SOME PHYSICAL PROPERTIES OF SEPARATED ISOTOPES OF LITHIUM

by

Donald DuWayne Snyder

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

1957

Approved D. J. M

ABSTRACT

As part of a program exploiting isotopic mass as a probe for investigation of the solid state, certain bulk properties of separated lithium isotopes were measured. The bulk density of natural lithium was first redetermined, by flotation-equilibrium and hydrostatic-balance methods. The value obtained was 0.531 ± 0.001 gm/cm^3, corrected for chemical impurities and reduced to 20°C. This value is slightly less than that for the crystal density computed from X-ray diffraction data, 0.533 gm/cm^3. The bulk density of the separated isotopes was measured by the hydrostatic-balance method. The values obtained were 0.460 ± 0.003 gm/cm^3 for lithium-6, 0.537 ± 0.002 gm/cm^3 for lithium-7, corrected for chemical impurities and reduced to 100% isotope-content at 20°C. The crystal densities are computed to be 0.462 gm/cm^3 and 0.539 gm/cm^3, respectively. Again the bulk density is slightly less than the crystal density, in accordance with usual experience. The relative electrical resistivity of natural lithium was determined from room temperature (295°K) to liquid-nitrogen temperature (77°K) with a Kelvin double bridge, the results agreeing with those in the literature. The relative resistivity of the separated isotopes

was measured over the same range, the results disagreeing qualitatively and quantitatively with the predictions of the Bloch-Gruneisen theory. A possible explanation lies in the presence of residual resistance due to impurities. If this resistance is large enough and different enough in the materials, it could account for the discrepancies. An estimate of the effect shows, however, that this explanation is not likely to hold. A measurement at liquid hydrogen temperature ($20^\circ K$) or below would settle the question directly. If the findings are substantiated, a serious modification in the treatment of transport phenomena in metals is called for.

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

ACKNOWLEDGMENTS

I wish to express my appreciation to Professor D. J. Montgomery for his suggestion of this problem and for his guidance and encouragement in its prosecution. The services of the Atomic Energy Commission in supplying the separated isotope samples for this work on loan are greatly appreciated. The cooperation and advice given by the personnel of the Oak Ridge National Laboratory, in particular Dr. P. S. Baker, were very helpful. 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. Professor M. T. Rogers and Mr. Theodore L. Brown of the Chemistry Department provided us with some specially prepared chemicals. Mr. Richard Leffler of the Physics Department very kindly assisted me in part of the experimental work. 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.

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CHAPTER I

INTRODUCTION

The production of electromagnetically-enriched isotopes by atomic energy projects has made available a new class of important substances. For the present study interest lies in the fact that isotopic mass becomes a probe for investigation of the solid state. The motivation is that the isotopes of a given element constitute a set of closely related simple substances which differ significantly - from the point of view of the proposed study - only in the atomic mass. This parameter then serves as a probe for testing theoretical predictions about certain physical properties. For example, the treatment of electrical conductivity in the usual theory leads to an expression for the conductivity which is a function of the temperature and the atomic mass, and at the same time a complicated functional of the atomic field. Because of the difficulty in evaluating this functional it has not been possible to make quantitative comparison between different elements. Previous investigations accordingly have been concerned with the dependence of conductivity upon temperature for fixed atomic mass and atomic field. The present work is concerned with the dependence of conductivity upon atomic mass for fixed temperature and atomic field. Specifically, the electrical conductivity of separated isotopes lithium-6 and lithium-7 is measured from room temperature to liquid-nitrogen temperature. The resulting data are then compared with the predictions from solid state theory.

In carrying out this program, various ancillary data are required. The mechanical properties of the substances should be known, in particular the lattice constant and bulk density, as a function of temperature. These data have intrinsic interest, of course, and they have still other interest for possible applications in isotope enrichment processes; but for the present work they are needed for calculation of resistivity from resistance measurements. Consequently the program was begun with measurements of bulk density, the results being compared with those obtained earlier on lattice constants. The investigation then proceeded with measurements of the electrical resistivity. It is this work which constitutes the substance of this thesis.

The choice of lithium was based on its availability in reasonable quantities and on the large relative isotopic mass difference. It has the additional advantage, from the scientific point of view, that it is the metal of lowest atomic number, and hence is relatively amenable to calculation. It crystalizes in a simple structure (body-centered cubic) and provides a structure of high symmetry and relative ease of calculation. On the other hand, the chemical reactivity of lithium makes it an awkard substance to handle. On balance, the scientific advantages were judged to outweigh the technical disadvantages, and it was chosen for the study. Some day it may be possible to extend the work to magnesium-24 and magnesium-26 and to calcium-40 and calcium-44.

So far as investigations of other phenomena are concerned, the value of isotopic mass as a probe will appear most characteristically where the lattice-vibration spectrum is an important factor in determining the behavior of the substance. Thus thermal conductivity and specific heat at low temperatures should be responsive to variation in isotopic mass. Perhaps a more significant region of phenomena 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 during vibration or flow. The present work, it is hoped, demonstrates the practicality of using isotopic mass for study of bulk properties of matter.

CHAPTER II

SAMPLES

A. Choice

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 others, such as highly toxic ones.

The investigations of the density and the electrical conductivity of separated isotopes were two parts of a broader program on the use of the isotopic mass as a probe for the study of the solid state. For the general study a metal was desired. Lithium, with natural isotopes Li-6 and Li-7 in reasonable abundance ratio (Li-6, 7.52%;Li-7, 92.48%), and the large relative mass difference (Li-7 - Li-6)/1/2(Li-7+Li-6) = 14%, was an obvious choice.

Examination of the ORNL Inventory of Electromagnetically Enriched Isotopes showed that both of these isotopes were available in very 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 is an alkali of 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 and Analyses

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 unfortunately the concentrations of impurities were too high to allow meaningful results to be obtained. The impurities appear to be introduced during the thermo-chemical 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 a nominal charge of $50., per sample. The material was accordingly returned for purification about 22 July 1955, without any measurements having been made on them. 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 we were to attempt further distillation. The new samples had the following analyses.

Li-6 Lot No. SS5(a) - redistilled 1045 mg

Isotopic Analysis (mass number and atomic percent): 6, 96.1±0.1; 7, 3.9±0.1

Spectrographic Analysis (element and weight percent, precision ±50%):

Ag	T	Fe	0.5	Ni	<0.01T
Al	<0.01T	K	<0.02T	Pb	<0.02T
Ba	<0.02	Mg	0.02	Si	<0.05
Ca	0.05	Mn	<0.01	Sn	<0.01
Cr	<0.01T	Mo	<0.01	Sr	<0.01
Cu	0.01	Na	0.03	V	<0.02

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

Isotopic Analysis (mass and atomic percent): 6, 0.2±0.1; 7, 99.8±0.1

Spectrographic Analysis (element and weight percent, precision ±50%):

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

With both isotope samples, iron appears in very great amount (Li-6, Fe = 0.5%; Li-7, Fe = 0.3%). It is believed that these high amounts 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%) in Li-7. 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 (668(j)) which was used for bulk density and resistivity determinations, and this sample of Li-6 SS5(a) which was used for resistivity 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. Allocations for 10 grams of 96 percent Li-6, and for 3 grams of 99 percent Li-6 were authorized about 31 January 1956. The latter sample, from Lot SS5(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. SS5(b) - redistilled 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 SS5(b) which was used for the resistivity 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

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

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 a nonreacting atmosphere (e. g., carbon dioxide) or by covering it with a nonreactive substance (e. g., petrolatum).

Initially the lithium was extruded from a steel die in such a way that petrolatum coated the emergent wire. The petrolatum coating could not be satisfactorily removed in making density measurements, and consequently another method of protecting the surface had to be used. It was found that carbon dioxide, dried by passing through a column of Drierite* and through one containing Anhydrone** did not react noticeably with lithium at room temperature. The experiments on density were then carried out in a CO_2-

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* Drierite: Trade name of the W. A. Hammond Drierite Company, Xenia, Ohio, for anhydrous Calcium Sulfate

** Anhydrone: Trade name of the J. T. Baker Chemical Company, Phillipsburg, New Jersey, for anhydrous Magnesium Perchlorate filled dry box, except when it was necessary to remove the lithium to place it in the temperature bath where it was submerged in a nonreacting liquid.

Preparation of the samples for the resistivity measurements was simple in that the petrolatum coating gave the needed protection and did not interfere with the measurements. The lithium which was to be placed in the press for extrusion was carefully cleaned of coatings (oxides, nitrides, etc.) by scraping or cutting away the surface which had been exposed.

CHAPTER III

BULK DENSITY: EXPERIMENTAL PROCEDURE

A. Choice of Method

Probably the most accurate methods for determination of the density of a solid are (a) specific-gravity bottle; (b) floating equilibrium; (c) hydrostatic balance.

In method (a) a weighed sample of the solid is placed in the specific-gravity bottle, which is then filled to a marked level with a liquid that does not react with the solid. The assembly is weighed, and the solid is removed. The bottle is then refilled with the liquid to the marked level, and reweighed. The density of the solid can be calculated from the results of the three weighings. This method is supposed to be accurate within 1 part in 1000 when proper care is taken to avoid entrapped gas bubbles. This degree of accuracy is suitable for our work, but the narrow mouth of the usual specific-gravity bottle makes for difficulty in inserting some of the samples. Hence this method was discarded.

In method (b), which is based on Archimedes' principle, the solid sample is placed in a vessel and covered with a nonreactive liquid of smaller density. Another nonreactive liquid of density higher than that of the solid and miscible with the first liquid is added until the solid just floats in the bulk of the liquid. The density of the liquid mixture, which is thus the density of the solid, is then determined by use of a pycnometer. This method is supposed to be accurate to within 0.2 part in 1000. The accuracy is higher than that needed in our work, but it seemed worth while to use this method to detect possible differences in density from sample to sample of the same material.

In method (c), which is again based on Archimedes' principle, the solid sample is first weighed while suspended in the atmosphere, and then while immersed in a nonreactive liquid. The density of the liquid is determined by pycnometer. The density of the solid can be determined from the results of the two weighings and of the pycnometer measurement. This method is supposed to be accurate to within 1 part in 1000 when proper care is taken, including possible corrections for buoyant forces and the effect of surface tension on the suspension wire. The accuracy is suitable for our work, and the apparatus is simple. Hence this method was also selected for actual use.

With all these methods, it is necessary to have liquids whose density is less than that of the solid sample. For lithium there are no such liquids under ordinary conditions. Consequently it is necessary to use a sinker, which for our work was a piece of platinum wire wound around the lithium sample. Especial care must then be taken to remove gas bubbles from the assembly. The methods described above give the effective density of the combination, and separate weighings of the sample and sinker must be made. Correction for buoyancy of the atmosphere (which may be either carbon dioxide or air) must of course be made in all weighings.

B. Flotation-Equilibrium Procedure

The flotation-equilibrium method was the one we chose to use first. The sample was extruded from a press and wrapped with a length of platinum wire. The relative amounts of lithium and platinum were so chosen as to give a resultant density of about 0.75 gm/cm^3, about midway between the densities of the two liquids used (benzene, 0.87 gm/cm^3 hexane, 0.68 gm/cm^3). The extruded lithium sample was a cylinder of 1/8 inch diameter and 1 1/2 inch length. The platinum sinker was a 6-inch length of No. 36 wire. The mass of the lithium was about 150 mg , and that of the platinum 50 mg. The lithium was extruded, weighed, wrapped, and placed in a bottle of hexane while in a CO_2-filled dry box. Carbon dioxide was used in preference to commerical helium, which apparently contains nitrogen which quickly tarnishes the lithium.

The lithium, wrapped with platinum, was submerged in a bottle of hexane, which was transferred to a temperature bath controlled at 25°C. Small bottles of hexane and benzene were already in the bath. After equilibrium was established, small amounts of benzene were added to the test bottle of hexane until the lithium samples were observed to be just floating in the bulk of the liquid. It was observed that two drops of benzene in about 25 cc of hexane produced a noticeable effect on the floating sample. The extra bottle of hexane was available in case too much benzene should be added to the test bottle. The liquids were transported by medicine droppers, and care was taken to assure good mixing. Reproducibility by this method was of the order of 3 parts in 10,000, as shown by two determinations on one sample (see trials No. 11 and No. 12 in Figure 1). Some of the samples tested, suspected of having heavy inclusions or voids, were carefully cut with a razor blade. In several cases the suspected imperfections were observed. Familiarity with the technique soon enabled us to ascertain whether or not the sample was reasonably good.

After determining the density of the liquid, the density of the lithium could be calculated from the formula

$$\rho_{Li} = \frac{M_{Li}\,\rho_c}{M_c - M_{pt}\,\rho_c/\rho_{pt}}$$

where M_{Li} = mass of the lithium, ρ_c = density of the liquid = density of the combination of the lithium wrapped with platinum, M_c = mass of the combination, M_{pt} = mass of the platinum and ρ_{pt} = density

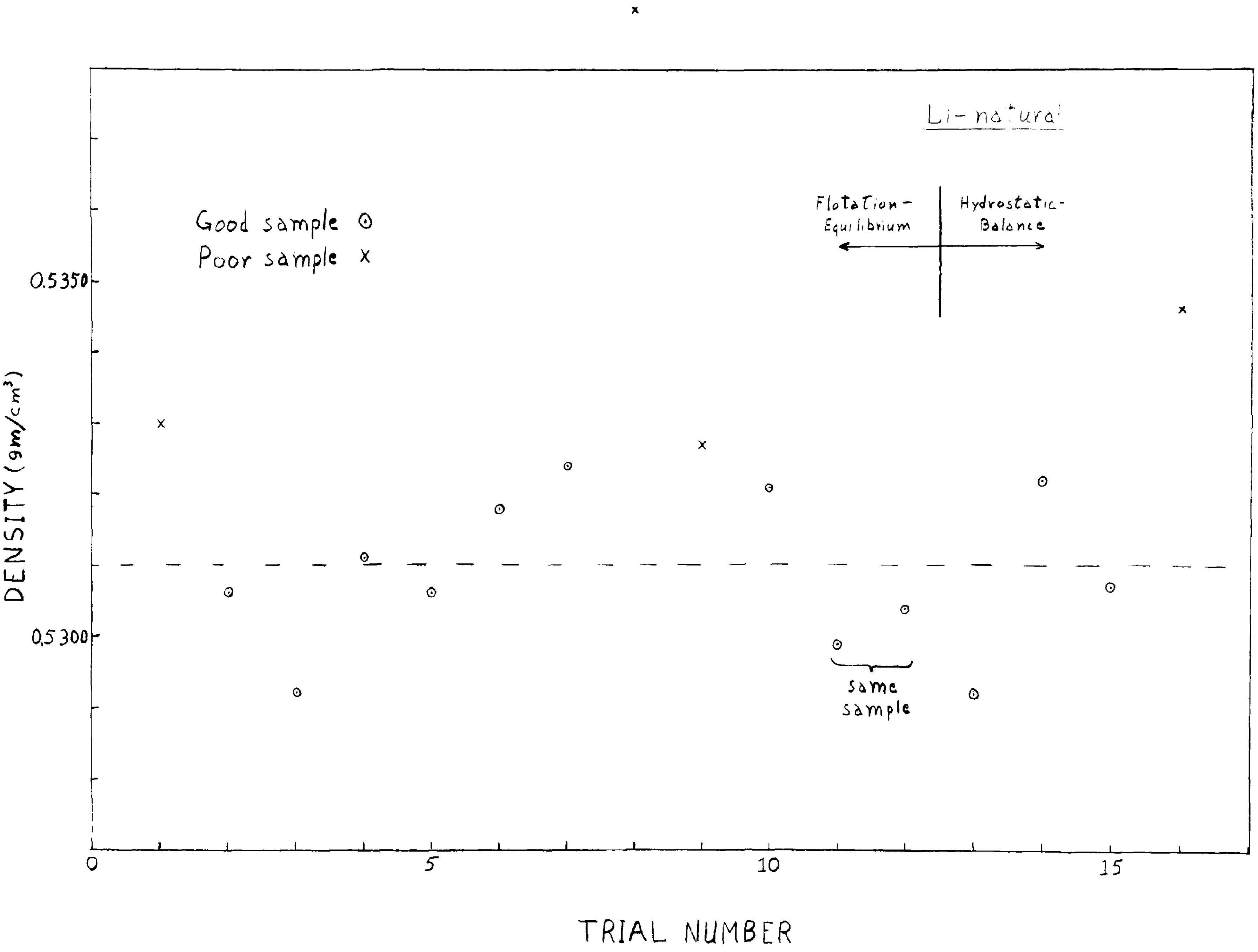

Figure 1

Density of natural lithium: results of successive trials of the platinum, 21.4 gm/cm^3. Choice of the sample size was made so that the formula would be nearly insensitive to the value for density of the platinum. As it turned out, the second term in the denominator was about 0.05% of the first term, and hence any uncertainty in the density of platinum exerts a negligible effect on the final result. Several determinations of density were made with the lithium and are plotted in Figure 1.. In using this method it was observed that the shiny surface of the lithium became visibly darkened when left in the liquid for more than a few minutes. This reaction was traced to the liquid other than benzene, i.e., to the hexane and the heptane. Benzene, itself, when dried over sodium, did not darken lithium even when the lithium was placed in it for a period of several months.

C. Hydrostatic-Balance Procedure

The reactivity of the liquids other than benzene, together with the rather long time required in the flotation method, led us to consider the possibility of using the hydrostatic-balance method which, although possibly less accurate, would be quicker and would eliminate the contact of the lithium with the reactive liquids. The lithium was prepared and weighed in an atmosphere of carbon dioxide. Then it was wrapped with the platinum sinker and hung from a fine wire. The combination was submerged in benzene and then weighed again. The density of the benzene was determined by use of a pycnometer, and the density of the lithium was calculated according to the following equation: $\rho_{Li} = w_1 \rho_{C_6H_6} / (w_1 + w_2)$ where w_1 is the weight of the lithium in carbon dioxide and w_2 is the weight lost when submerged in the benzene.

D. Pycnometer Calibration

The pycnometer used in the determination of the densities of the liquids was a 5-ml pycnometer type M-3080 manufactured by the H. S. Martin Company, Evanston, Illinois. It was calibrated by making four calibration runs with very pure benzene and water at a standard temperature of 25°C. The benzene had been recrystallized many times by Professor Rogers, who had checked the density of the resulting material very accurately. The water had been freed from ionic material by passage through a bed of ion-exchange resin, and its purity is believed to exceed that of ordinary conductivity water. The calibration curves are given in Figure 2.

Several points must be considered in connection with the weighing of the submerged sample. The effect of the surface tension of the benzene was calculated to be about 1 dyne, but since the wire holding the lithium was weighed in the same position both

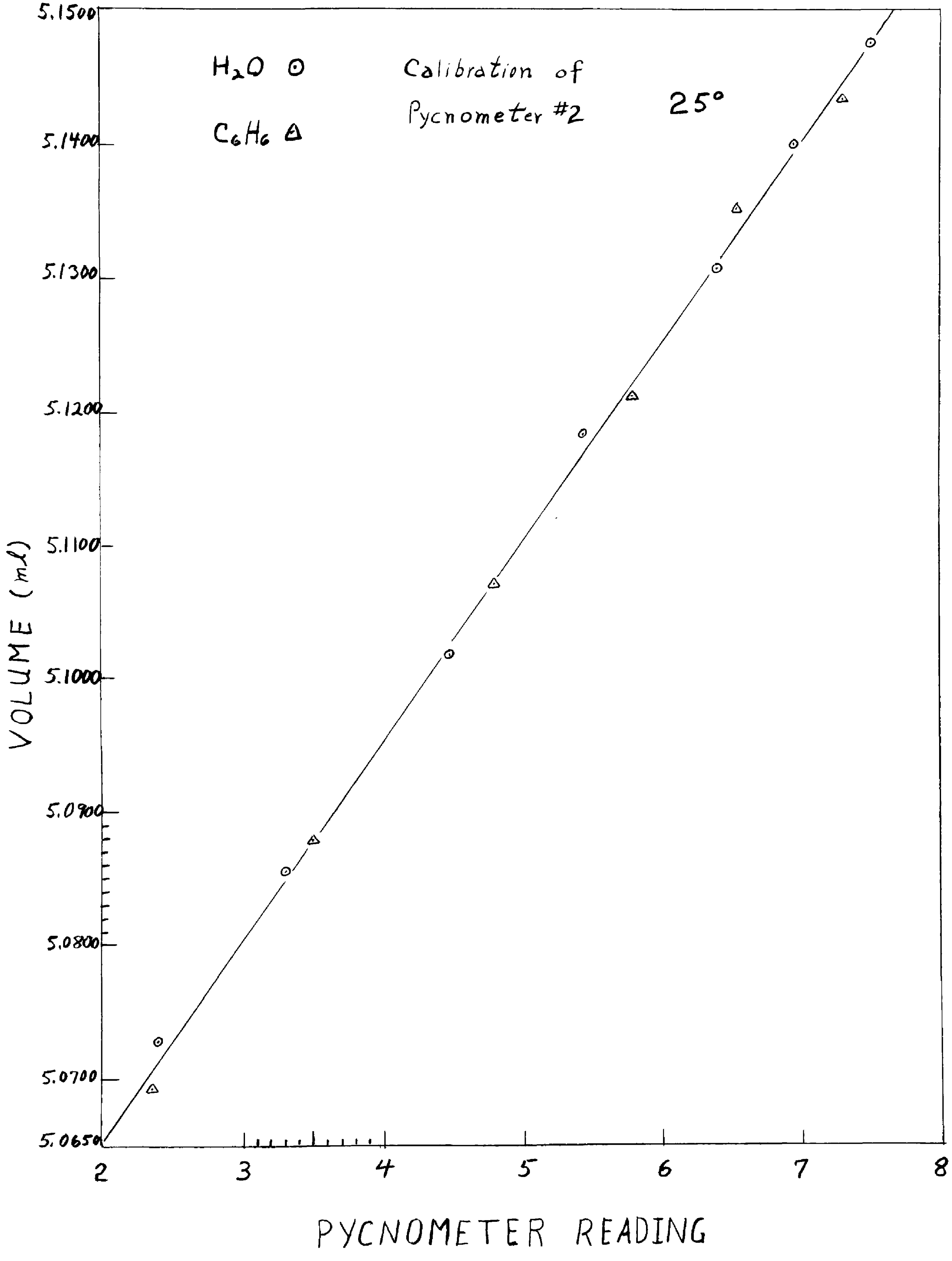

Figure 2

Pycnometer calibration: volume in milliliters as a function of scale reading. Standard liquids: benzene and water.

with and without the lithium, the change in weight due to the surface tension was negligible. The height of the liquid was kept nearly constant between the weighings so the small effect of the liquid displaced by the wire was rendered negligible. The box was kept at 25.0 $\pm$ 0.5 ^{o}C for all the weighings. A temperature difference of 1^{o}C would cause a variation in the density of benzene amounting to about 1 part in 1000, and hence induce a possible error of this amount in the density of the lithium sample.

CHAPTER IV

BULK DENSITY: RESULTS AND DISCUSSION

A. Natural Lithium

Both methods (b) and (c) were used for the determination of the density of natural lithium. The results are plotted in Figure 1. The flotation method gave an average value for the density of 0. 5316 gm/cm^3. The hydrostatic balance method gave an average value of 0. 5305 gm/cm^3. This agreement, we feel, is within the sample-to-sample variability. It will be noted that the flotation method gave a slightly higher value. A possible explanation is that dense reaction products were formed by the liquids used in the flotation method. The results can be consolidated in stating the density of natural lithium is 0. 531 gm/cm^3.

B. Separated Isotopes

The hydrostatic balance method was used exclusively for the density determinations of the isotopes. The results are plotted in Figure 3. There were two batches of lithium-6 as described in the section of procurement of samples. The average values for the densities are as follows:

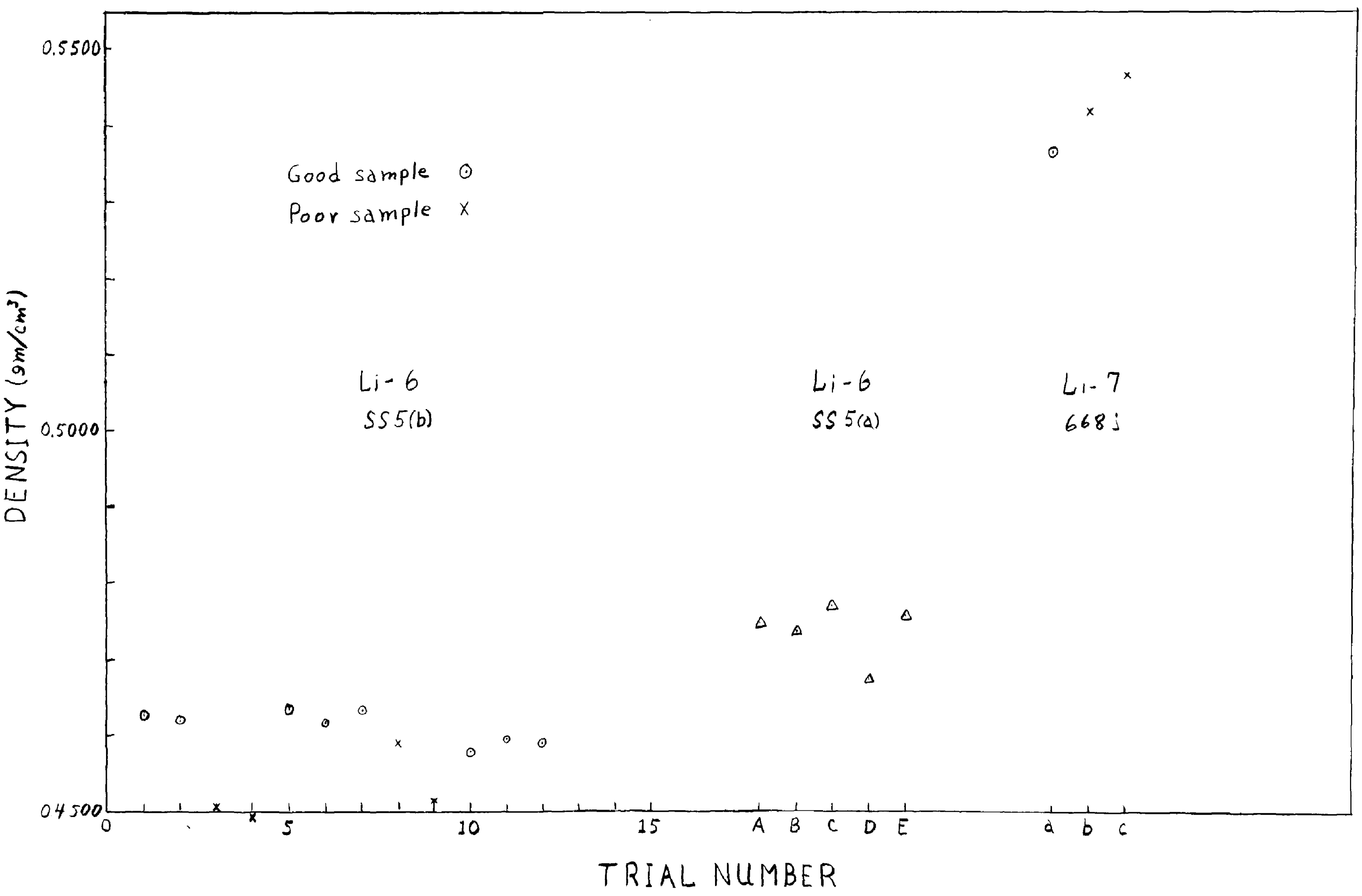

Figure 3

Density of isotopes: results of successive trial by hydrostatic balance.

Isotope	Sample		Density
Li^6	SS5(a)	ORNL Designations	0.4747 gm/cm^3
Li^6	SS5(b)		0.4600
Li^7	668(j)		0.5368
Li^{nat}	Lithium Corporation of America		0.531

Sample SS5(a) of lithium-6 seems anomalously dense. The values found are reproducible, and we feel that they are reliable. We had conjectured that enrichment of the heavy isotope might take place during distillation, but Dr. Baker informed us that negligible enrichment occurs upon distillation. Neglecting this sample that is much too dense, for reasons we have not yet established, the following values for the densities of natural lithium and its isotopes corrected to 100% at 20°C can be given as

Li^6	0.460 ± 0.002 gm/cm^3
Li^7	0.537 ± 0.003 gm/cm^3
Li^{nat}	0.531 ± 0.001 gm/cm^3

The limits are our informal estimates on the overall accuracy of the determinations.

Corrections to the raw density determinations must be made for four effects: 1) the buoyant effect of the atmosphere (CO_2) on both the specimen and the weights; 2) the calibrations to the weights; 3) the impurities in the sample; 4) reduction to standard temperature (20°C). Taking the density of CO_2 at one atmosphere at 25°C to be 2×10^{-3} gm/cm^3, and the certification of the weights* the first two corrections amounted to an increase of 2.7 parts per thousand. Corrections for the impurities were made according to the formula

$$\chi = M\left\{1 + M\left(\frac{A}{a} + \frac{B}{b}\right) - (A+B)\right\}$$

where χ = true density, M= measured density, A and B = % impurities, a and b = respective impurity densities. The correction to 20°C was made by using the coefficient of expansion[1]. This correction amounts to adding 4×10^{-4}.

C. Crystal Density

The density for an ideal cubic crystal can be computed from the expression $\rho = nM/(Na_o{}^3)$ where M = atomic weight, N = Avogadro's number, a_o = lattice constant, and n = number of atoms in the unit cell. (At room temperature, lithium crystallized in the body-centered cubic structure for which n = 2.) With the value of a_o for natural lithium[2] we find a value of 0.5334 gm/cm^3 for the crystal density of natural lithium. We note that this value is less than the experimental value of 0.534 gm/cm^3 found by Richards and Brink[3] for the bulk density. With most materials the value of the bulk density is found to be 0.1% to 1% smaller than the crystal density, owing to the imperfect formation in macroscopic crystals. Values of the lattice constant for the isotopes given by Covington[4] are: Li^6, $a_o = 3.5107$ Å; Li^7, $a_o = 3.5092$Å. Using these values we find the crystal densities for the isotopes to be Li^6, $\rho = 0.4623$ gm/cm^3 and for Li^7, $\rho = 0.5389$ gm/cm^3. It will be noted that the values of the bulk densities found in the present study are about 0.5% less than the crystal density values.

D. Projected Work

The work done on the lattice constant and bulk density of lithium isotopes could very profitably be extended to other isotopes now available. Some of these are listed below with their natural abundance ratios:

Element	Isotopes	Abundance Ratios	Relative Mass Difference
Silicon	28, 30	92.17%, 3.2%	7%
Calcium	40, 44	96.9%, 2.1%	10%
Magnesium	24, 26	78.8%, 11.1%	8%

These examples have mass differences large enough to be readily measured by the techniques described in this thesis. Measurements on electrical resistivity would be of interest.

Measurements of the density as a function of temperature over a reasonably wide range would be valuable. Plans are underway to make these measurements in the near future. The method envisioned is to find the coefficient of linear expansion from near the melting point (about 180°C) to liquid helium temperatures, and to compute the bulk density from this ceofficient.

CHAPTER V

ELECTRICAL RESISTIVITY: THEORETICAL CONSIDERATIONS

In a perfect lattice, the electrons have stationary states in which the mean velocity and hence the mean transport of charge and energy do not vanish. Hence the electrical and thermal resistivities would be zero. The resistivities occurring in practice arise from disturbances from perfect periodicity of the potential field in which the electrons move. These disturbances came from three sources: a) lattice vibrations; b) impurities and lattice imperfections; and c) interactions between electrons. For a good pure crystal at ordinary temperatures, the first of these disturbances is the most important. This fact explains the qualitative observation that the resistance of an ideal metal decreases with decreasing temperature. Additional analysis is required to explain the quantitative observation that the resistance goes to zero as the absolute temperature goes to zero, since the zero-point motion of the atomic cores might be expected to produce a large residual resistance for all metals. The explanation lies in the conditions on scattering imposed by the conservation laws and the distribution of electron energies.

Despite the severe approximations which must be made in developing the theory of resistivity, there is general agreement that for temperatures far above some characteristic temperature the analysis is adequate. Similarly, for very low temperatures the analysis appears reasonably satisfactory. But for intermediate temperatures no really satisfactory treatment has appeared. Wilson has summarized the work up until 1953. The analysis is too complicated to set forth briefly.

Although it is only an approximation, it is useful to consider the total resistance ρ as made up of three parts corresponding to the lattice disturbances listed above:

$$\rho = \rho_{\text{lattice vibrations}} + \rho_{\text{impurities}} + \rho_{\text{electron-electron}}$$

where $\rho_{\text{lattice vibrations}}$ is dependent on atomic mass and temperature, $\rho_{\text{impurities}}$ is independent of temperature, and $\rho_{\text{electron-electron}}$ is negligible except at the very lowest temperatures. For the present experiments it is necessary to find a range of temperature low enough for the first term to show appreciable dependence on atomic mass and at the same time high enough for the second not to swamp it. Fortunately the third term is small enough to be ignored.

The analysis of $\rho_{\text{lattice vibrations}}$ is based on the scattering of electron waves on sound waves (phonons) in the crystal. The scattering is not controlled by the amplitude of the sound wave alone, but also by the restrictions of conservation of momentum, the conservation of energy, and the statistical distribution of the electrons. At low temperatures these last factors combine to produce a fifth-power dependence of resistivity on absolute temperature T. At high temperatures of course the square of the amplitude of the atomic core displacement is the controlling factor, and the resistivity rises only as the first power of temperature. The detailed consideration of these factors leads to the Bloch-Grüneisen formula, which attempts to handle the temperature dependence of resistivity with a single parameter, the characteristic temperature Θ In principle this characteristic temperature should be the same as the Debye characteristic temperature Θ_D, but it is more satisfactory to take Θ as an adjustable parameter to be determined by experiment.

The expression for the resistivity ρ_M of an element of atomic mass M according to the Bloch-Grüneisen formula is

$$\rho_M(T) = \frac{BT}{M\Theta^2}\, G(\Theta/T) ,$$

where B is very nearly a constant for the same element. Here $G(z)$ is a function equal to $4z^4 \mathcal{J}_5(z)$, where $\mathcal{J}_5(z)$ is defined and tabulated in such references as Wilson.* Figure 8 shows $G(z)$ against z in the region of interest. The comparison of the formula with experiment is usually made by computing the θ required to obtain agreement, and then examining its constancy. Such a comparison for lithium has been made by Kelly & MacDonald[9].

For our purposes it is better to compare experimental and theoretical ratios of normalized resistivities ρ_M (or resistance R_M) for two isotopes as a function of temperature. Let this ratio be called r; we have

$$r_{\mathrm{exptl}} = \frac{R_{Li-6}(T) \,/\, R_{Li-6}\,(T_0)}{R_{Li-7}(T) \,/\, R_{Li-7}\,(T_0)}$$

and $r_{\mathrm{theor}} = \dfrac{\rho_6\,(T) \,/\, \rho_6\,(T_0)}{\rho_7\,(T) \,/\, \rho_7\,(T_0)}$

$$= \frac{G(\theta_6/T)/G(\theta_6/T_0)}{G(\theta_7/T)/G(\theta_7/T_0)} \cdot \frac{M_7\ \theta_7^2}{M_6\ \theta_6^2}$$

But since

$$h\,\nu_M = k\,\theta_M$$

where h is Planck's constant and k is Boltzmann's constant, in

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* A. H. Wilson, *The Theory of Metals*, 2nd ed. , (Cambridge, 1953)

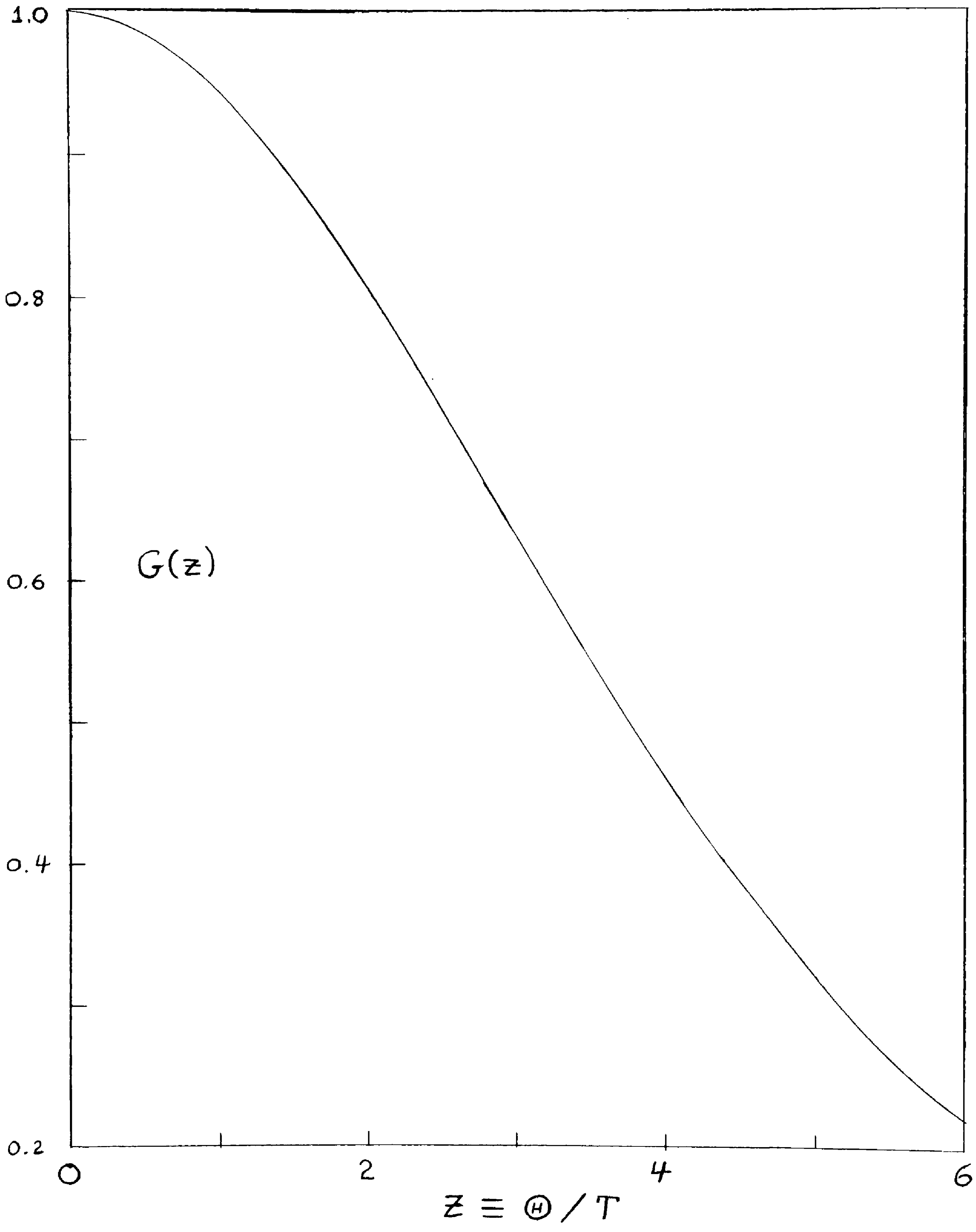

Figure 8

Graph of derived Gruneisen function G(z) versus z.

the relation connecting characteristic frequency ν_M with characteristic temperature θ_M ; and since

$$(2\pi\nu_M)^2 = b/M,$$

where b is some sort of spring constant which is constant for a given element, it is seen that

$$M\,\theta_M^2 = M(h/k)^2\nu_M^2$$

$$= M(h/2\pi k)^2(b/M) = b(\hbar/k)^2$$

is a constant for isotopes of the same element. Hence the final factor in the expression for r_{theor} may be dropped.

The three parameters θ_6 , θ_7 and T_0 may be reduced to two by defining

$$\alpha \equiv \theta_6/\theta_7 ,$$

$$y \equiv \theta_7/T_0 ,$$

and

$$x \equiv T_0/T$$

Then r_{theor} becomes

$$r_{theor} = \frac{G(\alpha y x)\;G(y)}{G(y x)\;G(\alpha y)}$$

We may consider α constant for a given pair of isotopes, and equal to

$$\alpha = \theta_6/\theta_7 = \sqrt{M_7/M_6} = \sqrt{7.0182/6.0170} = 1.0800 .$$

Suitable values of the parameter y can be estimated from the results for natural lithium. The parameter θ_{nat} lies in the range 330°K to 360°K. If θ_7 is taken to be about the same as θ_{nat} and T_0 is chosen as 295°K, the parameter y lies in the range

$$y = \theta_7/T_0 \sim 345°/295° \sim 1.15$$

In the next section is shown a plot of r_{theor} against $1/x \equiv T/T_0$ for values of y in the neighborhood of 1.15. The curve is not very sensitive to the exact choice of the value of y. It is this curve which is to be compared with experiment.

CHAPTER VI

ELECTRICAL RESISTIVITY: APPARATUS

The apparatus for this experiment can be grouped into three parts: the samples and holder, the cryostat, the measuring devices. A block diagram is shown in Figure 4, and photographs of the apparatus are shown in Figures 7b and 7c.

A. Kelvin Bridge

The form of the sample was chosen with the idea of eventually making a measurement of the absolute resistivity. For such a measurement, the dimensions must be known with high accuracy. However the small amount of material available limited the volume of the sample. Now it does not seem reasonable to suppose that the effective diameter of a long lithium wire can be measured to an accuracy greater than 10 microns. With this value, an accuracy of 2 percent in the cross section area determination would require the diameter of wire to be no less than 1 mm. This size was accordingly selected.

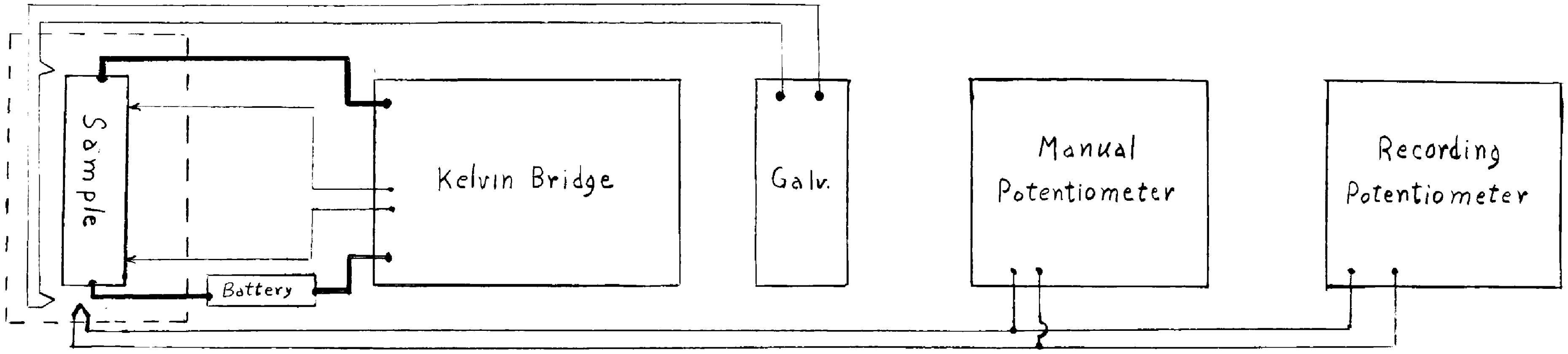

Figure 4

Block diagram of apparatus for measurement of electrical resistance.

The amounts of separated isotopes on hand were only a gram or two. Several replications are desirable. It was decided that about 100 to 150 mg could be used for a sample. The corresponding length of 1 mm wire is about 30 cm., with resistance about 40 milohms at room temperature, decreasing to about a tenth of that amount at 77°K.

The choice of a measuring method lay between a potentiometer method, with the current determined with the aid of a standard resistor, and the Kelvin double bridge. If the current can be kept constant, the potentiometer method offers some convenience[7]. On the other hand, the Kelvin bridge does not require a particularly steady current supply. The chief objection to its use is the existence of spurious thermal voltages. These effects can be eliminated by reversing the measuring current, and averaging the results. This procedure is satisfactory provided the thermal voltages do not change between reversals. With the present experimental procedure the changes were slow and no difficulty was found in repeating the measurements.

B. Sample Holder

The sample holder was designed to furnish physical support for the relatively soft lithium wire as well as to provide current and potential contacts on the lithium sample. The main sample support was constructed so as to hold six test samples at a time, two each of lithium-6, lithium-7, and natural lithium. The dimensions were kept small because of the limited size of the Dewar flask and because of the need to minimize temperature gradients. A top view of the sample holder is shown in Figure 5. The samples are located symmetrically about the central brass rod, which serves as a common lead and support shaft. The individual sample mountings are shown in detail in Figure 6. One current lead, which was common to every sample, was the 5/8-inch brass rod, silver-soldered to the bottom brass plate. The individual current leads for the samples were run to an external heavy-duty current switch. The switch was a six-position switch to allow selection of the sample for the current path. The lower potential contacts, made through the spring-loaded contact soldered to a brass screw mounted in lucite, were connected to a common lead that went directly to the Kelvin bridge. Six 3/8-inch holes were drilled in the upper lucite plate through which small connector clips could be attached to the upper potential leads, similar to the lower ones in construction and mounting. These leads were then run to an external light-duty switch. This switch was a six-position switch to allow selection of sample.

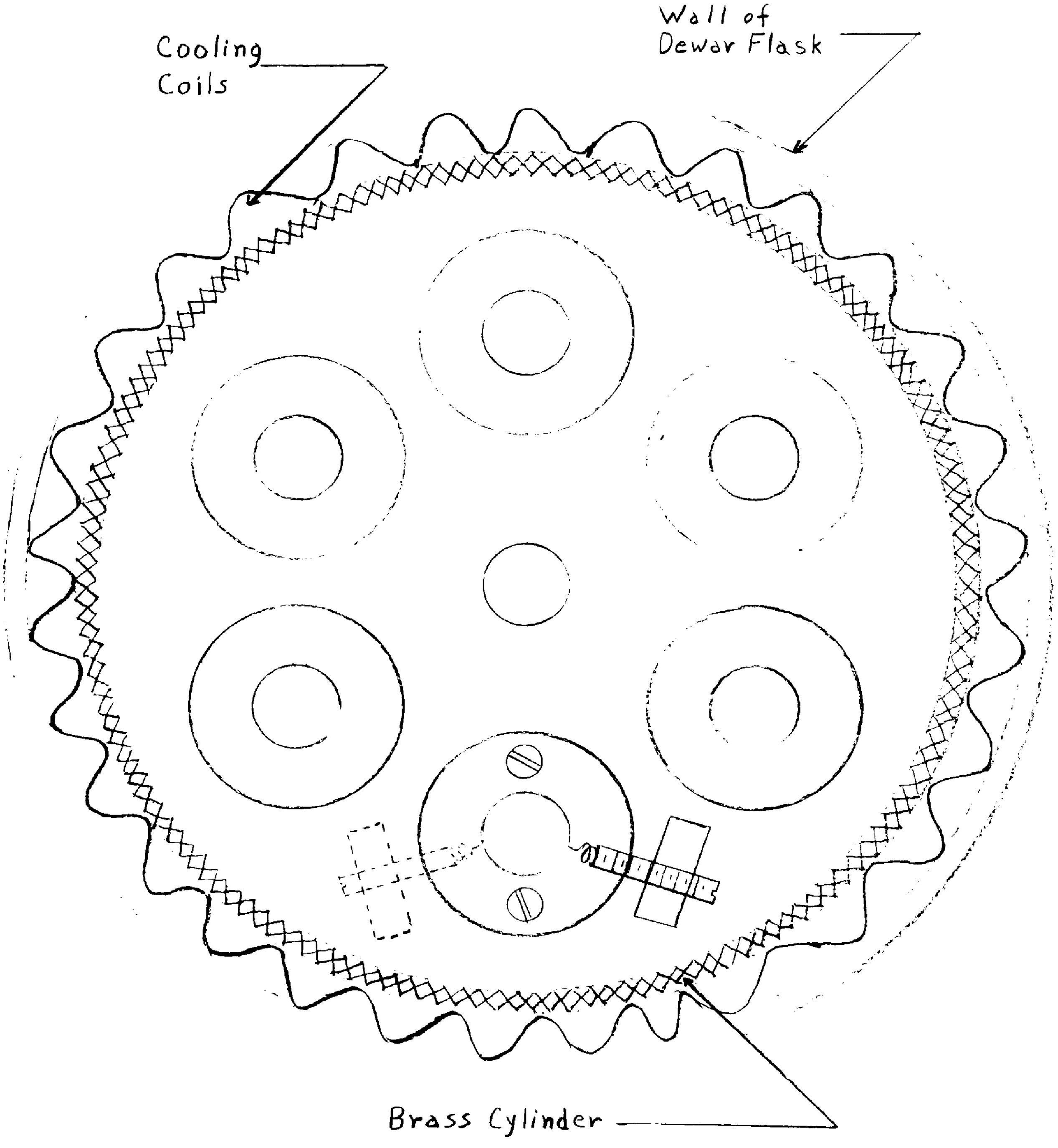

Figure 5

Sample holder (top view).

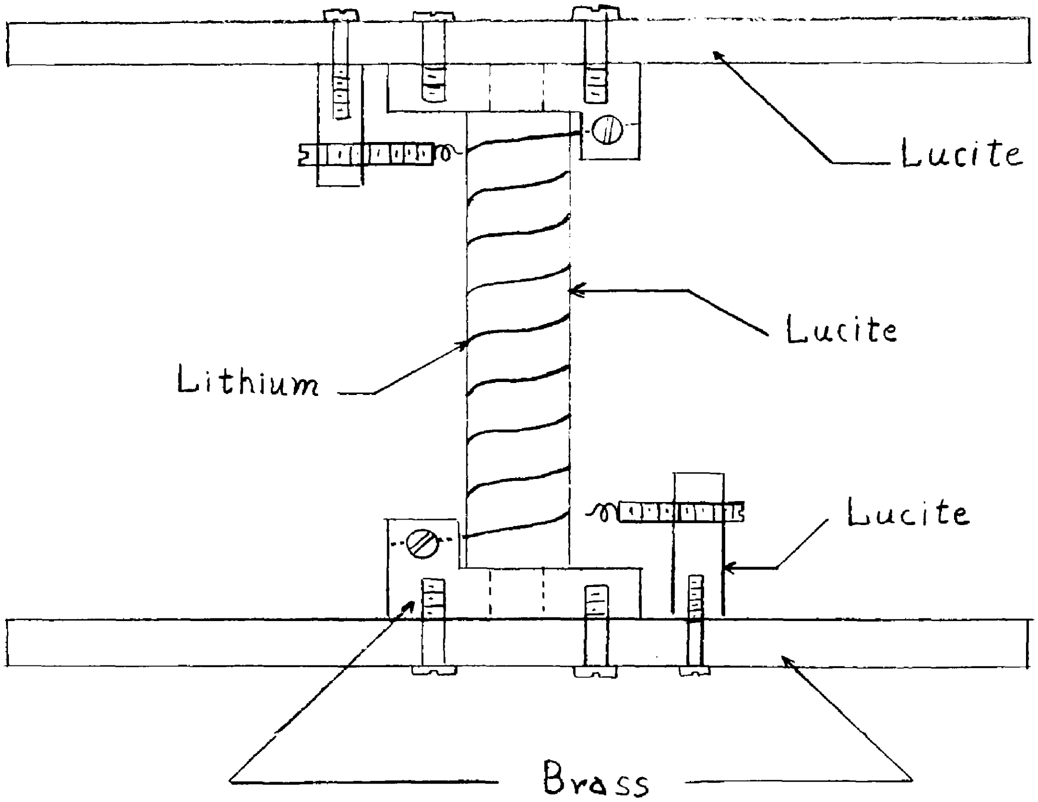

Figure 6

Sample holder (detail).

C. Cryostat

The cryostat arrangement is shown schematically in Figure 7a, and photographs of it and its contents are given in Figures 7b and 7c. The cryostat itself consisted of a stainless-steel Dewar flask* with inside dimensions of 6 inches diameter and 18 inches depth. A cooling coil of 1/4-inch copper tubing was wound around a hollow brass cylinder 5 inches in diameter and 6 inches deep in such a way that the intake and exhaust tubes were side by side at the top of the cylinder, and were joined at the bottom. Thus the incoming cold and outgoing warmer gases were placed adjacent in order to facilitate thermal equilibrium. The coils were soft-soldered to the brass cylinder. Provision was made for the exhaust gases to pass through another coil before going to the outside atmosphere. This second, and much smaller coil, consisted of three turns of 1/4-inch copper tubing wound around a solid 2-inch brass cylinder. This cylinder was drilled to take the 5/8-inch brass rod that constitutes the low-resistance current lead and mechanical support for the sample holders. This second coil was provided to decrease

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* All-stainless standard open Dewar flask, Catalog No. E2, 6" x 18", manufactured by Hofman Laboratories, Newark, New Jersey.

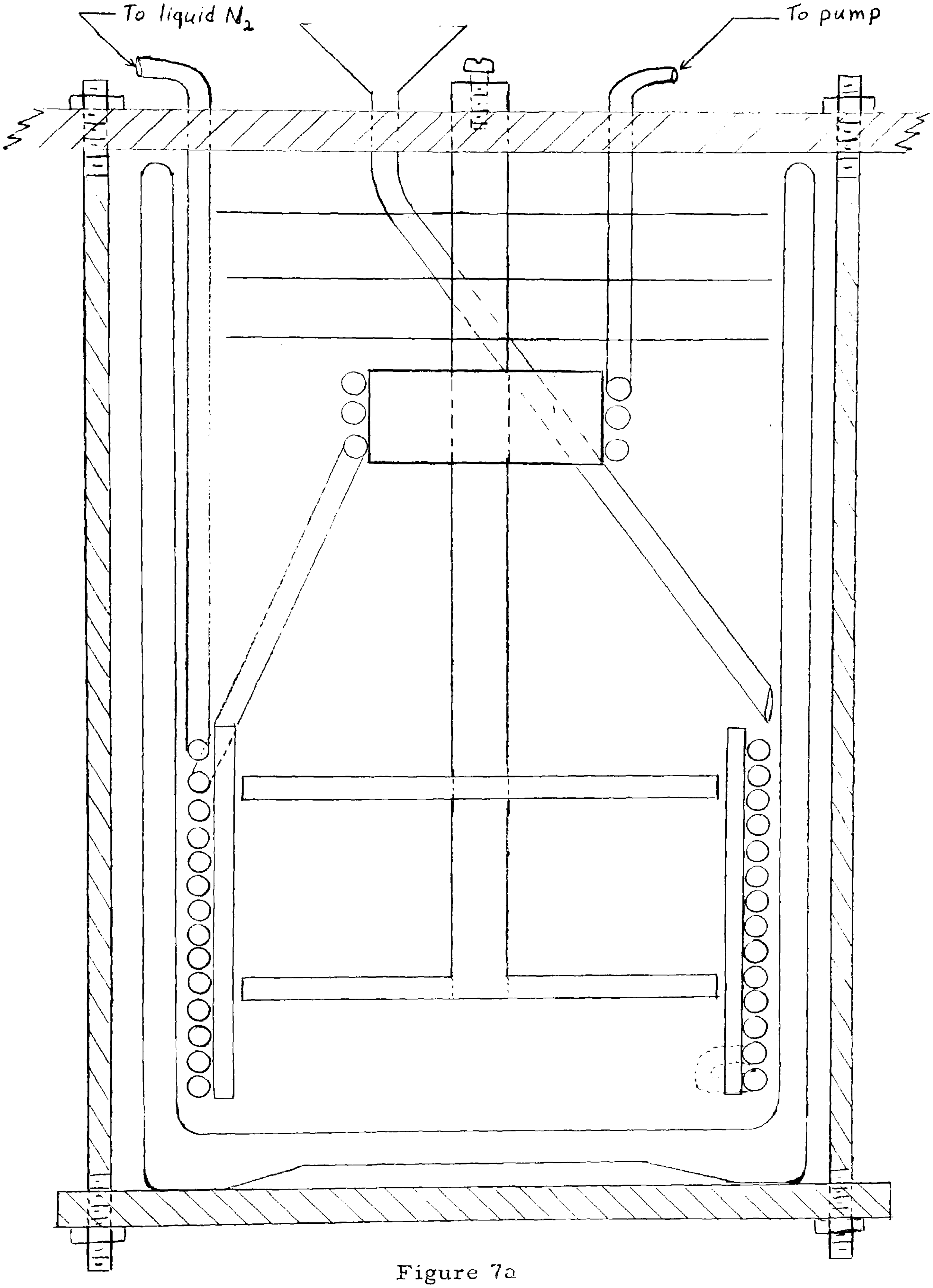

Figure 7a

Cryostat Arrangement.

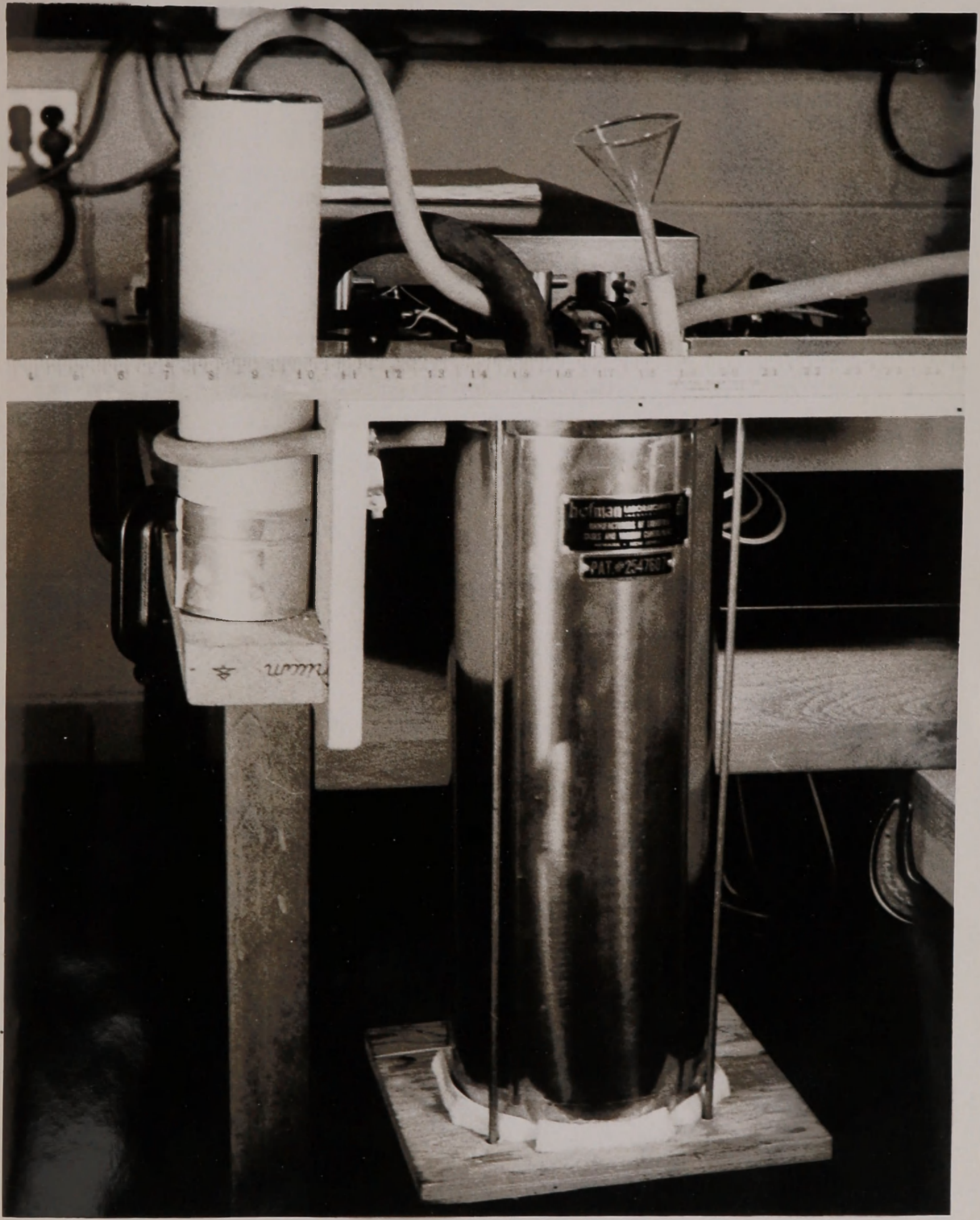

Figure 7b

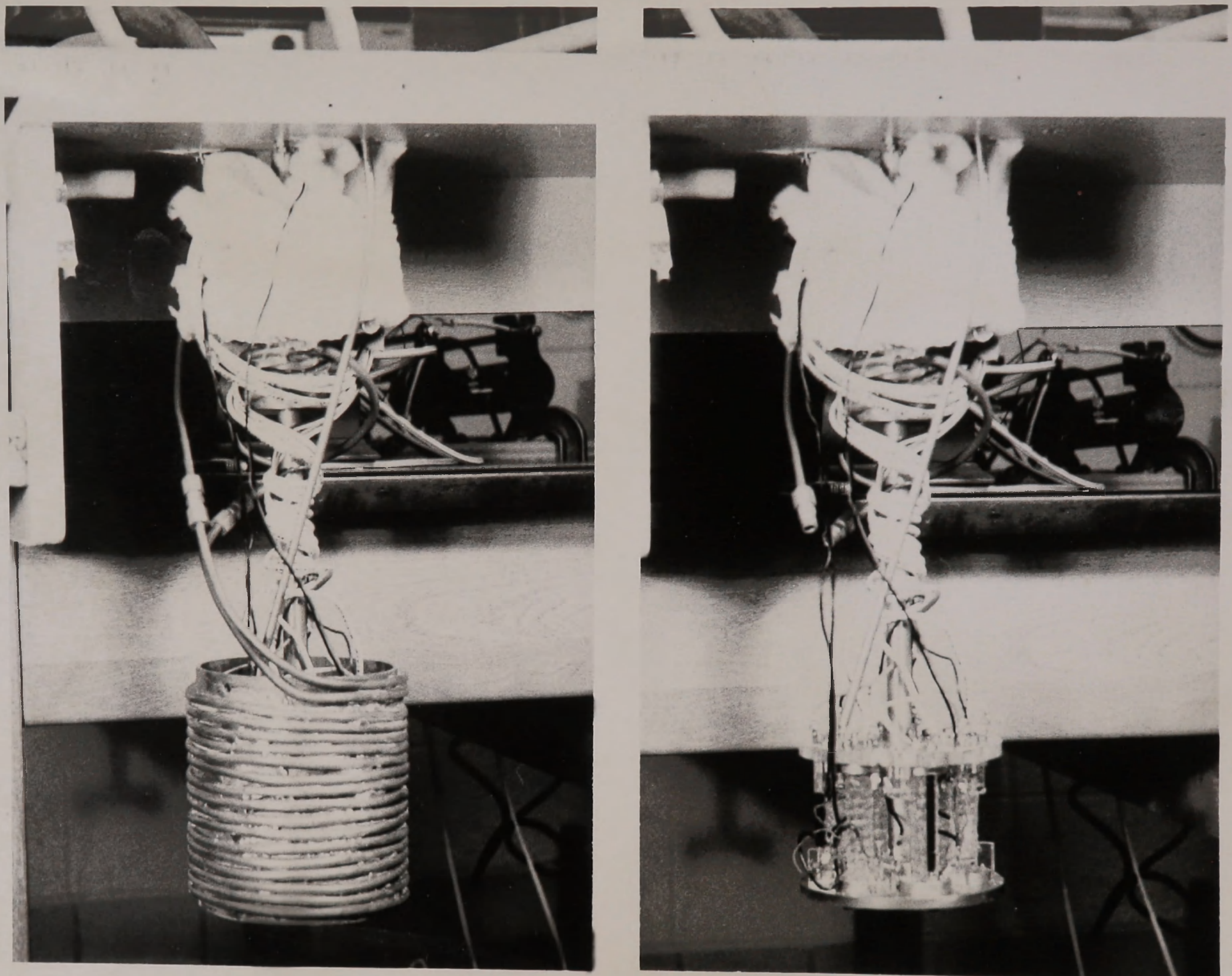

Figure 7c

the heat flow into the test chamber through the brass rod. For the same reason the electrical leads entering the chamber were wrapped around this coil. We were fortunate that the design and the construction of the cryostat were such that even on the first trial an acceptable rate of warming was obtained.

D. Measuring Devices

The bridge* used has a stated accuracy of 0.2 percent. From the standard analysis[8] of the circuit, the sensitivity is proportional to the measuring current. It is necessary to find a current large enough to get adequate precision, and yet small enough to prevent undue heating of the sample. Most of the resistance measurement were made with a current of one-half ampere through the sample. A check for heating effects due to this current showed that no noticeable heating occurred at temperatures below 150°K. The heating effect above that temperature was not large, and when the readings were taken without undue delay, the effect on the resistance was less than 1 part in 1000. At room temperature a current of one-tenth ampere did not produce any heating effect, but when the current was increased, heating became a serious factor.

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* Rubicon Standard Kelvin Bridge, Catalog No. 1605, Serial No. 87292 manufactured by the Rubicon Manufacturing Company, Philadelphia.

It was found that although a current of one-half ampere flowing for a short time gave results that agreed to 1 part in 1000 with those obtained with one-tenth ampere, a lengthy measuring time caused serious disagreement. At the lower temperatures, it required a current of almost two amperes to produce a noticeable heating effect.

The thermocouples were made of thermocouple constantan wire and common copper wire, silver soldered together. One thermocouple was connected to 10 channels of a 12-channel recording self-balancing potentiometer*, the other two channels being shorted to serve as references. This instrument served as a monitor during the entire course of a run. The differential thermocouples were connected to a galvanometer** which enabled temperature differences of less than one-half a centigrade degree to be measured. A manually-balanced potentiometer† was connected in parallel with the 12-channel recorder to permit a more precise reading

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* Micromax Model S, 40000 Series, manufactured by Leeds and Northrup Company, Philadelphia.

** Table Model Galvanometer No. 440, 30-0-30 scale, sensitivity approximately 0.5 microampere per division, resistance 50 ohms, manufactured by the Weston Instrument Company, Newark, N. J.

† Portable Model, self-contained galvanometer and standard cell, Catalog No. PM-40 modified, manufactured by Thwing-Albert Instrument Company, Philadelphia.

than was afforded by the recorder. Its scale was calibrated directly in 0.05 millivolt, corresponding to a temperature difference of about 2 Centigrade degrees depending on the temperature. The galvanometer* used with the Kelvin bridge had a sensitivity of 0.0029 microampere per millimeter, and a resistance of 25 ohms to give a voltage sensitivity of 0.07 microvolt per millimeter.

Our estimate for the overall accuracy of the temperature measurement is ± 2°K, and the accuracy of the resistance measurements is 1 percent.

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* Table Model, moving light beam, Catalog No. 2430-C, manufactored by Leeds and Northrup Company, Philadelphia.

CHAPTER VII

ELECTRICAL RESISTIVITY: EXPERIMENTAL PROCEDURE

In preliminary experiments a length of natural lithium wire 1 mm in diameter and about 30 cm in length was wrapped around the glass mandrel which was placed in an individual sample holder. The ends of the wire were clamped in current contacts, and insulated brass screws were turned into the lithium for potential contacts. The resistance of the sample was measured at room temperature, and then the holder carrying the sample was lowered into a 1-liter Dewar flask containing liquid nitrogen. After equilibration, the resistance was again measured. As the nitrogen was allowed to boil away and the sample warmed, resistance measurements were taken periodically. A copper-constantan thermocouple was attached to the sample holder and connected to a recorder. Also, a differential thermocouple was attached to the extremities of the sample holder so that the temperature gradient could be determined. In these preliminary experiments, several difficulties appeared. The small size of the Dewar flask resulted in rapid warming and the consequent appearance of excessive thermal gradients. The petrolatum covering the lithium became brittle at low temperatures and would not stick to the glass mandrel without support. The experience gained in these experiments was utilized in constructing an improved apparatus.

This final apparatus was described in the preceding section. The larger Dewar flask and the multiple sample holder allowed better temperature control, and permitted nearly simultaneous measurement on different samples. In the first experiments with the new apparatus several runs were made on two samples of natural lithium. The samples were changed and the runs repeated. The results were in very good agreement with published results for natural lithium[9]. In making runs with the natural lithium, great care was taken to attain temperature equilibrium and to get accurate measurements of temperature. This process took considerable time for each temperature, and a quicker means was sought. It was decided to use the natural lithium sample as the element of a resistance thermometer, the normalized resistance of the natural lithium sample being checked against the curve for natural lithium[9]. Thermal electrical effects were eliminated by reversing the current each time a reading was made and then averaging the two readings. Reproducibility was good enough to justify this procedure.

The method of cooling the test chamber was modified from that described earlier. A 1/4-inch stainless steel tube was run from just outside the brass cylinder through the top of the chamber, and then connected by a short rubber hose to a glass funnel.

Through this arrangement, liquid nitrogen could be poured into the test chamber without coming into direct contact with the samples. Moreover, the samples could be submerged in liquid nitrogen after being cooled to near the temperature of the liquid. A good calibration point at 77°K was thereby obtained. By pouring in various amounts of liquid, in conjunction with the pumping action described in the section on apparatus, different temperatures could be quickly attained. Once a low temperature was reached, subsequent readings were taken as the chamber warmed up at a rate of 10 to 20 degrees per hour.

CHAPTER VIII

ELECTRICAL RESISTIVITY: RESULTS AND DISCUSSION

The first measurements were made on samples of natural lithium. The resistance was measured from room temperature (295°K) to liquid nitrogen temperature (77°K). Studies were made of the several factors that could be controlled, such as the rate of cooling and warming, the attainment of temperature equilibrium in the test chamber, the current flowing through the sample, and day-to-day and run-to-run reproducibility. The results for the resistance, normalized to the room temperature value, are shown in Figure 9, wherein the experimental points represent the average value of two readings, one with the current in one direction and the other with the current reversed. Some of the points are omitted from the graph for clarity. The actual data are given in Table I. The solid curve represents the data of Kelly and MacDonald[9]. The present experimental results agree with theirs within the accuracy of the temperature measurement. It was concluded that the technique was satisfactory, and that the natural lithium samples could be used as resistance thermometers to give the temperature values of the samples better than could be done by the thermocouples, especially when the rate of change of temperature was high.

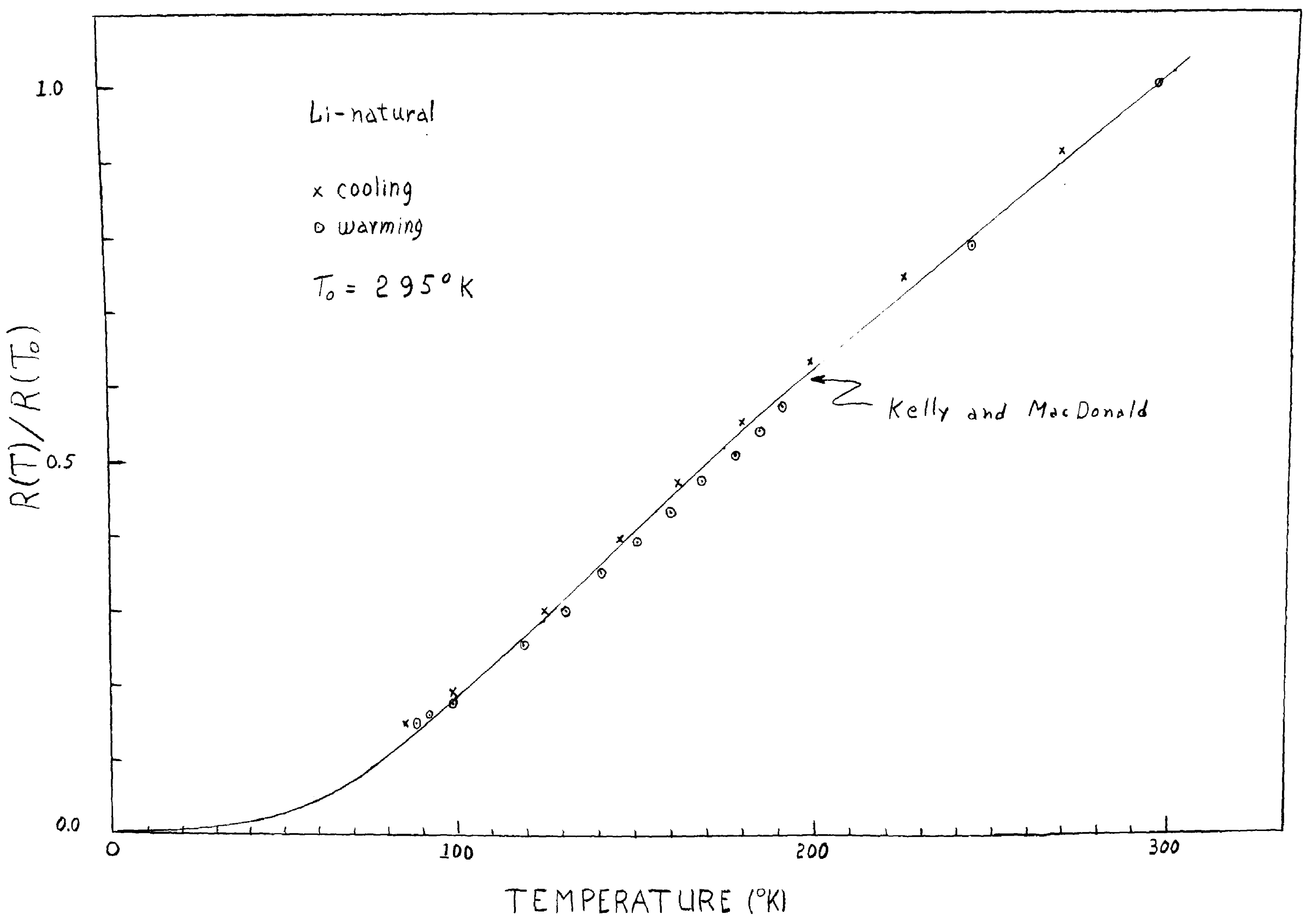

Figure 9

Normalized resistance as a function of temperature for natural lithium.

TABLE I: RESISTANCE MEASUREMENTS ON NATURAL LITHIUM

Sample 3					Sample 4					
T(°K)	R_+ (mΩ)	R_- (mΩ)	R(T) (mΩ)	R(T)/R(T_o)	T(°K)	R_+ (mΩ)	R_- (mΩ)	R(T) (mΩ)	R(T)/R(T_o)	I(a)
295	37.55	37.55	37.55	1.000	295	38.45	38.45	38.45	1.000	0.50
269	35.05	34.88	34.96	0.9310	267	35.55	35.26	35.40	0.9207	0.50
249	31.96	31.64	31.80	0.8469	246	31.78	31.29	31.53	0.8201	0.50
225	27.93	27.63	27.78	0.7398	219	27.73	27.50	27.61	0.7181	0.50
199	23.80	23.45	23.62	0.6290	197	23.79	23.48	23.63	0.6146	0.50
184	21.53	20.50	21.01	0.5595	180	21.09	20.21	21.15	0.5501	0.05
174	18.39	17.59	17.99	0.4791	162	18.50	17.74	18.17	0.4726	0.10
146	15.02	14.67	14.84	0.3952	143	14.89	14.56	14.72	0.3829	0.10
126	11.65	11.22	11.43	0.3044	123	11.40	11.38	11.39	0.2962	0.10
104	7.730	7.185	7.197	0.1917	99	7.147	7.250	7.198	0.1812	0.10
90	6.037	5.610	5.823	0.1551	88	6.076	5.773	5.924	0.1541	0.10
85	5.787	5.442	5.614	0.1495	88	5.905	5.616	5.760	0.1498	0.10
92	6.055	5.780	5.917	0.1576	92	6.271	6.070	6.170	0.1605	0.10
98	6.713	6.456	6.584	0.1753	99	6.957	6.712	6.834	0.1777	0.10
119	9.500	9.292	9.396	0.2502	119	9.828	9.687	9.757	0.2538	0.10
131	11.30	11.19	11.24	0.2993	131	11.67	11.55	11.61	0.3020	0.10
141	13.06	12.87	12.95	0.3449	141	13.41	13.30	13.35	0.3472	0.10
151	14.72	14.50	14.61	0.3891	151	15.14	14.96	15.05	0.3914	0.10
160	16.23	15.99	16.11	1.4290	160	16.68	16.50	16.59	0.4315	0.10
169	17.68	17.37	17.57	0.4666	169	18.18	17.92	18.05	0.4695	0.10
178	18.94	18.77	18.85	0.5020	178	19.42	19.32	19.37	0.5038	0.10
185	20.24	20.03	20.13	0.5361	185	20.76	20.60	20.68	0.5379	0.10
191	21.41	21.30	21.35	0.5686	191	21.99	21.89	21.94	0.5706	0.10
244	29.39	29.43	29.41	0.7832	244	30.17	30.22	30.20	0.7855	0.10

TABLE II: RESISTANCE MEASUREMENTS ON LITHIUM

I = 0.50 a

	Lithium-6		Lithium-7		Lithium-natural			
T(°K)	R(T) (mΩ)	R(T)/R(T_o)	R(T) (mΩ)	R(T)/R(T_o)	R(T) (mΩ)	R(T)/R(T_o)	R(T) (mΩ)	R(T)/R(T_o)
295	38.38	1.000	38.63	1.000	37.71	1.000	36.72	1.000
77	4.672	0.122	4.301	0.111	3.815	0.101	3.649	0.099
89	6.119	0.160	5.860	0.152	5.320	0.141	5.042	0.137
111	9.026	0.235	8.990	0.233	8.461	0.224	8.229	0.224
295	38.88	1.000	39.38	1.000	38.14	1.000	37.30	1.000
85	5.465	0.141	5.141	0.131	4.658	0.122	4.547	0.122
85	5.491	0.141	5.285	0.134	4 710	0.124	4.570	0.123
77	4.635	0.120	4.360	0.111	3.785	0.099	3.630	0.097
88	5.849	0.150	5.679	0.144	5.063	0.138	4.870	0.131
122	11.02	0.283	11.13	0.283	10.38	0.272	10.16	0.272
152	16.36	0.421	16.57	0.421	15.69	0.411	15.36	0.412
295	38.78	1.000	39.28	1.000	37.98	1.000	37.28	1.000
77	4.612	0.119	4.336	0.110	3.738	0.098	3.594	0.096
78	4.731	0.122	4.456	0.113	3.851	0.101	3.733	0.100
86	5.714	0.147	5.568	0.142	4.939	0.130	4.766	0.128
100	7.640	0.197	7.659	0.195	6.998	0.184	6.845	0.184

Measurements were then made on the separated isotopes. Six samples were placed in the sample holder, two each of natural lithium, lithium-6, and lithium-7. The procedure followed was as outlined earlier, the natural lithium samples serving as elements of a resistance thermometer. The results are shown in Figure 10 and Figure 11. As can be seen in Figure 10, which is a linear plot of the data at lower temperatures, the resistance at 77°K relative to its value at 295°K amounts to 0.097 for natural lithium, 0.108 for lithium-7 and 0.116 for lithium-6. As the temperature rises to room temperature, the curves begin to come together. As can be seen in Figure 11, which is a logarithmic plot of the entire variation, the curves begin to come together at higher temperatures, coinciding of course at 295°K. The numerical data for these results are given in Table II. Extensive data were not taken with the isotopes between 150°K and room temperature, since this range does not yield anything of particular interest.

It is regrettable that in no individual run was it possible to get readings on all six samples. The potential contacts can be maintained only with difficulty over the wide temperature range, and in every run some contact or other opened. Nevertheless, the reproducibility from one run to the next is high and it is believed that the data shown are reliable.

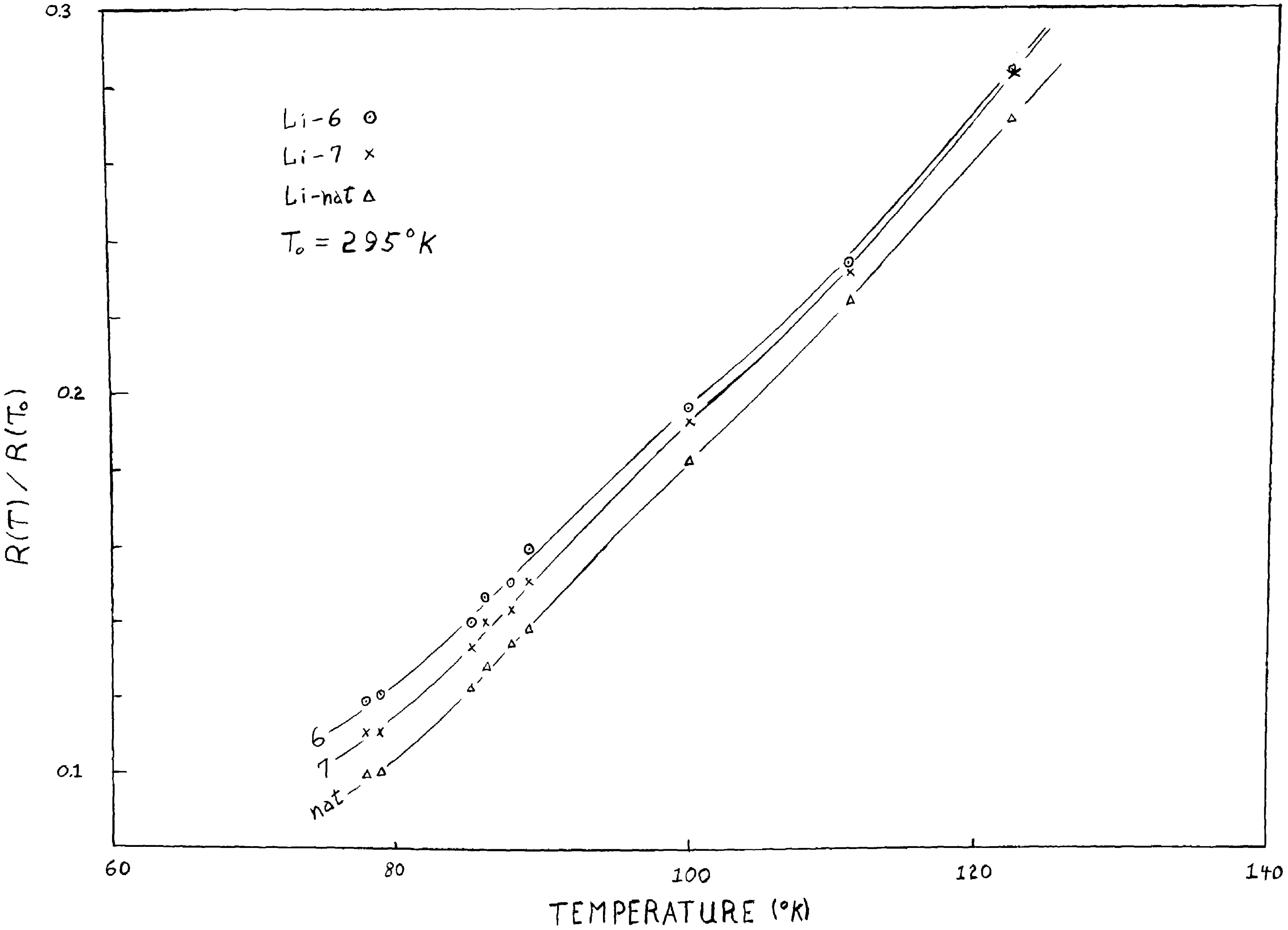

Figure 10

Normalized resistance as a function of temperature for natural lithium, lithium-6, and lithium-7 (linear plot of low temperature region).

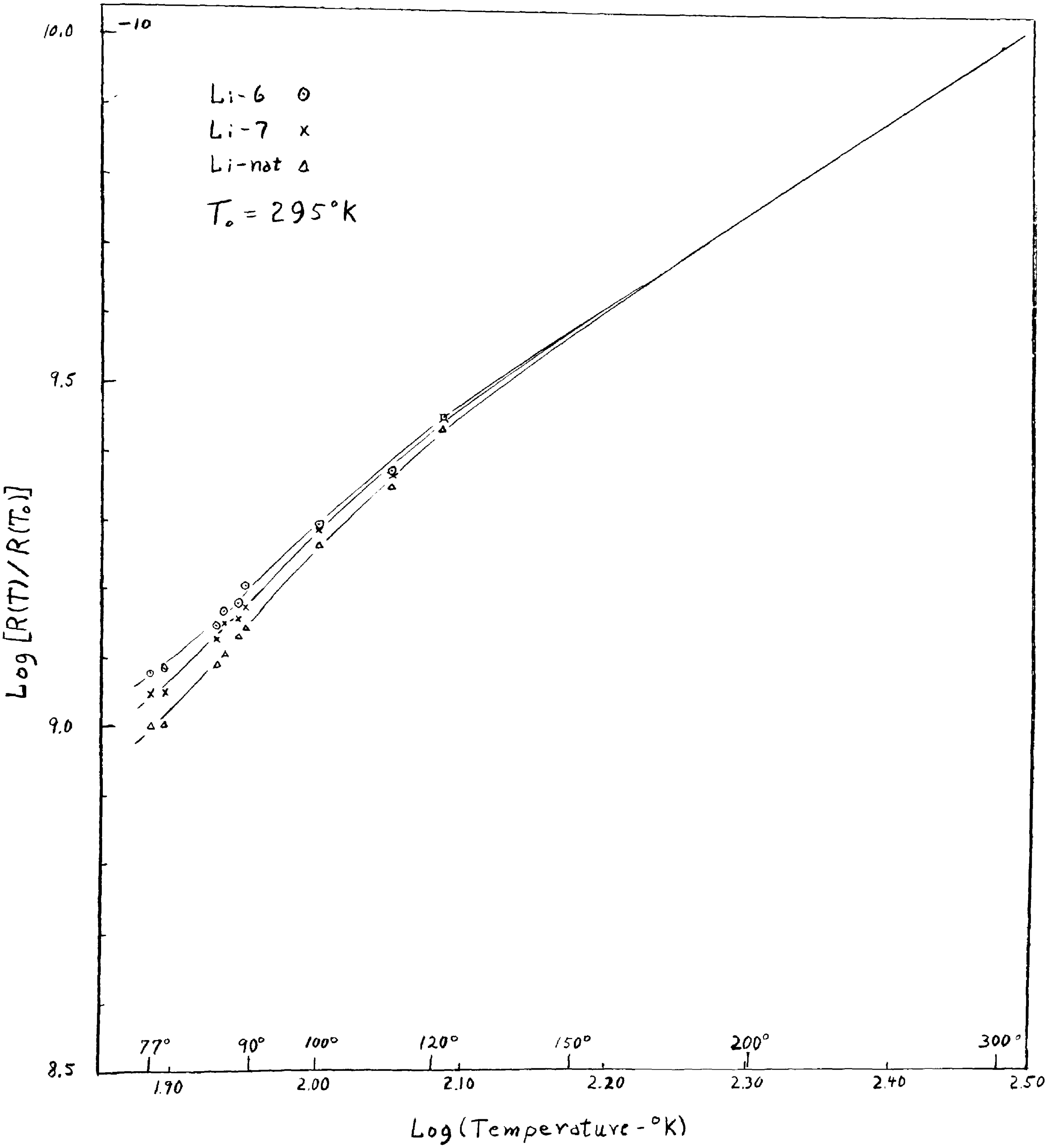

Figure 11

Normalized resistance as a function of temperature for natural lithium, lithium-6, and lithium-7 (logarithmic plot of entire region).

If the residual resistivity is considered to be negligible, the curves shown in Figure 10 may be used to compute the value of r_{exptl}. The result is shown in Figure 12, together with curves for r_{theor}. The experimental results are in contradiction both qualitatively and quantitatively. When the residual resistivity is not negligible, the curve for r_{theor} is changed seriously. If the residual resistivity is constant for the different materials, the curve will be raised, and the disagreement will be worse. However, if the residual resistivity were different for each material, and not negligible at 77°K, the curve could even lie below the one for r_{theor}.

Examination of Figure 10 shows no striking difference in the curvatures for the normalized resistivities of the three materials, and we believe that there is no experimental evidence to indicate substantial residual resistivities differing strongly between materials. On the other hand, the chemical analyses for the samples do show the presence of foreign atoms to the amount of some hundredths of an atomic percent.* The most serious impurities in the lithium-6 sample are calcium, 0.05 weight percent, and sodium 0.03 weight percent, corresponding to less than 0.01 atomic percent each. The chief impurity in the lithium-7 sample is calcium, 0.2 weight percent, corresponding to 0.03 atomic percent. The natural

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* Fe disregarded.

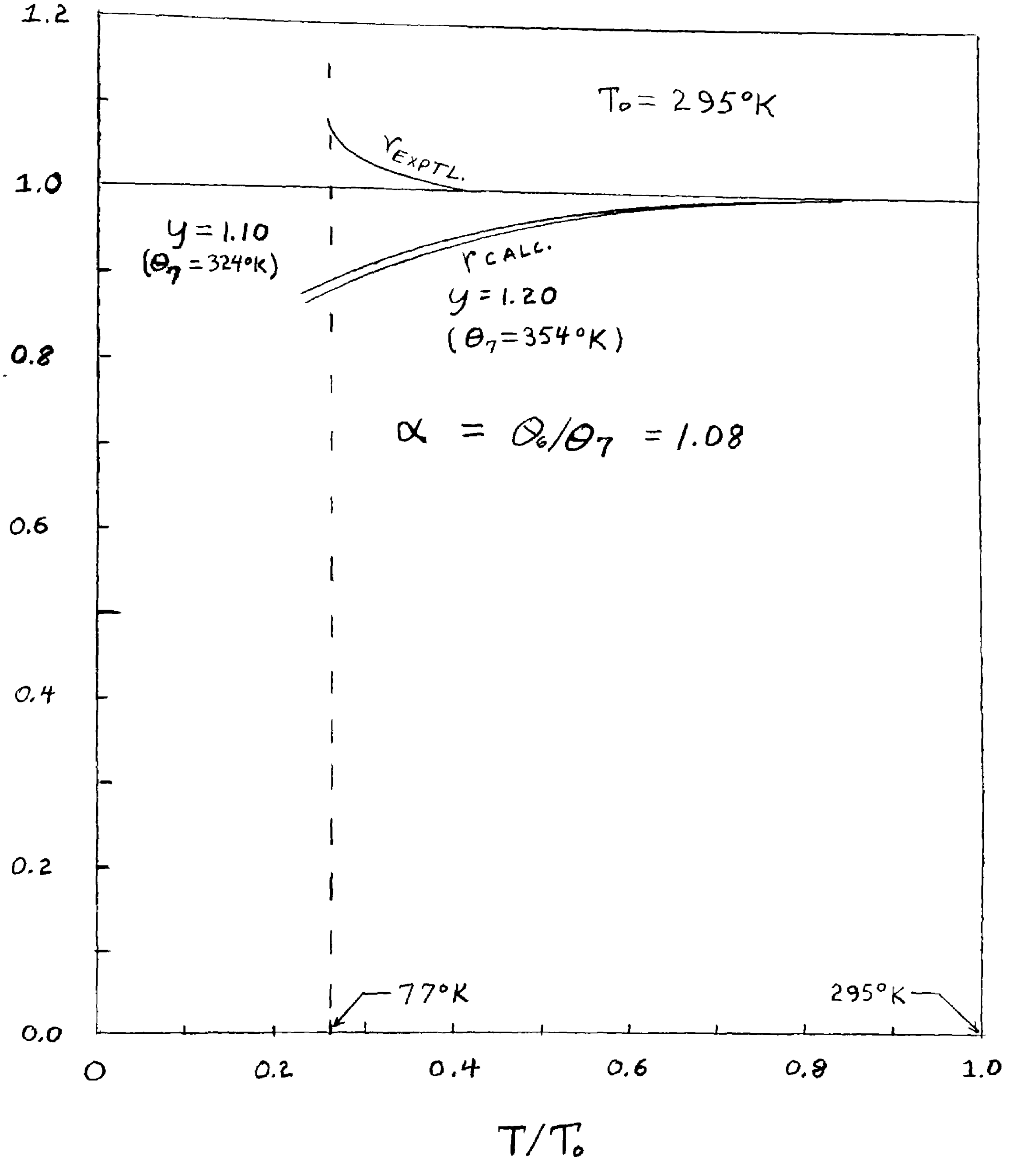

Figure 12

Ratio of normalized resistance of lithium-6 to normalized resistance of lithium-7 as a function of normalized temperature.

lithium is considerably purer, with calcium, 0.003 atomic percent, the chief impurity likely to be within the body of the metal*. Few data are available to suggest what numerical values should be used for the application of Matthiessen's rule that the increase in resistivity in dilute solid solutions is proportional to the atomic percent of impurity, and independent of temperature. As an outside limit for lithium, however, we suggest that the relative increase in resistivity might be 50 percent increase in room temperature resistivity per 1 atomic percent impurity. In this case the residual resistances for the isotopes would be less than 0.010 for the lithium-6, 0.015 for the lithium-7, and 0.005 for the natural lithium. With these estimates, the normalized resistances due to lattice vibrations become for lithium-6, 0.106; for lithium-7, 0.093; for natural lithium, 0.092.

Thus it appears that the residual resistance will not reverse the relative positions of the curves for the isotope samples, and that it may bring the lithium-7 curve nearly into coincidence with the natural lithium curve. If it is accepted that the curve for lithium-6 lies above the one for lithium-7, then serious doubt is thrown on the adequacy of the conventional analysis for electrical resistivity. In view of the gravity of this charge, it will be

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* N disregarded

important to extend the measurements to lower temperatures. The procedure can be maintained the same, but the apparatus must be modified to permit cooling with liquid helium. Such modification is simple and inexpensive.

It is not surprising that the conventional theory is not completely adequate, in view of the severe approximations made in carrying out the computations. A close critical examination of the present theory is not easy, but it would seem to be called for if the present experimental results are substantiated.

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