

UNCLASSIFIED

AD _____

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DCD DIR 5200.10



UNCLASSIFIED

THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

AD No. 72-266
ASTIA FILE COPY

Navy Contract Number N6onr-225. T.O. IV
ONR Project Number NR 058 038

Tech. Report No. 22

Project RF-283

**THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION**

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM

by

Herrick L. Johnston, Jih-Heng Hu, and William S. Horton

TR 283-22

April 20, 1953

Technical Report

Cryogenic Laboratory
Department of Chemistry
The Ohio State University
Columbus 10, Ohio

FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under contract with U.S. Navy, Office of Naval Research Contract Number N6onr-225, Task Order IV, ONR Project Number NR 058 038, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: " Low Temperature Thermodynamics of Inorganic Substances ". It represents the 22nd Technical Report of this series.

Director - H. L. Johnston

Editor - Esther R. Fultz

TABLE OF CONTENTS

<u>Title</u>	<u>Page</u>
ABSTRACT.	1
INTRODUCTION.	1
APPARATUS AND MATERIALS	1
PROCEDURE AND EXPERIMENTAL RESULTS.	2
DISCUSSION OF RESULTS.	6
ACKNOWLEDGEMENT.	8
REFERENCES.	9

then transferred to a vacuum desiccator in which the desiccant was crude ammonium chromium alum partially dehydrated by heating at 100°C 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°C , in order to test the approach to equilibrium. (This alum normally loses nine of its twelve moles of water of crystallization at 100°C and the other three moles at 300°C .) The final sample contained 45.01 % H_2O (theoretical = 45.19 %); 48.7269 grams (0.10186 mole) of this material were sealed in Calorimeter No. 6, one of a group of seven calorimeters³ 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 grams (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 Figure 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 ΔT of 8.362) was anomalously high when observed on a smooth plot of these data.

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 towards 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

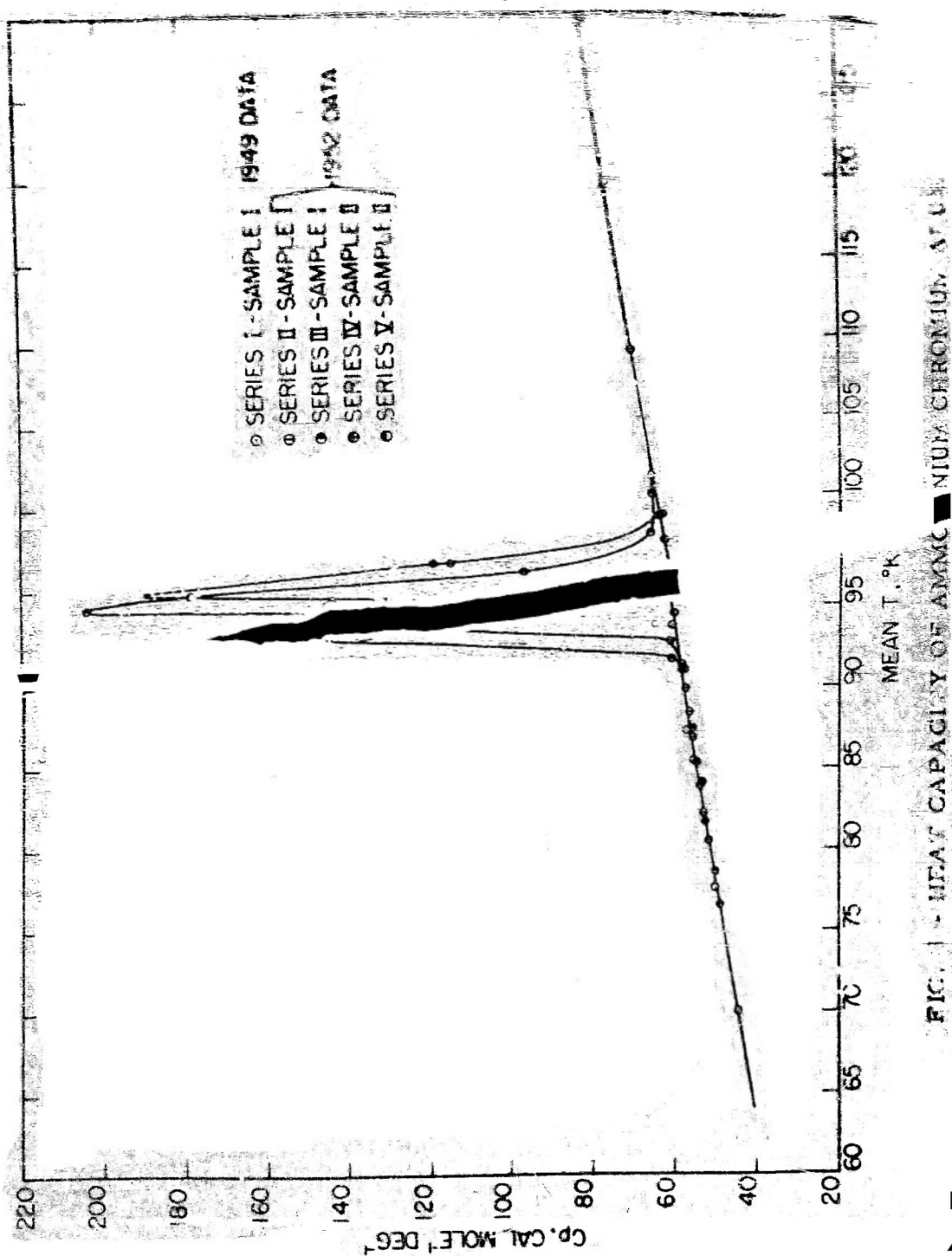


FIG. 1 - HEAT CAPACITY OF AMMC ■ NIUM CHROMIUM AT 1.1

**BEST
AVAILABLE
COPY**

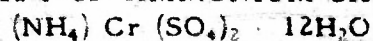
TABLE 1

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM	
(NH ₄) ₂ Cr ₂ (SO ₄) ₆ · 12H ₂ O	
Mole Wt = 478.36	
(1949)	
0.10186 Moles	
Temp T	C _p
	cal/mole deg
17.26	4.11
18.75	4.0
19.91	4.0
21.00	4.0
22.69	4.50
25.05	5.44
27.4	5.19
	5.32
29.93	5.50
32.37	5.39
35.43	5.61
39.07	5.60
42.42	5.52
47.14	5.05
51.76	5.89
56.25	5.23
62.78	5.02
70.07	5.41
77.64	5.00
85.51	5.43
87.33	5.07
93.87	6.90
101.28	6.25
109.20	6.63
119.53	7.75
129.51	8.50
137.90	8.21
145.66	90.76
152.91	94.83
161.62	99.78
172.32	105.28
182.52	110.70

BEST
AVAILABLE
COPY

TABLE I
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM



Mole Wt = 478.36

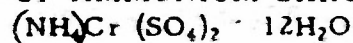
0.10186 Moles

(1949 data)

Mean T °K	ΔT	C_p cal/mole/deg
192.85	10.894	115.98
199.02	5.853	118.99
204.42	12.042	121.96
206.83	8.978	123.41
214.30	7.326	126.70
217.14	13.073	128.36
220.51	8.288	129.90
222.51	8.804	130.91
228.36	3.770	133.66
229.92	11.924	135.07
234.80	7.887	137.01
242.65	13.096	139.35
254.36	10.353	145.38
264.45	9.722	150.37
274.07	9.134	156.06
282.72	7.120	160.36
292.24	7.597	165.18
304.44	7.973	170.22

TABLE II

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM



(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
76.59	2.299	48.77	91.78	2.838	60.83
78.60	1.833	49.95	92.88	1.577	61.38
80.53	1.750	51.59	93.77	1.178	203.99
82.25	1.686	52.68	94.43	1.297	178.50

Sample I, cooled for 2 days before starting measurements (50.454 gm, 0.1055 moles)

TABLE II
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
 $(\text{NH}_4)_2\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
--------------	------------------	-----------------------	--------------	------------------	-----------------------

Sample I, cooled for 2 days before starting measurements (50.454 gm, 0.1055 moles)

83.90	1.632	53.68	95.28	2.271	82.78
85.35	1.595	54.51	95.33	2.030	96.74
86.94	1.543	55.49	96.01	1.795	115.13
88.46	1.499	56.35	97.64	2.519	65.64
89.94	1.457	57.35	100.13	2.451	65.34
91.39	1.413	58.36			

Sample II, cooled for two days before starting measurements (51.466 gm, 0.1076 moles)

81.72	1.819	52.46	93.73	2.014	132.95
84.12	2.987	53.42	95.99	2.133	119.69
87.50	3.773	55.56	98.64	3.114	63.48
91.14	3.529	58.36			

Sample II, measurements started immediately after the sample had cooled to about 90°K.

91.07	2.756	58.28	97.15	12.773	62.33
94.60	4.301	60.46	98.74	4.004	63.00

TABLE II
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
 $(\text{NH}_4)_2\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
--------------	------------------	-----------------------	--------------	------------------	-----------------------

Sample I, cooled for 2 days before starting measurements (50.454 gm., 0.1055 moles)

83.90	1.632	53.68	95.28	2.271	82.78
85.35	1.595	54.51	95.33	2.030	96.74
86.94	1.543	55.49	96.01	1.795	115.13
88.46	1.499	56.35	97.64	2.519	65.64
89.94	1.457	57.35	100.13	2.451	65.34
91.39	1.413	58.36			

Sample II, cooled for two days before starting measurements (51.466 gm., 0.1076 moles)

81.72	1.819	52.46	93.73	2.014	132.95
84.12	2.987	53.42	95.99	2.133	119.69
87.50	3.773	55.56	98.64	3.114	63.48
91.14	3.529	58.36			

Sample II, measurements started immediately after the sample had cooled to about 90°K.

91.07	2.756	58.28	97.15	12.773	62.33
94.60	4.301	60.46	98.74	4.004	63.00

was prepared and a fourth series of heat capacity measurements was 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 super-cooling 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.

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 171.93 ± 1.00 e. u. of which 0.64 e. u. was obtained by extrapolating below 18°K using a C_p versus $\log T$ plot.

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

TABLE III
THE HEAT OF TRANSITION OF AMMONIUM CHROMIUM ALUM
(NH₄) Cr (SO₄)₂ · 12H₂O

Run No.	t ^a hr	Heat of Transition cal/mole
1	8	257.58
2	16	267.61
3	46	279.90
4	100	267.10
Average		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.

TABLE IV
THERMODYNAMIC FUNCTIONS OF AMMONIUM CHROMIUM ALUM
(NH₄) Cr (SO₄)₂ · 12H₂O

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	5.13 [†]	3.183 ^{††}	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

[†] (H-H₀) extrapolated to 0°K

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.

ACKNOWLEDGEMENT

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

REFERENCES

1. R. Guillian
Compt. rend. 209, 21 (1939).
2. B. L. Kraus and J. C. Nutting
J. Chem. Phys. 9, 133 (1941).
3. H. L. Johnston and E. C. Kerr
J. Am. Chem. Soc. 72, 4733 (1950).

DISTRIBUTION LIST FOR TECHNICAL REPORTS

N6onr-225, Task Order IV, NR 058 038

Office of Naval Research

<u>Addressee</u>	<u>No. of Copies</u>
Commanding Officer Office of Naval Research Branch Office 150 Causeway Street Boston, Massachusetts	1
Commanding Officer Office of Naval Research Branch Office 844 North Rush Street Chicago 11, Illinois	2
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	1
Commanding Officer Office of Naval Research Branch Office 1000 Goary Street San Francisco 9, Calif.	1
Commanding Officer Office of Naval Research Branch Office 1030 N. Green Street Pasadena 1, Calif.	1
Officer-in-Charge Office of Naval Research Branch Office Navy Number 100 Fleet Post Office New York, New York	2
Director, Naval Research Laboratory Washington 25, D. C. Attention: Technical Information Officer	9
Chief of Naval Research Office of Naval Research Washington 25, D. C. Attention: Chemistry Branch	4
Research and Development Board Pentagon, Room 3D1041 Washington 25, D. C. Attention: Technical Reference Section	1
Dr. Ralph G. Siu, Research Director General Laboratories, QM Depot 2800 S. 20th Street Philadelphia 45, Pennsylvania	1

<u>Addressee</u>	<u>No. of Copies</u>
Dr. Warren Stubblebine, Research Director Chemical and Plastics Section, PDB-MPD Quartermaster General's Office Washington 25, D. C.	1
Dr. A. Stuart Hunder, Tech. Director Research and Development Branch MPD Quartermaster General's Office Washington 25, D. C.	1
Dr. A. G. Horney Wright Air Development Center Wright-Patterson Air Force Base Dayton, Ohio Attention: WCRRS-4	1
Dr. A. Weissler Department of the Army Office of the Chief of Ordnance Washington 25, D. C. Attention: ORDTB-PS	1
Research and Development Group Logistics Division, General Staff Department of The Army Washington 25, D. C. Attn: Dr. W. T. Read, Scientific Advisor	1
Director, Naval Research Laboratory Washington 25, D. C. Attention: Chemistry Division	2
Chief of the Bureau of Ships Navy Department Washington 25, D. C. Attention: Code 340	2
Chief of the Bureau of Aeronautics Navy Department Washington 25, D. C. Attention: Code TD-4	2
Chief of the Bureau of Ordnance Navy Department Washington 25, D. C. Attention: Code Rexd; Code Rd9a; Code Rd2d (one copy each)	3
Mr. J. H. Heald Library of Congress Navy Research Section Washington 25, D. C.	3

Revised 3/6/52
Project RF 283

Page 3

<u>Addressee</u>	<u>No. of Copies</u>
Dr. H. A. Zahl, Tech. Director Signal Corps Engineering Laboratories Fort Monmouth, New Jersey	
U.S. Naval Radiological Defense Lab San Francisco 24, California Attn: Technical Library	1
Naval Ordnance Test Station Inyokern China Lake, Calif. Attn: Head, Chemistry Division	1
Office of Ordnance Research 2127 Myrtle Drive Durham, North Carolina	1
Technical Command Chemical Corps Chemical Center, Maryland	1
U.S. Atomic Energy Commission Research Division Washington 25, D. C.	1
U.S. Atomic Energy Commission Chemistry Division Brookhaven National Laboratory Upton, New York	1
U.S. Atomic Energy Commission Library Branch, Tech. Info., ORE P.O. Box E Oak Ridge, Tenn.	1
Jet Propulsion Laboratory (CALCIT) California Institute of Technology Pasadena 4, Calif.	1
Johns Hopkins University Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Md.	1
Princeton University Princeton, N. J. Attn: Project SQUID	1
Aerojet Engineering Corp. Azusa, Calif. Attn: Dr. Zwicky	1

<u>Addressee</u>	<u>No. of Copies</u>
General Electric Co. Research Laboratory, Schenectady, New York Attn: Chemical Division	1
Carnegie Institute of Technology Department of Chemistry Pittsburgh 13, Pennsylvania Attn: Dr. F.D. Rossini	1
General Electric Co. Research Laboratory The Knolls Schenectady, New York Attn: L. Navias, Ceramics Division	1
Commanding General AMC Wright-Patterson Air Force Base Dayton, Ohio Attn: Office of Air Research (MCRRXS) Power Plant Laboratory (MCREXP-3) Central Air Documents Office (MCLDSD)	3
Carbide and Carbon Chemicals Corp. K-25 Plant, P.O. Box P Oak Ridge, Tenn. Attn: Plant Records Files	1
National Advisory Committee for Aeronautics Lewis Flight Propulsion Laboratory Cleveland 11, Ohio Attn: Dr. M. Gerstein	1
Ohio State University Research Foundation 310 Administration Building Columbus 10, Ohio	1
Ohio State University Department of Chemistry Columbus 10, Ohio Attn: Prof. H.L. Johnston	1
L. Kermit Herndon Director of Research Mathieson Chemical Corp. Niagara Falls, New York	1

Revised 3/6/52
Project RF 283

Page 5

<u>Addressee</u>	<u>No. of Copies</u>
Callery Chemical Co. Callery, Pennsylvania Attn: C. B. Jackson	1
Office of Naval Research Washington 25, D. C. Attn: Code 429	1
Defense Research Member Canadian Joint Staff 1746 Massachusetts Ave., N. W. Washington, D. C.	1