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.

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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]

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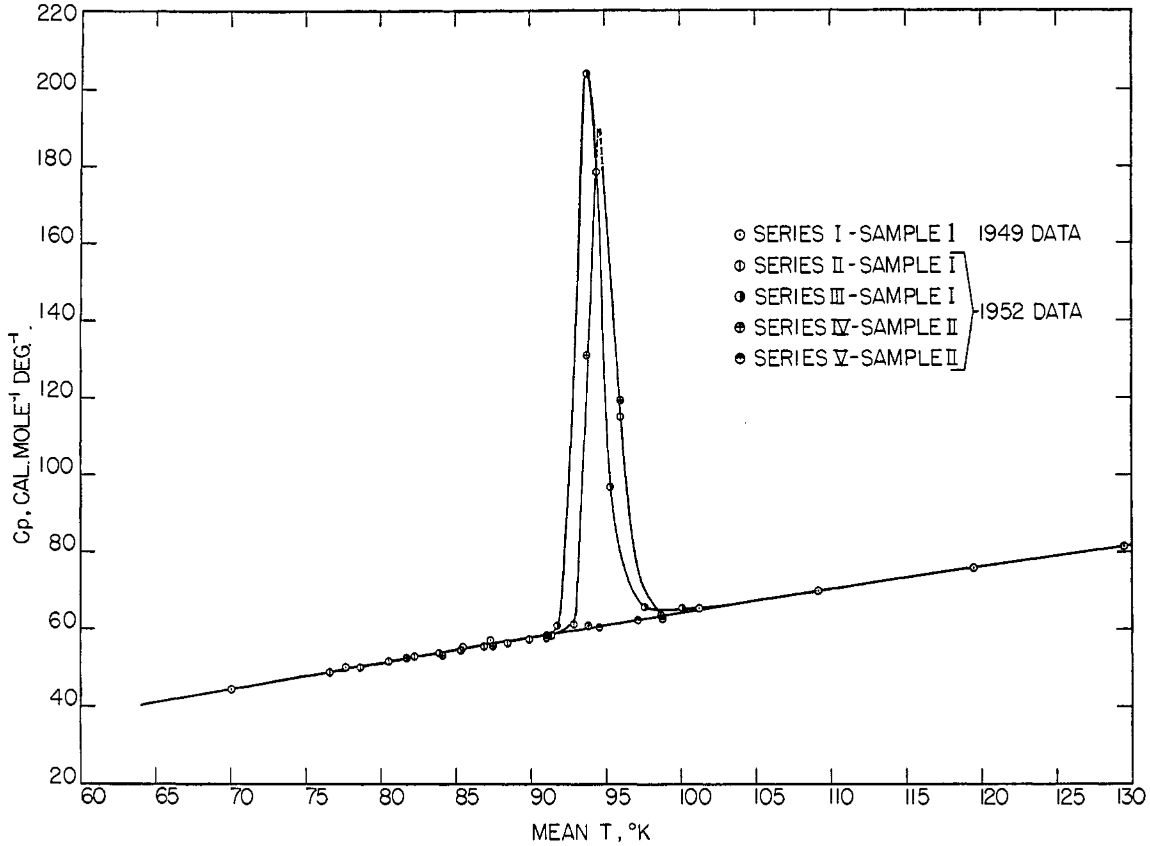
[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

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

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



, Fig. 1. .

crystals. Large crystals were undesirable since they entrapped large quantities of water and were difficult to dry properly so as to contain the correct formula weight of water of crystallization. The resulting crop of crystals was filtered through a buchner funnel and collected on a porous porcelain plate for partial drying, and then transferred to a vacuum desiccator in which the desiccant was crude ammonium chromium alum partially dehydrated by heating at 100° for several hours. The wet and dry forms of the alum were allowed to equilibrate for several months while other work was in progress. Analyses were made at intervals by complete dehydration of weighed samples in an oven set at 400°, in order to test the approach to equilibrium. (This alum normally loses nine of its twelve moles of water of crystallization at 100° and the other three moles at 300°). The final sample contained 45.01% $H_2O$ (theoretical 45.19%); 48.7269 g. (0.10186 mole) of this material was sealed in Calorimeter No. 6, one of a group of seven calorimeters[4] of identical design in use in this Laboratory.

Sample II was prepared in 1952 under exactly the same conditions as those of the previous sample. Analyses showed that it contained 45.45% $H_2O$ (theoretical 45.19%) and weighed 51.466 g. (0.1076 mole). It was sealed in Calorimeter No. 3 of the same group of calorimeters mentioned above. Data for the heat capacities obtained from the 1949 and 1952 measurements are shown graphically in Fig. 1.

### Procedure and Experimental Results

The experimental results obtained in 1949 are summarized in Table I. No transition was found in the heat capacity measurements but the experimental point at 93.87°K. (taken with a $\Delta T$ of 8.362) was anomalously high when observed on a smooth plot of these data.

TABLE I

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM, $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$

Mol. wt. = 478.36, 0.10186 mole (1949 data)

| Mean *T*, °K. | *C*p, cal./mole/deg. | Mean *T*, °K. | *C*p, cal./mole/deg. | Mean *T*, °K. | *C*p, cal./mole/deg. |
|---|---|---|---|---|---|
| 17.26 | 4.31 | 77.64 | 50.00 | 204.42 | 121.96 |
| 18.75 | 5.01 | 85.51 | 55.43 | 206.83 | 123.41 |
| 19.91 | 5.70 | 87.33 | 57.07 | 214.30 | 126.70 |
| 21.00 | 6.50 | 93.87 | 60.90 | 217.14 | 128.36 |
| 22.69 | 7.44 | 101.28 | 65.25 | 220.51 | 129.90 |
| 25.08 | 9.19 | 109.20 | 69.83 | 222.51 | 130.91 |
| 27.61 | 11.32 | 119.53 | 75.75 | 228.36 | 133.66 |
| 29.93 | 13.30 | 129.51 | 81.50 | 229.92 | 135.07 |
| 32.37 | 15.19 | 137.90 | 86.21 | 234.80 | 137.01 |
| 35.43 | 17.61 | 145.66 | 90.76 | 242.66 | 139.35 |
| 39.07 | 20.60 | 152.91 | 94.83 | 254.36 | 145.38 |
| 42.92 | 23.52 | 161.62 | 99.78 | 264.45 | 150.37 |
| 47.14 | 27.05 | 172.32 | 105.28 | 274.07 | 156.06 |
| 51.76 | 30.89 | 182.52 | 110.70 | 282.72 | 160.36 |
| 56.25 | 34.23 | 192.85 | 115.98 | 292.24 | 165.18 |
| 62.78 | 39.02 | 199.02 | 118.99 | 304.44 | 170.22 |
| 70.07 | 44.41 | | | | |

In 1952, the original sample (sample I) prepared in 1949 was cooled down to 75°K. and allowed to remain at this temperature for two days. The heat capacity measurements were then carried out from 75 to 101°K., with smaller temperature intervals, as shown in Table II. A region of anomalously high heat capacities was found between 92 and 98°K. The sample was again cooled down to 81°K. and after it had remained at 81°K. for about two days, a second series of heat capacity measurements was started. In the second series, the peak of this anomalously high region of the heat capacity curve showed a slight shift toward the high temperature end, relative to that of the first series; presumably, this was due to hysteresis. To eliminate the possibility that some slow change might have taken place in the sample between 1949 to 1952, a new sample (sample II) containing slightly more water was prepared and a fourth series of heat capacity measurements was

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[4] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

carried out under conditions identical to those for the second and third series. The same transition, spread over the same temperature region (92 to 97°K.), was found in this fourth series of measurements. In order to correlate the results observed in 1949, a fifth series of heat capacity measurements (on sample II) was started immediately after it had reached 90°K. The transition disappeared under these conditions. It is therefore concluded that the near disappearance of the transition in the 1949 observations was due to supercooling of the sample. Since in the 1949 measurements data below 80°K. were taken in a series of runs subsequent to those above liquid air temperatures and after the sample had been cooled for more than a day at 65°K., we believe that the values obtained from 14 to 65°K. in our 1949 measurements do give the true heat capacities of this low temperature form of the crystal. This conclusion is further justified from our heat of transition measurements in which it is observed (Table III) that data taken after the sample remained at 85°K. for eight hours are identical, within error limits, to those taken with longer equilibrium periods.

TABLE II

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM, $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$ (1952 data)

| Mean *T*, °K. | $C_p$, cal./mole/deg. | Mean *T*, °K. | $C_p$, cal./mole/deg. |
|---|---|---|---|
| Sample I, cooled for 2 days before starting measurements (50.454 g., 0.1055 mole) | | | |
| 76.59 | 48.77 | 91.78 | 60.83 |
| 78.60 | 49.95 | 92.88 | 61.38 |
| 80.53 | 51.59 | 93.77 | 203.99 |
| 82.25 | 52.68 | 94.43 | 178.50 |
| 83.90 | 53.68 | 95.28 | 82.78 |
| 85.35 | 54.51 | 95.33 | 96.74 |
| 86.94 | 55.49 | 96.01 | 115.13 |
| 88.46 | 56.35 | 97.64 | 65.64 |
| 89.94 | 57.35 | 100.13 | 65.34 |
| 91.39 | 58.36 | | |
| Sample II, cooled for two days before starting measurements (51.466 g., 0.1076 mole) | | | |
| 81.72 | 52.46 | 93.73 | 132.95 |
| 84.12 | 53.42 | 95.99 | 119.69 |
| 87.50 | 55.56 | 98.64 | 63.48 |
| 91.14 | 58.36 | | |
| Sample II, measurements started immediately after the sample had cooled about 90°K. | | | |
| 91.07 | 58.28 | 97.15 | 62.33 |
| 94.60 | 60.46 | 98.74 | 63.00 |

TABLE III

THE HEAT OF TRANSITION OF AMMONIUM CHROMIUM ALUM, $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$

| Run no. | *t*,[a] hr. | Heat of transition, cal./mole |
|---|---|---|
| 1 | 8 | 267.58 |
| 2 | 16 | 267.61 |
| 3 | 46 | 279.90 |
| 4 | 100 | 267.10 |
| | Av. | 267.43 ± 0.13[b] |

[a] *t* is the time for which the sample had been cooled before starting measurements of the heat of transition. [b] Run no. 3 has not been used for calculating the average value of heat of transition.

The heat of transition was obtained in the usual way, *i.e.*, by subtracting from the total amount of energy input that part of energy which was used for heating the sample. Four determinations were made with the sample kept at 85°K. for different lengths of time, prior to the runs.

The thermodynamic functions derived from the smooth heat capacity curve (using Table II data in the interval 80 to 100°K.), are given in Table IV at integral values of temperature. The entropy at 298.16°K. is 171 ± 1 e.u. of which 0.64 e.u. was obtained by extrapolating below 18°K. using a $C_p$ *versus* log *T* plot.

TABLE IV

THERMODYNAMIC FUNCTIONS OF AMMONIUM CHROMIUM ALUM, $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$

| *T*, °K. | $C_p$, cal./mole/deg. | $S - S_0$, cal./mole/deg. | $(H - H_0)/T$, cal./mole/deg. | $-(F - H_0)/T$, cal./mole/deg. |
|---|---|---|---|---|
| Solid I | | | | |
| 25 | 9.10 | 51.3[a] | 3.183[a] | 1.95 |
| 50 | 29.35 | 17.73 | 11.219 | 6.51 |
| 75 | 48.19 | 33.20 | 20.42 | 12.78 |
| Transition occurs between 92–97°K. | | | | |
| Solid II | | | | |
| 100 | 64.53 | 52.00 | 31.98 | 20.02 |
| 125 | 79.14 | 67.96 | 39.95 | 28.01 |
| 150 | 93.02 | 83.62 | 47.64 | 35.98 |
| 175 | 106.73 | 99.00 | 55.12 | 43.88 |
| 200 | 119.74 | 114.11 | 62.39 | 51.72 |
| 225 | 132.99 | 128.93 | 69.45 | 59.48 |
| 250 | 144.15 | 143.47 | 76.32 | 67.15 |
| 275 | 156.36 | 157.78 | 83.04 | 74.74 |
| 298.16 | 168.55 | 170.89 | 89.19 | 81.70 |
| 300 | 169.26 | 171.93 | 89.68 | 82.25 |

[a] $(H - H_0)$ extrapolated to 0°K.

## Discussion of Results

Kraus and Nutting have studied the spectra of a large number of chrome alums at low temperatures. They found that it was often possible to keep an ammonium sulfate alum crystal in its original perfect, highly transparent condition when placed in liquid nitrogen or liquid hydrogen. In this case the spectra at the higher and lower temperatures differ only in the line breadth. On other occasions, an apparently perfect crystal retains its transparency for a few minutes after being placed in the cooling liquid and then almost instantaneously becomes practically opaque, as though broken into an infinite number of tiny crystals by the disruption of the lattice. It is these nearly opaque crystals, which Kraus and Nutting called "shattered" crystals, that give absorption spectra at high temperatures which are quite different from those at low temperatures.

We give the following explanation for our heat capacity data in terms of Kraus and Nutting's observations: The 1949 data, which show no transition, correspond to the crystals (supercooled) which preserve their original transparent high temperature form, while the 1952 data, on the other hand, correspond to what Kraus and Nutting call "shattered crystals." We presume that the transition is accompanied by a volume change which, under condition of hysteresis, produces a multicrystalline material.

**Acknowledgment.**—We wish to acknowledge the assistance of Mr. E. C. Kerr in computation of data from the first series of runs.

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