The action of oxygen upon aluminum bromide was investigated.

The effect of ethylaluminum dibromide and of diethylaluminum bromide in the presence and in the absence of air upon the isomerization of *n*-butane was investigated.

The mechanism of isomerization was discussed.

RIVERSIDE, ILLINOIS RECEIVED JUNE 8, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BUFFALO]

The Defect in the Magnetic Susceptibility of Manganese Dioxide and Other Compounds of Manganese[1]

BY J. T. GREY, JR.[2]

The magnetic susceptibility of manganese dioxide has been measured in several previous investigations, but the values recorded are widely divergent, for $\chi_{obs.}$ varied from 26.03×10^{-6} at 37° to 66.2×10^{-6} at 20°. Moreover, when the atomic moment of the quadrivalent manganese ion was calculated from the accepted value of the mass susceptibility it was found that the value did not check that calculated theoretically for an atom with three unpaired electrons, assuming only the spin moments to be effective. A survey of the literature revealed that this defect in the magnetic susceptibility was not peculiar to manganese dioxide, but that it existed in the oxides and certain salts of all the transition elements.

These deviations have been attributed in the past to the interatomic field effects within the crystal lattice, but no clearly defined explanation had been advanced. Therefore, it was the purpose of this investigation to measure accurately the mass magnetic susceptibility of manganese dioxide and certain other compounds of manganese and to attempt to derive therefrom an explanation for the observed defect in the magnetic susceptibility.

Experimental

Method of Measurement.—The method of measurement and the apparatus used in this research were the same in principle as that used previously in this Laboratory.[3]

A refined apparatus was built to ensure greater accuracy and efficiency. The specific changes were as follows: (a) A glass capsule was employed to hold the sample and a glass compensator was attached to the suspension system so that the magnetic contribution of the capsule was cancelled. (b) Possible residual magnetism in the field source was eliminated by using an air core magnet instead of an iron core magnet. (c) The gas-filled photo tube was replaced by a high vacuum type tube which had more constant characteristics. (d) The mechanical interrupting contacts in the magnet circuit were replaced by an arrangement of Thyratrons which freed the circuit of variable contact resistances. (e) The current output of the generator was stabilized by floating a battery across the output terminals. (f) The current in the magnet circuit was measured directly. (g) The temperature was thermostatically maintained at 30.0 ± 0.1°.

Each of the experimental runs was made in accord with a routine procedure. A glass-stoppered Pyrex capsule was packed full of the sample, stoppered, weighed and laid on the glass suspension hooks in a definite position. The magnets and their supports were affixed and the thermostatically controlled temperature-housing was sealed. The apparatus was started and after the entire setup had had time to reach thermal equilibrium, the resistance in the magnet circuit was varied until the observed deflection of the capsule, and its contents, reached the predetermined standard value which had been decided upon during the calibration. When this deflection had been maintained constant for a period of ten minutes—approximately forty magnetization cycles—the system was considered to be at equilibrium and the voltage drop across the standard resistance in the magnet circuit was recorded.

The magnetic susceptibility of the material was then calculated by substituting in the equation, $m\chi = C/E^2$, which was readily deduced by considering the variables in a given experimental run. Thus, since the effect of the magnetic field on the capsule is nullified by the compensator and the capsule and its contents are always raised to the same total deflection, the only variables are the mass, the susceptibility and the magnetic field strength. Further, it was shown that the field strengths in the range employed in this investigation were directly proportional to the current in the magnet circuit, or inversely proportional to the voltage drop across the standard resistance, see Fig. 1.

The apparatus was calibrated with several purified compounds of accurately known susceptibility. The susceptibilities were corrected to 30°. The results are shown in Table I; the individual values of C are the average of at least two determinations in every case.

TABLE I

CALIBRATION CONSTANTS

Compound	χ at 30°	C
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	31.23×10^{-6}	4.14×10^{-8}
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	29.10×10^{-6}	4.13×10^{-8}
$K_4Fe(CN)_6$	6.87×10^{-6}	4.11×10^{-8}
$CuSO_4 \cdot 5H_2O$	5.90×10^{-6}	4.10×10^{-8}
Average value of C		4.12×10^{-8}

Preparation and Analysis of Compounds.—It is general knowledge that manganese dioxide is extremely difficult to purify and it is doubtful that the compound has ever been prepared pure enough to conform to the formula MnO_2. In an unpublished work, Frazer and Weld have recorded measurements of the partial pressure of oxygen in equilibrium with manganese dioxide at various temperatures, and it was shown, in general, that the manganese-to-oxygen ratio depended strongly on the past history of the sample and its mode of preparation. Empirical formulas such as $MnO_{1.}$[illegible] have been typical.

Manganese dioxide was, therefore, extremely difficult

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[1] An investigation under the direction of Dr. J. H. Frazer, presently Major, U. S. Army.

[2] Abstracted from a thesis by the author, submitted to the Faculty of the Graduate School of the University of Buffalo, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1940.

[3] J. H. Frazer and Long, *J. Chem. Phys.*, **6**, 462 (1938).

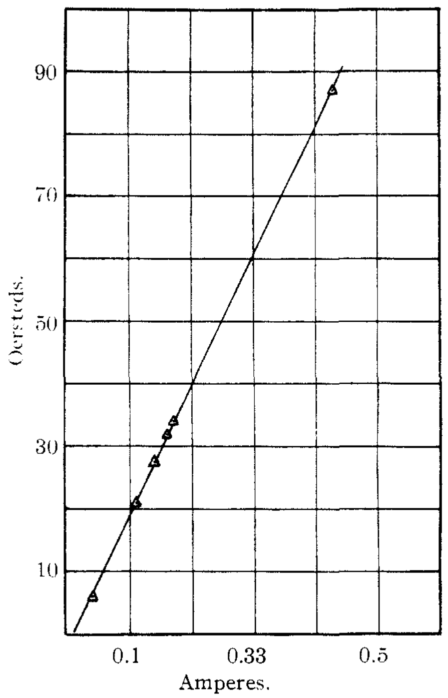

Fig. 1.

to purify, because rigorous treatment disturbed the mobile equilibrium between the oxygen of the manganese dioxide and the atmospheric oxygen and lower oxides of manganese resulted. This applied especially to dehydration. The contaminating oxide which most probably resulted from the methods used was the sesquioxide, Mn_2O_3.

Further, the tenacity with which traces of impurity were retained in the manganese dioxide was possibly due to the existence of definite complex compounds of quadrivalent manganese in which alkali ions acted as cations and chloride, sulfate, or hydroxo ions and water molecules were bound to the manganese ions in the complex anion. Unpublished research in this laboratory points to the existence of such complexes.[4]

Manganese dioxide, prepared by several methods, was investigated. The final samples were prepared by the methods which had given the best preliminary results. These were (a) the decomposition of permanganic acid in nitric acid[5] and (b) the alkaline oxidation of manganous hydroxide by hydrogen peroxide.[6]

In each method the precipitated manganese dioxide was washed only with distilled water, sucked dry on a Buchner funnel, dried for forty-eight hours at 120° in a convection oven, and stored while still warm in stoppered weighing bottles. Further drying caused excessive decomposition. The analyses are as shown in Table II.

Table II

Prepn.	Sample, g.	Wt. of Mn found, g.	Wt. of Mn as MnO_2, g.	% MnO_2	% Mn_2O_3	% H_2O
MnO_2(A)	0.1000	0.06085	0.06056	95.10	1.09	3.81
MnO_2(B)	0.1000	0.05968	0.05932	92.19	2.05	5.76

Empirical formula: MnO_2(A)-$MnO_{1.99}\cdot 0.21H_2O$
MnO_2(B)-$MnO_{1.98}\cdot 0.30H_2O$

The percentage of manganese sesquioxide was calculated by assuming that all the manganese found in the sample above that required by the manganese dioxide existed as the sesquioxide and substituting in the equations

$$\Sigma \text{Mn} = \frac{\text{Mn}}{\text{MnO}_2} X + \frac{2\text{Mn}}{\text{Mn}_2\text{O}_3} Y \qquad (6.1)$$

$$\text{Active O}_2 = \frac{\text{O}_2}{\text{MnO}_2} X + \frac{\text{O}_2}{\text{MnO}_2 \cdot \text{MnO}} Y \qquad (6.2)$$

where X equals the percentage of MnO_2 and Y equals the percentage of Mn_2O_3. By proper algebraic manipulation of equations 6.1 and 6.2 X and Y are obtained in terms of ΣMn and active O_2, multiplied by different characteristic numerical constants in each case.

The preparation and analyses of the compounds other than manganese dioxide and the magnetic data for each of them are collected in Table III.

Analytical Methods.—Standard analytical procedures were employed. The percentage of manganese dioxide as active oxygen and total manganese were determined on the same sample by destroying the first end-point and retitrating in alkaline solution. The methods of Mohr[7] and of Volhard[8] were successively applied to the same sample.

The complex salts were analyzed by previously described methods.[9] Fluorine was determined by the method of Willard and Winter.[10]

Sulfur was determined by the method of Brunch.[11]

Results and Discussion

The data for calculating the magnetic susceptibility of the compounds in which the magnetic defect was investigated and the calculated values of x are shown in Table III.

The values of the mass magnetic susceptibility of manganese dioxide shown in the tenth column of the table have been corrected for the paramagnetic contribution of the respective amounts of manganese sesquioxide shown in tabulated analysis above and also for the diamagnetic contribution of the respective amounts of water remaining in the samples.

The value of the magnetic susceptibility of potassium pentafluoaquo-manganiate has been corrected for the 3% deficiency noted above under the preparation.

A spectroscopic analysis of the samples of manganese dioxide revealed traces of potassium, calcium, magnesium, copper and iron. However, traces of alkali ions were shown to have no noticeable effect on the mass magnetic susceptibility of manganese dioxide by comparing the observed susceptibilities of a purposely contaminated and a purified sample.

The mass magnetic susceptibility of these

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(4) A personal communication from Dr. G. H. Cartledge.

(5) J. C. W. Frazer and Whitesell, This Journal, **45**, 2841 (1923).

(6) Weld, Thesis, Johns Hopkins University, Baltimore, Md., 1928.

(7) Treadwell-Hall, "Analytical Chemistry," 4th ed., vol. 2, J. Wiley & Sons, New York, N. Y., 1912, p. 625.

(8) Volhard, *Am. Chem. Pharm.*, **198**, 318 (1879).

(9) Weinland and Lauenstein, *Z. anorg. allgem. Chem.*, **20**, 40 (1899).

(10) Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(11) Brunch, *Z. anal. Chem.*, **45**, 541 (1906).

TABLE III

		Percentage composition Mn			Anion				$\chi \times 10^{-6}$ at 30°			Calcd. atomic moments	
Compound	Prepn.	Calcd.	Found	Anion	Calcd.	Found	Sample, g.	Volt.	Obs.	Cor.	Valence	χ Obs.	Unpaired elect.
MnO_2(A)	[a]	[l]					0.3565	0.05500	38.22	39.40	Mn^{+4}	2.86	3.88
							.3563	.05505	38.15				
MnO_2(B)	[b]						.3073	.06070	36.39	38.40	Mn^{+4}	2.86	3.88
							.3107	.05968	37.23				
$K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$	[c]	14.49	14.61	C_2O_4	46.42	46.37	.2576	.13734	8.48		Mn^{+4}	2.79	3.88
$K_2[MnF_6]$[d]	[e]	22.26	22.06	F	45.10	45.13	.3881	.06656	24.00		Mn^{+4}	3.84	3.88
$K[Mn(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O$	[f]	14.83	14.84	$C_3H_2O_4$	55.13	55.24	.3311	.07023	25.30		Mn^{+3}	4.37	4.90
$K_2[MnF_5(H_2O)]$[g]	[h]	22.21	21.60	F	38.61	37.56	.3970	.06655	23.40	24.10	Mn^{+3}	3.87	4.90
$K_3[CoF_6]$[i]							.1210	.10340	25.84		Co^{+3}	4.26	4.90
$MnS\beta$ (red)	[j]	63.22	63.31	S	36.78	35.92	.2436	.06132	44.98		Mn^{+2}	3.06	5.92
$MnS\alpha$ (green)	[k]	63.22	63.50	S	36.78	35.27	.5036	.03636	61.88		Mn^{+2}	3.62	5.92

[a] See Ref. 5. [b] See Ref. 6. [c] Cartledge and Ericks, THIS JOURNAL, **58,** 2069 (1936). [d] Since this complex hydrolyzed on exposure to air, the samples were protected by a desiccant, $CaCl_2$. [e] Weinland and Lauenstein, *Z. anorg. allgem. Chem.*, **20,** 40 (1899). [f] Cartledge and Nichols, THIS JOURNAL, **62,** 3057 (1940). [g] Although the analyses showed that the complex salt was low in both manganese and fluorine, the atomic ratio of manganese to fluorine was correct. The discrepancy was, therefore, caused by moisture in the sample. The observed magnetic susceptibility was corrected to allow for this 3% deficiency. [h] Prepared by oxidizing manganous sulfate with potassium permanganate in the presence of hydrofluoric acid and an excess of potassium fluoride. The complex salt was stored over a desiccant, $CaCl_2$. [i] The author is indebted to Dr. R. L. Mitchell, formerly of the University of Buffalo, for this sample of potassium hexafluocobaltiate. [j] Prepared by a modification of the method of Schnasse (*Z. physik. Chem.*, **20B,** 89 (1933)). [k] Prepared by boiling and aging the red form $(MnS)_\beta$. [l] For analyses see Table II.

compounds is significant, but the respective atomic moments calculated therefrom are more interesting, for they emphasize the defect in the magnetic susceptibility. They are given in the last two columns of the table.

These results indicate that some circumstance has befallen part of the unpaired 3*d* electrons which prevented the affected electrons from behaving normally, potassium hexafluo-manganiate excepted. The discrepancy is more pronounced in the case of the simple salts than in the case of the complex ones.

Pauling[12] has recently explained the interatomic forces in the transition elements by assuming that 2.56 of the 3*d* orbitals for the series potassium to copper form secondary bonds through hybridization with 4*s* and 4*p* orbitals. The remaining 2.44 of the 3*d* orbitals are assumed to have only a small interatomic overlapping and, hence, in accord with the rule of maximum multiplicity contain the greatest possible number of unpaired electrons.

A careful correlation of the spatial orientation of the five *d* orbitals of manganese that are available for bond formation with the crystal lattice of manganese dioxide revealed that each of three of the *d* orbitals has four segments directed along the bisectors of the interaxial angles in the respective axial planes—that is, directed toward the next-nearest neighboring cation. These are in addition to the normal octahedrally-directed orbitals and are not considered well suited to the formation of strong bonds. It is, therefore, highly probable that secondary cation to cation bonds are formed through the overlapping of these "interaxial" orbitals. An interaction of this type would naturally deplete the unpaired electrons on the manganese ions and the magnetic moment would be lowered.

It is interesting to note that the defect in the magnetic susceptibility of manganese dioxide involves about 0.60 electron; the remaining 2.40 *d* electrons on each manganese ion are unpaired. This figure, 2.40, agrees quite well with that given by Pauling as the average value of the "atomic" orbitals of the transition elements.

The shielding effect of large anions has been shown in the complex compounds. Although X-ray studies of these complexes have not been reported in the literature, it is reasonable to assume that the central manganese ion is well shielded by the large anions which surround it and that the crystals have large lattice constants. Therefore, the possibility of forming secondary bonds should be less and the observed magnetic susceptibility should be more nearly normal The empirical results support these assumptions with the exception of $K_2[Mn(C_2O_4)_2(OH)_2]$. In the latter case the discrepancy must be due to another mechanism.

In the case of manganous sulfide, it was known that the unstable form exhibited a greater defect than did the stable form. This fact has been verified. A study of the respective crystal lattices showed the unstable form offered a slightly greater possibility for the formation of secondary bonds, because the cation-to-cation distances were slightly shorter for neighboring cations.

Summary

1. The mass magnetic susceptibility of manganese dioxide has been found to be 39.0 × 10^{-6} at 30°.

2. The magnetic susceptibility of potassium dioxalato-dihydroxo-manganeate, potassium hexafluomanganeate, potassium dimalonato-diaquomanganiate, potassium pentafluo-aquo-manganiate, and potassium hexafluocobaltiate has been reported for the first time.

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(12) Pauling, *Phys. Rev.*, **54,** 98 (1938).

3. The magnetic susceptibility of each of two of the allotropic forms of manganous sulfide has been confirmed.
4. A possible theoretical explanation of the defect observed in the magnetic susceptibility of certain compounds of manganese has been advanced.

BUFFALO, NEW YORK RECEIVED NOVEMBER 21, 1945

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Poisson-Boltzmann Equation Derived from the Transfer of Momentum

BY ALBERT SPRAGUE COOLIDGE AND WALTER JUDA

The modern treatment of equilibrium states of electrolytic solutions is based on the Poisson–Boltzmann equation

$$\nabla^2\bar{\psi} = -\frac{4\pi}{D}\Sigma_i n_i^0 \epsilon_i e^{-\epsilon_i\bar{\psi}/kT} \qquad (1)$$

Here n_i^0 is the stoichiometric concentration (assuming complete dissociation) of ions of the species i with charge ϵ_i, and $\bar{\psi}$ is the time average of the electrostatic potential. This is a continuous point-function, having the value zero at all ordinary points in the solution, but differing from zero at special points in the neighborhood of some permanent feature such as a phase-boundary or fixed charge. It may also differ from zero at an ordinary point if the average is taken, not over all time intervals, but only over those during which some specified configuration of ions happens to prevail in the neighborhood—this may be loosely called the average at a special point near the given configuration, and in the ensuing discussion, the term "special point" will be understood to include this interpretation. D is the dielectric constant of the solvent.

The theoretical foundations of (1) have been clearly discussed by Fowler and Guggenheim[1] and by Onsager.[2] The rigorous form of the Boltzmann equation is

$$\bar{n}_i = n_i^0 e^{-W_i/kT} \qquad (2)$$

where $\bar{n}_i$ is the time average concentration of the ionic species i at any special point, and W_i is the potential of the average force acting on an i ion whenever it happens to be at the special point, this force itself being $-\nabla W_i$. In other words, W_i is the work which would be required to carry an i ion from an ordinary point to the special point, if at every point in the path it were subjected to just the average force associated with the proximity of the special feature or configuration involved, this latter being held constant. The Poisson equation takes the form

$$\nabla^2\bar{\psi} = -4\pi\bar{\rho}/D = -\frac{4\pi}{D}\Sigma_i\bar{n}_i\epsilon_i \qquad (3)$$

where $\bar{\rho}$ is the average charge density. It is not immediately obvious that this equation is correct, for if the ions are true point charges the instantaneous value of ρ is always either zero or infinity and cannot be averaged directly, while if the ions have a finite extension and the $\bar{n}_i$ are the distribution functions for their centers of mass, then $\bar{\rho}$ at each point will depend on the $\bar{n}_i$ averaged over a corresponding extension in the neighborhood of that point. We shall show later that (3) holds in the limit as the extension approaches zero. In order to obtain (1) it is now necessary to assume that

$$W_i = \epsilon_i\bar{\psi} \qquad (4)$$

This assumption can be justified only *a posteriori* by the self-consistency of the results to which it leads. It implies that on the average, the force acting on any ion which happens to be present at a special point can be computed from the average field that prevails there whether or not an ion is present. Since this force is due to the field of the other ions in the neighborhood, the assumption is essentially that there is no correlation between the presence or absence of an ion at the given point and the fluctuations of the field arising from the neighboring ions.

Onsager[2] has considered the conditions under which (4) is valid. So long as $\epsilon_i\bar{\psi} << kT$, (1) reduces to the familiar linear approximation of Debye and Hückel, and its solutions give distribution functions in the form of superposable ionic atmospheres. At least in the interior of the solution, the atmosphere of each ion is spherically symmetrical and exerts no force upon the ion at its center, which therefore experiences only the forces due to the distribution of other ions with their atmospheres which would exist, under the given circumstances, if the central ion were not there. Assumption (4) is therefore vindicated in the usual theory of ionic interaction. At points near a phase boundary this reasoning fails; even though superposable, the atmospheres of the ions are distorted and exert forces on the "central" ions, usually away from the boundary, which cannot be calculated from the average potential. Thus, Langmuir's[3] theory of forces on walls needs examination to determine the errors produced by overlooking this effect. In the remainder of this

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[1] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, 1939, p. 405.

[2] L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

[3] I. Langmuir, *Science*, **88**, 430 (1938); *J. Chem. Phys.*, **6**, 873 (1938).