FUNDAMENTALS OF THERMOMETRY PART VII
METAL MELTING AND FREEZING EQUILIBRIA
PHASE, PHASE DIAGRAMS, CRYOSCOPIC CONSTANT

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ABSTRACT

Thermometric fixed points, those points which are used as the basis for a temperature Scale and which provide the most absolute calibration systems, are temperatures at which pure materials exist in a condition of phase equilibrium; that is, where the material is simultaneously in two phases (liquid-solid, liquid-vapor, or solid-vapor, at a specified pressure) or in the three possible phases, liquid, solid and vapor.

In the real world, there are no ideally pure materials. Cells for realizing the two-phase equilibria of "pure" metals (indium, tin, zinc, aluminum, silver, etc.) are generally made using the purest available metals, usually containing impurities totalling not more than 1 part per million (99.9999% pure, or in the common jargon of metallurgy, "6N (6-nines)" pure). Even at this level of purity, these metals must be regarded as extremely dilute alloys. Since there will be some effect from impurities upon the temperature of the freeze, however minute, the analysis of the consequences of this unavoidable compromise is of interest.

There are two avenues by which theoretical analysis may be attempted. The first is by inspecting phase diagrams. Furthermore, phase diagrams provide an view *into eutectic points, which have a limited but real interest for thermometrists. The* second is calculation from the cryoscopic constant of the impurity material. Neither of these means are entirely satisfactory or comprehensive, but they may provide interesting insights.

In addition, there are methods for estimating the purity of cells by measurements performed on the manufactured freeze-point cell.

1: PHASE EQUILIBRIA

The following terms have the meanings given below:

- Phase: solid, liquid, or gaseous physical form.

- Component: A single pure metal or a chemical compound, in any phase or combination of phases, is a single component. Thus mercury is a single component, as a solid, a liquid or a vapor, or in two or three of these phases simultaneously. A container filled with silver pellets is a single-component system, even though the pellets may be surrounded by molecules of air. Sodium chloride is a single-component system. A dental amalgam of mercury and silver is a two-component system, since it is a mixture and not a chemical compound.

- Binary: A mixture of two components. Binary alloys often form intermetallic compounds with a crystal structure different from either pure element.

Thermometrists are concerned generally with single-component systems (ignoring, for the moment, the minute amount of impurity components) existing in several simultaneous phases.

In a single-component two-phase system, either temperature or pressure must be specified; there is a characteristic temperature at a given pressure, which temperature is maintained as a physical constant of the material as long as the two phases exist simultaneously and the pressure is constant.

For example, a properly prepared mixture of pure ice and pure-air saturated water contains a single component (H_2O), and is at the constant temperature 0°C as long as both liquid and solid water are present and the pressure remains 1 standard atmosphere. If we then pump the container so as to reduce the pressure, the equilibrium temperature will no longer be 0°C, but will rise (although the rise is small). If, however, the air is removed so that there is no air above the liquid/solid phases but only water vapor (the third phase of water) the system becomes a three-phase equilibrium, liquid water and solid water at the vapor pressure of water, and the system is then immune to any outside influence, as long as three phases continue to be present. If the solid phase disappears (melts) the equilibrium is destroyed and the temperature rises. If the liquid phase freezes into solid, the temperature will fall (as will, probably, shards of the container, if it is glass).

We can generalize this in the Phase Rule of Josiah Willard Gibbs:

$$F = C - P + 2 \qquad \text{Eq. 1}$$

where F = the number of degrees of freedom of the system, C = the number of components, and P = the number of phases present, F, C and P being integers.

In the case of liquid and solid water in an open container, there is one component and two phases. Then

$$F = 1 - 2 + 2 = 1 \text{ degree of freedom (pressure)} \qquad \text{Eq. 2}$$

In the case of liquid and solid water held in a sealed container under its own vapor pressure (approximately 4.6 mm Hg (0.000611 MPa) at that temperature[1]) there is one component and three phases. Then

$$F = 1 - 3 + 2 = 0 \text{ degrees of freedom} \qquad \text{Eq. 3}$$

The freezing points of high-purity metals are two-phase equilibria. The makers of ITS-90 and its predecessors might have chosen to establish, as defining fixed points of the Scale, the triple points of metals, but did not. Convenience took precedence. It would be difficult to make some of the metal equilibrium points as triple points, and the pressure-dependance of metal two-phase equilibria is relatively small and relatively easy to control. Table 1 shows the pressure dependance of metal freezing temperatures. For example, the pressure dependance of the tin point is about 3 mK per atmosphere, and so to realize the equilibrium within 0.1 mK requires knowledge - or control - of the pressure to only 25 mm Hg. (The most commonly used metal freeze-point cells are sealed cells, in which the internal inert atmosphere is established so that the pressure is 1 standard atmosphere at the freezing temperature. In such cells, the pressure is automatically established and controlled).

TABLE 1

Metal	*Pressure effect* mK per standard atmosphere
Mercury	A Scale triple point
Gallium	-2.0
Indium	+4.9
Tin	+3.3
Zinc	+4.3
Aluminum	+7.0
Silver	+6.0

2: PHASE DIAGRAMS

Phase diagrams allow us to examine the basic effects which occur in a system as temperature and composition change. Inspection of phase diagrams is one way to estimate the effects of an impurity on the equilibrium temperature of an otherwise pure metal. It is useful only in some instances, because the development of phase diagrams is based upon experimental determinations; most such metallurgical research has been directed at less dilute systems, and detailed information about highly dilute systems is often not available. Also, in general, published phase diagrams illustrate systems of only two components. The best reference on binary alloys lists some 1200 binary systems[2]; one can imagine how many experiments would be needed to develop such information for ternary or quatenary systems, and what a library would be needed to contain them!

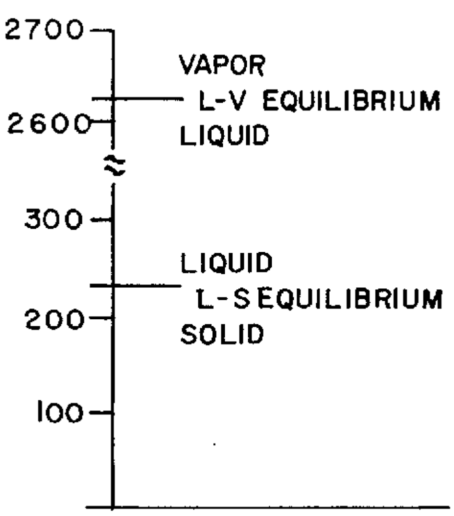

FIG. 1
THE PHASE DIAGRAM OF PURE TIN

A phase diagram is a graphical plot of temperature versus composition of the metal system. Fig. 1 shows the phase diagram for a single-component metal system, (in the example, pure tin) assuming that the metal is ideally pure. Composition does not change in such a system. This diagram is complete in its illustration of temperature versus phase.

If the temperature of a quantity of tin in its solid phase is raised, a phase transition point will be reached (at 231.9681 on ITS-90) at which temperature liquid tin begins to form. In the phase transition heat is absorbed (at the rate of 14.2 cal/gm). The transition continues until all the tin is liquid. During the transition, the temperature is invariant, since the supplied heat is absorbed as latent heat instead of temperature rise. When the tin is entirely liquid, application of additional heat will again result in temperature increase, until the liquid metal boils, when there will be a liquid-vapor transition, with another temperature equilibrium if pressure is held constant. (A boiling temperature is that temperature at which the vapor pressure equals the pressure above the system; 2623°C for tin, where the system is open to atmosphere; however this liquid-vapor transition temperature is not employed in thermometry).

During a freeze, there are identical transition points, except that the latent heat is released. It is this release of latent heat which accounts for the temperature rise from a condition of supercool to the freeze plateau.

A binary system is somewhat more complicated. Because ot is so familiar, we choose to show the binary system of lead and tin, with which all users of soft solders have had acquaintance[3].

Figs. 2 and 3 show the freezing behavior of various proportions of lead and tin in a mixture of the two metals.

Fig. 2(a) is the freezing curve of pure lead. Between A and B the metal is in the liquid phase. At a specific temperature, t_0, solid lead begins to form in the liquid (with a release of latent heat, which keeps the temperature constant) and the temperature remains invariant). When the entire mass reaches the solid phase, the temperature is again able to decrease). A similar picture would be seen for a system of 100% tin, shown as Fig. 2(e).

Figs. 2(b) and 2(d) show a similar diagram for systems system of mixtures of lead and tin of different proprtions. Note that there are two transition temperatures, t_0 and t_1. At t_0 solid crystals of lead-rich material begin to form in the alloy. At t_1 the entire alloy is solid.

Fig. 2(c) represents yet another situation. The system is 37% lead and 63% tin. This differs from the previous mixtures in that these proportions yield a composition called eutectic. A eutectic composition goes from a complete solid to a complete liquid upon ascending temperature (a complete liquid to a complete solid upon descending temperature) at a single temperature, which is always lower than the melting (freezing) points of the constituent metals. This is what we see occurring in 2(c). Fig. 2(e) shows the flat plateau of a freeze of pure tin.

Fig. 2(a), (b), (c). (d) and (e) can be combined into a picture, Fig. 3, which shows the performance with respect to phase of a mixture in any proportions of the two metals, so that the state of the entire system with respect to phase and temperature can be seen. The X-axis represents the proportion of the solute in the solvent; below the graph in terms of weight % and above it in terms of atomic %[4]. The dashed line at 3(a) corresponds to 2(a), in which the lead fraction is 100%. The lead is liquid above t_0 and solid below it.

The dashed line at 3(b) and 3(d) corresponds to 2(b) and 2(d) respectively. The system is liquid above t_0, but the area between t_0 and t_1 is a mixture of solid lead-rich material and the liquid. Solidification of the entire alloy is complete at t_1.

The dashed line at 3(c) corresponds to 2(c). The proportions of lead and tin are correct for a eutectic mixture, characterized by a single transition temperature, $t_0 = t_1$. At higher concentrations of tin than 63%, a cooling curve similar to 2(b) would be seen.

Fig. 3 was generated by connecting all the t_0 and t_1 temperatures derived from 2(a), 2(b), 2(c), 2(d) and 2(e), and many more experimental determinations of cooling curves of the system. The upper portion of the diagram represents the liquid phase. The liquidus line is the lower boundary of this liquid phase. The two areas immediately below the liquidus line are the pasty stage, where solid crystals exist in the liquid in equilibrium for that temperature. The line below the pasty stages is the solidus line, and below it, the alloy is completely solid. The roughly triangular end areas, S1 and S2, are solid, containing crystals of both metals in an incomplete solid solution, since tin and lead are mutually completely soluble in the liquid phase, but the solid solubility varies with and depends upon temperature.

(One would be inclined to think that eutectic mixtures, having a single distinct transition temperature, would be good thermometric fixed points. A lot of work has been done[4] which shows that they are less than satisfactory for the highest accuracy. The reason is that during freezing, two solid phases of quite different crystal structure form. When a metal is solid, it is crystalline; the constituent atoms are arranged in a lattice structure which is highly ordered. As the temperature is raised, the atoms in the lattice move further from each other. When the thermal activation energy exceeds the forces holding the atoms in the lattice, they go from an ordered state to a state of disorder (a liquid). Thus the metal goes from a state in which the structure is fixed (except dimensionally) to a state in which there is essentially no structure.

When the activation energy (heat) is slowly removed, the atoms return to the ordered lattice arrangement of the solid. Two metals may be in a state of ideal diffusion, or mixing, as liquids, but when one starts to crystallize before the other, there is segregation, and only slow diffusion can again homogenize the solid binary alloy. In the solid, such diffusion can be assisted by very long cooling rates, or by annealing, or by time on the order of weeks or months, and perhaps never complete. Only then does the solid remain near the true eutectic proportions. Melt plateaux which follow very slow (e.g., 12 hour) freezes seem to be reproducible to 5 mK or so.

Fig. 4 shows a phase diagram for the system silver-oxygen. Sufficient information exists to make this a useful diagram for a small contamination of silver with oxygen. It is clear from this diagram that 0.01 weight % of oxygen will cause a depression of the freezing point of about 21 C°. This diagram strongly suggests an advantage of sealed cells; it would be difficult, tedious and costly in time and equipment to establish an atmosphere free from any trace of oxygen in an open cell, and maintain it during the routine calibration process). Oxygen is not reported as an interference in systems involving indium, tin, zinc or aluminum.

Fig. 5 shows a diagram for the system silver-copper, including the silver-copper eutectic point. Note the similarity of this diagram to Fig. 2.

3: THE FIRST CRYOSCOPIC CONSTANT

Where phase diagrams are not available for the binary systems we wish to consider, some estimate of the effects of impurities may be had by calculation from the first cryoscopic constant. Once again we must state qualifications:

- Cryoscopic calculations cannot predict the effect of a number of impurities in combination, but only the binary contributions, and their sum.

- The information required for these calculations is analysis, which may or may not be available, for various impurities of a particular metal.

- The summation effect so calculated is probably worse, by some multiple, than the actual effect. The reason for this is that, when we freeze a highly pure metal, we take precautions that the freeze proceed radially away from the thermometer well. Thus the liquid-solid interface, as it proceeds, tends to sweep impurities ahead of it in a process equivalent to zone-refining, leaving the freezing shell of metal surrounding the thermometer much purer than the metal of the bulk solid ingot, while the still-molten metal becomes richer in the impurity.

- The calculation assumes that the solute (the impurity) is completely soluble in the solvent (the pure metal) at this dilution. This is surely true only approximately. Solubility would be found from phase diagrams, but in general such information is not available for these extreme dilutions.

- Calculations cannot indicate whether the impurity elevates or depresses the freezing point; a study of phase diagrams is necessary for this determination.

- We consider here only contaminants which are chemical elements, and in general are only metals. This is a reasonable limitation.

■ (And, yes, there is a second cryoscopic constant, but it is insignificant, compared to the other assumptions, at these extreme dilutions).

Accepting these caveats, we calculate the first cryoscopic coefficient A for a metal as:

$$A = L/(RT^2) \qquad \text{Eq. 4}$$

where L is the heat of fusion in kJ/mol, T is the kelvin temperature of fusion, and R is the universal gas constant (in this system of units 0.008315 kJ/mol). Table 2 shows the values of L, T and the calculated A for a variety of metals, including the defining fixed points.

With A known, the freeze point depression is calculated as follows:

$$\Delta_{fp} = X_2/A \qquad \text{Eq. 5}$$

where Δ_{fp} is the freezing point depression in kelvin, A is the first cryoscopic constant, and X_2 is the molar fraction of impurity in the alloy. Most analyses furnished by suppliers provide the impurity fraction in weight %, but here the molar or atomic % is required, calculated as follows:

$$X_2 = (Y_2/M_2)/[Y_2/M_2 + (1 - Y_2)M_1] \qquad \text{Eq. 6}$$

where M_1 is the atomic weight of the solvent (the major component, the "pure" metal), M_2 is the atomic weight of the solute (a single impurity), and Y_2 is the weight fraction of the impurity for a concentration of 1ppm, or 1×10^{-6}. For very dilute alloys $1 - Y_2$ is very close to 1, and $Y_2/_{M2}$ is very small compared to 1, so we may reduce Eq. 6 to

$$X_2 = Y_2M_1/M_2 \qquad \text{Eq. 7}$$

Table 3 employs the information computed from Eqs. 4-6 to calculate a Table of the effects of a number of metal contaminants at the 1ppm level on otherwise pure indium (as binary systems). Tables 4 through 7 does the same calculation for otherwise pure tin, zinc, aluminum and silver. Tables 8 and 9 use data from actual analyses of aluminum and zinc received by Isotech and used in the manufacture of thermometric freeze-point cells to calculate the efects of the impurities found by the supplier's analysis.

4: THE LAST WORD IN ASSURANCE

No theoretical analysis, or analysis of reported impurities in the bulk metal, can completely assure the quality of a freeze-point cell. Phase diagrams may not supply sufficiently accurate data (perhaps no data at all, or maybe worse, a long and misleading extrapolation) at very small concentrations. Analysis by cryoscopic constant may depend upon some assumptions (e.g. solubility of the solute in the solvent, at these concentrations and temperature) which may or may not be true; nor does this calculation speak to the effects of combining several impurities. The best we can say of cryoscopic analysis is that it presents worst-case, or worse than that. (It is occasionally a means for rejecting a batch of supplied material). Furthermore, there is always the possibility, although Isotech employ exhaustive techniques to minimize it, of contamination in a stage during manufacture, long after the analysis is made. (The possibility of contamination in use is a continual concern for open cells, and can be dismissed for sealed cells).

There is no proof of a cell quite like that obtained from the completed cell itself. By this we do not mean measurement of its freeze temperature. The freezing points of pure metals are intrinsic definitions of temperatures, and therefore must be considered to be more accurate than any measurement which can be made upon them. There are, however, well-described techniques for evaluating the purity of a metal in a freeze-point cell. These are described in an article by Sostmann and Tavener in a previous issue of the Isotech Journal of Thermometry. They are employed by Isotech to qualify cells it produces, and also by the National Physical Laboratory of England for assurance of the British National standards[6].

For completeness, we reprint here the section of the Tavener article referred to above:

"Isothermal Technology Ltd is in the unusual position of being both a Nationally-accredited Laboratory and a producer of commercially distributed metal freezing-point cells and ITS-90 thermometers. We must therefore satisfy ourselves that, our customers and the National Physical Laboratory of England, which supervises us, that the cells we use for our own calibrations and the cells which we distribute to others, are acceptable embodiments of the intrinsic standards which define ITS-90.

"There are several indirect approaches to the verification of a cell. As a part of our application to our National Accreditation and Assessment Authority (NAMAS) to assess our capability, establish evaluation procedures and designate our uncertainty of measurement, our Certificate of Accreditation requires the following:

"In order to evaluate the performance of (Isotech's) fixed point cells, the following procedure should be carried out:

"(1) Total melt followed by fast freeze, to segregate any impurities

"(2) Slow melt, to be fully plotted from initial undercool to final rise

"(3) Freezing curves for all cells except the gallium cell, followed by determination of plateau temperature using NPL-calibrated standard platinum resistance thermometers.

The metals used in freezing-point cells are the purest we can obtain; 99.9999%+ or better. "Better" must be taken qualitatively, since at 6N+ purity we approach the limit of spectrographic analysis. Nevertheless, these metals must be regarded as having minute fractions of impurity which usually (but not always) depress the freezing temperature. Ideally pure materials have a unique melting and freezing temperature, whilst alloys exhibit a melting and freezing range. Examination of the melting range, (2) in our qualification requirements, provides an estimate of the purity of the metal. Tables 3 and 4 (of this paper) shows the effects upon melting and freezing for a selection of possible impurities, taken one at a time in small amounts, and makes clear the sensitivity of the plateaux in the detection of impurities and the qualification of cells.

"When we use freeze point cells to calibrate thermometers, we first hold the metal molten at about 5°C above the melt temperature overnight, to thoroughly mix the metal by convective stirring, and to distribute any previously segregated pockets of impurity. We then freeze the metal slowly, by setting the furnace temperature slightly below the metal's freezing temperature, and by introducing a cold rod or cold thermometer into the re-entrant well of the cell. (Tin, because of its long supercool, requires a somewhat different technique). We obtain a very flat freeze plateau, with a thin layer of solid metal formed on the inner wall of the cell and the outer wall of the thermometer well, and the liquid-solid interface progressing away from the thermometer. This is a form of zone-refining, sweeping the minute quantity of impurity ahead of the liquid-solid interface. This method forms the most constant and reproducible plateaux for calibration.

" However, to assess the purity of the metal, we inspect the melting curves. The metal is held molten at 5°C above the melt temperature for 12 hours, to distribute any impurities homogeneously throughout the ingot, and then frozen rapidly by removing the cell from the furnace. It is then slowly melted, containing a monitoring thermometer connected to a strip-chart recorder. Fig. 6 (of this paper) shows that three cells with various levels of impurities all give rather flat freeze plateaux. Inspection of the melting curves tells us immediately which cell contains the most pure metal. Informed inspection of the curve so obtained indicates to what extent the cell is an acceptable embodiment of an intrinsic standard.

"Thus, a comparison of the melting curve obtained after a fast freeze with the freezing curve as the metal is frozen slowly (as it is during a thermometer calibration) is one necessarily oblique but useful means for qualifying the metal in a metal freeze point cell. Other methods are described by other authors."

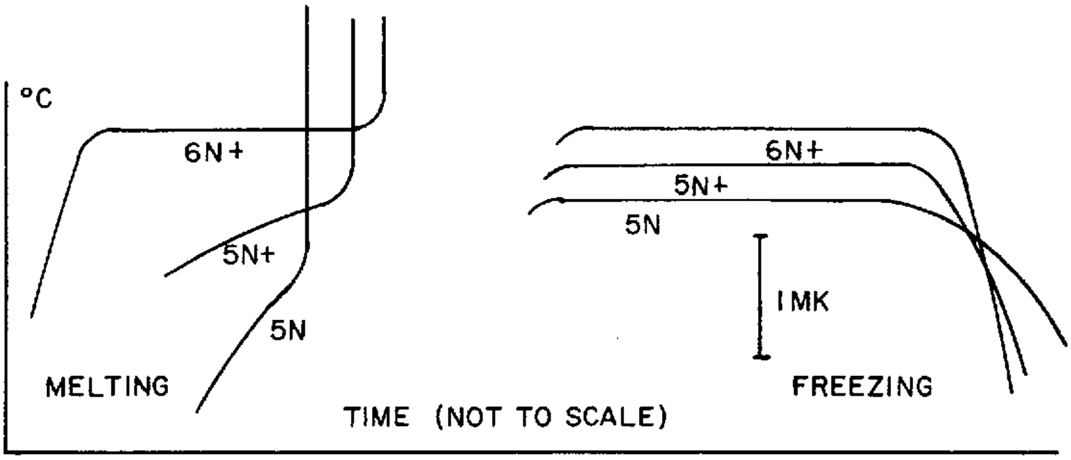

FIG. 6
MELT AND FREEZE CURVES OF METALS OF VARIOUS PURITY

FOOTNOTES

1: It is a curious fact that there are eight known triple points of water, including solid-liquid-vapor, solid-solid-liquid and solid-solid-solid equilibria, at pressures ranging from 0.0006 to 2077 MPa. These are listed below (from Schooley, Thermometry, CRC Press, 1986). When refer to the "triple point of water" in thermometry we mean always the ice-liquid-vapor triple point whose temperature is fixed by definition as 273.16 K and 0.01°C.

Phase in equilibrium	*Pressure (MPa)*	*Temp (C°)*
Ice I, liquid, vapor	0.000611	0.01
Ice I, liquid, Ice III	207.4	-22.0
Ice I, Ice II, Ice III	212.8	-34.7
Ice II, Ice III, Ice V	344.2	-24.3
Ice III, liquid, Ice V	346.2	-17.0
Ice V, liquid, Ice VI	625.7	+0.16
Ice VI, liquid, Ice VII	2199	+81.6
Ice VI, Ice VII, Ice VIII	2077	

Anyone wishing more information on the fascinating subject of this amazing chemical, H_2O, is referred to standard physics texts and also to Eisenberg and Kauzmann, *The Structure and Properties of Water* (Oxford 1969).

2: M. Hansen, *Constitution of Binary Alloys*. McGraw Hill (NYC) 1958

3: See H. H. Manko, *Solders and soldering*, (1964) McGraw-Hill, New York, for a complete discussion of the compositions and characteristics of binary and more complex alloys used as soft solders.

4: e.g Bongiovanni *et al* on the silver-copper eutectic, which melts at about 780°C; McLaren on the silver-aluminum eutectic, which melts at about 548°C; Sostmann on eutectics of gallium with indium and bismuth, etc.

5: The X-axis designation below the graph shows weight percent of tin (the solute) in lead (the solvent). The X-axis designation above the graph shows the atomic percent of tin.

The relationship between weight percentage and atomic percentage is useful in a number of metallurgical calculations, and therefore we show a generalized form. The reduction shown in the body of the text assumes that the percentage of solute is very small. For any ratio of solute to solvent, the following holds:

$$X = 100YA/[YA + (100 - Y)B] \qquad \text{Eq. 4}$$

$$Y = [(100)(x/a)]/[(X/A) + (100 - X)/B] \qquad \text{Eq. 5}$$

where X and Y are the percentages by weight and by atoms, respectively, of an element that has atomic weight A in a binary alloy with another element that has atomic weight B).

This can also be expressed as a function of the ratio of the amounts of the two elements, since the ratio by weight is the number of atoms multiplied by the ratio of atomic weights:

$$X/(100 - X) = (A/B)\ [Y/(100 - Y)] \qquad \text{Eq. 6}$$

6: Sostmann, Fundamentals of Thermometry, Part II, including Tavener, Confidence in the metal fixed points of ITS-90, *Isotech Journal of Thermometry*, Vol. 1 No. 2 (1990), Pages 49-78. Copies of this issue are still available.

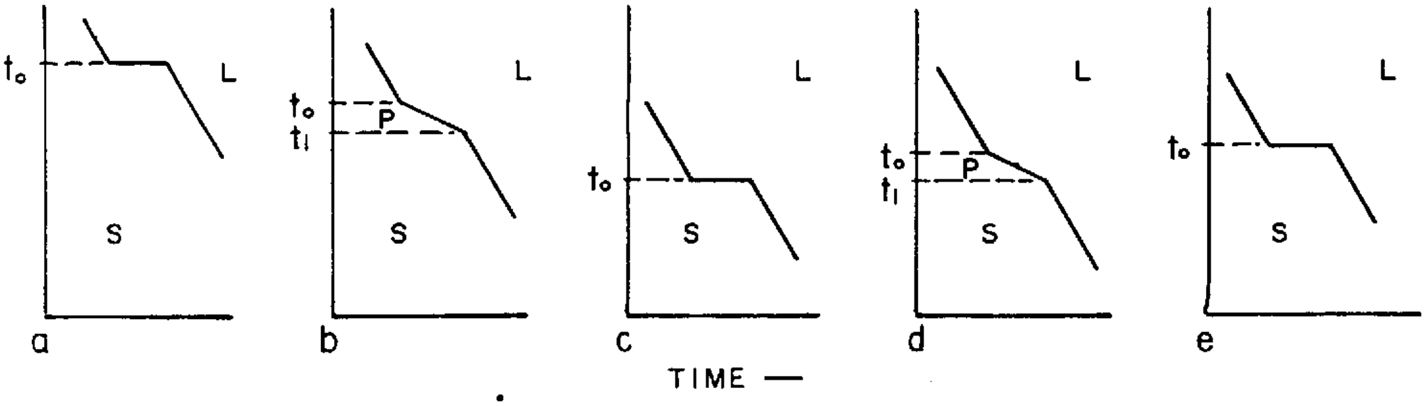

FIG. 2
MELT-FREEZE CURVES, WITH RESPECT TO TIME, OF (a) PURE LEAD (b) A MIXTURE OF LEAD AND TIN (c) LEAD AND TIN IN EUTECTIC PROPORTIONS, (APPROXIMATELY 63 WT% TIN), (d) A MIXTURE OF LEAD AND TIN (e) PURE TIN

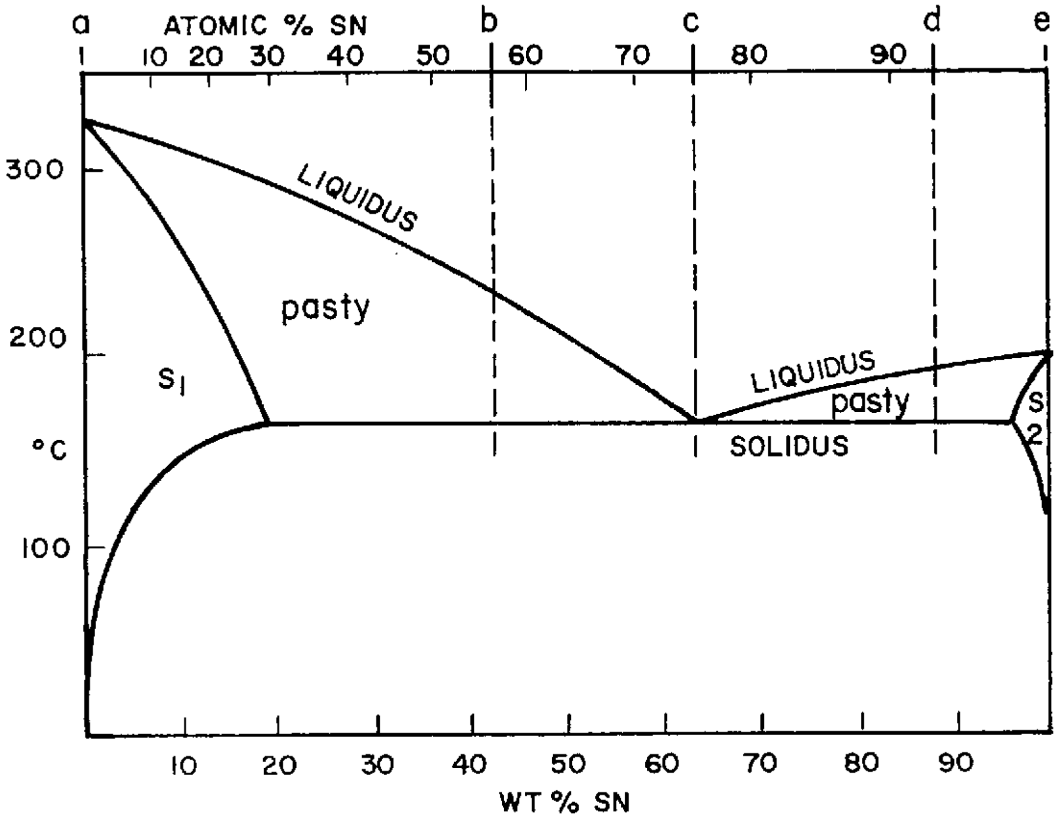

FIG. 3
THE COMPLETE PHASE DIAGRAM OF THE LEAD-TIN BINARY SYSTEM

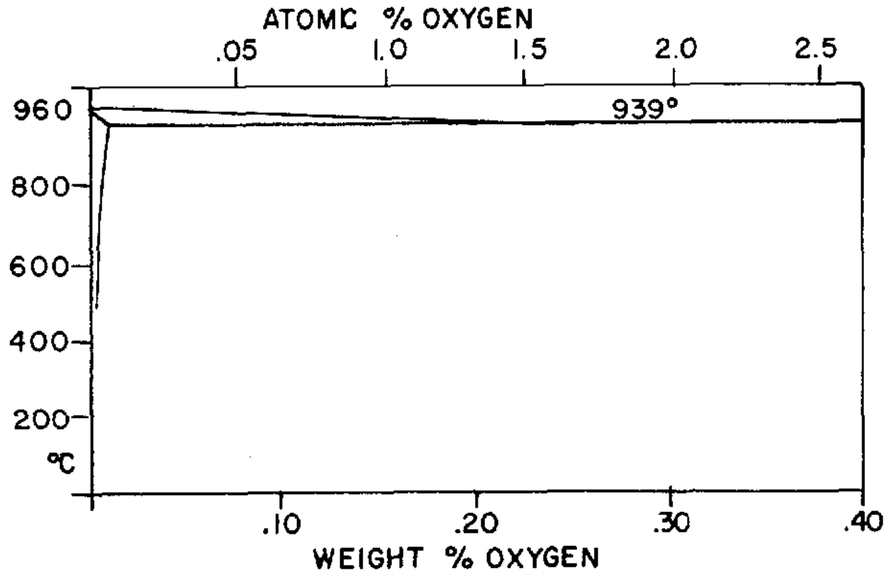

FIG. 4
THE SILVER-OXYGEN BINARY SYSTEM

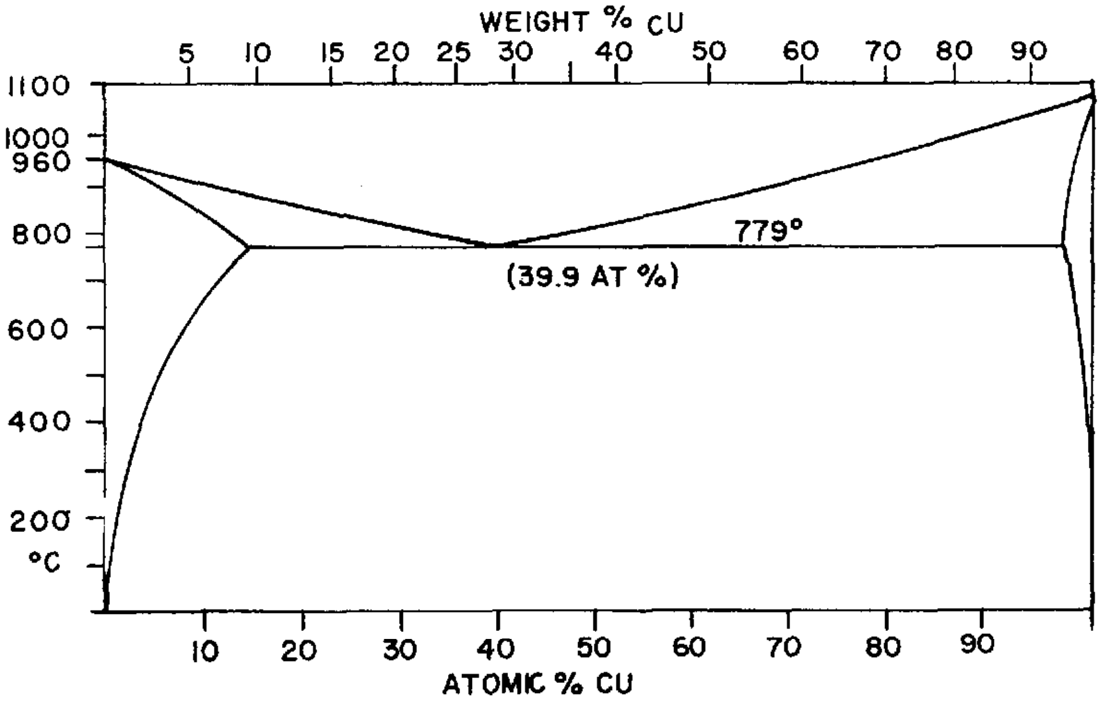

FIG. 5
THE SILVER-COPPER BINARY SYSTEM

TABLE 2

CALCULATION OF FIRST CRYOSCOPIC CONSTANT FOR VARIOUS METALS

A = [illegible]

A = FIRST CRYOSCOPIC CONSTANT
L = LATENT HEAT OF FUSION IN KJOULE/MOL
T = KELVIN TEMPERATURE
R = UNIVERSAL GAS CONSTANT = 0.008315 KJOULE/MOL

METAL	T	L	A
Al	933	10.79	0.001490
Ag	1235	11.30	0.000891
Au	1337	12.36	0.000831
Bi	545	11.30	0.004575
Ca	1112	8.54	0.000830
Cd	594	6.20	0.002113
Cr	2130	16.93	0.000448
Cu	1358	13.14	0.000856
Fe	1809	13.81	0.000507
In	430	3.26	0.002120
K	336	2.35	0.002503
Li	453	3.00	0.001758
Mg	922	8.95	0.001266
Mn	1517	2.40	0.000125
Na	370	2.60	0.002284
Ni	1726	16.47	0.000664
Pb	600	4.80*	0.001603
Si	1685	50.62	0.002144
Sn	505	7.11	0.003352
Ti	1943	15.50	0.000493
Zn	693	7.38	0.001848

*Note, for interest, the relatively low latent heat of Pb compared to In, Sn, Zn, Al and Ag. This results in shorter plateaux for Pb, which is otherwise a useful equilibrium fixed point.

TABLE 3

INDIUM

CALCULATE FREEZING POINT DEPRESSION FOR VARIOUS SOLUTES IN INDIUM AT A LEVEL OF 1 PART PER MILLION

NOTE: THIS CALCULATION ASSUMES THAT THE SOLUTE IS COMPLETELY SOLUBLE IN THE SOLVENT AT THIS CONCENTRATION

METAL	A 1ST CRYO CONST	AT WT SOLVENT	AT WT SOLUTE	MOLE FRAC SOLUTE	FP DEPRES
Al	0.0015	114.8	26.8	0.00000428	0.00285
Ag	0.0009	114.8	107.8	0.00000106	0.00118
Au	0.0083	114.8	196.97	0.00000058	0.00007*
Bi	0.0046	114.8	209	0.00000054	0.00011
Ca	0.0008	114.8	40	0.00000287	0.00358
Cd	0.0021	114.8	112.4	0.00000102	0.00048
Cr	0.0004	114.8	52	0.00000220	0.00551
Cu	0.0009	114.8	63.5	0.00000180	0.00200
Fe	0.0005	114.8	55.9	0.00000205	0.00410
In	0.0002	114.8	114.8	PURE INDIUM	
K	0.0025	114.8	39.1	0.00000293	0.00117
Li	0.0018	114.8	6.9	0.00001663	0.00924*
Mg	0.0013	114.8	24.3	0.00000472	0.00363
Mn	0.0006	114.8	54.9	0.00000209	0.00348*
Na	0.0023	114.8	23	0.00000499	0.00217
Ni	0.0007	114.8	58.7	0.00000195	0.00279*
Pb	0.0016	114.8	207.2	0.00000055	0.00034*
Si	0.0021	114.8	28.1	0.00000408	0.00194
Sn	0.0034	114.8	118.7	0.00000096	0.00020
Ti	0.0005	114.8	47.9	0.00000239	0.00479
Zn	0.0018	114.8	65.4	0.00000175	0.00097

*INSPECTION OF PHASE DIAGRAMS SUGGESTS THAT GOLD, LITHIUM, MANGANESE, LEAD AND SILICON RAISE THE FREEZING POINT OF INDIUM; HOWEVER THE DATA RESULTS FROM EXTRAPOLATION AT THESE CONCENTRATIONS AND MUST BE REGARDED AS QUESTIONABLE.

TABLE 4

TIN

CALCULATE FREEZING POINT DEPRESSION FOR VARIOUS SOLUTES IN TIN AT A LEVEL OF 1 PART PER MILLION

NOTE: THIS CALCULATION ASSUMES THAT THE SOLUTE IS COMPLETELY SOLUBLE IN THE SOLVENT AT THIS CONCENTRATION

METAL	A 1ST CRYO CONST	AT WT SOLVENT	AT WT SOLUTE	MOLE FRAC SOLUTE	FP DEPRES
Al	0.0015	118.7	26.98	0.00000439	0.00293
Ag	0.0009	118.7	107.8	0.00000110	0.00122
Au	0.0083	118.7	196.97	0.00000060	0.00007
Bi	0.0046	118.7	209	0.00000056	0.00012
Ca	0.0008	118.7	40	0.00000296	0.00370
Cd	0.0021	118.7	112.4	0.00000105	0.00050
Cr	0.0004	118.7	52	0.00000228	0.00570
Cu	0.0009	118.7	63.5	0.00000186	0.00207
Fe	0.0005	118.7	55.9	0.00000212	0.00424*
In	0.0002	118.7	114.8	0.00000103	0.00516
K	0.0025	118.7	39.1	0.00000303	0.00121*
Li	0.0018	118.7	6.9	0.00001720	0.00955
Mg	0.0013	118.7	24.3	0.00000488	0.00375*
Mn	0.0006	118.7	54.9	0.00000216	0.00360
Na	0.0023	118.7	23	0.00000516	0.00224
Ni	0.0007	118.7	58.7	0.00000202	0.00288
Pb	0.0016	118.7	207.2	0.00000057	0.00035
Si	0.0021	118.7	28.1	0.00000422	0.00201*
Sn	0.0034	118.7	118.7	PURE TIN	
Ti	0.0005	118.7	47.9	0.00000247	0.00496
Zn	0.0018	118.7	65.4	0.00000181	0.00101

*INSPECTION OF PHASE DIAGRAMS SUGGESTS THAT IRON, POTASSIUM, MANGANESE AND SILICON MAY ELEVATE THE FREEZING POINT OF TIN. THE DATA IS BASED ON EXTRAPOLATION AT THESE CONCENTRATIONS AND MUST BE REGARDED AS QUESTIONABLE.

TABLE 5

ZINC

CALCULATE FREEZING POINT DEPRESSION FOR VARIOUS SOLUTES IN ZINC AT A LEVEL OF 1 PART PER MILLION

NOTE: THIS CALCULATION ASSUMES THAT THE SOLUTE IS COMPLETELY SOLUBLE IN THE SOLVENT AT THIS CONCENTRATION

METAL	A 1ST CRYO CONST	AT WT SOLVENT	AT WT SOLUTE	MOLE FRAC SOLUTE	FP DEPRES
Al	0.0015	65.4	26.98	0.00000242	0.00161
Ag	0.0009	65.4	107.8	0.00000060	0.00067*
Au	0.0083	65.4	196.97	0.00000033	0.00004*
Bi	0.0046	65.4	209	0.00000031	0.00006
Ca	0.0008	65,4	40	0.00000163	0.00204
Cd	0.0021	65.4	112.4	0.00000058	0.00027
Cr	0.0004	65.4	52	0.00000125	0.00314
Cu	0.0009	65.4	63.5	0.00000102	0.00114*
Fe	0.0005	65.4	55.9	0.00000116	0.00233
In	0.0002	65.4	114.8	0.00000056	0.00284
K	0.0025	65.4	39.1	0.00000167	0.00066
Li	0.0018	65.4	6.9	0.00000947	0.00526
Mg	0.0013	65.4	24.3	0.00000269	0.00207
Mn	0.0006	65.4	54.9	0.00000119	0.00198
Na	0.0023	65.4	23	0.00000284	0.00123**
Ni	0.0007	65.4	58.7	0.00000111	0.00159
Pb	0.0016	65.4	207.2	0.00000031	0.00019
Si	0.0021	65.4	28.1	0.00000232	0.00110
Sn	0.0034	65.4	118.7	0.00000055	0.00016
Ti	0.0005	65.4	47.9	0.00000136	0.00273
Zn	0.0018	65.4	65.4	PURE ZINC	

*INSPECTION OF PHASE DIAGRAMS INDICATES THAT SILVER, GOLD AND COPPER ELEVATE THE FREEZING TEMPERATURE OF ZINC

**INSPECTION OF PHASE DIAGRAMS INDICATES THAT SODIUM MAY ELEVATE THE FREEZING TEMPERATURE OF ZINC. THE DATA IS BASED ON EXTRAPOLATION AT THESE CONCENTRATIONS AND MUST BE REGARDED AS QUESTIONABLE.

TABLE 6

ALUMINUM

CALCULATE FREEZING POINT DEPRESSION FOR VARIOUS SOLUTES IN ALUMINUM AT A LEVEL OF 1 PART PER MILLION

NOTE: THIS CALCULATION ASSUMES THAT THE SOLUTE IS COMPLETELY SOLUBLE IN THE SOLVENT AT THIS CONCENTRATION

METAL	A 1ST CRYO CONST	AT WT SOLVENT	AT WT SOLUTE	MOLE FRAC SOLUTE	FP DEPRES
Al	0.0015	26.98		PURE ALUMINUM	
Ag	0.0009	26.98	107.8	0.00000025	0.00027
Au	0.0083	26.98	196.97	0.00000013	0.00001
Bi	0.0046	26.98	209	0.00000012	0.00002
Cd	0.0021	26.98	112.4	0.00000024	0.00011
Cr	0.0004	26.98	52	0.00000051	→ 0.00129*
Cu	0.0009	26.98	63.5	0.00000042	0.00047
Fe	0.0005	26.98	55.9	0.00000048	0.00096
In	0.0002	26.98	114.8	0.00000023	0.00117
K	0.0025	26.98	39.1	0.00000069	→ 0.00027**
Li	0.0018	26.98	6.9	0.00000391	0.00217
Mg	0.0013	26.98	24.3	0.00000111	0.00085
Mn	0.0006	26.98	54.9	0.00000049	0.00081
Na	0.0023	26.98	23	0.00000117	0.00051
Ni	0.0007	26.98	58.7	0.00000045	0.00065
Pb	0.0016	26.98	207.2	0.00000013	0.00008
Si	0.0021	26.98	28.1	0.00000096	0.00045
Sn	0.0034	26.98	118.7	0.00000022	0.00006
Ti	0.0005	26.98	47.9	0.00000056	→ 0.00112*
Zn	0.0018	26.98	65.4	0.00000041	0.00022

*INSPECTION OF PHASE DIAGRAMS INDICATES THAT CHROMIUM AND TITANIUM ELEVATE THE FREEZING TEMPERATURE OF ~~TIN~~. Al

**INSPECTION OF PHASE DIAGRAMS INDICATES THAT POTASSIUM MAY ELEVATE THE FREEZING TEMPERATURE OF ~~TIN~~. THE DATA IS BASED ON EXTRAPOLATION AT THESE CONCENTRATIONS AND MUST BE REGARDED AS QUESTIONABLE.

Al

TABLE 7

SILVER

CALCULATE FREEZING POINT DEPRESSION FOR VARIOUS SOLUTES IN SILVER AT A LEVEL OF 1 PART PER MILLION

NOTE: THIS CALCULATION ASSUMES THAT THE SOLUTE IS COMPLETELY SOLUBLE IN THE SOLVENT AT THIS CONCENTRATION

METAL	A 1ST CRYO CONST	AT WT SOLVENT	AT WT SOLUTE	MOLE FRAC SOLUTE	FPDEPRES
Al	0.0015	107.8	26.98	0.00000399	0.00266
Ag	0.0009	107.8	107.8	PURE SILVER	
Au	0.0083	107.8	196.97	0.00000054	0.00006*
Bi	0.0046	107.8	209	0.00000051	0.00011
Ca	0.0008	107.8	40	0.00000269	0.00336
Cd	0.0021	107.8	112.4	0.00000095	0.00045
Cr	0.0004	107.8	52	0.00000207	0.00518*
Cu	0.0009	107.8	63.5	0.00000169	0.00188
Fe	0.0005	107.8	55.9	0.00000192	0.00385
In	0.0002	107.8	114.8	0.00000093	0.00469
K	0.0025	107.8	39.1	0.00000275	0.00110
Li	0.0018	107.8	6.9	0.00001562	0.00867
Mg	0.0013	107.8	24.3	0.00000443	0.00341
Mn	0.0006	107.8	54.9	0.00000196	0.00327*
Na	0.0023	107.8	23	0.00000468	0.00203
Ni	0.0007	107.8	58.7	0.00000183	0.00262**
Pb	0.0016	107.8	207.2	0.00000052	0.00032
Si	0.0021	107.8	28.1	0.00000383	0.00182
Sn	0.0034	107.8	118.7	0.00000090	0.00026
Ti	0.0005	107.8	47.9	0.00000225	0.00450
Zn	0.0018	107.8	65.4	0.00000164	0.00091

*INSPECTION OF PHASE DIAGRAMS INDICATES THAT THE FREEZING POINT OF SILVER IS ELEVATED BY GOLD, CHROMIUM AND MANGANESE.

**ISPECTION OF PHASE DIAGRAMS SUGGESTS THAT THE FREEZING POINT OF SILVER MAY BE ELEVATED BY NICKEL. THE DATA IS EXTRAPOLATED AT THIS CONCENTRATION AND MUST THEREFORE BE REGARDED AS QUESTIONABLE.

TABLE 8

AN ANALYSIS OF A QUANTITY OF ALUMINUM USED IN ISOTECH CELLS
LOT NO. N-9175

	IMPURITY REPORTED METAL	IMPURITY REPORTED PPM	FP DEPRESS FOR 1PPM (NOTE1)	EFFECT AT REPORTED LEVEL
	Bi	0.2	.00002	.00000
	Cr	0.1	-.00129	-.00013
	Cu	0.5	-.00047	-.00024
	Li	0.1	.00085	.00022
	Mg	0.1	.00085	.00009
	Pb	1	.00008	.00008
NET EFFECT		2		.00006

TABLE 9

AN ANALYSIS OF A QUANTITY OF ZINC USED IN ISOTECH CELLS
CONTRACT NO. 91 PO 2209

	IMPURITY REPORTED METAL	IMPURITY REPORTED PPM	FP DEPRESS FOR 1 PPM (NOTE 1)	EFFECT AT REPORTED LEVEL
	Ca	0.1	.00204	.00020
	Cu	0.1	-.00114	-.00011
	Fe	0.2	.00233	.00041
	Others	0.04		?????
NET EFFECT		0.44		.00030

NOTE 1: FREEZING POINT DEPRESSION PER 1PPM MEANS THE FREEZING POINT DEPRESSION CALCULATED FROM THE FIRST CRYOSCOPIC CONSTANT. (-) INDICATES THAT FREEZING POINT IS ELEVATED; SEE TABLES 5 AND 6.