TABLE II

COMBUSTION DATA FOR CADMIUM

Mass. of Cd, g.	Total energy, cor. to 30°, cal.	Cor. for fuse and *Elt*, cal.	Cor. for Tl, cal.	Cor. for incomp. comb., cal.	Net total energy, cal.	$-\Delta U_B$, cal./g.
6.99965	4221.98	−20.19	−534.22	126.12	3793.7	542.0
7.00033	4093.46	−19.21	−355.12	69.43	3788.6	541.2
7.00007	4412.99	−20.61	−709.37	115.94	3799.0	542.7
7.00008	4182.91	−20.15	−442.49	64.91	3785.2	540.7
6.99986	4335.34	−17.39	−616.88	77.25	3778.3	539.8
7.00023	4010.38	−19.03	−267.51	70.57	3794.4	542.0
7.00022	4345.23	−19.86	−623.15	87.86	3790.1	541.4
6.99968	4087.81	−19.60	−355.35	80.21	3793.1	541.9
					Mean	541.5 ± 0.7

$\Delta H_{298.16} = -61.2 \pm 0.2$ kcal./mole. The uncertainty interval allows for items corresponding to those listed above for chromium.

Recent compilers[1,2] of data have adopted −269.7 and −270.0 kcal./mole as the heat of formation of chromium oxide and −60.86 and −62.2 kcal./mole as the heat of formation cadmium oxide. The present results are considered superior from the viewpoint of experimental technique, precision and metal purity.

Combination of the new heat of formation values with entropy data listed by Kelley[6] leads to $\Delta F^\circ_{298.16} = -253.2 \pm 0.5$ kcal./mole for the free energy of formation of chromic oxide and $\Delta F^\circ_{298.16} = -54.1 \pm 0.3$ kcal./mole for cadmium oxide.

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Activation Energy for the Solid State Reaction γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$

BY FRANK E. DEBOER[1] AND P. W. SELWOOD

RECEIVED MARCH 15, 1954

Thermomagnetic measurements have been made on gamma ferric oxide prepared in several ways and with the addition of alumina, lanthana and gallia. The experimental data have been used to calculate the activation energy for the transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$. The activation energy for this reaction depends on previous heat treatment. It is raised by the presence of alumina, lowered by lanthana, and unaffected by gallia.

Quantitative description of reactions in the solid state has recently been facilitated by the demonstration by Parkins, Dienes and Brown[2] that activation energies for rate processes may, under certain conditions, be calculated from the isothermal variation of a measured physical property, without knowledge of the order of the reaction.

The method used in the present study was isothermal variation of the specific magnetization, in a manner similar to that used by Hofer[3] in a study of the decomposition of cobalt carbide. The method is based on the assumption that in a mixture of gamma and alpha ferric oxides the specific magnetization is linear with the mass of the ferromagnetic gamma phase.

Ferromagnetic ferric oxide has the spinel structure and alpha ferric oxide has the corundum structure. Thus in order for the transition to occur the oxygen lattice must shift from cubic close packed to hexagonal close packed and some of the iron ions must migrate from tetrahedral to octahedral positions. There have been several investigations of this reaction since the gamma oxide was characterized, in 1925. It has been established that aging[4] and purity govern the rate of transition. In particular it has been shown that alumina and other substances in small amounts may stabilize the gamma oxide.[5] The most nearly quantitative of these studies was that of Sachse and Haase.

Experimental

Preparations.—Series N was prepared in a conventional manner by precipitation of hydrous Fe_3O_4 which was then oxidized to γ-Fe_2O_3. Fifty grams of ferric ammonium sulfate hydrate in 0.5 l. of boiling water was added to 61.5 g. of ferrous ammonium sulfate hydrate in a like amount of boiling water. The solution so formed was poured into 2 l. of dilute ammonium hydroxide. The resulting jet black precipitate was washed by decantation six times with 4 l. of water each time. It was then filtered, dried at 110° for several hours and crushed to pass a 150-mesh screen. The gel was then divided into several portions and these were oxidized in air at 230° for varying lengths of time as shown in Table I.

Series PY was prepared from a pyridine complex according to the directions of Baudisch and Hartung.[6] About 120 g. of the complex, $Fe[py]_4Cl_2$ was added to 6 l. of water. Clean air was bubbled through this solution to oxidize and convert the mixture to gamma ferric oxide hydrate, γ-$Fe_2O_3 \cdot H_2O$. The precipitated monohydrate was dried in air at 110° for 24 hours, crushed in an agate mortar to pass a 150-mesh screen, then heated in air for varying lengths of time as shown in Table I.

Series AL was made as follows: 110 g. of ferrous sulfate hydrate was dissolved in 1.1 l. of water. To this solution, in different preparations, there was added from 0 to 16 g. of aluminum sulfate hydrate. The solution was brought

---

[1] This work was initiated under contract with the Office of Naval Research and continued on the Visking Corporation Fellowship, receipt of which is gratefully acknowledged.

[2] W. E. Parkins, G. J. Dienes and F. W. Brown, *J. Appl. Phys.*, **22**, 1012 (1951).

[3] L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Phys. Colloid Chem.*, **53**, 661 (1949).

[4] H. Sachse and R. Haase, *Z. physik. Chem.*, **A148**, 401 (1930).

[5] P. H. Emmett and K. S. Love, *J. Phys. Chem.*, **34**, 41 (1930).

[6] O. Baudisch and W. H. Hartung, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 184.

to a boil, 88 cc. of concd. ammonium hydroxide and 9.8 g. ammonium nitrate were added. The mixture was stirred and boiled for an hour. The precipitates were washed six times with 1 l. of boiling water, filtered, dried at 110°, sintered at 1000° for 75 minutes, crushed in an agate mortar to 150 mesh, and redried *in vacuo* over phosphorus pentoxide. The samples were then reduced in hydrogen at 350° for three hours. Reoxidation to gamma ferric oxide resulted in partial phase transition to alpha ferric oxide. For this reason thermomagnetic measurements were made both on the reduced and oxidized samples, and the loss in magnetization due to oxidation was graphically separated from that due to phase transformation. This method proved to be reliable.

Series LA was made in the same manner as series AL except that the aluminum sulfate was omitted and 1 g. of lanthanum oxide, dissolved in sulfuric acid, was added to the solution before precipitation. The precipitate was divided into three parts: LA-1 was washed five times with ammonium nitrate solution, LA-2 was washed once with water and LA-3 was not washed. The samples were filtered, dried at 110° in air, crushed to 150 mesh, heated in air at 900° for 45 minutes, screened again and reduced in hydrogen at 400° for 75 minutes. There was some indication that solid solution had not taken place completely, hence the samples were sintered again at 1050° for 3 hours in air, then reduced in hydrogen at 400° for 2.25 hours. The results on test oxidations were similar to those obtained for Series AL, hence kinetic runs were made with the reduced samples.

Series GA was made by a procedure similar to those used for Series AL and LA except that gallia was substituted for alumina or lanthana. Proportions were diminished, only 27.5 g. of ferrous sulfate hydrate and 0.380 g. of gallia being used. Sample GA-1 was washed twice with ammoniacal ammonium nitrate solution, GA-2 was washed once with water, and GA-3 was not washed. The samples were filtered, sintered overnight in air at 1100°, crushed to 150 mesh, reduced in hydrogen at 400° for $3^1/_4$ hours, oxidized in air at 225° for one hour and at 250° for one hour.

All samples were kept over phosphorus pentoxide until use.

Analysis.—Chemical analysis of the samples was difficult because of the complexity of the substances and mixtures, and by the trace of water present in several preparations. Series N and PY were analyzed by permanganate titration of samples dried to constant weight at 110°. X-Ray diffraction of these samples was in all cases identical with published (ASTM) values for gamma ferric oxide.

In series AL, LA and GA the proportion of the elements aluminum, lanthanum and of gallium, respectively, was found by difference. Analysis for iron was done as before by permanganate titration of the ignited sample. X-Ray diffraction studies on these samples showed slight shifts in the important peaks but the rather diffuse nature of all peaks made it difficult to use this method for quantitative estimation of the diamagnetic diluent.

Thermomagnetic Analysis.—Measurements were made on the thermomagnetic balance previously described. Runs were made at several different temperatures so that the activation energy could be calculated. Thus during any given run the programming feature of the temperature control circuit was used merely to hold the temperature constant.[7] Several runs were made on each sample at each temperature. The procedure was to raise the temperature as rapidly as possible to the reaction temperature. This was predetermined as giving a satisfactory rate and lay, in different runs, between 350 and 550°. In general the reaction was allowed to proceed to 50 or 60% completion under isothermal conditions. For series AL the Curie temperature

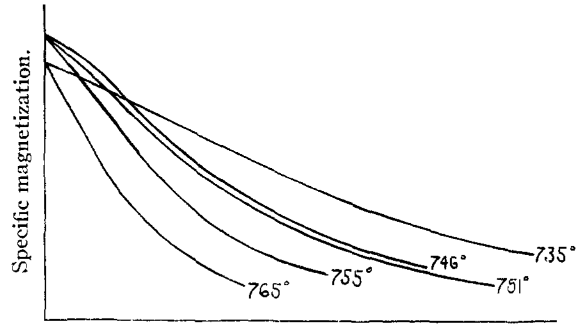

Fig. 1.—Isothermal decay of specific magnetization at several temperatures.

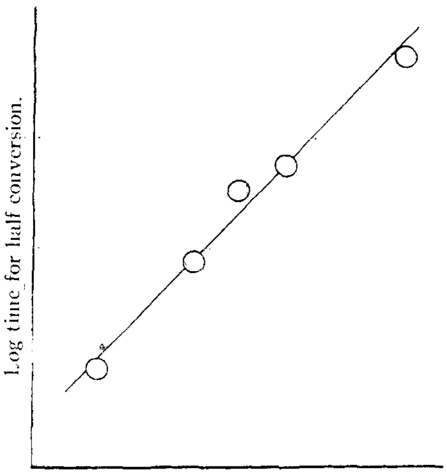

Fig. 2.—Plot derived from data of Fig. 1, for calculation of activation energy.

TABLE I

INFLUENCE OF PRELIMINARY HEAT TREATMENT ON THE STABILITY OF γ-Fe_2O_3

Sample	E, kcal./mole	σ_{298}	Treatment
N-1	50.6 ± 1.2	68.8	1.5 hr. at 230°
N-2	45.3	68.2	N-1 plus 16 hr. evac. at 25°
N-3	50.8	67.0	16.5 hr. at 230°
N-4	36.6	62.5	23 hr. at 250° plus 24 hr. at 300°
N-5	48.6	66.0	48 hr. at 230°
PY-1	50.2	52.0	1.25 hr. at 250°
PY-2	48.1	52.5	4.25 hr. at 250°
PY-3	46.1	52.2	19 hr. at 250°
PY-4	45.0	51.8	43 hr. at 250° plus 24 hr. at 270°

TABLE II

INFLUENCE OF DIAMAGNETIC IONS (M^{+3}) ON THE STABILITY OF γ-Fe_2O_3

Sample no.	$(Fe_xM_y)_2O_3$ y	E, kcal./mole	σ_{298}
AL-1	0.0	18.3 ± 2.4	87.5
AL-2	.014	..	87.0
AL-3	.037	35.6	58.5
AL-4	.058	34.6	64.6
AL-5	.056	54.9	81.0
AL-6	.078	60.5	59.0
AL-7	.094	14.9[a]	39.8
LA-1	.002	34.4	45.0
LA-2	.012	25.7	34.5
LA-3	.016	21.1	32.5
GA-1	.065	27.0	84.7
GA-2	.078	29.2	87.8
GA-3	.085	29.8	92.0

[a] A few samples, of which AL-7 is one, gave anomalous results, the cause of which was not found.

---

(7) R. F. S. Robertson and P. W. Selwood, *Rev. Sci. Instr.*, **22**, 146 (1951).

lay near the reaction temperature, so that in this case rather lower temperatures were used and the reaction was allowed to run to about 15% of completion. An example of a kinetic run is shown in Fig. 1. The plots generally showed a characteristic sigmoid shape as in Fig. 1. The order of reaction seemed to vary (1.5 to 1.7) from sample to sample. Figure 2 shows the data of Fig. 1 plotted for calculation of the activation energy.

Results

Results are tabulated in Tables I and II. The specific magnetization is designated as σ.

Surface areas were found by B.E.T. nitrogen adsorption. Values obtained on some samples were as follows: N-1, 58 m.^{2}g.$^{-1}$; N-4, 59; N-5, 53. It did not prove possible to prepare samples with more widely varying specific surfaces although this would have been desirable.

Discussion of Results

It has been shown that the activation energy for the gamma → alpha ferric oxide transition decreases with increasing severity of heat treatments. The principal result of heat treatment is to reduce the water content. It may, therefore, be concluded that water stabilizes the gamma ferric oxide lattice as it does the gamma aluminum oxide lattice.

There is no obvious relation between activation energy and particle sizes. This is true because large variations of activation energy occurred with only small variations of specific surface area. But it did not prove possible to prepare samples with large variations in surface area.

It is well known that alumina tends to stabilize the gamma ferric oxide. This has been placed on a quantitative basis, and substantial increases of activation energy have been shown to parallel increases of alumina content. It will be clear that the activation energy will reach a constant value when the ferric oxide becomes saturated with alumina.

Lanthana dissolved in gamma ferric oxide diminished the lattice stability as shown by a decrease of activation energy with increasing lanthana concentration. Gallia appears to be without effect on the stability of the ferric oxide. These results suggest that the stabilizing action of alumina is related to the small size of the aluminum ion. The larger lanthanum ion causes a decrease of stability, while the gallium ion which is almost equal in radius to iron (+3), has no effect on the stability of the gamma ferric oxide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Magnetic Susceptibilities of Some Aromatic Hydrocarbon Anions[1a,b]

BY TING LI CHU AND SHAN CHI YU

RECEIVED DECEMBER 19, 1953

The magnetic susceptibilities of tetrahydrofuran solutions of anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl anions were measured at room temperature by Gouy's method. The results obtained indicate that the monovalent anions under study are monomeric in solution with one unpaired electron and that two unlike monovalent anions exhibit no tendency to associate. Anthracene and phenanthrene also form divalent anions which, however, are diamagnetic.

Introduction

The alkali metals react with a large number of aromatic hydrocarbons in dimethyl ether, 1,2-dimethoxyethane or tetrahydrofuran by transferring one or two electrons to one molecule of hydrocarbon yielding intensely colored anions.[2,3] This reaction involves a measurable equilibrium and it was believed that this equilibrium is determined mainly by the magnitude of the solvation energy of the metal ion and perhaps that of the hydrocarbon anion.[3] In order to obtain information about the general nature of these anions, we have investigated the reaction products formed upon the reaction of sodium with several aromatic hydrocarbons in tetrahydrofuran solution by means of magnetic susceptibility measurements. The hydrocarbons under study consisted of anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl.

Experimental

Materials.—Eastman white label grade anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl, were purified by standard procedures, successive sublimation or fractional distillation under vacuum. Their melting points were 216.5, 69, 80, 99.5 and 87°, respectively.

Tetrahydrofuran was fractionated in a 30- by 2-cm. column of glass helices, b.p. 65–66°, and dried over sodium–potassium alloy.

Magnetic Measurements.—The magnetic susceptibilities of the hydrocarbon anion solutions were measured by the Gouy method at room temperature. The magnetic field was provided by a General Electric Isthmus Electromagnet with conical pole pieces of 5 cm. diameter and 15 mm. pole gap. An Ainsworth microbalance with optical lever was used. Both the magnet and the balance were encased in insulated boxes to minimize air current effects and to maintain constant humidity. Six amperes of current were used in most of the measurements and the field strength was reproducible with respect to the current to 0.1%.

A Pyrex tube 11 mm. in diameter and 20 cm. long was used for the susceptibility measurements. This tube was calibrated and used for all subsequent measurements. In the Gouy method, the apparent change in weight of the sample on application of the magnetic field, Δw, is measured. The tube calibration was made in terms of $A(H_1^2 - H_2^2)/g$ by measuring Δw of (1) the evacuated tube and (2) the tube filled to a definite height with distilled water, outgassed and sealed off under vacuum. The difference between these two measurements is related to the volume susceptibility of water taken as -0.720×10^{-6} c.g.s. units at

---

[1] (a) Taken in part from the Master Thesis of S. C. Yu, Duquesne University, 1954. (b) Presented before the Division of Physical and Inorganic Chemistry at 125th ACS Meeting, Kansas City, Mo., March 1954.

[2] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 442 (1936); A. Jeanes and R. Adams, *ibid.*, **59**, 2608 (1937); J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

[3] D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).