9. *Non-stoicheiometric Oxides. Part I. The Oxides of Chromium.*

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A large number of oxides of chromium, intermediate between CrO_3 and Cr_2O_3 have been reported, the results of different workers being in disagreement. A general survey of the oxides of chromium has therefore been undertaken. It has been found that chromic anhydride decomposes in two stages with the formation of two non-stoicheiometric oxide ranges; $CrO_{2\cdot6}$—$CrO_{2\cdot2}$ and $CrO_{1\cdot7}$—$CrO_{1\cdot9}$. Many of the oxides reported by earlier workers have been shown to lie in one or other of these stability ranges.

Of the other oxides of chromium, the only one which appeared to be substantiated was the dioxide. Three methods of preparing the so-called dioxide have therefore been carried out, with the following results: (*a*) The substance formed by low-temperature decomposition of ammonium dichromate is shown to contain nitrogen; (*b*) the oxide formed by heating chromic hydroxide in oxygen is in the first non-stoicheiometric range above, previous workers having erroneously based their analyses on the supposition that the decomposition product of this oxide was chromic oxide, whereas, in fact, it is the second non-stoicheiometric oxide above; (*c*) the oxide formed by the action of chromic anhydride on chromic hydroxide comes in the second range above. In instance (*b*) the hydrolysis of the material has been studied.

UNTIL the end of 1933, knowledge of the oxides of the common metals was considered to be almost complete, the formulation of complex oxides normally being made in terms of the simpler members of the series; *e.g.*, Cr_5O_{12} was formulated as $3CrO_3,Cr_2O_3$, and Pb_3O_4 as $2PbO_2,PbO_2$. Klemm and Hass (*Z. anorg. Chem.*, 1934, **219**, 82) showed, however, that nickel oxide can never exist as $NiO_{1\cdot000}$. They followed the decomposition of nickel carbonate analytically and magnetically, and proved that nickel oxide has a normal paramagnetism providing that the amount of oxygen is greater than that given by the ratio Ni : O = 1 : 1·005. As soon as the amount of oxygen falls below this value, the crystal breaks up and becomes ferromagnetic owing to the liberation of metallic nickel. A similar departure from the law of constant proportions appears to be shown by cupric and ferrous oxides and by ferrous sulphide, and the authors (J., 1938, 955) have already shown that the composition of chromic oxide varies somewhat with its method of preparation. These facts receive considerable support from the work of Hägg on the tungsten bronzes (*Nature*, 1935, **135**, 874; *Z. physikal. Chem.*, 1935, **29**, 192). He showed that a large number of compounds could be prepared with the formula Na_xWO_3, where x may vary from 0·93 to 0·32. By quantitative and X-ray analyses of different specimens, he found that the length of the crystal face increased from 3·813 to 3·850 A. as more sodium was incorporated in the crystal lattice. This is to be expected, for the subtraction of the sodium ion as a sodium atom leaves a positive charge on the rest of the molecule. This charge is spread over the whole of the lattice, reducing the negative charge on the whole of the tungsten ions forming the lattice and thus lessening the repulsive force between them.

It would thus seem likely that many of the oxides of metals of variable valency are not exactly stoicheiometric compounds and may also vary slightly in composition between well-defined limits. Moreover, examination of many of the more complex oxides reported in the literature may also prove these to be non-stoicheiometric.

Oxides of Chromium.—Innumerable oxides of chromium, intermediate between CrO_3 and Cr_2O_3 have been reported, although the existence of many of them remains unconfirmed. Some of these are shown in Table I, but the earlier literature described many others.

TABLE I.

Formula.	Decimal formula.	Reference.
CrO_2	CrO_2	Ball, J., 1909, **95**, 87; Hooton, P., 1908, **24**, 27; Ridley, *Chem. News*, 1924, **129**, 35; Popp, *Annalen*, 1870, **156**, 93; Kopp, *Chem. News*, 1864, **11**, 160; Moles and González, *Anal. Fís. Quím.*, 1923, **21**, 204; Bhatnagar, Prakash, and Hamid, J., 1938, 1428.
Cr_5O_{12}	$CrO_{2\cdot4}$	Simon and Schmidt, *Z. anorg. Chem.*, 1926, **153**, 191.
Cr_5O_{13}	$CrO_{2\cdot6}$	
Cr_5O_9	$CrO_{1\cdot8}$	Honda, *Sci. Rep. Tohoku Univ.*, 1913, **3**, 223.
Cr_6O_{15}	$CrO_{2\cdot5}$	
Cr_3O_5	$CrO_{1\cdot66}$	Schukoff, *Compt. rend.*, 1908, **146**, 1396.
Cr_4O_9	$CrO_{2\cdot25}$	
Cr_8O_{15}	$CrO_{1\cdot87}$	Traube, *Annalen*, 1848, **66**, 87; Popp, *loc. cit.*; Kopp, *loc. cit.*

Various experimental methods have been developed for both the preparation and the analysis of these oxides, but apart from the work of Simon and Schmidt (*loc. cit.*) little of it is recent. It would thus seem that a new and more comprehensive study of the oxides of chromium is required, apart from all questions of non-stoicheiometry.

The principal method of studying these oxides seems to have been to follow the thermal decomposition of chromic anhydride by gravimetric means, or, in cases where new oxides have been discovered, to ignite a fixed weight of the new oxide to chromic oxide. There is often a lack of analytical data, and in all cases where these methods have been followed, no mention is made of any analysis to check the composition of the final product, assumed to be chromic oxide. There is a potential source of error here, for not only might the final product of some of these decompositions be a lower, intermediate oxide, but the very composition of chromic oxide is variable, as we have shown (*loc. cit.*). Indeed, several of the earlier workers noticed that their final product had not the bright green colour of Cr_2O_3, but a dull grey-green.

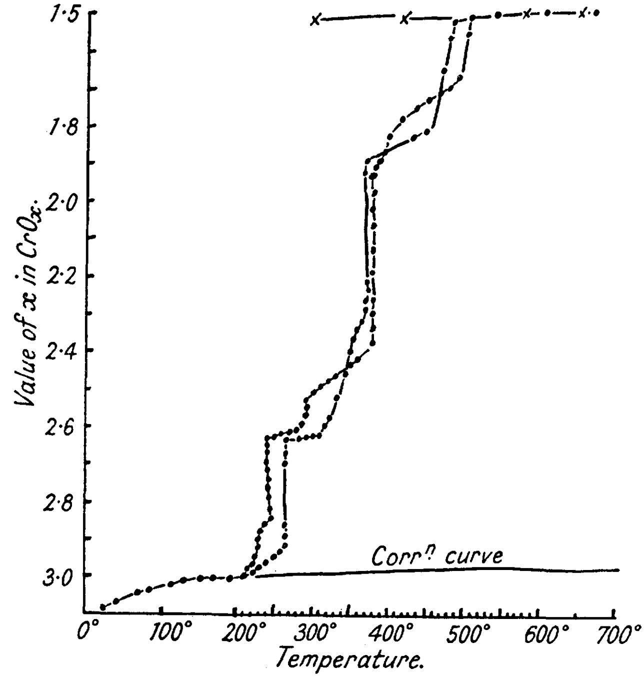
It was decided that the best method of detecting the existence of these oxides was to follow the decomposition curves of chromic anhydride or any other higher oxide of established formula.

Decomposition of Chromic Anhydride.—The first systematic work on the degradation of chromic anhydride was by Honda (*loc. cit.*), who followed the change in the magnetic susceptibility of the oxide as it decomposed. He found a lower oxide at 295° which was stable up to 400°; here it began to decompose slightly, and at 450° rapid decomposition took place with the formation of another oxide, which was ferromagnetic, having a Curie point at 220°. At 680° this finally yielded chromic oxide. Honda assigned the formulæ Cr_6O_{15} ($CrO_{2\cdot5}$) and Cr_5O_9 ($CrO_{1\cdot8}$) to these intermediate oxides. A ferromagnetic oxide of formula Cr_5O_9 had previously been described by Wöhler. Schukoff (*loc. cit.*) had also noticed that Wöhler's magnetic oxide was formed on heating chromic anhydride to 330°, but that it was of variable composition with a mean formula Cr_4O_9 ($CrO_{2\cdot25}$).

Simon and Schmidt (*loc. cit.*) measured the loss of weight of chromic anhydride when heated in a vacuum to different temperatures, special precautions being taken to prevent any loss due to distillation of the oxide. They concluded that there were two intermediate oxides, Cr_5O_{12} ($CrO_{2\cdot4}$) and Cr_5O_{13} ($CrO_{2\cdot6}$). They apparently found no trace of the foregoing ferromagnetic oxide, although Wedekind and Horst (*Z. anorg. Chem.*, 1933, **210**, 105), presumably working with Simon and Schmidt, stated that Cr_5O_{12} is ferromagnetic. Its susceptibility is about 100 times less than that of Wöhler's oxide, with which it cannot therefore have been confused.

We carried out the degradation of chromic anhydride in a constant-pressure apparatus (see p. 61). The correction curve in each diagram represents the expansion due to increased temperature. Several determinations were made, there being small variations between the resulting curves. Two typical curves are shown in Fig. 1. They show the formation of two non-stoicheiometric oxide ranges, the average compositions being Cr_5O_{12} ($CrO_{2\cdot6-2\cdot2}$) and Cr_5O_9 ($CrO_{1\cdot7-1\cdot9}$). In none of the curves was the oxide seen to decompose in the manner of an ordinary stoicheiometric compound, there being always a range of stability about the mean formula. It will be noticed that these results agree, in general, with Honda's work, his Cr_6O_{15} being within the range of the higher oxide composition, and that the Cr_5O_{12} oxide of Simon and Schmidt may be considered to be in the same oxide range. The variations between the different oxide decompositions are apparently of little significance. It has been noticed by other workers that the decomposition temperatures of various oxides are dependent on the surface condition, moisture content, rate of heating, etc. We shall discuss this matter in more detail in a later paper.

FIG. 1.

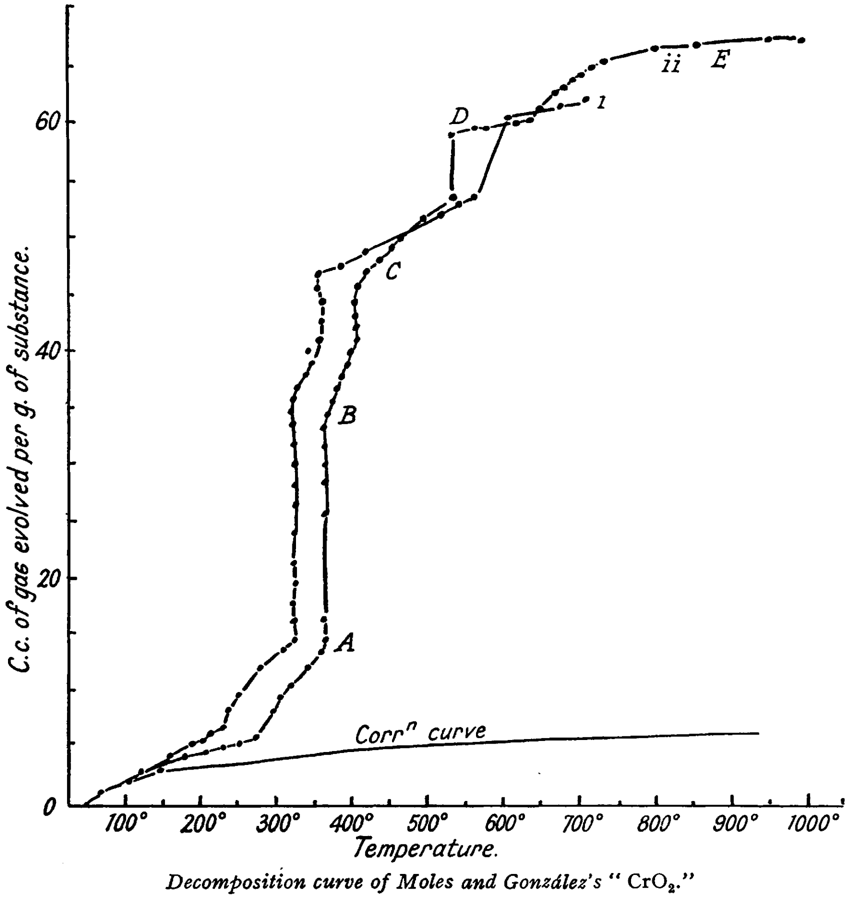


Decomposition curves of chromic acid.

Decomposition of Individual Oxides.—All the complex oxides of chromium described by earlier workers using reliable technique fall within the two non-stoicheiometric ranges described above, with the exception of the dioxide, the existence of which has been claimed by many workers for products obtained by different methods. As there was no sign of the formation of any such dioxide in the decomposition curve of chromic anhydride, it was thought advisable to examine the different oxides formulated thus.

(a) *Chromium dioxide from ammonium dichromate.* Rawson (J., 1889, **35**, 213) found that on heating ammonium dichromate at a temperature below that at which it normally decomposes, a grey-green dioxide was obtained. This was confirmed by Maumerie (*Bull. Soc. chim.*, 1892, **7**, 134) and later by Ball (*loc. cit.*), who noted that the hydrate CrO_2,H_2O was formed. Recent work by Moles and González (*loc. cit.*) was held to verify the existence of the dioxide, but the amount of nitrogen produced in the reaction did not agree with the theoretical value. We prepared this material by their method, *viz.*, by heating ammonium dichromate for 5 days at 195°. Decomposition then appeared to be complete, a portion of the powder yielding no coloration when washed with water. Determination of the chromium content of the powder gave a result corresponding to the dioxide. A portion was then decomposed in the same apparatus as was used for the chromic anhydride decomposition; two curves of the decomposition are shown in Fig. 2. It will be seen that

FIG. 2.



Decomposition curve of Moles and González's " CrO_2*."*

there are at least three distinct temperatures of decomposition, each intermediate product giving evidence of non-stoicheiometry as in the decomposition of chromic anhydride. Samples of the gas evolved at the points marked on the curve were removed and analysed in a Bone–Wheeler apparatus. These results, collected in Table II (i), prove that the material is not chromium dioxide, for both nitrogen and nitrous oxide are evolved in its decomposition.

It was suspected that Moles and González's " dioxide " might still have been contaminated with undecomposed ammonium dichromate, so a portion was thoroughly washed with methyl alcohol, in which the salt is very soluble, and the alcohol removed by evacuation. A portion of this modified sample was then decomposed as before, two curves being plotted in Fig. 3, and the analyses recorded in Table II (ii). The curves are similar to those obtained for the original sample, but the analyses show that the evolution of nitrogen and nitrous oxide is dependent on the past history of the sample. It is at least certain that the compound is not chromium dioxide. A similar nitrogen-containing product was obtained by Harbard and King (J. 1938, 955) by the decomposition of ammonium dichromate in a vacuum; but this compound decomposed in a manner different from that of Moles and González. It would thus seem that a number of products of variable composition can be obtained in these ways, but whether they are non-stoicheiometric nitrogen compounds or solid solutions of two or more compounds, it is not yet possible to say.

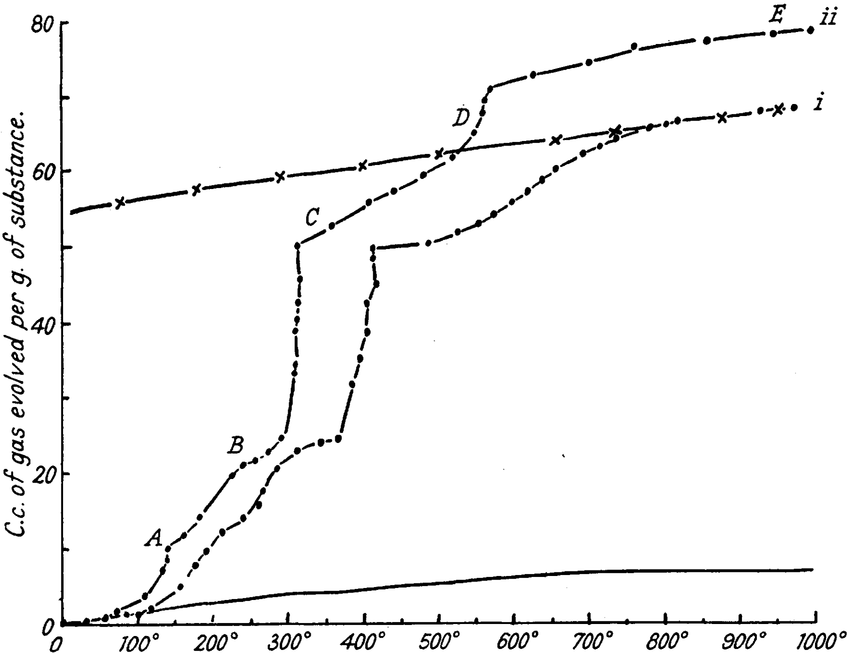
TABLE II.

Composition (%) of gases evolved in the decomposition of Moles and González's "dioxide."

	(i) Decomposition as shown in Fig. 2.					(ii) Decomposition as shown in Fig. 3.				
Sample.	A.	B.	C.	D.	E.	A.	B.	C.	D.	E.
N_2O	1·0	2·5	0	0	15	9·8	36·0	19·3	1·4	5·4
O_2	23·0	72·0	90	22	26	11·2	10·7	65·6	67·0	80·6
N_2	76·0	25·5	10	78	59	79·0	37·3	15·1	31·6	14·0

(b) *Chromium dioxide from oxidation of chromic hydroxide in oxygen.* Moissan (*Ann. Chim. Phys.*, 1880, **21**, 246) described an oxide, CrO_2, obtained by heating chromic hydroxide in a stream of oxygen at 280°, and Manchot and Kraus (*Ber.*, 1906, **39**, 3512) confirmed this result, heating a known weight of the oxide at 440° and weighing the residue. Simon and Schmidt (*loc. cit.*) carried out the decomposition of this oxide, which took place sharply at 335°. The product of this decomposition, which was stable to 530°, was assumed to be chromic oxide, although the authors state that the colour of this product was darker than that of normal chromic oxide.

FIG. 3.



Decomposition curve of washed Moles and González's "dioxide."

We prepared Moissan's oxide by precipitating chromic hydroxide from chrome alum by ammonia, dialysing it for 36 hours to free it from ammonium salts, and heating it for 9 hours in oxygen at 285°. The product, a black, crystalline powder, dissociated at 330° in agreement with Simon and Schmidt's observation. The curve was followed up to 680°, and the product allowed to cool; it was then dull green, as stated by these authors. Further heating of this powder gave a considerable evolution of oxygen between 850° and 870°. In order to determine the composition of these intermediate oxides, a weighed amount of the original compound was ignited at 500° and weighed again. It was then thoroughly ignited over a roaring Bunsen flame for about an hour, allowed to cool in air, and again weighed. The product of the first ignition was grey-green, but the final residue was of the usual bright green colour characteristic of chromic oxide. Calculation from these results showed that the first decomposition product corresponds to the formula $CrO_{1\cdot8}$ and the original substance to $CrO_{2\cdot6}$. Both of these oxides appear during the decomposition of chromic anhydride; it seems that the action of oxygen on chromic hydroxide is to produce the non-stoicheiometric $CrO_{2\cdot6}$, which on heating decomposes normally. In the present instance the $CrO_{1\cdot8}$ oxide did not begin to give off oxygen until heated to 550°, and decomposition was not complete until 870°, whereas the product of similar formula formed directly from chromic anhydride decomposed at 450°. Although variation in the physical condition of oxides is known to influence their decomposition temperatures, the above difference seems a little large.

Hydrolysis of the Moissan oxide. Manchot and Kraus found that their oxide did not react with water, but Blanc (*Ann. Chim. Phys.*, 1926, **6**, 202), who prepared the same compound by heating chromic hydroxide in air at 230°, noticed that hydrolysis took place even at room temperature with the formation of chromic acid. He proved that the oxide Cr_5O_9 was formed in the process. Blanc noted that between 360° and 410° this compound had a variable composition. This was confirmed by Michael and Bernard (*Comp. rend.*, 1935, **200**, 1316), who also showed that the crystal parameter increased from 5·27 to 5·33 A. during the process, a behaviour recalling that of the tungsten bronzes (p. 56).

We heated a small amount of the original oxide in a large excess of water for 15 hours at 90°. The water became coloured immediately, even in the cold, and was found to contain chromate but no chromic ions. The decomposition curve of the resulting powder agreed fairly well with the curve for the unhydrolysed oxide except that the temperature of the first decomposition was slightly higher. The oxygen loss during this decomposition was, however, considerably less than before, indicating that some of the oxide had decomposed to Cr_5O_9 : $3Cr_5O_{13} = 10CrO_3 + Cr_5O_9$. This agrees with the theory of Blanc, who measured the magnetic susceptibility of his compound which became ferromagnetic after hydrolysis, presumably being converted into the Cr_5O_9 stage.

(c) *Chromium dioxide from chromic hydroxide and chromic anhydride.* Bhatnagar, Prakash, and Hamid (*loc. cit.*) have recently described the preparation of chromium dioxide by adding a 5% solution of chromic acid to chromic hydroxide and drying the product at 200°. The magnetic susceptibility of this oxide is claimed to be in agreement with the formula CrO_2. Since, as we shall show in a later paper, none of the oxides of the transition metals has a magnetic susceptibility which is in agreement with theory, we decided to repeat this work. Accordingly, we prepared the oxide by the same method and dried it at 200° in an electric furnace. When heated in the usual manner, this oxide decomposed at about 300°, and the volume of oxygen liberated corresponded to a formula of $CrO_{1\cdot73}$ for the original oxide. This is within the non-stoicheiometric oxide range (Cr_5O_9) obtained in the chromic anhydride decomposition curve.

As a result of the work described above, it would appear that, apart from chromic anhydride and chromic oxide, only two other oxides of chromium can be substantiated, *viz.*: (1) An oxide of formula varying between $CrO_{1\cdot7}$ and $CrO_{1\cdot9}$, formed by decomposition of the other non-stoicheiometric oxide $CrO_{2\cdot6}$, by the decomposition of chromyl chloride, and by the action of chromic acid on chromic dioxide. As generally prepared, this oxide decomposes between 400° and 450°, but this temperature may vary considerably according to the method of preparation, and the variation is ascribed to the different particle size and other physical factors. (2) An oxide with formula ranging from $CrO_{2\cdot6}$ to $CrO_{2\cdot2}$; this is the first decomposition product of chromic anhydride and can also be formed by the action of oxygen on heated chromic hydroxide. It also possesses a somewhat variable decomposition temperature.

EXPERIMENTAL.

The purity and composition of the materials studied were always checked, and the composition of the final decomposition product verified. Neglect to carry out the last precaution had led to erroneous conclusions (cf. p. 60).

The apparatus used for the determination of the decomposition curves consisted of a silica tube sealed at one end and carrying a T-piece at the other. Another silica tube, also sealed at one end, was chosen of such a size that it just fitted inside the first tube. A weighed quantity of the oxide whose decomposition curve was to be plotted was placed inside the larger tube, in a small platinum boat. The smaller tube was then fitted inside the larger, and the end sealed with sealing wax. Thus a small chamber, leading to the T-piece by a very narrow capillary, was provided for the oxide. The T-piece was connected to a gas burette (enclosed in a thermostat), in which the gas evolved during the decomposition could be collected and measured.

In order to determine the exact path of the decomposition of the oxides, a very large number of points were taken during each run; often there were as many as 15 points per 100° change in temperature. In some cases the establishment of equilibrium was very slow. In order to ensure that the system had attained equilibrium at a given temperature, readings were taken at definite time intervals until two or more consecutive readings were identical. In nearly every instance the curves were determined two or more times. There were normally slight variations between the different curves for a given decomposition, but the nature of these variations was such that they could not be attributed to experimental error. They consisted of slight variations in the temperature of decomposition and in the slope of the curves in the region of stability of non-stoicheiometric oxides.

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