

MAGNETISM AND CATALYSIS

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The possibility of relationships between catalytic activity on the one hand, and magnetic fields and magnetic properties on the other, has interested many workers. It cannot be denied that those chemical elements which show the most pronounced catalytic activity, namely, the transition group elements, are also the elements which show the most interesting magnetic properties. In at least one case, the ortho-para hydrogen conversion, there is a clear-cut relationship between magnetic moment and catalytic activity. This is not to say that all catalytic activity is due to magnetism. It may yet appear that catalysis and magnetism are different manifestations of some more fundamental atomic property. But for the present, the chief applications of magnetism to catalysis are in structural studies of catalytic solids. A review of such applications, and of certain related effects, is the purpose of this article. Susceptibility data are included for some substances of major catalytic interest.

I. INTRODUCTION

It will be assumed that the reader is familiar with the principles of magnetochemistry (16, 132, 186, 192, 207); nevertheless, a few definitions will be given in this section, and some experimental methods will be briefly described.

Most substances are very slightly repelled by a magnet. These substances are said to be diamagnetic. The degree of diamagnetism does not vary greatly in different substances and has not, as yet, proved particularly useful in structural chemistry, in spite of considerable effort in this direction. Diamagnetism is independent of field strength and of temperature. It is actually a universal property of matter, because all substances have at least an underlying diamagnetism for which correction must be made for accurate determination of the permanent moment which may be present.

Many substances are slightly attracted to a magnet. These are paramagnetic. The effect is found especially among the transition group elements, and is related to the presence of incompletely filled energy levels. The existence of paramagnetism implies an unpaired electron. Atoms, ions, and molecules which have an odd number of electrons are invariably paramagnetic. Paramagnetism is independent of field strength at all ordinarily attainable fields. Very frequently the paramagnetism varies inversely as the absolute temperature, although many exceptions to this are known.

A few substances are very powerfully attracted to a magnet. The effect may be 10^3 to 10^6 times as strong as paramagnetism or diamagnetism. Such substances are said to be ferromagnetic. Ferromagnetism occurs only in iron, cobalt, nickel, and in a few alloys and compounds. Ferromagnetism is dependent on field strength in a complicated way, as shown in figure 1. It is also dependent on temperature, in that above a certain temperature, for nickel about 358°C ., the ferromagnetism drops to zero and the substance becomes para-

magnetic. The temperature of this sharp magnetic transition is called the Curie point.

If a substance is placed in a magnetic field of intensity H , and the magnetic induction in the substance is B , then

$$B = H + 4\pi\vartheta$$

where ϑ is the intensity of magnetization. The quantity

$$\vartheta/H = \kappa$$

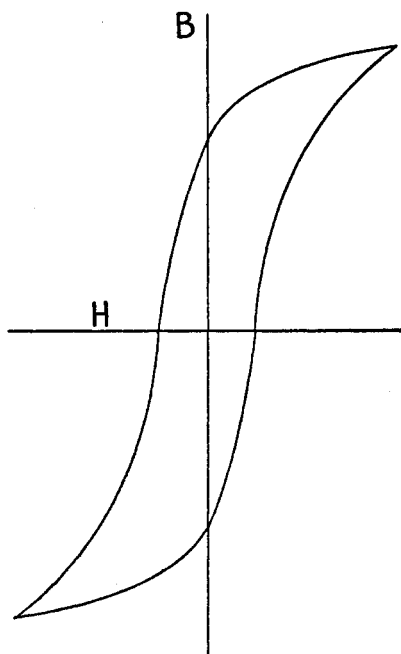


FIG. 1. Hysteresis curve showing dependence of induced magnetism on field strength for a ferromagnetic substance

is called the magnetic susceptibility per unit volume, and

$$\kappa/d = \chi$$

where d is the density, is the magnetic susceptibility per unit mass. This is the quantity with which magnetochemistry is chiefly concerned.

For paramagnetic substances χ often follows the Curie law

$$\chi = C/T$$

where C is the Curie constant and T the absolute temperature. More frequently χ follows the Weiss law

$$\chi = C/(T + \Delta)$$

where Δ is a constant. Deviations from both laws are common.

Atomic and molecular paramagnetism arises from the spin and orbital motions of the unpaired electrons. The orbital contributions are important only for the elements of the rare earth group. The effective magnetic moment, μ_{eff} , may be calculated from the susceptibility by the relationship

$$\mu_{\text{eff}} = \sqrt{\frac{3k\chi_m T}{N\beta^2}} = 2.83 \sqrt{\chi_m T}$$

where k is the Boltzmann constant, χ_m is the molar susceptibility, T is the absolute temperature, N is Avogadro's number, and β is the Bohr magneton,

$$\beta = \frac{eh}{4\pi mc} = 0.917 \times 10^{-20} \text{ erg oersted}^{-1}$$

where e is the electronic charge, h is Planck's constant, m is the electronic mass, and c is the velocity of light. For precise determinations the molar susceptibility should be corrected for the underlying diamagnetism. But, owing to a variety of effects, μ_{eff} is seldom constant over a wide temperature range. In some cases use of the Weiss law gives somewhat better results, so that the expression for μ_{eff} becomes

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_m (T + \Delta)}$$

Where the orbital contribution to the moment is negligible, the magnetic moment may be used to find the number of unpaired electron spins in the atom or molecule. The expression is

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

where n is the number of unpaired electron spins. The moment to be expected from one to five unpaired electron spins is as follows:

Unpaired electron spins.....	1	2	3	4	5
μ_{eff}	1.73	2.83	3.87	4.90	5.92

In a large number of cases the experimentally found magnetic moments agree with these values and, in general, deviations may be related to covalent binding and other types of interactions between atoms.

There are two principal methods for measuring the magnetic susceptibilities of solids. These are the methods of Gouy and of Faraday. The Gouy method, shown diagrammatically in figure 2, involves suspension of an elongated sample so that one end is in a strong magnetic field and the other in a region of negligible field intensity. The sample may be suspended from a sensitive balance. On application of the field the sample will appear to gain or lose in weight depending on whether the substance is paramagnetic or diamagnetic. The susceptibility is related to the force acting on the sample as follows:

$$f = 1/2\kappa H^2 A$$

where κ is the susceptibility per unit volume, H is the field strength, and A is the cross-section area of the sample. The apparatus is conveniently calibrated

with water, for which $\chi = -0.720 \times 10^{-6}$, or with ferrous ammonium sulfate, Mohr's salt, for which $\chi = 9500 \times 10^{-6}/(T + 1)$, where T is the absolute temperature. The sample must be surrounded by a gas of negligible magnetic susceptibility. The susceptibility of air is in general not negligible, because oxygen is strongly paramagnetic. Nitrogen and hydrogen are convenient gases to use for surrounding the tube. The sample, if powdered, may be packed into a cylindrical glass tube. The uniformity of packing will generally limit the accuracy of the measurements. The fields used may be from 1000 to 15,000 or 20,000 oersteds. In practically all measurements on solids it is necessary to investigate the susceptibility at more than one field strength. This is because most solids contain minute traces of iron or other ferromagnetic impurities.

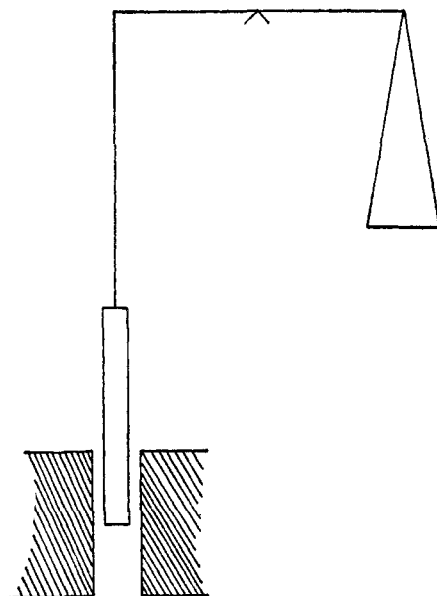


FIG. 2. Gouy magnetic balance

Such impurities lead to marked changes in susceptibilities. Correction for ferromagnetic impurities may be made by making the measurements above the Curie point of the impurities or, more simply, by plotting the susceptibility against reciprocal field strength. Extrapolation to infinite field gives substantially the susceptibility of the sample free from ferromagnetic impurities.

Measurements over a range of temperature may be made by surrounding the sample with an appropriately shaped Dewar flask into which are placed cooling liquids such as liquid air. High temperatures may be obtained by enclosing the sample in a long narrow heating coil. It is rather difficult to perform both high- and low-temperature experiments on the same apparatus.

In the Faraday method the sample may be much smaller. It is placed in a

magnetic field which has a fairly sharp gradient along an axis in which the sample is free to move (figure 3). The force acting on the sample is given by

$$f = m\chi H \frac{dH}{dx}$$

where m is the mass of the sample, χ is the susceptibility per unit mass, H is the field strength, and dH/dx is the field gradient. The method is convenient and sensitive, small samples only are required, and no separate determination of the density is necessarily obtained. The sample may be suspended on a torsion arm, although a very large number of modifications have been suggested, using both horizontal and vertical displacement. For powdered solids the Faraday method appears to have some definite advantages over the Gouy method.

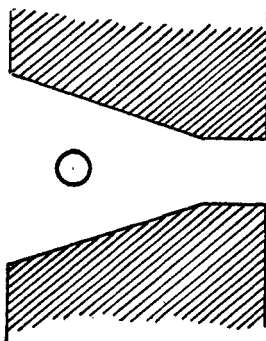


FIG. 3. Principle of the Faraday magnetic balance

Both the Gouy and the Faraday methods involve a motion of the sample. For the study of catalytically active substances it would be very convenient if the magnetic susceptibility could be determined *in situ*. For instance, it would be particularly useful if the preparation of the sample, measurement of catalytic activity, measurement of specific surface, and measurement of magnetic susceptibility could all be done on the same sample, without moving or transferring it in any way. There is, as yet, no method for doing this, but the development of such a method does not seem impossible. There are at least three approaches which would seem to offer promise. These are the inductance method, the Tobusch magnetometer, and the Rankine balance. They will be described briefly.

The inductance method—that is, the change in induction of a coil when a magnetic substance is placed in the coil—is, of course, a standard method for measuring the magnetic properties of ferromagnetic material such as steel. By use of a bridge and a sensitive galvanometer this method may be developed to measure susceptibilities of the order of 10^{-3} . A bridge for this purpose has been described by Elmore (42) after a design by Bitter. A diagram of the bridge

is shown in figure 4. The sensitivity of this bridge would have to be increased about one thousand fold to make it suitable for susceptibility measurements on non-ferromagnetic samples. Very great sensitivity may be achieved by use of a heterodyne beat system, but efforts so far to adapt this to susceptibility measurements have failed. The problem does not, however, appear to be insurmountable. The measurement of samples *in situ* within a coil, without necessity for removing the sample or adjusting the container, would appear to be a little easier than measurements in which the sample would have to be removed. It should be pointed out that inductance methods are commonly used for the measurement of magnetic susceptibilities at extremely low temperatures.

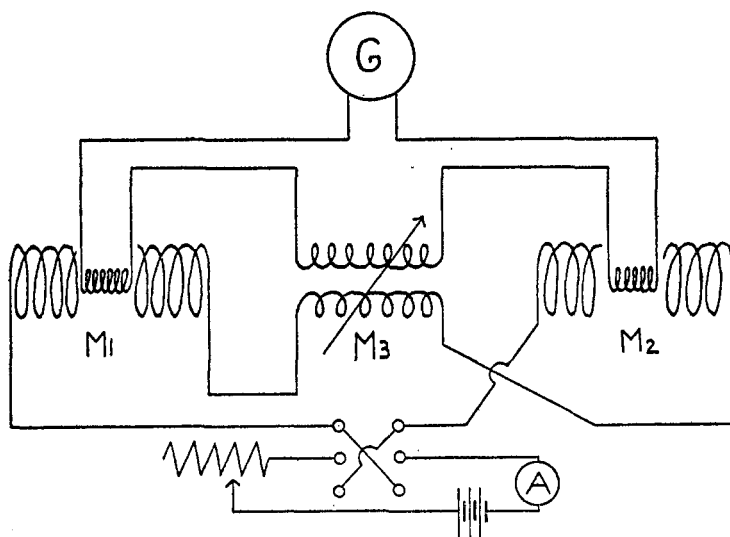


FIG. 4. Inductance bridge (Bitter-Elmore). G is a sensitive ballistic galvanometer; M_1 and M_2 are solenoids into one of which the sample is put. M_3 is a variable mutual inductance.

Another possible method for the *in situ* measurements of magnetic susceptibilities is the Tobusch magnetometer (see figure 5), as modified by Bozorth (29) and others (56, 177). The sample is placed inside one of two coils which are arranged on each side of an astatic magnet suspension system. The astatic system consists of two small rod-shaped permanent magnets arranged in opposition and placed a few centimeters apart on a rod attached to a delicate suspension fiber. Passing a current through the two solenoids has no effect on the suspended system unless one solenoid contains a substance of different susceptibility from the other. Movement of the system may be observed by a mirror and scale, and the system may be returned to a zero position by the use of a subsidiary coil placed inside one of the solenoids. The problem of increasing the sensitivity of this apparatus several hundred or thousand fold might include the use of Alnico or other alloys for the permanent magnets, and elaborate magnetic shielding.

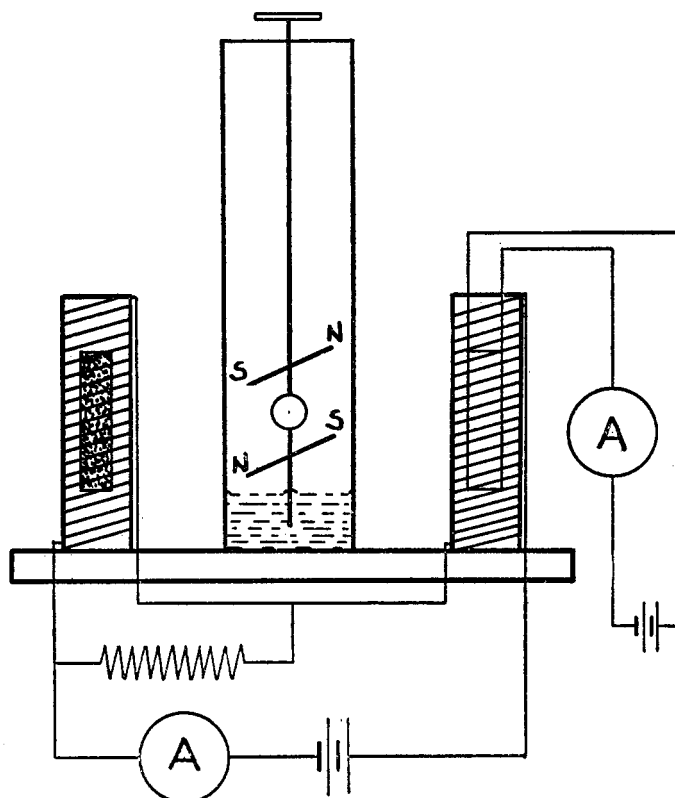


FIG. 5. Tobusch magnetometer

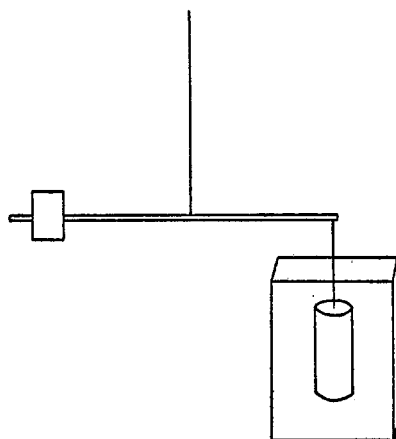


FIG. 6. Principle of the Rankine magnetic balance

The third possible *in situ* method is the Rankine balance (116, 174). In this method a small permanent magnet is suspended by a quartz-fiber system (figure 6) in such a way that the effect of stray fields is reduced. When a sub-

stance is placed near the permanent magnet a motion is induced in the suspended system. This method is sufficiently sensitive for measurements on catalytically active solids, but considerable difficulty is experienced in getting reproducible results. The field, all of which is produced by the permanent magnet, is quite small and may not exceed 100 oersteds.

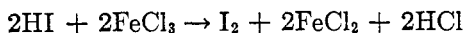
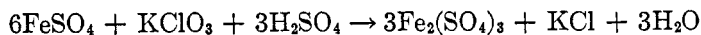
Of course, it will be noted that in both the Gouy and the Faraday methods the desired result could be achieved if the magnet were made to move while the sample remained clamped in position. This is, however, a little difficult, because the sample may weigh a gram and the magnet half a ton. With the development of super-powerful permanent-magnet alloys one difficulty may be eliminated, but the effect of stray fields may continue to be a problem.

II. INFLUENCE OF A MAGNETIC FIELD ON CHEMICAL EQUILIBRIUM AND REACTION VELOCITY

The possibility that a magnetic field might have an effect on chemical reactivity has received investigation for well over one hundred years. It must be admitted that, although some interesting and curious effects have been discovered, none of these is very startling, and none has so far contributed very much to our understanding of either magnetism or catalysis.

The literature up to 1847 has been reviewed by Wartmann (211), who investigated the electrolysis of water and the electrodeposition of copper in a magnetic field. He found that the field had no detectible effects, in disagreement with a considerable number of workers who preceded him. In 1881 Remsen (178) discovered some beautiful effects when copper is displaced by iron in a magnetic field. The iron in the form of a shallow dish was placed above a magnet, and then copper sulfate solution was poured into the dish. "When copper is deposited from a solution of copper sulfate on a plate of iron in a magnetic field, it is arranged in ridges around the poles of the magnet, and in directions which are at right angles to the lines of force, and consequently, coincident with the lines marking the equipotential surfaces. Further the outlines of the poles of the magnet are always sharply defined on the plate, as along these lines a portion of the iron of greater or less width is left unacted upon."

Further work along these lines, together with various explanations of the phenomena, have been published by Rowland (180), Nichols (163), Loeb (143), Wolff (218), and Rathert (176). Loeb found no change in the velocity of the following reactions in a magnetic field of several thousand oersteds.

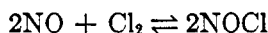


Wolff observed, incidentally, rotations of the solution during displacement reactions in a magnetic field. This seems to have been one of the first observations of the phenomenon recently reported as possibly being due to "magnetolytic" action. In the writer's opinion it is due to diffusion of ions of greater or less degree of hydration in the field.

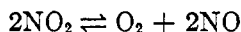
Further studies of reactions between solutions and metals have been made by Berndt (10), Shchukarev (189), Rosenberg and Yuza (179), Forestier (48), and Parker and Armes (165). Some of these authors report an increase in reaction velocity, some a decrease, and some no change at all. It should be pointed out that the stirring effect automatically produced in such solutions in a field may serve to accelerate the reaction. This possibility is made more probable by the observation of Parker and Armes that vigorous mechanical stirring tends to reduce the difference in reaction velocity between the mixtures in and out of the field.

An isolated observation by Jahr (117) is to the effect that a photographic plate may be affected by the presence of magnetized iron.

As for homogeneous reactions, negative results for the application of a magnetic field have been found by de Hemptinne (36) for the hydrolysis of methyl acetate and the inversion of sucrose, by Garner and Jackman (52) for the mutarotation of dextrose and the hydrolysis of sucrose both with and without the addition of paramagnetic salts, by Henglein (80) for the velocity of the reaction



and by Kornfeld (140) for the reaction



Clark and Archibald (31) found that the reaction products of nitric acid on benzoic acid did not vary appreciably whether in a field or out.

Rates of crystallization in a magnetic field have been studied fairly recently by Steacie and Stevens (191) and by Berлага and Gorskiĭ (9). No appreciable change in rate was found for such diverse substances as sodium thiosulfate, nickel sulfate, water, salol, and diphenylamine.

Jennison (118) has reported no change in the growth and other properties of bacteria, yeast, and molds on exposure to fields of 3000 oersteds.

In spite of this array of negative results, there are theoretical reasons for believing that a magnetic field might affect both reaction velocity and equilibrium, for certain types of chemical reactions (124).

Bhatnagar, Mathur, and Kapur (15) have studied a fairly large number of reactions in fields of from 600 to 1700 oersteds. They point out that in non-uniform fields the paramagnetic constituents of reaction mixtures may suffer local changes in concentration, and that in uniform, as well as non-uniform, fields the orientation of the elementary magnetic moments may affect the effective collision frequency. The theory of these effects may require further elaboration, and the experimental results are complicated by the difficulty of separating what might be called the magnetochemical phenomena from the purely mechanical. Nevertheless, the results reported by the Indian workers are illuminating. In brief, for those reactions in which the algebraic sum of molar susceptibilities increases, the rate of reaction is accelerated by the field. For those in which the susceptibility sum decreases, the reaction is retarded by

the field. That this rule is fairly general is indicated by the following series of reactions.

A. Reactions accelerated by the magnetic field:		$\Sigma\chi_{M_i}$	$\Sigma\chi_{M_f}$
1. Zinc plus dilute hydrochloric acid		149.6	44624.96
2. Permanganate plus oxalic acid			
3. Ferric chloride plus iron			
4. Ferric chloride plus aluminum			
5. Chromic acid plus phosphorous acid	-47.72		3774.48
6. Chromic acid plus organic acids			
7. Chromic acid plus ammonium oxalate			
8. Chromic acid plus potassium iodide	-336.48		3499.7
9. Potassium permanganate plus chloral hydrate	329.48		4658.8
B. Reactions retarded by the magnetic field:			
1. Ferric chloride plus zinc			
2. Iron plus dilute hydrochloric acid			
3. Ferric chloride plus hydroxylamine			
C. Reactions not affected by the magnetic field:			
1. Aluminum plus dilute hydrochloric acid			
2. Ferrous sulfate plus iodide plus iodate			
3. Cobaltous sulfate plus iodide plus iodate			
4. Hydriodic acid plus hydrogen peroxide	-111.66		-114.42
5. Acetic acid plus alcoholic hydrogen chloride	-65.08		-65.1
6. Mononitration of phenol			

In most cases the change in velocity constant, when a change was observed, was of the order of 1 per cent. For some of the homogeneous reactions there are given the initial ($\Sigma\chi_{M_i}$) and the final ($\Sigma\chi_{M_f}$) total susceptibilities. For these cases, at any rate, it seems to be true that when $\Sigma\chi_{M_f} > \Sigma\chi_{M_i}$ the reaction is accelerated, and *vice versa*.

The patent literature contains occasional references to control of reaction velocity by magnetic fields of greater or less intensity. Several of these have been investigated by the writer, all with uniformly negative results.

III. THE ORTHO-PARA HYDROGEN CONVERSION

Catalysis of the ortho-para hydrogen conversion by paramagnetic substances is a well-known phenomenon, adequately described by Farkas (44) and by Cremer (35). This conversion has been treated theoretically by Wigner (216) and by Kalckar and Teller (123). The homogeneous reaction is catalyzed by the paramagnetic gases, oxygen, nitric oxide, and nitrogen dioxide, and by solutions containing paramagnetic ions such as Cu^{++} , Ni^{++} , Co^{++} , Fe^{++} , Mn^{++} , and rare earth ions. Aqueous solutions of oxygen are also active. The heterogeneous reaction is catalyzed by paramagnetic solids such as Cr_2O_3 , Gd_2O_3 , Nd_2O_3 , and V_2O_5 , while it occurs at a much lower velocity over weakly paramagnetic or diamagnetic solids such as CeO_2 , ZnO , and La_2O_3 (195, 196). The low-temperature heterogeneous reaction is also strongly catalyzed by charcoal, which is diamagnetic. The conversion may be due in this case to the so-called

"surface paramagnetism" which has, in one or two instances, apparently been observed experimentally (57, 96).

In general, those paramagnetic solids showing catalytic activity also exhibit strong hydrogen adsorption at low temperatures. This is, however, not invariably true, as is shown by the work of Turkevich and Selwood (204). The organic free radical α, α -diphenyl- β -picrylhydrazyl is strongly paramagnetic, but it does not catalyze the ortho-para hydrogen conversion. This seems to be because the free radical, which is a stable solid, does not appreciably adsorb hydrogen. Zinc oxide, on the other hand, strongly adsorbs hydrogen but exhibits only a weak catalytic effect. If these two substances, the free radical and the zinc oxide, are thoroughly ground together, the mixture acquires strong

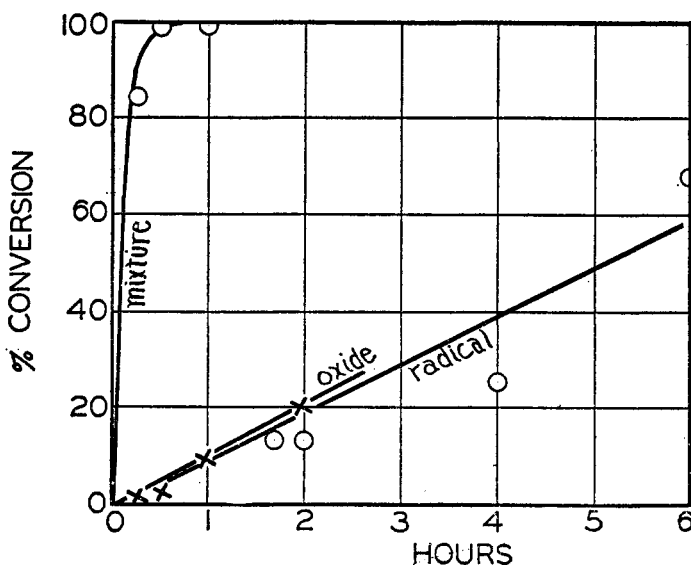


Fig. 7. Ortho-para hydrogen conversion on zinc oxide, on a free radical, and on a mixture of the two

catalytic activity (figure 7). There are apparently two factors necessary for the heterogeneous low-temperature catalysis: namely, an inhomogeneous field, produced in this case by the free radical, and adequate contact of the hydrogen with the field, ensured by van der Waals adsorption of the hydrogen on the zinc oxide.

Homogeneous magnetic fields, incidentally, do not promote the ortho-para hydrogen conversion. Some diamagnetic substances containing hydrogen, such as water, slowly catalyze the reaction, presumably because of the inhomogeneous field due to the nuclear magnetic moment of the hydrogen.

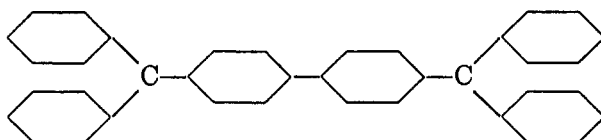
There have been a large number of applications of paramagnetic catalysis of ortho-para hydrogen conversion. Unfortunately, these have not proved quite so important as was at one time hoped. This is because, unlike the great majority of chemical reactions, no valence bond is ruptured in the low-temperature

paramagnetic reaction. In recent years the principal use of the ortho-para conversion has been in verifying the presence of free radicals or other paramagnetic substances in systems which do not lend themselves readily to the usual methods of susceptibility measurement. A few instances of such applications will be given.

The structure of diborane, B_2H_6 , has excited discussion for some time because there are insufficient electrons in this molecule to provide electron-pair bonds throughout. The existence of unpaired electrons, or single-electron bonds, would presumably give rise to paramagnetism. Diborane is scarcely stable enough for the usual magnetic susceptibility methods; Farkas and Sachsse (45) have found that this substance does not appreciably catalyze the ortho-para hydrogen conversion. The molecule cannot, therefore, be paramagnetic. This conclusion seems to have been verified by direct susceptibility measurements (51).

Similarly, a study has been made by Eley (41) on the heterogeneous conversion on a variety of porphyrin compounds, including hematoporphyrin, hematin, hemin, metal-free phthalocyanine, and copper phthalocyanine. As expected, the conversion is catalyzed by the paramagnetic but not by the diamagnetic solids.

In some cases the ortho-para hydrogen method yields results which could not have been obtained by the direct measurement of susceptibility, even though the experimental difficulties in the latter should be overcome. Schwab (185) has found that the Chichibabin hydrocarbon



catalyzes the ortho-para reaction to a degree indicating about 9.7 per cent dissociation to the biradical, although Müller, by direct measurement of susceptibility, has shown this compound to be diamagnetic.

The effects described for the ortho-para hydrogen conversion have suggested to several workers that local non-uniform magnetic fields in the neighborhood of paramagnetic atoms or ions might be a more general cause of catalytic action than has hitherto been suspected. This possibility has been advanced by Ogawa (167), Kitagawa (125), and Kuhn (141). Experiments by Gilbert, Turkevich, and Wallis (53) have not, however, substantiated this idea. No correlation was found between susceptibility and catalytic activity in the *cis-trans* isomerization of dimethyl maleate. The catalysts used, the magnetic susceptibilities, and the time necessary to form crystals of dimethyl fumarate from the maleate are shown in table 1. In addition to these substances, nickelous chloride, magnesium chloride, mercuric chloride, mercurous chloride, water, and Fe_2O_3 gave no crystals in 5 hr.

IV. POLYMERIZATION REACTIONS

There have been a few studies on magnetic changes during polymerization (5, page 61) but, so far as the writer is aware, only one short paper has appeared on the magnetic detection of free radicals in a polymerizing system. Farquharson and Ady (43) report that 2,3-dimethylbutadiene undergoes, in the absence of promoter, a 13.6 per cent diminution of diamagnetism, followed by a normal rise. If this observation can be definitely related to the presence of free radicals it promises to be of considerable interest in the study of polymerization kinetics. The methods used at present for susceptibility measurements may have to be refined considerably before accurate estimates of free-radical concentration in such systems may be made. But there is no particular reason why this cannot be done, because all that is required is the relative susceptibility before, during, and after polymerization. Such measurements, of the type already used by Michaelis in the study of semiquinone ions (186, page 130), may be made with considerably more accuracy than may those in which the sample has to be removed between determinations.

TABLE 1
Conversion of dimethyl maleate to dimethyl fumarate

CATALYST	$\chi \times 10^6$	TIME
Na.....	0.51	10 min.
AlCl ₃	-0.60	60 min.
FeCl ₃	86.0	180 min.
ZnCl ₂	-0.47	300 min.
CrCl ₃	44.0	9 hr.
Fe ₃ O ₄	Ferromagnetic	15 hr.

A problem closely related to the above, and one that merits magnetochemical study, is the dissociation of diaryl peroxides. No magnetic measurements appear to have been made on aroxy radicals, although Bachmann (4) describes several, such as the 9-methoxy-10-phenanthroxy radical, which are supposed to have a considerable degree of stability. The relation to polymerization kinetics is, of course, through the use of diaryl peroxides as accelerators. There is no *a priori* reason why even benzoyl peroxide should not be slightly dissociated, and it is rather surprising that no magnetic studies have been published on this compound.

V. MAGNETIC STATE AND CATALYTIC ACTIVITY

Hedvall (32, 33, 69-79) and his coworkers have extensively investigated the catalytic activity of ferromagnetic substances in the neighborhood of the Curie point. Work has been published on the decomposition of nitrous oxide, the hydrogenation and the decomposition of carbon monoxide, the hydrogenation of ethylene, of castor oil, and of cottonseed oil, and the cleavage of formic acid. These reactions have been studied on a variety of ferromagnetic solids, with a

variety of Curie temperatures. The results, in brief, show that at the Curie point there is a sharp increase in the temperature coefficient of reaction velocity. The results will be described more fully in connection with the decomposition of nitrous oxide and the disproportionation of carbon monoxide.

Nitrous oxide was passed over pure nickel, the Curie temperature of which was 358–361°C. The velocity of the decomposition reaction $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$ was measured by the increase of volume, and later by a continuous gas analyzer. As shown in figure 8, there is a sharp increase in the temperature coefficient of reaction velocity at the Curie temperature. This is not an accidental coincidence, because various alloys of nickel, with lower Curie points, show similar changes in reaction velocity. Copper-nickel alloy, for instance, with a Curie temperature of 337–340°C., shows a sharp change in the temperature coefficient of reaction velocity at almost exactly 339°C.

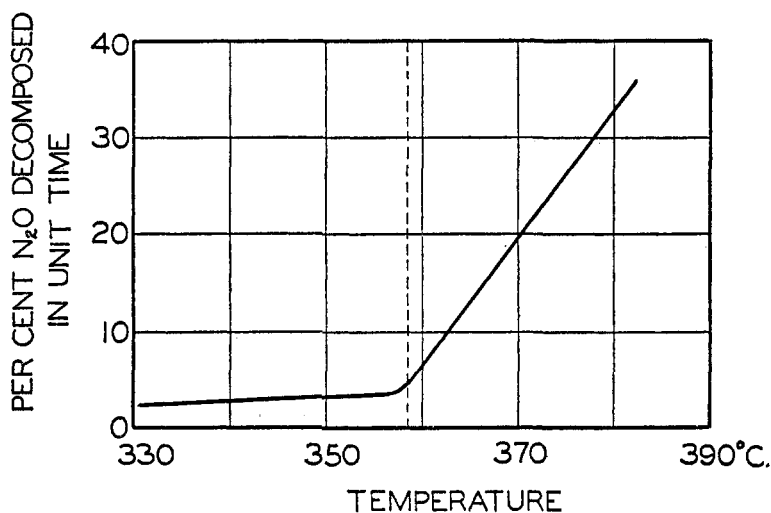


FIG. 8. Catalytic activity of nickel near the Curie point

With the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ the results are similar. It should be pointed out that these striking results are obtained only when the Curie temperature is well defined. Ordinary commercial nickel shows a rather gradual decrease of magnetization with increasing temperature, the change occurring over 50° or 100°. Such nickel shows only a correspondingly gradual change in catalytic activity. But highly purified nickel shows a sharp Curie point, the total drop in magnetization occurring within 3° or 4°. It is with such substances that Hedvall's most interesting results occur. A rather large group of ferromagnetic catalysts has been studied in this way. These include, besides nickel and nickel alloys, magnesium ferrite, cobalt-palladium alloy, pig iron, tungsten-chromium steel, and Heusler alloys. The sudden application of a magnetic field does not affect the reaction rate, either above or below the Curie point.

These changes, sometimes called the "Hedvall effect", have been studied by several other investigators, not all of whom have been able to obtain similar

results. Fischbeck (46) found a change in the synthesis of ammonia on γ - and α -iron, respectively almost non-magnetic and strongly ferromagnetic. The ferromagnetic type of ferric oxide is also a better catalyst than the other type for the decomposition of potassium chlorate (13). But Fischbeck (47) was unable to confirm Hedvall's observation on the reaction of carbon dioxide with hydrogen over nickel or nickel alloys.

The existence of some kind of change in catalytic activity at the Curie point has been confirmed by Aoyama (2) for the hydrogenation of ethylene over copper-nickel alloy and by Forestier and Lille (49) for the decomposition of acetic acid over a variety of ferrites. But the changes take the form of an acceleration of catalytic activity at the Curie point, followed by a decrease of activity above the Curie point. The effect reported is, therefore, somewhat different from the Hedvall effect. Related effects are reported by Veil (208).

Olmer (168, 169) was unable to observe the Hedvall effect for the catalytic decomposition of carbon monoxide over iron, cobalt, nickel, and the compounds CMn_3 , BMn , and SbMn , all of which are ferromagnetic. It is not clear why these experiments gave negative results, unless the Curie temperatures of the particular samples used were too indefinite to show the sharp changes in catalytic activity to be expected.

Körber, Wiemer, and Fischer (139) find that carbon monoxide undergoes a more rapid decomposition at about 900°C . over pure iron, but they attribute this less to catalytic activity than to reaction between the iron and the carbon monoxide. They show, by appropriate magnetic measurements, that powdered iron in contact with carbon monoxide above 500°C . is transformed entirely into cementite. Further extended criticism of the Hedvall effect has been given by Spingler and Reinhard (190). In experiments closely paralleling those of Hedvall they observed no discontinuity for the decomposition of carbon monoxide over nickel. In the hydrogenation of carbon monoxide there is an increase in activity beginning at about 350°C . and ending with a sudden decrease at about 370°C . These changes are, however, apparently independent of the Curie point. These authors believe that the decomposition of carbon on the catalyst may account for the observed changes in the neighborhood of the Curie point of nickel. These criticisms quite obviously do not explain the Hedvall experiments in which the catalytic discontinuity was found at lower temperatures when the Curie point of nickel was lowered by the use of copper-nickel alloys.

In spite of these criticisms it seems difficult not to believe in the reality of the Hedvall effect. But in the absence of any theoretical explanation for this effect we shall devote no further space to it.

Various other miscellaneous relationships between magnetic state and catalytic activity have been noted by Veil (209), by Baudisch (6, 7), and by Scheepers (183).

VI. PRINCIPLES OF STRUCTURAL MAGNETISM

The principal problem of magnetochemistry as applied to catalysis is chiefly a problem in structural inorganic chemistry. It is to gather information about

the identity, valence relationships, and atomic environment of the active substance. In this sense magnetic measurements have proved to be unusually revealing, and promise to be even more so, with respect to the structure of catalytically active solids. In this section some general principles will be given, to be followed by detailed remarks on a large variety of substances of interest to specialists in the field of catalysis.

A substance may, like aluminum oxide, be diamagnetic according to theory, yet slightly paramagnetic by observation. This is a common occurrence and almost always reveals the presence of some paramagnetic impurity in the substance. Paramagnetism generally varies inversely as the absolute temperature. Hence the presence of paramagnetic impurities may often be made much more conspicuous by making the measurements at low temperatures. In this way a very small fraction of 1 per cent of ferric oxide, present as impurity, could easily be detected in alumina.

TABLE 2
Valence states and effective magnetic moments in the first transition series

Unpaired electrons.....	0	1	2	3	4	5
Calculated moment.....	0	1.73	2.83	3.87	4.90	5.92
Observed moment.....	0	1.77-1.79	2.76-2.85	3.7-4.0	4.8-5.0	5.2-6.0
Ions.....	Sc ⁺³	Ti ⁺³	Ti ⁺²	V ⁺²	Cr ⁺²	Mn ⁺²
	Ti ⁺⁴	V ⁺⁴	V ⁺³	Cr ⁺³	Mn ⁺³	Fe ⁺³
	V ⁺⁵	Cu ⁺²	Ni ⁺²	Mn ⁺⁴	Fe ⁺²	
	Cu ⁺¹			Co ⁺²	Co ⁺³	
	Zn ⁺²					

There are some substances of catalytic interest which show a slight paramagnetism which is independent of temperature. Such a substance is ceric oxide. But this temperature-independent paramagnetism is easily distinguished from a normal paramagnetic impurity by making measurements at two or more temperatures.

If a substance is normally paramagnetic, the magnetic moment in Bohr magnetons may be calculated from the expression

$$\mu_{\text{eff}} = 2.83 \sqrt{\frac{3k\chi_m(T + \Delta)}{N\beta^2}}$$

as previously given. For nearly all transition group elements except the rare earths, the moment is related to the number of unpaired electron spins. The number of unpaired spins is, of course, related to the valence. The number of unpaired electrons, the calculated, and the average observed magnetic moments for several elements in the first transition series are given in table 2.

The magnetic susceptibility often gives, therefore, a means of finding the valence state. In mixtures of solids, because the susceptibilities are, to a first approximation, additive, the valence states may sometimes be found magnetically when other methods cannot be applied.

The data given in table 2 apply generally to substances which are magnetically dilute. By this is meant that the paramagnetic ions are situated relatively far apart in the crystal. Increasing interaction between paramagnetic atoms or ions is indicated by increasing magnitude of the quantity Δ in the Weiss law. This quantity may definitely be related to the degree of interaction between paramagnetic ions. For instance, chromic oxide (Cr_2O_3) has a strong paramagnetism almost independent of temperature. But dilute solid solutions containing the Cr^{+3} ion have a normal temperature coefficient. The quantity Δ is therefore useful in following the dispersal, or aggregation, of paramagnetic ions in solids, especially in diffusion processes. It often happens that compounds expected to be paramagnetic, such as molybdenum sulfide, turn out to be diamagnetic, or to have a greatly reduced paramagnetism. This is generally due

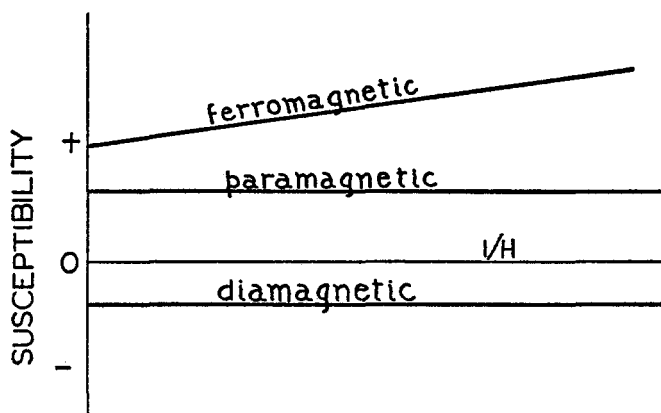


FIG. 9. Plot of reciprocal field strength against susceptibility for diamagnetic, paramagnetic, and ferromagnetic substances.

to interaction between the paramagnetic ions and to covalent-bond formation in the compound. The mechanism for this change will be described below.

Almost every solid has a trace of ferromagnetic impurity. This may be due to magnetic oxide of iron (Fe_3O_4) derived from dust or to other causes. Solids prepared in contact with steel containers at any step are generally rich in ferromagnetic content. For most carefully prepared solids the ferromagnetism reveals itself as a slight field strength dependence of susceptibility. This is neatly shown by plotting the susceptibility against reciprocal field strength, as shown in figure 9. Strictly pure diamagnetic and paramagnetic substances have susceptibilities independent of field strength. The magnitude of the ferromagnetism is expressed as the specific magnetization, σ , and is equal to the intensity of magnetization, \mathfrak{M} , divided by the density. It is also given by χH , where χ is the susceptibility per gram and H is the field strength. It is not infrequently possible to estimate the quantity of ferromagnetic substance present provided its nature is known. Specific magnetizations are well known for most ferromagnetic substances and the proportion is roughly given by σ/σ_0 , where σ is the

observed magnetization and σ_0 that of the pure ferromagnetic substance. This method is unusually sensitive; often as little as 1 part in 10^9 of iron may be detected. Sometimes, if the impurity happened to be, say, paramagnetic Fe_2O_3 , it could be made easily detectable by first heating the sample in hydrogen. In this way any "latent" ferromagnetism may be "developed" to a point where it is measurable. Measurements of ferromagnetism are especially useful in deciding whether one of the ferromagnetic elements is present as metal or in compound form.

The nature of a ferromagnetic constituent may often be found by observation of the Curie temperature. For pure substances the Curie temperature is often well defined, that for nickel being close to 358°C . For mixtures, such as alloys, the temperature-magnetization curve often reveals the nature, and distribution of concentrations, of the various substances present.

The application of magnetic measurements to complex compounds is due chiefly to Pauling (172). The method will be illustrated with respect to a nickel cyanide complex, although the chief application, so far as catalysis is concerned,

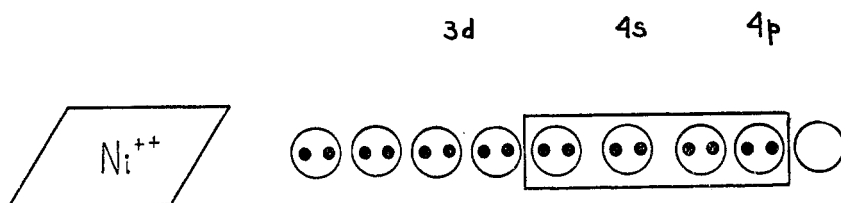


FIG. 10. Electron configuration in a planar covalent nickel complex. The free nickel ion has two unpaired $3d$ electrons.

has been in connection with natural complexes containing iron. Divalent nickel has two unpaired electrons in the $3d$ orbital, as shown in figure 10. The magnetic moment for magnetically dilute compounds containing this ion is normal, — namely, about 3 Bohr magnetons. In the cyanide complex, $\text{K}_2\text{Ni}(\text{CN})_4$, however, the nickel becomes diamagnetic, presumably owing to pairing of all electrons. A way in which this might be done is to use the $4s$, two of the $4p$, and one of the $3d$ orbitals for the formation of covalent bonds. According to the quantum-mechanical interpretation of directed valence, dsp^2 bonds should be square and planar, while four ionic bonds would, of course, be tetrahedral. It is, therefore, concluded from the diamagnetism of potassium nickelocyanide that the cyanide groups lie in a plane. This view is confirmed by x-ray studies. This interpretation is most effective for complexes containing nickel, but is also applicable to other transition group elements.

There remains to mention the rare earth elements. Their observed magnetic moments correspond to a rather complicated interaction of spin and orbital moments. So far as magnetism and catalysis are concerned, the chief interest of the rare earths lies in valence state determinations, and, of course, in the ortho-para hydrogen conversion.

VII. STRUCTURAL STUDIES

Morris and Selwood (162) have made parallel magnetic and catalytic measurements on nickel-activated copper. The reaction chosen was the hydrogenation of benzene at 175°C. Catalysts containing 1 per cent of nickel in metallic copper were prepared by mixing nickel nitrate with precipitated copper hydroxide, drying, igniting, and reducing in hydrogen at a low temperature. The copper was specially purified for this work.

The results show that an active catalyst is quite strongly ferromagnetic, and that heating the catalyst produces a loss of ferromagnetism, as observed at room temperature, and that this loss of ferromagnetism occurs in linear relationship to the loss of catalytic activity (figure 11). The explanation for these changes is made clear by determinations of the Curie point before, during, and after

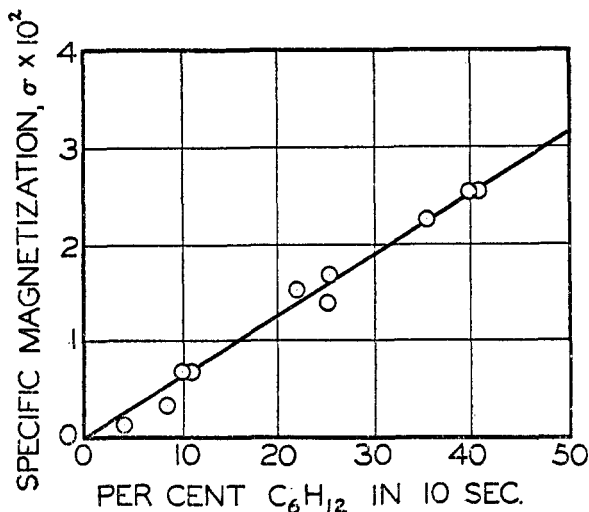


FIG. 11. Linear relationship between magnetization and catalytic activity

thermal inactivation. Use is made of the facts that the Curie point of a homogeneous copper-nickel alloy is approximately a linear function of the concentration (144), and that the specific magnetization below the Curie point is also approximately linear with concentration (115). Figure 12 shows magnetization as a function of temperature for a copper catalyst activated with 2 per cent of nickel. It will be noted that at the temperature of the hydrogenation reaction, 175°C., the active catalyst is only a little ferromagnetic, and the partially deactivated catalyst is not ferromagnetic at all. Apparently it is by no means essential that the active mass should be ferromagnetic at the temperature of the reaction.

The active catalyst can, on the basis of these results, contain no unalloyed metallic nickel in aggregates greater than those containing about 10^3 atoms (67, 160). Smaller aggregates are not ferromagnetic. The highest concentration of nickel alloy present in the active catalyst seems to be about 92.5 per cent,

but most of the nickel is present in a much lower concentration. It is clear also that most of the active mass is inhomogeneous, because the magnetization curve shows no abrupt change, but rather falls quite slowly as the temperature is raised. It seems probable, therefore, that the catalytic activity is due, not to metallic nickel as such, but to the nickel-rich nickel-copper alloys shown to be present. Figure 12 shows that thermal deactivation is attended by a diffusion process whereby the nickel gradually becomes uniformly distributed throughout the mass. The process is essentially a dilution by copper of the nickel-rich nickel-copper alloys present in the active mass. The quantitative treatment of this diffusion process in powdered metals is given by Selwood and Nash (187).

There are two observations to be made in connection with the above studies. The first is that no parallel study of specific surface was attempted. It will be difficult to relate magnetic properties to catalytic properties during thermal

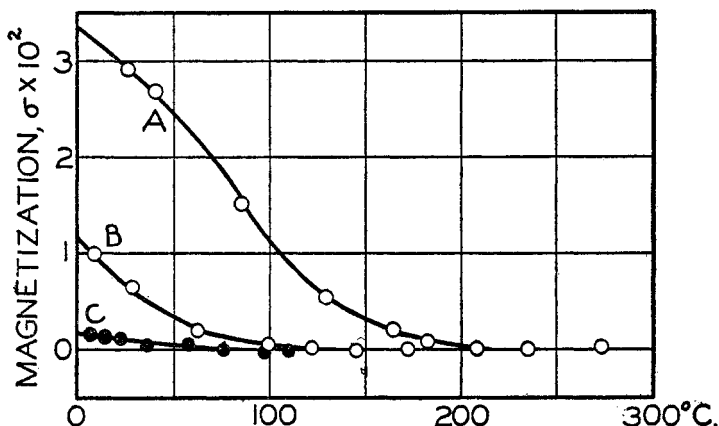


FIG. 12. Magnetization and Curie point of a nickel-activated copper catalyst. A, active catalyst; B, partially deactivated catalyst; C, inactive catalyst.

treatment until some way is found to control, or correct for, the surface changes which must obviously take place under such treatment. The second observation is that the published data show only a small proportion of the nickel to be accounted for as contributing to the ferromagnetism of the active catalyst. The remaining nickel must be present as unreduced nickel oxide, as atomically dispersed nickel on the surface or interstices of the copper crystals, or possibly as dissolved nickel in dilute solution. The state of this "non-ferromagnetic" nickel and its influence, if any, on catalytic activity are problems of considerable importance.

Further measurements by the same authors (71) have been made on nickel supported on magnesia. In this case, practically all the nickel is accounted for as contributing to the ferromagnetism. Thermal deactivation does not lead to a recession of the Curie point for this catalyst. The same is true of poisoned catalysts, in that only a slight change in magnetization occurs when a nickel-activated copper catalyst is treated with a variety of catalyst poisons.

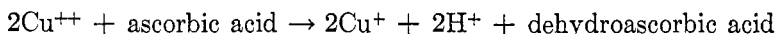
The magnetocatalytic properties of molybdenum oxide derivatives have been studied by Woodman, Taylor, and Turkevich (219). Their most significant results are in connection with the catalyst obtained by heating nickel ammonium molybdate, first in air, then in hydrogen, at 300°C. This catalyst is active in the hydrogenation of ethylene at -80°C. The catalyst is strongly ferromagnetic, a property which the authors attribute to metallic nickel. But Morris and Selwood (71) made magnetic measurements on a similar catalyst over a range of temperature and found that the Curie interval was large, and that all ferromagnetism was lost at 250°C. Metallic nickel is not, therefore, proved to be present. But what the ferromagnetic component is, is not known. The total ferromagnetism at room temperature amounts to little over 10 per cent of that to be expected if all the nickel present were in the form of metal.

The above work is a good example of the use of magnetic studies in catalysis. It also illustrates the necessity of extending magnetic measurements over a considerable temperature range, including the regions of all pertinent critical points. It should be pointed out that nickel-containing catalysts prepared as above, even with rather vigorous heating in hydrogen, do not necessarily show ferromagnetism. What, precisely, are the conditions necessary for the development of ferromagnetism in such catalysts we are not prepared to say. But in every case which has come to the writer's attention the presence of ferromagnetism has been paralleled by some striking changes in catalytic activity.

Several attempts have been made by Bhatnagar and his coworkers to find the nature of transitory compounds and valence states formed during the course of reactions. The catalytic decomposition of potassium chlorate by manganese dioxide (21), ferric oxide (13, 21), and cobalt oxide (13) is one such reaction. Mixtures of potassium chlorate and of each catalyst in turn were heated to various temperatures for definite time intervals. The mixtures were then analyzed and tested for magnetic susceptibility. For the manganese and cobalt oxides the susceptibility shows a negative deviation from additivity amounting to about 5 per cent. The intermediate compound must be either diamagnetic or less strongly paramagnetic. Ferric oxide showed no deviation from additivity although, as previously mentioned, ferromagnetic $\gamma\text{-Fe}_2\text{O}_3$ proved to be a better catalyst than paramagnetic $\alpha\text{-Fe}_2\text{O}_3$ (13). Evidence of intermediate compounds has also been obtained for the chlorination of chloroform to carbon tetrachloride in the presence of ferric chloride (24), for the catalysis of the reaction between ammonium oxalate and mercuric chloride by ferric ions (14), and for the catalysis of the persulfate-iodide reaction by ferric ions (22). A related type of study has been made by Merck and Wedekind (149, 150) on the oxidation of carbon monoxide as catalyzed by manganese dioxide, by cobaltic oxide, and by the mixed oxides and oxide hydrates.

The catalytic action of cupric ion on the oxidation of *l*-ascorbic acid has been known for some time. Tyson and Wiley (205) have used magnetic measurements to determine the function of the cupric ion in this reaction, as carried out in pyridine solution. Cupric ions in pyridine have a magnetic moment corresponding roughly to one unpaired electron spin. Mixed with an appropriate

quantity of ascorbic acid, the copper becomes diamagnetic, presumably owing to the reaction:



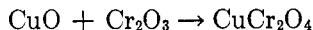
Exposure to oxygen or air results in changing the susceptibility back to a value corresponding to one unpaired electron spin for the copper. The colors of the solutions suggest that both cuprous and cupric ions form complexes with the dehydroascorbic acid.

A similar type of valence study by Noyes, Pitzer, and Dunn (164) shows, on the basis of magnetic and other measurements, that silver ions oxidized by ozone in concentrated nitric acid exist in the paramagnetic bipoisitive form.

Determination of bond type in enzymatic and related substances of biological interest is somewhat remote from the primary purpose of this review, but for the sake of completeness references will be given to work in this field. The extensive studies of Pauling and Coryell and their coworkers on hemoglobin and derivatives have been reviewed by Drabkin (37) and by the writer (186). Theorell has published studies on cytochrome (197), horseradish peroxidase (198), and horse-liver catalase (199). Catalase has also been investigated magnetically by Michaelis and Granick (156), who have further published an extensive study on ferritin (157).

VIII. ACTIVE OXIDES

In recent years there have been a large number of studies on mixed oxides. Most of this work is due to Hüttig (88-92) who, fortunately, has prepared reviews covering several hundred papers in this field. In general, the procedure has been to mix oxides, of which zinc oxide and ferric oxide will serve as examples, and to follow changes in catalytic activity, magnetic susceptibility, and other properties, as reaction in the solid state proceeds with the ultimate formation of a single compound. In the case given the final product would be a spinel, ZnFe_2O_4 . In a large number of instances there are indications that intermediate compounds are formed, and these often have very pronounced catalytic and magnetic properties. The procedures used in the preparation of these compounds are often different from those commonly used in the preparation of active catalysts. For instance, Hüttig and his coworkers have studied copper chromite as formed by the reaction



The reaction occurs at a high temperature, under conditions such that the final product is a poor catalyst, and is probably quite different from the well-known substance formed by thermal decomposition at moderate temperatures of copper ammonium chromate. Nevertheless, the substances studied by Hüttig are, in a large number of cases, of interest to catalytic chemists because his products are often formally related to some of the most important industrial and laboratory types of catalysts.

In the following discussion a few examples will be selected. References will be given to many other systems.

The system $\text{CaO-Fe}_2\text{O}_3$ (99, 109, 129, 130): If calcium oxide and ferric oxide are heated together, there begins to appear in the neighborhood of 800°C . unmistakable evidence for spinel formation. This change is clearly shown by x-ray diffraction, and is also indicated by the onset of ferromagnetism, of greatly reduced catalytic activity, and of numerous other changes in physical properties. Prior to this change, however, there are changes in susceptibility and a pronounced increase in catalytic activity. These changes, which are shown in figure 13, are paralleled by other changes. The experimental procedure consists in preparing stoichiometrical mixtures of the oxides, heating them for definite intervals (generally 6 hr.) at numerous gradually increasing temperatures, and,

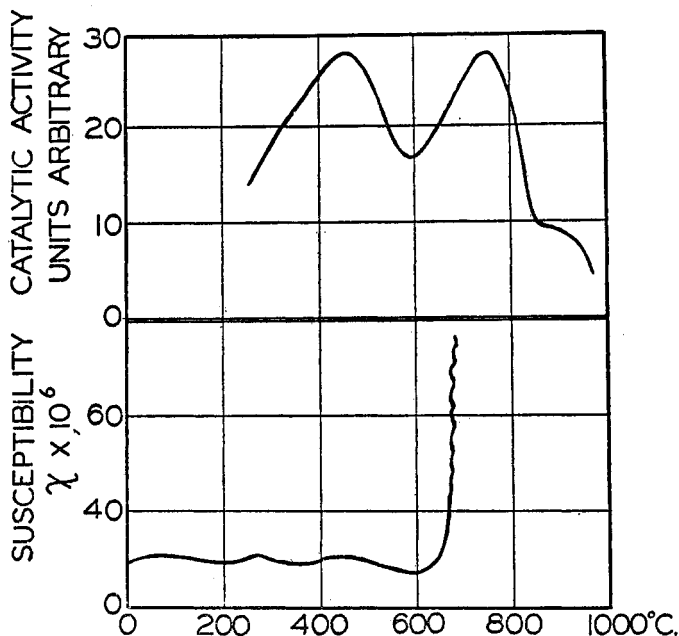


FIG. 13. Susceptibility and activity for the $\text{CaO-Fe}_2\text{O}_3$ system undergoing heating. The system becomes ferromagnetic after heating at 650°C .

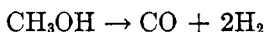
between heating periods, measuring the properties of the mixture under standardized conditions. Thus the magnetic susceptibility is generally found at 21°C . at several field strengths. The catalytic activity has been determined for the oxidation of carbon dioxide and the decomposition of nitrous oxide.

Hüttig interprets the increased catalytic activity and the other changes as being due to an active intermediate compound. This is believed to form first on the surface of the particles, although it would seem more reasonable to suppose it formed at the interface between the particles of the two oxides. As heating proceeds the intermediate compound becomes larger in amount, but spinel formation also begins and soon destroys the intermediate. But by holding the temperature just below that at which spinel forms, Hüttig succeeds in preparing a mixture which he believes contains not less than 60 per cent of the active

intermediate. This is indicated by a very great increase in catalytic activity. The intermediate is believed by Hüttig to be a compound of definite composition and properties, with a magnetic susceptibility of 51.5×10^{-6} at room temperature.

In spite of these assurances and of the very large number of papers published on so-called "active oxides," it must be admitted that the existence of these intermediate compounds can scarcely be regarded as established, by ordinary standards. But so far as the existence of an "active" state is concerned there can be no doubt, and Hüttig's work has produced a wealth of information concerning changes which take place in these systems.

The system ZnO-Cr₂O₃ (97, 106): This system, and the CuO-Cr₂O₃ system, are of particular interest in catalytic chemistry. The stoichiometric mixtures were prepared as usual, and ground for several hours. The reaction used for comparison of catalytic activity was the decomposition of methanol:



After 6 hr. of heating at 400°C. the catalytic activity rose over 400 per cent. At the same time the magnetic susceptibility rose from an initial value of 23.4×10^{-6} (at 21°C.) to $> 65 \times 10^{-6}$ at low fields, and ferromagnetism appeared. Further heating reduced both catalytic activity and susceptibility, with simultaneous appearance of spinel formation in the x-ray diffraction diagram. The final product, after 12 hr. over the blast burner, yielded a spinel, inactive catalytically and with a susceptibility of 45.0×10^{-6} which was independent of field strength. It should be pointed out that development of ferromagnetism is not often found in chromium compounds free from elements which form paramagnetic ions. The changes described above are shown in figure 14.

The system CuO-Cr₂O₃ (104, 126): This system has been studied with reference to the decomposition of nitrous oxide. A rather obvious extension of all this work would be to compare the catalytic activity of the mixture on several different types of reactions to see if the heat treatment which produced maximum activity for one type of reaction was the same as that for another type. For the copper chromite system the catalytic activity reaches a low maximum after rather moderate heating, and then drops slowly and irregularly until spinel formation is complete after 6 hr. heating at 1000°C. During this time the magnetism rises slowly, then more rapidly from 22.6×10^{-6} to 34.2×10^{-6} . There is no indication of ferromagnetism, and no pronounced peak of catalytic activity. These changes are shown in figure 15.

The system Cr₂O₃-Al₂O₃ (104): Not very much information has been published on this system, but what little has been published is included here because of the considerable interest in this well-known cyclization catalyst. The data of Hüttig, Meyer, Kittel, and Cassirer unfortunately refer to α - rather than to γ -alumina. Stoichiometric mixtures of chromia and alumina, prepared mechanically in the usual way, have an average susceptibility of about 16.8×10^{-6} . This value is very slightly changed by prolonged heat treatment up to 1000°C. There is, of course, no expectation of spinel formation in this system, but the

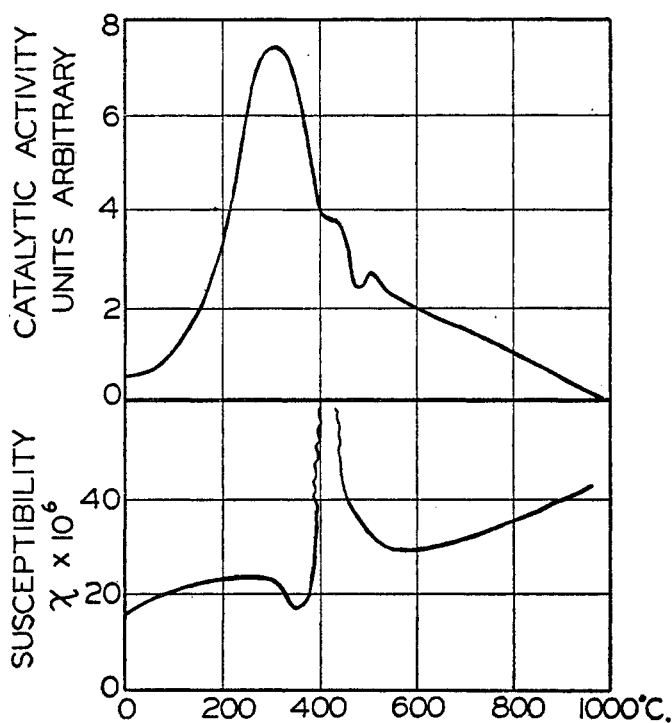


FIG. 14. Susceptibility and activity for the $\text{ZnO-Cr}_2\text{O}_3$ system undergoing heating. The system has a region of ferromagnetism at about 400°C.

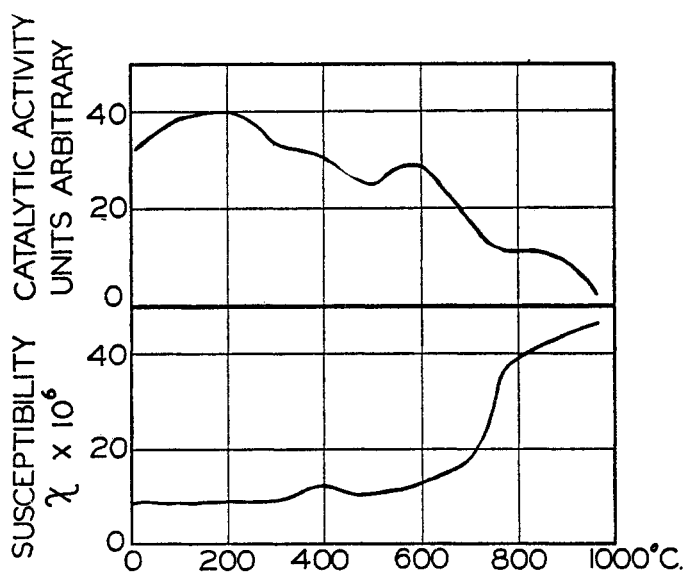


FIG. 15. Susceptibility and activity for the $\text{CuO-Cr}_2\text{O}_3$ system undergoing heating

system $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ shows a pronounced magnetic change after heat treatment in the neighborhood of 900°C . In this, and in all the other studies reported, the magnetic results would have been much more useful if they had been made at several temperatures. Some preliminary work by the writer suggests that a chromia-alumina catalyst prepared by the method of impregnating γ -alumina with chromium trioxide in solution, followed by reduction, gives a product with markedly different magnetic properties from the mechanical mixture of chromia plus alumina. These differences become very pronounced at liquid-air temperatures.

Other systems: In addition to those given above, the following systems have been subjected to magnetic and catalytic study by Hüttig and others.

$\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (104)	$\text{Fe}_2\text{O}_3\text{-SiO}_2$ (104)
$\text{BaO-Fe}_2\text{O}_3$ (129)	$\text{Fe}_2\text{O}_3\text{-TiO}_2$ (104)
$\text{BeO-Cr}_2\text{O}_3$ (126)	$\text{MgO-Al}_2\text{O}_3$ (109)
$\text{BeO-Fe}_2\text{O}_3$ (100, 101, 104, 109)	$\text{MgO-Cr}_2\text{O}_3$ (109, 130, 155)
$\text{CdO-Cr}_2\text{O}_3$ (126)	$\text{MgO-Fe}_2\text{O}_3$ (50, 104, 105, 107, 108, 128, 131)
$\text{CdO-Fe}_2\text{O}_3$ (127)	$\text{NiO-Fe}_2\text{O}_3$ (50)
$\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (104)	$\text{PbO-Cr}_2\text{O}_3$ (126)
$\text{Cr}_2\text{O}_3\text{-SiO}_2$ (104)	$\text{PbO-Fe}_2\text{O}_3$ (127)
$\text{Cr}_2\text{O}_3\text{-TiO}_2$ (104)	$\text{SrO-Fe}_2\text{O}_3$ (129)
$\text{CuO-Al}_2\text{O}_3$ (104)	$\text{ZnO-Fe}_2\text{O}_3$ (93, 94, 95, 100, 103, 104, 109, 110)
$\text{CuO-Fe}_2\text{O}_3$ (104, 127)	

IX. MAGNETISM AND ADSORPTION

The close relationship between adsorption and catalysis makes it necessary to say something about the former. Not very many magnetic studies have been made in this field, but what results are available are very interesting and could be profitably extended in several directions.

Determination of the valence states of dispersed substances on supported catalysts is an obvious application of magnetism to catalysis. For instance, Sachse (182) has used a ballistic method to determine the ferromagnetism of dispersed Fe_3O_4 on silica and on other supports. Adsorbed substances sometimes yield surprising results. In general the susceptibilities of systems involving adsorption do not obey the simple mixture law. Thus Bhatnagar, Mathur, and Kapur (17) have studied adsorption of the chlorides of iron, nickel, cobalt, and manganese on charcoal. These salts, all of which are normally strongly paramagnetic, become diamagnetic when they are adsorbed. Charcoal actually becomes more diamagnetic when it acts to adsorb such compounds. The charcoal must form definite covalent bonds to the metal ions, and the resulting system resembles the type of complex compound in which, through complete electron pairing, all paramagnetism is lost. This lack of additivity in adsorption is supported by some work of Boutaric and Berthier (28) on colloidal ferric hydroxide and on other substances.

The chemisorption of oxygen on metal oxides seems to have received magnetic study only from Bhatnagar *et al.*, on the compounds chromic oxide (12) and cobaltous oxide (19). Particularly in the case of the latter compound, the results

show a diminution of susceptibility provided the adsorption is carried on above room temperature. This confirms the view that van der Waals adsorption cannot take place under these conditions, because molecular oxygen is very strongly paramagnetic. The cobalt may undergo surface oxidation to cobaltous or cobaltic oxides.

The adsorption of oxygen on charcoal and on other relatively "inert" adsorbents has been studied by Aharoni and Simon (1) and by Juza and Langheim (120, 122). In spite of some differences of opinion it seems fairly well established that oxygen adsorbed on charcoal at room temperature has the same susceptibility as does gaseous oxygen. Courty (34) suggests that this may afford a convenient method of measuring the susceptibilities of gases. Courty's measurements appear not to have been carried out over a time or temperature interval, and it is here that the most interesting results are obtained. At room temperature, according to Juza and Langheim, the magnetic properties of adsorbed oxygen depend on time. The paramagnetism slowly diminishes owing, presumably, to chemical combination between the oxygen and the charcoal. It is possible to obtain the temperature coefficient of this reaction, and the activation energy of surface oxide formation works out to be about 5 kg.-cal. per mole.

At liquid-air temperatures the susceptibility of the oxygen depends, in addition, on the density of the adsorbed layer.

Similar systems which have been studied are palladium-hydrogen (1, 54, 122, 159, 188, 193), carbon-bromine (122), silica-bromine (122), and chabasite-oxygen (122).

The applications of such measurements to problems like the superficial oxidation and reduction of finely powdered metals are obvious.

One final observation in this connection may be made. There seems quite definitely to be an anomaly in the relationships between hydrogen and metallic nickel at the Curie temperature. Post and Ham (166) have shown that there is an abrupt discontinuity in the rate of hydrogen diffusion through nickel at the Curie point. Van Itterbeck, Mariens, and Verpoorten (206) have quite recently shown that the activated adsorption of hydrogen shows a sharp change at the Curie point (figure 16). It would be most interesting to know if these effects are part of a general phenomenon taking place with other gases and other metals. The possible relationships of such changes to the Hedvall effect are quite clear.

X. MAGNETIC SUSCEPTIBILITIES OF PURE SUBSTANCES OF CATALYTIC INTEREST

The following information covers the ionic diamagnetism of most elements and acid radicals, together with data on a variety of solids which find application in catalysis. While a fairly thorough search of the literature has been made, no attempt is made to give references to all the publications on each substance. Rather the values which seem most authoritative are given. Where it is impossible to choose between discordant values, both or all are generally given. It is hoped that these data will prove to be useful to readers who may wish to make magnetic studies. The data have already proved their value to the writer.

Ionic diamagnetism: The data given here (see table 3) are taken from the

publications of Klemm (133-135). Other workers give other values, and it is not possible to decide which values are the most accurate (202). Those of Klemm are chosen because of their completeness and general coherence. These data will prove useful in making diamagnetic corrections. It should be pointed out that the diamagnetism of atoms and ions depends on the environment, but the changes are generally small. Figures are given on some paramagnetic ions. It must be emphasized that these data are the underlying diamagnetic correction factors, not the observable susceptibility.

Aluminum, Al: The susceptibility per gram of pure aluminum metal (3, 111, 214) at room temperature is about 0.62×10^{-6} . Note that aluminum is paramagnetic. The susceptibility is always slightly dependent on field strength and the above represents a value extrapolated to infinite field. However, quite large percentages of iron do not greatly alter this value, presumably owing to formation

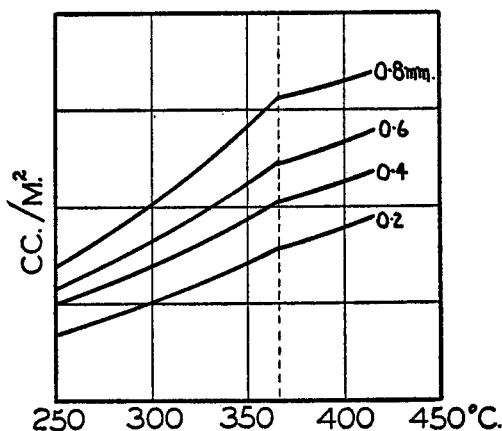


FIG. 16. Adsorption of hydrogen on nickel at several pressures in the neighborhood of the Curie point.

of the intermetallic compound FeAl_3 . Treatment with sodium hydroxide decomposes this compound, liberating metallic iron, with a great increase of susceptibility (145). The susceptibility of pure aluminum is independent of temperature down to $-170^\circ\text{C}.$, and almost independent of temperature up to the melting point of the metal. The susceptibility is somewhat dependent on state of aggregation (220).

Aluminum oxide, Al_2O_3 : The most complete study on alumina is that of Zimens (222). Pure $\gamma\text{-Al}_2\text{O}_3$ has $\chi = -0.34 \times 10^{-6}$ at room temperature. For $\alpha\text{-Al}_2\text{O}_3$, $\chi = -0.27 \times 10^{-6}$. It is not clear if this slight difference may not in some way be related to the great change in specific surface which for $\gamma\text{-Al}_2\text{O}_3$ is 18.2 meters² per gram, and for $\alpha\text{-Al}_2\text{O}_3$ is only 0.95 meters² per gram, as measured by Zimens by the emanation method. The two alumina hydrates, bayerite and böhmite, have a slightly greater diamagnetism than the oxide. The susceptibilities given, which are those for infinite field, are slightly dependent on field strength, presumably owing to impurities. Unfortunately no very

TABLE 3

Diamagnetic susceptibilities per gram-ion

Values in italics are for the underlying diamagnetism only of ions which may be paramagnetic

ION	$-x \times 10^6$	ION	$-x \times 10^6$	ION	$-x \times 10^6$
Ag ⁺¹	24	Eu ⁺³	20	Os ⁺⁴	29
Ag ⁺²	24	F ⁻¹	11	Os ⁺⁶	18
Al ⁺³	2	Fe ⁺²	13	Os ⁺⁸	11
As ⁺³	9?	Fe ⁺³	10	P ⁺³	4
As ⁺⁵	6	Ga ⁺³	8	P ⁺⁵	1
AsO ₃ ⁻³	51	Ge ⁺⁴	7	PO ₃ ⁻¹	30
AsO ₄ ⁻³	60	Gd ⁺³	20	PO ₃ ⁻³	42
Au ⁺¹	40?	Hf ⁺⁴	16	PO ₄ ⁻³	50
Au ⁺³	32	Hg ⁺²	37	Pb ⁺²	28
B ⁺³	0.2	Ho ⁺³	19	Pb ⁺⁴	26
BF ₄ ⁻¹	39	I ⁻¹	52	Pd ⁺²	25
BO ₃ ⁻³	35	I ⁺⁵	12	Pd ⁺⁴	18
Ba ⁺²	32	I ⁺⁷	10	Pr ⁺³	20
Be ⁺²	0.4	IO ₃ ⁻¹	50	Pr ⁺⁴	17
Bi ⁺³	25?	IO ₄ ⁻¹	54	Pd ⁺²	25
Bi ⁺⁵	23	In ⁺³	19	Pd ⁺⁴	18
Br ⁻¹	36	Ir ⁺¹	50	Pt ⁺²	40
Br ⁺⁵	6	Ir ⁺²	42	Pt ⁺³	33
BrO ₃ ⁻¹	40	Ir ⁺³	35	Pt ⁺⁴	28
C ⁺⁴	0.1	Ir ⁺⁴	29	Rb ⁺¹	20
CN ⁻¹	18	Ir ⁺⁶	20	Re ⁺³	36
CNO ⁻¹	21	K ⁺¹	13	Re ⁺⁴	28
CNS ⁻¹	35	La ⁺³	20	Re ⁺⁶	16
CO ₃ ⁻²	34	Li ⁺¹	0.6	Re ⁺⁷	12
Ca ⁺²	8	Lu ⁺³	17	Rh ⁺³	22
Cb ⁺⁵	9	Mg ⁺²	3	Rh ⁺⁴	18
Cd ⁺²	22	Mn ⁺²	14	Ru ⁺³	23
Ce ⁺³	20	Mn ⁺³	10	Ru ⁺⁴	18
Ce ⁺⁴	17	Mn ⁺⁴	8	S ⁻²	38?
Cl ⁻¹	26	Mn ⁺⁶	4	S ⁺⁴	3
Cl ⁺⁵	2	Mn ⁺⁷	3	S ⁺⁶	1
ClO ₃ ⁻¹	32	Mo ⁺²	31	SO ₃ ⁻²	38
ClO ₄ ⁻¹	34	Mo ⁺³	23	SO ₄ ⁻²	40
Co ⁺²	12	Mo ⁺⁴	17	S ₂ O ₃ ⁻²	49
Co ⁺³	10	Mo ⁺⁵	12	S ₂ O ₈ ⁻²	78
Cr ⁺²	15	Mo ⁺⁶	7	Sb ⁺³	17?
Cr ⁺³	11	N ⁺⁵	0.1	Sb ⁺⁵	14
Cr ⁺⁴	8	NH ₄ ⁺¹	11.5	Se ⁺³	6
Cr ⁺⁵	5	NO ₂ ⁻¹	10	Se ⁻²	48?
Cr ⁺⁶	3	NO ₃ ⁻¹	20	Se ⁺⁴	8
Cs ⁺¹	31	Na ⁺¹	5	Se ⁺⁶	5
Cu ⁺¹	12	Nd ⁺³	20	SeO ₃ ⁻²	44
Cu ⁺²	11	Ni ⁺²	12	SeO ₄ ⁻²	51
Dy ⁺³	19	OH ⁻¹	12	Si ⁺⁴	1
Er ⁺³	18	Os ⁺²	44	SiO ₃ ⁻²	36
Eu ⁺²	22	Os ⁺³	36	Sm ⁺²	23

TABLE 3—*Concluded*

ION	$-\chi \times 10^6$	ION	$-\chi \times 10^6$	ION	$-\chi \times 10^6$
Sm^{+3}	20	Ti^{+2}	15	V^{+5}	4
Sn^{+2}	20	Ti^{+3}	9	W^{+2}	41
Sn^{+4}	16	Ti^{+4}	5	W^{+3}	36
Sr^{+2}	15	Tl^{+1}	34	W^{+4}	23
Ta^{+5}	14	Tl^{+3}	31	W^{+5}	19
Tb^{+3}	19	Tm^{+3}	18	W^{+6}	13
Tb^{+4}	17	U^{+3}	46	Y^{+3}	12
Te^{-2}	70?	U^{+4}	35	Yb^{+2}	20
Te^{+4}	14	U^{+5}	26	Yb^{+3}	18
Te^{+6}	12	U^{+6}	19	Zn^{+2}	10
TeO_3^{-2}	63	V^{+2}	15	Zr^{+4}	10
TeO_4^{-2}	55	V^{+3}	10		
Th^{+4}	23	V^{+4}	7		

accurate measurements appear to have been made on "pure" aluminum oxide at low temperatures. The writer's experience is that material which is diamagnetic at room temperature invariably becomes paramagnetic at -190°C ., owing to paramagnetic impurities being present. "Pure" aluminum oxide would, presumably, have a susceptibility independent of both field strength and temperature.

Asbestos: No magnetic measurements appear to have been made on asbestos. Untreated asbestos would invariably contain appreciable iron as impurity. "Pure" asbestos would probably be diamagnetic.

Beryllia, BeO : Hüttig and Kittel give several values, averaging $\chi = -0.1 \times 10^{-6}$ at room temperature. This susceptibility is essentially independent of field strength. No data at low temperatures are available. "Pure" beryllium oxide should have no temperature dependence of susceptibility.

Boric oxide, B_2O_3 : The only measurement on this substance appears to be that of Meyer, $\chi = -0.55 \times 10^{-6}$ at 14°C ., as quoted in the *International Critical Tables* (112).

Charcoal, C: It is surprising that after many years of magnetochemical research there are available no measurements on relatively pure activated charcoal. Several measurements by the writer on charcoals of varying degrees of activity all show strong paramagnetism or ferromagnetism, owing to impurities. "Pure" charcoal should be diamagnetic. The susceptibility is probably about -0.4×10^{-6} . Graphite has a very large magnetic anisotropy and a correspondingly large diamagnetism for the powdered substance. Magnetic measurements on activated charcoal are further complicated by the possibility of "surface" paramagnetism, and of adsorbed gases.

Calcium oxide, CaO : Kittel and Hüttig (130) give $\chi = -0.58 \times 10^{-6}$ at room temperature. The data of these workers are not too reliable and it is possible that the older susceptibility of Meyer (113) is more accurate. Meyer gives $\chi = -0.27 \times 10^{-6}$. No measurements are available at low temperatures.

"Pure" calcium oxide should have no temperature coefficient of susceptibility.

Cadmium oxide, CdO: Meyer (153) gives $\chi = -0.30 \times 10^{-6}$ at 15°C.

Cerium oxide, CeO₂: Williams (217) gives $\chi = 0.14 \times 10^{-6}$ at 20°C. Ceric oxide is an example of a substance which has a small temperature-independent paramagnetism, although it must be admitted that there have not been many measurements made on material of established purity. Cerous oxide, Ce₂O₃, seems to have escaped magnetochemical investigation. It should be fairly strongly paramagnetic with the usual large temperature coefficient. The valence state of cerium in a solid is easily found by magnetic measurements.

Cobalt, Co: All the ferromagnetic metals have been subjected to innumerable magnetic studies. For our present purpose two quantities only are required, the specific magnetization and the Curie point. These both depend to a marked degree on purity and on other circumstances. We shall give $\sigma = 165$ and the Curie temperature 1100°C. (144).

Oxides of cobalt: A careful study has been made by Bhatnagar, Prakash, and Qayyum (20). The susceptibilities depend slightly on mode of preparation, but if care is taken to insure purity and identity the results may readily be duplicated. The data of these workers on the three common cobalt oxides are summarized below:

	CoO	Co ₃ O ₄	Co ₂ O ₃
$\chi \times 10^6$	68.4	30.7	28.8
Δ	315°	153°	180°

The susceptibilities of these substances follow the Weiss law, with Δ values as shown. The measurements were actually made between room temperature and about 500°C. The oxide Co₃O₄ becomes ferromagnetic after long heating at high temperature.

Cobalt sulfide, CoS₂: Haraldsen and Klemm have studied the system cobalt-sulfur. The compound CoS₂ has a susceptibility of 30.5×10^{-6} at room temperature. There are large and interesting variations of susceptibility with sulfur content, yielding in some cases ferromagnetism.

Chromic oxide, Cr₂O₃: This important oxide, from the catalytic standpoint, has been the subject of many magnetic studies. The work of Bhatnagar, Cameron, Harbord, Kapur, King, and Prakash (12) is the most complete, and brings some order out of a rather chaotic situation. Chromic oxide prepared in a large variety of ways has nearly the same susceptibility. The oxide prepared by ignition of the precipitated hydroxide has the values:

°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

Chromic oxide prepared by ignition of chromium trioxide has substantially the same susceptibility. There is some evidence that the susceptibility of chromic oxide rises sharply at still higher temperatures, but this may be due to decomposi-

tion. At lower temperatures the older data of Honda and Soné still seem to be satisfactory (84). They give the following: at 18°C . $\chi = 25.5 \times 10^{-6}$; at -64°C . $\chi = 22.2 \times 10^{-6}$; at -186°C . $\chi = 20.1 \times 10^{-6}$. It will be noticed that the temperature coefficient of susceptibility is small, and is opposite in sign from that predicted by the Curie law, at least at low temperatures. The susceptibility of the active oxide gel produced through slow interaction of dilute chromic nitrate and ammonia is not sensibly different from that reported for the crystalline oxide (203). The anomalous temperature coefficient is believed to be due in part to interaction between the chromium atoms. When chromic oxide is heated in hydrogen at 440°C . a drop in susceptibility occurs. This amounts to 4 or 5 per cent (12). The change is reversed by heating in oxygen. Strong heating of chromic oxide in hydrogen yields ferromagnetic oxides. There also apparently occur a series of ferromagnetic oxides approaching the formula Cr_2O_3 . However, Michel and Benard (158) claim that there is a definite ferromagnetic compound CrO_2 , isomeric with a non-ferromagnetic $\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$. The ferromagnetic substance has a Curie point at 116°C ., and is best prepared through decomposition of chromyl chloride. This substance was not obtained pure.

Chromic anhydride, CrO_3 : Grey and Dakers (55) and Tilk and Klemm (200) show that this substance has a small temperature-independent paramagnetism, with $\chi = 0.4 \times 10^{-6}$.

The chromium-sulfur system: The compound CrS is paramagnetic, according to Haraldsen and Kowalski (66), with a susceptibility at room temperature of 20.0×10^{-6} . This is almost independent of temperature. Chromic sulfide, Cr_2S_3 , is also paramagnetic with about the same susceptibility. But between these compositions there are some very interesting ferromagnetic systems. The ratio $\text{CrS}_{1.17}$ is strongly ferromagnetic between the temperatures 165°K . and 310°K .

Alkali thiochromites, NaCrS_2 , KCrS_2 : The use of sulfides and possible thio salts as catalysts makes it appropriate to mention the recent work of Rüdorff and Stegemann (181) on alkali thiochromites. Several different preparations gave reasonably consistent results. At room temperature for NaCrS_2 , $\chi = 45 \times 10^{-6}$, and for KCrS_2 , $\chi = 72 \times 10^{-6}$. Both salts follow the Weiss law: for NaCrS_2 , $\Delta = -37^{\circ}$; for KCrS_2 , $\Delta = -116^{\circ}$. The potassium salt becomes ferromagnetic at liquid-air temperature. These results are quite different from those obtained on Cr_2S_3 . Rüdorff and Stegemann relate these differences to the distances between chromium atoms in the compounds, which are as follows:

COMPOUND	Cr-Cr DISTANCE
	Δ
Cr_2S_3	2.78-3.42
NaCrS_2	3.53
KCrS_2	3.62

This is a good example of how the magnitude of the quantity Δ in the Weiss law may sometimes be used to estimate the proximity and degree of interaction of the magnetic atoms or ions in a compound.

Copper, Cu: Metallic copper (82) is slightly diamagnetic with a susceptibility of -0.08×10^{-6} . This value is substantially independent of temperature. Considerable difficulty is encountered in obtaining copper sufficiently free from ferromagnetic impurities to show no dependence of susceptibility on field strength. Corrections may be made in the usual way by extrapolating the susceptibility to infinite field. Morris and Selwood (162) describe methods for preparing "magnetically pure" copper. The impurities may sometimes be forced into solution by quenching the copper from a high temperature, but such procedures are seldom feasible with material prepared for catalytic purposes. The influence of particle size on the susceptibility of copper has been studied by Bhatnagar, Verma, and Anwar-ul-Haq (23).

Cuprous oxide, Cu₂O: This compound is diamagnetic, according to Klemm and Schüth (137) and Bhatnagar and Mitra (18). The susceptibility is -0.18×10^{-6} . The Indian experimenters state that superficial oxide films on copper are always paramagnetic, owing to the presence of cupric oxide. The general belief has been that such films consisted solely of cuprous oxide.

Cupric oxide, CuO: Klemm and Schüth (137) give the following data:

Temperature, °C.....	20	100	235	330	445
$\chi \times 10^6$	2.88	3.06	3.20	3.16	3.10

Different preparations have rather different susceptibilities, but all show the peculiar temperature coefficient. No measurements at low temperatures have come to the writer's attention. These would be useful in the study of copper and copper-containing catalysts.

Copper sulfides, Cu₂S (153) and CuS (137): Both these substances are diamagnetic. For Cu₂S, $\chi = -0.18 \times 10^{-6}$; for CuS, $\chi = -0.02 \times 10^{-6}$. This illustrates the rather frequent occurrence of diamagnetism in sulfides for which the corresponding oxide is paramagnetic.

Gold, Au: Metallic gold (82) is diamagnetic with a susceptibility of -0.15×10^{-6} , substantially independent of temperature.

Hafnium oxide, HfO₂: This substance is stated by Meyer (152) to be diamagnetic, with a susceptibility of -0.110×10^{-6} . This value is not surprising, although the presence of a small temperature-independent paramagnetism might be expected.

Iron, Fe: Metallic iron is strongly ferromagnetic. The magnetic properties depend in great degree on the purity and previous history of the sample. These changes have been the subject of almost innumerable researches. The specific magnetization is about 220, and the Curie point about 760°C.

Ferrous oxide, FeO: Welo and Baudisch (147) state that ferrous oxide hydrate has a susceptibility at room temperature of about 20×10^{-6} . Bizette and Tsai (25) have recently reported that the susceptibility has a maximum at 198°K., and that between 293°K. and 213°K., $\chi = 6.24/(T + 570^\circ)$. No other information on this compound seems to be available.

Ferric oxide, Fe₂O₃: There are at least two compounds of this formula (147).

γ - Fe_2O_3 is ferromagnetic. Its magnetic properties appear to be almost identical with those of magnetite, Fe_3O_4 . The Curie point is reported by various authors to lie between 500°C . and 620°C . The specific magnetization is about the same as that of nickel, namely $\sigma = 50$ – 60 . α - Fe_2O_3 is, on the other hand, paramagnetic, or more probably very weakly ferromagnetic (68). The susceptibility at room temperature is about 22×10^{-6} , but varies irregularly with temperature, becoming field dependent as the temperature is lowered. Different preparations show widely different magnetic behavior, but this may be due to failure accurately to characterize the substances on which measurements have been made. The susceptibility also varies with grain size (30).

Magnetite, Fe_3O_4 : This substance is ferromagnetic, about to the same degree as nickel. The Curie point is sometimes given as 590°C ., but this varies widely in different preparations (147, 148).

Iron-sulfur system: In general, low sulfur concentrations lead to paramagnetism and high to ferromagnetism. But this is not invariably true. The iron-sulfur system is extremely complex and, at its present state of development, not particularly useful from a magnetocatalytic standpoint. This system has been extensively studied by Haraldsen and others (58–61, 63, 119, 142).

Kaolin: Zimens and Hedvall (221) give χ as about 0.2×10^{-6} , but unfortunately it is not clear from this paper whether the susceptibility is negative or positive. As with all natural substances, iron may be an important impurity.

Magnesium, Mg (81): The metal has a small, temperature-independent paramagnetism, $\chi = 0.55 \times 10^{-6}$. As with most metals, correction for ferromagnetic impurity is practically always necessary. Rao and Savithri (175) give the much higher susceptibility 1.08×10^{-6} . It is not clear to what this difference may be due.

Magnesium oxide, MgO : The value given by Meyer (152) is probably close to the truth. The susceptibility is -0.25×10^{-6} , and is independent of temperature.

Manganese, Mn: Pantulu (170) gives the susceptibility of the amorphous metal at 20°C . as 11.80×10^{-6} . The susceptibility follows the Weiss law with $\Delta = 1540^\circ$. Other investigators give values for χ in the range 8 – 11×10^{-6} . Wheeler reports a difference in susceptibility of α - and β -manganese (215). Manganese appears to form ferromagnetic compounds with nitrogen at quite moderate temperatures (5).

Manganous oxide, MnO : Haraldsen and Klemm (65) give the following:

$T, ^\circ\text{K} \dots\dots\dots$	90	195	293	523	683
$\chi \times 10^6 \dots\dots\dots$	73.0	75.7	69.1	53.4	46.5

Bhatnagar (12) *et al.* give results about 5 per cent higher, but with approximately the same temperature coefficient.

Manganosic oxide, Mn_3O_4 : Like other oxides of similar formula, this substance is not very well characterized. Honda and Soné (85) give the susceptibility at room temperature as 55.8×10^{-6} .

Manganic oxide, Mn_2O_3 : Bhatnagar (12) *et al.* give the susceptibility at 20°C . as 89.3×10^{-6} . This value is considerably higher than those given in earlier reports.

Manganese dioxide, MnO_2 : Bhatnagar (12) *et al.* have carefully investigated this important compound. Their results are given below:

$T, ^\circ\text{K} \dots\dots\dots$	300	310	340	383	438	480
$\chi \times 10^6 \dots\dots\dots$	26.0	25.7	24.8	23.6	22.2	21.3

Manganous sulfide, MnS : Haraldsen and Klemm (65) give the following data:

$T, ^\circ\text{K} \dots\dots\dots$	90	195	293	528	726
$\chi \times 10^6 \dots\dots\dots$	67.3	73.6	64.7	48.5	40.3

However, MnS exists in at least two forms which have somewhat different susceptibilities (199).

Manganese disulfide, MnS_2 : Haraldsen and Klemm (64) give the following data:

$T, ^\circ\text{K} \dots\dots\dots$	90	195	290	423
$\chi \times 10^6 \dots\dots\dots$	60	53	47	40

These data are, however, only approximate, because some dependence of susceptibility on field strength was found.

Oxides of molybdenum: These compounds are not in a very satisfactory state, magnetically speaking. For Mo_2O_3 Meyer (152) gives $\chi = -0.35 \times 10^{-6}$ at 16°C . This result is rather surprising, because an appreciable paramagnetism would have been predicted. The compound MoO_2 is given a susceptibility of $+0.33 \times 10^{-6}$ by Wedekind and Horst (212). Molybdic anhydride, MoO_3 , might be expected to have a small temperature-independent susceptibility, and this appears to be the case (8, 201, 212), although values range from 0.876×10^{-6} to 0.02×10^{-6} .

Sulfides of molybdenum: The compounds MoS_2 and MoS_3 are diamagnetic with susceptibilities of -0.48×10^{-6} and -0.36×10^{-6} , respectively (154, 201). It would be interesting to know why oxides often show temperature-independent paramagnetism while the corresponding sulfides do not.

Nickel, Ni : From the very large number of reports on metallic nickel it is safe to say that the specific magnetization is about 55 and that the Curie point is about 358°C .

Nickel oxide, NiO : For a long time the commonly accepted susceptibility for this substance at room temperature was about 50×10^{-6} . Klemm (136, 138) has, however, shown that nickel oxide as ordinarily prepared is ferromagnetic, owing to the presence of metallic nickel. Only when the proportion of oxygen exceeds that in the stoichiometric ratio of NiO does the oxide become paramagnetic. The identity of the ferromagnetism with the presence of metallic nickel is proved by the fact that the ferromagnetism disappears above the Curie point

of pure nickel. Bhatnagar and Bal (11) show that when care is taken in the preparation, nickel oxide of proper stoichiometric proportions may be made, and that the susceptibility is 9.56×10^{-6} at room temperature.

Nickelous sulfide, NiS: This substance is not particularly easy to characterize accurately. A sample analyzing $\text{NiS}_{1.018}$ is stated by Klemm and Schüth (138) to have a susceptibility of about 3×10^{-6} at 20°C . and 2000 oersteds. There is a marked dependence on field strength and also on temperature. It will be noted that this susceptibility is considerably smaller than that for the corresponding oxide.

Nickel disulfide, NiS_2 : Haraldsen and Klemm (64) find that at 20°C . and extrapolated to infinite field, $\chi = 5.1 \times 10^{-6}$. There is, however, some dependence on field strength. Temperature dependence is also shown.

Platinum, Pt: The metal has been investigated extensively. The susceptibility at room temperature is about 1.0×10^{-6} , with a small temperature coefficient (210). Takatori (194) reports a decreased susceptibility for finely powdered platinum.

Rhenium, Re: Perakis and Capatos (173) give the susceptibility as $+0.369 \times 10^{-6}$, and as independent of temperature from -79° to 20°C . The value at room temperature has recently been confirmed by Miss Marylinn Ellis in the writer's laboratory.

Rhenium oxides and sulfides: Schüth and Klemm (184) give the following susceptibilities at room temperature:

Compound.....	ReO_2	ReS_2	ReO_3	Re_2O_7
$\chi \times 10^6$	+0.2	-0.15	+0.15	-0.06

All these values are substantially independent of temperature.

Silica, SiO_2 : Pascal (171) gives $\chi = -0.493 \times 10^{-6}$. This author has also studied the susceptibility of silica as a function of water content.

Silver, Ag: Metallic silver (151, 161, 175) is diamagnetic, $\chi = -0.19 \times 10^{-6}$.

Strontium oxide, SrO : Meyer (151) gives $\chi = -0.060 \times 10^{-6}$. This value seems a little small.

Sulfur, S: Zimens and Hedvall (221) give $\chi = -0.45 \times 10^{-6}$. Both rhombic and monoclinic sulfur have about the same susceptibility.

Thorium oxide, ThO_2 : Bourion and Beau (26) state that anhydrous ThO_2 is feebly paramagnetic but no data are given. Miss Ellis in the writer's laboratory finds $\chi = -0.1 \times 10^{-6}$ at room temperature.

Tin oxides (154): Both SnO and SnO_2 are diamagnetic, with $\chi = -0.11$ and -0.05×10^{-6} , respectively.

Titanium dioxide, TiO_2 : Zimens and Hedvall (221) have made a careful study of titanium oxide and of its hydrates. Pure "synthetic" rutile has a susceptibility of 0.13×10^{-6} , anatase a value slightly lower, perhaps about 0.09×10^{-6} . Hydrated TiO_2 (16.5 per cent water) is diamagnetic, $\chi = -0.05 \times 10^{-6}$. All these values are independent of field strength. They would be more useful if the measurements had been extended to low temperatures. The system titanium-oxygen has been studied by Ehrlich (39, 40).

Tungstic oxide, WO_3 : $\chi = +0.81 \times 10^{-6}$, according to Wedekind and Horst (213). In view of the interest in tungsten compounds as catalysts, it is unfortunate that more magnetic data are not available.

Oxides of uranium: Haraldsen and Bakken (62) give the following susceptibilities at room temperature:

COMPOUND	$\chi \times 10^6$
UO_2	+0.55
UO_2	1.7
U_3O_8	0.4

There is some doubt as to the identity of U_3O_8 . Both UO_2 and U_3O_8 follow the Weiss law with $\Delta = 180^\circ$ and 170° , respectively.

Vanadium oxides and sulfides: Hoschek and Klemm (86) give the following:

COMPOUND	$\chi \times 10^6$		
	20°C.	-78°C.	-183°C.
V_2O_5	0.35	0.38	0.49
VO_2	0.74	0.71	0.80
V_2O_3	12.2	13.3	8.7
V_2S_3	7.9	10.1	20.3

The system vanadium-oxygen (38, 87) has been further studied, with some very peculiar results in the neighborhood of VO_2 . The sulfide V_2S_5 probably does not exist. A substance analyzing to this formula is strongly paramagnetic, a result which is improbable for pentavalent vanadium.

Zinc oxide, ZnO : This oxide is diamagnetic, but the value seems to depend on previous heat treatment. Hüttig, Radler, and Kittel (106) report susceptibilities from -0.29 to -0.43×10^{-6} , depending on temperature of ignition. Turkevich and Selwood (204) found zinc oxide to be paramagnetic at liquid-air temperatures unless it was first ignited strongly.

Zirconia, ZrO_2 : Bourion and Hun (27) state that anhydrous ZrO_2 is slightly diamagnetic, but no data are given.

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