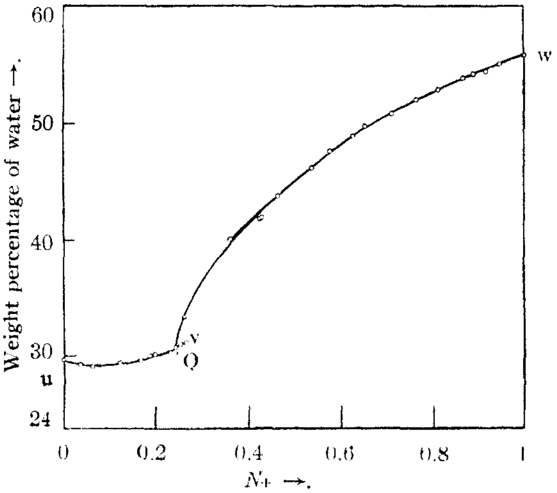

Fig. 6.—Water content for quaternary curves.

on the line **y**D and one of the sulfates on the line **z**C, and the liquid is consumed as it travels on the curve **w** → Q before it reaches Q. The 3-phase triangle (condensed phases) for this curve therefore starts as the line **w**DC and ends as Q**yz**. Similarly, liquids with P in A**xz**B dry up on the curve Q → **u** to leave AD_1 on the line A**x** and BC on line B**z**, the 3-phase triangle starting as Q**xz** and ending as **u**AB. Those with P in the triangle **xyz** dry up at point Q to leave the three solids **x** + **y** + **z**. The phase reaction on the curve **v** → Q is that of the ternary point **v**, namely, Liquid + **y** → **x** + $H_2O\nearrow$, except that the liquid on the curve is quaternary, containing sulfate. The 3-phase triangle starts as **vxy** and ends as Q**xy**. At point Q, which lies outside the triangle of its three saturating solids **xyz** (no matter where the point **z** is estimated to be), the invariant phase reaction is therefore still of the transition type, Liquid (Q) + **y** → **x** + **z** + $H_2O\nearrow$. Liquids reaching Q with P in **xyz** lose the liquid phase in the invariant reaction to leave the three solids, while those reaching Q with P in the triangle Q**xz** lose the solid **y** and proceed, while saturated with AD_1 and BC, to dry up on the curve Q → **u**.

The transition curve **v** → Q is crossed by liquids reaching it with original salt proportions P in the special region **vx**Q. These liquids approach the curve, from the right, with solid solution AD_2 as primary crystallization, and, with complete equilibrium, this solid attains the limiting composition **y** as the liquid reaches the curve **v** → Q, when solid solution **x** appears as a second solid phase. Before the liquid reaches the invariant point Q, however, all of the solid **y** is consumed in the reaction Liquid (on **v**Q) + **y** → **x** + $H_2O\nearrow$, and the remaining liquid, now saturated only with solid solution AD_1, leaves the curve to enter upon the saturation surface of AD_1, or A**v**Q**u**. The liquid finally dries up on the curve Q → **u**, to leave AD_1 + BC on the line B**z**.

If, as is practically inevitable, complete solid phase equilibrium is not maintained in isothermal evaporation, then only solutions reaching curve Q → **u** directly will leave only two solids when they finally dry up (practically at point **u**), and each solid, moreover, will not be uniform in composition although possibly "homogeneous" in structure. Solutions reaching directly either **v** → Q or **w** → Q will stop only momentarily at point Q, and will dry up (also at point **u**) to leave three solids, again each not uniform in composition.

New York, N. Y. Received March 19, 1951

[Contribution from the Department of Chemistry, University of Manitoba]

The System Aluminum–Indium–Tin

By A. N. Campbell, L. B. Buchanan, J. M. Kuzmak and R. H. Tuxworth

Of the three component binary systems, only the system aluminum–indium is at all in doubt. For this system we have determined the complete equilibrium diagram. An extensive region of partial miscibility, in the liquid state, occurs and for this we find the critical solution temperature and composition to be 875° and 61% indium by weight, respectively. For the ternary system Al–In–Sn, the isotherms have been established for 750, 700, 650 and 450°, using a constant temperature furnace and sampling and analyzing congruent solutions. In this way the critical compositions have been evaluated for the above temperatures. X-Ray diffraction measurements have shown that aluminum does not enter into In–Sn solid solutions to an extent greater than 5%, and probably not at all, since the lines of the diffraction picture were not shifted to any observable extent when aluminum was added to the In–Sn system. The ternary eutectic temperature is 117.1° and the composition 48.83% by weight in tin, 51.03% indium and 0.14% aluminum.

The equilibrium diagram of this ternary system has not been investigated previously; those of the component binary systems have, Al–Sn and In–Sn exhaustively, Al–In not so completely. The literature of the latter system requires some discussion, since the results are incomplete and not in agreement.

Interest in the Al–In system centers around a wide miscibility gap, which exists in the liquid state. According to Raub and Engel[1] the limits of the miscibility gap are 17.3% In up to nearly pure indium: the temperature of the invariant system: solid aluminum–liquid 1–liquid 2, is given in 634°. As far as Raub and Engel could determine, aluminum has no effect on the freezing point of indium and hence the binary eutectic composition must lie very close to that of pure indium, and the eutectic temperature close to the freezing point of pure indium, which is variously given as 155.5–156.4°. These authors also find, by microscopic and X-ray investigation, that the solid solubility of indium in aluminum is very small. According to Valentiner and Puzicka[2] the miscibility gap extends from 13 to 98 weight per cent. indium, at the invariant temperature, which they give as 634°; the eutectic temperature is very close to 156°. Valentiner also

(1) E. Raub and M. Engel, *Metallforsch.*, 1, 148 (1946).

(2) S. Valentiner and I. Puzicka, *ibid.*, 2, 127 (1947).

states that the mutual solubility of the two metals in the solid state is small.

Klemm and associates[3] give the upper limit for the solubility of indium in solid aluminum as 0.05 atomic per cent. They also state that there is at most 6 atomic per cent. Al in the indium-rich layer at the lower temperature limit of the miscibility gap, while the aluminum-rich layer contains 94 atomic per cent. Al. The temperature of the lower limit of the miscibility gap is given as 640°, while the eutectic is at about 155°.

From some unpublished work by Davies and Rowe,[4] Davies states "indium apparently has a slight solubility in aluminum. The α-phase at 250° contains enough indium to produce a barely discernible shift in the X-ray diffraction pattern from that of high purity aluminum."

Our own work on the complete system (this paper) indicates the limits of the gap at the invariant temperature to be 17.5 weight % In and 97.2% In, and the invariant temperature to be 638.6°. The binary eutectic Al–In contains certainly less than 0.05% Al, and lies at a temperature indistinguishable from the freezing point of pure indium (156.3°).

The latest work on the system aluminum–tin, that of Sully, Hardy and Heal[5] shows that, despite a distorted liquidus, neither compound formation nor solid solution occurs. The binary eutectic contains 99.50% tin and lies at 228°.

The most complicated binary system is that of indium–tin. The most precise study is that of Rhines and co-workers.[6] Their equilibrium diagram shows a eutectic and a peritectic point, but no maximum. At room temperature, four solid phases, $\alpha,\beta,\gamma,\delta$, exist, of which α, containing up to 3% by weight tin, is crystallographically identical with indium, and δ, containing up to 6% indium, is identical with pure tin.

Because of the nature of the three constituent binary systems, it was apparent from the beginning that the addition of aluminum to the indium–tin system would have but little effect on the nature of the solid phases. Interest therefore centered on the binary and ternary miscibility gaps and the compositions of congruent solutions, as well as on the determination, if possible, of the critical solution temperature in the Al–In system. The composition of the ternary eutectic had also to be evaluated. The principal technique employed was that of the determination of isothermal sections of the solid model.

Experimental Procedure

Purity of Metals.—The aluminum, indium and tin were analyzed as follows by the companies supplying them:

Aluminum (from the Aluminum Company of America): copper, 0.0042%; iron, 0.0010%; silicon, 0.0014%; magnesium, 0.0009%; sodium, 0.0001%.

Indium (from the Consolidated Mining and Smelting Company of Canada; marked "Tadanac 99.95 Indium"): lead, 0.005%; cadmium, 0.001%; iron, 0.001%; copper, 0.001%; tin, 0.004%; thallium, 0.0005%.

Tin (from Batch #73 of Vulcan "Commercial" Tin: iron, 0.0020%; antimony, 0.0023%; lead, trace; copper, trace; tin, 99.9957% (by diff.).

Methods of Analysis of Alloys.—Because of the close chemical similarity between indium and aluminum, it was impossible to determine either by precipitation with 8-hydroxyquinoline. The indium content was therefore determined polarographically, using a Sargent–Heyrovsky polarograph. It was not possible to determine aluminum polarographically, because of its high electrode potential. The aluminum content was checked by determining the density of the alloys. Owing to the great difference in density between aluminum and indium or tin, the method is surprisingly accurate. With ternary alloys, a direct determination of tin was also necessary and this was made gravimetrically as tin oxide, after treatment of the alloy with nitric acid.

Thermal Analysis.—The methods are well known. Both direct (rectilinear cooling) and differential thermal analysis were used. In the latter case, freezing aluminum was used as the neutral body. The thermocouple used throughout was Chromel P (Ni 90, Cr 10)–Alumel (Ni 94, Mn 2.5, Al 2, Si 1, Fe 0.5); it was calibrated using the freezing points of pure aluminum, zinc, lead and tin.

Isothermal Analysis.—The furnace was maintained at constant temperature by an arrangement of photoelectric cells and an electronic control. The main features of the apparatus have been described elsewhere[7] but we are indebted to Mr. K. I. Roulston, Assistant Professor of Physics, University of Manitoba, for a considerable simplification of the electronic control.

At 700°, the temperature was maintained constant to $\pm 1°$, and at 900° to $\pm 2°$. The resistance furnace was of the usual type, embodying a nichrome heating unit, and it was heavily lagged.

In order to prevent oxidation of alloys which were kept for three days at temperatures sometimes in excess of 800°, a reducing atmosphere of hydrogen and nitrogen was passed over the melt. This atmosphere was obtained from cracked ammonia using Larson's apparatus.[8]

In previous work on the system iron–tin[9] Pyrex containers were found very suitable for preventing oxidation at temperatures as high as 1000° but the use of Pyrex was found to be quite impracticable here, because the aluminum readily reduced the silica of the glass to metallic silicon and this metallic silicon, dissolving in the melt, produced great distortion in the miscibility gap. Alundum crucibles were therefore used. The alloys were given a preliminary melting and thoroughly stirred in an Ajax–Northrup induction furnace. The crucible and contents were then placed in a steel container through which the cracked ammonia gas was led, and the bomb itself placed in the furnace. The thermocouple hot junction also entered the steel container. The whole was left in the furnace for three days.

The most successful method of sampling was as follows: an alundum tube of outer diameter one-eighth inch and inner diameter one-sixteenth inch was passed into the molten sample to a carefully measured depth, depending on whether the top or the bottom layer was to be sampled. Suction was applied to the outer open end, the molten sample solidified in the tube, and the tube was broken for removal of the sample. This procedure was suitable for temperatures up to and including 850°, but at 900° the relatively low melting indium would not solidify in the tube and ran out as the tube was being withdrawn from the melt.

At 900° and higher temperatures, a quenching process was attempted, with only partial success; the two liquid layers of this system alter their composition with extreme rapidity, as the temperature changes. At temperatures below about 600°, solid aluminum appears as a phase in the isothermally invariant system (over certain ranges of composition). In working in those regions of the ternary system where solid aluminum is present, we attempted to bore through the crust of solid aluminum on the top of the alloy and sample the two liquid layers underneath, but with limited success. Here the process of quenching was resorted to with more success; at these relatively lower temperatures the change of equilibrium with temperature is much slower.

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(3) W. Klemm, Li Klemm, E. Hohmann, H. Volk, E. Orlamunder and H. A. Klein, *Z. anorg. Chem.*, **256**, 329 (1948).

(4) H. M. Davies, "Metals Handbook," Amer. Soc. for Metals, (1948).

(5) A. H. Sully, H. K. Hardy and T. J. Heal, *J. Inst. Metals*, **76**, 269 (1949).

(6) F. N. Rhines, N. M. Urquhart and H. R. Hoge, *Trans. Amer. Soc. for Metals*, **39**, 694 (1947).

(7) B. C. Lutz and J. H. Wood, *Can. J. Research*, **A26**, 145 (1948).

(8) A. T. Larson, W. L. Newton and W. Hawkins, *Chem. Met. Eng.*, **26**, 494 (1922).

(9) Campbell, Wood and Skinner, **THIS JOURNAL**, **71**, 1729 (1949).

X-Ray Analysis.—Simple Debye cameras were used. Without a back reflection camera, it is not possible to detect heterogeneity at a concentration of less than 5%, so that none of our conclusions is valid for concentrations less than this. The attempt was made to show that, if 5% aluminum is added to any one of the four homogeneous solid phases occurring in the indium–tin system, the characteristic aluminum lines would show up and that, therefore, aluminum did not enter into solid solution in any of these four phases to an extent greater than 5%. For this purpose homogeneous samples of the α, β, γ and δ phases of the indium–tin system were prepared and photographed and then the identical alloys, to which 5% of aluminum had been added. In every case, the alloys were rolled into foil and then annealed at 110° for several days.

Experimental Results

Table I

Binary System: Aluminum–Indium. Direct Thermal and Differential Thermal Analysis of Low Indium Alloys

	Direct thermal analysis		Differential thermal analysis	
Wt. % indium	Initial freezing point, °C.	Invariant temperature	Wt. % indium	Initial freezing point
0.00 (pure Al)	659.9	...	4.63	654.4
5.95	659.1	639.1	5.00	654.0
6.14	657.1	638.1	5.47	652.1
10.6	648.6	638.6	10.7	647.4
14.8	...	638.3		
17.7	...	639.2		

Table II

Isothermal Analysis of High Indium Liquidus

Mixtures of aluminum and indium which were heated for 24 hours at a series of different temperatures above the melting point of indium, were quenched and analyzed, in order to determine the compositions of solutions in contact with solid aluminum at various temperatures.

Temp., °C.	Wt. % aluminum	Temp., °C.	Wt. % aluminum
156.4	0.00 (pure In)	500	0.64
200	<0.05	550	0.93
300	<0.05	600	1.68
400	0.24	625	2.18

Table III

Compositions of Congruent Solutions—Two Liquid Layers. Both Layers Sampled at Equilibrium Temperatures

Temperature, °C.	Al-rich layer Wt. % In	In-rich layer Wt. % In	Mean Wt. % In
675	19.9	95.6	57.85
750	25.3	92.3	58.8
800	29.3	90.3	59.8
850	41.1	80.3	60.7

Table IV

Ternary System: Al–In–Sn. Ternary Eutectic

A 60-g. alloy of the binary In–Sn eutectic composition (48.9% tin and 51.1% indium) was prepared and its eutectic halt temperature obtained by thermal analysis as 117.8°. One-tenth of 1% of aluminum was then added and another run made. This procedure was repeated until no further lowering of freezing point was observed. By interpolation the ternary eutectic temperature was calculated to be 117.1° and the composition 48.83% tin, 51.03% indium and 0.14% aluminum.

Alloy composition	Freezing point, °C.
48.9% tin; 51.1% In	117.8
The above plus 0.1% Al	117.3
The above plus 0.2% Al	117.1
The above plus 0.3% Al	117.2

Table V

Congruent Solutions in Two-liquid Region at Various Temperatures

Equilibrium time 3 days throughout

Al-rich layer (Liq. 1)			In-rich layer (Liq. 2)		
Al, %	In, %	Sn, %	Al, %	In, %	Sn, %
Temperature 750°					
74.7	25.3	0.0	7.7	92.3	0.0
62.6	25.6	11.8	10.9	76.2	12.9
49.6	34.5	15.9	16.1	64.5	19.4
43.4	33.6	23.0	26.9	44.8	28.3
Temperature 700°					
55.3	20.5	24.2	18.9	48.1	33.0
40.3	29.6	30.1	22.2	38.5	39.3
Temperature 650°					
81.4	18.6	0.0	3.0	97.0	0.0
74.9	18.5	6.6	6.1	81.4	12.5
66.5	18.9	14.6	7.2	67.6	25.2
59.9	18.1	22.0	9.4	56.4	34.2
53.9	17.9	28.2	15.3	43.9	40.8
42.5	20.4	37.1	17.9	35.7	46.4

Temperature 450°

At this temperature, solid aluminum is in equilibrium with certain solutions. These alloys were quenched and analyzed (in one case) from the top, the middle and the bottom, of the ingot.

Top			Middle		
Al, %	In, %	Sn, %	Al, %	In, %	Sn, %
78.8	14.7	6.5	64.9	25.8	9.3
58.3	14.0	27.7			
75.9	20.1	4.0			

	Bottom		
Al, %	In, %	Sn, %	Phases present
1.8	81.6	16.6	Solid Al-liquid 1-liquid 2
12.2	31.6	56.2	Liquid 1-liquid 2
	94.6	5.8	Solid Al-liquid 2

Discussion of Results

Figure 1 represents the equilibrium diagram for the binary system Al–In. In this figure the values used for the invariant system solid Al–Liquid 1–Liquid 2, are: temperature = 638.6°, indium-rich layer, 97.2% indium, aluminum-rich layer, 17.5% indium (this latter figure is that of Raub and Engel (ref. 1)). We have chosen Raub and Engel's figure, because it is in good agreement with the extrapolation of our own isotherms for congruent solutions, to 638.6°. This is in apparent disagreement with our own Table I, which indicates that alloys containing 14.8 and 17.7% indium show no temperature halt above the invariant temperature. All this means, however, is that the freezing point curve becomes very flat as it approaches the miscibility gap, in agreement with the general behavior of non-ideal solutions, and thermal analysis is not sufficiently sensitive to detect the prior halt.

Our attempt to determine directly the binary eutectic conditions failed. Addition of aluminum to indium produces no effect on the freezing point that we could discover. Extrapolation of the high indium liquidus to the freezing temperature of indium showed that the eutectic mixture must contain less than 0.05% aluminum.

Table III gives the compositions of congruent binary solutions, up to 850°, obtained by direct sampling. The figures are very reliable up to and including 800°, but at 850° difficulty was experienced in withdrawing samples due to the extreme fluidity of the melt; the 850° figures must therefore be accepted with reserve. Hence, in the figure, the miscibility gap is drawn as a broken curve above 800°. We have every reason to believe, however, that the critical solution temperature lies below 900°. Thus, an alloy brought to equilibrium at 900° and quenched in ice-water gave, on analysis: top of ingot 64.8% In, middle 63.1% and bottom 65.4%. A similar experiment at 926° gave: top, 65.6%, middle 69.7% and bottom 70.4%. Allowing for the crudeness of the work, this represents homogeneity.

The mean composition of congruent solutions, plotted in Fig. 1, gives a good straight line and this "rectilinear diameter" extrapolated to meet the (dotted and hypothetical) portion of our curve of congruent solutions gives a critical solution temperature of 875° and a critical composition of 61% by weight of indium.

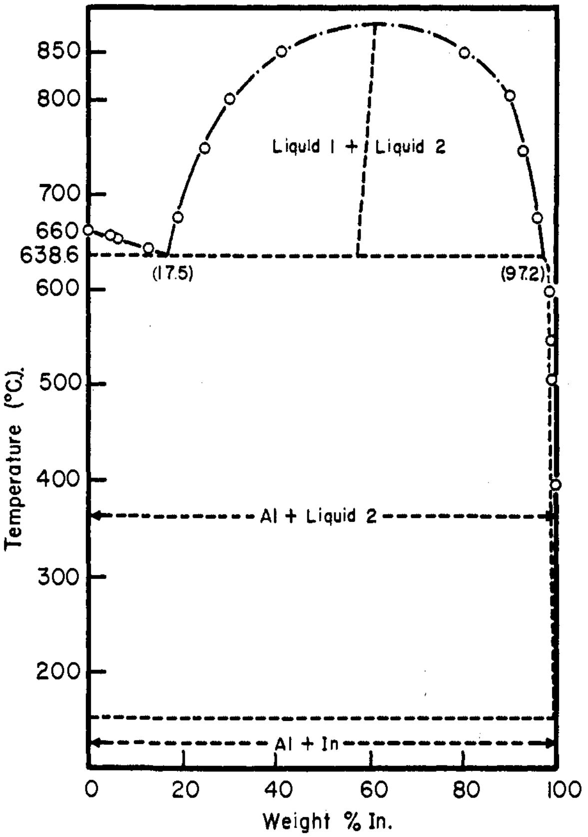

Fig. 1.

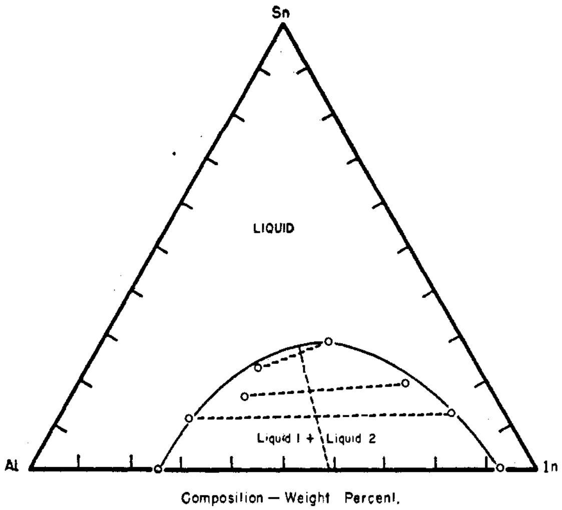

Fig. 2.

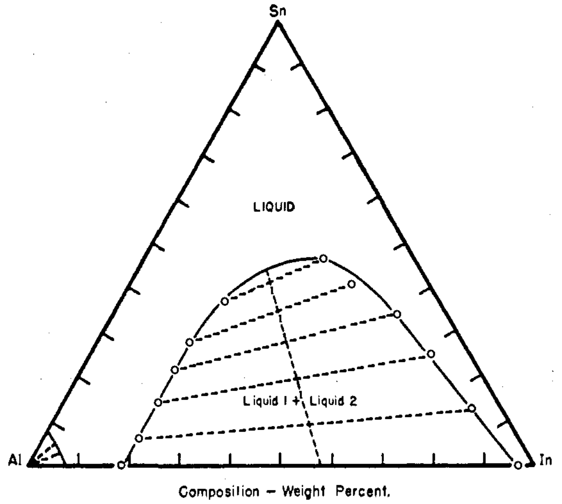

Fig. 3.

Turning to the ternary system, the isotherms of congruent solutions for 750 and 650° are given in Figs. 2 and 3. From these figures, it is seen that the area of partial miscibility extends further and further into the solid model with falling temperature. The 750° isotherm shows that there is no possibility of a ternary critical point: the highest temperature at which two liquid layers can occur lies in the binary system, Al–In.

In the ternary system, also, the plot of mean composition of congruent solutions is a reasonably straight line and, in this way, ternary critical compositions are deduced as follows: at 750°, 34% Al, 39% In, 27% Sn; at 700°, 32% Al, 32% In, 36% Sn; at 650°, 30% Al, 25% In, 45% Sn; at 450°, 32% Al, 15% In, 53% Sn (very approximately). The lower limits of the miscibility gap, at 450°, are approximated as 78% Al, 15% In, 7% Sn and 2% Al, 81% In, 17% Sn, respectively.

At 450°, it was found for all compositions investigated that a layer of solid aluminum sufficiently deep to defy drilling, had formed at the surface. The 450° alloys were therefore quenched, but quenching from the relatively low temperature of 450° should not cause such grievous errors as in our attempts to quench from higher temperatures. The results have been interpreted as shown in Fig. 4, *i.e.*, the first alloy is assumed to have a composition on, or very close to, the base of the miscibility gap, which has now moved into the body of the diagram. Similarly, it is assumed that the third alloy represents an equilibrium between solid aluminum and an indium-rich liquid, incomplete separation being apparent (the upper portion of the third alloy is analogous to the "wet residue" obtained in Schreinemakers' method for the determination of equilibrium solid phases). Figure 4 is strictly diagrammatic.

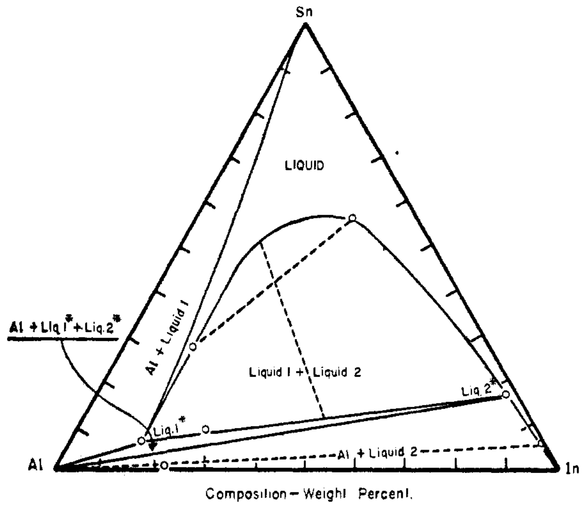

Fig. 4.

Figure 5 is a liquidus projection, showing the ternary eutectic and peritectic transition.

The X-ray data have shown that aluminum does not enter into the In–Sn solid solutions to an extent greater than 5%, and probably not at all, since the lines of the pure phases were not shifted to any observable extent. Sufficient aluminum lines were observed to indicate the presence of aluminum as a solid phase.

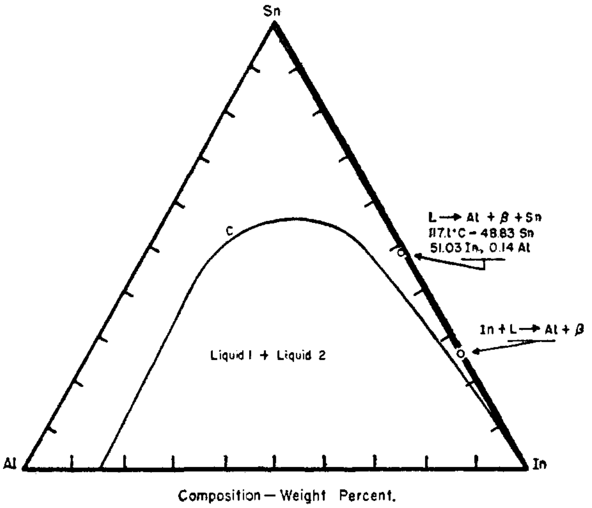

Fig. 5.

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WINNIPEG, CANADA RECEIVED SEPTEMBER 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Spectra of Cerium(IV) in Perchloric Acid. Evidence for Polymeric Species[1,2]

BY EDWARD L. KING AND MARY L. PANDOW

The spectra of cerium(IV) perchlorate in perchloric acid–sodium perchlorate solutions have been studied. It has been found that Beer's law is not obeyed in the wave length region of 440–530 mμ over the cerium(IV) concentration range of 4×10^{-4} to 10^{-1} molar at hydrogen ion concentrations of 0.85 and 2.57 molar. The spectral data are consistent with the existence in the solutions of equilibria between monomeric and polymeric species. The extinction coefficient of cerium(IV) in solutions which are relatively concentrated in perchlorate ion (>6 M) is much greater than in dilute solution. This is observed for both perchloric acid and perchloric acid–sodium perchlorate solutions. The system cerium(III)–(IV) does not exhibit "interaction–absorption" under the concentration conditions studied.

Several experimental studies have been made which are relevant to the question of what species of cerium(IV) exist in perchloric acid solutions. The study of the cerium(III)–cerium(IV) potential in perchloric acid by Sherrill, King and Spooner[3] indicates that the hydrated but unhydrolyzed Ce^{+4} does not exist to a predominant extent even in 2.4 M $HClO_4$. They propose the value 0.6 for the concentration equilibrium quotient for the reaction

$$CeOH^{+++} + H_2O \rightleftarrows Ce(OH)_2^{++} + H^+ \quad (1)$$

in which only monomeric species of cerium(IV) are present. Heidt and Smith[4] have studied the photochemical oxidation of water by cerium(IV) in perchloric acid solution and have concluded from the dependence of the quantum yield on the cerium(IV) concentration that cerium(IV) forms a dimeric species in 1 M $HClO_4$. These authors have also shown that the existence of such species would remove the anomalies in certain of the data of Sherrill, King and Spooner. Evans and Uri[5] have presented a mechanism for this photochemical reaction which does not necessitate the postulation of dimeric species of cerium(IV). This does not rule out the possibility of the existence of such dimeric species, however, as conclusions regarding equilibria drawn from kinetic studies are not always valid.

In solutions of constant hydrogen ion concentration, the relative concentrations of any number of soluble species involving cerium(IV) and hydroxide will be independent of the cerium(IV) concentration if all of these species contain the same number of cerium(IV) atoms. If species containing different

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[1] Presented before the Division of Physical and Inorganic Chemistry, 119th Meeting, American Chemical Society, Cleveland, Ohio, April 8-12, 1951.

[2] This work was supported in part by a grant from the U. S. Atomic Energy Commission.

[3] M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

[4] L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948).

[5] M. G. Evans and N. Uri, *Nature*, **166**, 602 (1950).