# MELTING POINT OF SEPARATED LITHIUM ISOTOPES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Julian Anthony Crawford
1958

# MELTING POINT OF
# SEPARATED LITHIUM ISOTOPES

by

Julian Anthony Crawford

AN ABSTRACT

Submitted to the College of Science and Arts
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Physics and Astronomy

1958

Approved ______________________________

# ABSTRACT

The melting points of the separated isotopes lithium-6 and lithium-7 were determined by a melting-wire technique. The samples were extruded at room temperature in the form of wires 0.4 mm in diameter and 3 cm in length. Samples were placed two at a time in an oil bath and the temperature was slowly raised through the melting point. Occurrence of melting was detected by interruption of a current through the samples. The difference in melting point of the two isotopes was found to be 0.23 ± 0.07 C-deg. The absolute melting points of the isotopes and of natural lithium were found to be: $Li^6$, 180.4 ± 0.2°C; $Li^7$, 180.7 ± 0.2°C; Li-natural, 180.7 ± 0.2°C. The melting point difference is smaller by a factor of ten than that predicted on the basis of the Lindemann theory. It is concluded that the lattice of the solid has become so imperfect at temperatures near the melting point that the Lindemann scheme affords a very poor description.

# MELTING POINT OF
# SEPARATED LITHIUM ISOTOPES

by

Julian Anthony Crawford

A THESIS

Submitted to the College of Science and Arts
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Physics and Astronomy

1958

## ACKNOWLEDGMENTS

I wish to express my appreciation to Professor D. J. Montgomery for his suggestion of this problem and for his guidance and encouragement throughout the work. I would also like to thank Professor B. H. Dickinson for his advice during the early stages of the work. The isotope loan fees were met in part by an All-College Research Grant awarded to Dr. J. C. Lee for 1954-55. Dean Thomas H. Osgood was instrumental in making this arrangement, and has otherwise encouraged and facilitated the program. Dr. P. S. Baker, of the Stable Isotope Research and Production Division of the Oak Ridge National Laboratory, has contributed generously of his facilities and experience in aiding the procurement and preparation of the separated isotopes. Partial support of this work was provided by a research contract granted to Michigan State University by the Metallurgy and Materials Branch of the Division of Research of the Atomic Energy Commission.

## TABLE OF CONTENTS

# I. INTRODUCTION

The production of electromagnetically-enriched isotopes by atomic-energy projects has made isotopic mass available as a new tool for the study of physical properties of many substances. The essential point in utilizing isotopes of the same element is that the mass can be changed while the atomic force field is kept almost exactly the same. The isotopic mass thus affords a powerful method for the verification and extension of theories of the properties of matter. This aspect of the production of isotopes was realized upon their discovery, but the low enrichments and the small mass differences of the isotopes then available prevented significant effects from appearing in phenomena other than gaseous or chemical. The discovery of deuterium and methods of producing it in quantity in the early 1930's made possible the measurement of strong isotopic effects resulting from the great relative mass difference of the hydrogen isotopes, and many physical measurements were made on deuterium and its compounds. The special nature of hydrogen, however, precluded the results from aiding the understanding of metals and most compounds.

The effect of isotopic mass on physical properties of metals is usually small. As early as 1919, Richards(1) reported that ordinary lead and uranium lead do not differ in their melting temperatures by more than about 0.06 C-deg, the uncertainty of his experimental measurements. However, the relative mass difference was only about one-half percent. The measurements by Soddy(2) on the densities of several isotopic species of lead gave negative results for the atomic volume to within an experimental accuracy of about 3 parts in 10,000. Johnson(3) suggested that the diffusion rate in solid metals should be influenced by atomic mass. His experiments show that the relative abundance of the various isotopes of nickel is altered by diffusion into copper in approximately the way that would be expected if the diffusion rate varies inversely with the square root of atomic mass. Chemla and Sue(4) have recently proposed that the isotopic enrichment obtainable by solid-state diffusion can be enhanced by the presence of an electric field. The isotopic effect on the superconducting transition temperature is appreciable, as discovered independently by Maxwell(5) and Reynolds(6) and their co-workers, and discussed by Fröhlich(7). The experimental evidence for an isotopic effect in superconductivity demonstrates the importance of the interaction of electrons and lattice vibrations in determining the behavior of superconducting material. Tuyn(8) and Justi(9) studied the electrical resistances of uranium lead and normal lead at several temperatures between 7°K and 273°K. The results of the two investigators are contradictory, so that it is difficult to decide whether an isotopic effect is indicated or not. Justi's results indicate an isotopic effect opposite in sign to that expected on the Grüneisen theory. However, his results depend upon a more limited number of measurements than do those of Tuyn. The results obtained by Tuyn, though not analyzed as to evidence of an isotopic effect, indicate a somewhat better agreement with the predictions of the Grüneisen theory than could be accounted for by random scatter of the data.

More recently, McCaldin(10) in 1954 reported studies of the isotopic effect on thermoelectric power, temperature coefficient of resistance, and the alpha-gamma allotropic transformation in $Fe^{54}$ and $Fe^{57}$. The small relative mass difference prevented him from getting conclusive results on the thermoelectric power and the allotropic transformation, but he was able to confirm the existence and the direction of the change in resistance. Covington and Montgomery(11) have measured the difference in lattice constants of $Li^6$ and $Li^7$ and Snyder, Leffler and Montgomery(12) have determined the difference in electrical conductivity. Montgomery, Leffler, and Smith(13) found a difference in the thermoelectric power of the separated isotopes of lithium in conformity with the theoretical prediction of Sondheimer(14).

Perhaps the region of phenomena where studies with varying isotopic mass can make their most useful contribution is that where the nucleus moves from one position of quasi-equilibrium to another, such as in solid or molten lithium around the melting point. In view of the great need for adequate understanding of melting phenomena, it was decided that a measurement of the difference in melting points between the two isotopes might be particularly valuable. Moreover, if the difference is substantial, it would be worthwhile to determine the temperature-composition phase-equilibrium diagram for the separated lithium isotopes in the solid-liquid region. Apart from its intrinsic interest, establishment of this diagram would show whether an isotope-enrichment process could be based on fractional crystallization from the melt.

The present work is limited to the determination of the melting-point difference, together with an estimation of the absolute values of the melting points. These last data are themselves useful for the light they might shed on the discrepancies appearing in the literature as to the melting point of natural lithium.

## II. EXPERIMENTAL PROCEDURES

### A. Choice of Material

Prior to the development of production-type mass spectrographs at the Oak Ridge National Laboratory (ORNL) and other installations of this kind, it was not possible to obtain bulk quantities of highly-enriched stable isotopes other than those of hydrogen. In early 1946 ORNL started a program for the enrichment of all naturally-occurring stable isotopes, and by the end of that year had begun shipments of samples. At present stable isotopes of the majority of the elements are available for sale or, in some cases, for loan. Among the elements not supplied are those with only one naturally-occurring stable isotope; the majority of the radioactive elements; the inert gases; certain rare earths; and a few other, such as the highly toxic ones.

The investigation of the melting point of separated isotopes was part of a broad program using the isotopic mass as a probe for the study of the solid state. Lithium, with natural isotopes Li-6 and Li-7 in reasonable abundance ratio (Li-6, 7.52%; Li-7, 92.48%), and a large relative mass difference $[(\text{Li-7} - \text{Li-6})/\frac{1}{2}(\text{Li-7} + \text{Li-6}) = 14\%]$, was selected as the most promising material for the initial studies. Examination of the ORNL Inventory of Electromagnetically Enriched Isotopes showed that both of these isotopes were available in high enrichments and in adequate amounts.

From the standpoint of theory, lithium is attractive in that it has a rather simple structure, both atomic and crystalline. It has low atomic number, and it crystallizes in the body-centered cubic form at all but the lowest temperatures. From the standpoint of experiment, on the other hand, lithium offers difficulties in its handling because of its high chemical reactivity. Nonetheless, it was decided that the advantages of high relative mass difference, ready availability, and simplicity of structure outweigh the disadvantages of experimental difficulties.

## B. Procurement of Samples

When the present work was begun in 1955, electromagnetically-separated isotopes were available for distribution only on loan as approved by the U. S. Atomic Energy Commission. Requests for loan were made to the AEC by using Form AEC-100. The requested amount of Li-6, the rarer isotope, was 500 milligrams; that of Li-7, the more common isotope, 1000 milligrams. For samples of this size the loan fee was $50 per sample. For preparation of the lithium in the elemental form, a special service charge of $60 per sample was made. The total charge was thus $220, which was met by an All-College Research Grant, Physics and Astronomy No. 453, initially given to Dr. J. C. Lee for the academic year 1954-55. The samples were shipped from ORNL on 19 May 1955. When these samples arrived, it was found that the concentrations of impurities were too high to allow meaningful results to be obtained. The impurities appear to be introduced during the thermochemical reduction of lithium chloride to elemental lithium by means of metallic barium in stainless steel containers. Dr. P. S. Baker, of ORNL, who supervised the preparation of the lithium, suggested that vacuum distillation would be the best method of purifying the metallic lithium, and agreed to have his organization perform the distillation, at the nominal charge of $50 per sample. The material was accordingly returned for purification about 22 July 1955, without any measurements having been made on it. The redistilled material was shipped from ORNL on 3 November 1955, in approximately double the amount initially requested, following the suggestion of Dr. Baker that it would be advantageous to have additional material to make up for the attrition during processing if further distillation were to be attempted. The redistilled Li-6 sample, SS 5(a), was of low isotopic purity (96.1% Li-6, 3.9% Li-7), and was not used for melting-point determination. The analysis of the redistilled Li-7 sample is as follows:

Li-7 Lot No. 668(j) - redistilled 1028 mg + 1000 mg

Isotopic Analysis (mass and atomic percent):

Li-6, 0.2 ± 0.1%; Li-7, 99.8 ± 0.1%

Spectrographic Analysis (element and weight percent, precision ± 50%; T = trace):

| | | | | | |
|---|---|---|---|---|---|
| Ag | T | Fe | 0.3 | Ni | 0.02 |
| Al | 0.02 | K | 0.02 | Pb | 0.01 |
| Ba | 0.01 | Mg | 0.02 | Si | <0.05T |
| Ca | 0.2 | Mn | <0.01 | Sn | <0.01 |
| Cr | <0.01T | Mo | <0.01 | Sr | <0.01 |
| Cu | 0.01 | Na | 0.02 | V | <0.01 |

The spectroscopic analysis shows a large amount of iron present (Fe = 0.3%). It is believed that this high amount can be largely discounted in view of the sampling procedure, which involved cutting the material with a steel knife. The only other impurity in high concentration is calcium (0.2%). The source is unknown. In the vacuum distillation, the hardest element to remove is strontium, because of the similarity of its vapor-pressure curve to that of lithium. It is gratifying to note that it appears only in very slight amount. It is this Li-7 sample (668j) which was used for melting point determinations.

During the progress of the experiments, the AEC policy on distribution of stable isotopes was changed, and it became possible to purchase certain samples, in particular Li-6 of high isotopic purity. An allocation for 3 grams of 99 percent Li-6 as well as one for 10 grams of 96 percent Li-6, was authorized about 31 January 1956. The Li-6 sample, from Lot SS 5(b) containing 99.3% Li-6, was ordered about 1 March and shipped 15 March. The cost was $30 per gram, plus $15 handling fee, for a total of $105. The analysis, as supplied by ORNL, is as follows:

Li-6 Lot No. SS 5(b) 3000 mg

Isotopic Analysis:

Li-6, 99.3 ± 0.2%; Li-7, 0.7 ± 0.1%

Spectrographic Analysis (element and weight percent, presumed precision ± 100%):

| | | | | | |
|---|---|---|---|---|---|
| Al | <.01T | Fe | .05 | Pb | <.01 |
| Ba | .01 | K | <.01 | Sn | <.01 |
| Be | <.001 | Mg | .01 | Sr | .01 |
| Ca | .25 | Mn | <.01 | V | <.01 |
| Cr | <.01FT | Na | .02 | Zn | <.25 |
| Cu | .02 | Ni | <.01 | | |

It is this Li-6 sample SS 5(b) which was used for melting-point determinations.

The natural lithium was produced by the Lithium Corporation of America, Minneapolis. It is their low-sodium grade, in the form of 3/8-inch diameter rods, with the following specifications:

| | |
|---|---|
| Na | 0.005% |
| K | 0.01 |
| Ca | 0.02 |
| N | 0.06 |
| Fe | 0.001 |

The isotopic analysis is that of ordinary natural lithium.

Mr. Theodore L. Brown and Professor Max T. Rogers, of the Chemistry Department of Michigan State University, kindly furnished the natural lithium and the information on its specifications for the initial experiments. Larger amounts were subsequently ordered from the Lithium Corporation of America.

## C. Preparation of Specimens

All lithium samples were shipped and stored in oil. Nevertheless, they became coated with a dark layer, probably lithium nitride for the most part. The coating can be scraped or cut off and the clean metal obtained, provided the fresh surface is protected either by keeping it in a nonreacting atmosphere (e.g., carbon dioxide) or by covering it with a nonreactive substance (e.g., petrolatum).

The lithium was extruded from a steel press in the form of 0.4-mm diameter wire. It emerged through a layer of petrolatum which forestalled surface contamination until the samples were inserted in the temperature bath. The samples averaged 2.5 cm in length, and were handled with petrolatum-coated tweezers while being inserted in the holder.

The later experiments were run with annealed material. Prior to being inserted into the press, the lithium was heated to its melting point in a beaker of mineral oil and then allowed to cool slowly back to room temperature. This procedure resulted in more uniform wires.

## D. Experimental Apparatus

The apparatus for this experiment can be divided into three parts: the temperature bath, the sample holder, and the measuring devices. Photographs of the apparatus are shown in Figures 1 and 2.

The temperature bath consisted of a series of containers and insulation as shown in Figure 3. There were two different oil baths, the small one containing mineral oil in which the samples were melted, and the large one containing low-volatility motor oil in which the heaters were immersed. A pair of glass jars, nested one within the other and separated by a layer of sand, served to separate the two oil baths and provide a means of heat transfer between them. The large bath, contained in an iron tank, was enclosed in a box with sides of asbestos board. The tank was insulated on the sides and the bottom with several inches of loosely packed vermiculite. A ventilating fan removed the fumes from the hot oil. Two Watlow No. We-123, 115-volt, 1000-watt immersion heaters were used to heat the main oil bath. They were controlled by a 100 - 550° F thermostat. The top of the main tank was covered with a sheet-metal lid which contained a large variable-speed stirrer. Insulation of the oil bath from the room was completed by covering the lid with several layers of glass-wool padding and putting an asbestos-board cover on the box.

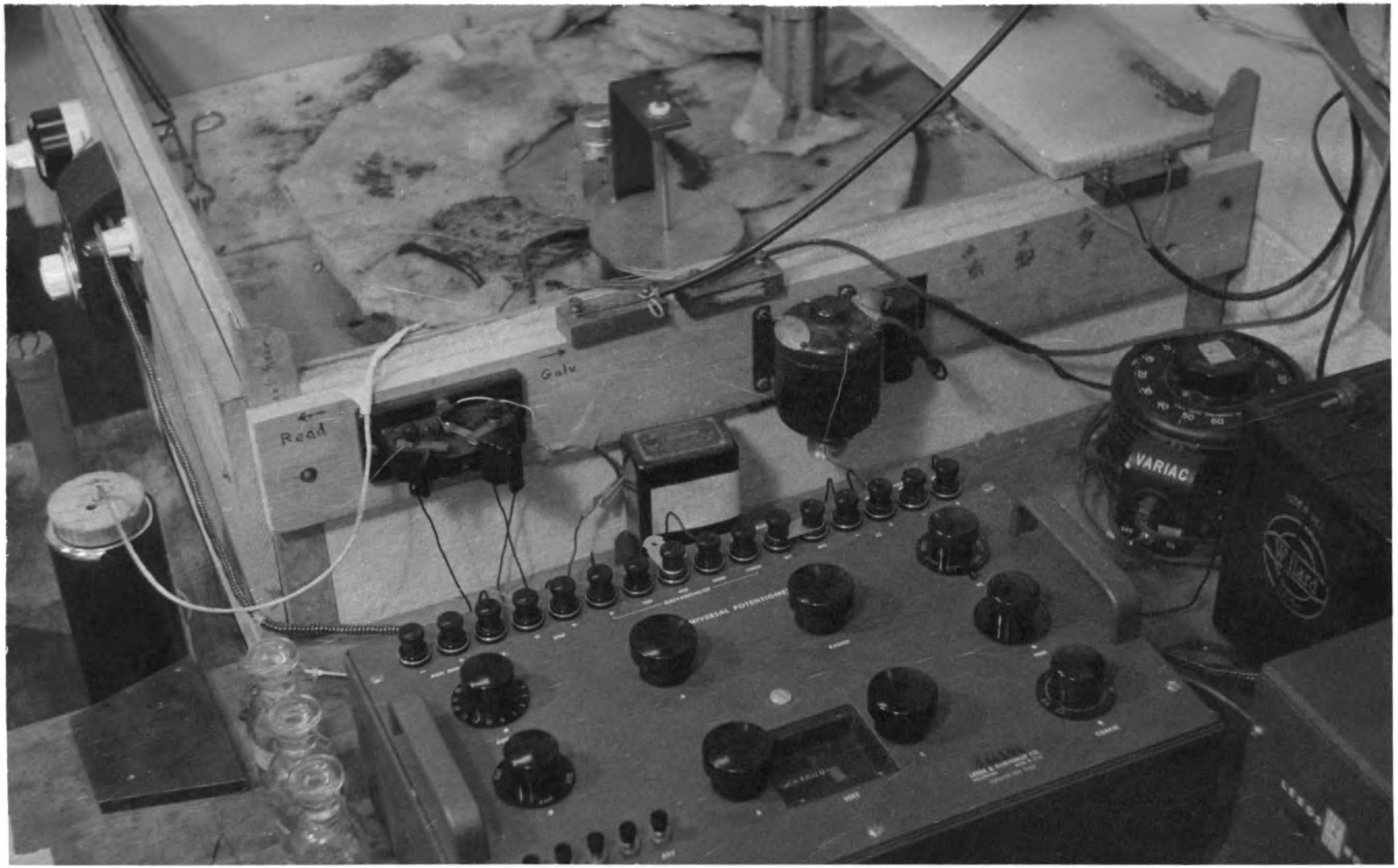

Fig. 1. - Apparatus

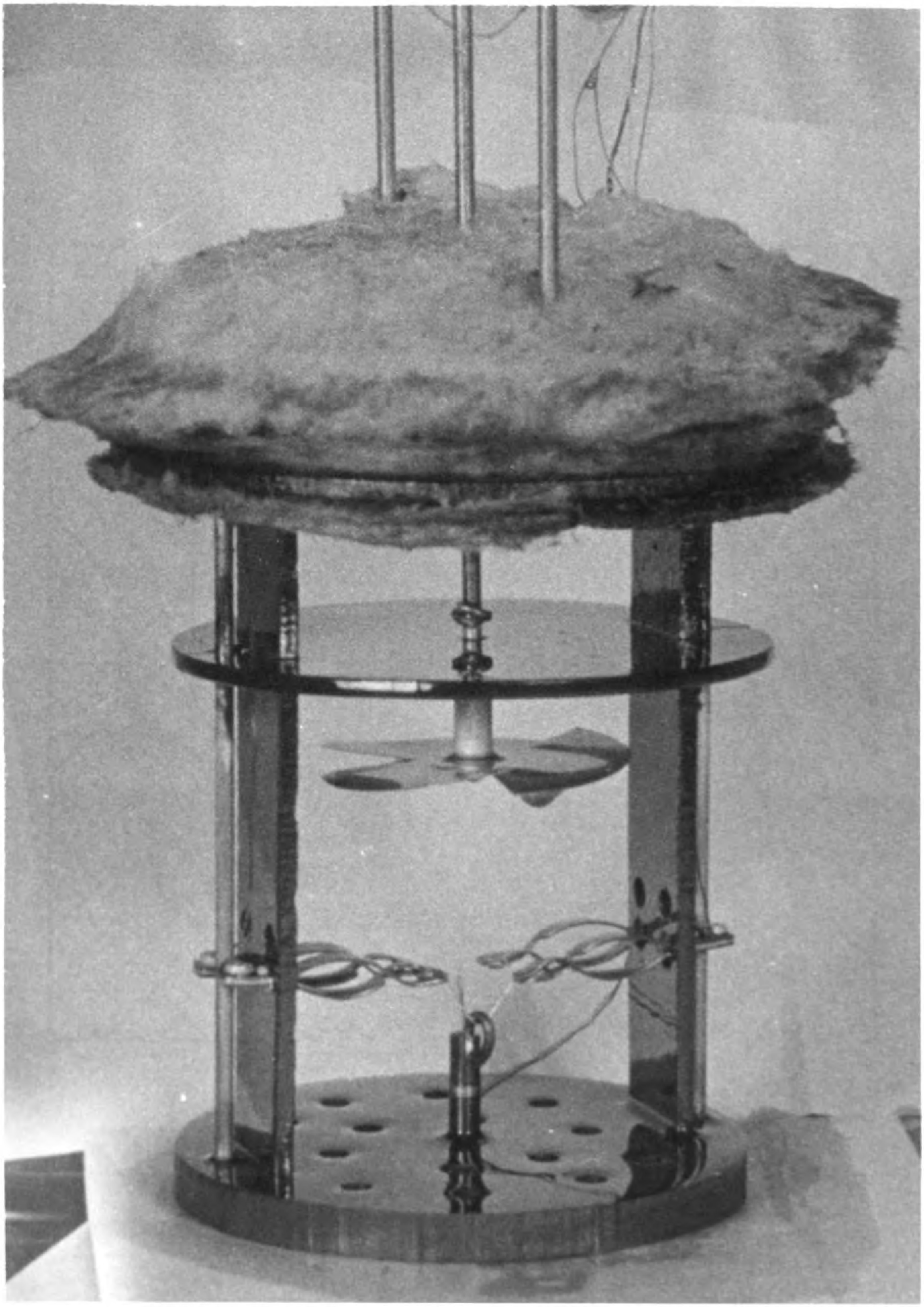

Fig. 2.- Sample holder

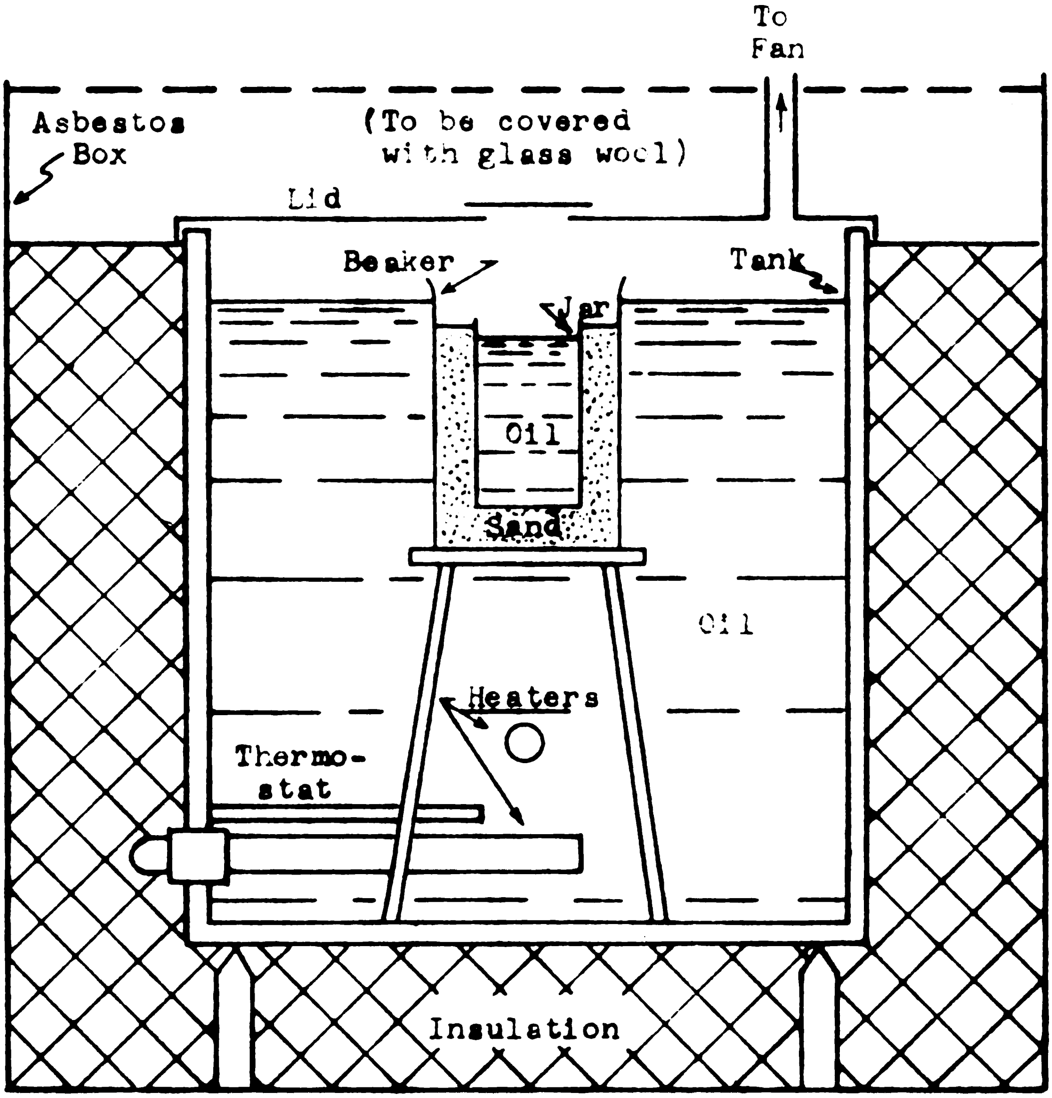

Fig. 3.-Diagram of temperature bath.

Initially a sample holder was built to carry five lithium wires simultaneously. Each of the five positions was identified by a separate pulse signal which occurred when the sample wire broke. However, consistent results could not be obtained with this arrangement. A two-wire holder was then built with particular attention paid to obtaining uniformity of conditions for the pair of samples.

A sketch of the sample holder is shown in Figure 4. The frame was constructed from 1/4-inch and 1/8-inch black phenolic plastic. The holder was designed so that it could be inserted directly into the temperature bath from outside the apparatus without having to remove any insulation. The wire samples were suspended between pairs of small spring clips projecting from the side of the holder toward the center. The jaws of the clips were located equidistant from the cylindrical center line of the holder. On this center line, and level with the jaws of the clips, was located one junction of a thermocouple. Directly above the center of this arrangement was a small slow-speed stirrer to minimize thermal gradients in the oil.

The spring clips formed part of a pulse circuit used to detect the occurrence of melting. The insertion of a lithium-wire sample between a pair of clips closed the circuit, allowing a 1-ma current to flow through the sample. A small hanger was placed on each sample wire to

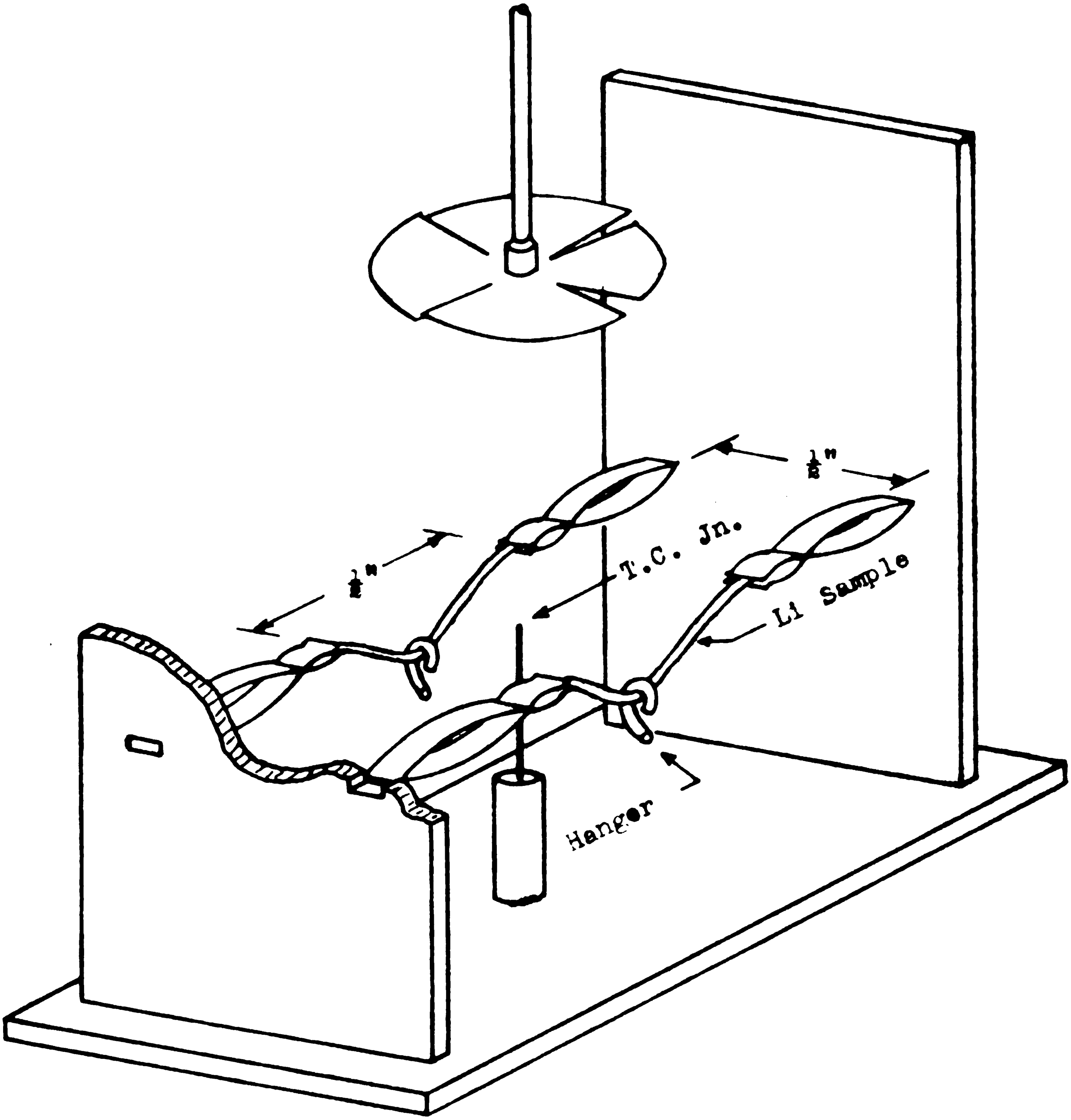

Fig. 4.-Diagram of sample holder.

overcome the effect of the surface film in preventing breakage of the sample. When the sample melted and opened the circuit, a small pulse was recorded on the temperature record.

Figure 5 shows a block diagram of the measuring circuit. A copper-constantan thermocouple made from 27-gauge wires was used to measure the temperature. The copper leads were covered with Teflon to provide durable insulation in the hot oil. A mixture of crushed ice and water provided a reference temperature. The thermocouple had a sensitivity of about 55 microvolts per degree at 180° C. A Leeds and Northrup No. 7553 type K-3 Universal Potentiometer (stated accuracy 0.02% of voltage) backed off most of the thermocouple voltage, which was about 8000 microvolts at the melting point. Copper leads and copper or brass contacts were used in the potentiometer and the switch circuits to reduce the possibility of spurious thermal voltages. The voltage difference between the thermocouple and the potentiometer was fed into a Leeds and Northrup No. 9835 B Stabilized D-C Microvolt Amplifier (stated accuracy 0.4% of the reading). The amplified signal drove a Leeds and Northrup Model S, 60000 Series Speedomax type-G Recorder (stated accuracy 0.5% of full scale). The pulse circuit previously mentioned was connected directly to the input of the recorder. This combination offered a continuous record of temperature

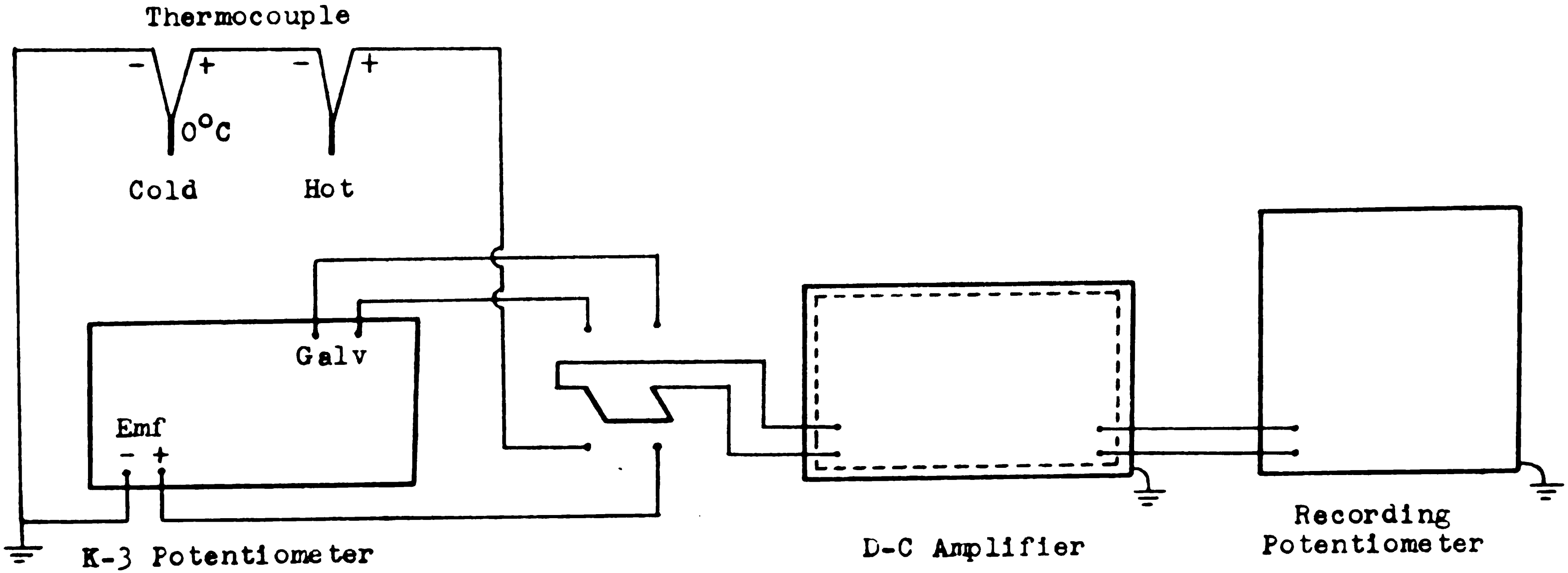

Fig. 5.-Block diagram of measuring circuit.

against time, and gave an automatic indication of melting with a maximum sensitivity of 50 μv (less than one degree) full scale. It was possible to detect accurately differences as small as ½ μv, or less than 0.01° C. Our estimate of the overall accuracy of the temperature measurement is ± 0.04° C. A sample strip chart record is shown in Figure 6.

### E. Thermocouple Calibration

The copper-constantan thermocouple was calibrated against a Leeds and Northrup No. 8163 Thermohm platinum resistance thermometer. The hot junction of the thermocouple was fastened alongside the coil of the resistance thermometer, and the combination was immersed to a depth of 9 or 10 inches in mineral oil surrounded by the oil of the main temperature bath. The thermocouple remained in the same recording circuit as previously described. The resistance thermometer was connected through a Leeds and Northrup No. 8068 Mercury Commutator switch to a Leeds and Northrup No. 8067 Mueller Temperature Bridge. The resistance and the emf were measured for a series of equilibrium temperatures ranging from 178° C to 182° C. A plot of resistance against temperature was made using the constants of the resistance thermometer. From this plot and the experimental data the variation of thermocouple emf with temperature was determined, as shown in the calibration curve of Figure 7.

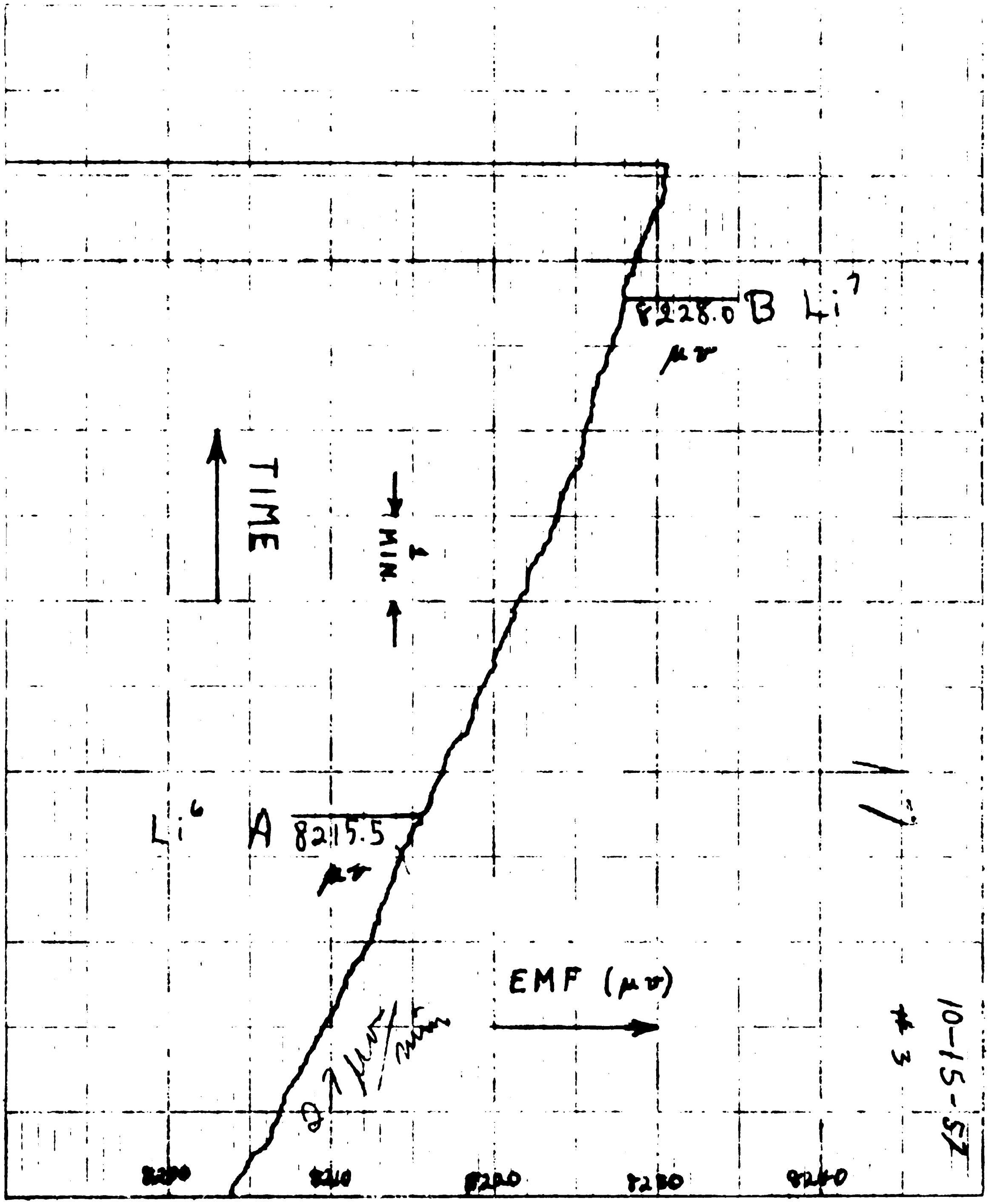

Fig. 6.-Sample Strip Chart Record.

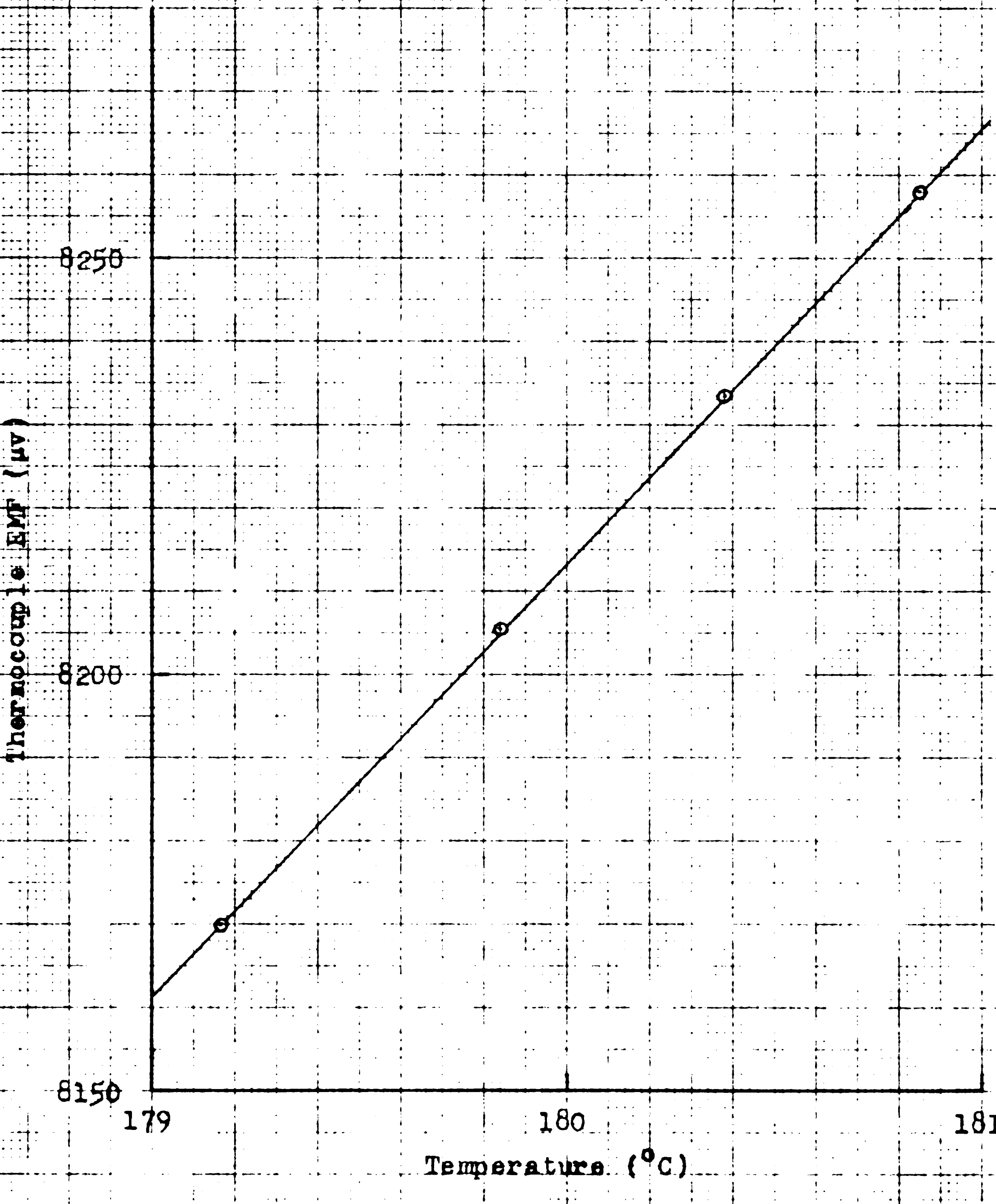

Fig. 7.-Thermocouple calibration curve.

## III. THEORETICAL CONSIDERATIONS

When heat is supplied to a solid, there is an increase in the amplitude of vibration of the atoms about their equilibrium positions. Naively stated, each atom then requires more room, and consequently the solid expands. As the temperature is increased, the long-range interatomic forces become ineffective and atoms begin leaving their original equilibrium positions. When this happens frequently enough, the solid loses its rigidity and melts.

In 1910 Lindemann(15) postulated a relation between the Einstein characteristic frequency $\nu_E$ and the melting temperature $T_m$. He assumed that a solid consists of a set of simple harmonic oscillators arranged in a tetrahedral lattice, and that melting occurs when the amplitude of thermal vibration of the atoms attains one-half the separation of nearest neighbors minus the sum of their radii; that is, the solid melts when the atoms touch. Lindemann assumed simply that the atomic radius is some constant fraction of the atomic spacing. These assumptions are equivalent to the assumption that at the melting point the mean amplitude of thermal vibration $X_m$ is a constant fraction a of the interatomic distance d; that is,

$$X_m = a d \tag{1}$$

In a tetrahedral configuration, d is related to the atomic volume V by

$$d = \sqrt[6]{2}\ \sqrt[3]{V/N} = \sqrt[6]{2}\ \sqrt[3]{A/\rho N} \qquad (2)$$

where N is Avogadro's number, A is atomic mass and $\rho$ is the density.

For a classical harmonic oscillator the average total energy is

$$\bar{E} = \frac{1}{2} b X_{max}^2 = kT \qquad (3)$$

where T is the absolute temperature, k is Boltzmann's constant, $X_{max}$ is the maximum amplitude of the oscillator at temperature T and b is the force constant which depends only on the atomic field. Quantum mechanically, the average total energy would be

$$\bar{E} = \frac{1}{2} b X_{max}^2 = \frac{1}{2} h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \qquad (4)$$

where h is Planck's constant and $\nu$ is the frequency of vibration. Figure 8 is a plot of the mean vibrational energy $\frac{1}{2}bX^2_{max}$ against kT (both quantities are normalized through division by $h\nu$ for Li-7). At absolute zero the difference in zero-point energy shifts the curve for Li-6 about 8% above that for Li-7. As the temperature increases, the difference becomes smaller, approaching zero at high temperatures. Covington and Montgomery(11) have used this model to account for the difference in lattice constants of Li-6 and Li-7.

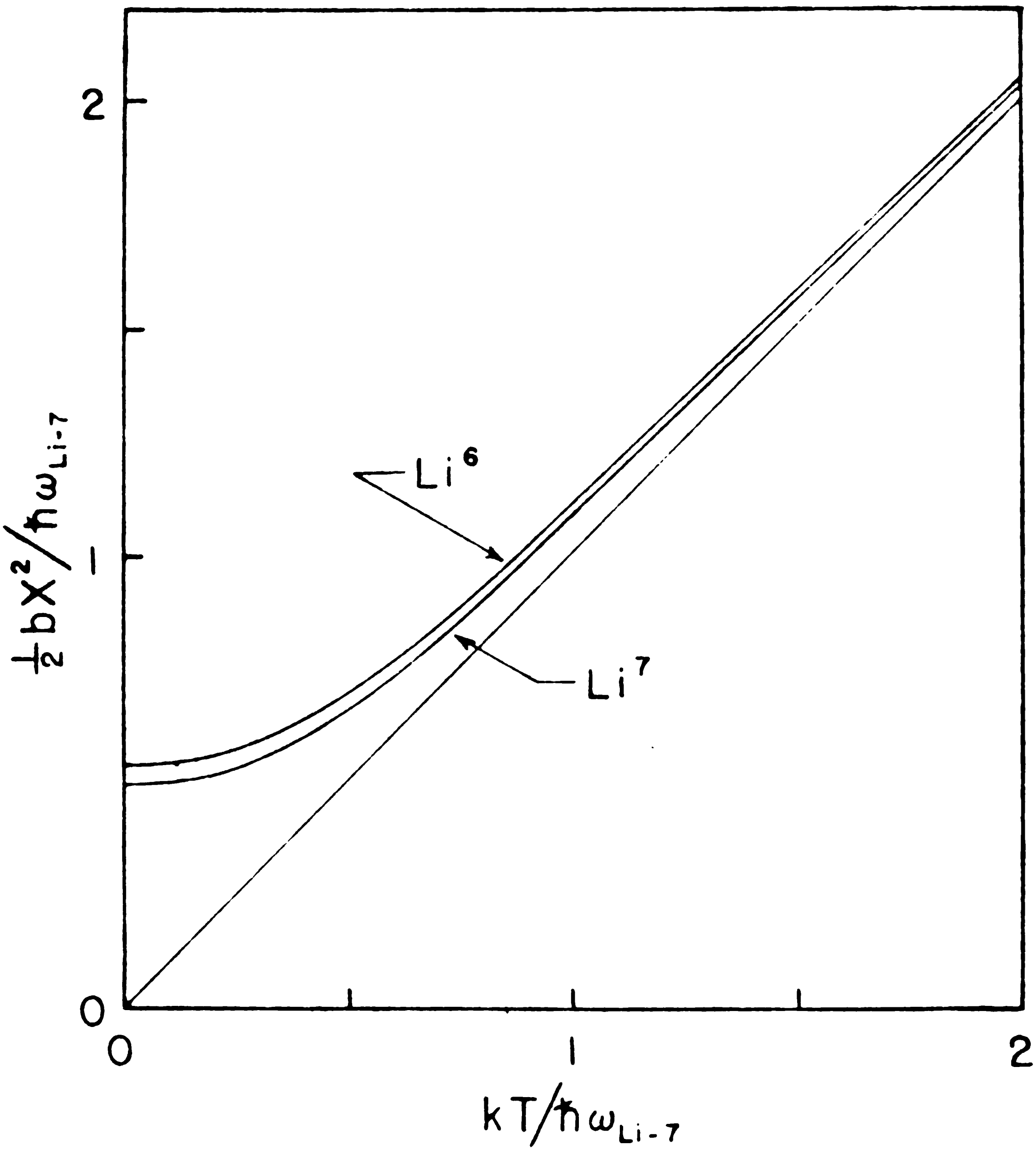

Fig. 8.-Plot of the mean vibrational energy $\frac{1}{2}bX^2_{max}$ against kT (both quantities normalized with respect to $\hbar\omega_{Li\text{-}7}$).

Under the assumption that the mean vibrational amplitudes are equal at the melting point, the intersection of a horizontal line with the curves in the neighborhood of the melting point for natural lithium gives the melting points of the individual isotopes. To get a value analytically for the difference in melting points equation (4) is written separately for each isotope and the right-hand sides are equated. The result can be solved numerically for $\Delta T_m$, the melting point difference. With $322^{o}$K for the Einstein characteristic temperature, and $453^{o}$K for the melting point of lithium, the predicted temperature difference $\Delta T_m$ turns out to be about 3 K-deg.

# IV. RESULTS AND DISCUSSION

The results of the measurements are given in Table I. Here the first column gives the date (in 1957) on which the experiment was performed. The next three columns give the thermal electromotive force between the hot junction of the copper-constantan thermocouple and its cold junction maintained at 0°C, when breaking of the various lithium wires occurs. The fifth column lists the observed differences in thermocouple voltages between Li-6 and Li-7 samples whenever the samples tested were of these materials; no entry is made for the cases where both wires were of the same material, or where Li-nat was under test. The sixth column gives the average heating rate, expressed in rate of rise of thermocouple voltage, in the neighborhood of the melting point. The seventh column lists the sample-wire diameter, and the last column gives the weight of the hanger used to insure breaking upon melting. The data are broken into sets, as indicated by subheadings. In a few cases some serious anomaly existed in the data, and such points were discarded in analyzing the data. These points are indicated by an "x" immediately preceding column 1.

## TABLE I

## EXPERIMENTAL DATA ON MELTING POINTS OF LITHIUM

| Date | Thermocouple Voltages | | | | Heating | Wire | Hanger |
|---|---|---|---|---|---|---|---|
| Date 1957 | Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Heating Rate (μv/min) | Wire Diam. (mm) | Hanger Weight (mg) |
| Standard Measurements, 400 mg | | | | | | | |
| 6-7 | 8220 | 8228 | - | 8 | 5.6 | 0.4 | ~ 400 |
| 6-7 | 8226 | 8234 | - | 8 | 3.5 | 0.4 | ~ 400 |
| 6-7 | 8218 | 8223 | - | 5 | 4.0 | 0.4 | ~ 400 |
| 6-10 | 8225 | 8235 | - | 10 | 3.8 | 0.4 | ~ 400 |
| 6-10 | 8219 | 8233 | - | 14 | 2.5 | 0.4 | ~ 400 |
| 6-10 | 8219 | 8228½ | - | 9½ | 2.2 | 0.4 | ~ 400 |
| 6-12 | 8217 | 8232 | - | 15 | 4.2 | 0.4 | ~ 400 |
| 6-12 | 8215 | 8225 | - | 10 | 1.6 | 0.4 | ~ 400 |
| 6-12 | 8218 | 8231 | - | 13 | 4.0 | 0.4 | ~ 400 |
| 6-12 | 8219 | 8232 | - | 13 | 5.0 | 0.4 | ~ 400 |
| 6-12 | 8218 | 8232 | - | 14 | 2.6 | 0.4 | ~ 400 |
| 6-13 | 8216 | 8228 | - | 12 | 3.8 | 0.4 | ~ 400 |
| 6-13 | 8215<br>8217 | - | - | - | 3.4 | 0.4 | ~ 400 |
| 6-13 | - | 8202<br>8228 | - | - | 4.5 | 0.4 | ~ 400 |
| 6-13 | - | - | 8222<br>8229 | - | 4.2 | 0.4 | ~ 400 |
| 6-13 | - | - | 8228<br>8230 | - | 5.0 | 0.4 | ~ 400 |
| 6-14 | - | - | 8228<br>8231 | - | 3.2 | 0.4 | ~ 400 |
| 6-14 | 8216 | - | 8230 | - | 2.8 | 0.4 | ~ 400 |

TABLE I - Continued

| Date 1957 | Thermocouple Voltages Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Heating Rate (μv/min) | Wire Diam. (mm) | Hanger Weight (mg) |
|---|---|---|---|---|---|---|---|
| 6-14 | - | 8230 | 8231 | - | 2.2 | 0.4 | ~ 400 |
| 6-14 | 8212 | 8216 | - | 6 | 7.0 | 0.4 | ~ 400 |
| 6-14 | 8216 | 8233 | - | 17 | 2.6 | 0.4 | ~ 400 |
| X 10-8 | 8160 | 8186 | - | 26 | 6.7 | 0.4 | ~ 400 |
| 10-8 | 8206 | 8218 | - | 12 | 9.5 | 0.4 | ~ 400 |
| 10-8 | 8213 | 8224 | - | 11 | 3.6 | 0.4 | ~ 400 |
| 10-9 | - | - | 8221<br>8227 | - | 3.3 | 0.4 | ~ 400 |
| 10-10 | - | - | 8213<br>8228 | - | 2.7 | 0.4 | ~ 400 |
| 10-10 | 8214<br>8216½ | - | - | - | 5.5 | 0.4 | ~ 400 |
| 10-10 | - | 8225<br>8228½ | - | - | 2.9 | 0.4 | ~ 400 |
| 10-10 | 8213½<br>8216 | - | - | - | 5.3 | 0.4 | ~ 400 |
| 10-12 | - | 8226½<br>8226½ | - | - | 4.9 | 0.4 | ~ 400 |
| 10-12 | 8210<br>8214 | - | - | - | 5.7 | 0.4 | ~ 400 |
| 10-12 | 8210½<br>8212 | - | - | - | 3.9 | 0.4 | ~ 400 |
| 10-12 | 8213½ | 8226½ | - | 13 | 3.0 | 0.4 | ~ 400 |
| 10-12 | 8213½ | 8227½ | - | 14 | 5.1 | 0.4 | ~ 400 |
| 10-12 | 8209½ | 8225½ | - | 16 | 5.8 | 0.4 | ~ 400 |
| 10-15 | 8217 | 8229 | - | 12 | 4.0 | 0.4 | ~ 400 |

TABLE I - Continued

| | Thermocouple Voltages | | | | | | |
|---|---|---|---|---|---|---|---|
| Date 1957 | Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Heating Rate (μv/min) | Wire Diam. (mm) | Hanger Weight (mg) |
| 10-15 | 8208 | 8224½ | - | 16½ | 2.6 | 0.4 | ~ 400 |
| 10-15 | 8215½ | 8228 | - | 12½ | 2.7 | 0.4 | ~ 400 |
| 10-15 | 8218 | 8231 | - | 13 | 3.7 | 0.4 | ~ 400 |
| 10-16 | 8216½ | 8228½ | - | 12 | 3.9 | 0.4 | ~ 400 |
| 10-16 | 8215½ | 8220½ | - | 5 | 1.6 | 0.4 | ~ 400 |
| 10-17 | 8211<br>8220½ | - | - | - | 4.4 | 0.4 | ~ 400 |
| X 10-17 | 8197<br>8197 | - | - | - | 2.0 | 0.4 | ~ 400 |
| 10-17 | 8205½<br>8206½ | - | - | - | 3.6 | 0.4 | ~ 400 |
| 10-21 | 8212<br>8214½ | - | - | - | 4.6 | 0.4 | ~ 400 |
| 10-21 | - | 8224<br>8229 | - | - | 4.5 | 0.4 | ~ 400 |
| 10-21 | - | 8226<br>8228 | - | - | 2.1 | 0.4 | ~ 400 |
| 10-23 | 8218½<br>8221½ | - | - | - | - | 0.4 | ~ 400 |
| 10-26 | 8216½<br>8220½ | - | - | - | 7.4 | 0.4 | ~ 400 |
| 10-26 | 8220½<br>8224 | - | - | - | 3.8 | 0.4 | ~ 400 |
| 10-26 | 8217<br>8219 | - | - | - | 5.8 | 0.4 | ~ 400 |
| 10-26 | 8211½<br>8214½ | - | - | - | 6.3 | 0.4 | ~ 400 |
| 10-26 | 8213½<br>8217 | - | - | - | 6.0 | 0.4 | ~ 400 |

TABLE I - Continued

| | Thermocouple Voltages | | | | Heating | Wire | Hanger |
|---|---|---|---|---|---|---|---|
| Date 1957 | Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Rate (μv/min) | Diam. (mm) | Weight (mg) |
| 10-29 | - | 8227<br>8228 | - | - | 3.1 | 0.4 | ~ 400 |
| 10-29 | - | 8229<br>8229 | - | - | 6.0 | 0.4 | ~ 400 |
| 10-29 | - | 8223½<br>8227½ | - | - | 3.2 | 0.4 | ~ 400 |
| 10-29 | - | 8228½<br>8228½ | - | - | 6.0 | 0.4 | ~ 400 |
| 10-30 | - | - | 8222<br>8227½ | - | 6.6 | 0.4 | ~ 400 |
| 10-30 | - | - | 8226½<br>8229½ | - | 6.0 | 0.4 | ~ 400 |
| 10-30 | - | - | 8222½<br>8228 | - | 6.6 | 0.4 | ~ 400 |
| 10-30 | - | - | 8217<br>8222 | - | 5.2 | 0.4 | ~ 400 |
| Weight Effect | | | | | | | |
| 11-2 | 8209<br>8217 | - | - | - | 8.2 | 0.4 | 400 |
| 11-2 | 8199<br>8205½ | - | - | - | 7.5 | 0.4 | 300 |
| 11-2 | 8220½<br>8221½ | - | - | - | 5.0 | 0.4 | 200 |
| 11-2 | 8209½<br>8228 | - | - | - | 3.4 | 0.4 | 200 |
| 11-2 | 8216<br>8217 | - | - | - | 6.7 | 0.4 | 300 |

TABLE I - Continued

| Date 1957 | Thermocouple Voltages<br>Li-6 (μv) | <br>Li-7 (μv) | <br>Li-n (μ v) | <br>Diff. (μv) | Heating Rate (μv/min) | Wire Diam. (mm) | Hanger Weight (mg) |
|---|---|---|---|---|---|---|---|
| 11-2 | 8203½<br>8213 | - | - | - | 6.3 | 0.4 | 400 |
| 11-5 | 8216½<br>8219 | - | - | - | 7.2 | 0.4 | 200 |
| 11-5 | 8211<br>8214½ | - | - | - | 5.6 | 0.4 | 200 |
| 11-5 | 8218½<br>8221½ | - | - | - | 5.2 | 0.4 | 100 |
| 11-5 | 8220<br>8221½ | - | - | - | 2.4 | 0.4 | 50 |
| 11-5 | 8225<br>8226½ | - | - | - | 5.2 | 0.4 | 50 |
| 11-5 | 8226<br>8228 | - | - | - | 7.1 | 0.4 | 50 |
| 11-6 | 8216<br>8220½ | - | - | - | 5.1 | 0.4 | 100 |
| 11-6 | - | 8242½<br>8244½ | - | - | 4.0 | 0.4 | 50 |
| 11-6 | - | 8243½<br>8246 | - | - | 6.6 | 0.4 | 50 |
| 11-6 | - | 8229<br>8233 | - | - | 2.8 | 0.4 | 100 |
| 11-6 | - | 8234<br>8236½ | - | - | 4.5 | 0.4 | 100 |
| 11-7 | - | - | 8222<br>8229½ | - | 6.0 | 0.4 | 50 |
| 11-7 | - | - | 8226½<br>- | - | 6.7 | 0.4 | 50 |
| 11-7 | 8231<br>- | - | - | - | 7.0 | 0.4 | 25 |

TABLE I - Continued

| Date | Thermocouple Voltages | | | | Heating | Wire | Hanger |
|---|---|---|---|---|---|---|---|
| Date 1957 | Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Rate (μv/min) | Diam. (mm) | Weight (mg) |
| 11-7 | - | - | 8230<br>8234 | - | 7.6 | 0.4 | 100 |
| 11-7 | - | - | 8234<br>8238 | - | 6.4 | 0.4 | 100 |
| 11-7 | - | - | 8224½<br>8229½ | - | 6.1 | 0.4 | 200 |
| 11-9 | - | - | 8229<br>8231 | - | 10.8 | 0.4 | 300 |
| Diameter Effect | | | | | | | |
| 11-9 | - | - | 8225<br>8238½ | - | 6.8 | 0.4<br>1.0 | 300<br>300 |
| 11-12 | - | - | 8222<br>8234½ | - | 6.8 | 1.0<br>0.4 | 625<br>100 |
| 11-12 | - | - | 8235<br>8246½ | - | 9.2 | 0.4<br>1.0 | 100<br>250 |
| 11-12 | - | - | 8235½<br>8241½ | - | 4.5 | 0.4<br>1.0 | 100<br>300 |
| 11-12 | - | - | 8229<br>8240 | - | 4.0 | 0.4<br>1.0 | 100<br>400 |
| Standard Measurements, 100 mg | | | | | | | |
| 11-13 | 8223.3 | 8233.3 | - | 10 | 7.3 | 0.4 | 100 |
| 11-13 | 8225.1 | 8238.7 | - | 13.6 | 6.3 | 0.4 | 100 |
| 11-13 | 8224.0 | 8233.4 | - | 9.4 | 5.4 | 0.4 | 100 |

TABLE I - Continued

| Date 1957 | Thermocouple Voltages Li-6 (μv) | Li-7 (μv) | Li-n (μv) | Diff. (μv) | Heating Rate (μv/min) | Wire Diam. (mm) | Hanger Weight (mg) |
|---|---|---|---|---|---|---|---|
| X 11-13 | 8223.0 | 8211.0 | - | - | 6.5 | 0.4 | 100 |
| X 11-13 | 8222.3 | - | - | - | 5.2 | 0.4 | 100 |
| 11-14 | 8221.5 | 8234.5 | - | 13 | 4.0 | 0.4 | 100 |
| 11-14 | 8224.0 | 8233.0 | - | 9 | 3.0 | 0.4 | 100 |
| 11-14 | 8226.4 | 8244.2 | - | 17.8 | 4.1 | 0.4 | 100 |
| 11-14 | 8226.9 | 8238.0 | - | 11 | 5.2 | 0.4 | 100 |
| 11-19 | 8221.7 | 8237.2 | - | 15.5 | 6.6 | 0.4 | 100 |
| 11-19 | 8227.0 | 8231.7 | - | 4.7 | 7.2 | 0.4 | 100 |
| 11-19 | 8220.3 | 8236.1 | - | 15.8 | 8.0 | 0.4 | 100 |
| 11-19 | 8224.1 | 8230.1 | - | 5.9 | 7.9 | 0.4 | 100 |
| 11-19 | 8224.6 | 8233.2 | - | 8.6 | 7.8 | 0.4 | 100 |
| 11-19 | 8222.6 | 8234.2 | - | 11.6 | 7.8 | 0.4 | 100 |
| 11-19 | 8232.8 | 8244.8 | - | 12 | 7.4 | 0.4 | 100 |
| 11-20 | 8217.5 | 8227.7 | - | 10.2 | 5.5 | 0.4 | 100 |
| 11-20 | 8222.8 | 8244.2 | - | 21.4 | 5.4 | 0.4 | 100 |
| 11-20 | 8230.9 | 8235.2 | - | 4.1 | 7.0 | 0.4 | 100 |
| Standard Measurements, 200 mg and 400 mg | | | | | | | |
| 11-20 | 8219.0 | 8227.4 | - | 8.4 | 6.7 | 0.4 | 200 |
| 11-20 | 8223.0 | 8232.8 | - | 9.8 | 6.5 | 0.4 | 200 |
| 11-20 | 8218.6 | 8233.1 | - | 14.5 | 2.6 | 0.4 | 200 |
| 11-21 | 8221.5 | 8224.9 | - | 3.4 | 4.6 | 0.4 | 400 |
| 11-21 | 8203.0 | 8224.7 | - | 21.7 | 5.7 | 0.4 | 400 |

The interpretation of data on melting points as obtained by the melting-wire technique adopted in the present work is complicated by the following factors: the possible existence of an appreciable temperature difference between the measuring thermocouple and the specimen under test, the difference having its source in the interaction of the specimen location and the heating rate; and the existence of a substantial difference between the "true" melting point and bath temperature when breaking occurs, the difference having its source in the incomplete compensation between support of the specimen by the coating formed on its outside, and load on the specimen by the weight hung on it to overcome this support.

Much of the preliminary experimentation was carried out in order to obtain temperature uniformity between the two sample locations. Statistical analysis of the final results showed that the effect of location is not significant, and moreover that the effect of heating rate is not important provided that it lies between 1 and 8 μv/min. These limits were maintained in the final experiments following their establishment tentatively in preliminary runs.

Estimation of the possible difference between melting point and breaking temperature is much more troublesome. Scatter diagrams for the breaking emf against hanger weight for 0.4-mm wire diameter showed identical trends for the three materials Li-6, Li-7, and Li-nat. The effect amounts to a lowering in emf of about 8 μv, equivalent to about

0.14 C-deg, from the 100-mg weight to the 400-mg weight. Increasing the thickness of wire at constant hanger weight would be expected to increase the breaking emf, and this effect is indeed found; in fact, at 300-mg load an increase in diameter from 0.4 mm to 1.0 mm produces a rise in emf of about 15 $\mu$v, corresponding to a temperature difference of 0.27 C-deg. It might be possible to combine the variables of diameter and weight into a single variable corresponding to an "equal loading" of some kind, for instance, equal stress on metal (proportional to weight divided by square of the diameter), equal stress on coating (proportional to weight divided by diameter), and so on. But without an adequate theory for failure, data on the mechnical properties of lithium, and extensive experiments with the present apparatus, further analysis does not appear worth while.

The conclusion---which must remain tentative---to be drawn from examination of the present data is that for wire diameters of 0.4 mm and 1.0 mm the breaking emf does not vary by much more than $\pm 6$ $\mu$v for loads that are heavy enough to keep the coating from supporting the wire to indefinitely high temperatures, and light enough to keep the hanger from causing creep to produce breakage at unreasonably low temperatures. Hence absolute values for melting points cannot be reported to better than ± 0.1 C-deg on the basis of uncertainties in the method itself, apart from the effects of chemical impurities and errors in calibration and instrumental inaccuracies.

On the other hand, the difference in melting points between isotopes can be determined with much higher precision. Examination of the data shows that the difference in breaking emf's between isotopes is nearly independent of hanger weight and wire diameter. On physical grounds this result would be expected, unless the effect of isotopic mass on ultimate strength, creep rate, and other mechanical properties is pronounced.

Analysis of all the data leads to the following results for the actual samples of lithium isotopes:

Melting point for lithium-6: $180.1 \pm 0.1^\circ C$
Melting point for lithium-7: $180.3 \pm 0.1^\circ C$

Difference in melting points: $0.23 \pm 0.07$ C-deg.

Here the indicated limits of error refer to those discussed above for the melting points, and to the statistical standard deviation for the difference in melting points. The instrumental and calibration errors are negligible in each case with respect to the indicated limits.

Isotopic and chemical impurities need next to be considered. The isotopic impurities produce negligible effects under the assumption of a straight-line extrapolation for melting-point as a function of isotopic composition; indeed, the isotopic contamination is considerably less than one percent, and even a fairly strong dependence of melting point on isotopic composition would not change the results.

The effect of chemical impurities is harder to assess, with respect both to the effect of a given amount and to the actual amounts present in the samples. If the usual assumption is made that for small concentrations of impurities, the freezing-point depression is proportional to the atomic fraction of impurities, and if further the melting point is affected in the same way as the freezing point, it is possible to correct for the effect of impurities. Douglas and his colleagues(16) have measured the melting point of natural lithium very carefully, and in this work have been able to estimate the constant for the freezing-point depression.

The analyses for the samples, as provided by Oak Ridge National Laboratory, were made spectrographically. The accuracy is given as only ± 50 per cent. From certain other experimental work performed in the Physics Department at Michigan State University, some question has arisen as to the accuracy of the analyses. It was attempted to check the results by use of the spectrograph in the Department of Agricultural Chemistry at Michigan State University, but difficulty was experienced in preparing samples which would give satisfactory spectra. Hence there remains some uncertainty in analysis. The samples of both isotopes, however, have had similar chemical treatment, and are reported to have nearly identical chemical analyses. Again there appears an uncertainty in the absolute value of the melting points, but the uncertainty in difference remains in all likelihood affected only slightly.

When the reported analysis is combined with the results of Douglas et al, and the uncertainty due to chemical impurities is taken into account, the values become finally:

Melting point for lithium-6: 180.4 ± 0.2°C
Melting point for lithium-7: 180.7 ± 0.2°C

Difference in melting points: 0.23 ± 0.07 C-deg.

The melting point for natural lithium does not differ significantly from that for lithium-7, according to the present data. Nonetheless, it is of interest to compute the melting point for natural lithium on the basis of a linear interpolation between the values given above. The figure turns out to be 180.65°C, which is in perhaps fortuitously good agreement with the value of 180.54 ± 0.03°C reported in reference 16. These investigators were able to use a thermal-arrest technique, and had large samples of exceptionally high purity. Hence their result is of high reliability.

The value of 0.23 ± 0.07 C-deg found experimentally is an order of magnitude lower than the value of about 3 C-deg predicted on the Lindemann theory. It appears that this theory is inadequate to treat any of the details of the fusion process. Such a finding is not surprising, of course, since the Lindemann theory attempts only to suggest a mechanism for fusion and has little thermodynamic basis, predicting as it does the occurrence of a phase change, but not the coexistence of two phases at the melting point. Still, the success of the Lindemann theory for a wide range of substances calls for some speculation as to the source of the discrepancy between theory and experiment. We tend to look for an explanation along the lines that near the melting point so many lattice defects appear that the average potential well in which the lithium ion moves is flattened, with consequent lowering of the natural frequency and the effective characteristic temperature. Then the ratio of actual temperature to characteristic temperature is increased, the effects of quantization and hence the difference in melting points thus becoming smaller.

In any event the hope of utilizing the difference in melting points as a basis for isotopic enrichment appears slight. Consequently extension of the work might more profitably take the form of determination of melting points on compounds of the lithium isotopes, or on other elements such as calcium and magnesium. It does not appear profitable to attempt to determine the solid-liquid phase-equilibrium diagram for the lithium isotopes in the absence of some motivation from the direction of metallurgy theory.

## LIST OF FIGURES

## Bibliography

1. T. W. Richards, "The Problem of Radio-Active Lead," Nature 103, 74 (1919).

2. F. Soddy, "Atomic Volume of Isotopes: Collected Data on Lead," Nature 107, 41 (1921).

3. W. A. Johnson, "Diffusion of the Stable Isotopes of Nickel in Copper," Metals Technology 13, T.P. #2007 (1946).

4. M. Chemla and P. Sue, "Enrichissement Isotopique par Migration dans un Solide Soumis a un Champ Electrique," Comptes Rendus 236, 2397 (1953).

5. E. Maxwell, "Isotope Effect in the Superconductivity of Mercury," Phys. Rev. 78, 477 (1950).

6. C. A. Reynolds, B. Serin, W. H. Wright and L. B. Nesbitt, "Superconductivity of Isotopes of Mercury," Letter in Phys. Rev. 78, 487 (1950).

7. H. Fröhlich, "Theory of the Superconducting State I. The Ground State at the Absolute Zero of Temperature," Phys. Rev. 79, 845 (1950).

8. W. Tuyn, "Measurements on the Electrical Resistance of Some Metals Below the Boiling Point of Oxygen," Communications from Leiden 18, Comm. No. 196b, 21 (1929).

9. E. Justi, "Versuche uber den Einfluss der Isotopenzusammensetzung auf den electrischen Widerstand und die Supraleitfahigkeit von Blei," Physikalische Zeitschrift 42, 325 (1941).

10. J. O. McCaldin, "The Influence of Isotopic Mass on Some Physical Properties of Iron," Physical Metallurgy Laboratory, Cal. Tech., April, 1954.

11. E. J. Covington and D. J. Montgomery, "Lattice Constants of Separated Lithium Isotopes," J. Chem. Phys. 27, 1030 (1957).

12. D. D. Snyder, R. G. Leffler, and D. J. Montgomery, "Electrical Resistance of Separated Lithium Isotopes," Bull. Amer. Phys. Soc. II, 2, 299 (1957); D. D. Snyder and D. J. Montgomery, "Electrical Resistivity of Separated Lithium Isotopes," Phys. Rev. 109, 222 (1958).

13. D. J. Montgomery, R. G. Leffler, and G. M. Smith, "Thermoelectric Power of Separated Lithium Isotopes," Bull. Amer. Phys. Soc. II, 3, 69 (1958).

14. E. H. Sondheimer, "The Theory of the Thermoelectric Power of Metals," Proc. Camb. Phil. Soc. 43, 571 (1947).

15. F. A. Lindemann, "Uber die Berechnung molekularer Eigenfrequenzen," Physikal. Zeits. 11, 609 (1910).

16. T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, "Lithium: Heat Content from 0 to 900°, Triple Point and Heat of Fusion, and Thermodynamic Properties of the Solid and Liquid," J. Amer. Chem. Soc. 77, 2144 (1955).