REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

Part XII. Magnetic Properties of Chromium Chromates.

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In the present paper we have shown that the magnetic susceptibilities of the several chromium oxides are in good agreement with the values calculated on theoretical considerations, assuming the chromium chromate formulæ given in Part XI. (This Journal, 1939, **22A**, 287-307).

We have used the equation

$$\chi = \frac{N\beta^2}{3KT}\left[4s(s+1)\right]$$

(Electric and Magnetic Susceptibilities by Van Vleck, p. 286) for calculation of the molecular magnetism of chromium in different valency states. The values obtained are given below:

Valency state for chromium	Spin quantum number	Molecular Susceptibility at 25°
	s	$\chi \times 10^{-6}$
6	0	0
3	3/2	6248

The value 4.6×10^{-6} was taken to represent the molecular diamagnetism of oxygen (Magnetism by E. C. Stoner, p. 35). The values for the magnetic susceptibility at 25° calculated assuming the chromium chromate structure for the different oxides, have been given in Table 2. The effect of temperature on the magnetic properties will be discussed later in this paper.

The correction for different linkages for polymerisation, etc., has not been applied in the above calculations as no accurate values for these corrections are known. All the corrections mentioned above are however diamagnetic and the corrected values will be slightly less than that shown in Table I.

CrO_3.—The theoretical value shows that the oxide is diamagnetic. From the experimental value it will be seen that the oxide is slightly paramagnetic and indicates the presence of hexavalent chromium atom in the oxide.

$6CrO_3$ Cr_2O_3.—Honda and Sone (Sci. Rep. Tohoku Univ. 1914, **3**, 223) measured the magnetic susceptibility of the product of decomposition of CrO_3 at 280°. Our results (This Journal, 1939, **22A**, 119) show that at 280° the decomposition proceeds to 25% and slows down. It therefore appears that the product of the decomposition of CrO_3 at 280° obtained by Honda and Sone is presumably the oxide corresponding to 25% decomposition. The experimental value for specific magnetic susceptibility fairly agrees with that calculated for the chromium chromate $6CrO_3$ Cr_2O_3.

$5CrO_3$ Cr_2O_3.—Wedekind and Albreight (Zeit. anorg. Chem., 1933, **210**, 105) measured the magnetic susceptibility of Cr_5O_{13} which corresponds to about 27% decomposition of CrO_3, for which they assigned a formula $3CrO_3$ $2CrO_2$. This compound is obviously Cr_2O_3 $5CrO_3$ corresponding to 28.6% decomposition. The experimental value for the magnetic susceptibility of the oxide is 17.3×10^{-6} as compared with the theoretical value 19.0×10^{-6}.

$4CrO_3$ Cr_2O_3.—The magnetic susceptibility for this oxide has not been determined. The value obtained by Honda and Sone is apparently that of $6CrO_3$ Cr_2O_3.

$3CrO_3$ Cr_2O_3.—The theoretical value for magnetic susceptibility of this oxide is 27.5×10^{-6}. The values obtained by Wedekind and Albreight for two samples were 35×10^{-6} and 51×10^{-6}, and the oxide was slightly ferromagnetic. The oxide was obtained by these authors by decomposition of CrO_3 at 370° at which temperature the oxide undergoes a further decomposition to Cr_4O_9, which, as shown by Shukoff (Compt. Rend. 1908, **182**, 386; J. Russ. Phys. Chem. Soc., 1909, **41**, 302), is ferromagnetic. If we take into consideration the probable existence of this ferromagnetic impurity, the higher magnetic value can be explained.

TABLE I.

Oxide	% decomposition	Method of preparation	Chromium chromate formula	Nomenclature	Specific susceptibility × 10^6			Authors.
					Calculated from Wedekind and Albreight's formula	Calculated from chromium chromate formula at 25°	Observed at room temperature	
(1) CrO_3	0	Anydrous	CrO_3	Chromic acid anhydride	..	—0 14	0 51	Wedekind and Albreight
(2) Cr_5O_{21}	25	By heating CrO_3 at 280°	$6CrO_3\ Cr_2O_3$	Dichromito sexies chromate	...	16 5	14.2	Honda and Sone
(3) Cr_6O_{11} or Cr_7O_{16}	28 6	By heating CrO_3 at 270°	$5CrO_3\ Cr_2O_3$	Dichromito penta chromate	15 0	19 0	17.3	Wedekind and Albreight
(4) Cr_6O_{15}	33 3	..	$4CrO_3\ Cr_2O_3$	Dichromito quarter chromate	..	22 5		
(5) Cr_5O_{12}	40	By heating CrO_3 at 370°	$3CrO_3\ Cr_2O_3$	Dichromito tris chromate	23 0	27 5	35 51	,,
(6) Cr_4O_9	50	By heating CrO_3 at 485° and at 500-510°	$2CrO_3\ Cr_2O_3$	Dichromito bis chromate	ferromagnetic		97 6650	Schukoff
(7) Cr_7O_9	66 6	By heating ammonium dichromate at 225°	$CrO_3\ Cr_2O_3$	Dichromito chromate		49 5	42 2	Moles and Gonzalez
		By treating $Cr(OH)_3$ with 5% chromic acid					35 1	Bhatnagar, Prakash and Hamid
		By oxidation of Cr_2O_3 by a current of oxygen at 150°			40		36 35 38	Wedekind and Albreight
(8) $Cr_5O_{15}\ 11H_2O$	75	By reduction of Cr_2O_3 with alcohol	$2CrO_3\ 3Cr_2O_3$	Hexachromito dichromate	42 0	43 6	39 37	,,
(9) Cr_5O_9	80	By heating CrO_3 at 420°	$CrO_3\ 2Cr_2O_3$	Tetrachromito chromate	ferromagnetic		66000	Honda and Sone Blanc
(10) Cr_2O_3	100	By decomposition of Cr_5O_{15} at 600°	Cr_2O_3	Chromic oxide	...	82 1	81 8	Bhatnagar *et al.*

$2CrO_3$ Cr_2O_3.—The oxide is shown by Shukoff to be ferromagnetic He showed that the oxide obtained by decomposition of CrO_3 at 510° was 70 times more magnetic than that obtained at 485° The oxide Cr_5O_{12} obtained by Wedekind and Albreight was also slightly ferromagnetic All these observations taken together show that the oxide Cr_5O_{12} of Wedekind and Albreight and the decomposition product of CrO_3 at 485° are mixtures mainly consisting Cr_5O_{12} with a slight impurity of Cr_4O_9

CrO_3 Cr_2O_3.—This oxide is not obtained in the thermal decomposition of CrO_3 Moles and Gonzalez (Anal Fis Quim, 1923, **21**, 201) obtained the oxide by the decomposition of ammonium dichromate at 225° The magnetic susceptibility of the compound is $42\ 2 \times 10^{-6}$, which is lower than the theoretical value Bhatnagar, Prakash and Hamid (Jour Chem Soc., 1938, 1428) observed a value $35\ 1 \times 10^{-6}$ for magnetic susceptibility of CrO_2 which is in agreement with that obtained by Wedekind and Albreight

$2CrO_3$ $3Cr_2O_3$.—This oxide has not been obtained in the thermal decomposition of CrO_3 The value obtained for Cr_8O_{15} $11H_2O$ by Wedekind and Albreight is in good agreement with the calculated value for the chromium chromate $2CrO_3$ $3Cr_2O_3$

CrO_3 $2Cr_2O_3$.—Honda obtained this oxide in the decomposition of CrO_3 at temperatures intermediate between 280° and 420° He found that the oxide was ferromagnetic Our results on the decomposition of CrO_3 show that Cr_4O_9 decomposes directly to Cr_2O_3 without formation of any intermediate stage It appears probable that the ferromagnetic oxide obtained by Honda is Cr_4O_9 According to Blanc [Bull Soc Chim 1926, (4) **39**, 718, Ann Chim Phys 1926, (12) **6**, 182] the ferromagnetic oxide is an unstable variety of Cr_5O_9 intermediate between α and β forms Sachse (Zeit fur Phys 1931, **70**, 546) found that Cr_5O_9 possesses a ferromagnetic curie point at about 108°.

Cr_2O_3.—The magnetic susceptibility value measured for the oxide is lower than the calculated value owing to polymerisation of the oxide.

Recently Bhatnagar *et al* (Current Science 1939, **8**, 253) have found that the magnetic susceptibility of the chromic oxide is in good agreement with the theoretical value for trivalent chromium by taking into account the effect of temperature on magnetic properties Blanc (loc cit) has observed that the susceptibility of the chromic oxide is constant from ordinary temperature to 800°, increases suddenly at this temperature and diminishes after 900°

Still more recently, Bhatnagar, Cameron *et al* (J Chem. Soc, 1939, 1433) reported values for the magnetic susceptibility of Cr_2O_3 prepared by ignition of CrO_3 and $K_2Cr_2O_7$, which when recalculated on the basis of Weiss' modification of the Curie law to allow for the effect of temperature, become 66×10^{-6} and $81\,8 \times 10^{-6}$ respectively The latter value is also in agreement with the recent work of Foex and Graff (Comptes Rend, 1939, **209**, 160), who have reported 19 1 as the magneton moment of Cr , from which the magnetic susceptibility of Cr_2O_3 comes to $83\,1 \times 10^{-6}$ The values of magnetic susceptibility of Cr_2O_3 obtained by the decomposition of $K_2Cr_2O_7$ are thus in remarkable agreement with the theoretical value, viz, 82 1, given in Table 1

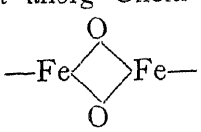
The molecular weight of most of the oxides of chromium is not known as most of these compounds exist only in the solid state. It is therefore a difficult matter to know the individual valency state of the different chromium atoms in the molecule The various attempts which have been made to find the concordance between the calculated and the observed values of the magnetic susceptibility are futile as they only yield an average value of the different valencies of the chromium atoms in the compound Wedekind and coworkers [Wedekind and Fetzer, (Ber 1907, **40**, 401), Wedekind and Horst (Ibid 1915, **48**, 105), Wedekind and Albreight (*Z* anorg Chem 1933, 210, 105)] measured the magnetic susceptibility of the following oxides, viz, CrO_3, Cr_5O_{13}, Cr_5O_{12}, CrO_2, Cr_8O_{15} $11H_2O$ and Cr_2O_3 and suggested that the oxides can be represented as CrO_3, $3CrO_3$ $2CrO_2$, $2CrO_3$ $3CrO_2$, CrO_2, Cr_2O_3 $6CrO_2$ and Cr_2O_3 respectively where chromium in CrO_3, CrO_2 and Cr_2O_3 groups has a valency of 6, 4 and 3.

Table II shows the average valency of chromium in different oxides calculated from magnetic data The average valency is fractional in most of the cases, which can be explained on the basis of chromium chromate structure to these oxides, in which chromium exists in two valency states, viz, 3 and 6 The average valency calculated from experimental data has been shown in the last column, which shows very good agreement with those calculated from the theoretical value in each case

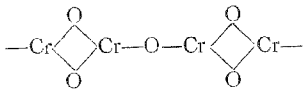
TABLE II

% decomposition of CrO_3	Chromium chromate formula	Average valency of chromium	
		Calculated	Experimental
0	CrO_3	6	5 95
25	Cr_2O_3 $6CrO_3$	5 25	4 97
28 6	Cr_2O_3 $5CrO_3$	5 14	4 78
33 3	Cr_2O_3 $4CrO_3$	5 0	...
40	Cr_2O_3 $3CrO_3$	4 8	4 08
50	Cr_2O_3 $2CrO_3$	(ferromagnetic)	.
66 6	Cr_2O_3 CrO_3	4 0	3 92 4 18
75	$3Cr_2O_3$ $2CrO_3$	3 75	3 64
80	$2Cr_2O_3$ CrO_3	(ferromagnetic)	...
100	Cr_2O_3	3 0	3 0

The magnetic properties of ferric oxide have been attributed by Krause and Tulecki (Zeit anorg Chem 1933, **213**, 292) to the group



From the structures given previously (cf. part XI) it is obvious that the ferromagnetic property of the oxides formed at 50% and 80% decomposition of the chromate which are represented by formula (VIIa) and (Xa) respectively, are due to the group :



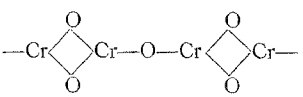
In the chromium chromate corresponding to 75% decomposition, which is represented by structure (IXa) which contains two such groups, the effect of one group has been counterbalanced by that of the other.

SUMMARY.

The magnetic properties of the various oxides of chromium have been explained on the basis of the chromium chromate structures of the general formula aCr_2O_3 $bCrO_3$, and by the ordinary valencies of chromium, viz., 3 and 6, as shown in Part XI.

The discrepancies between the calculated and observed values have been explained as due to traces of magnetic impurities in some of the oxides, and on the basis of polymerisation in some cases.

The ferromagnetic properties of some of the oxides of chromium have been shown to be due to the presence of a single group.



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