protons since this effect cancels in chemical reactions.

NOTE.—A letter by Shulman, Dailey and Townes[13] gives moments of inertia of ethylene oxide which are considerably different from those given by Cunningham, Le Van and Gwinn.[9] S., D. and T. give the values 31.9×10^{-40}, 36.7×10^{-40} and 56.7×10^{-40} from microwave data. The entropy calculated from these values agrees with the calorimetric result to within 0.07 cal. deg.$^{-1}$ mole.$^{-1}$. Unfortunately this agreement must be considered to be spurious since the interpretation given by Cunningham, Le Van and Gwinn appears to be unambiguous.

We thank Dr. W. M. Jones for assistance with the experimental measurements.

Summary

The heat capacity of solid and liquid ethylene oxide has been determined from 14 to 285° K.

The melting point is 160.65° K. (0° C. = 273.16° K.). The boiling point is 283.66° K.

The heat of fusion is 1236.4 cal. mole^{-1} and the directly measured heat of vaporization at the normal boiling point is 6101 cal. mole^{-1}.

The vapor pressure of ethylene oxide has been measured from 224 to 285° K. The data are represented by the equation

$$\log_{10}(P_{\text{inter. cm.}}) = -(2045.70/T) - 0.021507T + 2.3328 \times 10^{-5}T^2 + 13.3163$$

which is applicable over the above range.

The calorimetric measurements have been used to calculate the entropy of the ideal gas at the boiling point, 57.38 cal. deg.$^{-1}$ mole^{-1}.

The entropy at this temperature has also been calculated from molecular data, leading to a result of 57.56 cal. deg.$^{-1}$ mole. The assignment of the fundamental frequencies of ethylene oxide is uncertain and the discrepancy of 0.18 cal. deg.$^{-1}$ mole^{-1} may be due to this cause.

The most reliable value of the entropy of ideal ethylene oxide gas at 298.16° K. and 1 atmosphere is 57.94 cal. deg.$^{-1}$ mole.

BERKELEY, CALIFORNIA RECEIVED JANUARY 10, 1949

(13) Shulman, Dailey and Townes, *Phys. Rev.*, **74**, 846 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Iron[1]

BY P. W. SELWOOD, MARYLINN ELLIS AND KATHRYN WETHINGTON

In this paper we describe applications of the susceptibility isotherm method to supported iron oxides.[2]

Experimental Part

Magnetic susceptibility and other measurements have been described in earlier papers. The preparation of high area *gamma*-alumina has also been given. The preparation and analysis of the supported iron oxides are described below.

Following the procedure used for supported manganese, and other oxides, the first preparative attempts consisted simply of impregnation of *gamma*-alumina (~200 m.^{2} g.$^{-1}$, BET nitrogen) with ferric nitrate solution, followed by drying and ignition at about 200°. In most cases this procedure resulted in a sample which possessed an appreciable degree of ferromagnetism. Small traces of ferromagnetism are commonly encountered in work of this kind and their effects are eliminated by measuring the susceptibility over a range of field strength and extrapolating to $1/H = 0$. This procedure is, however, not very accurate if the ferromagnetism becomes appreciable. It should be pointed out that a trace of ferromagnetism may be quite negligible so far as the analytical results are concerned, but may completely mask the magnetic data.

It was thought that the trace of ferromagnetism might be related to the colloidal hydrous oxide commonly said to be responsible for the brown color of ferric nitrate solutions. It was obviously impractical to correct this situation by raising the nitric acid concentration. The problem was solved by using for impregnation a solution of ferrous ammonium nitrate.

Ferrous ammonium nitrate solution was prepared as follows: equimolecular weights of ferrous ammonium sulfate and barium nitrate were ground together, and then treated with a rather small amount of water. The resulting solution of ferrous ammonium nitrate was poured through a filter, and then quickly used for impregnating the alumina. The impregnation was carried out in an atmosphere of carbon dioxide. It was found necessary to discard samples in which any change of color, indicating oxidation, took place at this stage. The filtered but undried impregnated samples were bright green in color. They were dried and then ignited by raising the temperature to 200° for forty-eight hours, in a partial vacuum. The finished samples were bright orange. These samples were used in obtaining the data given below.

Samples were also prepared by the use of high area *rutile*[3] (129 m.^{2} g.$^{-1}$). The first method used with this support was the same as for the alumina support. The hoped for result, of iron with an oxidation state of four, was not obtained. It was then felt that the combination of ferrous ion and ammonium ion prevented the iron from being oxidized beyond the ferric stage during the ignition step. A return was, therefore, made to ferric nitrate solution as an impregnating agent in the knowledge that this method might give erroneous magnetic results but that it would give reliable analytical results. By some perversity of nature the ferric nitrate turned out to give excellent magnetic data on the *rutile*.

A single magnetic measurement was made on an iron-alumina sample which had been reduced in hydrogen for six hours at 300°.

In all samples total iron was determined by the Zimmer-

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(1) This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

(2) This is the sixth paper on the susceptibility isotherm from this laboratory. The fifth appeared in THIS JOURNAL, **71**, 693 (1949).

(3) Obtained from the National Lead Company, Titanium Division.

mann–Reinhardt method. The presence of iron in an oxidation state higher than three was found as "active" oxygen, by the same procedure used for finding "active" oxygen in samples of supported manganese oxides.[2]

Results

Table I gives the results for iron oxide on alumina. The first column gives the weight per cent. of total iron. The remaining three columns give the magnetic susceptibility per gram sample, at three temperatures. Directly below each measured susceptibility there is given the calculated susceptibility per gram of iron in each corresponding sample. Thus, the first sample had a susceptibility at 25° of 7.6 × 10^{-6} per gram of sample. This sample contained 7.1% of iron, and the susceptibility per gram of iron is then 110 × 10^{-6}. Table II gives similar data for the iron–*rutile* system.

In addition to the above samples, two samples were prepared by impregnation of alumina with ferric nitrate, and two samples were prepared by impregnation of rutile with ferrous ammonium nitrate. The ignited samples in all four cases contained no iron in an oxidation state other than three, as determined by "active" oxygen analysis.

TABLE I

SUSCEPTIBILITY OF IRON OXIDE ON ALUMINA

Wt. % iron	Susceptibilities × 10^6 at 102°K.	186°K.	298°K.
7.1	18.1	11.3	7.6
	259	160	110
5.1	13.0	8.4	5.7
	261	170	120
3.9	10.4	6.4	4.0
	275	170	110
3.6	9.2	5.4	3.7
	260	160	110
2.6	7.4	4.7	2.7
	290	190	110
2.3	6.7	3.9	2.5
	300	180	120
1.8	7.5	4.0	2.2
	430	240	140
1.7	7.5	3.8	2.0
	460	240	130
1.6	5.7	3.3	1.9
	360	220	130
1.5	5.2	3.0	1.8
	370	220	140
0.54	2.0	1.0	0.5
	430	241	150

TABLE II

SUSCEPTIBILITY OF IRON OXIDE ON RUTILE

Wt. % iron	Susceptibilities × 10^6 at 102°K.	186°K.	298°K.
12.9	21.1	12.8	8.4
	161	97.6	64
8.4	16.5	9.6	6.5
	193	110	76
5.4	13.0	8.6	5.4
	241	160	98
3.8	10.9	7.0	4.8
	279	180	120
2.4	9.7	6.2	4.0
	390	250	160
1.5	7.6	5.2	3.0
	490	330	190

One sample of iron on alumina, containing 0.13% iron, was reduced in hydrogen as previously described. Before reduction, the susceptibility of this sample at 25° was 0.0 × 10^{-6}. After reduction, the susceptibility became dependent on field strength to a slight degree as shown:

Oersteds	$\chi_{25°} \times 10^6$
3630	0.24
4710	.19
5450	.14

An attempt was made to prepare a sample containing more than 7.1% iron on alumina. This was tried by repeated impregnation with ferrous ammonium nitrate, but the product failed to give a reciprocal susceptibility linear with temperature.

Figure 1 shows the susceptibility isotherms for iron oxides supported on *gamma*-alumina and on *rutile*, both at −171°. Table III shows the derived data: magnetic moment (μ), Weiss constant (Δ), and chemically determined oxidation state of the iron for the iron–alumina system. Table IV gives similar data for the iron–*rutile* system.

Discussion of Results

Figure 1 shows that supported iron oxides give susceptibility isotherms of the same general shape as those already reported for chromium, manganese, and other transition group oxides. It is of interest to examine the magnetic moment and the Weiss constant to see if the shape of the isotherm is controlled by changes of environment as found for the systems Cr_2O_3/Al_2O_3, Mn_2O_3/Al_2O_3, and MnO_2/TiO_2, or whether both environmental and oxidation state changes are effective as in the system MnO_2/Al_2O_3.

TABLE III

MAGNETIC MOMENT (μ), WEISS CONSTANT (Δ), AND CHEMICALLY DETERMINED OXIDATION STATE FOR IRON OXIDE ON ALUMINA

Wt. % iron	μ	Δ	Oxidation state[a]
7.1	4.2	50°	...
5.1	4.4	58	...
3.9	4.0	28	...
3.6	4.1	43	...
2.6	4.1	29	3.0
2.3	4.2	32	...
1.8	4.2	−10	...
1.7	4.1	−18	3.0
1.6	4.2	2	...
1.5	4.4	10	3.0
0.54	4.4	2	...

[a] After three samples gave the expected result of an oxidation state exactly three, no further "active" oxygen determinations were made on this series.

TABLE IV

MAGNETIC MOMENT (μ), WEISS CONSTANT (Δ), AND CHEMICALLY DETERMINED OXIDATION STATE FOR IRON OXIDE ON RUTILE

Wt. % iron	μ	Δ	Oxidation state
12.9	3.3	52	3.2
8.4	3.3	36	3.4
5.4	3.9	36	3.7
3.8	4.3	58	3.6
2.4	5.0	38	3.7
1.5	5.3	16	3.9

The spin-only moment for trivalent iron is 5.9 Bohr Magnetons. In the system Fe_2O_3/Al_2O_3 there can be no question that the oxidation state is three, but the moment is definitely low, ranging from 4.0 to 4.4. If this were an isolated case, it would throw doubt on our whole interpretation of the susceptibility isotherm. But the effect, of a magnetic moment lower than the spin-only value, has now been reported to occur in chromium, molybdenum, and rhenium. It also occurs in nickel in the +3 and +4 oxidation states, as will be described in a forthcoming paper. In chromia supported on *gamma*-alumina this diminution of magnetic moment is very slight and was at first mistaken for the presence of some chromium in an oxidation state higher than three. Direct chemical analysis has shown, however, that the chromium in such systems as previously described is all in the +3 state, even though the magnetic moment tends to be 3.2–3.4 rather than 3.8. In molybdenum and rhenium the effect is so great that the supported dioxides of these elements have effectively zero magnetic moment. It is understood now that the reason for this is the existence of covalent bonds between the adjacent ions of these elements.

The case of trivalent supported iron lies almost midway between the slight diminution of moment found for chromium and the almost complete loss of moment found for molybdenum and rhenium. We attribute this effect to partial covalent bonds between adjacent iron atoms. It will be noted that at the lowest iron concentration in the Fe_2O_3/Al_2O_3 system the "population density" on the alumina surface must be exceedingly small. Yet the low magnetic moment shows that even in such extremely dilute systems the tendency is for iron ions to aggregate rather than to form true two-dimensional solid solutions. There is, apparently, a tendency to resist atomic dispersion, and this effect has now been demonstrated for molybdenum, rhenium, copper and iron. It probably occurs also with chromium, nickel and other transition group elements.

It may be noted that while diminished magnetic moments in these systems are of fairly frequent occurrence, we have encountered only one case, that of cobalt, in which the magnetic moment is higher than the spin-only value.

The Weiss constants for the Fe_2O_3/Al_2O_3 system are somewhat more erratic than those found in other systems. Nevertheless, the general trend for Δ is down with lower iron concentrations. This doubtless indicates a diminishing number of adjacent paramagnetic neighbors, as previously described for chromium and manganese.

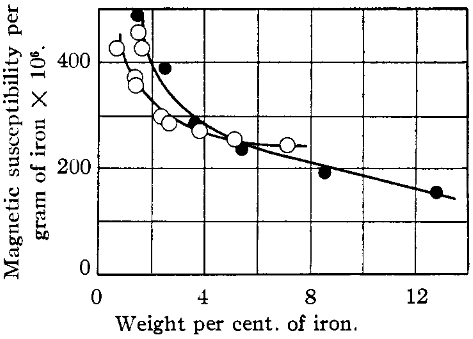

Fig. 1.—Susceptibility isotherms at −171° for iron (oxide) supported on γ-alumina (○), and on rutile (●).

For the iron-*rutile* system the magnetic moments are also lower than anticipated, and they actually change in the opposite direction to that anticipated if the oxidation state changes from three to four as the concentration is lowered. However, the chemical evidence seems to be unequivocal. At low iron concentrations the oxidation state of the iron definitely approaches four. This is further confirmation of the principle of valence inductivity described in earlier papers. The fact that the magnetic moment is not in agreement with the analytical data simply means that in this system also there is a degree of covalent binding between adjacent iron atoms, and that in this system the amount of such binding is somewhat more dependent on the iron concentration than it is in the Fe_2O_3/Al_2O_3 system.

Our conclusion with respect to the shape of the susceptibility isotherms for supported iron is that the alumina-supported samples resemble the Cr_2O_3/Al_2O_3 system, and that the *rutile*-supported samples resemble the MnO_2/Al_2O_3 system, but that both are complicated by the diminution of magnetic moment caused by partial covalency between adjacent iron ions.

It will be recalled that ferrous ammonium nitrate was used for the impregnation step on alumina, but that ferric nitrate was used for the *rutile*. A few samples were, therefore, made using ferric nitrate on alumina. The oxidation state of the iron was three, as expected. This shows that the *rutile*, rather than the impregnation solution, was responsible for the occurrence of tetravalent iron in the titania system.

Some evidence concerning the dispersion of iron is gained from the single observation on the ferromagnetism of the system after reduction in hydrogen. The degree of ferromagnetism produced was exceedingly small. It is well-known that ferromagnetism is a property of matter in the bulk and not of individual atoms or ions. In view of the very low ferromagnetism produced it must be concluded that no significant portion of the iron remains in aggregates larger than the minimum ferromagnetic domain.

The unique production of tetravalent iron in the iron–*rutile* system raises a number of interesting points. Iron is a common impurity in titania; such iron must generally be in the tetravalent state, and as such fit fairly well into the titania lattice. Perhaps this contributes to the difficulty in removing the last traces of iron from titania. It will also be observed that iron as a promoter in manganese dioxide catalysts probably also assumes a valence of four.

These considerations raise the possibility of using supported iron on *rutile* as a depolarizer in the Leclanché dry cell. Some cells were made up[4] according to standard practice, but using the iron–*rutile* instead of manganese dioxide as depolarizer. The sample was that containing 8.4% total iron, of which 40% was in +4 state. The number of coulombs withdrawn indicated that the iron was reduced to the +2 state. The performance of the cell seemed, within our limited experience, to be comparable to that of cells depolarized with manganese dioxide.

A second cell was made using iron–*rutile* containing 3.8% total iron of which 60% was in the +4 state. It was hoped that it would be possible to follow the valence changes of the iron by measuring the magnetic susceptibility of the cell during discharge. But no magnetic change was observed, possibly because the expected increase of susceptibility in going from +4 to +3 iron was accompanied by a decrease in going from +3 to +2 iron. For this reason, the experiments on tetravalent iron as a dry cell depolarizer were not continued.

Summary

Susceptibility isotherms have been measured for iron oxides supported on high-area *gamma*-alumina and on *rutile*. Iron oxide at low concentrations on *rutile* tends to assume an oxidation state of four.

EVANSTON, ILLINOIS RECEIVED OCTOBER 23, 1948

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[4] These experiments were performed by Mr. Robert P. Eischens, and will be described in a later paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEPARTMENT OF PHYSICS OF NORTHWESTERN UNIVERSITY]

Nuclear Induction and the Structure of Catalytically Active Solids

BY ROBERT B. SPOONER AND P. W. SELWOOD

Recent publications[1,2,3] from these laboratories have shown that the environment and oxidation state of a supported transition group element may, to some extent, be revealed by measurements of magnetic susceptibility. In the present paper it is shown how the nuclear induction experiment may be used to give additional information concerning catalyst structure: This additional information concerns the state of aggregation and the extent of active surface in the catalyst. But the chief application of nuclear induction to catalyst problems seems to be the promise of making rapid, *in situ*, observations during the actual time when the catalyst is promoting a chemical reaction.

The nuclear induction experiment has so far had only a few applications in chemistry. The principle of the method will, therefore, be outlined briefly.

It is well known that the familiar electronic paramagnetism is established almost instantly on application of an external field. This is not true of nuclear magnetism. The time for establishment of equilibrium in the nuclear case may be of the order of seconds, and is extremely sensitive to the structure and motions of the whole system. This time, necessary for the establishment of resolved nuclear moments in the applied field, is called the relaxation time.

For our present purpose the most interesting feature of the nuclear induction experiment is that the relaxation time, which it measures, may be greatly reduced by the use of paramagnetic catalysts. The phenomenon is similar to the use of paramagnetic catalysts in the spin isomerization of hydrogen. The nuclear induction experiment thus affords a method for measurement of paramagnetic moments, or of the concentration of paramagnetic substances of known moment. The method has been used[4] to measure the magnetic moments of copper, nickel and other ions in solution. The results depend to some extent on the distance of closest approach of a magnetic ion to the nucleus in question and hence give some information concerning the size and stability of any complex surrounding the nucleus or the paramagnetic ion. The nucleus used in all the experiments reported here was that of hydrogen, and the hydrogen was present in water, although any hydrogen compound, such as a hydrocarbon, would have been satisfactory.

The present paper reports relaxation measurements in which the catalysts were iron, and neodymium oxides, each supported on γ-alumina,

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[1] Eischens and Selwood, THIS JOURNAL, **70**, 2271 (1948).

[2] Selwood, Moore, Ellis and Wethington, *ibid.*, **71**, 693 (1949).

[3] Selwood, Ellis and Wethington, *ibid.*, **71**, 2181 (1949).

[4] Bloembergen, Purcell and Pound, *Phys. Rev.*, **73**, 679 (1948).