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CONTENTS.

REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

Part I. The Synthesis and Decomposition of Calcium, Sodium and Magnesium Chromates in Air.

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Although the manufacture of alkali chromates is a long established commercial process and a considerable amount of literature dealing with the technical side of the question is available,[1] very little appears to be known concerning the actual mechanism of the reactions which take place in the chromate furnace. The mixture of chrome iron ore, lime and sodium carbonate, usually employed for the production of sodium chromate, is a complex one and it is difficult to distinguish between the various reactions which may take place, unless information as to the behaviour of the simple components of the mixture at high temperatures is available.

As a contribution to the study of the question we have investigated the reactions between calcium and magnesium oxides, sodium carbonate and chromium sesquioxide at various temperatures, and the results obtained in presence of air are given in the present paper.

EXPERIMENTAL.

The following materials were used :

Calcium carbonate : pure precipitated, giving 100 per cent. $CaCO_3$ on analysis. When calcium oxide was required it was made by igniting this carbonate to constant weight.

Chromium oxide : A 'pure' commercial sample containing 97 per cent. Cr_2O_3, the remainder being water and a trace of sulphate.

Chromic acid : The first sample used contained sulphate. For the later experiments a sample free from sulphate was obtained.

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[1] cf. Wickop. *Die Herstellung der Alkali bichromate.* 1911.

Calcium chromate: was made by mixing equivalent quantities of calcium carbonate or calcium oxide and chromic acid dissolved in a a little water, evaporating and drying at 110°. The product was analysed to ensure the ratio of calcium to chromium being correct. It contained about 6 per cent. of water and a little carbonate.

Sodium carbonate: a sample of anhydrous material with no detectable impurities.

Sodium chromate: a 'pure' commercial specimen with traces of sulphate.

Magnesia: pure 'light' oxide.

Magnesium chromate: made from the above and chromic acid in a manner similar to that employed for calcium chromate.

Furnace. For heating the products to temperatures below 1,000° an electrically heated porcelain tube furnace was used. The tube was two inches in diameter and two feet long, and was large enough to accommodate four samples at a time. These were introduced into shallow nickel boats, which were placed two abreast in a thick iron boat in order to equalize the temperature as much as possible. A loose sheet of nickel was placed at the bottom of each boat, and provided this was well oxidised before use it was usually not appreciably attacked. In some experiments considerable corrosion took place and in such cases the nickel sheet could be changed without discarding the boat.

Temperatures were measured with a nickel-nichrome couple, standardized against a standard pyrometer and checked at the melting point of silver. The greatest variation observed between different parts of the iron boat was about 20°, consequently temperatures cannot be regarded as accurate to within 10°, in spite of the fact that the temperature of each small boat was measured separately.

For temperatures above 1,000° a Hirsch graphite resistance furnace was used and the temperature measured by an optical pyrometer of the disappearing filament type, standardized against Seger cones. The furnace would only take one sample at a time, and it was difficult to find a container which was not attacked. Siliceous materials reacted with the mixture and platinum was rapidly perforated. A disk of nickel was finally used as, although it was oxidised, the oxide did not appear to react with the substances under examination unless actual fusion occurred.

After heating, the chromate was determined by boiling the product with sodium carbonate solution and repeating the extraction until the solution became colourless. Ferrous ammonium sulphate was then added to the solution and the excess determined by titration with standard potassium permanganate. The total chromium was estimated by conversion into chromate by fusion with a mixture of borax and sodium carbonate.

CALCIUM CHROMATE.

For the first series of experiments an intimate mixture of chromium sesquioxide and calcium oxide, in the equivalent proportion $Cr_2O_3 : CaO = 1 : 1{\cdot}12$, was made. Four samples of one gram each were heated simultaneously. Three were removed from the furnace after four hours and the fourth sample after five hours. The results are shown in Table I, and in curve A, Fig. I. The 'percentage of chromate' in this and all following tables indicates the percentage of the total chromium present as chromate.

TABLE I.

$Cr_2O_3 : CaO = 1 : 1{\cdot}12$

Temperature. °C.	Percentage of chromate				
	Four hours				Five hours
	1	2	3	Mean	
660	42·0	43·0	42·0	42·3	49·1
690	56·0	55·0	57·0	56·0	61·7
700	58·5	58·0	61·0	59·2	67·6
710	64·0	64·0	65·5	64·5	71·0
750	72·0	79·0	76·0	75·7	75·5
780	88·0	87·0	86·0	87·0	87·1
800	88·0	89·0	87·0	88·0	87·1
810	92·0	91·0	90·0	91·0	89·2
870	86·5	87·0	89·0	87·5	...
870	87·5	...	88·5	88·0	...
920	85·5	87·5	87·5	86·8	...
920	86·0	87·0	87·5	86·8	...

The results indicate that the reaction is not complete in four hours at temperatures below 780°, but that above this temperature an equilibrium is reached within four hours.

In the second series of experiments a sample of calcium chromate was heated. This was prepared by treating calcium carbonate with excess of chromic acid and washing, and as the importance of knowing the exact ratio of chromium to calcium was not realized at this stage in the experiments, the calcium was not estimated. It is probable that the mixture contained a slight excess of calcium. Table II shows the results obtained on heating for three and four hours, and Fig. I, A 1 the same in the form of a graph.

TABLE II.

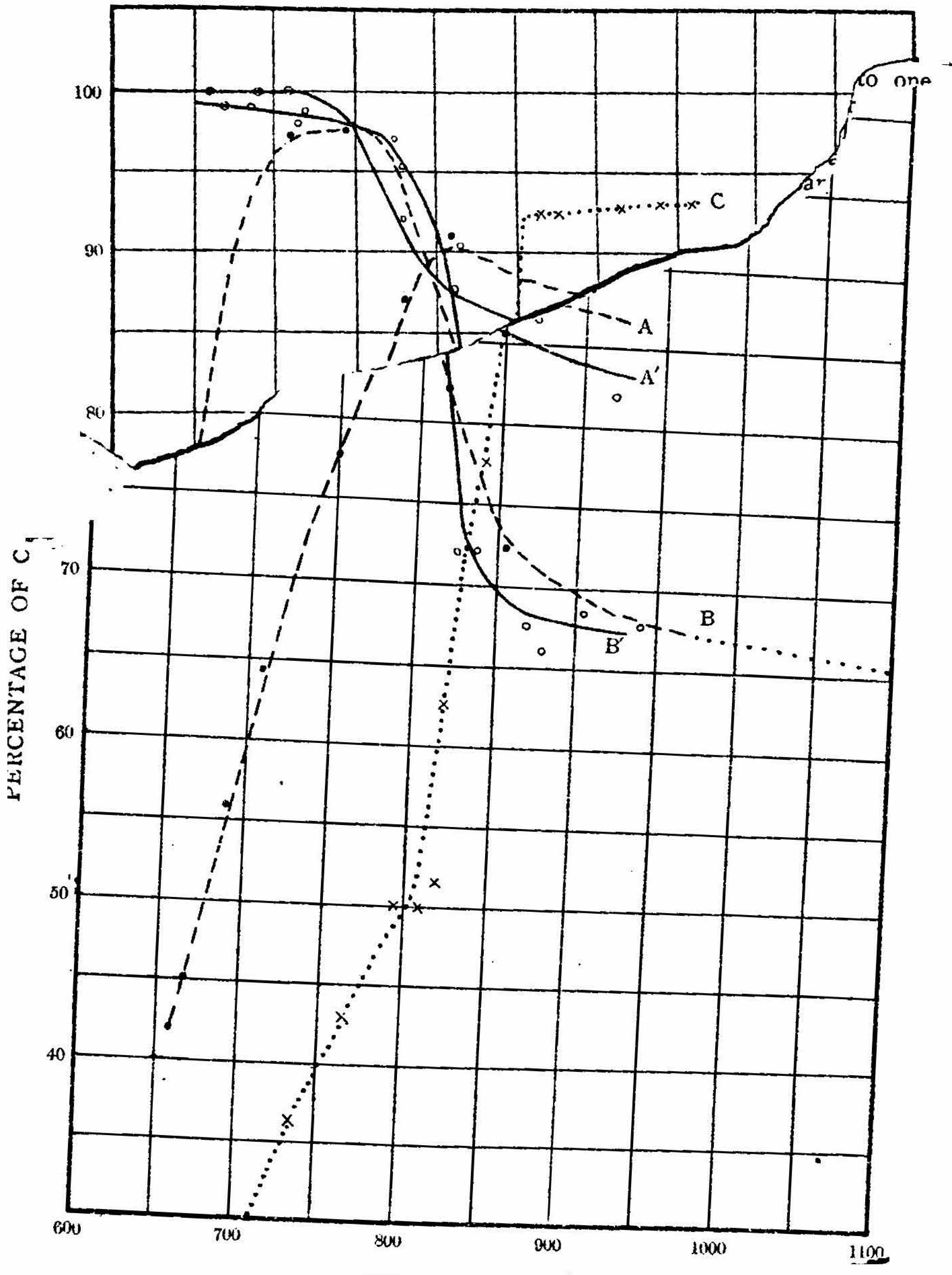
Calcium chromate.

Temperature °C.	Percentage of chromate				
	Four hours				Three hours
	1	2	3	Mean	
660	100	...	...	100	...
690	100	...	...	100	...
700	100	...	...	100	...
710	100	...	...	100	...
750	98·2	98·0	96·5	97·6	97·5
780	97·7	87·4	91·3	92·1	.
800	90·3	87·6	87·1	88·3	90·4
810	87·7	87·6	87·1	87·5	....
870	86·4	86·5	...	86·5	87·3
870	85·6	87·5	...	86·6	...
920	81·2	82·9	...	82·1	82·5
920	81·5	81·8	...	81·7	...

The results show that decomposition sets in at about 750° and that there is very little difference between the samples heated for three and four hours.

FIGURE I.

Effect of Heat upon Calcium Chromate.



Two sets of experiments were next carried out with mixtures containing approximately two atomic proportions of calcium to one of chromium. The first was a mixture of green chromium oxide and calcium oxide, the second a mixture of calcium chromate and calcium oxide. In the first case the ratio $\frac{1}{2}Cr_2O_3$: CaO was 1:2·07 and in the second 1:1·87. The results of heating these samples are shown in Table III and as graphs B and B′ in Fig. I.

TABLE III.

B. $0{\cdot}5Cr_2O_3 + 2CaO$. Cr : Ca = 1 : 2·07		B.′ $CaCrO_4 + CaO$. Cr : Ca = 1 : 1·87.	
Temperature °C.	**Percentage of chromate.**	**Temperature.**	**Percentage of chromate.**
655	79·5	670	98·9
690	94·6	685	98·9
700	95·0	715	98·0
720	97·3	720	98·9
745	97·6	760	97·4
760	97·6	775	97·0
800	87·4	780	95·2
855	72·3	815	90·4
875	71·1	815	82·5
910	69·2	825	72·0
1100	69·4	835	72·0
1200	58·7 *a*	870	67·6
1200	59·3	905	68·6
1300	58·8	940	67·8
1300	43·3 *b*	...	...

The time of heating was four hours at all temperatures below 1,000° and thirty minutes at 1,100° and above. Sample *a* was heated for ten minutes and *b* for fifteen minutes. Two experiments were carried out at each temperature, and the results, when not shown separately, temperature, as might be expected, but that for each temperature an equilibrium appears to be established. Further experiments were carried out in order to confirm this, with the following results.

A sample of carefully prepared calcium chromate, with no excess of calcium oxide and containing 3 per cent. of moisture as sole impurity, was found to show no signs of decomposition when heated to 1,000°, whereas previous samples had decomposed very appreciably between 750° and 800°. To this sample 0·1 molecular proportion of calcium oxide was added, thoroughly mixed and heated, with the results shown in Table IV.

TABLE IV.

$CaCrO_4 + 0{\cdot}1\ CaO$.		
Time in hours.	Temperature °C.	Percentage of chromate.
4	690	99·4
4	735	99·7
4	750	99·2
3	840—940	95·6
3	890—990	94·9
3	900—1000	90·7

In these experiments the temperature fluctuated somewhat so that the results are not very reliable. They serve to indicate, however, that the presence of free calcium oxide lowers the temperature of decomposition of calcium chromate, although the decomposition is not so marked as in the experiments recorded in Table II.

Three more samples of the same mixture were next heated for 3·5 hours to the temperatures 870°, 900° and 920° respectively. On removal from the furnace the first sample was seen to be yellowish green, and the other two green. The third sample (920°) was found to contain 96·9 per cent. of the chromium as chromate. The two others were replaced in the furnace at 700° for five hours. On removal [illegible] first sample was completely yellow and contained 99·7 per cent. [illegible] chromium as chromate, the second sample was almost yel [illegible] 8·9 per cent. as chrom [illegible] t the

A mixture of chromium sesquioxide and calcium oxide containing two atoms of calcium to one of chromium was next treated in a similar manner. Two samples were heated at 890° for 2·75 hours. One was analysed and contained 76·8 per cent. of the chromium as chromate, the other was again heated at 700° for nine hours and found to contain 92 per cent. of the chromium as chromate. A third sample was heated at 9[illegible]0° for 2·75 hours and then at 700° for nine hours. This was four[illegible] contain 83 per cent. of the chromium as chromate, while a check sample heated at 700° only for nine hours contained 96 per cent.

The experiments detailed in Table III show that the reaction is practically complete in four hours, but to obtain additional evidence as to the rate of the reaction, two samples of the mixture under consideration were rapidly introduced into the furnace which had been previously heated to 890°. In five minutes they attained the temperature of the furnace and were then withdrawn. They were found to contain 71·9 and 55·2 per cent. of the chromium as chromate showing that the reaction is very rapid. It may be assumed therefore that the sample with 76·8 per cent. of chromate represents the equilibrium at 890° and that on heating to 700° more chromate is formed. The low yields of 92 and 83 per cent. as compared with 96 per cent. for the check experiment may be due to slight sintering at the higher temperatures which would prevent complete oxidation.

Finally a mixture of calcium chromate and calcium oxide in equimolecular proportions was heated for a much longer period with the results given in Table V.

TABLE V.

$CaCrO_4 + CaO$. Cr : Ca = 1·00 : 2·00

Temperature °C	Time in hours	Per cent. chromate	Temperature °C	Time in hours	Per cent. chromate
765	4·0	99·1	765	12	98·8
770	4·0	99·9	770	12	99·8
795	4·0	96·0	795	12	97·1
900	3·25	78·0	890	18	75·0
900	3·25	79·0	900	18	77·0
920	3·25	76·0	920	18	73·0

These figures show that there is no appreciable decomposition below 770° even in twelve hours, but at 795° there is some decomposition.

The samples heated at the latter temperature became green. Heating for a longer time does not increase the amount of decomposition. At 900° about 22 per cent. of the chromate is decomposed in 3·25 hours, and although the figures given for eighteen hours indicate slightly greater decomposition, the low values are probably due to experimental error, as it was found difficult to maintain the temperature constant during such a long period, and on one or two occasions it rose by as much as 20 to 30 degrees.

The following conclusions may be drawn from the results: An intimate mixture of calcium oxide, and chromium sesquioxide in equivalent proportions[1] when heated in air reacts slowly with the oxygen to form chromate at a temperature of 650° and the rate at which the reaction takes place increases rapidly with rise of temperature. If the proportion of calcium oxide is doubled, the rate is greater at a given temperature than when equivalent proportions are present, for example at 700° about 95 per cent. of the chromium is converted into chromate in four hours in the former case, while in the latter, the conversion is only about 60 per cent. This is illustrated by the upward slopes of curves A and B in Fig. I, but it must be pointed out that these portions of the curves do not represent a state of equilibrium and that the results would vary considerably with the intimacy of mixture and the surface exposed to the air.

At temperatures of 800° and above lower yields of chromate are obtained with mixtures containing a slight excess of calcium oxide and a state of equilibrium is reached in about three hours or even less at the higher temperatures. These low yields are due to the instability of mixtures of calcium chromate and calcium oxide. This is confirmed by heating such mixtures. It is found that pure calcium chromate begins to decompose at about 1,000°. The addition of 0·1 equivalent of calcium oxide causes decomposition to start at about 800° and the quantity of chromate decomposed increases slowly with rise in temperature. If one equivalent of calcium oxide is added to calcium chromate the decomposition is still greater. The composition of the final product depends upon the temperature and is the same within the limit of experimental error whether a mixture of calcium oxide and calcium chromate is the starting material, or one of calcium oxide and chromium sesquioxide, provided that the ratio of calcium to chromium is the same in both cases.

Approximately 30 per cent. of the chromate decomposes between 750° and 900°. When the temperature is raised above 900°, the

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[1] 0·5 Cr_2O_3 equivalent to 1 CaO

extra quantity decomposed per 100° rise becomes much less than in the first stage of decomposition ; but analysis of the products does not indicate the formation of any definite compound. It seems probable that a series of solid solutions is produced.

SODIUM CHROMATE.

A complete series of experiments could not be carried out with sodium chromate owing to the fusibility of this compound and also of sodium hydroxide and carbonate. If a mixture of chromium sesquioxide and sodium carbonate is heated until it melts the chromium oxide sinks to the bottom of the vessel and irregular results are obtained.

The figures given in Table VI show that sodium chromate is readily formed from sodium carbonate and chromium sesquioxide.

TABLE VI.

0·5 Cr_2O_3 : Na_2CO_3 = 1·0 : 1·0. Time of heating four hours.

Temperature °C	Percentage of chromate
660	46·5
670	49·5
715	51·6
755	92·9
755	93·4

At 800° the mass fused. At higher temperatures the yield would probably be quantitative, as it was found that pure sodium chromate could be heated to 1,000° without decomposition.

Experiments were next conducted with mixtures of sodium carbonate and calcium oxide. As a mixture of one molecule of chromium sesquioxide with one molecule each of the two alkalis was found to fuse at 700°, another mixture with the composition,

0·5 Cr_2O_3 : Na_2Co_3 : CaO = 1·00 : 0·65 : 1·72, was used.

These proportions were selected because a mixture with the constituents in the same proportions, but in which the chromium was present as the mineral chromite, had given good yields of chromate when tested in a reverberatory furnace. The results are shown in Table VII.

TABLE VII.

$0{\cdot}5\ Cr_2O_3 : Na_2CO_3 : CaO = 1 : 0{\cdot}65 : 1{\cdot}72.$

Temperature °C	Time of heating in minutes	Percentage of chromate	Temperature °C	Time of heating in minutes	Percentage of chromate
665	240	99·0	1200	15	86·7
700	240	98·3	1200	10	86·6
750	240	97·9	1300	17	87·5
765	240	98·7	1300	15	87·1
800	240	97·9	1300	12	90·4
855	240	99·1	1400	15	0·0
880	240	98·9	1400	15	0·0
905	240	98·2	1400	15	51·0
915	240	99·3	1400	15	27·0
1070	40	94·5	1450	15	28·2
1070	10	95·2	1500	20	7·6
1070	5	94·6	1500	10	27·4

From these figures it is clear that the reaction takes place far more readily at low temperatures than in any of the cases hitherto considered. There is practically no decomposition up to 1,000°, but above this temperature a small proportion of the chromate is decomposed. If it is assumed that the whole of the sodium is present as chromate and that the remaining 0·35 equivalent of chromium is first converted into calcium chromate and then decomposed in accordance with curve B, Fig. I, so that at 1,200° only 60 per cent. of the chromium remains as chromate, then the total percentage of chromate in the mixture at this temperature would be 86, a value practically identical with the one given in Table VII.

Below 1,400° the mass fitted but did not fuse, above this temperature fusion took place and the nickel boat was badly attacked. It was exceedingly difficult to extract the chromate from the fused mass and the figures given for 1,400° and higher temperatures cannot be regarded as at all reliable.

It is interesting to notice that at 1,070° the reaction appears to be complete in five minutes.

MIXTURES CONTAINING FERRIC OXIDE.

As chrome iron ore contains a large proportion of iron in the ferrous state, which becomes converted into ferric oxide in the manufacture of sodium chromate, it was considered desirable to examine the effect of heating mixtures of ferric oxide and chromates. According to Donald,[1] chrome waste containing 60 to 70 per cent. of lime and about 20 per cent. of ferric oxide may replace fresh lime in the furnacing operation, while the Deutsche Solvay Werke,[2] recommend the use of a large proportion of ferric oxide and comparatively little lime.

Two mixtures were made containing sodium carbonate but no calcium oxide, the latter ingredient being replaced by ferric oxide the ratio 0·5 $Cr_2O_3 : Na_2CO_3 :$ 0·5 Fe_2O_3 in the first mixture (*a*), was 1 : 0·65 : 1·72 and in the second (*b*), 1 : 1 : 1·4. Mixture (*a*) corresponded with the lime mixture used in the experiments recorded in Table VII while in (*b*) the quantity of sodium carbonate was raised and that of the ferric oxide diminished to an equivalent degree.

These mixtures were heated for four hours and the results are shown in Table VIII.

TABLE VIII.

0·5 $Cr_2O_3 : Na_2CO_3 :$ 0·5 Fe_2O_3 = 1 : 0·65 : 1·72		0·5 $Cr_2O_3 : Na_2CO_3 :$ 0·5 Fe_2O_3 = 1 : 1 : 1·4	
Temperature °C	Percentage of chromate	Temperature °C	Percentage of chromate
665	59·2	670	75·9
700	59·1	680	82·6
...	...	700	84·5
...	...	765	87·8
...	...	780	89·6
...	...	810	89·4
...	...	825	89·4
...	...	955	90·0
...	...	1000	90·0

The heating at 955° and 1,000° was for three hours only.

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[1] E.P. 5086. 1888.

[2] E.P. 20, 168. 1895.

In the case of mixture (*a*) the formation of chromate is more rapid than when no ferric oxide is present, as may be seen by comparison with Table VI. This is probably due to the increased porosity of the mass. Ferric chromate does not exist at 700°, so that the maximum possible yield of chromate would be only 65 per cent. The reaction is therefore not quantitative in four hours at 700°.

In the case of mixture (*b*), where one equivalent of alkali is present and a quantitative yield is possible, the maximum yield found is 90 per cent. The reaction is analogous to the one in which one equivalent of calcium oxide is used, (Cf. Table I, p. 55) but it is more rapid.

A third mixture (*c*) was next made corresponding with the one for which the results have been given in Table VII, but in which half the calcium oxide was replaced by ferric oxide so that the composition was 0·5 Cr_2O_3: Na_2CO_3: CaO; 0·5 Fe_2O_3 = 1 : 0·65 : 0·86 : 0·86. On heating this for four hours the results shown in Table IX were obtained.

TABLE IX.

0·5 Cr_2O_3 : Na_2CO_3 : CaO : 0·5 Fe_2O_3 =
1 : 0·65 : 0·86 : 0·86.

Temperature °C.	Percentage of chromate.
660	91·9
675	95·6
705	99·1
710	100·0
765	99·2
780	98·7
815	99·1
895	99·1
940	99·4

Quantitative yields are readily obtained, but the reaction takes place a little more slowly than in the case of the similar mixture containing only lime, as may be seen by the slightly smaller yields at the lower temperatures.

From these three examples it appears that ferric oxide plays the part of an inert filler. As such it promotes the reaction, when sodium carbonate is the only alkali, by increasing the surface and preventing fusion; with calcium oxide it acts as a diluent and slightly reduces the rate of the reaction. At the same time this reduction is not so great as to prevent the use of ferric oxide as a partial substituent for calcium oxide for economic reasons in technical work.

CHROME IRON ORE

A number of experiments have been carried out dealing with the formation of chromates from chrome iron ore, but it is not proposed to discuss these in the present paper. The following typical experiment, however, is given in order to show the difference between the behaviour of chromium sesquioxide and chromite when heated with alkalis.

A mixture was made using finely ground ore (containing 50 per cent. Cr_2O_3) sodium carbonate and calcium oxide in the proportions previously used for pure chromium sesquioxide. The results obtained on heating for four hours are shown in Table X and illustrated by the curve C in Fig. I.

TABLE X.

Chromite + Na_2CO_3 + CaO. 0·5 $Cr_2O_3 : Na_2CO_3 : CaO = 1 : 0·65 : 1·72$.

Temperature °C.	Percentage of chromate.	Temperature °C.	Percentage of chromate.
650	8·9	825	62·5
665	12·5	840	77·8
690	23·8	865	92·3
735	36·4	875	92·3
765	43·0	915	92·6
795	49·9	940	93·1
810	49·9	960	93·1
825	51·5	...	...

From these figures it may be seen that the reaction is slow below 800° and that the percentage of chromate suddenly increases at about 825°. As a similar phenomenon does not occur when the pure oxide is used it appears that a compound, presumably $FeO.Cr_2O_3$, present in the mineral is rapidly decomposed at this temperature with liberation of Cr_2O_3 which is then converted into chromate.

MAGNESIUM CHROMATE.

Experiments similar to those with calcium oxide were carried out with mixtures of chromium sesquioxide and magnesium oxide and with magnesium chromate. The results using equivalent proportions are shown in Table XI and with two equivalents of magnesium oxide in Table XII, the time of heating being four hours except in three cases marked with an asterisk in which it was 5·5 hours.

TABLE XI.

$0{\cdot}5\ Cr_2O_3 : MgO = 1 : 1$		$Mg\ Cr\ O_4$	
Temperature °C	Percentage of chromate	Temperature °C	Percentage of chromate
545*	0·9	550	87·4
565*	0·8	560	77·2
575	0·4	585	67·3
585	0·4	645	17·3
590*	0·7	655	3·0
625	0·4	685	0·5
650	0·5	695	0·5
895	0·7	...	...

TABLE XII.

$0{\cdot}5\ Cr_2O_3 : MgO = 1 : 2$		$MgCrO_4 + MgO$	
Temperature °C	Percentage of chromate	Temperature °C	Percentage of chromate
510	1·9	600	54·9
530	2·1	660	1·4
550	2·1	700	1·0
560	1·8	940	1·3
585	2·0	...	...
660	0·5	...	...
670	0·5	...	...
705	0·2	...	...
710	0·2	...	...
895	0·4	...	...

These results show that magnesium chromate is almost completely decomposed on heating to 650°. It also decomposes appreciably at 550°, but the experiments are not comprehensive enough to show whether the decomposition is complete at this temperature if the period of heating is sufficiently prolonged, or whether an equilibrium is established as in the case of calcium chromate.

A final experiment was carried out with a mixture of magnesium and chromium oxides with the addition of sodium carbonate in the proportion of 0·65 equivalent to 1 equivalent of chromium oxide. The time of heating was four hours below 800° and three hours above this temperature. The results are shown in Table XIII.

TABLE XIII.

$0{\cdot}5\ Cr_2O_3 : Na_2CO_3 : MgO = 1 : 0{\cdot}65 : 1{\cdot}72$

Temperature °C	Percentage of chromate	Temperature °C	Percentage of chromate.
670	65·0	790	65·2
710	65·0	810	64·1
715	65·0	1020	61·1
745	64·8	1060	62·1

From these it may be seen that the sodium carbonate combines with the chromium oxide quantitatively to form chromate up to a temperature of 800°. Above this temperature there appears to be slight decomposition. As might be expected from the previous results, the magnesium oxide does not appear to influence the formation of chromate.

Although chromium sesquioxide readily forms chromate with sodium carbonate in presence of magnesium oxide, the same does not appear to be the case when the magnesium and chromium are initially combined. On several occasions when analysing the insoluble magnesium chromites mentioned later by fusing with sodium carbonate, great difficulty was experienced in decomposing the material completely. This fact may be of technical importance as magnesia is usually present in chromite, but the problem has not, so far, been investigated in detail.

As several observers[1] have stated that definite chromites are formed on heating magnesium chromate, some of the above products were analysed, and a few additional experiments were carried out with

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[1] cf. Abegg. *Handbuch der anorganischen Chemie*, 1921, 6, 126.

the special object of examining the composition of the residue. It was found that if the heated products were boiled with dilute hydrochloric acid (1 : 1), magnesium oxide could be removed and an insoluble residue left. After several extractions, solutions were obtained free from magnesium and the residue was then washed, dried and analysed by fusion with sodium carbonate and determination of the magnesium and chromium. The first series of experiments in which magnesium chromate was heated for five hours, gave the results shown in Table XIV, for the ratio $MgO : Cr_2O_3$ in the insoluble residue.

TABLE XIV.

Magnesium chromate			
Temperature °C	$MgO : Cr_2O_3$	Temperature °C	$MgO : Cr_2O_3$
635	1·76	830	1·31
685	1·77	910	1·35
830	1·41	910	1·28

These figures, although somewhat irregular, indicate that with increase of temperature the ratio $MgO : Cr_2O_3$ decreases. This confirms to some extent the results of Viard,[1] who found that at incipient red heat the compound $2\ MgO.\ Cr_2O_3$ was formed, while on increasing the temperature indefinite bodies with a lower proportion of magnesium oxide resulted, until at 900° and above the compound $5\ MgO,\ 4\ Cr_2O_3$ was the sole product.

Although it is evident that the proportion of magnesium oxide decreases with rise in temperature for a constant time of heating, it does not follow that the figures in Table XIV represent a state of equilibrium, consequently further experiments were carried out in which the heating was prolonged until an approximately constant value was reached. In one series of experiments pure magnesium chromate was heated, in the other, a mixture of magnesium chromate and magnesium oxide; in both cases the temperature was 700° and the results are given in Table XV.

From these experiments it is evident that equilibrium is slowly attained. The tendency in the case of pure magnesium chromate appears to be to form Viard's compound, $5MgO,\ 4Cr_2O_3$, a result which was confirmed by two experiments made at 900° for five and ten hours. These gave ratios 1·24 and 1·25 respectively. The high values in

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[1] *Compt. rend.*, 1891, 112, 1003.

TABLE XV.

Magnesium chromate.		Magnesium chromate and Magnesia.	
Time in hours.	$MgO : Cr_2O_3$	Time in hours.	$MgO : Cr_2O_3$
10	1·58	...	...
24	1·37	24	1·27
48	1·26	48	1·20
96	1·32	96	1·20

Table XV for ninety-six hours and in Table XIV for the temperature 910° are possibly due to incomplete extraction of magnesium oxide from the product after heating.

The addition of magnesium oxide appears to facilitate elimination of magnesia. The final product has the formula $6MgO, 5Cr_2O_3$ but the evidence is not sufficient definitely to prove the existence of such a compound.

SUMMARY.

1. Pure calcium chromate, when heated in air, begins to decompose at about 1,000°C. and gives off oxygen.

2. The addition of calcium oxide to the calcium chromate lowers the temperature of decomposition; and in the presence of 0·1 molecular proportion of lime appreciable decomposition occurs at 800°C.

3. Mixtures of calcium oxide and calcium chromate do not decompose completely, even when heated to 1,300°C. The quantity of chromate in the product decreases as the temperature is raised, but there is no evidence of the formation of definite compounds. At a given temperature the decomposition is greater the greater the proportion of calcium oxide. It appears probable that a series of solid solutions is formed.

4. The fact that the decomposition products mentioned above are in equilibrium has been confirmed by heating mixtures of calcium oxide and chromium sesquioxide. If the proportion of calcium to chromium is the same as in a similar mixture of calcium oxide and calcium chromate, the products obtained on heating to the same temperature (above 800°) contain almost the same percentage of chromate.

5. Mixtures of calcium oxide and chromium sesquioxide react to form chromate from about 600°C. upwards. The reaction is much more rapid if excess of calcium oxide is present.

6. Sodium chromate may be heated to 1,000°C. without decomposition.

7. A mixture of sodium carbonate and chromium sesquioxide gives an almost quantitative yield of chromate when heated for four hours at 755°, i.e., about 50° below its melting point.

8. By the addition of calcium oxide to a mixture of sodium carbonate and chromium sesquioxide a quantitative yield of chromate may be obtained at 700° in less than four hours. Above 1,050° there is slight decomposition of the chromate, but the reaction is complete in five minutes.

9. Ferric oxide acts as an inert filler when added to any of the above mixtures.

10. Chromite is only slowly attacked by a mixture of sodium carbonate and calcium oxide below 800°. At 850° the reaction is rapid, and the mineral then behaves similarly to pure chromium sesquioxide.

11. Magnesium chromate is almost completely decomposed at 650° yielding chromites.

12. The reaction between magnesium oxide and chromium sesquioxide at temperatures below 600° is very slow and appreciable quantities of chromate cannot be obtained in five hours.

13. On prolonged heating at 700° or 900°, magnesium chromate yields a substance insoluble in hydrochloric acid and corresponding with the formula $5MgO, 4Cr_2O_3$, whereas a mixture of magnesium chromate and magnesium oxide in equimolecular proportions under similar conditions gives $6MgO, 5Cr_2O_3$.

The experiments detailed above constitute the first part of the investigation and the work is being continued particularly with reference to the effect of the surrounding gas upon the equilibrium.

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