the terms of which correspond to proton abstraction by the various basic species present in the solvent. In principle, each of the $k^{\mathrm{B}}{}_1$ is still a function of the properties of the solvent and may therefore vary with the concentration of sulfuric acid. However, the kinetic analysis of a number of nitration reactions in sulfuric acid[17] has shown that this medium effect on rate constants can be relatively unimportant. The falling off of the rate constant k_{-1} with increasing acidity is therefore likely to be attributable to the changing concentration of the possibly active proton abstracting bases H_2O, $SO_4^=$ and HSO_4^- but the present data are insufficient to carry the analysis further. Experiments to extend these data with other compounds are in progress. Since

$$\log x = -2.3H_0 + \text{constant} \qquad (6)$$

and

$$\log K = -3.3H_0 + \text{constant} \qquad (7)$$

it follows that, very approximately

$$\log k_{-1} = H_0 + \text{constant} \qquad (8)$$

although the accumulation of experimental errors in the value of k_{-1} does not allow a sensitive test of this equation. From the definition of Hammett's acidity function we obtain that

$$\log \frac{k_1}{k_{-1}} = \log \frac{[\mathrm{RH_2}^+]}{[\mathrm{RH}]} = pK_{\mathrm{RH_2^+}} - H_0 \qquad (9)$$

It follows from a combination of equations 8 and 9 that the rate of proton attachment to anthracene is rather insensitive to the medium composition over the particular range studied, which would be expected if the logarithms of the concentrations of the kinetically active acids in the solvent (probably H_2SO_4 and/or H_3O^+) change less rapidly than those of the kinetically active bases. The steep dependence of the rate constant x on the acidity is therefore almost entirely ascribed to the effect of acid concentration on the solubility of anthracene molecules in the sulfuric acid phase and hence on the ratio $k_{\mathrm{P}}/k_{-\mathrm{P}}$.

ITHACA, NEW YORK

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[17] A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950); T. G. Bonner, F. Bowyer and G. Williams, *ibid.*, 3274 (1952).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Titanomagnetite and Ferric Titanate

BY S. S. TODD AND E. G. KING

RECEIVED MAY 20, 1953

Heat capacity measurements of titanomagnetite (Fe_2TiO_4) and ferric titanate (Fe_2TiO_5) were conducted throughout the temperature range from 51 to 298.16°K. Titanomagnetite has two heat capacity peaks, at 56.0 and 99.1°K. The entropies at 298.16°K. are, respectively, 39.0 ± 0.6 and 37.4 ± 0.3 cal./deg. mole for titanomagnetite and ferric titanate.

Introduction

Two compounds are known in the $FeO-TiO_2$ system,[1] ilmenite ($FeTiO_3$) and titanomagnetite (Fe_2TiO_4). In the $Fe_2O_3-TiO_2$ system, only one ferric titanate compound (Fe_2TiO_5) is definitely known. Compounds of composition corresponding to arizonite ($Fe_2O_3{:}3TiO_2$) and natural pseudobrookite ($2Fe_2O_3{:}3TiO_2$) sometimes have been postulated, but Overholt, Vaux and Rodda[2] have demonstrated by X-ray diffraction studies that arizonite is a mixture, and Pauling[3] similarly has demonstrated this for natural pseudobrookite.

Shomate[4] has reported low-temperature heat capacity values and the entropy at 298.16°K. for ilmenite, but there are no previous similar data for titanomagnetite or ferric titanate, with which the present paper is concerned.

Materials.—The compounds used in this investigation were prepared by K. R. Bonnickson of this Laboratory. The titanomagnetite was made from titania (99.8% pure), and powdered iron and magnetite derived from reagent grade ferric oxide. These ingredients were mixed in proper proportions and heated in a stream of nitrogen for several periods (including a total of 24 hours at 1250–1350° and 4 hours at 1350°), with intervening grindings, mixings, analyses and adjustments of composition. The final product analyzed 64.28% ferrous oxide and 35.66% titania, as compared with the theoretical 64.27 and 35.63%. Silica amounting to 0.06% was present. The X-ray diffraction pattern was virtually identical with that of magnetite, the only difference being a minor displacement of lines, corresponding to the slightly altered lattice dimensions.

The ferric titanate was made from pure titania and reagent-grade ferric oxide. An intimate, stoichiometric mixture was heated for several periods (including a total of 24 hours at 1200° and 7 hours at 1450°), with intervening grindings, mixings, analyses and adjustments of composition. Final analysis gave 66.63% ferric oxide and 33.30% titania, as compared with the theoretical 66.65 and 33.35%. The principal impurity was 0.06% silica. The X-ray diffraction pattern agreed with that for ferric titanate (Fe_2TiO_5) given in the A.S.T.M. catalog.

Measurements and Results

The heat capacity measurements were conducted with previously described apparatus.[5] The sample masses were 371.71 g. of titanomagnetite and 247.31 g. of ferric titanate. The results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are listed in Table I and plotted in Fig. 1. Molecular weights accord with the 1951 International Atomic Weights.[6]

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[1] J. Grieve and J. White, *J. Roy. Tech. Coll. (Glasgow)*, **4**, 444 (1939).

[2] J. L. Overholt, G. Vaux and J. L. Rodda, *Am. Mineralogist*, **35**, 117 (1950).

[3] L. Pauling, *Z. Krist.*, **73**, 97 (1930).

[4] C. H. Shomate, THIS JOURNAL, **68**, 964 (1946).

[5] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

[6] E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

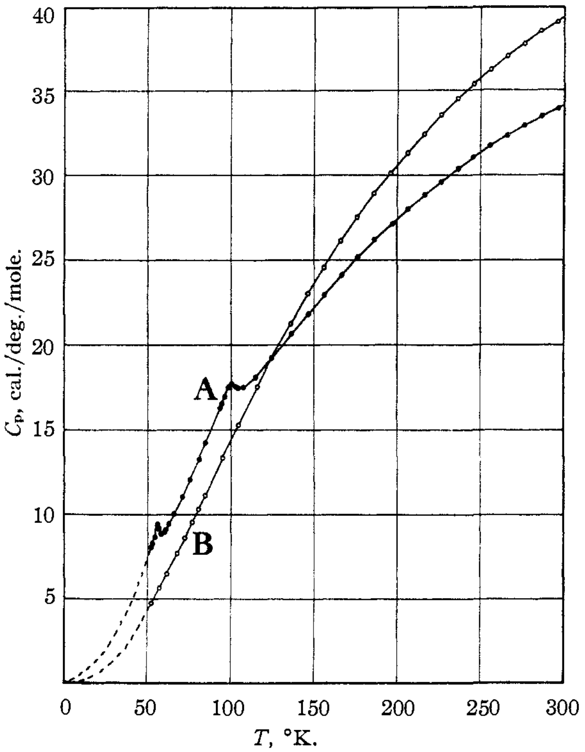

Fig. 1.—Heat capacities: A, black circles, Fe_2TiO_4; B, open circles, Fe_2TiO_5.

The heat capacity curve for ferric titanate follows a normal course, and no discussion appears necessary. The curve for titanomagnetite shows two heat capacity peaks, at 56.0 and 99.1°K. To better portray the shape of the peaks, the two series of determinations labeled (a) and (b) in Table I were made without temperature gaps and with small (*ca.* 2°) temperature rises. Integration of these two series of measurements gave a total heat absorption of 78.88 cal./mole between 51.00 and 60.00°K. and 243.12 cal./mole between 94.00 and 108.00°K. It is evident from Fig. 1 that the heat capacity of titanomagnetite is abnormal over a wide temperature range. One indication of this is the fact that the heat capacity is higher than for the ferric titanate at all measured temperatures below about 125°K.

It is of interest to note that chromite ($FeCr_2O_4$), which is isomorphous with titanomagnetite, also has two heat capacity peaks,[7] at 75 and 135°K. Magnetite itself has only one known peak,[8,9] at 114°K., but heat capacity measurements were not extended below 60°K.

Entropies at 298.16°K.—Calculation of the entropy of titanomagnetite comprised several steps. Entropy increments for the temperature ranges 60.00 to 94.00°K. and 108.00 to 298.16°K. were obtained by Simpson-rule integrations of C_p against log T plots as 5.49 and 25.94 cal./deg. mole, respectively. For the peak intervals 51.00 to 60.00°K. and 94.00 to 108.00°K., the entropy increments were derived by summations of the series of determinations labeled (a) and (b) in Table I (*i.e.*, $\Sigma C_p \Delta T/T$), with proper adjustment of the end members to conform to the even temperatures. Values for these intervals are, respectively, 1.42 and 2.41 cal./deg. mole. These quantities add to give $S^\circ_{298.16} - S^\circ_{51.00} = 35.26$ cal./deg. mole as the measured portion of the entropy.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
Fe_2TiO_4 (mol. wt., 223.60)					
51.95	8.076 (a)	94.63	16.57	176.01	25.19
52.62	8.259	95.97	16.92 (b)	185.88	26.23
54.00	8.683 (a)	98.09	17.50 (b)	195.96	27.13
56.00	9.420 (a)	100.31	17.67 (b)	206.10	27.97
56.40	9.180	102.38	17.53 (b)	216.34	28.87
57.99	8.863 (a)	104.24	17.47	226.22	29.56
60.09	8.915 (a)	104.32	17.45 (b)	236.07	30.38
60.82	9.071	107.44	17.48 (b)	245.64	31.04
62.71	9.423 (a)	114.54	18.10	255.84	31.71
65.61	10.04	124.64	19.25	266.09	32.31
70.40	11.05	136.16	20.65	276.37	32.93
75.20	12.06	146.39	21.84	286.26	33.51
80.58	13.26	155.88	22.98	296.57	33.91
84.91	14.24	166.37	24.15	(298.16)	(34.01)
93.47	16.29 (b)				
Fe_2TiO_5 (mol. wt., 239.60)					
52.36	4.778	115.65	17.52	216.02	32.46
56.86	5.572	124.60	19.24	226.08	33.59
61.56	6.502	135.73	21.25	236.00	34.52
67.32	7.679	145.96	23.02	245.71	35.40
71.94	8.620	155.75	24.60	256.19	36.24
76.62	9.563	165.81	26.16	266.19	37.04
80.12	10.31	175.83	27.59	276.14	37.79
84.21	11.16	185.77	28.94	286.19	38.52
94.69	13.33	195.75	30.16	296.64	39.10
104.49	15.29	206.00	31.36	(298.16)	(39.26)

Extrapolation to obtain the entropy below 51.00°K. was made by two methods. First, the measured heat capacities above 125°K. were fitted by an empirical sum of Debye and Einstein functions

$$D(129/T) + 3E(286/T) + 3E(721/T)$$

This sum represents the data between 125 and 298.16°K. with a maximum deviation of 1.0%. Low temperature heat capacity values from this function sum were calculated and plotted, and the measured curve then was extended and smoothly merged into the calculated curve at 36°K. This method gave $S^\circ_{51.00} = 3.81$ cal./deg. mole. The second extrapolation procedure was the comparison method of Kelley, Parks and Huffman,[10] the results of Shomate[7] for magnesium chromite being used for the "standard" substance. This method gave $S^\circ_{51.00} = 3.53$. An arbitrary intermediate value, $S^\circ_{51.00} = 3.72$, was adopted.

The entropy increment of ferric titanate for the temperature range 51.00 to 298.16°K. was obtained by Simpson-rule integration of a C_p against log T plot. Extrapolation below 51.00°K. was accomplished by means of the empirical Debye and Einstein function sum

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[7] C. H. Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

[8] R. W. Miller, THIS JOURNAL, **51**, 215 (1929).

[9] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (192[illegible]).

[10] K. K. Kelley, G. S. Parks and H. M. Huffman, *ibid.*, **33**, 1802 (1929).

$$D(193/T) + 3E(321/T) + 4E(670/T) + E(1260/T)$$

which fits the measured heat capacity data between 51 and 298.16°K., with a maximum deviation of 0.9%. The entropy values appear in Table II.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	Fe_2TiO_4	Fe_2TiO_5
0–51.00°K. (extrap.)	3.72	1.96
51.00–298.16°K. (meas.)	35.26	35.48
$S^\circ_{298.16}$	39.0 ± 0.6	37.4 ± 0.3

The results in Table II and the entropies of the elements listed by Kelley[11] give $\Delta S_{298.16} = -79.2 \pm 0.6$ and $\Delta S_{298.16} = -105.3 \pm 0.3$ cal./deg. mole as the entropies of formation of titanomagnetite and ferric titanate from the elements.

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(11) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Mechanism of Exchange of Hydrogen Gas and Aqueous Alkali[1a]

BY W. K. WILMARTH, JUNE C. DAYTON[1b] AND J. M. FLOURNOY

RECEIVED JANUARY 6, 1953

The conversion of parahydrogen in aqueous alkali has been shown to be a homogeneous non-photochemical process with a rate which is first order with respect to both hydrogen gas and hydroxide ion concentration. The rate constant in the temperature region 80–110° can be represented by the expression $k^\circ = 4.7 \times 10^{13} e^{-23,800/RT}$ l. mole^{-1} min.$^{-1}$. The exchange of deuterium gas to produce HD occurs at a slightly slower rate under comparable conditions. The mechanism has been discussed in terms of a solvated hydride ion as an intermediate.

Introduction

An account of exploratory studies in this laboratory has described the exchange of hydrogen gas with aqueous potassium hydroxide solutions.[1c] A similar exchange has been reported by two previous investigators. Wirtz and Bonhoeffer,[2] while investigating some phases of general acid–base catalysis, first discovered that potassium hydroxide catalyzed the homogeneous exchange between hydrogen gas and the deuterium in heavy water. Abe,[3] in a later paper, suggested that one would expect the change to be catalyzed as effectively by acid as by base, and since this was not the case, he postulated a catalysis by some trace impurity such as a colloidal iron compound. In support of this viewpoint he presented experimental evidence that the activity of the solution was destroyed by prolonged heating or by dialysis but was restored when the solution was brought in contact with an iron wire.

Neither of the above investigations was extensive enough to clarify the detailed mechanism of the exchange process. Since our preliminary data indicated a simple bimolecular reaction, Abe's experiments were repeated in greater detail, but in all cases our initial results were confirmed. A mass spectrometer was not available during the early phases of the work, and the bulk of the experiments were carried out using parahydrogen instead of an isotopic tracer. However, in the second part of this paper the essential identity of the exchange and the conversion processes has been established by observing the rate of exchange of both deuterium and hydrogen deuteride with aqueous alkali.

Experimental

The methods of preparation and analysis of parahydrogen have been previously described.[4] The reaction cell and the general techniques used in the kinetic studies were also essentially those of the previous paper. Except for the experiments described below, the potassium hydroxide solutions were obtained by dilution of a 0.707 *N* standard solution of Baker and Adamson C.P. potassium hydroxide and were used without further treatment. In run 106 the solution was dialyzed through a cellophane osmosis membrane supplied by Central Scientific Co. (70160-A, 1$^1/_8$″). The membrane was checked for holes after the dialysis by replacing the potassium hydroxide solution with a sugar solution and noting the development of osmotic pressure. The 0.103 *N* solution used in run 104 was prepared by partially neutralizing the standard 0.707 *N* potassium hydroxide with concentrated hydrochloric acid. This effected a decrease in hydroxide concentration with only a small dilution of the stock solution. The potassium hydroxide for run 95 was prepared by carefully distilling water into an evacuated vessel containing previously distilled metallic potassium. Approximately a twofold increase in surface area was effected in run 90 by the introduction of 1.0 g. of 100–150 mesh ground glass. In runs 102 and 103 the solution was first heated in a sealed glass container for one week at 100°. The solution for run 136 was heated for one week at 100° in a tube with enhanced surface area.

During an experiment the temperature was held to ±0.1° by pumping hot oil from a large thermostat through the outer jacket of the reaction cell. At appropriate time intervals a small fraction of the total hydrogen was removed and analyzed using the Pirani gage technique.

Results and Discussion

A rate constant k can be defined in terms of the measured resistance of the Pirani gage as

$$\frac{P_t - P_\infty}{P_0 - P_\infty} = \frac{R_t - R_\infty}{R_0 - R_\infty} = e^{-kt}$$

P_0, P_t and P_∞ denote the concentration of parahydrogen expressed in per cent. at time $t = 0$, t and ∞; R_0, R_t and R_∞ are the corresponding resistance values.

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(1) (a) A large portion of this investigation was carried out under Task Order IV, Contract No. N6onr-238, with the Office of Naval Research. (b) Based on a dissertation submitted by June C. Dayton, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

(1c) Y. M. Claeys, J. C. Dayton and W. K. Wilmarth, *J. Chem. Phys.*, **18**, 759 (1950).

(2) K. Wirtz and K. F. Bonhoeffer, *Z. physik. Chem.*, **177A**, 1 (1936).

(3) S. Abe, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **38**, 287 (1941).

(4) W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).