STUDIES ON CONSTANT PARAMAGNETISM, PART I.*

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ABSTRACT.—The constant atomic susceptibilities of the elements V to Mn are found to depend on the number of electrons in the d shell in a manner analogous to the dependence of the Bohr magneton numbers for these elements. The temperature co-efficient of susceptibility has a very low negative value for compounds like V_2O_5, $KMnO_4$, while it has a higher positive value for $K_2Cr_2O_7$. Susceptibilities of V_2O_5 in the amorphous and the crystalline states are different.

The study of paramagnetic substances containing atoms of the different transition series should properly be divided into three sections according to the nature of the chemical bond holding the magnetogenetic atom with the rest of the molecule. When such an atom is held by (1) a heteropolar bond the paramagnetic properties are defined by the theories of Hund, Bose, Stoner and Van Vleck and his co-workers. The magnetic behaviour is different when the bond is (2) homopolar or (3) metallic. While substances belonging to class (1) show a dependence of susceptibility on temperature given by the Curie-Weiss Law, that for classes (2) and (3) is either (*a*) complex or (*b*) practically independent of temperature. Known examples of (*b*) are many metallic elements, and a few compounds like $KMnO_4$, $K_2Cr_2O_7$, luteocobaltic chloride, V_2O_5 and some others, all containing atoms of the transition series.

The susceptibilities (χ) of some such compounds at room temperature together with the atomic susceptibilities (χ_A) for the magnetogenetic atom as determined from χ are given below.

TABLE I.

	$\chi . 10^6$	$\chi_A . 10^6$	Author.
TiO_2 (amorphous)	·074	15·1	This work
V_2O_5 ,,	·338	42·3	,,
V_2O_5 (crystalline)	·324	41·0	,,
V_2O_5 (amorphous)	(·354)	43·7	Perrakis [1]
NH_4VO_3	·120	40·3	This work
	(·163)	44·5	Perrakis [1]
$NaVO_3$	·160	40·6	This work
	(·193)	44·3	Perrakis [1]
$KMnO_4$		64·4	Ishiwara [2]
		56·5	Collet [3]
	·153	58·0	This work
$K_2Cr_2O_7$	·108	47·8	This work
	·13	(50·6)	Berkman & Zocher [4]
		63·3	Weiss & Collet [5]
		54	Gray & Dakers [6]

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The χ_A values are either given by the respective authors or have been calculated from their data by these authors, in which case they have been put within brackets, on the basis $()=4\cdot6$, $NH_4^+=12$, $Na'=7$, $K'=16$, all in units of $-1\cdot10^{-6}$.

The thermo-magnetic behaviour of some of the compounds belonging to this class has been studied by the authors from room temperature to about 500°C or less where decomposition sets in. The measurements were carried out by the translational method of Weiss and the apparatus used was the same as that described by Foex and Forrer in Jour. de Physique, 7, 180, 1926. The upper limit to the error may be placed at 2% for absolute and less than 1% for relative values, though the actual errors are considered to be less. To carry out the measurements a known weight of the substance is packed in a glass tube (which has previously been calibrated at different temperatures), placed in a non-homogeneous magnetic field and restored to its initial position by electrodynamic action when the field is excited. The current necessary for this compensation is a measure of the force displacing the specimen, and hence of its apparent susceptibility. As the observations are made in atmospheric air this apparent susceptibility with respect to air can easily be converted into the true value when the susceptibility of air at different temperatures as also the density of the material is known. When the force is too small to measure the compensating current with accuracy the deflection itself may be taken to be proportional to the force. In that case the working formula may be written as follows:

$$\chi_{true} = \frac{\dfrac{d_1-d_0}{m_1}}{\dfrac{d_2-d_3}{m_2}}\chi + \frac{k}{\rho}$$

where d_0 = deflection due to glass tube alone at the temperature of the experiment.

d_1 = deflection due to glass tube and material at the temperature of the experiment.

m_1 = mass of the material taken.

d_2 = deflection due to glass tube and standard substance at the above temperature.

d_3 = deflection due to glass tube at room temperature.

m_2 = mass of the standard substance.

k = volume susceptibility of air at the temperature of the experiment.

ρ = density of the material under observation.

χ = mass susceptibility of the standard substance.

The standard substance taken is conductivity water for which χ is taken to be $-\cdot719.10^{-6}$ and the volume susceptibility of air at t°C is taken to be given by the relation

$$k = \frac{2\cdot65\ 10^{-3}}{(273+t)^{\frac{3}{2}}}$$

(Landolt and Bornstein's Tables, Vol. 2)

The correction factor $\dfrac{k}{\rho}$ is of the order of $\cdot01.10^{-6}$ and must be carefully computed when low susceptibilities are concerned.

RESULTS.

TABLE 2.

V_2O_5 (cryst.).

Temp.	$\chi \cdot 10^6$	Temp.	$\chi \cdot 10^6$	Temp.	$\chi \cdot 10^6$
30°C	·321	183	·315	317	·312
61	·320	212	·314	362	·310
96	·319	253	·314	396	·311
124	·319	286	·313	446	·310
156	·317			485	·309
				522	·309

TABLE 3.

V_2O_5 (amorphous).

Temp.	$\chi \cdot 10^6$	Temp.	$\chi \cdot 10^6$	Temp.	$\chi \cdot 10^6$
30°C	·337	213	·332	362	·329
96	·336	253	·332	394	·320
132	·335	287	·330	448	·327
181	·333	315	·331	508	·328

TABLE 4.

NH$_4$VO$_3$.

Temp.	χ·10^6	Temp.	χ·10^6	Temp.	χ·10^6
31.3°C	.120	.536	.122	84.8	.130
38.5	.120	62.8	.124	96.5	.133
46.4	.121	75.2	.126	102.4	.136

TABLE 5.

KMnO$_4$.

Temp.	χ·10^6	Temp.	χ·10^6	Temp.	χ·10^6
30.2°C	.160	88.2	.157	152.0	.153
48.5	.158	102.5	.156	163.2	.153
56.4	.159	123.0	.155	172.5	.153
69.8	.158	136.8	.155	190.3	.16a

TABLE 6.

K$_2$Cr$_2$O$_7$.

Temp.	χ·10^6	Temp.	χ·10^6	Temp.	χ·10^6
29.6°C	.108	214	.120	362	.125
63	.111	256	.122	390	.125
85	.113	289	.123	402	.122
122	.115	328	.124	450	.124
165	.117			495	.125

TiO$_2$—The material was prepared by the action of ammonia on TiCl$_4$ and was amorphous. The precipitate was dried and heated at 400°C for about an hour.

V_2O_5—The amorphous powder was prepared from Merck's NH_4VO_3 by prolonged heating at about 180°C. When decomposed by heating at higher temperatures traces of other oxides of vanadium, which are more paramagnetic, are formed. These can again be oxidised to form V_2O_5 by adding HNO_3 and re-heating at rather low temperature to drive away the acid.

The crystalline variety was prepared by melting the amorphous substance (at 660°C) in a platinum crucible.

It is to be noted that there is a difference of 1·3 units in the χ_4 values of the amorphous and crystalline varieties. We shall come to this later on.

The results show that for both the varieties, amorphous and crystalline, there is a reduction in the χ value amounting at 500°C to about 4% of the values at room temperature.

Our values for χ_4 are in each case lower than Perrakis' as may be seen from table 1. In the course of preparing amorphous V_2O_5 by the method specified we found values for $\chi \cdot 10^6 = \cdot 358, \cdot 353, \cdot 343$, the progressive lowering corresponding to a gradual lowering of the temperature at which NH_4VO_3 was reduced. The purest we could get had a value $\chi = \cdot 338 \cdot 10^{-6}$ when heating took place at a temperature below 200°C. This on re-heating with HNO_3 gave the same value. Apart from the question of the presence of other more paramagnetic oxides, it may so happen that for the amorphous variety the susceptibility depends to some extent on the size of the particles.

NH_4VO_3—The material was Merck's preparation. It begins to decompose at about 50°C. Within this short range the result shows a constant paramagnetism. This is in conformity with Perrakis' observations (*loc. cit.*), whose measurements extended from 17°C to 45°C.

$KMnO_4$—The material was Kahlbaum's preparation 'for analysis.' It gave at first a χ value $= \cdot 215 \cdot 10^{-6}$ whence the value came out to be $66 \cdot 4 \cdot 10^{-6}$. This was in agreement with Ishiwara's value of $64 \cdot 4$. But as Coliet has remarked that she found a value of $56 \cdot 5$ after repeated re-crystallisation we followed a similar procedure. After re-crystallisation the χ value lowered and came to $57 \cdot 7$. This observation incidentally removes the discrepancy between the values of the above two authors.

Chemical evidence shows that evolution of oxygen begins at about 165°C producing MnO_2 as a product. Our magnetic evidence is in conformity with this. Above 150°C the slight lowering of the χ value of $KMnO_4$ is practically balanced for a small range of temperature by the higher susceptibility of the MnO_2 produced and from about 175°C the χ value begins to increase.

$K_2Cr_2O_7$—This is also Kahlbaum's ' for analysis.' The behaviour of this salt is different from that of the others in that here is a gradual increase in χ with temperature. This increase continues up to the melting point (cir. 396°C) (where it amounts to an excess of about 16% over the room temp. value), beyond which there is a slight reduction. Here also, as in $KMnO_4$, recrystallisation lowered the value. As may be seen from table 1 the values are lower than those found by other authors. That the gradual increase does not arise from gradual decomposition is manifested by the fact that the initial value of χ is regained on cooling. To be sure about the result the measurements were repeated on three different samples, each in a different ampoule, and eight independent sets of readings were taken with them. Gray and Dakers[6] expect on certain grounds that the polychromates should have a positive temperature coefficient.

CONCLUSION

From the results of our measurements we conclude :

(1) Some substances showing the phenomenon of constant paramagnetism have a negative coefficient of susceptibility, the mean values of which are as follows :—

V_2O_5 (amorphous)—$6 \cdot 10^{-5}$, V_2O_5 (cryst.)—$8 \cdot 10^{-5}$, both between 30° and 500°C; $KMnO_4$—$3 \cdot 10^{-4}$ between 30 and 160°C. The rather high value for $KMnO_4$ may be due to some undetected paramagnetic impurity.

(2) $K_2Cr_2O_7$, however, has a positive coefficient which is higher in value than the negative values. (Mean value = $3 \cdot 1 \cdot 10^{-4}$ between room temperature and 400°C.)

These values may be compared with the temperature coefficient of susceptibility for regular paramagnetics, which is of the order of $-37 \cdot 10^{-4}$.

(3) For the consecutive elements Ti-Mn in the first transition series the constant atomic susceptibilities as determined from their oxides show a gradual increase with atomic number.

At. No.	Element.	$x_A \cdot 10^6$
22	Ti	15
23	V	30
24	Cr	48
25	Mn	55 7

A parallel behaviour occurs for regular paramagnetics (*i.e.*, those obeying the Curie-Weiss Law), where the magneton numbers gradually increase with increasing number of $3d$ electrons in the ion.*

(4) From the above similarity of behaviour we can risk the suggestions that:—

(*i*) Iron, cobalt and nickel will have a constant atomic susceptibility in compounds where the valency is fully saturated. These values will diminish in the order iron-cobalt-nickel.

Moreover:

(*ii*) Such a compound will be paramagnetic or diamagnetic according as the paramagnetic atomic susceptibility of the transition element is greater or less than the total diamagnetic susceptibility of the rest of the molecule.

(5) The χ_{ι} value is not an absolute constant for the atom, but is susceptible to changes in the crystalline field, as is manifested by the different values for amorphous and crystalline V_2O_5.

DISCUSSION.

Our values for χ_{ι} differ slightly from those found by other observers, being lower than theirs except only for Mn where it is higher by only $1 \cdot 2$ units from Collet's value. Discrepancies occur in correcting for diamagnetism, as some of the authors do not state the values used by them. It is to be noted that paramagnetic contamination of water or of the material should increase the χ value and not diminish it.

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* This has been pointed out by the authors in Science and Culture, **1**, 587, 1936 and the analogy of behaviour extended to other transition series *vide*, Ray Chaudhuri and Das Gupta, Science and Culture, **1**, 654, 1936.

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