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The Effect of Sorption on the Structure of Surfaces of Solids. III. Magnetic Susceptibility of Sorbed NO_2–N_2O_4 on Rutile. The Stoichiometry of Rutile[1]

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RECEIVED DECEMBER 3, 1952

Magnetic susceptibility studies for NO_2–N_2O_4 sorbed on rutile are presented. These are interpreted in terms of deviations of rutile from the stoichiometric composition. The results of this investigation are compared to those obtained using similar techniques by other investigators as published in the literature.

Introduction

In a previous paper the adsorption of NO_2–N_2O_4 on rutile was discussed.[2] To explain the unusual results it was postulated that the rutile sample used in these experiments was probably surface deficient in oxygen. It was further postulated that during the sorption of NO_2–N_2O_4, the oxygen deficient sites were reoxidized, resulting in a progressive gain of sample weight.

Further evidence in favor of this hypothesis is given here in terms of magnetic susceptibility measurements. These results are then compared to other types of measurements reported in the literature, and the usefulness of adsorption isotherms in obtaining information regarding chemical properties of the solid is further discussed.

Experimental

The magnetic susceptibility measurements were carried out simultaneously with the determination of the isotherms reported in the previous paper. The magnetic susceptibility of the adsorbate–adsorbent system was determined by measuring the apparent weight change[2] of the system upon application of a magnetic field of 13 kgauss generated by the electromagnet described by Reyerson and Wertz.[3]

The yoke of this magnet was supported by a single screw and was raised or lowered with a motor-driven worm gear. The magnet was constrained to move vertically by use of steel ball bearings moving in carefully machined guides. With this arrangement the pole gap would be positioned to follow the downward movement of the sample during adsorption.

The field strength inside the pole gap was monitored using the principle of proton spin resonance. The circuit developed by Hopkins[4] was modified by altering the phase shift control mechanism and the method of modulating the steady magnetic field. The frequency of the oscillator was determined using a commercial frequency meter. By manual adjustment of the excitation current for the generator field windings so as to keep the absorption peak centered on the oscilloscope screen, it was an easy matter to keep the field strength constant to within ±0.1%.

After measuring the magnetic force acting on the sample in the field, corrections were applied for the force acting on the adsorbent, the glass container, the suspension fibers and for the vapor displaced by them.

In order to obtain better precision in the calculations the field of the electromagnet was mapped as a function of the distance from the center of the pole gap. The mapping operation was carried out with a calibrated flux meter, using a 3-mm. diameter flip coil driven by a synchronous motor. Using the field mapping, the corrections for the sample, glass bulb and fibers could be readily computed, using the standard formulas relating magnetic susceptibility to magnetic force.[5,6]

The magnetic susceptibility of Pyrex was determined in a separate experiment. Using a measured density value of 2.27, the mass susceptibility of Pyrex used in these experiments was found to be -0.337×10^{-6} c.g.s. units, as compared to a value of -0.341×10^{-6} c.g.s. units determined by Selwood.[7]

The vapor corrections were determined using a mass susceptibility value of $\chi = 8410 \times 10^{-6}/T$ for NO_2; experimental measurements by Havens[8] are in good agreement with this theoretical formula cited by Van Vleck.[9] An earlier determination by Soné[10] which yielded much lower susceptibilities is now thought to be in error.[9] The mass susceptibility of N_2O_4, which is also needed in the calculations was taken as -0.33×10^{-6} c.g.s. unit.[8]

The mass susceptibility of rutile prior to adsorption was found to be $+0.074 \times 10^{-6} \pm 0.007$ c.g.s. unit.

The susceptibility of the adsorbate is plotted against the quantity of gas adsorbed per gram TiO_2 in Fig. 1. Due to the small changes in force which were observed in these measurements the precision of the data is poor. The approximate quantity of gas required for monolayer coverage of the surface as computed from the BET equation (see Part II) is shown as a vertical line on the abscissa. The diamagnetic susceptibility of gaseous N_2O_4 is represented by the heavy horizontal dotted line. The diameter of the circles approximately represents the precision of the data.

Discussion

The above data are unusual in two respects: 1. At very low surface coverages the calculated susceptibility of the adsorbed phase is numerically larger than the diamagnetic susceptibility of N_2O_4 ($\chi_{N_2O_4} = -0.33 \times 10^{-6}$ c.g.s. unit).[11] The susceptibility values of NOCl ($\chi = -0.13 \times 10^{-6}$ c.g.s. unit)[12] or of N_2O_3 ($\chi = -0.21 \times 10^{-6}$ c.g.s. unit)[13] are too low to account for the high initial diamagnetic susceptibility of the adsorbate. A mixture of NO_2 and N_2O_4 would be expected to have a smaller diamagnetic susceptibility than pure N_2O_4.

2. The diamagnetic susceptibility of the adsorbate seems to fall with increasing surface coverage. This cannot correspond to an increasing dissociation of N_2O_4 into NO_2 on the surface because this process would violate Le Chatelier's principle. Thus,

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[1] This work was supported by funds from the Office of Naval Research and by a U. S. Rubber Company Fellowship granted to the junior author.

[2] L. H. Reyerson and J. M. Honig, THIS JOURNAL, **75**, 3917 (1953). Hereafter referred to as Part II.

[3] L. H. Reyerson and J. E. Wertz, *J. Phys. Colloid Chem.*, **53**, 234 (1949).

[4] N. J. Hopkins, *Rev. Sci. Instruments*, **20**, 401 (1949).

[5] E. Stoner, "Magnetism," Methuen & Co., Ltd., London, 1948.

[6] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.

[7] P. W. Selwood, THIS JOURNAL, **55**, 3161 (1933).

[8] G. G. Havens, *Phys. Rev.*, **41**, 337 (1932).

[9] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford Clarendon Press, New York, N. Y., 1932.

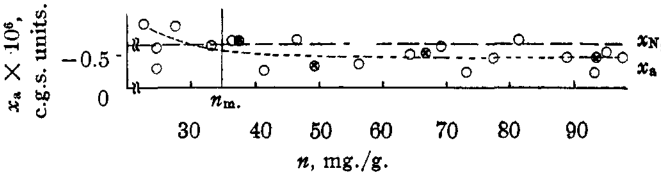
[10] T. Soné, *Sci. Rep. Tohoku Univ.*, **11**, 139 (1922).

[11] Note that in run M-1 no data were taken at very low surface coverages and hence the diamagnetic susceptibility of the adsorbed phase is never much larger than that of N_2O_4. However, just as in run M-2, the magnetic susceptibility isotherm tends toward higher negative values below monolayer coverage.

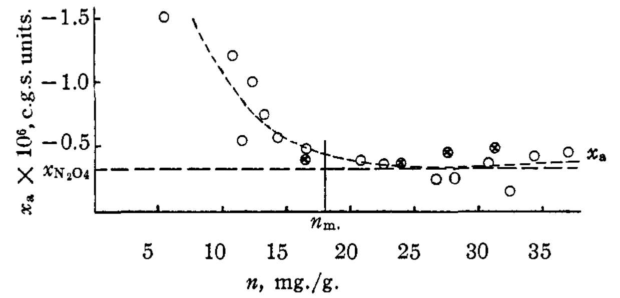
[12] (a) C. M. Beeson and C. D. Coryell, *J. Chem. Phys.*, **6**, 656 (1938). (b) E. B. Wilson, THIS JOURNAL, **56**, 747 (1934).

[13] "Handbook of Chemistry and Physics," Chemical Rubber Company, 33rd Edition, Cleveland, Ohio, 1951, p. 2169.

in cases where magnetic susceptibility and isotherm data for NO_2–N_2O_4 systems were obtained simultaneously in the literature[3,14] it was reported that the magnetic isotherm changed from smaller to larger diamagnetic values.



Run M-2; high area rutile.



Run M-1; low area rutile.

Fig. 1.—Magnetic susceptibility of sorbed NO_2–N_2O_4 on rutile, temp. 28.5°: crossed circles, desorption isotherm.

In order to explain the above results it is necessary to refer to the adsorption mechanism proposed in Part II. Ehrlich[15] has shown that the magnetic properties of the titanium oxides depend markedly on their composition. Thus he found that for $TiO_{1.90}$, $\chi_s = +1.60 \times 10^{-6}$ c.g.s. unit; for $TiO_{1.97}$, $\chi_s = +0.65 \times 10^{-6}$ c.g.s. unit; for TiO_2, $\chi_s = +0.08 \times 10^{-6}$ c.g.s. unit. Therefore, if the rutile was initially partially reduced and later reoxidized during absorption of NO_2, the magnetic susceptibility values measured prior to adsorption (and used in computing the corrections) were higher than those prevailing during adsorption. The use of smaller values in the calculations alters the magnetic isotherms in the right direction. For example if in run M-1 the sample susceptibility were taken to be $+0.061 \times 10^{-6}$ c.g.s. unit instead of $+0.074 \times 10^{-6}$ c.g.s unit the χ_a values for the adsorbate would change from $+0.5 \times 10^{-6}$ c.g.s. unit at $n = 5.6$ mg./g. to -0.2×10^{-6} c.g.s. unit at $n = 37$ mg./g., thus conforming to the usual magnetic susceptibility *vs.* surface coverage curves encountered in the literature. It is obvious from these calculations that the χ_a values are very sensitive to the sample susceptibility which is not known very accurately. For this reason no attempts have been made to recalculate the curves of Fig. 1 using smaller χ_s values. It is clear, however, that curves of the type shown in Fig. 1 can be interpreted only by assuming that the sample susceptibility decreased during adsorption. This interpretation tends to support the hypothesis presented in Part II.

Measurement of Rutile as a Function of the Sample Temperature.—In order to test the hypothesis still further the magnetic susceptibility of a fresh rutile sample was measured *in vacuo* at 28° after being heated for 24–48 hours at various temperatures. Susceptibility calculations were carried out as described earlier. The results are presented in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITY OF RUTILE AFTER HEATING AT VARIOUS TEMPERATURES. (MEASUREMENT TEMPERATURE 28°, SAMPLE WEIGHT 0.543 g., GLASS WEIGHT 0.193 g.)

Heating temp., °C.	Total magnetic force (dynes)	Net magnetic force acting on rutile (dynes)	$\chi_s \times 10^6$, c.g.s. unit
28	−0.21	0.48	0.078
200	− .16	.53	.086
275	− .15	.54	.088
450	− .14	.55	.089
450[a]	− .15	.54	.088

[a] After heating for 24 hr. in oxygen at atmospheric pressure.

Inspection of the table shows that an over-all increase of 0.011×10^{-6} c.g.s. unit in the paramagnetic susceptibility occurred upon heating the rutile up to 400°. Most of the change took place at temperatures near 200°; thus it is probable that the over-all change is attributable in part to desorption of water vapor. However, it is unlikely that the over-all change can be entirely accounted for on the basis of water vapor desorption. Using $\chi_{H_2O} = -0.72 \times 10^{-6}$ c.g.s. unit,[6] the observed change in magnetic susceptibility upon heating from 27 to 400° would correspond to a water loss of 30 mg. per g. of sample, in addition to the water lost after a three-day evacuation at room temperature. This compares to an estimated amount of 8 mg./g. which would be required for monolayer coverage of the surface by water vapor. All other gases present in air are not adsorbed to any appreciable extent at room temperature.

This increase in susceptibility may, therefore, be correlated with a slight oxygen deficiency of the sample, thus supporting the view expressed earlier.

It is of interest to note in this connection that the mass susceptibility values for rutile cited in the literature vary considerably. These are listed in Table II.

TABLE II

MASS SUSCEPTIBILITY VALUES OF RUTILE

Authors	Reference	$\chi_s \times 10^{-6}$, c.g.s. unit
S. Meyer	*Ann. Phys.*, **69**, 240 (1899)	0.039
E. Wedekind and P. Hausknecht	*Ber.*, **46**, 376 (1913)	.066
S. Berkmann and H. Zocher	*Z. physik. Chem.*, **124**, 322 (1926)	− .20
G. F. Hüttig	*Z. anorg. allgem. Chem.*, **224**, 225 (1935)	− .30
D. P. Raychaudhuri and P. N. Sengupta	*Ind. J. Phys.*, **10**, 253 (1936)	.073
P. Ehrlich	*Z. Elektrochem.*, **45**, 362 (1939)	.08
K. Ziemens and J. Hedvall	*Svensk Kem. Tidsk.*, **52**, 12 (1941)	.134
F. N. Hill and P. W. Selwood	THIS JOURNAL, **71**, 2522 (1949)	− .3
Present investigation		0.071 to 0.078

The disagreement, even as to sign and order of magnitude, probably can be explained on the basis

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(14) R. Juza and H. Tentschert, *Z. anorg. Chem.*, **262**, 165 (1950).

(15) P. Ehrlich, *Z. Elektrochem.*, **45**, 362 (1939).

of two factors: Since the magnetic susceptibility of rutile is inherently small, the presence of small amounts of impurities seriously affects the susceptibility values. Furthermore, according to our hypothesis, it is a relatively simple matter to obtain non-stoichiometric rutile by heating the sample prior to the measurements. In all probability, the fluctuations in the susceptibility values reported by the various investigators are due to small differences in the stoichiometric composition of the samples. Whether stoichiometrically pure TiO_2 is actually diamagnetic as reported by three different investigators is a question which should be further investigated.

Oxidation–Reduction Properties of Rutile.—There is a good deal of evidence in the literature which indicates that rutile may be reduced under certain conditions and reoxidized by oxidizing agents. Following earlier attempts by O. Ruff,[16] and Shusterius[17] to show changes in rutile, Meyer[18] and Meyer and Nedel[19] determined the conductivity of rutile as a function of the temperature. They found a drastic increase in conductivity if the samples were heated at 400–800° for 10–20 hours in an atmosphere of H_2. Other investigators found it necessary to place rutile in an atmosphere of oxygen in order to prevent changes in conductivity and dielectric properties.[19a] Verwey[20] and Verwey and Bügel[21] call attention to the existence of non-stoichiometric rutile. They point out that such deviations can be observed by measurements of dielectric losses before they can be detected by classical analytical methods. Thus the evidence here presented for the change in the surface stoichiometry is supported by a number of investigators. There is also some prior evidence for the reoxidation of metallic oxides by NO_2.[22,23]

Conclusion

The magnetic susceptibility studies on the system rutile–NO_2–N_2O_4 indicate strongly that the rutile was not presenting a stoichiometric surface when adsorbing the first NO_2. This supports the sorption evidence in the preceding paper. The combined evidence points to an unusual type of combined chemisorption and physical sorption. The NO_2 molecule is not chemisorbed in the usual sense but gives up an oxygen atom to the surface and escapes as NO. The more nearly perfect rutile surface then physically sorbs more NO_2. The slowness of the early sorption, the permanent increase in weight as shown in the sorption isotherm of the preceding paper, the spectroscopic analysis of the equilibrium gases, taken after sorption was partially complete, and the magnetic susceptibility of the system during the sorption of NO_2 all point to the above concept of the mechanism of sorption. Thus we have an example of sorption on a surface which itself is undergoing change.

Acknowledgments.—The authors are pleased to acknowledge their indebtedness to Professor J. E. Wertz and to Robert Batdorf for advice and assistance in the building of the proton resonance oscillator.

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(16) O. Ruff, *Z. anorg. Chem.*, **82**, 377 (1913).

(17) C. Shusterius, *Z. tech. Phys.*, **16**, 640 (1935).

(18) W. Meyer, *ibid.*, **16**, 355 (1935).

(19) W. Meyer and H. Nedel, *ibid.*, **18**, 588 (1937).

(19a) L. J. Berberich and M. E. Bell, *J. Appl. Phys.* **11**, 681 (1940).

(20) E. J. W. Verwey, *Philips Tech. Rev.*, **9**, 46 (1947).

(21) E. J. W. Verwey and R. D. Bügel, *ibid.*, **10**, 231 (1949).

(22) P. Sabatier and J. Senderens, *Ann. chim. phys.*, **7**, 391 (1896).

(23) J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XVIII. Heat Capacity of Ammonium Chromium Alum[1]

BY HERRICK L. JOHNSTON, JIH-HENG HU AND WILLIAM S. HORTON

RECEIVED APRIL 9, 1953

The heat capacity of ammonium chromium alum has been measured from 18 to 305°K. A second-order transition has been found between 92 and 97°K. with heat and entropy of transition equal to 267.4 ± 0.1 cal. and 2.8 ± 0.1 e. u., respectively. The entropy at 298.16°K., derived from the heat capacity data, is 171 ± 1 e.u.

Introduction

Measurements on the dielectric constant of ammonium chromium alum, $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$, at low temperatures by Guillian[2] show a second-order type transition which occurs in the region 85 to 90°K. and exhibits considerable hysteresis. By comparison with similar data on other alums, Guillian predicted that the same effect should be observable in the specific heat curve.

A similar transition in the absorption spectrum of the solid alum has been observed by Kraus and Nutting,[3] in the same temperature region. They have shown that the phenomenon is not readily reproducible, in that the energy of transition can be "frozen in" by cooling with either liquid air or with liquid hydrogen. The conditions of cooling which produced the low temperature form were erratic and could not be produced at will.

It was with the hope of studying this transition effect in the specific heat that the present investigation was undertaken.

Apparatus and Materials.—Two samples of ammonium chromium alum were used: the first sample (sample I) was prepared and studied in 1949, while the second (sample II) was prepared in 1952 for a new series of measurements.

Sample I was prepared as follows: J. T. Baker C.P. ammonium chromium alum was recrystallized from an aqueous solution saturated at 55° and cooled slowly with rapid mechanical stirring in order to produce a crop of finely divided

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) R. Guillian, *Compt. rend.*, **209**, 21 (1939).

(3) B. L. Kraus and J. C. Nutting, *J. Chem. Phys.*, **9**, 133 (1941).