EQUILIBRIUM DISTRIBUTION OF LITHIUM AND BISMUTH BETWEEN LIQUID
Li-Bi ALLOYS AND MOLTEN LiCl AT 650 TO 800°C*

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ABSTRACT

The distribution of lithium and bismuth between liquid Li-Bi alloys and molten LiCl was measured at several temperatures between 650 and 800°. The extent of their distribution to the LiCl increased at each temperature as the lithium concentration in the alloy increased; for example, at 650°, the bismuth concentration in the LiCl increased from about 5 to 4800 p.p.m. as the lithium concentration in the alloy increased from 10 to 50 at. %. The "free" lithium-to-bismuth ratio in the LiCl was 3, suggesting that saltlike Li_3Bi was distributing between the two phases. In a model describing this process, the species Li^+ , Bi^{3-} , and Bi^0 were assumed to be present in the alloy phase. The experimental data fit the model in that, at each temperature, a plot of $\log N_{\text{Li}_3\text{Bi}(d)}$ vs. $\log (N_{\text{Li}(m)}^4 [3 - N_{\text{Li}(m)}]^{-3} [3 - 3N_{\text{Li}(m)}]^{-1})$ was linear with the expected unit slope. In these expressions, N , (d) , and (m) denote mole fraction, dissolved in the salt phase, and dissolved in the alloy phase, respectively. Data obtained over the temperature range 650-800° can be expressed as:

$$\log N_{\text{Li}_3\text{Bi}(d)} = \log (N_{\text{Li}(m)}^4 [3 - N_{\text{Li}(m)}]^{-3} [3 - 3N_{\text{Li}(m)}]^{-1}) + 0.7256 - 1086/T(^{\circ}\text{K}),$$

with an estimated uncertainty in $\log N_{\text{Li}_3\text{Bi}(d)}$ of ± 0.05 . The data could also be accurately represented by a model in which random mixing of Li^+ , Bi^{3-} , and Bi^0 in the alloy phase was assumed.

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INTRODUCTION

A metal-transfer process for separating rare-earth fission products from thorium is being developed as one step in the chemical processing of molten-salt breeder reactors (MSBRs).

In this process,^{1,2} some of the thorium and rare earths are extracted from the $\text{LiF-BaF}_2\text{-ThF}_4$

1. L. E. McNeese, MSR Program Semiannu. Progr. Rep. Feb. 28, 1971, USAEC Rep. ORNL-4676, p. 234.
 2. D. E. Ferguson and Staff, Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971, USAEC Rep. ORNL-4682, p. 2.
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carrier salt into a Li-Th-Bi solution and, then, the rare earths are selectively extracted into molten LiCl. Finally, the rare earths are extracted from the LiCl by reduction into a Li-Bi solution in which the lithium concentration is 5 to 50 at. %. The net result is the transfer of a large fraction of the rare earths, but only a very small fraction of the thorium, from the fluoride salt to Li-Bi solutions of high lithium concentration. This separation is implicitly and significantly based on the reversal of the sequence of free energies of formation (per equivalent) of chlorides vs. fluorides of metal cations of varying polarizing power (di- and tripositive rare earths less than tetrapositive thorium) by virtue of the large difference in polarizabilities³ of the two anions, $\alpha(\text{Cl}^-) = 3.55 \text{ \AA}^3$ and $\alpha(\text{F}^-) = 0.97 \text{ \AA}^3$.

3. M. A. Bredig, MSR Program Semiannu. Progr. Rep. Aug. 31, 1970, USAEC Rep. ORNL-4622, p. 85.
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Results from the initial tests of the metal-transfer process indicated that, when molten LiCl was contacted with liquid Li-Bi alloys at about 650°, the distribution of both "free" lithium[#] and of bismuth to the salt phase was significant.⁴ This behavior was not entirely

4. E. L. Youngblood and L. E. McNeese, MSR Program Semiannu. Progr. Rep. Aug. 31, 1971, USAEC Rep. ORNL-4728, p. 202.
-

unexpected since Li₃Bi is quite soluble in LiCl-LiF (70-30 mole %), and the distribution of lithium and bismuth to this salt phase is significant when the salt is in contact with liquid Li-Bi (50-50 at. %) at 650 to 1000°. ^{5,6} We have investigated the equilibrium distribution

5. M. S. Foster, C. E. Crouthamel, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.* 68, 980 (1964).
6. E. J. Cairns, C. E. Crouthamel, A. K. Fischer, M. S. Foster, J. C. Hesson, C. E. Johnson, H. Shimotake, and A. D. Tevebaugh, Galvanic Cells with Fused-Salt Electrolytes, USAEC Rep. ANL-7316, (1967), p. 119.
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of lithium and bismuth between liquid Li-Bi alloys and molten LiCl in the temperature range 650-800°, and have summarized the results in this paper.

EXPERIMENTAL

Reagents. — Reagent-grade LiCl was oven-dried at about 120° before use. Analyses of the salt after melting under high-purity argon showed that the LiOH content was less than 0.05

[#]The notation "free" lithium is used to designate lithium species not present as LiCl.

mole %. The bismuth was Cominco American Co. 69 grade. Necessary amounts of lithium were cut under oil from reagent-grade stock and were washed with benzene just prior to use. High-purity argon was further treated by passage through a Molecular Sieve trap and a titanium sponge trap that was held at 600°.

Procedure. — Equilibrations were conducted in an argon atmosphere, using the apparatus and general procedure described previously.⁷ About 125 g. of LiCl and a total of 100 g.

7. L. M. Ferris, J. C. Mailen, J. J. Lawrance, F. J. Smith, and E. D. Nogueira,
J. Inorg. Nucl. Chem. 32, 2019 (1970).

of the desired amounts of lithium and bismuth were loaded into a molybdenum crucible. After the crucible had been sealed in the containment vessel, the system was heated to the desired temperature in an atmosphere of pure argon. After reaching this temperature, the system was allowed to equilibrate for at least 24 hr. before samples of the respective phases were taken. Molybdenum pipettes were used to obtain 2- to 15-g. samples of the salt phase, whereas samples of the alloy phase were taken with stainless steel filter sticks. The color of quenched samples of the salt changed from nearly snow-white to a deep red-brown as the lithium concentration in the alloy was increased from about 10 to 50 at. %.

One experiment was conducted to determine the solubility of Li_3Bi in LiCl over the temperature range 650-800°. In this experiment, the lithium concentration in the alloy was 70 at. %. According to the Bi-Li phase diagram,⁸ this gives a two-phase equilibrium

3. M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 1958, p. 316.

mixture of solid Li_3Bi and a liquid Li-Bi alloy in which the lithium concentration varies from about 52 to 62 at. % as the temperature increases from 650 to 800°. It is important to realize that with its solid phase as the standard state, the Li_3Bi in the mixture is at unit activity. The temperature of the system was randomly varied between 650 and 800°. At least 24 hr. was allowed for attainment of equilibrium at each temperature before several samples of the salt phase were removed for analysis. The quenched salt samples had a very deep red-brown color.

Analyses. — The salt samples were analyzed for "free" lithium and for bismuth by, first, hydrolyzing the samples in water and collecting the evolved hydrogen on a Molecular Sieve column at liquid nitrogen temperature. After hydrolysis was complete, the hydrogen was eluted from the column with helium and the amount eluted was determined by gas chromatography. The amount of hydrogen evolved was assumed to be equivalent to the amount of "free" lithium in the salt. The hydrolysis residue was then acidified to ensure that all of the bismuth was in solution. Aliquots of this solution were used for the determination of the bismuth concentration. When the bismuth concentration in solution was equivalent to a concentration of 100 p.p.m. or greater in the salt, the analysis was made using the spectrophotometric iodide method for bismuth. When bismuth was present at lower concentrations, it was determined by an inverse-polarographic method. The lithium concentrations in alloy samples were determined by flame-photometry.

RESULTS

The equilibrium concentrations of bismuth and lithium, expressed as mole fractions (N), measured in LiCl at several temperatures and alloy compositions are given in Table I. At each temperature the concentrations of these elements in the LiCl increased dramatically as the lithium concentration in the alloy [$N_{\text{Li(m)}}$] was increased. Also, the mole ratio of "free" lithium to bismuth dissolved in the salt phase, i.e., $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$, was about 3 in most cases. However, in some cases, the indicated ratio was much lower than 3. These latter results are probably spurious because of the inherent difficulty in obtaining accurate values for the "free" lithium concentration by the method employed. With the apparatus used, the hydrogen evolved during hydrolysis of a salt sample could be retained quantitatively on the Molecular Sieve column for only 15 to 20 min. When hydrolysis was slow (as, for example, with samples that were large), some loss of hydrogen from the system could have occurred. Consequently, the apparent value of $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$ would be low. Analysis of salt samples that were contaminated with entrained Li-Bi alloy would also give a low value for the ratio $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$. The preponderance of the information indicates that, within experimental uncertainty, the value of $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$ was 3.

The values determined for the solubility of Li_3Bi in molten LiCl over the temperature range 650–800° are given in Table II. These data also indicate that $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$ was 3. In Figure 1, the data are compared with the values obtained by Foster *et al.*⁵ over the temperature range 650–1000° using LiCl–LiF (70–30 mole %) as the salt phase. Within analytical uncertainty, the solubility of Li_3Bi was the same in both salt phases. The data can be represented by $\log S(\text{mole } \%) = [3.437 - 4110/T(^{\circ}\text{K})] \pm 0.06$.

Table I: Data Obtained by Equilibrating Liquid Li-Bi Alloys with
Molten LiCl at Various Temperatures

	Temp. (°C)	$N_{Li(m)}$	$10^6 N_{Bi(d)}$	$10^6 N_{Li(d)}$	$N_{Li(d)}/N_{Bi(d)}$
1	650	0.0981	0.79 ± 0.05	6.9 ± 3	8.7 ± 4
2		0.115	1.5 ± 0.3	19 ± 10	13 ± 5
3		0.164	6.3 ± 2	29 ± 4	4.3 ± 2.5
4		0.213	12.3 ± 2	63 ± 15	5.5 ± 1.7
5		0.224	21.8 ± 1	83.4 ± 5	3.8 ± 0.5
6		0.230	16.5 ± 1	43 ± 8	2.9 ± 0.8
7		0.249	37.6 ± 4	126 ± 50	3.4 ± 1.4
8		0.249	22.1 ± 2	--	--
9		0.268	45.6 ± 15	184 ± 40	4.0 ± 1.6
10		0.292	47.3 ± 3	279 ± 75	5.9 ± 1.5
11		0.311	67.3 ± 14	--	--
12		0.326	92.6 ± 10	--	--
13		0.376	202 ± 8	824 ± 100	4.1 ± 0.5
14		0.381	206 ± 3	662 ± 100	3.2 ± 0.5
15		0.392	211 ± 13	775 ± 90	3.7 ± 0.7
16		0.399	263 ± 2	820 ± 50	3.1 ± 0.2
17		0.475	505 ± 55	1580 ± 200	3.1 ± 0.4
18		0.482	864 ± 95	--	--
19		0.486	975 ± 225	2540 ± 215	2.6 ± 1
20		0.487	649 ± 40	2945 ± 630	4.5 ± 1.3
21		0.496	858 ± 5	--	--
22	700	0.166	4.9 ± 1	23 ± 1	4.7 ± 1.2
23		0.230	24.9 ± 1	67.7 ± 1.2	2.7 ± 0.2
24		0.290	63.3 ± 3	186 ± 10	2.9 ± 0.3
25		0.376	259 ± 40	757 ± 85	2.9 ± 0.3
26		0.399	324 ± 10	920 ± 15	2.8 ± 0.2
27		0.461	730 ± 60	1230 ± 185	1.7 ± 0.5
28		0.487	832 ± 60	3395 ± 100	4.1 ± 0.5
29	750	0.237	26.7 ± 1	73.4 ± 9	2.9 ± 0.5
30		0.290	74.8 ± 6	163 ± 18	2.2 ± 0.5
31		0.399	410 ± 10	969 ± 12	2.4 ± 0.3
32		0.487	1122 ± 60	3827 ± 275	3.4 ± 0.5
33	800	0.166	7.6 ± 1	8.7 ± 0.2	1.1 ± 0.3
34		0.244	29.5 ± 3	89.3 ± 6	3.0 ± 0.6
35		0.290	89.0 ± 4	177 ± 36	2.0 ± 0.5
36		0.399	487 ± 15	944 ± 40	1.9 ± 0.2

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SOLUBILITY OF Li_3Bi IN MOLTEN $LiCl$. THE LINE REPRESENTS DATA OBTAINED BY FOSTER et al.⁵ WITH MOLTEN $LiCl-LiF$ (70-30 MOLE %).

Figure 1.

DISCUSSION OF RESULTS

The equilibrium bismuth concentrations in LiCl determined in this investigation with either Li_3Bi or Li-Bi (about 50-50 at. %) as the metal phase are almost identical to those obtained at Argonne National Laboratory (ANL)^{5,6} with LiCl-LiF (70-30 mole %) as the salt phase. However, our value of about 3 for the $N_{\text{Li(d)}}/N_{\text{Bi(d)}}$ mole ratio over a wide range of alloy compositions and temperatures does not agree with the ANL results,⁶ which indicate that this ratio was between 1 and 2 when the alloy was Li-Bi (50-50 at. %). This disparity in results is presently inexplicable. Based on the information presented above, it would appear that the difference in results cannot be attributed to the use of LiCl-LiF instead of LiCl as the salt phase.

Table II. Solubility of Li_3Bi in Molten LiCl in the Temperature Range 650-800°

Temp. (°C)	$10^6 N_{\text{Bi(d)}}$	$10^6 N_{\text{Li(d)}}$	$N_{\text{Li(d)}}/N_{\text{Bi(d)}}$
650	1035 ± 100	3720 ± 40	3.6 ± 0.4
675	1570 ± 35	5160 ± 390	3.3 ± 0.3
700	1550 ± 10	4935 ± 365	3.2 ± 0.3
700	1410 ± 15	4205 ± 165	3.0 ± 0.2
725	2420 ± 55	7805 ± 350	3.2 ± 0.2
750	1760 ± 10	5610 ± 870	3.2 ± 0.5
800	3815 ± 450	10810 ± 1000	2.8 ± 0.7

The results obtained in the present study cannot be explained by the distribution between the two phases of lithium and bismuth per se. The solubility of bismuth in molten LiCl is extremely low, only about 0.1 p.p.m. at 650°. ⁹ Estimates based on the measured

9. L. M. Ferris and J. F. Land, MSR Program Semiannu. Progr. Rep. Aug. 31, 1971,
USAEC Rep. ORNL-4723, p. 192.

activities of lithium in liquid Li-Bi alloys¹⁰ and the solubility of lithium in molten LiCl¹¹

10. M. S. Foster, S. E. Wood, and C. E. Crouthamel, Inorg. Chem. 3, 1428 (1964).
11. A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem. 66, 572 (1962).

show that the equilibrium lithium concentrations in LiCl would be insignificant in comparison with those determined experimentally. If lithium per se distributed between the two phases, a likely equilibrium involved¹² would be .

12. M. A. Bredig, "Mixtures of Metals with Molten Salts." in M. Blander (ed.), Molten Salt Chemistry, Interscience Publishers, New York, 1964, p. 367.

in which (m) and (d) denote the alloy and LiCl phases, respectively. Since the lithium activity in each phase is the same, it can be easily shown that

$$N_{\text{Li}(d)} = \frac{2 N_{\text{Li}(m)}^2 \gamma_m^2}{\gamma_d} \quad (2)$$

in which γ_d and γ_m are activity coefficients referred to pure liquid lithium as the standard state. Using values of γ_d estimated from the solubility data of Dworkin et al.¹¹ and of

From the data of Foster et al.,¹⁰ we estimate that, at 800°, $N_{\text{Li(d)}} = 10^{-8}$ when $N_{\text{Li(m)}}$ is 0.5 and that $N_{\text{Li(d)}}$ is 2×10^{-12} when $N_{\text{Li(m)}}$ is 0.1. These values are negligible when compared with the values obtained experimentally (Table I). This conclusion is also valid for temperatures lower than 800°. As a consequence, we conclude that the experimental results are best interpreted in terms of the distribution of saltlike Li_3Bi between the two phases.

Several models describing the distribution of Li_3Bi between a liquid Li-Bi alloy and molten LiCl were tested. The most accurate representation of the data was obtained using models in which the species Li^+ , Bi^{3-} , and Bi^0 were assumed to be present in the alloy by virtue of the reaction

and by defining concentrations in terms of ion fractions. In one model, which gave an excellent representation of the data, the ion fractions of Li^+ and Bi^{3-} were defined as

$$X_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{n_{\text{Li}^+} + n_{\text{Bi}^0}} \quad (4)$$

and

$$X_{\text{Bi}^{3-}} = \frac{n_{\text{Bi}^{3-}}}{n_{\text{Li}^+} + n_{\text{Bi}^0}} \quad (5)$$

in which n denotes number of moles. It should be noted that n_{Bi^0} is the number of moles of Bi^0 present in the alloy after reaction (3) has occurred, and that these definitions of ion fraction can be applied only when the mole fraction of lithium is 0.75 or less. The activities of Li_3Bi in the salt and alloy phases are defined, respectively, as

$$a_{\text{Li}_3\text{Bi}(m)} = [X_{\text{Li}^+}^3][X_{\text{Bi}^{3-}}][\gamma_{\text{Li}_3\text{Bi}(m)}] \quad (6)$$

and

$$a_{\text{Li}_3\text{Bi}(d)} = N_{\text{Li}_3\text{Bi}(d)} \gamma_{\text{Li}_3\text{Bi}(d)} \quad (7)$$

When the Li_3Bi concentration in the LiCl is low, Eq. (7) can be written as

$$a_{\text{Li}_3\text{Bi}(d)} = N_{\text{Bi}(d)} \gamma_{\text{Li}_3\text{Bi}(d)} = [N_{\text{Li}(d)}^3] \gamma_{\text{Li}_3\text{Bi}(d)} \quad (8)$$

in which $N_{\text{Bi}(d)}$ and $N_{\text{Li}(d)}$ are the measured mole fractions of bismuth and "free" lithium in the LiCl . Since the activity of Li_3Bi is the same in each phase at equilibrium at a given temperature, Eqs. (6) and (8) can be equated. After appropriate substitutions and rearrangements, we obtain, in logarithmic form:

$$\log N_{\text{Bi}(d)} = \log [N_{\text{Li}(d)}^3] = \log \left[\frac{N_{\text{Li}(m)}^4}{(3 - N_{\text{Li}(m)})^3 (3 - 3N_{\text{Li}(m)})} \right] + \log \Gamma \quad (9)$$

in which $N_{\text{Li}(m)}$ is the mole fraction of lithium in the alloy. For simplicity, we will write Eq. (9) as

$$\log N_{\text{Bi}(d)} = \log [N_{\text{Li}(d)}^3] = \log \Phi + \log \Gamma \quad (10)$$

If the ratio of the activity coefficients, $\gamma_{\text{Li}_3\text{Bi}(d)} / \gamma_{\text{Li}_3\text{Bi}(m)}$, is constant at a given temperature, Γ is also constant and a plot of $\log N_{\text{Bi}(d)}$ or $\log [N_{\text{Li}(d)}^3]$ vs. $\log \Phi$ would yield a line of unit slope.

Plots of $\log [10^6 N_{\text{Bi}(d)}]$ and $\log [10^6 N_{\text{Li}(d)}^3]$ vs. $\log \Phi$ are shown in Figures 2 and 3. The lines, which are the best least-squares lines of unit slope, were derived from the bismuth concentrations because these could be determined analytically with more accuracy

EQUILIBRIUM DISTRIBUTION OF LITHIUM AND BISMUTH BETWEEN LIQUID Li-Bi ALLOYS AND MOLTEN LiCl AT 650°C AND 700°C.

Figure 2.

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EQUILIBRIUM DISTRIBUTION OF LITHIUM AND BISMUTH BETWEEN LIQUID LI-BI ALLOYS AND MOLTEN LiCl AT 750° AND 800°C.

Figure 3.

than the lithium concentrations in the LiCl. Actually, placement of the lines using the lithium analyses would not give markedly different results, particularly at 650° and 700°. As seen in Figures 2 and 3, the above model represents the experimental data very well. The reason for this is not obvious because the definitions of the ion fractions for Li^+ and Bi^{3+} , Eqs. (4) and (5), are unusual and are not easily related to a simple statistical model for the mixing of the various species in the alloy.¹³ The fact that the data at each

13. J. Braunstein, "Statistical Thermodynamics of Molten Salts and Concentrated Aqueous Electrolytes." In S. Petrucci (ed.), Ionic Interactions, Vol. I, p. 180, Academic Press, New York, 1971.

temperature obeyed Eq. (9) showed that the activity coefficient ratio $\gamma_{\text{Li}_3\text{Bi(d)}}/\gamma_{\text{Li}_3\text{Bi(m)'}}$ and hence Γ , was constant over a wide range of concentrations. Values of Γ obtained from the respective isotherms were:

Temp. (°C)	Γ
650	0.35 ± 0.08
700	0.40 ± 0.03
750	0.46 ± 0.04
800	0.52 ± 0.08

The data obtained in the temperature range 650-800° can be expressed as:

$$\log N_{\text{Bi(d)}} = \log [N_{\text{Li(d)}}/3] = [\log \Phi + 0.7256 - 1086/T(^{\circ}\text{K})] \pm 0.05.$$

Independent estimates of Γ can be made using the measured solubilities of Li_3Bi in molten LiCl and the liquidus curve from the Bi-Li phase diagram if the standard state for Li_3Bi is chosen as the pure solid. If we assume that $\gamma_{\text{Li}_3\text{Bi}(d)}$ is not a function of the Li_3Bi concentration in LiCl at each temperature, its value is simply the reciprocal of the solubility of Li_3Bi in LiCl at that temperature. This assumption seems reasonable because the solubilities of Li_3Bi in molten LiCl are low over the temperature range being considered. From the data presented in Table II and Figure 1, we obtain $\log \gamma_{\text{Li}_3\text{Bi}(d)} = [-1.437 + 4110/T(^{\circ}\text{K})] \pm 0.06$. In deriving Eq. (9), it will be found that

$$\log \Gamma = \log [27 \gamma_{\text{Li}_3\text{Bi}(m)}] - \log \gamma_{\text{Li}_3\text{Bi}(d)} = -\log \Phi - \log \gamma_{\text{Li}_3\text{Bi}(d)} \quad (11)$$

Experimentally, it was shown that Γ was a constant at a given temperature; thus, if our assumption regarding the constancy of $\gamma_{\text{Li}_3\text{Bi}(d)}$ is valid, $\gamma_{\text{Li}_3\text{Bi}(m)}$ would also be a constant at each temperature. It can be shown from Eq. (6) that $\Phi^{-1} = 27 \gamma_{\text{Li}_3\text{Bi}(m)}$ when $a_{\text{Li}_3\text{Bi}(m)} = 1$. Using the Bi-Li phase diagram,⁸ values of Φ^{-1} were calculated for the liquid alloys in equilibrium with solid Li_3Bi at several selected temperatures. These values were used in conjunction with the appropriate values of $\gamma_{\text{Li}_3\text{Bi}(d)}$ to estimate Γ at these temperatures. The values obtained are given in Table III, and are compared with the experimentally determined values in Figure 4. Considering the limits of uncertainty, the agreement is good.

The data obtained by Okada et al.¹⁴ for the distribution of sodium and bismuth between

14. M. Okada, R. A. Guidotti, and J. D. Corbett, *Inorg. Chem.* 7, 2118 (1968).

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COMPARISON OF EXPERIMENTALLY DETERMINED AND CALCULATED VALUES OF Γ . THE DASHED LINES REPRESENT THE LIMITS OF UNCERTAINTY IN THE CALCULATED VALUES.

Figure 4.

Table III: Values of Γ Calculated from Li_3Bi Solubility
Data and the Bi-Li Phase Diagram

Temp. (°C)	$N_{\text{Li(m)}}$	$\log \gamma_{\text{Li}_3\text{Bi(d)}}$	$-\log \Phi$	$\log \Gamma$	Γ
650	0.524 ± 0.01	3.01 ± 0.06	2.457 ± 0.07	-0.556 ± 0.09	0.28 ± 0.06
700	0.558 ± 0.01	2.79 ± 0.06	2.301 ± 0.07	-0.486 ± 0.09	0.33 ± 0.06
750	0.588 ± 0.01	2.58 ± 0.06	2.164 ± 0.07	-0.416 ± 0.09	0.38 ± 0.08
800	0.616 ± 0.01	2.39 ± 0.06	2.036 ± 0.07	-0.354 ± 0.09	0.44 ± 0.09

liquid Na-Bi alloys and molten NaCl-NaI (37-63 mole %) over the temperature range 600-1000° are represented excellently by the model described above. Consequently, we would concur with their conclusion that the observed results were due primarily to the distribution of Na_3Bi between the two phases and that the effect of NaBi was small. It should also be noted that the representation of their data by our model is much better than that obtained using a quasi-ideal model¹⁵ involving ideal solutions of the assumed species

15. A. K. Fischer, S. A. Johnson, and S. E. Wood, J. Phys. Chem. 71, 1465 (1967).

Na, Bi, NaBi, and Na_3Bi .

The experimental data obtained in the present investigation could also be represented accurately by a model involving random mixing of Li^+ , Bi^{3-} , and Bi^0 in the alloy phase.

With random mixing, the respective ion fractions are

$$X_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{n_{\text{Li}^+} + n_{\text{Bi}^{3-}} + n_{\text{Bi}^0}} = N_{\text{Li(m)}} \quad (12)$$

$$X_{\text{Bi}^{3-}} = \frac{n_{\text{Bi}^{3-}}}{n_{\text{Li}^{+}} + n_{\text{Bi}^{3-}} + n_{\text{BiO}}} = \frac{(1/3) n_{\text{Li}^{+}}}{n_{\text{Li}^{+}} + n_{\text{Bi}^{3-}} + n_{\text{BiO}}} = (1/3) N_{\text{Li}(m)} \quad (13)$$

and the activity of Li_3Bi in the alloy is defined as

$$a_{\text{Li}_3\text{Bi}(m)} = [X_{\text{Li}^{+}}^3][X_{\text{Bi}^{3-}}][\gamma'_{\text{Li}_3\text{Bi}(m)}] = (1/3)[N_{\text{Li}(m)}^4][\gamma'_{\text{Li}_3\text{Bi}(m)}] \quad (14)$$

Using the same definition for the activity of Li_3Bi in the salt phase as was used above [Eq. (7)], we obtain from Eqs. (8) and (14):

$$N_{\text{Bi}(d)} = \frac{[N_{\text{Li}(m)}^4][\gamma'_{\text{Li}_3\text{Bi}(m)}]}{[3\gamma_{\text{Li}_3\text{Bi}(d)}]} \quad (15)$$

If the ratio of the activity coefficients were constant, plots of $\log N_{\text{Bi}(d)}$ vs. $\log N_{\text{Li}(m)}$ would be expected to yield lines of slope 4. Plots of this type did not give a good representation of the data. However, analysis of the data showed that, if $\gamma_{\text{Li}_3\text{Bi}(d)}$ were assumed to be independent of concentration at each temperature, the activity coefficient for Li_3Bi in the alloy phase could be expressed as

$$\log \gamma'_{\text{Li}_3\text{Bi}(m)} = A + 1.12 N_{\text{Li}(m)} \quad (16)$$

and that A varied with temperature as follows:

$$A = \exp[-3.321 + 3090/T(^{\circ}\text{K})] \quad (17)$$

At a given temperature, $\gamma'_{\text{Li}_3\text{Bi}(m)}$ does not change markedly over a wide range of values of $N_{\text{Li}(m)}$. For example, at 800° , $\gamma'_{\text{Li}_3\text{Bi}(m)}$ increases only from about 6 to 21 as $N_{\text{Li}(m)}$ increases from 0.1 to 0.6. By combining Eqs. (15), (16), and (17) with the equation presented earlier for the temperature dependence of $\log \gamma_{\text{Li}_3\text{Bi}(d)}$, we obtain the following general

model for the distribution of Li_3Bi between liquid Li-Bi alloys and molten LiCl in the temperature range 650-600°:

$$\log a_{\text{Li}(a)} = \left\{ 4 \log N_{\text{Li}(m)} + 1.12 N_{\text{Li}(m)} + 0.960 - 4110/T(^{\circ}\text{K}) + \exp [-3.321 + 3690/T(^{\circ}\text{K})] \right\} \pm 0.05 \quad (18)$$

As seen in Figures 5 and 6, representation of the experimental data by Eq. (18) is excellent at each temperature.

We conclude that the observed distribution of lithium and bismuth between liquid Li-Bi alloys and molten LiCl is due to the distribution of Li_3Bi , and not the respective elements, between the two phases. It should be emphasized that the success of our models in describing the distribution does not constitute proof that the species assumed were actually those present. Additional experimentation would be required to confirm the existence of these species in the respective phases.

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EQUILIBRIUM DISTRIBUTION OF Li_3Bi BETWEEN LIQUID LI-BI ALLOYS AND MOLTEN $LiCl$. CURVES CALCULATED FROM EQ.(18), WHICH WAS DERIVED FROM A MODEL ASSUMING RANDOM MIXING OF Li^+ , Bi^{3-} , AND Bi^0 IN THE ALLOY PHASE.

Figure 5.

EQUILIBRIUM DISTRIBUTION OF Li_3Bi BETWEEN LIQUID Li-Bi ALLOYS AND MOLTEN LiCl . CURVES CALCULATED FROM EQ.(18), WHICH WAS DERIVED FROM A MODEL ASSUMING RANDOM MIXING OF Li^+ , Bi^{3+} , AND Bi^0 IN THE ALLOY PHASE.

Figure 6.

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