not of U^{4+} and U^{6+} ions,[18] on the assumption of spin-only magnetism. The same conclusion was reached by Dawson and Lister,[19] but deviations from the Curie–Weiss law were observed. The U^{6+} ions have no unpaired electrons, while U^{5+} has one, supposedly in a 5f orbital, which gives rise to the paramagnetism of U_3O_8. For spin-only magnetism the magnetic entropy should thus amount to $2R \ln 2$, or 1.84 e.u. per mole U_3O_8, but apparently only a fraction of this is associated with the effective magnetic moment of U_3O_8, decreases considerably as the temperature is lowered, and only amounts to 0.6 Bohr magneton per uranium atom at 25°K., and the magnetic entropy might therefore be spread over a rather large temperature region. In the crystal structure of U_3O_8 infinite linear $-U-O-U-$ chains are present in the

c-direction, a situation which should favor super-exchange.[20] Since magnetic susceptibility measurements[4] have not indicated significant changes in the magnetic properties of U_3O_8 around 25°K. no conclusion concerning the mechanism can be drawn at present.

(18) H. Haraldsen and R. Bakken, *Naturwiss.*, **28**, 127 (1940).
(19) J. K. Dawson and M. W. Lister, *J. Chem. Soc.*, 2181 (1950).
(20) P. W. Anderson, *Phys. Rev.*, **79**, 350 (1950).

ANN ARBOR, MICHIGAN
BLINDERN, NORWAY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

α-Ferric Oxide: Low Temperature Heat Capacity and Thermodynamic Functions[1]

BY FREDRIK GRØNVOLD AND EDGAR F. WESTRUM, JR.

The heat capacity of synthetic α-Fe_2O_3 was determined from 5 to 350°K. No heat capacity anomaly was observed at the magnetic transition about 250°K. Thermodynamic functions have been calculated and the values of C_p, $S°$, $H° - H_0°$, and $-(F° - H_0°)/T$ at 298.15°K. are: 24.80 cal. deg.$^{-1}$ mole^{-1}, 20.889 cal. deg.$^{-1}$ mole^{-1}, 3718.9 cal. mole^{-1} and 8.416 cal. deg.$^{-1}$ mole^{-1}, respectively.

Ferric oxide exists in two crystalline modifications, alpha and gamma, of which alpha is considered the stable form, but there are indications that it might transform into gamma under special conditions.[2] The heat capacity of α-ferric oxide previously has been measured[3] over only four narrow regions between 90 and 290°K., and it was considered of interest to extend the measurements to lower temperatures and obtain more accurate thermodynamic data for this compound. Moreover, α-Fe_2O_3 is a substance of rather complex magnetic properties,[4] having a weak ferromagnetism, which disappears below about 250°K., superimposed on its antiferromagnetism.

In the study by Parks and Kelley[3] two different samples were used, one consisting of large crystals of specular hematite, the other of a finely divided powder prepared from iron oxalate (Kahlbaum). The heat capacity of the synthetic sample was considerably higher (3.8% at 90°K., 2.4% at 275°K.) than of the mineral, which was explained on the basis of its somewhat amorphous state, as inferred from X-ray powder photographs. The lower values of the specular hematite were adopted, and the resulting entropy at 298°K. found to be 21.5 ± 0.5 e.u. Apart from these data a series of enthalpy measurements on a synthetic sample

have been made[5] over three regions in the range 81 to 317°K.

Neutron diffraction[6] work on α-Fe_2O_3 in the range 80 to 1000°K. confirmed earlier X-ray data[7-9] leading to a rhombohedral unit cell containing two formula units, with the oxygen atoms forming a slightly distorted close packing and $2/3$ of the octahedral interstices filled by iron atoms. The structure consists of sheets of iron atoms parallel to the (111) plane and sheets of oxygen atoms in between. In concordance with the view expressed by Néel,[4] the neutron diffraction data indicated the existence of an antiferromagnetic structure. All four iron atoms in the unit cell are located on the space diagonal. The neutron diffraction data suggest that they are non-equivalent and have relative spin orientation $(+ - - +)$. At room temperature the moments seem to be parallel to the (111) plane and directed toward one of the three nearest neighbors, while at lower temperatures they are oriented normal to the (111) plane or, in other words, in the (111) direction.

This change in the direction of the moments causes the parasitic ferro- or ferrimagnetism to disappear below about 250°K. according to the magnetic susceptibility data by Morin[10] and in the

(1) This work was supported in part by the Division of Research, U. S. Atomic Energy Commission.
(2) G. I. Finch and K. P. Sinha, *Proc. Roy. Soc. (London)*, **A241**, 1 (1957).
(3) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).
(4) L. Néel, *Ann. phys.*, **4**, 249 (1949); *Advances in Phys.*, **4**, 191 (1955).
(5) A. S. Russell, *Physik. Z.*, **13**, 59 (1912).
(6) C. G. Shull, W. A. Strauser and E. O. Wollan, *Phys. Rev.*, **83**, 333 (1951).
(7) L. Pauling and S. B. Hendricks, THIS JOURNAL, **47**, 781 (1925).
(8) V. Montoro, *Gazz. chim. ital.*, **70**, 145 (1940).
(9) N. V. Belov and V. I. Mokeeva, *Trudy Dok. Akad. Nauk SSSR* **57**, 819 (1947).
(10) F. J. Morin, *Phys. Rev.*, **78**, 819 (1950).

range 240 to 190°K. according to the magnetization data by Guillaud[11] on pure synthetic samples. The latter author found that the transition temperature decreased with increasing strength of the magnetic field and also a discontinuity in the resistivity of α-Fe_2O_3 and rather pronounced changes in the expansion coefficient in the range of the anomaly. No latent heat was detected, although the presence of a second-order transition could not be excluded. The transition was studied further by Néel and Pauthenet[12] and interpreted by Néel[13] by supposing that the ferromagnetism consisted of an isotropic and an anisotropic part. The anisotropic part is only observed above 260°K., i.e., when the magnetic moment is in the (111) plane. Studies of the thermomagnetic properties[14] of two natural hematite crystals showed in contrast to those measured by Néel and Pauthenet[12] only the anisotropic part of the ferromagnetism at room temperature. On cooling, this ferromagnetism in the (111) plane gradually disappeared from 253 to 173°K. The low-temperature susceptibility values found were in accord with those reported by Morin[10] and Guillaud.[11] Properties of the isotropic and anisotropic ferromagnetism in hematite were measured in the range 200 to 300°K. by Haigh[15] and a cyclic hysteresis effect studied in detail.

Magnetic resonance measurements on α-Fe_2O_3 confirm the presence of a highly anisotropic, weak ferromagnetism which disappears below room temperature. According to the results by Anderson, et al.,[16] on a synthetic single crystal (containing 3% Fe^{2+}) the resonance absorption corresponding to this anisotropy goes down to zero rather abruptly in the range from 260 to 255°K., which is not easily explained on the basis of a change in the direction of the magnetic moments. Similar measurements by Kumazai, et al.,[17] on a natural sample showed the transition to take place at about 220°K. and less abruptly. Some spread in the transition temperature also was observed by neutron diffraction between synthetic and natural hematite,[18] but there was no noticeable effect of a magnetic field on the transition temperature or line intensity above and below the transition. Measurements of magnetostriction in hematite in the transition region have shown[19] that the magnetostrictive effects are closely related to the parasitic ferromagnetism, both having the same type of dependence on applied field strength and temperature.

On the basis of a saturation magnetization of 0.43 e.m.u./g.[11] the uncompensated magnetic moment is 0.006 Bohr magneton per iron atom, and possible explanations given by Néel[4] about the origin of the parasitic ferromagnetism is that α-

Fe_2O_3 is a slightly defect structure or that the sublattices inside a domain are not equivalent, either for geometrical reasons or on account of local fluctuations in composition. According to Li,[20] who also has made a semi-empirical analysis of the super-exchange interaction responsible for the magnetic lattice of hematite, the weak ferromagnetism observed in the (111) plane of hematite is identified with the magnetization in domain walls, pinned down by lattice imperfections. The disappearance of this ferromagnetism on cooling is interpreted as due to mutual annihilation and migration of the domain walls to the surface. On heating through the transition, the domain walls are recreated by nucleation and stabilized by the imperfection centers. It is considered extremely improbable that all the moments would turn 90° at the same temperature. More recently, Dzyaloshinski[21] has developed a thermodynamic theory for explaining the weak ferromagnetism in α-Fe_2O_3 and concludes that the transition at about 250°K. is of the first kind. An expression for the entropy change is given but not evaluated. While Dzyaloshinski considers the ferromagnetism due to relativistic spin-lattice and magnetic dipole interactions, Bertaut[22] finds that dipole interactions can neither account for the weak ferromagnetism nor the magnetic anisotropy of hematite.

Ferric Oxide Sample.—The ferric oxide for this investigation was prepared by oxidizing "Iron by Hydrogen," Merck, in air at 1000° until constant weight was attained; this required 8 hr. Iron determination gave 69.91% total iron (theoretical, 69.94%) and the ferrous content was found to be zero within the limits of error (0.05%). Spectrographic analysis showed the presence of about 0.01% Mn, less than 0.01% Al, Co, Mg, Ni and Si, and less than 0.001% Ca, Cu and Sn.

X-Ray powder photographs of the product showed only lines from α-Fe_2O_3. Its lattice constants ($\lambda CoK_{\alpha_1} = 1.78890$ Å.) were determined at about 25° in a 11.48 cm. diameter camera with asymmetric film mounting. The rhombohedral unit cell dimensions are $a = 5.4266$ Å. and $\alpha = 55.256°$, which agree very well with the values $a = 5.4271$ Å. and $\alpha = 55.263°$ (25°) found by Willis and Rooksby.[23] The sample was found to be slightly ferromagnetic with a moment of 0.36 gauss/g. at room temperature, i.e., of the same magnitude as reported by earlier investigators.[11-14] The particle size was of the order of 5 μ.

Experimental Technique.—Mark I cryostat and the technique employed in low temperature adiabatic calorimetry are described elsewhere.[24] The copper calorimeter (laboratory designation W-10) has a capacity of 92.8 cc.; it is gold-plated inside and out and has no vanes. The heat capacity of the empty calorimeter was determined separately, using the same thermometer and heater and exactly the same amount of indium–tin solder for sealing and Apiezon-T grease for thermal contact with the thermometer and heater. It represented from 22 to 80% of the total heat capacity observed.

(11) C. Guillaud, J. phys. rad., **12**, 489 (1951).

(12) L. Néel and R. Pauthenet, Compt. rend., **234**, 2172 (1952).

(13) L. Néel, Revs. Mod. Phys., **25**, 58 (1953).

(14) H. Bizette, R. Chevallier and B. Tsaï, Compt. rend., **236**, 2043 (1953).

(15) G. Haigh, Phil. Mag., **2**, 877 (1957).

(16) P. W. Anderson, F. R. Merritt, J. P. Remeika and W. A. Yager, Phys. Rev., **93**, 717 (1954).

(17) H. Kumazai, H. Abe, K. Ono, I. Hagashi, J. Shinada and K. Iwanaga, ibid., **99**, 1116 (1955).

(18) L. M. Corliss, J. M. Hastings and J. E. Goldman, ibid., **93**, 893 (1954).

(19) H. M. A. Urquhart and J. E. Goldman, ibid., **101**, 1443 (1956).

(20) Y.-Y. Li, ibid., **101**, 1450 (1956); **102**, 1015 (1958).

(21) I. Dzyaloshinski, J. Phys. Chem. Solids, **4**, 211 (1958).

(22) F. Bertaut, Compt. rend., **246**, 3335 (1958).

(23) B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc., **B65**, 950 (1952).

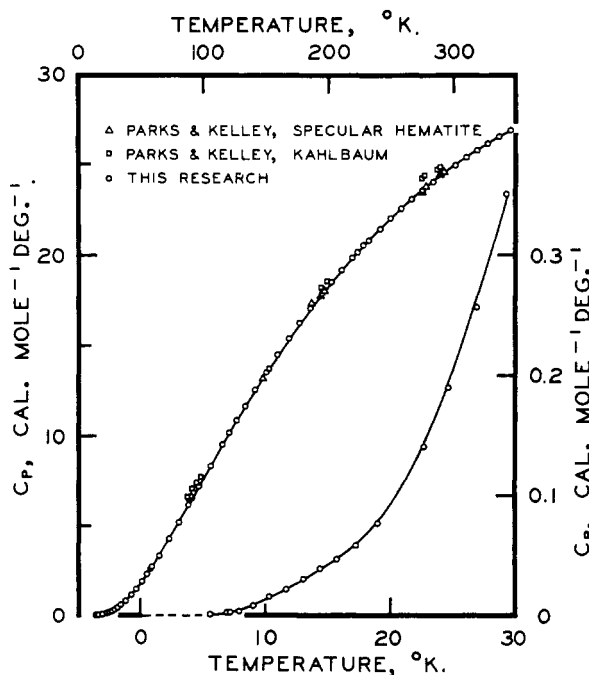(24) E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

Fig. 1.—Molal heat capacity of α-Fe_2O_3 from 5 to 350°K.

Temperatures were measured with a capsule-type platinum resistance thermometer (laboratory designation A-3) contained in an axial well in the calorimeter. The thermometer has been calibrated by the National Bureau of Standards, and the temperatures are judged to correspond with the thermodynamic temperature scale within 0.1°K. from 5 to 10°K., within 0.03°K. from 10 to 90°K., and within 0.04°K. from 90 to 350°K. Precision is considerably better, and the temperature increments are probably correct to 0.001°K. after corrections for quasi-adiabatic drift.

TABLE I

HEAT CAPACITY OF α-Fe_2O_3 IN CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		Series II		Series IV	
58.61	2.612	223.58	20.17	5.58	0.0011
65.30	3.326	232.31	20.82	7.10	.0024
73.20	4.248	241.06	21.44	7.87	.0038
80.93	5.177	249.68	22.03	9.02	.0073
88.57	6.128	258.22	22.57	10.31	.0135
96.83	7.138	266.75	23.09	11.65	.0218
106.36	8.308	275.38	23.61	13.02	.0301
116.07	9.503	283.78	24.06	14.39	.0390
121.39	10.15	292.35	24.50	15.72	.0469
127.04	10.83	301.23	24.96	17.25	.0583
133.82	11.63	310.20	25.42	18.97	.0767
141.85	12.54	319.04	25.81	22.70	.1406
150.70	13.52	327.77	26.19	24.65	.1898
159.58	14.50	336.53	26.58	26.89	.2567
168.38	15.38	345.42	26.94	29.24	.3509
177.24	16.24			31.56	.4473
185.88	17.05	Series III		34.80	.6163
194.32	17.80			38.75	.8662
202.65	18.52	6.97	0.0023	42.76	1.156
210.85	19.20			46.99	1.503
219.61	19.88			51.51	1.906
228.19	20.52			55.81	2.311
				59.71	2.729

The calorimeter was loaded with 170.914 g. of the α-Fe_2O_3 sample in a dry box filled with nitrogen. It was then evacuated and helium added at about 4 cm. Hg pressure at

25° to provide thermal contact between sample and calorimeter.

Results

The heat capacity determinations are listed in Table I in chronological order and expressed in terms of the thermochemical calorie, defined as 4.1840 absolute joules. The ice point was taken to be 273.15°K. and the atomic weight of iron as 55.85. The data are presented in terms of one mole of Fe_2O_3, i.e., 159.70 g. An analytically-determined curvature correction was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments usually can be inferred from the adjacent mean temperatures in Table I.

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF α-Fe_2O_3

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	$S°$, cal. deg.$^{-1}$ mole^{-1}	$H° - H_0°$, cal. mole^{-1}	$\dfrac{-(F° - H_0°)}{T}$ cal. deg.$^{-1}$ mole^{-1}
5	0.0008	0.0003	0.001	0.00006
10	.0120	.0028	.023	.00046
15	.0426	.0134	.158	.0029
20	.0912	.0311	.472	.0075
25	.1995	.0618	1.171	.0150
30	.3812	.1130	2.589	.0267
35	.6276	.1890	5.072	.0441
40	.9532	.2934	9.000	.0684
45	1.334	.427	14.69	.101
50	1.768	.590	22.43	.141
60	2.742	.996	44.82	.249
70	3.868	1.502	77.77	.391
80	5.066	2.097	122.44	.567
90	6.307	2.765	179.28	.773
100	7.528	3.492	248.44	1.008
110	8.765	4.268	329.88	1.269
120	9.984	5.083	423.64	1.553
130	11.18	5.930	529.5	1.857
140	12.34	6.801	647.2	2.178
150	13.45	7.690	776.1	2.516
160	14.54	8.594	916.1	2.868
170	15.56	9.506	1066.7	3.232
180	16.51	10.422	1227.1	3.605
190	17.42	11.340	1396.8	3.988
200	18.30	12.256	1575.4	4.379
210	19.13	13.169	1762.6	4.776
220	19.92	14.077	1957.8	5.178
230	20.66	14.979	2160.7	5.585
240	21.37	15.873	2370.9	5.994
250	22.04	16.760	2588.0	6.408
260	22.68	17.637	2811.7	6.823
270	23.29	18.504	3041.5	7.239
280	23.85	19.362	3277.2	7.658
290	24.39	20.208	3518.4	8.075
300	24.90	21.043	3764.9	8.493
350	27.12	25.054	5067.3	10.576
273.15	23.47	18.775	3115.1	7.370
298.15	24.80	20.889	3718.9	8.416

The heat capacity versus temperature curve is shown in Fig. 1. It has the usual sigmoid shape, with no sign of transitions, not even around 250°K. where the magnetic transition takes place. This indicates that the change in direction of easy magnetization does not involve any appreciable

entropy increment or that it is spread out over a rather broad temperature interval.

Values of C_p, S°, $H^\circ - H_0^\circ$ and $-(F^\circ - H_0^\circ)/T$ at selected temperatures are listed in Table II. The entropy and enthalpy increments were computed by numerical integration, using graphically interpolated values of heat capacity. The heat capacity values are considered to have a probable error of about 5% at 5°K., 1% at 10°K. and 0.1% above 25°K. Values below 5°K. were extrapolated with a T^3 function. The effects of nuclear spin and isotopic mixing are not included in the entropy and free energy functions and the values listed in Table II are therefore the conventional ones to be used in calculations of chemical equilibria. The estimated probable error in the thermodynamic functions is 0.1% above 100°K., but some of the values are given to an additional digit for comparison purposes.

The present measurements accord better with the data by Parks and Kelley[3] on specular hematite than on the finely divided powder but are 3% lower near 90°K. and within about 0.5% at higher temperatures, while they are 2 to 6% lower than those on the Kahlbaum sample. Inasmuch as even

the specular hematite contained 0.5% H_2O and 0.5% SiO_2 and no attempt was made to correct for these impurities, the agreement must be considered satisfactory. Since Parks and Kelley[3] used the data on the specular crystals in calculating the entropy, 21.5 ± 0.5 e.u., the entropy increment over the common region (90 to 295°K.) agrees quite well with that found in the present investigation. Most of the difference of 0.6 e.u. is in the extrapolated portion as a consequence of the errors in their lowest temperature data.

Heats and Entropies of Ionization of Phenol and Some Substituted Phenols

BY L. P. FERNANDEZ AND L. G. HEPLER

Standard heats of ionization of aqueous phenol, o-chlorophenol, p-chlorophenol, o-nitrophenol and p-nitrophenol have been determined calorimetrically at 298°K. These heats of ionization have been used with free energies, obtained from ionization constants, to calculate standard entropies of ionization of these compounds in aqueous solution. A detailed quantitative interpretation of the thermodynamics of ionization of phenol and substituted phenols is impractical until more data are available but some interesting comparisons of entropies of ionization are discussed.

This investigation of the heats and entropies of ionization of aqueous phenol and some substituted phenols was undertaken as part of a program aimed at the accumulation of thermodynamic data on the ionization of certain selected organic acids in water. It is to be hoped and possibly expected that systematic accumulation of such data on selected acids, combined with similar data of other investigators, will lead to a detailed interpretation of the thermodynamics of aqueous acids in terms of the structure of the weak acids and their anions and of solute–solvent interactions.

Experimental

The solution calorimeter used in this investigation has been described in detail.[1,2] All of the calorimetric work reported in this paper was carried out with 950 ml. of water or solution in the calorimeter. All heats of reaction and solution were investigated at 25.0 ± 0.3°.

Baker C.P. phenol was distilled under reduced pressure with only the middle fraction saved for calorimetric experiments. Eastman Kodak Co. practical grade o-chlorophenol and p-chlorophenol also were purified by fractional distillation. The o-chlorophenol and p-chlorophenol for calorimetric experiments boiled at 173° and melted at 42.8–44.8°, respectively.

(1) C. N. Muldrow and L. G. Hepler, THIS JOURNAL, **79**, 4045 (1957).

(2) R. L. Graham and L. G. Hepler, ibid., **78**, 4846 (1956).

Sodium o-nitrophenoxide was prepared by adding o-nitrophenol (m.p. 45–46°) to a solution of NaOH in ethanol. The resulting phenoxide was recrystallized once from 95% ethanol and twice from absolute ethanol. It then was dried and stored for future analysis and use.

The p-nitrophenol (m.p. 112–114°) used for our calorimetric experiments was supplied by Eastman Organic Chemicals. Sodium p-nitrophenoxide dihydrate was prepared by adding some of this p-nitrophenol to a solution of NaOH in ethanol. The salt formed was recrystallized twice from ethanol–water mixtures and washed with ethanol before drying and storing for future analysis and use.

Sodium o-nitrophenoxide was analyzed by titration with aqueous HCl. The yellow o-nitrophenol formed as a product of the titration reaction partly precipitated out and partly remained in solution and tended to obscure the indicator color change at the end-point. To eliminate this difficulty, 10 ml. of CCl_4 was added to the solution to extract and dissolve the o-nitrophenol, thus leaving the water layer nearly colorless. Methyl red indicator then was added and the solution titrated to the indicator color change without removing the CCl_4 layer. The titrations required 100.8% of the theoretical amount of HCl.

Sodium p-nitrophenoxide dihydrate also was analyzed by titration with aqueous HCl. This compound could serve as its own indicator, but the addition of one drop of methyl red solution made the color change at the end-point easier to see. The titrations required 101.0% of the theoretical amount of HCl.

Results and Calculations

We have measured the heat of solution of phenol in water and the heat of neutralization of phenol