THE ELECTRICAL RESISTANCE OF MOLTEN METALS AND ALLOYS.

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ABSTRACT

The electrical resistivities of liquid binary alloys are generally complex functions of the component resistivities. The resistivities of several mercury-based alloy systems have been studied as a function of composition and temperature. A precision, direct current potentiometric technique was employed with an overall accuracy of about 0.2%.

The results show that the resistivity of mercury decreases rapidly with increasing solute content, until this tendency is counteracted by the more usual resistivity increase obtained for the solute metals. The deviations of resistivity from the weighted mean values are negative, with minima appearing in the region of 20 atomic % solute.

A semi-empirical explanation of the data can be found in terms of the volume changes on alloying, and on the assumption that the number of conduction electrons per atom of mercury when alloyed is larger than the valency number.

Experimental evidence which suggests that clustering of bismuth atoms in Hg-Bi alloys, and segregation of the components of the Pb-Sn alloys, occurs is also presented.

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S E C T I O N 1.

I N T R O D U C T I O N.

INTRODUCTION.

The understanding of the liquid state, particularly in the case of metals and alloys, is very slight. This situation arises partly from experimental difficulties and partly from diffulties associated with the theoretical treatment of a non-regular system.

The search for engineering materials has been successful with the development of metals and alloys as basic construction materials. This interest in solid metals provided the incentive for the systematic measurement of their properties and the theoretical examination of the underlying physical principles. Most solid state measurements can be made under normal conditions of temperature and pressure, so that data are usually plentiful. The application of simple perturbation theory to the solid state, in which long-range order exists, is also possible. The result is that well-established theories of the solid state behaviour of metals are available.

The main feature which distinguishes the solid state from others is the existence of a well defined structure. In the case of solid metals, the simple picture is that of an ordered arrangement of metal ions with which valency electrons are associated

but not necessarily bound.

The small magnitude of the change of many properties on melting indicates that the liquid state is not very different from the solid. The most obvious difference between the two states is the disappearance of long range order in the liquid.

The high melting temperatures of most metals make their experimental examination in the liquid state difficult, with the result that liquid metals have until recently been largely of academic interest. However, new uses are being found for metals in the liquid state. Their high thermal conductivity makes them ideal as heat transfer fluids, especially since they are stable at high temperatures and have wide liquid ranges. These properties could make liquid metals particularly useful in the field of nuclear technology, but difficulties in applying them have underlined the deficiencies in our knowledge.

These commercial interests have stimulated the study of liquid metals and alloys, and the amount of data being produced is rapidly increasing. With this increased data it has become apparent that, from some points of view, the behaviour of liquid metals is more easily interpreted than that of solid metals.

It can be considered that all physical

properties depend ultimately on the atomic bonding mechanism. A complete understanding of this mechanism will lead to the explanation of these properties and the manner in which they are influenced by external factors. The examination of a property which is directly dependent on the bond mechanism would be a useful means by which these mechanisms could be studied. The property to be studied must be sufficiently fundamental in nature to bear a close relation to bond mechanism, and be measurable accurately.

The choice of this property can be very difficult and some apparently obvious properties can be misleading. For example, the crystal structure of a solid is a useful basic classification in many fields of study. Nevertheless, it is not a fundamental property from the view point of depending on a single atomic parameter, as it is known to involve factors such as atomic size, electronegativity and electron concentration. A type of structure can only be related to one parameter when that parameter predominates, e.g. Hume-Rothery phases.

The bonding mechanism between atoms is closely related to the properties of the electrons outside each atom core. There are three types of bond which can be present in varying proportions in a system.

Ionic bonding involves the transfer of valency electrons from one type of atom to another, while the sharing of electrons between atoms is known as covalent bonding. The third and most loosely defined type is the so-called "metallic" bond, in which the ions are sufficiently disassociated from their valency electrons to enable these electrons to move freely in an electric field. Bonding in pure metals is most frequently metallic in nature. Ionic or covalent bonding occurs in some alloys, but the bond type most frequently found is metallic.

The manner in which the valency electrons are involved in bonding can, in principle, be ascertained from the electrical conductivity of the material. In practice however, it is possible merely to distinguish between systems of pure bonding, for which the characteristics of resistivity behaviour are known. Most metals and alloys have resistivities in the range 10^{-6} - 10^{-4} ohms cms., with positive temperature coefficients. Resistance behaviour in this manner is considered to show the presence of metallic bonding.

The finer points of difference between metallic systems are rather more difficult to resolve. The resistivities of pure metals do not conform to any simple pattern. There is, for example, only rough correspondence between the Group of the Periodic table

in which a metal appears, and its resistivity. Alloy behaviour is more complex than that of pure metals, and in consequence, the understanding of liquid alloy behaviour is less than that of the pure metals.

An appraisal of the theories put forward to explain liquid metal behaviour should indicate the direction in which a new examination could be made. Accordingly, this work sets out to examine the factors involved in liquid metal behaviour, with particular reference to the electrical properties. The state of the theory of conductivity of liquid alloys is not very satisfactory, with the result that the present work has attempted to show relations between known or measurable properties rather than attempting to test out any comprehensive theory.

The calorimetric work, Hall coefficient and density measurements being made in conjunction with this work should eventually provide greater insight into the nature of the interatomic forces in metallic liquids.

SECTION II

PREVIOUS WORK.

PREVIOUS WORK.

(1) Introduction.

A comprehensive review of the theoretical aspects of liquid metal structure would involve an extensive mathematical treatment of the parameters and assumptions invoked by the various models. Some of the most recent models are mathematically very complex, and require detailed analysis to test their validity. This sort of review is the business of the theoretical physicist. This survey will only sketch the theoretical background of the liquid metal field, and point out what are considered to be the salient features of the various models.

The observation that the magnitude of a current in a metal was not time dependent, implied that the velocity of the charged particles in the electric field did not increase indefinitely, or until relativistic considerations became important. This observation was explained by the concept of an electrical resistance. The magnitude of a resistance is determined by the number of charged particles in the metal which can be accelerated by an applied field, and by the time between interactions with the ions. These factors, and the manner in which they vary, are of interest in any model of the behaviour of a metal.

(2) Empirical Rules.

The similarity in behaviour of many solid metals and alloys has resulted in the establishment of some empirical rules. The best known of these rules are the linear variation of resistance with temperature, and Mattheisen's rule, which states that the addition of a small quantity of impurity to a metal is accompanied by an increase in resistance, independent of temperature. A typical example of the increase in resistance on alloying is shown in Figure 1. Hence was established the concept of an electrical resistance composed of a thermal component, and a residual, or impurity, component independent of temperature.

The rules that were first established for the solid state were also found to be generally true of the liquid. Theories of the liquid state thus tended to be similar to the corresponding solid state theories, but with an added factor to account for the increase in disorder on melting. The current was assumed to be carried by "free" electrons, the number of which did not, in general, change on melting. The observed change in resistance on melting was considered to result from a change in the mean free paths of the conduction electrons. Resistance-temperature curves as shown in Figure 2

were to be expected, and were obtained. The resistance introduced by the melting process is given by (a - b) and (c - d) for a dilute alloy and pure metal, respectively. The increase in resistance on alloying (a - c) is typical of many systems in the liquid state, and is known as the residual alloy resistance.

Some attempts[1,2] have been made to relate electrical resistance to the difference in sizes, and positions in the Periodic Table, of the atoms of binary alloys. Linde's rule for dilute solid alloys has also been extended to the liquid state in an attempt[3] to relate the residual alloy resistance to the electronegativities of the components.

(3) Conductivity Models.

a. Early Work.

The classical model of the resistance of a solid was developed using the fact that the volume of the ions was much smaller than the volume of the atoms. The valency electrons carrying the current were assumed to move in the space between the ions, and to be scattered by these ions. However, calculations[4] based on the relaxation times of electrons indicated a mean free path that was greater than that

suggested by this model by two orders of magnitude. This discrepancy was resolved in an approach by Bloch[5], involving wave mechanics. He assumed that the motion of the conduction electrons was affected only when the periodicity of the potential field associated with the lattice broke down. The electron scattering probability was calculated on the assumption that the lattice vibrations obeyed the Debye model of specific heats. The theory indicated that, above the Debye temperature, the resistivity should be proportional to the Absolute temperature. This deduction is in general agreement with the observed pure metal resistivities and it goes some way towards justifying the basic assumptions of the theory.

In the solid state, the resistivity of a metal is dependent not only on the number of current carriers and their mean free paths, but also on the crystal structure itself. This is an additional factor in the relation between bond mechanism and resistivity. Most alloy systems show phase changes as their compositions are varied, and these further complicate the resistance behaviour of alloys. On melting, the crystal structure breaks down into an essentially disordered, single phase, state. It is worth emphasising however, that while solid state

structures are assumed to collapse on melting, there is no reason to believe that the forces which contribute to the production of these structures have also disappeared. These forces are in fact produced by the inter-atomic bond mechanisms, from which both crystal structures and electrical properties derive. The effect of long-range or changing crystal structure on resistivities can thus be eliminated by an examination of the liquid state.

Mott[6] considered that thermal motion in a liquid consisted of oscillations of ions about equilibrium positions which, unlike those in the solid state, move about at random. The frequency of oscillation of the ions is very much greater than their diffusion rates, and it was assumed that the diffusive motion and disordered positions of the ions could be ignored. Electrical resistance was assumed to be a function only of the thermal motion of the ions, so that the Bloch theory result for solid metals,

$$\rho_S \propto \frac{T}{M\Theta_S^2} \qquad (1)$$

where ρ_S = solid state resistance,

T = Absolute temperature

M = mass of the atom

and Θ_S = Einstein characteristic temperature,

was equally applicable to the liquid state. The quantity

$\frac{\sigma}{M\Theta_s^2}$, where σ is the conductivity, was shown[7] to vary according to the position of the metal in the Periodic table. The correlation is only qualitative, but it indicates that for the solid state at least the basis of the theory is sound. The Einstein characteristic temperature was used in preference to that of Debye to simplify calculations.

From the equation for ρ_s, and the assumptions regarding the liquid state, it follows that at the melting point:

$$\frac{\rho_l}{\rho_s} = \frac{\Theta_s^2}{\Theta_l^2} \qquad (2)$$

Values of the Characteristic temperature are known for the solid state, but the hypothesis that melting causes a change in the frequency of the thermal oscillations is open to question. It was assumed that the entropy of melting was associated with the thermal motion alone of the ions. Values of Θ_l can then be calculated from the latent heat of fusion of an atom leading to the result:

$$\frac{\rho_l}{\rho_s} = e^{\frac{80L_f}{T_m}} \qquad (3)$$

where L_f = latent heat of fusion

and T_m = melting temperature in ^oK.

This formula has been discussed by several workers (8,9,10).

Such a method of calculating liquid characteristic temperatures is not altogether satisfactory and attempts have been made to determine experimentally, characteristic temperatures for the liquid state from velocity of sound and compressibility[11] measurements, and inelastic neutron scattering[12] measurements. The results obtained indicate that the characteristic temperatures do not change sufficiently to account for the changes in resistance on melting.

The ratio $\frac{\rho_l}{\rho_s}$ in equation (3) shows good agreement with experiment for many metals, but the theory also implies that, at constant volume, $\rho_l \propto T$. This is not true generally. Sodium shows what is probably the best agreement for $\rho_l \propto T$, but has the worst agreement for the ratio $\frac{\rho_l}{\rho_s}$. The calculated and observed values of $\frac{\rho_l}{\rho_s}$ for some monovalent metals are shown in Table 1.

TABLE I.

Comparison of Resistivity Changes on Melting with Mott's Predictions.

	Na	K	Rb	Cs	Cu	Ag	Au
$(\frac{\rho_l}{\rho_s})_{calc.}$[6]	1.77	1.75	1.76	1.75	1.97	2.0	2.22
$(\frac{\rho_l}{\rho_s})_{obs.}$	1.45[13]	1.56[14]	1.60[14]	1.66[14]	2.04[15]	2.09[15]	2.28[15]
ρ_o at $0^\circ K$[16]	1.5	3.1	6.7	11.3			

The deviation from the prediction $\rho_l \propto T$ is shown by the magnitude of ρ_o, the resistivity when measured at constant volume and extrapolated to Absolute Zero.

The agreement with experiment shown by Mott's theory is no more than qualitative, but it does show that the thermal motion of the ions is still an important parameter in the understanding of the liquid state. It is also apparent that additional factors must be taken into account before the theory can give quantitative agreement.

The difference between the atomic and ionic volumes and its change on melting has also been examined[17] in a theory of the change of resistance on melting. The assumptions in this theory of one free electron per atom in both solid and liquid states, with a mean free path of about one interatomic distance, do not coincide with the views currently held. The theory also fails in its predictions of resistance behaviour in the solid state, unless it is assumed that the ion to atom volume ratio varies greatly with temperature. The calculated $\frac{\rho_l}{\rho_s}$ values show qualitative agreement with the measured values for the pure metals concerned, but in view of the rather arbitrary assumptions involved, the value of this theory is doubtful.

(b) Microcrystalline Models.

The first comprehensive attempt to calculate $\frac{\rho_l}{\rho_s}$ by taking into account thermal and structural factors in liquid metal resistances was made by Gerstenkorn[18] although many of the ideas used had been suggested by Shubin[19] much earlier. The theory was confined to an examination of the monovalent metals, and used the usual formula,

$$\rho = \frac{m}{ne^2\tau} \qquad (4)$$

relating ρ to the relaxation time, τ, of the conduction electrons. τ was calculated assuming the existence of a structure factor which resulted from interference between electron waves scattered from different atoms.

Calculations on polycrystalline solids showed that the X-ray distribution function of atoms could be expressed in terms of a thermal factor, and a factor dependent on the type of lattice and the number of atoms in each crystal. As this number of atoms in a crystal becomes small, the calculated shape of the structure factor approaches the shape observed experimentally for the distribution of atoms in a liquid. It was therefore assumed that a liquid could be treated in the same manner as a solid composed of crystals containing about twenty atoms. The complexity of the calculations limits the theory to the monovalent metals, but even these "simple" metals show no more

than qualitative agreement with experiment.

The microcrystalline approach has also been adopted in other models of liquid metal behaviour [20,21]. These models also postulate local arrangements of ions approximating to the solid lattice. These regions of regularity vary in their orientation, and consideration of the motion of electrons in each zone and across the zone boundaries led to formulae for the transport properties in the liquid state. The predictions of these "random local zone" theories are mathematically difficult, and show no better agreement with experimental observation than those of the "nearly free-electron" theories.

(c) Models Involving Simple Perturbation Theory.

The "nearly free-electron" approach to liquid metal theory has been developed using perturbation theory by means of the concept of the "pseudo-potential". It was shown by Phillips and Kleinman[22] that the real electron wave function of a conduction electron which oscillates rapidly near a nucleus could be replaced by a slowly varying wave function. The condition imposed on this assumption was that the true potential near the nucleus should be replaced by a smaller pseudo-potential. The concept has been developed by Ziman,[23] and other workers[24,25], who showed that the pseudo-potential was sufficiently

small for the application of perturbation theory to be justified. The thermal and structure factors of resistance used in other theories were treated by Ziman as plasma and pseudo-potential scattering respectively, although this division has been regarded as unnecessary[25]. Plasma scattering, considered to be a resistance resulting from local density fluctuations caused by thermal motion of the ions, was invoked because some of the calculated mean free paths were otherwise too long.

The pseudo-potentials are difficult to determine, and lead to some approximations in the numerical calculations. The pseudo-potential of sodium was found to be small, and the resistance was considered to be mainly the result of the small angle, plasma scattering. The resistivity ρ_1 at constant volume was calculated to be proportional to T. This result was not found by Gerstenkorn who considered that the thermal factor did not dominate in liquid sodium. The theory indicated that the other alkali metals possess larger pseudo-potentials, so that the plasma scattering assumes less importance. These deductions are in accord with the experimental values which show that, of the monovalent metals, sodium has the smallest resistivity at its melting point. The ratio of $\frac{\rho_1}{\rho_s}$ and the variations of ρ_1 from one metal

to another can also be explained in a qualitative manner by this model.

The theory has also been extended to consider polyvalent metals[26]. The pseudo-potentials of these metals are not known and the authors attempt to determine them from experimental properties. The potentials so calculated were rather smaller than expected from the empirical correlation of pseudo-potential and resistivity. The discrepancy was explained in part by the difference in the degree of order between the solid and liquid states. Plasma scattering was found to be negligible.

The simple perturbation theory used to study the liquid monovalent metals is valid because the electronic mean free path greatly exceeds the range of order. The model suggested that, in the liquid state, the range of order was approximately the interatomic distance. The polyvalent metals show mean free paths of the same order as the interatomic distance. This observation was put forward as one reason why the theory was less successful in the derivation of the properties of the polyvalent metals. The lack of success was considered to be a failure of the simple perturbation approximation for

polyvalent metals rather than of the model itself.

The theory of wave mechanics has been applied [27,28,29] to the problem of solving, in detail, Shrödinger's equation for the states of motion of the conduction electrons. These treatments are more fundamental in their approach than the simpler models and, in consequence, involve a great deal of mathematical analysis. Models which consider three-dimensional disorder, and the less complicated one- dimensional disorder have been derived. The comparative simplicity of one-dimensional disorder theories is largely offset by the limitations of these models. It has been shown[27,28] that the results obtained from such a model could be erroneous merely because it considered disorder in one-dimension only. However, the treatment of liquid metals in one-dimension can indicate the manner in which the real three-dimensional case should be examined.

(d) The "Random Close Packing" Model.

The difference between the degree of order in the solid and liquid states has been extensively studied by Bernal[30] by means of a statistical examination of the packing of hard spheres. Five types of polyhedral holes were shown to exist in a

model of an ideal close packed liquid, three of which would prevent the appearance of long-range order. The range of order was assumed to be little more than the interatomic distance, and the atom arrangement was unlike anything found in the solid state. The model was shown to produce diffraction patterns similar to those obtained from real liquids. It was suggested that microcrystalline models of liquids would not show the type of behaviour indicated by this model.

The change in volume on melting indicated by the model was about 15%, compared with real values of about 5%. If however, it is assumed that real atoms are not hard spheres, then metals can take up the structure advocated by Bernal without showing an anomalous volume expansion on melting. The rearrangement of hard spheres was shown to be rather difficult, and this implies that viscosity and diffusion in a real liquid cannot be explained by this model. The difficulty can be removed if it is again assumed that the spheres are not hard. Support[31] for this model can be found from the relation between viscosity and the self-diffusion coefficient as defined by Stoke's Law. This applies equally well to large hard spheres and to molecules moving through a liquid.

(4) Experimental Observations.

The fundamental difference between the modern models of liquid metal behaviour is the existence, or otherwise, of short range order approximating to solid state structures. Experimental evidence can be put forward in support of either of these view-points. Recently, measurements[32,33,34,35,36,37] of the Hall coefficient of metals, with valencies ranging from one to five, have been made. The measurements are experimentally difficult, and the errors range up to 10%.

TABLE 2

Hall Coefficient, R_H, of Some Pure Molten Metals.

	Valency	$R_{H_{obs.}}$	$R_{H_{calc.}}$	$\frac{R_{H_{obs.}}}{R_{H_{calc.}}}$
		$10^{-11} m^3/A.S$		
Na[36]	1	-25	-25.6	0.98
Zn[36]	2	-4.3	-4.90	0.88
Cd[36]	2	-7.1	-7.25	0.98
Hg[36]	2	-7.3	-7.60	0.96
Ga[36]	3	-3.9	-3.95	0.99
In[37]	3	-5.5	-5.65	0.97
Ge[36]	4	-3.6	-3.40	1.06
Sn[34]	4	-4.7	-4.42	1.06
Pb[36]	4	-1.9	-5.05	0.38
Sb[36]	5	-4.4	-3.87	1.14
Bi[37]	5	-4.1	-4.30	0.95
Te[36]	6	-12.6	-3.83	3.3

With few exceptions, and within the limits of error,

free electron values of the Hall coefficient are observed. These are listed in Table 2, together with the calculated values.

Schulz[38] has measured the optical properties of some pure liquid metals, and obtained the values expected from free electron theory. A series of optical measurements by Hodgson[39] also showed that the metals showed free-electron behaviour, provided that the number of free electrons and their mobilities were considered to be adjustable parameters.

In contrast to these data, X-ray diffraction studies[40] on tin, and soft X-ray emission studies[41] on aluminium have both been interpreted as showing that local crystalline order can exist in the liquid. If the current interpretation of the Knight shift[21] is correct, then its constancy when a metal is melted also lends support to the microcrystalline models.

Experimental measurements on binary alloy systems also provide conflicting evidence for models of liquid metals. There have been few Hall effect studies on liquid alloys. Apart from measurements on the alloy InSb[42], the only published data found by the author is that on the Hg-In system[43,44]. Unpublished work[45] on the same system shows fair agreement with these results. The observations indicate a departure from free-electron behaviour of the alloys, although it is obeyed by the components. The coefficients of some Ga-In alloys have also been

determined[45] and show free electron behaviour. Magnetic susceptibility measurements[37] on several bismuth- and lead-based alloys show the same behaviour. Optical measurements[38] on the systems Hg-In and Ga-In support the Hall coefficient data. It seems possible that the deviation of the Hg-In system from the free-electron model results from the properties of mercury rather than of alloys generally.

Apart from the general trends of alloy properties such as those already mentioned, additional factors are introduced on alloying. These usually take the form of property changes associated with eutectics and with compounds in the solid state. They will be discussed in the following sections when the corresponding resistivity data are considered.

(a) Change of Resistance on Melting.

The resistance ratio $\frac{\rho_l}{\rho_s}$ has been measured or tabulated by Roll[15] for many metals. With the exception of Bi, Ge and Sb, the resistance on melting increases by a factor of about two. The resistance ratio is Periodic in character, although the tendency is not very pronounced. A rough correspondence is observed between $\frac{\rho_l}{\rho_s}$ and the volume and entropy changes on melting. This is

also the case for those metals which show anomalous values for $\frac{\rho_l}{\rho_s}$.

A search of literature has revealed little data on the change of resistance at the liquidus temperatures of alloy systems. Where such measurements have been made, they have been associated with anomalous solid state behaviour, such as semiconductivity[42]. It is hardly productive to consider such systems at this stage.

(b) Variation of Resistance with Temperature.

The resistivity of many pure metals is a linear function of temperature. Close to the melting temperature most normal metals have a temperature coefficient of resistance at constant pressure of the order of $5 \times 10^{-4}\ ^{o}C^{-1}$. The coefficients of different metals do not appear to conform to any simple pattern.

It is of greater interest to examine the temperature coefficients for anomalies rather than for correlations between the coefficients of different metals. These anomalies could indicate the presence of structures in the liquid state. The divalent metals zinc, cadmium, magnesium and mercury show temperature coefficients which do not behave normally[15]. The first three metals show a decrease or no change in resistivity for about $200^{o}C$

above their melting points. Above this temperature the normal values of $\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{\rho}$ are observed. Mercury has an unusually large coefficient of resistance at constant pressure. However, when the resistances are measured[46] at constant volume, mercury, zinc and cadmium all show the same behaviour. This suggests that the temperature coefficients of resistance at constant pressure and at constant volume can be related. The usual procedure for estimating $\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{V}$ for metals for which it has not been determined is by means of a relation between the resistance coefficient at constant pressure and the compressibility. The coefficients at constant pressure and the compressibilities of a number of metals have been measured[47], the larger coefficients of the alkali metals being related to their large compressibilities.

It has been reported[48] that the temperature coefficient of liquid gallium showed a discontinuous change in the liquid phase. This would be of significance if correct, as it might be indicative of structural changes in the liquid. Later measurements[49] failed to show the anomaly, and its existence is doubted. Such behaviour is far more likely in systems containing atoms of

different species, than in a system of one type only. Resistance[50] and e.m.f.[51] measurements on some Hg-Tl alloys have shown behaviour similar to that found for pure gallium. It was suggested that these observations were a result of ordering of the alloys in the liquid phase.

The extensive work of Roll and his co-workers has shown some marked changes in $\left(\frac{\partial \rho}{\partial T}\right)_P$ for liquid alloys at compositions corresponding to solid state phases. Large changes of $\left(\frac{\partial \rho}{\partial T}\right)_P$ with composition are observed in tin alloys of copper, silver[52] and gold[53], and in Cd-Zn[54] alloys. Different alloys examined in these and other[55,56,57] papers show less marked, but still significant, variations in $\left(\frac{\partial \rho}{\partial T}\right)_P$. Gaĭbullaev[58] has shown that "quasi-eutectic" structures may exist in many systems for several hundred degrees above their eutectic temperatures. A smooth change in the temperature coefficient with a value related to those of the components, which might be expected from a completely homogenous liquid alloy, was not found in most cases.

(c) Variation of Resistance with Composition.

The forms of the resistance - composition isotherms of binary alloys are dependent on the

interactions between the component atoms. The case of the ideal system A-B, where the forces between like and unlike atoms are the same, is rarely found in practice. Many of the properties of this type of alloy system are the weighted means of the components.

It is more usual to find that the observed alloy resistances are larger than the weighted means. This can be explained by an increase in disorder resulting from the addition of foreign atoms to the solvent metal. Nordheim[59] calculated the residual resistance ρ_o for a totally disordered solid alloy to be given by:

$$\rho_o = \text{constant } x(1 - x) \qquad (5)$$

where x is the atomic fraction of A atoms, and $(1 - x)$ the fraction of B atoms. The conditions imposed on this result were that the atomic volume, crystal structure, and number of conduction electrons should remain constant throughout the composition range. Provided there is no strong A-B atom interaction, alloys in the liquid state should show resistance behaviour of the form given by equation (5). Many alloys have been shown[54,56,57] to behave in this manner.

The deviations from the behaviour of ideal

or regular systems are probably of more interest, because they can show any changes that occur in the disorder in the liquid, or in the types of bond between the A and B atoms. The alloy Mg_3Bi_2 has been shown[60] to behave as an ionic conductor, although the components behave as metallic conductors. Evidence of compound formation has also been deduced from gas solubility and magnetic susceptibility measurements[61] on the Fe-Si system, and resistance measurements[53] and X-ray studies[62] on Au-Sn alloys.

Many of the systems studied by Roll and his co-workers have also shown numerous minor variations in the resistivity isotherms. These were related to the positions of the metals in the Periodic table, and to the phase diagrams. It has been suggested[63] that these small changes could result from the measuring techniques, rather than from the alloys themselves. Similar behaviour has been observed by Toye and Jones[64] from viscosity, density and resistivity measurements on tin- and zinc-based alloys. It should be noted that the resistance measurements by Toye and Jones on the Pb-Sn system differ widely from those obtained by Roll and Fees[65]. The results at the liquidus temperatures obtained by these workers

are plotted in Figure 3. Viscosity measurements[66] on Bi-Sb, Bi-Cd and Sb-Zn alloys showed minima or maxima on the viscosity isotherms, which corresponded to eutectic or inter-metallic compound compositions. Similar effects have been found[67] in several antimony- and thallium-based systems.

Behaviour of a different type has been observed for many mercury-based alloys. Measurements on several dilute alloys of mercury quoted by Abowitz and Gordon[11] have shown that a marked fall in the electrical resistance occurs with increasing solute content. Measurements[54,65,68] covering the complete composition ranges of some of these alloys also show resistances that are much smaller than those expected from conventional alloying behaviour.

Much of this data merely indicates the general trends of the resistance-composition isotherms. More detailed studies of particular compositions have been made. Smallman and Frost[69] made an X-ray examination of some Hg-Tl alloys in the region of the compound Hg_5Tl_2. They concluded that there was a greater tendency to ordering of the atoms at a composition corresponding to the solid state compound than at other compositions. Entropy measurements made by Ward and Wilson[51]

were interpreted in the same way. The expected sensitivity of resistivity to such ordering was not found by Schulz and Spiegler[70] who attempted to detect anomalous changes in resistivity near the compound composition.

The resistivities of the liquid alkali metal amalgams do not vary in the same manner as other mercury alloys. The resistivity of the Hg-Na system[71] for example, decreases slowly with increasing sodium content, until a minimum is reached at a composition corresponding to the compound Hg_2Na. Thereafter the system behaves as a normal binary alloy with a positive excess resistance curve. Alloying of sodium and mercury is also accompanied by an increase in density over the weighted mean, and a large negative heat of formation[72]. Kleppa and others[73] have shown that the densities of many other mercury alloys are larger than expected even where there is little evidence of strong interaction between the components. No correlation was observed between the heats of mixing of these alloys, and their densities.

(5) Techniques of Resistance Measurement.

The electrical resistances of liquid metals have most frequently been measured using either

of two different physical principles. The more conventional method is that usually used for solid state measurements. This involves the determination of the current and potential developed across a specimen of known dimensions. These quantities are usually measured by means of potentiometer or bridge circuits. In either case it is necessary to bring electrodes into contact with the liquid specimen; thus increasing the risk of contamination.

The potentiometer provides a very simple method of determining the potential difference produced in a specimen. The resistance is calculated from the ratio of the potentials developed across the specimen and a known resistance when connected in series. However, difficulties arise when the specimen resistivity is determined from its resistance. The specimen container must be made from a non-contaminating material which is stable at high temperatures. Such materials are often difficult to work, particularly since the physical dimensions of the container should be accurately specified.

The real difference between the techniques of workers involved in the direct measurement of resistances lies in the manner in which the liquid specimen is contained. To ensure that the specimen

resistances were large enough to be measured accurately, capillaries were used,[60,64,74] made from glass or refractory materials. Resistances of the order of 0.01 ohms were obtained using a capillary tube with a bore of approximately 0.4 cms.

The alkali metals react with most of the non-conducting materials available as containers, and recourse has been made to stainless steel[1]. The steel container and the specimen were treated as a parallel resistance circuit, from which the specimen resistance could be determined.

A rather different form of container has also been used for measurements[75] on Pb, Sn, Zn and Bi. An oxide film was allowed to cover the specimen metal, which was in the form of a wire. Measurements were then made in the solid and liquid states, the oxide film being strong enough to retain the shape of the liquid specimen. Some of the results were not in agreement with those of other workers, probably as a result of the formation of gas bubbles under the oxide film.

The second method of resistance measurement makes use of the eddy currents induced in a

conductor when placed in a varying magnetic field. The method has been used by several workers (36,47,61,67), and in particular by Roll, et al, (15,76).

A liquid specimen, contained in a cylinder, is suspended by a torsion wire in a rotating magnetic field. The eddy currents set up in the specimen by the field produce a torque, which can be determined from the angle through which the specimen is twisted. Calculations show that the conductivity of the specimen is proportional to this deflection. The theory of the method is relatively straightforward, but a series of correction factors must be introduced before good absolute values of resistivity can be determined.

Corrections must be applied for the effect of the eddy currents on the primary magnetic field, and for the end effects of the specimen. The rotation of the liquid can be ignored, provided the current producing the primary magnetic field is kept low. The calculation of the conductivity involves the fourth power of the specimen radius, so that errors in its measurement can have considerable effect. This problem is avoided by the calibration of the specimen container using a metal whose resistivity is known.

The method does not involve the use of electrodes, and the simplicity of the specimen container shape allows the use of materials which otherwise would not be available. Some of the difficulties of high temperature measurements by direct methods can thus be avoided. An accuracy of $\pm$ 1% is claimed[76] for the values of resistivity measured. Larger discrepancies than those allowed by the experimental errors are found between these results[15], and the literature values for some liquid metals, notably Al, In and Bi. Disagreement also exists between measurements[64,65] on the Pb-Sn alloy system, as shown in Figure 3. However, there exists a general measure of agreement between the results for many systems when determined by this, and other techniques of resistance measurement.

(6) Conclusions.

It can be concluded from this survey that, although experimental data and theoretical interpretations are available, the understanding of the behaviour of liquid metals is far from complete.

Some fundamental theories are in direct conflict over the suggested structural arrangements of atoms in a liquid. In any case, these models have met with real success only with the simple pure metals. Although empirical rules tend to be rather limited in their application, it was decided that the approach to the resistance behaviour of alloys should be essentially empirical. Experimental data suggested that the variation with temperature and composition of factors such as density, valency difference, and current carrier concentration, should be examined.

Experimentally, there was advantage in the study of alloys which were liquid at low temperatures, the most obvious being those based on mercury. The apparent anomalous variation in the current carrier concentration of some of these alloys provided an added reason for their examination.

The paucity of reliable resistance data on such alloy systems suggested that they should be re-investigated. Two measurement techniques suggested themselves; these being the conventional capillary method and magnetic induction method. At the temperatures at which measurements on liquid mercury alloys could be made, the advantages of the induction technique do not outweigh its shortcomings. It was decided that accurate resistance data could be obtained by means of a precision capillary method, by which also some of the results observed using the induction method could be checked.

S E C T I O N III

E X P E R I M E N T A L
M E T H O D S.

EXPERIMENTAL METHODS

1. Temperature Control and Measurement.

Electrical resistance is a function of temperature, and so it is important to make measurements only at well-defined temperatures. Accurate control and measurement of specimen temperatures are therefore a necessity. However, the cost of temperature control equipment increases rapidly as the degree of control is increased, and this must be borne in mind when determing an acceptable tolerance of temperature variation.

The temperature coefficient of resistance, $\frac{1}{\rho_L}\left(\frac{\partial \rho}{\partial T}\right)_P$, for many liquid metals is about $5 \times 10^{-4}\ ^{\circ}C^{-1}$. A variation in specimen temperature of $1^{\circ}C$ will thus produce a resistance change of 0.05%. Errors of this magnitude were considered acceptable, requiring control to $\pm\ 0.5^{\circ}C$.

This degree of control was obtained by using an ordinary tubular resistance furnace, with a proportioning on-off controller. A hollow cylindrical aluminium block was fitted into the furnace tube, and thermally insulated at both ends. The block provided a material of large thermal capacity, which considerably reduced the temperature-time variations of the furnace. The high thermal

conductivity of aluminium also provided a means of reducing temperature gradients along the furnace tube. The resistance cell could then be placed in a zone of constant temperature, the time variations of which were reduced to a minimum.

At 400°C the temperature in the cell was found to vary by not more than 0.1°C, during the time required for the electrical measurements to be made. Temperature variations along the bore of the block did not exceed 0.5°C, and were constant. The specimen temperatures could thus be controlled to within the accuracy desired.

The specimen temperature was measured by means of two platinum-platinum/13% rhodium thermocouples, placed close to either end of the specimen. To ensure that the couples registered the true specimen temperature, and that a rapid response to changes in temperature was achieved, the hot junctions were not sheathed. While lacking the sensitivity of the base metal couples used in the control system, the measuring couples had the advantage of maintaining their calibration to a much greater degree. Calibration

was performed periodically, and the appropriate corrections made to the measured e.m.f.'s.

Measurements below room temperature were made by immersing the cell in a Dewar flask containing a low freezing point fluid (Isceon 11, melting point about -50°C). The fluid was cooled by the addition of small quantities of liquid nitrogen. Uniformity of temperature throughout the bath was ensured by continuous stirring. Temperature variations of not more than 0.3°C occurred during any measurement of resistance.

2. Preparation of Specimens.

The solid metals used in this work were supplied in lump or rod form, with a purity of 99.99% or better. The mercury used was of "triple distilled" quality.

The metals were vacuum melted and cast into conveniently sized pieces. These were usually free of oxide films, or were made so by scraping. The alloy specimens were prepared by melting the required quantities of the components in the resistance cell container. Non-volatile alloys were melted under vacuum,

and so degassed, but this was not possible with the mercury-based alloys. These were prepared under dry, oxygen-free argon or hydrogen. A small quantity of carbon was added to the bismuth alloys to reduce oxide formation.

The high oxygen affinity of sodium, and the large negative heat of formation of sodium-mercury alloys, made the preparation of these alloys rather difficult. The composition of an alloy made directly from the pure metals could not be defined with any certainty. This problem was largely overcome by preparing the alloys from mercury and a sodium-mercury alloy whose composition had been determined. This stock alloy was prepared by mixing pure sodium and mercury together slowly, until the composition was close to that required. Insoluble oxides were removed by filtration of the alloy, which was then allowed to solidify in a narrow glass tube. Sections of the tube were weighed before and after transfer of the alloy to the resistance cell to determine the quantity of alloy in use. Analysis of a specimen from the same alloy was performed by removing the sodium with water, and weighing the mercury remaining.

Hence, knowing the composition and quantity of alloy in the cell, it was possible to change the composition to the required value by simple additions.

Alloys of the other systems examined were analysed for the two main components only. The object of the analyses was merely to check the nominal compositions, and agreement to within about 1% was regarded as satisfactory. The analyses were carried out by heating the alloy samples under reduced pressure, to separate the mercury from the other component. Alloys which had been under examination for several weeks showed deviations from the nominal compositions of not more than 1.5%. In the worst case this indicated a shift in composition of less than 0.8 atomic %, and most changes were considerably less. It was considered that for the purposes of this work, changes in composition of this magnitude could be ignored.

3. The Resistance Cells.

Normal metallic systems have small resistivities, and to measure these by a potentiometric method to a high degree of precision the specimen material should be in the form of a thread. This

is easily accomplished for solids by using the material as a wire. A liquid can be made to conform to the thread shape by means of a capillary tube. Ideally, this tube should be a non-conductor, but it need not be so provided the current distribution between the tube and specimen can be determined. The resistance of a specimen is related to its length and cross-sectional area, and it is thus necessary that these quantities should be measured to some precision.

In this work electrical resistances have been determined by means of a conducting and a non-conducting cell.

(a) The Non-Conducting Cell.

This cell was made from a borosilicate glass (Pyrex) and could be used up to about 480°C., provided there was no reaction between the glass and specimen. Use was made of standard ground glass joints to allow the easy cleaning or replacement of components. This type of joint was used in particular as the means of attaching the glass capillary tube in the cell. Distortions of the bore of the capillary, which are inherent in the usual method of joining glass tubing by fusion, were thus avoided. The use of grease on the

capillary joint was found to be unnecessary.

A diagram of the cell is shown in Figure 4. The capillary was suspended vertically from the inner tube, which was connected directly to the atmosphere control system. Electrical connections to the liquid specimen were made by means of four 1 mm. diameter tungsten rods. The potential probes were electrically insulated except for their tips, which were brought close to either end of the capillary. A vacuum-tight sliding joint was obtained by means of a Wilson seal, allowing the capillary and electrodes to be moved vertically within the container. Approximately 15 cms., of movement were possible. The container was also connected to the atmosphere control system.

The length of the container was 30 cms., and it was, apart from the ground glass joint, placed vertically in the furnace. The depth of insertion was arranged such that the capillary, when in the lowered position, was at the centre of the constant temperature zone of the furnace. The overall height of the cell was 75 cms.

The potentiometric technique of resistance measurement involves the measurement of potential differences, rather than of resistances. A small fractional change in a p.d. can be measured, provided the total p.d. is relatively large. This can be achieved with a specimen of high resistance, or by passing a large current through a low resistance specimen. However, the latter method increases the possibility of a significant amount of electrolytic transport.

A large liquid metal resistance, of the order of 1 ohm, was obtained by means of a capillary about 12 cms. long and 0.04 cms. bore. The corresponding outside diameter of the capillary was such that the minimum possible container diameter was 1.2 cms. A charge of approximately 8 mls. of liquid specimen was required. A composition change device was attached to the gas inlet immediately above the top of the container.

(b) The Conducting Cell.

It was not possible to use the glass cell to examine many of the sodium amalgams above the maximum liquidus temperature of the system.

Above 300°C the rate of attack of pure sodium on glass is rapid[77], and although the reactivity of sodium amalgams is much lower, the risk of an indeterminate change in the capillary dimensions could not be taken. Alternative non-conducting materials, such as sapphire, were not available and recourse was made to a metal cell.

A suitable material from the point of view of corrosion and workability was stainless steel, and a cell was constructed as shown in Figure 5. The various sections were joined by an electron beam welding technique. The upper tubes were 0.5 cms. in diameter, to allow the cell to be used in the metal furnace block. The current was passed into the cell via the brazed current leads. Potential measurements were made on the quantity of specimen between the brazed potential contacts, which were about 10 cms. apart. Electrical insulation between the arms of the cell, and between the cell and the furnace block, was achieved by means of thin mica sheets. The cell was connected to the atmosphere control system by glass tubing and Wilson seals. A composition change device was also attached to one of the upper tubes.

The manner of the current distribution between the liquid specimen and the tube walls was of some importance. The specimen and tube were regarded as a parallel circuit and, provided a large fraction of the current flowing passed through the specimen, small changes in specimen resistance could be determined. A high sensitivity to resistance change required that the specimen tube radius, r, should be small in magnitude, but large compared with the wall thickness, Δr. A difference of a factor of ten between the respective cross-sectional areas was considered to be a suitable ratio. Hence, the value of r was defined by:

$$\frac{\pi r^2}{10} \geqslant 2\pi r \Delta r \qquad (6)$$

The minimum feasible value of Δr was 0.0075 cms. which gave the value $r \geqslant 0.15$ cms. The resistance of a 10 cms. length of the tube containing a specimen would be approximately 0.01 ohms, on the assumption that the specimen resistivity was about 10^{-4} ohms cms. Resistance changes in a resistance of this magnitude could be determined by the potentiometric technique without using a high specimen current. A smaller total resistance would result in a decrease in

the sensitivity of measurement, and hence the tube radius was also limited by the relation, $r \leqslant 0.15$ cms. The tubing used for the lower arms of the cell was 0.305 cms. in diameter with a wall thickness of 0.0076 cms. The measured resistance between the potential contacts was approximately 0.1 ohm when the cell was empty, and 0.01 ohms when containing a liquid specimen. The minimum volume of specimen required was about 2 mls.

4. The Electrical Circuit

The electrical measurements were made by means of a standard D.C. potentiometric technique. To avoid the inaccuracies inherent in the direct measurement of current, the specimen was connected in series with a standard resistance and a stable voltage supply. The ratio of the potential differences across the standard and specimen, through which the same current was flowing, provided the resistance of the specimen.

i.e.

$$R_{sp} = \frac{E_{sp}}{E_{st}} \cdot R_{st} \qquad (7)$$

where E_{sp} and E_{st} were the potentials developed across the specimen resistance, R_{sp},

and standard resistance, R_{st}, respectively.

A diagram of the circuit is shown in Figure 6. The potentiometer and galvanometer system allowed 1 microvolt changes in p.d. to be measured, with interpolations to 0.2 microvolts. Thermo-electric free switches and copper connections were used where possible to reduce thermoelectric effects to a minimum. Such effects could not be eliminated at the copper-tungsten, and tungsten-specimen junctions in the glass cell, but they were successfully removed in the stainless steel cell.

Transient thermal effects were reduced by protecting the dissimilar metal junctions from draughts. The presence of small temperature gradients in the cell produced small but constant thermal e.m.f.'s. The effects of the e.m.f.'s were eliminated by current reversal, the mean p.d.'s so obtained being used to calculate the true specimen resistance. Such constant thermal e.m.f.'s were less than 100 microvolts, so that changes in the temperature gradient which altered this value by, say, 10% would contribute less than 0.1% to the error in the p.d. measurements. The current used for measurements on the glass cell was approximately 10 milliamps, while that for the metal cell was

100 milliamps. A.C. "pick-up" was avoided by the use of screened leads.

5. Resistance Measurement Technique.

The main factor affecting the reproducibility of the resistance measurements was the presence of adsorbed gases on the capillary walls. On raising the temperature the gases tended to form small bubbles which adhered to the walls. The cell and the atmosphere control system were designed for the easy removal of these bubbles.

Much of the problem of outgassing in the glass cell was avoided by pretreatment of the capillary. A small electric furnace was used to apply local heating to the capillary when in the raised position in the cell. Evacuation of the cell assisted in the removal of adsorbed gases from the capillary, while a specimen of high vapour pressure remained unaffected in the bottom of the outer container. On transferring the cell to the furnace the specimen was brought to temperature, and allowed to mix thoroughly, before the capillary and electrodes were lowered into the liquid. The two separate connections of the cell to the atmosphere control system allowed a pressure difference to be applied between

the ends of the capillary. Surface tension effects in the capillary could then be easily overcome, and the circuit between the two sets of electrodes completed.

It was not always possible to remove all the gases likely to form bubbles inside the capillary before the commencement of the electrical measurements. This problem was particularly difficult in the case of mercury-rich specimens, which could not be vacuum melted. However, the presence of bubbles could be easily detected by changing the gas pressure in the cell. Gas bubbles in the capillary were observed as a change in the potential measurement when the pressure was varied. A narrow bore capillary was useful since the effects of small bubbles could be more easily observed.

Such bubbles were removed by applying a pressure difference between the ends of the capillary. This forced specimen liquid through the capillary and removed the bubbles at the same time. Electrical measurements were not made until all detectable gas bubbles had been removed from the capillary. A similar procedure was observed for the conducting cell. Passing liquid through

the capillary also provided a means of sampling different parts of the specimen, which was useful as a homogeneity test after a composition change.

A measure of the thermal stability of the system at a nominally constant temperature was shown by the repeatability of the measurements. A scatter of less than 0.05% was observed, which indicated that transient thermal effects could be ignored. The reproducibility of the results was considered to be given by a repeat measurement at a particular temperature, after an experimental run over a range of temperatures lasting several days. The reproducibility was found to be in the region of 0.1%, subject to the removal of gas bubbles which may have been introduced during the run. This technique thus provided a means by which the variation of resistance with temperature and composition could be accurately determined.

The accuracy of the absolute values of resistivity was mainly dependent on the constancy, and accuracy of measurement of the capillary bore. The method of attaching the capillary in the cell allowed its length to be measured with precision. The mean radius was determined from measurements of the length of a known weight of mercury in the

capillary. However, the mean cross-sectional area will give accurate resistivity values only when the deviations of the radius from the mean are small. Taking such a value of the cross-sectional area was shown to be justified by the constancy of the length of a column of mercury when observed in different sections of the capillary.

The area of cross-section was also calculated from resistance measurements on pure mercury. The resistivity of pure mercury at $20^{\circ}C$ was taken as 95.6×10^{-6} ohms cms., this being the value assumed by Roll[15]. These methods of determining the "cell constant" of a capillary agreed to within 0.5%, but to avoid any discrepancy between the results on different capillaries, all measurements were referred to the resistivity value for pure mercury at $20^{\circ}C$. Resistance measurements using the conducting cell when empty, and when containing a specimen of mercury, enabled this cell to be calibrated in a similar manner.

S E C T I O N IV.

R E S U L T S.

RESULTS.

1. Measurements on Pure Metals.

(a) Zinc, Tin, Lead and Bismuth.

Resistivity measurements at constant pressure were made on these metals from the melting points to approximately 550°C, in non-conducting cells. The results are shown in Figure 7, together with some published data.

Under bubble free conditions the results for these pure metals were highly reproducible. Deviations of results from the mean values were not measurable, with the exception of occasional measurements attributable to an unstable supply voltage or an incorrect temperature measurement. So, for the sake of clarity, many repeat measurements have not been included in the diagram. The results are also listed in Table 3, together with the temperature coefficients at the melting points.

Measurements were made to within 3°C of the melting points, and the resistivities corresponding to these temperatures determined by extrapolation. The resistivity variations with temperature are in good agreement with the data

TABLE 3.

Resistivity ρ_L, as a Function of Temperature for Some Pure Liquid Metals.

Temperature (°C)		Resistivity (Microhm Cms.) Zn	Sn	Pb	Bi
At	This Work	34.5	47.5	95.2	126.5
M. Pt.	Lit.(77).	35.3	47.6	94.6	127.4
250		-	48.0	-	-
300		-	49.4	-	128.1
350		-	50.9	96.4	130.7
400		-	52.3	98.8	133.4
450		34.2	53.7	101.2	136.1
500		33.8	55.1	103.6	138.8
550		33.4	56.5	106.0	141.5
$\frac{1}{\rho_L}\left(\frac{\partial \rho}{\partial T}\right)_P 10^{-5}.°C^{-1}$		-	59.6	50.4	42.3

tabulated in the Liquid Metals Handbook(77). The resistivity of tin was found to be a little less sensitive to temperature changes than the results of Roll and Motz(15) indicated.

Larger differences between the data from the three sources appear for the absolute resistivity values. There is agreement to within 1% between the present work and the Liquid Metals Handbook for Sn, Pb and Bi, but the values for Zn differ

by 2.5%. Roll observed the resistivity of Zn to be 8.5% higher than this work, and that of Bi to be 3% higher.

It is possible to explain the appearance of measured resistivity values larger than the real values in terms of impurities, or the presence of bubbles in the cell. However, low values are far more difficult to interpret in terms of faults in the measurement technique. The resistivities are calculated with reference to the value of pure mercury at $20^{\circ}C$, so the discrepancy cannot be attributed to errors in measuring the size of the capillaries. An alternative explanation could be found in terms of a contribution to the conductivity from ionic transport. The current density at which measurements were made was about 5 amps/cm^2, but no deviations from Ohm's law were observed for a range of current densities up to 50 amps/cm^2.

With cells designed specifically for the removal of physical irregularities such as bubbles in the specimen, the implication is that the results obtained by this work are real, while the higher values obtained by other workers could arise from such irregularities.

(b) Mercury.

Mercury was used for the calibration of the resistance cells, which resulted in a detailed examination of the metal. Degassing problems were most serious when using mercury because of its high vapour pressure, and added precautions were taken to obtain bubble free specimens.

The results of many calibration runs are shown in Figure 8. A single reference point was taken for each capillary, being a defined resistivity of mercury at 20°C. Agreement to within 0.1% was obtained over the whole liquid range of mercury, up to its boiling point. The result was a smooth curve for the resistivity variation with temperature.

The agreement between this work and the literature values was good, the greatest difference occurring near the boiling point. The results are listed in Table 4. The temperature coefficient $\frac{1}{\rho_L}\left(\frac{\delta\rho}{\delta T}\right)_P$ varied smoothly between $83.6 \times 10^{-5}/°C$ at the melting point and $112.3 \times 10^{-5}/°C$ at the boiling point.

TABLE 4.

Resistivity of Mercury as a Function of Temperature.

Temperature (°C)	-38.87	0	50	100	200	300	350
ρ_L, μohm cms.	90.9	93.9	98.2	103.1	114.0	127.2	134.7
Literature.	90.5	94.0	98.5	103.1	114.0	127.0	135.5

2. Measurements on Binary Alloys.

(a) The Mercury-Zinc System.

The resistivities of eight alloy compositions in this system were measured with respect to temperature. No anomalies were observed in the temperature coefficients of resistance, which varied smoothly between the values of the two components.

The coefficient is zero in the composition range 60-80 atomic% Zn and becomes slightly negative for alloys richer in zinc. These results are presented in Figure 9.

The variations of resistivity with composition at 250°C and 350°C are illustrated in Figure 10. The addition of small quantities of zinc to pure mercury is accompanied by a sharp decrease in the observed resistivity. The resistivity decreases to less than half the pure mercury values on the addition of 20 atomic % Zn.

The points on the isotherms for

Hg - 80 atomic % Zn and pure Zn were obtained by an approximate extrapolation from the liquid region, assuming the temperature coefficient of resistivity to be zero. The variation of resistivity with composition of the zinc-rich alloys was found to be very small. A change of 30% in composition was accompanied by a change in resistivity of 6%. No major discontinuities were observed in the variation of resistivity with composition.

No previous resistivity measurements on this system have been found by the author in the literature.

(b) The Mercury-Tin System

The variations of resistivity as a function of temperature of the six alloys examined in this system are shown in Figure 11. Alloys with tin concentrations larger than 7.5 atomic % show a linear variation of resistivity with temperature, while the dilute alloys tend to follow the pure mercury form. No discontinuities were found in the resistivity-temperature curves.

Figure 12 shows the variation of resistivity with composition at constant temperature. Smooth curves can be drawn through the values of the limited number of alloys examined. The addition of

tin to mercury is accompanied by a large decrease in resistivity. Between Hg - 40 atomic % Sn and pure Sn the rate of decrease is much lower and is approximately constant. In this region the temperature coefficient $\frac{\partial \rho_L}{\partial T}$ changes by less than 6%.

Also included in Figure 12 are the resistivities, relative to that of mercury at approximately 246°C, observed by Weber[68]. These results show a variation with composition very similar to that observed in the present work, although they are rather more scattered in the equi-atomic region. The displacement of Weber's results at all compositions other than pure mercury is sufficiently constant to suggest that the resistivity of tin would be a more appropriate reference value.

(c) The Mercury-Lead System

This system was the subject of a detailed study. Approximately fifty alloys were examined, at intervals of 2 atomic %. Composition ranges of about 10 atomic % were covered by successive additions of a component metal to the alloy specimen. The results from the final composition were then checked by measurements on a freshly prepared alloy. Agreement was usually to better than 0.5%.

In cases where the difference in measurements was near this limit, an analysis for the two main components was performed. It was found that the discrepancies could be attributed to mercury losses by evaporation resulting in composition shifts of not more than 0.8 atomic %. Some typical resistivity-temperature curves are shown in Figure 13. All the alloys examined showed a uniform variation of resistivity with temperature. The non-linear form of the curve for pure mercury also occurred with the dilute lead alloys, but an increase of the lead content to greater than 14 atomic % Pb reduced the resistivity-temperature curves to the linear form over the temperature range considered.

The alloy resistivity varied smoothly with composition, as shown by the resistivity isotherms illustrated in Figure 14. Many of the intermediate composition values have been omitted from the diagram, and are represented by the smooth curves.

The resistivity of the mercury-rich alloys decreased rapidly with increasing lead content to below the value of pure lead. The lead-rich alloys showed the normal alloy behaviour of increase in resistivity with increase in mercury content. The system thus shows a resistivity minimum which occurs

at approximately Hg - 30 atomic % Pb, and a maximum at about Hg - 80 atomic % Pb. These stationary points are not strongly marked, and the compositions at which they occur do not vary with temperature.

Particular attention was paid to the compositions equivalent to Hg_2Pb and Hg_4Pb_3. These compositions correspond to mercury with a valency of two and three, respectively. Discontinuous changes in the isotherms at these compositions were not observed. This suggested that ordering of atoms, or the presence of valency compounds resulting in high resistivities, did not occur in this system.

The resistivities at 265°C observed by Weber[68] are also included in Figure 14. Good agreement is shown with the present work for the mercury-rich alloys, but the other results are generally 2% higher. No irregular changes of resistivity with composition were observed by Weber.

In common with the other mercury alloys examined, the coefficient $\left(\frac{\partial \rho_L}{\partial T}\right)_P$ of the mercury-lead system decreased rapidly with increasing lead concentration. At concentrations greater than 20 atomic % Pb the coefficient becomes approximately constant at the value for pure lead. Minor irregularities occurred in $\left(\frac{\partial \rho_L}{\partial T}\right)_P$ which cannot be

attributed to experimental errors. The variations of $\left(\frac{\delta \rho_L}{\delta T}\right)_P$ with composition for some mercury alloys are shown in Figure 15.

(d) The Mercury-Bismuth System

The alloys of bismuth and mercury were also examined in detail. Figure 16 shows the temperature variation of resistivity of a selection of these alloys. The value of the coefficient $\left(\frac{\delta \rho_L}{\delta T}\right)_P$ becomes independent of temperature for bismuth concentrations larger than 18 atomic % Bi. The compositions were changed and the measured resistivities checked in the same manner as for the mercury-lead system.

The resistivities of different alloys of the same nominal composition were reproducible to within 0.7% in the regions where resistivity was most sensitive to composition change. This corresponded to a difference in composition of less than 1 atomic %. The results are presented in Figure 17, where they are compared with those obtained by Weber[68] at 265°C. The measurements made by Weber are resistivities relative to a factor which is not stated. Defining the factor as the resistivity of mercury at 0°C gives reasonable agreement for the observed values of pure bismuth and mercury and general agreement

for the shapes of the resistivity isotherms.

A broad maximum in resistivity occurs in the region of Hg - 80 atomic % Bi, while a fairly sharp minimum exists near Hg - 16 atomic % Bi. An increase of temperature shifts the minimum of the isotherm away from the mercury-rich end of the system. A secondary minimum was also observed close to the composition Hg_5Bi_2. This composition was attained by additions of bismuth to a specimen, and not as a freshly prepared alloy. It was therefore concluded that the minimum was a real effect, and did not arise from a composition error.

However, irregular behaviour was observed in the region 30-45 atomic % Bi, and it is likely that the secondary minimum is associated with this behaviour. Figure 17 shows the results from stable alloys only in this composition range. The anomalous alloys in this system were also examined in detail.

Four specimens with compositions in the range 20-50 atomic % Bi were examined at 295°C, and the results are presented in Figure 18. The resistivity variation with composition of each specimen is plotted separately, the direction in which the composition is changed being indicated by the arrows. Also included in the diagram are the results for

some 'normal' alloys. Each specimen was under examination for about ten days.

The initial composition of specimen I was Hg - 35 atomic % Bi. Change in composition to Hg - 40 atomic % Bi was accompanied by a rise of 10% in the resistivity. Returning the alloy to its initial composition produced a further rise in resistivity to approximately the value expected for a 'normal' alloy. The normal curve was followed on further increasing the mercury concentration in the specimen. The resistivities did not vary significantly with time, changes of less than 0.5% being observed over twentyfour hourly periods.

The specimen current was normally allowed to flow continuously between readings. To investigate the possibility of ionic transport the current was raised by a factor of ten, and also switched off, for periods prior to measurement. No detectable difference was noted in the resistivities.

Curve 2 illustrates the effect of continually increasing the concentration of bismuth in an Hg - 30 atomic % Bi specimen. The initial resistivity of specimen I was reproduced. It was followed by a rapid increase in resistivity with composition until a concentration of about

45 atomic % Bi was reached, when the normal curve was followed.

The composition of specimen 3 was changed from close to Hg - 20 atomic % Bi in the normal region to about Hg - 40 atomic % Bi. The normal curve was closely reproduced for the mercury-rich compositions but tended to diverge in the other composition range to about 1% less than the normal resistivities. The very low values of specimens 1 and 2 were not observed.

The resistivities found for specimen 4 are the results of the simulation of the usual procedure for the examination of a specimen, without in fact changing its composition by more than 1 atomic %. A low resistivity was obtained in the first measurements, which increased on changing the composition by 1.2 atomic % towards the bismuth end of the system. A range of resistivities was observed at this composition when different parts of the specimen were examined by raising the inner level of the specimen in the cell. Similar behaviour was also found in specimen 2. No decrease in resistivity could be obtained although the composition was moved back towards the mercury end of the system. However, when the specimen was allowed to cool considerably

below the liquidus temperature and then re-examined at temperature, some low resistivities were observed.

It should be noted that all the above alloys were prepared and examined above the melting point of pure bismuth. This avoided the separation out of solid bismuth, which would move the composition towards the region in which the stable resistivity minimum was observed. Analysis of several specimens for the two main components gave results which were in good agreement with the nominal compositions.

(e) The Mercury-Sodium System

This was the only system for which the stainless steel cells were used. The purpose of measurements on this system was to observe the change in resistivity with composition in the ranges in which compounds exist in the solid state. Measurements were made with respect to temperature up to 500°C, but generally the composition was changed at constant temperature only.

Figure 19 illustrates resistivity as a function of temperature for three Hg-Na alloys. In each case a smooth variation in resistivity over the whole liquid region was found. The resistivity-composition isotherm at 350°C is shown in Figure 20.

No marked changes in resistivity were observed at compositions associated with solid state compounds. A weak maximum occurred at the composition given by NaHg but, unlike the results of Bornemann and Müller[71], no minimum in resistivity was found at the composition of the stable compound $NaHg_2$. The eutectic composition Hg - 2.8 atomic % Na was also associated with a small resistivity maximum.

The failure rate of the non-conducting cells was high, a result, apparently, of the manner in which the potential leads were brazed to the steel capillary tube. Consequently, several composition ranges of the Hg-Na system were not examined in as much detail as was desired. However, sufficient data were obtained to indicate that large resistivity changes with composition were unlikely to occur, and to suggest that the system exhibits only metallic type conduction.

(f) The Lead-Tin System

The examination of this system was originally undertaken to confirm the observations of Roll and his co-workers of the existence in this and other systems of small irregular changes in resistivity with composition. Toye and Jones[64] noted greater sensitivity of resistivity to composition

changes than the results of Roll and Fees[65] suggest. Figure 3 shows the extent of the disagreement between the measurements taken at the liquidus temperatures.

Toye and Jones make no pretence of obtaining good absolute values of resistivity. This is clearly shown by the values stated for pure tin and lead at their melting points, which differ by up to 30% from the generally accepted resistivities. The main interest in these results lay in the appearance of two strong minima in the resistance-composition curve. It was decided to examine a series of alloys in the region of the eutectic composition Sn - 26.1 atomic % Pb which included a resistivity minimum found by Toye and Jones, and some of the irregularities observed by Roll and Fees.

Twenty compositions between Sn - 20 atomic % Pb and Sn - 28 atomic % Pb were examined, and a representative selection of the results are shown in Figure 21. A resistance-composition isotherm obtained from this diagram shows the same sort of minor irregularities as those observed by Roll and Fees, but with a sharper peak occurring at the eutectic composition.

Alloys close to the eutectic showed large

anomalies up to 70°C above the liquidus temperatures. Above 250°C all alloys exhibited a normal linear variation of resistance with temperature, although some of the absolute values of resistivity could be regarded as rather high. Care was taken to ensure that the high resistivities were not the result of blockages or bubbles in the capillary. Between 250°C and the liquidus temperatures the alloy resistances decreased rapidly, the temperature at which the temperature coefficient changed being apparently related to the absolute resistivity at that temperature. This effect was most marked at the eutectic, and disappeared within 1 atomic % on either side of the eutectic composition. It is illustrated in more detail in Figure 22, where the results of a series of runs on some eutectic alloys and other close compositions are presented.

It can be seen from Figure 22 that, although the anomalous effect is repeatable, it by no means reproducible to the extent expected from the method of measurement. However, it was found that good reproducibility was obtainable under vacuum or argon, provided the alloy was not disturbed. The selection of a different sample of the specimen by alteration of the two liquid levels in the cell resulted in a

different, reproducible resistivity-temperature curve. This effect is illustrated by the six separate runs on the eutectic Sn - 26.1 atomic % Pb shown in Figure 22.

The bulk composition accuracy of the eutectic alloy was confirmed by cooling curve experiments which did not indicate a phase change at other than the eutectic temperature (183°C), and X-ray analysis, which also showed that the impurity content was low. The presence of the structure of the eutectic alone in the solid alloy was also shown by metallographic examination. Resistivity measurements on oxide-free specimens under dry hydrogen eliminated the possibility that the anomalies resulted from the presence of oxides or dissolved oxygen.

The present work makes it easier to reconcile the very different results obtained for the Sn-Pb system. Roll and Fees determined the resistivities at the liquidus temperatures by extrapolation from the high temperature linear range, while Toye and Jones extrapolated the results observed at a few degrees above the liquidus. Both sets of measurements are shown in Figure 23 together with the present work, on which both methods were applied.

Extrapolation from the linear region gave a considerably larger maximum than that found by Roll and Fees. Measurements near the liquidus temperature also indicated a minimum in resistivity at the same composition as that of Toye and Jones, although the magnitudes show only qualitative agreement.

S E C T I O N V.

D I S C U S S I O N.

DISCUSSION.

1. Theoretical Considerations

The literature shows that the electrical resistivities of liquid binary alloys are generally complex functions of the pure metal values. The frequent failure of many fundamental and empirical theories to predict even the pure metal resistivities is indicative of the degree of difficulty experienced in relating theory to experimental observation. The origin of this difficulty most probably lies in the fact that a particular resistivity can arise from the operation of several different factors.

Before discussing the experimental observations made on specific binary alloys, it is relevant to examine the meaning of electrical resistivity when applied to metallic systems, and to consider the relative importance of the factors which are known to affect resistance behaviour. Alloy behaviour is rather more complicated than that of the pure metals, and it is proposed that the pure metal properties should be examined before those of alloys.

Electrical resistivity is defined as the resistance of a centimetre cube of a metal. This is a useful practical unit of comparison but is, by definition, a macroscopic quantity, whereas the

factors from which resistances arise are atomic in nature. It is therefore hardly surprising that little correlation exists between the resistivities of pure metals, which are otherwise very similar. The temperature and the external pressure on a specimen are also specified, since they are not implicit in the definition of resistivity.

Electrical resistance, being an atomic property, should be related to the number of atoms in the specimens under consideration. But the definition of resistivity does not allow differences in the number of atoms in the fixed volume, resulting from density changes or from the different sizes of atoms, to be taken into account. Another difficulty in the comparison of metals arises from the choice of temperature at which resistivities should be compared. The thermal motion of atoms affects the mobility of the current carriers but, according to the Debye theory of specific heats for solids, the motion is not the same at a particular temperature for different metals. However, the thermal motion can be considered to be in the same state for different metals when at defined temperatures. Comparisons of metals at their characteristic temperatures would thus appear to be more appropriate

than at the same temperature.

The validity of these assumptions has been strengthened by some experimental observations. Using the Einstein characteristic temperature for ease of calculation, Mott[6] has obtained a Periodic variation in the conductivity of the pure metals. A similar variation was observed by Bridgman[78] for the resistivities, measured at half the characteristic temperatures and taking account of the number of atoms in a centimetre cube of each metal. It should be emphasised that a quantitive correlation was not observed, particularly between the metals of higher valency.

Similar approaches to the liquid state, with appropriate factors to account for the changes on melting have also proved unsatisfactory. A change of characteristic temperature as assumed by Mott[6], or the increase in disorder suggested by McDonald[9], were both unable to supply a completely satisfactory explanation of the change in resistivity on melting. Nevertheless, some form of rationalisation is essential before a reliable comparison between liquid metals can be made.

An obvious first step in the standardisation of the conditions for a resistance comparison is to

fix the number of atoms in a specimen. This in itself is insufficient, since the shape of the specimen must also be defined in terms of the number of atoms in the cross-sectional area and in the length. The resistivity unit itself can still be applied if rationalisation is performed by means of a cube containing the number of atoms in one gram atom of the metal. The usual formula relating the resistance R, to the resistivity ρ:

$$R = \frac{\rho l}{A}$$

where A is the area of cross-section,

and l is the length of the specimen

reduces, in the case of a cube of volume V, to

$$R = \frac{\rho}{\sqrt[3]{V}}$$

When V is the gram atomic volume the "atomic resistivity" R_{at}, is given by:

$$R_{at} = \frac{\rho}{\sqrt[3]{\frac{W}{d}}} \qquad (8)$$

where W is the atomic weight,

and d is the density of the metal.

TABLE 5

Resistivity and Density Data of Some Pure Metals at the Melting Points

	At. No.	M. Pt. °C.	At. Wt. W	Density $d_L^{(77)}$ (g/mls)	$\Delta d_L^{(77)}$ in %	$\frac{W}{d_L}$ (mls)	$\sqrt[3]{\frac{W}{d_L}}$	$\frac{\rho_L}{\rho_S}$	$\rho_L^{(77)}$ (μohm cms)	$\frac{\rho_L}{\sqrt[3]{\frac{W}{d_L}}}$
Li	3	179	6.94	0.509	1.5	13.64	2.39	1.8[14]	45	18.8
Na	11	97.8	23	0.928	2.5	24.78	2.916	1.45[13]	9.5[16]	3.258
K	19	63.7	39.1	0.827	2.41	47.28	3.616	1.56[14]	13.2[16]	3.650
Rb	37	39.0	85.48	1.475	2.5	57.95	3.87	1.60	22.0[16]	5.685
Cs	55	28.5	132.9	1.84	2.6	72.23	4.165	1.66	36.7[16]	8.812
Cu	29	1083	63.5	8.22	4.1	7.73	1.977	2.04[15]	21.3	10.77
Ag	47	960.5	107.9	9.3	4.99	11.60	2.264	2.09	17.2	7.60
Au	79	1063	197.2	17.285	5.2	11.41	2.251	2.28	31.2	13.86
Mg	12	651	24.3	1.572	4.2	15.46	2.491	1.78	27.4[15]	11.0
Zn	30	419.5	65.4	6.92	6.9	9.45	2.114	2.24	35.3	16.70
Cd	48	321	112.4	8.02	4.74	14.01	2.411	1.93	33.7	13.98
Hg	80	-38.87	200.6	13.69	3.6	14.65	2.447	3.4	90.5	36.98
Al	13	660.2	27	2.380	6.6	11.35	2.247	2.20	19.6	8.723
Ga	31	29.92	69.7	6.095	-3.1	11.44	2.253	0.58	25.9	11.50
In	49	156.4	114.8	7.032	2.5	16.33	2.537	2.18	29.1	11.47
Tl	81	303	204.4	11.295	3.2	18.10	2.626	2.06	74.0	28.18
Sn	50	231.9	118.7	6.95	2.6	17.08	2.575	2.10	47.6	18.49
Pb	82	327.4	207.2	10.6	3.6	19.55	2.694	1.94	94.6	35.12
Sb	51	630.5	121.8	6.50	-0.94	18.74	2.656	0.61	117.0	44.05
Bi	83	271	209	10.07	-3.32	20.75	2.748	0.45	127.4	46.36

An examination of the resistivity and density change data on melting in Table 5 will show that a correction for the change in the number of atoms per unit volume cannot account for more than a few percent. of the total resistivity change. This results mainly from the smallness of the density changes at the melting points. Melting is also accompanied by an increase in the atomic disorder, and by the introduction of vacancies. Changes in the states of the valency electrons can also occur - an effect which is quite marked for antimony and bismuth.

A factor which is frequently not taken into account is the effect on resistivity of the volume change on melting. Work on resistivity as a function of pressure can be interpreted in terms of volume changes, although the resistivity changes cannot be accounted for merely by a correction for the change in the number of atoms. If atomic volume or its change is the more important parameter then, since the compressibilities are different, the use of pressure as a reference parameter can give rise to errors of interpretation.

The problem can be examined in terms of the meaning of applied pressure when referred to

atoms not on the surface of the liquid. The properties of a metal are affected by the distance between such atoms, and an external pressure change, or a change of state, can both result in a change in the interatomic distance. This suggests that an external pressure can have a meaning only in terms of the interatomic distances between atoms in the liquid. The question of the validity of measurements made at atmospheric pressure thus arises. On the basis of the above argument there is no reason to suppose that resistance measurements at pressures approximating to zero can be taken as a special case. It is more appropriate for measurements to be made at constant volume. Many fundamental approaches to the problem of resistivity behaviour have considered constant volume to be an essential standard.

Atomic resistivities measured at constant pressure should thus include a factor which introduces the effect of change in interatomic distance on resistance. This would be difficult to apply to the resistivity change on melting since a distinction exists between interatomic distance and atomic volume. On melting the density of a metal changes by about 4%, whereas X-ray data suggest

that there is little change in the mean interatomic distance. As suggested by Bernal[30], the volume change can be related to an increase in the number of vacancies arising from the atomic disorder. Unless it is assumed that atoms are hard spheres, it is not possible to reduce the atoms of the liquid to the same state as those in the solid simply by the application of an external pressure. While disorder is present the vacancies must exist, giving rise to a situation where an atom of a liquid at the same density as the solid occupies a smaller volume than when in the solid state.

That such atoms are not in the same state is shown by the values calculated for ρ_L, assuming that the metal can exist as a supercooled liquid when under pressure at the normal melting point. The difference between ρ_L and ρ_s at the same density and temperature is reduced only by about 25% for metals such as Na, K and Hg. Hence it would seem that standardisation for any metal with respect to volume alone is insufficient to account for the change of resistance on melting, without some knowledge of the effects of disorder and of vacancies.

The changes in density and resistivity on

melting for many metals are very similar. These observations are taken as sufficient grounds for the assumption that the melting process introduces in each metal disorder of approximately the same magnitude. Thus, in relation to each other, the mean interatomic distances in the liquid metals can be discussed in terms of their gram atomic volumes. Column 7 of Table 5 indicates these volumes at the melting points.

The volumes at the melting points of the alkali metals were chosen by Endo[16] as those at which to measure resistivity at constant volume. This is the procedure adopted in most work at constant volume. It leads to much rationalisation of results when the resistivity-temperature curves are extrapolated to zero to eliminate the thermal effect on resistivity. However, from the theoretical standpoint, there appears to be little justification for choosing the constant volume to be that at the melting point. It is known that resistivity is a function of volume, so the different volumes taken up by metals at their normal melting points under zero pressure are not necessarily standard conditions for measurement.

At Absolute Zero it is considered that

the "liquids" all exist with approximately the same degree of disorder and the same fraction of free space. It is further assumed that each ion core electron has a volume equivalent, which is a constant for each of the electrons in an atom. It is immediately obvious that the volume equivalents are not the same for different metals such as silver and gold. This arises from the large difference in the number of electrons in atoms of the two metals, which occupy nearly identical atomic volumes. An atomic size standard can be derived in terms of the number of electrons by arranging that the volume equivalent is a constant for all metals.

It is probably not justified to apply the rather oversimplified procedure of assigning a physical volume to the electrons in an atom. An electron can be considered as a point of negative charge, for which volume has no meaning, and the volume of an atom can be thought of as a measure of the equilibrium distance between atoms under different force fields. However, for similar metals at least, both views will be regarded as equivalent. Different metals can then be considered in the same state when the atomic volumes bear a simple

relationship to their atomic numbers.

The gram atomic volumes at $0^{\circ}K$, determined by extrapolation of the density curves from the liquid ranges, are presented in Table 6.

It can be seen that the attainment, for all metals, of atomic volumes proportional to their atomic numbers would be experimentally very difficult. However, at zero pressure the atomic volumes of the alkali metals are roughly related to the atomic numbers. The resistivity behaviour might therefore be expected to be more rational than that of other metals. With the exception of lithium, this has been found to be so for resistivity measurements at constant volume by Endo[16], and the pseudo-potential theory developed by Ziman[23].

The experimental problems involved in measuring resistivities at constant volume and as a function of pressure are such that work at high temperatures is difficult. Of the polyvalent metals only those with low melting points, such as Hg and Ga[46], have been studied, and insufficient data is available to adequately test the arguments developed above. Despite this difficulty, the degree to which atomic resistivity is related to atomic volume can be shown, as in Figure 24.

TABLE 6

Atomic Volumes and Atomic Resistivities of Some Pure Metals at 0°K

	Atomic Number	$\left(\frac{W}{d_L}\right)_{0°K}$ * (mls)	$\left(\frac{\rho_L}{\sqrt[3]{\frac{W}{d_L}}}\right)_{0°K}$ * (μohms)
Li	3	12.3	(6.5)
Na	11	22.1	-1.42
K	19	42.3	-2.8
Rb	37	(51)	-1.9
Cs	55	(62)	(1.26)
Cu	29	(5.7)	(2.5)
Ag	47	9.7	4
Au	79	9.4	1
Mg	12	(8.3)	(4.8)
Zn	30	9	(5)
Cd	48	12.7	(6)
Hg	80	13.8	26.5
Al	13	10.0	1
Ga	31	10.8	8
In	49	15.4	9
Tl	81	16.9	(20)
Sn	50	15.9	14.3
Pb	82	17.8	25.5
Sb	51	16.9	23
Bi	83	19.5	31

* The figures in brackets have been estimated from rather sparse experimental data.

With few exceptions all the metals lie on a smooth curve. The absolute value of mercury is rather high, but its variation with volume is the same as that given by the slope of the curve.

The periodicity of the atomic resistivity parameter is shown in Figure 25. In general the function varies systematically with both atomic number and the sequence of metals in each Group. These diagrams illustrate the strong interdependence of atomic resistivity and volume which can override many of the differences between metals.

2. Liquid Alloy Applications

The purpose of this discussion has been to establish a basis for the manner in which resistivities should be treated, before a quantitative relationship between metals can be set up. From this point of view alone the approach has not been altogether satisfactory. Its value lies in the applications to liquid alloys, particularly those in which volume changes occur on alloying.

Although the rationalisation process cannot be effectively applied to the pure metals, alloy behaviour can be examined in terms of the changes in the factors affecting resistivity when at the measuring temperatures. Justification for

this assumption can be found from the ratios of the atomic volumes and resistivities of the component metals, which are much the same as when calculated at $0^{o}K$. This is not the case for the alkali metals which have large and differing compressibilities and temperature coefficients of resistance.

The melting process introduces disorder into a system, which is usually accompanied by a resistivity increase. On alloying, the mixing of A and B atoms produces further disorder, and hence the alloy resistivity might be expected to be positive with respect to the weighted mean value of the component resistivities. Provided the A-B interaction is not strong enough to cause the formation of intermetallic compounds, the solid state result for the excess resistivity of a totally disordered alloy usually applies, in the form of a parabola given by equation (5).

In contrast to this behaviour, the resistivity isotherms of mercury alloys are all the more remarkable. The negative resistivity deviations from the weighted mean values of several Hg-based systems are illustrated in Figure 26. The similarity between the curves is rather striking, with the minima appearing between 15 and 25 atomic % solute.

The size of each minimum is related to the absolute resistivity of the solute metal. Quantitative calculations involving the Hg-Zn curve should be used with caution, since the pure zinc end-point was determined by an uncertain extrapolation from the liquid state. The formation of these mercury alloys is accompanied by fairly substantial volume contractions of up to 3%[73].

Before the volume change effect on resistivity can be studied, the variation of the number of conduction electrons per atom must be known, since this is a major factor affecting resistivity. These properties have all been measured for the Hg-In system, and are illustrated in Figures 27 and 28. The values for the indium rich alloys at 100°C are obtained by extrapolation from the liquid region.

The number of conduction electrons per atom was calculated from the Hall coefficient data of Cusack[44] and Tièche[45]. Although the pure metals show free-electron behaviour, the measured Hall coefficients suggest that the Hg-In alloys have more conduction electrons available than would be expected from free-electron considerations. Recalculated values by Cusack and Kendall[43],

which agree more closely with the Tièche coefficients, are attributed to local anisotropy in the liquid alloys. This anisotropic effect is presumably similar to that arising in solids, where free-electron values are not obtainable although resistivity data suggest that this behaviour does occur. It is difficult in any case to understand why a larger number of electrons than expected should be present.

Behaviour similar to that found for resistivities was also observed for the compressibilities of some dilute mercury alloys, including Hg-In. It was interpreted by Abowitz and Gordon[11] in terms of the breakup of covalently bonded pure mercury into the metallic state when alloyed. The Characteristic temperature increase of the alloys as calculated in this work was also attributed to the same cause. The Hall coefficient data on pure mercury indicate that the metal behaves according to the free-electron theory, and tend to refute the covalent bond theory.

Several theories on electrical resistivity behaviour have been developed with the use of a Characteristic temperature factor. When applied to liquid alloys the concept tends to become rather artificial. It is suggested that the Characteristic

temperature effect should be recognised as a means of correcting for volume differences. The relationship can be described in a fairly simple manner. If at any temperature the volume of a system is decreased, then the amplitudes of the thermal vibrations of the atoms will be reduced. The total thermal energy must remain constant, so a corresponding increase in the vibrational frequencies must occur, resulting in an increased Characteristic temperature.

This is an oversimplified picture, but it is borne out by the existence of an inverse relationship between the Characteristic temperatures[7] and atomic volumes of similar metals when in the solid state. The increase in Characteristic temperature observed for the mercury alloys[11] can also be attributed to the volume contractions on alloying.

No change in volume is to be expected when the components of a simple mixture are alloyed. For systems in which a volume change does occur, it is possible to determine its effect from the pure metal properties by arranging for the volume change to be zero. The degree to which each component changes its volume in the alloying process, or the

resistivity variation of the alloy as a function of volume must be known.

The similarities between the volume changes of the mercury alloys suggest that the effect is largely independent of the solute metal. It is therefore assumed that these changes can be related to the mercury atoms only. The 'simple mixture' resistivity of an alloy is then given by the point at which the straight line joining the resistivity of mercury, compressed sufficiently to account for the total volume change, to the resistivity of the pure solute metal intersects the alloy composition.

The effect of the volume change correction on the atomic resistivities of the Hg-In system at 100°C is illustrated in Figure 29. It can be seen that the deviation of the observed atomic resistivity from the simple mixture value is reduced by about 35%. The variation of the resistance of mercury with volume is taken from Bridgman's data[14,79] at 30°C, and used on the assumption that the relationship between resistance and volume is independent of temperature.

The volume-corrected curve will indicate the weighted mean resistivities if it is assumed that the system contains the number of electrons

given by the free-electron theory. The apparent number present is shown in the upper diagram of Figure 28, and the simple-mixture alloy should be treated as if this increased number of electrons were introduced into the system. The resultant values determined from the two sets of Hall coefficient data are shown in Figure 29. This correction for the apparently increased number of conduction electrons accounts for 50% of the resistance difference from the linear values.

The observed and theoretical resistivities of the Hg-In system are shown in Figure 27. The observed resistivities are about 7% smaller than the calculated values. A negative deviation of resistivity with respect to the weighted mean values could be considered a somewhat surprising result in view of the marked change in the properties of mercury caused by solute atoms. However, the large negative heats of formation associated with a strong A-B interaction are not generally found for the mercury alloys. This lends support to the initial assumption that these alloys can be treated as mixtures. The closeness of the agreement between the experimental and derived resistivities also justifies the hypothesis that

the change in volume on alloying can be attributed mainly to pure mercury.

On the assumption that the percentage volume changes measured at 158°C do not vary significantly with temperature, the volume change effect on the weighted mean resistivities at 350°C of the Bi, Sn, Pb and Zn amalgams can be calculated. These curves are shown in Figures 30 and 31, together with the observed atomic resistivities. As in the case of the Hg-In system the correction for the volume effect accounts for approximately 35% of the total resistance deviation from the linear values.

However, there is little justification for an assumption that the mercury alloy resistivities should follow the weighted mean values, since most alloys show positive deviations from them. No Hall coefficient data on these four systems are known to the author, but, on the basis of the measurements on Hg-In it will be assumed that the effective valency of mercury rises to three when more than 20 atomic % solute atoms are present. In this case Hg-In can be considered as an alloy system of two metals of the same valency, for which the resistivity variations are frequently linear with respect to composition[54,65]. Hence,

agreement between the calculated and observed resistivities in this system can be expected.

The apparent number of conduction electrons present in each system, assuming that mercury shows an effective valency of three, is shown in the lower diagram of Figure 32. The upper diagram represents the difference between the observed atomic resistivities, and those calculated from weighted mean values corrected for volume changes and for the presence of excess electrons. These figures need only be multiplied by approximately 2.5 to convert them to the more familiar resistivity differences.

While the results are not entirely compatible with the suggested increase in the effective valency of mercury, the derived resistance deviations of the Bi and Pb amalgams are typical of alloys which exhibit a normal increase of resistivity with composition. Difficulties arise when lower resistivities than expected are observed, as in the cases of Hg-Sn and Hg-Zn. One explanation is that the atoms in the systems are ordered. In this case it would be reasonable to suppose that the ordering effect would be more pronounced at some composition, causing a well defined minimum in the resistivity

isotherms. The isotherms of the Sn, Pb and Zn amalgams show no discontinuities at which ordering could occur. It is more likely that the negative resistivity differences from the calculated values result from errors in the application of the correction factors.

Individually, the Sn, Pb and Zn amalgams show little in the way of interesting behaviour. All three are characterised by smoothly varying isotherms and similar temperature coefficient behaviour. The minor variations in the coefficient for Hg-Pb cannot be associated with any single cause. It is only in their behaviour as a group that mercury alloys of this type are of interest.

On the other hand the Hg-Bi alloys exhibit some unusual resistivity behaviour in the composition range 30-45 atomic % Bi. The normal results for this system are shown in Figure 17, while the abnormal resistivity values on four specimens are indicated in Figure 18. It was found that abnormally low resistivities were obtainable on the freshly prepared specimens. Operations performed on any of these specimens resulted in a larger resistivity, and it was not found possible to lower the values either by the same path or by a

form of hysteresis. This behaviour continued until the normal values of resistivity for the system were obtained.

The resistivity at the minimum was found to be the same as that at the minimum of the isotherm. This suggested that the alloy was not homogenous, and that the sample of specimen under examination was of the wrong composition. This could be true if the measurements had been made below the bismuth melting point, since bismuth alloys made in this manner have been observed to maintain a suspension of pure solid bismuth[63].

Ionic transport was not observed, and the resistivities were generally found to be not time dependent. The resistivity was also not particularly sensitive to mechanical mixing of the specimen. The observed resistivities can be satisfactorily explained if it is assumed that, even when liquid, the bismuth atoms tended to cluster. The effective composition of the alloy would be lower than intended, and would give rise to the resistivities observed in the region of the true minimum. Breakup of the clusters, caused by mechanical mixing, and with time, would result in resistivity increases until the normal values were attained.

Confirmation of the abnormally low bismuth content of the sample in the capillary could be obtained from the temperature coefficients of resistivity of the anomalous results. Unfortunately, the resistivity changes made the accurate calculation of the coefficients difficult. In any case, it can be seen from Figure 15 that the coefficient is almost constant in the region required for the composition check.

Over the range of composition examined, the resistivities of the Hg-Na alloys are relatively insensitive to composition changes. The system was examined in the region which contained four solid state compounds. Small maxima were observed at the composition NaHg and near the eutectic Hg - 2.8 atomic % Na. These maxima could equally well arise from the tendency to form a minimum in the region of $NaHg_2$. The experimental technique requires further development before the resistivities near the compound compositions can be defined with any certainty.

3. The Tin-Lead Anomalies

The discrepancies which exist between the data on the eutectic in the Pb-Sn system are illustrated in Figure 23. In this work it was

found that both the anomalous effects could be qualitatively reproduced.

Since the results suggested that the eutectic composition showed a very narrow maximum, it is tempting to imagine the presence of a "eutectic structure"[58], which is stable over a very small composition range, and which possesses a high resistivity. The irregular behaviour of the results could then be explained in terms of fractional composition changes causing the capillary sample to change from the eutectic composition, with a corresponding fall in resistivity.

However, the manner in which the discontinuity temperature was related to the high and low temperature resistivities as shown in Figure 22, suggested a different cause for the anomalies. The consistency of the measurements suggested that phase changes were occurring in the capillary, although not at the same composition, and although there was little doubt that the bulk composition was that of the eutectic.

This hypothesis was tested in the following way: It was assumed that the change in temperature coefficient represented a real phase change. The compositions corresponding to the

discontinuity temperatures were obtained from the equilibrium diagram, and the liquidus temperature resistivities of alloys at these compositions found from the Roll and Fees data.

An almost exact correspondence exists between these values, and the measured resistivities at the discontinuity temperatures. The data are presented in Table 7. The final column proves conclusively that localised composition changes can occur in alloys close to the eutectic composition. This behaviour could arise from different diffusion coefficients of the metals when under the influence of an electric field. It has been found[80] that the component phases of a fused salt eutectic can be separated when a current density of 10^3 amps/cms^2 is applied. It is surprising that similar behaviour can have such a marked effect on the Pb-Sn eutectic, using current densities of only 5 amps/cms^2.

Table 7

Correlation between Observed and Derived Resistivities in Some Pb-Sn Alloys

Nominal composition at. % Pb	Discontinuity temperature °C	Observed resistivity (μ ohm cms)	Composition equivalent to dis. temp. at. % Pb	ρ_L (Roll) (μ ohm cms)	$\frac{\rho_{(obs)}}{\rho_{(Roll)}}$
26.1	256	69.8	57	74.0	0.95
"	240	67.0	48.5	68.4	0.98
"	227	63.4	41.5	66.0	0.96
"	225	64.0	41	65.2	0.98
"	223	62.8	40	63.5	0.99
25.7	210	60.0	35	63.0	0.95
"	205	59.0	33	61.0	0.97
25.3	197	58.0	30	56.3	1.03
26.7	192	57.5	28	57.0	1.01
26.1	192	57.2	28	57.0	1.00
25.0	188	56.7	27	57.0	1.00

VI. SUMMARY AND CONCLUSIONS

1. Summary

Electrical resistivity measurements were made on several liquid alloys by means of a precision, direct current potentiometric method. The resistance cell was designed to ensure homogeneity of the specimens, the overall accuracy of measurement being approximately 0.2%. The results can be summarised as follows:

(a) The addition of a polyvalent metal to mercury results in a sharp decrease in the resistivity. The slopes of the resistance-composition isotherms of the mercury-rich alloys are dependent on, but not very sensitive to, the resistivities of the pure solutes.

(b) The resistivities of alloys in the sodium-mercury system are very insensitive to composition changes.

(c) The temperature coefficient of resistivity decreases with increasing solute concentration up to about 20 atomic % solute. Above this concentration the coefficient becomes almost independent of composition.

(d) No significant discontinuities were observed in the variation of resistance with composition of the tin, lead and zinc amalgams, and the normal

mercury-bismuth alloys.

(e) Irregular resistivity behaviour occurred in some alloys of the mercury-bismuth system. Abnormally low resistivities were observed, which increased under various factors and could not be regained.

(f) Abnormally large resistivities were found in the region of the lead-tin eutectic. They were accompanied by sharp changes in the temperature coefficient at up to 70°C above the eutectic temperature.

2. Conclusions.

The following conclusions have been drawn from the results obtained in this work.

(a) The electrical properties of mercury are strongly in evidence in all the polyvalent mercury alloys. The interest in these systems lies in their behaviour as a group, rather than as individual systems. The resistivities of all these alloys deviate negatively with respect to the weighted mean values of the pure components.

It is possible to separate the effects that some factors can have on resistivities. The volume change which occurs on alloying can account for up to 35% of the resistivity deviation from

the mean values, if it is assumed that the volume contraction is related only to mercury.

A further 50% of the deviation can be attributed to an apparent increase in the valency of mercury. Reasonable agreement with the measured resistivities can be obtained if the valency of mercury is assumed to rise to three when the concentration of solute atoms is more than 20 atomic %. This was suggested by the Hall coefficient data[43,44,45] on the Hg-In system.

A correction for the increased number of atoms in a centimetre cube of alloy, resulting from the volume contractions, cannot account for more than 1% of the total resistivity change.

When these factors have been taken into account the Hg-In results suggest that there is little need for a Characteristic temperature change correction as proposed by some workers[9,11].

It is obvious that a direct measure of the number of conduction electrons is necessary before close agreement with the observed resistivities can be obtained. The effects of disorder introduced by the solute atoms can then be examined.

The treatment of the differences between the resistivities of the pure metals themselves

is a difficult problem, which cannot be resolved using the available data merely in terms of the difference in atomic volumes.

(b) The data for several Hg-Bi alloys suggest that clustering of bismuth atoms or bismuth- rich complexes can occur at temperatures above the melting points of the components. The disappearance of the effect suggests that is is not a very stable state, and that the atoms can be uniformly distributed by mechanical methods.

(c) It is concluded that similar behaviour can occur in alloys near the Pb-Sn eutectic. The mechanism in this case appears to depend on different diffusion rates of the species when in an electric field.

Both observations suggest that liquid alloys remain homogeneous only when external factors are not in operation.

VII PROPOSALS FOR FURTHER WORK.

It is evident that the electrical resistivities alone of a system are insufficient to show the degree of interaction between the component metals.

1. There is very little Hall coefficient data available on liquid alloys. Much of this work is on mercury alloys, which have many anomalous properties. It would be useful to know if, as the resistivities suggest, most alloy systems show free electron values for the conduction electrons.

2. Since resistivities are fairly sensitive to volume changes, it is necessary that the change in volume on alloying should be known before any treatment of the resistivity variations can be attempted. Hence, density changes of the liquid alloys as a function of temperature and composition need to be known. Volume changes as measured by Kleppa et al[73] would be sufficient, if the technique could be developed to work at high temperatures.

3. It is felt that to resolve the differences between the liquid pure metal properties, more should be known of the variation of resistivity at constant volume. This would allow a reasonably fundamental approach to be made to the effect on resistivity of the differences in atomic volumes.

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X. DIAGRAMS

Figure 1. Resistivity of solid alloys of Ni in Cu.

Figure 2. Resistivity-temperature curve of a metal and dilute alloy.

Figure 3. Resistance-composition curves at the liquidus temperatures of the system Sn-Pb.

Figure 4. Glass resistance cell.

Figure 5. Stainless steel resistance cell.

Figure 6. Diagram of circuit used to measure resistance of specimen.

Figure 7. Variation of resistivity with temperature of liquid Bi, Pb, Sn and Zn.

Figure 8. Variation of resistivity with temperature of liquid mercury.

Figure 9. Resistivity variation with temperature of some Hg-Zn alloys.

Figure 10. Resistance-composition isotherms of the system Hg-Zn.

Figure 11. Resistivity variation with temperature of some Hg-Sn alloys.

Figure 12. Resistance-composition isotherms of the system Hg-Sn.

Figure 13. Resistivity variation with temperature of some Hg-Pb alloys.

Figure 14. Resistance-composition isotherms of the system Hg-Pb.

Figure 15. Temperature coefficient of resistivity, $\left(\frac{\partial \rho_L}{\partial T}\right)_P$ of some mercury alloys.

Figure 16. Resistivity variation with temperature of some Hg-Bi alloys.

Figure 17. Resistance-composition isotherms of the system Hg-Bi.

Figure 18. Resistance-composition isotherms of four liquid Hg-Bi specimens at 295°C.

Figure 19. Variation with temperature of the resistivity of some Hg-Na alloys.

Figure 20. Resistance-composition isotherm at 350°C of some Hg-Na alloys.

Figure 21. Resistivity variation with temperature of some Sn-Pb alloys.

Figure 22. Variation of resistivity with temperature of Sn-Pb alloys in the region of the eutectic Sn-26.1 at. % Pb.

Figure 23. Liquidus temperature resistivities at compositions around the eutectic of the Sn-Pb system.

Figure 24. Atomic resistivities of some metals as a function of atomic volume, at 0°K.

Figure 25. Atomic resistivity at 0°K as a function of atomic number.

Figure 26. Deviations of resistivity from weighted mean values of some Hg alloys at 350°C.

Figure 27. Resistance-composition isotherm at 100°C of the Hg-In system.

Figure 28. Number of free electrons and atomic volumes in the system Hg-In.

Figure 29. Atomic resistivity and derived properties of the Hg-In system.

Figure 30. Atomic resistivity and volume-corrected resistance of the systems Hg-Bi and Hg-Sn.

Figure 31. Atomic resistivity and volume-corrected resistance of the systems Hg-Pb and Hg-Zn.

Figure 32. Derived resistivity differences and numbers of free electrons in some Hg alloys.

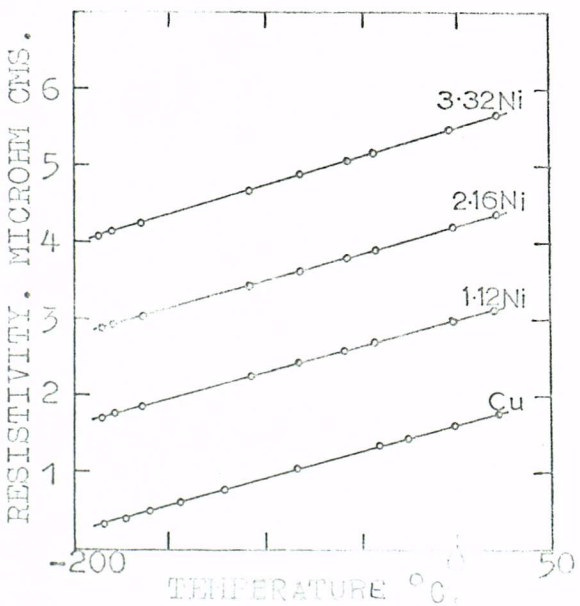


FIGURE 1. RESISTIVITY OF SOLID ALLOYS OF Ni IN Cu.(7)

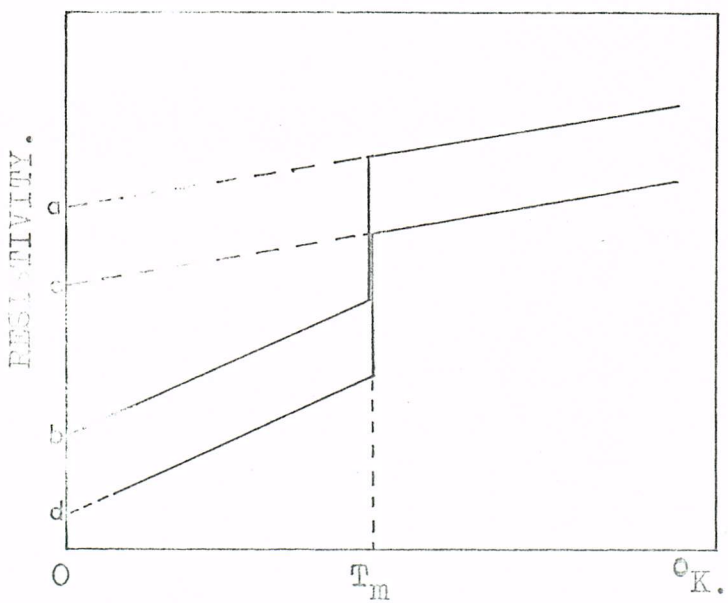


FIGURE 2. RESISTIVITY-TEMPERATURE CURVE OF A METAL AND DILUTE ALLOY.

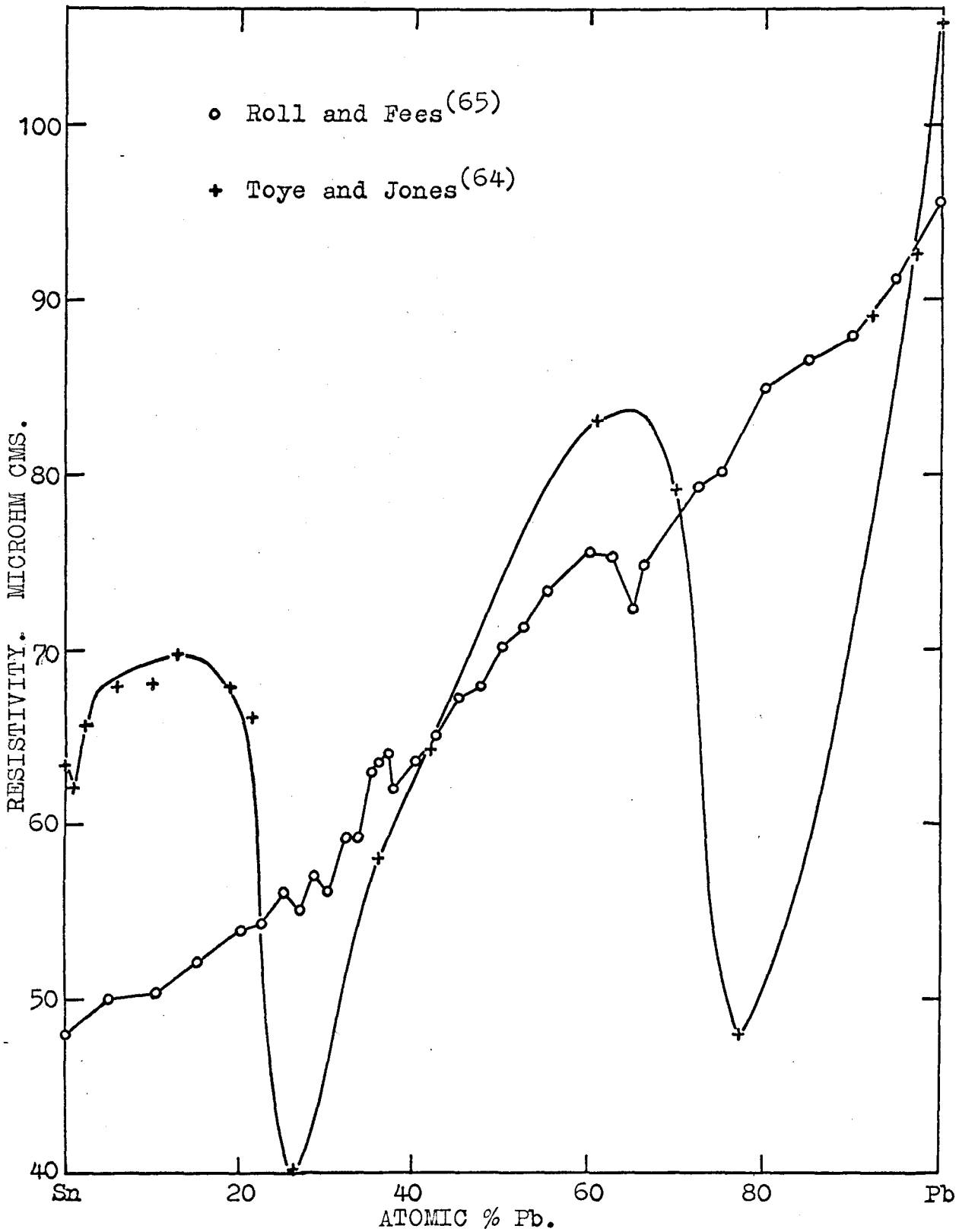


FIGURE 3. RESISTANCE-COMPOSITION CURVES AT THE LIQUIDUS TEMPERATURES OF THE SYSTEM Sn-Pb.

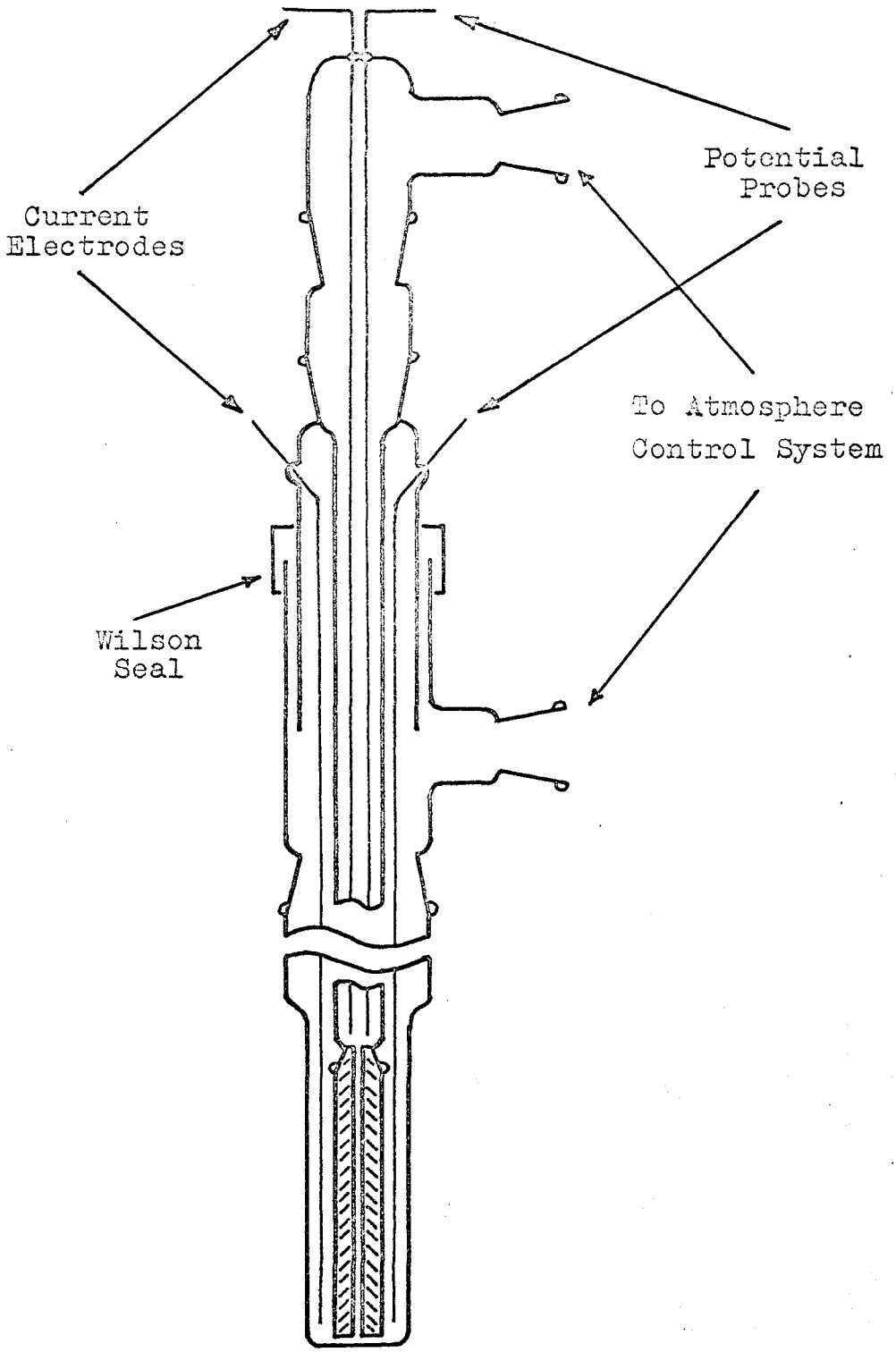


FIGURE 4. GLASS RESISTANCE CELL.

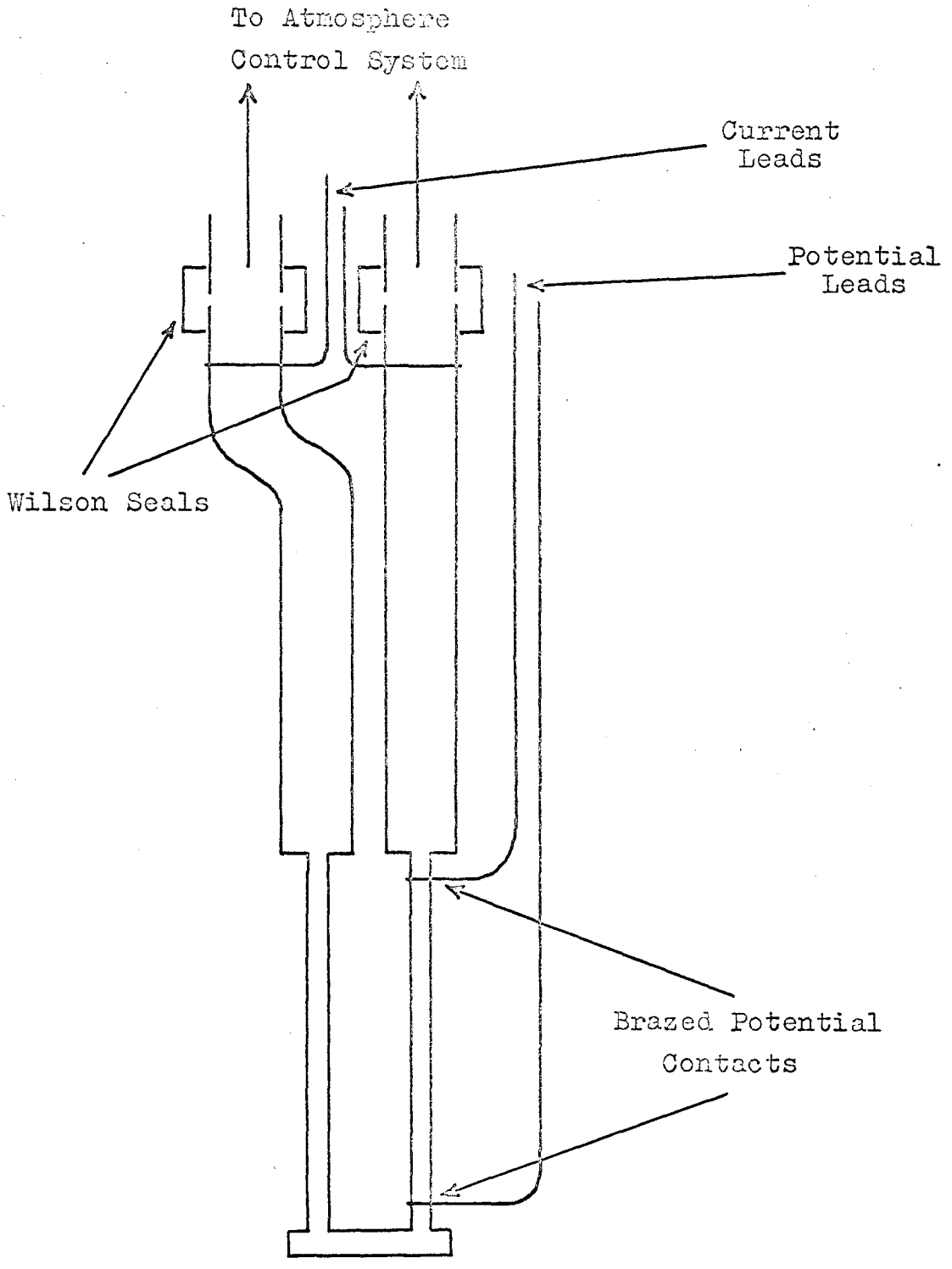


FIGURE 5. STAINLESS STEEL RESISTANCE CELL.

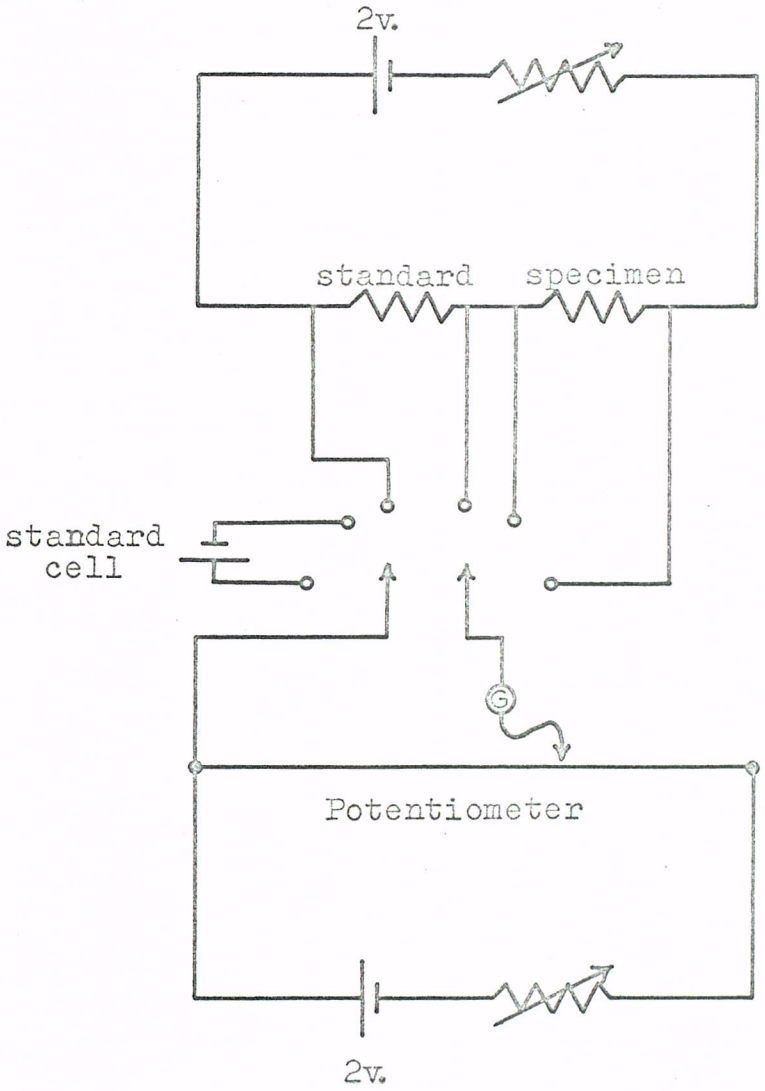


FIGURE 6. DIAGRAM OF CIRCUIT USED TO MEASURE RESISTANCE OF SPECIMEN.

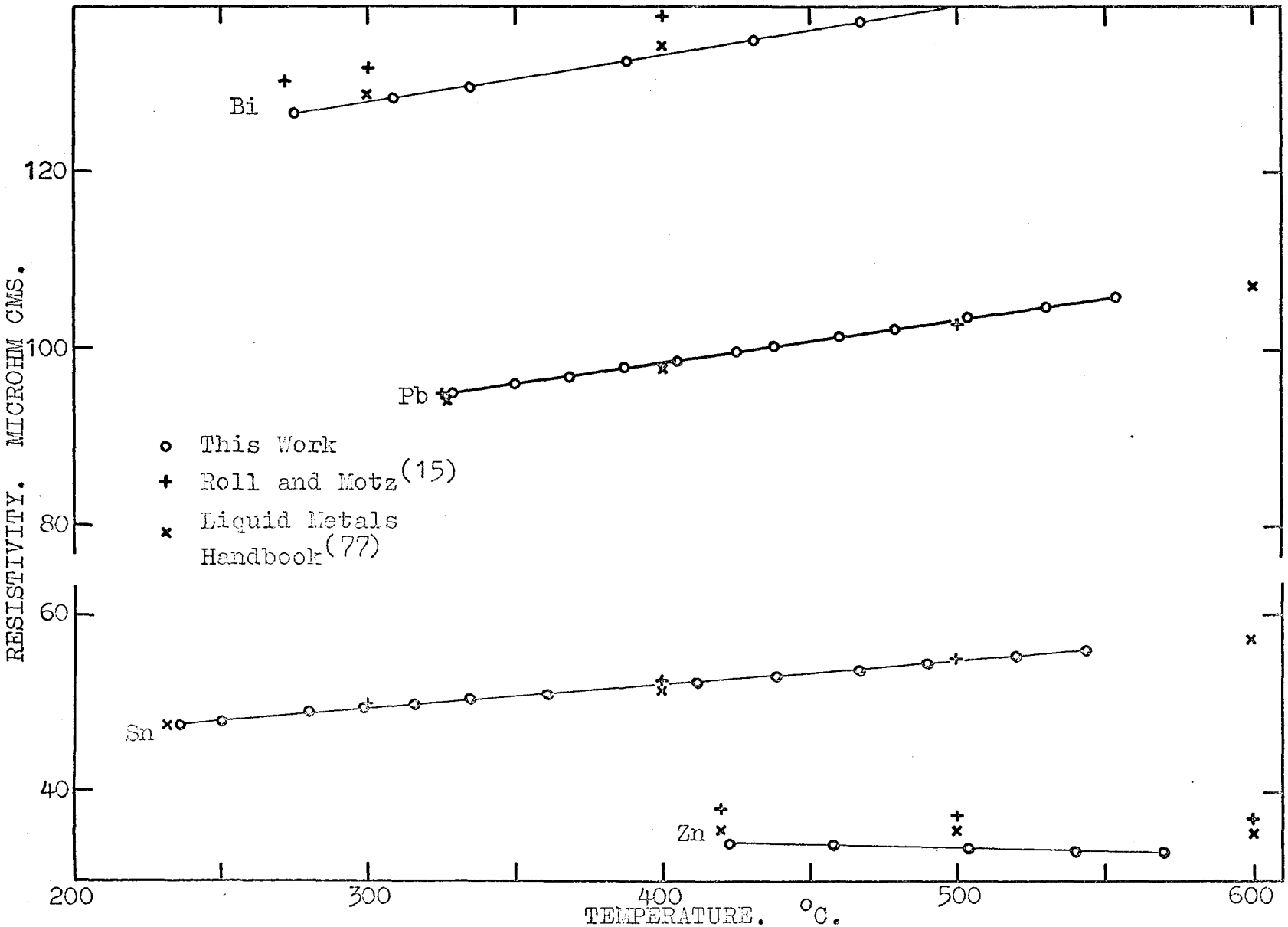


FIGURE 7. VARIATION OF RESISTIVITY WITH TEMPERATURE OF LIQUID Bi, Pb, Sn AND Zn.

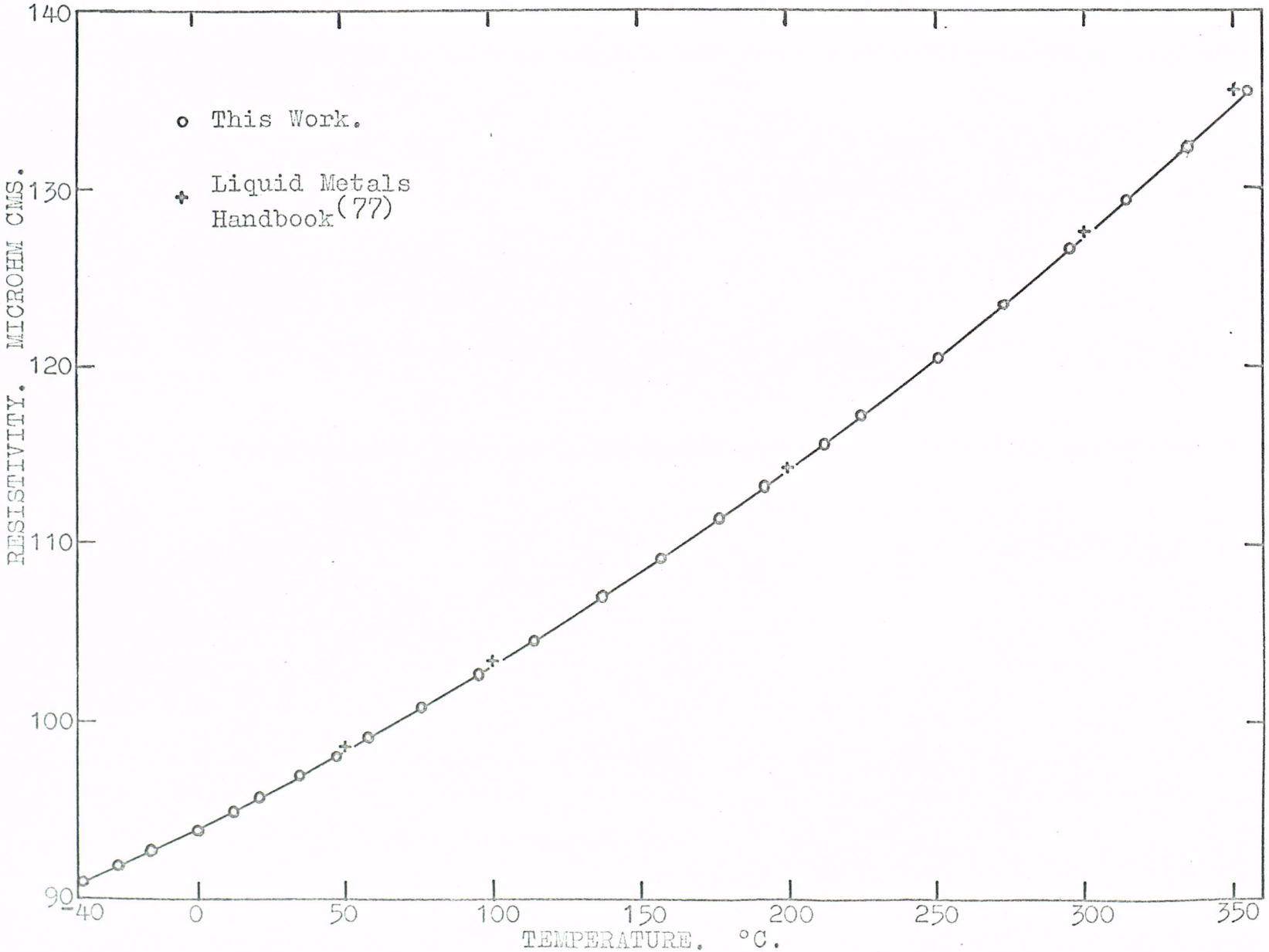


FIGURE 8. VARIATION OF RESISTIVITY WITH TEMPERATURE OF LIQUID MERCURY.

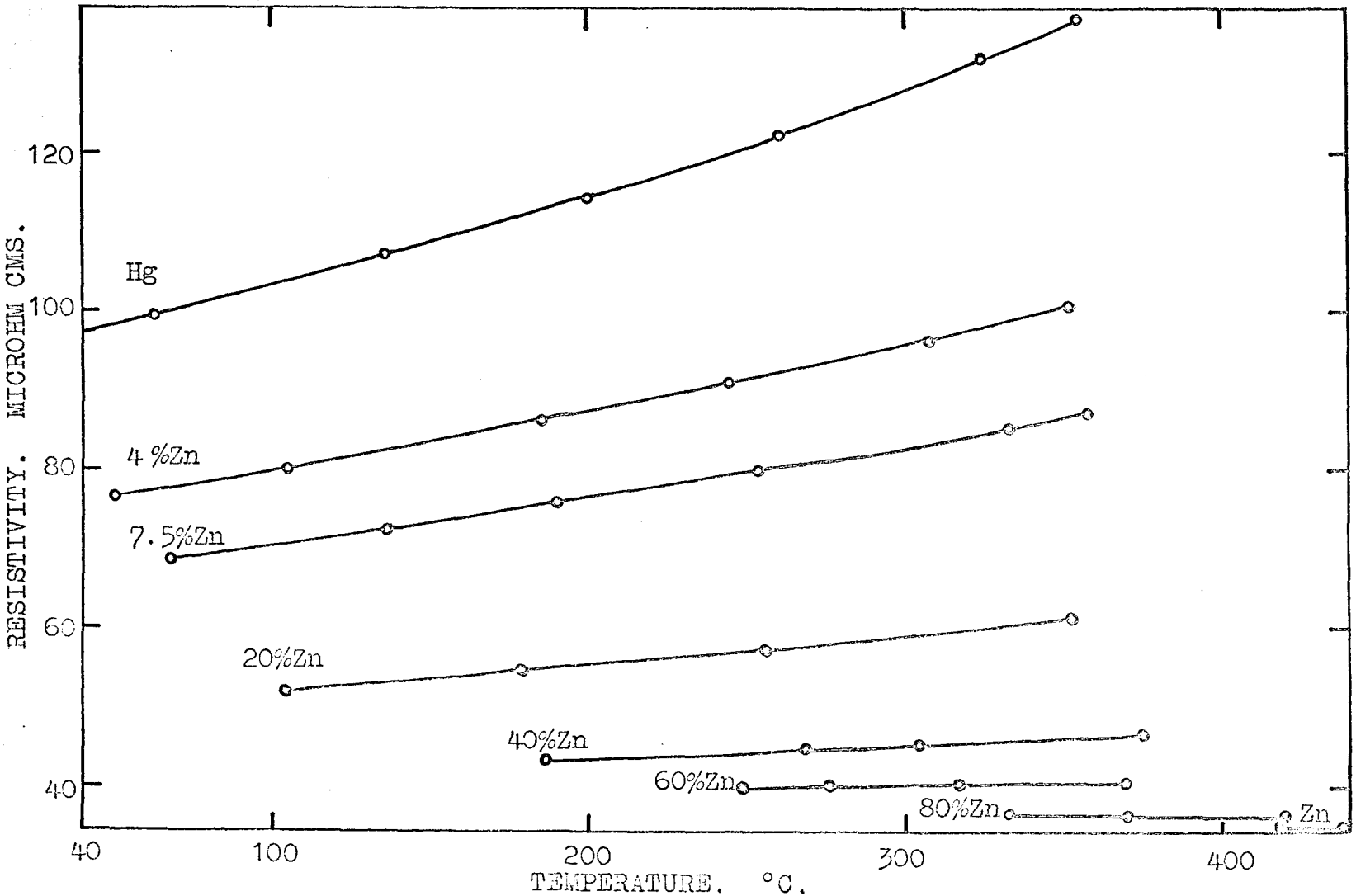


FIGURE 9. RESISTIVITY VARIATION WITH TEMPERATURE OF SOME Hg-Zn ALLOYS.

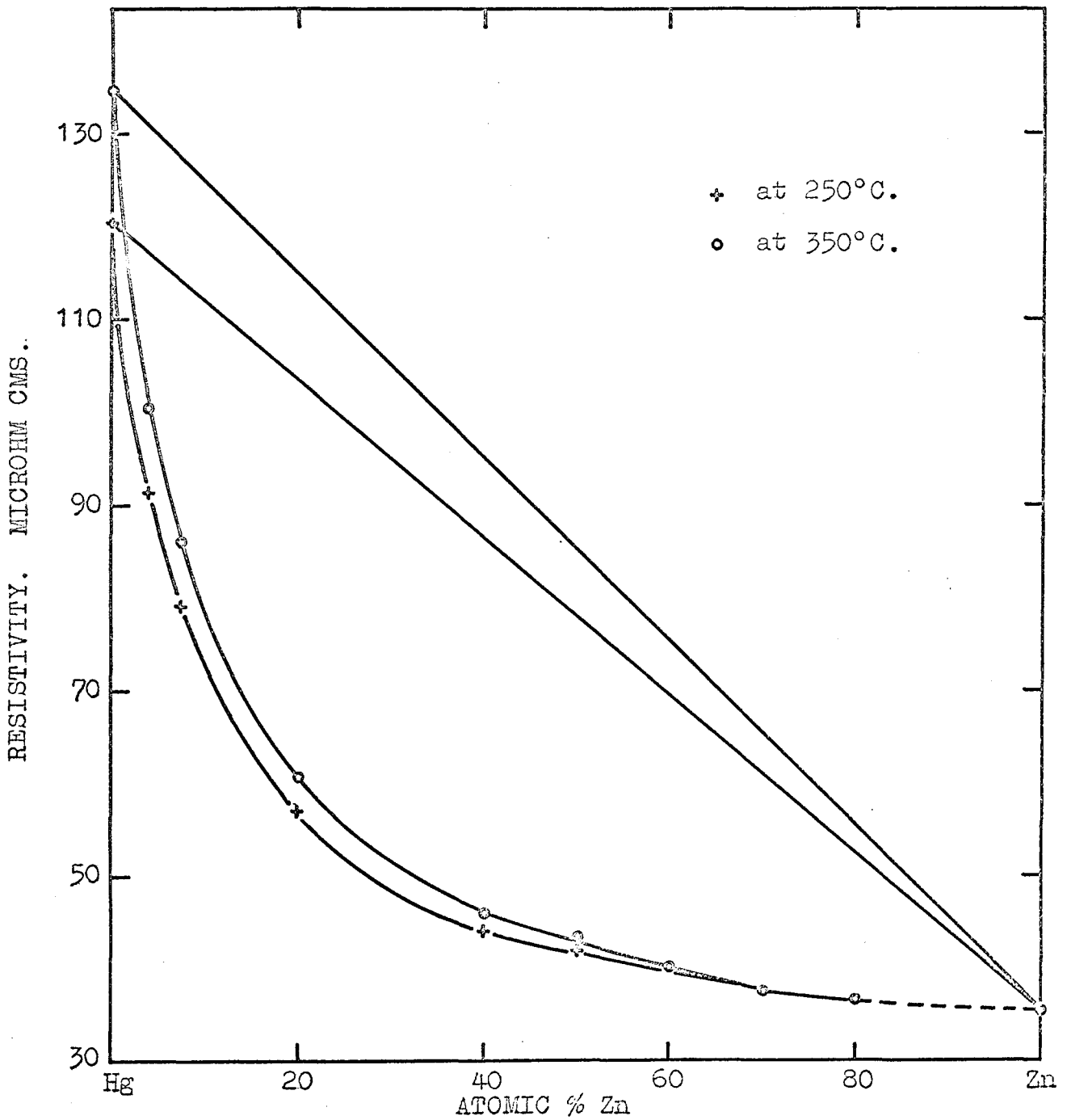


FIGURE 10. RESISTANCE-COMPOSITION ISOTHERMS OF THE SYSTEM Hg-Zn.

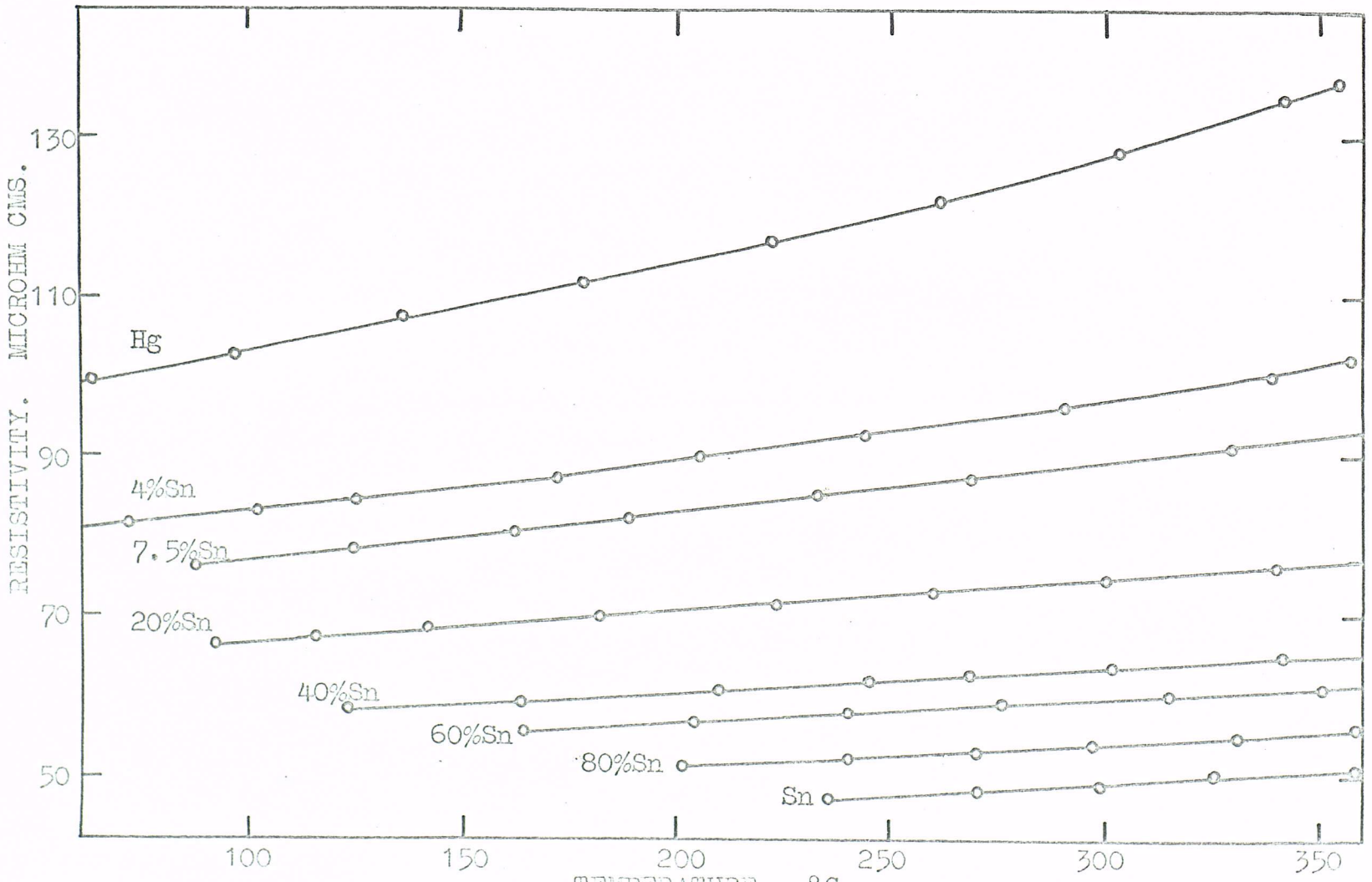


FIGURE 11. RESISTIVITY VARIATION WITH TEMPERATURE OF SOME Hg-Sn ALLOYS.

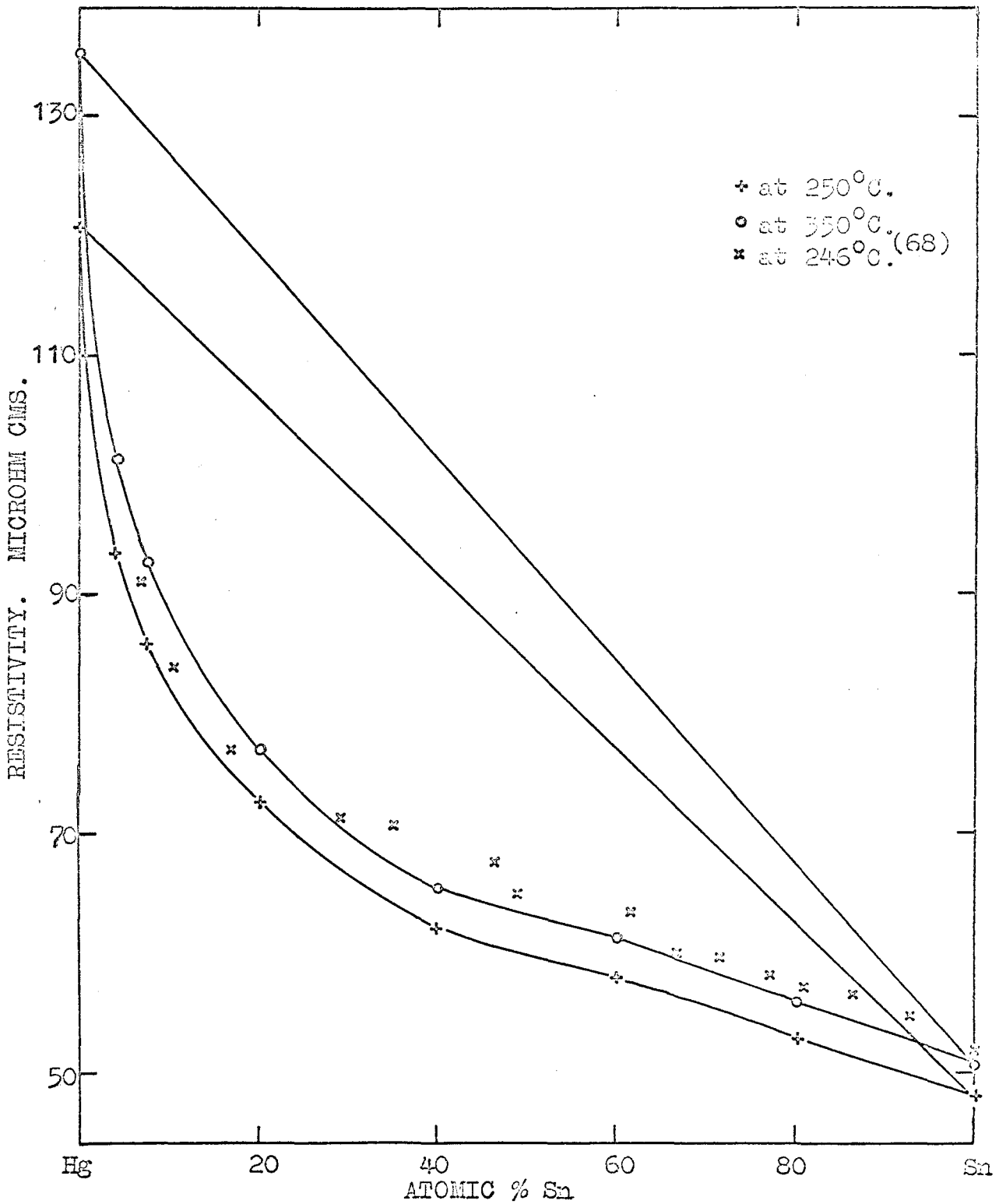


FIGURE 12. RESISTANCE-COMPOSITION ISOTHERMS OF THE SYSTEM Hg-Sn

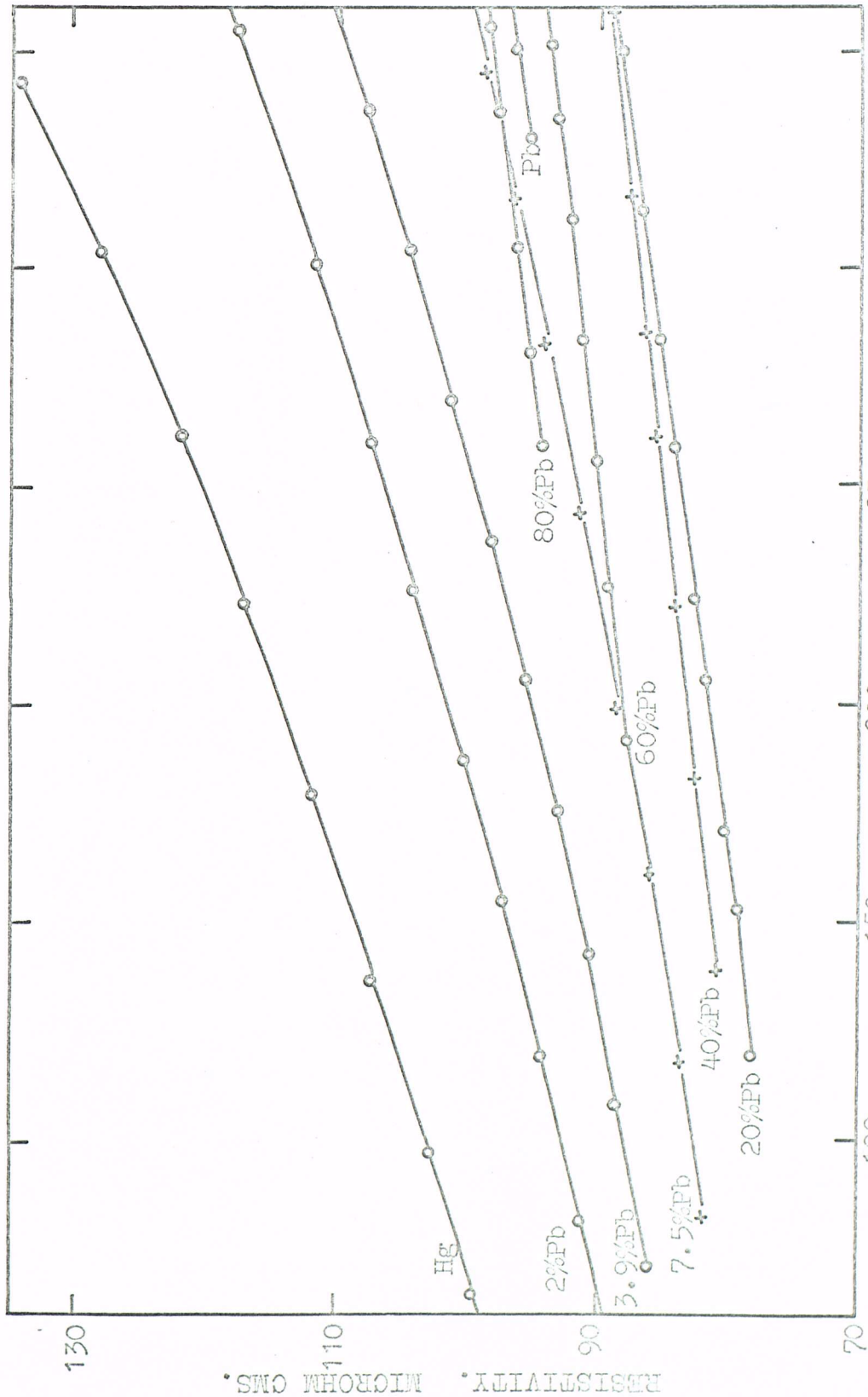


FIGURE 13. RESISTIVITY VARIATION WITH TEMPERATURE OF SOME Hg-Pb ALLOYS.

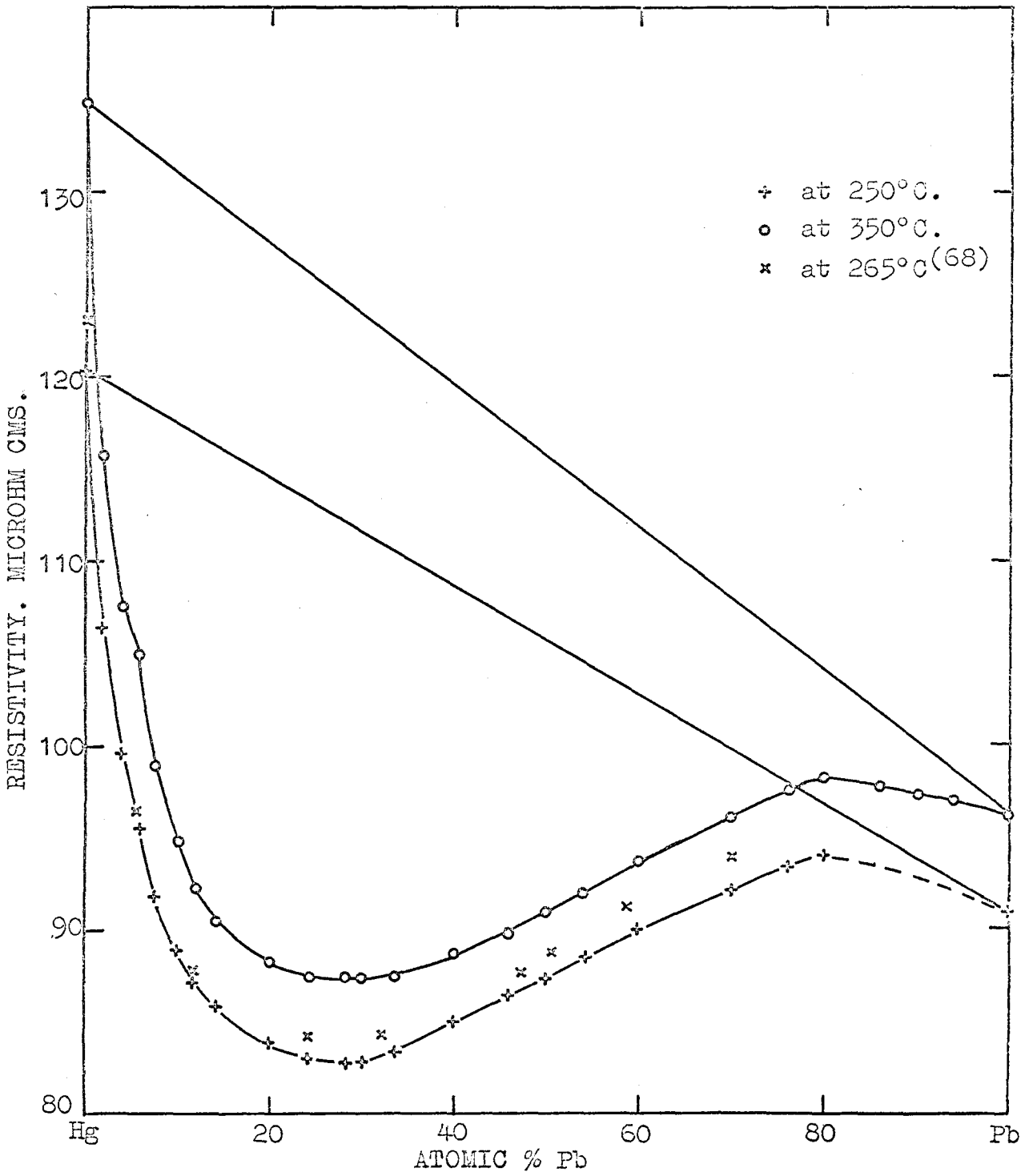


FIGURE 14. RESISTANCE-COMPOSITION ISOTHERMS OF THE SYSTEM Hg-Pb.

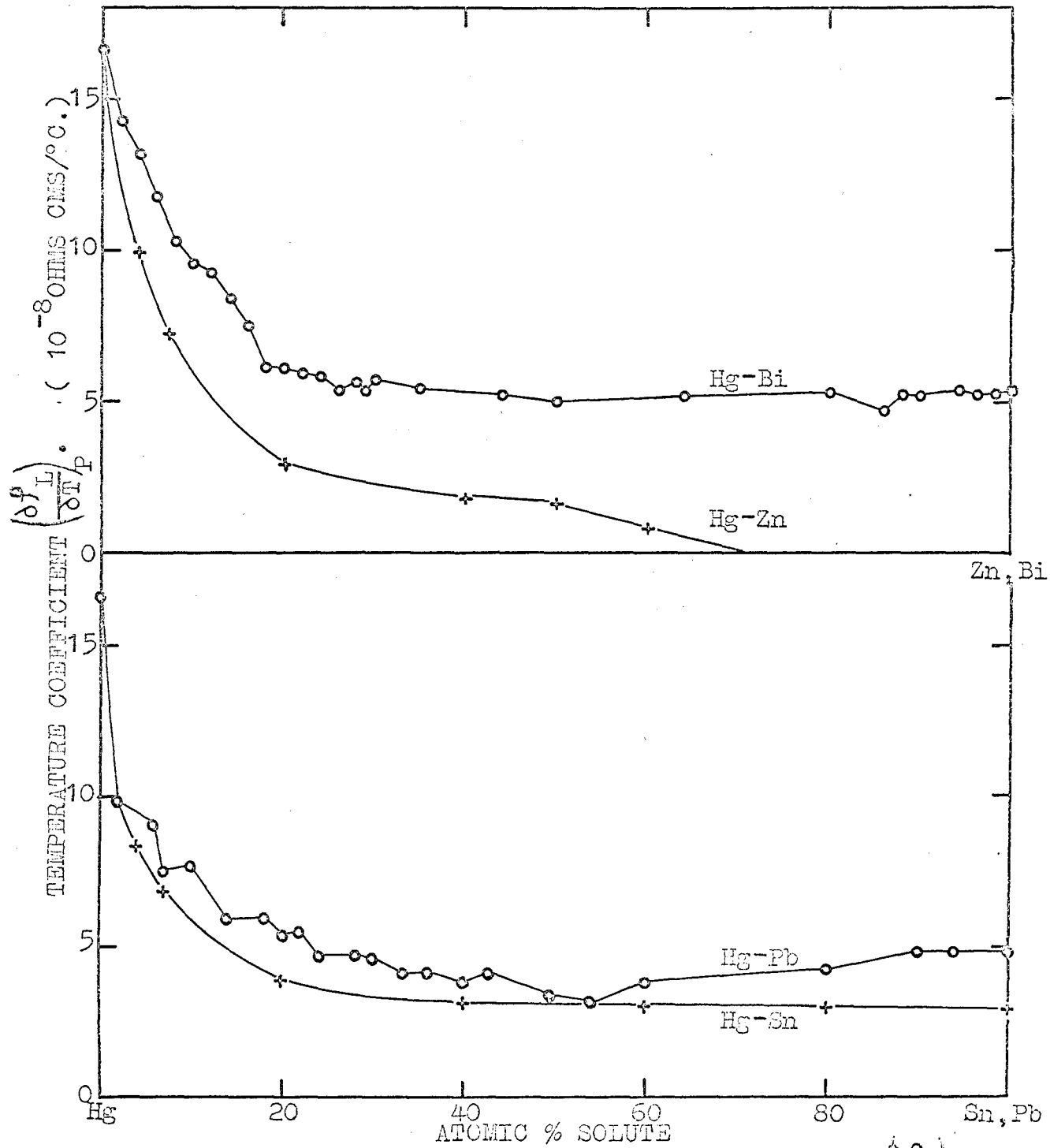


FIGURE 15. TEMPERATURE COEFFICIENT OF RESISTIVITY, $\left(\frac{\delta \rho_L}{\delta T}\right)_P$, OF SOME MERCURY ALLOYS AT 350°C

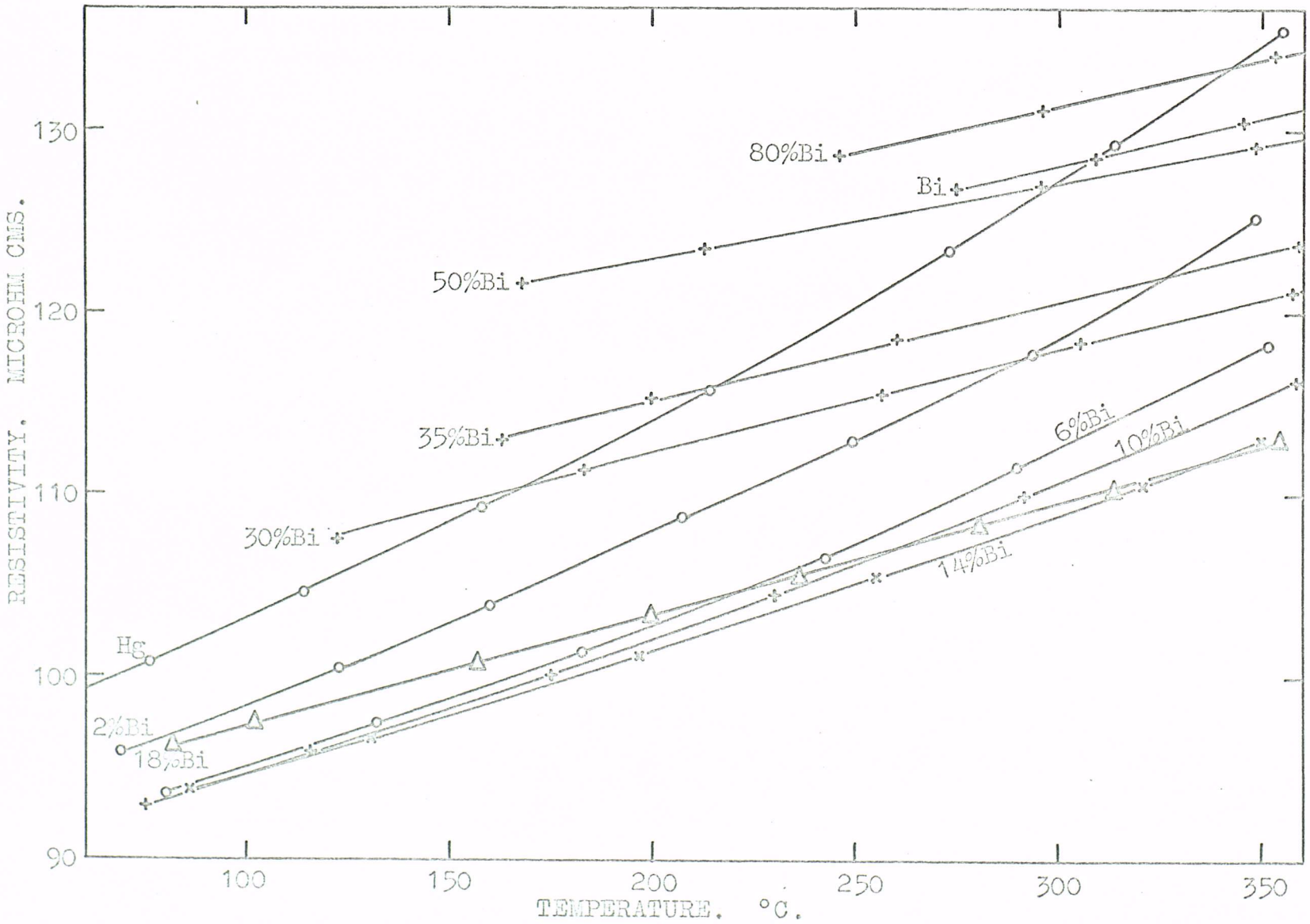


FIGURE 16. RESISTIVITY VARIATION WITH TEMPERATURE OF SOME Hg-Bi ALLOYS.

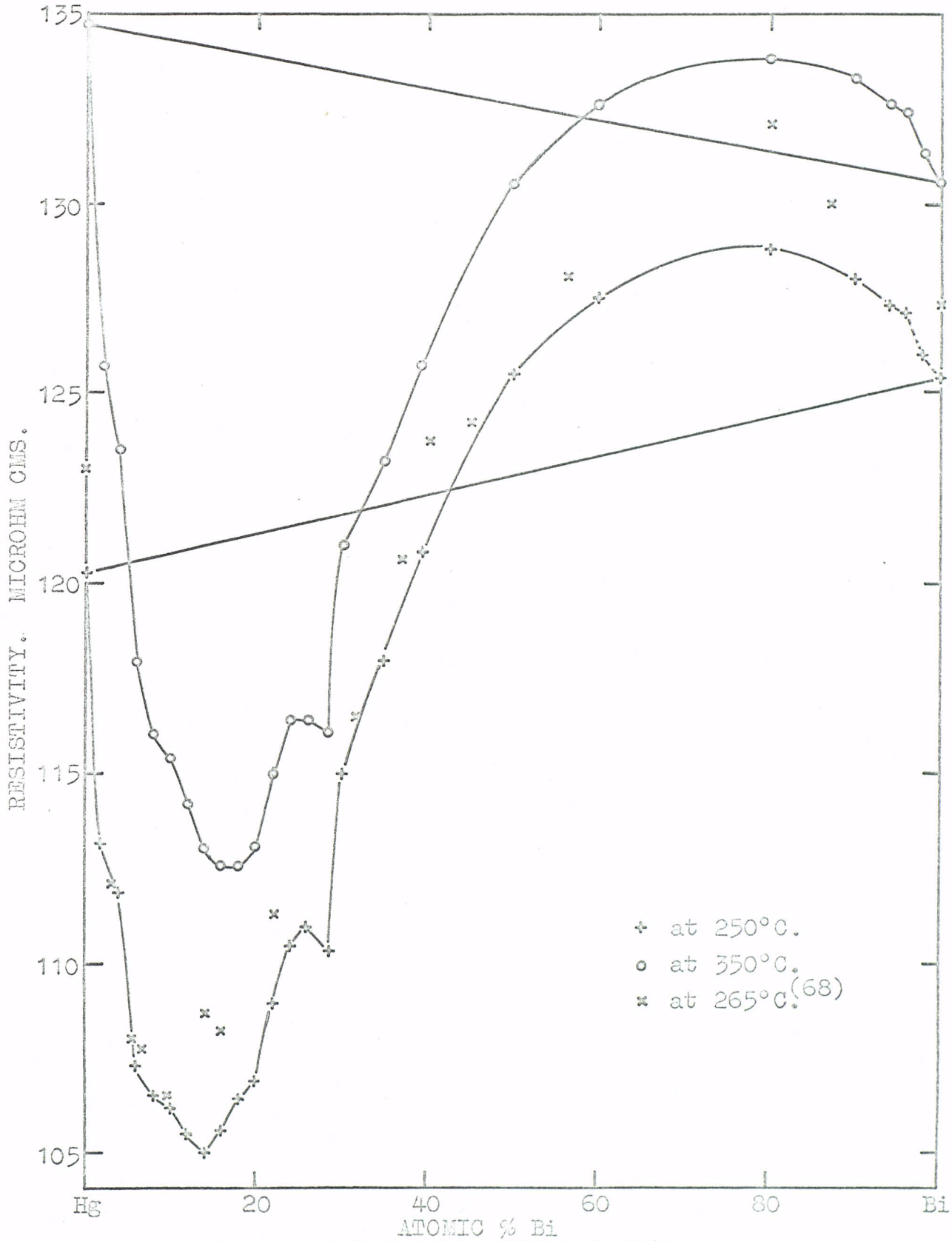


FIGURE 17. RESISTANCE-COMPOSITION ISOTHERMS OF THE SYSTEM Hg-Bi.

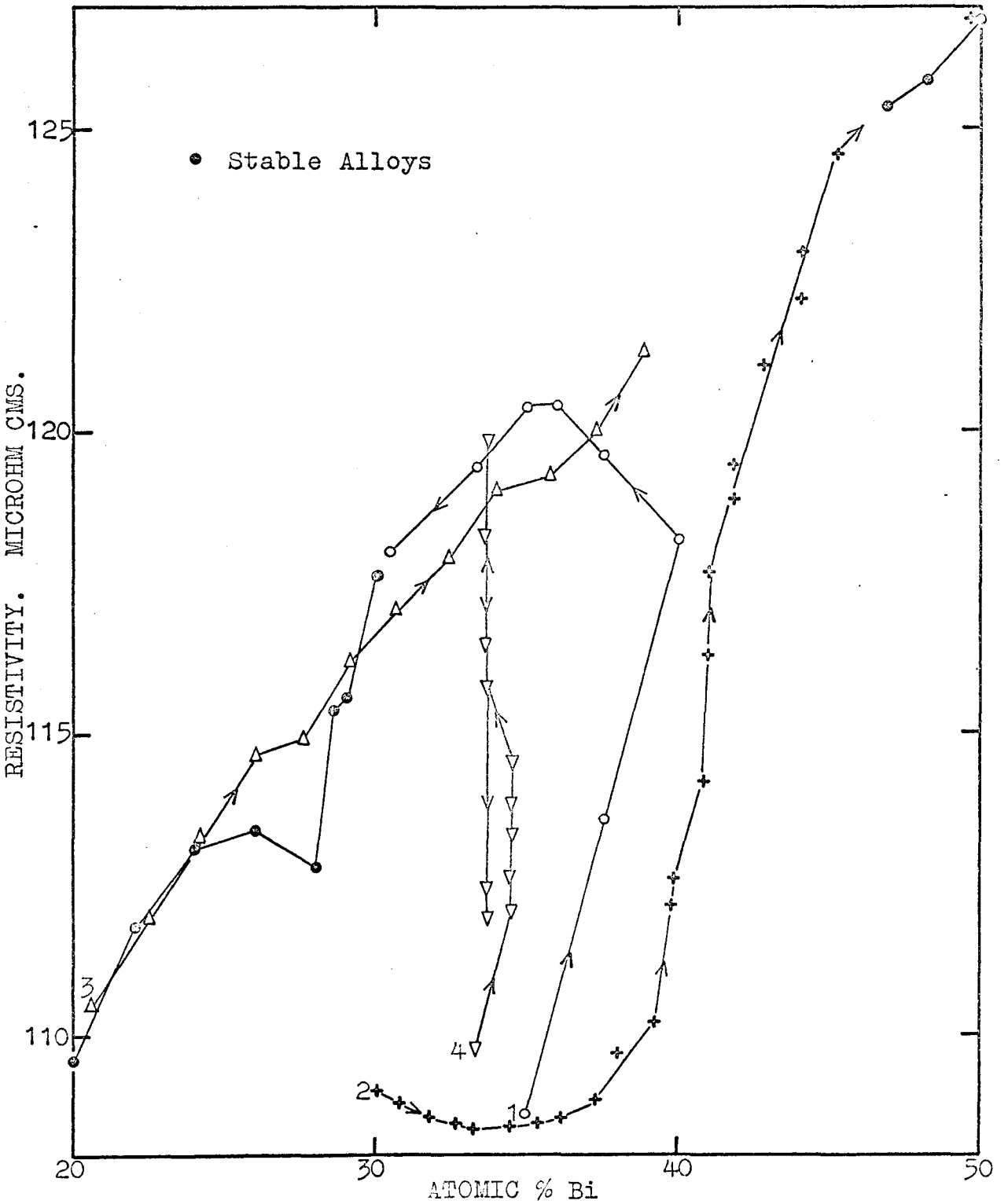


FIGURE 18. RESISTANCE-COMPOSITION ISOTHERMS OF FOUR LIQUID Hg-Bi SPECIMENS AT 295°C.

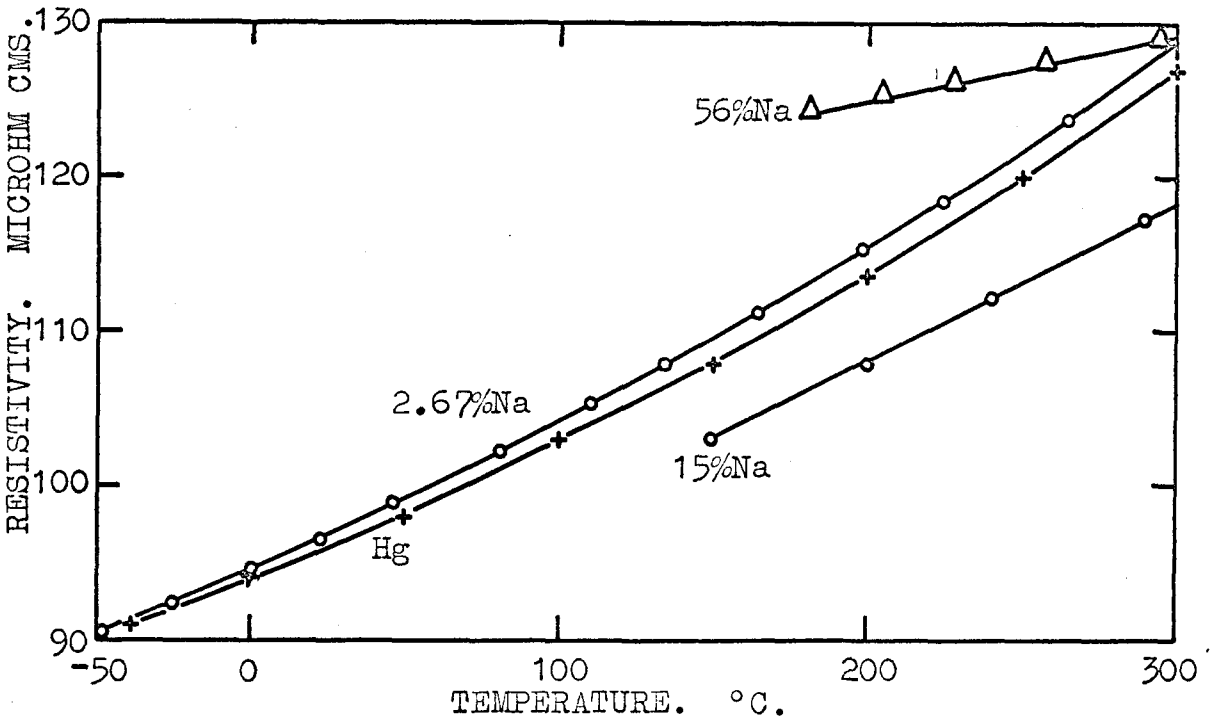


FIGURE 19. VARIATION WITH TEMPERATURE OF THE RESISTIVITY OF SOME Hg-Na ALLOYS.

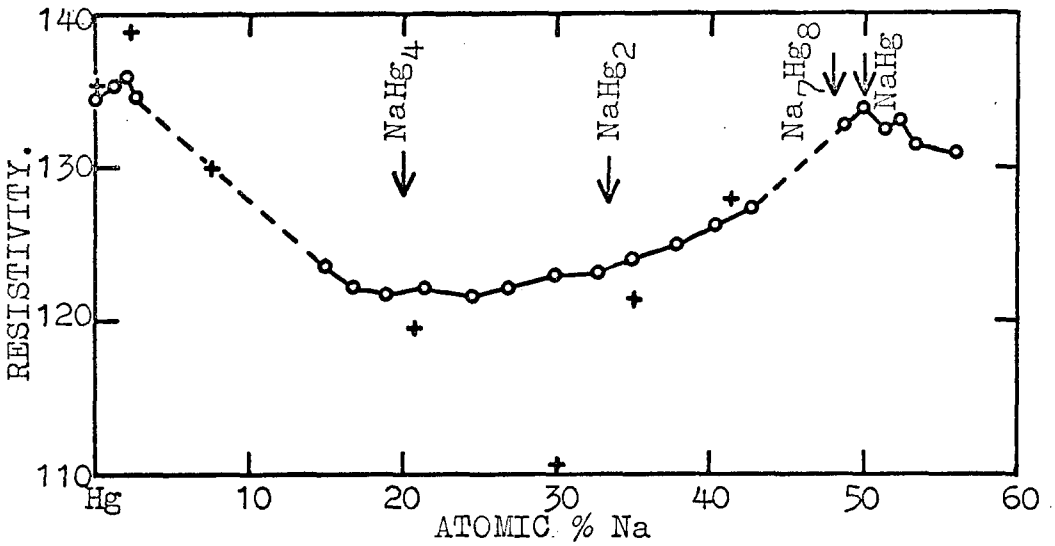


FIGURE 20. RESISTANCE-COMPOSITION ISOTHERM AT 350°C OF SOME Hg-Na ALLOYS.

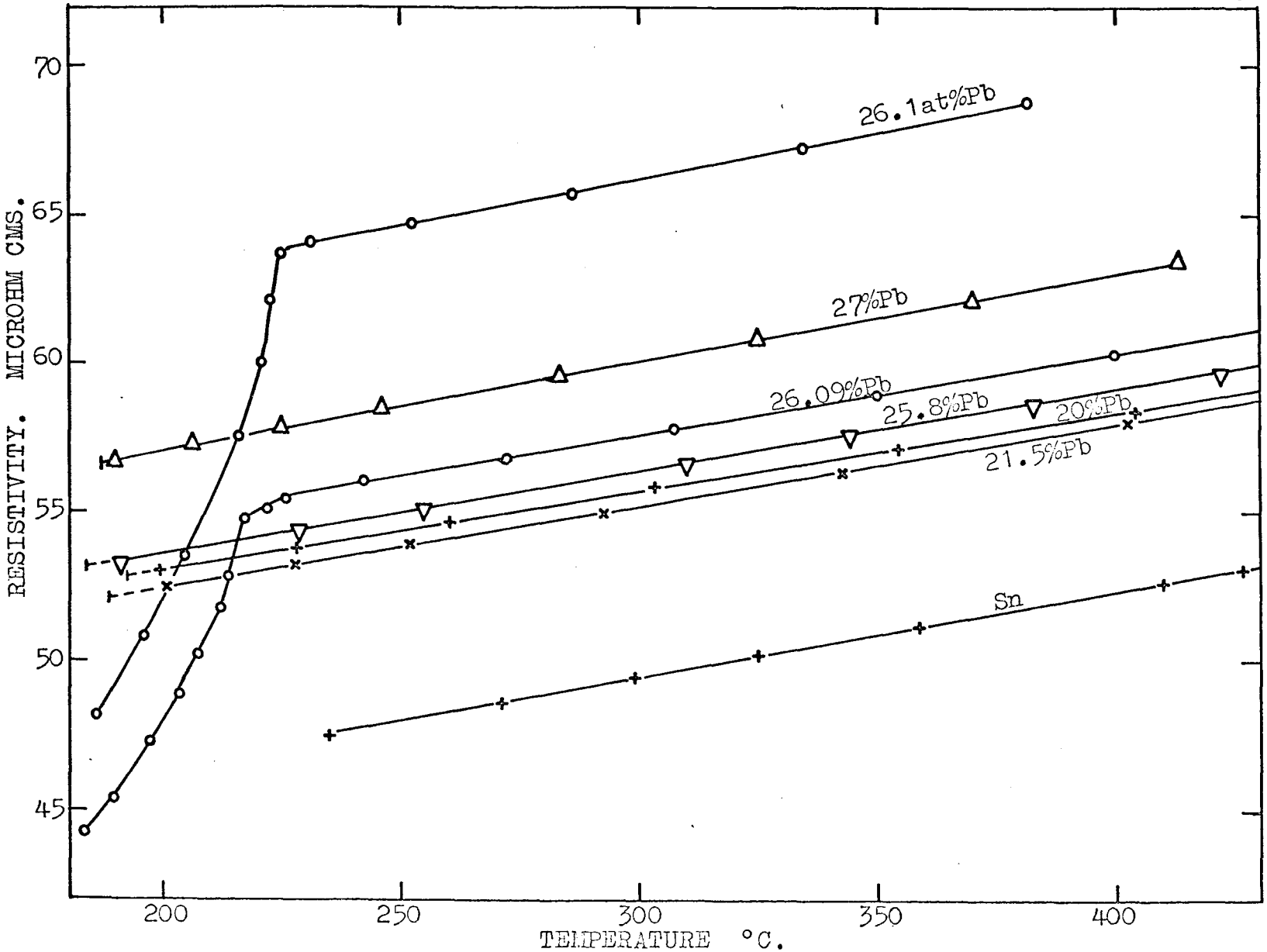


FIGURE 21. RESISTIVITY VARIATION WITH TEMPERATURE OF SOME Sn-Pb ALLOYS.

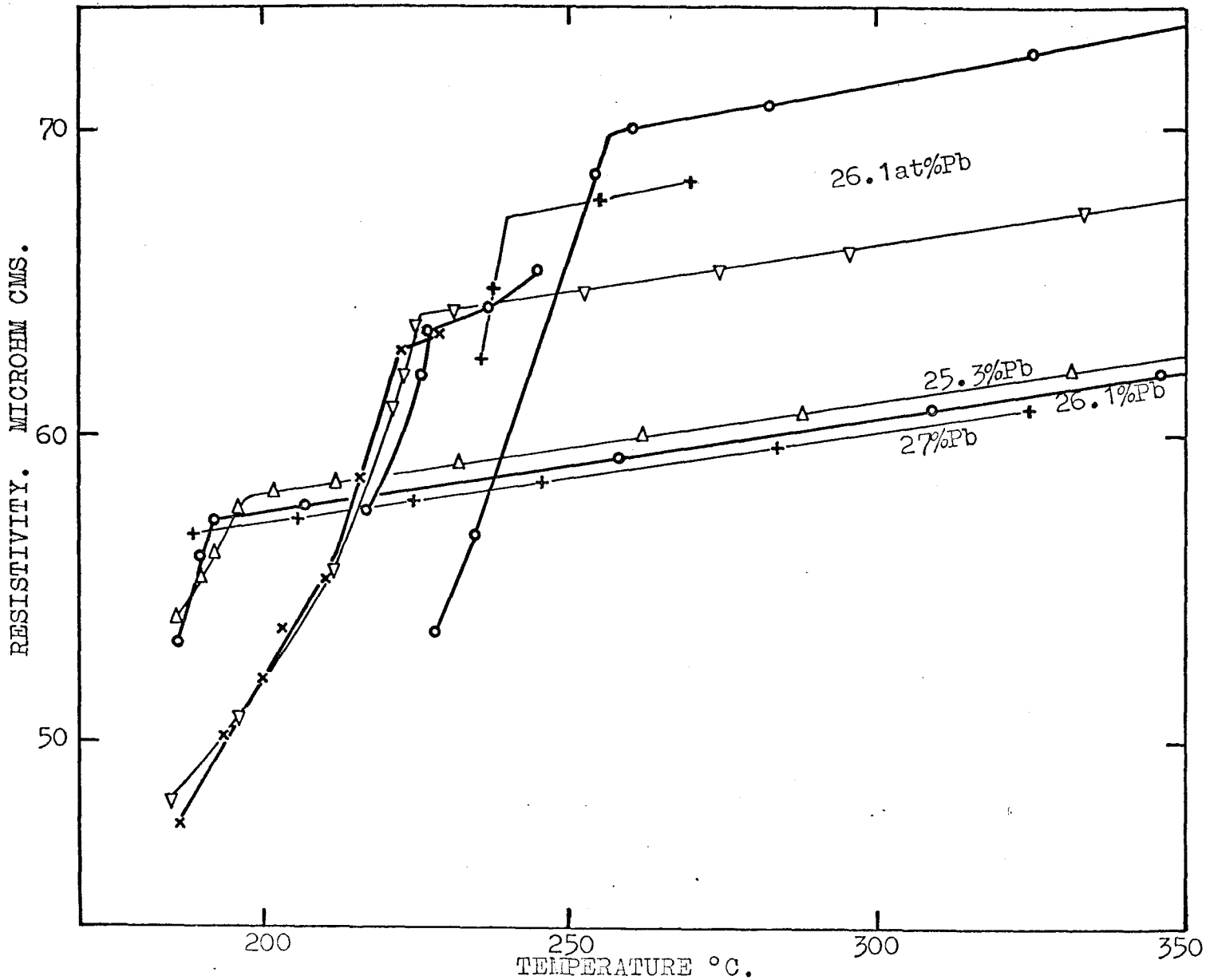


FIGURE 22. VARIATION OF RESISTIVITY WITH TEMPERATURE OF Sn-Pb ALLOYS IN THE REGION OF THE EUTECTIC Sn-26.1At%Pb.

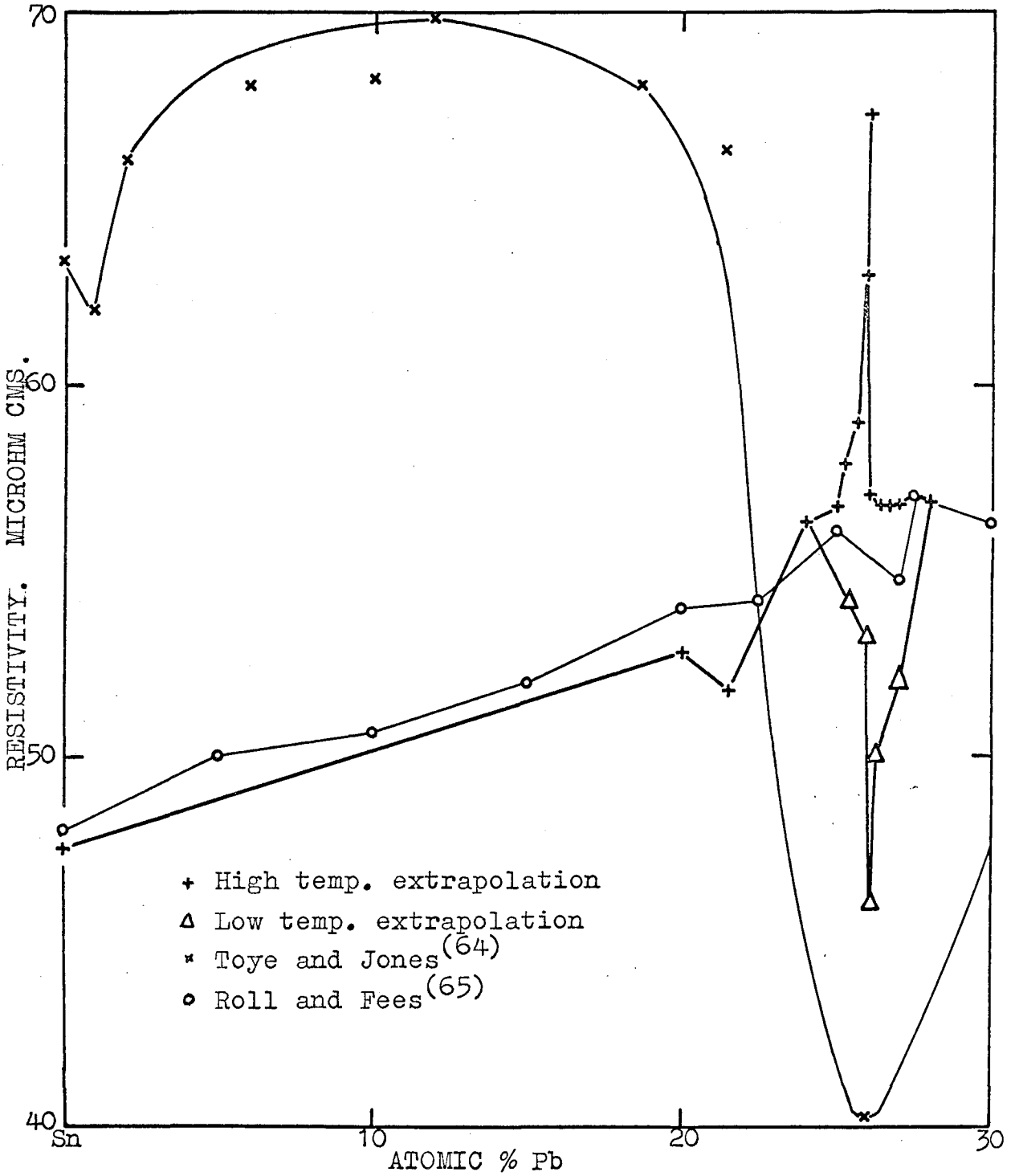


FIGURE 23. LIQUIDUS TEMPERATURE RESISTIVITIES AT COMPOSITIONS AROUND THE EUTECTIC OF THE Pb-Sn SYSTEM.

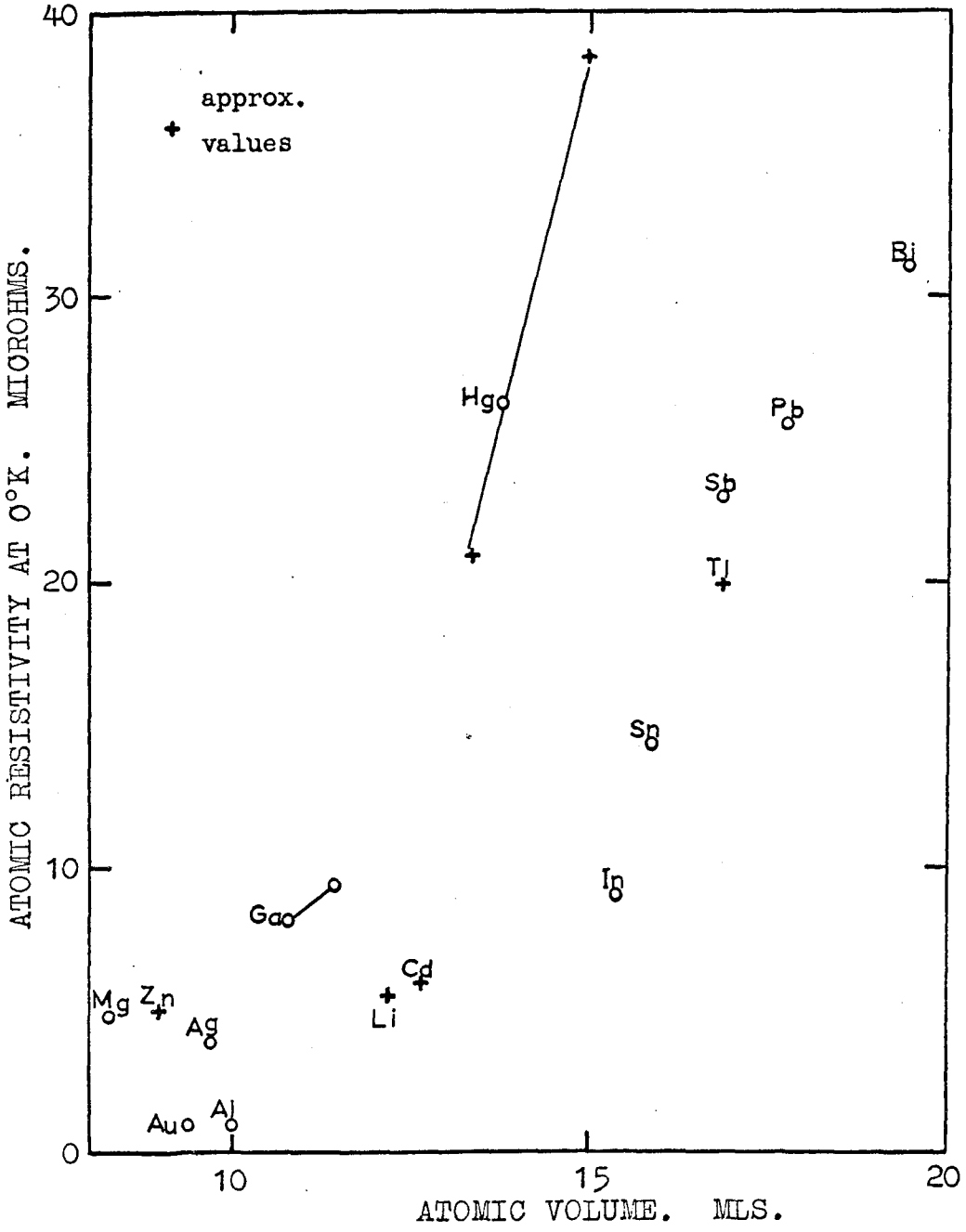


FIGURE 24. ATOMIC RESISTIVITY OF SOME METALS AS A FUNCTION OF ATOMIC VOLUME, AT 0°K.

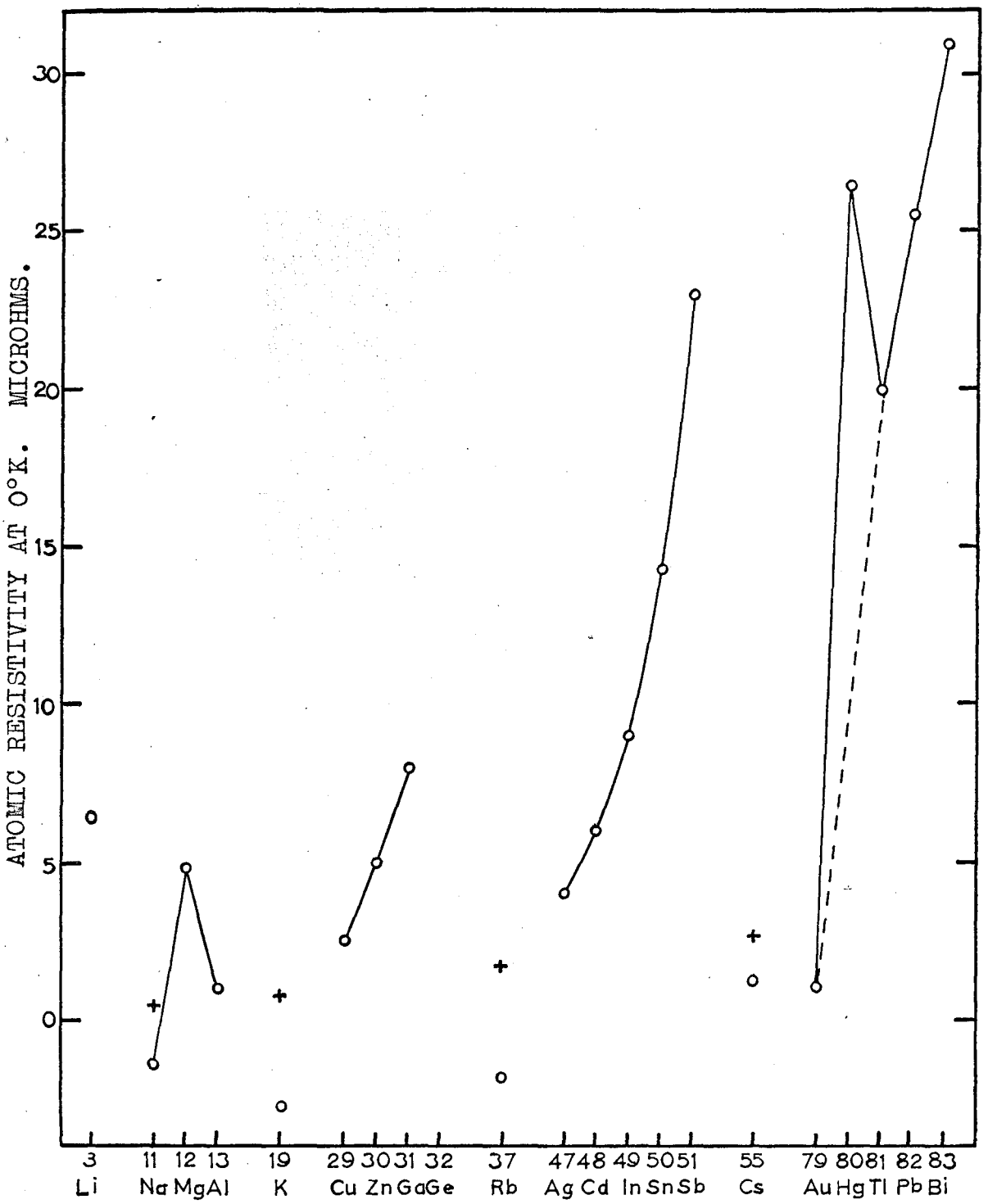


FIGURE 25. ATOMIC RESISTIVITY AT 0°K, AS A FUNCTION OF ATOMIC NUMBER.

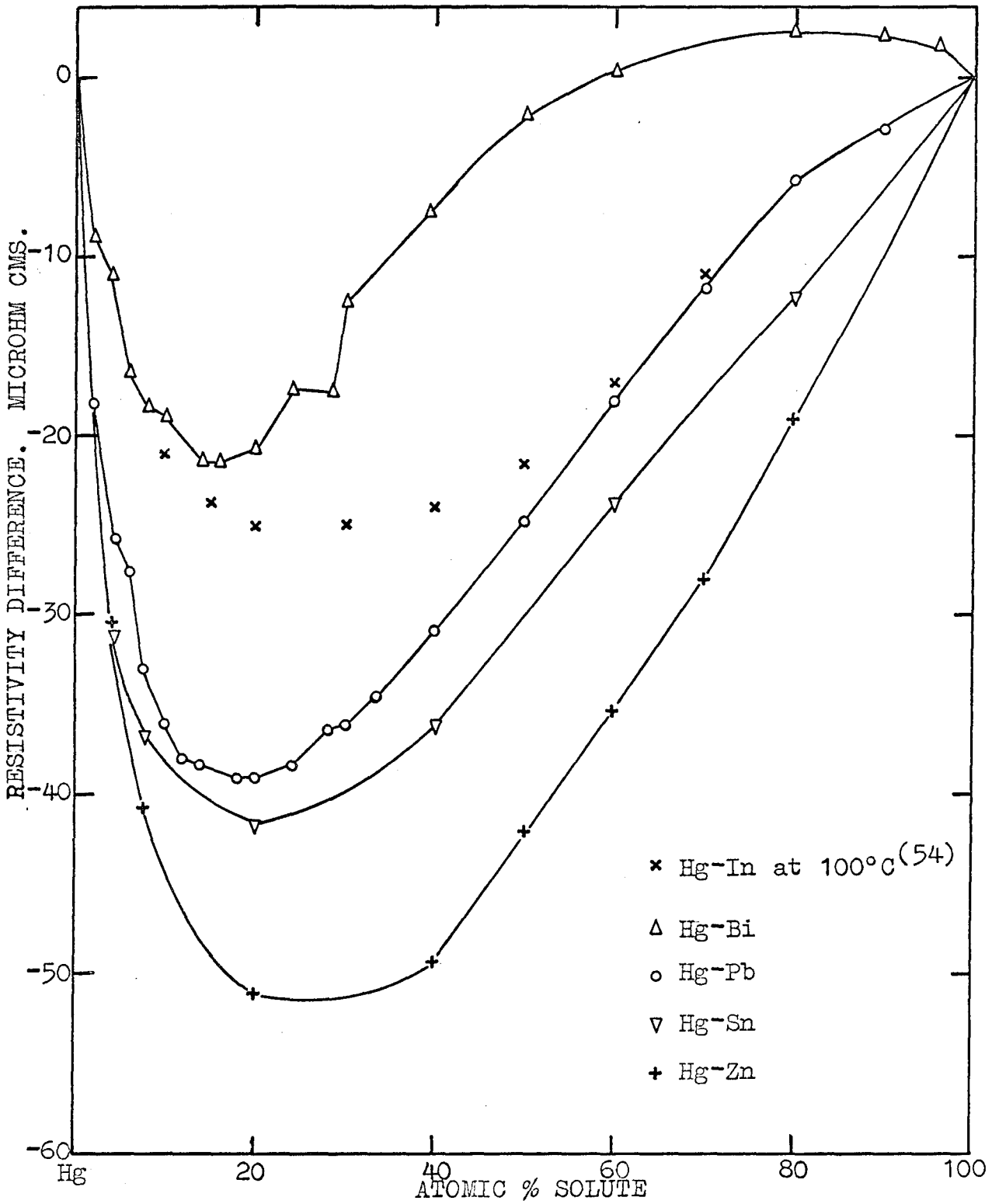


FIGURE 26. DEVIATIONS OF RESISTIVITY FROM THE WEIGHTED MEAN VALUES OF SOME Hg ALLOYS AT 350°C.

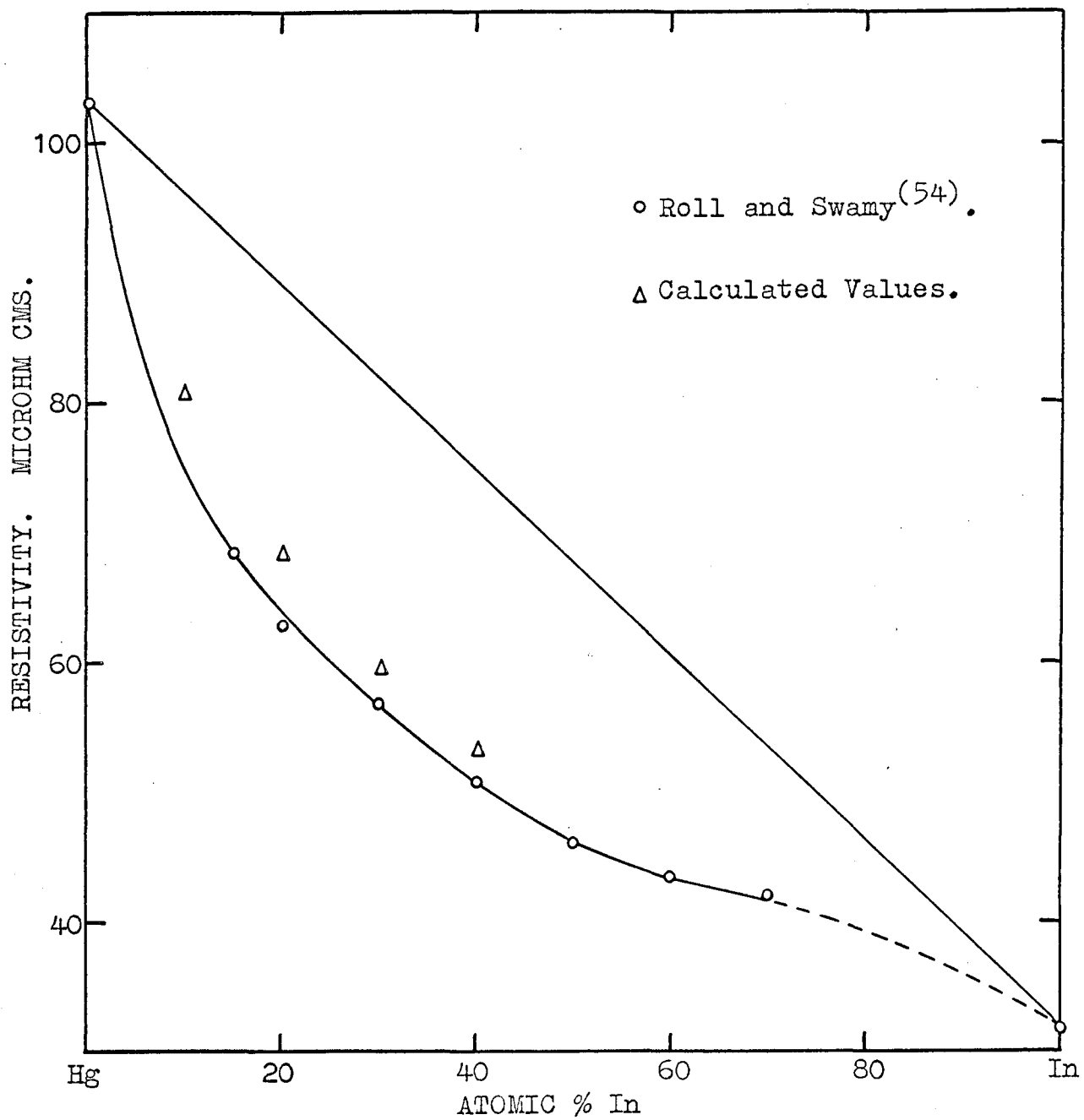


FIGURE 27. RESISTANCE-COMPOSITION ISOTHERM AT 100°C. OF THE Hg-In SYSTEM.

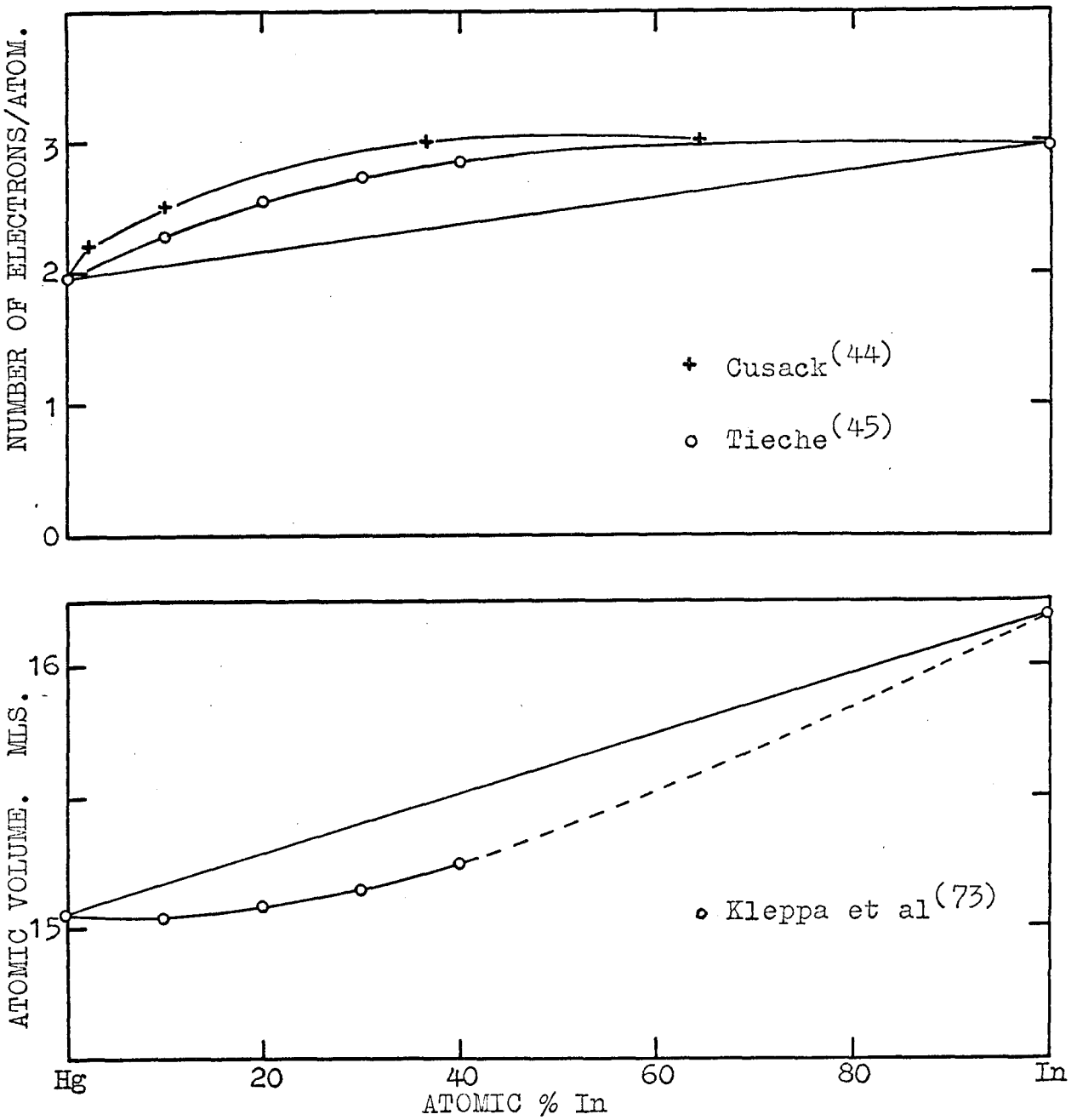


FIGURE 28. NUMBER OF FREE ELECTRONS AND ATOMIC VOLUMES IN THE SYSTEM Hg-In.

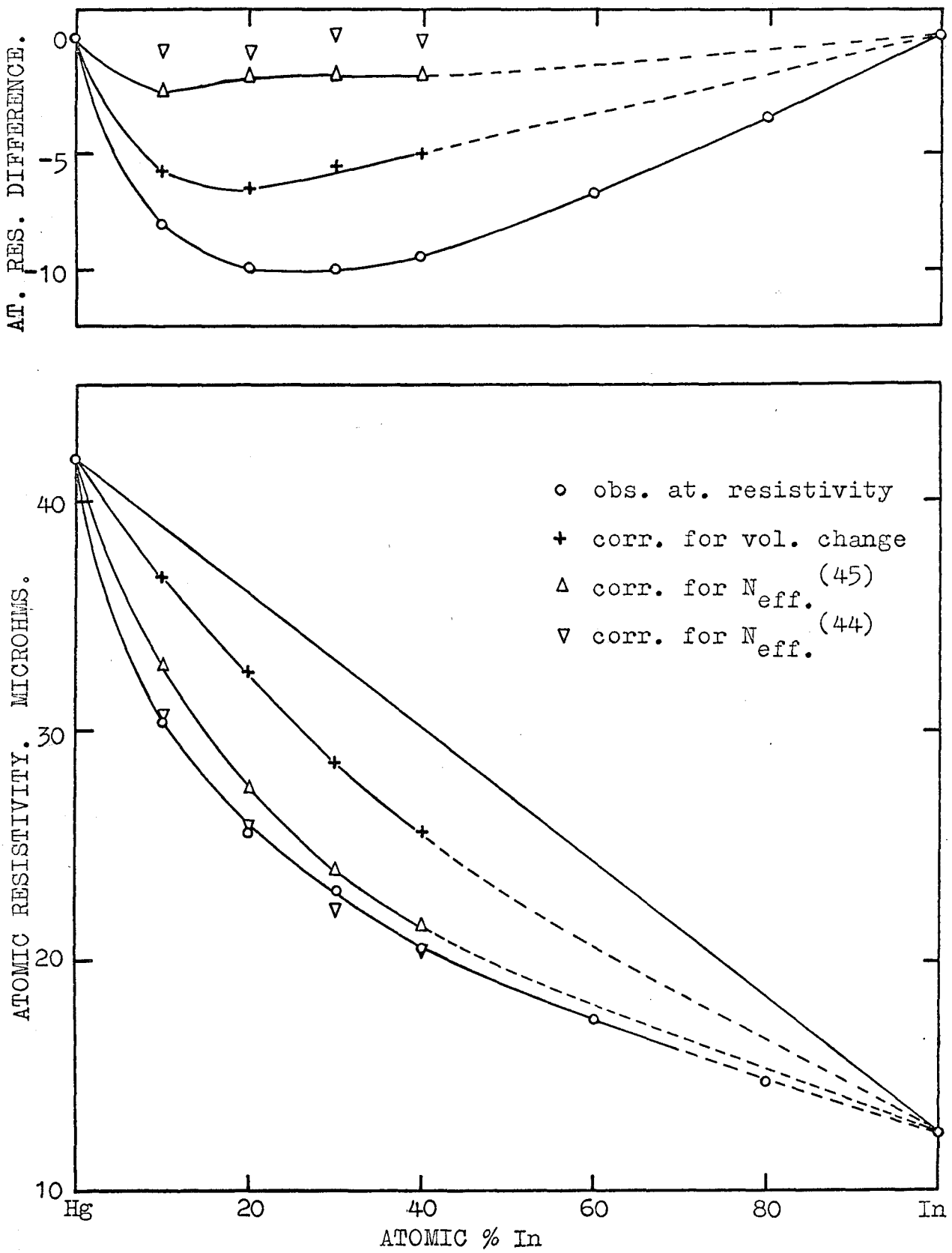


FIGURE 29. ATOMIC RESISTIVITY AND DERIVED PROPERTIES OF THE Hg-In SYSTEM.

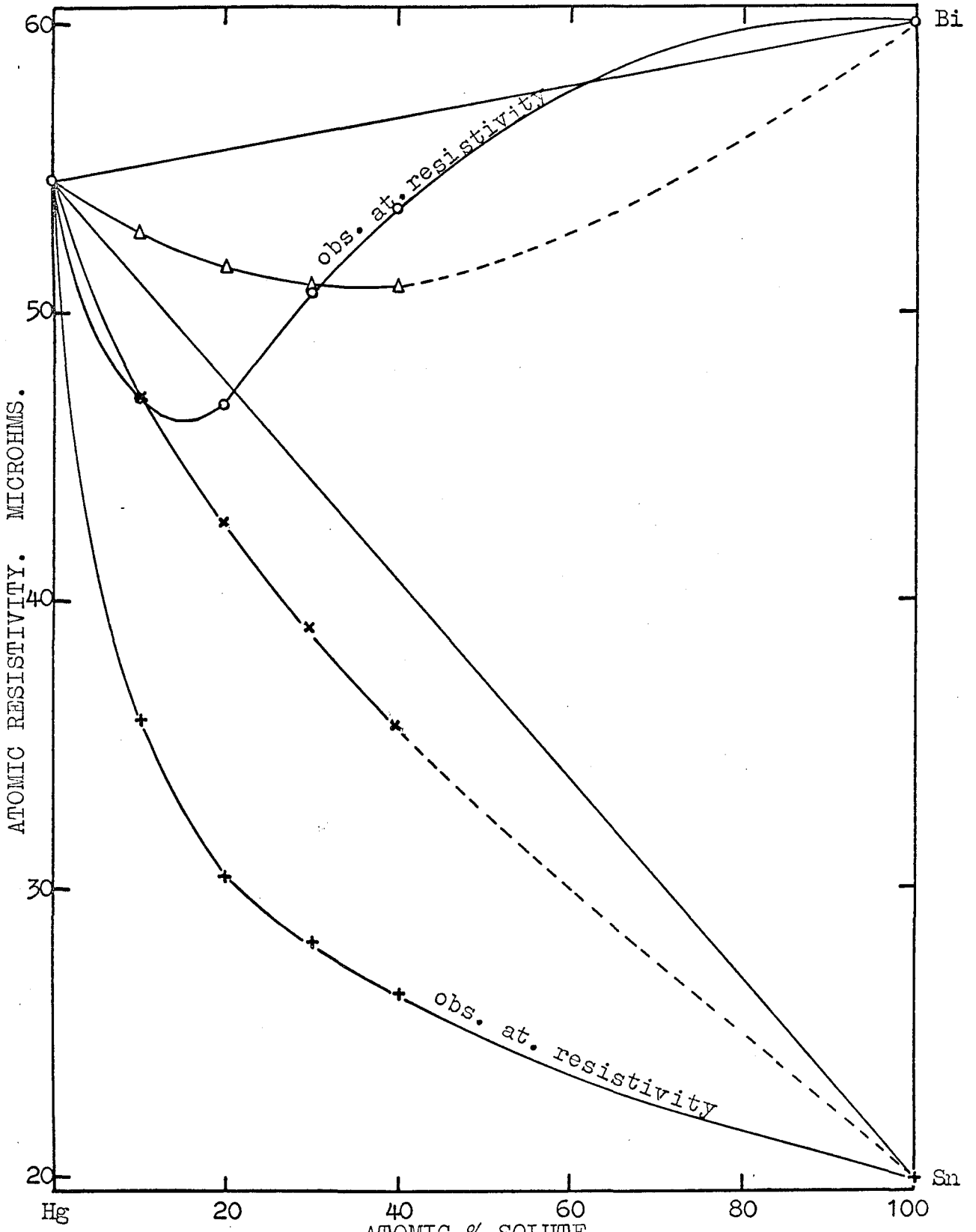


FIGURE 30. ATOMIC RESISTIVITY AND VOLUME-CORRECTED RESISTANCE OF THE SYSTEMS Hg-Bi AND Hg-Sn.

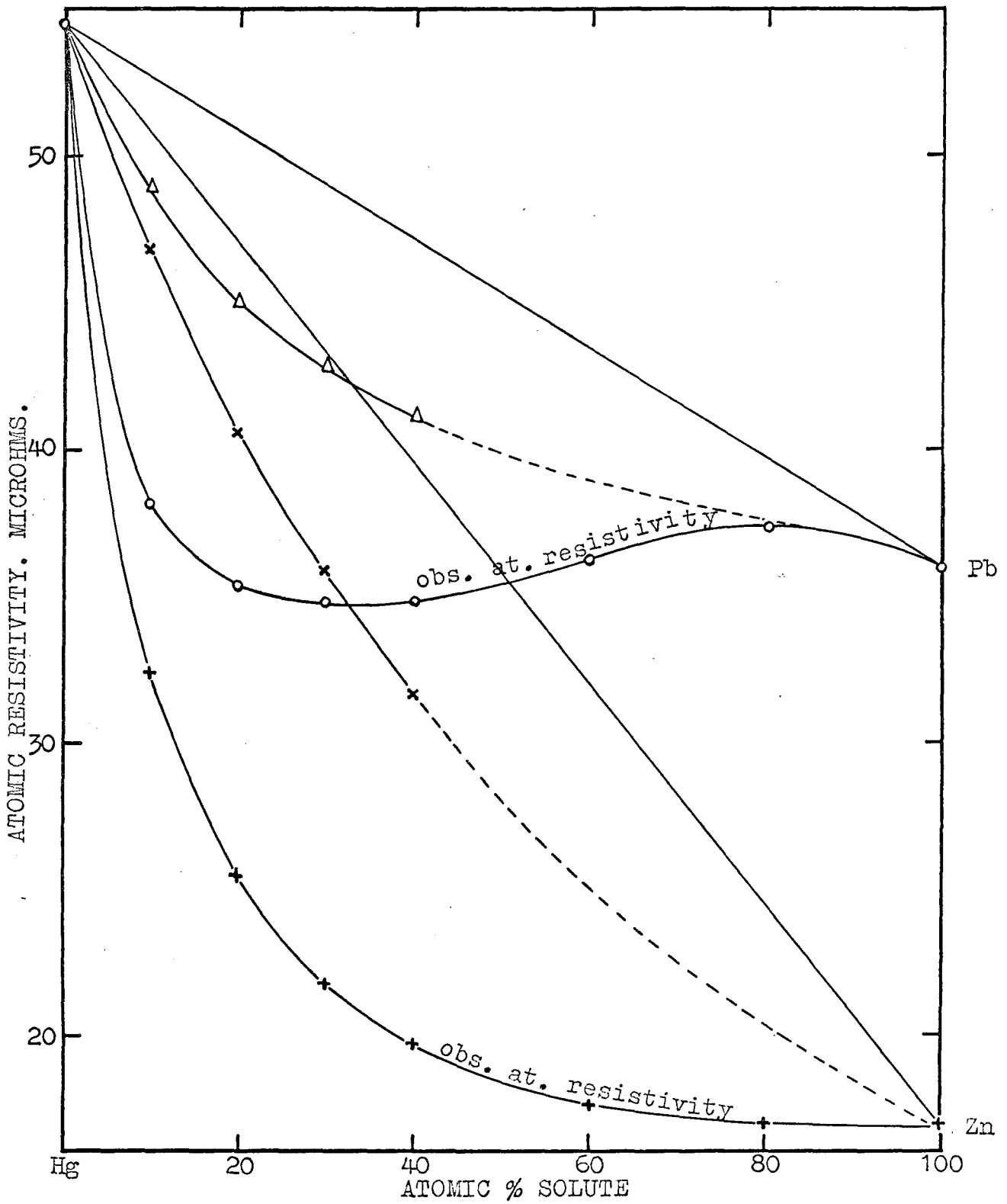
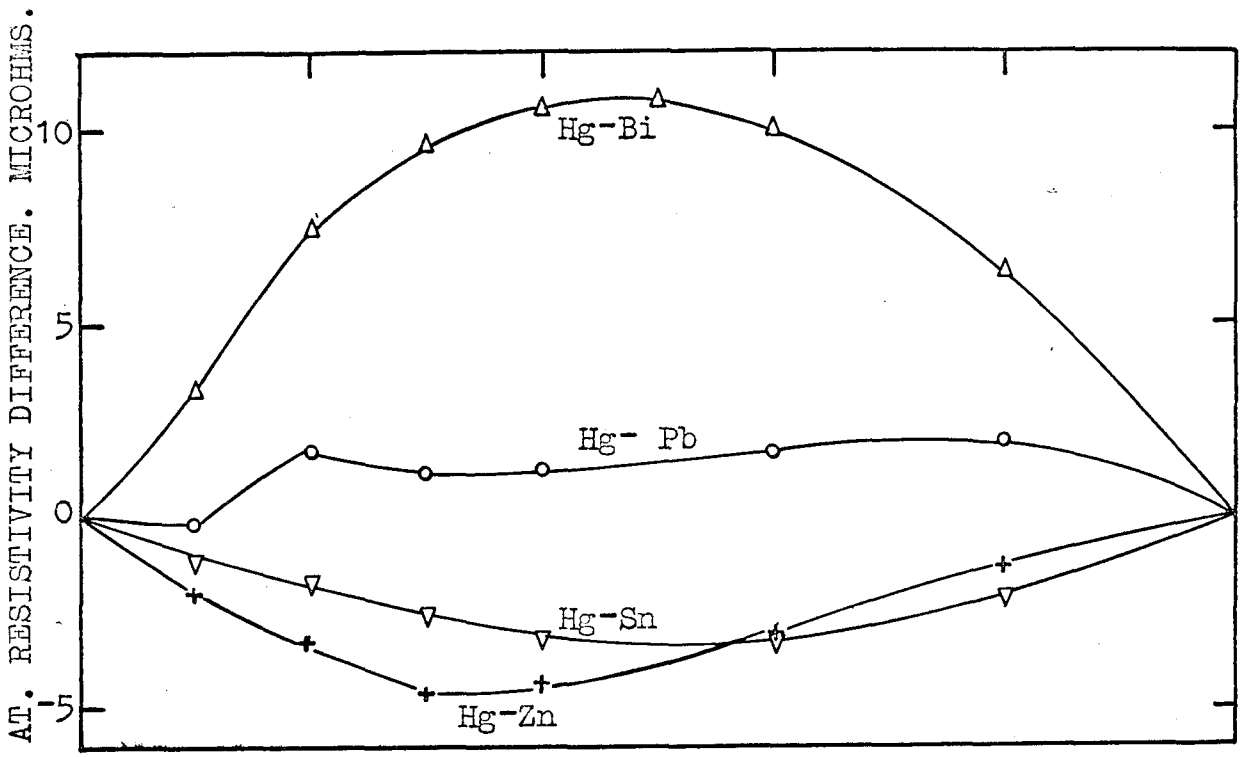


FIGURE 31. ATOMIC RESISTIVITY AND VOLUME-CORRECTED RESISTANCE OF THE SYSTEMS Hg-Pb AND Hg-Zn.



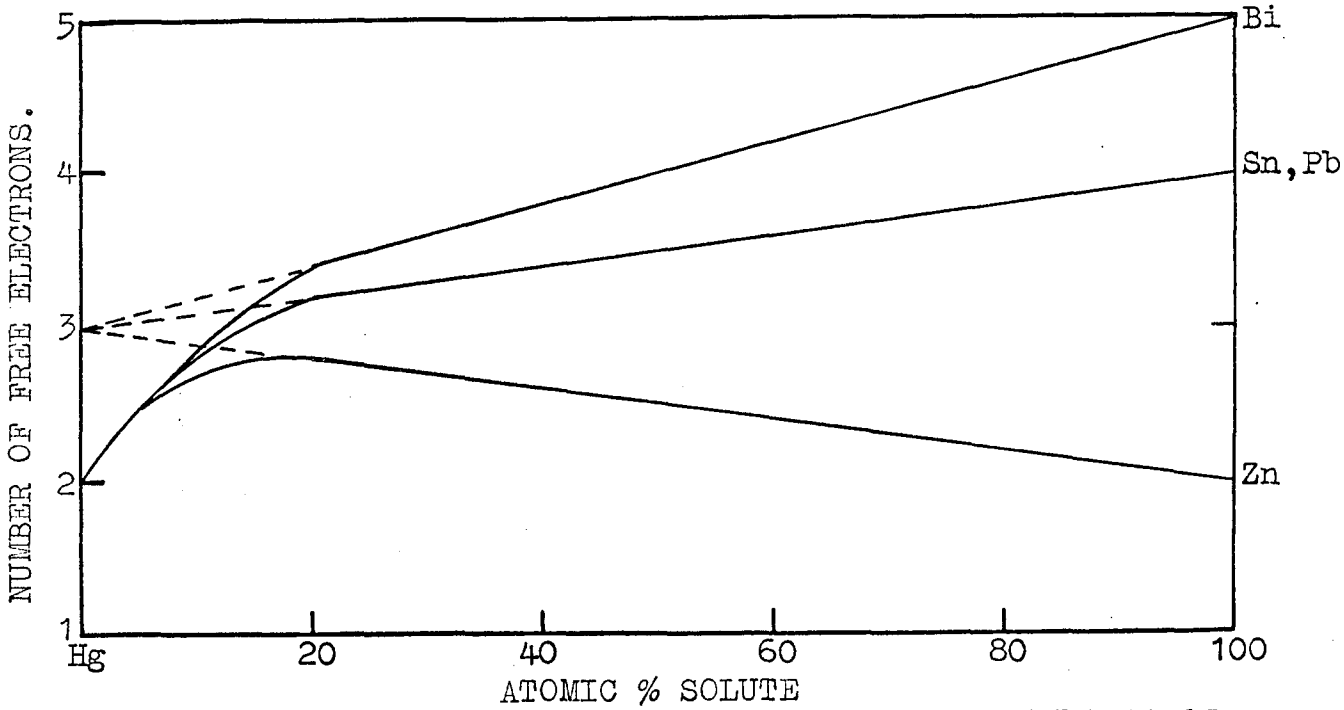


FIGURE 32. DERIVED RESISTIVITY DIFFERENCES AND NUMBERS OF FREE ELECTRONS IN SOME Hg ALLOYS.