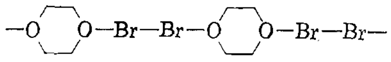
by Hassel and Hvoslef.[8] The space group of the dioxane complex is C^3_{2h}-C2/m with two formula units of $C_4H_8O_2 \cdot 2ICl$ per unit cell. Thus isomorphism with either selenothiane complex is ruled out.

The crystallographic data for the isomorphous 1:1 ICl and IBr complexes of selenothiane do not require the molecules to have any special symmetry. However, it seems probable that the molecules will be found to approximate structure A in Fig. 1, which has a mirror plane through the four heavy atoms. A complete structural study of these complexes is in progress and it will be of interest to see if the ICl (or IBr) is bonded in *axial* or in *equatorial* positions, and also if the sulfur atom becomes involved in the bonding, say with a chlorine atom of another molecule.

A similar situation with regard to molecular symmetry applies to the isomorphous pair of addition compounds of selenothiane with chlorine and bromine. Again it is expected that the molecule will approximate mirror symmetry by a plane through the four heavy atoms, but here linear Cl–Se–Cl and Br–Se–Br bonding should occur with the orientation perpendicular to the plane of the C–Se–C bonds,[9] as shown in structure B of Fig. 1. The structure predicted here is in sharp contrast to that found by Hassel and Hvoslef for the 1:1 complex of dioxane with bromine.[10] The latter was found to contain linear polymers of the type



Structural studies of the chlorine and bromine addition compounds of 1,4-selenothiane are in progress.

Acknowledgment.—The author is pleased to acknowledge the financial assistance of the National Science Foundation under Grant NFS-G24997, and also the assistance of Miss Heather King, who performed the carbon and hydrogen analyses.

[8] O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **10**, 138 (1956).

[9] R. E. Marsh and J. D. McCullough, *Acta Cryst.*, **3**, 41 (1950).

[10] O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 873 (1954).

CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Thermodynamics of Binary Alloys. I. The Lithium–Bismuth System[1]

BY MELVIN S. FOSTER, SCOTT E. WOOD, AND CARL E. CROUTHAMEL

Received May 15, 1964

Electromotive force measurements have been made on cells of the type Li|LiCl–LiF|Li in Bi (X_{Li} = atom fraction Li) for compositions of the alloy from pure Bi to Bi saturated with Li_3Bi(s) and for temperatures between 775 and 1100°K. The electrolyte consisted of 70 mole % LiCl and 30 mole % LiF. A secondary reference electrode which consisted of Bi saturated with Li_3Bi(s) was used in most of the cells in place of the Li anode. Its potential was independently measured against the Li electrode. From the measurements, a least-squares derived equation relating the excess chemical potential (cal./mole) of Li in the alloy as a function of temperature and composition for the region studied was found to be

$$\Delta\mu^{E}_{\text{Li}} = [9397 + 18.16T - 0.0109T^2] + [7103 - 19.44T + 0.0068T^2]X_{\text{Li}}$$

The standard free energy of formation of Li_3Bi(s) has been derived as a function of temperature.

Introduction

Electromotive force measurements of concentration cells without transference which may be of interest in a regenerative cell system have yielded information concerning the thermodynamic properties of the binary lithium–bismuth system.

Lithium has been used as one of the components of the binary system for several reasons. Lithium has a low equivalent weight and forms relatively stable intermetallic compounds with many of the more noble elements. The stability of these compounds gives rise to substantially larger cell voltages in concentration cells without transference than those predicted from ideal solution theory. Lithium has the least solubility in its fused halides of any of the alkali metals,[2] permitting operation of cells containing Li metal and fused Li halides at elevated temperatures without appreciable solubility of Li in the salt. This solubility would result at best in an irreversible transfer of Li between electrodes and at worst might result in an internal electrical short circuit of the cell through increased electronic conductance of the electrolyte.[3]

Based upon information given by Hansen and Anderko,[4] some of the metals which combine with Li to form intermetallic compounds whose melting points are higher than either element include Sn, Ga, In, Pb, Bi, Tl, Zn, Cd, and Hg. Of these combinations, the Li–Bi system has been investigated first.

Experimental

Materials.—Only reagent grade LiCl and LiF were used in this study. The electrolyte used was the eutectic composition

---

[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *J. Phys. Chem.*, **66**, 572 (1962).

[3] H. R. Bronstein and M. A. Bredig, *ibid.*, **65**, 1220 (1961).

[4] M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, N. Y., 1958.

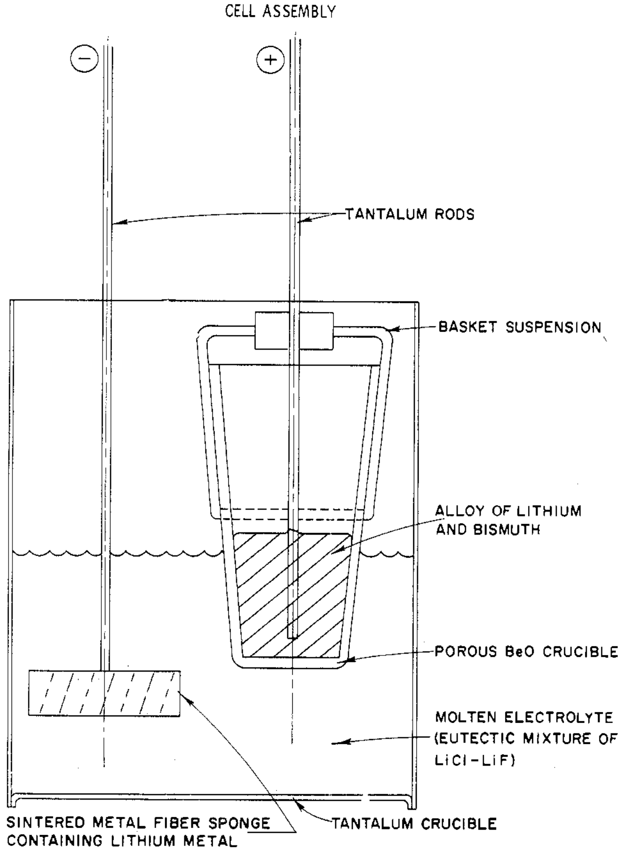


Fig. 1.—Cell construction.

30 mole % LiF–70 mole % LiCl.[5] This composition was made up in air and purified by the method of Maricle and Hume,[6] *i.e.*, chlorine gas was passed through the molten eutectic, after which the excess chlorine was removed by bubbling helium through the melt. The melt was then sealed in Pyrex under vacuum and transferred to a helium-filled drybox where all subsequent operations were accomplished. Lithium metal was obtained from Foote Mineral Company, Philadelphia, Pa., in the form of 1-lb. ingots sealed in cans under an argon atmosphere. The impurity analysis supplied by the Foote Mineral Company was 0.003% Na, 0.0028% K, 0.003% Cl, and 0.0031% N_2. No further purification of the Li metal was attempted, but only bright metal pieces were used. Bismuth metal was obtained in shot form from United Mineral and Chemical Corporation, New York, N. Y. The impurity analysis funished by United Mineral and Chemical Corporation showed 0.0004% Ag, 0.0001% Cu, 0.0002% Pb, and 0.0001% Fe. This metal was melted under helium and filtered to remove oxide impurities.

Apparatus and Procedure.—The cells used in this investigation were operated in a furnace well attached to a helium-filled drybox. The helium atmosphere was continuously recirculated through a purification train consisting of a Pd catalyst, a molecular sieve bed, and an activated charcoal bed immersed in liquid nitrogen.[7] The impurities in the drybox atmosphere consisted of 0.1 to 0.5 p.p.m. of water while oxygen and nitrogen were not detected (limit of detection 10 p.p.m.).

Typical cell construction is shown in Fig. 1. A porous BeO crucible was used to contain the anode or cathode in order to minimize the effect of Li and intermetallic compound solubility in the electrolyte. These crucibles were obtained from National Beryllia Corporation, North Bergen, N. J. The wall thickness of the crucible was approximately 2.4 mm. and the pore diameter 50 μ. The BeO was preferentially wet by the molten electrolyte; the contact between the electrode and electrolyte was made at the inner surface of the crucible.

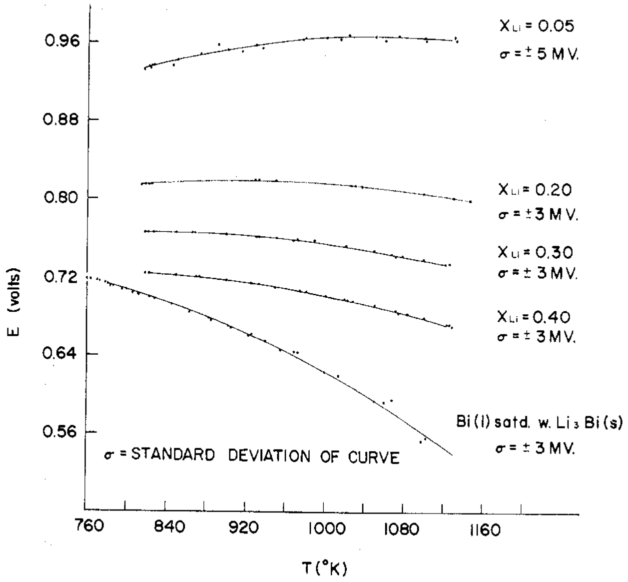


Fig. 2.—Voltage–temperature–composition data of the cell: Li(l)/LiCl–LiF/Li in Bi(l) (X_{Li} = atom fraction Li). σ = standard deviation of points from curve.

The electrode material not contained in the BeO crucible was held on a sintered metal fiber sponge (as shown in Fig. 1) or was contained on the bottom of the outer metal crucible containing the entire cell. The anode of pure Li shown in Fig. 1 is held below the surface of the molten electrolyte. Lithium, which would normally float on the surface of the molten electrolyte as a second liquid phase, wets the sintered fiber metal sponge with such tenacity that no loss of Li occurs when the sponge is submersed. The metal sponge used was obtained from Huyck Equipment Company, Milford, Conn., and consisted of pressed and sintered 50-μ diameter fibers of Type 430 stainless steel with an over-all density of approximately 10% of theoretical.

All electrode alloys used were prepared by combining appropriate weighed quantities of the elements in the drybox.

It was necessary to ensure the thermodynamic stability of the electrolyte in these studies, since the use of materials in the electrolyte which might be irreversibly reduced at the anode may give rise to false e.m.f. values. Also, any metal ion in the electrolyte which could interact with the bismuth in the cathode might be reduced electrochemically at the cathode and influence the activity of Li in the alloy. In the face of the very strong reducing nature of Li metal, it was possible to use only the eutectic mixture of 70 mole % LiCl–30 mole % LiF in collecting data for use in calculating thermodynamic properties.[8]

---

[5] H. M. Haendler, P. S. Sennett, and C. M. Wheeler, Jr., *J. Electrochem. Soc.*, **106**, 264 (1959).

[6] D. L. Maricle and D. N. Hume, *ibid.*, **107**, 354 (1960).

[7] M. S. Foster, C. E. Johnson, and C. E. Crouthamel, "Helium-Purification Unit for High-Purity Inert-Atmosphere Boxes," ANL-6652 (1962).

[8] The importance of choosing electrolyte materials which are thermodynamically stable in the cell environment was observed in preliminary laboratory studies of the reference electrode potential using a LiCl–KCl (59–41 mole %) electrolyte. Cells using the LiCl–KCl electrolyte yielded voltages which fluctuated markedly and decreased more rapidly than in cells using LiCl–LiF electrolyte when the operating temperature was increased to greater than 773°K. The disparity in voltages is due to the fact that at temperatures above 773°K., Li reduces KCl to K metal. The K is partially distilled, as evidenced by the condensation of K metal on the cooler sections of the electrode leads in the upper part of the cell.

Further evidence for the reduction of KCl by Li was found when a sample of 17 mole % Li and 83 mole % KCl was heated to 1073°K. and then subjected to thermal analysis. A liquidus break of 951°K. was observed, which on comparison with the published LiCl–KCl phase diagram[9] corresponds to a composition of 17 mole % LiCl and 83 mole % KCl. The eutectic temperature noted was 614°K., some 11° lower than the literature value. This lower temperature is probably caused by the solubility of K or Li metal in the molten salt mixture. Condensed metal found on the upper and lower spacers which are part of the thermal analysis apparatus was weighed and titrated with standard acid in an alcohol–water solvent and found to be potassium.

[9] E. Elchardus and P. Laffitte, *Bull. soc. chim. France*, **51**, 1572 (1932).

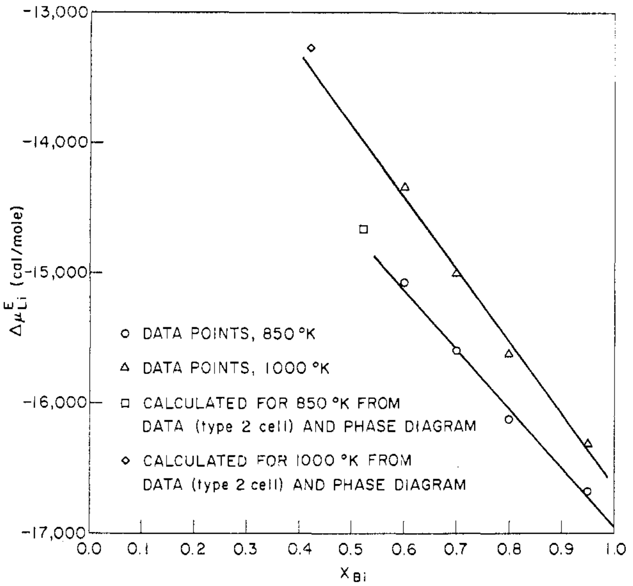


Fig. 3.—Excess chemical potential of Li in Li–Bi alloys as calculated from least-squares fit of data to

$$\Delta\mu^E{}_{Li} = (a_1 + a_2T + a_3T^2) + (b_1 + b_2T + b_3T^2)X_{Li}$$

It is also possible that a deleterious effect on the cell e.m.f. may be encountered due to the transfer of cathode material to the anode through solubility of the intermetallic compound, Li_3Bi, in the electrolyte. It was found that the interposition of the porous BeO crucible effectively eliminated any transfer of intermetallic compound from a cathode saturated with Li_3Bi to a pure Li anode. The solubility of Bi metal itself in the molten electrolyte is negligible (approximately 10^{-3} wt. %).[10]

It was experimentally observed that Li transferred from a pure Li anode at a rate which was sufficient to alter appreciably the composition of a 5 atom % Li in Bi cathode, thus precluding stable, reproducible cell potential measurements. Even the interposition of the porous BeO crucible wall as a barrier to diffusion was ineffective in reducing this rate of transfer to a tolerable level. The problem of the transfer of Li from the anode was overcome through the use of a secondary reference electrode. This electrode consisted of a two-phase binary system with an over-all composition of 60 atom % Li in Bi. The phases present are a liquid solution of Li_3Bi in Bi and solid Li_3Bi. At constant temperature the addition of a small quantity of Li does not change the composition of either phase present in the electrode, but only the relative quantities of each phase. Thus, the reference electrode described is insensitive with respect to additions of Li by transfer from a pure Li anode through solubility in the electrolyte, and a stable reference electrode potential was established.

Results

The e.m.f.–temperature–composition data were obtained with the two types of cells: (1) Bi saturated with $Li_3Bi(s)$/LiCl–LiF/Li in Bi(l), X_{Li} = atom fraction Li where $X_{Li} = 0.05$, 0.20, 0.30, and 0.40. (2) Li(l)/LiCl–LiF/Bi saturated with $Li_3Bi(s)$. The combination of these two cells results in the cell: (3) Li(l)/LiCl–LiF/Li in Bi(l), X_{Li} = atom fraction Li = 0.05, 0.20, 0.30, and 0.40.

The e.m.f.–temperature characteristics of cells of types 2 and 3 are shown in Fig. 2. The smooth curve for each composition represents the e.m.f. as a quadratic function of temperature. This function was derived by a standard least-squares treatment of the data. The standard deviation, σ, of the individual data points from the smooth curve is shown.

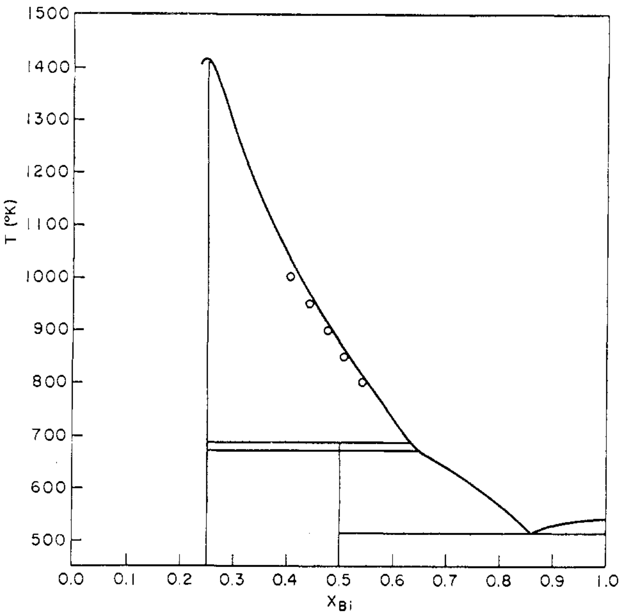


Fig. 4.—Partial phase diagram of the Li–Bi system showing solubility points calculated from least-squares fit of data to

$$\Delta\mu^E{}_{Li} = (a_1 + a_2T + a_3T^2) + (b_1 + b_2T + b_3T^2)X_{Li}$$

The cell reaction for type 3 cells is the transfer of Li from pure Li (saturated with electrolyte) to the alloy, for which the change in the Gibbs free energy is

$$\Delta G = -FE = RT \ln a_{Li} \qquad (1)$$

The standard state of Li is taken to be the pure liquid metal in the cell environment, *i.e.*, saturated with electrolyte, at the temperature of interest. The excess chemical potential of Li in the alloy is then given by the relationship

$$\Delta\mu^E{}_{Li} = -FE - RT \ln X_{Li} \qquad (2)$$

where F is the value of the Faraday, E the e.m.f. of the cell, and R the gas constant. The values so calculated were fitted by the least-squares method to the equation

$$\begin{aligned}\Delta\mu^E{}_{Li} &= (a_1 + a_2T + a_3T^2) + (b_1 + b_2T + b_3T^2)X_{Li}\\ &= (9397 + 18.16T - 0.0109T^2) + (7103 -\\ &\qquad 19.44T + 0.0068T^2)X_{Li} \text{ (cal./mole)} \qquad (3)\end{aligned}$$

The corresponding standard deviation of the e.m.f. data from the values indicated by this equation was 2 mv., or well within experimental error.

The lines shown in Fig. 3 represent the values calculated for $\Delta\mu^E{}_{Li}$ from eq. 3 as a function of composition at temperatures of 850 and 1000°K. The data points shown were taken from the smooth curves in Fig. 2. Also shown in the figure are the values for $\Delta\mu^E{}_{Li}$ calculated from the published phase diagram[4] and the reference electrode potential obtained from a type 2 cell. It must be emphasized that the region of applicability of eq. 3 extends only over that portion

---

[10] M. S. Foster, C. E. Crouthamel, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, **68**, 980 (1964).

of the phase diagram in which Bi-rich, unsaturated alloys exist and for temperatures between 775 and 1100°K.

The solubility of Li in Bi has been calculated at chosen temperatures from eq. 3 and the reference electrode potential. The results are shown in Fig. 4.

Discussion

The excess chemical potential of Li is very large and negative. This behavior may be explained qualitatively in terms of the strong interaction of Li and Bi which is evidenced by the formation of the solid compound Li_3Bi.

Originally, an attempt was made to fit the data to a function of the form $\Delta\mu^E{}_{Li} = X_{Bi}{}^2 f(T, X_{Li})$, where $f(T, X_{Li})$ is a function of the temperature and composition. This attempt failed in that the calculated values tended to become more positive than the observed values as the concentration of Li in the alloy increased. Apparently, this behavior occurred in the attempt to reach the zero point of the curve (at a composition of pure Li). In reality, the curve for $\Delta\mu^E{}_{Li}$ at constant temperature must be discontinuous through the composition range where solid Li_3Bi is present in equilibrium with a liquid solution. The mole fraction of Li in the Li-rich solution in equilibrium with solid Li_3Bi ranges from 0.02 to 0.25. It is expected that the values of $\Delta\mu^E{}_{Li}$ for these solutions, while still negative, would be much smaller in absolute value.[11] Thus, the calculated curve of $\Delta\mu^E{}_{Li}$ as a function of composition should probably be sigmoid in shape. With these difficulties, it was decided to use the simpler, but empirical, function given in eq. 3.

TABLE I

STANDARD FREE ENERGY OF FORMATION OF $Li_3Bi(s)$

Temp., °K.	$\Delta G_f°$, kcal./mole
800	−50.5
850	−49.7
900	−48.8
950	−47.8
1000	−46.6
1050	−45.3
1100	−44.0

The cell reaction for the reference electrode potential studies may be written

$$Li(l) + {}^1/_3Bi(l)\ (\text{saturated with } Li_3Bi) \longrightarrow {}^1/_3Li_3Bi(s) \quad (4)$$

If Li(l) and $Li_3Bi(s)$ are said to exist in their standard states in the cell environment, then for the cell reaction given we may write

$$\Delta G = -FE = {}^1/_3\Delta G_f° - {}^1/_3RT \ln a_{Bi} \quad (5)$$

where a_{Bi} is the activity of Bi in the alloy saturated with $Li_3Bi(s)$ with the reference state the pure liquid metal in the cell environment and $\Delta G_f°$ is the standard free energy of formation of $Li_3Bi(s)$ from the elements. The activity of Bi was calculated by application of the Gibbs–Duhem equation and eq. 3. Values of $\Delta G_f°$ for the formation of 1 mole of Li_3Bi at various temperatures are given in Table I. The estimated error of these values is 0.9 kcal./mole.

[11] This was confirmed in a cell in which a Li-rich alloy in equilibrium with $Li_3Bi(s)$ was used as an anode *vs.* a reference electrode (a Bi-rich alloy in equilibrium with $Li_3Bi(s)$). The cell potential observed was, within experimental error, the same as that observed for a cell of type 2, indicating that the values for $\Delta\mu^E{}_{Li}$ in Li-rich solutions saturated with $Li_3Bi(s)$ are near zero.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS

Hydrogen Tracer Studies on the Reactions of Uranium Hydride with Aqueous Oxidizing Agents

BY JOHN B. HUNT AND HENRY TAUBE

Received April 8, 1964

The reaction of UD_3 with concentrated HCl in H_2O forms HD as the principal gaseous product. When the concentration of the acid is reduced to *ca.* 9.5 *M*, reaction is much slower, and H_2 and D_2 are the chief gaseous products. Little D is lost to the solvent by exchange, although D loss does become a feature of the results at still lower acidity. The rates of the reaction are very sensitive to the anion which is present. When a metal ion such as Ce(IV) is the oxidizing agent, the D_2 originally contained in the solid is liberated essentially quantitatively and no other gaseous product is formed. These and related results are interpreted on the assumption that a barrier layer, presumably UO_2, governs the rate and mechanism of the reaction.

The main reactions of the salt-like hydrides LiH[1] and NaH[2] with D_2O can be expressed by equations of the type

$$MH + D_2O = HD + M^+ + OD^- \quad (1)$$

Also in the reaction of the complex hydride $LiAlH_4$[2] with D_2O, HD is the dominant gaseous product.[3]

---

[1] H. Beutler, G. Brauer, and H. O. Junger, *Naturwissenschaften*, **24**, 347 (1936).

[2] I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1140 (1949).

[3] The reaction of $LiAlH_4$ with D_2O has been recommended as a way to prepare pure HD. However, when KBH_4 is the reactant, there is a substantial admixture of H_2 and D_2 in the gases: W. L. Jolly and R. E. Mesmer, *ibid.*, **83**, 4470 (1961).