Germanium and Silicon Liquidus Curves

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New measurements are reported on the solubility of germanium in liquid gallium, thallium, tin, arsenic, bismuth, cadmium and zinc, and the solubility of silicon in liquid indium, tin, lead, antimony, bismuth and zinc. The measurements of other workers are reviewed, including those of the solubility of germanium and silicon in liquid copper, silver, gold and aluminum; of germanium in liquid indium, lead and antimony; and of silicon in liquid arsenic and nickel. All but two of the liquidus curves can be described within experimental error by a two-constant equation. The form of this equation suggests that the liquid solutions exhibit certain simple thermodynamic properties, and some evidence is cited indicating that the constants of this equation can be used to estimate the excess free energy of the solutions. Figures for the complete liquidus curves of these binary systems (T–x and log x–1/T) have not been included in this paper, but sets of these figures can be supplied upon request.

I. INTRODUCTION

Germanium and silicon have become very important elements in the last ten years. Great strides have been made in the exploitation of the electrical properties of these semiconductor elements, and many useful solid state electronic devices that employ these two elements are manufactured in increasing numbers every year. The electrical properties of pure germanium and silicon are of academic interest only, however. It is the modification of these properties by small amounts of added impurities that has made these elements technologically important.

A knowledge of the chemical reactivity of electrically active impurities with germanium or silicon is necessary in order to be able to control the impurity concentrations. Much of the chemistry of such reactions can be described in a simple way by the use of phase diagrams. These diagrams give the chemical compositions of phases at equilibrium at various temperatures. Of particular interest are the liquidus and solidus curves of germanium and silicon.

The liquidus curve gives the solubility of germanium or silicon in another element as a function of temperature. Each point on the curve corresponds to the temperature and composition at which a liquid phase is saturated with germanium or silicon respectively. The solidus curve gives the concentration of the other component which will be dissolved in germanium or silicon at various temperatures when the solid phase is in equilibrium with a saturated liquid phase.

In this paper, the liquidus curves of germanium and silicon will be discussed; the solidus curves are discussed in an accompanying paper.[1]

The liquidus curves formed by the dissolution of germanium and silicon in elements of Groups III, IV and V of the periodic system were reviewed a number of years ago.[2] It was found that these liquidus curves could be reasonably well approximated by a one-constant equation that had a form consistent with the thermodynamic properties expected of a "regular" liquid solution in equilibrium with a pure solid phase. Additional solubility measurements now show that the liquidus curves cannot be satisfactorily represented by such an equation. A simple two-constant equation has been found that describes the curves within the present limits of experimental error. This equation suggests that simple departures from ideal solution entropy occur, as well as a simple heat-of-mixing effect.

Our objectives have been: (a) to construct the best liquidus curves of germanium and silicon from measurements reported in the literature, supplemented by our own measurements and (b) to obtain the activity coefficients of germanium and silicon along the liquidus curves. This information will be used to estimate the thermodynamic properties of the liquid binary alloys.

One method of evaluating liquidus curves is to plot the solubility measurements on a temperature-composition (atom fraction) scale and draw the best curve through the points from the eutectic to the melting point. For many of the liquidus curves of interest here this is neither practical nor desirable. A number of the liquidus curves cover a very long temperature range (as much as 1380 degrees in the case of the silicon-gallium system) and long composition range (from an atom fraction of about 10^{-10} to 1 in the same system). There is only a limited amount of experimental data available for these systems and rather long extrapolations of the data, to both higher and lower temperatures and compositions, are required if an estimate of the complete curve is to be made.

It is possible, however, to make such extrapolations with greater confidence by taking advantage of all other available information that influences the position of a liquidus curve. The first and most important

bit of additional information is that the measured liquidus curves appear to represent equilibrium conditions between liquid and solid phases. Studies of solubility as a function of time lead to this conclusion, as do the agreement between measurements made by different methods. The disagreement that exists between the measurements of solubility made by different workers frequently arises, we believe, from experimental error, part of which may be attributable to the fact that thermodynamic equilibrium was not attained. However, in general, this problem is avoidable.

With the knowledge that thermodynamic equilibrium exists between the phases, additional information becomes pertinent: (a) germanium and silicon exhibit only one crystalline modification; (b) the solid solubility of the other component in germanium and silicon is small; (c) the melting points and heats of fusion of germanium and silicon are now better known; (d) the liquidus curves can be expected to exhibit certain simple properties in the region of the melting point of germanium and silicon; (e) the liquidus curves that extend to low temperatures and represent liquids that become very dilute in germanium or silicon can also be expected to exhibit certain simple properties.

The implications of this additional information are as follows: (a) the fact that germanium and silicon exhibit only one crystalline modification means that the liquidus curves will be smooth curves with no abrupt changes of slope; (b) the fact that the solid solubility of the second component is small means that the thermodynamic properties of the solid phase are essentially those of pure germanium or silicon; (c) the more accurate knowledge we now have of the melting points of germanium and silicon can be used to construct better curves, since curves now in the literature use melting points varying from 936 to 958°C for germanium and from 1400 to 1430°C for silicon; (d) a knowledge of the heats of fusion of germanium and silicon and the fact that the solid solubilities are small means that the liquidus curves can be expected to come into the melting point of germanium or silicon with a certain known limiting slope; (e) when the amount of solute in the liquid phase is small at low temperatures, it can be expected that the logarithm of the atom fraction of the solute will be well approximated by a straight line when it is plotted as a function of the reciprocal of the absolute temperature.

We have used a method of evaluating the liquidus curve measurements that takes advantage of all the above information related to these curves. In addition, this method of evaluation has led to the discovery of an apparent regularity that leads to an interesting suggestion about the thermodynamic properties of the liquid alloys. Specifically, we have

calculated the activity coefficients of germanium and silicon along a liquidus curve from the solubility measurements, and calculated the parameter $\alpha \equiv RT \ln \gamma_1/(1 - x)^2$, where R is the gas constant, T the absolute temperature, γ_1 the activity coefficient of germanium or silicon referred to the pure supercooled liquid state, and x the atom fraction of germanium or silicon in the saturated liquid. It has been found that α is a linear function of T. This leads to a two-constant liquidus curve equation that has all the desired features. Previously[2] it had been found that the liquidus curves of a number of these systems could be approximated by a one-constant equation, but more accurate solubility measurements now show that two constants are needed.

The liquidus curves formed by 14 different elements with germanium and silicon, for a total of 27 different curves, have been evaluated. The parameter α is found to be a linear function of temperature over a significant temperature range within experimental error for 17 of these binary systems (germanium-indium, -gallium, -aluminum, -lead, -tin, -bismuth, -cadmium, -silver, -copper, -gold; silicon-indium, -gallium, -tin, -bismuth, -antimony, -silver, -zinc). The solubility data for seven other systems (germanium-arsenic, -antimony; silicon-aluminum, -lead, -arsenic, -copper, -gold) are more limited or exhibit considerable scatter. An estimate of the best liquidus curve representing the available measurements is obtained by assuming that α is a linear function of T. The complete germanium-thallium liquidus curve has been estimated from very limited solubility measurements, and the silicon-thallium curve has been estimated, although no solubility measurements have been made. Two systems, germanium-zinc and silicon-nickel, have liquidus curves that appear to be qualitatively the same as the other curves when plotted as T versus x, but it is found that α is not a linear function of temperature. New solubility measurements are reported for 14 binary systems (germanium-thallium, -gallium, -tin, -bismuth, -cadmium, -arsenic, -zinc; silicon-tin, -lead, -bismuth, -antimony, -zinc and the previously unreported work of Hassion[3] on germanium-indium and germanium-lead).

After a description of our experimental procedure we will illustrate this method of evaluation of the solubility measurements by discussing the germanium-gallium system in some detail. Each of the other systems will then be considered briefly.

II. EXPERIMENTAL PROCEDURE

The solubility measurements were made by a method similar to that used by Kleppa and Weil.[4] An excess of germanium or silicon was sealed

into an evacuated silica tube with a known weight of solvent. The germanium and silicon were in the form of single-crystal ingots of high purity. The temperature of the furnace containing the quartz tube was raised slowly to insure against overshooting, and then held constant for various periods of time before the furnace was tipped. A constriction in the tube permitted separation of the saturated melt from the excess germanium or silicon by tipping of the furnace. The equilibration time varied from one-half to one hour for germanium and up to 19 hours for silicon. During equilibration the temperature was held constant to within one degree centigrade, by manual control for the shorter times and by a Leeds and Northrup Speedomax controller for the longer heating times. The emf's of the calibrated platinum and platinum–10 per cent rhodium thermocouples used for temperature measurement were determined with a Leeds and Northrup portable precision potentiometer. Temperatures are considered to be accurate to within ±2 degrees.

The compositions of the saturated melts were obtained from the loss in weight of the germanium or silicon ingots, except for the germanium-arsenic system, in which case the poured-off melts were chemically analyzed. In order to obtain the loss in weight of the single-crystal ingots, the small amount of melt adhering to the crystal was dissolved in a solvent that would not attack the pure germanium.*

III. TREATMENT OF DATA

3.1 *Germanium-Gallium*

The solubility of germanium in liquid gallium has been measured by Klemm et al.,[5] Keck and Broder,[6] Greiner[7] and de Roche.[8] These measurements are shown in Fig. 1, along with our own measurements. The measurements of Klemm et al. are in substantial disagreement with the others. The disagreement between the measurements of de Roche and the others at the lower temperatures is quite evident in Fig. 2, where $\log x$ has been plotted as a function of the reciprocal of the absolute temperature, $1/T$. The measurements of Klemm et al. are not included in this figure.

An interesting feature of these measurements is that they fall close to the ideal liquidus curve. Included in Fig. 2 are two dashed curves, each an ideal liquidus curve corresponding to different assumptions about the heat capacity of supercooled liquid germanium. One of the curves

* In general, hot concentrated HCl was used. A mixture of 30 per cent H_2O_2 , glacial HAc and H_2O in the volume ration 2:2:5 was used for lead on germanium.[3] Aqua regia was used for antimony on silicon.
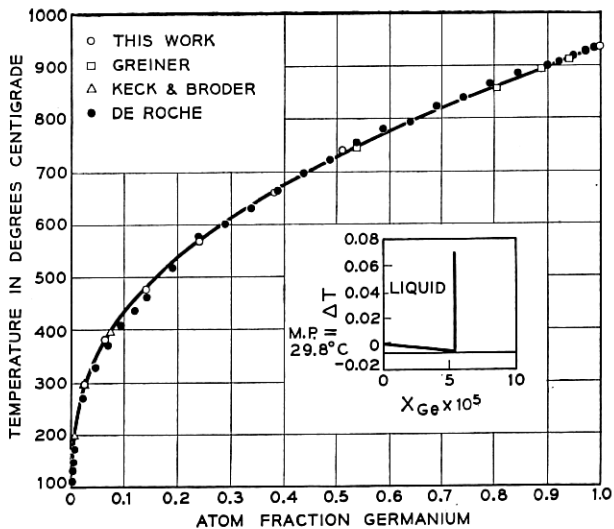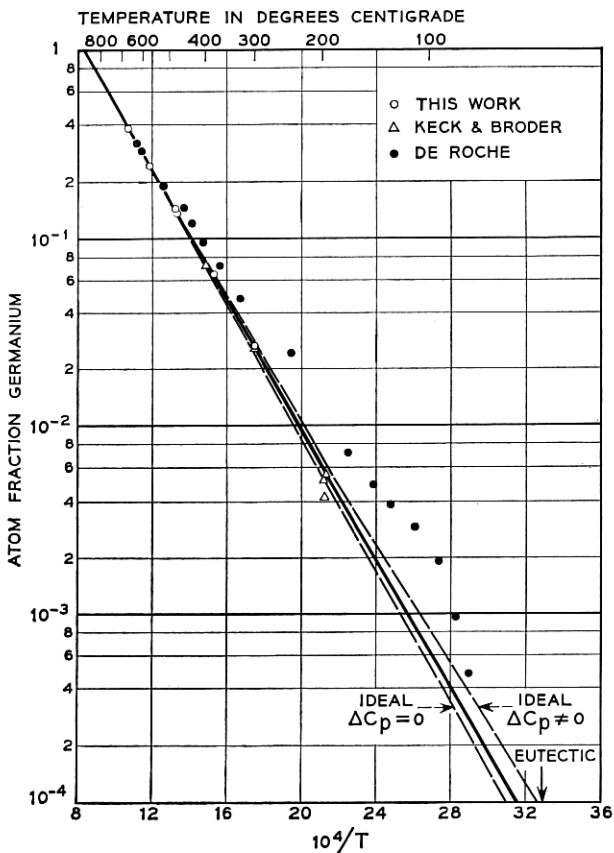
Fig. 1. — Germanium-gallium liquidus curves.

Fig. 2 — Germanium-gallium liquidus curves, log x vs. $1/T$.

results from the assumption that the heat capacity of liquid germanium is the same as solid germanium ($\Delta C_p = 0$); the other results from the assumption that the heat capacity of liquid germanium is constant ($\Delta C_p \neq 0$). If the liquid alloys are ideal solutions of atoms, if these liquids are at equilibrium with pure solid germanium and if the heat capacity of pure supercooled liquid germanium is the same as pure solid germanium, the liquidus curve will be given by the following equation (Ref. 9, pp. 357–358):

$$\ln x = \frac{\Delta H_1^F}{R} \left(\frac{1}{T_1^\circ} - \frac{1}{T} \right). \tag{1}$$

If, however, the heat capacity of pure supercooled liquid germanium is constant and the heat capacity of pure solid germanium has the form $a + bT$, the ideal liquidus curve will be given by

$$\ln x = \frac{\Delta H_1^F}{R} \left(\frac{1}{T_1^\circ} - \frac{1}{T} \right) + \frac{1}{R} \left\{ (a - bT) \frac{T_1^\circ - T}{T} + a \ln \frac{T}{T_1^\circ} \right. \\ \left. + \tfrac{1}{2}b \left[(T_1^\circ)^2 - T^2 \right] \right\}. \tag{2}$$

The dashed curve of Fig. 2 designated $\Delta C_p = 0$ corresponds to (1) with ΔH_1^F, the latent heat of fusion of germanium, taken as 8100 calories per gram atom[10] and T_1°, the melting point of germanium, 937°C.[7,11] The dashed curve of Fig. 2 designated $\Delta C_p \neq 0$ is obtained from (2), using the specific heat equation listed by Kubaschewski and Evans[12] for solid germanium and assuming that the specific heat of liquid germanium is constant and equal to that of solid germanium at its melting point.

At temperatures near the melting point of germanium, de Roche reports that the lowering of the freezing point leads to a heat of fusion of 8100 ± 200 calories per gram atom. This is in agreement with Greiner and Breidt.[10] The agreement between the heat of fusion obtained by freezing point lowering measurements and the heat obtained by direct measurement is evidence that germanium and gallium form atomically dispersed liquid solutions.* If other elements form atomically dispersed binary liquid phases with germanium and also exhibit negligible solid solubility, their liquidus curves will all come into the melting point of germanium with the same limiting slope. In other words, (1) will be a good approximation to all the liquidus curves at temperatures near the melting point of germanium.

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* The possibility cannot be ruled out that germanium and gallium form polymeric species $(Ge)_x$ and $(Ga)_x$, but this is believed to be unlikely.

At low temperatures, where the atom fraction of germanium in the saturated liquid phase is small, we expect that the form of (1) will be correct but that, in general, the slope and intercept (on a log x–$1/T$ plot) will be different for each element.

Let it now be assumed that (1) is the correct equation for the ideal liquidus curve (this corresponds to saying that the heat of fusion of germanium is not a function of temperature — i.e., the heat capacity of solid and supercooled liquid germanium are the same — and that the solid solubility of the component forming the ideal liquid solutions with germanium is zero). We can measure the departures of any experimental liquidus curve from the ideal liquidus curve in terms of the activity coefficient, γ_1, defined by the expression (Ref. 9, pp. 357–358):

$$\ln x\gamma_1 = \frac{\Delta H_1^F}{R}\left(\frac{1}{T^\circ} - \frac{1}{T}\right). \tag{3}$$

Consequently, a value of γ_1 can be calculated for every solubility measurement.

The activity coefficient defined in this way has the pure (supercooled) liquid germanium as the reference state. Thus, when x is unity, γ_1 is unity. Since x will be unity at the melting point of germanium, (1) becomes a good approximation to (3) when the temperature is near the melting point of germanium.

The relationships between γ_1 and other thermodynamic parameters are given below:

$$RT \ln \gamma_1 = \Delta \bar{F}_1^e, \tag{4}$$

$$\Delta \bar{F}_1^e = \Delta \bar{H}_1 - T\Delta \bar{S}_1^e. \tag{5}$$

The terms $\Delta \bar{F}_1^e$ and $\Delta \bar{S}_1^e$ are the relative partial molar excess free energy and entropy, respectively, and $\Delta \bar{H}_1$ is the relative partial molar enthalpy. From (4) and (5), and using the fact that the heat of fusion is equal to $T_1^\circ \Delta S_1^F$, (3) may be rewritten in the following form:

$$\ln x = -\frac{\Delta H_1^F + \Delta \bar{H}_1}{RT} + \frac{\Delta S_1^F + \Delta \bar{S}_1^e}{R}. \tag{6}$$

When the liquidus curve extends to low temperatures where x is small, $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ will no longer depend significantly on composition. Since the temperature dependences of $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ are expected to be small, (6) will give a linear relationship between $\ln x$ and $1/T$. In the germanium-gallium system, the values of $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ are close to zero.

Equation (6) can also be used as a general expression for the liquidus curves, where, in general, $\Delta \bar{H}$ and $\Delta \bar{S}_1^e$ are functions of composition and temperature. Since we expect the temperature dependence of $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ to be small, the variation in $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ will arise primarily from their composition dependence. The composition dependence of $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ can each be represented conveniently by a power series in $(1 - x)$:

$$\Delta \bar{H}_1 = \sum a_n (1 - x)^n, \tag{7}$$

$$\Delta \bar{S}_1^e = \sum b_n (1 - x)^n. \tag{8}$$

Since $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ are zero when $x = 1$, a_0 and b_0 are both zero. If long-range forces between the atoms are not present, a_1 and b_1 will be zero.[13] Consequently, a first approximation to the composition dependences of $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ can be expected to be

$$\Delta \bar{H}_1 = a_2 (1 - x)^2 \tag{9}$$

and

$$\Delta \bar{S}_1^e = b_2 (1 - x)^2. \tag{10}$$

Upon substitution of (9) and (10) in (6) and rearranging, we obtain

$$\alpha \equiv \frac{T \Delta S^F - \Delta H^F - RT \ln x}{(1 - x)^2} = a_2 - b_2 T. \tag{11}$$

A value of the parameter α can be calculated from every solubility measurement. If $\Delta \bar{H}$ and $\Delta \bar{S}^e$ are independent of temperature and their composition dependences are given by (9) and (10), it follows that α will be a linear function of T.

We have evaluated α for a number of the liquidus curves of germanium and silicon and found that the experimental data can be satisfactorily approximated with α as a linear function of T. As will be discussed below, it does not follow that (9) and (10) must represent the thermodynamic properties of the liquid phases in order for α to be a linear function of T. For any given set of experimental points there are an infinite number of equations for $\Delta \bar{H}_1$ and $\Delta \bar{S}_1^e$ that would provide a fit to an α–T plot within experimental error. The discussion of the preceding paragraph describes the simplest thermodynamic properties the liquid alloys could have which would lead to the liquidus curve shapes we observe. A previous study[2] of a number of these liquidus curves suggested that α was independent of temperature along the liquidus curve. This property of α would be expected if the liquid alloys were regular solutions.*

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* The term "regular solutions" was coined by Hildebrand to denote solutions for which "thermal agitation is sufficient to give practically complete random-

The solubility measurements of germanium and gallium evaluated in this way are shown in Fig. 3. The measurements of Greiner,[7] Keck and Broder[6] and our measurements can be represented by a line with $a = -150$ and $b = 0$. The measurements of de Roche[8] are included, except those at low temperatures and those near the melting point of germanium. The parameter α is quite sensitive to experimental error near the melting point, and, between about 1100 and 1211°K, $a = -150$ is a satisfactory representation of all the measurements when a T–x plot is used.

The solubility measurements we have made of germanium in gallium are given in Table I; the measurements of Keck and Broder, scaled from their published figure, and of Greiner are also given. These measurements have been used to obtain a and b.

3.2 *Germanium-Aluminum, Germanium-Indium*

The solubility of germanium in aluminum has been measured by Stöhr and Klemm.[16] Their results, scaled from a figure, are given in Table I.† The parameter α has been plotted as a function of temperature in Fig. 3. A line, $a = -5360$, $b = -3.16$ has been drawn through the points. Some curvature is suggested, but it is believed that the straight line fits the data within experimental error.

The solubility of germanium in indium has been measured by Keck and Broder,[6] whose data, scaled from a figure, are given in Table I, and by Hassion,[3] whose measurements are also given in the table. The measurements of Klemm et al.[5] are in sufficient disagreement with these measurements to justify not including them in Table I and Fig. 3. A line, $a = 1570$, $b = 0.56$, has been drawn through the measurements of Keck and Broder and Hassion, plotted as α versus T in Fig. 3.

3.3 *Germanium-Tin, Germanium-Lead*

The solubility of germanium in tin has been measured by Stöhr and Klemm.[16] However, we have also measured the solubility of germanium

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ness.[14] This definition would, in general, include those solutions for which $\Delta \bar{S}_1{}^e$ is zero and for which (9) gives the partial molar heats of solution, but would not be restricted to them. It is useful to classify solutions empirically in terms of the mathematical functions used to describe their thermodynamic properties. The terms "regular solutions" and "strictly regular solutions" are sometimes used (Ref. 9, p. 246 and Ref. 15, p. 85) to describe solutions for which a_2 is constant and b_2 is zero in (9) and (10).

† The parameter α is very sensitive to error in T and x near the melting point. Consequently, solubility measurements in this range have not been weighted very heavily and frequently have not been included in the table of data.
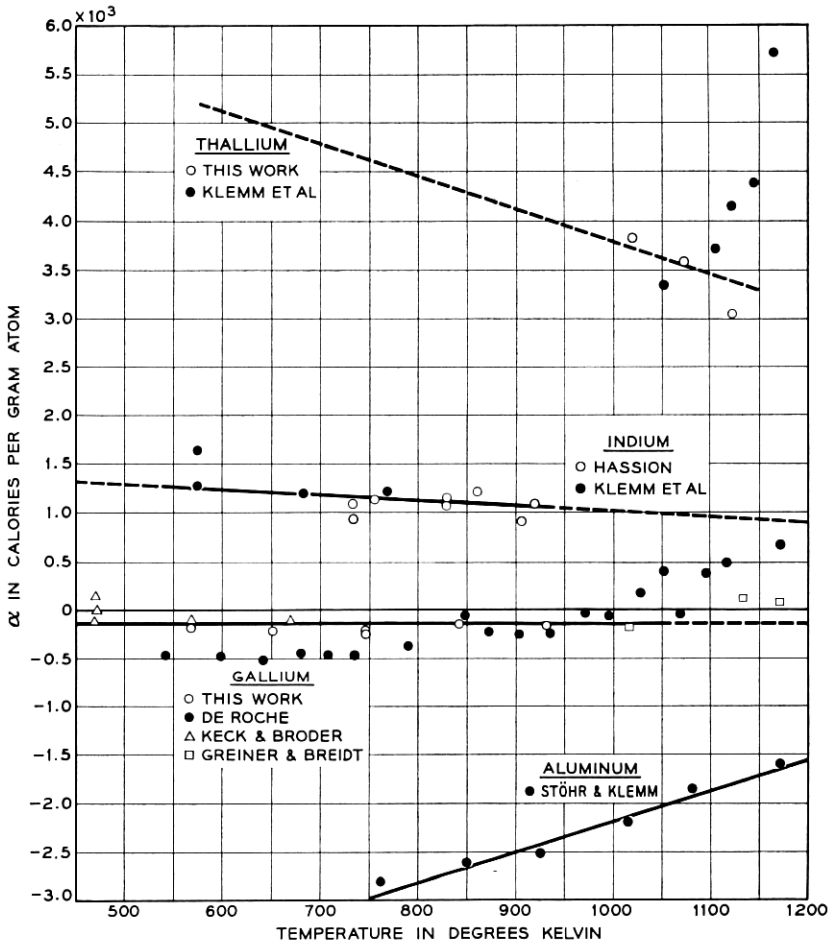
Fig. 3 — α vs. T for germanium-aluminum, germanium-gallium, germanium-indium and germanium-thallium.

in tin and are in significant disagreement. Our measurements are given in Table I and a plot of α versus T is shown in Fig. 4. A line, $a = 1680$, $b = 1.08$, has been drawn through the points. The measurements of Stöhr and Klemm when plotted as α versus T fall on a curve which crosses our data at about 800°K and is of opposite slope. Thus, around 800°K, our measurements agree with those of Stöhr and Klemm, but at higher temperatures we measure somewhat higher solubilities and at lower temperatures somewhat lower solubilities.

TABLE I — EXPERIMENTAL COMPOSITIONS (ATOM FRACTION
OF GERMANIUM) AND TEMPERATURES OF GERMANIUM
LIQUIDUS CURVES

Element	Source	Temperature, °K	x
Aluminum	Stöhr & Klemm (Ref. 16)	762	0.324
		849	0.410
		926	0.501
		1014	0.614
		1081	0.718
		1172	0.904
Gallium	This work	570	0.0268
		653	0.0655
		749	0.142
		749	0.144
		843	0.243
		933	0.382
	Keck & Broder (Ref. 6)	470	0.0042
		473	0.0052
		470	0.0055
		570	0.026
		670	0.071
	Greiner & Breidt (Ref. 7)	1018	0.541
		1134	0.796
		1171	0.894
		1191	0.944
Indium	Keck & Broder (Ref. 6)	575	0.0061
		575	0.0083
		683	0.033
		769	0.076
	Hassion (Ref. 3)	735	0.064
		735	0.068
		756	0.073
		830	0.138
		830	0.133
		862	0.160
		907	0.254
		921	0.249
Thallium	This work	1023	0.131
		1073	0.260
		1123	0.656
	Klemm et al. (Ref. 5)	1052	0.238
		1106	0.377
		1122	0.492
		1143	0.635
		1165	0.776
Tin	This work	601	0.014
		658	0.0305
		758	0.077
		810	0.125
		860	0.181
		908	0.257
		960	0.362
		999	0.459

TABLE I — *Continued*

Element	Source	Temperature, °K	x
Lead	Hassion (Ref. 3)	901	0.021
		953	0.040
		984	0.052
		1012	0.066
		1050	0.105
		1058	0.112
		1062	0.126
		1108	0.270
		1123	0.37
		1137	0.50
		1146	0.63
Antimony	Ruttewit & Masing (Ref. 18)	872	0.20
		907	0.25
		977	0.40
		1043	0.55
		1058	0.60
		1100	0.70
Arsenic	This work	1023	0.595
		1073	0.693
		1123	0.783
		1148	0.841
	Stöhr & Klemm (Ref. 16)	1023	0.605
		1102	0.738
		1128	0.798
Bismuth	This work	873	0.0273
		923	0.0440
		973	0.0656
		973	0.0728
		1023	0.118
		1073	0.201
Copper	Reynolds & Hume-Rothery (Ref. 21)	917	0.365
		948	0.407
		982	0.460
		1010	0.507
		1048	0.583
		1090	0.674
		1154	0.833
Silver	Maucher (Ref. 20)	925	0.241
		929	0.246
		951	0.271
		1028	0.389
		1104	0.598
		1131	0.690
		1151	0.774
	Briggs et al. (Ref. 22)	923	0.260
		948	0.270
		953	0.286
		978	0.308
		988	0.328
		1013	0.357
		1026	0.398

TABLE I — *Concluded*

Element	Source	Temperature, °K	x
		1070	0.497
		1103	0.618
		1128	0.708
		1149	0.803
		1186	0.923
Gold	Jaffee et al. (Ref. 23)	629	0.270
		919	0.537
		1070	0.731
		1164	0.891
Zinc	This work	723	0.0914
		773	0.148
		823	0.213
		873	0.288
		928	0.368
		973	0.440
		1023	0.530
		1073	0.636
Cadmium	This work	669	0.0076
		669	0.0076
		722	0.0144
		776	0.0284
		776	0.0282
		776	0.0292
		821	0.0469
		877	0.0717
		927	0.131
		978	0.205
		1015	0.306
		1015	0.298
		1015	0.279

The solubility of germanium in lead has been measured by Briggs and Benedict,[17] Ruttewit and Masing[18] and Hassion.[3] We have accepted the measurements of Hassion given in Table I, and have plotted these data as α versus T, shown in Fig. 4. A line, $a = 8780$, $b = 4.08$, has been drawn to represent these measurements. The measurements of Briggs and Benedict are in fair agreement with Hassion's measurements, but the low-temperature solubilities reported by Ruttewit and Masing are much lower than the values obtained from an extrapolation of Hassion's measurements using the α–T plot.

3.4 *Germanium-Arsenic, Germanium-Antimony, Germanium-Bismuth*

The measurements of Stöhr and Klemm[16] of the solubility of germanium in arsenic have been scaled from their published figure and are listed in Table I along with our measurements. The α–T plot is shown

in Fig. 5 and a line, $a = -5600$, $b = -4.16$, has been drawn to represent the data.

The solubility of germanium in antimony has been measured by Ruttewit and Masing[18] and Stöhr and Klemm.[16] The measurements of Ruttewit and Masing, scaled from a figure, are given in Table I and the $\alpha-T$ plot resulting from these measurements is shown in Fig. 5. The line, $a = 2640$, $b = 1.98$, has been drawn. Stöhr and Klemm found smaller solubilities at all temperatures than those found by Ruttewit and Masing. A plot of α versus T with their data leads to a curve lying 500 to 1,000 calories higher than the line drawn to represent the measurements of Ruttewit and Masing. We consider the antimony-germanium liquidus curve to be in some doubt.

The solubility of germanium in bismuth has also been measured by Ruttewit and Masing[18] and by Stöhr and Klemm.[16] We have also measured the solubility of germanium in bismuth, and our results are given in Table I and plotted in Fig. 5. The line, $a = 5505$, $b = 1.49$, has been used to represent the data. Neither the measurements of Ruttewit and Masing nor those of Stöhr and Klemm can be represented as a line on a plot of α versus T. Their measurements are in only fair agreement with those we have made.

3.5 *Germanium-Copper, Germanium-Silver, Germanium-Gold*

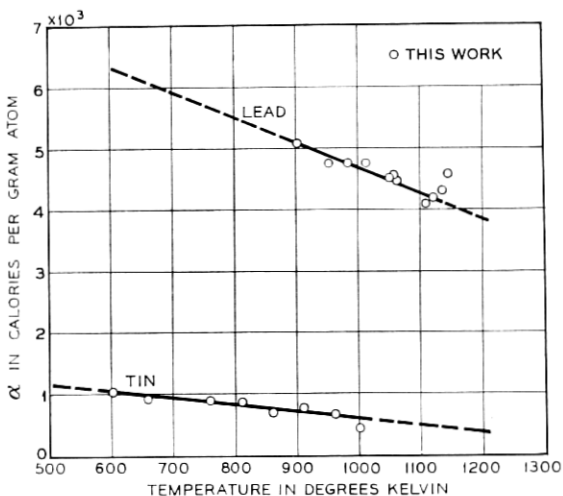The solubility of germanium in copper has been measured by Schwarz and Elstner,[19] Maucher[20] and Reynolds and Hume-Rothery.[21] The meas-

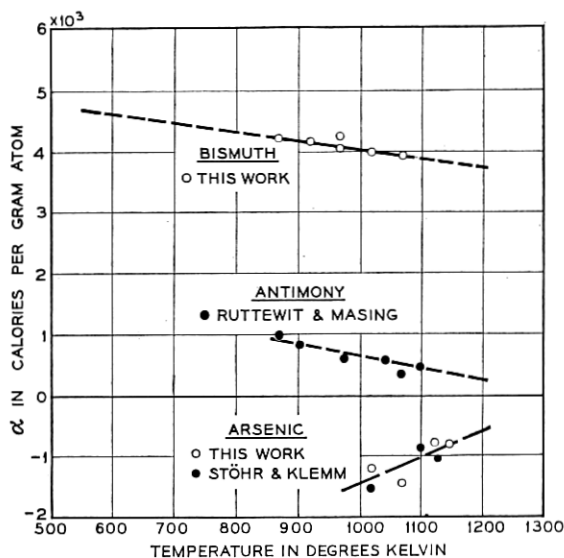Fig. 4 — α vs. T for germanium-tin and germanium-lead.

Fig. 5 — α vs. T for germanium-arsenic, germanium-antimony and germanium-bismuth.

urements of Reynolds and Hume-Rothery are given in Table I and the corresponding α–T plot is shown in Fig. 6. The measurements of the other workers scatter rather badly. They are in agreement with Reynolds and Hume-Rothery at low temperatures but show lower solubilities at higher temperatures. The line, $a = -7360$, $b = -7.67$, has been drawn in Fig. 6.

The solubility of germanium in silver, measured by Maucher,[20] and by Briggs, McDuffie and Willisford,[22] is given in Table I; the α–T plot of these data is shown in Fig. 6. The line, $a = -5500$, $b = -7.13$, has been drawn.

The solubility of germanium in gold has been measured by Jaffee, Smith and Gonser.[23] Their measurements are given in Table I and the α–T plot in Fig. 6. The line, $a = -4865$, $b = -1.02$, has been drawn.

3.6 Germanium-Zinc, Germanium-Cadmium

Gebhardt[24] and Kleppa and Thalmayer[25] have measured the solubility of germanium in zinc. The measurements of the latter are in fairly good agreement with our measurements, which are recorded in Table I. It can be seen in Fig. 7 that α versus T cannot be represented by a straight
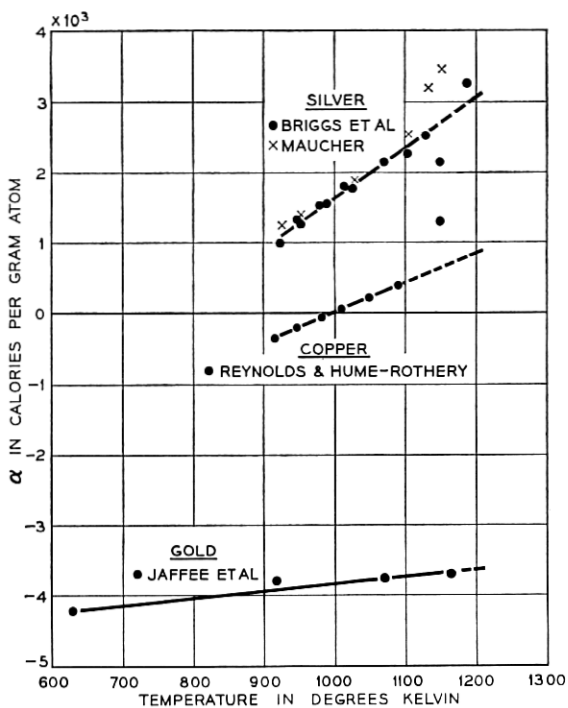
Fig. 6 — α vs. T for germanium-gold, germanium-copper and germanium-silver.
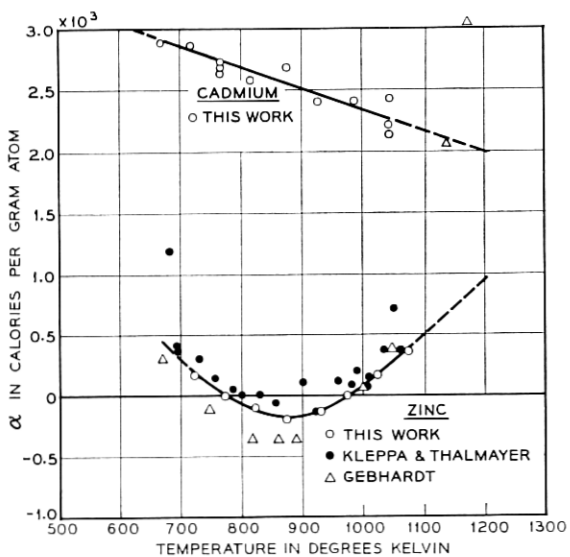

Fig. 7 — α vs. T for germanium-cadmium and germanium-zinc.

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line. The measurements of Gebhardt and of Kleppa and Thalmayer are included in the plot.

We have measured the solubility of germanium in cadmium, and the results are given in Table I. The points of the α–T plot appear to be represented within experimental error by the line, $a = 4110$, $b = 1.75$. Spengler[26] has reported that the germanium-cadmium system is simple eutectic and has mentioned three solubility measurements. These three points are at much higher germanium concentrations than those we have found.

3.7 Silicon-Aluminum, Silicon-Gallium, Silicon-Indium

We have evaluated the measurements of the solubility of silicon in a number of elements of interest in a manner completely analogous to that used for germanium. We have used a heat of fusion of 12,100 calories per gram atom.[27] The melting point of silicon has been reported as 1415°C by Gayler[28] and 1408°C by Pell.[29] We have used a value of 1410°C.

The solubility of silicon in aluminum has been measured by Fraenkel,[30] Roberts,[31] Gwyer and Phillips,[32] Broniewski and Smailowski[33] and Craighead, Cawthorne and Jaffee.[34] The measurements of Fraenkel and Broniewski and Smailowski were scaled from the figure published by Hansen.[35] These measurements are listed in Table II and α versus T is plotted in Fig. 8.* The line, $a = -4140$, $b = -1.22$, has been drawn.

The silicon-gallium liquidus curve has been studied by Keck and Broder[6] and Klemm et al.[5] The measurements tabulated in Table II were scaled from figures. The points plotted in the α–T plot of Fig. 8 have been represented by the line, $a = 3250$, $b = 0.83$.

The solubility of silicon in indium has been measured by Keck and Broder[6] and by Klemm et al.[5] We have also studied this system. Our solubility measurements are given in Table II and the α–T plot is shown in Fig. 8, where the line, $a = 11,450$, $b = 3.37$, has been drawn. The measurements of Klemm et al., are in essential agreement with our measurements, but by themselves give no indication of a linear relation between α and T. The three measurements of Keck and Broder are all at higher solubilities than we have measured, their lowest temperature measurement being in greatest disagreement with the liquidus curve corresponding to the line of Fig. 8.

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* The tabulation in Table II does not include the measurements made near the melting point of silicon. The measurements of Gwyer and Phillips near the eutectic, which are in agreement with the measurements of Craighead et al., are not plotted in Fig. 8.

Element	Source	Temperature, °K	x
Aluminum	Fraenkel (Ref. 30)	957	0.194
		1232	0.391
		1439	0.597
		1503	0.717
	Roberts (Ref. 31)	969	0.179
		1116	0.319
		1232	0.391
		1307	0.482
		1503	0.698
		1526	0.731
		1607	0.850
	Broniewski & Smailowski (Ref. 33)	1131	0.337
		1333	0.510
	Gwyer & Phillips (Ref. 32)	850	0.113
		852	0.116
		852	0.119
		867	0.124
		875	0.134
		889	0.142
		950	0.183
	Craighead et al. (Ref. 34)	851	0.118
		854	0.123
		871	0.132
Gallium	Keck & Broder (Ref. 6)	548	0.000016
		769	0.00254
		1023	0.034
		1023	0.050
		1170	0.100
		1273	0.200
		1423	0.400
Indium	This work	1173	0.0088
		1273	0.0190
		1273	0.0205
		1373	0.0425
		1373	0.0494
		1373	0.0400
		1473	0.0955
		1473	0.101
		1473	0.101
Tin	This work	1025	0.00391
		1073	0.00607
		1075	0.00792
		1075	0.00760
		1099	0.00754
		1099	0.00778
		1150	0.0112
		1150	0.0113
		1173	0.0143
		1173	0.0136
		1202	0.0166
		1223	0.0258

TABLE II — *Continued*

Element	Source	Temperature, °K	x
		1235	0.0235
		1235	0.0232
		1247	0.0279
		1251	0.0251
		1251	0.0244
		1273	0.0280
		1273	0.0330
		1273	0.0292
		1296	0.0369
		1300	0.0358
		1300	0.0368
		1329	0.0454
		1373	0.0645
		1373	0.0597
Lead	This work	1323	0.0022
		1349	0.0025
		1373	0.0036
		1423	0.0046
		1474	0.0076
		1475	0.0072
		1523	0.0112
Arsenic	Klemm & Pirscher (Ref. 38)	1346	0.60
		1483	0.65
		1512	0.70
Antimony	This work	1073	0.0151
		1073	0.0143
		1170	0.0239
		1174	0.0243
		1272	0.0461
		1371	0.0835
		1473	0.150
Bismuth	This work	1273	0.00262
		1373	0.00544
		1423	0.00832
		1473	0.0113
		1548	0.0193
Zinc	This work	915	0.00845
		925	0.00962
		971	0.0131
		973	0.0168
		1017	0.0208
		1020	0.0200
		1024	0.0247
		1069	0.0321
		1071	0.0325
		1072	0.0394
		1117	0.0486
		1119	0.0526

TABLE II — *Concluded*

Element	Source	Temperature, °K	x
Copper	Hansen & Anderko (Ref. 41) Rudolfi (Ref. 40)	1075 1103 1268 1336 1433 1503 1547	0.300 0.355 0.424 0.486 0.598 0.685 0.763
Silver	Rudolfi (Ref. 40)	1215 1307 1402 1513 1563 1592 1613 1623	0.168 0.224 0.300 0.490 0.622 0.721 0.794 0.852
Gold	Hansen & Anderko (Ref. 41) di Capua (Ref. 43)	643 1063 1303 1403 1448 1538 1568	0.309 0.439 0.553 0.637 0.701 0.775 0.824

3.8 *Silicon-Tin, Silicon-Lead*

We have measured the solubility of silicon in tin, and our results are given in Table II and Fig. 9. The line corresponds to $a = 8,145$, $b = 1.50$. The measurements of Tamaru,[36] who used 92.5 per cent silicon (the principle impurities were iron and aluminum), give higher solubilities than we have found.

Our measurements of the solubility of silicon in lead are also given in Table II, and the α–T plot (Fig. 9) shows the line, $a = 19,830$, $b = 4.58$, drawn through the points. Moissan and Siemens[37] reported a number of solubility measurements, all of which lie at appreciably lower silicon concentrations than those which we report.

3.9 *Silicon-Arsenic, Silicon-Antimony, Silicon-Bismuth*

Klemm and Pitscher[38] have obtained three points on the silicon-arsenic liquidus curve that are listed in Table II. These three points have lead us to estimate the complete liquidus curve with the line, $a = -49,990$, $b = -32.40$, in the α–T plot of Fig. 10.

Solubility measurements of silicon in antimony have been reported by Williams.[39] Our measurements, given in Table II, are in essential
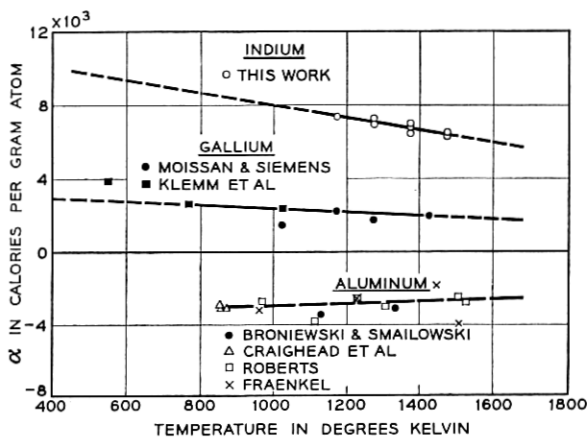
Fig. 8 — α vs. T for silicon-aluminum, silicon-gallium and silicon-indium.

agreement with these. However, we have used our measurements to establish the line that we believe to be a best approximation at present to the silicon-antimony liquidus curve. The line, $a = 3290$, $b = -1.61$, is shown with the experimental points in Fig. 10.

Our measurements of the solubility of silicon in bismuth are recorded in Table II and plotted in Fig. 10. The line, $a = 14,840$, $b = 2.06$, has been drawn.
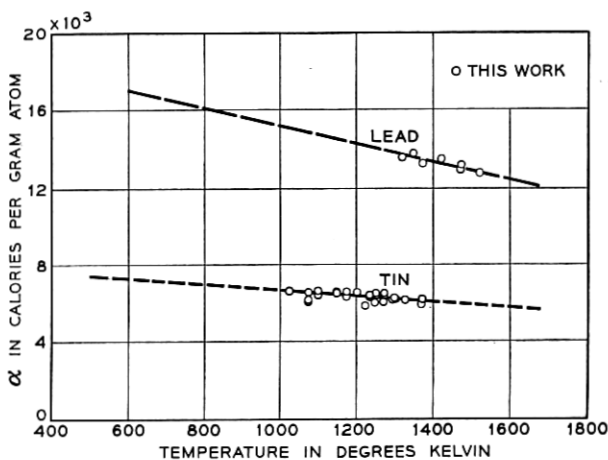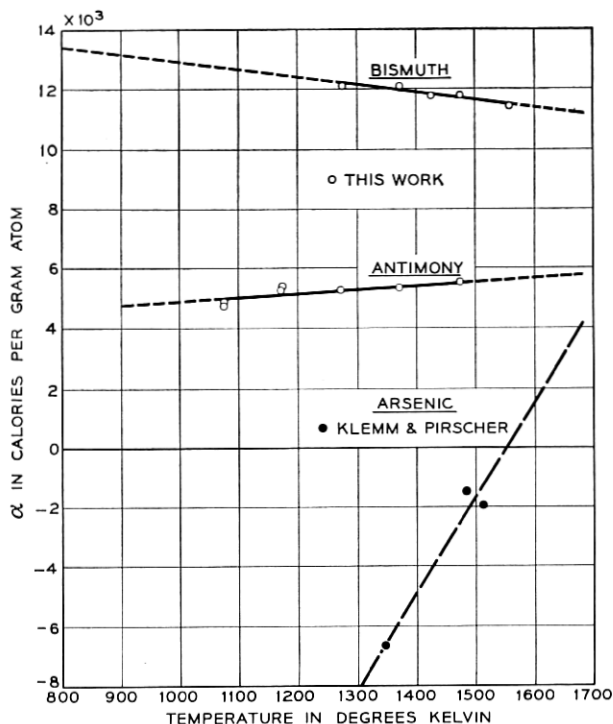

Fig. 9 — α vs. T for silicon-lead and silicon-tin.

Fig. 10 — α vs. T for silicon-arsenic, silicon-antimony and silicon-bismuth.

3.10 Silicon-Copper, Silicon-Silver, Silicon-Gold

Rudolfi[40] has reported measurements of the solubility of silicon in copper. These are given in Table II, along with a value for the eutectic composition proposed by Hansen.[41] The α–T plot is shown in Fig. 11 and the line, $a = -11,910$, $b = -7.19$, has been drawn.

Arrivant[42] has measured the solubility of silicon in silver; his measurements are given in Table II. The line, $a = -7910$, $b = -7.63$, has been drawn through these data plotted as α versus T in Fig. 11.

The solubility of silicon in gold has been measured by di Capua,[43] and his measurements are listed in Table II. The plot of α versus T in Fig. 11 suggests that the data can be represented by the line, $a = -19,540$, $b = -10.28$. More weight has been attached to the four points at low temperatures than the high temperature points, where experimental error will lead to a greater scatter of points than at lower temperatures.

3.11 Silicon-Zinc, Silicon-Nickel

Our measurements of the solubility of silicon in zinc, given in Table II, lead to an α–T plot, Fig. 12, which suggests the line, $a = 4280$, $b = 1.14$. The measurements reported by Moissan and Siemens[37] lie at somewhat lower values of the solubilities than those we report.

The measurements of Iwase and Okamoto[44] of the solubility of silicon in nickel, scaled from Hansen's plot,[41] are shown in Fig. 12 as an example of a binary silicon system for which the α versus T plot is clearly nonlinear.

IV. DISCUSSION

4.1 The Liquidus Curve Equation

Equation (11) can be rearranged to give the following relationship:

$$T = \frac{\Delta H_1^F + a(1 - x)^2}{\Delta S_1^F - R \ln x + b(1 - x)^2}. \tag{12}$$

This will be called the liquidus equation since liquidus temperatures can be calculated as a function of x for each set of values of a and b. The values of a and b used to approximate the available experimental data have been summarized in Table III.
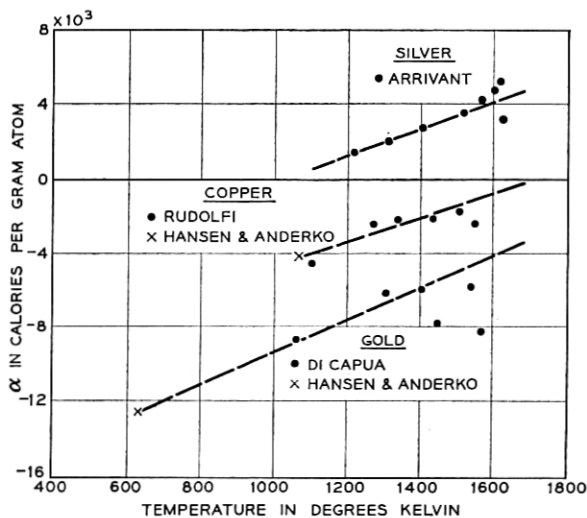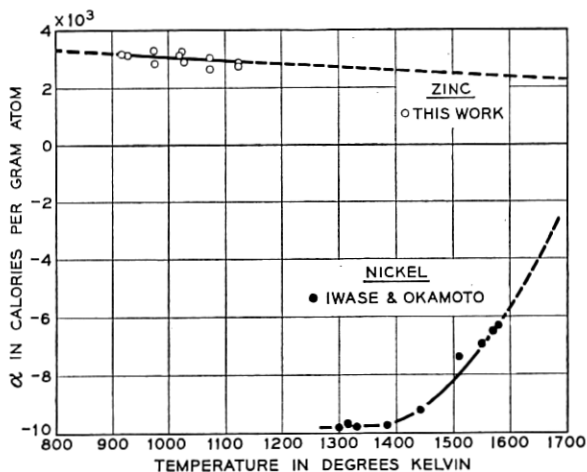

Fig. 11 — α vs. T for silicon-silver, silicon-copper and silicon-gold.

Fig. 12 — α vs. T for silicon-nickel and silicon-zinc.

The solid curves of Figs. 1 and 2 correspond to $a = -150$, $b = 0$ for the gemanium-gallium liquidus curve. The extrapolation of the α–T line to the melting point of germanium means that the liquidus curve approaches the melting point of germanium with the limiting slope determined by the heat of fusion and melting point of germanium. The extrapolation to lower temperatures of the α versus T line is in accord with the expected behavior of such liquidus curves — namely, that at low temperatures the log x versus $1/T$ plot will be linear.

TABLE III — COEFFICIENTS a AND b OF THE LIQUIDUS
CURVE EQUATION FOR VARIOUS BINARY SYSTEMS

Element	Germanium		Silicon	
	a	b	a	b
Aluminum.........	−5360	−3.16	−4140	−1.22
Gallium...........	−150	0	3250	0.83
Indium............	1570	0.56	11450	3.37
Thallium..........	(5700)	(1.90)	(16600)	(3.80)
Tin...............	1680	1.08	8145	1.50
Lead..............	8780	4.08	19830	4.58
Arsenic...........	−5600	−4.16	−49990	−32.40
Antimony.........	2640	1.98	3290	−1.61
Bismuth...........	5505	1.49	14840	2.06
Copper............	−7360	−7.67	−11910	−7.19
Silver.............	−5500	−7.13	−7910	−7.63
Gold..............	−4865	−1.02	−19540	−10.28
Zinc..............	—	—	4280	1.14
Cadmium..........	4110	1.75	—	—

The lines in Figs. 3 through 11 have been drawn to indicate the complete liquidus curve and the amount of extrapolation of the experimental data required to give the full curve. The liquidus curves, plotted as T versus x or log x versus $1/T$, have not been included in this paper. These curves can be readily obtained from (12) and the constants of Table III. However, we have available complete sets of T versus x and log x versus $1/T$ plots which will be supplied to anyone upon request.

We have assumed that the distribution coefficients of the second components in germanium and silicon are small enough to have no influence on the liquidus curve. However, the solid solubility of gallium in germanium is high enough to cause us to expect that some influence should be expected. This is also true for aluminum-germanium. We will use the solid solubility measurement of Trumbore et al.[1,45] to estimate the magnitude of the error introduced in the germanium-gallium system by ignoring the solid solubility.

de Roche[8] has reported that the liquidus curve points he has measured that lie between 1.0 and 0.80 atom fraction of germanium lead to a heat of fusion of germanium of 8100 kilocalories. This calculation used (1), and no correction was made for the solidus curve. If we accept the statement that the experimental liquidus curve follows (1) over the range 1.0 to 0.8 with $\Delta H_1{}^F$ having the value 8,100, we can use the solid solubilities measured by Trumbore, et al.[1,45] and re-evaluate the heat of fusion of germanium.

Equation (1), modified to account for solid solubility, will be

$$\ln \frac{x_L}{x_S} = \frac{\Delta H_1{}^F}{R} \left(\frac{1}{T_1{}^\circ} - \frac{1}{T} \right), \tag{13}$$

where x_L is the atom fraction of germanium in the liquid phase and x_S the atom fraction in the solid phase. The value of x_L can be calculated using (1) with $\Delta H_1{}^F = 8100$ and $T_1{}^\circ = 1210°K$ for various values of the temperature down to a value of x_L of 0.8. The measurements of Trumbore et al. give x_S at these temperatures. A plot of the logarithm of x_L/x_S versus $1/T$ leads to a value of $\Delta H_1{}^F$ of 7850 calories per gram atom. This value is essentially within the experimental error of 8100 ± 200 cals estimated by de Roche. Consequently, the neglect of the solid solubility introduces a negligible error.

4.2 Eutectic Temperatures and Compositions

The eutectic temperatures and compositions that are consistent with the a and b values summarized in Table III are given in Table IV. The

TABLE IV—EUTECTIC TEMPERATURES, $T_{eu}°C$, DIFFERENCES BETWEEN MELTING POINT OF SECOND COMPONENT AND EUTECTIC TEMPERATURE ($\Delta T = T_2° - T_{eu}$), AND EUTECTIC COMPOSITIONS IN ATOM FRACTIONS OF GERMANIUM AND SILICON

Element	Germanium			Silicon		
	$T_{eu}°C$	ΔT	x_{eu}^*	$T_{eu}°C$	ΔT	x_{eu}^*
Aluminum....	424	236	0.28(0.30)	577	82	0.120(0.121)
Gallium......	30	0.007	5×10^{-5}	30	6×10^{-8}	5×10^{-10}
Indium.......	157	0.2	5×10^{-4}	157	1×10^{-7}	2×10^{-10}
Thallium.....	304	(0.3)	(4×10^{-4})	304	(2×10^{-6})	(3×10^{-9})
Tin..........	232	0.9	0.003	232	4×10^{-5}	1×10^{-7}
Lead........	327	0.1	2×10^{-4}	327	5×10^{-8}	9×10^{-10}
Arsenic†	736	78	0.58(0.59)	1073	-259	0.595(0.595)
Antimony....	590	40	0.18(0.17)	630	1.1	0.003
Bismuth......	271	0.05	2×10^{-4}	271	3×10^{-8}	1×10^{-10}
Copper.......	644	434	0.36(0.36)	802	281	0.32(0.30)
Silver........	651	310	0.25(0.26)	830	131	0.125(0.154)
Gold........	356	707	0.27(0.27)	370	693	0.31(0.31)
Zinc.........	398	22	0.044(0.055)	420	0.2	4×10^{-4}
Cadmium.....	320	1.0	0.002	—	—	—

* Compositions in parentheses given by Hansen.[41]
† Not simple eutectic systems.

eutectic temperatures have been taken from the literature and the corresponding composition calculated. There are a number of systems for which the eutectic temperatures are very near the melting point of the solvent. An estimate can be made of the eutectic temperatures and compositions by extrapolating the liquidus curve to the melting point of the solvent, then using this composition to calculate the freezing point depression, as was done in an earlier paper.[2] On the assumption that the solid solubility of germanium or silicon in the solvent element is negligible, the freezing point depression can be calculated from the following equation:

$$\Delta T = \frac{R(T_2°)^2}{\Delta H_2^F} x_{eu}, \qquad (14)$$

where x_{eu} is the atom fraction of germanium (or silicon) in the eutectic liquid phase, $T_2°$ the melting point of the solvent, and ΔH_2^F its heat of fusion. Equation (14) follows from (1) applied to component 2. The freezing point depressions calculated in this manner, (see Ref. 14, Table B, pp. 284–305, for ΔH_2^F), have been tabulated in Table IV, along with other eutectic compositions and temperatures. The germanium-gallium eutectic, calculated on the assumption of negligible solid solubility of germanium and gallium, is shown in the insert of Fig. 1.

4.3 *The Relationship Between a and b*

In Fig. 13 we have plotted the values of *b* against *a*. It can be seen that, in general, the more positive the value of *a*, the more positive *b* becomes, and the more negative the value of *a*, the more negative *b* becomes. We have used this relationship between *a* and *b* to estimate the germanium-thallium and silicon-thallium liquidus curves.

4.4 *The Germanium-Thallium and Silicon-Thallium Liquidus Curves*

The available experimental measurements[5] of the solubility of germanium in thallium are given in Table I, and the corresponding $\alpha-T$ points are plotted in Fig. 3. The position of these points leads to a value of α of about 3500 calories per gram atom at 1075°C. On the assumption that the $\alpha-T$ relationship is linear and passes through this point, and that the value of *a* and *b* must be related in such a way as to fall on the curve of Fig. 13, we obtain for our estimate of the complete germanium-thallium liquidus curve, $a = 5700$, $b = 1.90$.

From the position of the silicon-lead and silicon-bismuth $\alpha-T$ lines, we estimate a value for α of 12,500 at 1450°K for thallium. Then, proceeding as for the germanium-thallium system, we conclude that a reasonable estimate of the $\alpha-T$ line for thallium would be $a = 16,600$, $b = 3.80$. The values of *a* and *b* for the thallium systems have been included in Table III in parentheses, and the eutectic compositions and temperatures are shown in Table IV. The $\alpha-T$ line for germanium-thallium is shown in Figure 3.
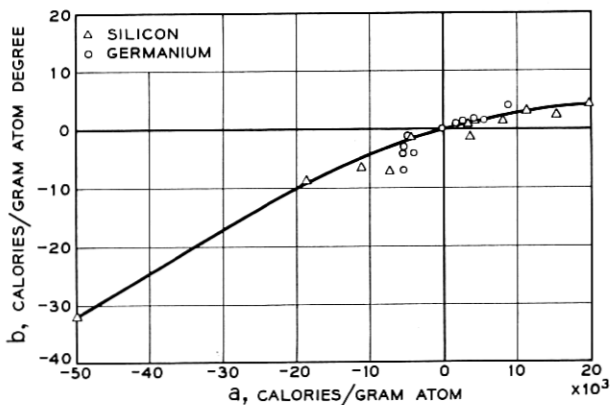

Fig. 13 — *b* plotted as a function of *a*.

4.5 *Implications of the $\alpha = a - bT$ Relationship*

In the preceding discussion we have used the α–T plots to estimate the complete liquidus curve from limited solubility measurements. We conclude that, within experimental error, the liquidus curves of a rather large number of binary systems for which germanium or silicon is the solid phase can be described by a two-parameter equation. Two systems, germanium-zinc and silicon-nickel, quite clearly fail to fall into the same class as the other liquidus curves.

In Section 3.1 it was shown that, if the thermodynamic properties of the liquid phases are given by (9) and (10), it would follow that α would be a linear function of T along a liquidus curve. One cannot draw the conclusion, however, that, because α appears to be a linear function of T, the thermodynamic properties of the liquid phase must be given by (9) and (10). The partial molar heat and excess entropy are related to the partial molar excess free energy by partial derivatives at constant composition. The liquidus curves have given partial molar excess free energies along a line in $\Delta \bar{F}_1^e$, x, T, space. It is not possible to obtain partial derivatives of $\Delta \bar{F}_1^e$ at constant composition from such limited information. The linear relationship between α and T only suggests that (9) and (10) describe the thermodynamic properties of these solutions. At present there is no information available which can be used as a direct check of this suggestion.

From (3), (4) and (11) we can conclude that the following relationship is true along the liquidus curve if α is a linear function of T:

$$\Delta \bar{F}_1^e = (a - bT)(1 - x)^2. \tag{15}$$

If this relationship applied off the liquidus curve as well, it would follow from the Gibbs-Duhem equation that, for the other component,

$$\Delta \bar{F}_2^e = (a - bT)x^2 \tag{16}$$

and, for the integral molar excess free energy of mixing,

$$\Delta F_m^e = (a - bT)x(1 - x). \tag{17}$$

It is possible for us to test the applicability of (16) to several of the systems studied by calculating the value of the activity coefficient of the second component at the eutectic temperature and composition. We can use the eutectic composition and temperature of a number of systems to obtain an experimental value of $\Delta \bar{F}_2^e$, which we can write in terms of the activity coefficient, γ_2, since

$$\Delta \bar{F}_2^e = RT \ln \gamma_2. \tag{18}$$

TABLE V — ACTIVITY COEFFICIENT OF COMPONENT 2 AT THE EUTECTIC

System	γ_2	γ_2, calculated
Aluminum-Germanium...............	0.84	0.84
Antimony-Germanium...............	1.08	1.02
Gold-Germanium...................	0.36	0.78
Aluminum-Silicon.................	0.99	0.97
Silver-Silicon...................	1.01	1.00
Gold-Silicon.....................	0.41	0.38

We have used (3), modified to account for a nonzero value of ΔCp (Cp of the liquid was assumed to be constant) as in (2), and applied it to the liquidus curve of the second component at the eutectic. The values of γ_2 have been obtained in this way for a number of systems, using the tabulated data of Kubashewski and Evans,[12] and are given in the first column of Table V. In the second column are values of γ_2 calculated from (16) and (18) using the eutectic temperatures and compositions in Table IV.

A comparison of the activity coefficients in Table V reveals a fairly good agreement between the experimental activity coefficients and those obtained using the appropriate values of a and b in Table III.* An additional bit of information is available for the silicon-silver system. Schadel et al.[46] have measured the vapor pressure of silver over silicon-silver melts at several temperatures in the range of 1000°C. The positive deviations from ideality found by Schadel et al. are in fair agreement with the values we calculate using the a's and b's found from the solubility of silicon in silver, but the temperature coefficient of the activity coefficient they found is opposite to the one we predict. However, it is probable that not much weight can be attached to the experimental temperature coefficients in view of the authors' comments on experimental errors.

4.6 *The Silicon-Thallium, Silicon-Lead and Silicon-Bismuth Binary Phase Diagrams*

We have used the α versus T linear relationship to fit the full liquidus curves of the silicon-lead and silicon-bismuth systems. When the values of a and b of Table III are put into (12), the liquidus curve equation, the curve rises from low temperatures to a maximum, passes through a point of inflection at $x = 0.5$ and then through a minimum before reach-

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* The germanium-silver system was not included in Table V because the solid solubility of germanium in silver at the eutectic is large and the activity coefficient of silver in the solid solution is not known.

ing the melting point of silicon, with the appropriate limiting slope. This behavior is in keeping with the fact that a miscibility gap is known to exist in these systems. If we assume that the values of a and b obtained from the liquidus curve at low temperatures give a reasonable estimate of the free energy of the liquid phases of the silicon-lead and silicon-bismuth systems, and that our estimate of the α–T line for silicon-thallium is correct, we can calculate the complete phase diagram.

The thermodynamic conditions for two liquid phases to be in equilibrium lead to the following equation for the miscibility gap when the molar excess free energy of the liquid phases is given by (17):

$$T = \frac{a(1 - 2x')}{R \ln \dfrac{1 - x'}{x'} - b(1 - 2x')}. \tag{19}$$

The temperature at which this curve intersects the curve given by (12) is the so-called monotectic temperature, where two liquid phases, one rich in silicon and the other dilute in silicon, are in equilibrium with pure solid silicon. The maximum in the miscibility gap occurs at $x = 0.5$. The temperature of the maximum in the miscibility gap, T_c, the critical temperature, cannot be obtained directly from (19), but can be shown to be given by the equation

$$T_c = \frac{a}{2R + b}. \tag{20}$$

The critical temperatures predicted for the thallium, lead and bismuth systems are given in Table VI, along with the monotectic temperatures, T_m, and monotectic compositions, x_m' and x_m''.

4.7 *Liquidus Curves and Critical Temperatures*

The liquidus curves for three systems, silicon-indium, silicon-tin and silicon-antimony, are rather flat in the region of $x = 0.5$, when T is

TABLE VI — ESTIMATED CRITICAL TEMPERATURES, MONOTECTIC TEMPERATURES AND MONOTECTIC COMPOSITIONS FOR THREE SILICON BINARY SYSTEMS WITH LIQUID-LIQUID MISCIBILITY GAPS

Element	T_c, °C	T_m, °C	x_m'	x_m''
Thallium	1862	1387	0.06	0.94
Lead	2047	1397	0.03	0.97
Bismuth	2187	1393	0.04	0.96

plotted as a function of x. This indicates that the miscibility gap occurs at temperatures just below the liquidus curve in the supercooled liquids. If the free energies of the liquid phases were reasonably well approximated by (17), the calculated critical temperatures would all lie below the liquidus curve temperature at $x = 0.5$. The comparison is made in Table VII for these three systems. Included in the table are the critical temperatures and liquidus temperatures for the three germanium systems, germanium-thallium, germanium-lead and germanium-bismuth, which have the highest calculated miscibility gaps. In every case the liquidus curve lies above the calculated critical temperature of the miscibility gap. This shows that the use of (17) for the free energy of the liquid phases is consistent with the presently known properties of these systems.

The systems germanium-arsenic, -copper, -silver and silicon-arsenic, -copper, -silver, -gold all have critical temperatures calculated from (20) that are higher than the temperature of the liquidus curve at $x = 0.5$. It can be shown, however, that this critical temperature is a lower one; that is, it is predicted that, above this temperature, the liquid phase will split into two liquids and below it there will be homogeneity. In all other systems, no critical temperature is predicted.

Some indication of the degree of approximation to be expected from the above treatment of binary systems with miscibility gap can be obtained by applying this treatment to the copper-lead system, which has a miscibility gap that has been measured. We have evaluated α from the measurements of the solubility of copper in molten lead reported by Kleppa and Weil.[4] A plot of α versus T can be approximated by the line, $a = 6160$, $b = 0.85$, although the experimental points clearly depart from this line near the monotectic temperature. Using these values of a and b in (12) and (21), the complete phase diagram was calculated. A comparison between certain critical compositions and temperatures ob-

TABLE VII — COMPARISON OF LIQUIDUS CURVE TEMPERATURES
AND CALCULATED CRITICAL TEMPERATURES

System	T (liquidus, $x = 0.5$)	T_c (calculated)
Germanium-Thallium	1114	972
Germanium-Lead	1132	1090
Germanium-Bismuth	1122	1007
Silicon-Indium	1590	1563
Silicon-Tin	1581	1487
Silicon-Antimony	1583	1213

TABLE VIII — COMPARISON OF CALCULATED AND EXPERIMENTAL
PHASE DIAGRAM FEATURES FOR THE COPPER-LEAD SYSTEM

	Calculated	Experimental
Critical temperature, T_c	1263°K	1277°K
x_c	0.5	0.35
Monotectic temperature, T_m	1190	1227
x_m'	0.26	0.15
x_m''	0.74	0.67

tained by this calculation and those measured experimentally[41] can be made. This comparison is shown in Table VIII, where it can be seen that a fairly good approximation has resulted.

4.8 The Thermodynamic Properties of Liquid Alloys

Darken and Gurry[47] have used the α function $[RT \ln \gamma/(1 - x)^2]$ to describe the thermodynamic properties of liquid alloys at constant temperature. The temperature dependence of α was not considered. Guggenheim (Ref. 15, pp. 83–84) has pointed out that the excess molar free energy of the carbon tetrachloride-benzene and carbon tetrachloride-cyclohexane systems over the temperature range from 30 to 70°C can be quite satisfactorily accounted for by an interchange energy, w, which is a linear function of temperature. This is equivalent to finding that α is a linear function of temperature.

We have evaluated α along the liquidus curves of a number of other binary systems for which germanium or silicon is not one of the components. These systems have long liquidus curves and negligible solid solubility. The general features of the liquidus curves, on a T versus x plot, are the same as those of germanium and silicon binary systems. The α versus T plots of these liquidus curves* were nonlinear in every system.

Scatchard[48] has discussed the relationship between the temperature dependence of α (in essence) and the volume change on mixing. The conclusion has been reached[49] that a volume change upon mixing that is greater than additivity indicates a positive excess entropy of solution, while a volume contraction indicates a negative excess entropy. Prigogine[50] and his co-workers have discussed this relationship in some detail in terms of their average potential model. (See also Ref. 51.) Exceptions can be expected to the above generalization, and such have been observed, but, in general, a close relationship between the excess volume and excess entropy of mixing can be expected. The correlation found here

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* Silver-tin, -lead; zinc-gallium, -indium, -tin, -cadmium.

between a and b (Fig. 13) suggests, then, that volume expansion upon mixing occurs for positive a and b while contraction occurs for negative values of a and b.

Kleppa[52,53,54] and Wittig[55] have measured the heats of mixing of quite a number of binary liquid alloys. Trends in heats of mixing with position of one of the components in the periodic system, keeping the other component fixed, were observed. Some of these trends can be satisfactorily accounted for[52] in terms of Friedel's alloy solution model, which, among other things, takes into account the difference in valence expected for the two components. The relative valence effect does not seem to appear, in any simple way, at least, in the system we have studied.

Wittig[55] has found some general trends in the heat of mixing that he has related to the position of the variable component in the periodic system. Germanium occupies a position as a variable component in the several series he has investigated. The heats of solution we have deduced from our analysis of liquidus curves do not appear to violate the trends Wittig has observed.

V. SUMMARY AND CONCLUSIONS

A two-constant equation, (12), has been used to fit the liquidus curves of a number of binary systems for which either germanium or silicon is one of the components. This equation gives a limiting slope of the liquidus curve at the melting point that is consistent with the known heats of fusion of germanium and silicon and the known solid solubilities. The form of the equation at low temperatures is also consistent with the expected thermodynamic properties of the two phases.

The general form of the equation suggests that the thermodynamic properties of the liquid alloys are simple functions of composition and temperature. It was pointed out that a first approximation to the relative partial molar heat of solution of germanium or silicon in the liquid alloys would be given by the equation

$$\Delta \bar{H}_1 = a(1 - x)^2 \tag{21}$$

and a first approximation to the relative partial molar excess entropy by the equation

$$\Delta \bar{S}_1^e = b(1 - x)^2, \tag{22}$$

where a and b are independent of temperature and composition. This means that the excess free energy would be given by

$$\Delta \bar{F}_1^e = RT \ln \gamma_1 = (a - bT)(1 - x)^2. \tag{23}$$

If solutions having the thermodynamic properties given by these three

equations were in equilibrium with pure solid germanium or silicon, the liquidus curve equation would have the form

$$T = \frac{\Delta H_1^F + a(1-x)^2}{\Delta S_1^F - R \ln x + b(1-x)^2}. \tag{24}$$

This is the same equation found empirically.

The constants a and b of (24) were obtained from the straight line drawn through the points representing each solubility measurement when plotted as the function α versus T:

$$\alpha \equiv \frac{RT \ln \gamma_1}{(1-x)^2} = \frac{T\Delta S_1^F - \Delta H_1^F - R \ln x_1}{(1-x)^2} = a - bT. \tag{25}$$

It cannot be concluded however, that the thermodynamic properties of the liquid alloys must be given by (21), (22) and (23) as a result of the observed linearity of α with T. The linearity of α as a function of T shows that (23) gives the activity coefficients of germanium or silicon along the respective liquidus curves. It was found, however, that the activity coefficient of the other component at the eutectic in several binary systems was fairly well approximated by the equation resulting when it was assumed that (23) applied at all temperatures and compositions, and the Gibbs-Duhem relationship was used. Based on this assumption, the extent of the miscibility gaps in the silicon-thallium, -lead, -bismuth binary systems were estimated.

The two-constant liquidus curve equation, (24), can be used to provide a best present estimate of the complete liquidus curves for 26 different binary systems for which germanium or silicon is one of the components. The constants for each system are given in Table III. Sets of the liquidus curves, plotted as T versus x or $\log x$ versus $1/T$, may be obtained from the authors upon request.

VI. ACKNOWLEDGMENTS

REFERENCES

1. Trumbore, F. A., this issue, p. 205.
2. Thurmond, C. D., J. Phys. Chem., **57**, 1953, p. 827.
3. Hassion, F. X., unpublished work.
4. Kleppa, O. J. and Weil, J. A., J. Am. Chem. Soc., **73**, 1951, p. 4848.
5. Klemm, W., Klemm, L., Hohman, E., Volk, H., Örlamunder, E. and Klein, H. A., Z. anorg. allgem. Chem., **256**, 1948, p. 239.
6. Keck, P. H. and Broder, J., Phys. Rev., **90**, 1953, p. 521.
7. Greiner, E. S. and Breidt, P., Jr., J. Metals, **7**, 1955, p. 187.

8. de Roche, N., Z. Metall., **48**, 1957, p. 59.
9. Prigogine, I. and Defay, R., *Chemical Thermodynamics*, Longmans, Green & Co., New York, 1954.
10. Greiner, E. S. and Breidt, P., Jr., J. Metals, **4**, 1952, p. 1044.
11. Hassion, F. X., Thurmond, C. D. and Trumbore, F. A., J. Phys. Chem., **59**, 1955, p. 1076.
12. Kubaschewski, O. and Evans, E., *Metallurgical Thermochemistry*, 3rd Ed., Pergamon Press, London, 1958.
13. Buff, F. P. and Schindler, F. M., J. Chem. Phys., **29**, 1958, p. 1075.
14. Hildebrand, J. H., Farad. Soc. Disc., No. 14, 1953, p. 14.
15. Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford, 1952.
16. Stöhr, H. and Klemm, W., Z. anorg. allgem. Chem., **241**, 1939, p. 305.
17. Briggs, R. T. and Benedict, W. S., J. Phys. Chem., **34**, 1930, p. 173.
18. Ruttewit, K. and Masing, G., Z. Metall., **32**, 1940, p. 52.
19. Schwarz, R. and Elstner, G., Z. anorg. allgem. Chem., **217**, 1934, p. 289.
20. Maucher, H., Forschungsarbeiten über Metallkunde und Röntgen Metallographie, **20**, 1936.
21. Reynolds, J. and Hume-Rothery, W., J. Inst. Metals, **85**, 1956–7, p. 1731.
22. Briggs, T. R., McDuffie, R. O. and Willisford, C. W., J. Phys. Chem., **33**, 1929, p. 1080.
23. Jaffee, R. I., Smith, E. M. and Gonser, B. W., Trans. A.I.M.E., **161**, 1945, p. 366.
24. Gebhardt, E., Z. Metall., **34**, 1942, p. 255.
25. Kleppa, O. J. and Thalmayer, C. E., to be published.
26. Spengler, H., Metall., **8**, 1954, p. 937.
27. Olette, M., Compt. rend., **244**, 1957, p. 1033.
28. Gayler, M. L. U., Nature, **142**, 1938, p. 478.
29. Pell, E. M., J. Phys. Chem. Solids., **3**, 1957, p. 77.
30. Fraenkel, W., Z. anorg. allgem. Chem., **58**, 1908, p. 154.
31. Roberts, C. E., J. Chem. Soc., **105 II**, 1914, p. 1383.
32. Gwyer, A. G. C. and Phillips, H. W. L., J. Inst. Metals, **36**, 1926, p. 283.
33. Broniewski, W. and Smailowski, M., Rev. Met., **29**, 1932, p. 542.
34. Craighead, C. M., Cawthorne, E. W. and Jaffee, R. I., Trans. A.I.M.E., **81**, 1955, p. 285.
35. Hansen, M., *Der Aufbau der Zweistofflegierungen*, Springer, Berlin, 1936.
36. Tamaru, S., Z. anorg. allgem. Chem., **61**, 1909, p. 40.
37. Moissan, H. and Siemens, F., Compt. rend., **138**, 1904, p. 657.
38. Klemm, W. and Pirscher, P., Z. anorg. allgem. Chem., **247**, 1941, p. 211.
39. Williams, R. S., Z. anorg. allgem. Chem., **55**, 1907, p. 19.
40. Rudolfi, E., Z. anorg. allgem. Chem., **53**, 1907, p. 216.
41. Hansen, M. and Anderko, K., *Constitution of Binary Alloys*, McGraw-Hill Book Co., New York, 1958.
42. Arrivant, G., Z. anorg. allgem. Chem., **60**, 1908, p. 430.
43. di Capua, C., Rend. Accad. Lincei, **29**, 1920, p. 111.
44. Iwase, K. and Okamoto, M., Science Reports, Tohoku Imperial Univ., K. Hondu Anniversary Volume, 1936, p. 777.
45. Trumbore, F. A., Porbansky, E. M. and Tartaglia, A. A., to be published.
46. Schadel, H. M., Jr., Berge, G. and Birchenall, C. E., Trans. A.I.M.E., **188**, 1950, p. 1282.
47. Darken, L. S., Gurry, R. W., *Physical Chemistry of Metals*, McGraw-Hill Book Co., New York, 1953, p. 270.
48. Scatchard, G., Trans. Farad. Soc., **33**, 1937, p. 160.
49. Hildebrand, J. H. and Scott, R. L., *Solubility of Nonelectrolytes*, 3rd Ed., Reinhold Publishing Corp., New York, 1950, p. 136.
50. Prigogine, I., *The Molecular Theory of Solutions*, Interscience Publishers, New York, 1957.
51. Scott, R. L., J. Chem. Phys., **25**, 1956, p. 193.
52. Kleppa, O. J., Kgl. Norske Videnskab. Selskabs, Skifter (English), **2**, No. 6, 1957.
53. Kleppa, O. J., Acta Met., **6**, 1958, p. 225.
54. Kleppa, O. J., Acta Met., **6**, 1958, p. 233.
55. Wittig, F. E., Z. Electrochem., **63**, 1959, p. 327.