A Structural Change in Iron(II) Bromide Near 400°

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Heat capacity measurements of FeBr₂ show an anomaly in the vicinity of 400° suggestive of a coöperative (second-order) type transition. The transition temperature is markedly lowered by the presence of small amounts of water vapor. X-Ray powder studies indicate the high temperature form to be different from either the HCP or random packed layer structures, of the Cd(OH)₂ type, observed below the transition temperature.

The limited evidence provided by X-ray powder patterns indicates that iron(II) bromide, when purified by vacuum sublimation at *ca.* 500°, condenses in a Cd(OH)$_2$ type structure with the halogen atoms in a hexagonal close-packed array (HCP).[1] However when FeBr$_2$·H$_2$O is dehydrated *in vacuo* at temperatures around 110°, the anhydrous material formed appears to have its layers of halogen atoms packed randomly (RP form).[2] After cooling, RP material heated to temperatures of the order of 500° is found to have changed to the HCP structure. A similar modification of close-packed layer structures also has been observed for FeCl$_2$[1] and for some of the cadmium halides.[3]

In the present work the heat capacity of FeBr$_2$, in both the HCP and RP forms, has been measured between 50 and 450° to see whether a transition between the two structures could be observed and to obtain data needed to relate equilibrium properties previously determined at high temperatures[4] to thermodynamic data at 298°K. An X-ray powder examination of samples throughout this temperature range also has been made.

Experimental

FeBr$_2$ was prepared from analytical grade iron wire and reagent grade bromine as described previously.[1,2,4] Quantitative analyses of samples indicated the formula to be FeBr$_2$ within the accuracy of the determination (*e.g.*, % Fe found, 25.64, 25.74; theo. 25.89; % Br found, 74.03, theo. 74.11). An X-ray fluorescence examination, capable of detecting less than one part per thousand of elements with atomic number larger than titanium, showed the presence of only iron and bromine. The only impurity detected was a small amount of Fe$_3$O$_4$ (less than 0.2 weight %), observed as an insoluble residue when the HCP material, to be recovered in the RP form, was dissolved in water.

Heat capacity measurements were made in a continuously heating adiabatic vacuum calorimeter, described earlier.[5,6] The calorimeter cell was first filled (in a dry box) with ordered (HCP) material, sample 0-1, 103.22 g. The cell was then attached to a high vacuum line and pumped on (*p* <10^{-5} mm.) at 100° for 10–12 hr. and then at 500° for 24 hr. to remove adsorbed gases (primarily water vapor). A pressure of 300 mm. of purified argon then was admitted and the entry tube collapsed. A series of five separate runs was made in which the heat capacity was measured between 50 and 450°. X-Ray powder patterns of samples taken before and after these measurements indicated the HCP structure.

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(5) Details may be found in the Ph.D. thesis of Harry Edward O'Neal, "A New Adiabatic High Temperature Calorimeter and the Heat Capacity of Iron(II) Bromide," The University of Washington, 1957.

(6) H. E. O'Neal and N. W. Gregory, *Rev. Sci. Instr.*, in press.

The sample was then transferred (in a dry box) from the cell to a Pyrex tube and the latter attached to the vacuum line. Deoxygenated water in sufficient amount to dissolve the sample completely then was introduced by distillation. The water was subsequently removed by evaporation under vacuum and the resulting hydrate finally heated to 120° until only the RP anhydrous salt remained. This material, R-1, 87.23 g. (some loss in transfer), was returned to the calorimeter cell, pumped on at 125° for 24 hr. and 300 mm. of argon added before sealing. Degassing was limited to this low temperature to ensure that the sample remained in the RP form. A single series of heat capacity measurements to 450° was made.

On conclusion of the R-1 run X-ray powder patterns of samples showed the presence of ordered packing lines. The R-1 sample then was redissolved in water and the evaporation repeated, yielding a second RP sample of 83.03 g., R-2. Four consecutive runs yielding indistinguishable results were made with this material.

A final series of runs was made with a 92.01-g. sample, 0-2, prepared by resubliming the R-2 sample in high vacuum after combining it with FeBr$_2$ from an independent preparation.

Heat capacity data were obtained by measuring the energy necessary to raise the temperature of the calorimeter cell through each ten degree interval.[5,6] The temperature gradient within the cell, established by the continuous heating, decreased gradually from about 10° at the beginning to 6° at the highest temperatures. As an illustration of the original data, Fig. 1 shows the three runs made with sample 0-2. From the combined data for all runs with a given sample, a smooth curve was drawn and heat capacities were calculated from this curve at various temperatures.

Results and Discussion

Within experimental error molal heat capacities from the four samples were found identical between 50 and 360°. Points from each sample and the final line chosen are shown in Fig. 2. The maximum point deviation from the line is 2.0%, the average point deviation 0.65%. The variation of heat capacity with temperature may be expressed in a linear form

$$C_p = 17.59 + 5.32 \times 10^{-3}\, T \text{ cal. mole}^{-1} \text{ deg.}^{-1} \text{ (323–633°K.)}$$

The corresponding enthalpy and entropy equations are

$$H_T - H_{298}° = 17.59T + 2.66 \times 10^{-3}\, T^2 - 5478 \text{ cal. mole}^{-1}$$

$$S_T - S_{298}° = 40.51 \log T + 5.32 \times 10^{-3}\, T - 101.8 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

An extrapolation of the heat capacity equation to 298.16°K. gives a value of C_p of 19.14, agreeing within experimental error with an independent value of 19.06, determined in a series of low temperature measurements.[7]

Beginning at a temperature slightly above 360° and extending over about a 45° temperature range, an anomaly, showing a reversible character, was observed on each successive run with both the ini-

(7) Private communication from E. F. Westrum, Jr., Department of Chemistry, University of Michigan, Ann Arbor.
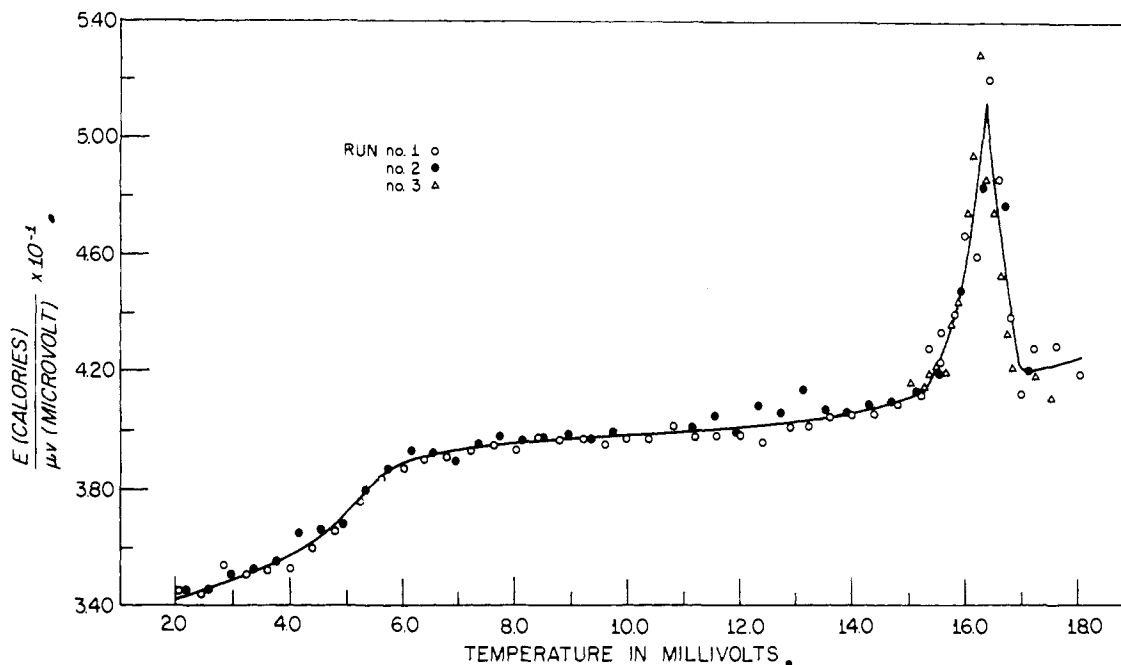
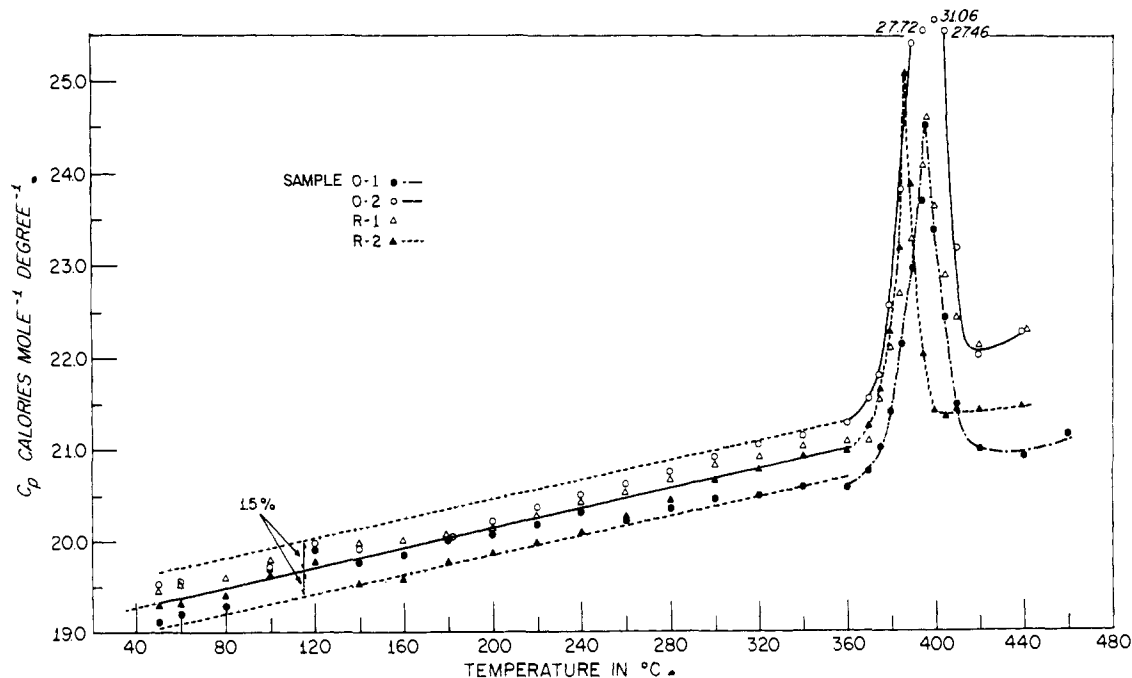Fig. 1.—Heat capacity of calorimeter cell filled with iron(II) bromide.

Fig. 2.—Heat capacity of iron(II) bromide.

tially HCP and RP samples. The large temperature range (compared with the temperature differential within the cell) and general shape of the curve is suggestive of a coöperative type (second-order) transition, although with the constant heating technique even a normal first-order transition would be spread out over a small temperature interval. The excess energy absorbed in this region, above the extrapolated heat capacity curve, was estimated by graphical integration, giving 70, 57, 48 and 158 cal. mole^{-1} for O-1, R-1, R-2 and O-2, respectively. This rather large variation may in

part be associated with the limited data available above the transition (limited by the use of uranium glass for the cell and mica for electrical insulation) which made it difficult to establish the high temperature heat capacity base line. The transition energy appears to be less for the RP samples than for the HCP material. On the first heating both RP samples were observed to have slightly higher heat capacities at temperatures just above the principal anomaly than observed with HCP samples. This difference was not observed in the second and third runs with R-2.

While the anomaly has the shape expected for an order–disorder type transition, it does not appear to be simply associated with the interconversion of the HCP and RP forms. If the transition were a change of HCP to RP, for example, samples initially in the RP form should not show the heat capacity irregularity, unless they became ordered before the sample reached the reversible transition temperature. To provide some structural information an X-ray powder pattern study of the system has been made.

Preliminary X-ray studies were made on quenched samples. In the first series, initially RP material was transferred in the dry box to thin-walled Pyrex or quartz capillary tubes. The tubes were sealed and then annealed at various temperatures for 2 hr. and the samples subsequently quenched by dropping the tubes into cold water. Faint lines of an ordered structure could be detected in samples annealed at temperatures between 250 and 350°, although patterns were poor. The structure was definitely ordered after RP samples were annealed at and then quenched from temperatures between 410 and 500°. Samples which were initially HCP retained their structure after annealing at any temperature in the range. Once RP samples had changed to an ordered structure, they did not revert back to the RP form after reannealing at temperatures as high as 350° for as long as two days.

Because some of the RP samples in the above experiments appeared to contain traces of moisture, presumably picked up during filling and sealing of the capillary tubes, further studies were made in which capillary tubes were attached to the vacuum line after filling and thoroughly degassed before sealing. RP samples treated in this way did not develop detectable HCP lines when heated for 2 hr. periods at temperatures as high as 500°; after annealing for 12 hr. at 500°, HCP lines were clearly present after quenching. As before, once the ordered structure had been formed, it was not destroyed by further annealing for long periods at any temperature. The general conclusion drawn from this work was that the RP form changes irreversibly to the HCP structure and that this transition occurs more readily when traces of moisture are in the sample. The possibility remained, however, that the RP structure might be stable above the transition temperature but that it was not retained by quenching.

To investigate the latter possibility, a small furnace was constructed in which X-ray powder patterns could be taken of a rotating powder sample held at various temperatures up to 500°. A small hole, just large enough for the capillary tube, ca. one mm. o.d., was drilled in a stainless steel rod, ca. 1.5 inch long and $1/4$ inch o.d., and another small hole drilled in the center at right angles for the X-ray beam, with a conical opening on the beam exit side. The beam exit was kept as small as feasible to minimize the temperature gradient in the sample caused by this exposure; the diffracted beams were thus restricted to values of 2θ less than 45°. Diffracted beams were recorded on a flat photographic plate about 3 cm. from the sample. The film was protected by black paper and cooled with an air fan during the 20–36 hr. exposures. (Ni filtered Cu radiation.)

A small heating element was fitted around the rod and its temperature measured by an attached thermocouple. Since the rotating sample was freely suspended in the hole, touching only the edges in places, and the part of the sample exposed to the beam was also exposed to the air at room temperature, an estimate of the relationship of the sample temperature to that of the furnace was obtained by a rough calibration. A small thermocouple was inserted in an empty capillary tube and placed in the same position as the sample during the X-ray exposure. A rather large temperature differential was found at the highest temperatures, ca. 60° at 400° and 80° at 500°.

Two capillaries containing independent samples of HCP material were attached to the vacuum line and degassed thoroughly under high vacuum at temperatures up to 500°. The capillaries were filled with argon, sealed and subjected to X-ray analysis. The first four lines[2] of the HCP structure were easily seen at all sample temperatures up to 350° (these are the only lines characteristic of the HCP pattern which fall in the diffraction angle limit). When the sample

temperature was raised to 430° and above (highest about 460°), a clearly different pattern (also different from the RP form) was observed. Two of the most intense lines of the HCP structure θ = 15.5 and 19.8°, disappeared and a new strong line, θ = 16.9°, appeared, with a line at 14.4° also evident; the latter corresponds closely with a line also charteristic of the HCP pattern. The high temperature form (HTF) also appears to have a line around 7–8° (as does the HCP form) with such low intensity that it was difficult to detect for certain or measure accurately because of the high background in this region. On cooling samples below the transition temperature, i.e., between room temperature and 350°, the HTF pattern disappeared and the HCP lines reappeared. The transition was reversed several times with both samples. Although the temperature of the sample in the X-ray beam cannot be considered known with certainty, it appears that the transition in structure detectable by X-rays occurs in the same range as the anomaly in the heat capacity curve, and the two are believed associated. Unfortunately, the limited information provided by the new powder pattern is not sufficient to permit meaningful speculation concerning the nature of the high temperature structure. If it were a cubic close packed structure of the $FeCl_2$ type, additional lines should be observable on the HTF pattern. However, failure to observe these lines may be simply an intensity problem.

When the powder samples were held in the intermediate temperature zone of the transition range, rather faint patterns were obtained on which lines from both the HCP and HTF structure could be detected. Since the temperature uniformity of the sample is questionable, this is not considered definite evidence for the heterogeneous nature of the transition, however.

Prior to the availability of the high temperature X-ray data, differential cooling experiments were carried out to ascertain whether the anomaly were associated with presence of small amounts of Fe_3O_4 or some undetected impurity separable from $FeBr_2$ by fractional crystallization from water. These experiments also gave further insight into the behavior of the transition by demonstrating that a trace of water vapor causes a marked effect on the transition temperature.

A dissolved sample of $FeBr_2$ was separated from the trace of insoluble Fe_3O_4 and separated into two portions by fractional crystallization. Water was first removed by vacuum evaporation until about half of the solute had crystallized (as a hydrate). The supernatant liquid was then decanted and the separate portions further dehydrated to the anhydrous salt. About 15-g. samples of each of these portions were transferred to Pyrex capsules (containing thermocouple wells) and sealed off after degassing at 125–250° followed by addition of argon. One of these capsules, together with another filled with sodium chloride, used as a reference material, was suspended in the calorimeter in the place normally occupied by the calorimeter cell. The two capsules were connected with a differential thermocouple and heated in vacuo to a temperature near 500° and then allowed to cool slowly. During cooling their temperature and temperature differential were measured at intervals of 0.2 millivolt (chromel–alumel couples). The transition temperature was easily detected as a sharp deflection on the differential thermocouple. Both fractions exhibited the same behavior, showing a temperature halt just below 400°, which demonstrated that the fractional crystallization and removal of Fe_3O_4 had not separated the material responsible for the effect.

The sequence of cooling curves shown in Fig. 3 illustrates the marked effect of small amounts of water on the transition temperature. Figure 3a shows the original curve of one of the degassed samples. This sample was then opened, transferred to a new capsule, attached to the vacuum line, degassed and then a small quantity of water vapor, 0.07 mole %, added with some argon and the capsule sealed. The halt in the new cooling curve, Fig. 3b, occurred ca. 27° below that before the water was added. On re-opening the capsule and degassing the material again, the anomaly was observed at the original point, near 400°, Fig. 3c, showing
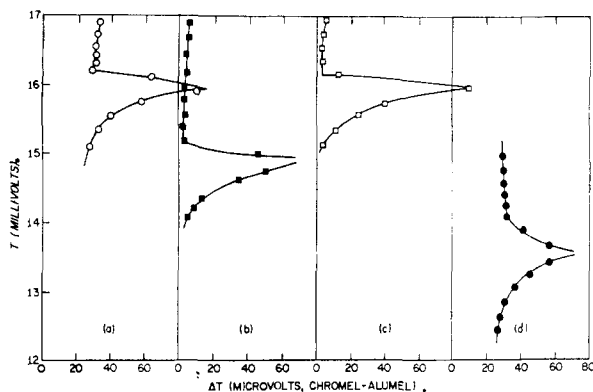
Fig. 3.—Differential cooling curves.

that the effect of water is reversible. A final experiment was conducted in which twice as much water was added, Fig. 3d. The temperature halt then was observed nearly 50° lower than for the degassed samples. The monohydrate of FeBr$_2$ is not stable at these temperatures (decomposition pressure of H$_2$O estimated to be 10 atm. at 280°).[2] Previous experiments in this temperature range also have shown no interaction of water vapor with FeBr$_2$ of such a nature to cause a pressure change detectable on a diaphragm gauge.[2]

The marked effect of small amounts of water vapor on the transition temperature again suggests the transition is of the coöperative type. Small amounts of impurities have been shown to have a pronounced effect on second-order type transitions in certain metal systems.[8-10] Water vapor appears to interact with the FeBr$_2$ lattice reversibly in some way which markedly affects the transition. Slightly varying amounts of water vapor could be responsible for some of the differences observed in

the estimated energies of transition and temperatures of the maxima in the heat capacity measurements.

It is of interest to note that the heat capacities of the RP and HCP forms are identical within the limits of our experimental error (rather large, $\pm 1-2\%$) below the transition temperature. Nothing is observed in this temperature range that can be associated with the conversion of one form to the other; presumably both change to the HTF at the transition temperature. From the X-ray data on quenched samples it appears possible to change the RP form to the HCP structure by prolonged heating; this transition occurs more readily at temperatures in the vicinity of 300° when small amounts of water vapor are in the system, which may be related to the observation that the transition to the HTF also then occurs at a lower temperature; the HTF may provide the mechanism for the conversion by reverting to the HCP form on cooling. The transition from RP to HCP appears quite slow in samples thoroughly degassed prior to annealing, surprisingly so even at 500° where 2 hr. annealing was apparently insufficient. This observation may actually be a matter of lack of detection of ordered lines on the powder pattern because of the small particle size of the original dehydrated (RP) sample. A longer annealing interval allows larger crystallites to grow by vaporization.

The calorimeter is currently being redesigned to permit measurement of heat capacities at higher temperature to give better definition of the transition. It is also planned to investigate other substances having similar structural characteristics to those of iron(II) bromide to see whether they undergo similar transitions.

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X-Ray Diffraction Pattern for Monoclinic Sulfur

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The X-ray diffraction pattern of monoclinic sulfur has been determined by making use of a special heated sample holder.

In connection with some X-ray diffraction studies[2] on orthorhombic and carbon disulfide-insoluble sulfur, we were surprised to find that an X-ray diffraction pattern for monoclinic sulfur had not been reported.[3] It is noteworthy that although the crystal structure of orthorhombic sulfur is well-established,[4,5] only a preliminary report on the unit cell and space group of monoclinic sulfur has been published using single crystal data.[6] The reasonable assumption has been made[4] that monoclinic sulfur consists of a cyclic ring of eight sulfur atoms. Das[7] recently enumerated the difficulties encountered in his unsuccessful attempts to obtain a powder X-ray pattern of monoclinic

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(3) After our work was complete (J. S. Kim, thesis, Baylor University, 1957) a notice of a preliminary report of the diffraction pattern of monoclinic sulfur came to our attention [C. A., **51**, 10965 (1957)]. The abstract of the paper presented at a meeting of the American Physical Society, Southeastern Section at the University of Florida, Gainesville, Florida [J. E. Miller, N. S. Kendrick, Jr., and G. W. Crawford, Phys. Rev., **99**, 163 (1955)], however, does not present any data for comparison with our results.

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