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Technical Report

THIRD ELEMENT INTERACTIONS WITH THE LIQUID BISMUTH-ALUMINUM AND LEAD-ALUMINUM BINARY SYSTEMS

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NOMENCLATURE

a_i	Thermodynamic activity of component i
E	Pauling's electronegativity
$e_i^k(Z)$	Interaction parameter defined in equation (7)
(e/a)	Electron-to-atom ratio
f_i	The ratio of a_i to the weight per cent of component i. See equation (6).
H	Integral molar enthalpy
H_i^M	Relative partial molar enthalpy, or partial molar enthalpy of mixing of component i.
ΔH_f^T	Heat of formation at temperature T
$\Delta \bar{H}_{ik}$	Partial heat of solution of element i in element k.
M_i	Molecular weight of component i.
N^o	Avogadro's number
N_i	Mole fraction of component i
$\bar{n}$	The number of bonds per atom formed between two atoms
P_i^k	Activity coefficient factor of component i at constant mole fraction of component i; defined by equation (19)
Q_i^k	Activity coefficient factor of component i at constant activity of component i; defined by equation (18)
R	The gas constant
r_i	A parameter defined by equation (31)
$S^M_{i(Z)}$	Relative partial molar entropy or partial molar entropy of mixing of component i in solvent (Z)
T	Absolute temperature, °K
V^M	Molar volume of a solution
W_{ik}	Interchange energy of atoms i and k; similarly for W_{kZ}, W_{iZ}, etc.

Greek Symbols

γ_k	Activity coefficient of component k
δ_i	Solubility parameter of element i
$\epsilon_i^k(Z)$	Wagner's interaction parameter defined by equation (3). It represents the effect of component k on the activity coefficient of component i in solvent Z.
$\epsilon_k^k(Z)$	Wagner's self-interaction parameter representing the effect of component k on its own activity coefficient in solvent Z.
$\lambda_i^k(Z)$	Interaction parameter defined by equation (12)
$\zeta_i^k(Z)$	Interaction parameter defined by equation (11)
μ_i	Chemical potential of component i
Ω_k	Energy per atom of element k in a solution

ABSTRACT

The purpose of this study was to determine the effect of several carefully selected third elements on the activity coefficient of aluminum in liquid bismuth and liquid lead.

Initial studies were concerned with the bismuth-aluminum and lead-aluminum binary systems. The solubilities of aluminum in liquid bismuth and liquid lead were measured over the approximate temperature range 450-600°C. Studies were then made of the effects of several different elements upon these two binary solutions at 549°C. Interaction parameters were determined for each of the twelve ternary solutions studied.

The solubility of aluminum in liquid bismuth, over the temperature range 450-600°C, is given by:

$$\log_{10}(\text{wt. \% Al}) = 2.55 - \frac{2110}{T°K}$$

The solubility of aluminum in liquid lead, over the same temperature range, is given by:

$$\log_{10}(\text{wt. \% Al}) = 1.86 - \frac{2540}{T°K}$$

Designating the standard state of aluminum as the pure solid at a given temperature, the relative partial molar enthalpy of aluminum at saturation in liquid bismuth is $9.2 \frac{\text{k cal}}{\text{g atom}}$ and in liquid lead is $11.6 \frac{\text{k cal}}{\text{g atom}}$ over the temperature range 450-600°C. The elements Ca, Sr, Ba, and Sn increase the activity coefficient of aluminum in liquid bismuth, and Pd and Sb decrease it. Except for barium, these elements have just the opposite effect on the activity coefficient of aluminum in liquid lead.

The effects of the elements studied on the activity coefficient of aluminum in liquid bismuth and liquid lead can be explained reasonably well, in a qualitative manner, through the electronegativities of the elements involved, in conjunction with Wagner's electron model of a liquid alloy. The results are discussed in terms of Alcock and Richardson's equation and Wada and Saito's equation. Some of the data from this investigation, as well as additional data obtained from the literature, support the correlation between interaction parameters and the periodic table suggested previously by other investigators.

I. INTRODUCTION

The problem of solute interactions in molten alloys first gained attention from persons studying the physical chemistry of steelmaking. Studies of iron-base systems were undertaken by these investigators in order that they might gain a more thorough knowledge of the effects of certain alloying elements upon the reactions taking place in the steel bath. In many cases, extremely small concentrations of particular alloying elements were found to produce significant effects on the behavior of another solute.

In more recent years, interest in the interaction problem has arisen in other areas. One of the areas in which this problem is of the most concern is the nuclear energy field. In dealing with nuclear power reactors, one is concerned with extremely concentrated power sources which require the most efficient heat transfer fluids available to cool them. The advantages inherent in employing liquid metals for this purpose are fairly evident. Much less evident, however, are the technological problems involved. Of the various problems that do arise, those resulting from interactions of the liquid metal with its immediate surroundings are of major importance. Such interactions, if they are strong enough, can result in serious corrosion problems, and may lead further to plugging of the liquid metal circuit at various critical points. Problems of this nature have given rise to studies of the same type as those undertaken earlier by those persons concerned with iron-base systems in particular. Some of these studies are concerned with measuring the solubilities of various elements in certain liquid metal solvents. Other studies are directed toward measurements of the interaction between two dilute solute elements in a given liquid metal solvent. For example, if one has a dilute solution of element B in solvent A, what effect will the addition of a third element, C, have upon the behavior of solute B? Will its activity be increased, decreased, or unaffected? Sufficient insight into interaction phenomena such as these will perhaps sometime in the future allow one to control the corrosion process to some extent through the use of appropriate additives to the liquid metal solution. A general solution to the interaction problem would have application in many areas.

There are two methods of attacking the interaction problem: theoretically, through the use of liquid solution mechanics, and experimentally, through the use of primarily chemical arguments. By the latter method is meant the assumption of a postulate which is then tested by direct experiment and/or empirical comparison with the chemical information already available. Hopefully, such a postulate would finally yield a theory which could be used to predict new phenomena. For the time being, the advances to be made in the area of solute interactions will probably be made largely by a combination of these two methods of attack. Perhaps sometime in the more distant future, developments in liquid solution mechanics will offer a general solution to the problem.

It would be of considerable practical value, at least for engineering purposes, if one could generalize on solute interactions in liquid metal solutions. For example, perhaps one could correlate, to some extent, the effect of particular chemical elements upon a specific binary liquid metal solution with some measurable atomic property or properties of the elements involved. Consideration of this problem prompted the present investigation. The systems studied have no immediate specific interest; they were chosen for several reasons of a practical nature, in the interest of studying the general problem. It is hoped that information gathered from studies such as these can be extended and generalized upon to cover specific problems arising in engineering situations.

The purpose of this study was to determine the effect of several carefully selected third elements upon the activity coefficient of aluminum in liquid bismuth and in liquid lead. Initial studies were concerned with the liquid bismuth-aluminum and lead-aluminum binary systems. The solubility of aluminum in liquid bismuth and in liquid lead was measured over the approximate temperature range 450-600°C. Studies were then made of the effects of several different elements upon these two binary solutions at 549°C. Interaction parameters were determined for each of the twelve ternary solutions studied. The results of these studies are discussed in terms of Alcock and Richardson's equation, Wada and Saito's equation, and in terms of electron effects. These discussions are extended to include interaction parameters whose values are published in the literature. Attention is given also to the regular behavior with respect to the periodic table which is displayed by some of the parameters determined, as well as other parameters presented in the literature.

II. REVIEW OF THE LITERATURE

A. Interaction Studies

Up to the present time, the study of solute interactions in molten alloys has been directed primarily toward iron-base systems. These studies were undertaken by persons interested in the physical chemistry of steel making, trying to gain insight into the effects of alloying elements upon the reactions taking place in the steel bath. The theories proposed are, of course, relevant to non-ferrous as well as to ferrous-base systems.

1. Theoretical

One of the first, and probably one of the best, methods thus far proposed for assessing solute interactions in multicomponent systems is that proposed by Carl Wagner (40). This method makes use of the so-called interaction parameter and is restricted to systems which are dilute with respect to all solutes. This interaction parameter is the coefficient in the Taylor series expansion of the partial molar excess free energy (or logarithm of the activity coefficient) of the primary solute. The series is expanded around zero concentration of all solutes. Writing this expansion for component 1, the primary solute in a multicomponent system, we have:

$$\ell n\gamma_1\,(N_1,N_2,\,\ldots) = \ell n\gamma_1{}^{o} + \left[N_1\left(\frac{\partial \ell n\gamma_1}{\partial\, N_1}\right) + N_2\left(\frac{\partial \ell n\gamma_1}{\partial\, N_2}\right) + \,\ldots\ldots\right]$$

$$+\left[\frac{1}{2}\,N_1{}^2\left(\frac{\partial^2 \ell n\gamma_1}{\partial\, N_1{}^2}\right) + \frac{N_1N_2}{2}\left(\frac{\partial^2 \ell n\gamma_1}{\partial N_2\partial N_1}\right) + \ldots\right] + \mathcal{O}(N^3) \qquad (1)$$

where all derivatives are evaluated as the mole fractions of all solutes tend to zero. In this equation, γ_1 is the activity coefficient of component 1, and N_1, N_2, etc. are the mole fractions of components 1, 2, etc., respectively.

Like any other Taylor series, this series can be expected to approximate the function at infinite dilution more closely the more terms one takes. Likewise, this series representation can be extended further away from the infinitely dilute solution the more terms one takes. In practice, however, the series is truncated after the first order terms, and all terms of second and higher order are neglected. For a multicomponent system, the inclusion of even second order terms involves the experimental evaluation of quantities such as:

$$\frac{\partial^2 \ell n\gamma_1}{\partial N_2 \partial N_3}$$

where, once again, this quantity is evaluated as the mole fractions of all solutes tend to zero. Evaluation of these terms requires quaternary data. It is obvious how complicated higher order terms would rapidly become. Thus, as a second approximation to $\ell n\gamma_1$ of equation (1), the series is truncated after the first order terms. The degree to which the function is represented and the distance that one can move away from the infinitely dilute solution depends upon the system under consideration, i.e., upon the extent of interaction among the solvent and solute species concerned. Neglect of second order and higher terms implies that one solute has negligible influence on the effect caused by another. This assumption is valid in the "dilute" range. In fact, one may, in this case, consider this as the definition of "dilute;" i.e., when second order interactions are negligible. This range extends further out along the concentration scale for some systems than it does for others, depending upon the magnitude of the various interactions involved.

Referring back to equation (1), if second and all higher order terms are neglected, we can write:

$$\ell n\gamma_1(N_1,N_2, \ldots) = \ell n\gamma_1{}^{o} + N_1 \epsilon_1^1 + N_2 \epsilon_1^2 + \ldots\ldots \tag{2}$$

where the epsilons, Wagner's interaction parameters, are defined by:

$$\epsilon_1^k = \left[\frac{\partial \ell n\gamma_1}{\partial N_k}\right]_{\text{all } N_{\text{solute}} \to 0} \tag{3}$$

In equations (1) and (2), $\gamma_1{}^{o}$ is the limiting value of γ_1 in the solvent-1 binary. The second term in equation (2) involves ϵ_1^1, the self-interaction parameter, which represents the effect of element 1 on its own activity coefficient. This parameter can be determined by studying the dilute solvent-1 binary. Similarly, the general term ϵ_1^k of equation (3) represents the effect of element k on the activity coefficient of component 1, and requires studies on the solvent-1-k ternary for its determination. In other words, the activity coefficient of component 1 in a multicomponent system can be calculated from its value in the solvent-1 binary along with appropriate "correction factors" which can be determined from studies of the constituent ternary systems.

Wagner demonstrates a reciprocity between his interaction parameters, which says that:

$$\epsilon_1^k = \epsilon_k^1 \tag{4}$$

This expression can very easily be demonstrated by cross-differentiation of the expression for the complete differential of the Gibbs free energy of the system.

Dealy and Pehlke (9) have discussed the variation of Wagner's interaction coefficient with temperature. It can be shown that:

$$\left[\frac{\partial \epsilon_i^k}{\partial \frac{1}{T}}\right] = \frac{1}{R}\left[\frac{\partial^2 H}{\partial N_k \partial N_i}\right]_{N_i,\, N_k \to 0} \qquad (5)$$

The authors point out that when the derivative of the enthalpy with respect to the mole fractions of the two dilute solutes is not a strong function of temperature, an extrapolation of this linear relationship to temperatures lying outside the experimental range can be accomplished.

Chipman (6) has proposed a representation of Wagner's expression which involves the use of the weight percentage of a component rather than its mole fraction as the concentration variable, and which uses common logarithms rather than natural logarithms. This representation is written as:

$$\log f_1(N_1, N_2, \ldots) = \log f_1^{\circ} + (\%1)\, e_1^1 + (\%2)\, e_1^2 + \ldots \qquad (6)$$

where

$$f_1 = \frac{a_1}{(\%1)}$$

a_1 = activity of component 1,

and

$$e_1^k = \left[\frac{\partial \log f_1}{\partial (\%k)}\right]_{\%\text{ all solutes} \to 0} \qquad (7)$$

The relationship between the two interaction parameters turns out to be:

$$e_1^k = \left[\frac{M_{solvent}}{230\ M_k}\right] \epsilon_1^k \qquad (8)$$

where M represents molecular weight. The reciprocal relationship of equation (4) becomes:

$$e_1^k = \left[\frac{M_1}{M_k}\right] e_k^1 \qquad (9)$$

Ohtani and Gokcen (24) have derived an equation which they claim is not limited to the solution which is dilute with respect to all solutes. For the case of a three component system, this equation is:

$$\left[\frac{\partial \ell n \gamma_2}{\partial N_3}\right]_{\frac{N_2}{N_1}} = \frac{N_1+N_3}{N_1+N_2} \left[\frac{\partial \ell n \gamma_3}{\partial\ N_2}\right]_{\frac{N_3}{N_1}} \qquad (10)$$

where component 1 is the solvent. They define a new set of interaction parameters in the solvent 1 by:

$$\zeta_2^k = \left[\frac{\partial \ell n \gamma_2}{\partial\ N_k}\right]_{\frac{N_2}{N_1}} \qquad (11)$$

In the limiting case where N_2 and N_k tend to zero, ζ_2^k obviously reduces to Wagner's interaction parameter ϵ_2^k. Also, equation (10) reduces to equation (4).

Ohtani and Gokcen define another parameter λ_2^k as:

$$\lambda_2^k = \left[\frac{\partial \ell n \gamma_2}{\partial\ N_k}\right]_{a_2} \qquad (12)$$

which must be evaluated as the mole fractions of all solutes tend to zero, as in the case of Wagner's parameter. In a solution which is saturated with respect to component 2, the thermodynamic activity of component 2 is unity if one chooses pure 2 at that temperature as the standard state; hence:

$$\lambda_2^k = \left[\frac{\partial \ell n \gamma_2}{\partial N_k}\right]_{\substack{a_2 = 1 \\ N_{\text{solutes}} \to 0}} = - \left[\frac{\partial \ell n\ N_2}{\partial N_k}\right]_{\substack{a_2 = 1 \\ N_{\text{solutes}} \to 0}} \qquad (13)$$

To evaluate λ_2^k in this case, one needs data on the variation of the saturation content of component 2 with change in the mole fraction of component k, as the concentrations of all solutes tend to zero. Fuwa and Chipman (11) have derived a relationship between this parameter and Wagner's interaction parameter. This relationship is given by:

$$\epsilon_i^k = \lambda_i^k \left[1 + \left(\frac{\partial \ell n \gamma_i}{\partial \ell n N_i}\right)\right]_{N_k = 0} \qquad (14)$$

Therefore, if one can evaluate the quantity $\left[\frac{\partial \ell n \gamma_i}{\partial \ell n N_i}\right]_{N_k = 0}$, he can interconvert between values of λ_i^k and the corresponding values of ϵ_i^k.

Turkdogan has proposed other parameters for evaluating solute interactions (35) . He noted that Wagner's equation,

$$\gamma_2 = \gamma_2^2 \cdot \gamma_2^3 \cdot \gamma_2^4 \cdot \ldots\ldots , \qquad (15)$$

is valid only for very dilute solutions. This equation is another form of equation (2). The general term, γ_2^k, in equation (15) is defined by:

$$\gamma_2^k = \frac{\gamma_2\ (N_2 = 0,\ N_3 = 0,\ \ldots\ldots\ N_k \neq 0,\ \ldots)}{\gamma_2^o} \qquad (16)$$

It is evaluated in the limit, as N_k tends to zero. Thus, the first term on the right side of equation (15) is the value of γ in the solvent-2 binary, and the subsequent terms represent the values of γ in the ternary systems solvent-2-3, solvent-2-4, etc., evaluated at vanishingly small concentrations of component 2. As is illustrated by the results on the systems Fe-Si-C, Fe-Mn-C, and Fe-Cr-C, the general term γ_2^k may also vary with the concentration of component 2. The variation is generally not as great as with the third components themselves, but nevertheless, it does limit the use of this equation to very dilute solutions.

In the interest of overcoming the difficulties inherent in equation (15), Turkdogan introduced the parameter $(\Delta N_2^k/N_2^2)$. In this ratio, $\Delta N_2^k = N_2 - N_2^2$, where N_2 and N_2^2 are the atom fractions of component 2 in the ternary and binary solutions, respectively, at the same activity of component 2. He found the ratio $(\Delta N_2^k/N_2^2)$ to be independent of the activity of component 2 in most systems for which data were available.

From the difference $\Delta N_2^k = N_2 - N_2^2$, it follows that:

$$\frac{\Delta N_2^k}{N_2^2} + 1 = \frac{N_2}{N_2^2} = \frac{\gamma_2^2}{\gamma_2} \tag{17}$$

for constant activity of component 2. There are then two ways of representing the effect of solute k on the activity coefficient of component 2:

$$Q_2^k = \left[\frac{\gamma_2}{\gamma_2^2}\right]_{T,\ a_2} \tag{18}$$

and

$$P_2^k = \left[\frac{\gamma_2}{\gamma_2^2}\right]_{T,\ N_2} \tag{19}$$

At a given temperature, Q_2^k is a function of the concentration of component k only, but P_2^k is a function of the concentrations of both components k and 2. When Henry's Law is obeyed, then $P_2^k = Q_2^k$.

In quaternary and higher order systems, the simultaneous effects of all the solutes on the activity coefficient factor, Q_2^k , of component 2 in dilute solution is given by:

$$Q_2^k = Q_2^{k_1} \cdot Q_2^{k_2} \cdot Q_2^{k_3} \cdot \ldots \quad (20)$$

Here, k_1, k_2, k_3, etc. represent the various solutes present in the solution under consideration.

Through a chemical approach, Alcock and Richardson (1) developed a relation showing the effect of an alloying element at high dilution on the activity coefficient of sulfur at low concentrations. Beginning with the assumption that the distribution of metal atoms around each other and around sulfur atoms is random, they wrote an expression for the partial molar enthalpy of mixing of sulfur in the alloy (X+Y) containing sulfur at high dilution. By making several other simplifying assumptions, they arrived finally at the equation:

$$\left[\frac{\partial \ln\gamma_s}{\partial N_Y}\right]_{N_Y \to 0} = \epsilon_s^Y (X) = \ln\gamma_{s(Y)} - \ln\gamma_{s(X)} - \ln\gamma_{Y(X)} \quad (21)$$

where component X is the solvent, and the symbols have their usual meaning. The simplifying assumptions involved in this equation include: (1) the distribution of all atoms is random; (2) the coordination numbers of all three types of atoms are equal; (3) the energy of interaction between atom pairs is independent of concentration; (4) high dilution of Y in X; (5) $S^M_{s(X+Y)} = S^M_{s(X)}$ for low concentrations of component Y;

(6) $S^M_{s(X)} = S^M_{s(Y)}$; and (7) $S^M_{Y(X)}$ is Raoultian. The symbol $S^M_{s(X)}$ represents the partial molar entropy of mixing of solute s in solvent X, and similarly for the other partial molar entropies of mixing. The application of this equation is not restricted, of course, to ternaries in which sulfur is the primary solute.

The relationship given in equation (21) permits one to determine Wagner's interaction parameter, ϵ_s^Y (X), for the solute s in the (X-Y-s) ternary, providing the appropriate activity coefficients of the constituent binaries are available. The advantages of an expression such as this are obvious. Because of the several restrictions imposed in the derivation of equation (21), however, one would suspect that its quantitative accuracy may not be very great. This is pointed out by the authors, and they go to considerable length in evaluating the shortcomings of the equation.

In a second paper (2), Alcock and Richardson consider the same problem and attack it in the same manner, except that they take clustering about the primary solute atoms into account. One difficulty involved in their resulting expression is that its use requires a knowledge of the coordination number of the primary solute. This number, in general, is not known. Although the result appears to be a little better than equation (21), it still yields only qualitative results.

The interaction between positively charged metal ions may, under certain conditions, be relatively unimportant compared to the interactions between free electrons and metal ions. Wagner (39) points out that in many thermodynamic investigations the electronic constitution of alloys is disregarded for the following reasons. In the first place, it is not possible to measure thermodynamic properties of electrically charged particles such as ions and electrons. Secondly, in the limiting case of dilute solutions, the activity of a solute metal is proportional to its concentration regardless of ionization, since the electron concentration is essentially constant due to its relatively high value in the solvent. Finally, it is known that many binary liquid alloys show relatively small deviations from ideality, although according to conventional assumptions, the concentration of valence electrons varies considerably with composition. Nevertheless, it is worthwhile to examine to what extent the thermodynamic functions of an alloy are related to its electronic constitution.

Himmler (17) proposed the following theory to explain the fact that zinc decreases the solubility of hydrogen in copper. He formulates the stoichiometric equation for the dissolution of hydrogen in copper as:

$$\frac{1}{2} H_2 \text{ (gas)} = H^+ + e^- \qquad (22)$$

where H^+ represents a proton and e^- an electron, and the condition of thermodynamic equilibrium as:

$$\frac{1}{2} \mu_{H_2} = \mu_{H^+} + \mu_e \qquad (23)$$

Here, μ_{H_2} is the chemical potential of gaseous molecular hydrogen, μ_{H^+} is the chemical potential of protons dissolved in copper, and μ_e is the chemical potential of the electrons. The following equation results for a dilute solution of hydrogen in copper:

$$C = \exp \left\{ \left[\frac{1}{2} \mu_{H_2} - \mu^o_{H^+} - \mu_e \right] \Big/ RT \right\} \qquad (24)$$

where C is the hydrogen solubility and $\mu^o_{H^+}$ is the chemical potential of protons at unit concentration.

Wagner goes on to say that metallic copper contains essentially one valence electron per atom (39). When copper is alloyed with other elements, such as zinc, having higher valences, the valence electron-to-atom ratio increases. Thus, μ_e increases. For a given value of μ_{H_2} (resulting from a given pressure of H_2), equation (24) indicates that the hydrogen solubility is decreased by elements which increase μ_e, assuming that $\mu^o_{H^+}$ is of minor importance. Generally speaking, however, an increase in μ_e will be attended by a decrease in $\mu^o_{H^+}$. Therefore, it cannot necessarily be said that an increase in μ_e results in a decrease in hydrogen solubility. On the other hand, if a considerable decrease in hydrogen solubility is noted, this may be attributed to an increase in μ_e which is only partly compensated for by a decrease in $\mu^o_{H^+}$.

In the light of Himmler's development outlined above, Wagner interprets: the change in hydrogen solubility in copper by various elements; the change in zinc activity dissolved in copper brought about by aluminum and nickel; and the change in activity of the alkali metals dissolved in mercury brought about by thallium. He concludes that the activity of solute metal 2 dissolved in solvent 1 will be increased by a third component if elements 2 and 3 change the electron/atom ratio in the same direction, and conversely.

Wagner goes on to show that if we have only positively charged metal ions present in a solution, and assume that direct interaction between metal ions can be disregarded, then:

$$\epsilon_2^3 = \epsilon_3^2 = \pm \left[\epsilon_2^2 \cdot \epsilon_3^3\right]^{1/2} \tag{25}$$

Whether the sign is positive or negative must be deduced from qualitative considerations. Also, equation (25) is significant only if the deviations of systems (1-2) and (1-3) from ideal behavior have the same sign, because otherwise the square root of the product is imaginary. Wagner proves, however, that for a given solvent these deviations do always have the same sign provided direct interaction between metal ions can be disregarded.

Since direct interaction between metal ions is, in general, not zero, the change in chemical potential of the electrons can be expected to predominate only if deviations from ideality are large. Therefore, the use of equation (25) should be limited to systems where ϵ_2^2 and ϵ_3^3 are considerably greater than unity. Deviations from this principle are indicated if equation (25) is indeed found to be invalid. This demonstrates the limitations of equation (25) and of the assumptions involved in its derivation.

Quite recently, Wada and Saito (37) have published a paper concerning the calculation of Wagner's interaction parameter by a statistical thermodynamic method. Expressions for the interaction parameters of alloying elements in dilute ternary metallic solutions were calculated by the zeroth approximation of Guggenheim's quasi-chemical method. Since it is known that the coordination number in liquid metallic solutions is in the range of 10 to 12, and their structures are nearly closed packing, the face-centered cubic lattice was used as the model for the derivations. First, a ternary system in which both solutes are distributed substitutionally in the quasi-crystalline lattice was considered. This model yielded the following expression for Wagner's interaction parameter:

$$\epsilon_i^k(Z) = \frac{1}{RT}(W_{ik} - W_{kZ} - W_{iZ}) \qquad (26)$$

where W_{ik} represents the i-k interchange energy, and W_{kZ} and W_{iZ} the corresponding energies. Equation (26) is actually the same as Alcock and Richardson's equation, under certain conditions. This is discussed later in the thesis. The authors also derive the corresponding expression for ϵ_k^i (Z) and illustrate Wagner's reciprocity relationship. The authors compare equation (26) and the corresponding equation for ϵ_k^i (Z) with Alcock and Richardson's equation, equation (21). They point out that

Alcock and Richardson's equation becomes identical to these two equations as N_Y and N_s tend to zero, providing that the s-Y, s-X, and Y-X binaries are regular solutions.

Wada and Saito considered a second ternary solution in which solute k is distributed substitutionally, and solute i is distributed interstitially. This model yielded the equation:

$$\epsilon_i^k \, (Z) = \frac{1}{RT} \, (W_{ik} - W_{iZ}) \tag{27}$$

Derivation of the corresponding equation for ϵ_k^i (Z) demonstrated Wagner's reciprocity relationship once again.

The authors next derived an expression for the interchange energies which appear in the above equations. Based on Mott's equation for the excess free energy of a binary metallic solution, they derive the following equation for W_{ik}:

$$W_{ik} = V^M (\delta_i - \delta_k)^2 - 23060 \, \bar{n} \, (E_i - E_k)^2 \tag{28}$$

In this equation V^M is the molar volume of the solution, δ_i and δ_k are solubility parameters, $\bar{n}$ is the number of i-k bonds, and E_i and E_k are electronegativities. Similar equations for W_{iZ} and W_{kZ} can be obtained. Thus, by means of equations (26), (27), (28), and similar equations for W_{iZ} and W_{kZ}, one can calculate theoretical values of ϵ_i^k (Z) for either substitutional-substitutional alloys, or substitutional-interstitial alloys, providing the appropriate values for molar volumes, solubility parameters, electronegativities, and $\bar{n}$ are available.

Wada and Saito calculated theoretical values of the interaction parameters for Fe-Cr-X, Fe-Ni-X, Fe-C-X, and Fe-S-X systems by the above methods and compared them with the experimental values. They assumed the appropriate value of $\bar{n}$ in each case to the smaller of the valences of the two components involved. The agreement between observed and calculated values for the systems considered was fair, in general. In order to discuss the Fe-Cr-X and Fe-Ni-X systems in detail, more experimental data are required. In the cases of the Fe-C-X systems, the agreement was quite good, illustrating periodic changes of the parameter with the atomic number of the third component. For the Fe-S-X systems, calculations were made using both the substitutional-substitutional model and the substitutional-interstitial model. From the comparison of these results, it could not be concluded which model is the more suitable.

In a second paper, Wada and Saito derive theoretical expressions for the self-interaction parameter in binary alloys. They use the same statistical thermodynamic approach employed in their first paper, once again assuming the face-centered cubic crystal and the zeroth approximation of the quasi-chemical model. For a substitutional binary alloy, they derive the expression:

$$\epsilon_k^k\,(Z) = -\frac{2}{RT}\,W_{kZ} \tag{29}$$

and for an interstitial alloy, the expression :

$$\epsilon_k^k\,(Z) = 2 - \frac{2}{RT}\,N^o\,\Omega_k \tag{30}$$

The interchange energy, W_{kZ}, is given by the same equation as in the case of a ternary alloy (see equation (28)). In equation (30), N^o represents Avogadro's number, and Ω_k represents the energy per atom of element k.

Wada and Saito compare several theoretical values of the self-interaction parameter calculated from equation (29) with the experimental values. Once again, in calculating the theoretical values, $\bar{n}$ was taken to be the smaller of the valences of the two elements involved. In the cases of the Fe-Cr and Fe-Ni binaries, the agreement was considered to be quite good; in the Fe-Al, Fe-P, and Fe-S systems, the agreement was only fair. The theoretical values of the self-interaction parameters for the two systems Fe-Si and Fe-Cu, however, showed considerable disagreement with the experimental values. The authors conclude that although these two disagreements may be due partly to uncertainties in the values of the electronegativities and solubility parameters used, the deviation of these two systems from regular solution behavior may be the primary cause of the disagreements. No theoretical values of ϵ_k^k are calculated from equation (30), because of the fact that values of the parameter Ω_k are unknown.

2. Experimental

There has been relatively little experimental work carried out on solute interactions in molten alloys. It is the purpose of this section to summarize some of the most important work which has been done, and to point out some of the conclusions which have been drawn from this work by various investigators.

In 1956, Turkdogan published a paper regarding the solubility of graphite in Fe-Mn, Fe-Co, and Fe-Ni melts (36) . He determined graphite solubilities over the entire composition ranges, finding that manganese increases graphite solubility, while cobalt and nickel decrease it. He then found that the initial change in graphite solubility, upon adding one of these third components, is related to the atomic number of the third component. This relationship is illustrated in Figure 1, curve (6), where r_c is plotted against the atomic number of the third component. From previous work he had done, combined with work done by others, Turkdogan was able to define another curve which is shown on the same plot, curve (4). The parameter $r_c(Fe)$ referred to in this figure is defined by:

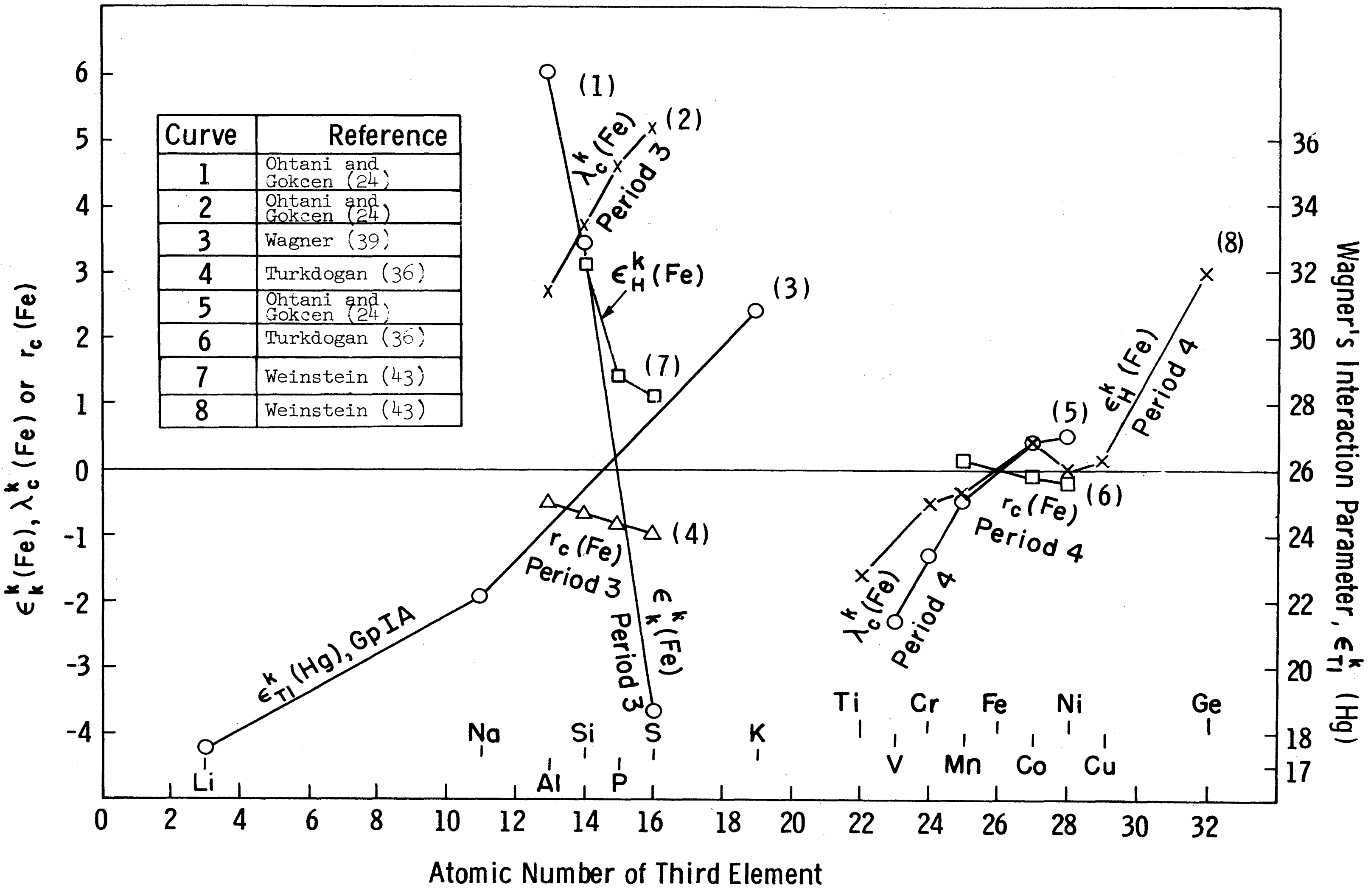


Figure 1. $\epsilon_i^k(Z)$, $\epsilon_k^k(Fe)$, $\lambda_c^k(Fe)$, and $r_c(Fe)$ versus Atomic Number of Third Component.

Correlated by Periods.

$$r_c = \left[\frac{\delta(\Delta N_c^k)}{\delta N_k} \right] \tag{31}$$

where N_k is the mole fraction of component k, $\Delta N_c^k = N_c - N_c^c$, and N_c and N_c^c are the mole fractions of carbon in the ternary and binary solutions, respectively. As is illustrated in the figure, the value of r_c decreases as the atomic number of the third element increases across a given period of the periodic table. In his paper, Turkdogan also illustrates interesting relationships whereby r_c decreases with decreasing empirical crystal radius (in the free state) of the third component and, except for silicon, decreases with increasing second ionization potential of the third component.

In the paper by Ohtani and Gokcen (24) referred to earlier, various interaction parameters are examined and correlated. They first review several binary systems and tabulate values of the self-interaction parameter, calculated from published data, for some of these binary systems. Once again, there appears to be a relationship between the self-interaction parameter, ϵ_k^k, and the atomic number of the solute, k. The parameters for Al, Si, and S are plotted in Figure 1, curve (1), along with Turkdogan's work.

Besides the binary systems, Ohtani and Gokcen also reviewed the published data on several ternary systems. Curves 2 and 5 in Figure 1 show a plot of λ_c^k (Fe) against the atomic number of component k. The parameter λ_i^k has been discussed in the preceding section of this thesis.

Curve 3 in Figure 1 is a plot of ϵ_{Tl}^k (Hg) against the atomic number of k, where k represents Li, Na, or K. The parameter actually measured by Wagner was ϵ_k^{Tl} (Hg) rather than ϵ_{Tl}^k (Hg) so in Figure 1 it has been assumed that Wagner's reciprocity relationship is valid, i.e.,

$\epsilon_{Tl}^{k} = \epsilon_{k}^{Tl}$. The values of these parameters, ϵ_{k}^{Tl} (Hg), were determined by Wagner (39) using an emf cell. Wagner actually made these investigations on ternary amalgams to check the validity of equation (25), which is:

$$\epsilon_{2}^{3} = \epsilon_{3}^{2} = \pm \left[\epsilon_{2}^{2} \cdot \epsilon_{3}^{3}\right]^{1/2} \qquad (25)$$

In these three cases, equation (25) did indeed give results which were deemed by Wagner to be in satisfactory agreement with the observed results. It is important to note here, however, that the values of ϵ_{k}^{k} for Tl, Li, Na, and K are 13.1, 26.5, 36.0, and 67.0, respectively, indicating large deviations of these binaries from ideal behavior. This is one of the stipulations on equation (25) which must be satisfied before this equation can be expected to be valid.

The parameters included in curves (7) and (8) in Figure 1 represent the work of a number of persons. These parameters are all tabulated in the thesis of Weinstein (43) .

Chipman (6) published a paper in which he tabulates quite a large number of interaction coefficients for elements dissolved in liquid iron at 1600°C. Figure 2 is a graphical presentation of a good share of this data, in which the interaction parameter is plotted against the atomic number of the third component. This graphical presentation is an attempt at correlating these interaction parameters according to the subgroup of the periodic table to which the third components belong. Any data in Chipman's article which were not part of a set made up of parameters representing three or more elements from the same subgroup of the periodic table, of course, could not be included in this correlation.

It appears that there are indeed trends as one proceeds up or down a subgroup of the periodic table. This phenomenon will be discussed in a subsequent section of this report.

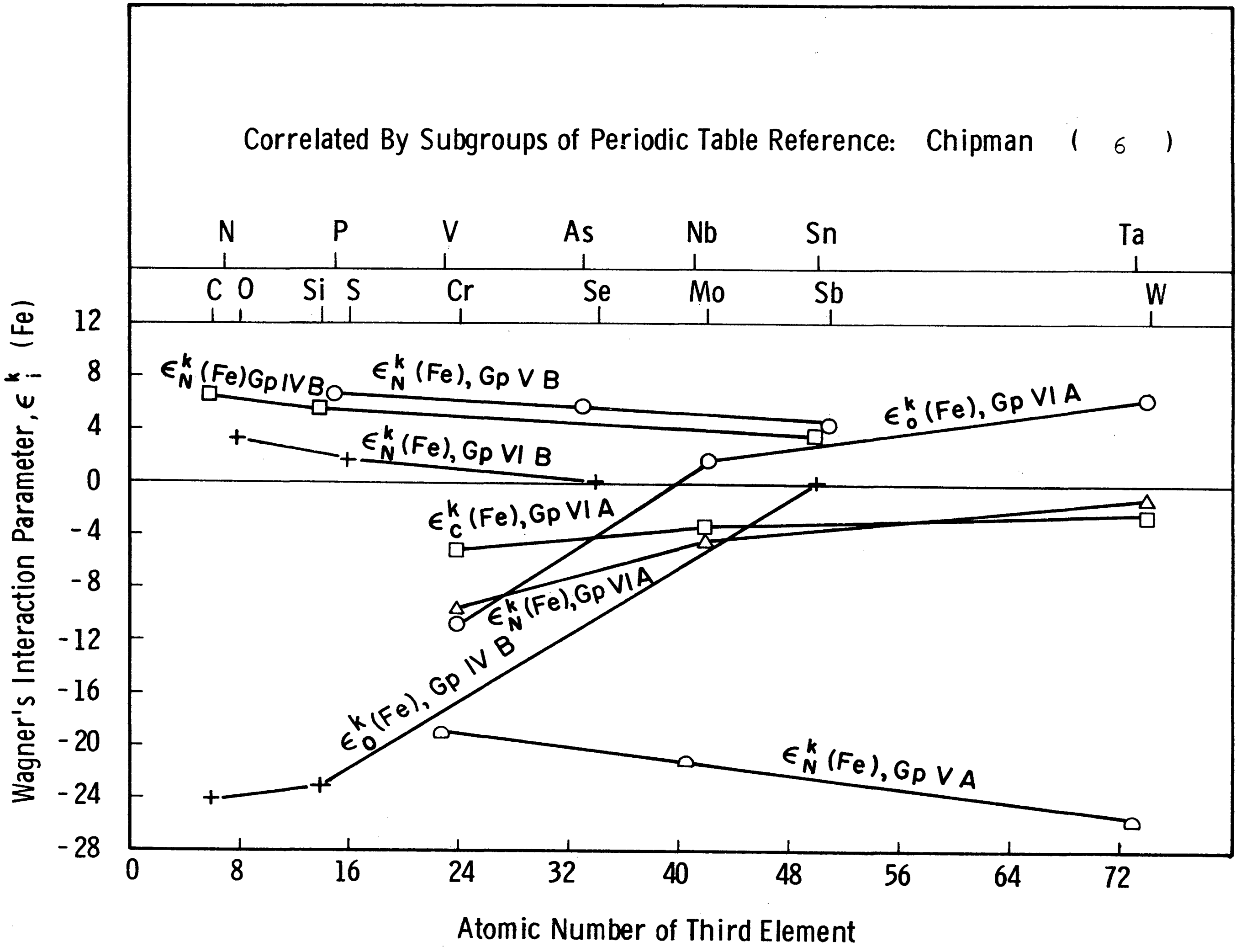


Figure 2. ϵ_i^k(Fe) versus Atomic Number of Third Component. Correlated by Subgroups.

All the interaction parameters except two which are presented in Figure 2 were taken from Chipman's article. The two parameters ϵ_{O}^{C} (Fe) and ϵ_{N}^{V} (Fe) were taken from reference (24). All the parameters were determined from apparently reliable experimental results, but the degree of precision is somewhat variable, according to Chipman.

Dealy and Pehlke (10) have published a compilation of nonferrous interaction parameters. These parameters were calculated by the authors from published experimental data. A graphical presentation of these data such as that given in Figures 1 and 2 for the iron-base alloys is not possible, because the data were not taken systematically with respect to the periodic table, since they were gathered by many different investigators. The paper also includes a comparison of experimental results with values calculated from Wagner's reciprocity relationship, equation (25). The comparison indicates reasonable agreement between this relationship and the observed results, if the self-interaction parameters are large (considerably greater than unity) and of the same algebraic sign, as Wagner originally pointed out.

B. Studies of the Bismuth-Aluminum Binary

The original studies of this binary system were made during the period 1892-1906, with later studies following in 1931 and 1939. According to thermal and microscopic examinations (13) , the two metals bismuth and aluminum are almost entirely immiscible in the liquid state. Layer formation was also observed by (45, 5) and (above 30 wt. per cent Bi) by (27) . The monotectic temperature was found to lie about 5° (13) , 3.5 ± 0.5° (16) , or 3C° (19) below the melting point of aluminum. At the monotectic temperature, the miscibility gap extends from 3.4 wt. per cent (0.45 atomic per cent) bismuth (19) to at least

98.5 wt. per cent (90 atomic per cent) bismuth, probably higher (13). At 700°, 800°, and 880°C, respectively, about 5.5, 9.9, and 15.2 wt. per cent bismuth are soluble in liquid aluminum (19). The solid solubility of bismuth in aluminum at 657°C is less than 0.2 wt. per cent (0.026 atomic per cent) (19). The phase diagram resulting from these studies is shown in Figure 24 in Appendix A.

No experimental data were available on the Bi-Al liquidus between the monotectic and eutectic temperatures until 1961 when Weeks and Minardi published their work done at Brookhaven National Laboratory (41) (see Figure 8). Their data were found to be represented by the equation :

$$\log_{10} (\text{ppm Al}) = 6.40 - \frac{1992}{T°K} \pm 10\% \qquad (32)$$

The experimental procedure followed in their study was not mentioned in the writeup of their results. These same authors, however, have measured the solubility of several other elements in liquid bismuth as part of a long-term program. From the published results concerning some of these latter elements, it was learned that they were all studied by the same basic method; it was therefore concluded that the Bi-Al binary was studied by this same method. According to this method, the Bi-Al binary was equilibrated at a selected temperature in a graphite crucible. After waiting a predetermined length of time for the system to come to equilibrium, the melt was sampled by means of a graphite, pyrex, vycor, tantalum, or molybdenum sampling probe. This probe consisted of a 1/2 to 3/4 inch diameter cylinder with a 30 to 40 micron pore-size frit. During the equilibration and sampling processes, the liquid metal temperature had been maintained to within a reported ± 0.5C° of the selected run temperature. The composition of the liquid metal sample was then determined by chemical analysis. It was stated that the errors introduced by the equipment were generally smaller than those introduced by the chemical analysis. The overall error, according to equation (27), over the entire temperature range covered was estimated to be ± 10 per cent.

Prior to their study of the Bi-Al binary, Weeks and Minardi measured the solubility of aluminum in bismuth which was contaminated with 3.6 atomic per cent Mg. At the time they made this study, the authors stated that the results were questionable, i.e., that this magnesium concentration might have an effect on the aluminum solubility. According to their later studies with no magnesium present, this is indeed the case. The presence of 3.6 atomic per cent Mg lowers the solubility of aluminum in bismuth by approximately 20 per cent over the temperature range covered. Both curves are shown in Figure 8.

Sri Krishna and Grace (33) also carried out an investigation of this binary liquidus in 1961 at Purdue University. The results of this work appear in Figure 8. The least-squares line was fitted to their data by the author, and the equation of this line found to be:

$$\log_{10} (\text{ppm Al}) = 2.29 - \frac{1679}{T^\circ K} \qquad (33)$$

This line gives aluminum solubilities approximately 0.7-1.3 times as great as those reported by Weeks and Minardi, depending upon the temperature. Sri Krishna and Grace carried out their investigation for the purpose of studying the kinetics of dissolution of a rotating aluminum cylinder in liquid bismuth. Aluminum cylinders with freshly machined surfaces were immersed and rotated in liquid bismuth and the dissolution process followed by sampling small amounts of the liquid phase at various times. Chemical analyses were performed by a spectrophotometric technique with results reported to be within ± 0.01 weight per cent aluminum.

No details concerning experimental procedure, sampling technique, etc., were given by the authors.

C. Studies of the Lead-Aluminum Binary

The study of the lead-aluminum binary was first undertaken by C. R. A. Wright (45) . He found a very wide miscibility gap to exist in the liquid state. This miscibility gap has subsequently been verified by many other investigators. It was shown later by (16, 19) that the melting point of aluminum is lowered 1.5C° by 1.1 wt. per cent lead to a monotectic temperature of 658.5°C. Likewise, the melting point of lead (327.3°C) is lowered by 0.021 wt. per cent aluminum to 326.8°C, the eutectic temperature. The solubility of aluminum in liquid lead, as determined between 350° and 1100°C by (8) is shown in Figure 9 . Solubilities reported by (7) and (30) are four to five times higher than those reported by (8) . Data were taken only at 650°C and 1000°C by (30) and at 1020°C and 1200°C by (7) and, considered as a whole, are quite scattered. The phase diagram resulting from the above data is shown in Figure 26 in Appendix A.

Schneider (30) told nothing about the experimental method employed in gathering the data reported. The experimental data reported by (7) resulted from experiments in which the Bi-Al solutions were equilibrated in magnesia-lined clay crucibles. The melts were brought to the run temperature, stirred, and let stand for one-half hour. The bottom layer was then sampled by means of a magnesite suction probe and analyzed chemically. No details were given on the chemical analysis technique.

Dardel's (8) experimental procedure was as follows. A 500gm sample of lead with 2 wt. per cent aluminum was melted in a small steel crucible and held for one hour at 1100°C. Then the temperature was changed to one of the run temperatures and the Al-rich and Pb-rich phases allowed to separate. The crucible containing the melt was then plunged into water, and the lower part of the ingots chemically analyzed to determine the composition of the Pb-rich layer. The dispersion of the results obtained in two or more runs at the same temperature was quite pronounced at most temperatures investigated. It is possible that the solidification rate of the ingots, though it was reported to take place in less than one minute, was still slow enough that departures from the equilibrium composition were experienced during the cooling process.

The least squares line fitted to Dardel's data (8) is represented by the equation:

$$\log_{10} (\text{wt.\% Al}) = 1.04 - \frac{1629}{T°K} \tag{34}$$

The least squares line fitted to the combined data of (7) and (30) has the equation:

$$\log_{10} (\text{wt.\% Al}) = 1.56 - \frac{1883}{T°K} \tag{35}$$

The solubility of lead in solid aluminum is not higher than 0.2 wt. per cent (0.025 atomic per cent) lead (19) ; see reference (25) also. The solid solubility of aluminum in lead is practically nil (4, 8).

III. EXPERIMENTAL PROGRAM

A. Preliminary Considerations

As mentioned in a previous section of this thesis, it would be of considerable practical value, at least for engineering purposes, if one could generalize on solute interactions in dilute liquid metal solutions, i.e., if one could correlate the effect of the chemical elements upon a particular binary liquid metal solution with some measurable atomic property or properties of the elements involved. This study was initiated with this thought in mind.

Various persons have proposed methods for assessing solute interactions in multicomponent systems. The methods of Wagner, Ohtani and Gokcen, Turkdogan, and Alcock and Richardson have been reviewed in the preceding section of this report. As mentioned in that section, some investigators have concluded that these various interaction parameters vary in a periodic manner, and do, in fact, have experimental data which supports this hypothesis to some extent. This data indicates a periodicity in the effect of the elements upon a given binary, in that the interaction parameters, in most cases, fall into definite sequences which correspond to subgroups or periods in the periodic table. There has been a considerable amount of data taken on ternary systems which allows one to determine interaction parameters for these systems. Unfortunately, however, very little of this data was taken consistently enough with respect to the periodic table to allow one to investigate any periodic trends. Therefore, it was felt desirable to study solute interactions for several ternary systems chosen with respect to the periodic table such that trends across a period or down a subgroup could be investigated.

With these facts in mind, the Bi-Al and Pb-Al systems were chosen as the basic binaries to be studied. If one inspects the Bi-Al and Pb-Al phase diagrams, he will find that they are essentially the same in their constitution. (See Figures 24 and 26 .) In both cases, between the eutectic and monotectic temperatures, the equilibrium occurring along the liquidus is between the Bi-Al or Pb-Al liquid solution and essentially pure solid aluminum. Therefore, if one chooses pure solid aluminum as the standard state, the activity of aluminum in the liquid in both systems is fixed at unity, and the activity coefficient of aluminum can be determined directly from its solubility. Specifically, this activity coefficient, γ_{Al}, is given by $\gamma_{Al} = 1/N_{Al}$, where N_{Al} is the atomic fraction of aluminum in the liquid solution. In order to evaluate the parameter $\lambda^{k}_{Al}(Z)$, one needs to measure the solubility of aluminum as a function of the concentration of the added element (k), for in this case,

$$\lambda^{k}_{Al}(Z) = \left[\frac{\partial \ln \gamma_{Al}}{\partial N_k}\right]_{a_{Al}} = -\left[\frac{\partial \ln N_{Al}}{\partial N_k}\right]_{a_{Al}}$$

As pointed out in the previous section, this expression must be evaluated as N_k and N_{Al} tend to zero. What this really means is that this expression must be evaluated at liquid compositions dilute enough with respect to all solutes such that second order interactions are unimportant and can be neglected. The solubility of aluminum in both bismuth and lead is small enough between the monotectic and eutectic temperatures that the solutions should be dilute in this sense with respect to aluminum. To satisfy the further requirement that N_k tend to zero, $\lambda^{k}_{Al}(Z)$ is determined as the limiting slope (as N_k tends to zero) of the line described by plotting $\ln \gamma_{Al}$ as a function of N_k, or the negative of the limiting slope of the line described by plotting $\ln N_{Al}$ as a function of N_k.

In selecting the third components to be studied, several factors had to be taken into consideration. Experimental investigation of solute interactions by periods or subgroups (i.e., the third components lying in the same period or subgroup of the periodic table) seemed to be the reasonable plan to follow for two reasons. In the first place, the atomic interactions which take place in a liquid alloy are a function of the chemical and physical properties of the elements involved. Therefore, it seems obvious that experimental data taken in a logical manner with respect to the periodic table will ultimately be of greater aid in attempting to elucidate the nature of the solute interactions in liquid alloys than will data which has been taken in a more or less random manner. Secondly, since there is evidence that interaction parameters may perhaps correlate to some extent with the atomic number of the third component, it seems reasonable to study them on this basis until a more quantitative theory for their prediction is developed. In the meantime, as the volume of experimental data grows, and if it does indeed indicate periodic trends in these parameters, then perhaps various undetermined interaction parameters can be estimated by interpolation or extrapolation. In addition to the two reasons mentioned above, it was necessary to select third components that do not dissolve in solid aluminum to an appreciable extent. The activity of aluminum can then be held at essentially unity throughout the two-phase field bordering on the solvent-aluminum side of the ternary phase diagram. It was felt, however, that an aluminum-k primary solid solution in the range of 1-2 atomic percent k, as long as it is accurately known, could be tolerated, since Raoult's law should be valid in this range. Other factors which necessitated the exclusion of certain of the elements from further consideration as third components include too limited a solubility in bismuth and in lead, anticipated chemical analysis problems, and a general lack of knowledge concerning their alloying behavior.

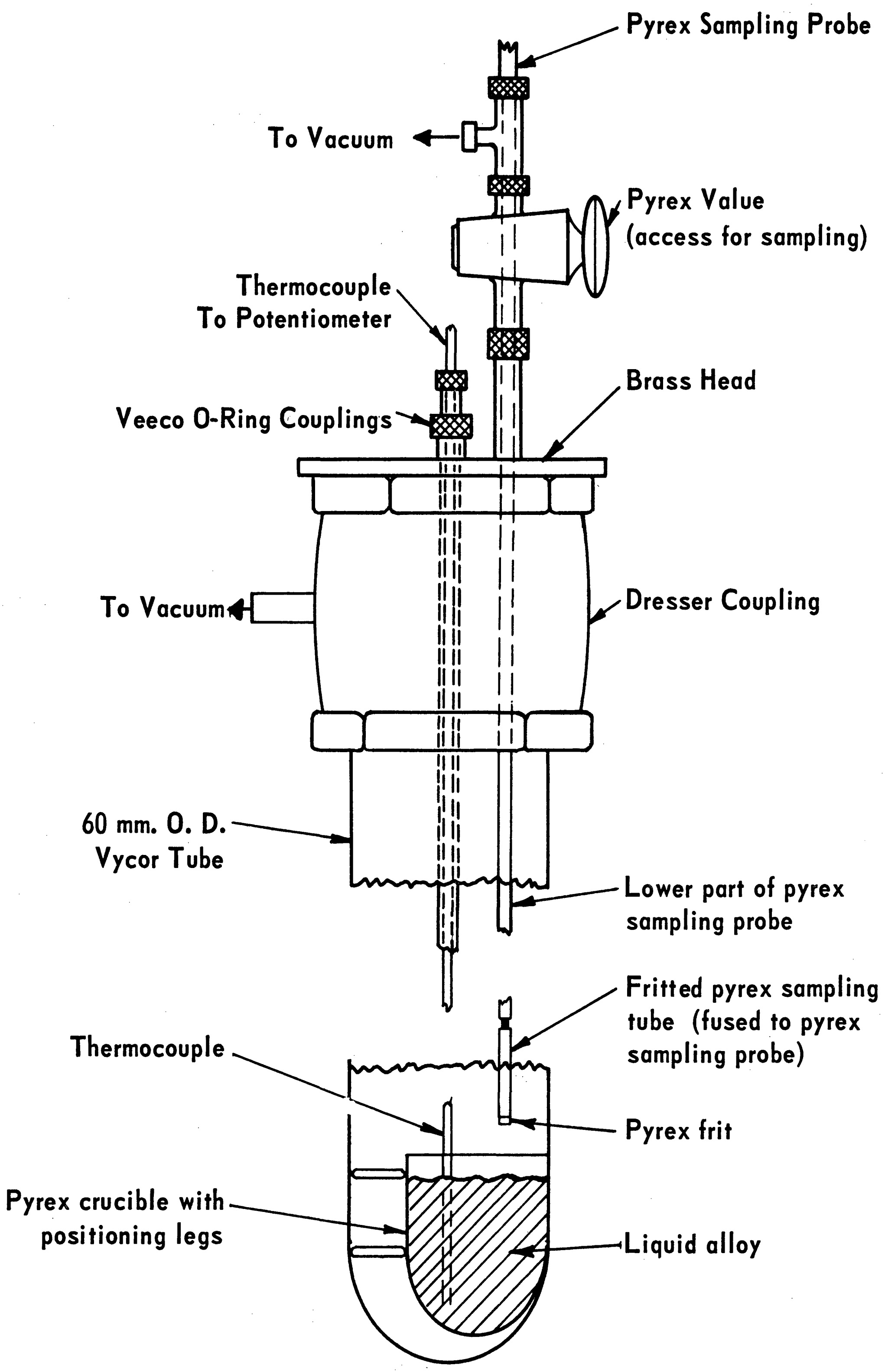
Considering all the limitations outlined above, the following elements appeared to be the most suitable for the study: calcium, strontium, and barium, from subgroup IIA of the periodic table, and palladium, tin, and antimony, all lying in period five. Strontium lies in both subgroup IIA and period five of the table. Of all these third elements, calcium has the highest solid solubility in aluminum, being on the order of 0.4 atomic per cent at 616°C and 0.2 atomic per cent at "room temperature." The two matrix elements, bismuth and lead, have solid solubilities of less than 0.025 atomic per cent, in aluminum at 650°C (19).

As will be discussed in the following section of this thesis, most of the experimental data obtained in this study was the product of equilibrations carried out in graphite filter crucibles. Therefore, the interaction of graphite with the liquid metal solutions had to be considered. The solubility of carbon in molten aluminum is very small, estimated to be less than 0.1 atomic per cent at 1300-1500°C (15) and is practically nil at 1000-1100°C (15) . Therefore, in the temperature range at which these studies were made, the solid solubility of carbon in aluminum is certainly negligible. The solubility of carbon in liquid bismuth was found to vary from 0.0028 atomic per cent to 0.0052 atomic per cent for temperatures between 300 and 750°C (15). The solubility of carbon in lead in the temperature range of interest is not available. Comparing carbon solubilities in bismuth and lead at higher temperatures, however, it appears that the solubility of carbon in liquid lead between 400 and 600°C is probably on the order of thousandths, or at least hundredts, of one atomic per cent. (The solubility of carbon in bismuth at 1408°C is about 0.3 atomic per cent and its solubility in lead at 1415°C is about 0.9 atomic per cent.)

The evaluation of $\lambda^{k}_{Al}(Z)$ for a particular ternary involves obtaining a sample of the liquid ternary solution in equilibrium with pure solid aluminum at the selected temperature. This sample is obtained by filtering the equilibrium liquid phase away from the solid aluminum phase. The details of this procedure are given in a subsequent section of this thesis. Once a sample of this equilibrium liquid solution is obtained, it is analyzed chemically for the concentration of aluminum and the third component. This data, for several values of third component and aluminum concentrations, makes it possible to determine $\lambda^{k}_{Al}(Z)$ for that particular ternary at that particular temperature.

B. Equipment

Two different types of experimental apparatus were used in this study. In one type, the liquid metal equilibrium solution could be sampled repeatedly as a function of time. This apparatus was used to determine the time necessary for the Bi-Al binary system to come to equilibrium. It was also used to determine the Bi-Al liquidus line between 400 and 600°C, since it was possible with this apparatus to determine solubilities as a function of temperature in the course of one continuous run. The second type of apparatus allowed one to vary the third element concentration at a fixed temperature for each run. This apparatus was used in the ternary studies. The two apparatuses were compared to make sure that they gave the same results at several points on the Bi-Al binary liquidus, and indeed they did. The former apparatus was not used at all in the lead-base studies. The two types of apparatus are described below.



Equilibrium Chamber – Apparatus A

Figure 3.

1. Apparatus A

The first type of apparatus, called apparatus A, was constructed as shown in Figure 3. The liquid metal solution equilibration was carried out in a pyrex crucible 3 inches long by 38 millimeters in outside diameter. This crucible sat in the bottom of a larger vycor tube which measured 60mm OD by 20 inches long. The larger tube was held in the vertical position and was enclosed by a vertical split-wound resistance furnace. The furnace was two feet long and was equipped with compensating end windings to minimize the temperature gradient within the furnace. The power to the furnace was varied through a 0-220 volt variac. The temperature of the equilibrium solution was controlled by means of a proportionating Wheelco controller. This controller was capable of maintaining the reservoir temperature within $\pm$ 2C° of the set temperature over the temperature range covered. The control thermocouple which activated the temperature controller was situated between the furnace windings and the outside of the 60mm OD vycor tube in order to obtain maximum control sensitivity and thus minimize temperature fluctuations within the liquid metal solution. The thermocouple which measured the temperature of the liquid metal solution was immersed directly into the solution. The thermocouple wires were enclosed in stainless steel hypodermic tubing to eliminate corrosion as well as to provide access into the evacuated system. The hypodermic tubing entered the system through a Veeco coupling mounted on the brass head, as shown in Figure 3 . The hypodermic tubing was fabricated of AISI No.430 ferrite stainless steel. This material contains Fe, Cr, and carbon, none of which are soluble to any appreciable extent in the bismuth and lead alloys studied. A stirrer also entered the system through a Veeco coupling mounted on the brass head. This stirrer was made entirely of 7mm OD pyrex tubing and was used to agitate the liquid metal periodically. It was found that if the depth of the liquid metal reservoir was maintained equal to or less than one inch, then the temperature gradient within the reservoir was less than 1C°.

The entire reaction chamber was kept under an inert atmosphere during all runs in order to minimize oxidation of the liquid metal and to prevent excessive mass transfer of the liquid metal from the reaction zone to the cooler parts of the Vycor tube. It was found that 20mm of argon pressure was sufficient to reduce the mass transfer of bismuth to a satisfactory extent. The solubility of argon in bismuth at this pressure and higher is immeasurably small (31).

Before introducing the argon, the system was evacuated to about one micron pressure by means of a roughing pump connected to the system through a cold trap in combination with a diffusion pump. The argon was introduced into the system through a charcoal trap. This argon was used as the pressurizing gas to effect filtration as well as to provide continuous environmental control. This combination of initial evacuation to one micron pressure (as measured by a thermocouple gage) followed by environmental control through argon gas was found adequate to inhibit oxidation (at least to the extent that it was not visually detectable), prevent excessive volatilization of bismuth, and effect the filtrations.

2. Apparatus B

This apparatus was constructed as shown in Figure 4 . As many as twenty-two separate equilibrium solutions could be accommodated at one time in this apparatus. Each equilibrium solution was contained in a graphite filtering crucible as shown in Figure 5 . The filtering

Equilibrium Chamber and Furnace — Apparatus B

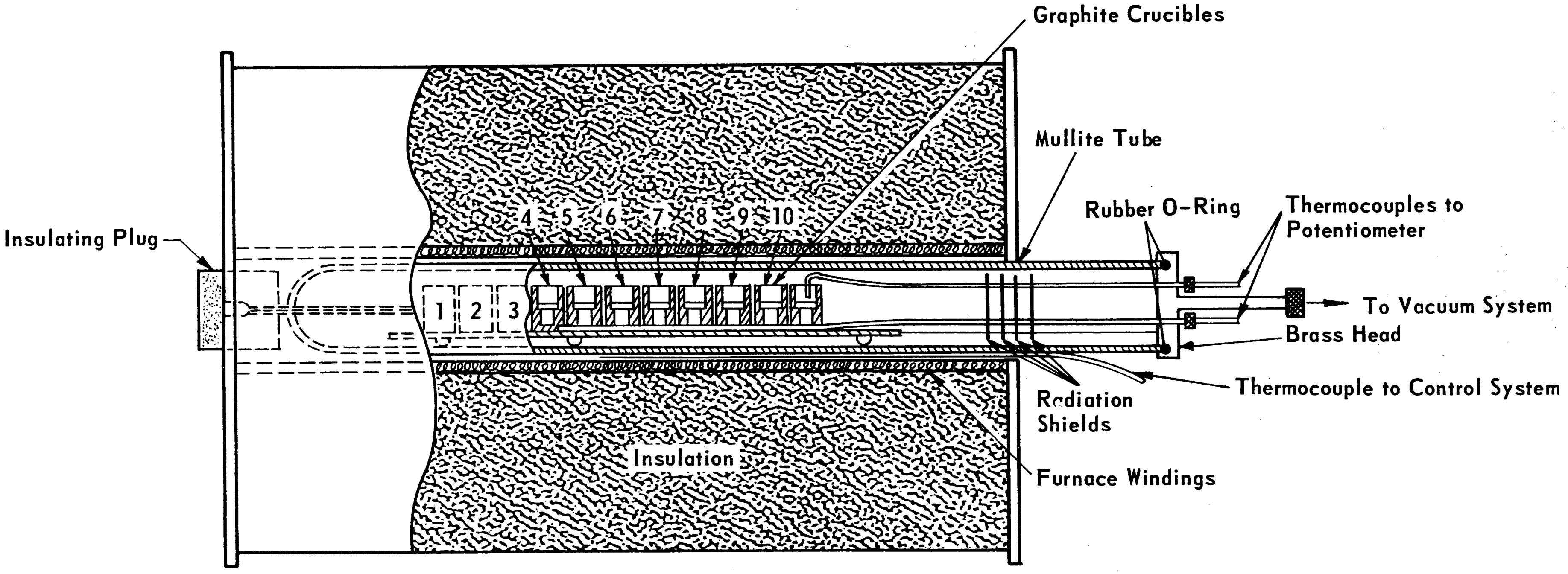
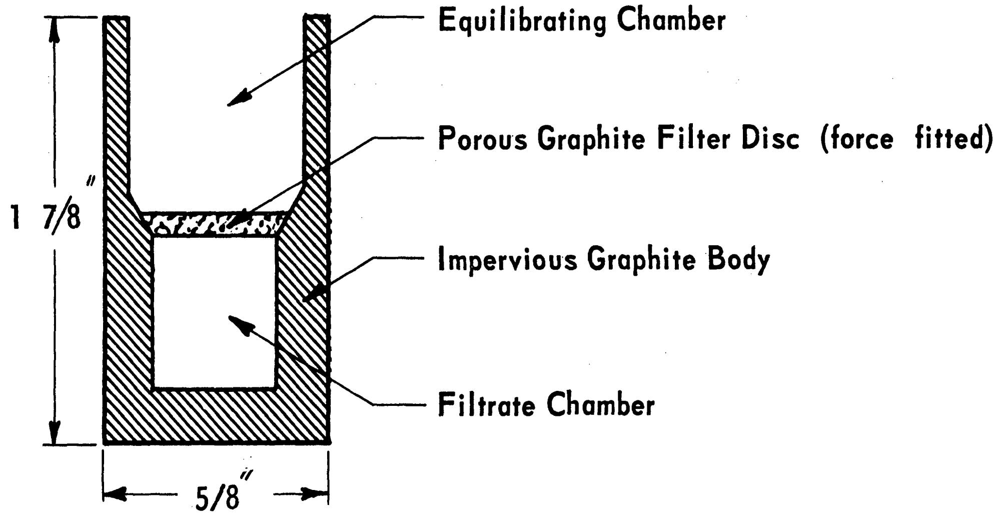
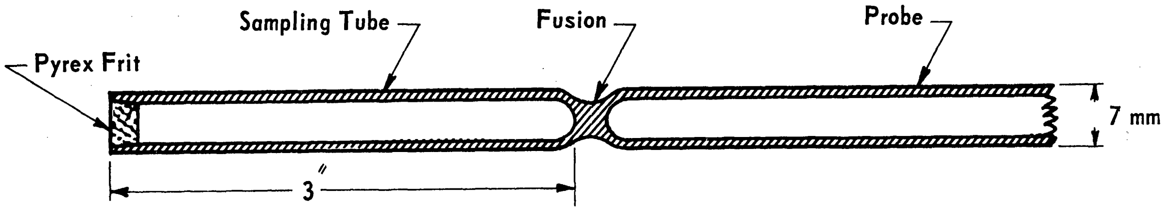


Figure 4.



Graphite Filtering Crucible (Apparatus B)

Figure 5.



Pyrex Probe and Sampling Tube (Apparatus A)

Figure 6.

crucibles, in turn, were contained in a 2 1/2 inch ID Mullite tube which was enclosed in a horizontal position in a split-would resistance furnace of the same size and type as that used with apparatus A. The temperature controller for this system was a Foxboro on-off controller activated by a thermocouple placed between the Mullite tube and the resistance wires of the furnace. This controller was capable of maintaining the temperature fluctuation at any point within the reaction zone in the Mullite tube to ± 1C°. An insulating plug was inserted at the end of the furnace closer to the closed end of the Mullite tube in order to minimize radiation and convection losses.

The open end of the Mullite tube was enclosed by a brass head through an O-ring seal. This brass head provided access to the reaction chamber for the thermocouple(s) and the vacuum line from the pump. Although only one thermocouple was generally employed in these runs, the brass head was designed to accommodate up to three if necessary. The rack holding the graphite filtering crucibles was attached to the brass head by means of stainless steel connecting rods. This arrangement assured proper positioning of the crucibles for each run.

The temperature profile within the reaction zone, i.e., across the entire group of crucibles containing the equilibrium solutions, was checked repeatedly during the course of each run. It was found that the minimum temperature gradient that could be attained along the length of the twenty-two crucibles used in some runs was 3-4C°. In runs employing less than twenty-two crucibles, the temperature gradient was usually less. If at the beginning of a run the temperature gradient was found to be greater than 4C° (as was usually the case) conditions external to the furnace were altered until the 4C° gradient was attained.

Temperatures were measured by means of a chromel-alumel thermocouple of the same type as that described in the description of apparatus A. The thermocouple tube entered the reaction zone through a Veeco coupling which was attached to the brass head enclosing the open end of the Mullite tube. The flexibility of the Veeco coupling allowed the thermocouple to be moved back and forth along the entire length of the reaction zone. Thus, the temperature profile along the reaction zone was checked repeatedly for every experimental run made.

As implied in the preceding paragraph, temperatures in apparatus B were measured outside the graphite crucibles, rather than inside the liquid metal solutions themselves. This, of course, was necessary in order to avoid using one thermocouple for every crucible. Several runs were made to determine the difference between the temperatures at the points where the run temperatures were measured and the actual liquid metal temperatures. The results of these runs indicate that this temperature difference varies from about 5C° at 400°C to about 7C° at 600°C. Temperature corrections were applied accordingly to all runs made on apparatus B.

3. Thermocouples and Their Calibration

Throughout the course of this study, all temperature measurements were made with chromel-alumel thermocouple wires. The thermocouples were constructed of 28 gage chromel-alumel wire, all taken from the same matched spools. Each thermocouple was enclosed in a stainless steel hypodermic tube, the thermocouple wires being insulated from the tubing by means of two-hole ceramic insulation. Enclosure in the tubing eliminated corrosion of the thermocouple wires and provided access for the wires into the evacuated system. The hypodermic tubing was constructed of AISI No. 430 ferrite stainless steel. This material contains iron, chromium, and carbon, none of which are appreciably soluble in the bismuth or lead alloys studied.

Two different thermocouples were calibrated against a Pt/Pt-10 per cent Rh thermocouple which had been previously calibrated by the National Bureau of Standards. The apparatus used in this calibration was essentially the same as apparatus A, described previously in this thesis. The Pt/Pt-10 per cent Rh standard thermocouple was enclosed in a molybdenum protection tube. The tips of the standard couple and the couples to be calibrated were wired into contact with each other and inserted into a reservoir of liquid bismuth. This reservoir, in turn, was contained in an evacuated reaction chamber. The temperature of the reservoir was maintained successively at several selected temperatures ranging approximately from 350° to 650°C. The temperature measurements were made by reading alternately the standard couple and the couples being calibrated several times at a particular temperature and averaging the resultant readings for each couple.

It was found that the necessary temperature correction depended upon the temperature being read. The correction for one of the thermocouples calibrated as outlined above varied from - 0.2C° to - 1.7C° over the temperature range 650° to 350°C and the correction for the other varied from - 3.2C° to - 1.9C° over this range, but neither varied in a monotonic fashion.

The thermocouples used in this study burned out numerous times. Generally, the break was observed quite close to the thermocouple junction, so that the thermocouple could be clipped off near the break, a new junction made, and the same thermocouple wires used over again. This was done whenever possible. When it became necessary to make a new thermocouple, this was done, and the new couple calibrated against the chromel-alumel couple used previous to it. Thus, all the thermocouples used during the course of this study were calibrated against either the Pt/Pt-10 per cent Rh standard couple or another standardized chromel-alumel couple.

Considering the ± 2C° uncertainty in temperature due to the temperature gradient in the Mullite tube, the ± 1C° uncertainty due to temperature control, and the uncertainties due to thermocouple calibrations and ΔT from inside to outside of the graphite crucibles, it is estimated that the liquid metal temperature was known in general to ± 3 to 4C°.

C. Run Procedures

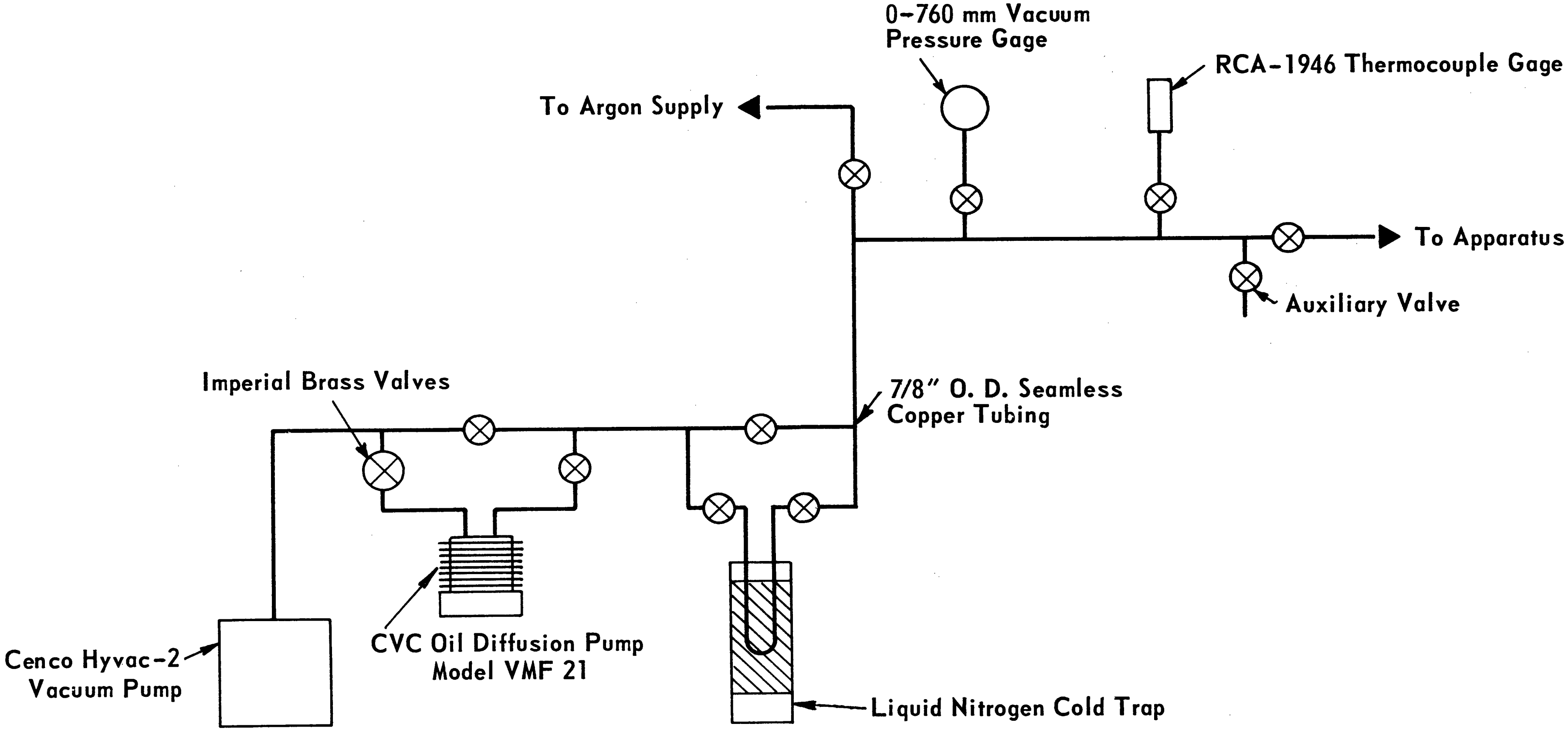
Prior to each run, the aluminum to be used was cleaned by immersing it in 1:1 HCl for several minutes, washing it in distilled water, following this by several acetone washes, and finally drying it before weighing. The bismuth and lead used in each run had been previously vacuum filtered to remove the oxides which they contained at the time they were received. In this filtering operation, the bismuth and lead were cast into 30mm diameter cylinders. These cylinders were subsequently broken up into pieces small enough that 10 gms of the metal could be fitted into each graphite crucible. In the alkaline earth runs, the alkaline earth to be used was weighed under the protection of reagent grade benzene in order to minimize oxidation. The benzene was automatically removed from the surface of these metals by evaporation when a vacuum was pulled on the system prior to melting.

1. Apparatus A

In performing a run on apparatus A (Figure 3), the procedure was as follows. After pre-treatment of the metals to be used, they were charged to the crucible, the aluminum in the neighborhood of 100 per cent excess, so as to insure saturation. The system was then evacuated to a pressure of about one micron (see Figure 7), the furnace turned on, and heating begun. The heating was generally accompanied by a slight outgassing of the metals. Therefore, before shutting off the vacuum pump to run under a static vacuum, the system temperature was always taken first to the run temperature or above and left there until outgassing was complete. Then the vacuum pump was shut off from the system, and the run was made under a static vacuum, the system proving adequately vacuum-tight to permit this. The system was generally allowed about 24 hours to come to equilibrium, although preliminary studies had shown that equilibrium was actually attained in a much shorter time. This 24 hour equilibration period was followed primarily for convenience.

The sampling probe used in conjunction with this apparatus was a 7mm OD pyrex tube, to the end of which was attached a shorter piece of pyrex tubing, closed at one end and fitted with a pyrex frit at the other. This probe is illustrated in Figure 6. The shorter piece of pyrex was also 7mm OD, was 3 inches long, and was fused directly to the longer pyrex tube. The pyrex frit was of the medium grade, having a pore size ranging from 10 to 15 microns. The overall length of the sampling probes was about fifty inches.

To remove a sample of the liquid equilibrium solution, the probe was inserted into the reaction chamber through a Veeco coupling and glass valve arrangement (see Figure 3) which permitted access without disturbing



Vacuum System — Apparatus A
(Vacuum system for B the same, except no diffusion pump)

Figure 7.

the vacuum. The probe was then lowered until the tip was within two inches of the surface of the liquid metal and allowed to come to temperature equilibrium. Temperature equilibrium of the probe was found to be attained to a satisfactory extent within ten minutes. This was indicated by the fact that after a ten minute wait, immersion of the probe into the liquid metal caused no appreciable temperature fluctuation. After immersion of the tip of the sampling probe below the surface of the liquid metal, inert gas pressure (300-400mm Hg) was applied to the metal surface. This pushed a sample of the liquid up through the pyrex frit into the sampling tube. The sampling probe was then withdrawn slowly so that the hot portion would have time to cool before contacting the rubber O-ring of the Veeco coupling. The entire sampling procedure was found to cause very little temperature disturbance; on the order of 0.5C°.

After the removal of the sampling probe from the experimental apparatus, the small tube containing the sample was detached from the longer tube and readied for chemical analysis. The entire sample was analyzed because of the possibility of segregation taking place within the sample upon cooling.

2. Apparatus B

The first step involved in making a run on apparatus B was to outgas the graphite crucibles. The outgassing operation was carried out at 800°C and was continued until the pressure inside the system decreased to one micron (see Figure 7). Then the furnace was turned off and the system cooled down in preparation for adding the metals. Before opening the system and exposing the crucibles to the atmosphere, argon was introduced into the system and allowed to remain there for one-half hour or more. It was hoped that the crucibles would adsorb the argon and thus minimize oxygen readsorption upon exposure to the atmosphere.

After their pre-treatment, the metals were charged to the graphite crucibles and the crucibles, in turn, to the Mullite tube. It was always attempted to hold to a minimum the time between removing the outgassed crucibles from the system and reinserting them after the metals had been charged to them. Once again, the aluminum was added in approximately 100 per cent excess. The system was then pumped down to about one micron gage pressure before the furnace was turned on. Upon heating the metals, more outgassing was experienced; so once again, the vacuum line to the pump was not sealed off until the run temperature or greater was reached, and a system pressure of one micron was obtained simultaneously. The run was then carried out under a static vacuum.

The first few runs that were conducted were made under a pressure of 20mm of argon, in order to suppress the volatilization of bismuth or lead. It was soon learned, however, that a pressure difference of 20mm of mercury across the graphite filter discs was sufficient in some cases to cause filtration. Therefore, in order to avoid the risk of premature filtering, the 20mm pressure of argon was eliminated. It was then learned that at temperatures of 650°C or less, where these runs were made, the mass transfer of the liquid metals being studied was of a small enough magnitude that it caused no detectable problem. These runs, as in the other apparatus, were also generally made about 24 hours in length.

Filtration was accomplished by the introduction of inert gas pressure above the liquid metal solutions. It was found that, in order to insure that a maximum number of crucibles were filtered, about 700mm of mercury inert gas pressure was required. Quite frequently, even this amount of pressure difference across the graphite filter discs was insufficient to accomplish filtration. No greater inert gas pressure than this could be used, however, because 50-60mm pressure difference across the brass head was needed to hold the head in position and prevent leakage of the atmosphere into the Mullite tube.

Several investigations were made into the possibility of leakage of liquid metal around the outside of the filtering disc. It was found that, as long as the discs were seated properly in the crucibles, leakage did not occur. Two major factors contributed to proper seating of the filter discs. First, the inside of the crucible wall was tapered inward very slightly at the bottom of the upper chamber. This taper amounted to only about one millimeter decrease in diameter of the upper chamber over its bottom three millimeters of length. After introducing a filter disc into the top of the crucible, however, and sliding it down to the lower part of the upper chamber, it could be seated snugly in this portion of slightly smaller diameter. The second factor contributing to proper filter disc seating was simply maintaining a strict tolerance on the diameter of the discs when they were machined. They were machined such that they fit just snugly into the larger portion of the upper chamber.

After filtration and cooling, the samples were removed from the crucibles and readied for chemical analysis. The removal was quite simple, because few of the alloys studied wetted the crucible walls. In fact, most of the crucibles were so clean after use that they could be used over again for studying the same ternary. Once again, the entire sample was analyzed because of probable segregation upon cooling.

D. Materials

1. Aluminum: The aluminum used throughout this entire study was obtained in the form of 20 gage wire from the Fisher Scientific Company. It was reported to be 99.8 per cent pure, the major impurities being Si (0.10 per cent) and Fe (0.05 per cent). As mentioned under the section on run procedures, the aluminum was pre-treated to remove the oxide film. After the cleaning process the wire was cut into small pieces approximately 0.5 cm in length before being used in a run.

2. Bismuth: The bismuth, obtained from the Belmont Smelting and Refining Company, was reported to be 99.998 per cent pure. It was received in the form of large lumps which were broken up and vacuum cast into 34mm cylinders for use in apparatus A, and into 12mm cylinders for use in apparatus B. These cylinders were then cut into appropriate lengths for charging to the crucibles.

3. Lead: This metal was obtained from the Baker and Adamson Chemical Company in the granular form. Major impurities reported include As (0.0001 per cent), Bi (0.0001 per cent), Cu (0.0003 per cent), Fe (0.001 per cent), Ni (0.001 per cent), and Ag (0.00005 per cent). The lead was vacuum cast into slugs and the oxide removed in the same manner as described for the bismuth.

4. Calcium, Strontium, and Barium: All three of these alkaline earths were obtained from the Fisher Scientific Company. They were all obtained in the form of electrolytic lumps and were reported to be 99 per cent pure. Prior to use in a run, they were cut into small pieces of appropriate size and weighed under the protection of benzene, in order to minimize oxidation. The benzene was removed by

evaporation when the crucibles were placed in the furnace and a vacuum pulled on the system.

5. Palladium: The palladium was obtained from the Chemical Commerce Company in the form of a powder. It was reported to be 99.98 per cent pure.

6. Tin: Granular, 30 mesh tin, obtained from the Baker and Adamson Company was used. It was reported to be 99.96 per cent tin; the major impurities were Fe, Pb, and Zn, all present to the extent of about 0.01 per cent.

7. Antimony: This metal was obtained from the Mallinckrodt Chemical Works in the granular form. Its purity was quoted to be 99.7 per cent, the major impurities being As (0.04 per cent), Cu (0.02 per cent), Fe (0.03 per cent), Pb (0.02 per cent), and S (0.10 per cent).

8. Graphite crucibles and filter discs: The crucibles (Figure 5) were machined from impervious graphite rod, Grade AUC, 5/8 inch in diameter, obtained from the National Carbon Company. After cutting the rod into pieces measuring 1 7/8 inches in length, the chambers were drilled into these pieces in a two step operation using two different drill bits. The upper chamber was drilled first, using a 1/2 inch drill bit. This was followed by a second drilling operation using a 5/16 inch drill bit, which formed the lower chamber of the crucible. In the first drilling operation a bit was used which was one millimeter smaller in diameter at the tip and back for 3mm than it was along the rest of the bit. This made the bottom part of the upper chamber of the crucible, for the distance of 3mm above

the shoulder, one millimeter smaller in diameter than the rest of the upper chamber above it. Such an arrangement helped insure tight seating of the filter discs. It was found that if the filter discs were made to a diameter such that they fit snugly into the upper part of the upper chamber of the crucible, then they could be force-fitted into the slightly smaller lower part of the chamber and seated such that no seepage would occur around the edges of the filter disc. It was also found, however, that if the discs were made a little too large or a little too small, then it was very difficult to seat them and maintain the fit closely enough to insure that there would be no leakage around the edges.

The filter discs were machined from porous graphite blocks also obtained from the National Carbon Company. The effective porosity of this graphite was 48 per cent and it was reported to retain particles 0.0005 inches in diameter. The discs were cut approximately 1 mm thick.

The finished crucibles, with seated graphite filter discs and graphite lids, were outgassed immediately prior to the run in which they were to be used. The outgassing procedure was carried out at 800°C and continued until the system pressure decreased to one micron. Then argon was introduced into the system prior to discharge of the crucibles in order that argon rather than oxygen have the chance to be readsorbed by the crucibles.

IV. PRESENTATION OF EXPERIMENTAL RESULTS

The results of the previously described experimental program are presented in this chapter. The results for the two binary and twelve ternary systems studied are presented in graphical form in Figures 8 through 21. The raw data are presented in Appendix D. Also presented in this chapter are the following: the equations of the lines representing log (wt. per cent Al) as a function of $\frac{1000}{T°K}$ for the Pb-Al and Bi-Al binaries; the interaction parameters, λ_{Al}^{k} (Z), calculated for each of the ternaries studied; and the values of the relative partial molar enthalpy of aluminum in the two binaries studied. None of these data, or results derived from these data, are discussed to any extent in this chapter. Such discussions are presented in the chapter following this one.

A. The Bi-Al and Pb-Al Binary Studies

1. The Bismuth-Aluminum Binary

Determinations of the solubility of aluminum in liquid bismuth over the approximate temperature range 450-600°C yielded the results shown in Figure 8. The solubility relationships determined by two other investigators are shown in the same figure. The equation of the solubility line determined by the author is:

$$\log_{10}(\text{wt. per cent Al}) = 2.55 - \frac{2110}{T°K} \qquad (36)$$

A discussion of this line, as well as the three other lines appearing in Figure 8, is presented in the next chapter.

It is possible to determine the relative partial molar enthalpy of aluminum in liquid bismuth from the solubility line appearing in Figure 8. The relative partial molar enthalpy of aluminum in liquid bismuth over the temperature range and concentration range covered by the author's

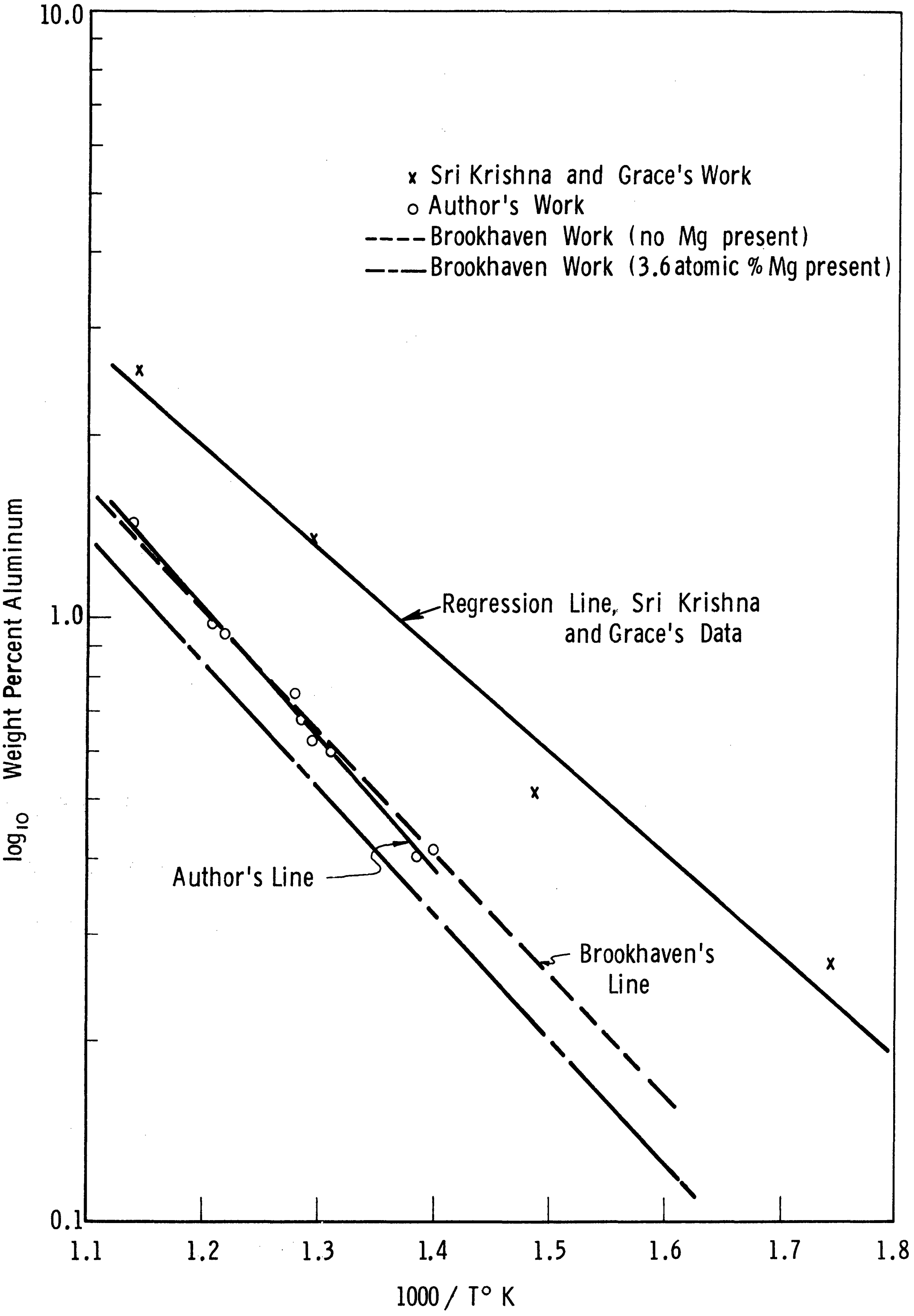


Figure 8. Bismuth-Aluminum Liquidus $\log_{10}$(wt. per cent Al) versus $\frac{1000}{T°K}$.

solubility line is $9.2 \frac{\text{k cal}}{\text{gm mol}}$. The same quantity based on the Brookhaven line is $8.7 \frac{\text{k cal}}{\text{gm mol}}$, about 5 per cent lower. The determination of these two quantities is summarized in Appendix C.

2. The Lead-Aluminum Binary

Determinations of the solubility of aluminum in liquid lead over the approximate temperature range 450°-600°C yielded the results shown in Figure 9. Solubilities determined by Dardel (8) are shown in the same figure. The equation of the solubility line determined by the author is:

$$\log_{10} (\text{wt. per cent Al}) = 1.86 - \frac{2540}{T°K} \qquad (37)$$

A discussion of this line and the solubilities determined by Dardel is presented in the next chapter.

The relative partial molar enthalpy of aluminum in liquid lead over the temperature range and concentration range covered by the author's solubility line is $11.6 \frac{\text{k cal}}{\text{gm mol}}$. The determination of this quantity is summarized in Appendix C.

B. The Bismuth-Base Ternary Studies

There were six bismuth-base ternary systems studied in this investigation. Calcium, strontium, barium, and tin were found to decrease the solubility of aluminum in bismuth at 549°C; palladium and antimony were found to increase it. The results of the experimental studies on these six systems are illustrated graphically in Figures 10 through 15.

It is possible to determine the value of λ_{Al}^{k} (Bi), for each of the third components studied, from the data presented in Figures 10 through 15. The parameter λ_{Al}^{k} (Bi) is defined by:

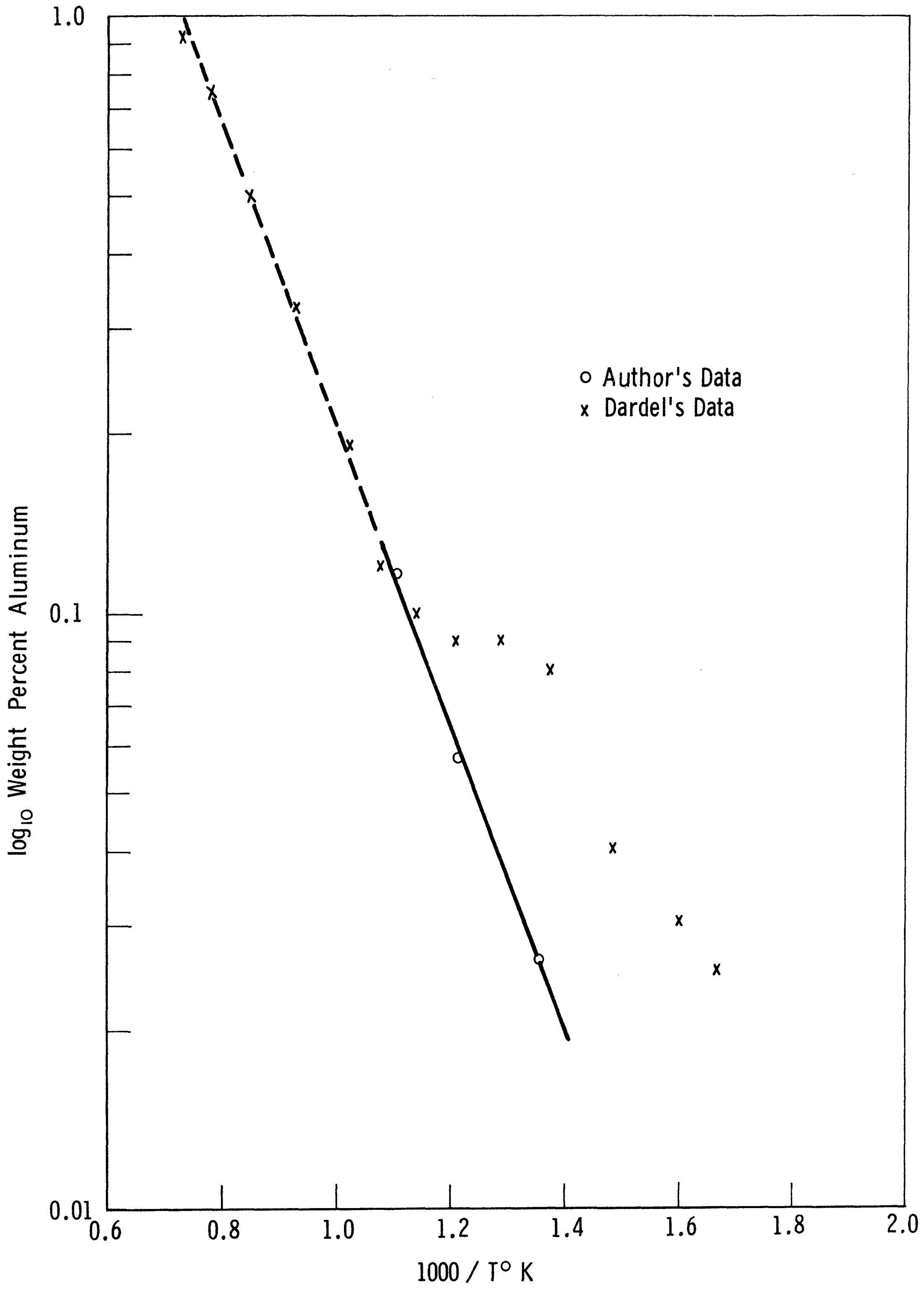


Figure 9. Lead-Aluminum Liquidus $\log_{10}$(wt. per cent Al) versus $\frac{1000}{T°K}$.

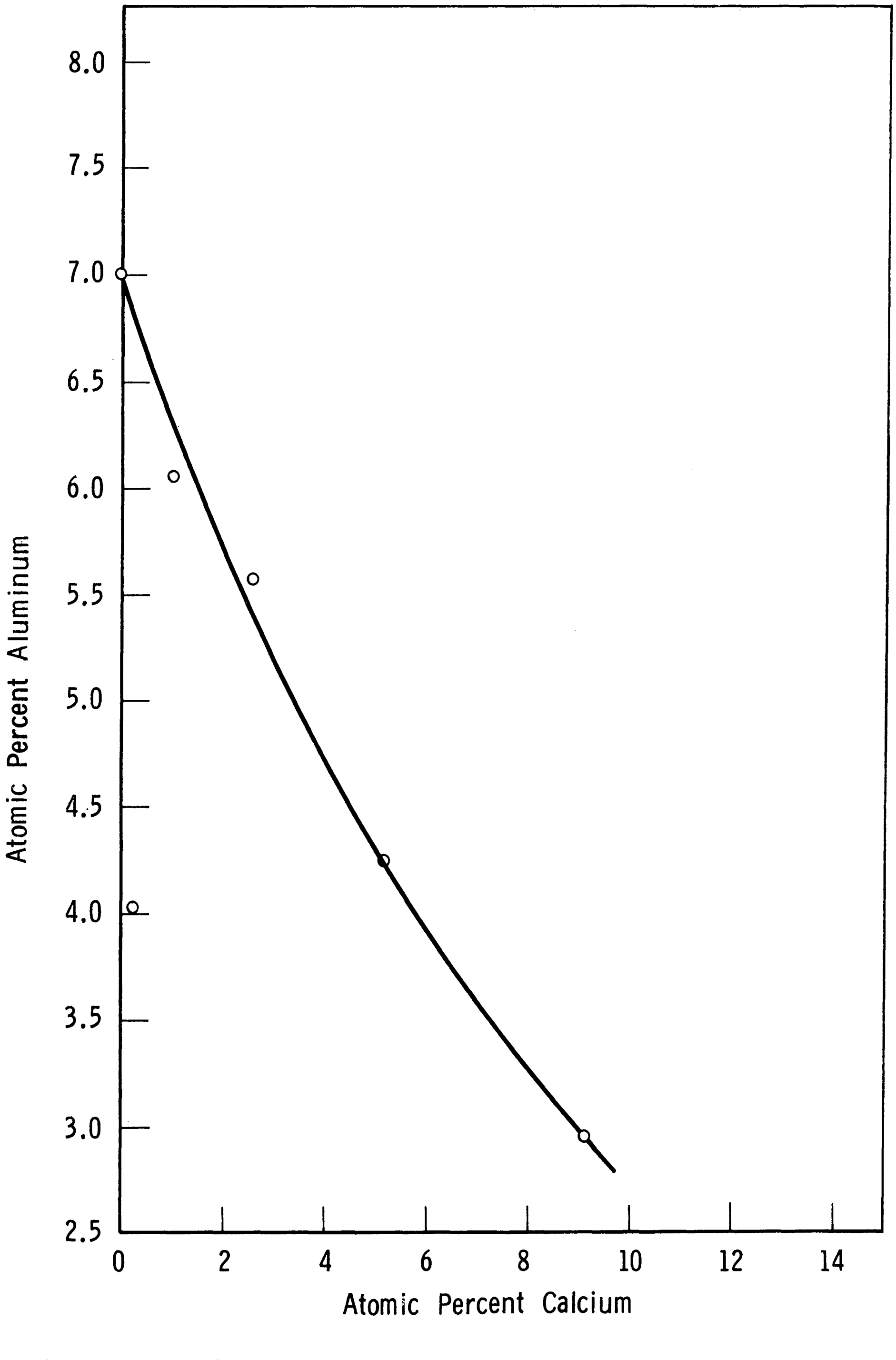


Figure 10. The Bi-Al-Ca System
Atomic Per Cent Aluminum versus Atomic Per Cent Calcium

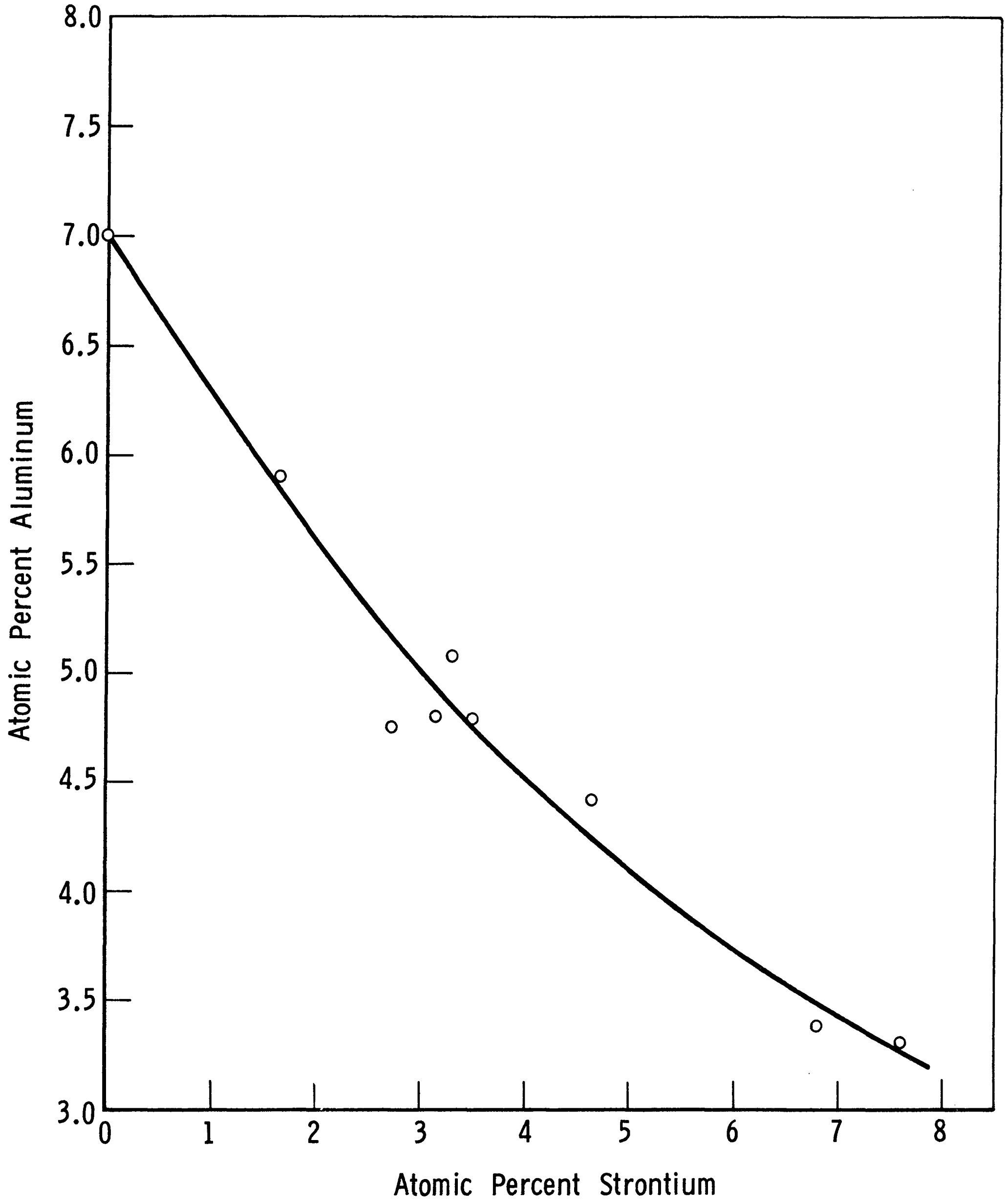


Figure 11. The Bi-Al-Sr System
Atomic Per Cent Aluminum versus Atomic Per Cent Strontium

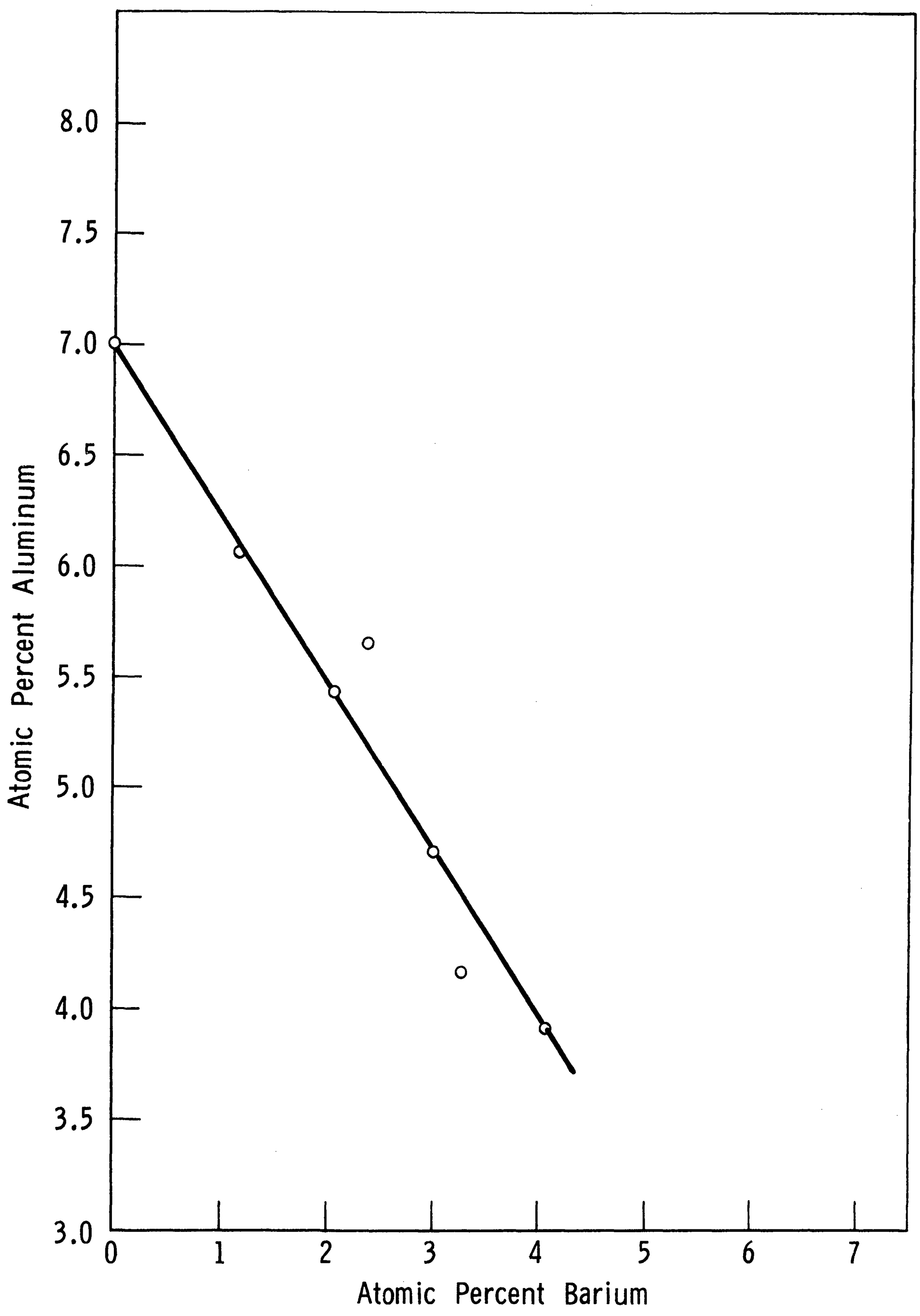


Figure 12. The Bi-Al-Ba System
Atomic Per Cent Aluminum versus Atomic Per Cent Barium

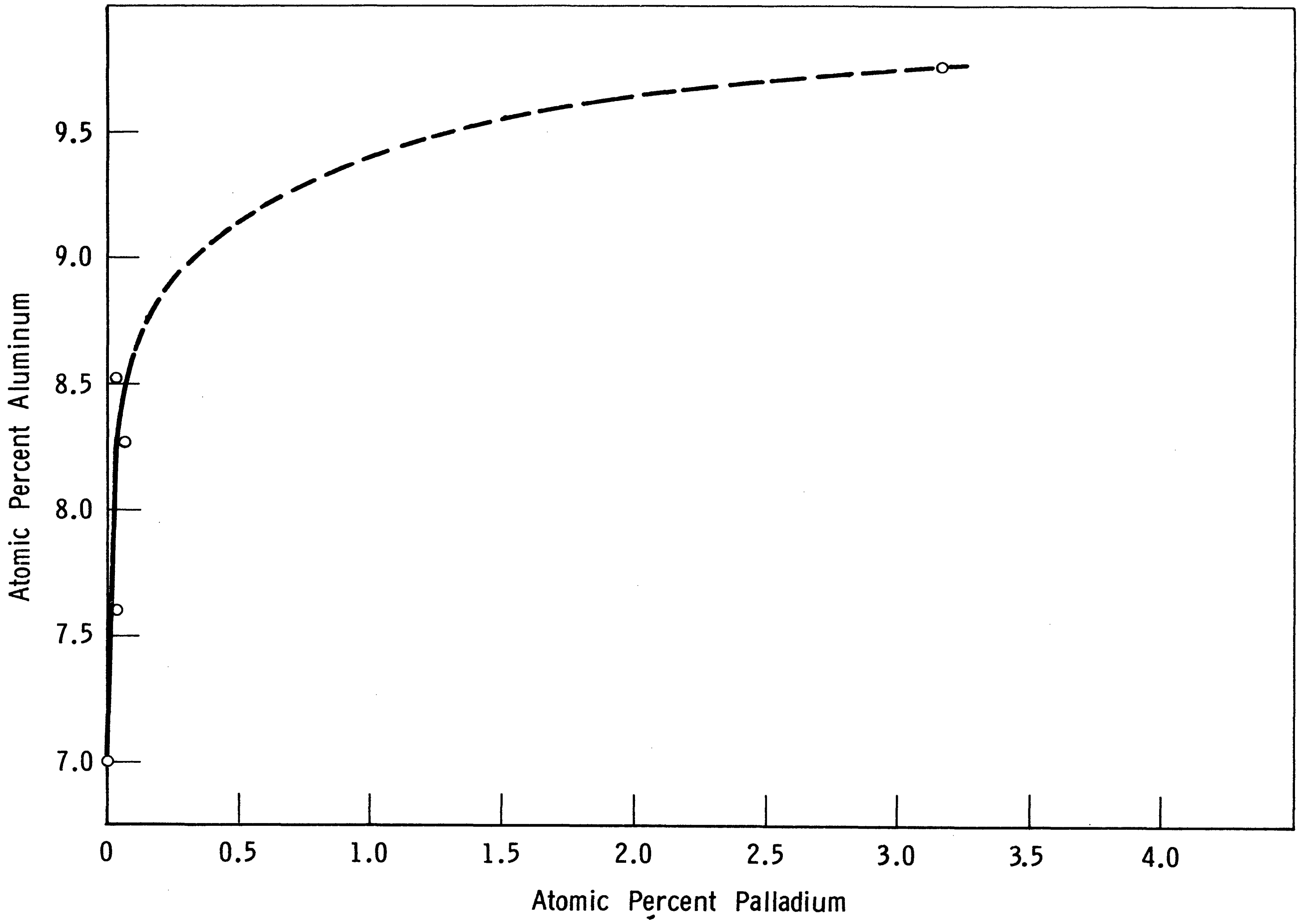


Figure 13. The Bi-Al-Pd System. Atomic Per Cent Aluminum versus Atomic Per Cent Palladium.

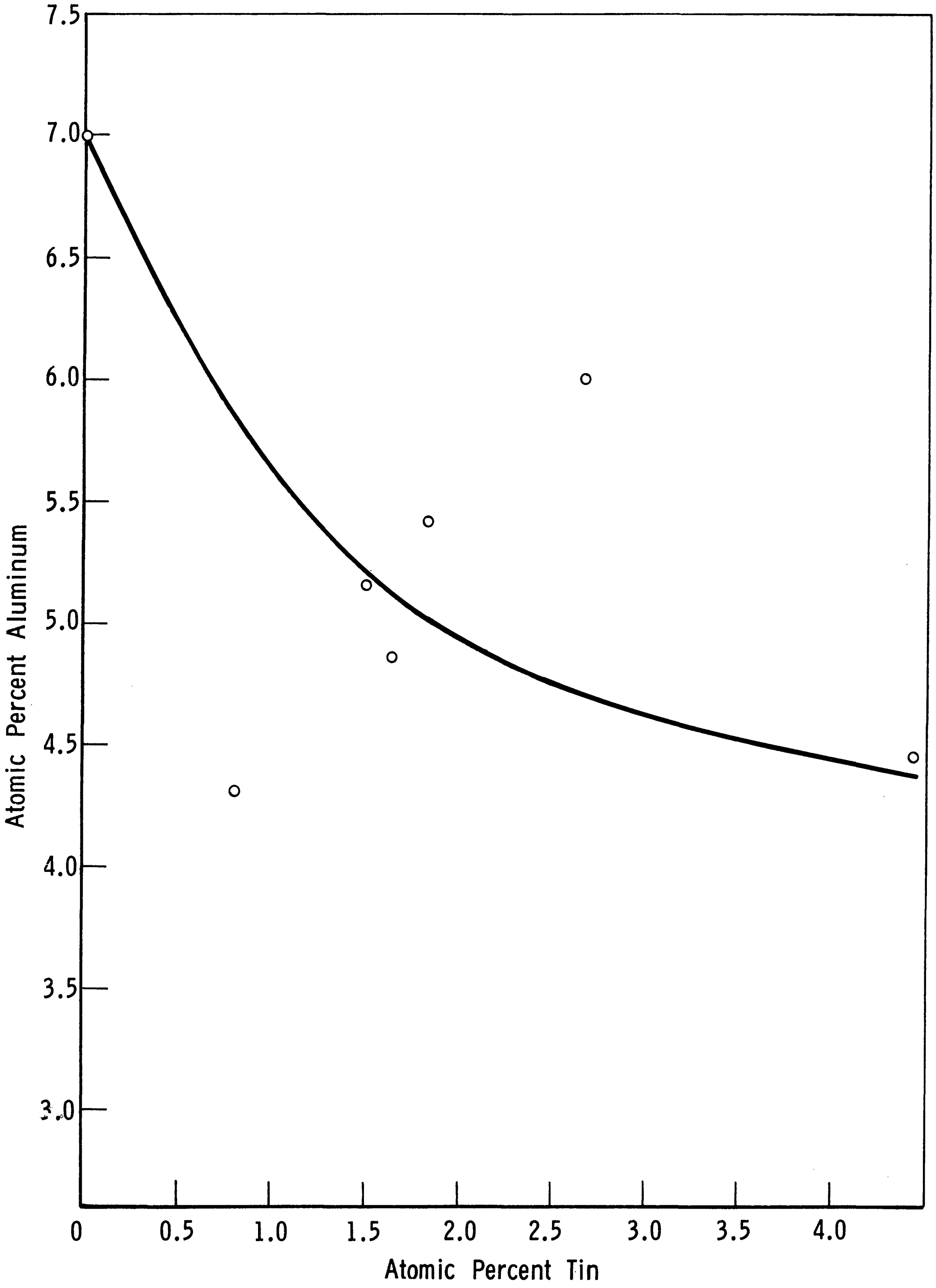


Figure 14. The Bi-Al-Sn System
Atomic Per Cent Aluminum versus Atomic Per Cent Tin

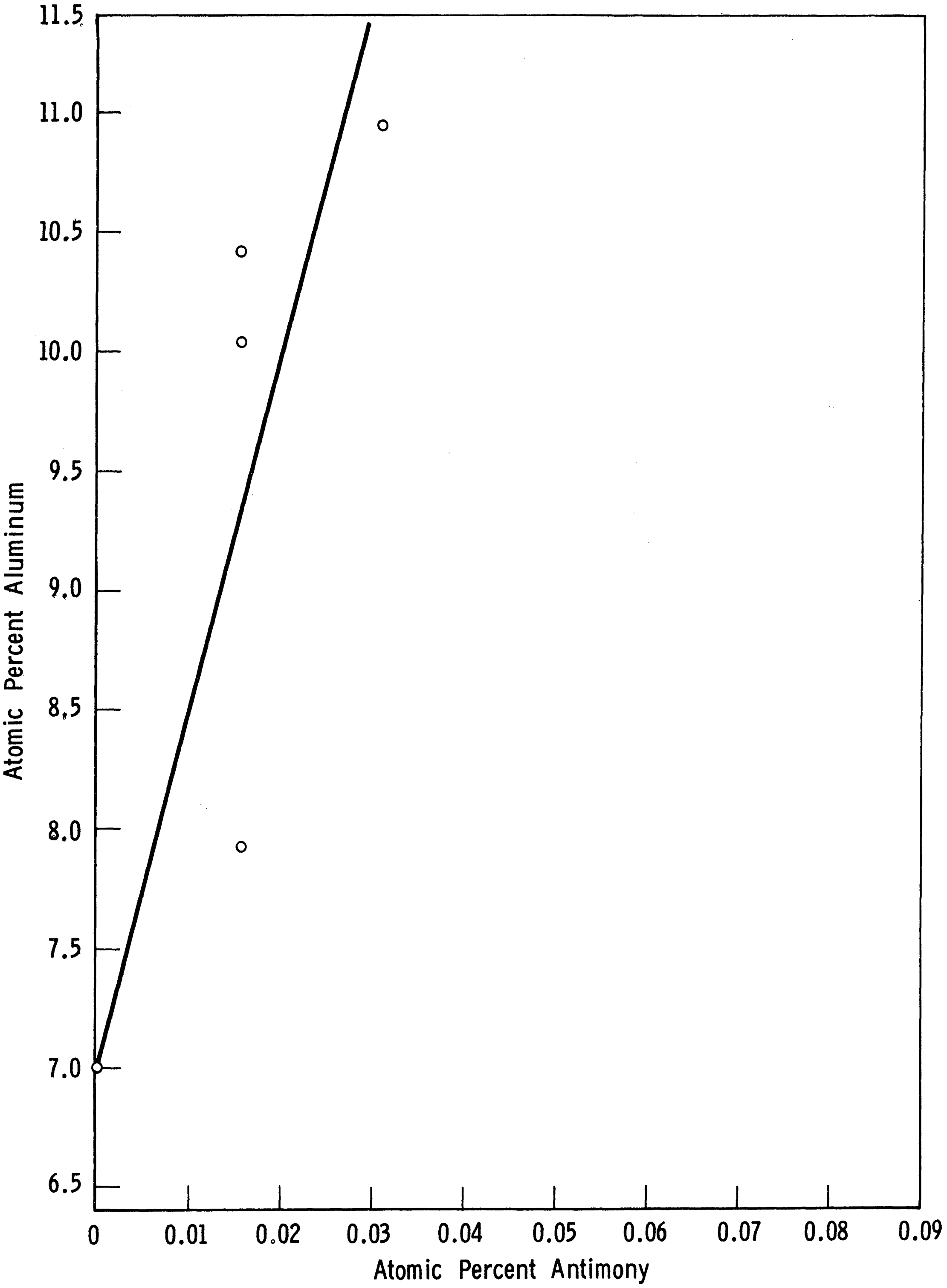


Figure 15. The Bi-Al-Sb System
Atomic Per Cent Aluminum versus Atomic Per Cent Antimony

$$\lambda_{Al}^{k}\ (Bi) = \left[\frac{\partial \ell n \gamma_{Al}}{\partial N_k}\right]_{a_{Al}} = - \left[\frac{\partial \ell n N_{Al}}{\partial N_k}\right]_{a_{Al}}$$

and is subject to the further stipulation that it must be evaluated in the limit as N_{Al} and N_k tend to zero. This was discussed earlier in the "Review of the Literature" chapter. The value of λ_{Al}^{k} (Bi) for each of the third components studied was determined by plotting ℓnN_{Al} versus N_k, and evaluating the slope of this line in the limit as N_k tends to zero. The resulting values of λ_{Al}^{k} (Bi) for each ternary studied are presented in Table I.

TABLE I

Values of λ_{Al}^{k}(Bi) and λ_{Al}^{k}(Pb) For the Third Elements Studied in this Investigation

Element k	λ_{Al}^{k}(Bi)	λ_{Al}^{k}(Pb)
Ca	+ 9.5	- 4.2
Sr	+ 10.4	- 1.1
Ba	+ 14.2	+ 2.4
Pd	- 317	+ 58*
Sn	+ 33.0	- 9.3
Sb	-1550	+ 30*

* These two parameters are only rough estimates, based on just one equilibrium concentration in each of the respective ternary solutions (see Figures 19 and 21).

C. The Lead-Base Ternary Studies

There were six lead-base ternary systems studied in this investigation. Calcium, strontium, and tin were found to increase the solubility of aluminum in liquid lead at 549°C; barium, palladium, and antimony were found to decrease it. The results of the experimental studies on these six systems are illustrated graphically in Figures 16 through 21. As in the cases of the bismuth-base solutions mentioned above, the value of λ_{Al}^{k} (Pb) for each of the third components studied, was determined by plotting $\ell n N_{Al}$ versus N_k, and evaluating the slope of this line in the limit as N_k tends to zero. The resulting values of λ_{Al}^{k} (Pb) for each ternary investigated are presented in Table I. The values of λ_{Al}^{Pd} (Pb) and λ_{Al}^{Sb}(Pb) are only approximate. This is because of the fact that these parameters were determined on the basis of knowing only one ternary equilibrium solution concentration in each of the two cases (see Figures 19 and 21).

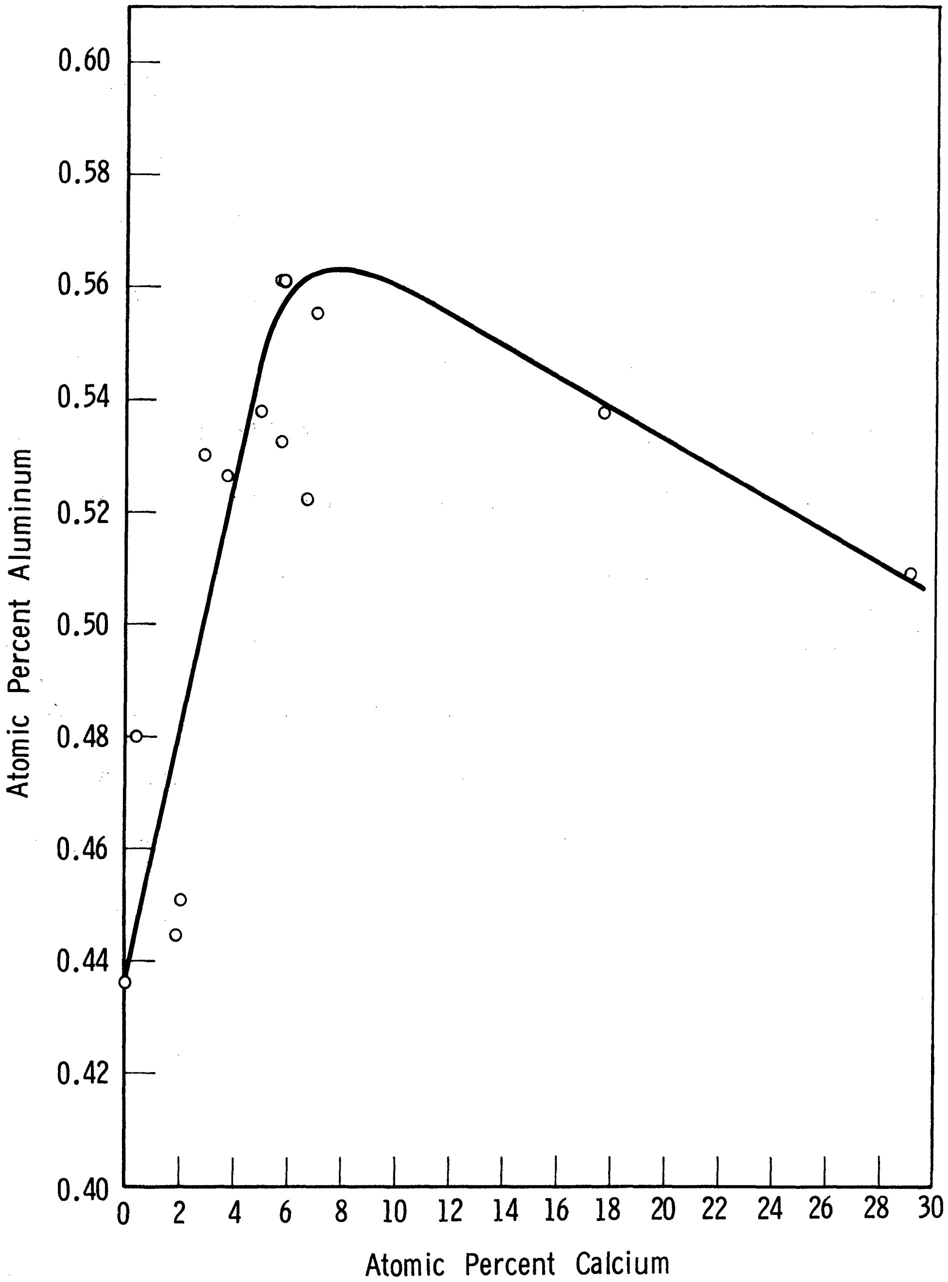


Figure 16. The Pb-Al-Ca System
Atomic Per Cent Aluminum versus Atomic Per Cent Calcium

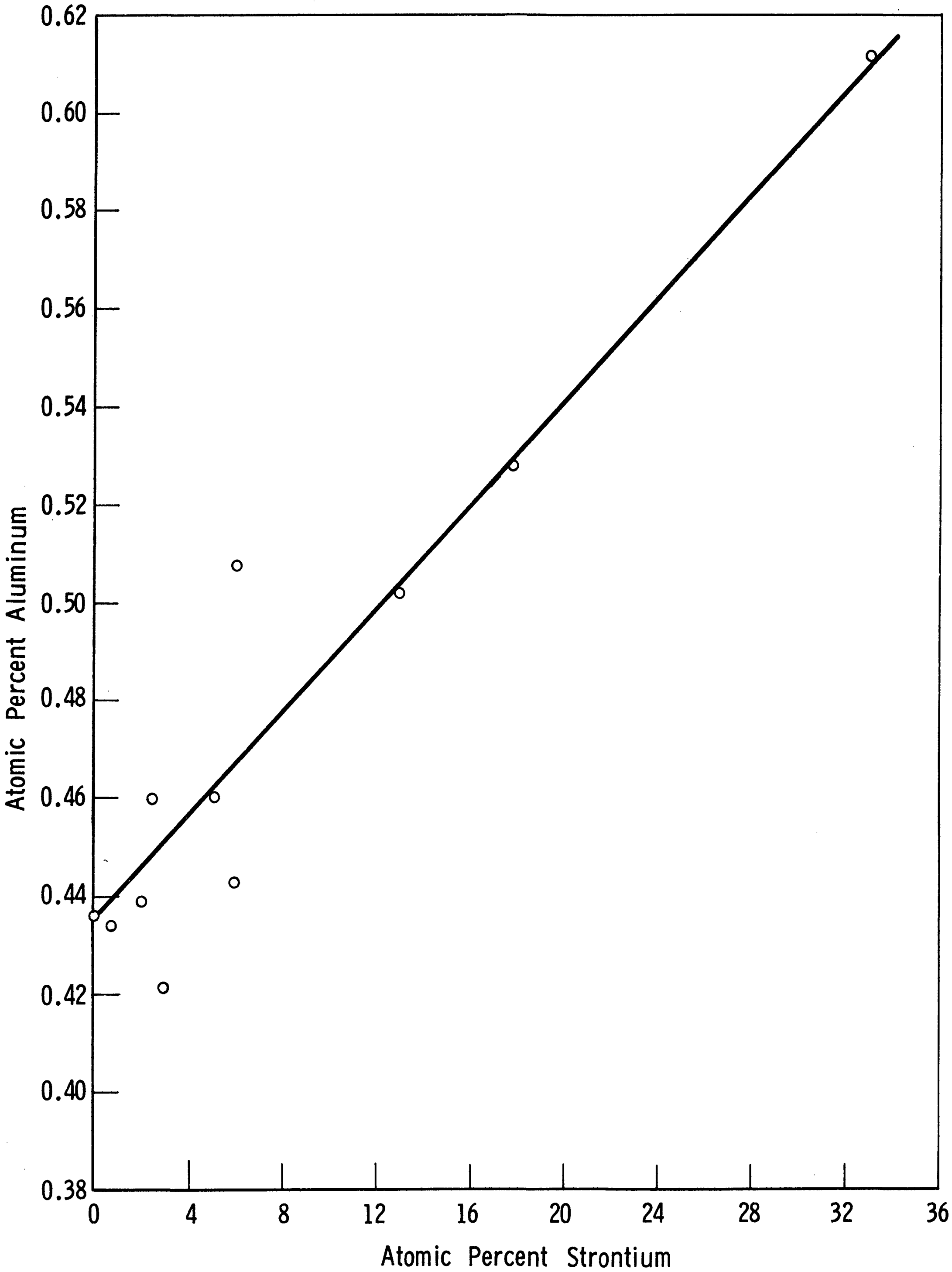
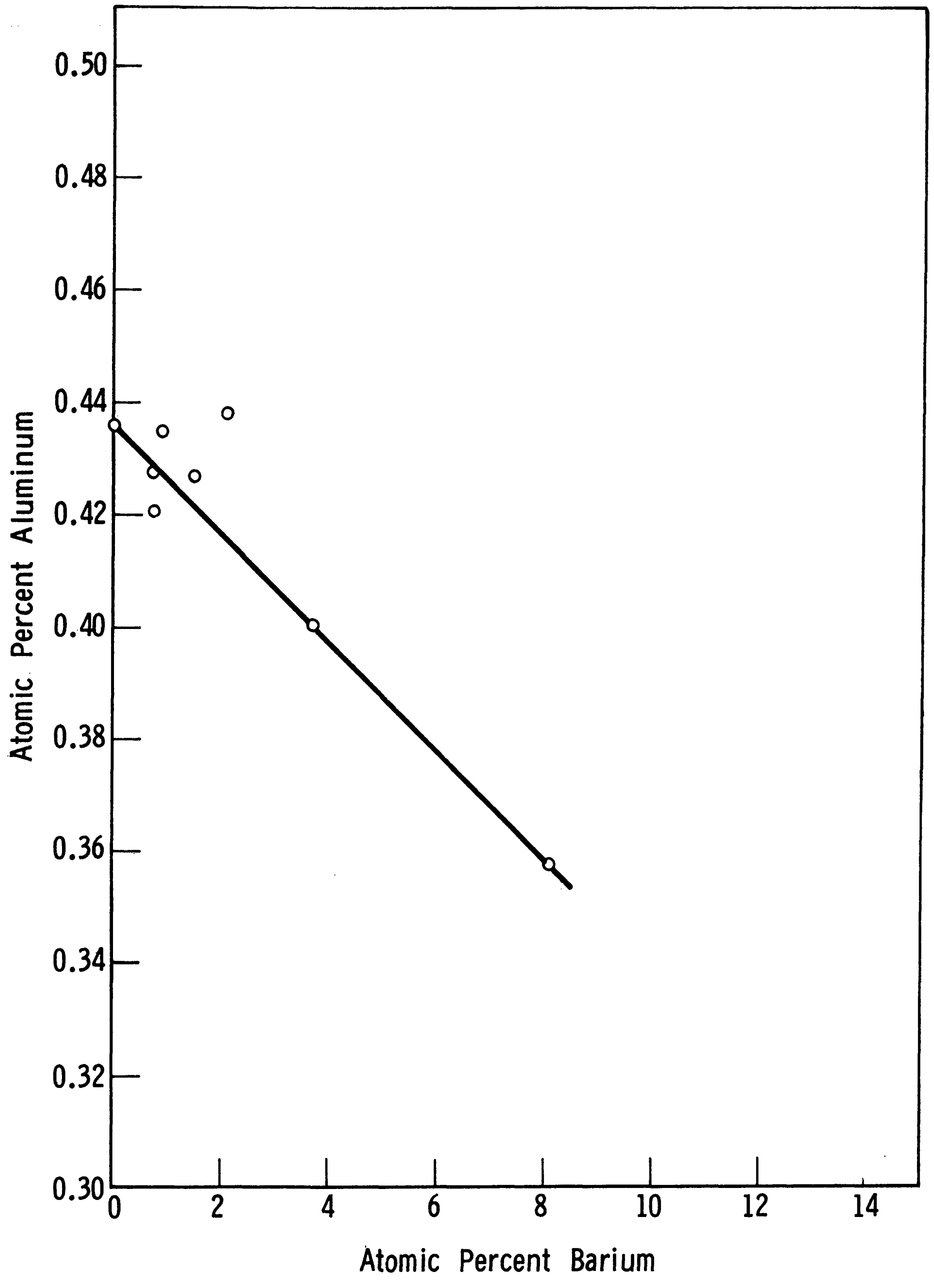


Figure 17. The Pb-Al-Sr System
Atomic Per Cent Aluminum versus Atomic Per Cent Strontium



..gure 18. The Pb-Al-Ba System
Atomic Per Cent Aluminum versus Atomic Per Cent Barium

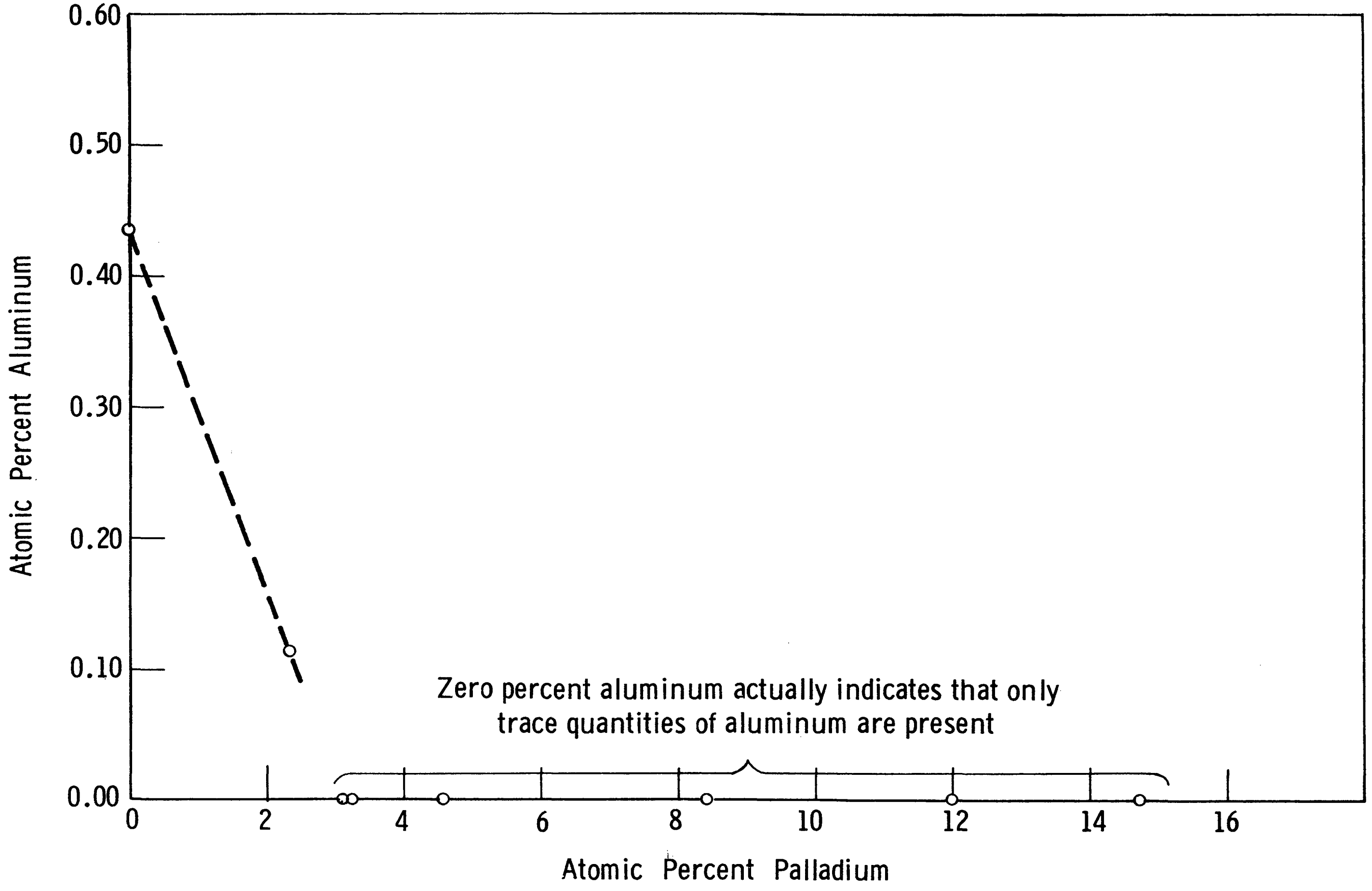


Figure 19. The Pb-Al-Pd System. Atomic Per Cent Aluminum versus Atomic Per Cent Palladium.

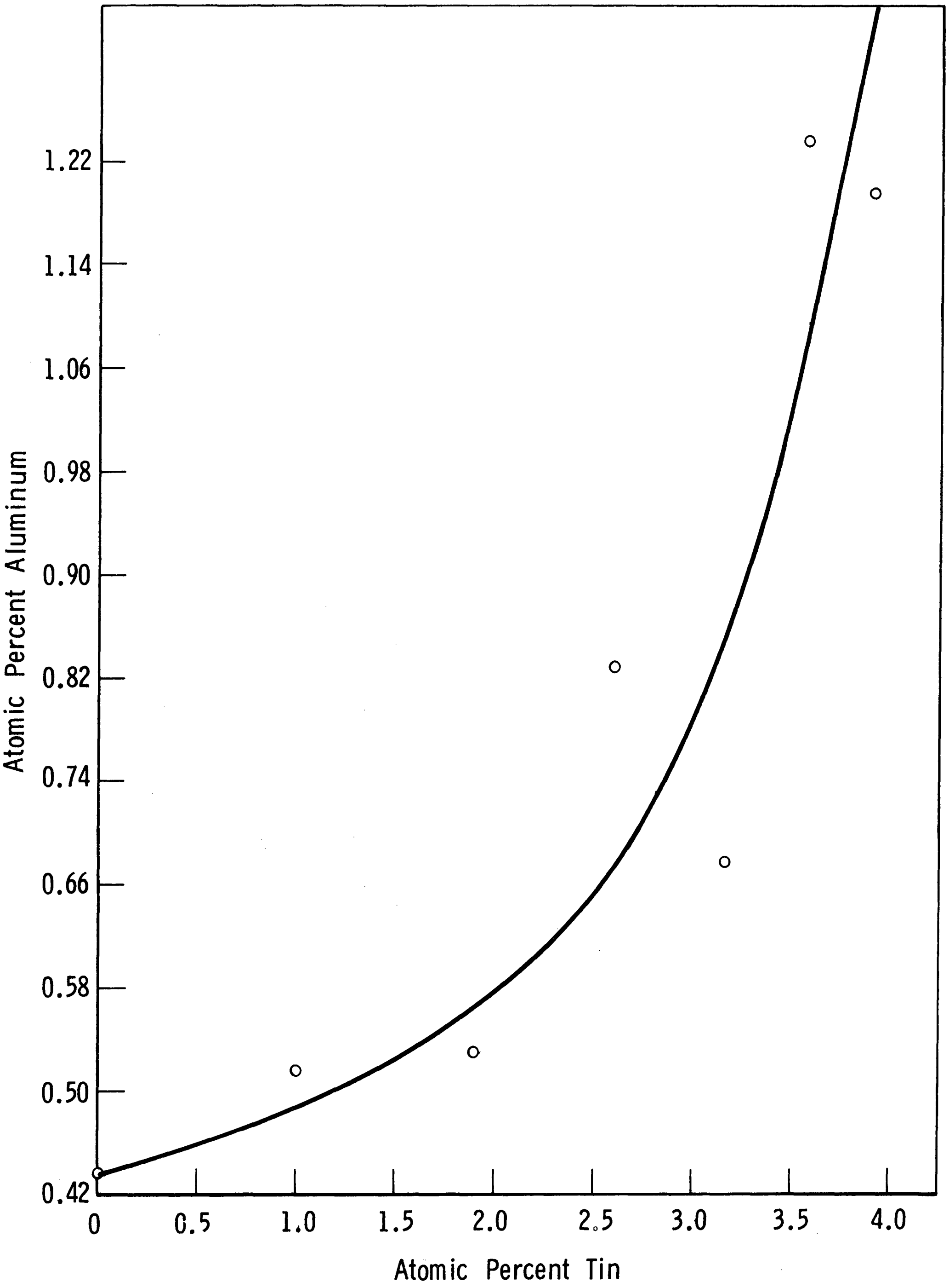


Figure 20. The Pb-Al-Sn-System
Atomic Per Cent Aluminum versus Atomic Per Cent Tin

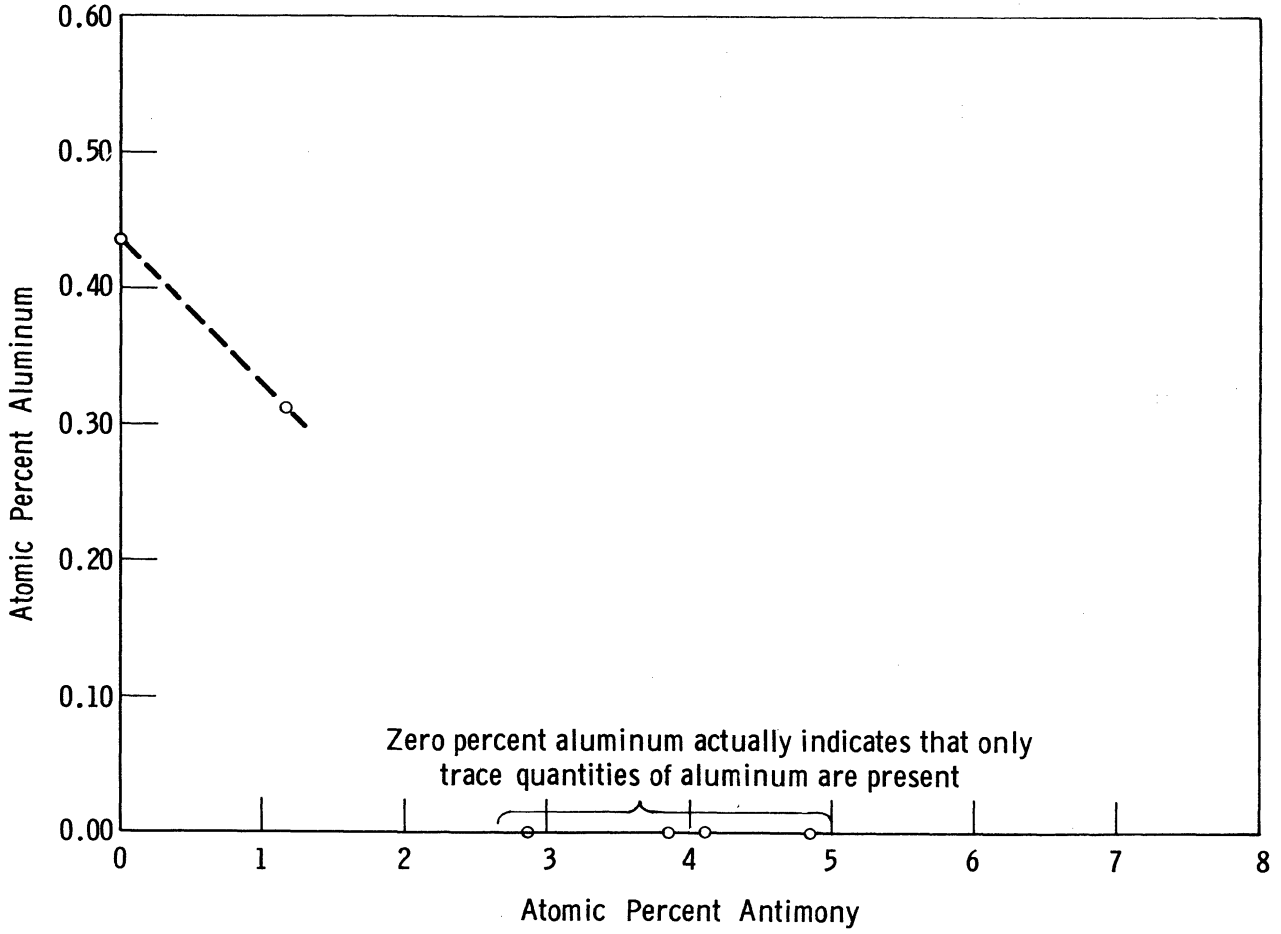


Figure 21. The Pb-Al-Sb System. Atomic Per Cent Aluminum versus Atomic Per Cent Antimony.

V. DISCUSSION

A. Analysis of Theoretical Methods of Predicting Interaction Parameters

At the present time, there are several methods of predicting interaction parameters. Most of these methods were discussed to some extent in the "Review of The Literature". In this chapter some of these theories will be discussed more thoroughly and applied to experimental data which has been published in the literature. Although these theories have been discussed before by other authors, they have not been applied to the volume of data presented here. This data represents all the appropriate ternary data which, to the author's knowledge, is available at the present time in the published literature.

1. Quasi-Chemical Models

The simplest possible model of a condensed system is one in which it is assumed that the total cohesive energy arises from nearest neighbor contacts or "bonds". A fundamental assumption of this theory is that the bond energies do not depend upon the concentration of the solution in which the atoms are found. Alcock and Richardson (1) derived their equation for $\epsilon_i^k(Z)$ by a quasi-chemical approach. Their derivation, which resulted in equation (21), is discussed in the "Review of The Literature".

$$\epsilon_i^k(Z) = \ell n\gamma_{ik} - \ell n\gamma_{kZ} - \ell n\gamma_{iZ} \qquad (21)$$

It was stated earlier that this equation has not been extensively tested. The reason for this is the lack of appropriate data. First of all, there is a relatively small amount of ternary data in the literature. Secondly, although a considerable amount of binary data does exist, only a small portion of this data can be used; in order for a given binary activity coefficient to be of any use in this respect, the two additional activity coefficients of equation (21) must also be available. Even if one is fortunate enough to find an activity coefficient for all three constituent binaries of a given ternary, chances are they will not all be at the same temperature. In their second paper, Alcock and Richardson (2) do compare experimental values of $\epsilon_i^k(Z)$ for seven ternary systems with values of $\epsilon_i^k(Z)$ calculated from equation (21). For six of those particular systems, the values of $\epsilon_i^k(Z)$ calculated from equation (21) differed from the experimental values by factors ranging anywhere from about 1.5 to 5. In the Fe-Al-O system $\epsilon_i^k(Z)$ was in error by a much larger factor. In all seven cases, however, equation (21) gave values of $\epsilon_i^k(Z)$ which were correct in sign.

To the author's knowledge, Alcock and Richardson's equation has not been tested experimentally beyond the seven systems mentioned above. In part (a) of Table II are tabulated the experimental and predicted values of $\epsilon_i^k(Z)$ for four more ternary systems. The predicted values were calculated from equation (21) using data from Hultgren (18) and Wagner (40), and the experimental values were obtained from Dealy and Pehlke (10), except for the Bi-Cd-Sn system. Once again, the agreement is quite good; the experimental and calculated values differ by a factor of less than two in three of the four cases. All four of the calculated values of $\epsilon_i^k(Z)$ are correct in algebraic sign.

In part (b) of Table II are tabulated eight more ternary systems. For each of these systems, an approximate value of $\epsilon_i^k(Z)$ was calculated from equation (21) using data from Hultgren (18) and Wagner (40).

TABLE II

Prediction of Interaction Parameters From Alcock and Richardson's Equation

Solvent Z	Element i	Element k	γ_{ik}	γ_{iZ}	γ_{kZ}	Predicted $\epsilon_i^k(Z)$	Experimental $\epsilon_i^k(Z)$
(a) Quantitative Values (773°K)							
Bi	Cd	Pb	3.3	1.0	0.5	+1.9	+ 1.6
Bi	Cd	Sn	1.7	1.0	1.14	+0.5	+ 0.3*
Pb	Cd	Sn	1.7	3.35	1.0	-0.6	- 2.0
Pb	Cd	Sb	0.22	3.35	1.0	-2.7	- 1.6
(b) Qualitative Values							
						Approximate	
Cd	Hg	Na	0.0014 (648°K)	0.27 (600°K)	0.12 (668°K)	-3	- 6 (623°K)
Pb	Na	Hg	7.2×10^{-6} (648°K)	0.00182 (698°K)	1.14 (597°K)	-6	- 5.2 (673°K)
Hg	Na	Cd	0.12 (668°K)	7.2×10^{-6} (648°K)	0.27 (600°K)	+11	+ 6 (623°K)
Hg	Na	K	3.0 (298°K)	7.2×10^{-6} (648°K)	1.1×10^{-7} (600°K)	+27	+46.5 (?°K)
Hg	K	Tl	1.6×10^{-6} (798°K)	1.1×10^{-7} (600°K)	0.45 (600°K)	+4	+30.8 (?°K)
Hg	Na	Pb	1.8×10^{-3} (698°K)	7.2×10^{-6} (648°K)	6.4 (597°K)	+4	+6 (673°K)
Hg	Na	Tl	0.002 (648°K)	7.2×10^{-6} (648°K)	0.45 (600°K)	+7	+22.1 (?°K)
Na	Hg	Cd	0.27 (600°K)	0.0014 (648°K)	2.82 (668°K)	+4	+4.2 (623°K)

*Data from Mellgren (22). The unstarred experimental values of $\epsilon_i^k(Z)$ are from compilation of Dealy and Pehlke (10).

The binary activity coefficients are from Hultgren (18), and Wagner (40).

In all eight systems, Hultgren's and Wagner's values of the three activity coefficients involved were not all determined at the same temperature. Furthermore, these temperatures differ from the temperatures of the experimental $\epsilon_i^k(Z)$ values. Therefore, they represent only approximately calculated values; to a degree depending upon how strong a function of temperature the activity coefficients involved are. In most cases, the temperatures are on the order of ±50C° different from each other. Considering the fairly large magnitudes of the experimental values of $\epsilon_i^k(Z)$ involved, it was felt that in most cases the variation of the binary activity coefficient values over the small temperature ranges required to bring them all to the same temperature would probably not change the picture significantly. Also, in several of the cases, one of the three activity coefficients predominated to a great extent. At any rate, after making the calculations, it was felt that the results were of enough interest to present here, since the parameters are predicted quite closely in most cases. It is interesting to note that in each of the eight cases there is at least a qualitative agreement between the experimental and calculated values of $\epsilon_i^k(Z)$, and that in most cases the predicted parameter is in the right order of magnitude.

One cannot expect equation (21) to yield extremely accurate values of $\epsilon_i^k(Z)$; there are a great many assumptions involved in its derivation (see "Review of The Literature"). As mentioned above, equation (21) has been applied to seven systems by Alcock and Richardson, and to four more by the author. According to these few results, it appears reasonable to expect Alcock and Richardson's equation to predict a given $\epsilon_i^k(Z)$ to within a factor of about 1.5 or less to about 5 for these types of systems. In cases where the interactions are very strong the accuracy may not be this good. Interaction parameters calculated to even this degree of accuracy could prove to be very useful in many instances. It also appears that one could generally expect that Alcock and Richardson's equation will at least correctly predict the algebraic sign of a given $\epsilon_i^k(Z)$ if the binary data used are reliable.

Another development based on quasi-chemical theory is that due to Wada and Saito (37, 38). This development also is discussed in the "Review of The Literature".

Wada and Saito's equation for a substitutional-substitutional ternary is given by:

$$\epsilon_i^k(Z) = \frac{1}{RT} (W_{ik} - W_{iZ} - W_{kZ}), \qquad (26)$$

where the interchange energy, W_{ik}, is given by:

$$W_{ik} = V^M (\delta_i - \delta_k)^2 - 23060\ \bar{n}\ (E_i - E_k)^2 \qquad (28)$$

The other two interchange energies are given by analagous expressions. In equation (28), V^M represents the molar volume of the i-k binary; δ_i and δ_k are solubility parameters; E_i and E_k are electronegativities; and $\bar{n}$ represents the number of i-k bonds formed per atom. The product $V^M (\delta_i - \delta_k)^2$ is commonly called the Hildebrand factor.

It should probably be noted at this point that equation (26) really is not very different from Alcock and Richardson's equation. In their derivation of equation (21), Alcock and Richardson arrived at the equation:

$$\epsilon_i^k(Z) = \frac{1}{RT} \left[\Delta \bar{H}_{ik} - \Delta \bar{H}_{iZ} - \Delta \bar{H}_{kZ}\right] \qquad (38)$$

In this equation $\Delta \bar{H}_{ik}$, $\Delta \bar{H}_{iZ}$, etc. are the partial heats of solution of element i in element k, i in Z, etc.. In arriving at (21) from (38), it was assumed that the partial molar entropy of solution of i in k was equal to that of i in Z, and that the partial molar entropy of solution of element k in Z was Raoultian. If the interchange energies, W, in equation (26) are replaced by partial heats of solution of the same binaries, then equation (26) is identical to equation (38).

Wada and Saito's equation represents a significant step in the solution of the interaction problem. Although their equation for evaluating $\epsilon_i^k(Z)$ itself is similar to that of Alcock and Richardson's, their method for evaluating the partial heats of solution, or, in their case, the interchange energies, is unique, simple, and can be applied to a vast majority of the elements without further experimentation. Binary molar volumes, solubility parameters, and electronegativities are known for nearly all the chemical elements. Therefore, providing a reasonable value of $\bar{n}$ is known, it is possible to calculate the interchange energy for most any binary pair from equation (28); these energies, in turn, make it possible to calculate $\epsilon_i^k(Z)$ from equation (26). Of course, one would not expect these equations to be extremely precise, because of the nature of their derivations. Chances are, the experimental partial heats of solution in equation (38) are more representative of particular binaries than are the interchange energies of equation (26). Nevertheless, equation (26), in combination with equation (28), allows one to calculate a theoretical value of $\epsilon_i^k(Z)$ in the absence of heat of solution data. Because of this, equation (26) could prove to be particularly advantageous in certain situations, depending upon its ability to yield reasonably accurate values of $\epsilon_i^k(Z)$.

As mentioned in the "Review of The Literature", Wada and Saito (37) applied their equations to several iron-base ternary systems, viz. systems of the type Fe-Cr-X, Fe-Ni-X, Fe-C-X, and Fe-S-X. The agreement between observed and calculated values of $\epsilon_i^k(Z)$ for these systems was fair, in general. In the cases of the Fe-C-X systems, the agreement was quite good. In application of their equation for the self-interaction parameter, which is similar to equation (26), Wada and Saito also met with fair to good success, in most cases. They applied this equation to binaries of iron with Cr, Ni, Al, P, S, Si, and Cu. The two latter binaries showed considerable disagreement with the experimental values. The authors concluded that the deviation of these two systems from regular solution behavior was the primary cause of the disagreement.

In summary, Wada and Saito's equations represent a valuable contribution to the interaction problem. This type of a treatment of the problem is particularly desirable because of its simplicity; it is possible to calculate theoretical values of $\epsilon_i^k(Z)$ for almost any ternary solution, because molar volumes, solubility parameters, and electronegativities are easily obtainable for most of the elements. Of course, there is some degree of uncertainty involved in these parameters, particularly the latter, but such values should become more precise as they are further studied. One of the next logical steps in the investigation of solute interactions would be to attempt to improve on Wada and Saito's development. This could be attempted in either or both of two ways; by attempting to improve the equation for $\epsilon_i^k(Z)$ itself, and/or improving the expression for the interchange energies.

2. Predictions Based On Electronegativities of The Elements In Conjunction With Wagner's Electron Model Of A Liquid Alloy

Whereas the discussion in the preceding section was semi-quantitative (and probably as quantitative as is possible at the present time), the discussion in this section will necessarily be only qualitative. Interaction parameters whose values are published in the literature will be discussed in terms of the electronegativities of the elements involved. More specifically, solute interactions will be related to changes in electron-to-atom ratios which take place in the alloying process, and these changes in electron-to-atom ratios will be evaluated on the basis of the electronegativities of the elements involved. Initially, the electronegativity concept itself will be discussed, inasmuch as a certain amount of ambiguity seems to surround this concept in the literature.

The term "electronegativity", according to Pauling (26), represents the relative attraction of an atom for valence electrons in a covalent bond. Considering an electron-pair bond, for example, if the two atoms involved attract the two electrons to the same extent, then the electronegativity values of the two atoms are taken to be equal, and the bond involved is electrically symmetrical or nonpolar. On the other hand, if one of the atoms attracts the electrons to a greater extent than the other, then the bond will be electrically unsymmetrical or polar. The atom having the greater affinity for electrons is said to have the greater "electronegativity", and does, in fact, have a "partial" negative charge with respect to the other atom. The most familiar values of electronegativity are those derived by Pauling, although other persons have derived electronegativity scales on bases different from that used by Pauling.

Pauling derived his electronegativity values from information on bond energies based on experimental values of heats of formation and dissociation. He considered that in the reaction

$$A_2 + B_2 \longrightarrow 2AB,$$

if the bonds formed are all nonpolar covalent bonds, then the energy of the A-B bond should be exactly the average of the A-A and B-B bond energies. If this were the case, then there would be no heat effect. On the other hand, if the A-B bond energy were greater than the average of the A-A and B-B bond energies, then the reaction should be exothermic. This increase in the A-B bond energy (i.e., above the average of the A-A and B-B bond energies) was attributed to an "ionic character" of the A-B bond, which resulted from a difference in the electronegativities of atoms A and B. This extra "ionic" energy, or the energy in excess of a nonpolar covalent bond, was taken to be a measure of the electronegativity difference between atoms A and B. By determining the corresponding differences for atoms A and C, atoms A and D, etc., Pauling derived his relative scale of electronegativities.

It is apparent from the above discussion that "electronegativity" is not a precisely definable term; therefore its numerical value for a particular element cannot be determined with great precision. In fact, electronegativity should be thought of primarily as a fundamental quality; as a quality which can be and is evaluated quantitatively to an extent great enough to allow a more exact comparison of relative values. It is the relative values of electronegativity that have real meaning. Their absolute values are somewhat arbitrary. The electronegativity of an atom in a molecule is different from the electrode potential of the element, which depends upon the difference in free energy of the element in its standard state and in ionic solution. It is different also from the ionization potential of the atom, and from its electron affinity, although it is related to these properties in a general way (26). Electronegativity values are generally reported to one decimal place only, as this is regarded by most to be the limit of their reliability.

There is a tendency for the electronegativity of a given element to increase with increasing valency of that element. Haissinsky (14) deduced that this increase would be less marked for the metalloid elements and the noble metals. Furthermore, the electronegativity of an element will vary to some extent depending upon the element with which it is combined. In view of an element's increasing electronegativity with increasing valence, perhaps this can be interpreted as resulting from the element's exhibiting of different effective valences upon combination with different elements, at least if the bond is covalent. This variation in electronegativity can be appreciated from the difference in electronegativity values derived from the oxides and bromides as compared with the values obtained from the fluorides and chlorides. The electronic behavior of the transition elements is dependent upon their environment, and on this basis, their electronegativities cannot be represented by single numbers. Other elements whose electronegativity may change with environment include arsenic, antimony, bismuth, lead, mercury, thallium, and tin. There is no satisfactory basis for evaluating the probable variation of electronegativity with environment.

As is implied in the above discussion of electronegativity, the solution of a particular element by a liquid metal alloy involves a transfer of electrons between the solvent and the solute. Thus, upon going into solution, elements which are more typically metallic, and give up their valence electrons more easily than the solvent will tend to do so. On the other hand, elements which are more typically non-metallic than the solvent will tend to gain electrons in the solution process by admitting them into their lower-energy orbitals. Thus, the free electron concentration existing in a particular liquid metal solution may be either increased or decreased by the addition of another element, depending upon the nature of that element.

There have been attempts by various investigators to relate the thermodynamic properties of solutes in alloys to the interactions of free electrons and ions (which are created by these solutes) with their surroundings. Himmler (17) has suggested that the chemical potential, μ_i, of component i in solution can be separated into the chemical potential of its ions and the chemical potential of the electrons, such that

$$\mu_i = \mu_{i(\pm\ \text{ion})} \pm z_i\mu_e \qquad (39)$$

In equation (39), $\mu_{i(\pm\ \text{ion})}$ represents the chemical potential of the ions of element i, μ_e the chemical potential of the electrons, and z_i the net charge on the ions of element i. Whether the sign of the $z_i\mu_e$ term is positive or negative depends upon the net charge on the ion, i.e., upon whether component i loses electrons or gains electrons upon going into solution. Accordingly, if element i loses electrons upon going into solution, the sign is positive, and if it gains electrons, the sign is negative. The effective value of z_i does not have to be an integer. According to equation (39), a change in μ_e will affect the value of μ_i directly, by virtue of the second term in the equation, and it will also affect μ_i indirectly because of the fact that a change in μ_e causes a change in $\mu_{i(\pm\ \mathrm{ion})}$ through ion-electron interactions.

One can also represent the chemical potential, μ_i, of component i in solution as:

$$\mu_i = \mu_i^\circ + RT\ \ell n\ a_i \tag{40}$$

where μ_i° is the chemical potential of component i in its standard state, and a_i is the thermodynamic activity of component i in solution.

By combining equations (39) and (40), one can write:

$$a_i = \exp\left\{\frac{1}{RT}\left[\mu_{i(\pm\ \mathrm{ion})} \pm z_i\mu_e - \mu_i^\circ\right]\right\} \tag{41}$$

where μ_i° is constant at a given temperature (see reference 39).

Assuming that μ_e increases as the ratio of free electrons to atoms, (e/a), in the alloy is increased, and that μ_e decreases when the (e/a) ratio is decreased, there are three cases to consider in regard to changes in free electron concentration as one adds a third component to a solution. The first of these is the case in which both solutes increase the (e/a) ratio (free electron-to-atom ratio) above what it was in the solvent; the second is the case in which both solutes decrease this ratio below what it was in the pure solvent; and the third case is that in which one solute increases it and the other solute decreases it.

Consider individually, in conjunction with equation (41), each of the three cases mentioned above. In each case, assume that changes in μ_i are due primarily to changes in μ_e. In other words, changes in $\mu_{i(\pm\ \mathrm{ion})}$ are neglected. According to Brönsted's principle of specific interaction for electrolytes in aqueous solution, interaction between ions of the same sign is disregarded. The above assumption, then, corresponds roughly to this principle, except that in the single case where the two solutes change the (e/a) ratio in opposite directions, this principle has been carried a little further by neglecting interactions between all ions, even those which are oppositely charged.

The three cases to be considered when one adds a third component to a given binary solution are as follows:

(a) Solutes i and k may both increase the (e/a) ratio. According to equation (41), if element i increases the (e/a) ratio above what existed in the pure solvent, then addition of element k, which also increases this ratio, will increase a_i; or γ_i will increase if a_i is held constant. Therefore, the resulting value of $\lambda_i^k(Z)$ will be positive.

(b) Solutes i and k may both decrease the (e/a) ratio. According to equation (41), if element i decreases the (e/a) ratio below what existed in the pure solvent, then the addition of element k, which also decreases this ratio, will increase a_i; or γ_i will increase, if a_i is held constant. Therefore, the resulting value of $\lambda_i^k(Z)$ will again be positive.

(c) Solutes i and k may change the (e/a) ratio in opposite directions. According to equation (41), if element i increases the (e/a) ratio above what existed in the pure solvent, and element k decreases it, or vice-versa, then a_i will be decreased; or γ_i will be decreased, if a_i is held constant. Therefore, the resulting value of $\lambda_i^k(Z)$ will be negative.

It can be shown that if the quantity $\left[\frac{\partial a_i}{\partial N_i}\right]_{N_k = 0}$ is positive, then the conclusion drawn in each of these three cases apply to the prediction of Wagner's parameter, $\epsilon_i^k(Z)$, as well as to the prediction of $\lambda_i^k(Z)$. Also, it is interesting to note at this point that the conclusions drawn above predict that $\lambda_i^k(Z) = \lambda_k^i(Z)$, or $\epsilon_i^k(Z) = \epsilon_k^i(Z)$ for all three cases. This is a statement of Wagner's reciprocity relationship.

It should probably be emphasized once more that in arriving at the conclusions in (a), (b), and (c) above, changes in $\mu_{i(\pm\ \mathrm{ion})}$ were considered to have no direct effect upon μ_i. Just how restrictive an assumption this may be depends, no doubt, upon the ternary system under consideration.

Consider the electronegativity of the elements as a measure of their electron affinity. This is not strictly true, but one might expect a rough parallel between these two quantities. Unfortunately, reliable values of the electron affinity of most elements are unknown; hence the above assumption. If one adds a solute to a solvent of higher electronegativity, he would expect the (e/a) ratio in the binary to be greater than it was in the original pure solvent. On the other hand, if he adds a solute of higher electronegativity to a solvent of lesser electronegativity, he would expect the (e/a) ratio in the binary to be less than it was in the pure solvent. Based on this line of reasoning and the conclusions drawn in (a), (b), and (c) above, a qualitative prediction of $\epsilon_i^k(Z)$ or $\lambda_i^k(Z)$ was made for each of the 80 ternary systems presented in Table IV. In most of these systems, numerical values of $\epsilon_i^k(Z)$ were reported, but in a few cases, only qualitative observations were available. The data presented were taken from compilations by Balzhiser (3), Chipman (6), Dealy and Pehlke (10), Ohtani and Gokcen (24), Weinstein (43), Sponseller (32), and Wagner (39). The predictions made in Table IV are based on the hypothesis that $\epsilon_i^k(Z)$ or $\lambda_i^k(Z)$ will be positive if elements i and k change the (e/a) ratio in the same direction, and negative if they change it in opposite directions. Changes in the (e/a) ratio were assessed from the relative electronegativities (Table III), as described previously. The electronegativities of lead and cadmium (about which there seems to be some dispute) were taken to be 1.6, and 1.4, respectively. There were several other "rules" which were followed in making the predictions contained in Table IV. No prediction was made unless the solute and solvent electronegativities differed by at least ±0.1 electronegativity unit, because this is thought to be about the limit of their reliability. This rule was also followed when dealing with elements displaying more than one valence, and therefore more than one electronegativity. In other words, if any of the multiple values of electronegativity exhibited by one element were less than ±0.1 electronegativity unit different from the solute or solvent, as the case may be, no prediction was attempted. Interaction parameters having a value of zero are not included in Table IV, because the hypothesis used in making the predictions is not really sensitive enough to predict zero values of the interaction parameter.

Of the 80 systems presented in Table IV the qualitative prediction of the interaction parameter is correct in 65 cases, or over 81 per cent of the time. It is interesting to note that of the 15 erroneous predictions made, 9 of them are involved with two particular elements. Thus, 5 out of 8 parameters involving aluminum as a solute are in error, and 4 out of 12 parameters involving oxygen are in error.

TABLE III

Table of Electronegativities

Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb			Ib	IIb	IIIa	IVa	Va	VIa
Li													C	N	O
1.0P 1.0G													2.5P	3.0P	3.5P
Na	Mg											Al	Si	P	S
0.9P 0.9G	1.2P 1.2G											1.5P 1.5W 1.5G 1.5K	1.8P 1.8W 1.8K	2.1P 2.0W 2.1K	2.5P 2.5W 2.5K
K	Ca		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
0.8P 0.8G	1.0P 1.0G		1.5P 1.5W 1.6K	1.6P 1.7W 1.9K	1.6P 1.7W 1.4K	1.5P 1.7W 1.4K	1.8P 1.9P 2.0W 1.7K	1.8P 2.1W 1.7K	1.8P 2.1W 1.8K	1.9P 2.0P 1.9W 1.8K 2.0K	1.6P 1.6W 1.5K	1.6P 1.6W 1.5K	1.8P 1.8W 1.8K	2.0P 1.9W 2.0K	2.4P
Rb	Sr		Zr	Nb	Mo				Pd	Ag	Cd	In	Sn	Sb	Te
0.8P 0.8G	1.0P 1.0G		1.4P 1.4W 1.5K	1.6P 1.7W 1.7K	1.8P 1.8W 1.6K				2.2P 2.0K	1.9P 1.9W 1.8K	1.7P 1.4W 1.1K	1.7P 1.5K	1.8P 1.9P 1.7W 1.7K 1.8K 1.7G	1.9P 1.8K 2.1K 1.8G	2.1P
Cs	Ba			Ta	W				Pt	Au	Hg	Tl	Pb	Bi	
0.7P 0.7G	0.9P 0.9G			1.5P 1.3K	1.7P 2.0W 1.6K				2.2P 2.2W 2.1K	2.4P 2.1W 2.3K	1.9P 1.8K 1.0G	1.8P 1.5K 1.9K	1.8P 1.6K 1.5W 1.5G	1.9P 1.8K 1.8G	

P, Pauling (26); W, Wada and Saito (37); K, Kleppa (20); G, Gordy-Thomas (12).

The values given in this table refer to the common oxidation states of the elements. For some elements, variation of electronegativity with oxidation number is observed, the higher positive valence corresponding to the more electronegative state.

TABLE IV

Qualitative Prediction of $\lambda_i^k(Z)$ and $\epsilon_i^k(Z)$ from Electronegativities

Solvent Z	Element i	Element k	E(i)	E(k)	Predicted Sign of $\lambda_i^k(Z)$	Experimental $\lambda_i^k(Z)$	Temp., °C
Iron E=1.8,1.9	Carbon	P	2.5	2.1	+	+4.6	1600°
	"	Mn	"	1.5	-	-0.5	"

Solvent Z	Element i	Element k	E(i)	E(k)	Predicted Sign of $\epsilon_i^k(Z)$	Experimental $\epsilon_i^k(Z)$	Temp., °C
Mercury E=1.9	Tl	Li	1.8	1.0	+	+0.3	25°
	"	Na	"	0.9	+	+2.6	"
	"	K	"	0.8	+	+6.9	"
Aluminum E=1.5	H	Cu	2.1	1.9,2.0	+	+4,+39	1000°, 700°
	H	Si	2.1	1.8	+	+2,+11	1000°, 700°
Antimony E=1.9	Cd	Pb	1.4	1.6	+	+2.8	500°
Bismuth E=1.9	Cd	Pb	1.4	1.6	+	+1.62	500°
Cadmium E=1.4	Bi	Pb	1.9	1.6	+ *	-3.2	500°
	Hg	Na	1.9	0.9	-	-6.0	350°
	Pb	Sn	1.8	1.8,1.9	+	+2.9	500°
Cobalt E=1.8	Cr	N	1.6	3.0	-	-19.5	1600°
	N	V	3.0	1.6	-	-72	"
	S	Cu	2.5	1.9,2.0	+ *	-4	1500°
Copper E=1.9,2.0	S	Au	2.5	2.4	+	+6.9	1115°
	S	Co	2.5	1.8	-	-4.8	1300°
	S	Ni	"	1.8	-	-6.6	"
	S	Pt	"	2.2	+	+9.2	1200°
	S	Si	"	1.8	- *	+6.9	"
Lead E=1.6	Bi	Cd	1.9	1.4	-	-0.9	500°
	Cd	Sb	1.4	1.9	-	-1.6	"
	Hg	Na	1.9	0.9	-	-5.3	400°
Mercury E=1.9	Cd	Na	1.4	0.9	+	+6.0	350°
	K	Na	0.8	0.9	+	+46.5	?
	K	Tl	0.8	1.8	+	+30.8	?
	Li	Tl	1.0	1.8	+	+17.5	?
	Na	Pb	0.9	1.6	+	+6.0	400°
	Na	Tl	0.9	1.8	+	+22.1	?
Nickel E=1.8	Cr	N	1.6	3.0	-	-23.6	1600°
Sodium E=0.9	Cd	Hg	1.4	1.9	+	+4.2	350°
Tin E=1.8,1.9	Cd	Zn	1.4	1.6	+ *	-1.7	700°

Solvent Z	Element i	Element k	E(i)	E(k)	Predicted Sign of $\epsilon_i^k(Z)$	Experimental $\epsilon_i^k(Z)$	Temp., °C
Iron E=1.8,1.9	N	Sb	3.0	>1.9	+	+0.9	1600°
	"	P	3.0	2.1	+	+5.1	1600°
	"	As	"	2.0	+	+1.8	"
	"	C	"	2.5	+	+13.0	"
	"	O	"	3.5	+	+5.0	"
	"	S	"	2.5	+	+1.3	"
	"	Cr	"	1.6	-	-4.5	"
	"	W	"	1.7	-	-0.2	"
	"	V	"	1.6	-	-10	"
	"	Cb	"	1.6	-	-6.7	"
	"	Ta	"	1.5	-	-3.4	"
	"	Al	"	1.5	- *	+0.3	"
	"	Mn	"	1.5	-	-2.0	"
	"	Ti	"	1.5	-	-63	"
Iron E=1.8,1.9	Carbon	Cr	2.5	1.6	-	-2.4	1600°
	"	W	"	1.7	-	-0.3	"
	"	Cb	"	1.6	-	-6	"
	"	H	"	2.1	+	+1011	"
	"	V	"	1.6	-	-3.8	"
	"	S	"	2.5	+	+9.1	"
Iron E=1.8,1.9	Aluminum	C	1.5	2.5	- *	+10.7	1600°
	"	O	"	3.5	-	-1971	"
	"	S	"	2.5	- *	+4.9	"
Iron E=1.8,1.9	Hydrogen	Al	2.1	1.5	- *	+1.5	1600°
	"	C	"	2.5	+	+85	"
	"	Cb	"	1.6	-	-0.4	"
	"	Mn	"	1.5	-	-0.3	"
	"	Cr	"	1.6	-	-0.5	"
	"	Ta	"	1.5	-	-2.0	"
	"	S	"	2.5	+	+1.1	"
	"	Ti	"	1.5	-	-8.1	"
Iron E=1.8,1.9	Oxygen	Au	3.5	2.4	+ *	-0.4	1600°
	"	C	"	2.5	+ *	-13	"
	"	Cr	"	1.6	-	-5.4	"
	"	W	"	1.7	- *	+0.8	"
	"	P	"	2.1	+	+7.0	"
	"	Pt	"	2.2	+	+0.4	"
	"	S	"	2.5	+ *	-9.1	"
	"	Ti	"	1.5	-	-18.7	"
	"	V	"	1.6	-	-27.1	"
Iron E=1.8,1.9	Sulfur	Cr	2.5	1.6	-	-2.2	1600°
	"	Mn	"	1.5	-	-2.5	"
	"	P	"	2.1	+	+4.5	"
Iron E=1.8,1.9	Calcium	Al	1.0	1.5	+ *	-7.5	1608°
	"	Au	"	2.4	- *	+	"
	"	C	"	2.5	-	-15.5	"
Bismuth E=1.9	Uranium	Pd	1.7	2.2	-	-4.8	800°
	"	Cu	"	1.9,2.0	- *	+11.0	600°

For explanation of table, see top of next page.

(a) All electronegativities, except for Pb and Cd, are Pauling's.

(b) For the hypotheses followed in making these predictions, see text of this section of thesis.

(c) No zero values of $\lambda_i^k(Z)$ or $\epsilon_i^k(Z)$ included; no self-interaction parameters included.

(d) All experimental values of $\epsilon_i^k(Z)$ are from the following: Chipman (6), Dealy and Pehlke (10), Ohtani and Gokcen (24), Wagner (39), Weinstein (43), Sponseller (32), and Balzhiser (3).

* Indicates disagreement between experiment and predicted values.

Consider the i-k-Z ternary solution and its two parameters $\epsilon_i^k(Z)$ and $\epsilon_k^i(Z)$, where element Z is the solvent. If one also considers a system consisting of the same three elements, but having element k as the solvent, what will be the relation of $\epsilon_Z^i(k)$ and $\epsilon_i^Z(k)$ to $\epsilon_i^k(Z)$ and $\epsilon_k^i(Z)$? Similary, if element i is the solvent, what relation will $\epsilon_Z^k(i)$ and $\epsilon_k^Z(i)$ have to the four other parameters? According to the hypotheses formulated earlier in this section, if $\epsilon_i^k(Z)$ is negative, then these conclusions follow: $\epsilon_k^i(Z)$ is also negative (Wagner's reciprocity relationship); $\epsilon_Z^k(i)$, $\epsilon_k^Z(i)$, $\epsilon_Z^i(k)$, and $\epsilon_i^Z(k)$ should all be positive. On the other hand, if $\epsilon_i^k(Z)$ is positive, then the situation is a little more complicated. Careful consideration will show that in this case there are four circumstances to consider: (1) If $E(Z)>E(i)>E(k)$, where E represents electronegativity, then $\epsilon_i^k(Z)$, $\epsilon_k^i(Z)$, $\epsilon_i^Z(k)$, and $\epsilon_Z^i(k)$ will all be positive, and $\epsilon_Z^k(i)$ and $\epsilon_k^Z(i)$ will both be negative; (2) if $E(k)>E(i)>E(Z)$, then the same conclusions drawn in (1) result; (3) if $E(Z)>E(k)>E(i)$, then $\epsilon_i^k(Z)$, $\epsilon_k^i(Z)$, $\epsilon_Z^k(i)$, and $\epsilon_k^Z(i)$ will all be positive, and $\epsilon_Z^i(k)$ and $\epsilon_i^Z(k)$ will both be negative; (4) if $E(i) >$

E(k)>E(Z), then the same conclusions drawn in (3) result. There is only a limited amount of appropriate data available to investigate these conclusions. What data are available are presented in Table V. These data have all been presented previously in Table IV, but are presented by themselves in Table V because it is interesting to observe that the hypotheses presented earlier predict a good share of the changes in sign from parameter to parameter among these related systems for which data are available. According to the hypotheses, one would predict that the two parameters missing from Table V, $\epsilon_{Pb}^{Sb}(Cd)$ and $\epsilon_{Pb}^{Hg}(Na)$, would be negative and positive, respectively. Unfortunately, data on these parameters are unavailable.

TABLE V

Table of Related Interaction Parameters

(* Incorrect predictions)

$\epsilon_i^k(Z)$	E(k)	E(i)	E(Z)	Predicted Sign of $\epsilon_i^k(Z)$	Experimental Value of $\epsilon_i^k(Z)$
$\epsilon_{Pb}^{Cd}(Sb)$	1.7	1.6	1.9	+	+2.8
$\epsilon_{Cd}^{Sb}(Pb)$	1.9	1.7	1.6	+ *	-1.6
$\epsilon_{Hg}^{Na}(Cd)$	0.9	1.9	1.7	-	-6
$\epsilon_{Na}^{Cd}(Hg)$	1.7	0.9	1.9	+	+6
$\epsilon_{Hg}^{Cd}(Na)$	1.7	1.9	0.9	+	+4.2
$\epsilon_{Pb}^{Cd}(Bi)$	1.7	1.6	1.9	+	+1.6
$\epsilon_{Pb}^{Bi}(Cd)$	1.9	1.6	1.7	-	-3.2
$\epsilon_{Bi}^{Cd}(Pb)$	1.7	1.9	1.6	+ *	-0.9
$\epsilon_{Na}^{Hg}(Pb)$	1.9	0.9	1.6	-	-5.3
$\epsilon_{Pb}^{Na}(Hg)$	0.9	1.6	1.9	+	+6

There are other interaction parameters for ternary systems reported in the literature which are not presented in Table IV. The reason they are not presented is that for these particular systems, the electronegativity of either element i or element k was so close to that of solvent Z that a prediction could not be made. Since electronegativities are not precisely determinable in the first place, the comparison of two values which are closer together than about 0.1 electronegativity unit probably has no meaning. The ternary systems falling into this category, and having iron as a solvent are presented in Table VI. It should be noted that in this table element i has an electronegativity considerably different from that of iron, while the electronegativity of element k is essentially the same as that of iron, as near as one can tell. Accordingly, qualitative predictions of $\epsilon_i^k(Z)$ are made on two different bases in Table VI. First, a prediction is made on the assumption that $E(k) > E(Fe)$, and second, a prediction is made on the opposite assumption. It can be seen from Table VI that, except for copper, one assumption or the other for any given element k gave a great majority of correct predictions, rather than an approximately equal number of correct and erroneous predictions. In fact, in two out of the five elements investigated, one assumption made 100 per cent of the predictions correct, while the opposite, of course, predicted them all wrong. According to this table, it appears that Si, Ni, Co and probably Cu are more electronegative than iron, and Mo is less electronegative. This certainly is not unreasonable, judging from the relative positions of these elements in the periodic table. It is felt that the information contained in Table VI, because of the facts outlined above, is a valid addition to Table IV.

TABLE VI

Qualitative Prediction of $\epsilon_i^k(Z)$ From Electronegativities

(Borderline Cases)

Solvent: Iron at 1600°C

Element k	Element i	E(k)	E(i)	Experimental $\epsilon_i^k(Z)$	Predicted $\epsilon_i^k(Z)$	
					Assuming E(k)>E(Fe)	Assuming E(k)<E(Fe)
Si	Ca	1.8	1.0	-10.5	-	opposite
"	C	"	2.5	+3.7	+	"
"	N	"	3.0	+4.7	+	"
"	Al	"	1.5	+6.0	- *	"
"	H	"	2.1	+2.7	+	"
"	O	"	3.5	-19.9	+ *	"
"	S	"	2.5	+6.6	+	"
"	P	"	2.1	+8.6	+	"
Cu	N	1.9, 2.0	3.0	+0.9	+	opposite
"	C	"	2.5	+1.6	+	"
"	O	"	3.5	-0.9	+ *	"
"	S	"	2.5	-1.2	+ *	"
"	H	"	2.1	+0.13	+	"
Ni	Ca	1.8	1.0	-10.5	-	opposite
"	N	"	3.0	+1.0	+	"
"	C	"	2.5	+1.2	+	"
"	O	"	3.5	+0.6	+	"
"	Si	"	>E(Fe)#	+0.5	+	"
Mo	H	1.8	2.1	-0.5	opposite	-
"	N	"	3.0	-1.1	"	-
"	C	"	2.5	-0.9	"	-
"	O	"	3.5	+0.35	"	- *
Co	N	1.8	3.0	+1.1	+	opposite
"	C	"	2.5	+1.2	+	"
"	O	"	3.5	+0.7	+	"

For explanation of table, see top of next page

* Indicates disagreement between experimental and predicted values.

\# It is assumed here that E(Si)>E(Fe) because six of the first eight entries in this table support this assumption.

(a) All electronegativities are Pauling's

(b) Borderline case means that element k has an electronegativity so close to solvent Z that one cannot safely make a judgement concerning the sign of $\epsilon_i^k(Z)$.

There are data for other "borderline" cases (i.e., where electronegativities are too close to permit prediction of $\epsilon_i^k(Z)$ or $\lambda_i^k(Z)$) in the literature, but they cannot be treated like the data in Table VI because not enough data involving the same solvent and primary solute are available. Thus, these data cannot be used.

In Table VI, 20 out of 25 parameters, or 80 per cent are predicted successfully. Note, once again, that of the five erroneous predictions made, four of them involve systems containing either oxygen or aluminum. The single parameter involving aluminum, and three of the five parameters involving oxygen were predicted erroneously. Combining these data with those in Table IV, the total number of systems covered is 105. In these 105 systems, the interaction parameter was predicted successfully in 85 cases, or about 81 percent of the time.

If one considers the hypothesis assumed in making the predictions presented in Table IV, he will note that this hypothesis predicts that the self-interaction parameter will always be positive, regardless of the solute and solvent being considered. In other words, this hypothesis predicts that as one adds a particular solute to a given solvent, the initial effect of the solute upon itself will be to increase its own activity coefficient.

TABLE VII

Qualitative Prediction of Self-Interaction Parameters Based On Deviations From Raoult's Law

Solvent Z	Element k	Deviation From Raoult's Law	Predicted $\epsilon_k^k(Z)$	Experimental $\epsilon_k^k(Z)$	Temp. °C
Aluminum	Ag	Negative	+ *	-3.1	1000°
Antimony	Cd	Neg.	+	+1.5	500°
"	Pb	Neg.	+	+0.6	"
"	Sn	Neg.	+	+2.2	905°
Bismuth	Au	Neg.	+	+2.1	700°
"	Cd	Neg.	+ *	-1.2	500°
"	Hg	Pos.	-	-0.3	321°
"	Mg	Neg.	+ *	-0.9	700°
"	Pb	Neg.	+	+0.9,+1.4	475°,500°
"	Sn	Pos.	-	-0.06	330°
"	Tl	Neg.	+	+3.2,+2.1	270°,480°
"	Zn	Pos.	-	-3.3	600°
Cadmium	Bi	Pos.	-	-6.5	500°
"	Hg	Neg.	+	+3.4	327°
"	Na	Neg.	+	+17.8	350°
"	Pb	Pos.	-	-4.6	500°
"	Sb	Neg.	+ *	-6.5	500°
"	Sn	Pos.	-	-1.5	500°
"	Zn	Pos.	-	-1.8	682°
Copper	Zn	Neg.	+	+0.4,+1.4	802°,604°
Gold	Bi	Pos.	- *	+0.1	700°
"	Pb	Neg.	+	+5.0	600°
"	Sn	Neg.	+	+38.9	"
"	Tl	Neg.	+	+0.1	"
Silver	Al	Neg.	+	+6.4,+4.2	700°,1000°
"	Cd	Neg.	+	+1.5	827°
"	Pb	Pos.	-	-0.4	1000°
Sodium	Hg	Neg.	+	+2.0	350°
Zinc	Cd	Pos.	-	-3.3	682°

Solvent Z	Element k	Deviation From Raoult's Law	Predicted $\epsilon_k^k(Z)$	Experimental $\epsilon_k^k(Z)$	Temp. °C
Lead	Ag	Pos.	-	-0.6,-0.9	1085°,1000°
"	Au	Neg.	+	+3.2	600°
"	Bi	Neg.	+	+2.6	500°
"	Cd	Pos.	-	-2.6	"
"	Mg	Neg.	+	+0.6	833°
"	Na	Neg.	+	+3.6	400°
"	Sb	Neg.	+	+0.16	500°
"	Sn	Pos.	-	-1.2	"
"	Tl	Neg.	+	+0.1	450°
"	Zn	Pos.	-	-5.3	653°
Mercury	Tl	Neg.	+	+0.6,+13.1	325°, ?°
"	Ba	Neg. #	+	+127	298°
"	Ce	Neg. #	+	+127,+51	25°, 378°
"	K	Neg.	+	+73,+44	0°,390°
"	Li	Neg.	+	+26.5	25°
"	Na	Neg.	+	+46.1,+43	25°,400°
Thallium	Au	Neg.	+	+2.6	700°
"	Hg	Neg.	+	+0.09	325°
"	Sn	Pos.	-	-1.7,0	325°,478°
Tin	Au	Neg.	+	+5.8	600°
"	Cd	Pos.	-	-1.1,-2.5	500°,700°
"	Zn	Pos.	-	-0.6	684°
"	Pb	Pos.	- *	+0.65	500°
"	Tl	Pos.	-	-3.2,-0.5	478°
Iron	C	Neg.	+	+22.4	1600°
"	Al	Neg.	+	+4.8	"
"	O	Neg. #	+ *	-20	"
"	S	Neg. #	+ *	-2.8	"
"	Si	Neg. #	+	+2.9	"
"	Ti	Neg. #	+	+4.6	"

For explanation of table, see top of next page.

* Indicates disagreement between experimental and predicted values.

Deviation based on phase diagram rather than on actual activity data (since none were available).

(a) Data on deviation from Raoult's Law from Hultgren (18) and Hansen (15).

(b) Experimental $\epsilon_k^k(Z)$ values obtained from Dealy and Pehlke (10), and Chipman (6).

(c) $\epsilon_k^k(Z) > 0$ for negative deviators and $\epsilon_k^k(Z) < 0$ for positive deviators.

In Table VII are presented 59 values of self-interaction parameters taken primarily from Dealy and Pehlke's compilation (10). These experimental data do not support the above hypothesis; only 36 of the 59 entries have a positive value.

On considering the self-interaction parameter further on a qualitative basis it was concluded that positive deviators from Raoult's Law should yield negative self-interaction parameters, and negative deviators should yield positive self-interaction parameters. These conclusions were based on the facts that the slope of the activity line on an activity-composition diagram for a positive deviator decreases as the concentration of the component increases away from zero (as long as one remains in the dilute region), and the opposite effect occurs for a negative deviator. In attempting to show this analytically, no definite conclusions could be reached, due to the fact that some of the important variables involved could not be evaluated. Application of the Raoult's Law criterion to the data mentioned above, however, yielded 51 correct predictions out of 59 attempts, representing over 86 per cent success. The results of this study are tabulated in Table VII.

In several of the systems presented in Table VII, there were no activity data available to indicate whether those systems were positive or negative deviators from Raoult's Law. Such systems are noted in the table. In these cases, decisions regarding their deviation from Raoult's Law were made on the basis of their phase diagrams. The connection between the phase diagram of a particular binary and the deviation of that binary from Raoult's Law is discussed in reference (28), pages 6 ff.

Obviously, all the foregoing attempts at predicting ternary interaction parameters, as well as self-interaction parameters, are highly qualitative. Considering specifically the ternary interaction parameters, it was necessary to make many simplifying assumptions in their prediction. Is one justified, in the first place, in separating the chemical potential, μ_i, of a solute into a chemical potential of its ions, $\mu_{i(\pm \text{ ions})}$, and a chemical potential of the electrons, μ_e? It appears that one can make qualitative predictions of $\epsilon_i^k(Z)$ on this basis with a fair amount of success. The fact that 81 per cent of the interaction parameters for the 105 systems investigated were predicted correctly on this basis would seem to indicate also that the free electron concentration in liquid metal alloys is an important variable. Ternary systems which include one of the two elements aluminum or oxygen, are responsible for 13 of the 20 erroneous predictions made in Tables IV and VI, although systems involving these two elements account for only 26 of the 105 systems reviewed. If all systems including one of these two elements were excluded from Tables IV and VI, then of the 79 parameters remaining, 73 of them, or over 92 percent, are predicted correctly qualitatively. Thus, one is faced with the question of why aluminum and oxygen apparently misbehave. In the case of aluminum, it was mentioned previously that six of the nine parameters were predicted erroneously on the basis of the reported value of 1.5 for the electronegativity of aluminum. If the electronegativity of aluminum were in the neighborhood of 1.8, rather than 1.5, then eight of the nine parameters would be predicted correctly. More specifically, the electronegativity of aluminum would have to be greater than that of iron. According to Table III, the electronegativity of iron falls somewhere in the range 1.7 - 1.9, depending upon its valence, and who reports it. If the electronegativity of aluminum is indeed greater than that of iron, then, interestingly enough, the single erroneous prediction of $\epsilon_i^k(Z)$ made in connection with aluminum also involves oxygen as a solute. In view of the above facts, it appears reasonable that the electronegativity of aluminum may be greater than 1.5; in the neighborhood of 1.8 for the systems reviewed (It has been pointed out previously that the electronegativity of an element is a function, to some extent, of its environment). Of course, this could also be explained by assuming that the electronegativity of iron is less than 1.5, the reported electronegativity of aluminum. If this assumption is made, however, then a good share of the other interaction parameters involving iron (but not aluminum) are disrupted; i.e., such an assumption leads to a large number of erroneous predictions of other parameters involving iron. Therefore, it is more likely that the reported value of the electronegativity of aluminum is in error, rather than that of iron. The erroneous predictions of $\epsilon_i^k(Z)$ observed for oxygen cannot be rectified on the basis of oxygen having an electronegativity different from that reported. The errors here are perhaps associated with the fact that ion-ion interactions were ignored in the application of equation (41). Of course, this probably affects all the predictions made in Tables IV and VI to varying extents, but perhaps the disregard for ion-ion interactions is more unreasonable in the solutions involving oxygen than it is in the others. In fact, one might expect ion-ion interactions to be quite pronounced in some cases, since oxygen is such an active element.

It is frequently necessary to resort to a method such as that outlined in this section of the thesis in order to get an engineering estimate of a particular problem. When the problem involved is so very complex, the predictions resulting from such an oversimplification cannot be hoped to be extremely accurate. If one can predict $\epsilon_i^k(Z)$ even qualitatively over 80 per cent of the time, however, this would seem to be a step in the right direction, and could prove to be of some value in certain engineering situations. Also, this type of a qualitative development may prove helpful in the future by contributing to the development of a more quantitative theory.

3. Periodic Behavior of The Interaction Parameters

As mentioned in the "Review of The Literature," Chapter II, there is evidence which indicates that the various interaction parameters may be correlated as a function of the atomic number of the third component. The plausibility of such a correlation and the evidence indicating such a correlation will be discussed here.

To begin with, it would seem helpful to discuss the periodic law itself to some extent for the purpose of clarifying the discussion to follow. The periodic law states that "The properties of the chemical elements are a periodic function of their atomic number." The various forms of the periodic table are somewhat arbitrary, and are merely attempts to organize the elements according to their chemical and physical properties in the most helpful manner possible. The periodic law itself, however, does indeed have a fundamental basis.

The foundation of the properties of the chemical elements is their atomic structure. More specifically, it is the pattern by which the electrons are distributed around the nucleus. The accepted electronic configurations of the elements were assigned on the basis of quantum theory in conjunction with spectroscopic and general chemical evidence. The fundamental principle in the building up of electronic shells of the atoms as their atomic numbers increase is that each successive electron must go into the lowest energy level available. With few exceptions, the distribution of electrons in any given atom is like that of the element immediately preceding it in atomic number, except for the addition of one more electron. There is, of course, a corresponding change in the nucleus.

No complete theoretical basis for determining exactly how the electrons are distributed in any given atom is known. It has been possible, however, to decide quite unambiguously on the electronic configuration of the atoms of most of the chemical elements by combination of a knowledge of the quantum numbers, the Pauli exclusion principle, atomic spectra, and the general physical and chemical properties of the elements. By comparing these configurations with the generally recognized facts of chemical periodicity, it becomes apparent that there is a fundamental correlation between the way in which the electronic configurations change with atomic number, and the pattern by which the chemical and physical properties change with atomic number.

The chemical and physical similarities existing among particular elements leads to the grouping together of such families as the alkali metals, the alkaline earths, and the halogens. These similarities correspond to similarities in the electronic configurations of the elements involved. Any particular alkali metal, for instance, differs electronically from the inert gas immediately preceding it in atomic number only by having one more electron. Any particular halogen differs electronically from the immediately succeeding inert element only by having one less electron. The classification of certain elements as transition elements is based on electronic configurations, the transition elements being those having partially filled d orbitals. The rare earths are those elements having partially filled f orbitals. If one were to plot any particular chemical or physical property of the elements versus atomic number, he would find that a general correlation does exist, but that this correlation would fall into specific groups. These observed groupings would correspond to periods, groups, or subgroups of the periodic table. There would be a number of inconsistencies observed in such a correlation, of course, if one were to cover the entire periodic table but there would indeed be a general correlation.

Although the original formulation of the periodic law had an entirely empirical basis, this law is now recognized to be based very solidly on the atomic structures of the elements. Perhaps a better statement of this law, as suggested by Sanderson (29), would be "The physical and chemical properties of the elements are a function of the electronic configuration of their atoms, which varies with increasing atomic number in a periodic manner."

Having briefly considered the variation of the chemical and physical properties of the elements in a general way with atomic number, consider now the reaction of one chemical element with another. One might suspect that the reactions of one specific element individually with each one of the other elements in the table would also be periodic to some extent, because the degree of reaction between two elements depends, among other things, upon the properties of one relative to those of the other.

Consider individually the reaction between iron and some of the other elements of the periodic table. This particular element was chosen because of the availability of appropriate data. Beginning with the alkali metals, one finds that none of them react with iron to any extent, except under very extreme conditions (15). Going across the third period of the table, after sodium, the alkali metal, one comes to magnesium. Whereas sodium is considered to be insoluble in solid iron, magnesium does have a measurable solubility, although it is small (15). Also, it is indicated that the solubility of iron in liquid magnesium is greater than it is in liquid sodium. Continuing across period three, after magnesium one advances successively to Al, Si, P, S, and Cl, excluding the inert gas, argon. Unlike Na and Mg, each one of these elements forms compounds with iron. The heats of formation of particular iron compounds formed with each one of these elements are given in Table VIII (21). It can be seen that there is a regular increase in the heats of formation as one proceeds across period three, except that either FeP or FeS appears to be "anomolous". The heats of formation of the compounds formed give measures of the affinity that the atoms have for each other.

TABLE VIII

Heats of Formation of Compounds of Period 3 Elements with Iron

Compound	$-\Delta H_f^{298}$ per atom of iron $\left[\frac{\text{k cal}}{\text{g mole}}\right]$
FeAl	12.2
FeSi	19.2
FeP	29.0
FeS	23.1
$FeCl_2$	81.6

Reference: Kubaschewski and Evans (21).

TABLE IX

Heats of Formation of Compounds of Subgroup VI-A Elements with Iron

Compound	$-\Delta H_f^{298}$ per atom of iron $\left[\frac{\text{k cal}}{\text{g mole}}\right]$
FeO	63.5
FeS	23.1
FeSe	18.0
FeTe	7.7

Reference: Kubaschewski and Evans (21).

TABLE X

Heats of Formation of Compounds of Subgroup VII-A Elements With Iron

Compound	$-\Delta H_f^{298}$ per atom of iron $\left[\frac{\text{k cal}}{\text{g mole}}\right]$
FeF_2	168.0
$FeCl_2$	81.5
$FeBr_2$	59.1
FeI_2	30.0

Reference: Kubaschewski and Evans (21).

To further illustrate this regular behavior, consider the heats of formation of the compounds formed with iron by several other elements for which data are available. In descending subgroup VI-A one observes the trend illustrated in Table IX. In descending subgroup VII-A one observes the trend illustrated in Table X. In both subgroups, as one descends from a more electronegative to a less electronegative element, the numerical value of $(-\Delta H_f^{298})$ decreases. In the same manner, as one proceeds across period three from left to right, this time from a less electronegative to a more electronegative element, the numerical value of $(-\Delta H_f^{298})$ increases.

Without going into unnecessary detail, it seems reasonable to state that the regular pattern of behavior illustrated by iron in combination with the above elements could probably be extended to include most of the other periods and/or subgroups of the periodic table. Obviously, there would be apparent inconsistencies here and there, just as there is in the case of most any fundamental physical or chemical property of the elements. Nevertheless, there would in general be a regular pattern displayed. Furthermore, it seems reasonable to suspect that this regular behavior could be generalized upon to a large extent to include the other elements in the table in addition to iron.

In view of the periodicity in the properties of the chemical elements, as discussed briefly above, it is not difficult to accept evidence indicating a correlation between the various interaction parameters and the atomic number of the third component. Although it does not follow a priori from the periodic law, it seems very reasonable that such a correlation could exist. It was pointed out in an earlier chapter of this thesis that Turkdogan (36), and Ohtani and

Gokcen (24) found a regular behavior to be displayed when they plotted interaction and saturation parameters in a liquid iron solvent against the appropriate atomic number. Their observations are illustrated in Figure 1, where the groupings of the parameters correspond to periods in the periodic table. Also, the author found some of the interaction parameters from Chipman's article (6), Wagner's article (39), and Weinstein's thesis (43), to exhibit a regular behavior when plotted by subgroups or periods against the atomic number of the third component. These parameters are shown in Figures 1 and 2, which include all the data from these articles which could be used. The only parameters which could not be included in these correlations are those which are not part of a set made up of parameters representing three or more elements from the same subgroup or period of the periodic table. No conclusion can be drawn in regard to a correlation, of course, if only one or two parameters from the same subgroup or period of the table are available.

To summarize what has been said in the last few paragraphs with regard to the behavior of the interaction parameters in relation to the atomic numbers of the third components, the following statement can be made: In the same way that the chemical and physical properties of the chemical elements are a function of the electronic configurations of their atoms, and thus, of their atomic numbers, it appears that the various interaction parameters, measuring the effect of element k on a given basic binary, are functions of the electronic configurations or atomic numbers of the elements k, the added third components. It is felt that the data appearing in Figures 1 and 2 illustrate this statement. To the author's knowledge, the data appearing in these two figures represent all the data taken to date which can be subjected to such a correlation. A good share of the data shown in Figure 1 has been presented before by Turkdogan (36) and Ohtani and Gokcen (24); some of it has not been presented in this manner. To the author's knowledge, none of the data presented in Figure 2, however, has ever been correlated in this manner. Except for a few inconsistencies, the fact that all this data behaves in such a regular manner when plotted against the atomic number of the third component lends considerable support to the statement made above.

In view of the data presented in Figures 1 and 2, primarily Figure 2, it appears that processes of interpolation and extrapolation could provide one with approximate values of interaction parameters which have not been measured. Of course, in order to perform either operation, the values of appropriate parameters to be used as a basis for the operation would have to be known. Also, one would have to be particularly careful in considering interpolations or extrapolations in certain regions of the periodic table, viz., where apparent anomolies in the physical and chemical properties of the elements exist. In Figure 2, certain trends in the parameters from subgroup to subgroup suggest themselves. However, there are not enough data points available to make any definite conclusions.

B. Discussion of The Results of This Investigation

The results of the entire experimental program are discussed in detail in this section. First the Bi-Al and Pb-Al binary systems are discussed and compared with the published work done on the same two systems. Then the various ternary systems studied in this investigation are discussed. Phase diagrams of each of the three binary systems making up each of the twelve ternary solutions are presented in Appendix A for the convenience of the reader. The interaction parameters determined for each of these ternary solutions are discussed in the following terms: in terms of Alcock and Richardson's equation; in terms of Wada and Saito's equation; in terms of the electronegativities of the elements, in combination with Wagner's electron model of a liquid alloy; and in terms of the regular behavior which they display with respect to the periodic table.

1. The Bismuth-Aluminum and Lead-Aluminum Binary Systems

In the investigation of the Bi-Al binary system, the solubility of aluminum in liquid bismuth was studied over the approximate temperature range 450-600°C. The results of this investigation are presented in Figure 8 along with the results obtained by two other investigators. In this figure, log weight percent aluminum is plotted as a function of $\frac{1000}{T°K}$. The equation of the author's line is:

$$\log_{10}(\text{wt. per cent Al}) = 2.55 - \frac{2110}{T°K} \qquad (36)$$

The points in Figure 8 representing the author's work are actually mean concentrations, i.e., any particular point is the mean of a small set of concentrations observed at that particular temperature. The number of observations contained in these sets is variable, ranging from about five to ten. The standard deviation of these sets, expressed as a percentage of the mean, varies from about 2% to 10%. The standard deviation of the slope of the line, expressed as a percentage of the slope, is 2.2%.

As mentioned previously in the "Review of The Literature" chapter, only two other studies of the Bi-Al binary liquidus have been made over a temperature range including that of this investigation. The solubility relationships derived in those two studies are shown along with the author's results in Figure 8. The line lying well above all the others represents the work of Sri Krishna and Grace (33). They did not present their data in that form, so the line fitted to their data was fitted by the author. The equation of this line is:

$$\log_{10}(\text{wt. per cent Al}) = 2.29 - \frac{1679}{T°K} \qquad (42)$$

Comparing this equation with that of the author, it can be seen that not only are the aluminum solubilities considerably higher at any given temperature, but the slope of their line is less by about 20 percent. The solubilities range from about 70% to 130% higher than those observed by the author, depending upon the temperature. Since Sri Krishna and Grace did not elaborate on their experimental or chemical analysis procedures, it is difficult to conjecture as to why their results are so different from those of the author.

The dotted line shown in Figure 8 represents work done by Weeks and Minardi at Brookhaven National Laboratory (41). The equation of this line is:

$$\log_{10}(\text{wt. per cent Al}) = 2.40 - \frac{1992}{T°K} \qquad (43)$$

This line intersects the author's line at 0.86 wt. percent aluminum. At 549°C, or $\frac{1000}{T°K} = 1.22$, where all the ternary studies were carried out, Brookhaven's line gives an aluminum solubility of 0.96 wt. percent, while the author's line gives an aluminum solubility of 0.94 wt. percent. Thus, at the temperature of primary interest (because the ternary studies were made at this temperature) the two curves agree to within 0.02 wt. percent aluminum, which is within the scatter of the author's data. The maximum disagreement between the two curves is in the neighborhood of 450°C, where the discrepancy amounts to about 0.03 wt. percent aluminum, or about 7.5% of the aluminum present.

Finally, there is one line remaining in Figure 8 which has not been discussed. This is the line lying at the lowest aluminum solubilities, and represents the solubility of aluminum in bismuth containing 3.6 atomic percent magnesium. These data were taken at Brookhaven National Laboratory by Weeks and Minardi (42) . The magnesium content was constant over the entire temperature range. The significance of this depressive effect of magnesium will be discussed later on in this chapter along with the discussion of the other ternary systems.

Data for the Pb-Al binary are presented in Figure 9 along with Dardel's (8) results. The author's data were again taken over the approximate temperature range 450-600°C. The equation of the author's line between these two temperatures is:

$$\log_{10}(\text{wt. per cent Al}) = 1.86 - \frac{2540}{T°K} \qquad (37)$$

Once again, the points appearing in Figure 9, as far as the author's data are concerned, are the means of small sets of concentrations observed at those particular temperatures. The number of observations in these sets is variable, ranging from five to twenty-seven. At 549°C, the temperature at which the ternary studies were made, twenty-seven observations of the aluminum concentration were made, in order that this concentration with zero percent third component would be well-known. The standard deviation of these sets, expressed as a percentage of the mean, varies from about 7% to 11%. The standard deviation of the slope of the line, expressed as a percentage of this slope, is 5.1%.

As mentioned above, there has been one other study of the Pb-Al liquidus which includes the temperature range investigated by the author. This study was carried out by Dardel, using a procedure as outlined in the "Review of The Literature" section of this thesis. If one looks closely at Dardel's data, he will note that there appears to be two distinct solubility lines intersecting somewhere in the neighborhood of $\frac{1000}{T°K} = 1.1$, which is very close to 660°C, the monotectic temperature in the Pb-Al binary system. It will also be noted that the author's solubility line, if extrapolated, runs very nicely through Dardel's data points taken above the monotectic temperature. A possible explanation for this deviation is suggested by examining the experimental procedure of Dardel. A 500 gm. sample of lead containing 2 wt. percent aluminum was heated in a small steel crucible and the melt was held at 1100°C for one hour. The temperature was then lowered to the run temperature and the phases allowed to separate. The crucible containing the melt was then plunged into water and the lower part of the ingot chemically analyzed for the aluminum content of the lead-rich phase. As long as the run temperature was above the monotectic, the equilibrium involved two liquid phases, a lead-rich phase and an aluminum-rich phase. This liquid-

liquid equilibrium still exists at 1100°C. Therefore, after dropping the temperature from 1100°C to a run temperature above the monotectic, it is postulated that both equilibrium and phase separation occurred prior to quenching. At temperatures below the monotectic, however, one is dealing with an equilibrium between a lead-rich liquid and pure, solid aluminum. The complicating factor here may well have been involved in the actual physical separation of the solid and the liquid phases upon dropping the temperature from above to below the monotectic. In other words, in dropping the melt temperature from 1100°C to a run temperature below the monotectic, pure, solid aluminum must precipitate out. In this precipitation process, some of the aluminum coming out of solution, being very finely divided, might have remained suspended in the liquid phase. Thus, when the melt was quenched, the liquid phase still contained excess, solid aluminum, which led to a high apparent equilibrium aluminum solubility. Since Dardel's results were higher, rather than lower, than the author's results at temperatures below the monotectic, this would appear to be a logical explanation of the discrepancy.

A brief study of the kinetics of the dissolution of solid aluminum in liquid bismuth was carried out toward the beginning of the experimental program. It was found, by taking samples of the Bi-Al solution as a function of time, that the aluminum reaches its equilibrium concentration very rapidly at these temperatures. This was established by taking liquid samples for run times varying from about 10 minutes to about 50 hours and finding that there were no significant differences in aluminum solubility; that is, the results were the same to within the natural scatter of the data. Run B-12 in the appendix illustrates this point. Other runs demonstrated that for run times varying between about 25 and 100 hours, there also are no significant differences in aluminum solubility. A similar study was not performed on the Pb-Al binary. It was assumed in this case that since the data taken at different temperatures, but at run times varying from about 25 to 50 hours, correlated so nicely with reciprocal temperature, that equilibrium is achieved in less than 25 hours. In fact, equilibrium is probably achieved on the order of a few hours or less, as in the case of the Bi-Al system.

Before leaving the two binary systems, there remains one more topic to discuss, viz. the relative partial molar enthalpy of aluminum in liquid bismuth and in liquid lead. The calculation of this quantity for both solvents is summarized in Appendix C. Designating the standard state for aluminum as the pure solid at the temperature of interest, the relative partial molar enthalpy (H_{Al}^{M}) of aluminum in solution is the difference between the partial molar enthalpy of aluminum in solution and the molar enthalpy of pure, solid aluminum at the same temperature. The relative partial molar enthalpies of aluminum in solution in bismuth and in lead are both positive, being 9.2 and 11.6 $\frac{\text{k cal}}{\text{gm mole}}$, respectively. Both values are constant over at least the temperature range 450-600°C; probably a wider range. These enthalpy differences, of course, apply only to the case where aluminum is present to the extent of its saturation concentration at any particular temperature for either binary. The fact that H_{Al}^{M} is positive for both binaries suggests that both binaries are positive deviators from Raoult's law.

2. The Ternary Systems

(a) Review of The Ternary Data

Before attempting to interpret the results obtained for the ternary systems studied, the experimental data itself will be reviewed.

The results obtained for these systems are presented in Figures 10 thru 21. In determining the interaction parameters, $\lambda^k_{Al}(Z)$, from these experimental data, the following procedure was followed. First, the raw data (see Appendix D) were converted from a weight percent to an atomic percent basis, and the atom fractions of aluminum and the third component determined. From this point on, the treatment of the data for any particular ternary system depended upon whether the plot of $\ell n\, N_{Al}$ as a function of N_k was a straight line or a curve. This question was settled in each case by a visual inspection of the plot. If the plot of $\ell n\, N_{Al}$ versus N_k appeared to be approximately linear (as it did in six of twelve cases), then the least squares line was fitted to the data, and its slope determined. From the slope of this line, the value of $\lambda^k_{Al}(Z)$ was easily calculated. On the other hand, if the plot of $\ell n\, N_{Al}$ versus N_k was not linear, a curve was fitted to the data points. Since there were so few data points for the ternaries involved, multiple regression was not used; the curve was fitted by trial and error until the sum of the squares of the deviations of the points from the curve was a minimum. The limiting slope (as N_k tends to zero) of each of these curves was then determined visually, and the resulting value of $\lambda^k_{Al}(Z)$ calculated.

The value of $\lambda^k_{Al}(Z)$ is known more accurately in some cases than it is in others. In six cases, viz. the Bi-Al-Ca, Bi-Al-Sr, Bi-Al-Ba, Bi-Al-Sb, Pb-Al-Sr, and Pb-Al-Ba systems, it was possible to determine the standard deviation of the slope of the line relating $\ell n\, N_{Al}$ to N_k, since this relationship was essentially linear in each case (in several cases, the relationship of N_{Al} to N_k was not quite linear, but that between $\ell n\ N_{Al}$ and N_k was linear.) The standard deviations expressed as percentages of the slopes for the six systems mentioned above were ±13%, ±4%, ±24%, ±18%, ±15%, and ±3% respectively. In the remaining six systems, such an analysis was not possible. One can obtain a fairly good idea of the relative accuracy of the data on four of the six remaining systems, however, by inspecting Figures 10 thru 21. In Figure 13, the Bi-Al-Pd system, considering only the three points at low Pd concentrations, these points fall 6-8% from the curve. These percentages and those immediately following refer to the deviation of the point from the curve, expressed as a percentage of the aluminum concentration indicated by the curve at that particular concentration of element k. In Figure 14, the Bi-Al-Sn system, there are two particularly bad points; one lies about 25% above, and one 25% below the curve. The other points deviate only 5% or less from the curve. In Figure 16, the Pb-Al-Ca system, the maximum deviation from the line occurs for a point lying about 7% low. The other points deviate only 5% or less from the curve. The reversal in slope of this line at about 8 atomic % Ca is postulated to be due to a change of equilibria; that is, there is a change from the solid aluminum-liquid alloy equilibrium to some other equilibrium. It is difficult to say what this other equilibrium might involve. There are many possibilities. The Pb-Al-Sn system, like the Bi-Al-Sn system, contains more scatter in the data points than most of the other systems. In Figure 20, the two worst points deviate about 25% from the curve, one above and one below. The other points fall much closer to the line.

In Table XI are presented the values of $\lambda_{Al}^{k}(Z)$ determined in this investigation together with the uncertainties estimated to be involved with the value of each parameter measured. The uncertainties which are unstarred were calculated from the standard deviation of the slope of the least squares line fitted to the data for that particular system. More specifically, these uncertainties represent the standard deviation of the slope of the least squares line relating $\ell n\ N_{Al}$ to N_k expressed as a percentage of this slope. The negative value of this slope, of course, is $\lambda^k_{Al}(Z)$, so uncertainties in the slope represent uncertainties

TABLE XI

Uncertainties Involved In The Interaction Parameters Measured

Element k	Solvent Z	$\lambda^k_{Al}(Z)$
Ca	Bi	+ 9.5 ± 1.3
Sr	Bi	+ 10.4 ± 0.4
Ba	Bi	+ 14.2 ± 3.4
Pd	Bi	- 317 ± 160*
Sn	Bi	+ 33 ± 16*
Sb	Bi	-1550 ± 280
Ca	Pb	- 4.2 ± 0.8*
Sr	Pb	- 1.1 ± 0.2
Ba	Pb	+ 2.4 ± 0.1
Sn	Pb	- 9.3 ± 7*

* These values are only estimated values. The unstarred values were calculated from the standard deviations of the slopes of the lines relating $\ell n\ N_{Al}$ to N_k for each system. For a discussion of these uncertainties, refer to the text of this section of thesis. $\lambda^{Pd}_{Al}(Pb)$ and $\lambda^{Sb}_{Al}(Pb)$ are excluded for reasons mentioned in the text.

in $\lambda_{Al}^{k}(Z)$. The other four uncertainties (starred) are only estimated values. They were estimated by somewhat arbitrarily assuming the upper and lower limits on the limiting slope of the curve relating $\ell n\ N_{Al}$ and N_k. These limits were assumed to be given by the slopes of the lines drawn through the two points deviating a maximum distance above and below the curve in question. This seems to be a reasonable, but probably harsh, criterion for estimating the uncertainties. They are probably not quite so large as indicated for the starred parameters in Table XI.

In the two systems Pb-Al-Pd and Pb-Al-Sb, the parameters reported are very approximate. As shown in Figures 19 and 21, only one data point representing the equilibrium concentration of a ternary solution was obtained for each of these two systems. In either case, if N_k exceeded about 0.025-0.030, the aluminum concentration was reduced to such an extent that only trace quantities of aluminum were detectable. The points falling between zero and three atomic percent of element k were difficult to obtain in these two cases. Thus, the lines joining the two points in Figures 19 and 21 are shown dotted to indicate the doubt connected with them. Either or both of these two lines may in fact be a concave or convex upwards curve, rather than a straight line. Even though the parameters, $\lambda_{Al}^{k}(Pb)$, are not accurately determined for these two systems, the data do indicate that they are both positive, which is of considerable interest to this study.

There are several factors which may have contributed to the scatter observed in the experimental data. Most of these factors would apply to the binary as well as the ternary systems. The uncertainty in run temperature was estimated earlier to be in the range of ± 3-4C°. Judging from the slopes of the Bi-Al and Pb-Al binary lines of wt.

percent Al versus 1000/T°K, a ±4C° temperature uncertainty would give a ±2%-4% error in the aluminum concentration for either binary. The uncertainty in aluminum concentration due to chemical analysis is ±4% for the bismuth-base samples, and ±7% for the lead-base samples. Also, the uncertainties involved in the chemical analyses for the third components vary from about ±5% to 11%, depending upon the element being sought. These uncertainties are discussed more completely in Appendix B. It is also possible that some of the scatter in the experimental data is due to the presence of oxygen in the experimental system. It is felt, however, that errors of this origin were held to a minimum, at least in the bismuth-base systems. This is indicated by the close agreement of the Bi-Al binary line with that determined at Brookhaven. There is also the possibility of errors arising from the failure of the solution to reach equilibrium. An error of this origin is much more likely in the ternary data than in the binary data. The time necessary for the binary systems to attain equilibrium was determined experimentally, and the duration of all binary runs exceeded this time by a considerable amount. The times necessary for each ternary system to reach equilibrium were not determined, since such a study would be a thesis in itself. Nearly all ternary runs were made 24 hours or longer in duration, as they were for the binary systems. One cannot definitely say that these run times were adequate in every case, although it is felt that they were in most cases. Therefore, the possibility of errors of this origin does exist.

(b) Discussion of The Ternery Data In Terms of The Theories Previously Discussed

As mentioned previously, there are, at the present time, two equations which enable one to calculate a theoretical value of Wagner's interaction parameter for a given ternary; Alcock and Richardson's equation (1, 2), and Wada and Saito's equation (37,38). Neither equation can be expected to be more than semi-quantitative because of the assumptions made in its derivation. The parameter determined for the ternaries studied in this investigation was $\lambda_i^k(Z)$ rather than Wagner's parameter, $\epsilon_i^k(Z)$. The relationship between these two parameters is given by equation (14) in the "Review of the Literature":

$$\epsilon_i^k(Z) = \lambda_i^k(Z) \left[1 + \frac{\partial \ell n \gamma_i}{\partial \ell n N_i} \right]_{N_k = 0} \qquad (14)$$

Unfortunately, the data necessary for determining the term $\frac{\partial \ell n \gamma_i}{\partial \ell n N_i}$ in the Bi-Al and Pb-Al binary systems is unavailable. Therefore, the experimental values of $\lambda_{Al}^k(Bi)$ and $\lambda_{Al}^k(Pb)$ cannot be converted to the corresponding values of $\epsilon_{Al}^k(Bi)$ and $\epsilon_{Al}^k(Pb)$ for purposes of comparison with Alcock and Richardson's equation, and Wada and Saito's equation. It can be shown that if the term $\frac{\partial a_i}{\partial N_i}$ in the i-Z binary is positive, then $\lambda_i^k(Z)$ and $\epsilon_i^k(Z)$ should have the same algebraic sign. Therefore, since this stipulation is observed in the Bi-Al and Pb-Al binaries, it is possible to at least compare the experimental values of $\lambda_{Al}^k(Z)$ in a qualitative manner with the theoretical values of $\epsilon_{Al}^k(Z)$ in both the bismuth solvent and the lead solvent. Also, since the term $\left[\frac{\partial \ell n \gamma_i}{\partial \ell n N_i}\right]_{N_k = 0}$ is constant for a given binary at a given temperature, any trends in $\lambda_{Al}^k(Z)$

(within a subgroup, for instance) should be reflected in the values of $\epsilon^{k}_{Al}(Z)$. Although this is certainly not as desirable as a quantitative comparison of experimental and theoretical values of $\lambda^{k}_{Al}(Z)$, it is, unfortunately, all that one can do because of the lack of data necessary to convert values of $\lambda^{k}_{Al}(Z)$ to $\epsilon^{k}_{Al}(Z)$.

The experimental results will be discussed first in terms of Alcock and Richardson's equation. This relationship is given by equation (21) as:

$$\epsilon^{k}_{Al}(Z) = \ell n\gamma_{Alk} - \ell n\gamma_{kZ} - \ell n\gamma_{AlZ} \tag{21}$$

In this equation, γ_{Alk} represents the limiting value of the activity coefficient of aluminum in the Al-k binary, and the other activity coefficients bear similar representations. In some cases it will be more convenient to talk in terms of Alcock and Richardson's equation in the form of equation (38), discussed earlier, than in the form of equation (21).

$$\epsilon^{k}_{Al}(Z) = \frac{1}{RT}\left[\Delta\bar{H}_{Alk} - \Delta\bar{H}_{kZ} - \Delta\bar{H}_{AlZ}\right] \tag{38}$$

In reference to the Bi-Al-k systems studied in this investigation, the term γ_{AlZ} in equation (21) represents γ_{Al} in the Bi-Al binary. The exact value of this parameter is not known. It is known, however, that the Bi-Al system is a positive deviator from Raoult's law $\left[H^{M}_{Al}(Bi) = +9.2\,\frac{\text{k cal}}{\text{g atom}}\right]$. Therefore, $\gamma_{AlBi} > 1$, and $\ell n\gamma_{AlBi}$ is positive. In Table XII are presented the qualitative values of γ_{Alk} and γ_{kBi} for the k elements studied.

TABLE XII

Table of Activity Coefficients

Element k	γ_{Alk}	γ_{kBi}	γ_{kPb}
Ca	< 1	< 1	< 1
Sr	< 1	< 1	< 1
Ba	< 1	2×10^{-18}(500°C)*	< 1
Pd	< 1	< 1	< 1
Sn	2.1(730°C)	1.1(335°C)	> 1
Sb	< 1	> 1	< 1

Also, $\gamma_{AlBi} > 1$, and $\gamma_{AlPb} > 1$

*Reference: Wiswall and Egan (44).

These values were obtained either directly from Hultgren (18), or estimated from the binary phase diagrams given in Hansen (15), unless otherwise specified. The question of such estimations is covered in reference (28) . According to Table XII, γ_{Alk}, as well as γ_{kBi}, is less than unity for all the alkaline earth elements studied. The value of γ_{kBi} for barium is 2×10^{-18} (44). Therefore, for barium:

$$\epsilon_{Al}^{Ba}(Bi) = (neg.) - (-40.7) - (pos.) \tag{44}$$

where (neg.) signifies that that particular term is negative, and (pos.) signifies the opposite. The term (-40.7) is the natural logarithm of 2×10^{-18}. Although the first and last terms in equation (44) tend to give $\epsilon_{Al}^{Ba}(Bi)$ a negative value, the large middle term must predominate, since $\epsilon_{Al}^{Ba}(Bi)$ is positive $\left[\lambda_{Al}^{Ba}(Bi) = +14.2\right]$. For the Bi-Al-Ca and Bi-Al-Sr systems, the situation apparently is much the same (the second term predominates), since $\lambda_{Al}^{k}(Bi)$ is positive for these two systems also. The last term, γ_{AlBi}, is identical for all three bismuth-base alkaline earth systems.

There was a regularity observed in the interaction parameters, $\lambda_{Al}^{k}(Bi)$; the values increased in positive value as one descended the alkaline earth subgroup (see Table I). There is evidence to indicate that the second term in equation (38), $\Delta \overline{H}_{kBi}$, is considerably more negative for barium than for calcium; the value for Sr falls in between. This increase in $\Delta \overline{H}_{kBi}$ contributes to the observed increase in the value of $\lambda_{Al}^{k}(Bi)$ as one progresses down the alkaline earth subgroup from calcium to barium. The last term, $\Delta \overline{H}_{AlZ}$, is the same for all three systems. The third term in equation (38) is also negative for the Bi-Al-Ca and Bi-Al-Sr systems, as it was for the Bi-Al-Ba system. The relative values of this term for these three systems are not known. Since the parameter $\lambda_{Al}^{k}(Bi)$ does increase in positive value for Ca, Sr, and Ba in the same order as the increase in the second term of equation (38), then the first term either: (1) contributes to this observed order of increase; or (2), if it opposes this order of increase, the relative values of $\Delta \overline{H}_{Alk}$ are close enough that they do not completely disrupt it.

Consider the Bi-Al-Sn, Bi-Al-Pd, and Bi-Al-Sb systems. According to Table XII, γ_{AlSn}, γ_{SnBi}, and γ_{AlBi} are all positive. In fact, γ_{AlSn} is about 2.1 at 730°C and γ_{SnBi} is about 1.1 at 335°C. The value of γ_{AlBi} is not known. Thus, the first term in equation (21) tends to make $\lambda_{Al}^{Sn}(Bi)$ positive, and the two remaining terms tend to make it negative. According to Table XII, for the two temperatures listed, the first term ($\ln 2.1$) predominates over the second term ($-\ln 1.1$), tending to make $\lambda_{Al}^{Sn}(Bi)$ positive. Although these two terms will not have these same values at 550°C, the predominance of the first term is apparently still observed at that temperature. Since $\lambda_{Al}^{Sn}(Bi)$ is, in fact, positive at 550°C, the third term in equation (21) must not be large enough to alter this qualitative picture. In the case of the Bi-Al-Pd system, according to Table XII, the first and last terms in equation (21) tend to make $\lambda_{Al}^{Pd}(Bi)$ negative, and the second term tends to make it positive. Experiment shows it to be negative. Since the relative values of none of these terms are known, nothing more can be said, except that the sum of the first and last terms apparently predominates over the middle term. Finally, in the case of the Bi-Al-Sb system, according to Table XII, the first term in equation (21) would be negative, and the second and third terms positive; all three terms, therefore, contribute to a negative value of $\lambda_{Al}^{Sb}(Bi)$. Experiment shows that $\lambda_{Al}^{Sb}(Bi)$ is indeed negative.

Consider the Pb-Al-Ca, Pb-Al-Sr, and Pb-Al-Ba systems. In each of these systems, according to Table XII, the three activity coefficients of equation (21) have the same algebraic sign as they do in the bismuth solvent. What, then, is a possible explanation for $\lambda_{Al}^{Ca}(Pb)$ and $\lambda_{Al}^{Sr}(Pb)$ being negative (the analagous parameters were positive in bismuth), and $\lambda_{Al}^{Ba}(Pb)$ being considerably less positive than $\lambda_{Al}^{Ba}(Bi)$? The reasons are most clearly postulated in terms of equation (38). The first term in this equation is identical for the Bi-base and Pb-base systems. Therefore, the reason for the difference in $\lambda_{Al}^{k}(Z)$ between the two solvents must lie in the second and third terms. The third term in equation (38), $\Delta \bar{\bar{H}}_{kZ}$, is more positive in the Pb-Al system $\left[+\ 11.6\ \frac{k\ cal}{g\ atom}\right]$ than it is in the Bi-Al system $\left[+\ 9.2\ \frac{k\ cal}{g\ atom}\right]$. This would certainly contribute to the decrease in positive value of $\lambda_{Al}^{k}(Z)$ in changing solvents from bismuth to lead. Also, there is evidence to indicate that the second term in equation (38) is more positive in the lead-base systems than it is in the bismuth-base systems. This is indicated by the heats of formation of the binary intermetallic compounds concerned. This also would contribute to the decrease in positive value of $\lambda_{Al}^{k}(Z)$ in changing solvents from bismuth to lead. Therefore, for these two reasons, on the basis of Alcock and Richardson's equation, one would certainly expect the values of $\lambda_{Al}^{k}(Z)$ for the alkaline earth elements to be less in positive value in lead than they are in bismuth. This agrees with the experimental results. In the cases of the Pb-Al-Ca and Pb-Al-Sr systems, the last two terms apparently are enough more positive than they were in the bismuth-base systems to result in negative values of $\lambda_{Al}^{k}(Pb)$, rather than positive values. In the Pb-Al-Ba system, $\lambda_{Al}^{Ba}(Pb)$ is positive, but considerably less positive than $\lambda_{Al}^{Ba}(Bi)$. The regular behavior displayed by $\lambda_{Al}^{k}(Pb)$ in descending the alkaline earth subgroup is explainable by the same line of reasoning used in the bismuth-base systems.

The value of $\lambda_{Al}^{Sn}(Pb)$ was found experimentally to be negative; the value of $\lambda_{Al}^{Sn}(Bi)$ was positive. As in the case of the Bi-Al-Sn system, all three binaries of the Pb-Al-Sn system are positive deviators from Raoult's law. The reason that $\lambda_{Al}^{Sn}(Pb)$ is negative, according to Alcock and Richardson's equation, is that the second and third terms in equation (38) predominate over the first term. In the Bi-Al-Sn system, the first term (which is the same for both ternary systems) predominated. Therefore, the only way that $\lambda_{Al}^{Sn}(Pb)$ could be negative while $\lambda_{Al}^{Sn}(Bi)$ is positive is for one or both of the last two terms in equation (38) to be more positive in the lead-base system than in the bismuth-base system. According to available heat of solution data, this is indeed the case for both of the last two terms in equation (38).

The experimental value for $\lambda_{Al}^{Pd}(Pb)$ is positive. According to Table XII, the first and last terms in equation (21) tend to make $\lambda_{Al}^{Pd}(Pb)$ negative, and the middle term tends to make it positive. Therefore, the magnitude of the second term apparently predominates over the other two. This can only be postulated, since relative values of these three terms are unavailable. The opposite was found to be true in the bismuth-base system. Accordingly, one would suspect that the partial heat of mixing of Pd in lead is, to some degree, more negative than it is in bismuth, on the basis of equation (38).

The experimental value of $\lambda_{Al}^{Sb}(Pb)$ was also found to be positive. According to equation (38), this would suggest a large negative partial heat of mixing in the Pb-Sb system, since the other two terms tend to make $\lambda_{Al}^{Sb}(Pb)$ negative. In the analagous situation in the Bi-base system, the partial heat of mixing of the Bi-Sb solution was positive, contributing to the observed positive value of $\lambda_{Al}^{Sb}(Bi)$. In the Pb-Sb system, however, it is found that the partial heat of mixing is indeed negative, lending support to the fact that the experimental value of $\lambda_{Al}^{Sb}(Pb)$ is positive.

Although all the discussion presented above is highly qualitative, it is interesting that, in the light of Alcock and Richardson's equation, it is possible to explain, to some degree, the results observed. The tendency for some of the parameters to be positive in one solvent and negative in the other was discussed.

Also, the tendency for the parameters within the alkaline earths to behave in a regular manner as one descends this subgroup was discussed. These two tendencies seemed to be fairly well indicated by the small amount of available data analyzed in conjunction with Alcock and Richardson's equation.

It is felt that it would now be of some interest to discuss the experimental results in terms of Wada and Saito's equation. This relationship is given by equation (26).

$$\epsilon_i^k(Z) = \frac{1}{RT}\left[W_{ik} - W_{iZ} - W_{kZ}\right] \tag{26}$$

The interchange energies, W , are given by equation (28).

$$W_{ik} = V^M\,(\delta_i - \delta_k)^2 - 23060\,\bar{n}\,(E_i - E_k)^2 \tag{28}$$

These two equations are discussed more thoroughly in the "Review of The Literature." As in the case of Alcock and Richardson's equation, one can make only a qualitative comparison of the experimental values of $\lambda_{Al}^k(Z)$ with the theoretical values of $\epsilon_{Al}^k(Z)$, since the data necessary to convert from one to the other are unavailable. Trends within subgroups and periods can also be compared. Although this is not as desirable as a quantitative comparison, it is all that is possible.

In determining the interchange energies for the binaries involved in this study, the following sources of data were used: Hildebrand factors were obtained from reference (34); Mott's electronegativity values were used, unless otherwise noted; and the parameter $\bar{n}$ was taken to be the lesser of the valences of the two elements involved. The adoption of this particular value for $\bar{n}$ assumes that the two elements form the maximum number of two-electron bonds possible for the element of lesser valence.

In Table XIII are presented the values of $\epsilon_{Al}^{k}(Z)$ calculated from Wada and Saito's equation. The experimental values of $\lambda_{Al}^{k}(Z)$ for the same systems are also presented. As pointed out previously, although these two parameters will not in general be equal, they should have the same algebraic sign.

TABLE XIII

Qualitative Comparison of $\epsilon_{Al}^{k}(Z)$ Values From Wada and Saito's Equation With Experimental Values of $\lambda_{Al}^{k}(Z)$

Element k	Solvent Z	Experimental $\lambda_{Al}^{k}(Z)$	Calculated* $\epsilon_{Al}^{k}(Z)$
Ca	Bi	+ 9.5	+ 22.2
Sr	Bi	+ 10.4	+ 34.5
Ba	Bi	+ 14.2	+ 40.7
Pd	Bi	- 317	- 40.6
Sn^{II}	Bi	+ 33	- 9.3
Sb^{V}	Bi	-1550	- 13.3
Ca	Pb	- 4.2	+ 9.7
Sr	Pb	- 1.1	+ 21.6
Ba	Pb	+ 2.4	+ 25.5
Pd	Pb	+ 58	- 26.4
Sn^{II}	Pb	- 9.3	- 15.3
Sb^{V}	Pb	+ 30	+ 0.1

* Calculated from equation (26)

Consider first the parameters associated with the bismuth solvent. In those six cases, the values of $\epsilon_{Al}^{k}(Bi)$ agree qualitatively with the experimental values of $\lambda_{Al}^{k}(Bi)$ in every case except for the element Sn^{II}. Furthermore, it is interesting to note that the calculated values of $\epsilon_{Al}^{k}(Bi)$ for the alkaline earths reflect the trend of an increasing value of $\lambda_{Al}^{k}(Bi)$ as one proceeds down the alkaline earth subgroup. In the six systems associated with the lead solvent, the calculated values of $\epsilon_{Al}^{k}(Pb)$ agree qualitatively with the experimental values of $\lambda_{Al}^{k}(Pb)$ in only three of the six cases. The algebraic sign of $\lambda_{Al}^{k}(Pb)$ is predicted incorrectly for the third elements Ca, Sr, and Pd. Nevertheless, it is interesting to note that some of the trends in $\lambda_{Al}^{k}(Z)$ which were experimentally observed in changing solvents from bismuth to lead, are also observed in the calculated values of $\epsilon_{Al}^{k}(Z)$. For instance, the values of $\lambda_{Al}^{k}(Z)$ for the alkaline earth elements are considerably less positive in lead than they are in bismuth. In fact, $\lambda_{Al}^{Ca}(Pb)$ and $\lambda_{Al}^{Sr}(Pb)$ are negative. The trend of $\lambda_{Al}^{k}(Z)$ increasing in positive value as one descends the alkaline earth subgroup, which was found to exist in bismuth, also exists in lead. Both of these trends are also indicated by the calculated values of $\epsilon_{Al}^{k}(Z)$, but positive, rather than negative, values of $\epsilon_{Al}^{Ca}(Pb)$ and $\epsilon_{Al}^{Sr}(Pb)$ are predicted. Furthermore, Wada and Saito's equation predicts that $\lambda_{Al}^{Pd}(Pb)$ should be less negative than $\lambda_{Al}^{Pd}(Bi)$, $\lambda_{Al}^{Sn}(Pb)$ should be more negative than $\lambda_{Al}^{Sn}(Bi)$, and $\lambda_{Al}^{Sb}(Pb)$ should be less negative than $\lambda_{Al}^{Sb}(Bi)$. These predictions are all consistent with the experimental values of $\lambda_{Al}^{k}(Z)$, although the algebraic signs are not correct in every case. In the iron-base systems to which they applied their equation, Wada and Saito also found the algebraic sign to be predicted erroneously in several cases. This equation does predict the opposite signs which were found to exist between $\lambda_{Al}^{Sb}(Bi)$ and $\lambda_{Al}^{Sb}(Pb)$. Of course, the calculated value of $\epsilon_{Al}^{Sb}(Pb)$ is so small (+0.1) that the significance of the algebraic sign is perhaps disputable. Still, as in all the other cases, the trend is in the right direction.

In calculating the values of $\epsilon_{Al}^{k}(Pb)$ given in Table XIII, it was assumed that the electronegativity of lead is 1.6, Mott's value (23) There seems to be considerable disagreement in regard to this value; values for the electronegativity of lead range all the way from 1.5 up to 1.8 in the literature. The value of 1.6 was used for all the calculations in Table XIII, because it was found that this figure gave more realistic values of $\epsilon_{Al}^{k}(Pb)$ than did the value of 1.8.

The values of $\epsilon_{Al}^{k}(Z)$ calculated from Wada and Saito's equation and tabulated in Table XIII are indeed interesting, particularly in view of the trends in $\lambda_{Al}^{k}(Z)$ which they reflect. The inconsistencies which were found to occur are probably due to two primary factors: first, Wada and Saito's equation assumes a regular solution, and is based on the relatively crude zeroth approximation of this model; second, the expression for the interchange energy, W, cannot be expected to be very precise. In addition to the empirical basis of this equation, it is impossible to obtain a precise value for $\bar{n}$, the number of element-element bonds. Furthermore, most electronegativity values are open to some question. Nevertheless, as pointed out previously, this equation does represent a significant step toward the solution of a very complex problem.

The results of this investigation have been discussed above in terms of Alcock and Richardson's equation, and Wada and Saito's equation. That discussion is as quantitative as is possible at the present time. The results will now be discussed in terms of the electronegativities of the elements involved, in conjunction with Wagner's electron model of a liquid alloy.

When one adds aluminum to bismuth, he would expect the (e/a) ratio to increase, since bismuth has the higher electronegativity (see Table III). According to the results tabulated in Tables IV and VI, it appears that aluminum may very well have an electronegativity of about 1.8, rather than the 1.5 value given in Table III. This was discussed previously in this chapter of the thesis. Accepting Pauling's value of 1.9 for the electronegativity of bismuth, however, it appears that bismuth still has a higher electronegativity than aluminum. According to the electronegativities of the six elements used as third components in conjunction with the study of the Bi-Al system, then, Ca, Sr, and Ba should definitely increase the (e/a) ratio when added to bismuth, as aluminum did, and Pd should definitely decrease it. On the basis of Pauling's electronegativities, it is difficult to say whether Sn and Sb will increase or decrease this (e/a) ratio, since their electronegativities are listed as being so close to that of bismuth. On the basis of other electronegativity scales (Gordy-Thomas, Kleppa), however, it appears quite likely that Sn would increase and Sb would decrease the (e/a) ratio of the Bi-Al binary. Thus, on the basis of these changes in (e/a) ratio, and in accordance with the hypotheses and assumptions formulated in the earlier discussion involving electronegativities, one would expect Ca, Sr, Ba, and probably Sn to give positive values of $\lambda_{Al}^{k}(Bi)$. By the same token, one would expect Pd, and probably Sb to give negative values of $\lambda_{Al}^{k}(Bi)$. According to the experimental values of $\lambda_{Al}^{k}(Bi)$ for these six elements, these predictions are correct in every case. It is interesting to note further that as one descends the alkaline earth subgroup from Ca to Ba, the values of $\lambda_{Al}^{k}(Bi)$ increase monotonically in positive value. The logical explanation for this, based upon the previously-formulated hypothesis, is that since the electronegativities decrease as one descends this subgroup, the ability of these atoms as electron donors also increases in the same order. Therefore, Ba, for example, increases μ_e to a greater extent than does Ca upon addition to the Bi-Al binary solution. For this reason, and since aluminum also increases μ_e upon addition to Bi in the first place, then according to equation (41), $\lambda_{Al}^{Ba}(Bi)$ would be expected to have a larger positive value than $\lambda_{Al}^{Ca}(Bi)$.

Considering now the lead-base ternaries studied in this investigation, the same line of reasoning used above will be applied in attempting to explain the experimental results obtained. To begin with, it should be noted that the values of $\lambda_{Al}^{k}(Pb)$ are opposite in sign from the values of $\lambda_{Al}^{k}(Bi)$ in every case except for barium. This would tend to make one suspect that aluminum is more electronegative than lead. If one checks the electronegativities in Table III, he will find that the electronegativity of lead is reported as being anywhere from 1.5 up to 1.8, depending upon who reported it. Most investigators indicate a value in the neighborhood of 1.5 to 1.6. On the other hand, the electronegativity values reported in Table III for aluminum seem fairly well agreed upon at a value of 1.5. In a previous section of this chapter of the thesis, however, where interaction parameters taken from the literature were discussed in terms of electronegativities, it was concluded that aluminum might very well have an electronegativity of about 1.8. This particular value explained eight of nine interaction parameters involving aluminum, whereas the 1.5 value explained only three of nine. Interestingly enough, this same value for the electronegativity of aluminum explains a maximum number of the interaction parameters measured in this investigation for the lead-base systems. If the electronegativity of aluminum is indeed about 1.8, and the electronegativity of lead is less than this (it is probably in the neighborhood of 1.6), then one would expect the interaction parameters for Ca, Sr, and Ba to be negative, and the parameters for Pd, Sb, and probably Sn to be positive. The electronegativity of Sn is probably very close to that of lead, and, because of this, it is a little more difficult in the case of Sn than of the other elements to say what algebraic sign $\lambda_{Al}^{k}(Pb)$ will have. One would be inclined, however, to say that $\lambda_{Al}^{Sn}(Pb)$, on the basis of electronegativities, is positive (which is erroneous). Thus, the predicted parameters agree qualitatively with the experimental values in every case except for barium and tin. There is one other apparent inconsistency; if the electronegativities of Pb, Al, and the alkaline earth elements have the values given above and in Table III, one would expect the values of $\lambda_{Al}^{k}(Pb)$ for the alkaline earth elements to decrease in positive value in the opposite order from which they actually do. This statement is based on the same line of reasoning used to explain the similar behavior observed in bismuth for the alkaline earth elements. Nevertheless, the observed values of $\lambda_{Al}^{k}(Pb)$ are explained qualitatively for at least four of the six elements studied. This fact, combined with the fact that a value of 1.8 for the electronegativity of aluminum explains eight of nine, rather than three of nine, parameters presented in Tables IV and VI, tends to support a value of 1.8 for the electronegativity of aluminum, rather than 1.5. If the electronegativity of aluminum is 1.5, as it is reported, then only two ($\lambda_{Al}^{Sn}(Pb)$ and $\lambda_{Al}^{Ba}(Pb)$) of the six lead-base parameters measured are explained qualitatively.

It is not obvious why $\lambda_{Al}^{Ba}(Pb)$ and probably $\lambda_{Al}^{Sn}(Pb)$ do not conform to the hypothesis based on electronegativities, while all the other parameters do. There is a considerable amount of uncertainty in some of the electronegativities involved (viz. aluminum and lead), which makes it difficult to make very definite predictions of the interaction parameters in the lead-base systems. Also, the electronegativities appear to be so close together for some of the elements involved, that predictions are made difficult. Perhaps ion-ion interactions, which were neglected in all predictions, are more pronounced in the lead-base systems than they were in the bismuth-base systems, although it is not apparent why this should be so.

The discussion presented above regarding the interactions observed in bismuth-base and lead-base systems can be summarized in the following manner: the hypothesis formulated in terms of (e/a) ratios and the electronegativities of the elements explains all the bismuth-base data in a qualitative manner; except for the Pb-Al-Ba and Pb-Al-Sn systems, it also qualitatively explains the lead-base data, if the electronegativity of aluminum is greater than that of lead. If the electronegativity of lead is, in fact, greater than that of aluminum, then the hypothesis fails, explaining only two of the six lead-base parameters. According to the literature values of electronegativities, it is difficult to say which element has the greater electronegativity. If the electronegativity hypothesis means anything, however, literature data and the data taken in this thesis on interaction parameters support a value of about 1.8 for the electronegativity of aluminum.

Finally, the results of this investigation will be discussed in terms of the regular behavior exhibited by the interaction parameters with respect to the periodic table. Such behavior was discussed previously in this chapter. As illustrated in Figure 22, the values of $\lambda_{Al}^{k}(Bi)$ and $\lambda_{Al}^{k}(Pb)$, where k represents Ca, Sr, or Ba, increase in positive value monotonically with increasing atomic number. In fact, an approximate value for $\lambda_{Al}^{Mg}(Bi)$ also falls into the regular sequence

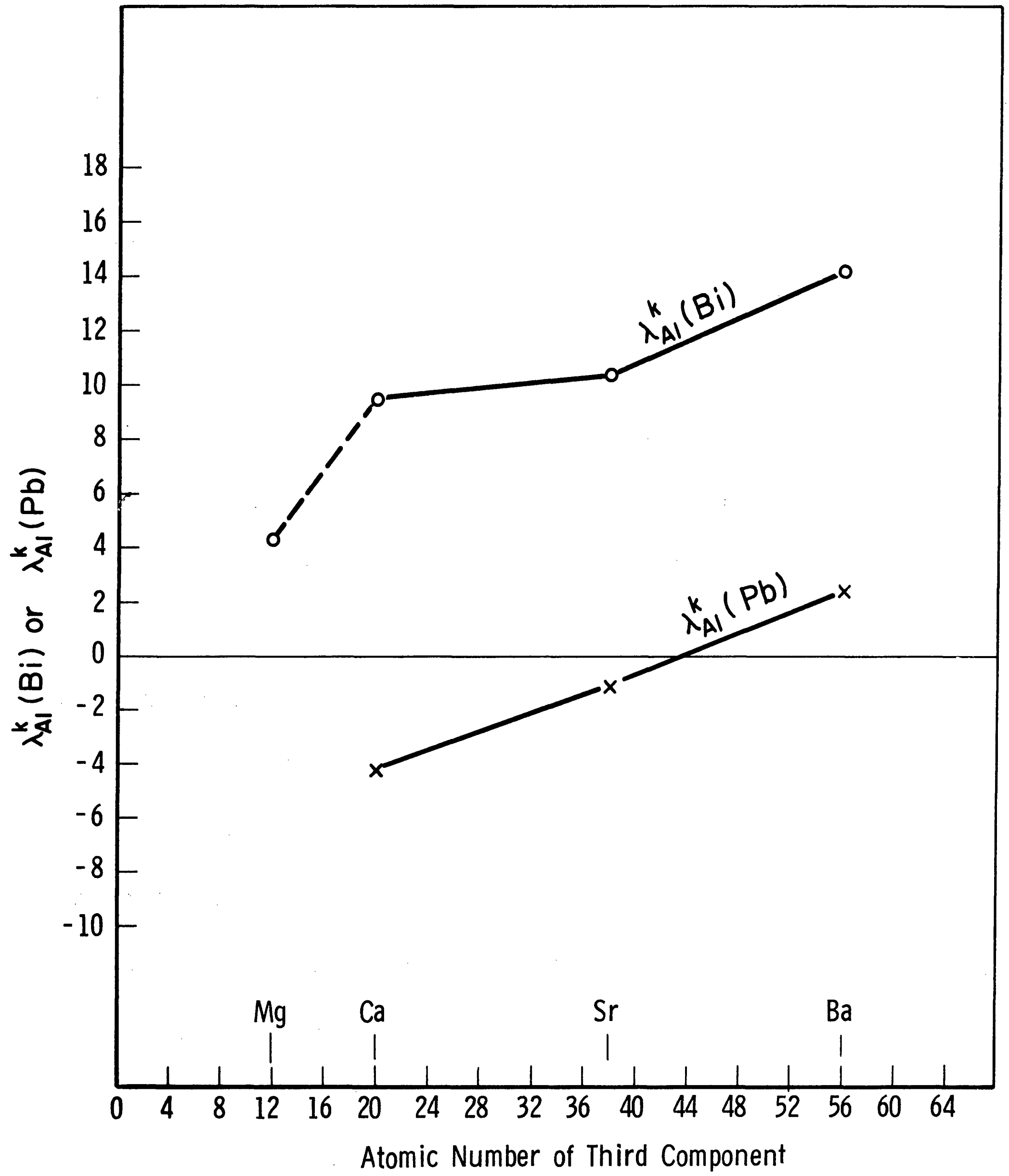


Figure 22. $\lambda_{Al}^{k}(Bi)$ and $\lambda_{Al}^{k}(Pb)$ versus Atomic Number at Element k

for the bismuth solvent, as shown in the same figure. The reason that this value of $\lambda_{Al}^{Mg}(Bi)$ must be regarded as only approximate is because its determination, out of necessity, was based on two assumptions. First of all, in determining the value of γ_{Al} in the Bi-Al-Mg ternary, Raoult's law was assumed to hold in the Mg-Al binary out to 12 atomic percent magnesium. This assumption was necessary because magnesium dissolves to the extent of 12 atomic percent in solid aluminum at 549°C. Secondly, it was assumed that the relationship between $\ln\gamma_{Al}$ and N_{Mg} in the Bi-Al-Mg ternary was linear between zero and 3.6 atomic percent magnesium. This assumption was necessary because of the fact that the only equilibrium concentration known at 549°C for this ternary is the point at 3.6 atomic percent magnesium. The data on this ternary were taken at Brookhaven National Laboratory (42). This data point, in combination with the author's Bi-Al binary data at 549°C was used to determine $\lambda_{Al}^{Mg}(Bi)$.

The values of $\lambda_{Al}^{k}(Bi)$, where k represents the elements Pd, Sn, and Sb, were found not to follow a regular pattern when plotted against the atomic number of element k. The values of $\lambda_{Al}^{k}(Pb)$ for the elements Pd and Sb were considered to be too approximate to plot in this manner, because they were determined on the basis of only one value of $\ln\gamma_{Al}$ in the respective ternaries (see Figures 19 and 21). The values of $\lambda_{Al}^{k}(Bi)$ for Pd, Sn, and Sb were found in this investigation to be -317, +33, and -1550, respectively. Although they do not follow a regular pattern when plotted against the atomic number of element k, as do the parameters for Ca, Sr, and Ba, they do increase monotonically in positive value with certain of the properties of the elements k. They increase with decreasing first ionization potential, decreasing electronegativity (Gordy-Thomas), and decreasing heat of fusion of element k.

These three properties could very likely be important variables in the determination of $\lambda_i^k(Z)$. The values of $\lambda_{Al}^k(Bi)$ and $\lambda_{Al}^k(Pb)$ for Ca, Sr, and Ba exhibit this same behavior when plotted against the same three variables. Thus, the apparently anomolous behavior exhibited by some of the fundamental properties (first ionization potential, electronegativity, and heat of fusion) of Pd, Sn, and Sb as one proceeds across the period is perhaps reflected in the respective values of $\lambda_{Al}^k(Bi)$.

VI. SUMMARY AND CONCLUSIONS

This investigation was undertaken for the purpose of studying third component interactions with dilute solutions of aluminum in liquid bismuth and liquid lead. Initially, the solubility of aluminum in these two solvents was measured over the approximate temperature range 450-600°C. Studies were then made of the effects of various third components on these two binary systems at 549°C. The interaction parameters, $\lambda_{Al}^{k}(Z)$, were determined for each of the twelve ternary systems studied. The results were discussed in terms of: (1) Alcock and Richardson's equation; (2) Wada and Saito's equation; (3) the electronegativities of the elements involved, in conjunction with Wagner's electron model of a liquid alloy. Attention was also given to the regular behavior with respect to the periodic table which is exhibited by some of the parameters measured. Interaction parameters whose values were obtained from the literature were also discussed on the same bases.

As a result of the investigation presented here, the following conclusions are drawn:

1. The solubility of aluminum in liquid bismuth and liquid lead over the approximate temperature range 450-600°C is given by equations (36) and (37), respectively.

$$\log_{10}(\text{wt. \% Al}) = 2.55 - \frac{2110}{T°K} \qquad (36)$$

$$\log_{10}(\text{wt. \% Al}) = 1.86 - \frac{2540}{T°K} \qquad (37)$$

2. Over the temperature range 450-600°C, the relative partial molar enthalpy of aluminum in liquid bismuth was found experimentally to be $9.2 \frac{\text{k cal}}{\text{g atom}}$. The same quantity for aluminum in liquid lead was found to be $11.6 \frac{\text{k cal}}{\text{g atom}}$. This quantity

represents the difference between the partial molar enthalpy of aluminum in solution at saturation and the molar enthalpy of pure, solid aluminum at the same temperature.

3. The elements Ca, Sr, Ba, and Sn increase the activity coefficient of aluminum in liquid bismuth, and Pd and Sb decrease it. Except for barium, these elements have just the opposite effect on the activity coefficient of aluminum in liquid lead. The parameters $\lambda_{Al}^{k}(Bi)$ and $\lambda_{Al}^{k}(Pb)$ were determined for these six elements.

4. Because of the lack of appropriate binary data, it was impossible to calculate theoretical values of the $\lambda_{Al}^{k}(Z)$ parameters. Therefore, no quantitative comparison could be made between theory and experiment. Alcock and Richardson's, and Wada and Saito's equations do, however, indicate some of the trends from parameter to parameter which were found to exist.

5. The effects of the elements studied on the activity coefficient of aluminum in liquid bismuth and liquid lead can be explained reasonably well in a qualitative manner by the electronegativities of the elements involved, in conjunction with Wagner's electron model of a liquid alloy.

6. In the course of the analysis involved with 4 above, it was concluded that the electronegativity of aluminum may be closer to 1.8 for the systems studied than to the generally reported value of 1.5. This was also indicated by interaction parameters whose values are recorded in the literature. This question should be investigated further.

7. The present investigation indicates areas where further studies are needed. This is discussed in the following chapter.

The review of the interaction parameters published in the literature leads to the following conclusions:

1. Electronegativities of the elements, in conjunction with Wagner's electron model of a liquid alloy explain, in a qualitative manner, a good share of the $\epsilon_i^k(Z)$ values published in the literature. It appears that free electron concentration may be an important variable in the study of liquid metal alloys.
2. It appears that, to some extent, interaction parameters can be correlated with the periodic table. This has been suggested previously by other investigators. Additional data from the literature, as well as some of the data from this investigation, lend further support to this statement.
3. Alcock and Richardson's equation is probably the best method, at the present time, for obtaining a semi-quantitative theoretical value of $\epsilon_i^k(Z)$. This equation has not been tested very thoroughly, however, because of the lack of appropriate data. Further experimentation should be carried out for the purpose of obtaining this type of data.
4. Wada and Saito's equation makes it possible to calculate a theoretical value of $\epsilon_i^k(Z)$ from fundamental properties of the elements involved. This type of a development is particularly desirable. One of the next logical steps in the study of solute interactions would be to attempt to improve on Wada and Saito's development by attempting to improve on the equation for $\epsilon_i^k(Z)$ itself, and/or improving on the expression for the interchange energies.

VII. SUGGESTIONS FOR FURTHER STUDY

It is obvious that a lot of work remains to be done on the study of solute interactions in molten alloys. At the present time, it appears that Alcock and Richardson's equation is one of the best methods of predicting $\epsilon_i^k(Z)$, although it is only semi-quantitative, at best. Therefore, it is felt that this equation should be tested more thoroughly by experiment. Such investigations might indicate the types of systems to which this equation is most applicable and the types of systems for which it could not be expected to yield very accurate results. This is apparent to some degree from the assumptions made in the derivation of the equation, but experiment should reveal the true capabilities and limitations of the equation more definitely.

In order to test the applicability of Alcock and Richardson's equation to a particular ternary system, the appropriate binary data must also be available. According to equation (21), if one knows the limiting values of the activity coefficients for each of the three constituent binaries of a ternary solution, he can calculate a theoretical value of $\epsilon_i^k(Z)$. According to equation (38), one can calculate a theoretical value of $\epsilon_i^k(Z)$ if he knows the limiting partial heats of solution rather than the activity coefficients of the binaries involved. Perhaps it would be necessary to obtain some of this binary data experimentally in order to study the particular ternary systems desired. Well-planned experimental programs could be revealing, not only in regard to Alcock and Richardson's equation in particular, but also to the interaction problem in general.

Another investigation which might be undertaken in the study of solute interactions would be largely theoretical in nature. This would involve a study of Wada and Saito's equation and an attempt to improve upon it. This might be carried out in either or both of two ways: through attempting to improve upon the equation for $\epsilon_i^k(Z)$ itself (perhaps a higher order approximation of the regular solution model), and/or attempting to improve upon the expression for the interchange energies. Such equations should finally be tested by comparison with experiment. As pointed out previously, a development such as Wada and Saito's is particularly desirable because of the fact that it is based upon quite fundamental properties of the elements.

It might be worthwhile to carry out further studies involving either or both of the elements aluminum and lead. Although the electronegativity of aluminum is reported in the literature to be 1.5, the present investigation and some of the literature data on interaction parameters indicate that it may be in the neighborhood of 1.8 for the types of systems considered. There also seems to be considerable disagreement in the literature concerning the electronegativity of lead. It might be desirable to perform experiments aimed at determining the electronegativities of these two elements more closely.

In the present investigation the effects of several different elements on the activity coefficient of aluminum in liquid bismuth and liquid lead were determined. It would be interesting to expand this study to include other elements in the periodic table, at least in the case of the bismuth solvent. Such investigations should be well designed with respect to the periodic table. For instance, one might make further studies using elements from the same subgroup of the periodic table as third components. Since the very metallic elements Ca, Sr, and Ba have already been studied, it would be interesting to study some of the more non-metallic elements, such as S, Se, and Te. Their interactions with aluminum would be expected to be quite strong. It would be interesting to compare the results of the two studies (metallic vs. non-metallic), and investigate the periodicity and algebraic sign of the interaction parameters. According to their relative electronegativities, and Wagner's electron model of an alloy, one would expect $\lambda_{Al}^{k}(Bi)$ to be negative for the non-metals S, Se, and Te. This parameter was positive for the metallic elements Ca, Sr, and Ba. The same studies carried out in a lead solvent could be revealing in regard to the relative electronegativities of aluminum and lead.

Another area of study is involved with varying the primary solute rather than the third components in the ternary systems studied. For instance, as a continuation of the present study, one might vary the primary solute from aluminum down the III-A subgroup successively to Ga, In, and Tl, using as third components one or more of the third components used in the present study (preferably Ca, Sr, or Ba). For one thing, it would be interesting to see if one observes a regular behavior in the magnitude of the interaction parameters as he varies the primary solute down this subgroup; such behavior was observed in varying the third components down a subgroup. It would also be interesting to compare, in the light of the relative electronegativities of the elements involved, the algebraic signs of the parameters obtained.

Another investigation one might consider is involved with variation of the solvent, rather than the solutes, from system to system. This was done in the present study, to some extent; the studies carried out in the bismuth solvent were also carried out in lead. In Figure 22 are plotted the interaction parameters $\lambda_{Al}^{k}(Bi)$ and $\lambda_{Al}^{k}(Pb)$ for the elements Ca, Sr, and Ba. The parameters for lead consistently fall below those involving the bismuth solvent. If these same studies were now carried out in solvents of Tl and Hg (which are in the same period as Bi and Pb), where would the parameters fall in relation to those shown in Figure 22? Is there some degree of periodicity in the parameters as one changes solvents across a period or down a subgroup, such as one observes in varying the third element in this manner? Also, how do the parameters behave with respect to the electronegativities of the elements involved?

The study of some of the specific ternary systems mentioned above may turn out to be impracticable for reasons which would become obvious upon further consideration of the problems. If this were the case, however, it should be possible to select other more desirable systems to replace them and accomplish the same goals.

Other topics worthy of further investigation include: an experimental study of Wagner's equation for $\ell n\gamma_i$ in a multicomponent system (see equation (2) in "Review of The Literature"); an experimental study of Wagner's reciprocity relationship.

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APPENDICES

APPENDIX A

BINARY PHASE DIAGRAMS

The binary phase diagrams presented in this appendix were reproduced from:

> "Constitution of Binary Alloys," M. Hansen. 1958. McGraw-Hill Book Co., Inc.

They are all used with the permission of the publishers. Each of these diagrams is associated with one or more of the ternary systems studied, and are included for the convenience of the reader in studying the results obtained in this investigation.

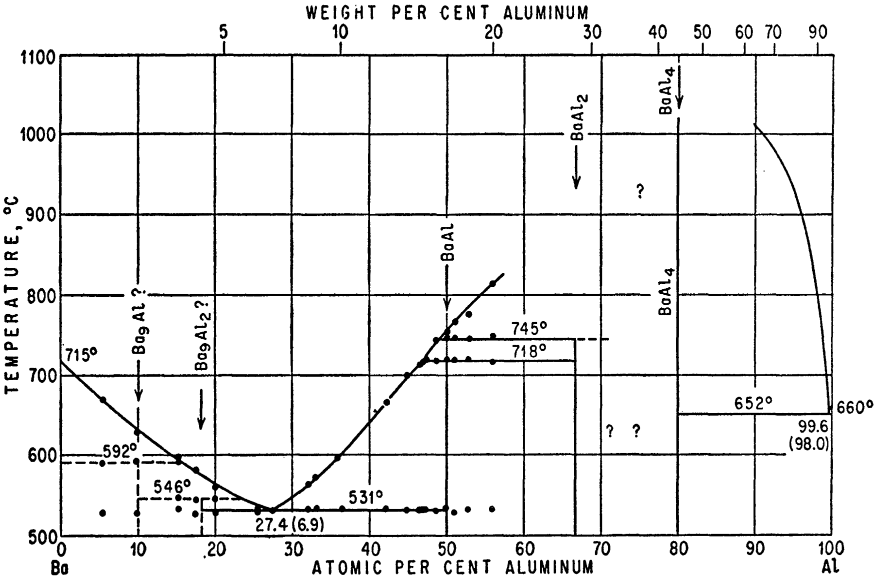

Figure 23. The Al-Ba System

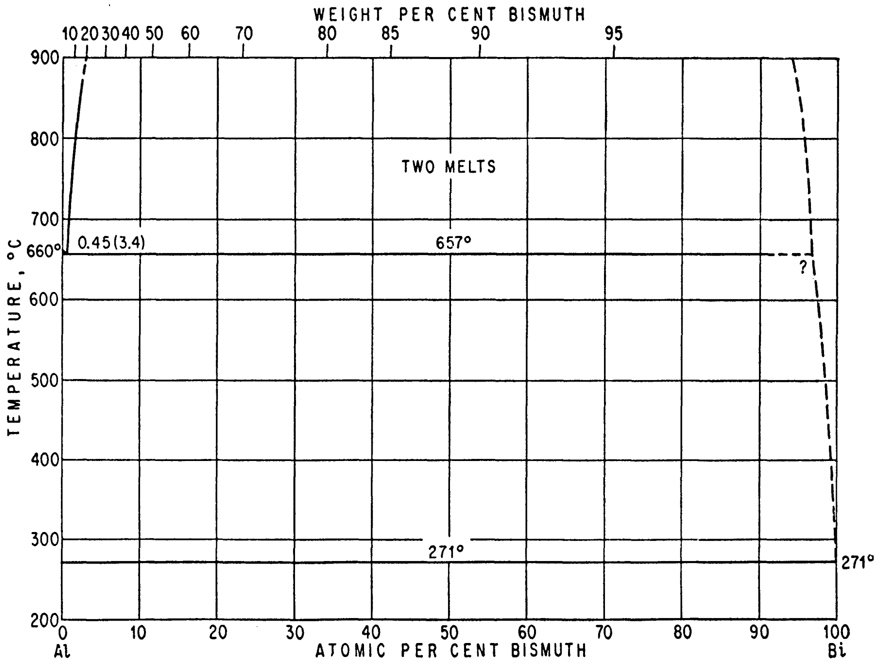

Figure 24. The Al-Bi System

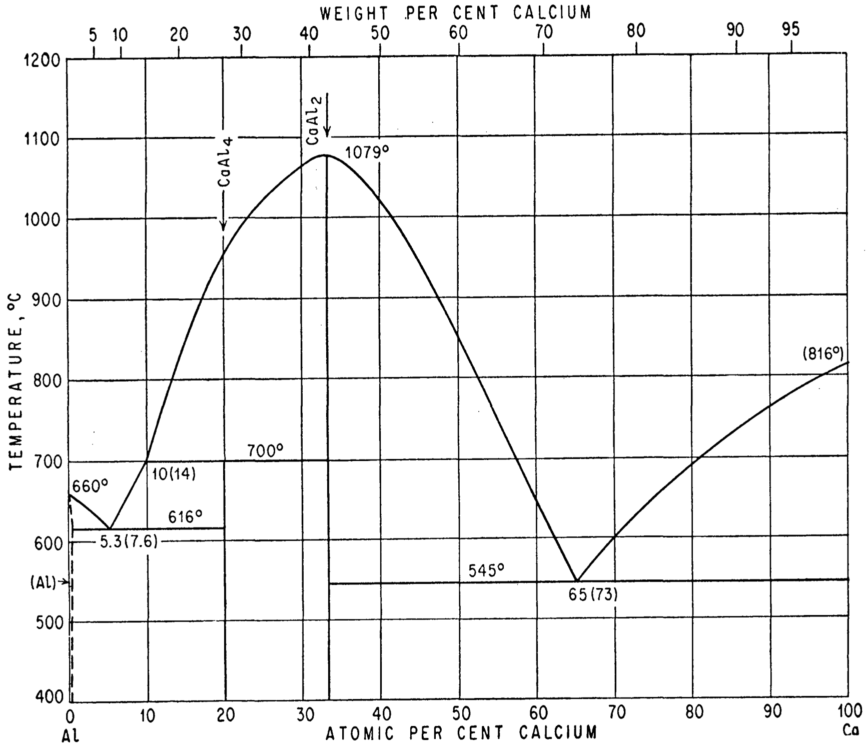

Figure 25. The Al-Ca System

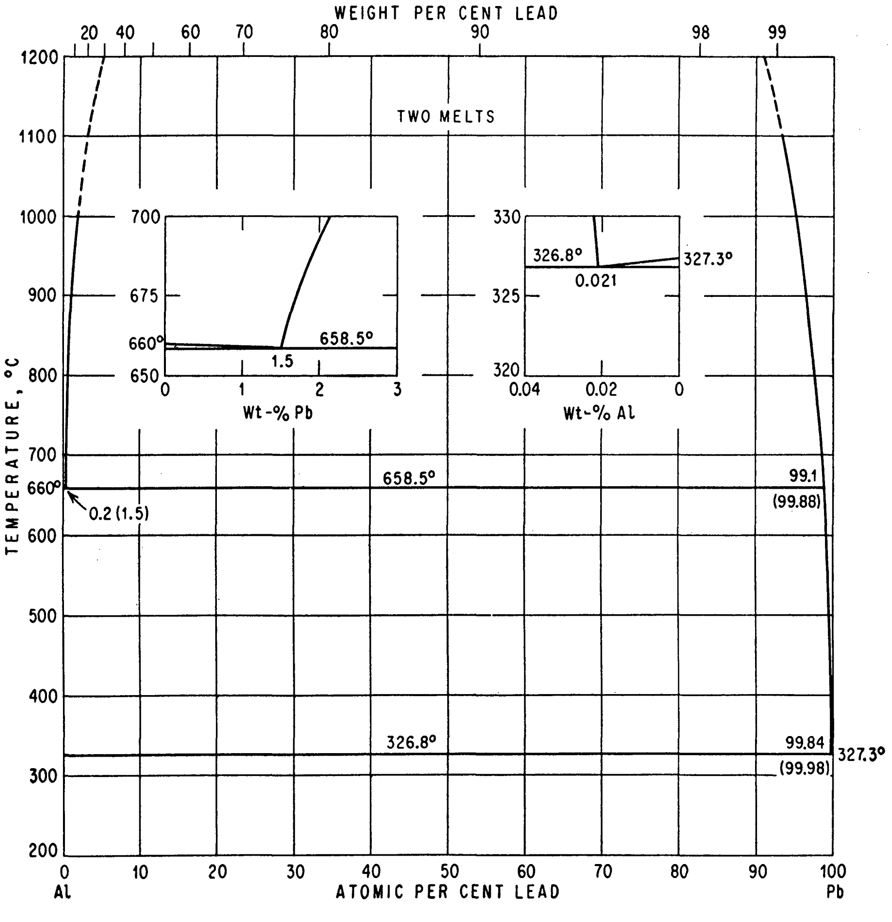

Figure 26. The Al-Pb System

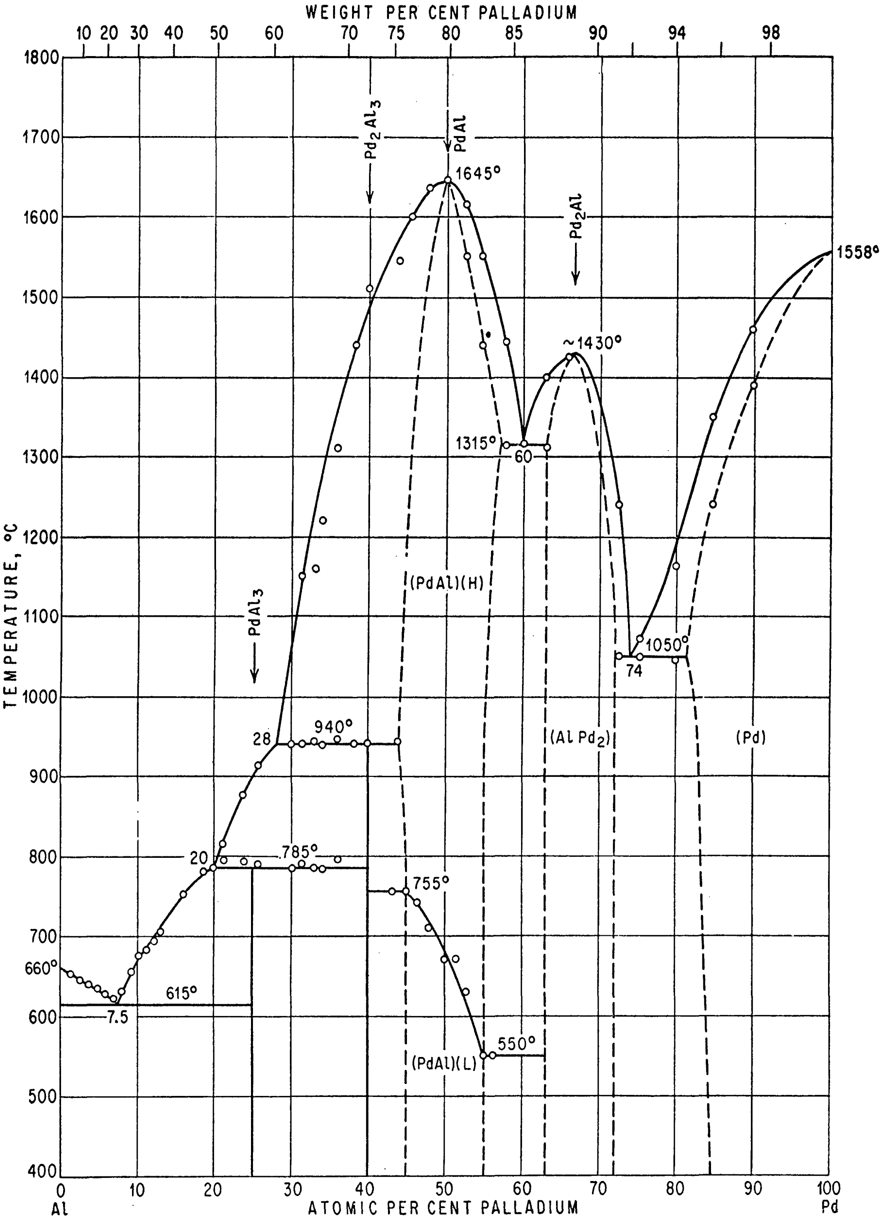

Figure 27. The Al-Pd System

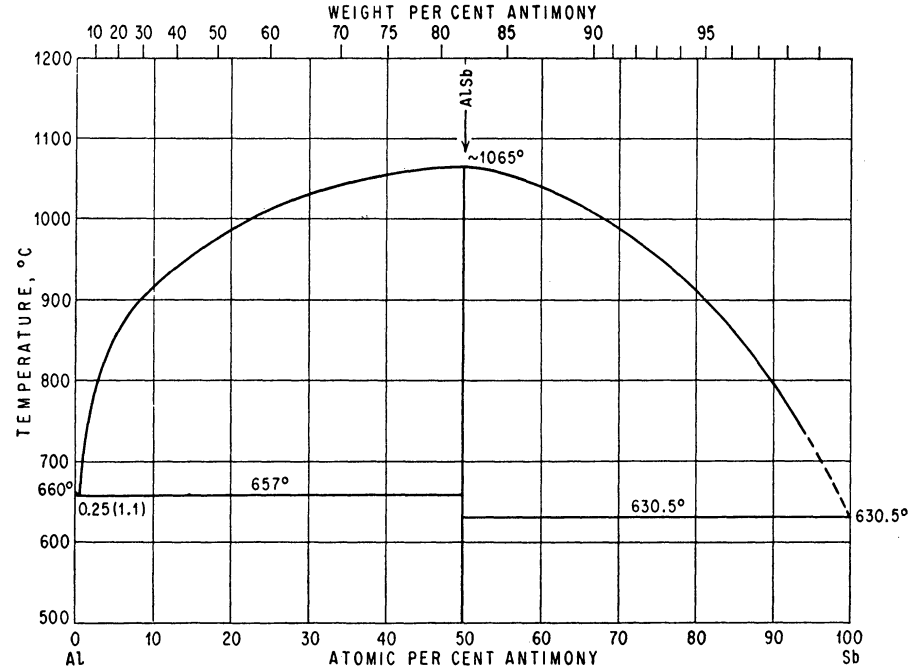

Figure 28. The Al-Sb System

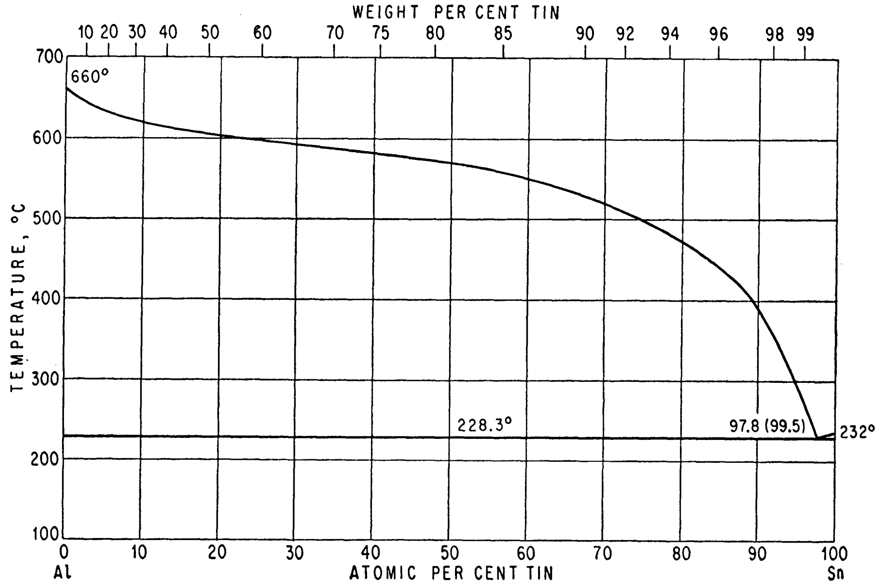

Figure 29. The Al-Sn System

The following conclusions [1] have been drawn from the results of X-ray studies of alloys with up to 50 at. (76.46 wt.) % Sr: (*a*) The solid solubility of Sr in Al is apparently negligibly small. (*b*) There are two intermediate phases, based on the compositions $SrAl_4$ (44.81 wt. % Sr) and SrAl. $SrAl_4$ possesses a homogeneity range which extends, at 700°C, from about 15 to 25.7 at. % Sr. SrAl dissolves some Sr and decomposes at temperatures up to at least 300°C into $SrAl_4$ and Sr. (*c*) The Al-$SrAl_4$ eutectic lies below 0.3 at. (about 1.0 wt.) % Sr. The eutectic temperature was not determined.

$SrAl_4$ is tetragonal of the $BaAl_4$ ($D1_3$) type, $a = 4.46$ A, $c = 11.07$ A, $c/a = 2.48$; and SrAl is b.c.c. of an unknown type with $a = 15.8$ A ($a = 16.4$ A if saturated with Sr) and 116 atoms per unit cell. The structure is probably a superstructure of the CsCl type.

1. H. Nowotny and H. Wesenberg. *Z. Metallkunde*, **31**, 1939, 363–364.

Figure 30. The Al-Sr System

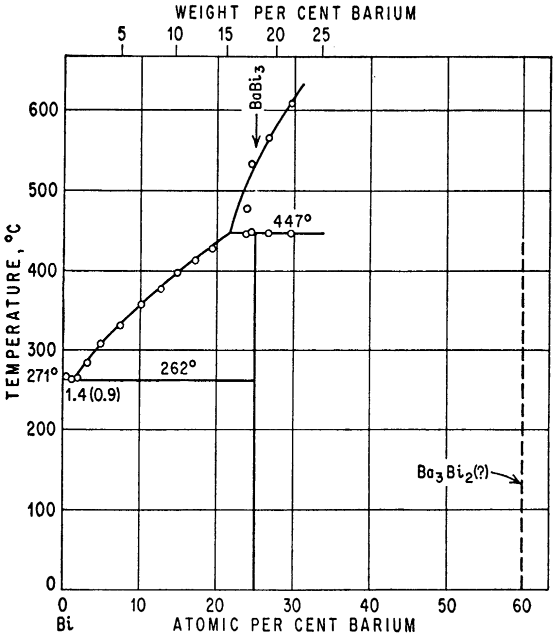

Figure 31. The Ba-Bi System

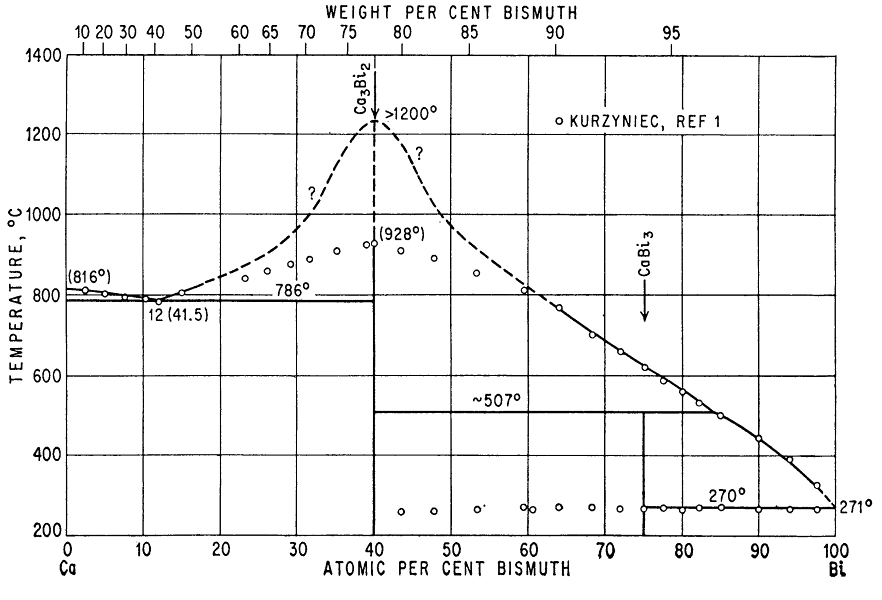

Figure 32. The Bi-Ca System

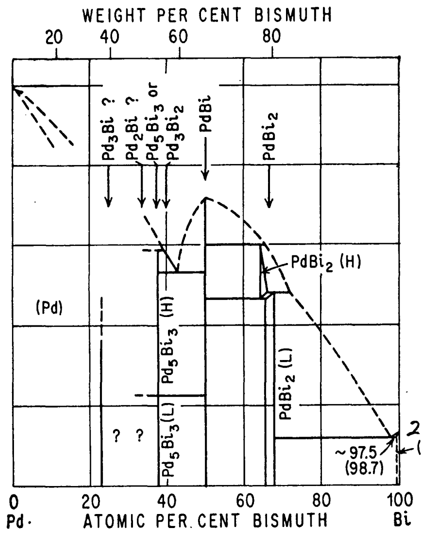

Figure 33. The Bi-Pd System

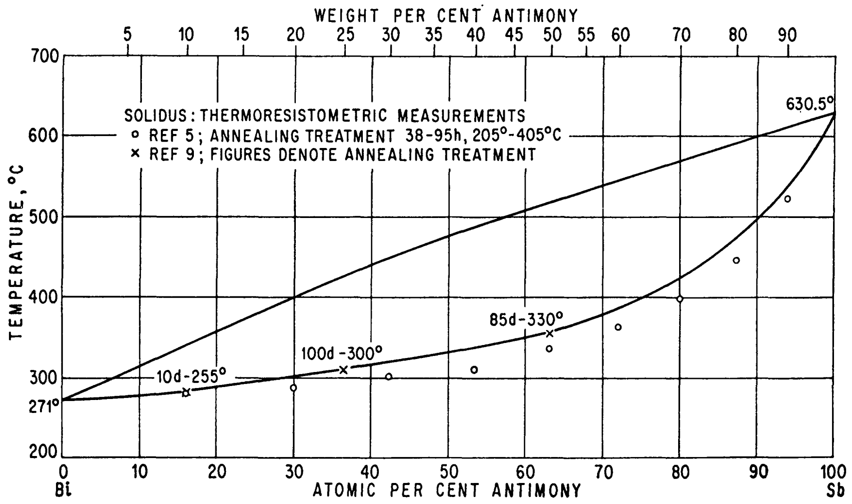

Figure 34. The Bi-Sb System

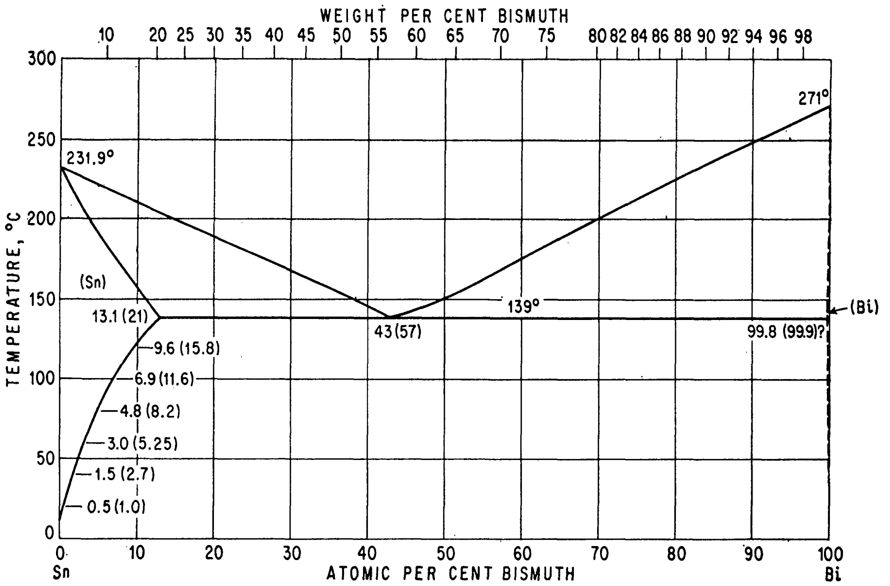

Figure 35. The Bi-Sn System

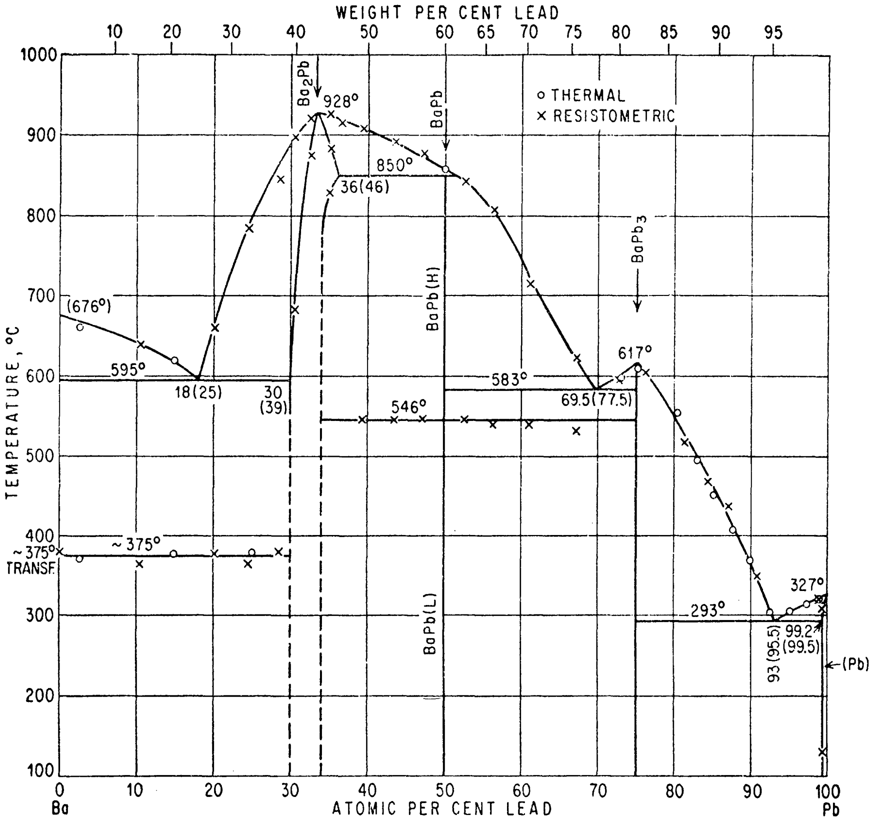

Figure 36. The Ba-Pb System

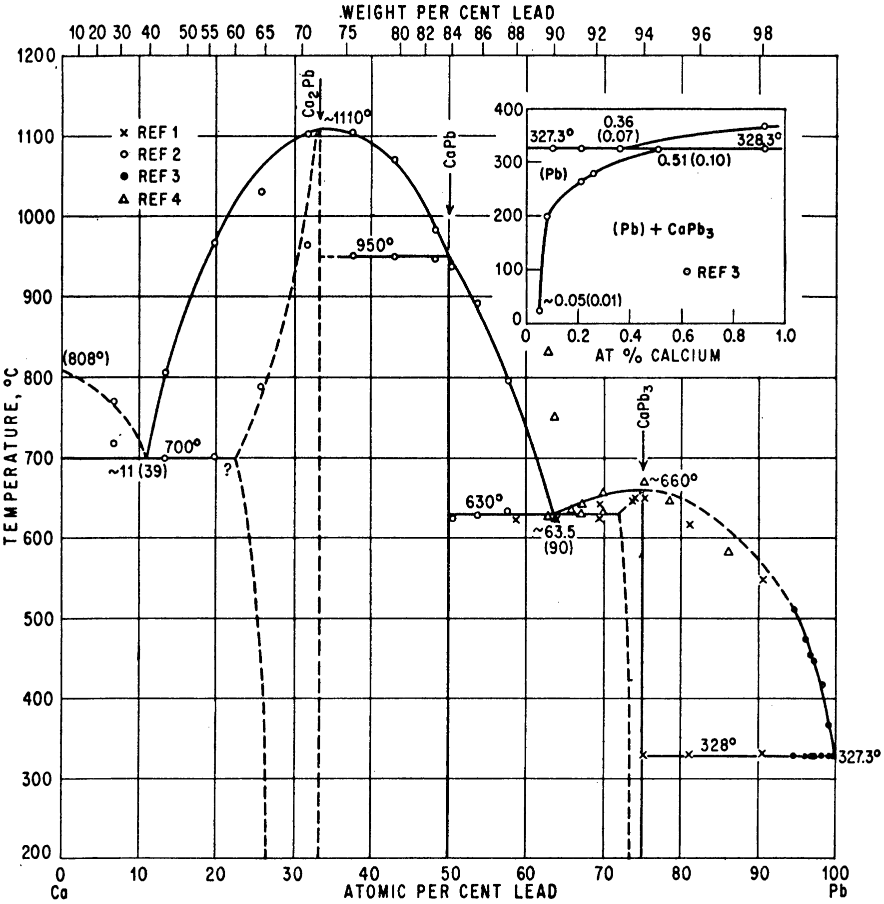

Figure 37. The Ca-Pb System

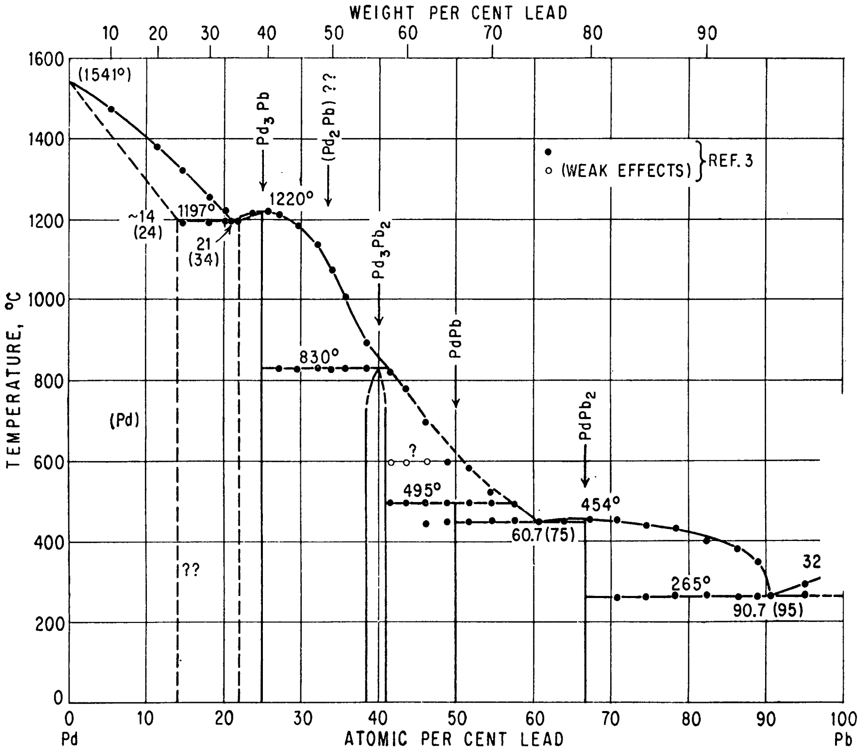

Figure 38. The Pb-Pd System

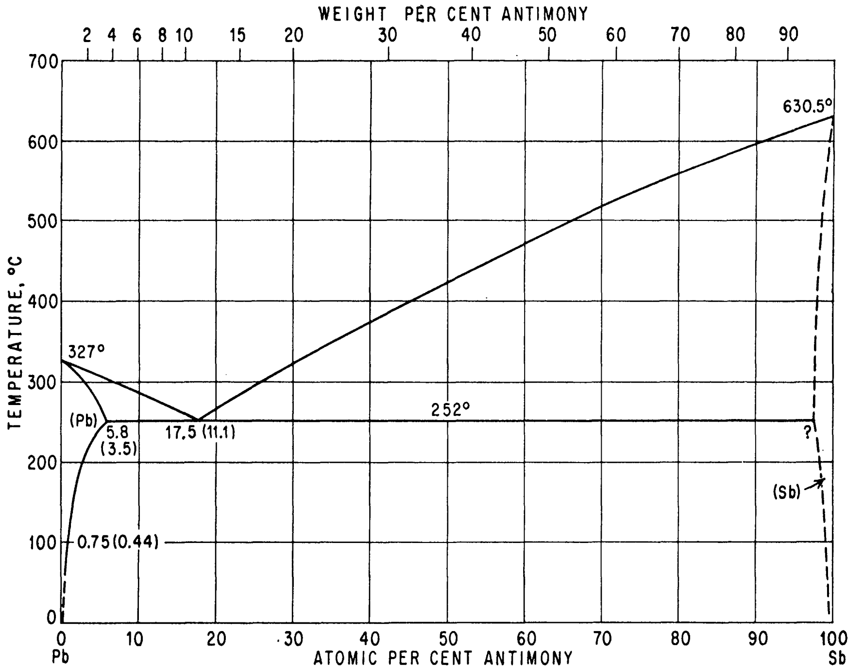

Figure 39. The Pb-Sb System

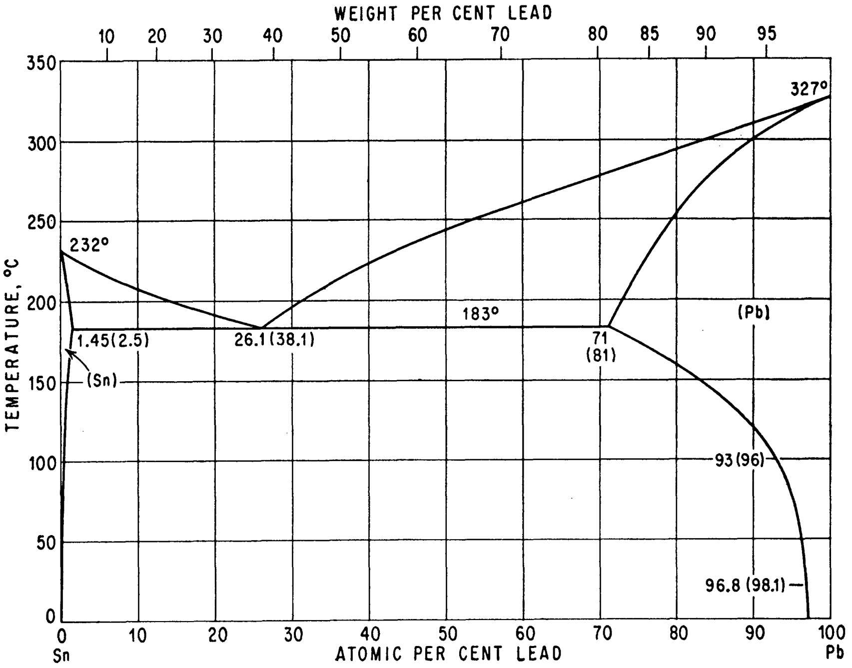

Figure 40. The Pb-Sn System

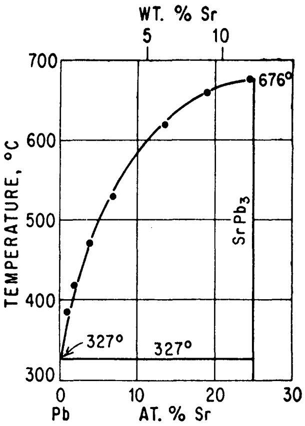

Figure 41. The Pb-Sr System

APPENDIX B

CHEMICAL ANALYSIS PROCEDURES

I. THE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINUM IN BISMUTH ALLOYS AND LEAD ALLOYS

Introduction

Aluminum is determined spectrophotometrically after bismuth and lead have been removed by precipitation as their respective sulfides. All other interfering ions, of course, must also be removed by some appropriate means. Calcium, barium, and strontium were found to cause no interference. The aluminum is then determined by measuring the absorbence of the aluminum--8 hydroxyquinoline complex in chloroform at 395 millimicrons. Beer's law is observed in the range from 0 to 30 micrograms of aluminum per 10 ml of chloroform.

Apparatus

The Beckman Model DU Spectrophotometer with a tungsten lamp and a blue sensitive cell; fused silica cells having a path length of 1 cm. A pH meter must also be available.

Reagents

Nitric acid, conc., reagent grade

Hydrochloric acid, conc., reagent grade

Ammonium hydroxide, 5 M

Hydrochloric acid, 3 M

Acetate buffer (4.2 - 5.0 pH range)

Bromphenol blue indicator solution, 0.05 wt. per cent

8 hydroxyquinoline solution (1 wt. per cent in purified chloroform).

The chloroform is purified by shaking with concentrated ammonium hydroxide and a saturated solution of ammonium chloride.

Preparation of Samples

1. Weigh the sample and dissolve it in 75 ml of 1:1 nitric with 25 ml of 1:1 hydrochloric acid on a hot plate.
2. Dilute samples to required volume (the solution should be such that no more than 10 ml will be required for the analysis).
3. Pipette an aliquot of the sample into a 125 ml ehrlenmeyer flask. This aliquot should be such that after removing the Bi or Pb which it contains, it can be diluted to a volume consistent with 2 above. The pH of this solution is then adjusted to the point of incipient precipitation of BiOCl, using 5 N ammonium hydroxide. This is followed by saturation with H_2S for 10 minutes. The sample is allowed to stand for 1/2 hour and again saturated with H_2S for 10 minutes. After the second treatment with H_2S, the sample is allowed to stand until all the precipitate settles and the solution is clear.
4. The two phases are then separated by suction filtration (see note 1) and the precipitate is washed 5 - 10 times with water which is saturated with H_2S. The precipitate of Bi_2S_3 or PbS is discarded, and the filtrate is transferred to a beaker, boiled down to near dryness, and then diluted up to 100 ml, or some other appropriate known volume. (See note 2.)

Procedure

1. An aliquot (1 - 10 ml) of the solution prepared in 4 is taken and diluted with distilled water up to a total volume of 10 ml in a 125 ml separatory funnel.

2. Three drops of bromphenol blue indicator solution is added and the solution adjusted with 3 N HCl until it is yellow.
3. To the yellow solution, add 5 ml of acetate buffer and make the solution just blue using 5 N NH_4OH. Now the pH should be in the range 4.2 - 5.0.
4. Pipette 10 ml of 1 per cent 8 hydroxyquinoline in chloroform into the blue solution (at this point, the aluminum forms a complex with the 8 hydroxyquinoline and the resulting precipitate is soluble in the organic layer). Stopper the solution immediately and shake it for 3 minutes. (See note 3.)
5. Separate the bottom organic layer into a 50 ml centrifuge tube which contains approximately 1/2 gm of anhydrous sodium sulfate. Stopper and shake for 1/2 minute. (See note 4.) This removes any water entrained in the organic layer.
6. The organic solution is now centrifuged for 1 minute at 1000 rpm and transferred to a Beckman absorption cell. The absorbence is measured at 395 millimicrons against a reagent blank. A standard sample is run with each group of unknown samples.

Calculations

The absorbence reading is used with the standard curve to determine the amount of aluminum present in 10 ml of the chloroform. This reading, however, must be corrected for Bi or Pb interference, as the case may be. The micrograms of Al + Bi or Al + Pb per 10 ml of chloroform is multiplied by the dilution factor and the Bi or Pb correction factor subtracted off to give the total weight of aluminum present in the sample. Then,

$$\%\text{Al} = \frac{\mu\text{g Al+Bi(or Pb)-Bi(or Pb)(correction factor)(dilution factor)(100)}}{\text{(ml. aliquot) (sample wt) }(10^6)}$$

Notes

1. Sufficient acid (use 1:1 HCl) must be present to prevent the precipitation of BiOCl.
2. If a white precipitate appears at this point, add sufficient 1:1 HCl to dissolve it.
3. The separatory funnel should be shaken continuously while the 8 hydroxyquinoline-chloroform solution is being added.
4. The solution should be stoppered immediately after running it into the centrifuge tube in order to prevent any evaporation of the chloroform.
5. The glassware used in this analysis must be carefully washed in order to prevent any contamination. After each use, soak in soap solution, rinse with tap water, and follow this with several rinses in 3 N HCl, several in distilled water, and several in acetone. From time to time, all glassware should be soaked several hours in cleaning solution (a saturated solution of sodium hydroxide in ethanol).

Preparation of Solutions Used in the Analysis

1. Ammonium hydroxide, 5 M-- Dilute 14 ml of the concentrated (28%) NH_3 up to total volume of 50 ml with distilled water.
2. Acetate buffer--Dissolve 32.8 gm of sodium acetate in distilled water. Add 34.6 ml of concentrated acetic acid and finally dilute to one liter with distilled water.
3. Bromphenol blue indicator--Dissolve 0.025 grams of the solid in 50 ml of absolute alcohol.
4. 8 hydroxyquinoline--Purify the reagent grade chloroform by shaking it with concentrated ammonium hydroxide and a saturated

solution of ammonium chloride. Dissolve one gram of the solid reagent in 100 ml of purified chloroform. Always prepare a fresh solution just prior to each run.

Accuracy of the Aluminum Determinations

The accuracy of these determinations depends to a great extent upon how accurately the bismuth and lead correction factors are known. A study of the reproducibility of the bismuth correction factor revealed that the uncertainty involved in this factor at the one weight per cent aluminum level for a 2.5 gram sample amounts to two per cent of the aluminum present. This is reported at the 95 per cent confidence level using the student-t distribution. Very few of the samples analyzed weighed less than 2.5 grams. Most of them, in fact, were greater than 3 grams in weight. A study of the reproducibility of the lead correction factor revealed that the uncertainty involved in this factor at the 0.06 weight per cent aluminum level amounts to 5.6 per cent of the aluminum present, for a 4.5 gram sample. Once again, this uncertainty is reported at the 95 per cent confidence level based on the student-t distribution. The lead-base samples were consistently larger than the bismuth-base samples, very rarely weighing less than 4.5 grams.

A study of the consistency in hitting the aluminum standard curve revealed that as long as one stays above 10 micrograms of aluminum per 10 ml of chloroform, the maximum error introduced here is about one per cent of the aluminum present. It is estimated that all human errors involved in the aluminum analysis probably amount to less than one per cent of the aluminum present. Considering all the errors outlined above, the maximum uncertainty in the aluminum analyses in the bismuth-base and lead-base samples is estimated to be on the order of 4 per cent and 7 per cent of the aluminum present, respectively, depending upon the sample size, aliquot, etc. These estimates are based on the bismuth and lead correction factors being reported at the 95 per cent confidence level using the student-t distribution.

Reference

Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis," Third Edition., John Wiley and Sons, New York, New York, 387 (1961).

II. TITRAMETRIC DETERMINATION OF CALCIUM, STRONTIUM, AND BARIUM IN BISMUTH AND LEAD ALLOYS

Introduction

Calcium, strontium and barium can be determined quantitatively in the presence of aluminum in both bismuth-base and lead-base alloys using a substitution titration with EDTA (ethylenediaminetetracetic acid). The Bi or Pb, as the case may be, is first removed by precipitation as the sulfide and the aluminum is complexed with triethanolamine. The Ca, Sr, or Ba is then titrated.

Apparatus

50 ml burette, pipettes of various sizes, ehrlenmeyer flasks, beakers.

Reagents and Their Preparation

1. 0.001 molar EDTA solution. (See note 1.) Dissolve 0.3721 gm of the di-sodium salt in 1000 ml of deionized water.
2. 0.01 M Na_2MgY, the magnesium complex of the di-sodium salt of EDTA. (See note 2.) Equivalent amounts of solutions of EDTA and magnesium sulfate are mixed and neutralized with NaOH to a pH between 8 and 9 (phenolphthalein just reddened). The solution is then diluted to 0.01 molar. This solution does not need standardizing.
3. Eriochrome Black T Indicator. Dissolve 0.2 gm of the dyestuff in 15 ml triethanolamine and 5 ml absolute alcohol. Such solutions keep for at least a month.
4. Triethanolamine. This reagent can be obtained directly.

5. 2 wt. per cent sodium cyanide. Dissolve 2 gm of the solid in 100 ml distilled water.
6. NH_4OH/NH_4Cl buffer of pH = 10. Prepared by adding 570 ml concentrated (28 per cent) ammonia to 70 gm ammonium chloride and diluting up to 1000 ml.

Preparation of Samples

Follow the procedure outlined under the aluminum analysis.

Procedure

1. After removing the Bi or Pb, and diluting up to a known volume, pipette into an ehrlenmeyer flask an aliquot of the unknown solution. This aliquot should be such that it contains a total weight of calcium in the range 0.8 - 1.8 mg, a total weight of strontium in the range 1.7 - 4.0 mg, or a total weight of barium in the range 2.7 - 6.2 mg. These aliquots will require 20 to 45 ml of 0.001 M EDTA for titration.
2. Add 2 - 5 ml of triethanolamine to complex the aluminum.
3. Neutralize the solution with 2 N NaOH.
4. Add 20 ml of pH = 10.0 - 10.5 buffer.
5. Add 2 ml of 0.01 M Na_2MgY to sharpen the end-point of the titration.
6. Add 1 ml of 2 per cent NaCN solution. (See note 3.)
7. Add 6 - 8 drops of Eriochrome Black T indicator, depending upon total volume of solution.
8. Titrate until the last traces of reddish hue disappear. The final color is a very clear blue.

Calculations

Every milliliter of 0.001 M EDTA corresponds to 10^{-6} gm atom of metal, i.e., 40.08 micrograms of Ca, 87.63 micrograms of Sr and 137.4 micrograms of Ba.

Therefore,

$$\%Ca = \frac{(\text{ml. of } 10^{-3}\text{M EDTA})(40.08)(10^{-6})(\text{dilution factor})}{(\text{aliquot})\ (\text{Sample wt.})}$$

and similarly for the % Sr and % Ba.

Notes

1. This solution (0.001 M EDTA) is prepared from the di-sodium salt, since the acid itself is only sparingly soluble in water. The di-hydrate of the di-sodium salt is available in a high degree of purity. After drying at 80°C, its composition agrees exactly with the formula $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$ and it can be weighed out directly and treated as a primary standard. If it is desired to standardize a solution of EDTA, however, the purest calcium carbonate, zinc, or freshly distilled mercury can be used as primary standards. Ordinary distilled water is unsuitable for making up this solution, because it often contains traces of polyvalent ions. Solutions of the di-sodium salt keep extremely well and retain their titre for months, provided they are kept in vessels of pyrex or polyethylene. In the course of time, ordinary glass will yield appreciable amounts of calcium to solutions of EDTA.
2. The magnesium complex of the di-sodium salt of EDTA is supposedly available commercially as the tetra-hydrate, but may be difficult to obtain. It can be used directly provided its purity is

adequate. After making up this solution, one should always test whether or not the solution does, in fact, contain Mg and EDTA in the ratio 1:1. A solution of the salt should have a pH between 8 and 9; after adding buffer of pH = 10, a few drops of Erio T should produce a dirty violet color which should turn to blue with a single drop of 0.01 M EDTA, and to red with a single drop of 0.01 M $MgSO_4$.

3. The NaCN solution is added as a precaution to complex the cations of Co, Ni, Cu, Hg, Zn, Cd, Ag and Pt.

Accuracy of the Alkaline Earth Determinations

In order to assess the accuracy of these determinations, synthetic samples of Bi-Al-Ca, Bi-Al-Sr, and Bi-Al-Ba were prepared and analyzed. These samples were prepared such that they were representative of a typical sample, as far as weight and composition are concerned. No lead-base samples were prepared, because it was felt that the bismuth-base samples would be sufficient to assess the accuracy of the corresponding analyses of the lead-base alloys.

The synthetic calcium standard was dissolved according to the standard procedure and diluted to 1000 ml. The bismuth was removed and the solution diluted again so that it contained 0.1202 mg of calcium per ml and 0.0665 mg of aluminum per ml. The solution was then analyzed five times according to the procedure outlined above. The percent error of each of these five determinations was then recorded. The standard deviation of this set of errors was 1.72 per cent of the calcium present.

A similar procedure was carried out for strontium and for barium. The standard deviation for the set of percent errors for strontium was 4.24 per cent of the strontium present. The standard deviation for the set of percent errors for barium was 4.75 per cent of the barium present. Therefore, at the 95 per cent confidence level based on the student-t distribution, the uncertainties in the calcium, strontium and barium analyses are 5.5 per cent, 9.9 per cent and 11.1 per cent, expressed as a percentage of the amount of the element present.

The calcium analysis is obviously the best of the above analyses. The color change at the end point is less sharp with strontium than it is with calcium in the corresponding titration, and still less so with barium. This is a result of the relative stabilities of the versenate complexes formed, barium forming the least stable complex of the three.

References

1. Schwarzenbach, G., Complexometric Titrations, Interscience Publishers, Inc., New York (1957).

2. Barnard, A. J., Broad, W. C., and Flaschka, H. The EDTA Titration: Nature and Methods of End Point Detection, published by the J. T. Baker Chemical Company, Phillipsburg, New Jersey (1957).

III. SPECTROGRAPHIC ANALYSES OF PALLADIUM, TIN, AND ANTIMONY IN BISMUTH AND LEAD ALLOYS

The analyses of all ternary alloys involving palladium, tin and antimony were performed spectrographically by either Warren Quality Control Laboratory or the Detroit Testing Laboratory, both of Detroit, Michigan. Spectrographic analyses of several of the two binary alloys as well as several of the alkaline earth ternaries were also performed by these laboratories. In several cases it was possible to compare the results of their analyses with those of the author performed on samples from the same experimental run. In each case the agreement was found to be within the scatter of the experimental data. The former laboratory quoted the accuracy for their determinations to be in the range of five to seven per cent of the amount of the element present. This quotation applied to aluminum as well as the various third components being analyzed for, and was dependent upon the concentration level of the element. The latter laboratory quoted their accuracy to be about 1.5 per cent on the same basis. The former estimate seems to be a little more realistic.

APPENDIX C

CALCULATION OF THE RELATIVE PARTIAL MOLAR ENTHALPY OF ALUMINUM IN DILUTE BISMUTH AND LEAD SOLUTIONS

Designating the standard state of aluminum as the pure solid at the temperature of interest, the relative partial molar enthalpy of aluminum (H^M_{Al}) is the difference between the partial molar enthalpy of aluminum in solution and the molar enthalpy of pure, solid aluminum at the same temperature. It can be shown that H^M_{Al} is given by:

$$H^M_{Al} = - RT^2 \left[\frac{\partial \ell n a_{Al}}{\partial T} \right]$$

and that this can be expressed equivalently by:

$$H^M_{Al} = R \left[\frac{\partial \ell n \gamma_{Al}}{\partial \frac{1}{T}} \right]_{N_{Al}}$$

Since the activity of aluminum is constant and equal to unity in the Bi-Al and Pb-Al systems over the temperature range covered in this study, then $\gamma_{Al} = \frac{1}{N_{Al}}$. Thus, we can express the above equation as:

$$H^M_{Al} \left[\frac{\text{k cal}}{\text{gm. atom}} \right] = - 2.303 R \left[\frac{\partial \log N_{Al}}{\partial \frac{1000}{T}} \right]_{N_{Al}}$$

where R is in $\frac{\text{cal}}{\text{gm atom °K}}$ rather than $\frac{\text{k cal}}{\text{gm atom °K}}$.

For the Bi-Al system, the following values were gotten for H^M_{Al}(Bi):

Sri Krishna and Grace's Data

$$H^M_{Al}(\text{Bi}) = 7.3 \text{ k cal/gm atom}$$

Brookhaven Data

$$H^{M}_{Al}(Bi) = 8.7 \text{ k cal/gm atom}$$

Author's Data

$$H^{M}_{Al}(Bi) = 9.2 \text{ k cal/gm atom}$$

For the lead-aluminum system, the value of $H^{M}_{Al}(Pb)$ was determined to be 11.6 k cal/gm atom.

APPENDIX D

TABLE I RAW DATA

(a) Bi-Al Binary

Run Number	Temp. °C	Run Time (Hours)	Weight % Al
* B-9	549	24	1.01
	549	25	0.96
	549	47.5	0.90
	549	48.5	0.98
	549	75	0.99
	549	96.5	0.85
	549	100	0.87
B-10	492	100	0.60
	492	100	0.58
	492	100	0.61
	492	100	0.58
	501	100	0.61
	501	100	0.63
	506	100	0.66
	506	100	0.69
* B-11	443	48	0.47
	443	48.5	0.46
	443	72	0.49
	443	72.5	0.39
	443	117.5	0.40
	443	118	0.36
	443	141.5	0.41
	443	146	0.34
* B-12	510	0.1	0.76
	510	1.0	0.75
	510	2.0	0.78
	510	4.5	0.70
	510	12	0.77
	510	28	0.73
	510	49.5	0.72
* B-13	607	30.5	1.41
	607	31.2	1.36
	607	50	1.43
	607	50.5	1.44
	607	67.5	1.49
* B-14	451	25.5	0.41
	451	30	0.40
	451	52	0.40
	451	52.5	0.40
B-15	556	38.5	1.10
	556	38.5	1.04
	556	38.5	0.90
	556	38.5	0.94
	556	38.5	0.93
	556	38.5	0.93

* Runs performed on apparatus A. All other runs were performed on apparatus B.

(b) Bi-Al-Ca System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Ca
C2	61.5	0.84	0.21
	61.5	0.60	1.09
	61.5	0.78	0.54
C7	33.5	0.42	1.96
	33.5	0.54	0.043

(c) Bi-Al-Sr System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Ca
C2	61.5	0.70	1.48
	61.5	0.67	1.40
	61.5	0.65	1.20
	61.5	0.81	0.74
C7	33.5	0.46	3.43
	33.5	0.66	1.57
	33.5	0.47	3.06
	33.5	0.61	2.08

(d) Bi-Al-Pd System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Pd
C26	20	1.05	0.02
	20	1.15	0.04
	20	1.40	1.80
	20	1.19	0.02

(e) Bi-Al-Ba System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Ba
C2	61.5	0.74	1.44
C7	33.5	0.64	2.08
	33.5	0.77	1.66
	33.5	0.83	0.81
	33.5	0.55	2.18
	33.5	0.53	2.80
	33.5	0.56	3.87**

** Result questionable because of very small sample size.

(f) Bi-Al-Sn System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Sn
C17	31	0.58	0.48
	31	0.66	0.99
	31	0.84	1.62
	31	0.61	2.67
C26	20	0.70	0.90
	20	0.74	1.10

(g) Bi-Al-Sb System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Sb
C28	30.5	1.42	0.01
	30.5	1.56	0.02
	30.5	1.10	0.01
	30.5	1.48	0.01

(h) Pb-Al Binary

Run Number	Temp. °C	Run Time (Hours)	Wt. % Al
C10	549	26.5	0.051
	549	26.5	0.064
	549	26.5	0.049
	549	26.5	0.061
	549	26.5	0.057
C18	549	25	0.064
	549	25	0.068
	549	25	0.056
	549	25	0.054
	549	25	0.056
	549	25	0.053
	549	25	0.055
	549	25	0.055
	549	25	0.055
	549	25	0.055
	549	25	0.066
	549	25	0.054
	549	25	0.062
	549	25	0.057
	549	25	0.057
	549	25	0.054
	549	25	0.055
	549	25	0.054
	549	25	0.055
	549	25	0.055
	549	25	0.055
	549	25	0.059

Pb-Al Binary (Cont'd)

Run Number	Temp. °C	Run Time (Hours)	Wt. % Al
C14	463	51	0.028
	463	51	0.030
	463	51	0.025
	463	51	0.023
	463	51	0.025
C19	630	36	0.11
	630	36	0.12
	630	36	0.12

(i) Pb-Al-Ca System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Ca
C11	26	0.060	0.41
	26	0.059	0.39
	26	0.063	0.08
	26	0.074	1.01
C15	25.5	0.072	1.38
	25.5	0.071	0.75
	25.5	0.077	1.15
	25.5	0.073	1.19
	25.5	0.077	1.20
C21	29	0.071	0.57
	29	0.087	7.34
	29	0.082	3.98
	29	0.077	1.45

(j) Pb-Al-Sr System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Sr
C15	25.5	0.053	0.29
	25.5	0.068	1.75
C21	29	0.057	0.32
	29	0.071	5.95
	29	0.077	8.42
	29	0.058	0.86
	29	0.061	1.08
	29	0.099	17.39
	29	0.060	2.65
	29	0.053	0.29
	29	0.056	1.28

(k) Pb-Al-Ba System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Ba
C15	25.5	0.053	2.50
	25.5	0.056	1.00
	25.5	0.065	1.85
C21	29	0.056	0.52
	29	0.055	0.47
	29	0.048	5.53
	29	0.057	0.60

(l) Pb-Al-Pd System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Pd
C16	16	trace	8.15
	16	trace	6.60
	16	trace	4.50
	16	trace	2.40
	16	trace	1.60
C25	14	0.015	1.20
	14	trace	1.68
	14	trace	2.40

(m) Pb-Al-Sb System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Sb
C29	49	0.041	0.64
	49	trace	1.70
	49	trace	2.30
	49	trace	2.45
	49	trace	2.90

(n) Pb-Al-Sn System at 549°C

Run Number	Run Time (Hours)	Wt. % Al	Wt. % Sn
C25	14	0.070	1.10
	14	0.110	1.52
	14	0.165	2.10
	14	0.090	1.85
	14	0.160	2.30
	14	0.068	0.60

APPENDIX E

SUPPLEMENTARY BIBLIOGRAPHY

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