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ULTRASONIC MEASUREMENTS IN BINARY SOLUTIONS OF Na-K AND Na-Rb

BY

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OF

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ABSTRACT

The pulse-echo technique has been used to measure ultrasonic absorption and velocity in Na-K and Na-Rb alloys. Data were taken at temperatures from -5° C to 250° C using frequencies from 15 MHz to 105 MHz. It has been found that both Na-K and Na-Rb have absorption peaks near 67 atomic percent Na. The magnitude of the absorption was found to be much greater in the Na-Rb solutions. The results in Na-K are consistent with previously reported measurements that were attributed to the equilibrium process $2Na + K \rightleftharpoons Na_2K$. However, it is further speculated that the high attenuation in Na-Rb is due to a critical phase separation.

TABLE OF CONTENTS

ABSTRACT

PREFACE

LIST OF TABLES

LIST OF FIGURES

PREFACE

This thesis was written in accordance with the Manuscript Thesis Plan approved by the Graduate Council. The main body of the paper was written to be published by a scientific journal and hence, lacks many details of procedures and tables of data. The appendices following the manuscript contain all introductory information, procedures and complete tables of data used to plot the graphs found in the manuscript.

INTRODUCTION

Alkali metals, being monatomic and nearly spherically symmetric, comprise the simplest group of liquid metals and it would be expected that binary combinations of alkalis would form a simple set of liquid metal solutions. Previous ultrasonic measurements have shown that the K-Rb system behaves like an ideal mixture[1], but that the Na-Cs system exhibits a large temperature dependent absorption peak at a concentration Na_3Cs[1], and that the Na-K system has a small absorption peak near Na_2K[2]. Measurements confirming the Na-K results and new measurements of the Na-Rb system are reported here.

EXPERIMENT

The ultrasonic pulse-echo method was used to measure velocity and absorption of sound in the frequency range 15-105 MHz and in the temperature range -5° (or the liquidus temperature) to 250°C. Details of the method and of the apparatus have been given elsewhere[1,3]. The samples were obtained from MSA Research Corporation in sealed glass ampoules which were opened in the test container under high purity argon cover gas. The velocity measurements are accurate to within ±0.5% and the absorption measurements to within about ±4%.

RESULTS

A. Na-K Alloys

The results for the velocity of sound in Na-K can be given by the equations:

100% Na: $C = 2568 - 0.542T$ (ref.3) (1a)
84.66% Na: $C = 2407 - 0.5643T$ (1b)
75.13% Na: $C = 2283 - 0.4072T$ (1c)
62.85% Na: $C = 2208 - 0.4752T$ (1d)
30.16% Na: $C = 2027 - 0.5525T$ (1e)
100% K: $C = 1910 - 0.534T$ (ref.3) (1f)

where concentration is given in atomic percent, velocity, C, is in units of m/sec, and temperature, T, is in degrees Celsius.

The corresponding results for the amplitude of the absorption coefficient divided by frequency squared, α_0/f^2, are given by:

100% Na^3: $$\frac{\alpha_o}{f^2} = [8.99 + 2.13 \times 10^{-2}T + 0.23 \times 10^{-4}T^2]\times 10^{-17} \tag{2a}$$

with a standard deviation $= 0.133 \times 10^{-17}$

84.66% Na: $$\frac{\alpha_o}{f^2} = [0.807 \times 10^{1} - 0.158 \times 10^{-1}T + 0.123 \times 10^{-3}T^2] \times 10^{-17} \tag{2b}$$

with a standard deviation $= 0.186 \times 10^{-17}$

75.13% Na: $$\frac{\alpha_o}{f^2} = [0.103 \times 10^{2} - 0.782 \times 10^{-1}T + 0.568 \times 10^{-3}T^2 - 0.102 \times 10^{-5}T^3] \times 10^{-17} \tag{2c}$$

with a standard deviation $= 0.305 \times 10^{-17}$

62.85% Na: $$\frac{\alpha_o}{f^2} = [0.156 \times 10^{2} - 0.193T + 0.142 \times 10^{-2}T^2 - 0.299 \times 10^{-5}T^3] \times 10^{-17} \tag{2d}$$

with a standard deviation $= 0.424 \times 10^{-17}$

30.16% Na: $$\frac{\alpha_o}{f^2} = [0.109 \times 10^{2} - 0.204 \times 10^{-1} + 0.217 \times 10^{3}] \times 10^{-17} \tag{2e}$$

with a standard deviation $= 0.385 \times 10^{-17}$

100% K^3: $$\frac{\alpha_o}{f^2} = [24.72 + 9.80 \times 10^{-2}T + 0.39 \times 10^{-4}T^2] \times 10^{-17} \tag{2f}$$

with a standard deviation $= 0.486 \times 10^{-17}$

where $\frac{\alpha_o}{f^2}$ is in sec^2/cm and T in degrees Celsius. The measured absorption as a function of temperature is shown in Fig. 1. The increase in absorption with increasing temperature is due primarily to the increase in losses due to heat conductivity. For concentrations near 63 at .% Na, the absorption increases with decreasing temperature at low temperatures. This cannot be accounted for by the classical absorption mechanisms of shear viscosity and thermal conductivity which are given by the expression[4,5]

$$(\alpha_s + \alpha_t)/f^2 = \frac{2\pi^2}{\rho C^3}[\frac{4}{3}\eta_s + \frac{C^2\beta^2 T}{JC_p^2} K],$$

where ρ is the density of the fluid, C the sound velocity, η_s the shear viscosity, β the volume expansion coefficient, K the thermal

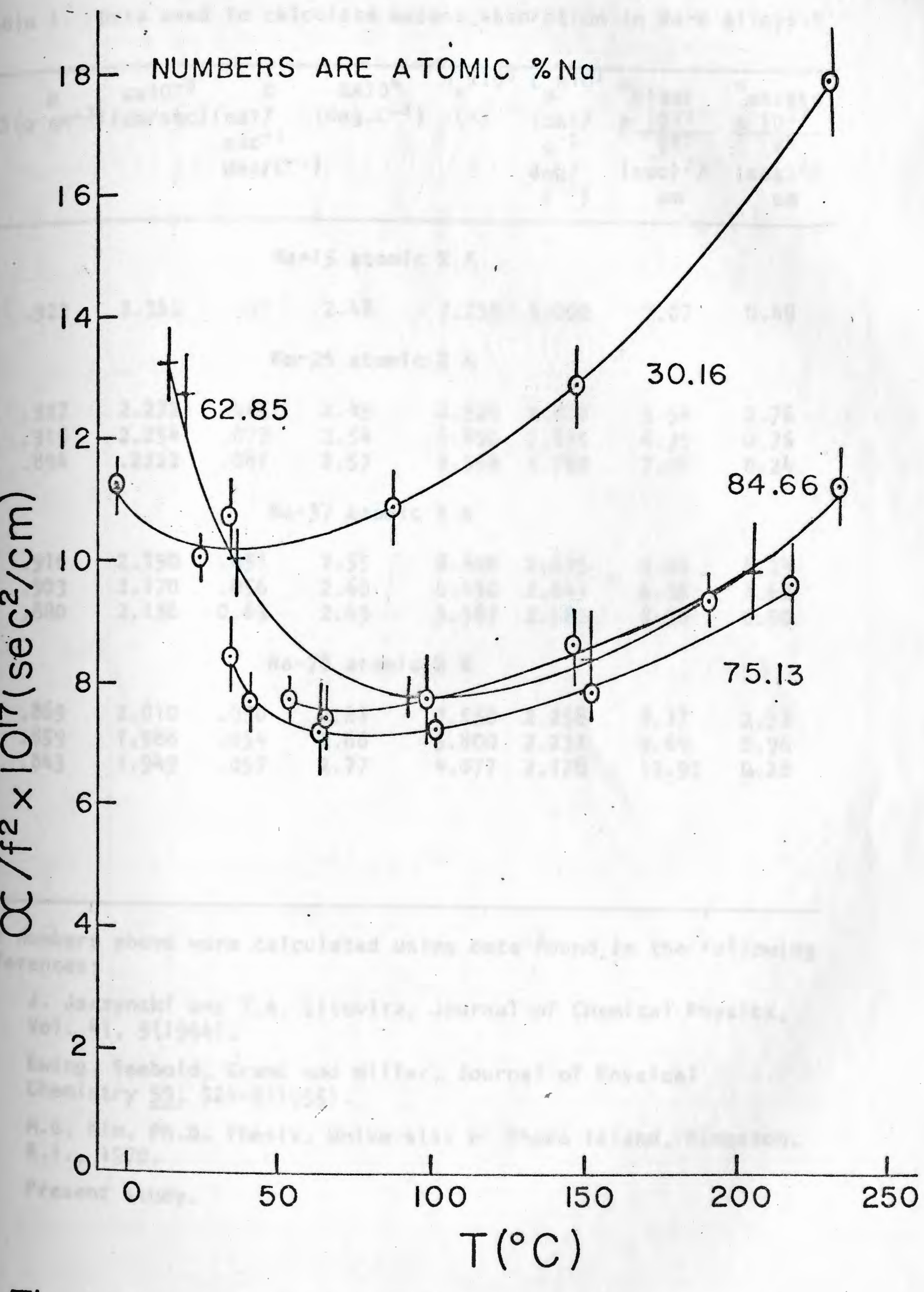

Fig. 1 Sound absorption in Na-K

Table I. Data used to calculate excess absorption in Na-K alloys.*

T (°K)	ρ (g cm^{-3})	c$\times 10^{-5}$ (cm/sec)	K (cal/ sec^{-1} deg/C^{-1})	$\beta \times 10^4$ (deg.C^{-1})	$\eta_s \times 10^3$ (P)	$C_p \times 10^1$ (cal/ g^{-1} deg/ C^{-1})	α_{class} $\times 10^{17}$ / f^2 (sec)^2/ cm	α_{excess} $\times 10^{17}$ / f^2 (sec)^2/ cm
				Na-15 atomic % K				
348	.922	2.365	.107	2.48	7.230	3.000	7.07	0.48
				Na-25 atomic % K				
308	.927	2.272	.065	2.49	8.920	2.870	5.54	2.76
348	.915	2.254	.073	2.54	6.850	2.835	6.39	0.76
423	.894	.2222	.081	2.57	3.554	2.769	7.96	0.24
				Na-37 atomic % K				
308	.916	2.190	.051	2.55	8.400	2.675	5.66	4.24
348	.903	2.170	.056	2.60	6.450	2.643	6.38	1.62
423	.880	2.136	0.63	2.69	3.387	2.582	8.30	0.50
				Na-70 atomic % K				
308	.869	2.010	.050	2.61	7.550	2.258	8.37	2.33
348	.859	1.988	.054	2.66	5.800	2.231	9.64	0.96
423	.843	1.949	.057	2.77	4.077	2.178	12.92	0.28

*All numbers above were calculated using data found in the following references:

J. Jarzynski and T.A. Litovitz, Journal of Chemical Physics, Vol. 41, 5(1964).

Ewing, Seebold, Grand and Miller, Journal of Physical Chemistry 59, 524-8(1955).

M.G. Kim, Ph.D. Thesis, University of Rhode Island, Kingston, R.I., 1970.

Present study.

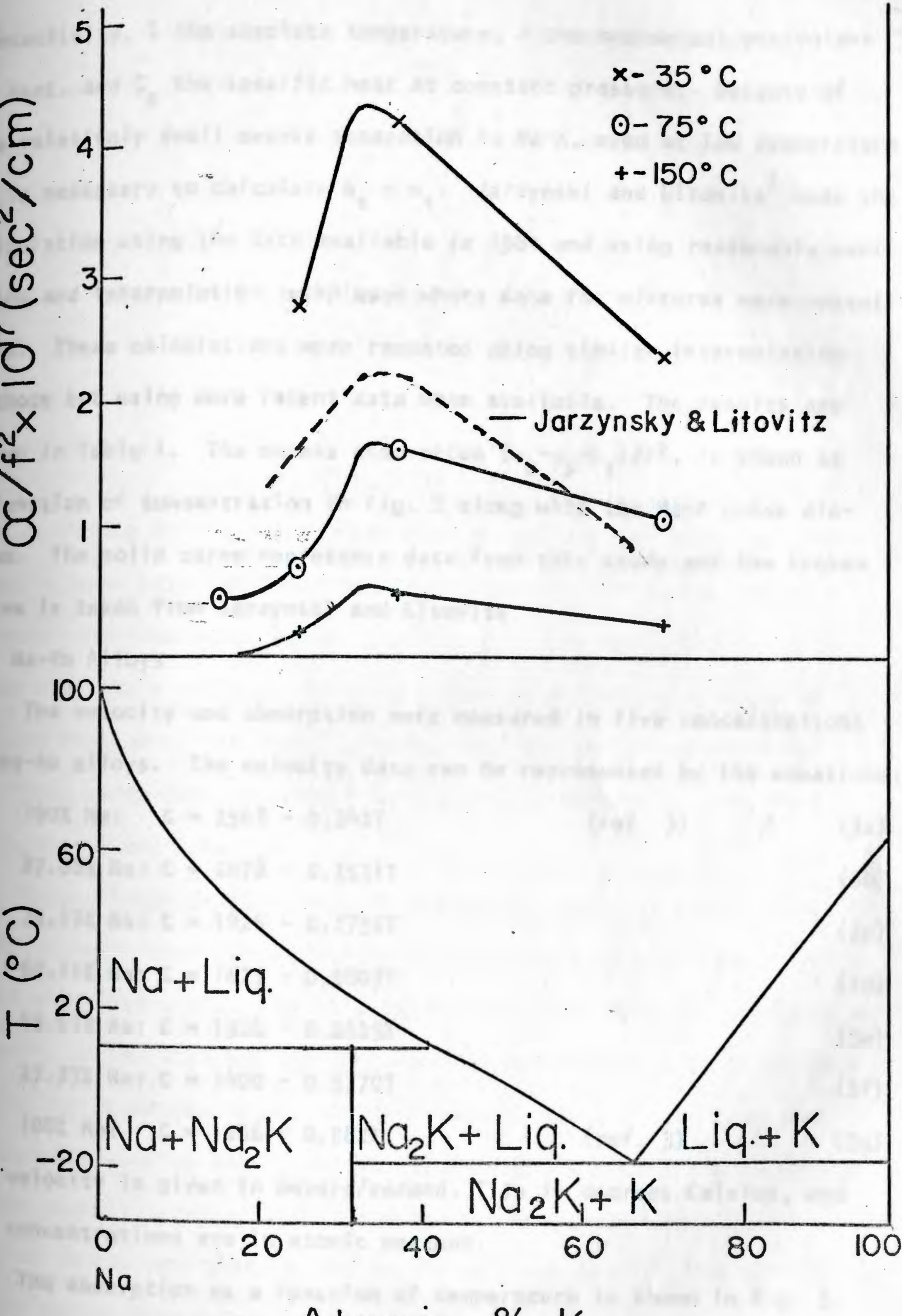

Fig. 2. Sound absorption in Na-K alloys with phase diagram

conductivity, T the absolute temperature, J the mechanical equivalent of heat, and C_p the specific heat at constant pressure. Because of the relatively small excess absorption in Na-K, even at low temperature, it is necessary to calculate $\alpha_s + \alpha_t$. Jarzynski and Litovitz[2] made the calculation using the data available in 1964 and using reasonable averaging and interpolation techniques where data for mixtures were unavailable. These calculations were repeated using similar interpolation methods but using more recent data when available. The results are shown in Table I. The excess absorption $(\alpha_o - \alpha_s - \alpha_t)/f^2$, is shown as a function of concentration in Fig. 2 along with the Na-K phase diagram. The solid curve represents data from this study and the broken curve is taken from Jarzynski and Litovitz.

B. Na-Rb Alloys

The velocity and absorption were measured in five concentrations of Na-Rb alloys. The velocity data can be represented by the equations:

100% Na: $C = 2568 - 0.542T$ (ref. 3) (3a)

87.08% Na: $C = 2078 - 0.3531T$ (3b)

75.17% Na: $C = 1826 - 0.2736T$ (3c)

60.11% Na: $C = 1625 - 0.3007T$ (3d)

49.61% Na: $C = 1520 - 0.2625T$ (3e)

27.27% Na: $C = 1400 - 0.5770T$ (3f)

100% Rb: $C = 1266 - 0.382T$ (ref. 3) (3g)

The velocity is given in meters/second, T is in degrees Celsius, and the concentrations are in atomic percent.

The absorption as a function of temperature is shown in Fig. 3. The dashed curves show the nearly classical behavior of pure Na and

Rb[3]. The low sodium concentration sample (27 at. %) also appears to have nearly classical temperature dependence, but the other samples have a strong increase of attenuation with decreasing temperature, and the effect is strongest for 60-75 at. % concentrations. The measured absorption as a function of concentration for various temperatures is shown in Fig. 4. Finally, the absorption versus composition curve, along with the liquidus curve of the phase diagram is given in Fig. 5.

DISCUSSION

Observing Fig. 2, it is seen that the results of Jarzynski and Litovitz have been confirmed to within experimental error. They attributed their measured excess absorption to the perturbation by the sound wave $2Na + K \rightleftharpoons Na_2K$. Since the absorption peak does occur at a concentration of K-67% Na, it seems that the solid composition Na_2K does carry over into the liquid state as previously predicted by Jarzynski and Litovitz.

Next, if one observes Fig. 5, a similar result is seen in the Na-Rb system. Again, the absorption peak occurs near 67% Na. This would also lead one to suspect a mechanism of the form $2Na + Rb \rightleftharpoons Na_2Rb$. However, unlike the Na-K system where the excess had to be calculated to see the absorption peak, the Na-Rb sample gives a very high peak so that subtracting the classical absorption would have little effect on the overall picture. Another major difference between the two systems is the existence of the stable compound Na_2K in the solid state in one and no such molecular association in the Na-Rb solutions. Hence, the high absorption at Rb-67% Na cannot be connected to a compound carrying over from the solid state.

The absorption peaks occur at the same concentration at which the inflection point of the liquidus curve of the phase diagram is located. In a previous work done by Kim and Letcher[1], it was also found that the absorption peak in the Na-Cs system occured at the same concentration where an inflection point in the liquidus curve occured. Also, the curve at the inflection point was somewhat flatter than might be predicted. When a metastable liquid immiscibility exists (i.e., a liquid miscibility gap which lies below the liquidus curve) it has the effect of broadening the shape of the liquidus curve. Hence, a submerged miscibility gap was expected. When a miscibility gap lies very near the liquidus curve, the liquid above the liquidus continues to be influenced by the immiscibility (in the form of critical concentration fluctuations). In the system studied here, Na-Rb, an identical situation exists. The curve at the inflection point is broader than expected and hence, one expects a metastable liquid immiscibility. The flattening at the inflection point of the liquidus curve suggests a critical composition near Rb-67 atomic % Na which is the same concentration at which the absorption peak occured. This is strong evidence connecting the high absorption to a critical phenomenon.

The two prominent theories attempting to explain excess absorption in binary systems attribute the attenuation of sound to a molecular association[7] or to a critical phenomenon[6,8,9]. Unfortunately, the lack of thermophysical data in the alkali metal systems prevents a quantitative comparison between theory and experiment, but some speculation can be made. Recall the major differences between the systems

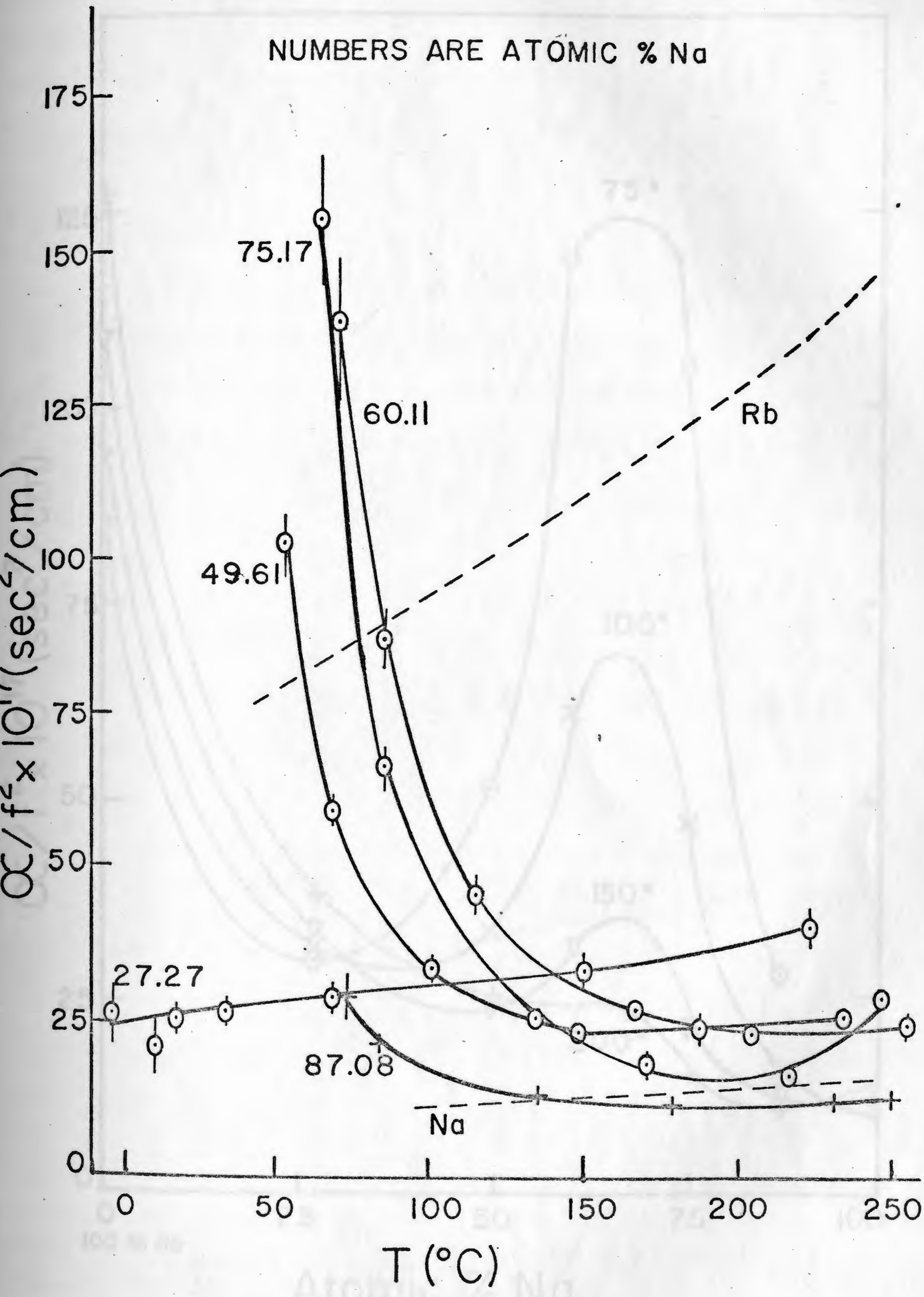

Fig. 3. Sound absorption in Na-Rb

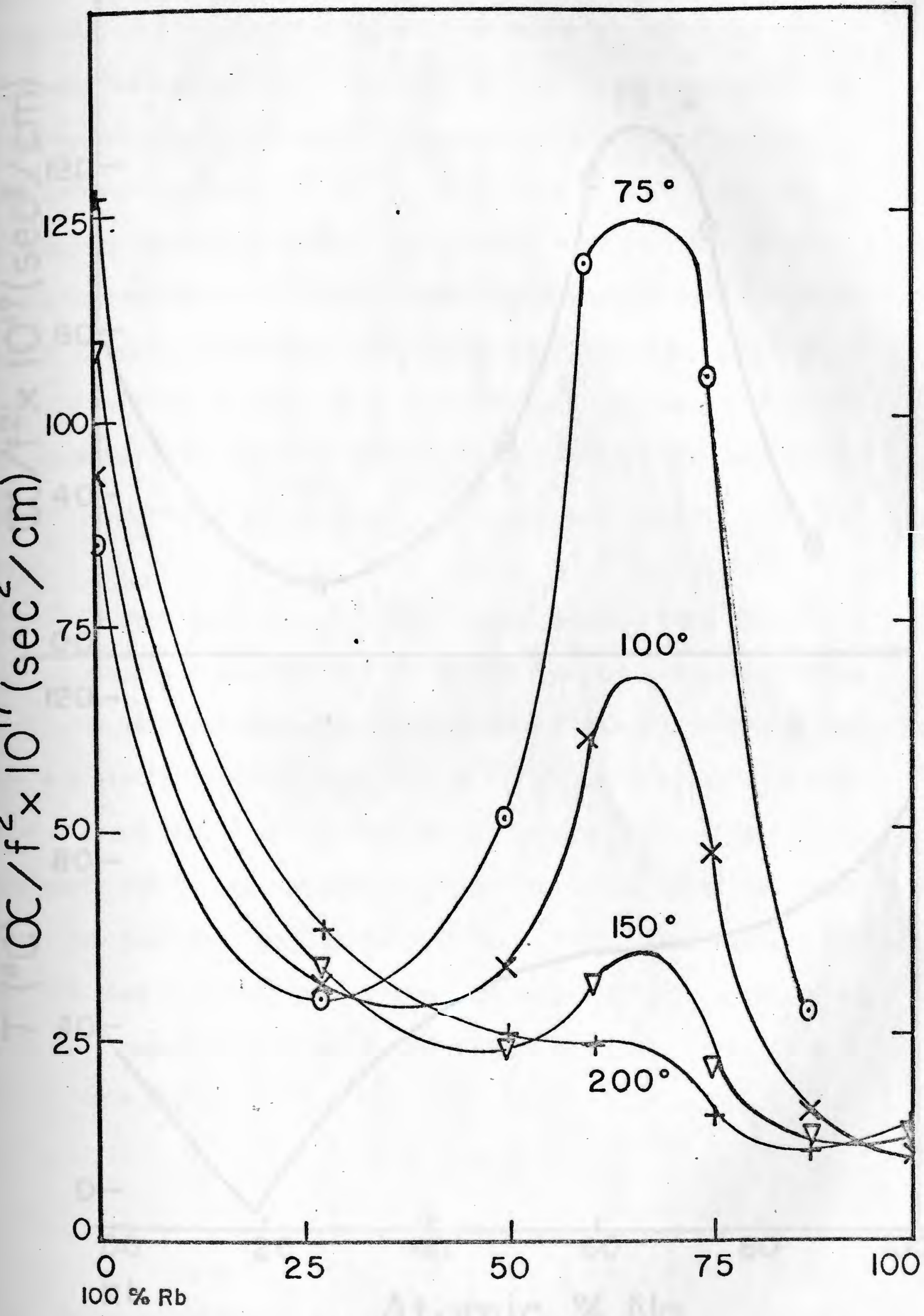

Fig. 4. Sound absorption in Na-Rb versus alloy composition

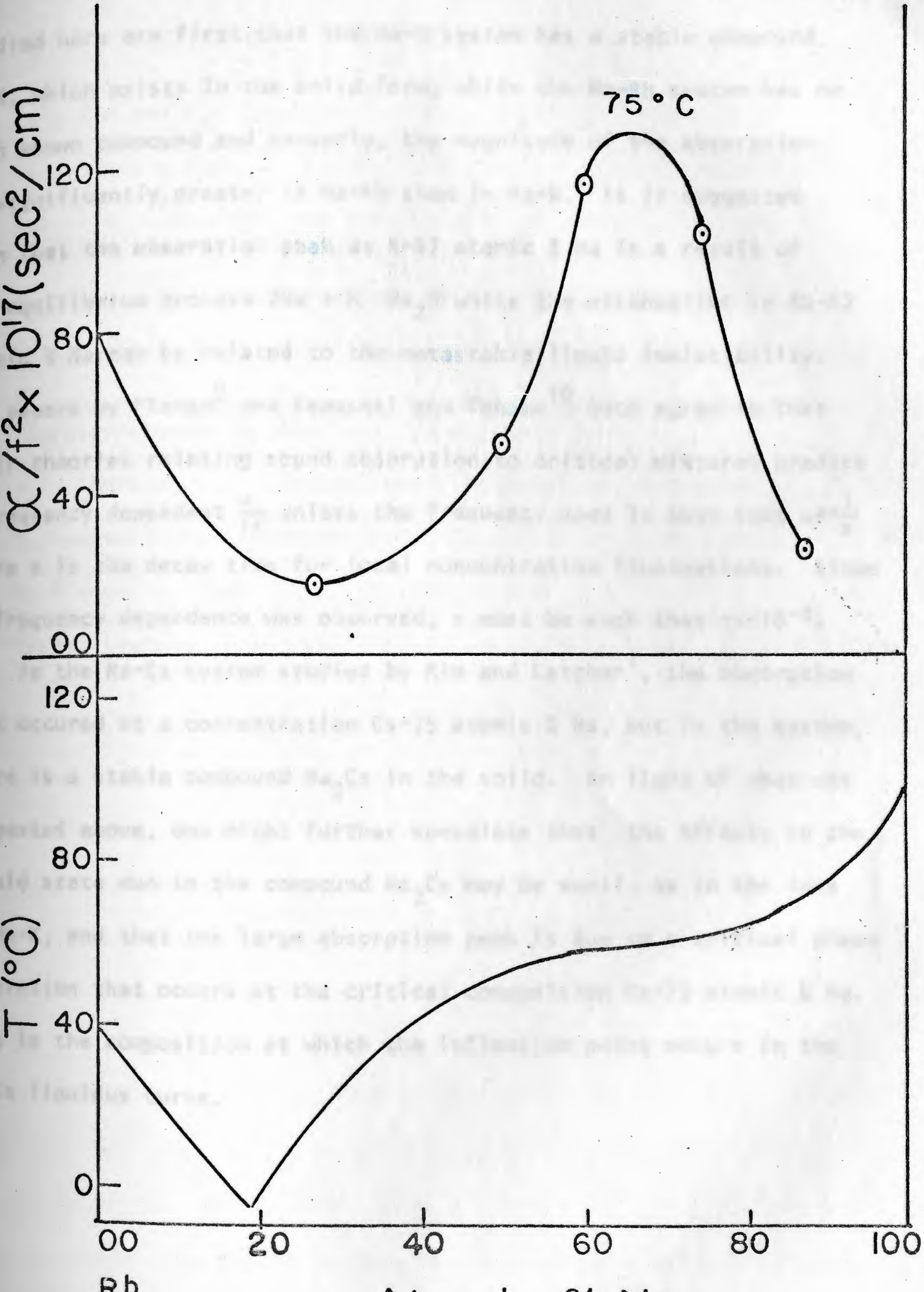

Fig. 5. Sound absorption in Na-Rb with phase diagram

studied here are first that the Na-K system has a stable compound Na_2K, which exists in the solid form, while the Na-Rb system has no such known compound and secondly, the magnitude of the absorption is significantly greater in Na-Rb than in Na-K. It is suggested then that the absorption peak at K-67 atomic % Na is a result of the equilibrium process $2Na + K \;\; Na_2K$ while the attenuation in Rb-67 atomic % Na can be related to the metastable liquid immiscibility. The papers by Fixman[9] and Kawasaki and Tanaka[10] both agree in that their theories relating sound absorption to critical mixtures predict a frequency dependent $\frac{\alpha}{f^2}$ unless the frequency used is such that $\omega \ll \frac{1}{\tau}$ where τ is the decay time for local concentration fluctuations. Since no frequency dependence was observed, τ must be such that $\tau \ll 10^{-8}$.

In the Na-Cs system studied by Kim and Letcher[1], the absorption peak occured at a concentration Cs-75 atomic % Na, but in the system, there is a stable compound Na_2Cs in the solid. In light of what was suggested above, one might further speculate that the effects in the liquid state due to the compound Na_2Cs may be small, as in the case of Na-K, and that the large absorption peak is due to a critical phase separation that occurs at the critical composition Cs-75 atomic % Na. This is the composition at which the inflection point occurs in the Na-Cs liquidus curve.

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APPENDIX A: INTRODUCTION AND REVIEW OF THE PROBLEM

Ultrasonics is one of the many areas of physics which has grown rapidly with the development of more specialized and sophisticated electronic equipment. One is able to send out a short pulse of ultrasound through a liquid, receive the echo of this pulse, and measure how much has been absorbed by the medium. By changing pathlength, one can express absorption per unit distance. The electronic apparatus also gives an accurate measure of the travel time from which the velocity can easily be calculated. These data can be used to test the theories describing the mechanisms which cause absorption.

In the nineteenth century, it was believed that sound absorption was caused by only two processes. Stokes[1] derived the expression for the absorption which results from the shear viscosity of the liquid. This absorption α_s is given by $\alpha_s = 8\pi^2\eta_s f^2/3\rho C^3$, where f is the frequency, η_s is the shear viscosity, ρ is the density, and C is the sound velocity. The second process known to cause sound absorption was first proposed by Kirchhoff[2]. He showed that the thermal conductivity of a liquid will give rise to an absorption, α_T, which is given by $\alpha_T = 2\pi^2\beta^2 KTf^2/\rho CJC_p$, where β is the volume expansion coefficient, K is the thermal conductivity, T is the absolute temperature, J is the mechanical equivalent of heat, C is the sound velocity, f is the frequency, and C_p is the specific heat at constant pressure. The sum of these two absorption coefficients, $\alpha_s + \alpha_T$, is often referred to as the classical absorption. When accurate measurements of absorption were possible, it was realized that most liquids had absorption coefficients much too high to be accounted for by $\alpha_S + \alpha_T$ alone. By reexamining the equation derived by Stokes, it is found that he assumed a quantity η_β, the bulk viscosity, to be zero. That is, he assumed that there is no energy loss by shearless compressions. This is the special case rather than the generality; so the assumption is therefore invalid for most liquids. The difference between the observed and the classical absorption, the so-called excess absorption, α_e, can be attributed phenomenologically to a bulk viscosity[3] in the form $\frac{\alpha_e}{f^2} = \frac{2\pi^2\eta_\beta}{\rho C^3}$.

Pure liquid alkali metals are spherically symmetric monatomic liquids so any excess absorption should not be due to intramolecular processes. If two alkali metals are mixed and if the two components dissolve completely and have no molecular association, then a relatively simple binary system is obtained. Ultrasonic absorption in such a system is a smoothly varying function of concentration with no absorption peaks present. If molecular association is present in the system, it could be detected by unusually high absorption peaks at the particular concentration at which it is predominant. In either case, alkali metal mixtures provide a desirable system to be used in the study of the mechanisms involved in sound absorption.

Several previous attempts have been made to measure ultrasonic absorption in liquid alkali metals and in binary alkali metal solutions. As one would guess, many technical problems are encountered when working with such chemically active materials and often samples are contaminated before measurements can be made. Jarzynski and Litovitz[4] used ultrasonic techniques to study the system Na-K. They expressed their difficulties in keeping their samples clean and in obtaining a usable bond between the transmission line and the sample. Recently, it was shown by Kim[5] that impurities in the sample could gravely affect the measured absorption. Therefore, the Na-K system was a good sample to re-investigate.

The work leading to this most recent study of alkali metal systems was first begun by Kemp[6]. He investigated pure alkali metal systems and encountered the usual difficulties in handling the samples and in preventing contamination. The physical apparatus was improved by Kim[5]. This revised equipment is capable of going through all the steps from transferring the sample to taking the data with a minimum of contamination. The success in minimizing contamination is proven by comparing duplicate data points at various time intervals. Kim succeeded in making measurements in pure Na, K, Rb, and Cs[7]. He also obtained data for the two binary systems, K-Rb and Na-Cs[8]. The Na-Cs system gave an unusually high absorption peak at a concentration of about Na_3Cs. If one looks at the liquidus curve of the phase diagram, an inflection point occurs at approximately the same concentration. As Kim[5] points out, the connection here is far more than coincidence and it would be desirable to investigate other systems with similar phase diagrams. The Na-Rb system also has an inflection point on its liquidus curve and hence, was an interesting system to explore. For these reasons, the Na-K and the Na-Rb systems were chosen as the samples in this investigation.

APPENDIX B: EXPERIMENTAL PROCEDURES

High purity samples were obtained in 20 ml sealed glass ampoules from MSA Research Corporation, Pittsburgh, Pa. A total of nine were tested, five were Na-Rb mixture and four Na-K. Compositions were chosen near the inflection and eutectic points of the liquidus curve of the phase diagram and at various intermediate concentrations. The end point, or pure sample, measurements have been made in another study[7].

The mechanical system was first used by Kemp[6], later improved by Kim[5], and finally with some alteration, used in the present study. Since all of the details can be found in these previous two works, only a general description of the system and how it operates will be included here. The main body of the apparatus is schematically pictured in Fig. 6.

The necessity to guard against contamination is an important part of the equipment design. Alkali metals are extremely active and react with most materials. If the sample oxidizes to the point where the surface is no longer clean and shiny, not only will the results be questionable, but it becomes extremely difficult to obtain a bond between the transducer and the sample. (Naturally, if no bond is obtained, no data can be taken.) Therefore, steps must be taken to insure that the system is clean before an experiment is attempted. All parts which come in contact with the sample are washed for at least 24 hours in a distilled acetone bath*. All other interior portions of the apparatus

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*Corning No. 3885 obtained from Eastern Scientific Corp.

are washed with acetone prior to assembly. The only materials which come in contact with the sample once it has been transferred are the quartz transducer, porcelain cement, and the stainless steel parts making up the system (all interior parts except the vacuum seal joints are made of stainless steel). Two different types of transducer holders were used. For samples which did not readily "wet" the transducer, a Savereisen porcelain cement was used to mount the transducer on the very end of the transducer assembly. Since the transducer itself was first to contact the sample, a bond could be obtained. When the sample showed good wetting properties, the transducer was mechanically sealed using two highly polished stainless steel surfaces with the transducer clamped in the middle. Although the porcelain system facilitated bonding, it would tend to leak after long exposure to high temperatures. Therefore, in most cases the virtually leakless mechanical seal was used. Both systems are described in detail by Kim[5].

The next step in the procedure is to evacuate the system thoroughly. Since data are taken at temperatures as high as 250° C, the system should be evacuated at temperatures at least this high to outgas the system successfully. Commercial heaters with fiberglass insulation could not be used since the dense fibers have such a large surface area, they contain a great deal of adsorbed gas. Even when "baked" for long periods at high temperature, the heater could not be completely outgased. Instead, a heater made of nichrome wire and porcelain cement packed around a porcelain cylinder was used. The system was evacuated for several hours by the mechanical pump at a temperature above 250° C. When a sufficiently low pressure was obtained, the system was further

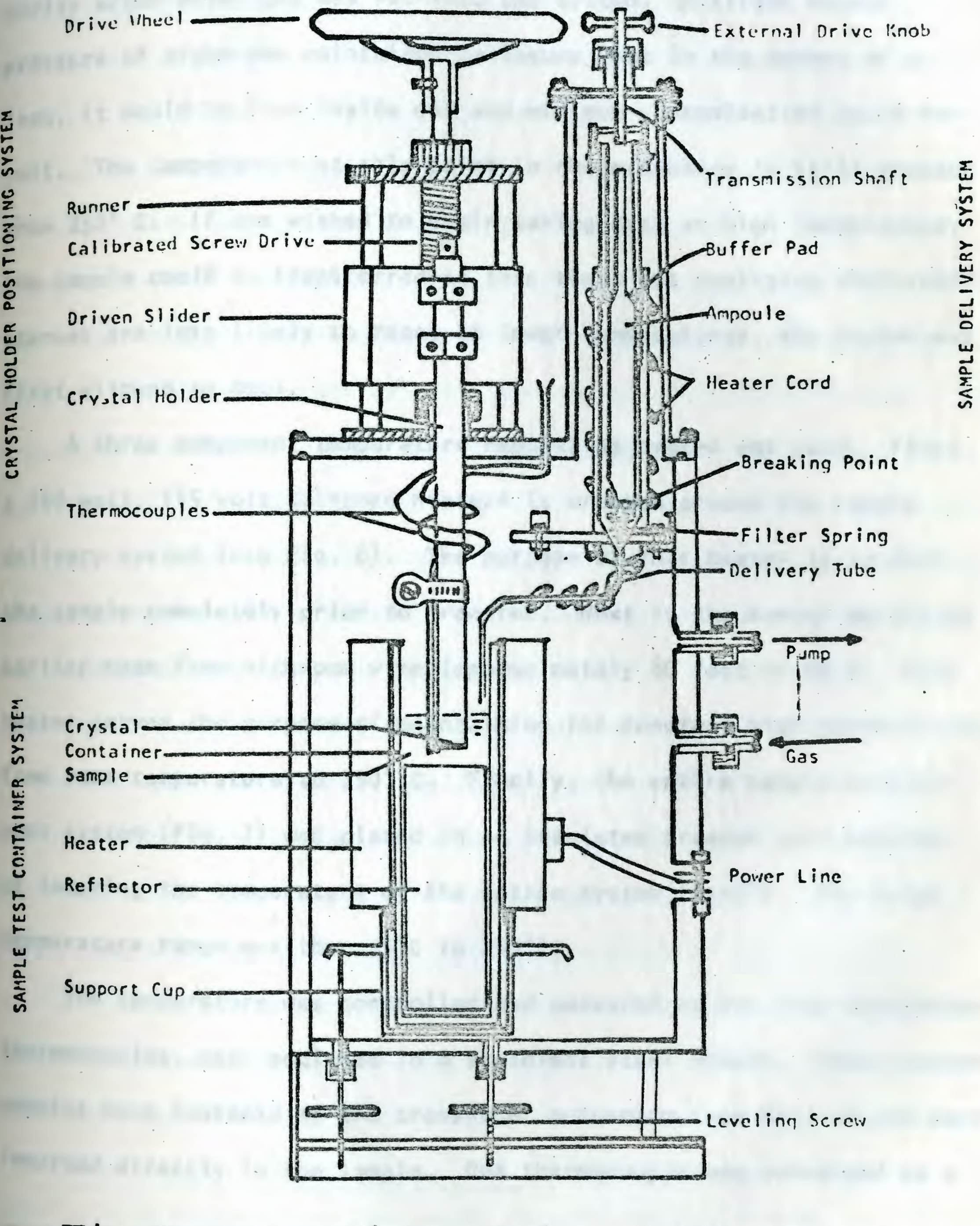

Fig.6. Sample containment system

evacuated by a diffusion pump for several hours. When a pressure of about 10^{-4} torr was reached, the vacuum line was shut off and a high purity argon cover gas was let into the system. A slight excess pressure of argon was maintained to insure that in the advent of a leak, it would be from inside out and minimum contamination would result. The temperature at this point in the procedure is still greater than 250° C. If one wished to begin taking data at high temperature, the sample could be transferred at this time, but realizing that substances are less likely to react at lower temperatures, the system was first allowed to cool.

A three component temperature regulating system was used. First, a 160 watt, 115 volt Cal-cord heater* is wrapped around the sample delivery system (see Fig. 6). The purpose of this heater is to melt the sample completely prior to transfer. Next is the heater mentioned earlier made from nichrome wire (approximately 80 feet or 80 Ω. This heater served the purpose of maintaining the constant high temperatures from room temperature to 250° C. Finally, the entire sample containment system (Fig. 1) was placed in an insulated freezer unit capable of lowering the temperature of the entire system to -5°C. The total temperature range was then -5°C to 250°C.

The temperature was controlled and measured by two iron-constantan thermocouples, each enclosed in a stainless steel sheath. These thermocouples were fastened to the transducer mechanism (see Fig. 6) and were immersed directly in the sample. One thermocouple was connected to a

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*A glass fiber insulated cord heater, made by Glass-Col Apparatus Co., Terre Haute, Indiana.

pyrotroller* which automatically controlled the high voltage keeping the temperature within a preset range. A variable voltage was supplied to the heaters and a calibration curve had been measured. That is, any voltage setting would raise the temperature to a steady state temperature, but to set the voltage at the desired temperature and wait for the system to come to equilibrium was a very time consuming operation. The pyrotroller was used to shorten this time. By setting the temperature desired on the pyrotroller and supplying the heaters with a voltage higher than necessary to attain this temperature, the system would heat very rapidly and shut off at approximately the predetermined temperature. Finally, resetting the voltage to the correct setting would produce the steady state temperature desired. This method greatly reduced the time necessary to take the data and hence reduced the chance of contamination of the sample. The second thermocouple was used in conjunction with a millivolt potentiometer**. It was determined that the system could be kept at a constant temperature to within ±1°C.

After the preliminary preparations are completed and the system has cooled to a few degrees above the melting point, the sample could be transferred. The sample is first melted by turning on the cal-cord heater and allowing sufficient time for the delivery system and the delivery tube to heat substantially above the melting point. This is essential since any unmelted sample would hinder the flow through the delivery tube. To release the liquid from the glass ampoule, pressure

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*Manufactured by the Alnor Instrument Co., Chicago, Illinois.

**Millivolt potentiometer 8686, Leeds & Northrup Co., Philadelphia.

is applied to the external drive knob causing the ampoule to break and the sample to flow through the delivery tube and into the test container.

Although not pictured in Fig. 6, there is a small window (about 1 inch in diameter) at the top of the sample containment system and a light bulb inside the system which allows one to view the sample. Thus, it is very easy to inspect the sample once it has been transferred; making any surface oxidation easily detectable.

The transducer assembly can now be lowered very slowly into the sample. This procedure usually produced a good bond, but in some cases, the sample had to be heated increasing its tendency to wet the transducer. When a bond was obtained at this higher temperature, the temperature could again be lowered to just above the melting point without loss of signal. The transducers used were X-cut five MHz quartz crystals, 1/2 inch in diameter. Since the samples were good conductors, they served as the ground electrode and the crystals were plated in a 1/4 inch diameter circle on one side only. The details of the transducer mechanism can be found elsewhere[5].

Next, one must be certain that the surface of the transducer is parallel to the plane of the reflector. This paralleling procedure is performed by setting the transducer at maximum path length and adjusting the levelling screws (see Fig. 6) so that maximum echo amplitude is observed on the oscilloscope. This was checked periodically throughout the experiment but generally, once adjusted remained parallel. The reflector is a stainless steel cylinder 4 inches long so that any transmitted energy is dissipated before returning to the sample and hence does not show up in the echo pattern.

The signal which is applied to the transducer is produced by an attenuation comparator (Model PR201) produced by Matec, Ind., Warwick, R.I. This comparator sends out pulsed oscillations, receives the echoes, and displays them on a built-in CRT. Although no measurement can be made on the absolute magnitude of the echo, by changing path length it is possible to measure the change in sound level. This is accomplished by using the Model 666 pulse comparator (also manufactured by Matec, Inc.) in conjunction with the main comparator. The pulse comparator generates a two-microsecond electrical pulse at a frequency of 60 MHz which has an amplitude that is variable in steps of 0.1 decibels to 61 decibels. This calibrated pulse is displayed on the oscilloscope with the echo pattern. Since the sample amplifier is used for both signals, there is no difficulty with nonlinearity. By matching the height of the comparator pulse with a returning echo, changing path length, and then again matching pulse height, a measure of the absorption in decibels per centimeter is easily obtained. Also, using the calibrated delay built into the attenuation comparator, the comparison pulse can be delayed a known amount of time. Hence, if the two pulses are observed at the same relative position with respect to each other at various path lengths, the time changes can be observed and the velocity of sound can be calculated.

The path length is varied by means of a calibrated screw-drive turned by a slow speed electric motor. Using a microswitch system, the motor could be stopped at precisely one turn intervals. One turn of the screw represents a distance of 0.159 cm so that the total path length change would be twice this amount. For most samples, data were taken at one turn intervals for ten turns.

For each sample, data were taken as a function of temperature and frequency. Starting at a temperature just above the liquidus temperature, six temperatures were used at regular intervals to as high as 250°C. At each of these temperatures, the frequency of the pulse was varied from 15 MHz to as high as 105 MHz in 10 MHz intervals. In those samples with the highest absorption, a maximum of only 45 MHz could be used. At each of the six temperatures as many as ten frequencies were used and at each of these frequencies, the path length was changed by ten turns of the calibrated screw drive giving attenuation settings in decibels and delay times in microseconds for each turn.

These data are then put into a multi-purpose computer program[9]. The program first makes corrections for instrument calibrations and then, assuming the transducer behaves as a plane piston source in an infinite medium, diffraction corrections are made[10]. The time delay differences along with the path differences are used to calculate the velocities. This is done for all the temperatures at each frequency and then the average is computed. Data which deviate by more than three standard deviations from the mean are excluded. Similarly, the decibel differences for a known path length change are used to calculate a value for $\frac{\alpha}{f^2}$. These values are averaged and a standard deviation is calculated. Finally, the program uses the above information to produce a least squares-linear equation for the velocity as a function of temperature.

APPENDIX C: EXPERIMENTAL RESULTS

Na-K

The computer corrected data for Na-K solutions can be found in Table II. These are the data used to plot all figures found here and in the manuscript. The values for $\frac{\alpha}{f^2}$ found here were used as the observed absorption α_0 in calculating the excess absorption (see Manuscript).

It was seen from Eq. (1) that the velocity varies linearly with temperature. This is also illustrated in Fig. 7 where the velocities are plotted as a function of temperature. Interpolating from this graph, one can then plot velocity versus concentration for various temperatures. The result can be seen in Fig. 8. These curves do not show any unusual temperature or concentration dependence.

The absorption data can be plotted in a variety of ways depending on what one wishes to illustrate. Here, since the main interest is the variation of absorption with concentration, first $\frac{\alpha}{f^2}$ versus temperature is plotted, then by interpolation, $\frac{\alpha}{f^2}$ versus concentration can be graphed (shown in Fig. 9). In the case of the Na-K system, no absorption peaks are immediately evident from Fig. 9 although the low temperature curve does show a tendency to peak in the area of 65 atomic % Na. Hence, the excess absorption was calculated and the peak was easily observed (see Manuscript Fig. 2).

The error bars in Fig. 2 are quite large since the data used to make the classical calculation may lead to an error as high as ±50%. However, a very convincing argument in favor of the validity of the peak absorption can be made by observing Figs. 1 and 9. In Fig. 1,

Table II. Velocity and Absorption Data for Na-K Alloys

T (°C)	c (m/sec)	error range (m/sec)	$\alpha_o/f^2 \times 10^{17}$ (sec^2/cm)	error range (sec^2/cm)
		K-30.16% Na		
-1.5	2027	8	11.2	0.5
25.6	2003	10	10.0	0.4
34.2	2021	8	10.7	0.6
88.2	1977	9	10.8	0.6
148.0	1943	9	12.8	0.6
231.8	1901	8	17.8	0.9
		K-62.85% Na		
13.6	2190	13	13.2	0.6
19.2	2213	21	12.7	0.7
35.4	2189	14	10.0	0.7
91.8	2166	17	7.8	0.4
152.3	2134	17	8.4	0.8
205.3	2111	17	9.9	0.8
		K-75.13% Na		
34.6	2268	14	8.5	0.6
40.7	2264	14	7.7	0.5
64.0	2263	14	7.3	0.8
102.4	2236	13	7.3	0.2
153.0	2225	19	7.9	0.4
218.7	2192	13	9.7	0.7

Table II. Continued

T (°C)	c (m/sec)	error range (m/sec)	$\alpha_o/f^2 \times 10^{17}$ (sec^2/cm)	error range (sec^2/cm)
		K-84.66% Na		
54.9	2377	12	7.7	0.4
66.9	2374	13	7.4	0.5
99.7	2344	15	7.7	0.7
148.1	2325	15	8.6	0.6
192.1	2300	11	9.4	0.4
235.4	2274	15	11.2	0.7

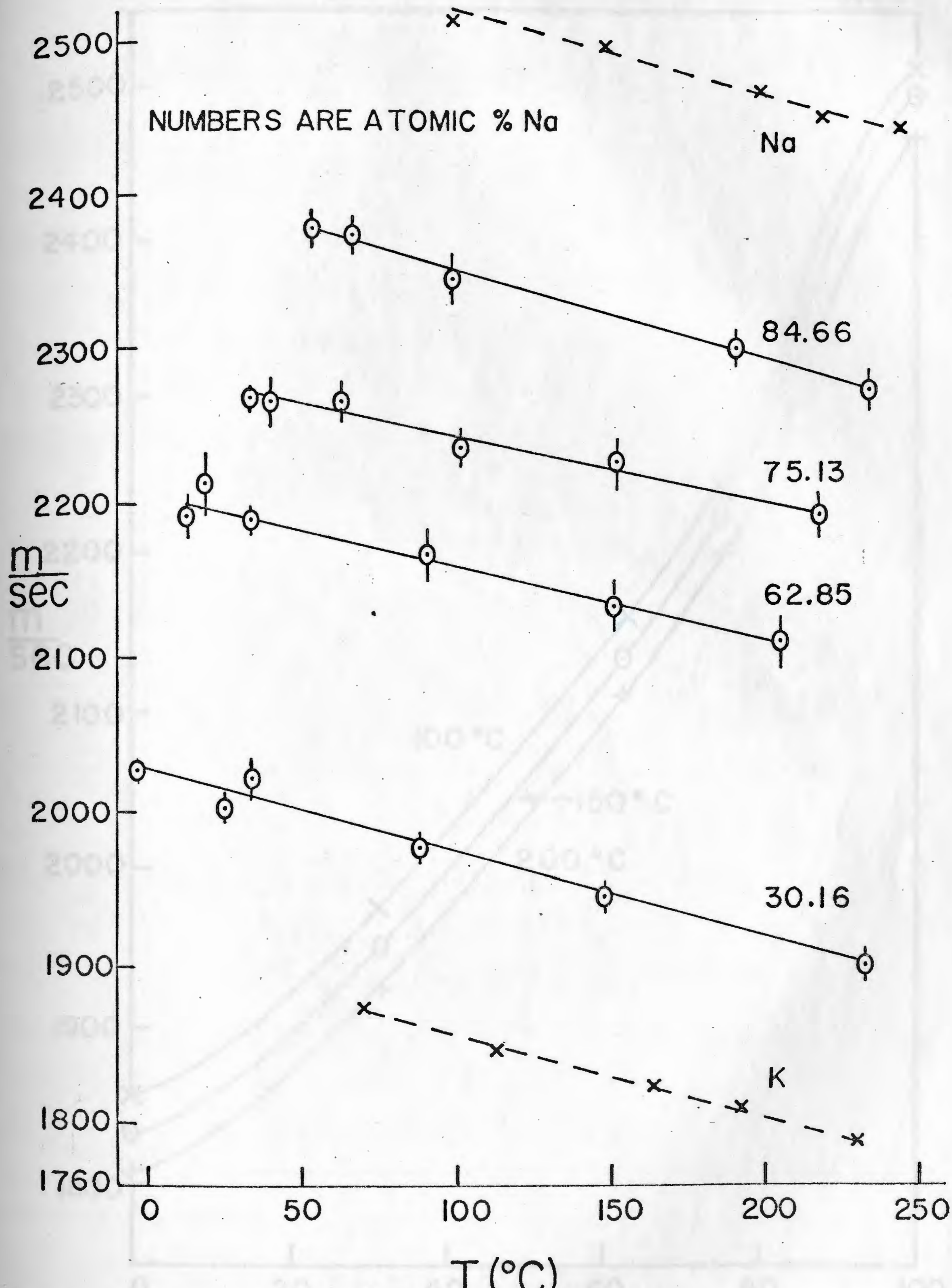

Fig. 7. Sound velocity versus temperature in Na-K alloys

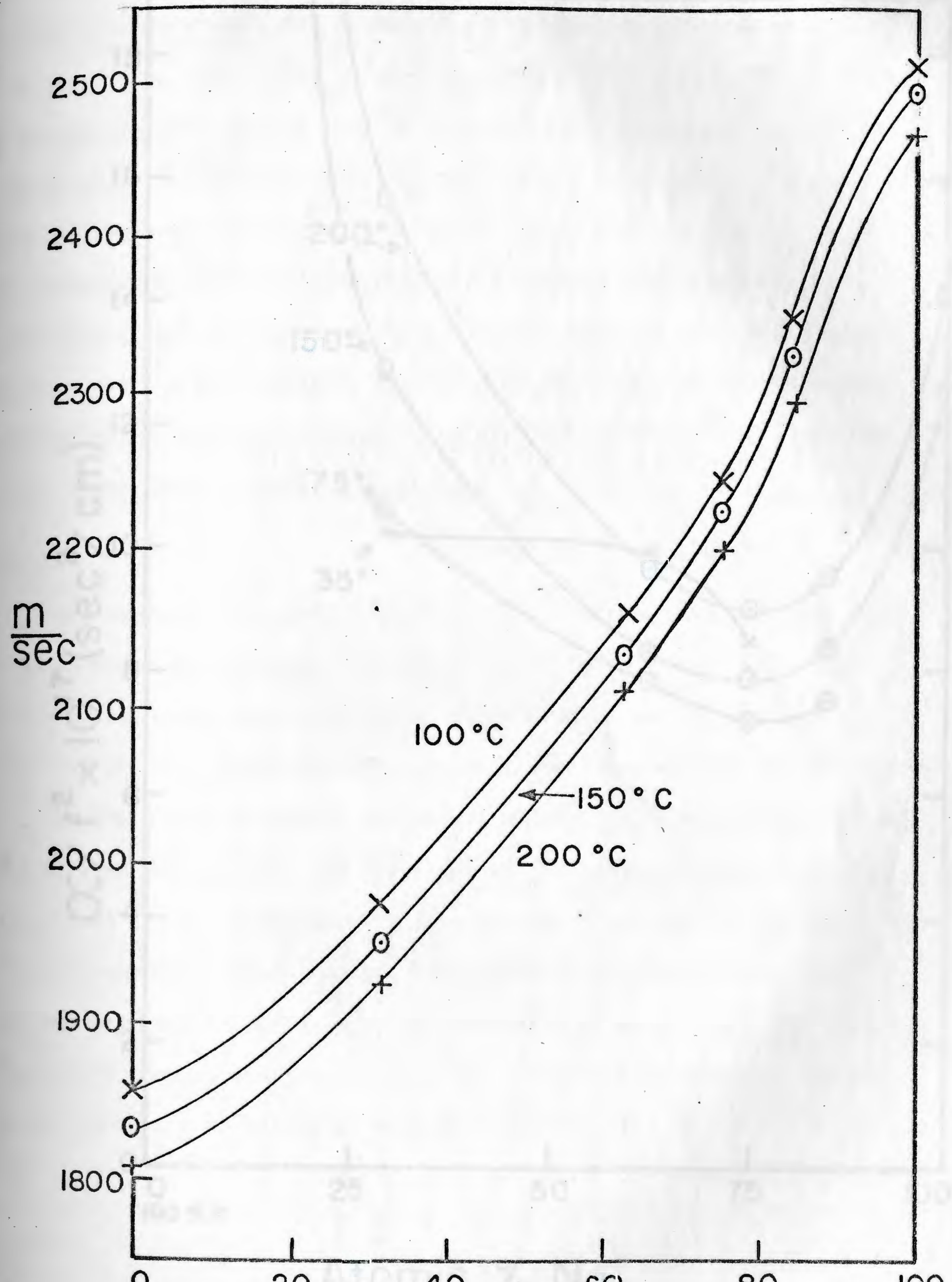

Fig. 8. Sound velocity versus composition in Na-K

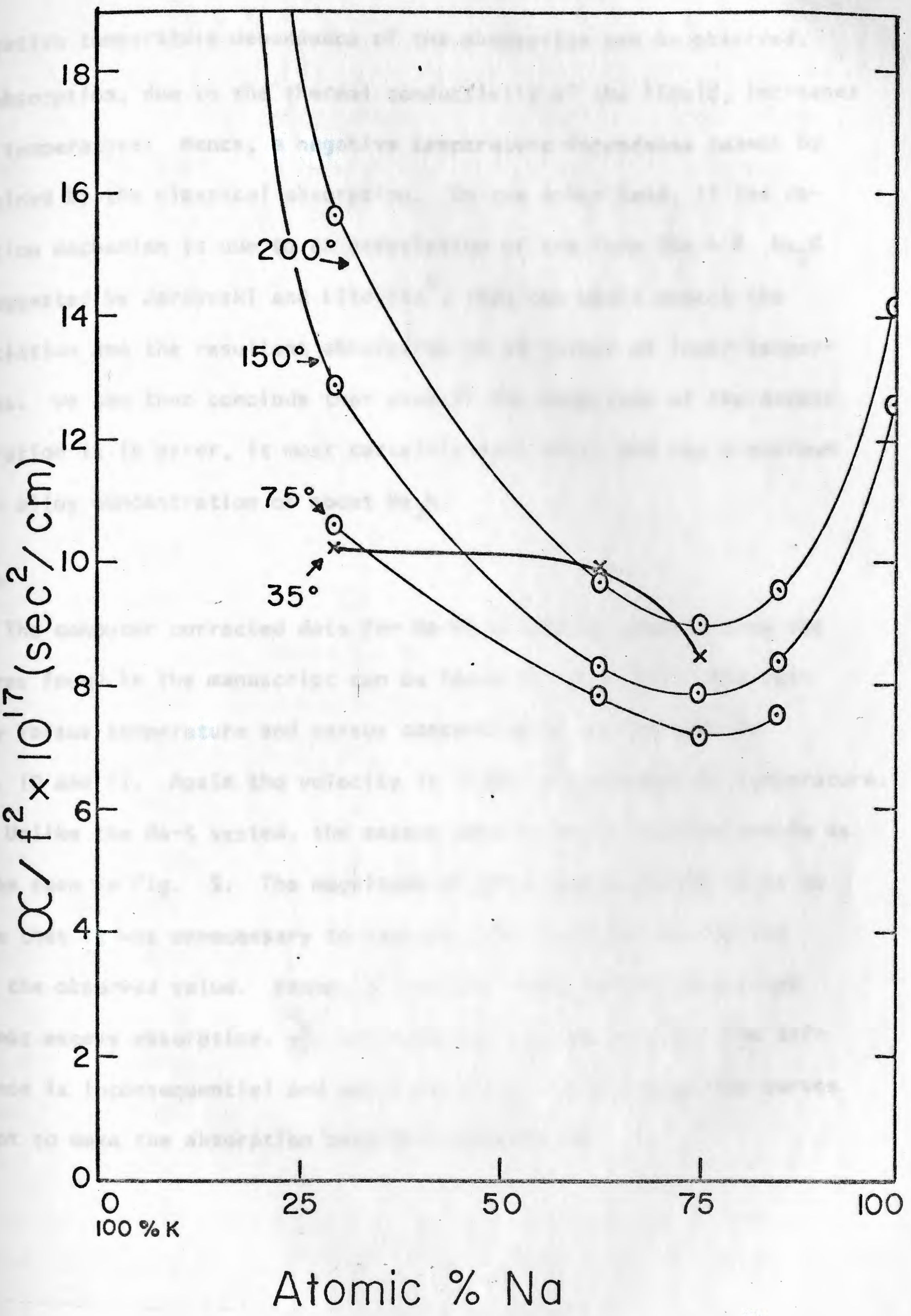

Fig. 9. Observed sound absorption in Na-K alloys

a negative temperature dependence of the absorption can be observed. The absorption, due to the thermal conductivity of the liquid, increases with temperature. Hence, a negative temperature dependence cannot be explained by the classical absorption. On the other hand, if the relaxation mechanism is due to an association of the form $2Na + K \quad Na_2K$ as suggested by Jarzynski and Litovitz[4], then one would expect the association and the resultant absorption to be larger at lower temperatures. We can then conclude that even if the magnitude of the excess absorption is in error, it most certainly does exist and has a maximum at an alloy concentration of about Na_2K.

Na-Rb

The computer corrected data for Na-Rb solutions used to draw the figures found in the manuscript can be found in Table III. The velocity versus temperature and versus concentration can be seen in Figs. 10 and 11. Again the velocity is linearly dependent on temperature.

Unlike the Na-K system, the excess absorption is unquestionable as can be seen in Fig. 5. The magnitude of this excess proved to be so large that it was unnecessary to subtract the classical absorption from the observed value. Hence, all graphs found in the manuscript are not excess absorption, $\frac{\alpha_e}{f^2}$, but observed absorption, $\frac{\alpha_o}{f^2}$. The difference is inconsequential and would have little bearing on the curves except to make the absorption peak more symmetrical.

Table III. Velocity and Absorption Data for Na-Rb Alloys

T (°C)	c (m/sec)	error range (m/sec)	$\alpha_o/f^2 \times 10^{17}$ (sec^2/cm)	error range (sec^2/cm)
		Rb-27.27% Na		
-1.3	1451	53	26.9	4.9
11.7	1399	29	21.5	5.0
19.2	1346	9	26.0	2.1
34.5	1348	11	27.0	2.1
69.6	1374	25	29.5	2.5
150.5	1319	14	33.9	3.0
224.1	1295	12	40.5	3.4
		Rb-49.61% Na		
53.5	1507	7	102.1	5.0
68.5	1499	10	59.2	2.6
100.8	1493	5	33.7	1.7
150.2	1483	6	23.7	1.7
187.8	1470	7	24.3	2.6
235.8	1457	6	25.6	1.6
		Rb-75.17% Na		
65.5	1803	6	154.9	10.8
86.0	1804	7	66.7	2.7
136.2	1794	9	25.8	2.1
171.6	1785	5	18.2	1.8
218.6	1767	9	16.5	1.3
248.3	1754	9	29.0	1.5

Table III. Continued

T (°C)	c (m/sec)	error range (m/sec)	$\alpha_0/f^2\times10^{17}$ (sec^2/cm)	error range (sec^2/cm)
		Rb-60.11% Na		
71.3	1598	10	138.1	10.4
85.1	1603	9	86.7	4.7
115.3	1592	7	45.4	2.9
166.3	1576	6	27.6	1.6
204.3	1561	6	23.6	1.2
255.2	1548	7	24.5	2.3
		Rb-87.08% Na		
73.7	2054	12	29.2	3.5
84.7	2047	30	21.7	1.7
136.7	2028	16	12.6	1.1
180.6	2016	13	12.0	0.9
233.0	1997	13	12.0	1.0
250.7	1989	15	12.5	0.8

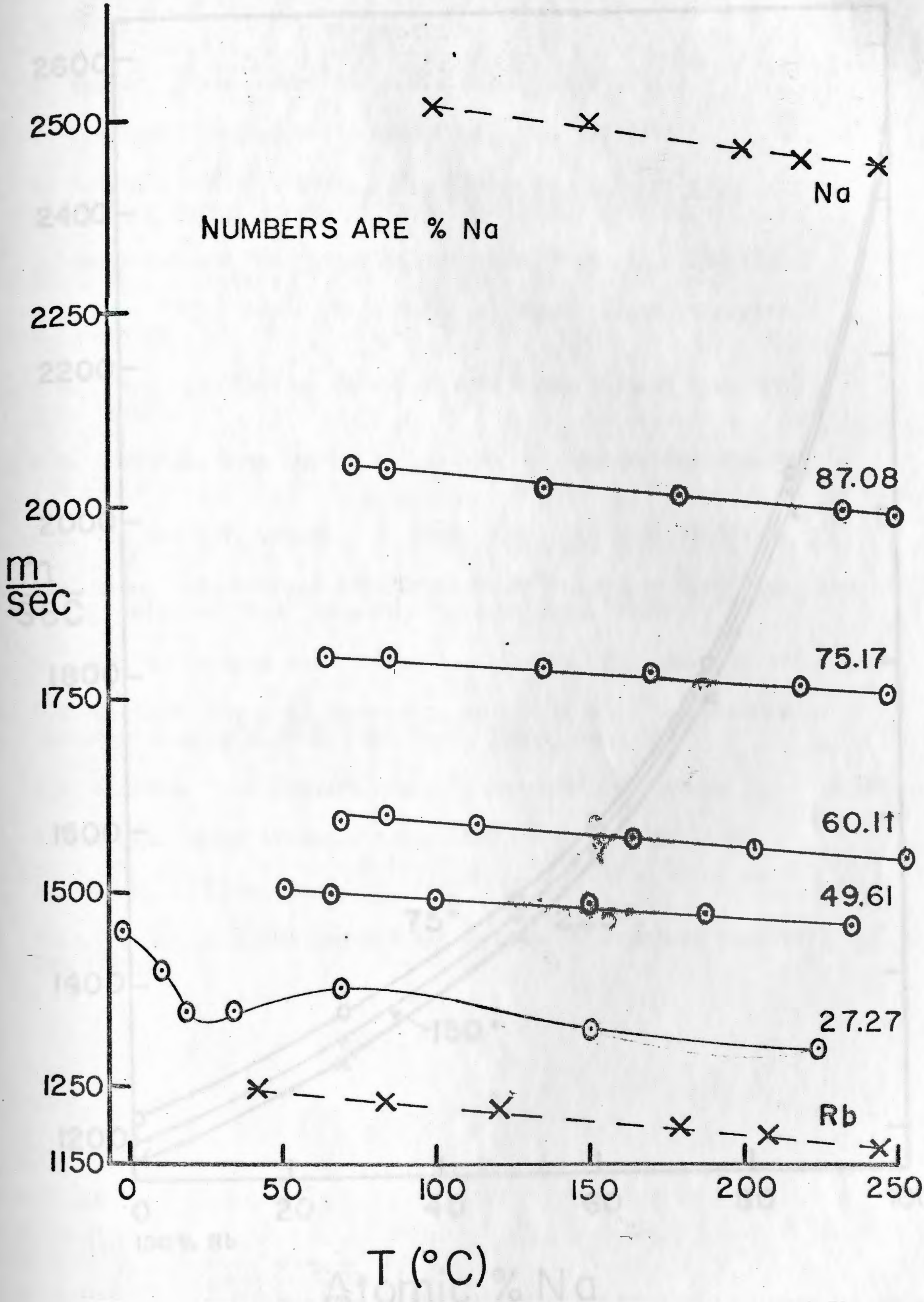

Fig. 10. Sound velocity in Na-Rb alloys

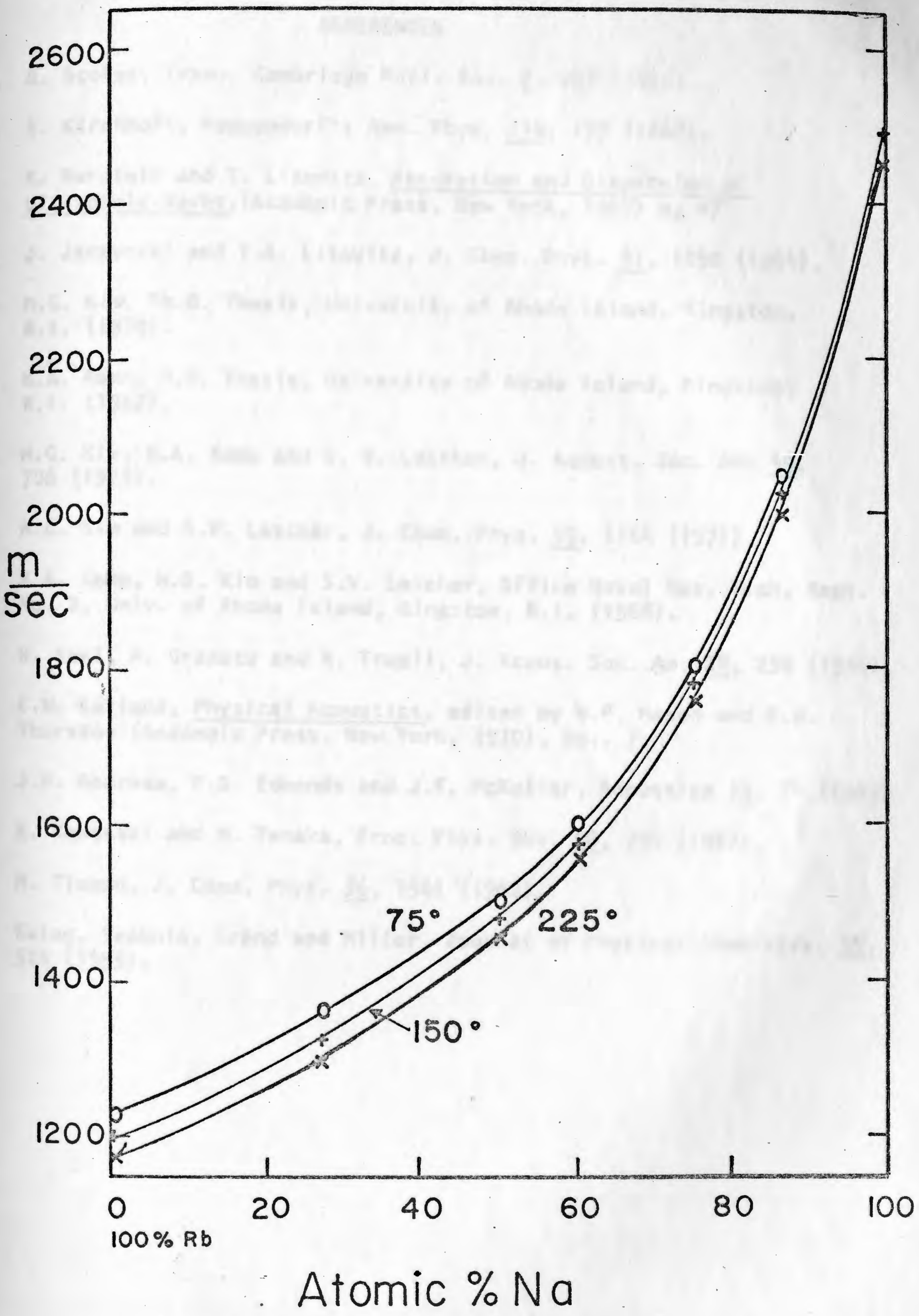

Fig.11. Sound velocity versus composition in Na-Rb alloys

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