean |                         |
| 900             | 5                      | 7   | 5   | 6   | 6    | ...                     |
| 920             | 10                     | ... | 11  | ... | 11   | 20                      |
| 930             | 12                     | 11  | 11  | 13  | 12   | 22                      |
| 950             | 15                     | 16  | 15  | ... | 15   | 24                      |
| 970             | 23                     | 23  | ... | ... | 23   | ...                     |
| 990             | 35                     | 35  | 37  | 36  | 36   | 14                      |
| 1,000           | 45                     | 42  | 45  | 44  | 44   | 44.5                    |
| 1,030           | 72                     | 70  | 65  | 67  | 70   | 70                      |

In the neighbourhood of 1000°, absorption of oxygen takes place readily and the pressures obtained on cooling are almost the same as those recorded with the temperature rising. At lower temperatures absorption was slow and equilibrium was not complete in the time allowed. The small quantity of carbonate in the sample was not sufficient to affect the pressures appreciably since the quantity present in 1 gram would have produced an additional pressure of only 1 mm. even if there had been no absorption by the soda-lime.

In order to ascertain the nature of the first decomposition product of calcium chromate, varying quantities of the material were heated as before and the pressure of oxygen measured. As already mentioned, the total quantity of oxygen evolved could be deduced and hence the extent of the decomposition. The results at 1030° are shown in Table II.

TABLE II.

| Weight of CaCrO <sub>4</sub><br>gm. | Pressure obtained<br>mm. | Percentage<br>decomposition. |
|-------------------------------------|--------------------------|------------------------------|
| 0.627                               | 72                       | 17.9                         |
| 0.314                               | 70                       | 35.1                         |
| 0.150                               | 63                       | 63.3                         |
| 0.150                               | 59                       | 60.3                         |
| 0.100                               | 40                       | 63.4                         |
| 0.100                               | 43                       | 68.2                         |
| 0.050                               | 19                       | 60.3                         |
| 0.025                               | 11                       | 69.0                         |
| 0.025                               | 12                       | 75.0                         |

It will be observed that when the quantity of chromate exceeds 0.2 gm. the pressure is approximately constant, indicating that decomposition is incomplete; with smaller quantities the percentage decomposition is sensibly the same, pointing to the existence of a compound which does not decompose further at pressures above 12 mm. It would appear that this compound is one in which 66 per cent. of the chromate has given off oxygen, but as the method of estimating oxygen from the pressure is not accurate, the results cannot be considered as having much more than a qualitative significance.

In order to obtain more accurate results, samples of the chromate were introduced into the tube and the whole apparatus evacuated at room-temperature or after slight warming. The temperature was

raised to  $1030^{\circ}$  and the gas pumped away as evolved, care being taken not to allow the pressure to fall below about 30 mm. At first the pressure rose to 70 mm. after each stroke of the pump, but later it decreased as the evolution of gas became slower and finally, when no more gas was liberated, the pressure was reduced to 30 mm. and pumping stopped. The measured gas was burnt by means of phosphorus, allowance being made for the residue, if any, in calculating the volume. The volume of gas remaining in the tube was known approximately from the preliminary calibration, so that the total volume of oxygen evolved by the chromate could be calculated with some accuracy.

On reducing the pressure below 30 mm. no more gas was given off until 5 mm. was reached, at which point a further evolution took place. The pressure was consequently reduced to 2 mm. and the evolved gas collected and measured as before. When the pressure became steady it was still further reduced to the lowest value attainable and the tube heated for two hours longer. At this stage the evolution of gas did not exceed a few c. mm. per hour. The tube was then allowed to cool and the product removed and analysed. Table III shows the results obtained; 2.503 gms. of completely decomposed chromate would evolve 256 c.c. of gas at N.T.P.

It will be seen that at 30 mm. pressure the percentage decomposition is 64 per cent., at 2 mm. it is 74 per cent. and at about 0.2 mm. it is 79 per cent., the values for the lowest pressure being obtained by the analysis of the residue. Although the results are fairly concordant they are quite possibly subject to a constant error owing to the fact that decomposition takes place very slowly when near the equilibrium point so that equilibrium is not quite reached. Support is given to this view by the final analytical results which are more accurate than the determinations made by the gas-measurement method. From these it may be seen that the percentage decomposition of the larger quantities is less than that of the smaller, a phenomenon which has been observed in numerous reactions of this type, evidently depending upon the diffusion of the gas.

It seems probable therefore that the decompositions observed are due to the formation of compounds in which the percentage decompositions are 66.7, 75, and 80 per cent. The oxide  $\text{CrO}_3$  cannot exist at the temperature of the experiments and it will be shown later that, if free  $\text{CaO}$  or  $\text{Cr}_2\text{O}_3$  is present, different compounds are obtained. Hence all the decomposition products appear to be definite compounds, not mixtures, and if so their formulae may be written:—

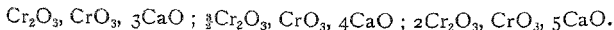


TABLE III.

*Percentage Decomposition of Calcium Chromate at Different Pressures.*

| Weight of $\text{CaCrO}_4$<br>gms. | Final pressure<br>mm. | Oxygen evolved c.c.<br>N.T.P. | Percentage<br>decomposition |
|------------------------------------|-----------------------|-------------------------------|-----------------------------|
| 2.508                              | 30                    | 164.0                         | 64.0                        |
| 2.508                              | 25                    | 162.5                         | 63.5                        |
| 1.254                              | 30                    | 83.5                          | 65.2                        |
| 1.254                              | 28                    | 81.8                          | 63.9                        |
| 0.627                              | 32                    | 49.4                          | 63.1                        |
| 0.627                              | 30                    | 41.5                          | 64.8                        |
| 0.314                              | 30                    | 20.4                          | 63.8                        |
| 0.314                              | 35                    | 20.2                          | 63.3                        |
| 2.508                              | 2                     | 188.0                         | 73.5                        |
| 1.254                              | 2                     | 96.5                          | 75.4                        |
| 0.627                              | 2                     | 47.5                          | 74.2                        |
| 0.314                              | 2                     | 23.5                          | 73.5                        |
| 1.254                              | 0.2                   | ...                           | 77.0                        |
| 0.627                              | 0.2                   | ...                           | 78.0                        |
| 0.100                              | 0.2                   | ...                           | 80.5                        |
| 0.100                              | 0.2                   | ...                           | 79.0                        |

At  $1030^\circ$  the first of these decomposes at a pressure of about 5 mm. of oxygen, the second at about 1 mm. Whilst the third appears to be stable at a very low pressure. Calcium chromate itself decomposes at 70 mm. giving the first of the above compounds.

It has been mentioned that calcium chromate decomposes slightly when heated in air and a few further experiments were undertaken with the object of confirming this result. In order to obtain some idea as to the error introduced by cooling the material rapidly and analysing the product, the following determinations were made. A known weight of calcium chromate was introduced into the tube, the apparatus evacuated and the temperature raised to  $1030^\circ$ . A suitable quantity of the evolved oxygen was pumped away and measured, the pressure of the residual gas being determined. From these figures the percentage decomposition could be calculated. Air, or in some cases nitrogen was admitted to the tube, the stopper was removed and the boat withdrawn and cooled as rapidly as possible, the whole operation

occupying about two minutes. The contents of the boat were then analysed and the results are shown in Table IV.

TABLE IV.

*Oxidation Effects during Cooling.*

| Weight of $\text{CaCrO}_4$<br>gms. | Gas<br>admitted | Percentage decomposition : |          |
|------------------------------------|-----------------|----------------------------|----------|
|                                    |                 | gas measurement            | analysis |
| 1.254                              | air             | 14.0                       | 13.5     |
| 0.627                              | "               | 28.5                       | 26.5     |
| 0.314                              | "               | 30.0                       | 28.8     |
| 0.314                              | "               | 56.0                       | 40.2     |
| 0.150                              | "               | 64.0                       | 48.0     |
| 0.100                              | "               | 64.0                       | 47.5     |
| 0.050                              | "               | 64.0                       | 48.0     |
| 0.025                              | "               | 64.0                       | 49.0     |
| 1.254                              | nitrogen        | 14.0                       | 13.8     |
| 0.627                              | "               | 28.5                       | 27.8     |
| 0.100                              | "               | 64.0                       | 62.0     |

From these it may be seen that when air is admitted, very inaccurate results are obtained by the analysis method when the quantities are small and the percentage decomposition large. On the other hand if about one gram of material is used and the decomposition is not very great the errors are comparatively small, and are diminished by substituting nitrogen for air. Hence it appears legitimate to accept the analytical results under suitable conditions.

Varying quantities of calcium chromate were consequently heated in air for periods of three hours and cooled rapidly. The product was in all cases hard and somewhat discoloured on the outside, but yellow inside. The results obtained on analysis are shown in Table V.

From these it appears that there is a small but definite amount of decomposition. As this takes place at comparatively low temperatures it seems to be due to some ill-defined side reaction. The loss in weight in each case is practically equal to the amount of water in the chromate calculated by difference from the known amounts of  $\text{CrO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$ . This water is not lost at  $110^\circ$ . It is shown later that calcium oxide produces decomposition of the chromate, but in this case the excess is not sufficient to account for the observed results.

TABLE V.

*Decomposition of Calcium Chromate in Air.*

| Temperature<br>°C. | Weight taken<br>gms. | Weight of<br>product | Percentage<br>loss | CrO <sub>3</sub> in product,<br>per cent. | Percentage<br>decomposition |
|--------------------|----------------------|----------------------|--------------------|---|-----------------------------|
| 500                | 0.100                | 0.0963               | 3.7                | 62.6                                      | 2.0                         |
| 1030               | 0.100                | 0.0961               | 3.9                | 61.4                                      | 4.1                         |
| 930                | 0.100                | 0.0964               | 3.6                | 61.1                                      | 4.2                         |
| 1030               | 0.500                | 0.4820               | 3.6                | 62.0                                      | 3.2                         |
| 930                | 0.500                | 0.4800               | 4.0                | 62.2                                      | 3.0                         |
| 1030               | 1.000                | 0.9648               | 3.5                | 61.8                                      | 3.1                         |
| 930                | 1.000                | 0.9632               | 3.7                | 62.0                                      | 2.9                         |

Two other samples of calcium chromate prepared as already mentioned from lime water and chromic acid containing 5.7 per cent. of water and with the ratio Ca : Cr = 0.9956 : 1, gave identical results for the amount of decomposition at 1030°, so that this does not appear to depend upon slight variations in the composition of the chromate.

## CHROMIUM TRIOXIDE.

A sample of chromium trioxide in a porcelain boat was placed in the quartz tube and the apparatus evacuated. After allowing some time for small quantities of moisture to be absorbed by the phosphorus pentoxide the temperature was slowly raised. In several experiments the pressure up to 210° was too low to read on the manometer, at 220° there was distinct evolution of oxygen and at 250° the gas was given off rapidly. At the latter temperature pressures as high as 400 mm. could be obtained without any indication that the state of equilibrium was being approached. It is evident therefore that the dissociation pressure increases very rapidly between 210° and 250° and exceeds 400 mm. at 250°.

From these results it might be expected that chromium trioxide would decompose rapidly and completely when heated in air to about 300°. This however, is not the case. Table VI shows the result of heating samples in air at different temperatures. The percentage decomposition was determined by removing the samples from the tube, cooling rapidly, and analysing them for CrO<sub>2</sub> and total chromium.

TABLE VI.

*Effect of Heat upon Chromium Trioxide in Air.*

| Temperature °C. | Time of heating hours | Percentage decomposition |
|-----------------|-----------------------|--------------------------|
| 300             | 2                     | 28                       |
| 320             | 2                     | 32                       |
| 350             | 2                     | 48                       |
| 350             | 9                     | 52                       |
| 350             | 18                    | 55                       |
| 400             | 2                     | 52                       |
| 550             | 2                     | 100                      |
| 600             | 2                     | 100                      |

There appears to be some tendency to form a compound  $\frac{1}{2}\text{Cr}_2\text{O}_3, \text{CrO}_3$  at temperatures below  $400^\circ$ , but the evidence is not definite. The existence of intermediate compounds appears to be necessary to account for the high temperature required for complete decomposition. As, however, those experiments were made chiefly to confirm the fact that  $\text{CrO}_3$  was completely decomposed at temperatures well below those employed in the subsequent experiments, the investigation of intermediate products was not continued.

Some time after the completion of our work, a comprehensive examination of the thermal decomposition of  $\text{CrO}_3$  was made by A. Simon and T. Schmidt, (*Z. anorg. Chem.*, 1926, **153**, 191-218) using similar methods. The temperature of initial decomposition of  $\text{CrO}_3$  agrees fairly closely with the value obtained by us, but subsequent values differ considerably. For instance, the dissociation pressure is given as 10 mm. at  $265^\circ$  and 400 mm. at  $310^\circ$ , whereas we obtained a value greater than 400 mm. at  $250^\circ$ . The formula for the new compound  $\text{Cr}_5\text{O}_{13}$  which was found by these authors to exist up to  $320^\circ$  at 10 mm. pressure corresponds in our notation with 26.6 per cent. decomposition while  $\text{Cr}_5\text{O}_{12}$ , the oxide stable from  $365^\circ$  to  $410^\circ$  at 10 mm., corresponds with 40 per cent. decomposition. The existence of the former is not incompatible with the figures in Table VI, but it is hard to reconcile the formation of the latter compound with our values at  $350^\circ$  and  $400^\circ$ . The progressive slow decomposition at  $350^\circ$  is noticeable and it is possible that the reaction is considerably affected by catalysts such as water vapour which was present in our experiments as the air was not dried.



## CALCIUM BICHROMATE.

Samples of calcium bichromate made by adding the calculated quantity of calcium oxide to a solution of chromic acid, evaporating to dryness and drying at  $110^{\circ}$  were examined in the same way as the chromic acid. On heating in vacuo, oxygen was evolved readily at  $250^{\circ}$ , and after two hours' heating in air at  $500^{\circ}$  the residue was found to be a mixture of calcium chromate and  $\text{Cr}_2\text{O}_3$ . Calcium bichromate therefore appears to behave on heating very much as if it were a mixture of calcium chromate and  $\text{CrO}_5$ .

## CALCIUM CHROMATE AND CALCIUM OXIDE.

In the first series of experiments weighed quantities of calcium chromate and calcium oxide were ground together in an agate mortar and the chromate content of the mixture determined. The presence of small quantities of carbonate would have no effect on the subsequent results. The mixture (0.2 to 1.0 gm.) was heated in the furnace and a slow current of air allowed to pass through the tube. At the end of the required period the sample was withdrawn rapidly, cooled and analysed. It has been pointed out on p. 154 that with the quantities used the error so introduced is small, particularly as the decomposition of the smaller amounts is low. Table VII shows the results obtained.

TABLE VII.

*Effect of Heat upon Mixtures of  $\text{CaCrO}_4$  and  $\text{CaO}$  in Air.*

| Mols. CaO per mol. $\text{CaCrO}_4$ | Mixture gms. | Time of heating: hours | Percentage decomposition |                   |
|-------------------------------------|--------------|------------------------|--------------------------|-------------------|
|                                     |              |                        | at $920^{\circ}$         | at $1030^{\circ}$ |
| 0.1                                 | 0.2          | 2                      | 10.4                     | 12.5              |
| 0.1                                 | 0.2          | 3                      | 11.2                     | 13.0              |
| 0.2                                 | 0.2          | 2                      | 13.4                     | 14.2              |
| 0.2                                 | 0.2          | 3                      | 14.2                     | 15.0              |
| 0.5                                 | 0.5          | 2                      | 29.8                     | 32.7              |
| 0.5                                 | 0.5          | 3                      | 31.5                     | 32.0              |
| 1.0                                 | 1.0          | 2                      | 32.1                     | 31.9              |
| 1.0                                 | 0.5          | 3                      | 33.2                     | 33.1              |
| 1.5                                 | 1.0          | 2                      | 33.2                     | 33.2              |
| 1.5                                 | 0.5          | 3                      | 32.2                     | 32.9              |
| 2.0                                 | 1.0          | 2                      | 33.0                     | 32.7              |
| 3.0                                 | 1.0          | 2                      | 32.2                     | 31.3              |

It will be observed that the percentage decomposition at both temperatures increases with the amount of lime until about 0.5 mol. is present, after which it remains constant and very nearly 33 per cent. This indicates the formation of a compound in which the ratio of  $\text{CrO}_3$  to  $\frac{1}{2}\text{Cr}_2\text{O}_3$  is 2 : 1, and confirms the results found in Part I, viz., that a mixture of  $\text{Cr}_2\text{O}_3$  and  $\text{CaO}$  containing approximately 2 mols. of calcium to 1 of chromium yielded in air at  $910^\circ$  a substance in which 69.2 of the chromium was present as chromate, while a mixture of  $\text{CaCrO}_4$  and  $\text{CaO}$  with a similar ratio of calcium to chromium gave at  $940^\circ$  a product with 67.8 per cent. of chromate.

The quantity of calcium oxide necessary for the formation of this compound is not very obvious from the experimental results, as the decomposition for 0.1 mol.  $\text{CaO}$  appears abnormally high. It is moreover in disagreement with the figure 9.3 found in Part I. If this value is adopted, the figures at  $1030^\circ$  lie on a straight line (bearing in mind the fact that pure calcium chromate decomposes to the extent of 4 per cent.) when plotted against the proportion of calcium oxide, with a break very close to 0.5 mol.  $\text{CaO}$ . This would indicate that the compound contains 0.5 mol.  $\text{CaO}$  per 1 mol.  $\text{CaCrO}_4$  and that when less than this quantity of calcium oxide is used the products are mixtures of the compound with calcium chromate. If this is so the formula for the compound is  $\frac{1}{2}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\frac{1}{2}\text{CaO}$ . It is black and completely soluble in 10 per cent. sulphuric acid.

To determine whether any other compounds were formed, a series of gas pressure measurements were made. Two mixtures were prepared with 0.5 mol. of calcium oxide and with 1 mol. respectively to 1 mol. of calcium chromate. The dissociation pressure at different temperatures was measured in exactly the same way as in the case of calcium chromate, and the results are given in Table VIII.

TABLE VIII.

*Dissociation Pressures of Mixtures of CaO and CaCrO<sub>4</sub>.*

| Temperature °C | Pressure |     |       |     | Mean |
|----------------|----------|-----|-------|-----|------|
|                | 0.5 : 1  |     | 1 : 1 |     |      |
|                | a        | b   | a     | b   |      |
| 740            | 16       | 19  | 15    | 16  | 16   |
| 795            | 35       | 37  | 42    | 40  | 38   |
| 835            | 100      | 105 | 99    | 108 | 103  |
| 855            | 180      | 197 | 186   | 190 | 188  |
| 875            | 281      | 287 | 263   | 270 | 275  |
| 885            | 360      | 340 | 375   | 380 | 356  |

Owing to considerable experimental difficulties the figures are not very concordant, but they suffice to show that, as anticipated, there is no appreciable difference in the behaviour of the two mixtures.

On comparing the mean values with those for pure calcium chromate it will be seen that they are very much higher. At  $910^{\circ}$  the dissociation pressure of the mixture was greater than 680 mm. while that of calcium chromate at  $290^{\circ}$  was only 11 mm. This shows that the two substances must react to form a basic chromate which is comparatively easily decomposed. The formula  $\text{CrO}_3, \frac{2}{3}\text{CaO}$  appears to represent this basic chromate.

The amount of gas given off by different weights of the equimolecular mixture was next measured and the percentage decomposition calculated. In one set of experiments the total pressure was measured, in the other, gas was pumped away and the total quantity ascertained by measuring the volume and the pressure of the residual gas. Table IX shows the results in the former case.

TABLE IX.

*Pressure of Gas evolved from Mixture  $\text{CaO} + \text{CaCrO}_4$  (1:1)  
Temperature,  $910^{\circ}$ .*

| Mixture gms. | Pressure mm. | Percentage decomposition |
|--------------|--------------|--------------------------|
| 3.0          | 460          | 24                       |
| 2.0          | 320          | 25                       |
| 1.5          | 270          | 29                       |
| 1.0          | 200          | 32                       |
| 0.75         | 148          | 31                       |

It has already been explained that this method is not capable of giving very accurate results, but these figures indicate that the decomposition increases when the pressure falls below about 270 mm. Consequently, in the second set of experiments the pressure was first adjusted by pumping to 300 mm., then to 250 mm. and finally the tube was evacuated completely. The results are shown in Table X.

These confirm the hypothesis that the decomposition takes place in two stages and show that a third stage exists when the pressure is reduced still further.

TABLE X.

*Quantity of Gas evolved from Mixture CaO + CaCrO<sub>4</sub> (1 : 1)  
Temperature, 900°.*

| Mixture gms. | Pressure mm. | Volume c.c., N.T.P. | Percentage decomposition |
|--------------|--------------|---------------------|--------------------------|
| 4.0          | 300          | 77                  | 26.0                     |
| 3.0          | 300          | 55                  | 25.0                     |
| 4.0          | 250          | 83                  | 31.8                     |
| 3.0          | 250          | 69                  | 31.3                     |
| 4.0          | < 0.1        | 121                 | 41.0                     |

The product obtained at 250 mm. evidently consists of a mixture of calcium oxide and the compound already obtained by heating the mixture in air. In order to determine its decomposition pressure, a sample was prepared by heating an equimolecular mixture of calcium oxide and calcium chromate to 1000° for two hours in air. A portion was then placed in the quartz tube, evacuated and heated at a constant temperature until the pressure became constant. The values obtained were 22 mm. at 920° and 45 mm. at 1000°.

Finally, an examination was made of the product mentioned in Table X in which the decomposition amounted to 41 per cent. Mixtures of calcium chromate with varying proportions of calcium oxide were heated in a vacuum at 1030° until no more gas was evolved. After cooling *in vacuo* the product was analysed. Table XI shows the results.

TABLE XI.

*Effect of Heat upon Mixtures of CaO and CaCrO<sub>4</sub> in vacuo.*

| CaO per mol. CaCrO <sub>4</sub> | Mixture gms. | Percentage decomposition |
|---------------------------------|--------------|--------------------------|
| 0.1                             | 0.2          | 54.4                     |
| 0.1                             | 0.2          | 55.8                     |
| 0.2                             | 0.2          | 44.1                     |
| 0.2                             | 0.2          | 45.2                     |
| 0.5                             | 0.5          | 41.0                     |
| 1.0                             | 1.0          | 42.0                     |
| 1.5                             | 1.0          | 42.1                     |
| 2.0                             | 1.0          | 41.0                     |
| 3.0                             | 1.0          | 42.3                     |

Pure calcium chromate decomposes to the extent of 80 per cent. in a vacuum and it is interesting to note that the addition of calcium oxide reduces the amount of decomposition whereas the reverse is the case when the heating is conducted in air. The final product may be considered as decomposed to the extent of 40 per cent. since it is not likely that a mixture of two solids will be sufficiently intimate for the reaction to be complete. A curve in which the quantity of calcium oxide is plotted against the decomposition exhibits a break very close to 0.25 mol. CaO, but as this break is not quite sharp the true value might possibly be 0.33. The former figure however appears more probable, particularly in view of the large effect of 0.1 mol. CaO and if it is correct, the formula for the compound may be written  $\frac{1}{3}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\frac{25}{12}\text{CaO}$ . As the number of mols. of CaO is approximately 2, it is very likely that the true formula is  $\frac{1}{3}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $2\text{CaO}$ . The substance is completely soluble in 10 per cent. sulphuric acid.

#### CALCIUM CHROMATE AND CHROMIUM OXIDE.

Two mixtures of calcium chromate with 0.5 and 1.0 molecular proportions of well washed and ignited chromic oxide were prepared, and the quantity of  $\text{CrO}_3$  determined as a check. The dissociation pressures were measured and found to be the same for both mixtures, mean values being 22 mm. at  $930^\circ$ , 90 mm. at  $990^\circ$  and 150 mm. at  $1030^\circ$ .

A series of mixtures containing from 0.25 to 2.0 mols. of  $\text{Cr}_2\text{O}_3$  per molecule of  $\text{CaCrO}_4$  were heated in air to  $1000^\circ$ , and, as was to be expected, the amount of decomposition was found to be the same as for pure  $\text{CaCrO}_4$ , viz., 4 per cent. The partial pressure of oxygen at Bangalore is approximately 140 mm. so that evidently there would have been decomposition if the temperature had been a few degrees higher.

On evacuation oxygen was readily evolved, but there was no indication of evolution by stages. The product after cooling *in vacuo* did not contain chromate. A portion was replaced in the tube, evacuated and heated to  $1000^\circ$ . When oxygen was admitted at a pressure of 150 mm. it was readily absorbed. Mixtures of varying composition were then heated *in vacuo* and analysed after cooling, the results being shown in Table XII.

Bearing in mind that calcium chromate alone decomposes to the extent of 80 per cent., it would seem that approximately 0.5 mol. of  $\text{Cr}_2\text{O}_3$  suffices to produce complete decomposition although the results are not very definite possibly owing to incomplete mixing.

TABLE XII.

*Effect of Heat upon Mixtures of  $\text{Cr}_2\text{O}_3$  and  $\text{CaCrO}_4$  in vacuo.  
Temperature,  $1030^\circ$ .*

| Mol. $\text{Cr}_2\text{O}_3$ per mol.<br>$\text{CaCrO}_4$ | Percentage<br>decomposition. |
|---|------------------------------|
| 0.25  | 82                           |
| 0.25  | 84                           |
| 0.50  | 96                           |
| 0.50  | 95                           |
| 1.00  | 99                           |
| 1.00  | 100                          |
| 2.00  | 100                          |

The final product is a calcium chromite. If 0.5 mol. of  $\text{Cr}_2\text{O}_3$  is required, the formula becomes  $\text{Cr}_2\text{O}_3, \text{CaO}$ , the chromite described by Guber (*Bull. Soc. Chim.*, 1877 (2), 27, 435) and Dufan (*Ann. Chim. Phys.*, 1897 (7), 12, 266).

#### MIXTURES OF $\text{CaO}$ AND $\text{Cr}_2\text{O}_3$ .

Owing to the difficulty of preserving a mixture containing calcium oxide, pure calcium carbonate was used in the following experiments, the mixture being heated to about  $800^\circ$  and all carbon dioxide pumped away before proceeding with any measurements.

In the first series, mixtures containing different proportions of the ingredients were heated to  $1030^\circ$  in vacuo, cooled, and the product treated with hydrochloric acid. The calcium in the solution was then estimated with the results shown in Table XIII.

The interpretation of these results is not very simple. When a small quantity of calcium oxide is added, the whole of it does not combine with the chromic oxide and become insoluble as might be expected, but only somewhat less than a half. With a large excess of calcium oxide, only 0.5 to 0.6 mol. becomes insoluble. A possible explanation is that a compound is formed having the formula  $\text{CaO}, \text{CaO}, 2\text{Cr}_2\text{O}_3$ , in which one molecule of calcium oxide is soluble in acid. According to the figures in Table XIII, the proportion of chromic oxide should be somewhat less than is indicated by the formula, but it is possible that the higher values for the amount

TABLE XIII.

*Quantity of CaO rendered insoluble by heating with Cr<sub>2</sub>O<sub>3</sub> at 1030°C.*

| CaO per mol. Cr <sub>2</sub> O <sub>3</sub> in original mixture | Time of heating hours | CaO rendered insoluble |
|---|-----------------------|------------------------|
| Mols.   |                       | Mol.                   |
| 0.25  | 3                     | 0.09                   |
| 0.25  | 5                     | 0.11                   |
| 0.50  | 3                     | 0.19                   |
| 0.50  | 5                     | 0.22                   |
| 0.66  | 3                     | 0.22                   |
| 0.66  | 5                     | 0.23                   |
| 1.00  | 3                     | 0.42                   |
| 1.00  | 5                     | 0.45                   |
| 2.00  | 3                     | 0.53                   |
| 2.00  | 5                     | 0.55                   |
| 4.00  | 3                     | 0.57                   |
| 4.00  | 5                     | 0.60                   |

of insoluble CaO when excess of CaO is taken are due to solid solution and the difficulty of complete extraction.

On treatment with acid a compound having the approximate formula CaO,  $\frac{1}{2}$ Cr<sub>2</sub>O<sub>3</sub> is obtained. If this formula is correct, the original compound has the same empirical formula as the chromite already mentioned, but differs from it in being partially soluble in acid.

On admitting oxygen to the mixtures of calcium oxide and chromic oxide, it was rapidly absorbed, but after a short interval in several cases, the gas was again liberated, sometimes quantitatively. At first sight this seemed to be a very remarkable phenomenon, but it appears to be due to the fact that, of two possible reactions, one takes place much faster than the other. Details will be given later. When two or more mols. of CaO are present for one of chromic oxide, gas evolution does not occur. The following results were obtained on admitting measured quantities of oxygen, the pressure at no time being allowed to rise above 20 mm.

TABLE XIV.

*Absorption of Oxygen by Mixtures of CaO and Cr<sub>2</sub>O<sub>3</sub>.  
Temperature, 1030°.*

| CaO per mol.<br>Cr <sub>2</sub> O <sub>3</sub> | Weight of sample<br>gms. | Oxygen absorbed<br>c.c., N.T.P. | Percentage<br>absorption |
|--|--------------------------|---------------------------------|--------------------------|
| Mol.   |                          |                                 |                          |
| 2:0  | 1.00                     | 36.4                            | 38.6                     |
| 2:0  | 2.00                     | 71.0                            | 36.6                     |
| 2:0  | 3.00                     | 105.0                           | 37.2                     |
| 3:0  | 1.00                     | 43.5                            | 59.2                     |
| 3:0  | 2.00                     | 87.0                            | 59.1                     |
| 3:0  | 3.00                     | 129.0                           | 58.5                     |

The last column shows the percentage of oxygen actually absorbed when a state of equilibrium was reached, calculated on the quantity which would be absorbed for complete oxidation.

The mixture containing 3 mols. CaO is equivalent to an equimolecular mixture of calcium oxide and calcium chromate, which has been shown (Table XI) to decompose to the extent of 42 per cent. below 45mm. pressure at 1000°. Similarly the mixture with 2 mols. corresponds with pure calcium chromate which decomposes to the extent of 64 per cent. (Table III) at pressures between 65 and 5 mm. The agreement in both cases is close, showing that, at the temperatures under consideration, reaction between the two solids is practically complete. It is remarkable that in neither case is the molecular ratio of Cr<sub>2</sub>O<sub>3</sub> to CrO<sub>3</sub> exactly simple, and the difference appears to be beyond the limit of experimental error. In the case of the 3 to 1 mixture the only simple number near 59 is 60. If the experimental value is low in this case, it is possible that it is also low in the case of the 2 to 1 mixture thereby indicating 40 as the correct value. If this is so, the figure 64 per cent. for the decomposition, although the mean of a number of consistent experiments, is too high. In the circumstances it seems advisable to give greater weight to the decomposition experiments, as they are made with a homogeneous material and not with a mixture of two solids. Moreover, a 67 per cent. decomposition leads to the simple formula Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>, 3CaO as opposed to  $\frac{2}{3}$ Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>,  $\frac{3}{2}$ CaO required by 60 per cent. decomposition, so that it seems desirable to adopt the former value.

When the mixture contains less than one atom of calcium per atom of chromium, the phenomenon of absorption followed by evolution



of oxygen already mentioned is observed. Table XV gives the results of some typical experiments, the time T being in minutes and the pressure P in mm.

TABLE XV.

*Absorption and Evolution of Oxygen by Mixtures of CaO and Cr<sub>2</sub>O<sub>3</sub>.*

| A   |     | B  |    | C   |     | D  |     | E  |     | F  |     |
|-----|-----|----|----|-----|-----|----|-----|----|-----|----|-----|
| T   | P   | T  | P  | T   | P   | T  | P   | T  | P   | T  | P   |
| 0   | 40  | 0  | 60 | 0   | 138 | 0  | 215 | 0  | 102 | 0  | 226 |
| 1   | 25  | 1  | 45 | 1   | 110 | 1  | 166 | 1  | 83  | 1  | 174 |
| 2   | 20  | 2  | 35 | 2   | 92  | 2  | 137 | 2  | 73  | 3  | 146 |
| 3   | 18  | 4  | 30 | 3   | 80  | 3  | 125 | 3  | 65  | 4  | 130 |
| 6   | 16  | 8  | 25 | 4   | 72  | 4  | 117 | 4  | 61  | 5  | 118 |
| 8   | 15* | 15 | 20 | 5   | 66  | 8  | 112 | 6  | 55  | 12 | 100 |
| 77  | 1   | 25 | 15 | 7   | 48  | 10 | 114 | 14 | 47  | 40 | 102 |
| 122 | 2   | 35 | 13 | 25  | 40  | 14 | 120 | 22 | 46  |    |     |
| 125 | 4   | 42 | 14 | 26  | 45  | 19 | 124 | 23 | 53  |    |     |
| 130 | 10  | 44 | 17 | 28  | 49  | 29 | 131 | 24 | 70  |    |     |
| 147 | 15  | 45 | 20 | 30  | 56  | 59 | 156 | 25 | 80  |    |     |
| 150 | 18  | 50 | 30 | 35  | 74  |    |     | 27 | 84  |    |     |
|     |     | 55 | 50 | 59  | 80  |    |     |    |     |    |     |
|     |     | 59 | 60 | 110 | 110 |    |     |    |     |    |     |
|     |     |    |    | 159 | 130 |    |     |    |     |    |     |

In experiments A, B, C, D and F the mixture was  $3/2$  mol. Cr<sub>2</sub>O<sub>3</sub> to 1 mol. CaO. In E the ratio was  $5/2:1$ . The temperature in experiment F was 990°; in all others 1030°. 1 gm. of the sample was used in each case and the pressure of the oxygen sufficient to form CaCrO<sub>4</sub> + Cr<sub>2</sub>O<sub>3</sub> in the first four experiments would be 423 mm. In experiment A, when the pressure had fallen to 15 mm. the tube was evacuated to 0.5 mm. and it is interesting to notice that gas was not evolved for more than an hour. In the next three experiments it will be noticed that, the higher the pressure initially, the shorter the time taken to reach the minimum pressure.

A possible explanation is as follows:—The calcium oxide and part of the chromic oxide combine rapidly with oxygen to form the compound Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>, 3CaO which is stable between pressure of 70 and 5 mm. at 1030°. This compound then reacts, but more slowly with the excess of Cr<sub>2</sub>O<sub>3</sub>, evolving oxygen. If only a small quantity of oxygen is admitted, insufficient to form more than a small proportion of the compound, the oxygen first evolved is absorbed by some of the un-attacked substances, and is not liberated until the whole of the calcium oxide is in a state of combination. The larger the amount of oxygen, the more rapidly is complete oxidation attained and the shorter is the time for the evolution of gas to take place. In the first four experi-

\* The tube was evacuated to 0.5 mm.

ments, the initial pressure of oxygen necessary to form the compound, assuming it was not subsequently decomposed, would be 141 mm. so that the quantity actually added was considerably in defect in the first three experiments, but in excess in the fourth.

In experiment F no evolution of gas was observed, the reason being that the decomposition pressure of the compound is about 90 mm. at the temperature employed, 990° (p. 161). In experiment D, the pressure did not rise above 156 mm. for the same reason, the difference between this value and 150 mm., that found for the decomposition pressure at 1030°, being well within the limit of experimental error.

This theory of an intermediate compound being formed is supported by the fact that if, after the completion of the above experiments, the oxygen is pumped away and the substance cooled *in vacuo* and analysed, there is no calcium soluble in acid, whereas it has been shown (Table XIII) that if mixtures of  $\text{Cr}_2\text{O}_3$  and  $\text{CaO}$  are heated without admission of oxygen, a considerable proportion of the calcium remains soluble in acid.

It may be mentioned that the evolution of gas was not caused by slight changes of temperature during the experiments, as the phenomenon was observed at other temperatures.

Additional confirmation was obtained by heating a mixture of 3.2 mol.  $\text{Cr}_2\text{O}_3$  and 1 mol.  $\text{CaO}$  to 1030° *in vacuo*, cooling and extracting the product with hydrochloric acid. The residue was replaced in the tube and heated to 1030°. On admitting oxygen none was absorbed until the pressure reached 150 mm.

Finally it may be mentioned that the whole of the experiments described in the present paper are tentative and merely indicate the complex quality of the system with which we are dealing. It is intended to undertake a more systematic examination of each compound in the near future.

### SUMMARY.

The existence of a number of compounds of calcium, chromium and oxygen has been shown by measurements of decomposition pressures, the quantity of gas evolved or absorbed on heating various mixtures and, where possible, by analysis. Details are as follows, the formulæ for the sake of comparison being written as though each contained only one molecule of  $\text{CrO}_3$ .

1.  $\text{CrO}_3$ ,  $\text{CaO}$ , calcium chromate. Dissociation pressure 15 mm. at 950°, 44 mm. at 1000°, 70 mm. at 1030°. Decomposes to compound 6.

2.  $\text{Cr}_2\text{O}_3$ ,  $\frac{3}{2}\text{CaO}$ , quantity of  $\text{CaO}$  somewhat uncertain. Dissociation pressure 188 mm. at  $835^\circ$ , 358 mm. at  $855^\circ$ . Decomposes to 3.

3.  $\frac{1}{6}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $2\text{CaO}$ . Formed by heating 2. Dissociation pressure at  $910^\circ$  about 270 mm., below which it decomposes to 4.

4.  $\frac{1}{3}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $9/4\text{CaO}$ , or possibly  $2\text{CaO}$ , formed from 3 or by heating calcium oxide and calcium chromate in air. Black substance soluble in dilute acid. Dissociation pressure 22 mm. at  $920^\circ$  and 45 mm. at  $1000^\circ$ , the compound 5 being formed.

5.  $\frac{1}{3}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $2\text{CaO}$ , formed from 4 or by supplying oxygen at a pressure less than 20 mm. to a mixture of  $\text{Cr}_2\text{O}_3$  with more than one mol. of  $\text{CaO}$ . Soluble in acid. Dissociation pressure not measurable at  $1030^\circ$ .

6.  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $3\text{CaO}$ , (formula somewhat doubtful) the first decomposition product of pure calcium chromate, also formed on supplying oxygen at less than 20 mm. pressure to a mixture of  $\text{Cr}_2\text{O}_3$  with two mols. of  $\text{CaO}$  at  $1030^\circ$ .

7.  $\frac{3}{2}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $4\text{CaO}$ , decomposes at about 2 mm. at  $1030^\circ$  to give 8.

8.  $2\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $5\text{CaO}$ , the final decomposition product of calcium chromate with no appreciable dissociation pressure at  $1030^\circ$ .

9.  $\frac{1}{3}\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\text{CaO}$ , quantity of  $\text{Cr}_2\text{O}_3$  uncertain, formed by heating calcium chromate with  $\text{Cr}_2\text{O}_3$ ; dissociation pressures 22 mm. at  $930^\circ$ , 90 mm. at  $990^\circ$  and 150 mm. at  $1030^\circ$  yielding compound 9.

10.  $\text{Cr}_2\text{O}_3$ ,  $\text{CaO}$  the simplest chromite obtained from heating *in vacuo* compound 9.

11.  $2\text{Cr}_2\text{O}_3$ ,  $2\text{CaO}$ , obtained when mixtures of  $\text{CaO}$  and  $\text{Cr}_2\text{O}_3$  are heated *in vacuo*; one molecule of  $\text{CaO}$  is soluble in acid yielding compound 12. The quantity of  $\text{CaO}$  is not quite definite.

12.  $2\text{Cr}_2\text{O}_3$ ,  $\text{CaO}$  obtained from 10 by treatment with acid.

An interesting case of two reactions between solids and gas which take place with different velocities is encountered in the reactions between oxygen and certain mixtures of  $\text{CaO}$  and  $\text{Cr}_2\text{O}_3$ . The gas is first absorbed and then liberated at the same temperature.

*Department of General Chemistry,  
Indian Institute of Science,  
Bangalore.*

[Accepted, 5-10-26.]

PRINTED AND PUBLISHED  
BY GEORGE KENNETH AT THE DIOCESAN PRESS  
POST BOX 455, MADRAS—1926. C1052