307. *The Magnetic Susceptibilities of Metallic Oxides, with Special Reference to those of Chromium and Manganese.*

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Different workers report widely divergent results for the magnetic susceptibilities of the transition metals. It has now been shown that, if the best values for the susceptibility are taken, the magnetic moment, as calculated from the Curie law, gives values which are of no theoretical significance, but application of Weiss's modification of this law to the oxides of chromium and manganese gives values for the magnetic moment which are in accord with theory and enable magnetic measurements to be used for the evaluation of the correct formulæ of oxides.

The formulæ of the oxides of manganese are discussed, and the occurrence of quadrivalent chromium in a hydrated dioxide of that metal established.

The magnetic susceptibility of the various stages of decomposition of chromium trioxide has been measured, and it has been found that there is little change in the magnetic susceptibility with variation of composition in non-stoicheiometric oxides. The Cr_5O_9 non-stoicheiometric oxide is ferromagnetic.

Samples of chromic oxide prepared by different methods have slightly different susceptibility values. It is suggested that these differences are due to the presence of impurities and, in particular, to small amounts of chemisorbed gaseous elements. The adsorption of oxygen or of hydrogen at 440° on this oxide causes definite variation in the susceptibility value. High-temperature evacuation likewise causes a considerable fall in the susceptibility of chromic oxide. It is suggested that activated adsorption on oxides is connected with reduction of chemisorbed oxygen, and the use of magnetic measurements is recommended as a means of following surface chemical processes on oxides.

THE magnetic properties of the metallic oxides have received much less systematic study than those of the corresponding salts. In many instances different observers report values which differ considerably for a particular oxide, and there are few precise determinations of the variation of susceptibility with temperature.

The χ values for the oxides of iron vary over wide ranges. Ferric oxide, for example, is usually paramagnetic, but it also exists in a ferromagnetic form, both in Nature and as a synthetic product. Similar observations have been made for cobalt and nickel oxides; for the latter, the matter is of considerable interest, since Klemm and Hass (*Z. anorg. Chem.*, 1934, **219**, 82) have shown nickel oxide to be non-stoicheiometric, having a natural paramagnetism provided that the ratio O : Ni is above 1 : 1·005. As soon as the ratio is below this, the compound becomes ferromagnetic, owing to the liberation of metallic nickel.

In view of the lack of information concerning the magnetic properties of oxides on the one hand and of increased knowledge of oxide structure and chemistry on the other, it was thought desirable to review the whole subject; the oxides of chromium and manganese are especially suitable for this purpose. This work has been undertaken independently in Lahore and in London, and the various authors have collaborated in this publication in the interests of economy.

It is well known that changes in principal valency bring about changes in magnetic moment which can be correlated with atomic structure. In general, atoms or ions which contain completed sub-groups possess zero, or very small, magnetic moments and are consequently diamagnetic, whilst those in which the sub-group is incompletely filled are paramagnetic. The magnetic moment in Bohr units is given by the formula

$$\mu_B = \sqrt{4s(s-1) + l(l-1)}$$

which reduces to $\mu_B = \sqrt{4s(s-1)}$ when the orbital moment is fully quenched. The magnetic susceptibilities of salts, calculated on the above formula for spin only, agree well with the experimental values. This is shown by the examples recorded in the left-hand part of Table I. Values for the oxides of metals with completed inner shells are also in good agreement with theory, but with oxides of the transition metals the difference between

theoretical and measured values is so great as to make magnetic susceptibility useless as a means of determining valency, and Sidgwick's remark, " agreement, even for the oxides, is surprisingly good," is somewhat optimistic.

TABLE I.

The Magnetic Moments of some Metallic Salts and Oxides.

Compound.	μ, found.	μ, calc.	No. of un- paired spins.	Compound.	μ, found.	μ, calc.	No. of un- paired spins.
$CrCl_3$	4·05	3·87	3	CrO_3	0·344	0	0
$CrCl_2$	4·90	4·90	4	Cr_2O_3	2·12	3·87	3
$CoBr_2$	4·90	4·90	4	CoO	2·91	4·9	4
$CuCl_2$	1·79	1·73	1	CuO	0·90	1·73	1
$FeCl_2$	5·75	5·92	5	Cu_2O	0·447	0	0
$MnCl_2$	5·66	5·92	5	Fe_2O_3	1·96	5·92	5
$MnBr_2$	5·80	5·92	5	MnO	2·78	3·87	3
				MnO_2.............	3·56	5·92	5
				Mn_2O_3	3·57	4·90	4

It may be that these divergencies between theory and practice are due to wide deviations from Curie's law, *viz.*, $\mu_B = 2.839\sqrt{\chi_m T}$, which neglects interaction between the molecules. The first part of the present investigation was undertaken to see whether Weiss's modification of this law, *viz.*, $\mu_B = 2.839\sqrt{\chi_m(T - \theta)}$, gave better concordance with theory : the constant θ takes cognizance of the distortions produced by interatomic forces, and this factor is primarily responsible for the wide divergencies from the Curie law. If this correction gave significant values for μ_B, application might again be made to the determination of oxide structure from magnetic data.

The magnetic susceptibilities at different temperatures are collected in Table II. The value of μ_B is calculated from the Weiss equation, the constant θ being determined by plotting the $1/\chi$–T curve and reading off θ as the intercept on the T axis. As the susceptibility of chromic oxide shows a maximum, the value of θ for this oxide was calculated from the χ values at the higher temperatures.

Chromic Oxide.—According to Faraday (*Pogg. Ann.*, 1847, **70**, 33) and Nilson and Pettersson (*Ber.*, 1880, **13**, 1459) the sesquioxide is ferromagnetic, but Wedekind and Horst (*Z. anorg. Chem.*, 1933, **210**, 105) found that the susceptibility varied after the oxide had been subjected to different treatments, sometimes being ferromagnetic. Hüttig (*Z. Elektrochem.*, 1933, **39**, 368), on the other hand, found that, although the mass susceptibility of the oxide prepared by different methods could vary from 28 to 47 $\times$ 10^{-6}, no ferromangetic sample could be obtained. Michael and Bernard (*Compt. rend.*, 1935, **200**, 1316) have shown that the magnetic oxide obtained by thermal decomposition of chromyl chloride is a mixture of oxides which changes to the green, non-magnetic chromic oxide at a high temperature. Other reported values of the susceptibility of this oxide vary widely; *e.g.*, Meyer (*Ann. Physik*, 1899, **68**, 325; **69**, 236) gave 24 $\times$ 10^{-5}, Moles and Gonzáles (*Anal. Fís. Quím.*, 1923, **21**, 204) gave 26·2 $\times$ 10^{-6}, and Blanc and Chaudron (*Compt. rend.*, 1925, **180**, 289) found an abrupt increase at 800°, followed by a fall at 900°. Chaudron and·Forrestier (*ibid.*, 1924, **179**, 763) observed that the temperature coefficient of the calcined is greater than that of the uncalcined oxide. Honda and Sone (*Sci. Rep. Tôhoku Imp. Univ.*, 1913, **2**, 1) found that the susceptibility attained a maximum at 64°. Haas and Handel (*Proc. Acad. Sci. Amsterdam*, 1933, **73**, 36, 168) found that two apparently identical samples of the oxide had $\chi = 26 \times 10^{-6}$ and 22 $\times$ 10^{-6} at room temperature, but that at low temperatures the results for the two samples were widely different.

The results of Table II indicate that the susceptibility of chromic oxide obtained by the precipitation method, by ignition of chromic acid, and by ignition of ammonium dichromate is 25·6 $\pm$ 0·2 $\times$ 10^{-6} at 32°, the agreement contrasting strongly with the divergencies in the literature. The value for the last sample is especially interesting, since Harbard and King (*J.*, 1938, 955) have shown that the oxide so prepared contains more oxygen than the stoicheiometric formula demands. The value of θ for the three samples varied from $-$ 400° to $-$ 485°. The oxide obtained by igniting a mixture of potassium dichromate and sulphur at 800° had $\chi = 29.73 \times 10^{-6}$, whereas that resulting from ignition

TABLE II.

Variation of Magnetic Susceptibility with Temperature.

(1) *Chromic oxide.*

(a) Prepared by ignition of the precipitated hydroxide.

Temp., °K.	302	325·5	335·5	355·5	395	464·5	540	615
$\chi \times 10^6$	25·86	26·71	26·94	26·40	26·02	24·78	22·40	20·78

$\theta = -405°$; mean $\mu_B = 3.61$ B.u.

(b) Prepared by ignition of chromic anhydride.

Temp., °K.	305	328	359·5	428	485	523
$\chi \times 10^6$	25·39	26·38	25·61	25·05	23·83	22·6

$\theta = -485°$; mean $\mu_B = 3.73$ B.u.

(c) Prepared by ignition of ammonium dichromate.

Temp., °K.	308	331	367	427	488	526	573
$\chi \times 10^6$	25·80	26·69	26·25	24·91	23·12	21·80	21·00

$\theta = -400°$; mean $\mu_B = 3.54$ B.u.

(d) Prepared by ignition of potassium dichromate and sulphur at 1080°.

Temp., °K.	309	332	370	428	489·5	526
$\chi \times 10^6$	25·98	26·67	26·18	25·22	24·06	23·11

$\theta = -670°$; mean $\mu_B = 4.12$ B.u.

(e) Prepared by ignition of potassium dichromate and sulphur at 800°.

Temp., °K.	306	329	365	430	488
$\chi \times 10^6$	29·73	29·11	26·87	24·56	23·57

(2) *Chromium dioxide,* CrO_2,H_2O.

	Sample 1.						Sample 2.			
Temp., °K.	309·5	335	356	388	448		309·5	351	384	443
$\chi \times 10^6$	34·80	32·19	30·1	27·67	24·01		34·80	30·10	27·71	23·27

$\theta = 2°$; mean $\mu_B = 2.94$ B.u. $\theta = 5°$; mean $\mu_B = 2.94$ B.u.

(3) *Manganese dioxide.*

Temp., °K.	300	310	340	383	438	480
$\chi \times 10^6$	26·03	25·72	24·82	23·63	22·24	21·34

$\theta = -470°$; mean $\mu_B = 3.76$ B.u.

(4) *Manganic oxide.*

Temp., °K.	293	304	333	365	423	475	523	580
$\chi \times 10^6$	89·32	87·27	82·44	77·18	70·40	64·80	60·45	55·88

$\theta = -176°$; mean $\mu_B = 5.17$ B.u.

(5) *Manganous oxide.*

Temp., °K.	293	306	342	363	424	473	528
$\chi \times 10^6$	73·38	72·34	69·38	67·64	63·61	60·42	57·42

$\theta = -540°$; mean $\mu_B = 5.91$ B.u.

of the mixture at 1080° had $\chi = 25.9 \times 10^{-6}$, the θ value being $-670°$. The only previous work on chromic oxide from which θ can be calculated is that of Honda (*loc. cit.*). By plotting $1/\chi$–T from his results and extrapolating, a value of $-487°$ K. is obtained for θ. This is in remarkable agreement with our value of $-485°$ for a similar preparation, especially as the θ values for samples of the oxide prepared by different methods vary from 400° to 485°.

In agreement with Honda also, the χ–T curve for chromic oxide was found to exhibit a maximum at 65°, except in the case of the oxide obtained by ignition of potassium dichromate and sulphur at 800°, in which this curve is smooth, the susceptibility falling with rise of temperature. In this system (Bruckner, *Monatsh.*, 1906, **27**, 199) it is probable that there is a trace of chromic sulphide formed along with the oxide. The susceptibility value of this preparation is, indeed, 29.73×10^{-6}, which is higher than that for any of the other samples of the oxide, and as Haraldsen (*Naturwiss.*, 1936, **24**, 280) found the sulphides of chromium to be strongly paramagnetic, this high value is probably due to contamination by sulphide, traces of which were actually detected in the sample.

The smooth χ–T curve for this chromic oxide preparation can be explained by assuming

that the fall in susceptibility of the sulphide with rise of temperature is much more than the corresponding rise of the susceptibility of Cr_2O_3, which is thus masked. Further support to this view is afforded by the fact that, if the sample of chromic oxide with the high susceptibility is ignited at 1080°, the susceptibility falls to $25 \cdot 98 \times 10^{-6}$ and the sample then exhibits a maximum on the χ–T curve. The value of θ is much higher than that for chromic oxide prepared by other methods, and the rise in susceptibility is comparatively less. This sample did not give a qualitative reaction for sulphide, but probably a trace of this impurity is still present, and is responsible for the high value of χ and comparatively small rise of the susceptibility value with temperature.

The χ–T curve for chromic oxide exhibits a maximum at 65°, indicating the appearance of a new phase at this temperature. The value of θ calculated from the susceptibility values beyond 65° gives a value of 3·63 for μ_B, which is in good agreement with the theoretical value of 3·87 for tervalent chromium.

Squire (*J. Chem. Physics*, 1939, 139) measured the paramagnetic susceptibility of manganous oxide from 14° K. to 298° K., and observed that the paramagnetism drops to nearly diamagnetism with decreasing temperature. This he explains by assuming that electron spins giving rise to paramagnetism at the higher temperatures are no longer free to orient themselves at low temperatures. In the case of chromic oxide it would appear that below 65° the electron spins giving rise to paramagnetism corresponding to tervalent chromium are not perfectly free to orient, but that above 65°, where the value of μ_B corresponds to the theoretical, orientation is possible.

The magnetic susceptibilities of some samples of chromic oxide prepared by other methods and subjected to various treatments are given on p. 1438.

Chromium Dioxide.—Cameron, Harbard, and King (this vol., p. 55) have examined various oxides claimed to be CrO_2, and shown that the material prepared by partial decomposition of ammonium dichromate (Moles and González, *loc. cit.*, and others) contains nitrogen. Moles and González found $\chi = 42 \cdot 2 \times 10^{-6}$ for this " dioxide." We obtained values of 26·9, 33·6, and $34 \cdot 5 \times 10^{-6}$ for different samples of this material : this diversity probably reflects its extreme variability of composition.

Other dry methods reported to yield CrO_2 gave compounds which appear to be non-stoicheiometric, belonging to the oxide range $CrO_{2 \cdot 6 — 2 \cdot 2}$ or $CrO_{1 \cdot 9 — 1 \cdot 7}$. Bhatnagar, Prakash, and Hamid (*J.*, 1938, 1428), however, described the preparation of anhydrous CrO_2 by intensive drying of the product obtained by adding 5% solution of chromic acid to chromic hydroxide. If the brown product was dried carefully below 200°, a hydrated dioxide CrO_2,H_2O was obtained, and measurements in both our laboratories led to a μ_B-value of 2·94 for the latter, which compares well with the theoretical value of 2·83 for quadrivalent chromium calculated on the basis of spin only. The results in Table II show that the Weiss constant θ is very small in this case (2—5°), and that valency deductions based on the uncorrected law are therefore correct.

Oxygen analyses by Cameron, Harbard, and King indicated that their original preparation had the formula $CrO_{1 \cdot 73}$, being thus in the Cr_5O_9 non-stoicheiometric group. It is possible that the dioxide had hydrolysed under these conditions to Cr_5O_9 in a similar manner to the oxide investigated by Blanc (*Ann. Chim.*, 1926, **6**, 202). It should be realised, however, that oxides of the Cr_5O_9 non-stoicheiometric range are normally ferromagnetic (see below).

Magnetic Properties of the Oxides of Manganese.—Like the oxides of chromium, those of manganese also give widely divergent values. For example, Wedekind and Horst (*Ber.*, 1915, **48**, 105) found $\chi = 56 \cdot 16 \times 10^{-6}$ for manganous oxide, $\chi = 65 \cdot 5 \times 10^{-6}$ for manganosic oxide, and $44 \cdot 58 \times 10^{-6}$ for manganese dioxide; Theodorides (*Compt. rend.*, 1920, **171**, 948) found $67 \cdot 46 \times 10^{-6}$ for the first, and Feytis (*ibid.*, 1911, **152**, 710) $74 \cdot 3 \times 10^{-6}$ for the second oxide. Meyer (*loc. cit.*) and Wistrand (" Magnetiska Susceptibiliteten hos Kvarts, etc.," Upsala, 1916) found $\chi = 27 \times 10^{-6}$ and $37 \cdot 3 \times 10^{-6}$ respectively for the dioxide. Williams (*Physical Rev.*, 1926, **28**, 167) discussed the structure of manganous oxide from magnetic data, and Honda and Sone (*Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 139) and Tyler (*Physical Rev.*, 1933, **44**, 776) measured the susceptibilities of the oxides at various temperatures.

Manganese Dioxide.—The constitution of this oxide has been the subject of much controversy. Richarz (*Ber.*, 1888, **21**, 1675) attributed to it the formula O=Mn=O, Guyard (*Bull. Soc. chim.*, 1864, **1**, 89) and Volhard (*Annalen*, 1879, **198**, 318) regarded it as a permanganate, $3MnO,Mn_2O_7$, Laspeyres (*J. pr. Chem.*, 1876, **13**, 176) considered it to be manganous manganate, $Mn(MnO_4)$, and on the other hand, Elliot and Storer (*Proc. Amer. Acad.*, 1862, **5**, 1921) considered it to be a basic manganic manganate.

Many workers who have studied the decomposition of manganese dioxide, *e.g.*, Drucker and Huttner (*Z. physikal. Chem.*, 1927, **131**, 237) and Simon and Feher (*Z. Elektrochem.*, 1932, **38**, 137) have failed to obtain an exactly stoicheiometric formula : the ratio of oxygen to manganese is always low, *ca.* 1·85—1·95. Samples prepared in both our laboratories gave analyses agreeing with $MnO_{1·99}$.

The observed value of μ_B (3·76) for this compound is, however, in excellent agreement with the theoretical value of 3·87 calculated for quadrivalent manganese on the basis that the orbital moment is fully quenched. Nevertheless, a decomposition curve of the dioxide shows that in the range of temperatures used for the magnetic measurements, there is a considerable and regular oxygen evolution. It would appear therefore that, within the non-stoicheiometric range of composition of this oxide, variation of magnetic moment is small. A similar lack of variation of magnetic properties during non-stoicheiometric decomposition of the oxide of chromium is discussed later (p. 1438).

Manganic Oxide.—The constitution O=Mn—O—Mn=O in which manganese is tervalent has been ascribed to this oxide, although suggestions have been made that it may possess the constitution MnO,MnO_2. The μ_B value of 5·17, however, compares well with the theoretical value of 4·90 Bohr units for tervalent manganese and hence supports the former constitution.

Manganous Oxide.—The magnetic moment of 5·91 Bohr units for this oxide agrees excellently with the calculated value of 5·92 for bivalent manganese and hence confirms the constitution Mn=O. Tyler (*loc. cit.*) arrived at a similar conclusion from a magnetic study of this oxide at low temperatures.

From the foregoing results it is clear that, although the μ_B values obtained for oxides of the transition metals do not agree well with those obtained by use of the Hund formula for " spin only," yet, when calculated after the necessary correction for θ in the Weiss formula has been made, the observed values agree excellently with those of theory; this is particularly so in the case of the oxides of manganese. It is suggested, therefore, that if due regard be paid to the purity of the oxides, and if the distortions produced by interatomic forces be taken into consideration, magnetic measurements are capable of giving important evidence as to the structure of oxides.

Magnetic Study of the Decomposition of Chromic Anhydride.—Cameron, Harbard, and King (*loc. cit.*) reported that the decomposition of chromium trioxide takes place non-stoichiometrically in two stages, most of the previously reported intermediate oxides of chromium lying within one or other of these non-stoicheiometric ranges. Magnetic measurements on these intermediate oxides are rather chaotic : Wohler reported the existence of a ferromagnetic oxide prepared in the same manner as the oxide Cr_5O_{12} of Simon and Schmidt (*Z. anorg. Chem.*, 1926, **153**, 191), and Honda (*Sci. Rep. Tôhoku Imp. Univ.*, 1913, **3**, 223) described two oxides (Cr_6O_{15} and Cr_5O_9), paramagnetic and ferromagnetic respectively. It was thought, from the results of Klemm and Hass (*loc. cit.*), that large variations in the magnetic properties might be observed during non-stoicheiometric decomposition, the susceptibility varying as oxygen was removed from the lattice. The thermal decomposition of chromium trioxide was therefore repeated in an apparatus which facilitated the removal of the decomposing oxide for accurate measurement of the magnetic susceptibility. The results are shown in the figure, where oxide composition is plotted against temperature of heating. During the thermal decomposition, paramagnetic properties appeared at the point *B*, the susceptibility of the sample being then 36×10^{-6}. This value increased slightly throughout the non-stoicheiometric (Cr_5O_{12}) range *BC*, being $40·8 \times 10^{-6}$ at *C*, and at *D* the oxide suddenly became faintly ferromagnetic. Ferromagnetism became stronger as the second (Cr_5O_9) non-stoicheiometric range was traversed, and finally, at the point *F*, the normal paramagnetic susceptibility of chromic oxide was registered. These

results are in general agreement with those of Honda, but their chief interest lies in the absence of any significant change in magnetic properties during non-stoicheiometric decomposition, even although the oxide composition varied considerably. The absence of a ferromagnetic sample at even the least stable end of the first oxide range is important.[1]

The Magnetic Susceptibility of Chromic Oxide, and the Adsorbed Layer.—It was noticed by Wedekind and Horst and by Hüttig (*locc. cit.*) that chromic oxide can possess a variable magnetic susceptibility according to its past treatment. The values for various samples of this oxide prepared in different ways, collected in Table II, show that, except where impurities are suspected, the susceptibilities are very nearly constant. A number of other
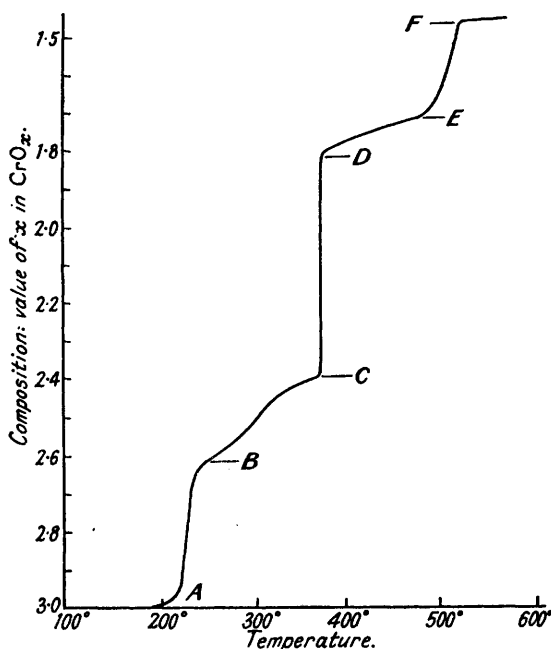
preparations of chromic oxide were therefore made, and their susceptibilities measured; these are collected in Table III.

TABLE III.

Susceptibility of Chromic Oxide at 18°.

No.	Method of preparation.	Colour.	$\chi \times 10^6$.
1	Ignition of Hg_2CrO_4	Bright green	24·7
2	,, ,,	,,	24·5
3	Strong ignition of (2)	,,	23·6
4	Ignition of CrO_3	,,	25·5
5	Ignition of $(NH_4)_2Cr_2O_7$	Olive-green	25·4
6	Ignition of (5) in hydrogen	Bright green	24·3
7	Ignition of $K_2Cr_2O_7$ and S	Olive-green	25·9
8	Ignition of precipitated $Cr(OH)_3$	Bright green	25·6

These results show that, although there is a definite and considerable variation in magnetic susceptibility, at no time could a ferromagnetic sample be prepared. It seemed possible that the variations might be connected either with slight variations in structure or with an adsorbed layer on the oxide surface, especially if this were chemically bound. Dowden and Garner (this vol., p. 893) have shown that both oxygen and hydrogen can be bound on the surface of chromic oxide by chemical means.

Of the reported cases of activated adsorption, a large proportion concern oxides or oxide-coated metal surfaces, the adsorbed gas generally being of a reducing nature, such as hydrogen or carbon monoxide. Many of these adsorptions are not reversible, and it thus

seems possible that in these instances the mechanism of activated adsorption may be the reduction of the chemisorbed oxygen or, alternatively, removal of some of the oxygen from the oxygen-rich member of a non-stoicheiometric series. On the assumption that the differences in magnetic susceptibility of the various preparations of chromic oxide are due to chemisorbed films, or to slight variations in composition (Harbard and King, J., 1938, 955), measurement of magnetic properties would be a useful method of studying this type of sorption. Preliminary work has therefore been done on the chromic oxide system. A special arrangement was constructed so that the sample of oxide could be removed from the adsorption apparatus in contact with gas at a given pressure for magnetic measurement, without allowing contact with the atmosphere. A sample of chromic oxide prepared by ignition of ammonium dichromate was placed in the apparatus, which was then evacuated, and hydrogen admitted at a pressure of about 28 cm. The temperature was gradually raised to 350°, whereat a small amount of adsorption took place. An attempt was then made to activate the oxide by the addition of inert impurities. In this case, a small amount of silica powder was intimately mixed with the crystals of ammonium dichromate, and the mixture ignited. The product did not show activated adsorption. A second sample prepared with a trace of carbon as impurity was likewise inactive. The next material tested was a mixture of chromium and manganese oxides, prepared by ignition of manganese chromate; this was reported by Taylor and Williamson (*J. Amer. Chem. Soc.*, 1931, **53**, 2168) to adsorb large amounts of hydrogen at comparatively low temperatures. It was found that the sample began to adsorb hydrogen at about 200°; after about 12 hours, equilibrium appeared to be reached, but on leaving the oxide at the same temperature for a further 12 hours a little more hydrogen was adsorbed. It was found that there is a gradual, but constant adsorption of hydrogen at this temperature, and that raising the temperature did not appreciably alter the rate of adsorption after the " false equilibrium " had been reached. It seems probable that there is a gradual reduction of the oxide at the temperatures employed, but the matter requires further investigation.

The olive-green chromic oxide prepared by ignition of ammonium dichromate changed to a bright green colour on being heated in hydrogen at 440°; at the same time χ fell from 25.4×10^{-6} to 24.3×10^{-6}. The oxide was then heated in a vacuum for several hours at the same temperature, and the value of its susceptibility redetermined. The oxide was then heated in oxygen, and a third value of the susceptibility obtained. The results are shown below :

	Freshly prepared oxide.	$\chi \times 10^6$.		Freshly prepared oxide.	$\chi \times 10^6$.
1.	After heating in hydrogen	24.3	2.	After heating in hydrogen	24.7
	,, ,, oxygen	27.3		,, ,, oxygen	26.0
	,, ,, a vacuum	22.4		,, ,, a vacuum	21.7

It was found that the whole cycle could be repeated and that, although the exact values of the susceptibility were not identical with those obtained in the first experiment, the general tendency of the change was the same. The hydrogen-treated samples were always bright green, whereas the oxygen-exposed varieties were of a dark olive colour. On being heated in a vacuum, the product had a colour intermediate between these two.

The effect of oxygen treatment was always to increase the susceptibility, of hydrogen treatment to lower it, with respect to the original preparation; the high temperature of reaction makes it most likely that the retention of these gases on the surface is by chemical forces. Heating in a vacuum always resulted in a product with a lower susceptibility than those produced by heating in a gas atmosphere. This makes it appear probable that the adsorbed layer is partly removed by heating in a vacuum, retreatment with oxygen or hydrogen re-establishing the chemisorbed layer. The adsorption theory of variation of composition and properties seems to be more probable than that of non-stoicheiometric variation, since, if the latter were alone operative, retreatment under constant conditions of temperature and gas pressure would be expected to yield products of identical magnetic susceptibility. Moreover, it is unlikely that vacuum treatment would produce a material of magnetic susceptibility lower than that of either the oxygen-rich or the oxygen-poor members of a non-stoicheiometric series. Further evidence for chemisorption is yielded by

the results of the second cycle. The vacuum value of susceptibility is here lower than on the first sorption, showing perhaps that more of the film has been removed; this is probably connected with the fact that, whereas the oxygen-covered oxide had a susceptibility value of 27·3 on the first treatment, this had fallen to 26·0 on the second cycle. This means that part of the surface previously occupied by chemically held oxygen is no longer available for chemisorption, an observation in line with the results of Garner and Dowden (*loc. cit.*), who noticed a decrease in surface activity of chromic oxide on repeated sorptions and desorptions at 400°. Adsorption work, at present in progress, on this system shows that the chromic oxide surface is exceptionally mobile; it is not surprising, therefore, that a proportion of the active centres disappear on treatment such as is described above. From the adsorption isotherm of chloroform on chromic oxide, which shows a Langmuir saturation value, the surface area of the chromic oxide sample under investigation has been calculated and compared with the area of surface covered with oxygen or hydrogen in the experiments at higher temperatures. It is found that only 5% of the total surface is available for chemisorption in this manner. The low susceptibility value of the oxide surface when free from both oxygen and hydrogen is remarkable and requires further investigation.

EXPERIMENTAL.

The oxides were prepared with due regard to their purity; wherever possible " AnalaR " reagents were used, and were specially tested for the presence of any ferromagnetic elements. The different samples of chromic oxide were prepared as follows :—

(1) *Precipitation method.* Chromic sulphate, obtained by the reduction of an acidified solution of analytically pure chromic acid with alcohol, was treated with ammonia, and the precipitated hydroxide ignited at 800° (Found : Cr, 68·10. Calc. : Cr, 68·42%).

(2) *Ignition of chromium trioxide.* Pure chromium trioxide was ignited in an electric furnace at 800° (Found : Cr, 68·28%).

(3) *Ignition of ammonium dichromate.* The dichromate when ignited at 800° gave chromic oxide directly. The excess of ammonium dichromate, if any, was removed by washing the preparation with methyl alcohol, in which the salt is extremely soluble (Found : Cr, 64·14%). All the above preparations are slightly deficient in chromium; this is almost certainly due to a slight excess of oxygen, either chemisorbed or in the lattice, or both.

(4) *Reduction of potassium dichromate with sulphur.* The dichromate was fused with excess of sulphur, cooled, and the mass washed free from sulphate, sulphide, and unattacked dichromate. One sample was ignited at 800° and another at 1080° (Found : Cr, 67·74, 68·28% respectively).

(4) *Ignition of mercurous chromate.* A solution of mercurous nitrate was added to a neutral solution of potassium dichromate, the precipitate filtered off, and washed well with a dilute solution of mercurous nitrate; it was ignited in a vacuum at 400° and then over a Meker burner (Found : Cr, 68·40%).

Chromium Dioxide.—Chromium hydroxide was treated with 5% chromic acid solution, and the brown product washed and dried carefully below 200°. Chromium was determined by direct ignition to chromic oxide. Water was estimated by heating the sample and absorbing the liberated water in calcium chloride (Found : Cr, 51·34; H_2O, 17·90. Calc. for CrO_2, H_2O : Cr, 51·00; H_2O, 17·65%).

Manganese Dioxide.—Analytically pure manganous nitrate was twice recrystallised from water and heated at 150—160° for 50 hours. The residue was washed free from nitrate and dried at 200°. On analysis it was found to conform to the formula $MnO_{1·99}$. The product was repeatedly treated with boiling nitric acid in order to dissolve the lower oxides, and finally washed and dried at 200° in a vacuum.

Manganic Oxide.—The dried product obtained from the decomposition of manganous nitrate at 150—160° (above) was ignited to constant weight at 600° in an electric furnace.

Manganous Oxide.—This oxide was prepared by reducing the $MnO_{1·99}$ in a slow current of dry hydrogen at 600°. Any adsorbed hydrogen in the greyish-green oxide was removed by heating it in a vacuum, first at 120° and finally at 200°.

Analysis of the Oxides.—Total manganese was estimated by the pyrophosphate method. Available oxygen was estimated by two methods : (a) The oxide was treated with a known excess of standard oxalic acid in the presence of dilute sulphuric acid, and the excess back-titrated with standard permanganate. (b) A known weight of the oxide was heated with an excess of hydrochloric acid, the chlorine evolved being absorbed in potassium iodide solution,

and the liberated iodine titrated against standard thiosulphate. The results of these analyses are given below :

	Total Mn, %.	Available oxygen, %.		
Compound.		Method (a).	Method (b).	Calc.
$MnO_{1.99}$ (MnO_2)	63·33	18·24	18·26	18·39
Mn_2O_3	69·63	10·13	10·14	10·14
MnO	77·45	0·00	0·00	0·00

Magnetic Measurements.—The magnetic susceptibility of the samples was determined in both laboratories on a modified form of Gouy's magnetic balance. The current was stabilised by a " floating charge " method. In this method an accumulator in series with a resistance is connected in parallel with the magnet, and the resistance adjusted so that no current is being taken from the accumulator when the magnet is in use. Any slight change of current in the magnet causes a small current to flow from the accumulator and this is detected by an ammeter. The resistance controlling the current in the magnet is then adjusted to restore the original conditions. The magnetic balance was calibrated by the use of a standard sample of nickel chloride.

During the measurements of magnetic susceptibility at low temperatures, the sample was kept at constant temperature by means of a water jacket. For measurements at higher temperatures an electrically-heated silica-tube furnace was used. The variations in temperature near the pole pieces on account of the furnace were not found to affect the field strength appreciably, because the pull per g., observed for the standard diamagnetic at various temperatures, was found to be unaffected. In order to determine whether the substances in the tube had actually attained the temperature recorded by the thermometer in the furnace, a magnetic examination of manganese pyrophosphate, prepared from analytically pure manganous sulphate, was undertaken. The calculation of temperature was made by the aid of the Curie–Weiss law, the value of θ ($-25°$) being known for this compound. The observed and the calculated temperatures are tabulated below : the agreement is excellent.

$\chi \times 10^6$	101·73	95·80	88·20	76·30	68·70
Temp., °K. { Obs.	305	325	355	414	463
{ Calc.	—	325·3	355·3	414·3	462·7

Adsorption Apparatus.—The method of determining the magnetic susceptibility required that the tube in which the sample was kept should be about 6 mm. in diameter and not more than 20 cm. long. It was also highly desirable that the susceptibility should be measured with the sample in an atmosphere of hydrogen or oxygen at the pressure at which the gas was being adsorbed without coming into contact with the atmosphere and, at the same time, without admission of air into the adsorption apparatus. A device was thus necessary which would enable the tube to be shut off from the rest of the apparatus, and yet leave it easily detachable in order that it might be removed to the magnetic balance. A tap-joint connexion was finally adopted. At the end of the silica reaction tube was a small ground joint, fitting into a small cap. A hole in the side of the joint in both tube and cap was made so that, by turning the tube, the tube could be opened to the atmosphere. The outside of the cap was also ground so that a similar, but larger cap could be fitted over the first. This second cap was then made to fit into a third cap which had been attached, by means of an internal seal, to a wide piece of tubing leading to the apparatus. By opening all the " taps " the reaction tube could be connected to the main apparatus. When all the taps were shut and the two middle joints separated, the reaction tube could be removed from the main apparatus and weighed, without either the tube or the apparatus being opened to the atmosphere.

The adsorption apparatus was of the static type, changes in pressure being measured by means of an oil manometer. The reaction tube was heated by an electric furnace wound round a copper block. The tube was inserted in a hole in the block which ensured uniform heating.

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