REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XIX—SYNTHESIS AND DECOMPOSITION OF CALCIUM CHROMATE

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INTRODUCTION

Similarity in the thermal decomposition of chromic acid and its salts has been brought out by the results of several investigations Datar and Jatkar (This Journal 1939, **22A,** 119) have shown that chromium trioxide decomposes in stages with the formation of oxides $6CrO_3\ Cr_2O_3$, $4CrO_3\ Cr_2O_3$, $3CrO_3\ Cr_2O_3$ and $2CrO_3\ Cr_2O_3$ at intermediate decomposition, the compounds at the various stages being characterised by distinctive rates of decomposition The basic chromium chromates corresponding to all these oxides, possessing definite equilibrium decomposition pressures have also been prepared (*Ibid*, Parts II, IV, VI, VII, VIII, X, XI, XIII, XIV, XV, XVI and XVIII) But although the existence of the higher decomposition stages at 66 6%, 75% and 80% was not indicated in the thermal decomposition of chromium trioxide, the formation of the corresponding basic chromium chromates has been reported though data is conflicting and incomplete, (Parts III, V and VII) Athavale and Jatkar expressed their doubts regarding the individuality of these compounds and suggested that the compounds formed when the pure chromates decomposed to 66 6% and 75% stages might be identical to the compounds formed at the lower stages in the decomposition of the chromates in presence of the oxides Datar and Jatkar assigned structural formulæ to these compounds on the consideration of a number of indications in the previous results in support of their individuality It is necessary, therefore, to reinvestigate the decomposition of the chromates in order to ascertain the identity of the compounds formed in the lower and higher stages of the decomposition of the chromates of calcium, strontium and barium

In this investigation calcium chromium chromates are prepared by the decomposition of calcium chromate in stage as well as by the stagewise oxidation of mixtures of chromic oxide and calcium oxide and their identity has been thoroughly established

EXPERIMENTAL

The apparatus and the experimental procedure was the same as described previously

In the oxidation experiments, oxygen prepared by heating pure crystals of potassium permanganate was admitted into the apparatus through a phosphorus pentoxide tube An estimation of volume of gas introduced was always made by the measurement of pressure it produced To avoid the error in pressure measurements at high temperatures owing to the extremely uneven temperature of the reaction tube, which retained a major portion of gas, oxygen was usually admitted in the apparatus at room temperature, when a very accurate estimation of the total quantity of gas introduced could be made from pressure measurements The apparatus was also calibrated for estimating roughly volume of gas in the apparatus at intermediate stages of the reaction by admitting known volume of gas at different temperatures and measuring the pressures produced The estimation thus obtained was sufficiently accurate for the required purpose

Accurate and reliable results on the equilibrium pressures of calcium chromium chromates are necessary in order to determine the identity of the compounds produced in the decomposition of $CaCrO_4$ and $12CaO8CrO_3$, particularly as the decomposition pressures of the compounds $12CaO6CrO_3Cr_2O_3$, $9CaO4CrO_3Cr_2O_3$ and $15CaO6CrO_3\,2Cr_2O_3$ produced at the intermediate decomposition of $12CaO8CrO_3$ are very near each other (*cf* part XV) Very accurate measurements of the characteristic vapour pressures of these compounds prepared by the oxidation of the mixtures of chromic oxide with calcium oxide were undertaken in order to supplement and confirm the previous data

Oxidation of a mixture of chromic oxide with calcium oxide (1 3 mols)—A mixture of one mol of chromic oxide with 3 mols of calcium carbonate was heated in vacuum The decomposition started at about 300° On keeping at constant temperature, carbon dioxide initially evolved was absorbed back though extremely slowly and the final pressures were identical to those of calcium carbonate viz, 9 0 mm at 630° and 34 0 mm at 746° The carbonate was completely decomposed by evacuation at 1000°

$6CaO\ 2CrO_3Cr_2O_3$—The system was cooled to the room temperature and oxygen was admitted into the apparatus sufficient for about 33 3% oxidation, the complete oxidation being supposed to take place when the chromite was completely converted into basic chromate

The oxidation started at low temperature, proceeding with an appreciable rate at 480° The pressure of oxygen over the system dropped at the rate of about 0 3 mm per minute at that temperature The rate of oxidation increased with rise of temperature and at constant temperature was proportional to pressure of oxygen in the gas phase The reaction in one of the experiments was carried out between 500° and 600° for 28 hours to find out whether slow oxidation at low temperature produced a different set of compounds As no such difference in the process of oxidation by change of temperature was observed, the oxidation was usually carried out at high temperature, when the reaction occurred with rapidity When the amount of oxygen in the gas phase was considerably reduced, further oxidation proceeded very slowly and it was found suitable to remove the gas from the apparatus before raising the temperature for the determination of the equilibrium decomposition pressures of the oxidation product. Usually the system was kept for a long time at high temperature to avoid any spurious reactions vitiating the equilibrium pressure measurements

The decomposition pressures of the compound produced when the system had undergone 31% oxidation, are given in table I

TABLE I

Decomposition pressures of $6CaO\ 2CrO_3Cr_2O_3$

Temp °C	Pressure mm	Q Cals
1026	0 44	68 2
1051	0 56	68 9

$15CaO\ 6CrO_3\ 2Cr_2O_3$—The system was cooled to the room temperature and more oxygen was admitted for further oxidation The oxidation was rapid at 550° The decomposition pressures of the product at 57% oxidation are given in table II

TABLE II

Decomposition pressures of $15CaO\ 6CrO_3\ 2Cr_2O_3$

Temp °C	Pressure mm	Q Cals
997	1 72	63 1
1026	3 28	63 0
1049	3 64	63 9
1061	4 16	(64 2)

$9CaO\ 4CrO_3\ Cr_2O_3$—The decomposition pressures of the further oxidation products at 62% and 66% oxidation are given in table III

The decomposition pressures of the products at 62% and 66% oxidation are same and show the identity of the compound produced at the two oxidation stages

$12CaO\ 6CrO_3Cr_2O_3$—The oxidation was further proceeded to 70% stage The oxidation in this case started at about 550° The decomposition pressures of the product at this stage are given in table IV

TABLE III

Decomposition pressures of $9CaO\ 4CrO_3\ Cr_2O_3$

62% oxidation			66% oxidation		
Temp °C	Pressure mm	Q Cals	Temp °C	Pressure mm	Q Cals
901	1.04	(59.23)	962	1.70	61.32
942	1.36	(60.60)	983	2.36	61.62
975	2.56	60.98	1006	2.84	62.22
999	2.90	61.93			
1027	4.08	62.50	1044	4.60	(63.08)
1046	4.88	(63.02)			

TABLE IV

Decomposition pressures of $12CaO\ 6CrO_3\ Cr_2O_3$

Temp °C	Pressure mm	Q Cals
896	1.20	58.61
916	1.84	58.66
946	2.30	59.73
972	2.92	(60.50)
1010	3.68	(61.89)

$12CaO\ 8CrO_3$.—On admitting oxygen, the reaction started at about 550°. When the oxidation reached 85% stage, the reaction was very slow above 800°, further oxidation being possible only at lower temperatures. The decomposition pressures of the products at 88% and 100% oxidation are given in table V.

TABLE V

88% Oxidation		100% Oxidation	
Temp °C	Pressure mm	Temp °C	Pressure mm
725	1 00	632	2 50
771	6 08	671	3 20
815	17 50	760	5 90
836	29 10	810	24 0
895	42 0	824	30 0

It will be seen that the oxidation of chromic oxide in presence of calcium oxide (1 3 mols) takes place with the formation of all the basic chromium chromates which occur in the decomposition of $12CaO\ 8CrO_3$, the corresponding oxidation stages occurring at 50%, 60%, 66 6% and 75% oxidation Thus the vapour pressures of $6CaO\ 2CrO_3\ Cr_2O_3$ are shown by the system between 0 and 50% oxidation, of $15CaO\ 6CrO_3\ 2Cr_2O_3$ between 50% and 60% oxidation, of $9CaO\ 4CrO_3\ Cr_2O_3$ between 60% and 66 6% oxidation and of $12CaO\ 6CrO_3\ Cr_2O_3$ between 66 6 and 75% oxidation Further oxidation of $12CaO\ 6CrO_3,Cr_2O_3$ produces $12CaO\ 8CrO_3$ which dissociates into calcium chromate and calcium oxide The product at the last stage of oxidation shows higher decomposition pressures probably owing to the formation of $2CaO\ CrO_3$ to a certain extent

Fig 1 shows the reliable values for the equilibrium decomposition pressures of the intermediate compounds formed both in the synthesis and the decomposition of calcium chromate determined in the previous experiments and confirmed in a series of experiments which follow

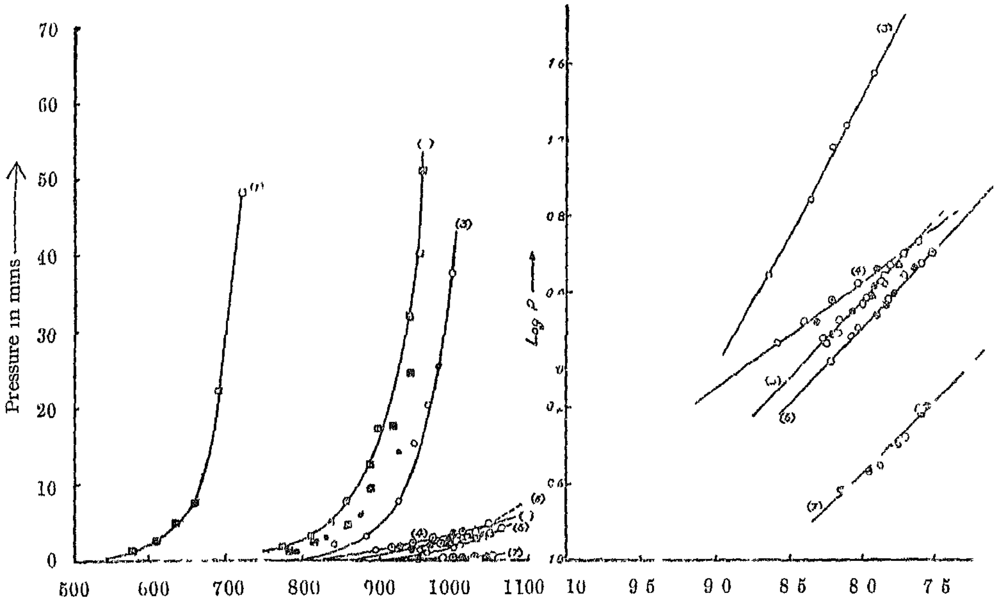

FIG 1

SYNTHESIS AND DECOMPOSITION OF CALCIUM CHROMATE

(1) Decomposition pressures of 2CaO.CrO$_3$

(2) Decomposition pressures of CaO.Cr$_2$O$_3$.CrO$_3$

(3) Decomposition pressures of 12CaO.8CrO$_3$

(4) Decomposition pressures of 12CaO.6CrO$_3$.Cr$_2$O$_3$

(5) Decomposition pressures of 9CaO.4CrO$_3$.Cr$_2$O$_3$

(6) Decomposition pressures of 15CaO.6CrO$_3$.2Cr$_2$O$_3$

(7) Decomposition pressures of 6CaO.2CrO$_3$.Cr$_2$O$_3$

⊠ Decomposition pressures of CaCrO$_4$+MgO

● Decomposition pressures of CaCrO$_4$ (Athav Jatkar)

○ Decomposition pressures of calcium chromium ch (obtained in the decomposition of calcium chro

⊙ Decomposition pressures of calcium chromiu mite (obtained in the oxidation of Cr$_2$O$_3$+3Ca(

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⊖ Decomposition pressures of calcium chromi mite (obtained in the oxidation of Cr$_2$O$_3$+2Ca(

Oxidation of a mixture of chromic oxide with calcium oxid (1 : 2 mols.)—In order to decide whether similar set of compounds i also produced when the proportion of calcium oxide in the mixture i reduced, similar experiments were conducted with a mixture c chromic oxide with two molecules of calcium carbonate containin chromium and calcium in the same ratio as existing in calciu chromate

TABLE VI

Decomposition pressures of calcium chromium chromates

Chromium chromate	Oxidation Stage	Decomposition pressures		
		Temp °C	Pressures mm	Q Cals
$6CaO\ 2CrO_3\ Cr_2O_3$	10%	1022	0 40	68 22
		1055	0 66	68 74
	25%	983	0 30	(66 76)
		1009	0 40	67 48
		1045	0 60	68 50
	33%	955	0 24	(65 72)
		1018	0 42	67 85
$15CaO\ 6CrO_3\ 2Cr_2O_3$	40%	954	1 08	(61 98)
		992	1 92	62 55
		1005	2 20	62 79
		1014	2 56	63 04
		1041	3 60	(65 03)
$9CaO\ 4CrO_3\ Cr_2O_3$	44%	944	1 56	(60 54)
		967	2 08	61 06
		991	2 80	61 56
		1040	5 00	62 65
		1049	5 48	62 88
$12CaO\ 6CrO_3\ Cr_2O_3$	50%	929	1 76	59 47
		996	3 60	(61 22)
$12CaO\ 8CrO_3 +$ $CaO\ Cr_2O_3\ CrO_3$	62 5%	801	1 24	. .
		834	2 40	
		933	10 80	.

A mixture of chromic oxide and calcium carbonate (1 2 mols) was heated in vacuum The reaction started at about 300° The decomposition pressures of the mixture particularly at high temperatures were comparable to those of calcium carbonate viz , 18 mm at 701° and 60 mm at 755° The carbonate was completely decomposed by evacuation at 990° The oxidation was carried out in stages and the decomposition pressures of the products at different oxidation stages were measured under equilibrium conditions taking all the precautions mentioned in the last experiment The decomposition pressures at different stages are given in table VI

The comparison of the decomposition pressures show the identity of the compounds formed with those produced during the oxidation of chromic oxide in presence of 3 mols of calcium oxide The mixture contains inadequate amount of calcium oxide for the complete formation of the basic chromium chromates The results indicate that whole of the base enters into combination with two thirds of the total chromic oxide producing the basic chromite $3CaO\ Cr_2O_3$, which reacts with oxygen to produce the compounds $6CaO\ 2CrO_3\ Cr_2O_3$, $15CaO\ 6CrO_3\ 2Cr_2O_3$, $9CaO\ 4CrO_3\ Cr_2O_3$, $12CaO\ 6CrO_3\ Cr_2O_3$ and $12CaO\ 8CrO_3$ at 33 3%, 40%, 44 4%, 50% and 66 6% oxidation

It has been shown that the system $Cr_2O_3 + 3CaO + O_2$ showed higher decomposition pressures at the last oxidation stage owing to the formation of $2CaO\ CrO_3$ by the reaction between calcium chromate and calcium oxide As the present mixture consists of an excess of chromic oxide, the slightly higher decomposition pressures at 62 5% oxidation indicate the formation of $CaO\ Cr_2O_3\ CrO_3$ along with $12CaO\ 8CrO_3$

Oxidation of a mixture of chromic oxide with 4 mols of calcium oxide—It has been shown in an earlier investigation (part XV) that calcium chromate reacts with calcium oxide forming $2CaO\ CrO_3$, which decomposes to $4CaO\ Cr_2O_3$, without producing any compounds at intermediate decomposition The basic chromite $4CaO\ Cr_2O_3$ is however not produced in the reactions between chromic oxide and 4 mols of calcium oxide, but the oxidation proceeds with the formation of $3CaO\ Cr_2O_3$ in stages in accordance with the results of the experiments already described

A mixture of chromic oxide with 4 mols of calcium carbonate was heated in vacuum The mixture decomposed with the vapour pressures of calcium carbonate (table VII)

TABLE VII

Temp °C	Pressure mm	Temp °C	Pressure mm
352	2 56	710	26 58
413	3 38	780	76 00
604	13 40	803	112 0

Final decomposition of calcium carbonate being very slow was carried out by complete evacuation at 1000° The oxidation was carried out in stages and the decomposition pressures were measured in the manner already described The decomposition pressures are given in table VIII

TABLE VIII

Basic Chromium Chromate	Oxidation stage	Decomposition pressures		
		Temp °C	Pressures mm	Q cals
$6CaO\ 2CrO_3\ Cr_2O_3$	42%	1012	0 60	(66 6)
		1043	0 64	68 3
$9CaO\ 4CrO_3\ Cr_2O_3$	62%	984	2 20	61 8
		1009	3 28	62·1
		1022	3 66	62·5
$12CaO\ 8CrO_3+2CaO\ CrO_3$	100%	550	1 08	
		618	2·28	
		638	3 64	
		682	10 20	
		733	17 0	

The formation of $6CaO2CrO_3Cr_2O_3$ at 42% and of $9CaO\ 4CrO_3\ Cr_2O_3$ at 62% oxidation is in conformity with the results of the previous experiments The product at the last oxidation stage is a mixture of $12CaO8CrO_3$ and $2CaO\ CrO_3$ The vapour pressures of the system on complete oxidation are higher than those of a similar system containing less calcium oxide, (table V) indicating an increase in $2CaO\ CrO_3$ produced, with the addition of excess of calcium oxide The system showed vapour pressures of $12CaO8CrO_3$ on removing a small portion of oxygen indicating thereby that $2CaOCrO_3$ is produced in the reaction only in small quantities

Oxidation of a mixture of Chromic oxide with Calcium oxide (1 1 mol)—Nargund and Watson (*Ibid*, 1926, **9A**, 149) observed that the mixtures of chromic oxide with calcium oxide containing less than one atom of calcium per atom of chromium absorb oxygen at 1030°, which is given out in most of the cases completely Whereas it is obvious from the preceeding experiments that the oxidation of chromic oxide with calcium oxide in all proportions produce the basic chromium chromates, which are comparatively stable

A mixture of chromic oxide with calcium carbonate (1 1 mol) was decomposed in vacuum The carbonate was completely decomposed and the oxidation was carried out in stages The decomposition pressure measurements are given in table IX

As the amount of calcium oxide present in the mixture is one-third of that required for the complete formation of the basic chromium chromates, the formation of $12CaO\ 8CrO_3$ should be complete during the oxidation of this mixture at 33 3% stage Actually the decomposition pressures of the product at 16% oxidation indicate the existence of $12CaO\ 8CrO_3$ indicating that not whole of the oxide present is taking part in the reaction On further oxidation the formation of $CaO\ Cr_2O_3\ CrO_3$ is probable in view of the large proportion of chromium oxide in the mixture The very high vapour pressures given by the product at 30% oxidation are in accordance with the results on the decomposition of calcium chromate in presence

TABLE IX

Basic chromium chromate	Oxidation stage	Decomposition pressures		
		Temp °C	Pressure mm	Q Cals
$12CaO\ 8CrO_3$	16%	876	2 61	55 76
		912	4 80	56 20
		944	7 80	56 66
		963	19 30	55 10
	30%	788	10 82	
		876	26 60	
		1001	57 0	
		1011	87 0	

of chromic oxide where the decomposition pressures increase on keeping at constant temperature owing to the side decomposition of calcium chromate (*cf* part XVII) The results of Nargund and Watson also show the formation of an unstable system on progressive oxidation

The findings of the foregoing experiments clearly show that irrespective of the proportion of calcium oxide, the mixtures of chromic oxide and calcium oxide react with oxygen in accordance with the following scheme —

$Cr_2O_3 + 3CaO \longrightarrow 3CaO\ Cr_2O_3$

$+O_2 \longrightarrow 6CaO\ 2CrO_3\ Cr_2O_3$

,, $\longrightarrow 15CaO\ 6CrO_3\ 2Cr_2O_3$

,, $\longrightarrow 9CaO\ 4CrO_3\ Cr_2O_3$

,, $\longrightarrow 12CaO\ 6CrO_3\ Cr_2O_3$

,, $\longrightarrow 12CaO\ 8CrO_3$

,, $\longrightarrow 8CaCrO_4 + 4CaO$

and $2CaO\ CrO_3$ (excess of CaO in the mixture)

or $CaOCr_2O_3CrO_3$ (excess of Cr_2O_3 in the mixture)

Comparison of the vapour pressures for the intermediate oxidation products (*cf.* also fig. 1) establishes the identity of the compounds, the slight variation in some of the cases being due to unavoidable experimental error.

Oxidation of a mixture of $Cr_2O_3+2CaO+MgO$.—The formation of mixed calcium magnesium chromium chromates has been reported (*cf.* part XIII). The reverse reaction of the oxidation of chromic oxide in presence of calcium and magnesium oxides however, does not produce similar compounds but takes place with the formation of calcium chromium chromates.

A mixture of $Cr_2O_3+2CaCO_3+MgO$ was decomposed in vacuum. The decomposition pressures of the mixture corresponded to those of calcium carbonate viz., 16.48 mm at 676° and 82 mm at 783°. The vapour pressure of carbon dioxide dropped down on decomposition at constant temperature viz., 783°, being 72 mm after 55% decomposition of the carbonate and 34 mm after 84% decomposition of the carbonate. The carbonate was completely decomposed and the oxidation of the basic chromite was carried out in stages. The decomposition pressures of the compounds at the various stages are given in table X.

Thus the decomposition pressure measurements indicate that *addition of magnesium oxide has no effect upon the course of* the oxidation of chromic oxide in presence of calcium oxide except perhaps by way of accelerating the reaction occurring at the various stages. The decomposition pressures at the last oxidation stage are comparable to those obtained in the decomposition of mixtures of calcium chromate and magnesium oxide (*cf.* part XII).

Decomposition of Calcium Chromate.—It has been already shown that the decomposition of mixtures of calcium chromate with calcium carbonate produce calcium chromium chromates, the similar compounds also occurring in *the oxidation of chromic oxide in* presence of calcium oxide. It will further be interesting to follow the decomposition of calcium chromate in order to decide whether identical compounds also occur at intermediate decomposition.

TABLE X

Decomposition pressures of Calcium Chromium Chromates

Basic Chromium Chromate	Oxidation Stage	Temp °C.	Pressure mm	Q Cals
$6CaO\ 2CrO_3\ Cr_2O_3$	20%	981	0.56	(65.7)
		1011	0.66	(66.4)
$15CaO\ 6CrO_3\ 2Cr_2O_3$	34%	941	1.12	(61.3)
		1006	2.36	62.8
		1010	3.00	63.5
$9CaO\ 4CrO_3\ Cr_2O_3$	44%	935	1.52	(60.1)
		949	1.90	(60.3)
		985	2.28	61.8
		1001	3.36	61.8
		1022	4.12	62.2
$12CaO\ 8CrO_3 + CaOCr_2O_3CrO_3$	80%	873	4.24	
		902	7.52	
		915	11.32	
		955	22.52	
		989	42.0	

The previous workers prepared calcium chromate from calcium oxide and chromic acid. In the following experiments the chromate prepared by precipitation from a solution of calcium chloride with potassium chromate was used. The purity of the sample was about 98.5%.

Calcium chromate begins to dissociate in vacuum at about 500°. The initial pressures were not reproducible. The formation of compounds during the decomposition was decided by observing change in the decomposition pressures. The formation of compounds was indicated at about 57%, 63%, 70% and 75% decomposition The decomposition pressures at the various stages are given in table XI

TABLE XI

Decomposition pressures of calcium chromium chromates

Basic chromium chromate	Decomposition stage	Temp °C	Pressures mm	Q Cals
$12CaO\ 8CrO_4$	1%	839	1·88	(54·5)
		882	3·18	55·6
		924	7·98	55·6
		949	15·24	55·9
		964	20·24	55·3
		996	37·52	55·3
$12CaO\ 6CrO_4,Cr_2O_3$	57%	851	0·68	57·4
		892	1·40	58·0
		929	2·38	58·7
		964	3·62	59·5
$9CaO\ 4CrO_4,\ Cr_2O_3$	63%	855	0·28	(59·7)
		952	1·52	61·0
		1001	2·80	62·0
$15CaO\ 6CrO_4\ 2Cr_2O_3$	70%	962	1·52	(61·5)
		972	1·72	(61·9)
		1000	2·20	63·8
$6CaO\ 2CrO_4\ Cr_2O_3$	75%	997	0·32	67·3
		1009	0·50	(66·9)
		1029	0·64	67·4

The comparison of the vapour pressures at the different stages brings out the identity of the compounds produced on progressive decomposition with the calcium chromium chromates The formation of the basic chromium chromates is possible on the assumption of the following reactions —

$$2CaCrO_4 \rightarrow 2CaO\ Cr_2O_3 + \tfrac{3}{2}O_2 \qquad \text{I}$$

$$8CaCrO_4 + 4\ CaO \rightarrow 12CaO\ 8CrO_3 \qquad \text{II}$$

Calcium oxide required for the latter reaction is supplied by $2CaO\ Cr_2O_3$ in either of the following two ways

$$2CaOCr_2O_3 \rightarrow CaO + CaO\ Cr_2O_3 \qquad \text{III}$$

or

$$2CaOCr_2O_3 \rightarrow 2CaO + Cr_2O_3 \qquad \text{IV}$$

The results indicate that the formation of $12CaO8CrO_3$ mainly takes place by the conversion of $2CaOCr_2O_3$ to $CaOCr_2O_3$, further reduction of $CaOCr_2O_3$ to Cr_2O_3 taking place only under special circumstances such as the presence of a catalyst like magnesium oxide

It will be noticed that unless chromic oxide is produced according to the equation IV, which may combine with calcium chromate to form $CaO\ Cr_2O_3\ CrO_3$, the reaction will primarily proceed with the formation of $12CaO\ 8CrO_3$ And accordingly the vapour pressures of $12CaO\ 8CrO_3$ are shown by calcium chromate in its initial stages of decomposition The compounds $12CaO\ 6CrO_3Cr_2O_3$, $9CaO\ 4CrO_3\ Cr_2O_3$, $15CaO\ 6CrO_3\ 2Cr_2O_3$ and $6CaO\ 2CrO_3\ Cr_2O_3$ will form at 62 5%, 66 6%, 70%, and 75% decomposition The variation observed in case of the first two stages might be accounted for by suggesting the existence of reaction IV also in the first stages of decomposition.

The behaviour of the mixtures of calcium chromate with magnesium oxide which decompose with the pressures of calcium chromate to a stage at 50% decomposition (*cf* part XIII) can be explained Further reduction of $CaO\ Cr_2O_3$ to Cr_2O_3 is possible and owing to a larger supply of calcium oxide the compound $12CaO\ 6CrO_3\ Cr_2O_3$, which is produced at about 60% decomposition in the decomposition of pure calcium chromate is formed at a lower stage in the decomposition of the mixture Also the initial pressures in the decomposition of $CaCrO_4$ and of mixtures of $CaCrO_4$ with MgO are entirely different, which follows from the consideration that the decomposition pressures in the former reaction are due to the decomposition of $12CaO\ 8CrO_3$ while those in the latter reaction indicate the presence of $CaO\ Cr_2O_3\ CrO_3$

In an another experiment on the decomposition of calcium chromate the decomposition was carried out by evacuation at high temperature, i e , 1030° The pressure dropped down gradually But the vapour pressure measurements at that temperature did not indicate the formation of the basic chromium chromates until $6CaO\ 2CrO_3\ Cr_2O_3$ was formed at about 60% decomposition The results point out to the possibility of extracting more calcium oxide from $2CaOCr_2O_3$ at high temperature when the decomposition of $12CaO\ 8CrO_3$ is fairly rapid The results are in conformity with the apparent formation of $6CaO\ 2CrO_3Cr_2O_3$ at 40% decomposition of mixtures of calcium chromate and calcium carbonate (Athavale and Jatkar *Ibid*, 1938, **21A,** 119) and show that the results on the decomposition, especially at high temperatures and pressures, if not obtained under equilibrium conditions, are unreliable Similarly though the mixture of $2CaCrO_4 + MgO$ decomposes into calcium magnesium chromium chromates under proper conditions (*cf* part XIII), it decomposes with the vapour pressures of $CaOCr_2O_3CrO_3$, if sufficient time is not allowed for the formation of $8CaO\ 4MgO\ 8CrO_3$ The main difficulty in producing $8CaO\ 4MgO\ 8CrO_3$ is found in avoiding the spurious formation of chromic oxide which accelerates the decomposition of calcium chromate and entirely changes the course of the reaction

The significance of the results of Athavale and Jatkar on the decomposition of calcium chromate (*Ibid*, 1937, **20A,** 55) can now be easily understood In their study they used calcium chromate prepared from chromic acid and calcium oxide which facilitates the initial formation of $CaO\ Cr_2O_3CrO_3$ The initial pressures observed by Athavale and Jatkar for calcium chromate are thus due to $12CaO\ 8CrO_3 + CaOCr_2O_3CrO_3$ The pressures of basic chromate $12CaO\ 8CrO_3$ appeared at 50% stage Having no means for reliable temperature control and accurate pressure measurements, it was not possible for them to isolate $12CaO\ 6CrO_3Cr_2O_3$, $9CaO\ 4CrO_3Cr_2O_3$

and $\mathrm{15CaO\ 6CrO_3\ 2Cr_2O_3}$, the decomposition pressure values of which are very near and cannot be distinguished unless by elaborate measurements The decomposition pressures measured by them show the presence of $\mathrm{9CaO\ 4CrO_3Cr_2O_3}$ at 66 6% and $\mathrm{6CaO\ 2CrO_3Cr_2O_3}$ at 75% decomposition The formulae suggested by them for the compounds produced at the intermediate decomposition of calcium chromate on the basis of the composition of the total solid phase must now be modified in the light of the new results

The existence of additional compounds at different stages in the decomposition of calcium chromate is an outcome of a side reaction, the main reaction being the irreversible decomposition of calcium chromate to calcium chromite The basic chromate $\mathrm{12CaO\ 8CrO_3}$ decomposes in four stages producing $\mathrm{12CaO6CrO_3Cr_2O_3}$, $\mathrm{9CaO4CrO_3Cr_2O_3}$, $\mathrm{15CaO6CrO_32Cr_2O_3}$ and $\mathrm{6CaO2CrO_3Cr_2O_3}$ The formation of the basic chromate is restricted by addition of chromic oxide (*cf* part XVII) when decomposition of calcium chromate to calcium chromite proceeds to completion

The heats of decomposition of the several chromium chromates have been calculated from the Nernst's equation and shown in the last column in the tables Fair agreement is shown by the data calculated from the vapour pressures for the basic chromium chromates prepared by different methods

SUMMARY

The oxidation of chromic oxide in presence of calcium oxide, by supplying known volume of oxygen in stages, reveal the formation of $\mathrm{6CaO2CrO_3Cr_2O_3}$, $\mathrm{15CaO6CrO_32Cr_2O_3}$, $\mathrm{9CaO4CrO_3Cr_2O_3}$, $\mathrm{12CaO6CrO_3Cr_2O_3}$ and $\mathrm{12CaO\ 8CrO_3}$, which also occur in the decomposition of calcium chromate with calcium oxide On complete oxidation $\mathrm{2CaO\ CrO_3}$ or $\mathrm{CaO\ Cr_2O_3\ CrO_3}$ is also produced along with the basic chromate $\mathrm{12CaO\ 8CrO_3}$, the extent of the formation of the two compounds depending upon the amount of calcium oxide and chromic oxide in the mixtures The addition of magnesium oxide has no effect on the oxidation of chromic oxide in presence of calcium oxide

The reactions occurring in the decomposition of calcium chromium chromates may be represented by the following equations.

$$\tfrac{2}{3}(12CaO \cdot 8CrO_3) = \tfrac{2}{3}(12CaO \cdot 6CrO_3 \cdot Cr_2O_3) + O_2 - 55.6 \text{ Cals} \quad \text{I}$$

$$2(12CaO \cdot 6CrO_3 \cdot Cr_2O_3) = \tfrac{8}{3}(9CaO \cdot 4CrO_3 \cdot Cr_2O_3) + O_2 - 58.9 \text{ Cals} \quad \text{II}$$

$$\tfrac{10}{3}(9CaO \cdot 4CrO_3 \cdot Cr_2O_3) = 2(15CaO \cdot 6CrO_3 \cdot 2Cr_2O_3) + O_2 - 61.8 \text{ Cals} \quad \text{III}$$

$$\tfrac{4}{3}(15CaO \cdot 6CrO_3 \cdot 2Cr_2O_3) = \tfrac{10}{3}(6CaO \cdot 2CrO_3 \cdot Cr_2O_3) + O_2 - 63.1 \text{ Cals} \quad \text{IV}$$

$$\tfrac{2}{3}(6CaO \cdot 2CrO_3 \cdot Cr_2O_3) = \tfrac{4}{3}(3CaO \cdot Cr_2O_3) + O_2 - 68.1 \text{ Cals} \quad \text{V}$$

Calcium chromate decomposes irreversebly to calcium chromite, the basic chromate being produced in a side reaction. The basic chromate $12CaO \cdot 8CrO_3$ then decomposes in stages producing calcium chromium chromates. The decomposition of the chromium chromates has to be carried out at lower temperatures and pressures under equilibrium conditions to obtain reproducible and reliable results. The discrepancies in the previous results have been explained. It is concluded that chromic acid and chromates decompose in four stages at intermediate decomposition producing the chromium chromates $6CrO_3 \cdot Cr_2O_3$, $4CrO_3 \cdot Cr_2O_3$, $6CrO_3 \cdot 2Cr_2O_3$ and $2CrO_3 \cdot Cr_2O_3$ and the corresponding basic compounds respectively.

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