ELECTROCHEMICAL STUDIES OF THE SODIUM-BISMUTH SYSTEM*

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Introduction

Studies of various thermally regenerative galvanic cell systems have been underway at Argonne National Laboratory for some time. In these systems, thermal energy, as from a nuclear reactor, is used to decompose the products of a power-producing galvanic cell to form into the original reactants for re-use in the cell. Since the cell generally operates at a lower temperature than the decomposition temperature of the cell products, the system is a two-temperature system and is limited to Carnot cycle efficiency.

The search for materials which combine with a large negative Gibbs free energy change at the cell temperature, and yet may be thermally decomposed at a temperature obtainable in a reactor using today's technology, has led to an examination of various alkali metal-containing binary alloys. Many of these alloys have a large negative free energy of formation, as indicated qualitatively by the high melting points of the compounds formed between the lighter alkali metals, and, for example, bismuth.

In order to predict the ideal behavior of a thermally regenerative galvanic cell system, it is necessary to know the thermodynamic properties of the alloy used in the cell. For instance, the chemical potential of the alkali metal in the binary alloy is used to calculate the open-circuit potential of the cell in the system if the cell is a concentration cell without transference. Likewise, the temperature variation of the chemical potential of the alkali metal in the alloy may be used to calculate the partial pressure of the alkali metal over the alloy for various postulated regeneration conditions. The particular alloy which is the subject of this report is the sodium-bismuth alloy.

In a study of the thermodynamic properties of the binary sodium-bismuth alloy, the most obvious method would appear to be an emf technique. This technique corresponds directly to the cell in a regenerative system.

In using the emf technique, one may choose to operate cells which by design are not capable of producing significant electrical currents. For example, several workers in the past have operated cells with sodium anodes in which the electrolyte consisted of a sodium ion-containing glass. Other electrolytes which might be used include mixtures of molten sodium salts or a solid sodium salt. The cell-potential data reported here were taken using electrolytes of solid NaCl.

Although power-producing cells may well use molten salt electrolyte, the solubilities of sodium metal from the anode and of sodium-bismuth intermetallic species from the cathode alloy are sufficiently high to introduce complications when attempting to make thermodynamic measurements[1]. These complications take several forms. First, the sodium metal dissolved in the electrolyte near the anode tends to diffuse toward the cathode. At the cathode, the sodium is extracted from the electrolyte by the cathode alloy. The result is a transfer of sodium from the anode to the cathode without producing any current in the external circuit,

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causing a constant change in the cathode composition of the cell. Second, the solution of sodium in the electrolyte is a "mixed" electrical conductor, that is, it has both ionic and electronic conductivity. This results in a lowering of the open-circuit potential by causing an internal short circuit in the cell. Third, there exists the possibility of back-diffusion of bismuth from the cathode alloy to the anode through the solubility of intermetallic species in the electrolyte. For these reasons, solid NaCl electrolytes were used in the cells reported here.

Experimental Studies

Since the sodium metal itself and the sodium-bismuth alloys are subject to attack by water vapor and oxygen, all of the cells were operated in furnace wells attached to an inert atmosphere enclosure containing helium. The helium was continuously recirculated through a purification system and contained as impurities less than 1.5 ppm water vapor, and less than 5 ppm each of oxygen and nitrogen.

Electrolytes were obtained from Harshaw Chemical Company in the form of cups with 1/8-in. thick walls and bottoms. These were machined from single crystals of NaCl. The sodium anode was contained inside the cup electrolyte, which was in turn lowered into the liquid sodium-bismuth alloy. Tantalum rods were used as electrode contacts. Cell potentials were measured with a potentiometric electrometer having an input impedance of 10^{13} ohms. Forward and reverse current-voltage curves were measured by passing small currents through the cell. The current-voltage relationship so obtained was linear for cell temperatures between 810 and 1050°K. At a cell temperature of 523°K, the internal cell impedance was approximately 2.2×10^7 ohms, indicating the requirement of an electrometer or similar device for measuring the cell potential. At higher temperatures, approaching 1050°C, the internal cell resistance dropped to $\sim$ 300 ohms.

Results

It was found necessary to add a small correction to the raw cell potential-temperature-composition data in order to compensate for the "mixed" ionic and electronic conductivity in the electrolyte. Sodium may dissolve in the solid electrolyte in contact with the sodium anode. These dissolved atoms may dissociate into sodium ions (which may be located in cation vacancies) and electrons, at least some of which are located in F-centers (or anion vacancies). The electronic conductivity could arise from the thermal excitation of electrons in F-centers into conduction bands.

The correction terms was found by comparing the voltage of the experimental cell:

$$Na(\ell)NaCl(s)/40\ a/o\ Na\ in\ Pb(\ell)$$

as a function of temperature with both emf data from the literature and with the emf calculated for 700°C from vapor pressure measurements. Previous concentration cell studies using the Na-Pb system have been reported by Hauffe and Vierk[2] (in 1949) and by Lantratov[3] (in 1959). These investigators used glass electrolytes containing sodium oxide. Their results are in agreement with those reported in 1956 by Porter and Feinleib[4], who used an electrolyte of alumina impregnated with sodium carbonate. A. K. Fischer[5] of Argonne determined the vapor pressure of Na over a 40 a/o Na in Pb alloy held at 700°C. From his measurement, the cell emf was calculated to be $\sim$ 8 mv higher than that reported by Feinleib and Porter. The correction term for the cell potentials observed using solid NaCl as the electrolyte ranged from 4 mv at 400°C to 36 mv at 700°C. The corrected cell potential-temperature-composition data for the sodium-bismuth cells are shown in Figure 1.

Discussion

The data in Figure 1 clearly reflect that when a cell with a cathode alloy containing 30 to 40 a/o Na in Bi is cooled, a solid starts to precipitate from the liquid alloy as evidenced by the change in slope of the emf vs temperature curves. This is predicted, of course, from the phase diagram. Using the data of Figure 1, the corresponding excess chemical potentials of sodium have been calculated for the liquid Na-Bi alloys. These data were then treated by a least-squares technique

to find an expression for the excess chemical potential of sodium in liquid sodium-bismuth alloys as a function of temperature and composition. The best fit was obtained by assuming a quadratic dependence of excess chemical potential on both temperature and composition -- a subtle way of saying that nine coefficients are necessary to describe the excess chemical potential surface (see Equation 1 and Table 1).

$$\Delta\mu^{E}_{Na} = \sum_{i=1}^{3} \sum_{j=1}^{3} C_{ji}\, T^{j-1}\, X_{Na}^{i-1} \qquad (1)$$

Other thermodynamic quantities for sodium-bismuth alloys may be calculated from the equation for the excess chemical potential of sodium, using the standard thermodynamic relationships.

Using the cell potential surface calculated from the equation:

$$E = \frac{-1}{F}\ \Delta\mu_{Na} = 1\ \frac{1}{F}\left[RT\ell n\ X_{Na} + \sum_{i=1}^{3} \sum_{j=1}^{3} C_{ji}\, X_{Na}^{i-1}\ T^{j-1}\right] \qquad (2)$$

one may calculate the composition, X_{Na}, at a given temperature, for which E is the same as that observed for cells in which the cathode alloy was saturated with a solid intermetallic compound -- either NaBi or Na_3Bi. This composition-temperature relationship is the usual phase diagram, and the points calculated are shown in Figure 2, compared with the phase diagram published in Hansen and Anderko[6]. The compositions and cell potentials calculated were used, along with the equation for the excess chemical potential, to calculate the standard free energy of formation of solid NaBi and Na_3Bi, assuming pure liquid Na and Bi as the standard states. These are compared in Table 2 with those reported previously[7] for solid Li_3Bi. It is to be noted that the sodium-bismuth interaction is significantly lower in energy than the interaction between lithium and bismuth.

Table 1.
C_{ji} Coefficients Used in Evaluating $\Delta\mu^{E}_{Na}$ from Equation 1.

	i = 1	i = 2	i = 3
j = 1	-7454.10	-14928.3	6227.26
j = 2	-17.7422	25.5126	37.9301
j = 3	.0113414	-.000940211	-.0435859

Table 2.
Standard Free Energies of Formation of Li_3Bi, NaBi, and Na_3Bi

Standard Free Energy of Formation* (kcal/mole) of:

T (°K)	Li_3Bi	NaBi	Na_3Bi
550		-15.4	-
600		-15.0	-
650		-14.7	-
700		-14.4	-
750		-	-36.1
800	-50.5	-	-34.6
850	-49.7	-	-33.4
900	-48.8	-	-32.6

*Standard states were chosen to be the pure liquid elements and the solid compounds in the cell environment.

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3. M. F. Lantratov, Russian J. Inorg. Chem., 4, 927 (1959).

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Figure 1.
CORRECTED POTENTIALS FOR THE CELL:
Na(ℓ)/NaCl(s)/Na in Bi as a Function of Temperature.

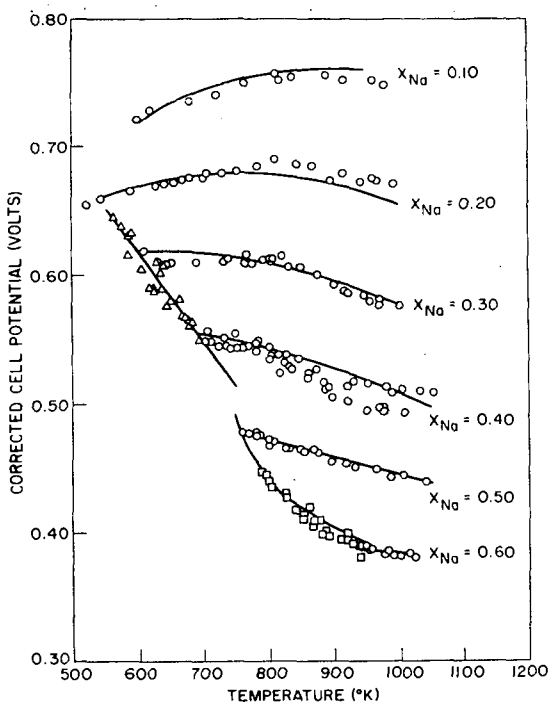
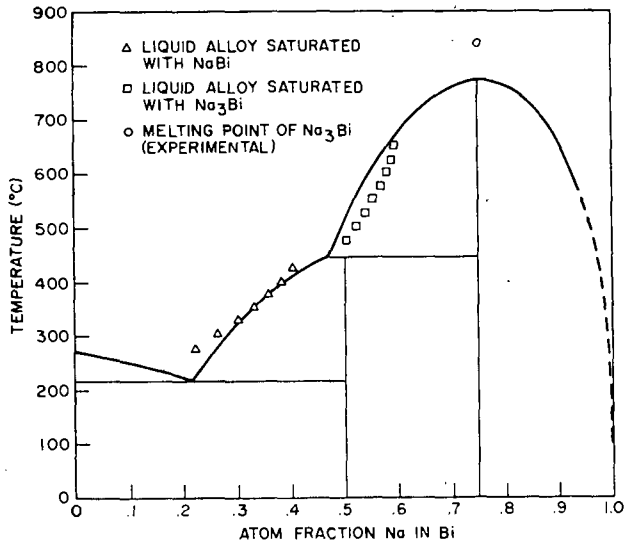


Figure 2.
COMPARISON OF CALCULATED SATURATION CONCENTRATIONS
WITH PUBLISHED PHASE DIAGRAM[6].



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