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REPRINT II

The Determination of the Liquid Immiscibility Boundaries of the Lithium-Sodium and Thallium-Selenium Systems by the Liquid Density Method¹

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Abstract—The immiscibility boundaries and monotectic temperatures of the lithium-sodium and thallium-selenium systems were determined by techniques using density-temperature and density-composition isotherms. The immiscibility boundary of the lithium-sodium system was found to extend from 10.5 to 96 weight percent sodium at the monotectic temperature, $170^{\circ} \pm 1^{\circ}\text{C}$. The critical solution (consolute) temperature was found to be $306^{\circ} \pm 1^{\circ}\text{C}$. The thallium-rich immiscibility region of the thallium-selenium system has a consolute temperature of $750^{\circ} \pm 1^{\circ}\text{C}$ and a monotectic isothermal of $380^{\circ} \pm 2^{\circ}\text{C}$ extending over the composition range 0.1–32.9 atom percent selenium. The second immiscibility region in this system was found to have a consolute temperature of $454^{\circ} \pm 1^{\circ}\text{C}$ and a monotectic isothermal of $201^{\circ} \pm 1^{\circ}\text{C}$. The latter extends between the composition limits 77–99.9 atom percent selenium.

Introduction

It has been shown² that liquid immiscibility boundaries can be accurately delineated by the use of density-temperature and density-composition isotherms. This technique was used to determine the immiscibility boundaries in the lithium-sodium and thallium-selenium systems.

These were chosen as the first metallic systems to be investigated by this method for several reasons. The determination of alkali and alkaline earth metal systems has been a research endeavor in this laboratory for many years therefore the lithium-sodium system was of immediate interest. A system involving the alkali metals presents many experimental challenges and it was felt this would present the ultimate test for the adaptability of this method. When this system was first³ investigated in

this laboratory little experimental work but much postulation⁴ had been made regarding the immiscibility region. Another investigation⁵ was reported which was in serious disagreement with both these results. As a consequence when improved equipment was constructed and the isotherm approach was developed² it was felt that this system should be carefully re-investigated.

The thallium-selenium system as reported by Hansen⁶ shows a monotectic immiscibility system at each end of the diagram. However, both immiscibility boundaries were only speculative and neither consolute temperature was known. In addition, the monotectic temperatures, reported for several investigators, are in disagreement. The double immiscibility, an unusual feature in phase diagrams, coupled with the challenge posed by the high vapor pressure of selenium, made this system a worthy one with which to test the density method further.

THE LITHIUM-SODIUM SYSTEM

Apparatus

The density determinations by the Archimedean method were accomplished using apparatus previously described.² The densitometer cell, which contained the sample crucibles and the molten alloys is shown in Fig. 1. Cells were constructed of both Pyrex or Vycor depending upon the ultimate temperature to which samples were heated. A standard taper cap allowed for opening the cell in order to load it with crucibles or to make additions to metal slugs in existent alloys. Purified argon (Matheson research grade), flowed into the cell and out through the opening in the cap. This argon flow was maintained during the entire experiment with a given alloy.

In the bottom of the glass envelope is shown an iron crucible, (A), $1\frac{1}{4}$ " O.D. and 5" long. It was into this crucible that the weighed metals were placed. A second iron crucible, (B), was suspended, as shown, above (A). The outer diameter of (B) was $\frac{1}{8}$ " less than the i.d. of (A) in order to permit nesting of (B) into (A). The bottom of crucible (B) was drilled with two $\frac{1}{8}$ " diameter holes, one in the center and the other on the outer edge of the crucible bottom. The shaft of an iron ring stirrer passed through the edge hole. The holes served as inlets for the molten metal in (A) to pass through and fill (B) when it was submerged and

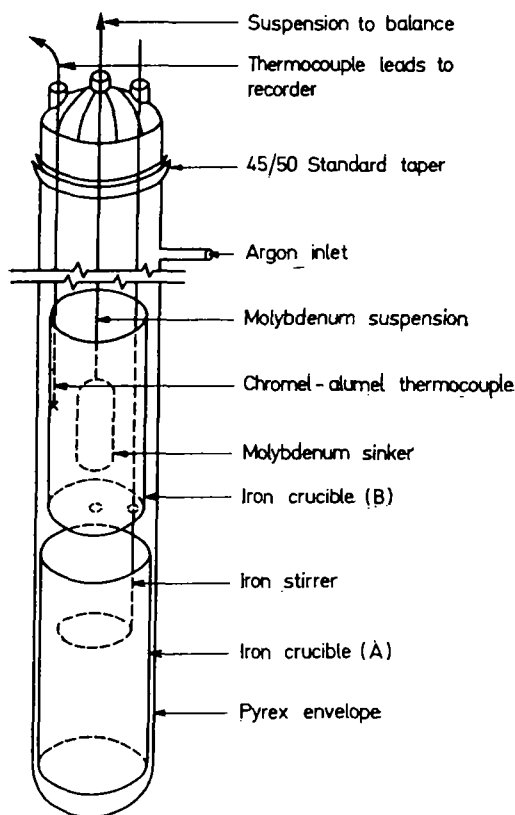


Fig. 1 Densitometer Cell for Sodium-Lithium System

nested in (A). This descummed the surface of the metal or alloy which, otherwise, regardless of the care exercised in its preparation and in cleaning the crucibles, always displayed a dull surface dross. The dross can cling to the fine suspension in a "tenting" fashion and drag the suspension downward as the surface drops due to volume contraction during cooling. Erratic density-temperature recordings result and this casts some doubt on the reliability of inflections indicating the onset of immiscibility. For this reason it is imperative to maintain brilliant molten surfaces. The crucible (B) could be raised or lowered by means of the thermocouple shield, usually iron, attached to the inner wall of the crucible and extending out through the opening in the standard taper cap. The 4 cc. molybdenum sinker, suspended from a 5 mil molybdenum filament,

rested in (B) and became submerged and in suspension in the melt when (B) was finally nested into (A).

The furnace consisted of four individual cylindrical resistance heaters stacked vertically and comprising a total vertical heat zone 6 inches in length. Each section had a separate variable resistor in its circuit in order to adjust the current it drew and consequently minimize thermal gradients between successive units. The uniformity and constancy of melt temperatures in the central zone of the furnace was maintained within at least $\pm 0.5^\circ\text{C}$. The furnace could also be cooled or heated at a constant rate ranging from 0.2°C to 8°C per minute.

In the case of static density measurements which were made at constant temperature, the sinker was suspended from a Mettler balance and temperature was read periodically with a Leeds and Northrup precision potentiometer. Chromel-Alumel thermocouples used in this investigation were calibrated against a Pt; 90Pt 10Rh thermocouple calibrated and certified by the N.B.S. It is felt that the temperatures reported in the results are reliable to within at least 1°C .

Alloys

The sodium used in this investigation was obtained from Baker and Adamson Co. and was reported to be 99.9 + % pure. Its melting point, 97.5°C , was very close to the recognized value 97.8°C for high purity sodium.^{7, 8} The lithium was obtained from Foote Mineral Co. and according to the analysis of the supplier, it was 99.9% pure. It melted at 180.5°C which is in excellent agreement with previously reported results.^{9, 10, 11} For more convenience in manipulation, many of the alloys were prepared outside the drybox. The metals were scraped clean under sodium-dried paraffin oil, rinsed in petroleum ether and accurately weighed in tared beakers of clean petroleum ether. The very brief exposure to the atmosphere during transfer between petroleum ether and the crucible did not affect the composition of the alloy nor did it increase the amount of dross which had to be removed by the method described above even for drybox prepared alloys.

Experimental Procedure

The cell and its contents were heated to approximately 400°C and after the metals melted the alloy was thoroughly stirred by means of the ring stirrer while crucible (B) containing the sinker, was held in suspension

above the molten alloy. This crucible was then lowered into the melt, and as the alloy rose through the holes in its bottom any surface scum which was present in crucible (A) was effectively filtered from entering (B). After temperature equilibration was reached the alloy was cooled at a slow controlled rate (between 0.8–2°C/min) while the weight loss of the sinker was plotted continuously against the temperature as described previously.² Cooling was continued until the monotectic (solidification) temperature (170°) was reached.

Inflections occurred on the density-temperature curves as shown in Fig. 2, at temperatures corresponding to the onset of immiscibility B, Table I, as well as at the monotectic temperature C. The direction of the in-

TABLE I Immiscibility boundary temperatures determined from inflections in density-temperature curves

Wt. % Na	Temp. °C	Wt. % Na	Temp. °C
19	228	63	303
25	253	64	306
39.5	292	71.5	303
47	298.5	75	301
50	302	79.5	296
54.5	300.5	89.5	257

flexion at (C) depends upon the system, change in volume upon solidification, the position of the sinker within the separated layers and whether crystals growing from the side or bottom of the crucible reach and support or lock the sinker in suspension. Whatever the case, there is no longer a continuum of the curve B–C but rather a change in direction at (C) and at constant temperature for isothermal processes either in the direction of higher density or more usually in the direction of lower density due to an increase in sinker weight due to adherent solid on its surface.

The inflection in the density-temperature curve resulting from the growth of crystals on the sinker, or a change in composition of solution due to crystallization, allows for this method to be used also for the determination of solidification temperatures of metals and alloys. This is important whenever the heat of crystallization is small enough to render thermal analysis data unreliable. Some liquidus temperature data for the thallium-selenium system reported below was obtained by this method.

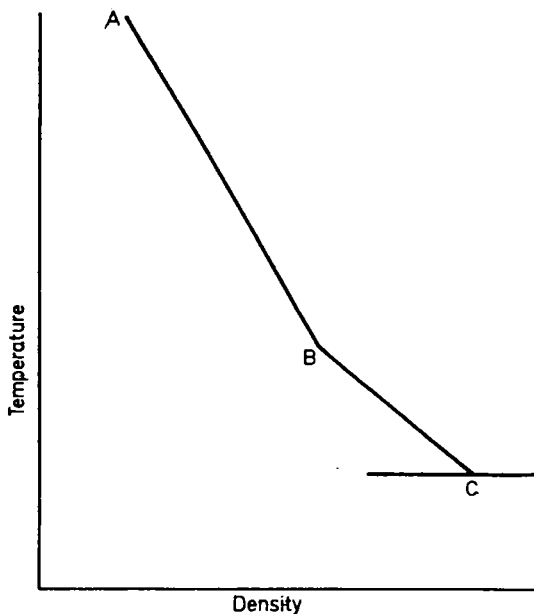
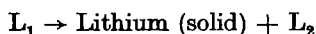


Fig. 2

The isothermal monotectic reaction occurring in this system is:



The reaction occurs at 170°C and the eight experimentally determined monotectic temperatures shown in Fig. 3 were determined by the method described above. They were verified by time-temperature cooling curves run simultaneously with the density-temperature experiments. The temperatures of solidification by both methods agree in each observed pair of runs well within 0.5°C of each other. The maximum deviation of the eight monotectic temperature determinations was within 1°C of 170° over the composition range 10.5–96 wt. % sodium.

The immiscibility phase boundary was also investigated by the density-isotherm method.² The densities of the lithium and sodium rich layers of 50 and 75 weight per cent sodium alloys respectively were determined after equilibration and gravitational separation at various temperatures. The compositions which correspond to these densities at these temperatures were deduced from density-composition isotherms as described previously and are given in Table 2.

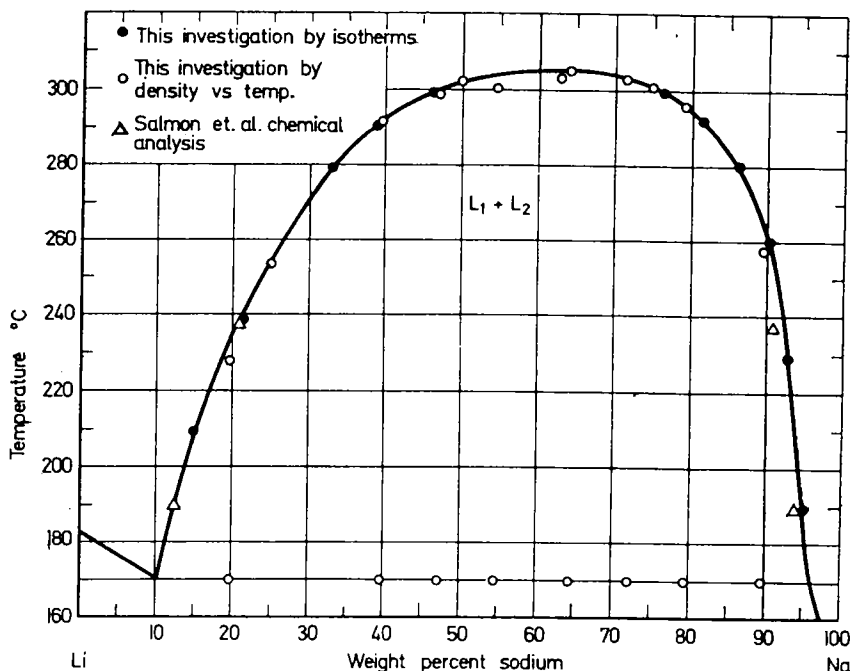


Fig. 3

TABLE 2 The composition and density of immiscible layers which exist at the temperatures listed

Sodium Layer			Lithium Layer		
Temp. °C	Density	Wt. % Na	Temp. °C	Density	Wt. % Na
299.5	.736	76.5	299	.613	46.5
292	.770	81.5	290	.591	39.0
280	.788	86.5	279	.573	33.0
260	.812	90.5	238	.552	21.5
229.5	.838	93.0	209	.537	15.0
189	.862	95.5			

Discussion of Results

The immiscibility boundary data by both the density-temperature and density isotherm methods found in this work are in excellent agree-

ment. The consolute temperature is $306^{\circ}\text{C} \pm 1^{\circ}$ and the monotectic temperature is $170^{\circ}\text{C} \pm 1^{\circ}$. The results of Salmon *et al.*⁴ based on chemical analysis of equilibrated layers, but only at two temperatures, are in agreement with the results reported here. However their calculated consolute temperature, 327°C , is high.

The boundary of Howland *et al.*⁵ based on thermal analysis requires a critical solution temperature of 442° which is 136° higher than that found in this laboratory. No inflection in the density curves was observed in this temperature region. In fact the density was found to be uniform from top to bottom of the melt, at any temperature investigated above 306° . This indicates that a homogeneous solution exists above 306° . It would be impossible for a heterogeneous mixture of two solutions which differ in density by approximately 75% to resist gravitational separation. It is felt, therefore, that the boundary limits found in this laboratory are correct and pertain to equilibrium conditions as shown in Fig. 2.

THE THALLIUM-SELENIUM SYSTEM

Apparatus

The same apparatus was used for the investigation of this system as for the lithium-sodium system. Due to alloying characteristics and the reactivity of selenium with many metals it was found convenient to use Vycor as a crucible material and shield for the thermocouples. A tungsten sinker circa 4 cc. volume and a 5 mil tungsten suspension wire were used since this was sufficiently dense to sink in the alloys and was not attacked by them.

Metals

Both metals were obtained from the United Mineral and Chemical Corporation of New York. The thallium rod was four nine pure and selenium shot was five nines pure.

Since thallium is quite reactive towards atmospheric gases, pre-weighed samples for alloys and for additions to existent alloys were made up in advance in a drybox and sealed in test tubes under an argon atmosphere until ready for use. The metal was exposed to the atmosphere very briefly during transfer from the opened test tubes into the crucible.

Experimental Procedure

The techniques used in the lithium sodium system studies were followed here for both immiscibility regions of this system. Samples of various compositions between 0–33 atomic % selenium and 75–100 atomic % selenium were subjected to density-temperature and density-isotherm investigations. The inflections in the density-temperature curves gave immiscibility boundary points and monotectic temperatures. These results are given in Table 3 and plotted in Figure 4 the other features of

TABLE 3 Immiscibility boundary temperatures and monotectic reaction temperatures determined for both immiscibility regions by the density-temperature method

Thallium-Rich Boundary			Selenium-Rich Boundary		
Compo- sition	Immisci- bility	Mono- tectic	Compo- sition	Immisci- bility	Mono- tectic
At % Se	Temp. °C	Temp. °C	At % Se	Temp. °C	Temp. °C
5.0	621°	381°	85	412°	200°
14.1	736°	379°	90.5	448°	201°
20	750°	383°	92.5	454°	—
25	738°	—	95	448°	201°
30	660°	378°			

which are from Hansen.⁶ Due to the uncertainty of the liquidus boundary between 33 and 42 atomic % selenium this was also redetermined by the density-temperature method as described above and the data are given in Table 4. The proximity of this liquidus to the immiscibility region coupled with another type investigation underway in the laboratory were the reasons for investigating this liquidus.

TABLE 4 Liquidus temperatures determined by the density-temperature methods

Composition At % Se	Temperature °C
35	394°
37	381°
39	358°
40	349°

In order to apply the density isotherm method for additional immiscibility boundary points, samples with compositions of 10, 14, 85 and 90 atomic per cent selenium were cooled below the critical solution temperatures and equilibrated stepwise at various temperatures. The density

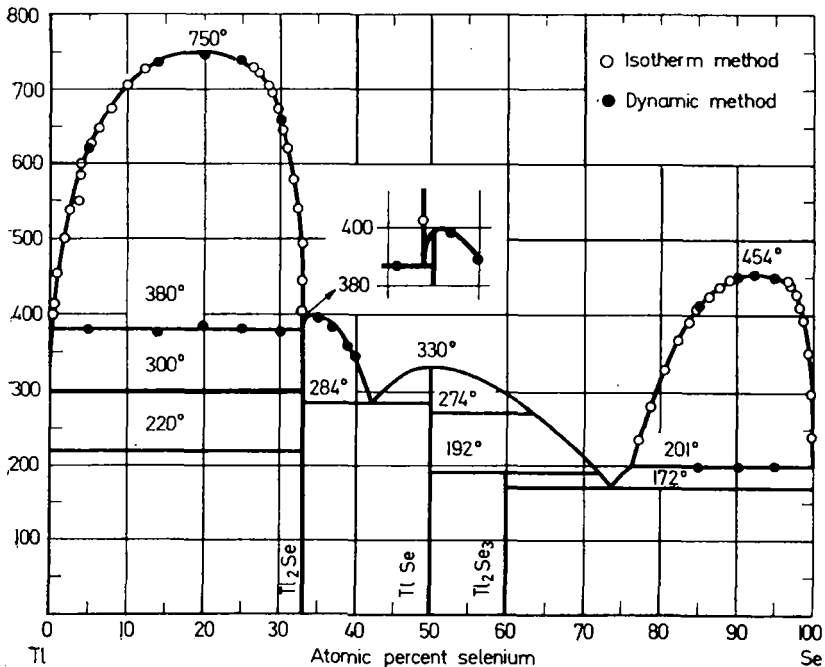


Fig. 4

of the lower layer (thallium layer) was determined at each of these temperatures. For these compositions the lower layer was present in the largest volume assuring complete submergency of the sinker within the layer. These densities, and the temperatures at which they were determined, are given for the thallium layer in Tables 5 and 6. The atomic per cent selenium listed in the tables corresponding to each of these densities were determined from the density isotherms.

Samples corresponding to the composition of 25 and 95 atomic per cent selenium were investigated similarly except that the density of the more voluminous upper layer (selenium layer) was determined from these at various temperatures. These data are also given in Tables 5 and 6 for the selenium layer in each case.

Discussion of Results

Based on literature research the two immiscibility boundaries of this system have not been determined previously. The monotectic temperature for the thallium rich immiscibility region has been given as $354^{\circ}C^{12}$,

TABLE 5 Immiscibility boundary temperatures and compositions for the thallium-rich immiscible region

Thallium Layer			Selenium Layer		
Temp. °C	q	At % Se	Temp. °C	q	At % Se
729	9.769	12.3	730	8.681	26.5
703	9.986	10.0	723	8.616	27.2
674	10.177	8.0	708	8.564	28.5
648	10.312	6.7	696	8.494	29.0
625	10.452	5.6	673	8.452	29.6
600	10.611	4.0	645	8.401	30.5
587	10.638	3.9	619	8.389	31.0
550	10.731	3.6	579	8.367	31.6
536	10.815	2.5	538	8.356	32.3
500	10.921	1.8	494	8.387	32.8
452	11.041	.9	444	8.420	32.9
414	11.157	.1	403	8.470	32.9
400	11.201	.1			

TABLE 6 Immiscibility boundary temperatures and compositions for the selenium-rich immiscible region

Thallium Layer			Selenium Layer		
Temp. °C	q	At % Se	Temp. °C	q	At % Se
446	4.604	89.4	446	4.008	96.8
437	4.728	87.9	440	3.990	97.0
426	4.861	86.5	429	3.945	97.8
408	5.016	84.8	413	3.916	98.3
392	5.110	83.8	394	3.894	98.9
368	5.245	82.4	353	3.890	99.5
329	5.439	80.6	296	3.922	99.8
280	5.636	78.8	240	3.984	99.9
236	5.794	77.4			

390°C¹³ and in the range of 360°–390°C¹⁴. In the present investigation this temperature was found to be 380° ± 2°C over the composition range 0.1–32.9 atom per cent selenium. The selenium rich monotectic of 201 ± 1°C between 77–99.9 atom per cent selenium is in good agreement with that determined by Obukhov *et al.*¹³ and Baroni.¹⁵ Pelabon¹³ on the other hand reported this monotectic to be 190°C.

The two critical solution (consolute) temperatures have not been reported by other investigators. It is felt that the values 750°C and 454°C for the thallium-rich and selenium-rich regions respectively, are within 1°C

of the equilibrium critical solution temperatures for the high purity alloy system.

Since the vapor pressure of the selenium was found to be respectable there was some concern regarding changes in composition of alloys over the period of time during which density measurements were made. A 50 at % alloy involving about 40 g of selenium was heated at 500°C and its weight loss amounted to circa 10 mg per hour. Even after three hours of heating the alloy composition change is still less than one part per thousand. Under these circumstances it was felt that density and composition errors induced by the vaporization loss of selenium would be insignificant relative to the limitations placed on the experimental results.

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