REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XV—DECOMPOSITION OF MIXTURES OF CALCIUM CHROMATE WITH CALCIUM OXIDE AND WITH CALCIUM CARBONATE

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INTRODUCTION

A large number of papers have been published on the decomposition of calcium chromate with calcium oxide In 1922, Nayar, Watson and Sudborough (This Journal 1924, **7**, 54) investigated the reactions between calcium oxide and calcium chromate at various temperatures in air and came to the conclusion that the addition of 0 1 equivalent of calcium oxide caused the decomposition to start at about 800°, the decomposition at 1000° being about 10%, though a pure sample of calcium chromate showed no signs of decomposition when heated up to 1000° The decomposition is obviously due to the formation of a certain compound of low stability

The results of Nargund and Watson (*Ibid*, 1926, **7**, 149) on the decomposition of the mixtures in air are in agreement with the observations of the previous workers They further studied the decomposition of $CaCrO_4+CaO$ (1 1 mol) at 900° by evacuation in stages, and observed that the decomposition was 25% when the pressure dropped down to 300 mm and 33 3% when it further dropped down to 250 mm They observed the formation of a third stage at 40%, when the pressure was reduced still further Athavale and Jatkar (*Ibid*, 1938, **21A**, 119) observed that the compounds at the different stages obtained in the decomposition of calcium chromate with calcium carbonate in place of calcium oxide are exceedingly stable, the decomposition pressures for the different stages given by them being considerably lower than those obtained by Nargund and Watson for the corresponding stages in the decomposition of calcium chromate with calcium oxide The large variation in the vapour pressure data seems to indicate that the reactions in the two cases are entirely different

Datar, Athavale and Jatkar (*Ibid*, 1939, **22A**, 111) obtained a compound $12CaO\ 6CrO_3\ Cr_2O_3$ at 25% decomposition of the chromate by the reaction between calcium chromate with calcium carbonate, the compound formation being preceded by the formation of the basic chromate 1 5CaO CrO_3 On further investigations with the mixtures of the chromate with the carbonate, it now appears that this reaction is accompanied to a certain extent by the formation and side decomposition of the other basic chromate 2CaO CrO_3

EXPERIMENTAL

The apparatus used and the experimental procedure followed was the same as *described previously* *Pure calcium oxide* was prepared by heating pure calcium carbonate at 775° for 5 hours Calcium oxide was cooled and preserved in a soda lime desiccator A mixture of 2 mols of calcium chromate with 1 mol of calcium oxide was heated in vacuum The mixture contained calcium carbonate to the extent of 0 1%, which was completely decomposed below 500° The decomposition pressures of the mixture are given in table I and graphically shown in fig 1A and 1B

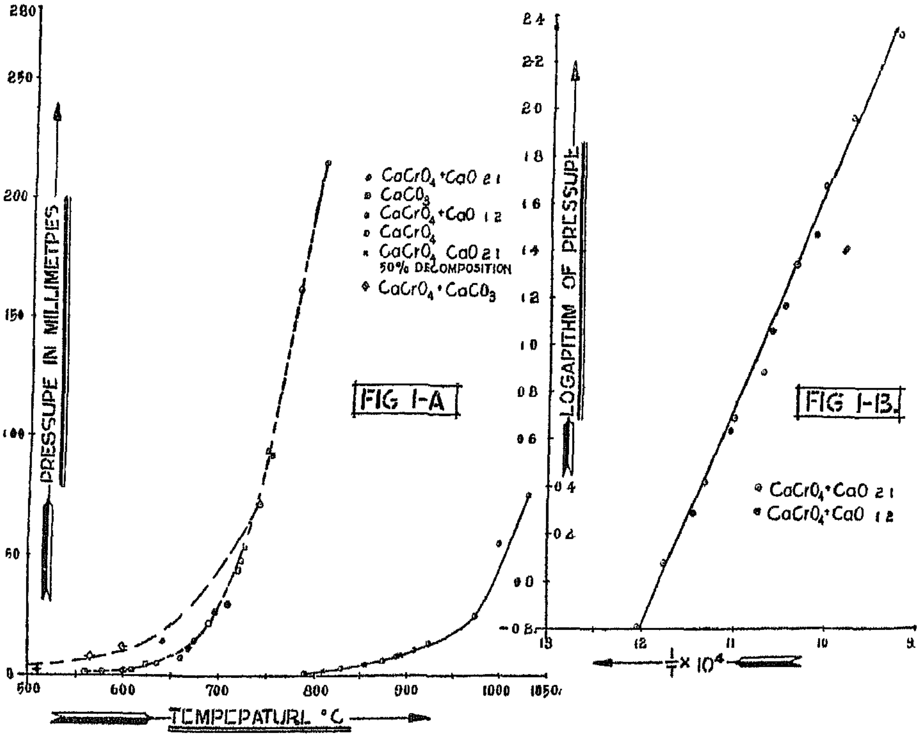


TABLE I

Author			Nargund and Watson	
Temp °C	Pressure mm	Q in Cals.	Temp °C	Pressure mm
558	0·64	41·7		
578	1·20	41·7		
610	2·64	42·0		
635	4·92	42·2		
660	7·66	42·6		
691	22·0	42·1	740	16·0
723	48·0	42·1		
750·5	94·0	42·0	795	38·0
780	162·0	42·2	835	103·0
806	216·0	42·7	855	188·0
			875	275·0
			885	356·0

In table I the values for the decomposition pressures for similar mixtures measured by Nargund and Watson have been given, which show a great variation from the results of this experiment, being comparatively lower for the same temperature. The variation may be attributed to the difference in the methods of preparation of calcium chromate. Nargund and Watson prepared calcium chromate by exact neutralisation of chromic acid with lime, while the chromate in these experiments has been prepared by precipitation from a solution of calcium chloride by potassium chromate.

On decomposition the system showed the same vapour pressures of the original mixture at 14%, 25% and 33·3% decomposition of the chromate On further decomposition to the 40% stage a gradual drop in the pressure values at the various temperatures was observed The results are given in tables II and III

TABLE II

14% decomposition		25% decomposition		33 3% decomposition	
Temp °C	Pressure mm	Temp °C	Pressure mm	Temp °C	Pressure mm
571	0 72	578	0 92	631	3 52
616	2 80	645	4 78	646	3 66
667	10 00	680	12 96		

The mixture was further decomposed and at about 50% decomposition the pressure values obtained were identical with those of calcium chromate

TABLE III

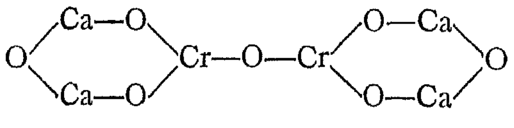
40% decomposition				53% decomposition	
A		B			
Temp °C	Pressure mm	Temp °C	Pressure mm	Temp °C	Pressure mm
647	0 60	703	1 84	810	2 04
743	2 90	748	4 60	855	4 12
777	8 24	769	16 04	893	8 40

In table III under the heading 40% decomposition (A) the decomposition pressures when the system reached 40% decomposition have been given The measurements were repeated after cooling back to room temperature (B) The results show that the vapour pressures at 40% stage are not definite probably on account of the existence of solid solutions The formation of solid solutions being pronounced at the decomposition stages nearing 50% stage The observation of the low values for the decomposition pressures by Nargund and Watson also indicate the formation of solid solutions between the two possible basic chromates, where in the stable basic chromate is present to a greater extent The mixtures containing the chromate prepared from chromic acid and lime behave similarly to the system $Cr_2O_3+CaO+O_2$ described later

As the vapour pressures of calcium chromate appear in the decomposition of the mixture at about 50% stage, it would indicate that half of the chromate in combination with the base present has completely decomposed with the formation of 2CaO CrO_3 and the vapour pressures observed at the 50% stage were due to the decomposition of calcium chromate in excess This experiment thus shows that the formula for the basic chromate is 2CaO CrO_3 The basic chromate decomposes according to the following equation

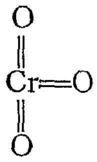
$$2(2CaO\ CrO_3)=4CaO\ Cr_2O_3+\tfrac{3}{2}O_2$$

The product of decomposition of 2CaO CrO_3 retains the whole of the base present in the basic chromate, no base being separated in the decomposition The basic chromate has therefore been represented by the formula 4RO Cr_2O_3 and by the structure given below



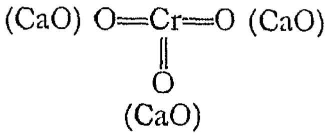
The compound 3CaO $Ca(CrO_2)_2$ or 4CaO Cr_2O_3 has been previously obtained by Moissan [*Ann Chim Phys*, 1895, (7) **4**, 142, *Bull Soc Chim*, 1902, (3), **27**, 664] by heating chromium with calcium oxide and by Dufau [*Ann Chim Phys*, 1897, (7), **12**, 263] by heating a mixture of chromic oxide and calcium oxide

The formula for chromium trioxide suggests the possibility of the formation of the higher basic chromate 2CaO $CaCrO_4$ or 3CaO CrO_3



$$\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}=O$$

Chromium trioxide



$$(CaO)\ O=\underset{\underset{\underset{(CaO)}{O}}{\|}}{Cr}=O\ (CaO)$$

Basic chromate

The previous experiment with a lower proportion of the base however did not give any indication for the existence of this compound The reactions of calcium chromate with the requisite proportion of the base also lead to the same conclusion

A mixture of 1 mol of calcium chromate with 2 mols of calcium oxide was heated in vacuum The equilibrium vapour pressures of the mixture are given in table IV and plotted in fig 1A and 1B The vapour pressures show the complete identity of the compound formed with 2CaO CrO_3

TABLE IV

Temp °C	Pressure mm	Q in Cals	Temp °C	Pressure mm	Q in Cals
498	0 28	(39 8)	669	11 48	42 31
601	1 96	42 45	680	14 72	42 37
633	4 32	42 33	711	30 00	42 46

The vapour pressures measured at the different stages of decomposition given in table V correspond to those of 2CaO CrO_3 and confirm the previous observation that the basic chromate decomposes directly to the basic chromite 4CaO Cr_2O_3

TABLE V

% decomposition	Temp °C	Pressure mm
25	672	9.24
	694	18.52
33.3	694	18.12
40	694	16.00
50	699	18.52
66.6	692	14.80
75	694	15.00
80	694	13.04
90	694	11.84
	715	20.0
96	617	3.0
	670	8.54

A drop in the pressure values is observed at the higher stages of decomposition.

It must be mentioned here that the decomposition pressures of the basic chromate $2CaO \cdot CrO_3$ are near those of calcium carbonate. The heat of decomposition calculated according to Nernst's formula from the characteristic decomposition pressures is given by the following equation

$$\tfrac{4}{3}(2CaO \cdot CrO_3) = \tfrac{2}{3}(4CaO \cdot Cr_2O_3) + O_2 - 42.1 \text{ Cals}$$

Decomposition of calcium chromate with calcium carbonate.—A mixture of calcium chromate and calcium carbonate in the ratio of 2 : 1 mols was heated in vacuum. The mixture decomposed with evolution of pure carbon dioxide, which was pumped out from the apparatus. The decomposition pressures of the mixture were then measured. The results given in table VI confirm the conclusion of Athavale and Jatkar (This Journal 1938, 11, 119) that the mixture decomposes with the vapour pressures of calcium carbonate, a small quantity of oxygen being also given out in the decomposition.

The decomposition of the mixtures started with the evolution of pure carbon dioxide, which indicated the formation of a stable basic chromate. The gas evolved on decomposition was collected in different tubes. The subsequent analysis of the gas showed that it contained carbon dioxide and oxygen in the ratio of about 2 3 1, whereas, in the formation of the compound $12CaO\ 6CrO_3\ Cr_2O_3$ at the 25% stage according to the equation

$$4CaCO_3+8CaCrO_4=12CaO\ 6CrO_3\ Cr_2O_3+4CO_2+\tfrac{3}{2}O_2$$

a definite ratio of 2 66 1 should exist between carbon dioxide and oxygen in the admixture of the gases evolved in the decomposition

TABLE VI

$CaCrO_4+CaCO_3$		$2CaO\ CrO_3$		$CaCO_3$ Landolt and Bornstein Tables (1936, **III**, 2571)	
Temp °C	Pressure mm	Temp °C	Pressure mm	Temp °C	Pressure mm
431	1 28	578	1 20	624	4 94
510	2 00	610	2 64	719 6	44 14
564	8 00	635	4 92	728	54 00
600	12 00	660	7 66	755·7	91 90
642	14 26	691	22 00		
697	27 12	723	48 00		
742	72 00	750 5	94·00		

More oxygen was given out in the decomposition probably owing to the side decomposition of the less stable basic chromate $2CaO\ CrO_3$, which is also produced in the reaction

The formation and the decomposition of the higher basic chromate in the decomposition of mixtures of calcium chromate with calcium carbonate can be represented by the equations given below

$$2CaCO_3+2CaCrO_4=2(2CaO\ CrO_3)+2CO_2$$
$$2(2CaO\ CrO_3)=4CaO\ Cr_2O_3+\tfrac{3}{2}O_2$$

The equations give the ratio of carbon dioxide to oxygen evolved in this decomposition as 1 33 1 Now if we assume that the excess of oxygen given out is supplied by the decomposition of $2CaO\ CrO_3$, the higher proportion of oxygen can be explained on the assumption that the higher basic chromate separately decomposed to the extent of 6·8%. A part of the oxide takes part in the formation of $2CaO\,CrO_3$, the remaining entering into combination with the chromate to form the lower basic chromate $1{\cdot}5CaO\,CrO_3$ which decomposes in stages. The extent of the formation of the two basic chromates in this reaction can be given as follows:

TABLE VII

Basic chromate	$CaCrO_4$ %	CaO %	decomposition %
$2CaO\,CrO_3$	6·8	13·6	6·8
$1{\cdot}5CaO\,CrO_3$	86·4	86·4	21·6
$CaCrO_4$	6·8	—	—
	100·0	100·0	28·4

If we assume that the basic chromates decompose as fast as they are formed, the complete decomposition of the carbonate should occur according to the above calculations at about 28·4%. In this experiment the corresponding decomposition of the chromate is 26%.

The product of decomposition at this stage was further decomposed along with the chromate in excess. The vapour pressure measurements at different stages viz., 25, 33·3 and 40% did not show an appreciable change, showing that the compounds formed at these stages are more or less having nearly the same stability ranges. The vapour pressures are given in table VIII.

It is very difficult to isolate the compounds of similar stability particularly in view of the existence of various compounds in the reactions. It is scarcely to be expected also that a mixture of two solids will be sufficiently intimate for the reaction to be complete. In addition the reactions also depend to a great extent on the available surface of decomposition and require a long time for reaching equilibrium particularly when the compound undergoing decomposition is

TABLE VIII

28 6% decomposition		33 3% decomposition		40% decomposition	
Temp °C	Pressure mm	Temp °C	Pressure mm	Temp °C	Pressure mm
951	1 28	921	1 0	978	1 28
978	2 22	954	1 40	1007	1 92
998	2 76	988	2 44	1032	2 80
1024	3 60	1020	3 04	1047	3 00

present in small quantities in the last stages of decomposition The vapour pressures at different stages however, show a variation on progressive decomposition showing the formation of compounds

SUMMARY

It has been found that calcium oxide possesses the remarkable property of combining with calcium chromate to form both the basic chromates $1\ 5RO\ CrO_3$ and $2RO\ CrO_3$ The higher basic chromate is obtained by heating calcium chromate with calcium oxide, the formation of the still higher basic chromate $3RO\ CrO_3$ being not detected in the reaction The observation of Datar, Athavale and Jatkar that the basic chromate $1\ 5CaO\ CrO_3$ is initially formed in the decomposition of mixtures of calcium chromate with calcium carbonate which further decomposes in stages at 25%, 33 3% and 40% decomposition has been confirmed The results however show that the decomposition is accompanied by the formation of the less stable basic chromate, which introduces many complexities in the reaction by liberation of oxygen in excess and by the formation of solid solutions It is clear from the measurements of the characteristic vapour pressures of the compounds formed at the several stages that $12CaO\ 6CrO_3\ Cr_2O_3$, $9CaO\ 4CrO_3Cr_2O_3$ and $15CaO\ 6CrO_3\ 2Cr_2O_3$ formed during the course of the reaction have similar stability ranges and very near by the same decomposition pressures

The decomposition of $2CaO\ CrO_3$ will be represented by the following thermochemical equation

$$\tfrac{4}{3}(2CaO\ CrO_3) = \tfrac{2}{3}(4CaO\ Cr_2O_3) + O_2 - 42\ 1\ \text{Cals}$$

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