

CRYSTALLINE POLYMORPHISM
OF NITRATES

APPROVED:

L. J. Bonnell, Jr.
Major Professor

R. B. Esch, Jr.
Minor Professor

L. L. Milder
Director of the Department of Physics

Jack Johnson
Dean of the Graduate School

CRYSTALLINE POLYMORPHISM
OF NITRATES

THESIS

Presented to the Graduate Council of the
North Texas State College in Partial
Fulfillment of the Requirements

For the Degree of

MASTER OF ARTS

by

193495

Jimmie G. Shepherd, B. S.

Beaumont, Texas

August, 1951

PREFACE

The purpose of this study was to investigate the polymorphism of a group of related compounds. Special emphasis was placed upon the temperature at which transitions occurred and a possible correlation of these temperatures with other properties of the compounds.

A review of the literature revealed that little information was available for many nitrates. A group of five nitrates with no reported transition temperatures was investigated. All the compounds were anhydrous and had melting points which could be reached with the equipment available. Anhydrous compounds were studied because the presence of water of crystallization alters the structure and hence all the physical properties of the compound.

The compounds investigated in this study were lead nitrate, sodium nitrate, lithium nitrate, barium nitrate, and strontium nitrate. Silver nitrate and potassium nitrate were also investigated, but extensive information was available as to their transition temperatures.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF ILLUSTRATIONS	vi
Chapter	
I. INTRODUCTION	1
II. APPARATUS AND PROCEDURE	9
Apparatus	
Procedure	
III. DATA AND RESULTS	21
IV. CONCLUSION	34
BIBLIOGRAPHY	37

LIST OF TABLES

Table	Page
1. Calibration of Thermocouple Number One . .	13
2. Calibration of Thermocouple Number Two . .	14
3. A Summary of Data and Results	33

LIST OF ILLUSTRATIONS

Figure	Page
1. Cut-away View of Furnace and Ice Bath . .	11
2. Calibration Curve for Thermocouples One and Two	15
3. Heating Curves for Potassium Nitrate . .	22
4. Heating Curves for Silver Nitrate	23
5. Heating Curves for Lead Nitrate	24
6. Heating Curves for Strontium Nitrate . .	26
7. Heating Curves for Strontium Nitrate . .	27
8. Heating Curves for Barium Nitrate	28
9. Cooling Curve for Barium Nitrate	29
10. Heating Curves for Sodium Nitrate	31
11. Heating Curves for Lithium Nitrate . . .	32

CHAPTER I

INTRODUCTION

Polymorphism is the term used to describe the existence of a compound in two or more distinct crystalline forms. A more nearly complete definition has been given by Buerger: "Polymorphism includes every possible difference encountered in crystalline structure of a substance, excepting homogeneous deformations."¹ When a crystal is heated certain changes, such as expansion or contraction, always occur in the crystalline structure, which are often referred to as homogeneous deformations.² Polymorphism was first recognized by Klaproth in 1798 when he discovered that calcite and aragonite were chemically identical.

In the order of decreasing magnitude, polymorphic changes occurring in crystals can be grouped into three classes. The first is polytypy, which is a complete alteration of the space lattice with the formation of a new type of structure. The second is polysynony in which there

¹M. J. Buerger, "The General Role of Composition in Polymorphism," The Proceedings of the National Academy of Sciences of the United States, XXII (1936), 688.

²T. F. W. Barth, "Polymorphic Phenomena and Crystal Structure," American Journal of Science, XXVII (April, 1934), 273.

is a distinct change in the geometrical symmetry of the space lattice although the atomic arrangement, density, and cleavage properties are so slightly affected that merely a new variant of structure is formed while the type of structure is preserved. The third class is called polytropy, which pertains to crystals representing one and the same structure type, but distinct from polysynony in that the crystals must retain the same geometrical symmetry. The gradual transition with rising temperature of sodium nitrate is a case of polytropy.³ The three types of polymorphic changes may be distinguished by the physical behavior of the inversion.

The first detailed study of polymorphism was carried on by Frankenheim, who studied a number of crystals with a polarizing microscope. This study revealed that there was a definite temperature of transition where a low-temperature crystalline form changed to a higher-temperature crystalline lattice structure. The former can not exist at a higher temperature than its transition point, but the higher-temperature structure can exist below the transition point and can even be generated in this region. If the high-temperature form, below its transition point, is brought into contact with the low-temperature form the first changes into the latter upon contact. The change proceeds in all

³Ibid., p. 274.

directions from the point of contact. It is even possible for the high-temperature form to change to the low-temperature modification upon contact with foreign bodies, stirring, or shaking. Whenever this change occurs, heat is released.⁴

A polymorphous transition is simply a rearrangement of the atomic units in the space lattice. As can be seen from the above classifications, this may be a slight reorientation of the groups or a complete rearrangement. When the atoms have no agitation, this is the arrangement of least possible potential energy. With an increase in kinetic energy, the bonds which hold the atomic units together are strained or even broken. A new so-called dynamic structure then occurs. There is an infinite number of ways that the atomic units may rearrange themselves in the space lattice and each new arrangement has its definite lattice energy. The stable configuration is the one with least potential energy and this is not necessarily the static lattice energy.

There are cases, however, in which different modifications of the same compound exist at the same temperature. Only one form can be most stable, i.e., have the least potential energy at the given temperature, and any other forms existing at the same temperature are called metastable. In a few cases, accidental degeneracy of the energies accounts for the existence of metastable states; in others the excess

⁴M. J. Buerger and M. C. Bloom, "Crystal Polymorphism," Zeits. fur Kristall., XCVI (1937), 184.

of potential energy in the metastable state is probably so small that the transition to the more stable form is not spontaneous. Calcium carbonate is a good example of metastability. It exists in two forms, calcite and aragonite. Both of these forms are found at ordinary temperatures. However, if they are heated and then returned to room temperature all the crystals will have changed to one form. At room temperature, calcite is the most stable.⁵

In order for a polymorphic change to occur, energy must be put into or taken away from the system. This is usually accomplished by the addition or subtraction of heat. The energy content of a crystal is in the form of motion of its fundamental atomic units. That is, heat motion is a form of wave motion among the atoms of the crystal structure. The temperature of the crystal is a good indication of this energy content. The motions of the fundamental atomic units are not entirely at random but are synchronized with their neighbors. This is true because of the mechanical binding between them. Buerger⁶ suggests that the whole secret to polymorphism resides in the form of this wave motion.

Crystals are composed of atomic units called clusters. A cluster may consist of an atom, a molecule, a molecular

⁵R. C. Evans, An Introduction to Crystal Chemistry, p. 256.

⁶M. J. Buerger, "The Kinetic Basis of Crystalline Polymorphism," Proceedings of the National Academy of Science of the United States, XXII (1936), 683.

group of atoms, or a coordinated group of atoms. To examine the form of wave motion, it is convenient to fix the attention in the immediate vicinity of one of the major repetitive units of the crystal lattice. The three degrees of freedom of each of the n atoms comprising the cluster may be combined in several ways to give the characteristic modes of vibration. Six degrees of freedom can be accounted for by the motion of translation and rotation of the bodily unit. These are termed "outer" modes. The remaining $3n-6$ degrees of freedom account for disorders inside the cluster. These are termed "inner" vibration modes. If one cluster turns out to be geometrically identical with another except for orientation, then the number of distinctly different types of vibrations is greatly reduced. Different levels of kinetic energy input tend to excite the different possible cluster vibration modes.⁷ Therefore, cluster vibration modes are different with different temperatures.

The relative strength of the intercluster and intra-cluster bindings determine the possible vibration modes for any one crystal. In general the forces between clusters are weaker than the forces within clusters; therefore the excitation of the "outer" vibration mode is brought about very easily in the case of clusters of molecules and molecular groups. As a consequence rotation of the molecules

⁷Ibid., p. 684.

is quite common as a form of heat motion.

Different symmetries are generally characteristic of different vibration modes. In other words, the static symmetry is not necessarily the same as the dynamic symmetry. The dynamic symmetry may be either higher or lower than the static symmetry. If the rotation is complete, the "outer" vibration modes tend to increase the cluster symmetry to radial symmetry about the axis of rotation. On the other hand the "inner" modes have either the symmetry of the ideal static cluster or a lower symmetry. If a crystal responds to a certain temperature with a given vibrational mode, the clusters have a specific dynamic symmetry.⁸ This requires a crystal structure in which the cluster occupies that specific symmetry in the space group.

Transition temperatures for a group of compounds containing the same radical may vary over a wide range. This can be caused by different valences of the cations. The transition temperature from one crystalline form to another is increased with increased valence of the cation. In the group of compounds of the form A_mBX_n , the transition temperature is affected by increased size of the A cation. This is due to the strengthening of the A-X binding because the polarization of the A cation is increased in the

⁸Ibid.

negative field of the anion. An increase in size of the A cation can also decrease the transition temperature. This occurs where the weakening of the positive field around A, which is due to the increase in size of A, overcomes the strengthening of the A-X binding induced by polarization.⁹

An extreme example of polymorphism due to ionic rotation is exhibited by ammonium nitrate. This compound exists in five distinct crystalline structures, two forms of tetragonal, two forms of orthorhombic, and cubic. Below minus eighteen degrees Centigrade the low symmetry form of tetragonal is stable. At minus eighteen degrees Centigrade the ammonia radical probably begins to rotate about the tetrahedral axis and the symmetry changes to the low symmetry form of orthorhombic. At approximately thirty-three degrees Centigrade the ammonia radical is thought to commence free rotation and the symmetry changes to the higher form of orthorhombic. At about eighty-five degrees Centigrade the nitrate group begins to rotate about a perpendicular to its plane. The crystalline structure changes to a higher tetragonal symmetry. At

⁹M. A. Bredig, "High Temperature Crystal Chemistry of AmBX_n Compounds with Particular Reference to Calcium Orthosilicate," The Journal of Physical Chemistry, XLIX (July, 1945), 552.

approximately 125 degrees Centigrade the nitrate group begins to rotate freely, and the crystalline structure changes to cubic. When the temperature is raised to 169 degrees Centigrade the ammonium nitrate melts. The above events may be interpreted to mean the substance is melting in stages, since melting for a solid means the constituents are free to rotate about one another.

CHAPTER II

APPARATUS AND PROCEDURE

Apparatus

The apparatus consisted of a Leeds and Northrup Type 7651 potentiometer, a Huppert Model 22 heating furnace, a Bureau of Standards Number 81025 calibrated thermometer, two iron-constantan thermocouples, and a crushed ice bath for the low temperature junction of the thermocouples. A traveling microscope was used for reading the instruments.

The potentiometer could be read accurately to one-hundredth of a millivolt. The one-thousandth place could be estimated easily. The range of the instrument at this accuracy was from zero to sixteen millivolts. Since the iron-constantan thermocouple produced an electromotive force of about thirty millivolts at the higher temperatures, it was necessary to restandardize the potentiometer with the scale set to read half the potential of the standard cell. All readings were then multiplied by two.

The heating furnace gave a range in temperature from room temperature to 1200 degrees Centigrade, which included the temperature range desired. It was necessary to heat the sample very slowly. For temperatures below 350 degrees Centigrade, the furnace was lined with asbestos. Glass wool

was packed inside the asbestos. A one-half pint Dewar flask was mounted in the center of the glass wool. The Dewar flask was packed with glass wool with a small hole in the center for the sample. Since glass wool melts at a lower temperature than three of the compounds tested, it was replaced with asbestos when barium, strontium, or lead nitrates were heated. The two materials placed in the furnace served two purposes, mechanical support and insulation.

The thermometer was a mercury-in-glass, 76 millimeter-immersion type, hence no stem correction was necessary. Its range was from -10 degrees Centigrade to +350 degrees Centigrade. During calibration of the thermocouples the thermometer was read with the traveling microscope. This afforded an excellent method of reading the temperatures to the nearest tenth of one degree.

The thermocouples were made of Brown and Sharpe gauge number thirty-one iron wire and number twenty-seven constantan wire. The different sizes of wire were used to give approximately the same rate of thermal conduction in the leads. The hot junction was placed in a small capillary tube to prevent corrosion caused by contact with the sample. Ice for the cold junction was kept in a Dewar flask which was packed in rock wool insulation. Figure 1 is a cut-away view of the apparatus.

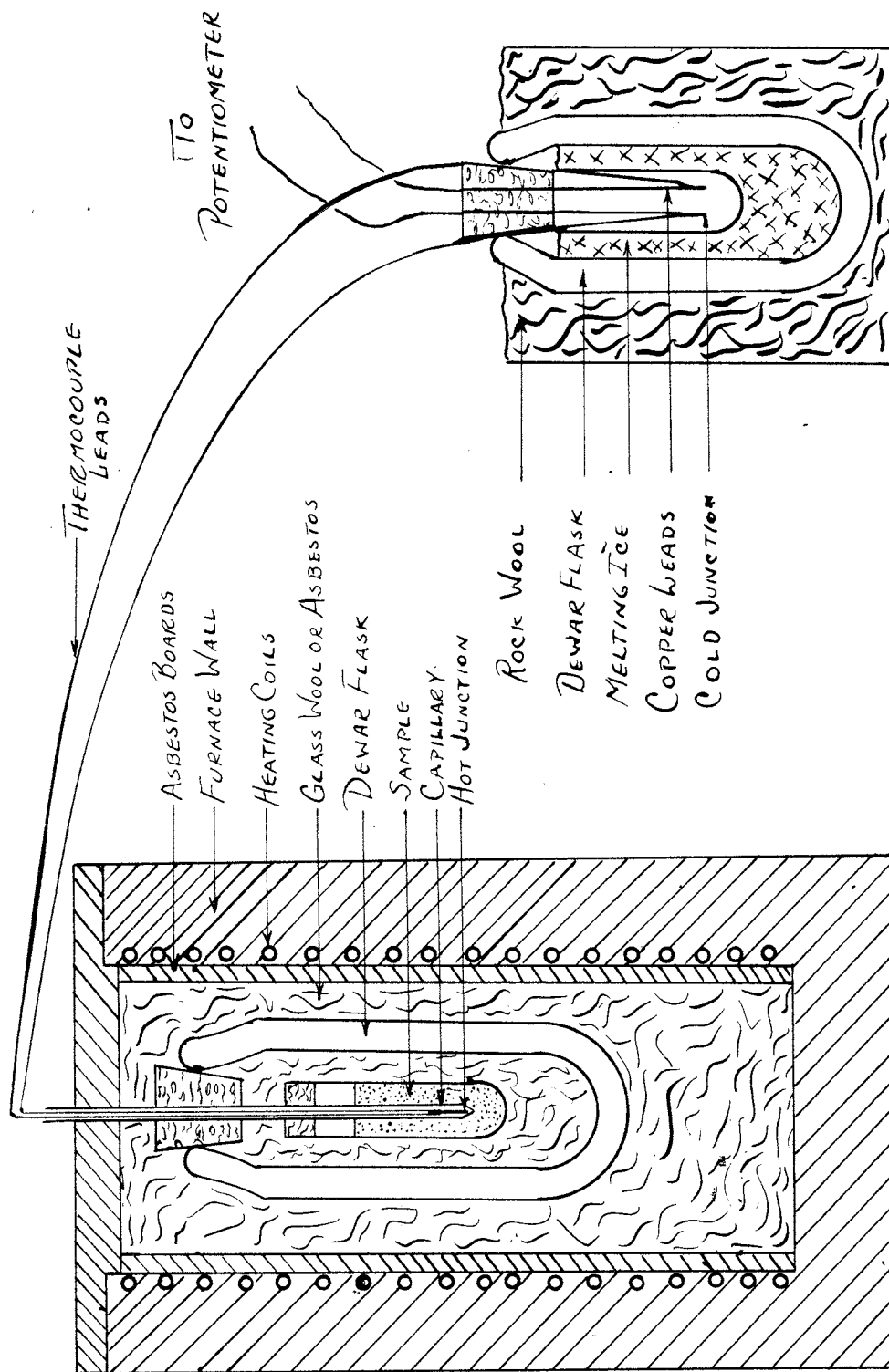


Fig. 1--Cut-away View of Furnace and Ice Bath

Procedure

The initial step in the problem was to obtain a thermocouple that would give reproducible results, that is, give the same electromotive force each time the two junctions were brought to a given temperature difference. The two wires were securely fastened together mechanically. The joint was then made permanent with silver solder. For calibration the thermocouple was heated through steps of twenty centigrade degrees to 350 degrees Centigrade. An electromotive force reading was taken at each interval to check the consistency of results. The hot junction was allowed to cool and the heating process repeated. Tables 1 and 2 present the data obtained in the heating processes. The results were reproduced to one-thousandth of a millivolt. After the thermocouple was calibrated it was used as a temperature measuring device. Figure 2 shows the calibration curves obtained when temperature versus thermocouple electromotive force was plotted.

The method used to find the transition temperatures of the compounds is known as the heating and cooling curve method. The temperature of the compound was raised from room temperature to its melting point as slowly as possible. When a crystalline transition occurred the energy that normally raised the temperature of the compound produced the change in crystalline structure. On a graph of temperature versus time the change in structure was revealed as a plateau.

TABLE 1

CALIBRATION OF THERMOCOUPLE NUMBER 1
 USING 76 MILLIMETER-IMMERSION
 CALIBRATED THERMOMETER

Thermometer Reading (°C.)	Calibration Correction (°C.)	Temperature (°C.)	Thermocouple E.M.F. (Millivolts)
31.8	-0.51	32.3	1.24
50.0	-0.46	50.5	2.27
70.0	-0.36	70.4	3.28
90.0	-0.24	90.2	4.29
110.0	-0.08	110.1	5.31
130.0	-0.14	129.9	6.35
150.0	-0.36	149.6	7.39
170.0	-0.52	169.5	8.43
190.0	-0.60	189.4	9.45
210.0	-0.60	209.4	10.45
230.0	-0.54	229.5	11.45
250.0	-0.48	249.5	12.42
270.0	-0.43	269.6	13.42
290.0	-0.40	289.6	14.43
310.0	-0.44	309.6	15.44
330.0	-0.80	329.2	16.51
350.0	-1.40	348.6	17.52

TABLE 2

CALIBRATION OF THERMOCOUPLE NUMBER 2
USING 76 MILLIMETER-IMMERSION
CALIBRATED THERMOMETER

Thermometer Reading (°C.)	Calibration Correction (°C.)	Temperature (°C.)	Thermocouple E.M.F. (Millivolts)
29.5	-0.52	30.0	1.25
50.0	-0.46	50.5	2.45
70.0	-0.36	70.4	3.50
90.0	-0.24	90.2	4.53
110.0	-0.08	110.1	5.57
130.0	-0.14	129.9	6.65
150.0	-0.36	149.6	7.63
170.0	-0.52	169.5	8.70
190.0	-0.60	189.4	9.73
210.0	-0.60	209.4	10.76
230.0	-0.54	229.5	11.76
250.0	-0.48	249.5	12.76
270.0	-0.43	269.6	13.78
290.0	-0.40	289.6	14.87
310.0	-0.44	309.6	15.96
330.0	-0.80	329.2	17.04
350.0	-1.40	348.6	18.21
570.0 ^a	570.0	30.37
592.0 ^b	592.0	31.78

^aMelting point of strontium nitrate.

^bMelting point of barium nitrate.

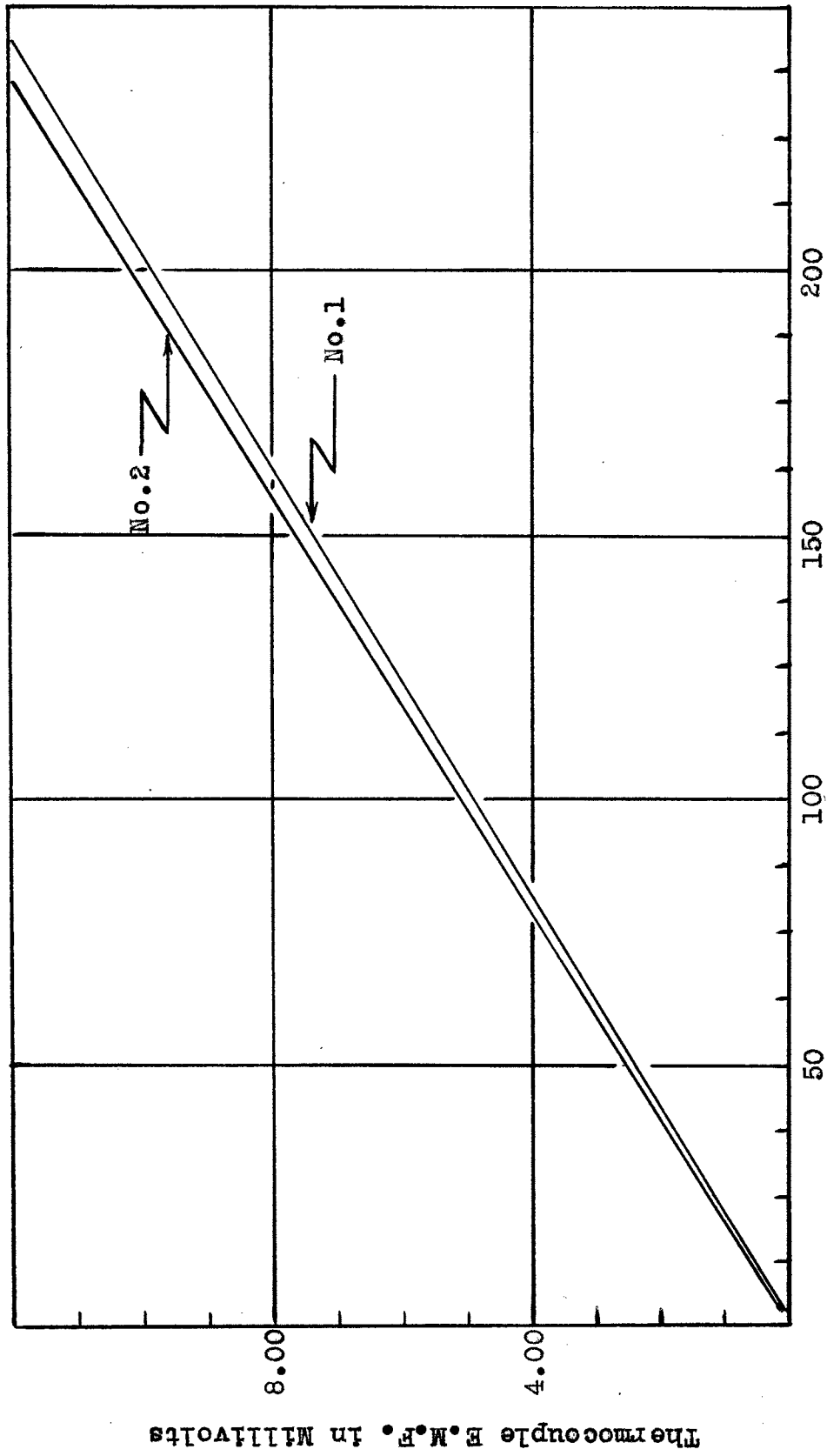
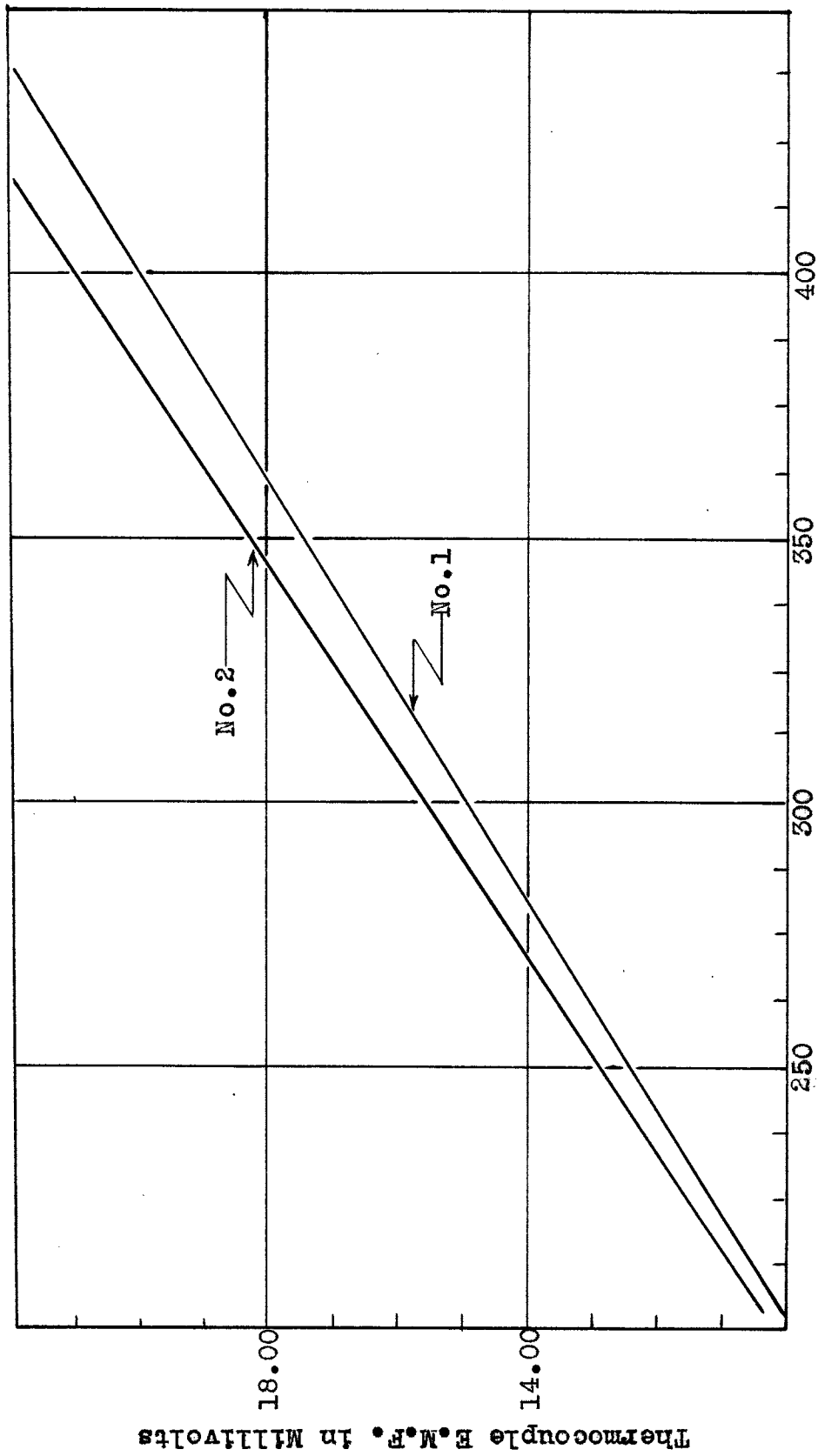
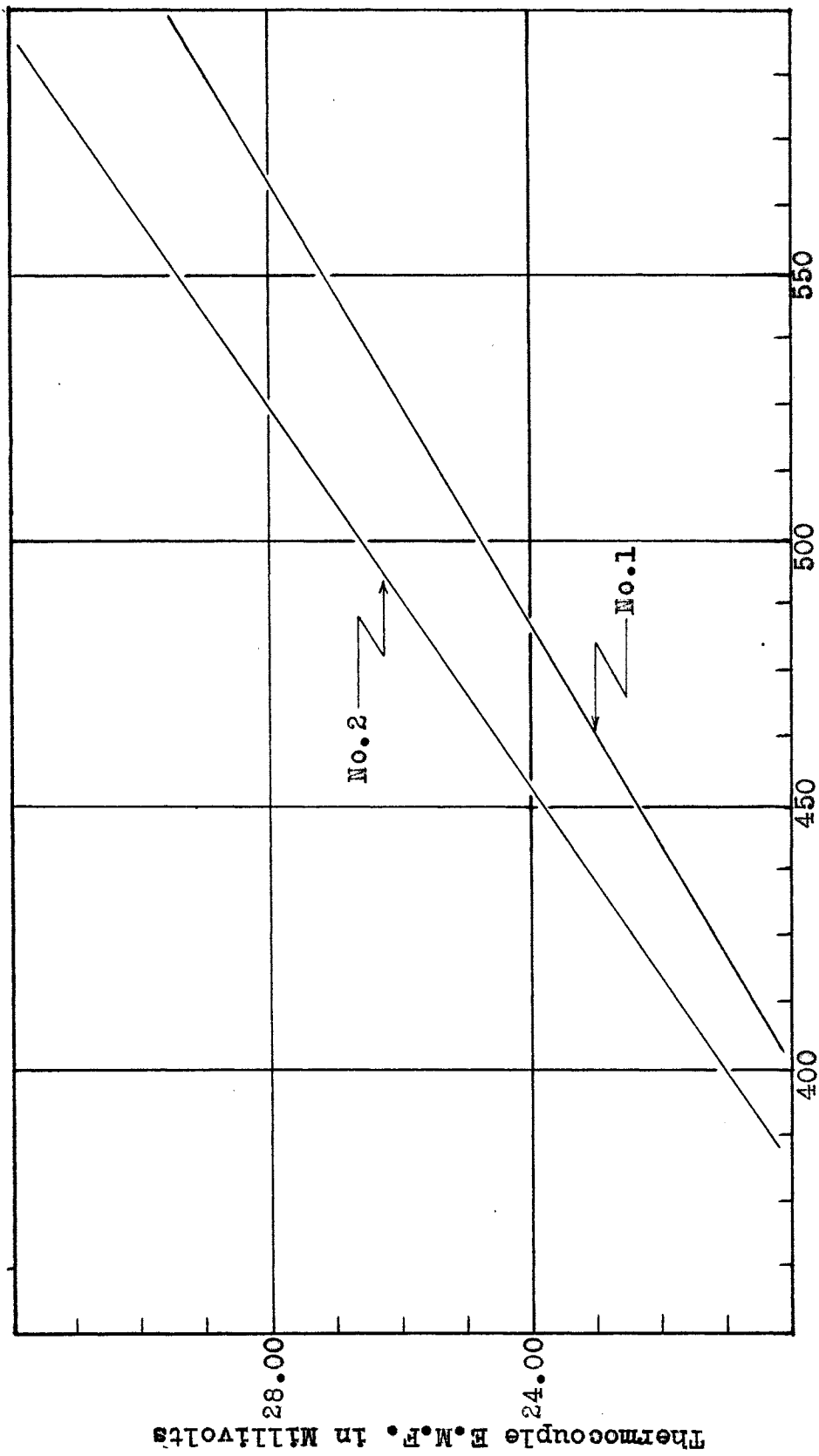


Fig. 2--Calibration Curves for Thermocouples One and Two



Temperature in Degrees Centigrade

Fig. 2--Continued



Temperature in Degrees Centigrade

Fig. 2--Continued

The cooling curve method is not so reliable as the heating curve method. Two reasons for this are metastability and supercooling. However, cooling curves were taken for barium, strontium, and lead nitrates.

Two compounds with known transition temperatures, silver nitrate and potassium nitrate, were used to check the results of the instrument. Values previously reported for the transition temperatures of these compounds are 159.4 degrees Centigrade¹ and 129.5 degrees Centigrade² respectively. Results obtained were within two per cent of these temperatures.

Each of the five compounds studied was heated from room temperature to its melting point at least twice. The thermocouple electromotive force was recorded at one-minute intervals. Since the melting points of the compounds were known they were used as check points for the thermocouple calibration in the high temperature range.

A gradual transition with rising temperature has been reported for crystals of sodium nitrate.³ To check the results obtained using the furnace, sodium nitrate was

¹Landolt-Bornstein, Physikalisch-Chemische Tabellen, Vol. I, p. 355.

²Ibid., p. 343.

³T. F. W. Barth, "Polymorphic Phenomena and Crystal Structure," American Journal of Science, XXVII (April, 1934), 276.

heated twice again using an oil bath. This enabled the compound to be heated even more slowly than before. Readings were taken every minute while the compound was heated from room temperature to 200 degrees Centigrade. Even at a slow rate of heating no transition temperature was found.

The accuracy of results depended on the purity of the compounds and the reliability of the instruments. The compounds were all Baker's Analyzed chemically pure and contained less than 0.1 per cent impurities. Therefore the error due to impurities is believed negligible.

As stated above, the temperature was measured with a Bureau of Standards Calibrated 76 millimeter-immersion mercury-in-glass thermometer. The temperatures could only be estimated to the nearest tenth of one degree. Greater accuracy could have been obtained if a more accurate temperature measuring device had been available.

Another source of error was in the calibration of the thermocouple in the high temperature range. The only calibration points between 350 degrees and 600 degrees Centigrade were the melting points of barium nitrate and strontium nitrate.

The potentiometer was sensitive to one-thousandth of a millivolt and was recalibrated before each heating. Consequently the measurement of the thermocouple electro-

motive force was more accurate than the thermometer used.
The measurement of the transition temperatures is believed
to be accurate to within two degrees.

CHAPTER III

DATA AND RESULTS

The heating and cooling curves through the different transition points are presented in Figures 3 through 11. Figure 11 shows the cooling curve obtained for barium nitrate. While cooling curves for lead nitrate and strontium nitrate were taken, they are not given since no transitions were indicated by these data.

Figures 3 and 4 show the transition points for potassium nitrate and silver nitrate. The observed transition point for silver nitrate was 160.1 degrees Centigrade, while the reported value was 159.4 degrees Centigrade. The reported transition temperature for potassium nitrate was 129.5 degrees Centigrade and the observed value was 131.8 degrees Centigrade.

Figure 5 shows the transition points for lead nitrate. The first heating gave a transition at 20.44 millivolts. The second heating gave one at 20.47 millivolts. The average temperature given by the two readings was 379.8 degrees Centigrade.

The first heating of strontium nitrate gave a transition point at 23.96 millivolts. The second heating yielded one at 23.79 millivolts. The temperature difference was

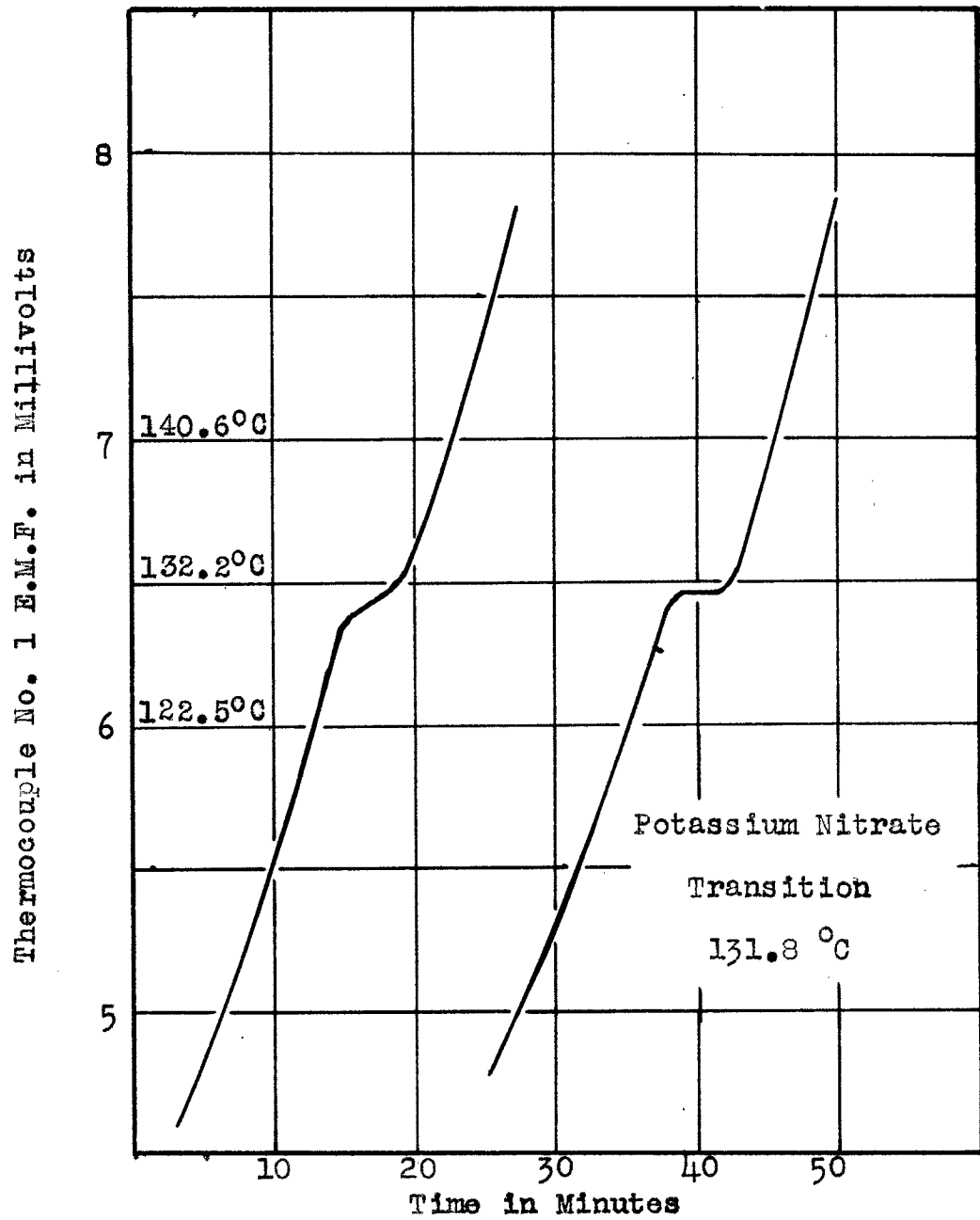


Fig. 3--Heating Curve for Potassium Nitrate

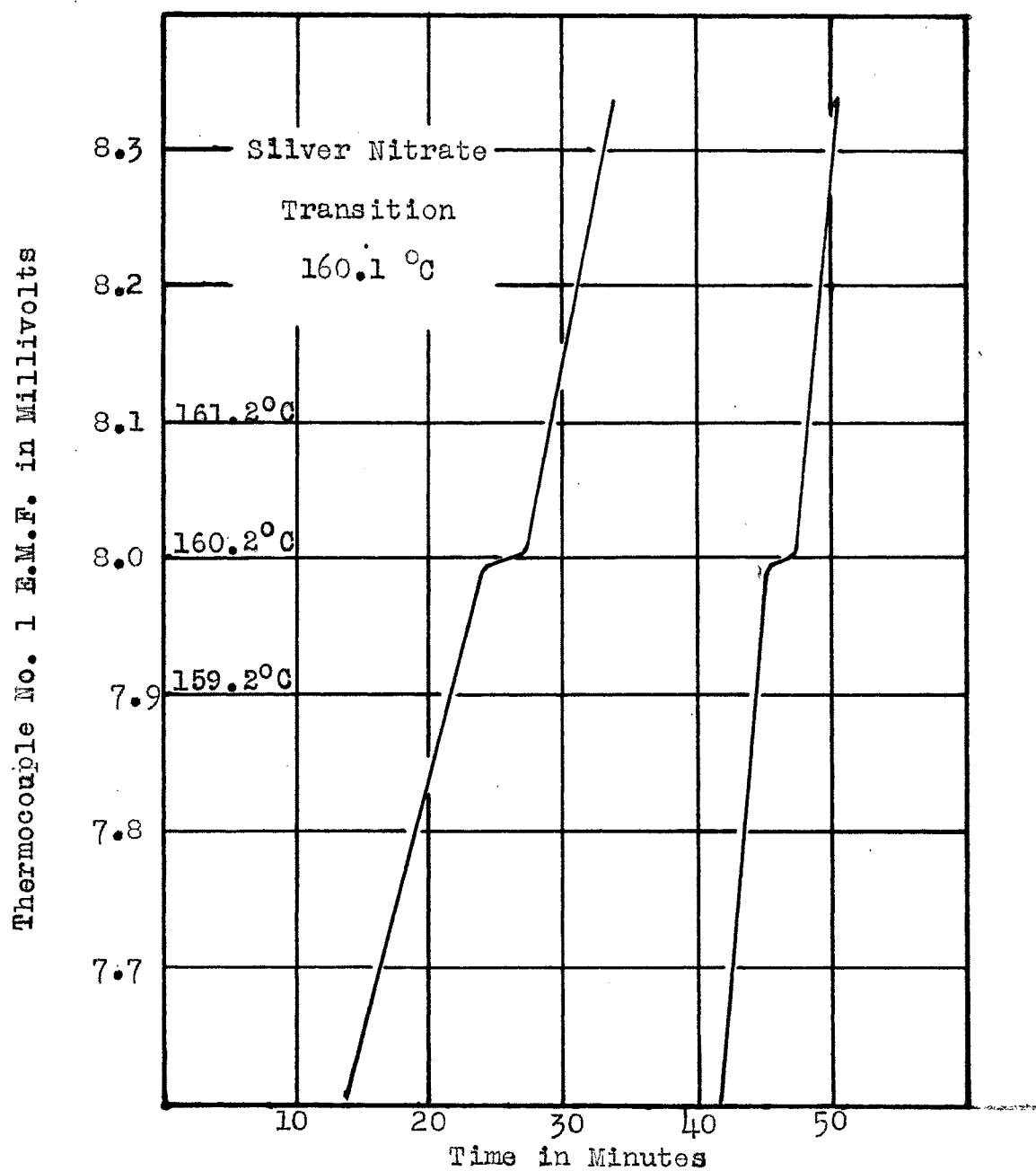


Fig. 4--Heating Curve for Silver Nitrate

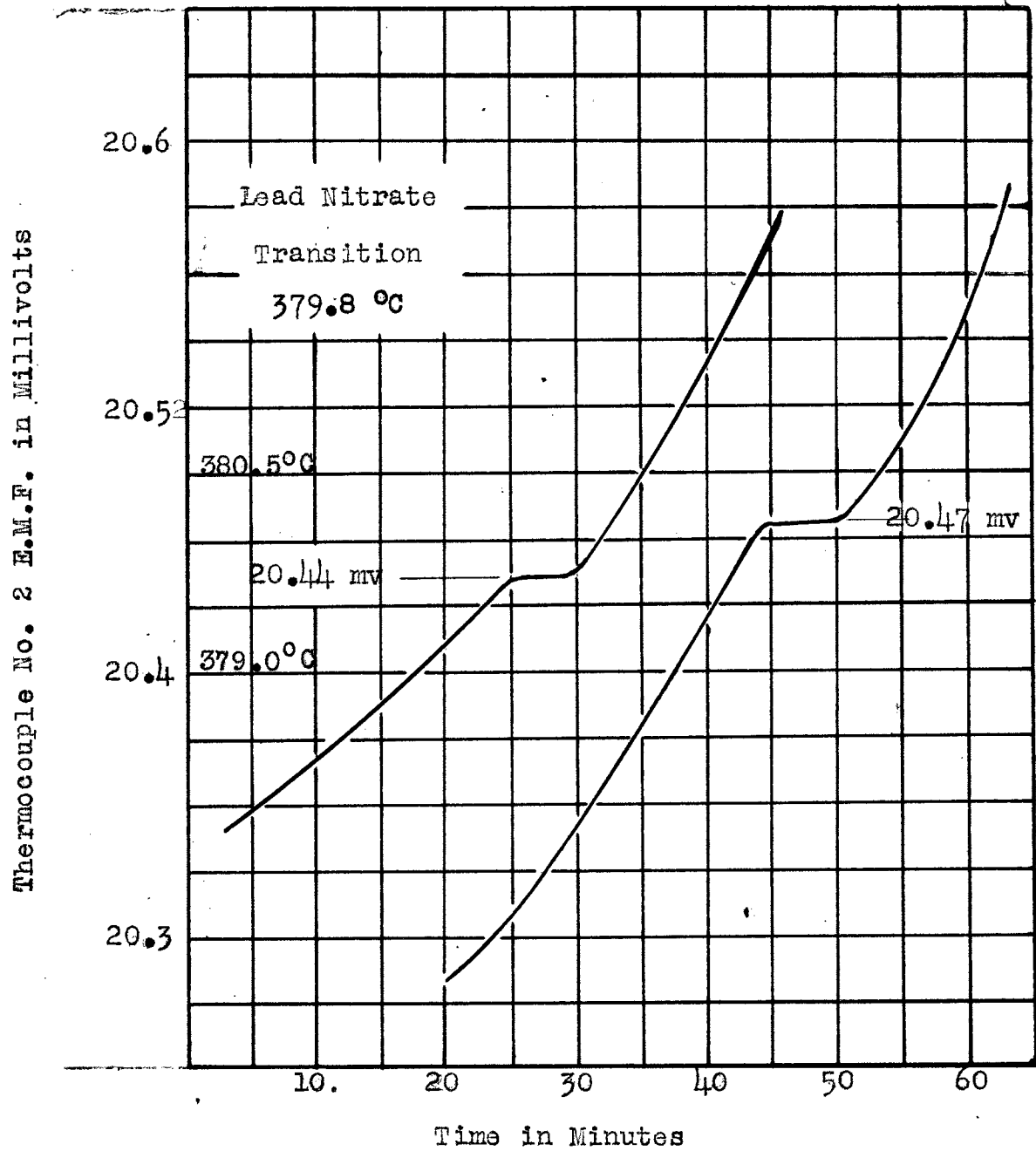


Fig. 5--Heating Curve for Lead Nitrate

three degrees Centigrade. The average temperature given by the two readings was 433.8 degrees Centigrade. The rate of heating for the second trial was greatly reduced. As a result a definite plateau was not observed in this curve. However, there was a marked change in the slope of the curve at the transition point. Figures 6 and 7 show the transition points for strontium nitrate.

Barium nitrate revealed a transition point at 538.8 degrees Centigrade. Both heating curves gave the same reading at this point. A temperature of 538.8 degrees Centigrade corresponded to 29.78 millivolts. A cooling curve was also taken for barium nitrate. However, the transition was noted to occur approximately forty Centigrade degrees lower than the transition temperature obtained from the heating curve. This was a result of supercooling. The slight rise in temperature, after the minimum point was reached, indicates that the temperature tried to rise to the original transition point. The heat of transition was too small for the temperature to rise to this value. Such differences between heating transitions and cooling transitions have been noted previously and measured for a number of crystals.¹ Figure 8 shows the heating curves for barium nitrate and Figure 9 shows the cooling curve.

¹L. F. Connell and J. H. Gammel, "Hysteresis Ranges of Polymorphic Transitions of Some Crystals," Acta Crystallographica, III (January, 1950), 75.

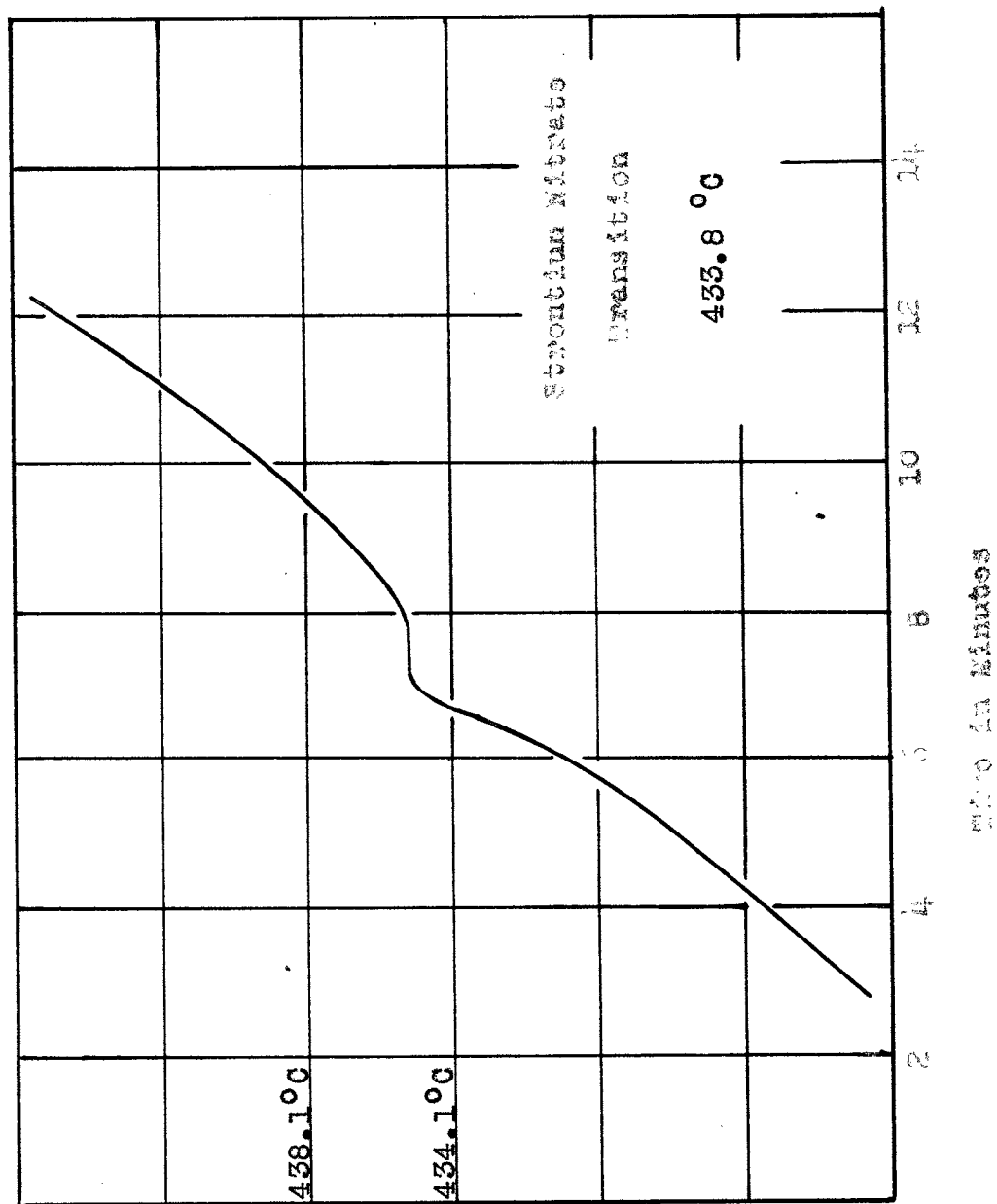


Fig. 6---Heating Curve for Strontium Nitrate

Thermocouple No. 2 E.M.F. in Millivolts

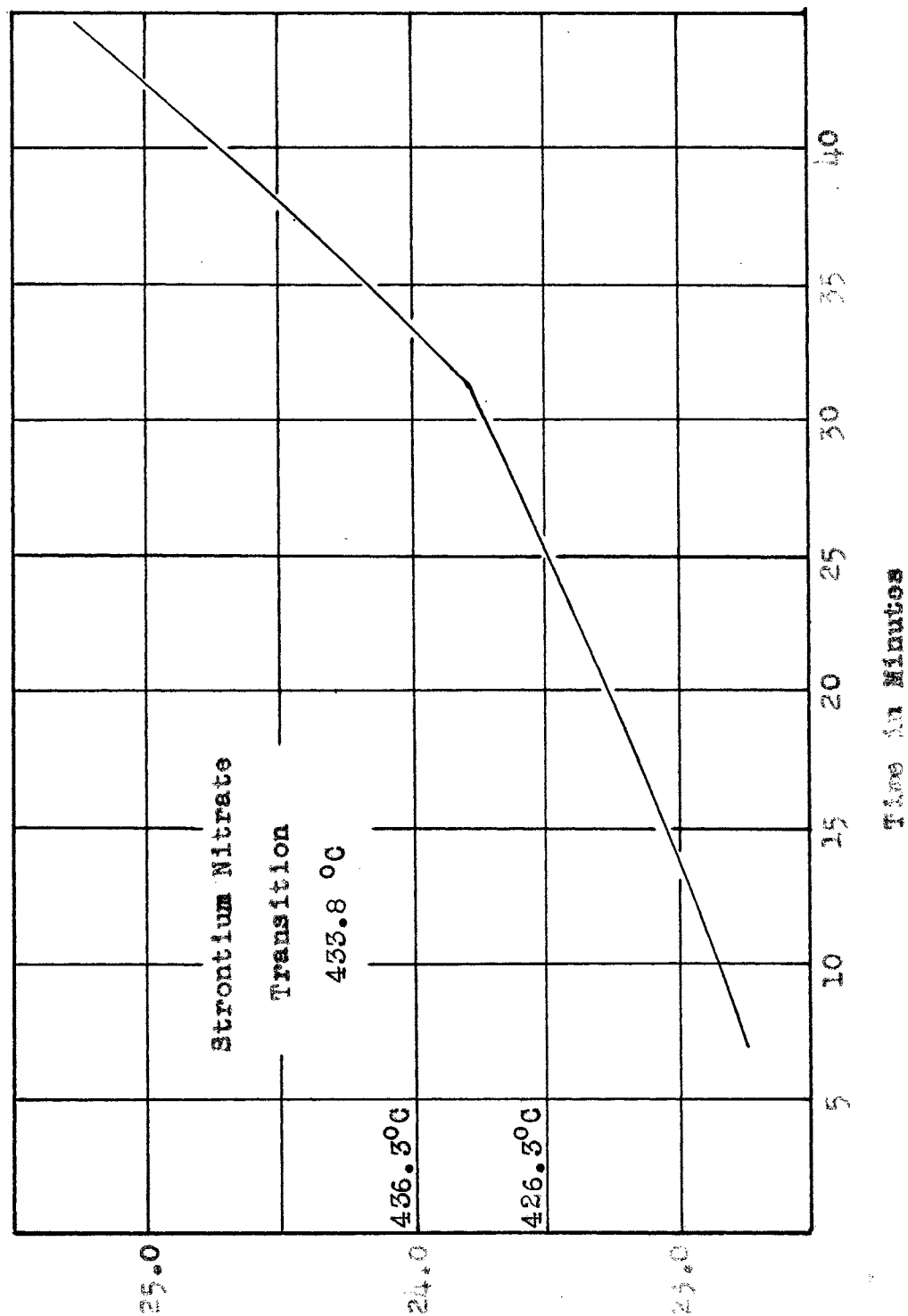


Fig. 7--Heating Curve for Strontium Nitrate

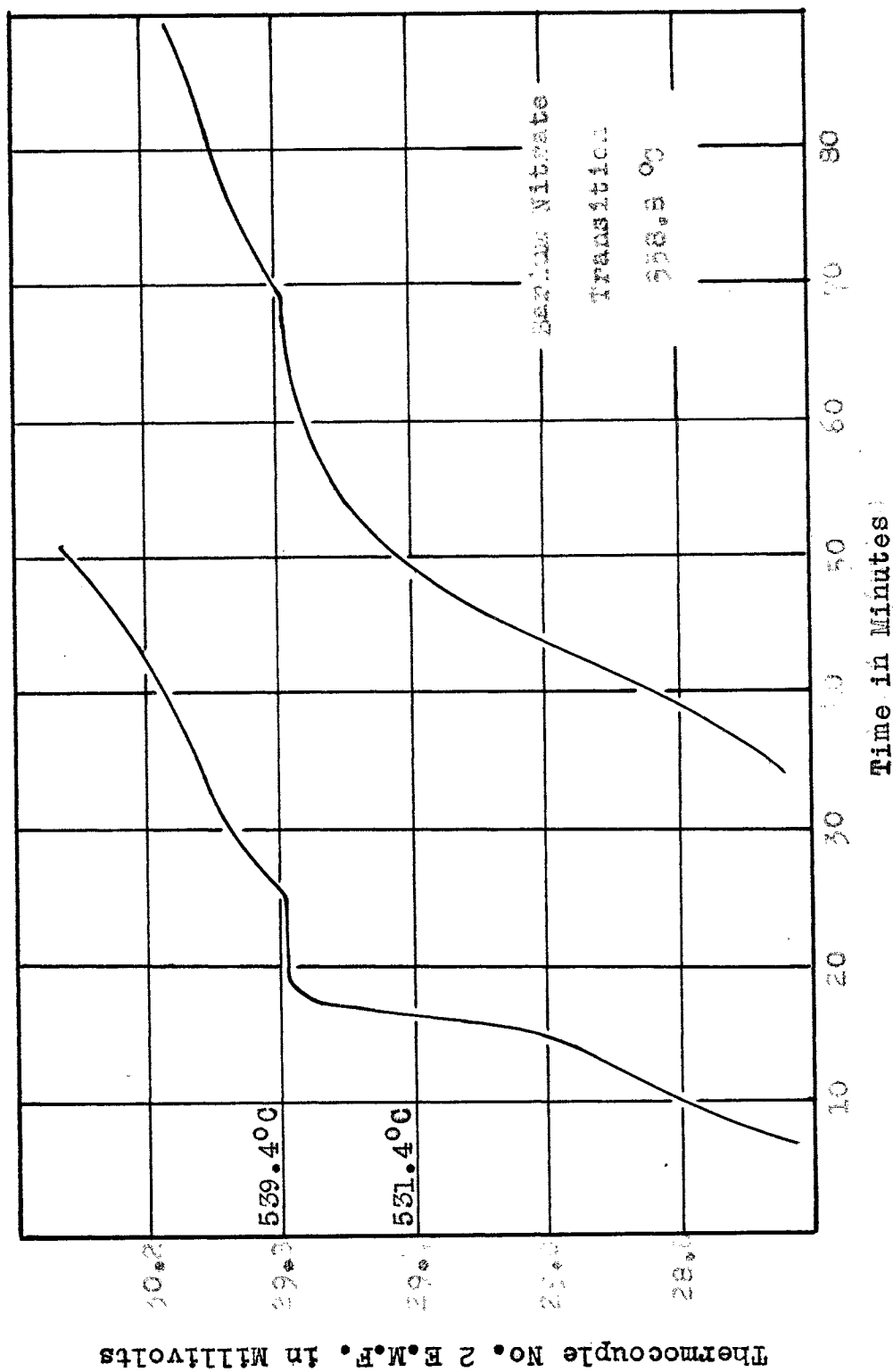


Fig. 8--Heating Curves for Barium Nitrate

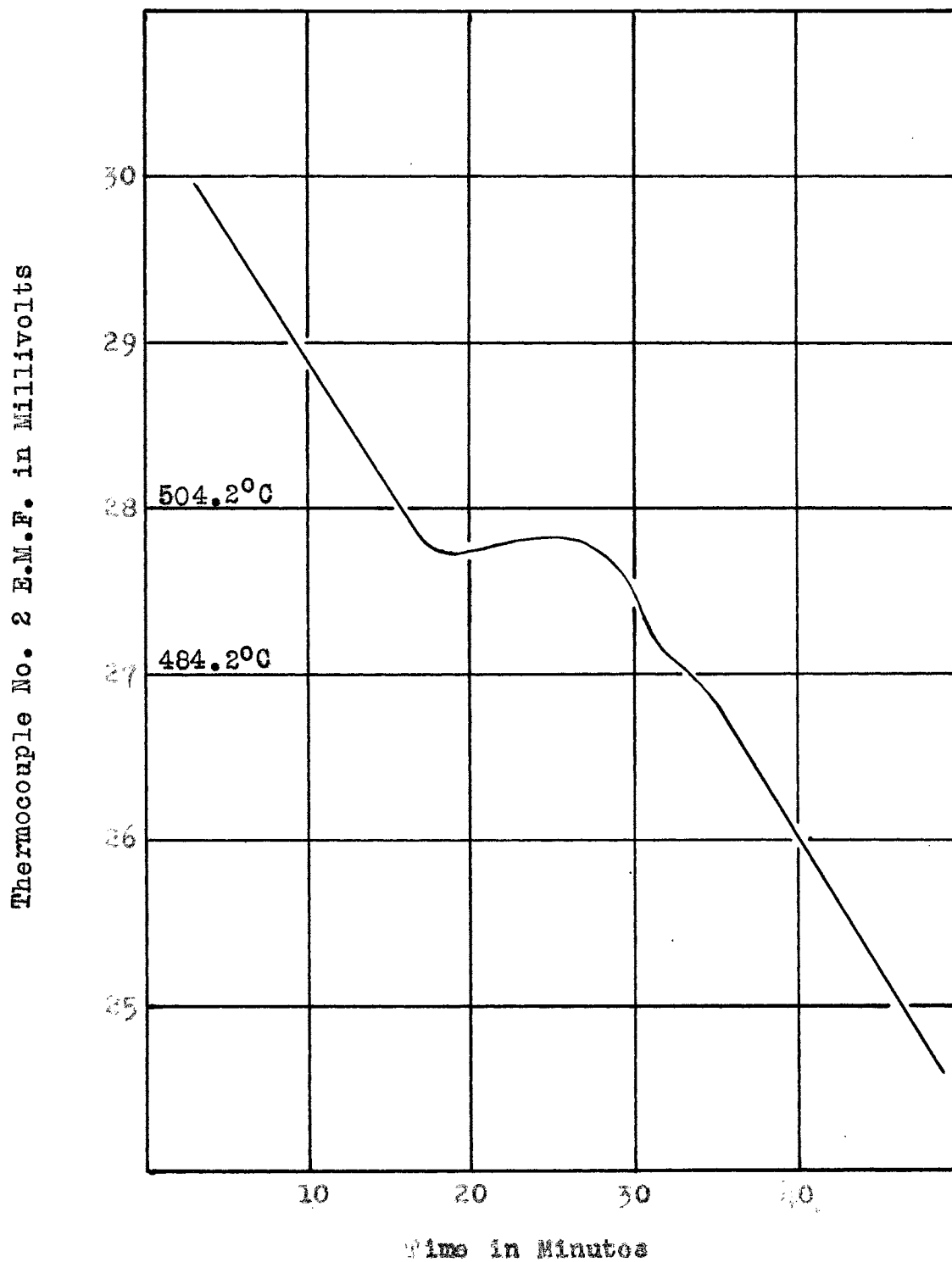


Fig. 9--Cooling Curve for Barium Nitrate

No transitions were observed for sodium nitrate and lithium nitrate. Two sets of readings were taken very carefully over the complete temperature range for each compound. These curves are shown in Figures 10 and 11.

A summary of data for the nitrates studied is given in Table 3. The molecular weights,² melting points,³ known transition temperatures, and observed transition temperatures are included in this table.

²C. D. Hodgkin, editor, Handbook of Chemistry and Physics, pp. 436-500.

³Ibid.

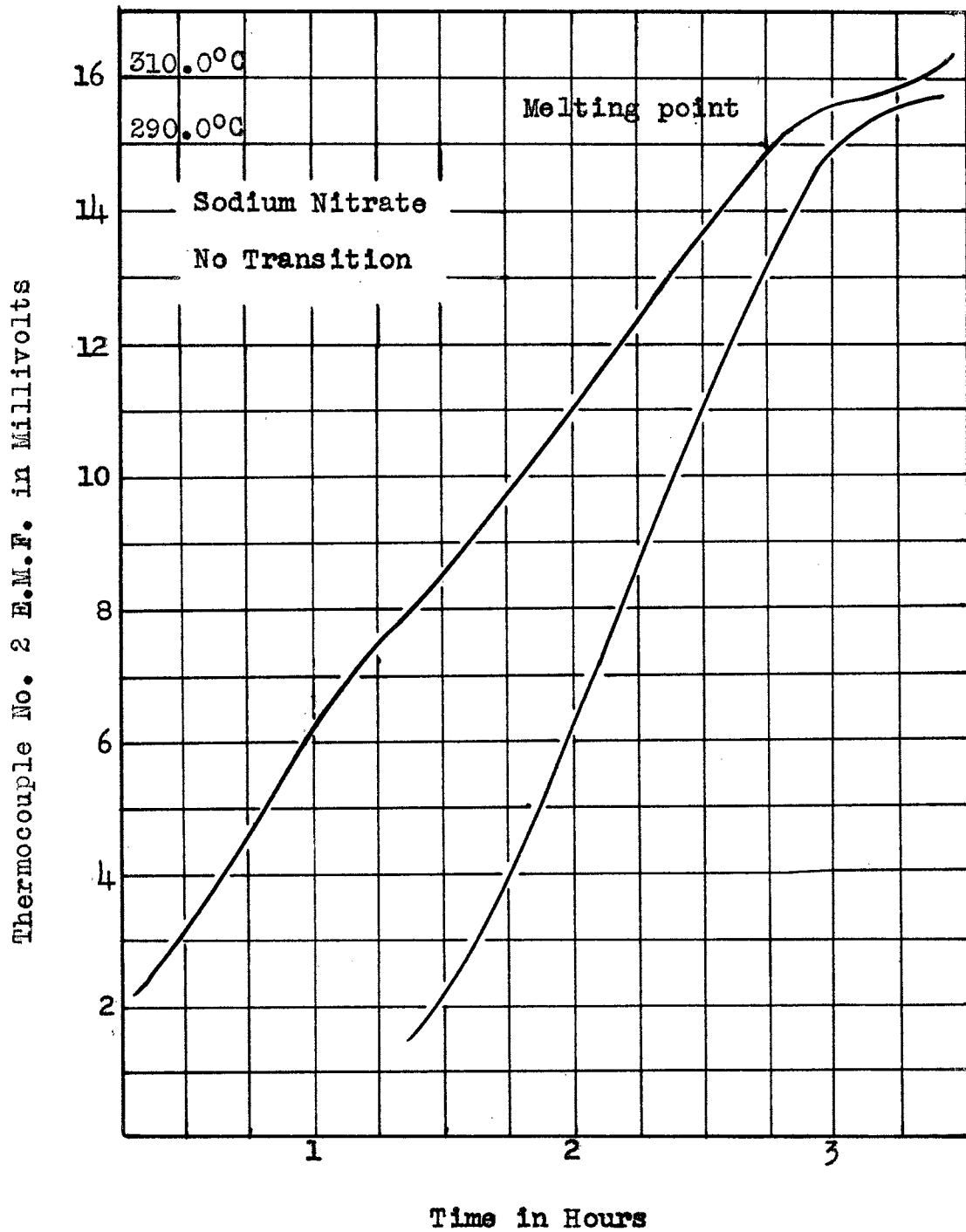


Fig. 10--Heating Curves for Sodium Nitrate

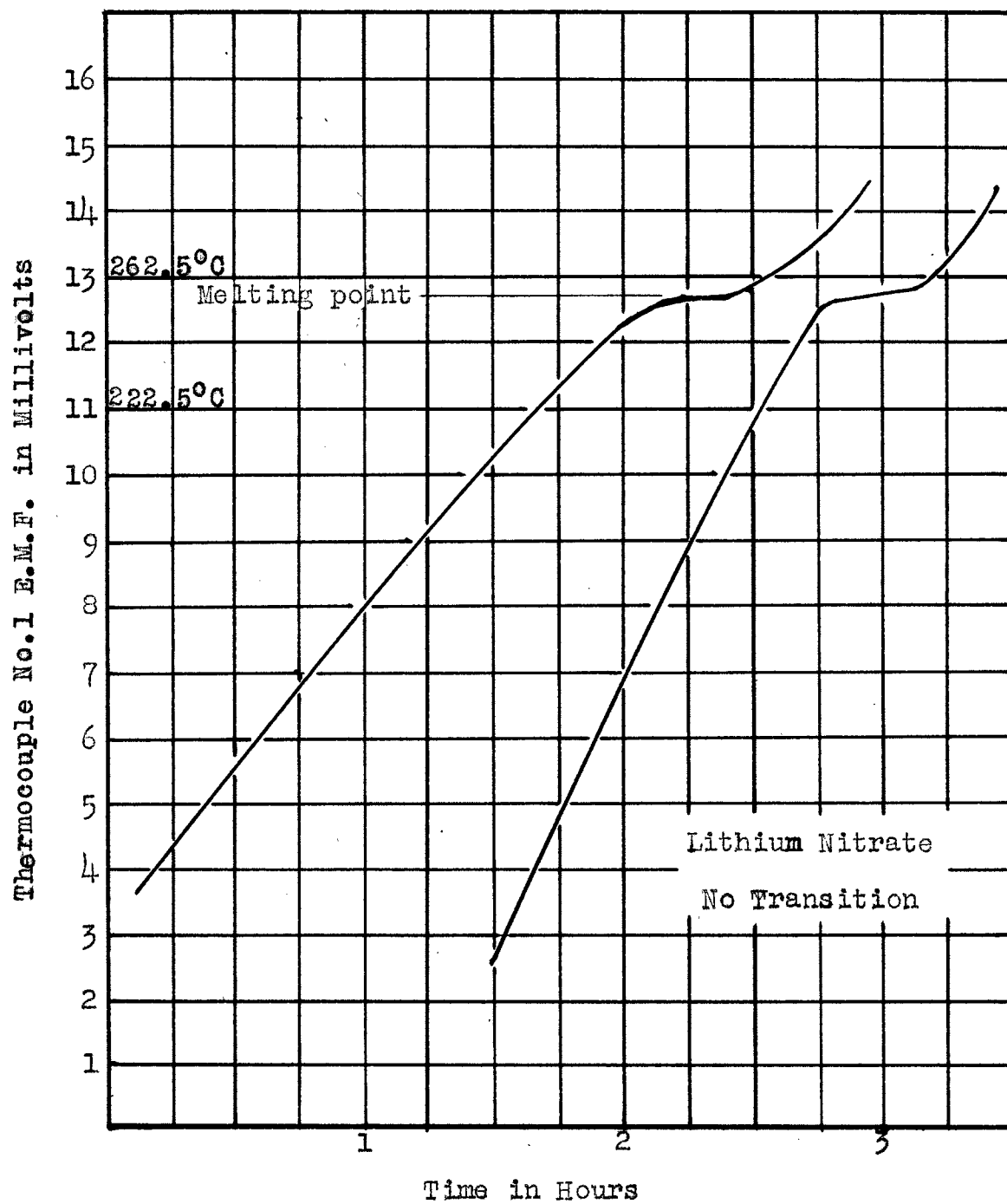


Fig. 11--Heating Curves for Lithium Nitrate

TABLE 3
A SUMMARY OF DATA AND RESULTS

Compound	Molecular Weight	Melting Point	Structure at 20 °C	Known Transition Temperature	Observed Transition Temperature
LiNO_3	68.95	255	trigonal
NaNO_3	85.01	306.8	trigonal or rhombic- hedral
KNO_3	101.1	334	rhombic or trigonal	126-130 ⁴	131.8
AgNO_3	169.89	212	rhombic	159.4 ⁵	160.1
$\text{Sr}(\text{NO}_3)_2$	211.65	570	cubic	433.8
$\text{Ba}(\text{NO}_3)_2$	261.38	592	cubic	538.8
$\text{Pb}(\text{NO}_3)_2$	331.23	470d	cubic or mono- clinic	379.8

⁴J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, p. 809.

⁵Ibid., Vol. III, p. 460.

CHAPTER IV

CONCLUSION

All the compounds that possessed transition points between room temperature and the melting point proved to be dimorphous. That is, they existed in two distinct crystalline forms in this temperature range.

Barium nitrate, strontium nitrate, and lead nitrate were found to have inversions of the type known as polytypy. In all three cases there was a sharp transition point which pointed to a complete rearrangement of the crystal lattice.

Sodium nitrate and lithium nitrate were not observed to pass through a distinct transition. Sodium nitrate is known to possess a gradual transition which is characteristic of the type known as polytropy.¹ At twenty degrees Centigrade the oxygen atoms are fixed around the nitrogen atom in sodium nitrate. At 270 degrees Centigrade the oxygen atoms are rotating around the nitrogen atom. The transition occurs somewhere between these two temperatures. It is possible that a transition of the polytypy class may

¹L.M. W. Barth, "Polymorphic Phenomena and Crystal Structure," The American Journal of Science, XXVII (April, 1934), 274.

occur below room temperature.² However, for sodium nitrate, Hissink³ tried to find a transition point between minus fifty degrees Centigrade and 270 degrees Centigrade and P.W. Bridgman⁴ investigated the material between twenty degrees and 200 degrees Centigrade. Negative results were obtained in both cases.

No transitions have been previously reported for strontium, barium, or lead nitrates; the transition temperatures observed during this investigation were between 379.8 degrees Centigrade and 538.8 degrees Centigrade. Such high temperatures were to be expected for divalent compounds. The explanation for this is the greater binding between the positive ion and the nitrate group, which was induced by the greater valence of the cation.

A higher transition temperature was noted to accompany larger atomic weights of the cation in each compound. Strontium nitrate was the lightest divalent compound investigated, and its transition temperature was lower, at 433.8 degrees Centigrade. Barium nitrate, which was

²R. C. Evans, An Introduction to Crystal Chemistry, pp. 255-256.

³J. W. Mellor, A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. II, p. 809.

⁴Ibid.

slightly heavier than strontium nitrate was observed to have a transition at 538.8 degrees Centigrade.

In the case of lead nitrate, which was the heaviest of all compounds studied, a lower transition temperature of 379.8 degrees Centigrade was noted. The reduced transition point was a result of the greater weight of the lead atom.⁵ This weight overbalanced the strengthening of the binding created by the increase in polarization described above and in Chapter I. Hence the total binding force between the lead and the nitrate group was reduced.

No new transition points were observed for the monovalent compounds studied. Without additional information no valid conclusions could be reached regarding them. For more definite conclusions to be drawn an X-ray study of all the above compounds would be highly desirable.

⁵Evans, op. cit., p. 22.

BIBLIOGRAPHY

Books

- Bragg, W. H., Bragg, W. L., The Crystalline State, Vol. I, New York, The Macmillan Company, 1934.
- Davey, W. P., A Study of Crystal Structure and Its Applications, New York, McGraw-Hill Book Company, 1934.
- Evans, R. C., An Introduction to Crystal Chemistry, London, Cambridge University Press, 1939.
- Hodgman, C. D., editor, Handbook of Chemistry and Physics, Cleveland, Chemical Rubber Publishing Company, 1947.
- Landolt-Bornstein, Physikalisch-Chemische Tabellen, Vol. I, Julius Springer, Berlin, 1923.
- Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vols. II, III, and VII, London, Longmans and Company, 1923.
- Rice, O. K., Electronic Structure and Chemical Binding, New York, McGraw-Hill Book Company, 1940.
- Smit, A., The Theory of Allotropy, translated by J. Smeath Thomas, London, Longmans Green and Company, 1922.
- Strong, John, Procedures in Experimental Physics, New York, Prentice Hall, Inc., 1938.
- Van Arkel, A. E., Molecules and Crystals in Inorganic Chemistry, London, Butterworths Scientific Publications, 1949.
- Weber, R. L., Heat and Temperature Measurement, New York, Prentice Hall, Inc., 1950.
- Wooster, W. A., A Textbook on Crystal Physics, London, Cambridge University Press, 1938.

Articles

- Barth, T. F. W., "Polymorphic Phenomena and Crystal Structure," American Journal of Science, Vol. XXVII (April, 1934), 273-286.
- Fredig, M. A., "High Temperature Crystal Chemistry of $AmBX_n$ Compounds with Particular Reference to Calcium Orthosilicate," The Journal of Physical Chemistry, XLIX (July, 1945), 537-553.
- Bruch, W. M., Spomer, H., "Calculation of Transition Energies of Polymorphous Molecular Crystals," Physical Review, XLII (1937), 324-330.
- Buerger, M. J., "The Kinetic Basis of Crystal Polymorphism," Proceedings of the National Academy of Science of the United States, XXII (1936), 682-685.
- Buerger, M. J., "The General Role of Composition in Polymorphism," Proceedings of the National Academy of Science of the United States, XXII (1936), 685-689.
- Buerger, M. J., Bloom, M. C., "Crystal Polymorphism," Zeits. fur Kristall., XCVI (1937), 182-200.
- Connell, L. F., Gammel, J. H., "Hysteresis Ranges of Polymorphic Transitions of Some Crystals," Acta Crystallographica, III (January, 1950), 75.
- Kracek, F. C., "Polymorphism of KNO_3 ," Journal of Physical Chemistry, XXXIV (1930), 225-247.

Unpublished Material

- Seale, Robert Lewis, "Polymorphism of Anhydrous Chlorates," Unpublished Master's Thesis, Department of Physics, University of Texas, 1950. Pp.51.