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Title Differential Heat Capacity Curves for Salts of Hydrazine

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The work of Ewald (1914) and the subsequent investigations by Simon (1922) showed that the specific heats of the ammonium halides underwent a gradual transition covering about a ten-degree range in the vicinity of 240° K.

Pauling has suggested that the discontinuities in the heat capacity curves are the result of change from molecular oscillation to rotation, which may set in around the three crystal axes at different temperatures. For example, HBr undergoes three transitions at -184.1°C., -100.1° C. and -156° C.

The moment of inertia of the molecule, its shape, the differences in Van de Waal's forces exhibited by different kinds of atoms and the size of the molecular dipole moment are important factors in determining whether or not rotation will occur.

The purpose of this investigation was to determine if the salts of hydrazine, closely chemically related to ammonia, showed such specific heat anomalies as have been found present in the ammonium halides.

The method of approach to the problem was to compare the rate of heating of the hydrazine salt to that of sodium chloride, a salt known to

give a normal heating curve in the range -60° C. to 0° C., the temperature range investigated. The two salts were placed in a small copper block, cooled to -60° with an acetone-CO_2 bath, and heated at the rate of approximately 1°/Minute, their temperature difference being measured by means of a two-junction copper-constantan thermocouple. The absolute temperature of the salt was given by another copper-constantan couple. The E.M.F. readings of the temperature thermocouple as well as the differential thermocouple readings were plotted against time.

Small anomalies were found in the curves at temperatures very near the transition temperature of NH_4Cl. The breaks in the differential curve are quite sharp and small. No logical explanation has been suggested for the downward break in most of the curves.

It is apparent that the transformations in the hydrazine salt do not closely approximate those of the ammonium halides.

Further investigations, perhaps of a calorimetric or dilatometric nature, are necessary to complete the study of the specific heat discontinuities shown by the salts of hydrazine.

DIFFERENTIAL HEAT CAPACITY CURVES FOR SALTS OF HYDRAZINE

by

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DIFFERENTIAL HEAT CAPACITY CURVES FOR SALTS OF HYDRAZINE

INTRODUCTION

Anomalies in the specific heat curves of the ammonium halides were first reported in 1914 by Ewald (5), who showed that the curves rose sharply between -78° C. and 0° C. In 1922 Simon (12), using a vacuum calorimeter, substantiated this work, finding for the chloride, bromide and iodide a gradual transition covering about a ten-degree range in the vicinity of 240° K., the nature of the phenomenon not depending essentially on the anion.

Subsequent X-ray studies by Simon and Simson (14) showed that the crystal structure of these salts remained unaltered throughout the transition. A volume change of less than 1% was found to have occurred.

Simon explained the discontinuity in the heat capacity curves on the basis of an inner transformation of the crystal. The increase of the temperature of transition of the halide series, NH_4I (-42.5° C.), NH_4Br (-38.0° C.) and NH_4Cl (-30.4° C.), showed the expected effect of increasing interionic forces accompanying decreased anion radius.

Numerous other investigators (3), (13) and (15), have attacked this problem, most of the work being calorimetric in nature. Dielectric constant measurements (16), Raman spectra (9), infra-red work (7), piezoelectric studies (2) and X-ray analysis have contributed to the knowledge gained thus far.

The conception that the abrupt changes in the specific heat curves of various ammonium salts are the result of a change from molecular vibration to rotation (still in the solid state) has steadily gained prominence. As yet, however, no systematic investigations of the groups of compounds in which molecular rotation might be expected have been made. A very complete summary of the status of our present knowledge in this regard is given by Eucken (4).

The purpose of the work herein described was to determine whether the salts of hydrazine showed such anomalies as had previously been detected in the closely related ammonium salts.

EXPERIMENTAL METHOD AND RESULTS

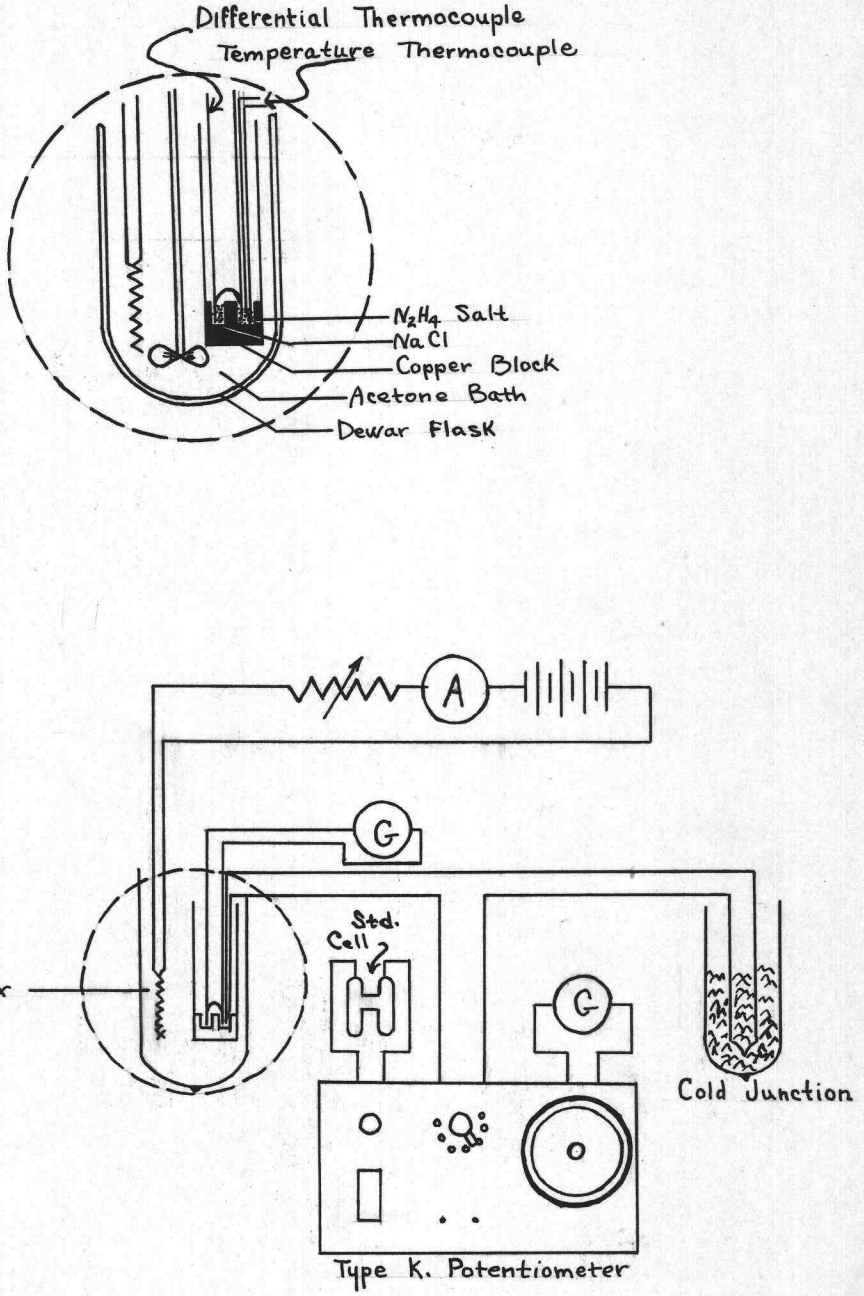


FIGURE I.

Diagram of apparatus used in obtaining differential heat capacity curves for the hydrazine salts.

EXPERIMENTAL METHOD AND RESULTS

THE APPARATUS

The type of calorimeter required for specific heat work on solids at low temperatures is very complex and the cost was prohibitive at this time. A simpler approach may be made by studying the rate at which a salt absorbs heat in comparison to some other salt chosen as a standard.

The principle of the apparatus is shown in Figure I. The two salts are placed in small recesses in heavy copper block with a differential thermocouple between them. As heat enters the system any sudden change in the heat capacity of either salt, with its resultant effect on rate of temperature rise, will develop a potential in this thermocouple.

The apparatus used was similar to that described by Taylor and Klug (18), which was used in determining a transition in $CuSO_4 \cdot 5H_2O$ as well as ammonium compounds.(8).

The receptacle used to contain the salts under investigation consisted of a bakelite-insulated copper block, about 1 1/8 inches in diameter and one inch high, into which were drilled two holes 3/8 of an inch in diameter. A ring of copper wire was soldered into the block for convenience in lowering into the flat-bottomed pyrex glass container.

Heat was added to the system by a heater made by winding nichrome wire on a notched section of transite. The rate of heating

was regulated by insertion of a rheostat and ammeter in the circuit. Two six-volt storage batteries supplied the required current.

Both glass container and heater were inserted in the cork which fitted the wide-mouth Dewar flask.

A horseshoe-shaped, bakelite-coated two-junction copper-constantan differential thermocouple in conjunction with a Leeds and Northrop Type R 2500-A galvanometer of .4μV sensitivity was used to detect the temperature difference between the two salts in the copper block. A deflection of one scale division (1/2-inch at a distance of one meter) corresponded to approximately .07° C. Readings were approximated to 1/20 of a scale division.

The temperature of the hydrazine salt was measured by another copper constantan thermocouple enclosed in a thin glass protecting tube. The cold junction was maintained at 0° in an ice-filled Dewar flask.

Double silk-covered constantan (B.S. #30) was used in the construction of both thermocouples. For the differential thermocouple double silk-covered copper (B.S. #36) was used. For the temperature thermocouple enameled copper wire (B.S. #38) was used.

The melting points of Hg, ice and napthalene, the transition point of $Na_2SO_4 \cdot 10H_2O$ and the boiling-point of water were used in the calibration of the temperature thermocouple. For convenience in determining the temperature corresponding to a given potentiometric reading, the deviations of the actual readings from those of a

standard calibration table were plotted against the temperature.

TECHNIQUE OF OPERATION

About 1.5 grams of hydrazine salt were placed in one hole of the copper block previously described. In the other hole was placed approximately the same weight of NaCl. The differential thermocouple was inserted and the block lowered into the glass container. The setup was suspended on a ring and the temperature thermocouple inserted in the hydrazine salt, the lead wires of the differential thermocouple being placed between the two sections of the split cork.

Then the cell was transferred to the small Dewar, the stirrer inserted, a space being left for addition of "dry ice."

The Dewar flask contained 250 cc. of acetone. The bath liquid was then cooled by the addition of the "dry ice," a pentane thermometer being used to indicate the progress of cooling. The time required to reach the minimum temperature (usually about -60° C.) was about seven minutes.

After the bath had been cooled, the cork was tightly fitted and stirring started. At this time the galvanometer attached to the differential thermocouple was placed in operation. Stirring was maintained until equilibrium was attained. The heater was then started.

Potentiometric and differential readings were taken at intervals varying from two to four minutes. In the vicinity of

transition points, readings were taken every half minute.

In some of the runs the rate of heating was altered. Of course, this affected the curves of E.M.F. vs. T and E.M.F. vs. D, the differential reading.

In the check runs on NH_4Cl it was found that too high a rate of heating shifted the apparent location of the transition point, while rates of approximately 1 to 1.5 amperes gave results which checked well with the commonly accepted values.

The galvanometer deflections on the NH_4Cl runs were very large compared with those for the hydrazine salts. To reduce the amount of deflection the galvanometer was shunted on these runs with a known resistance.

PREPARATION OF COMPOUNDS

The hydrazine salts used in this investigation were "C.P." salts which had been previously purified in this laboratory. Each salt (except $N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}H_2O$) was ground to a particle size between 100 and 150 mesh and dried over P_2O_5.

To remove definitely the possibility that traces of ammonium compounds might be responsible for the observed effects, the sulfate, which is most easily purified, was further recrystallized three times. No change in behavior could be noted.

Both Baker's and Coleman and Bell's "C.P." NaCl were used as the "neutral body" in these runs, the Coleman and Bell salt being substituted in later work because the Baker product was unavailable.

The purity of these salts was deemed sufficient for the purposes of this investigation.

TABULATION OF RESULTS

Salt	Preparation	Run No.	Maximum	Minimum	Total Differential Change	Transition Temperature (°C.)	Heating Rate (Amperes)	Initial Potentiometric Reading (μV)	Time of Stirring Before Heating (Min.)
$N_2H_4 \cdot H_2SO_4$	Dried over $Mg(ClO_4)_2 \cdot 3H_2O$	4	x	-	0.8*	30.0°	-	-2348	-
"	"	6	x	-	0.35*	30.4°	1.0	-2378	-
"	Recrystallized Dried over $Mg(ClO_4)_2 \cdot 3H_2O$	7	x	-	0.7	30.2°	1.5	-2272	15
"	Same treatment as above plus 1 day over P_2O_5	8	-	-	-	-	1.5	-2318	-
"	Dried over P_2O_5	9	-	x	-0.2	30.3°	1.0	-2284	16
$N_2H_4 \cdot HCl$	Dried over P_2O_5	2	x	-	1.0	30.4°	1.5	-2297	-
"	"	4	-	x	0.6	30.2°	1.5	-2213	16
"	"	5	-	x	0.65	30.5°	1.5-1.0	-2205	25
				x	0.05	0.0°			
$N_2H_4 \cdot 2HCl$	"	2	-	-	-	-	1.0	-570	-
"	"	3	-	x	0.5	30.5°	1.5	-2267	12
"	"	4	-	x	0.65	30.0°	1.4	-2185	25
$N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}H_2O$	Not Dried	1	x	-	1.4	29.9°	1.5	-2332	10
			-	x	0.5	.5°			
"**	"	2	-	x	0.35	30.5°	1.0	-2563	10
$N_2H_4 \cdot HBr$	Dried over P_2O_5	1	-	x	0.4	30.1°	1.5	-2160	10
"	"	2	-	x	0.5	29.9°	1.5	-2240	7

*6 ohm shunt across galvanometer
** Methyl alcohol bath used

DIFFERENTIAL HEAT CAPACITY CURVES

Following are typical differential heating curves for six salts, including NH_4Cl and each of the hydrazine salts investigated.

In each case the differential reading and E.M.F. of the temperature thermocouple are plotted against time. It will be noted that the discontinuity in the differential curve occurs at very nearly the same temperature in each case. The change in slope of the temperature-time curve at the transition point is also fairly well marked.

DISCUSSION

Figure II.

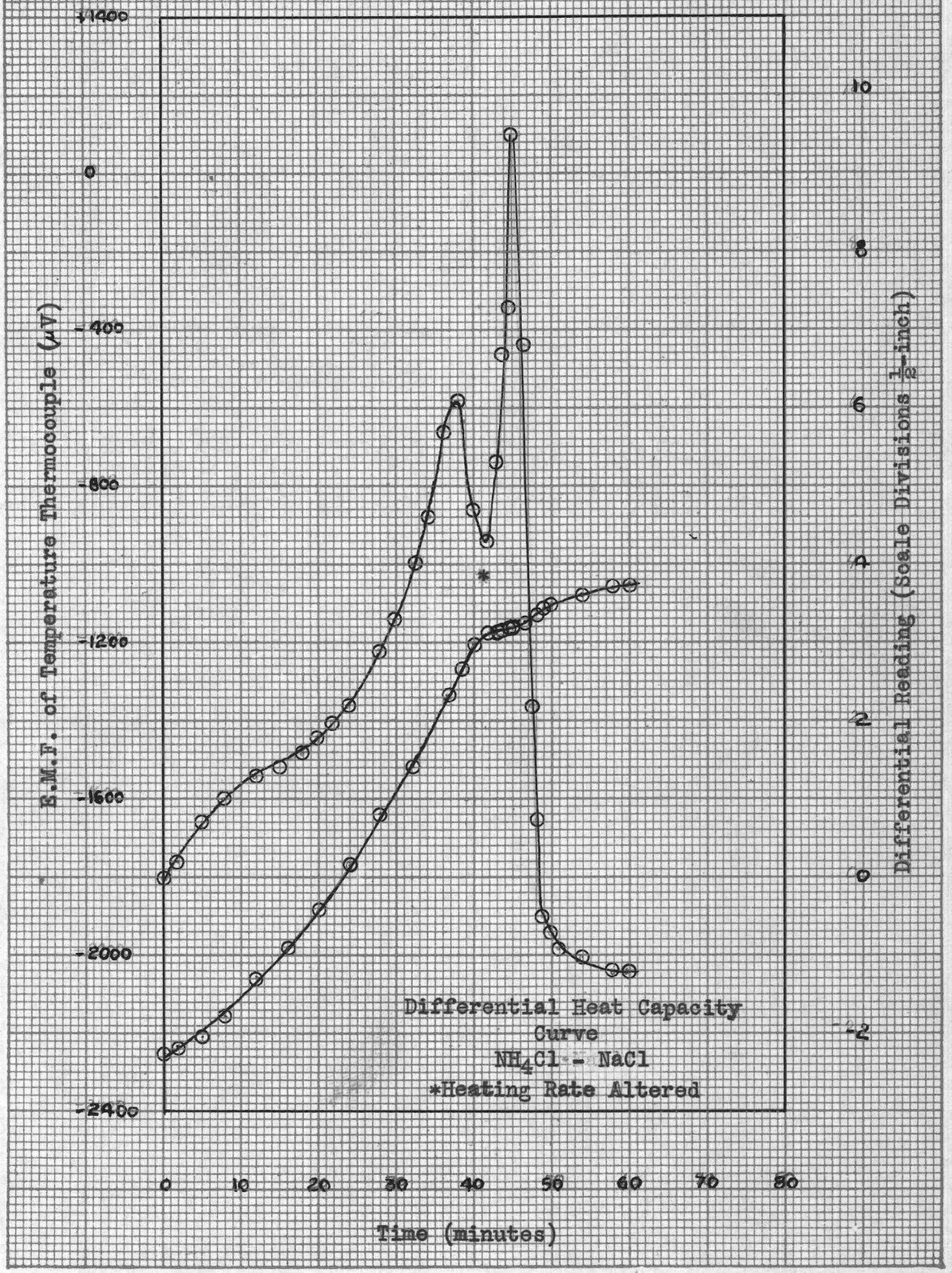

+1400
0
-400
-800
-1200
-1600
-2000
-2400
E.M.F. of Temperature Thermocouple (μV)
10
8
6
4
2
0
-2
Differential Reading (Scale Divisions 1/2-inch)
0
10
20
30
40
50
60
70
80
Time (minutes)
*
Differential Heat Capacity Curve
NH4Cl - NaCl
*Heating Rate Altered

Figure III.

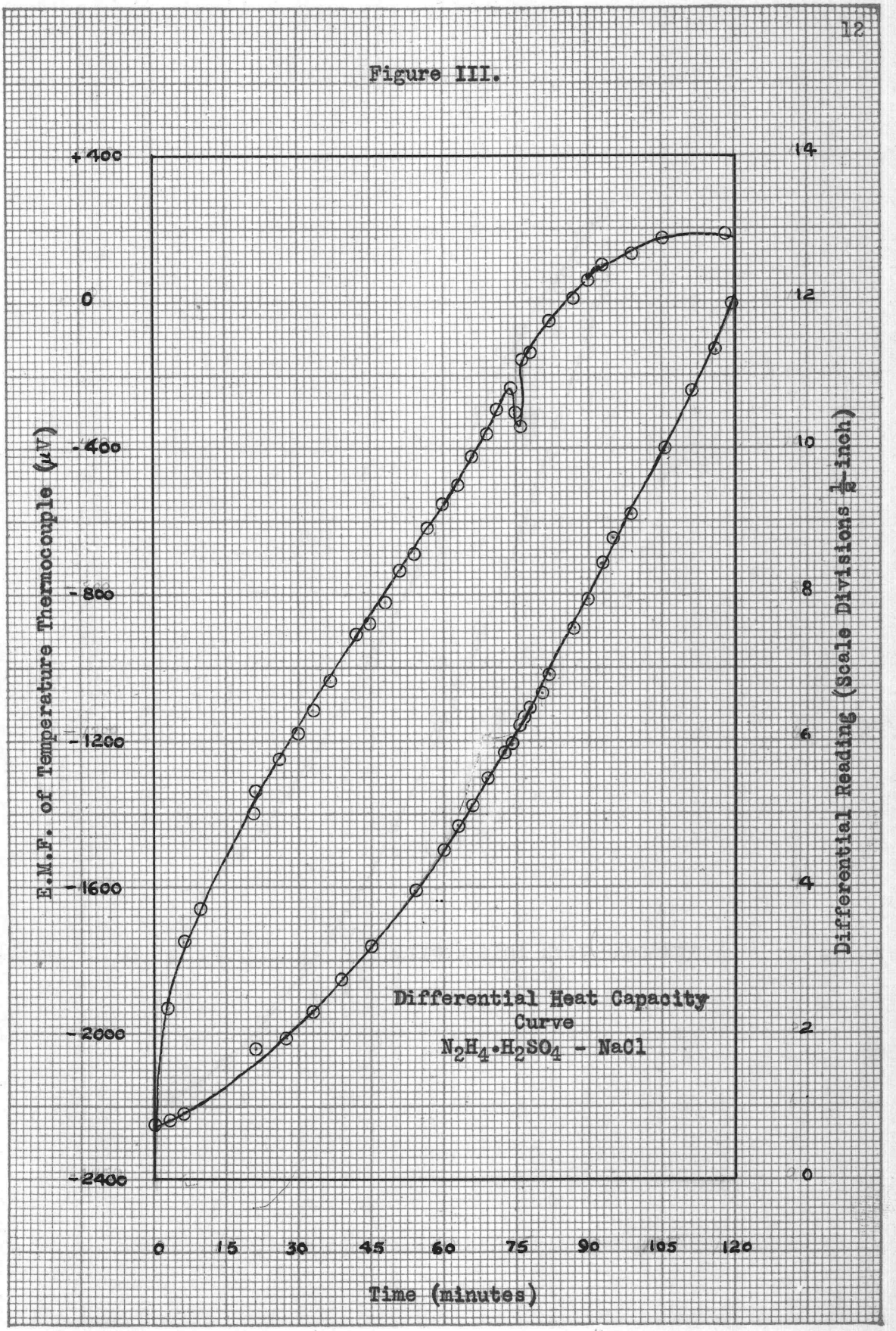

+400
0
-400
-800
-1200
-1600
-2000
-2400
E.M.F. of Temperature Thermocouple (μV)
14
12
10
8
6
4
2
0
Differential Reading (Scale Divisions ½ inch)
Differential Heat Capacity Curve
$N_2H_4 \cdot H_2SO_4$ - NaCl
0
15
30
45
60
75
90
105
120
Time (minutes)

Figure IV.

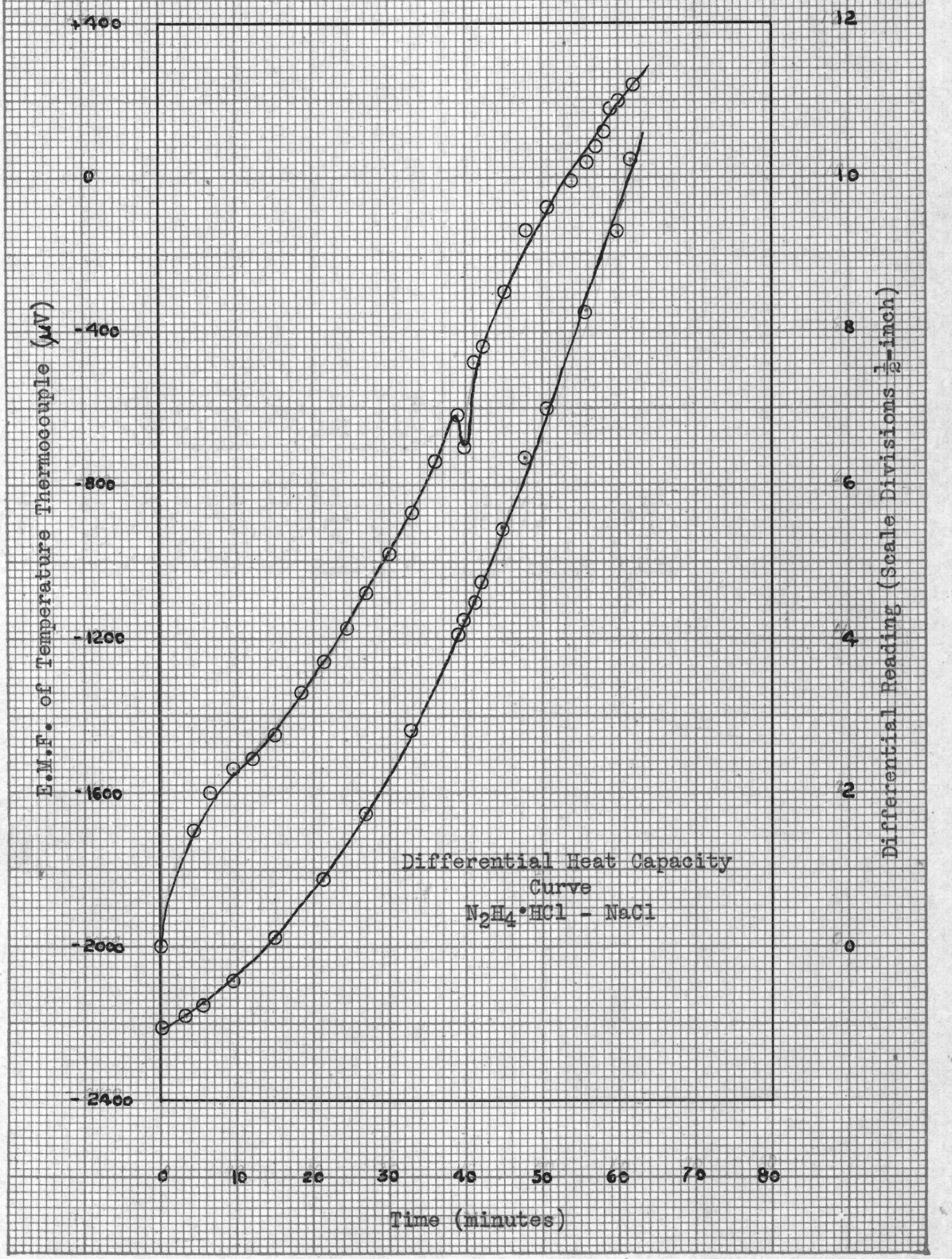

+400
0
-400
-800
-1200
-1600
-2000
-2400
E.M.F. of Temperature Thermocouple (μV)
12
10
8
6
4
2
0
Differential Reading (Scale Divisions 1/2-inch)
0
10
20
30
40
50
60
70
80
Time (minutes)
Differential Heat Capacity Curve
$N_2H_4 \cdot HCl$ - NaCl

Figure V.

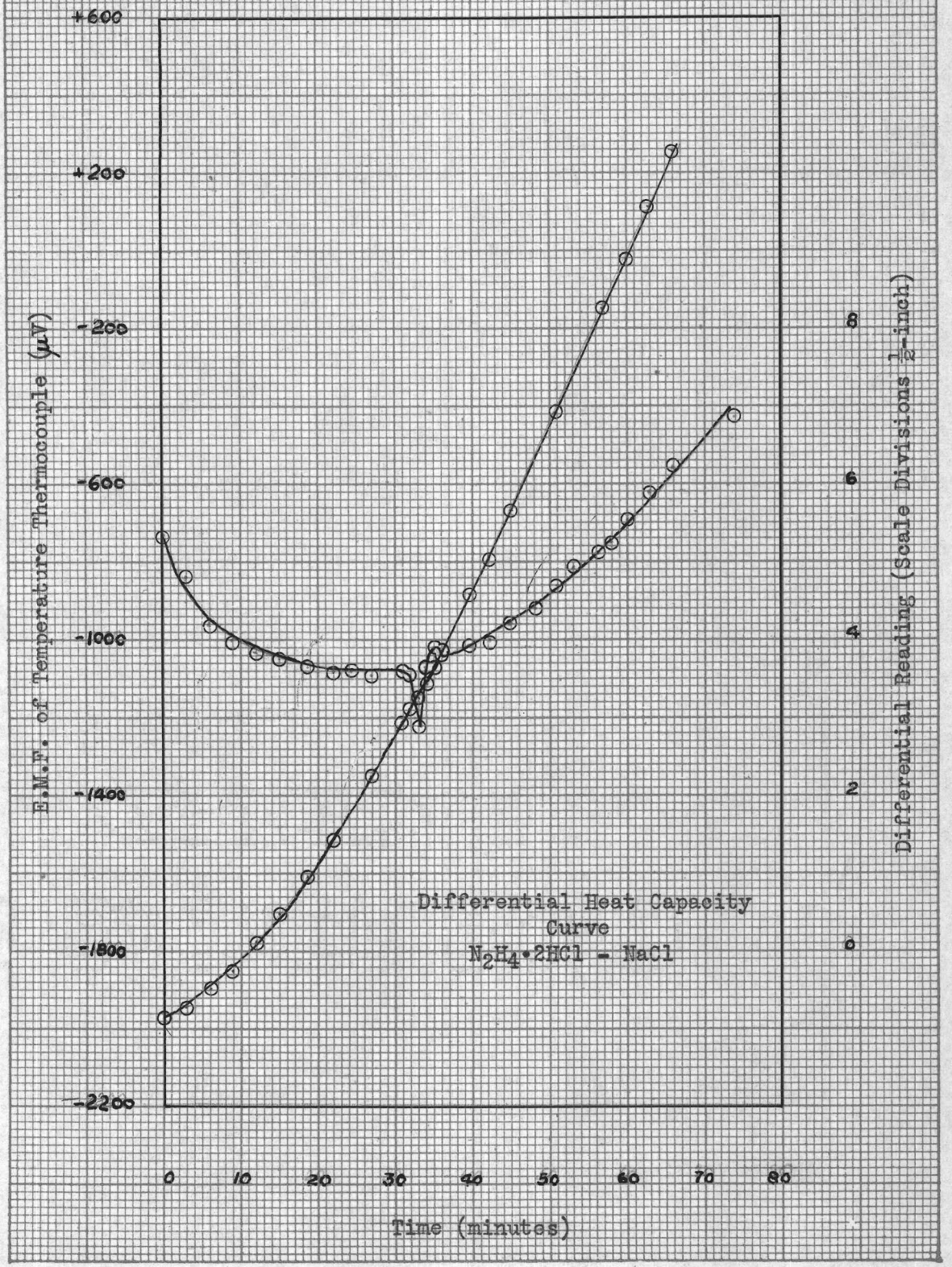

+600
+200
-200
-600
-1000
-1400
-1800
-2200
E.M.F. of Temperature Thermocouple (μV)
8
6
4
2
0
Differential Reading (Scale Divisions ½-inch)
0
10
20
30
40
50
60
70
80
Time (minutes)
Differential Heat Capacity Curve
$N_2H_4 \cdot 2HCl$ - NaCl

Figure VI.

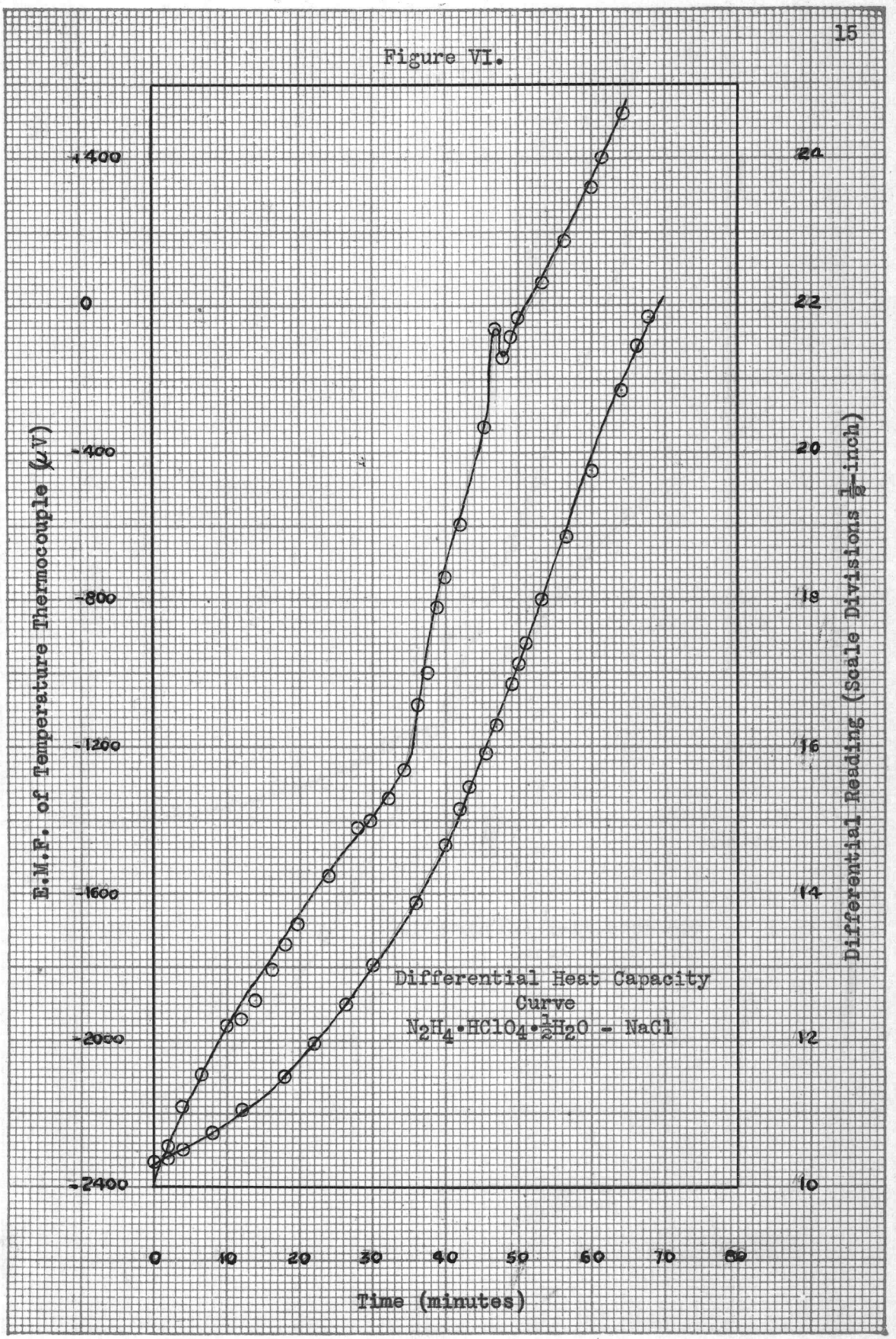
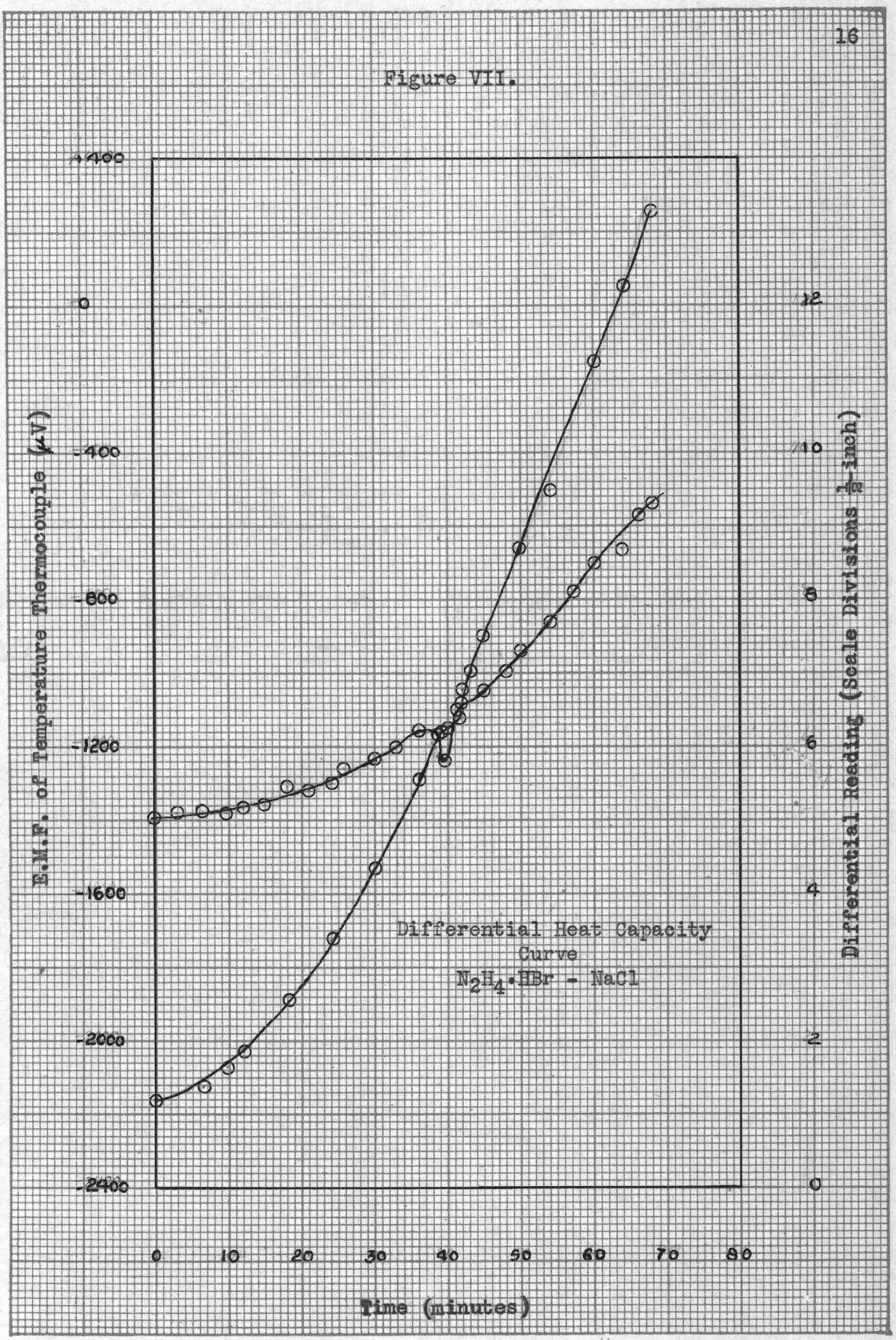

+400
0
-400
-800
-1200
-1600
-2000
-2400
E.M.F. of Temperature Thermocouple (μV)
24
22
20
18
16
14
12
10
Differential Reading (Scale Divisions 1/2-inch)
0
10
20
30
40
50
60
70
80
Time (minutes)
Differential Heat Capacity Curve
$N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}H_2O$ - NaCl

Figure VII.


+400
0
-400
-800
-1200
-1600
-2000
-2400
E.M.F. of Temperature Thermocouple (μV)
12
10
8
6
4
2
0
Differential Reading (Scale Divisions 1/2-inch)
0
10
20
30
40
50
60
70
80
Time (minutes)
Differential Heat Capacity Curve
$N_2H_4 \cdot HBr$ - NaCl

DISCUSSION

The interpretation of specific heat measurements on many crystals, such as NH_4Cl, requires an assumption that there exists a critical temperature above which it is possible for the molecular configuration within the crystal to rotate.

The only real attempts at dynamic description of this condition are those of Pauling (10) and Sterne (17).

Pauling considered the simple diatomic molecule to be bound like a harmonic oscillator in the crystal fields. The average interaction of the molecule with the surrounding molecules is given in its simplest form by $V = V_o(1-\cos 2\theta)$ where V_o is a constant obtainable from specific heat data and θ is the angle made by the figure axis of the molecule with some fixed direction.

Transition from oscillation to rotation is assumed to start when the kinetic energy of the molecules becomes of the order of magnitude of $2V_o$, or at a temperature of $T = 2V_o/k$, (k = Boltzmann's constant), when rotation weakens the binding force. Thus the binding force depends upon the temperature.

For lower temperatures the molecules oscillate about $\theta = 0$, while above the transition point they rotate, being hindered in their motion by the crystal fields.

To explain the behavior shown by compounds such as HBr, which undergoes three transitions at -184.1° C., -160.1° C. and -156° C., Pauling has suggested the possibility of molecular rotation setting

in first about one directional axis of the crystal; then later about the other axes. The fact that molecules in crystals could rotate was first discovered by Bonhoeffer and Harteck (1) in the case of ortho and para H_2, the former showing rotational phenomena, the latter not.

Stern considered the molecule as a three dimensional oscillator, showing diagramatically how the energy-level scheme varies as the crystal fields increase in magnitude.

The problem of the spherical oscillator does not yield an exact quantum mechanical solution. The two limiting cases, 1., when the crystal fields approach zero, thus affecting the motion of the top only slightly, and 2., when the crystal fields approach infinity, so that the axis of symmetry oscillates isotropically about its position of equilibrium, are examples which may be solved exactly.

Fowler (6) has recently developed a statistical theory of the rotation of molecules in which he considers the effect of an increase of temperature, any influence of the concomitant change in volume (13) being neglected or relegated to a minor role. He assumed that the probability of a molecule's rotating is greater if its neighbors are rotating. He also demonstrates that under certain circumstances it is possible to get a sharp rotation without a change in volume.

Rice (11) believes that in the actually observed transitions the dependence of $(\frac{\partial S}{\partial V})T$ on volume plays an important part.

Nevertheless he feels that Fowler's theory contains much truth. Thus, the greater ease of rotation for a molecule would be evinced in a fairly great, though not completely sharp, increase in $(\frac{\partial S}{\partial V})_T$ when volume increases over a fairly narrow critical range just before the marked decrease of $(\frac{\partial S}{\partial V})_T$ sets in. This would naturally affect the details of the transition.

Bridgman (2) points out that small range anomalies need not involve as radical an internal change as passing from oscillational to rotational motion, but may be caused by intermediate types of change such as an increase in the amplitude of the oscillating molecule with accompanying thermal and volume effects.

Pauling (10) states that in general it is to be expected that the rotational motion of molecules and complex ions of sufficiently low moment of inertia will set in below the melting point of the crystals. The fact that such a compound as $N(CH_3)_3Cl$, very similar chemically to NH_4Cl, failed to show a transition may be explained on the basis of its relatively great moment of inertia as compared with that of NH_4Cl.

On the other hand, Smyth (16) is of the opinion that the moment of inertia of the molecule does not have the dominant effect in determining rotation which has been attributed to it. Examination of Pauling's theory shows that the moment of inertia is a factor in determining oscillational or rotational energy levels of the molecule and hence the distribution of energy among the molecules, but does not actually change the potential energy barrier through which the

molecule has to pass to rotate, except through its small effect in determining the zero energy level.

Increased molecular size, incidentally involving increased moment of inertia, gives greater potential energies between the molecules, and, consequently, in most cases greater variation of potential energy with orientation of the molecule in the lattice or, in other words, greater barriers to prevent rotation. The shape of the molecule is one of the most important factors in determining these barriers, since upon it will depend largely their distance of approach in a rotational oscillation, and this distance determines the intermolecular force. If there is no actual blocking of molecules by other molecules, the differences in Van de Waal's forces exhibited by different kinds of atom and the size of the molecular dipole moments become important factors.

Setting in of rotation may occur gradually because of the unequal distribution of energy among the molecules, as in borneol or in arsine, in which latter substance the transition after a gradual start ends with a sharp increase in rotation.

Commonly transition is almost as sharp as melting because of the attenuation of the intermolecular forces in the vicinity of the molecule which has begun to rotate.

The energy absorbed by a solid where rotation sets in lies between 37% and 100% of the heat of fusion. Usually the energy content of a solid with rotating molecules just below the melting point differs from that of the liquid just above the melting point by

little, if any, more than it differs from that of the solid below the temperature where rotation sets in. From a molecular point of view, the difference between a solid having rotating molecules and a liquid is that the molecules of the solid are vibrating about points fixed in a lattice, while those of the liquid are vibrating about points which migrate slowly and irregularly through the liquid.

Because the molecule of hydrazine would have a greater moment of inertia than ammonia, it was not thought necessary to search for possible transitions at temperatures lower than observed for ammonium salts. The lowest temperature was also limited by the cooling agent used, solid carbon dioxide.

Differential heating curves were run for five hydrazine salts, including examples both of the neutral 1:1 and acid 1:2 types. In every case small, but very sharp and definite, discontinuities occurred, all within a range of 0.6° C. These persisted in undiminished degree even upon repeated recrystallization so they are not to be ascribed to the presence of impurities.

The fact that the differential effect is small (never more than .07° C.) does not exclude the possibility of transition as Eucken (4) points out in his excellent paper.

To insure that the cause did not lie in the thermocouple, a check was made using sodium chloride in both sides of the copper block. In this case, the curve was smooth.

In most of the curves also a definite indication of a halt in the temperature rise may be seen in the curve of absolute

temperature against time, which indicates a transition.

There are several interesting characteristics of these breaks which should be noted. One is their close proximity to the transition range of ammonium salts. An important difference also is that these breaks are very sharp and not broad like those observed with ammonium salts. The change in the salt is obviously not of the same degree and probably not of the same kind. Another interesting observation, if substantiated, is that the break is downward in the curve. From the way in which the thermocouple is set up, this would indicate a rise in temperature for the hydrazine salt, opposite to the effect noted with ammonium salts.

Until further information is at hand, obtained by different methods of approach, it is not feasible to offer a complete and satisfactory explanation for this, however. In fact, little can be said except that a definite change takes place, independent of the anion or the valence of the hydrazinium ion in the salt.

SUMMARY

Differential heating curves for $N_2H_4 \cdot HCl$, $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot HBr$, $N_2H_4 \cdot H_2SO_4$ and $N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}H_2O$ have been obtained, using NaCl as a reference salt. The accuracy of check runs made with NH_4Cl has shown the apparatus used to be very accurate.

No logical explanation of the minima in the differential curves has been advanced. They do not appear to be the result of NH_4Cl impurities in the salt.

Most of the temperature-time curves show a fairly marked change of slope at the transition point.

Calorimetric and dilatometric investigation should be applied to these hydrazine salts in order to substantiate the results obtained in this work.

A fairly complete outline of the theoretical treatment of molecular rotation in the solid state is given.

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