REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

Part XI. Structures of Chromium Chromates.

By D. S. Datar and S. K. K. Jatkar.

The existence of a number of compounds of calcium, chromium and oxygen was first reported by Nargund and Watson (This Journal, 1926, **9A,** 149). Athavale and Jatkar, and Datar, Athavale and Jatkar (Ibid., 1937, **20A**, 55-56; 1938, **21A,** 119-129, 159-169, 179-188, 273-283; 1939, **22A,** 111-118) reported the formation of various intermediate stages in the decomposition of pure chromates, and of the mixtures of the chromates with the corresponding oxides of calcium, strontium and barium. The pure chromates decomposed in stages corresponding to 50, 66.6, 75 and 80 %, and the mixtures, in stages at 25, 33.3 and 40 % of the complete decomposition. The higher stages could not be obtained in the case of barium chromate owing to the high temperature required. The composition and the chemical properties of the compounds formed at various stages were studied and the characteristic decomposition pressures were measured. The existence of the intermediate compounds appeared possible on the basis of the several corresponding chromium oxides reported in literature. Although there has been considerable controversy regarding the individuality of the oxides, there is increasing evidence to show the existence of the various oxides of chromium corresponding to all the above stages of decomposition of the chromate. Fig. I A indicates the stepwise decomposition of the various chromium oxides as observed by different workers. Fig. I B shows the corresponding stages in the decomposition of chromates of calcium, strontium and barium and the range of temperature over which the different intermediate compounds are stable at low pressures (<0.2 mm.), as reported by Athavale and Jatkar.

In the decomposition of chromium trioxide (This Journal, 1939, **22A,** 119-126) we were able to confirm the formation of four intermediate

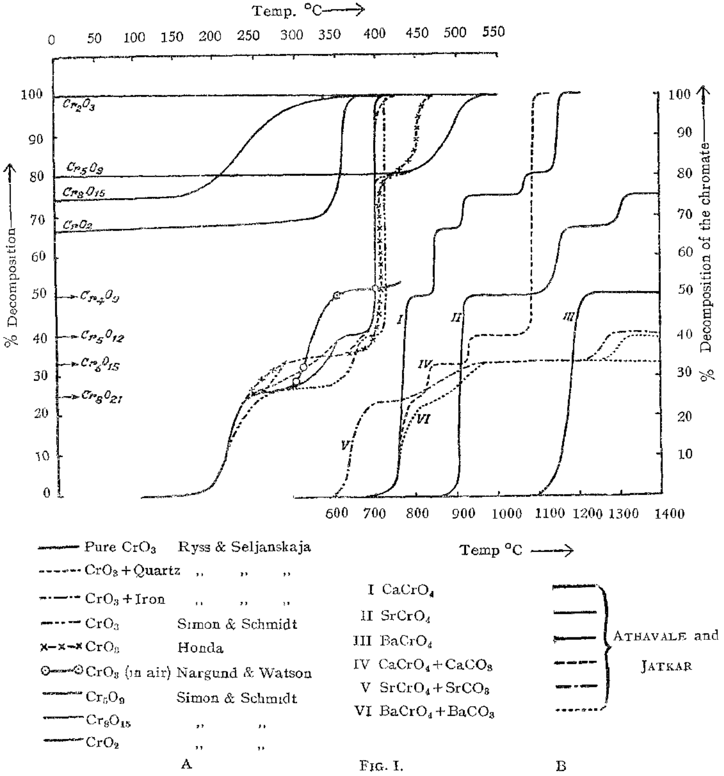


Fig. I.

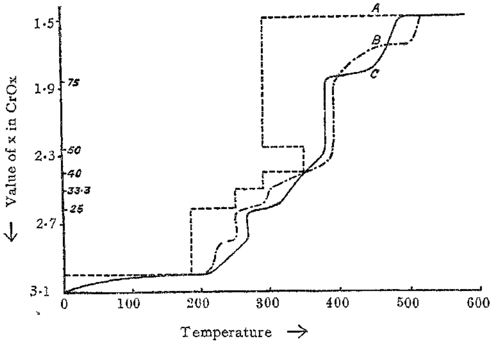
oxides of chromium, viz., Cr_8O_{21}, Cr_6O_{15}, Cr_5O_{12} and Cr_4O_9 corresponding to 25, 33.3, 40 and 50% of the complete decomposition of CrO_3, which were characterised by distinctive rates of decomposition.

Recently Cameron, Harbard and King (J. Chem. Soc. 1939, 55) carried out the decomposition of chromium trioxide and of chromium dioxide in a constant pressure apparatus and measured the volume of the gas evolved during the decomposition at different temperatures. The nature of the decomposition curve (Fig. II) was attributed to the existence of *only two* nonstoichiometric oxides ranging from $CrO_{2\cdot6}$ to $CrO_{2\cdot2}$ and from $CrO_{1\cdot9}$ to $CrO_{1\cdot7}$. The results shown graphically indicate, however, several breaks in the curve, at which the decomposition was 10% at 220°, 25% at 240°, 33.3% at 290°, 40% at 350°, 75% at 360°, 80% at 425° and 85-90% at about 440°, the decomposition being complete at 470° (Fig. II and Table 1). The decomposition curves obtained for CrO_2 also showed breaks approximately corresponding to the stages at 75, 80 and 90%. The results of Ryss and Seljanskaja (Acta Physico Chemica, 1938, **5**, 623-40) seem to indicate an additional stage at 28.6% decomposition. The variations in the two curves obtained by Cameron and co-workers show the effect of the time factor. Thus though according to our results and those of Ryss and Seljanskaja, the decomposition of CrO_3 starts at about 185°, they could not get any indication of the decomposition up to 210° as the decomposition below this temperature is very slow and is visible only after prolonged heating of the system.

We failed to obtain 66.6%, 75%, 80% and 85-90% stages in the thermal decomposition of CrO_3. The compounds formed at these stages are not perhaps characterised by reaction rates which are different from those of other stages, at the pressures investigated by us. We obtained a definite stability range for each of the oxides and found that the several products of the decomposition of CrO_3 have definite compositions. Four sharp breaks at 185, 250, 290, and 349° were obtained denoting the decomposition of CrO_3 to Cr_8O_{21}, Cr_8O_{21} to Cr_6O_{15}, Cr_6O_{15} to Cr_5O_{12} and Cr_5O_{12} to Cr_4O_9 and subsequently to Cr_2O_3 [curve A (Fig. II)].

The breaks in the decomposition curves indicated the formation of new compounds having distinctive rates of decomposition from the original compound and therefore gave the range of stability and the composition of the new compound in each case.

FIG. II.



DECOMPOSITION of CrO_3
A - Authors
B and C - Cameron, Harbard and King

The formulæ of the compounds formed at the different stages in the decomposition of chromium trioxide and other oxides are summarised in Table I. In the present paper we have suggested structures to the various compounds formed, on the basis of the properties and reactions shown by the corresponding basic chromates, in which a group of the chromium atoms are trivalent and the remaining hexavalent.

It will be apparent that the general formula of chromium chromates corresponding to the various steps observed in the decomposition of CrO_3 can be expressed by $Cr_2O_3\ nCrO_3$ and $CrO_3\ nCr_2O_3$, where the values of n are 1 to 6 in the case of the former and 1 to 4 in the latter. In addition to these, a compound $2CrO_3\ 3Cr_2O_3$ corresponding to 75% decomposition is possible.

There have been a number of papers in which the various oxides of chromium are described as chromium chromates. The methods of preparation of these oxides by partial oxidation of chromic hydroxide, by partial reduction of chromate or chromium trioxide and

TABLE I.

Chromium Chromates.

Formula	Decimal formula CrO_x	Structural formula	% decomposition of CrO_3.
CrO_3	CrO_3	CrO_3	0
	(1) $CrO_{2\cdot 93}$	$36CrO_3\ Cr_2O_3$	5.2
	(1) $CrO_{2\cdot 87}$	$20CrO_3\ Cr_2O_3$	9.1
	(1) $CrO_{2\cdot 83}$	$16CrO_3\ Cr_2O_3$	11.1
Cr_8O_{21}	(1,2) $CrO_{2\cdot 62}$	$6CrO_3\ Cr_2O_3$	25
	(1,3) $CrO_{2\cdot 57}$	$5CrO_3\ Cr_2O_3$	28.6
Cr_6O_{15}	(1,4) $CrO_{2\cdot 5}$	$4CrO_3\ Cr_2O_3$	33.3
Cr_5O_{12}	(1,5) $CrO_{2\cdot 4}$	$3CrO_3\ Cr_2O_3$	40
Cr_4O_9	(6) $CrO_{2\cdot 25}$	$2CrO_3\ Cr_2O_3$	50
Cr_3O_6	(7) CrO_2	$1CrO_3\ Cr_2O_3$	66.6
Cr_8O_{15}	(1,8) $CrO_{1\cdot 88}$	$2CrO_3\ 3Cr_2O_3$	75
Cr_5O_9	(1,9) $CrO_{1\cdot 8}$	$CrO_3\ 2Cr_2O_3$	80
	(1) $CrO_{1\cdot 71}$	$CrO_3\ 3Cr_2O_3$	85.7
	(1) $CrO_{1\cdot 66}$	$CrO_3\ 4Cr_2O_3$	88.9
Cr_2O_3	$CrO_{1\cdot 5}$	Cr_2O_3	100

[1] Cameron, Harbard and King (*Jour. Chem. Soc.*, 1939, 55).

[2] Ryss and Seljanskaja (*Acta Physico Chemica*, 1938, **5**, 623–40) and authors.

[3] Simon and Schmidt (*Z, anorg. Chem.*, 1926, **153**, 191) and Ryss and Seljanskaja (*loc. cit.*).

[4] Braun (*Jour. Prakt. Chem.*, 1863, (1) **90**, 356), Honda (*Sci. Rep. Tohoku Univ.*, 1913, **3**, 223) and authors.

[5] Traube (*Annalen*, 1848, **66**, 87), Simon and Schmidt (*loc. cit.*), Ryss and Seljanskaja (*loc. cit.*) and authors.

[6] Schukoff (*Compt. rend.*, 1908, **146**, 1396) and authors.

[7] Ball (*Jour. Chem Soc.*, 1909, **95**, 87), Ridley (*Chem. News*. 1924, **129**, 35), Popp (*Annalen*, 1870, **156**, 93), Kopp (*Chem. News*. 1864, **11**, 160), Moles and Gonzalez (*Anal. Fis. Quim*, 1923, **21**, 204), Bhatnagar, Prakash and Hamid (*Jour. Chem. Soc.*, 1938, 1428).

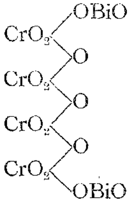
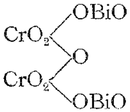
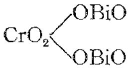
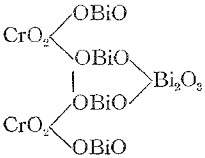
[8] Traube (*loc. cit.*), Popp (*loc. cit.*), Kopp (*loc. cit.*).

[9] Honda (*loc. cit.*), Blanc (*Bull Soc. Chem.*, 1926, (4) **39**, 718).

by the action of chromic hydroxide on chromic acid or chromate solution, show that the product is a salt of chromic acid and chromic hydroxide.

Maus (Pogg. Ann. 1827, **9**, 127) prepared Cr_6O_{15} or $Cr_2O_3\ 4CrO_3$ by evaporating a solution of hydrated chromic oxide or chromium carbonate in cold aqueous solution of chromic acid. Maus obtained CrO_2 or $CrO_3\ Cr_2O_3$ by digesting a hot solution of potassium chromate with chromic acid. Bensch (Ibid., 1842, **55**, 98) digested chromium sulphate with chromic acid, while Eliot and Storer (cf. Mellor XI, 208) used chrome alum instead of chromium sulphate.

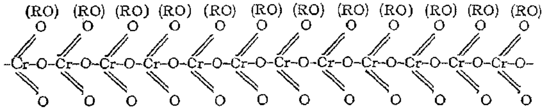
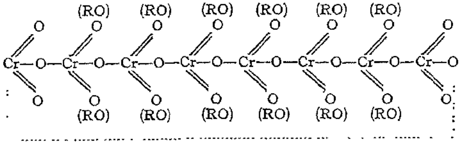
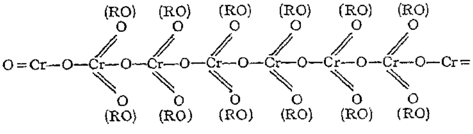
The formation of bismuthyl chromates corresponding to chromium chromates has been reported by Muir (J. Chem. Soc., 1876, **30**, 12; 1877, **31**, 645). The following bismuthyl chromates have been reported :

Chromium chromate	Corresponding bismuthyl chromates	Structural formulæ assigned by Muir
$4CrO_3\ Cr_2O_3$	$4CrO_3\ Bi_2O_3$	
$2CrO_3\ Cr_2O_3$	$2CrO_3\ Bi_2O_3$	
$CrO_3\ Cr_2O_3$	$CrO_3\ Bi_2O_3$	
$2CrO_3\ 3Cr_2O_3$	$2CrO_3\ 3Bi_2O_3$	

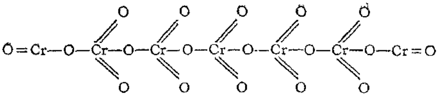
Jovitschlich (Helv. Chim. Acta. 1920, **3**, 40) gave a salt like structure to CrO_2 and represented it as Cr_2O_3 CrO_3 $7H_2O$. Support for this formula was obtained by its ready conversion into chromate and chromic hydroxide by ammonia, alkali carbonate, hydroxide or boiling water. Manchot and Kraus[2] (Ber., 1906, **39**, 3512) observed that boiling potassium and sodium hydroxide converts the dioxide into a solution of alkali chromate and a precipitate of hydrated chromic oxide.

Calcagni (Gazz. Chim. Ital. 1925, **55**, 226) prepared $Cr_2(Cr_2O_7)_3$ or $6CrO_3$ Cr_2O_3 by evaporating a solution of chromic oxide in chromic acid. Blanc (Ann. Chim. Phys., 1926, (10) **6**, 182) observed that if a salt of tervalent aluminium, iron or chromium were added to a solution of a neutral chromate and the precipitate were washed with boiling water, yellow $2Al_2O_3$ CrO_3 or brown $2Fe_2O_3$ CrO_3 or brown $2Cr_2O_3$ CrO_3 is formed, and he inferred that the oxide Cr_5O_9 or $2Cr_2O_3$ CrO_3 is a chromium chromate. He also obtained chromium dioxide by oxidation of Cr_2O_3 in air at 230° for 24 hours, to which he assigned the formula CrO_3 Cr_2O_3 based upon the products of hydrolysis.

TABLE II.

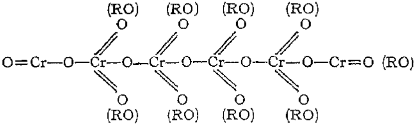
Chromium chromate	Structural formulæ
(1) 0% CrO_3 (RO CrO_3)	 I
(2) (12RO $8CrO_3$) (12CaO $8CrO_3$)(1)	 II
(3) 25% $6CrO_3$ Cr_2O_3 (12RO $6CrO_3$ Cr_2O_3) (2, 3) (12CaO $6CrO_3$ Cr_2O_3) (1)	 III

(4) 28·6%
$5CrO_3\ Cr_2O_3$



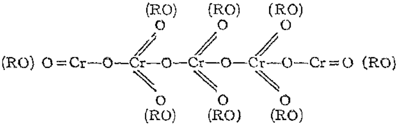
IV

(5) 33·3%
$4CrO_3\ Cr_2O_3$
$(8\ \text{or}\ 9RO\ 4CrO_3\ Cr_2O_3)$ (2,3)
$(9CaO\ 4CrO_3\ Cr_2O_3)$ (1)



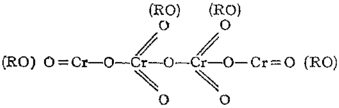
V

(6) 40%
$3CrO_3\ Cr_2O_3$
$(8RO\ 3CrO_3\ Cr_2O_3)$
$(8{\cdot}5RO\ 3CrO_3\ Cr_2O_3)$ (2)
$(6CaO\ 3CrO_3\ Cr_2O_3)$ (1)



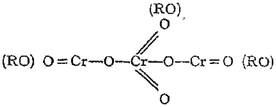
VI

(7) 50%
$2CrO_3\ Cr_2O_3$
$(4RO\ 2CrO_3\ Cr_2O_3)$ (2)
$(2CaO\ 2CrO_3\ Cr_2O_3)$ (1)



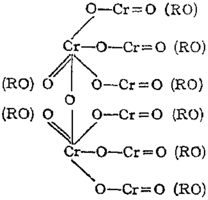
VII

(8) 66·6%
$CrO_3\ Cr_2O_3$
$(3RO\ CrO_3\ Cr_2O_3)$ (2)
$(3CaO\ CrO_3\ Cr_2O_3)$ (1)
$(3H_2O\ CrO_3\ Cr_2O_3)$



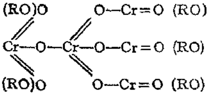
VIII

(9) 75%
$2CrO_3\ 3Cr_2O_3$
$(8RO\ 2CrO_3\ 3Cr_2O_3)$ (2)
$(8CaO\ 2CrO_3\ 3Cr_2O_3)$ (1)



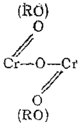
IX

(10) 80%
$CrO_3\ 2Cr_2O_3$
$(5RO\ CrO_3\ 2Cr_2O_3)$ (2)
$(5CaO\ CrO_3\ 2Cr_2O_3)$ (1)



X

(11) 100% Cr_2O_3 (1 or $2RO\ Cr_2O_3$) (1 or $2CaO\ Cr_2O_3$) (1)



XI

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[1] Nargund and Watson (loc. cit.) $[CaO—Cr_2O_3—O_2]$

[2] Athavale and Jatkar (,,)

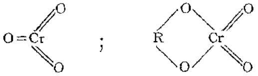
[3] Datar, Athavale and Jatkar (,,)

[2, 3] $[RO—Cr_2O_3—O_2]$

The structure of the various chromium chromates may also be represented as follows :—

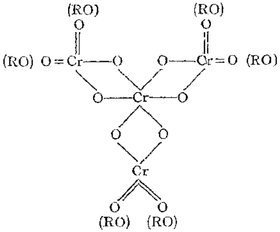
TABLE III

0% $(RO)CrO_3$



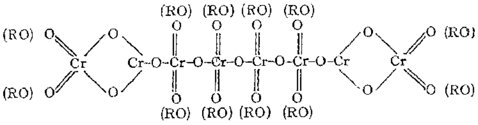
(I)a

$(12RO)\ 8CrO_3$



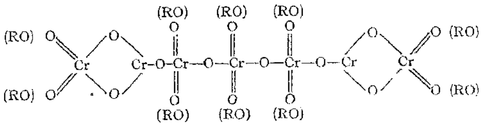
(II)a

25% $(12RO)\ 6CrO_3\ Cr_2O_3$



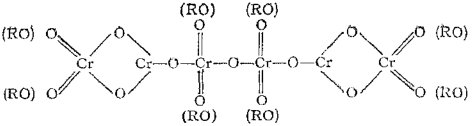
(III)a

28·6% $(10RO)\ 5CrO_3\ Cr_2O_3$



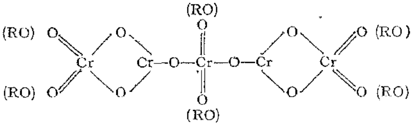
(IV)

33·3%
$(8RO)\ 4CrO_3\ Cr_2O_3$



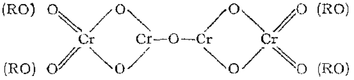
(V)a

40%
$(6RO)\ 3CrO_3\ Cr_2O_3$



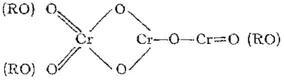
(VI)a

50%
$(4RO)\ 2CrO_3\ Cr_2O_3$



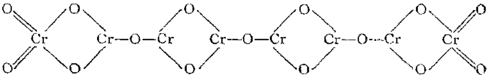
(VII)a

66·6%
$(3RO)\ CrO_3\ Cr_2O_3$



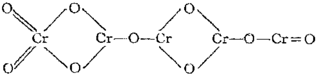
(VIII)a

75%
$(4RO)\ 2CrO_3\ 3Cr_2O_3$



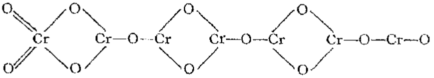
(IX)a

80%
$(3RO)\ CrO_3\ 2Cr_2O_3$



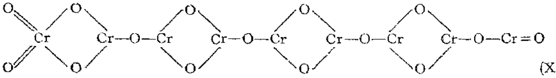
(X)a

85·7%
$(3RO)\ CrO_3\ 3Cr_2O_3$



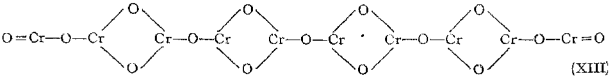
(XI)a

88·9%
$(3RO)\ CrO_3\ 4Cr_2O_3$



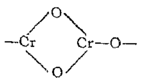
(XII)a

100%
Cr_2O_3

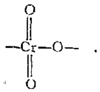


(XIII)

The structures given above are made up of the units :

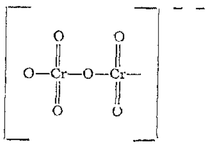


and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O- .$$

The chromium trioxide is represented by



$$\left[O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}- \right]^{--}$$

which is in agreement with the molecular weight of chromic acid in aqueous solutions.

The following facts have to be taken into account in forming the structures: (1) X-ray investigations of Cr_2O_3 show that every atom of chromium is surrounded by 6 oxygen atoms and that the metal atoms are immediately below and above the centre of the equilateral triangle formed by three oxygen atoms as shown in structure XI. (2) In CrO_3 also every chromium atom is surrounded by six oxygen atoms, forming a somewhat deformed octagon. The elementary cell of Cr_2O_3 and CrO_3 contains many molecules (Braken, *Z.* Krist, 1931, **78**, 484).

Structure I is in accordance with the X-ray findings. The decomposition of CrO_3 indicates breaks at compositions corresponding to $Cr_2O_3\ n CrO_3$, where the value of n is 36, 20, 16, 6 to 1, and is in accordance with the findings from X-ray studies that the elementary cell of CrO_3 contains many molecules. The structure of Cr_2O_3 is given by XII.

The compounds formed at the intermediate stages in the decomposition of CrO_3 have not been studied by X-ray. The structures II to X are only tentative and the formulæ represent a graphical expression of equivalent proportions of CrO_3, Cr_2O_3 and the base. The two end chromium atoms in each one of these structures are joined together to form Cr_2O_3. All the chromium atoms therefore must be arranged in a ring if an examination with X-rays would reveal that every chromium atom is surrounded by six oxygen atoms as in the case of CrO_3 and Cr_2O_3.

The proportion of the base required to form the intermediate basic chromium chromates is approximately twice the number of CrO_3 groups. When however the number of chromium atoms is not sufficient to form a ring, the end chromite groups are capable of taking up extra base (as shown in the various structures proposed).

The determination of the exact proportion of the base to form any suitable solid compound is a matter of considerable experimental difficulty, as the reactions between solids are rarely quantitative, and side reactions usually occur at the high temperatures (as found in the case of 40 per cent. stage in the decomposition of calcium chromate). The previous results were based upon the fact that breaks were shown in the curves showing the percentage decomposition with different amounts of the bases. Unfortunately these results only fix the outside limit. We have therefore discussed our experimental data on the basis of probable reactions between the various chromium chromates to which we have assigned tentative structures.

The structures fully satisfy the usual valencies of the chromium atoms, viz., 3 and 6. In all the oxides each chromium atom is joined to another through oxygen atom and the remaining oxygen atoms are attached to chromium atoms. The formation of the corresponding basic chromium chromates in the decomposition of chromates can also be easily explained, the oxide taking up base in the place where chromium atoms are joined to oxygen as shown in brackets.

In the decomposition of a mixture of the chromates with the corresponding oxides, the basic chromate is initially formed, which is unstable and is represented by the formula (II) or (IIa). It has been shown in part X that a compound $4Na_2O$ $8CaO$ $8CrO_3$ is formed in the decomposition of mixtures of calcium chromate and sodium carbonate. The four Na_2O groups probably enter the end chromate groups in (II).

25% stage.—The basic chromate on decomposition gives the 25% stage. The oxide corresponding to this stage can take up 12 molecules of the base forming 12RO $6CrO_3$ Cr_2O_3, according to both the structures (III) and (IIIa). Datar, Athavale and Jatkar (This Journal, 1939, **22A**, 111) obtained 12RO $6CrO_3$ Cr_2O_3 as the formula, in confirmation of the findings of Nargund and Watson in their study of the system CaO - Cr_2O_3 - O_2. We have already reported the formation of the compound $4Na_2O$ 8CaO $6CrO_3$ Cr_2O_3 in the decomposition of mixtures of calcium chromate and sodium carbonate, which is in agreement with the above findings. The difference between the structures (III) and (IIIa) is that the latter is a real chromium chromate structure in which the chromite is not capable of reacting with any extra base, while in the case of the former the compound can take two more moles of the base. It will therefore be interesting to determine whether the decomposition pressures of the 25% stage are altered when more basic oxide is added.

28.6% stage.—The chromium chromate corresponding to this stage has been obtained by Simon and Schmidt (Z. anorg. Chem. 1926, **153**, 191) and Ryss and Seljanskaja (loc.cit.) and was also indicated by a break in the decomposition curve given by Cameron *et al* (loc.cit.). Experiments are under way to study the decomposition of the corresponding basic chromium chromate. According to structure (IV) the basic chromate can take up a maximum of 12 moles of the base, while according to (IVa) it can take up only 10 moles.

33.3% stage.—The oxides corresponding to this stage can take up a maximum number of 10 base molecules according to structure V forming the compound 10RO $4CrO_3$ Cr_2O_3, the compound actually obtained being 9RO $4CrO_3$ Cr_2O_3. Athavale and Jatkar suggested the formation of 8SrO $4CrO_3$ Cr_2O_3 and 9SrO $4CrO_3$ Cr_2O_3. The formation of 8SrO $4CrO_3$ Cr_2O_3 does not appear to be possible as their experiments on the decomposition of the mixtures of calcium chromate with calcium oxide at two different temperatures and the decomposition of the mixtures of barium chromate with barium oxide at 1275° only indicate the formation of 9RO $4CrO_3$ Cr_2O_3. Our experiments on a mixture of

0.1 mol of strontium chromate with 0.375 mol of carbonate decomposed by evacuation to 33.3% stage, showed that the product was not completely soluble and did not indicate the formation of $8SrO\ 4CrO_3Cr_2O_3$.

Athavale and Jatkar have shown that in the decomposition of the mixtures of strontium chromate with strontium carbonate at 825° and 1070°, carbon dioxide and oxygen are evolved simultaneously and are present in the gas phase in the ratio of 2 : 1. This suggests that the course of the reaction can be shown by the following equation:

$$3RO\ CO_3 + 6RO\ CrO_3 \longrightarrow 9RO\ 4CrO_3\ Cr_2O_3 + 3CO_2 + \tfrac{3}{2}O_2.$$

Athavale and Jatkar have also shown that the compound $8SrO\ 4CrO_3\ Cr_2O_3$ has got nearly the same vapour pressure as that of $4SrO\ 2CrO_3\ Cr_2O_3$. As the decomposition curves (Fig. 1, Part VI) show that the decomposition products of mixtures of strontium chromate with strontium carbonate at 1120° are mixtures of the 33.3% and 50% decomposition stages, the above result is easily explained. A mixture of strontium chromate with strontium carbonate (2 : 1 moles) decomposes to $9SrO\ 4CrO_3\ Cr_2O_3$ and shows distinctive vapour pressures. A decomposition product of the mixture of 1 mol of $SrCrO_4$ with 0.6 mols of SrO shows pressures corresponding to those of $9SrO\ 4CrO_3\ Cr_2O_3$. However at higher temperatures the pressures correspond to those of $4SrO\ 2CrO_3\ Cr_2O_3$, which is formed in traces owing to the chromate decomposing independently.

40% stage.—The structure of the compound formed at this stage of decomposition is given by (VI) and (VIa). While the former can take a maximum number of 8 moles of the base which is nearer the experimental value, the latter can combine with only 6 moles of the base. It is interesting to note in this connection that Nargund and Watson got the corresponding calcium compound with only 6 moles of the base by decomposition of the chromate, which appears to support the formula (VIa). Athavale and Jatkar assigned a formula $17RO\ 6CrO_3\ 2Cr_2O_3$ or $8.5RO\ 3CrO_3\ Cr_2O_3$ for the 40% stage, as compared with the basic chromium chromate $8RO\ 3CrO_3\ Cr_2O_3$. The exact amount of the base cannot be determined from the nature of the decomposition curves given by Athavale and Jatkar. It may be noted that Nargund and Watson obtained the 40% stage corresponding to the formation of the compound *ca* 7.5CaO $3CrO_3$ Cr_2O_3, which was also confirmed by the oxidation of the mixture of calcium oxide with chromic oxide. The decomposition of mixtures of calcium chromate and sodium carbonate has yielded a compound of the formula $5Na_2O$ 10CaO $6CrO_3$ $2Cr_2O_3$, for which a structural formula has been given in part X of this series. A similar structure can also be given to the corresponding basic chromium chromates of calcium, strontium and barium.

In the decomposition of strontium chromate with different proportions of strontium oxide, the results seem to indicate the formation of 15RO $6CrO_3$ $2Cr_2O_3$ the excess of chromate decomposing to 75% stage as given in the following table :

Mols $\frac{SrO}{SrCrO_4}$	% decomposition	
	observed	calculated
0	75.0	75.0
0.2	61.5	61.0
0.3	53.2	54.0
0.4	46.5	47.0
0.5	42.1	40.0

As the decomposition of the mixtures of calcium chromate with calcium carbonate was made at high temperatures, and as the final pressure is not a sure indication of how far the decomposition has proceeded, the results are likely to have been vitiated by possible side reactions. The decomposition of the mixtures of barium chromate with barium carbonate is peculiar as the latter offers considerable resistance towards decomposition. At 975° the mixtures decompose with the formation of

$12BaO\ 6CrO_3\ Cr_2O_3$ (25% decomposition, pressure 1.0 mm.), which decomposes further to form the compound $9BaO\ 4CrO_3\ Cr_2O_3$ (33.3%) at the same temperature with the excess, of the base. At 1275° the compound $9BaO\ 4\ CrO_3\ Cr_2O_3$ is formed. But when the amount of carbonate present is in excess, the decomposition exceeds 33.3%. The fact that 41.8% decomposition was obtained by heating a mixture of 1 mol of the chromate with 0.7 mol of the carbonate does not indicate the formation of $17BaO\ 6CrO_3\ 2Cr_2O_3$. It appears possible that the whole of the base does not combine, particularly as, with excess of base, the decomposition proceeds further at that temperature. The basic chromate decomposes as follows :—

$$\begin{aligned} 12RO\ 8CrO_3 &\longrightarrow 12RO\ 6CrO_3\ Cr_2O_3\ (25\%). \\ &\longrightarrow 9RO\ 4CrO_3\ Cr_2O_3\ (33.3\%). \\ &\longrightarrow 15RO\ 6CrO_3\ 2Cr_2O_3\ (40\%). \end{aligned}$$

50% stage.—The structural formula of the basic chromium chromate obtained at 50% decomposition is shown by (VII) and (VIIa). Nargund and Watson obtained a compound $2CaO\ 2CrO_3\ Cr_2O_3$, while Athavale and Jatkar obtained compounds of the formula $4RO\ 2CrO_3\ Cr_2O_3$ in the decomposition of pure chromates of calcium, strontium and barium. It would appear that this chromium chromate is less stable when combined with 2 moles of the calcium oxide than with 4 moles. This point is under investigation.

The corresponding compounds cannot be obtained in the decomposition of pure chromates. Nargund and Watson studied the oxidation of mixtures of Cr_2O_3 with CaO which was insufficient for the formation of chromate, and observed that the mixtures absorb oxygen initially and then evolve oxygen, the final product being always $CaO\ Cr_2O_3$ (cf. Table XIII and XV, Part II of this series). When CaO is sufficient or in excess, the analysis of the products indicated the formation of the 50% stage.

66.6% stage.—In the decomposition of pure chromates, the compound formed at this stage, is given by the structures (VIII) and (VIIIa). The latter is a true chromium chromate structure. The hydrate of the so-called chromium dioxide $CrO_2\ H_2O$ which has been obtained by several workers is obviously represented by (VIII), CrO_3 Cr_2O_3 $3H_2O$, the water of hydration corresponding to 3(RO) in the basic compound. The decreased stability of the 66.6% stage is apparently due to the strong affinity of the base for both trivalent and hexavalent chromium. It will be interesting to study the stability of the compound with addition of one more mole of the base, which results in the initial formation of the lower decomposition stages, viz., 25, 33.3 and 40%.

75% and 80% stages.—The structures of the compounds formed at 75 and 80% decomposition are given by (IX), (IXa) and (X), (Xa). Athavale and Jatkar (loc.cit.) had tentatively suggested that the chromium chromate corresponding to the 80% stage required only 3 moles of the base on the basis of the structure (IXa). The structure IX takes up the entire amount of the base available in the decomposition products of the pure chromates. It will however be interesting to study decomposition pressures of these compounds with lower proportions of the base, which can be effected by studying the decomposition of the mixtures of the chromates with chromic oxide in varying proportions.

85.7% and 88.9% stages.—The scheme of the successive stages in the decomposition of chromium trioxide shown in Table I indicates additional stages at 85.7 and 88.9%, which are given by structures (XIa), (XIIa). Athavale and Jatkar (loc.cit.) actually obtained an arrest in the decomposition of calcium chromate at 85%. The corresponding oxides of chromium have been also indicated by the decomposition curves given by Cameron *et al.* From the structures given it is obvious that these higher stages can only be stable when the base present is lower than that given by the decomposition of pure chromates and probably occur in the decomposition of mixtures of Cr_2O_3 and chromate (*cf.* Part II, p. 162).

Although the early experiments of Nargund and Watson on the system $CaO - Cr_2O_3 - O_2$ were regarded as tentative and the decomposition pressures were very high as compared with the subsequent results, all the compounds described by them fit in with the formulæ and structures given above.

Athavale and Jatkar (loc. cit.) had raised the question, whether the compounds formed when the pure chromates decomposed to 66.6 and 75% stages were pure compounds or mixtures of the lower stages of decomposition with those of higher stages. The vapour pressure data showed that the stability range of the products formed at 66.6 and 75% stages were not appreciably different from the compounds formed at 33.3 and 40%, and the acid soluble portions from the former stages were also identical with the products of the latter stages, which were also completely soluble in acids. It is usual to regard that the products formed at the higher stages of decomposition should be more stable than those corresponding to the lower stages of decomposition. In the particular case, however, owing to the complicated structure of the chromium chromates, the stability of the compounds corresponding to 66.6 and 75% decomposition is nearly the same as that of the lower stages. As shown by us previously, the 50% stage in the decomposition of chromium chromate is actually less stable than the 40% stage, and evidence for the formation of the 66.6 and 75% stages could not be obtained at all owing obviously to the decreased stability of the compounds under the conditions of our experiment.

Athavale and Jatkar (loc. cit.) measured the vapour pressures in a very low range and their measurements were not sufficiently accurate and hence were doubtful about the identity of the products formed. In the case of calcium chromium chromates, the decomposition pressures of which are large enough to be measured accurately, the measurements of Athavale and Jatkar show that the vapour pressures of the 33.3 % and 66.6%, and 40% and 75%, stages are not identical. The argument based upon the acid soluble portions of the complicated molecules, which apparently exist in solid condition, is not also very reliable. The compound corresponding to the 50% decomposition of calcium chromate yield acid soluble portion corresponding to $10CaO$ $6CrO_3$ Cr_2O_3, while the corresponding compounds of strontium and barium give $8RO$ $4CrO_3$ Cr_2O_3. The insoluble portion is the chromite in all cases except those of 50% stages of strontium and barium, where it is Cr_2O_3, whose formation cannot be expected in the decomposition of chromates. The assumption that both the higher and lower stages are identical, also leads us to formulate an improbable scheme to explain the reactions

$$24RO\ CrO_3 \xrightarrow{50\%} 3Cr_2O_3 + 3\ (8RO\ 4CrO_3\ Cr_2O_3) + 9O_2$$

or

$$4\ (CaO\ Cr_2O_3) + 2\ (10CaO\ 6CrO_3\ Cr_2O_3).$$

$$\xrightarrow{66.6\%} 6\ (RO\ Cr_2O_3) + 2\ (9RO\ 4CrO_3\ Cr_2O_3) + 12O_2.$$

$$\xrightarrow{75\%} 7\ (RO\ Cr_2O_3) + 17RO\ 6CrO_3\ 2Cr_2O_3 + \tfrac{3}{2}O_2.$$

$$\xrightarrow{80\%} X(5RO\ CrO_3\ 2Cr_2O_3).$$

$$\xrightarrow{100\%} Cr_2O_3.$$

In the decomposition of mixtures of the chromates with the oxides, where oxide is not sufficient for the formation of the compounds corresponding to the lower decomposition stages, the decomposition occurs with incomplete formation of the lower stage and with decomposition of the remaining chromate independently. It is of interest to note in this connection that the two reactions are distinct and independent of one another depending only upon the temperature of the reaction. The mixtures of calcium chromate with calcium oxide decomposes to 33.3% and the extra chromate to 50% at 870° and 66.6% at 920° and to 40% and 75% respectively at 1030°. The basic chromate of strontium decomposes to 33.3% at 1070° and to 40% stages at 1380° when the excess of chromate decomposes to 50% and 75% stages respectively. In the case of barium chromate the basic chromate decomposes to 33.3% stage and excess of chromate to 50% at 1275°. It will be seen that the two reactions, viz., the decomposition of chromate and of basic chromate are distinct reactions.

It should be mentioned that it is possible to formulate Werner's structures of the various chromium chromates on the assumption that the chromium from Cr_2O_3 forms the central atom of the complex and that the base is placed inside the complex for saturating the auxilary valencies of the chromium, like those given to compounds like chromium sulphuric acids with analogous composition. The observation of Simon and Schmidt that in the decompositoin of the hydrates of the oxides of chromium, namely, CrO_2, Cr_8O_{15} and Cr_5O_9, both water and oxygen are evolved simultaneously, can be explained on the assumption of Werner's structures to the hydrates. Werner has shown that basic compounds can be obtained from hydrates by replacing molecules of water by the basic oxide. If the basic chromium chromates are to be represented by the Werner's structures, they would be very unstable and would dissociate into simpler molecules at higher temperatures. The intermediate compounds formed in the decomposition of chromates at high temperatures are in no way simpler than the original chromate, and the remarkable stability of the basic chromium chromates is in conflict with the assumption of the Werner's structures for these compounds.

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SUMMARY.

The thermal decompositions of chromium trioxide and of chromates of calcium, strontium and barium have shown that they decompose in a number of stages corresponding to the formation of chromium chromates having a general formula $aCr_2O_3\ bCrO_3$. Although the oxides of chromium are not characterised by any definite decomposition pressures, the corresponding chromium chromates of the alkaline earths possess characteristic decomposition pressures, which depend upon the ratio of the base to the chromium.

The probable chemical structures for the compounds obtained in the thermal decomposition of chromium trioxide and the chromates of the alkaline earths have been assigned on the basis of their properties and reactions, based upon the ordinary valencies of chromium, i.e., 3 and 6.

It will be shown in the next Part of this series that the magnetic properties of the various oxides of chromium can also be explained on the basis of the structures given in this paper.

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