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**Evaluation of the first order ternary interaction parameters for  
bismuth in molten copper using a novel distribution technique**

**Jiang, Xin Hua, M.S.**

**The University of Arizona, 1987**

**U·M·I**

**300 N. Zeeb Rd.  
Ann Arbor, MI 48106**



**EVALUATION OF THE FIRST ORDER TERNARY INTERACTION  
PARAMETERS FOR BISMUTH IN MOLTEN COPPER  
USING A NOVEL DISTRIBUTION TECHNIQUE**

by

Xin Hua Jiang

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A Thesis Submitted to the Faculty of the  
**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING**

In partial Fulfillment of the Requirements

For the Degree of

**MASTER OF SCIENCE**

In the Graduate College

**THE UNIVERSITY OF ARIZONA**

1987

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## ACKNOWLEDGEMENTS

I wish to thank my thesis director and chief advisor, Professor David C. Lynch, for his guidance and assistance. His help and effort are greatly appreciated. I also wish to thank all graduate students, in the Department of Materials Science and Engineering for their encouragement along the way. In addition, a warm thank to you is extended for your contribution to this work. Finally, I wish to express my appreciation to the Arizona Mining and Mineral Resources Research Institute for their support of this investigation.

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## ABSTRACT

The first-order ternary interaction parameters of bismuth in molten copper containing either iron, arsenic or antimony have been evaluated using a pseudo equilibrium process at temperatures between 1398 K and 1473 K. The isopiestic distribution technique developed in this investigation yielded the following results:

$$\epsilon_{Bi}^{Fe} = \frac{1.11 \times 10^6}{T} - 754$$

$$\epsilon_{Bi}^{As} = \frac{4.4 \times 10^4}{T} - 24$$

$$\epsilon_{Bi}^{Sb} = -11$$

These results, coupled with other activity data, have been used to calculate the isoactivity curves for each constituent in the copper rich corner of each ternary system. The basis for the ternary interactions associated with  $\epsilon_{Bi}^{Fe}$ ,  $\epsilon_{Bi}^{As}$  and  $\epsilon_{Bi}^{Sb}$  are also discussed.

## Chapter 1

### INTRODUCTION

The production and use of copper has gradually increased from its time of discovery about 8000 years ago, to where now 8,473 thousand tons are consumed annually, world-wide (Bureau of Mines, 1979). Almost ninety percent of the world's primary copper is present in the form of sulfide minerals, which in traditional copper production are converted to copper bars in the following manner. First, the ore is concentrated by froth flotation. That process is followed by roasting to reduce sulfur content. The roasted ore is then smelted in a reverberatory furnace or a more modern flash furnace, where two liquid layers, matte and slag, form at 1200°C. Matte consists of copper and iron sulfides, precious metals and other minor impurities such as As, Bi, Sb, Ni and Pb. The other phase, slag, consists of silica, alumina, iron oxides, lime and other minor oxides. Slag also typically contains 0.3–0.8% Cu, and higher concentrations if single-step smelting or oxygen enrichment is employed. In contrast, matte has a high copper concentration ranging from 35–40% Cu. Finally, in two-step smelting operations, the matte is converted to blister copper (98.5–99.5% Cu), usually in a separate

vessel. The blister copper product is subsequently fire-refined and electro-refined to produce commercial grade copper (99.99% Cu).

In order to meet the demand for copper, reduce energy consumption and minimize pollution, several new processes for production of copper have been investigated and some are currently in operation. These new processes, such as the Mitsubishi continuous smelter and the Noranda process (Biswas and Davenport, 1980), not only do all the work of reverberatory furnace matte smelting, but also have many advantages over reverberatory furnace smelting. For example, they save capital expenditure, yield a high concentration of  $\text{SO}_2$  gas for the reduction of pollution, and reduce energy consumption. However, there is a negative side to these new processes. It has been found that the potential for minor elements such as Bi and As to transfer to the copper phase is significantly greater since slag, matte and blister copper are often in contact. As part of an effort to evaluate the behavior of minor elements during smelting, this research was conducted to examine the thermochemistry of minor elements in molten copper and copper alloys.

The thermodynamic properties of minor elements in liquid copper alloys are important both from the viewpoint of their behavior as impurities during copper smelting and from the physical chemistry aspect of liquid copper alloys. It has long been recognized that minor elements such as Bi, As and Sb adversely affect

the workability and mechanical properties of copper. Minor elements reduce the electrical and thermal conductivity of copper, and cause brittleness in the final copper anodes (Biswas and Davenport, 1980). So it is important to control Bi, As and Sb during the copper-making process.

Several investigators have studied the thermodynamic behavior of bismuth, iron, arsenic and antimony in copper (authors of the specific papers are given in the list of references). However, the ternary systems Cu-Bi-Fe, Cu-Bi-As and Cu-Bi-Sb have not been studied. It is the goal of this research to investigate the effects of As, Fe and Sb on the activity of Bi in copper.

## Chapter 2

### REVIEW OF THE LITERATURE

The activity of Bi, Fe, As and Sb in molten Cu alloys has been examined by several investigators: Predel and Emam, 1973; Azakami and Yazawa, 1967; Sibanda and Baker, 1979; Arac and Geiger, 1981; Bode, Gerlach and Pawlek, 1971; Taskinen and Niemela, 1981; Nikoskaya, Lomov and Gerasimov, 1959; Nagamori, Mackey and Tarassoff, 1975; Morris and Zellars, 1956; Hultgren and Desai, 1973; Sigworth and Elliott, 1974; Hultgren, et al., 1973; Subramanian and Laughlin, 1987; Lynch, 1980; Hino and Azakami, 1985; Hino and Toguri, 1987; Dabbs and Lynch, 1983; Azakami and Yazawa, 1976; and Nagamori and Chaubal, 1982. In some instances first order interaction parameters for those solutes in molten copper have been evaluated. A critical review of their literature is helpful in understanding the behavior of minor elements in liquid copper alloys, but first a review of the interaction parameter system is presented.

#### I. Development of The Interaction Parameter Formalism

The interaction parameter was introduced by Wagner (1952), then extended by Lupis and Elliott (1966) to represent the thermodynamic properties of a

dilute solution; and further modified by Pelton and Bale (1986) to represent the thermodynamic properties of non-dilute solutions.

The interaction parameters proposed by Wagner (1952) for a system with  $(n - 1)$  solutes and a solvent involves representing the partial molar excess Gibbs free energy,  $G_i^E$ , of the  $i^{th}$  species, using a Taylor series expansion, expanded at  $X_i$  (the mole fraction) equal to zero, are shown below:

$$\begin{aligned}
 G_i^E &= (G_i^E)_{T,P,X_{solvent} \rightarrow 1} \\
 &+ \sum_{j=2}^n \left( \frac{\partial G_i^E}{\partial X_j} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j] \\
 &+ \sum_{j=2}^n \frac{1}{2} \left( \frac{\partial^2 G_i^E}{\partial X_j^2} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j]^2 \\
 &+ \sum_{j=2}^{n-1} \sum_{k>j}^n \left( \frac{\partial^2 G_i^E}{\partial X_j \partial X_k} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j][X_k] + \dots \quad (2.1a)
 \end{aligned}$$

or in terms of the activity coefficient the equation becomes

$$\begin{aligned}
 \ln \gamma_i &= (\ln \gamma_i)_{T,P,X_{solvent} \rightarrow 1} \\
 &+ \sum_{j=2}^n \left( \frac{\partial \ln \gamma_i}{\partial X_j} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j] \\
 &+ \sum_{j=2}^n \frac{1}{2} \left( \frac{\partial^2 \ln \gamma_i}{\partial X_j^2} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j]^2 \\
 &+ \sum_{j=2}^{n-1} \sum_{k>j}^n \left( \frac{\partial^2 \ln \gamma_i}{\partial X_j \partial X_k} \right)_{T,P,X_{solvent} \rightarrow 1} [X_j][X_k] + \dots \quad (2.1b)
 \end{aligned}$$

According to the notation developed by Lupis and Elliott (1966), the above equation can be recast as follows:

$$\ln \gamma_i = \ln \gamma_i^\infty + \sum_{j=2}^n \epsilon_i^j [X_j] + \sum_{j=2}^n \rho_i^j [X_j]^2 + \sum_{j=2}^{n-1} \sum_{k>j}^n \rho_i^{j,k} [X_j][X_k] + \dots \quad (2.2)$$

where  $\epsilon_i^j$  and  $\rho_i^j$  are first-order and second-order interaction parameters, respectively, and are defined as follows:

$$\epsilon_i^j = \left( \frac{\partial \ln \gamma_i}{\partial X_j} \right)_{T,P,X_{\text{solvent}} \rightarrow 1} \quad (2.3a)$$

and

$$\rho_i^j = \frac{1}{2} \left( \frac{\partial^2 \ln \gamma_i}{\partial X_j^2} \right)_{T,P,X_{\text{solvent}} \rightarrow 1} \quad (2.3b)$$

The summation in the equation (2.2) is from  $j$  equal 2 to  $n$  and represents all solutes, whereas species 1 designates the solvent. That notation is adopted and utilized in the following discussion.

In the interaction parameter formalisms, the first-order interaction parameter  $\epsilon_i^i$  is a measure of how an increase in the concentration of  $i$  affects the activity coefficient of  $i$ , and  $\epsilon_i^j$  is a measure of how the presence of  $j$  affects the behavior of  $i$ . When the solute atoms  $i$  and  $i$ , and  $i$  and  $j$ , have a stronger attraction for each other than for solvent atoms,  $\epsilon_i^i$  and  $\epsilon_i^j$  are negative; when the solute atoms strongly repel each other,  $\epsilon_i^i$  and  $\epsilon_i^j$  are then positive.

Pelton and Bale (1986) recently examined the inconsistencies associated with use of a Taylor series expansion to represent the partial molar free energy. Their analysis generates a thermodynamically consistent expression for the activity coefficient, but one that is not justifiable as a mathematical series expansion. Ignoring the latter and accepting the former as a significant advancement, the new expression should provide a better representation of activity coefficients at higher solute concentration. Experimental results appear to confirm this conclusion.

Pelton and Bale's analysis begins with the functional representation for Gibbs free energy,

$$G = f(T, P, n_1, n_2, n_3, \dots, n_k)$$

for which taking total derivative yields:

$$\begin{aligned} dG = & \left( \frac{\partial G}{\partial T} \right)_{P, n_k} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_k} dP \\ & + \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \dots} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \end{aligned}$$

Let  $T, P, n_1, n_2, n_3, \dots, n_k$  be constant except  $n_i$  and  $n_j$ , then the total derivative becomes

$$dG = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_1, \dots} dn_i + \left( \frac{\partial G}{\partial n_j} \right)_{T, P, n_1, \dots} dn_j$$

From Maxwell's relations, the following relationship exists.

$$\frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial n_j} \right)_{T, P, n_1, \dots} = \frac{\partial}{\partial n_j} \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_1, \dots} \quad (2.4)$$

According to the definition of the partial molar property of Gibbs free energy, the following equations can be obtained,

$$\left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_1,\dots} = \mu_j = \mu_j^0 + RT \ln a_j \quad (2.5a)$$

and

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,\dots} = \mu_i = \mu_i^0 + RT \ln a_i \quad (2.5b)$$

Substituting the above two equations into equation (2.4) and evaluating the derivatives yields:

$$\frac{\partial \ln \gamma_j}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_j} \quad (2.6)$$

For a multi-components solution, the activity coefficients of solutes  $i$  and  $j$  can be represented in the usual manner as:

$$\ln \gamma_i = \ln \gamma_i^\infty + \epsilon_i^i X_i + \epsilon_i^j X_j + \epsilon_i^k X_k + \dots \quad (2.7a)$$

and

$$\ln \gamma_j = \ln \gamma_j^\infty + \epsilon_j^j X_j + \epsilon_j^i X_i + \epsilon_j^k X_k + \dots \quad (2.7b)$$

respectively. Taking the derivatives of the above equations with respect to the appropriate molar species yields:

$$\frac{\partial \ln \gamma_i}{\partial n_j} = -\frac{\epsilon_i^i X_i}{n_T} + \frac{\epsilon_i^j (1 - X_j)}{n_T} - \frac{\epsilon_i^k X_k}{n_T} \quad (2.8a)$$

and

$$\frac{\partial \ln \gamma_j}{\partial n_i} = -\frac{\epsilon_j^j X_j}{n_T} + \frac{\epsilon_j^i (1 - X_i)}{n_T} - \frac{\epsilon_j^k X_k}{n_T} \quad (2.8b)$$

Substituting equations (2.8a) and (2.8b) into equation (2.6) and rearranging the resulting equation yields:

$$\epsilon_i^j - \epsilon_j^i = \ln \left[ \frac{\gamma_i / \gamma_i^\infty}{\gamma_j / \gamma_j^\infty} \right] \quad (2.9)$$

This equation is a direct result of the Maxwell relation and is applicable only if the representation of the activity coefficients in equations (2.7) and (2.7b) are correct. It is to be noted that when  $X_1 = 1$ , then  $\gamma_i / \gamma_i^\infty = \gamma_j / \gamma_j^\infty = 1$  and equation (2.9) becomes the well-known interaction parameter relationship:

$$\epsilon_i^j = \epsilon_j^i \quad (2.10)$$

which is obtained from analysis of the Gibbs-Duhem relationship using equations (2.7a) and (2.7b). Whereas, in the general case at finite concentration the ratios of the activity coefficients no longer equal one and only fortuitously would the two ratios cancel to yield equation (2.10). Therefore, equation (2.9) is limited to infinite dilution and the standard formalism, equation (2.2), is inconsistent at finite concentrations.

Pelton and Bale modified the formalism to overcome the inconsistency. Their first-order modified formalism is presented as:

$$\ln \gamma_i = \ln \gamma_1 + \ln \gamma_i^\infty + \sum_{j=2}^n \epsilon_j^i [X_j] + \dots \quad (2.11a)$$

and

$$\ln \gamma_j = \ln \gamma_1 + \ln \gamma_j^\infty + \sum_{i=2}^n \epsilon_j^i [X_i] + \dots \quad (2.11b)$$

Using the new formalism equation (2.9) becomes:

$$\epsilon_i^j - \epsilon_j^i = \frac{d \ln \gamma_1}{dX_i} + \ln \left[ \frac{\gamma_i / \gamma_i^\infty}{\gamma_j / \gamma_j^\infty} \right] \quad (2.12)$$

where

$$\ln \gamma_1 = -\frac{1}{2} \sum_{j=2}^{n-1} \sum_{k>j}^n \epsilon_j^k [X_j] [X_k] \quad (2.13)$$

Application of the Gibbs-Duhem equation with the new formalism still yields the restriction in equation (2.10). The validity of the new formalism is then tested by taking the derivative of equation (2.13) with respect to  $X_i$  and substituting the result into equation (2.12). The resulting equation must be consistent with the restriction in equation (2.10) at all compositions. The derivatives of equation (2.13) yields:

$$\left( \frac{d \ln \gamma_1}{dX_i} \right) = \frac{-\epsilon_1^1 X_1 - \epsilon_1^i X_i + \epsilon_1^i X_1}{\epsilon_i^i X_i} \quad (2.14)$$

Redefining the interaction parameters in this equation using the new formalism presented in equation (2.11a) and (2.11b) leaves the following expression for the derivative:

$$\left( \frac{d \ln \gamma_1}{dX_i} \right) = - \ln \left[ \frac{\gamma_i}{\gamma_i^\infty} \right] \quad (2.15)$$

Substitution of this equation into equation (2.12) reveals that the new formalism is consistent with both the Maxwell relation and the Gibbs-Duhem equation. Whereas the standard interaction parameter formalism given by equation (2.2) is not. Also it was noted that  $\ln \gamma_1$  contains only quadratic terms. In very dilute solution, these quadratic terms may be ignored. That is, as  $X_1 \rightarrow 1$ , the modified formalism reduces to the standard formalism, equation (2.2), so that the existing compilations of interaction parameters in the standard formalism can be used directly in this modified formalism.

Comparison of equation (2.2) and (2.1b) reveals that  $\ln \gamma_i^\infty$  is the limiting value of  $\ln \gamma_i$  at infinite dilution of all solutes. Therefore, the Taylor series for  $\ln \gamma_i$  may be viewed as equivalent to the assumption of series expression of Henry's law of all orders, that is, to a generalized Henry's law at the composition  $X_1 = 1$ .

## II. Review of Thermodynamical Data

### 1. Cu-Bi Binary System

The activity of Bi in Cu-Bi alloys has been studied by Predel and Emam (1973), Azakami and Yazawa (1969), Sibanda and Baker (1979), Arac and Geiger (1981), Bode, Gerlach and Pawlek (1971), Paskinen and Niemela (1981), Nikolsya, and Lomov and Gerasimov (1959) and Nagamori, Mackey and Tarasoff (1975).

The work by Azakami and Yazawa (1967) was conducted using a transportation system. The apparatus employed by those investigators consisted of an alumina crucible which contained an alumina boat filled with a Cu-Bi alloy which was maintained at a constant temperature. A flow of high purity argon gas was passed over the alloy and saturated with volatile bismuth vapors. The argon gas flushed the bismuth vapor at a constant rate. With knowledge of the total pressure, the argon flow rate and the amount of Bi vapor condensed as a function of time the activity of bismuth in the alloy can be calculated as shown below.

From the weight of the condensate collected on the cold finger, the mole fraction of Bi in the vapor,  $X_{Bi}$ , assuming only monatomic bismuth vapor is present, is calculated using the following equation:

$$X_{Bi} = \frac{n_{Bi}}{n_{Bi} + n_{Ar}} \quad (2.16)$$

where  $n_{Bi}$  is the number of moles of bismuth transported by the carrier gas; and  $n_{Ar}$  is the number of moles of the carrier gas, argon, passed over the melt during an experiment.

Azakami and Yazawa (1967) considered bismuth to consist of two vapor species, Bi and Bi<sub>2</sub>, at the experimental temperatures employed. The equilibrium between monatomic and diatomic bismuth species can be represented by the following reaction:



for which the equilibrium constant is

$$K = \frac{P_{Bi_2}}{P_{Bi}^2} \quad (2.17b)$$

where  $P_{Bi}$  and  $P_{Bi_2}$  are the partial pressures of Bi and Bi<sub>2</sub>, respectively.

An apparent vapor pressure  $P_m$ , which is also equivalent to  $X_{Bi}$  in equation (2.16), is based on the assumption that only monatomic bismuth vapor was evolved from the melt, and is represented by the following expression:

$$P_m = \frac{P_{Bi} + 2P_{Bi_2}}{P_{Bi} + 2P_{Bi_2} + P_{Ar}} \quad (2.18)$$

where  $P_{Ar} = 1 - P_{Bi} - P_{Bi_2}$ . Rearranging equation (2.17b) and substituting that equilibrium into the above expression yields:

$$P_m = \frac{P_{Bi} + 2KP_{Bi}^2}{1 + KP_{Bi}^2} \quad (2.19)$$

In turn, by substituting known values of  $P_m$  and  $K$  into (2.19),  $P_{Bi}$  can be solved. The activity of bismuth (using the Raoultian standard state) can be computed from the results using the following relationship:

$$a_{Bi} = \left( \frac{P_{Bi}}{P_{Bi}^0} \right) = \left( \frac{P_{Bi_2}}{P_{Bi_2}^0} \right)^{1/2} \quad (2.20)$$

where  $P_{Bi}^0$  and  $P_{Bi_2}^0$  are the partial pressures of the monatomic and diatomic species over pure liquid bismuth at the temperature of interest. From the foregoing, the activity coefficient  $\gamma_{Bi}$ , which is given by the ratio of activity to the mole fraction of Bi in the alloy,  $\left( \frac{a_{Bi}}{X_{Bi}} \right)$ , can be computed. Azakami and Yazawa (1967) found the Henry's law activity coefficient of Bi to be 4.1 at 1273 K, 3.2 at 1373 K and 2.7 at 1473 K, respectively.

Arac and Geiger (1981) investigated the activity of bismuth using the same method used by Azakami and Yazawa. They carried out the experiments under controlled oxygen potential, and reported the values of  $\gamma_{Bi}^\infty$  equal to 2.17 at 1473 K and 2.27 at 1523 K. Those results are suspect as there is a discrepancy in the saturation pressure used to calculate Bi activities (Arac and Geiger, 1981).

Sibanda and Baker (1979) also used the transportation method to evaluate the activity of the bismuth in liquid Cu-Bi alloys at 1100°C. They found the limiting value of the activity coefficient of bismuth,  $\gamma_{Bi}^\infty$ , to be 2.5 at 1373 K.

Predel and Emam (1973) determined the thermodynamic activity of liquid copper-bismuth alloy using the transportation method, too. Their results

were reevaluated by Nagamori, Mackey and Tarassoff (1975). That analysis has yielded a value of the limiting activity coefficient for bismuth of 2.2 at 1373 K using a range of mole fraction of Bi between 0.2 and 0.95. This result is in agreement with that reported by Sibanda and Baker (1979).

Taskinen and Niemela (1981) examined the thermodynamical behavior of bismuth at dilute concentration in molten copper by an electrochemical technique. The authors used an electrochemical concentration cell which is represented in the usual manner,



to determine the bismuth activity in liquid Cu-Bi alloys. Values of the activity coefficient of bismuth at infinite dilution in molten copper were found to be 3.7, 4.5 and 5.2 at 1373 K, 1273 K, and 1173 K, respectively.

The experimental results reviewed are summarized in Table (2.1). That summary indicates that the values of activity coefficient of bismuth,  $\gamma_{Bi}^{\infty}$ , vary from 5.2 at 1173 K to 2.0 at 1573 K. However the results obtained with different methods are in reasonable agreement, as shown in Figure (2.1).

Few investigators have made an evaluation of the first-order interaction parameter  $\epsilon_{Bi}^{Bi}$ . Arac and Geiger (1981) evaluated the first-order self interaction parameter for Bi in liquid Cu by determining the distribution coefficient of bismuth between copper-white metal, copper-matte, and matte-slag phases. They

reported the 1 wt.% standard state first-order self interaction parameter  $\epsilon_{Bi}^{Bi}$ , had a value of zero. This value for  $\epsilon_{Bi}^{Bi}$  corresponds to a value of  $-2.3$  for  $\epsilon_{Bi}^{Bi}$  which is obtained from the conversion relationship given by Lupis (1983).

Sibanda and Baker (1979) did not report a value of the first-order self interaction parameter for bismuth in liquid copper. Although no value of  $\epsilon_{Bi}^{Bi}$  was stated in their paper, their representation of  $\gamma_{Bi}$  as being constant over the composition range examined implies that  $\epsilon_{Bi}^{Bi}$  is zero.

## 2. Cu-Fe Binary System

The thermodynamics of Cu-Fe alloys has been investigated by several investigators. Among them the works of Morri and Zellars, 1956; Hultgren and Desai, 1971; and Sigworth and Elliott, 1974; are particularly reviewed here and the results are summarized in Table (2.2).

Morris and Zellars (1956) were first to measure the activity of iron in Cu-Fe alloys. The activity of Fe in liquid Cu was determined at temperatures between 1739 K and 1873 K utilizing a transposition technique. The authors reported that the activity coefficients of Fe at 1823 K could be described by the following equation:

$$\log \gamma_{Fe} = 1.4856X_{Cu}^2 - 1.9076X_{Cu}^3 + 1.4131X_{Cu}^4 \quad (0 \leq X_{Cu} \leq 1)$$

from which the infinite dilute activity coefficient of Fe in liquid Cu was calculated to be 9.80 at 1823 K. Also the authors reported that the activity of iron shows strong positive deviation from Raoult's law.

Hultgren and Desai (1971) also studied the activity coefficient of Fe in molten Cu at 1823 K. The value of 10.57 was reported for  $\gamma_{Fe}^{\infty}$  at the elevated temperature, which is in agreement with the result from Morris and Zellars (1956).

Sigworth and Elliott (1974) re-computed the thermodynamic values based on the works of other investigators (Morris and Zellars, 1956; Hultgren and Desai, 1971; Oelsson, et al., 1961; and Kulkarni, 1973). A value of 19.5 was reported for  $\gamma_{Fe}^{\infty}$  at 1473 K; and values of  $-5.7$  for  $\epsilon_{Fe}^{Fe}$  and  $4.7$  for  $\rho_{Fe}^{Fe}$  were reported at 1823 K. The value of 19.5 for  $\gamma_{Fe}^{\infty}$  was used in this investigation.

The value for  $\epsilon_{Fe}^{Fe}$  at 1369 K in Table (2.2) was estimated from the work of Harig, et al. (1972), and was determined by examining the equilibrium between the austenitic solid alloy and molten copper at the stated temperature. The method for estimating  $\epsilon_{Fe}^{Fe}$  is sensitive to the choice of equilibrium concentration of copper in both the liquid and solid phases. Thus the value of  $\epsilon_{Fe}^{Fe}$  in Table (2.2) should be used with caution. That value for  $\epsilon_{Fe}^{Fe}$  does, however, compare favorably with the value of  $-5.7$  at 1823 K which was estimated by Sigworth and Elliott (1974). An evaluation of the selected values reported by Hultgren, et al.

(1973) yield values at 1823 K of  $-6.6$  and  $6.2$  for  $\epsilon_{F_e}^{F_e}$  and  $\rho_{F_e}^{F_e}$ , respectively. In all cases the values of  $\epsilon_{F_e}^{F_e}$  in Table (2.2) compare favorably.

### 3. Cu-As Binary System

Thermodynamic investigations of the Cu-As system have been studied by Azakami and Yazawa (1976), Bode, Gerlach and Pawleck (1971), Lynch (1980), Subramanian and Laughlin (1987), and Hino and Toguri (1987). Values for the activity coefficient of As in liquid Cu-As alloys are summarized in Table (2.2).

The activity of As in liquid Cu-As alloys has been determined by Azakami and Yazawa (1976) using an EMF method. In applying this method, those investigators first prepared the Cu-As alloys by placing high purity copper and arsenic powder in a quartz ampule, which was then sealed under vacuum and kept at a temperature of  $600^{\circ}\text{C}$  for three days; next fixed electro-polished tungsten lead wires were attached by resin at the top of the cell. This was followed by placing the electrode materials and prefused electrolyte in the cell, which was then kept under vacuum for 4 hours at  $350^{\circ}\text{C}$  and then sealed. The cell was then placed in the furnace and heated at a desired temperature. Finally, they measured the EMF values and calculated the activity of arsenic. Azakami and Yazawa reported the activity coefficient of As to be  $1.45 \times 10^{-4}$  at 1273 K and  $8.00 \times 10^{-5}$  at 1573 K respectively.

Bode, Gerlach and Pawleck (1971) determined the activity of As in liquid Cu at 1573 K using a transport technique. The authors reported a value of  $1.00 \times 10^{-6}$  for  $\gamma_{As}^{\infty}$ .

Jones and Philipp (1979) using a saturation technique examined the activity of As in molten Cu at 1373 K assuming  $As_4$  being the predominant vapor species at this temperature. Their results gave a value of  $5.0 \times 10^{-7}$  for  $\gamma_{As}^{\infty}$ , which is substantially smaller than  $8.00 \times 10^{-5}$  reported by Azakami and Yazawa (1976).

Lynch (1980) reevaluated the data of Azakami and Yazawa (1976) and Jones and Philipp (1979) in light of new information regarding the vapor of arsenic at elevated temperatures. The redetermined activity coefficient of As by that author at 1100°C from the raw data of Jones and Philipp (1979), and at 1000°C from the raw data of Azakami and Yazawa (1976) are represented by the following relationships:

$$\log \gamma_{As} = -6.22X_{Cu}^2 + 2.25 \quad (0.21 \leq X_{As} \leq 0.30)$$

and

$$\log \gamma_{As} = -5.58X_{Cu}^2 + 1.65 \quad (0.21 \leq X_{As} \leq 0.30)$$

respectively. The results of the new analysis indicate that the work of Jones and Philipp (1979) based on the former equation and the work of Azakami and

Yazawa (1976) based on the later equation are closer to one another than were originally reported.

The value of  $\varepsilon_{As}^{As}$  was estimated by evaluating Subramanian and Laughlin's equation for the excess free energy of the Cu-As binary system. That equation, itself, has been estimated from activity studies by Lynch (1980), and Hino and Azakami (1985). The analysis yields values of  $\gamma_{As}^{\infty}$  and  $\varepsilon_{As}^{As}$  of  $4.9 \times 10^{-3}$  and 6.1 respectively at 1273 K. The value for  $\gamma_{As}^{\infty}$  compares favorably with the values reported in other investigations at temperatures from 1273 K to 1423 K (Hino and Toguri, 1987; Dabbs and Lynch, 1983; Azakami and Yazawa, 1976). The comparison suggests that  $\gamma_{As}^{\infty}$  is not strongly dependent on the temperature. A similar condition is assumed to exist for  $\varepsilon_{As}^{As}$ , such that the values of  $4.9 \times 10^{-3}$  and 6.1 for  $\gamma_{As}^{\infty}$  and  $\varepsilon_{As}^{As}$  have been used in this study.

#### 4. Cu-Sb Binary System

The values of  $\varepsilon_{Sb}^{Sb}$  and  $\gamma_{Sb}^{\infty}$  were estimated experimentally by Azakami and Yazawa (1976), Nagamori and Chaubal (1982) and Hino and Toguri (1987). Their experimental results are presented in Table (2.2).

The activity of Sb in Cu,  $\gamma_{Sb}^{\infty}$ , was examined by Azakami and Yazawa (1976) using the same transport technique as that used in examining  $\gamma_{Bi}^{\infty}$ . Only the value of  $\gamma_{Sb}^{\infty}$  was reported as 0.013 at 1473 K.

The thermodynamics of antimony in metallic copper was also investigated by Nagamori and Chaubal (1982). The value of  $\gamma_{Sb}^{\infty}$  examined was 0.017 at 1573 K which compares favorably with the value of 0.013 reported by Azakami and Yazawa (1976).

A recent thermodynamic investigation of Cu-Sb alloys was carried out by Hino and Toguri using a mass spectrometric technique with a double Knudsen cell (Hino and Toguri 1987). The values of  $\gamma_{Sb}^{\infty}$  and  $\epsilon_{Sb}^{Sb}$  were reported to be 0.013 and 10.7 respectively at 1423 K. The value of 0.013 for  $\gamma_{Sb}^{\infty}$  is in good agreement with the value of 0.013 reported by Azakami and Yazawa (1976) at 1473 K, and also compares favorably with the value of 0.017 reported by Nagamori and Chaubal (1982) at 1523 K. Because no other data is available for  $\epsilon_{Sb}^{Sb}$ , the values of 0.013 and 10.7 for  $\gamma_{Sb}^{\infty}$  and  $\epsilon_{Sb}^{Sb}$  are used to evaluate the first-order ternary interaction parameter,  $\epsilon_{Bi}^{Sb}$ , in this investigation.

Table (2.1)

Summary of Activity Measurements  
for the Cu-Bi System

$\gamma_{Bi}^{\infty}$	$\epsilon_{Bi}^{Bi}$	Composition, $X_{Bi}$	Temp, K	Investigators
2.2	—	0.02–0.95	1373	Predel & Emam
4.1	—	—	1273	Azakami & Yazawa
3.2	—	—	1373	
2.7	—	—	1473	
2.5	0	0.01–0.04	1373	Sibanda & Baker
2.17	-2.3	0.006–0.0166	1473	Arac & Geiger
2.27	-2.3	0.0031–0.0089	1523	
3.0	—	0.00286–0.0088	1373	Bode, Gerlach & Pawlek
2.4	—	0.00286–0.0088	1473	
2.0	—	0.00286–0.0088	1573	
5.2	—	0.25–0.90	1173	Taskinen & Niemela
4.5	—	0.10–0.75	1273	
3.7	—	0.05–0.70	1373	
3.3	—	0.10–0.90	1200	Nikolskaya, Lomov & Gerasimov

Table (2.2a)  
 Summary of Activity Measurements  
 for the Cu-Fe System

$\gamma_{Fe}^{\infty}$	$\epsilon_{Fe}^{Fe}$	$\rho_{Fe}^{Fe}$	Temp, K	Investigators
9.80			1823	Morris & Zellars
10.57			1823	Hultgren & Desai
19.5			1473	Sigworth & Elliott
10.57	-6.6	6.2	1823	Hultgren, et al.
	-5.7	4.7	1823	Sigworth & Elliott
	-8		1369	Honig, Kirchner & Hillent

Table (2.2b)

Summary of Activity Measurements  
for the Cu-As system

$\gamma_{As}^{\infty}$	$\varepsilon_{As}^{As}$	$\rho_{As}^{As}$	Temp, K	Investigators
$4.9 \times 10^{-3}$	6.1		1273	Lynch
$4.8 \times 10^{-4}$			1000	Sigworth & Elliott
$1.45 \times 10^{-4}$			1273	Azakami & Yazawa
$8.0 \times 10^{-5}$			1573	Azakami & Yazawa
$7.3 \times 10^{-3}$	10.5		1423	Hino & Toguri
$5. \times 10^{-7}$			1373	Jones & Philipp
$1.0 \times 10^{-2}$			1273	Hino & Azakami
$6.8 \times 10^{-3}$			1423	Hino & Azakami

Table (2.2c)

Summary of Activity Measurements  
for Cu-Sb System

$\gamma_{Sb}^{\infty}$	$\epsilon_{Sb}^{Sb}$	$\rho_{Sb}^{Sb}$	Temp, K	Investigators
$1.4 \times 10^{-2}$	15	-7.5	1273-1473	Sigworth & Elliott
$1.3 \times 10^{-2}$			1473	Azakami & Yazawa
$1.76 \times 10^{-2}$			1523	Nagamori & Chaubal
$1.3 \times 10^{-2}$	10.7		1423	Hino & Toguri
$3.7 \times 10^{-3}$			1573	Bode, Gerlach & Pawlek

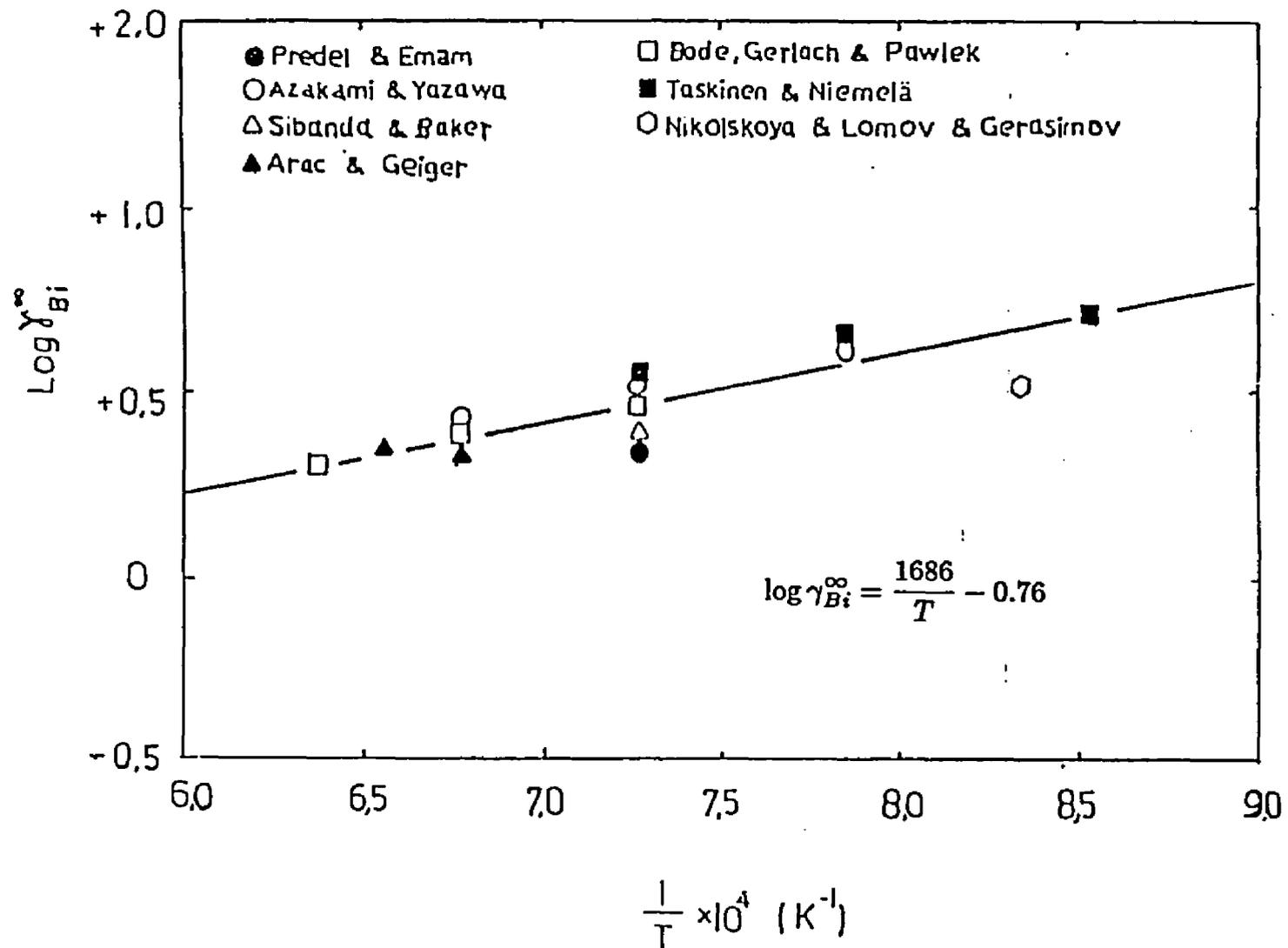


Figure 2.1 Comparison of experimental results for  $\gamma_{Bi}^{\infty}$

## Chapter 3

### EXPERIMENTAL

#### I. Apparatus

Traditionally, activity determination of metallic components at high temperatures has been accomplished with one of two techniques, the transportation method (which was described in Chapter 2), or the electrochemical method. Analysis of the resulting data has provided a means for evaluating the interaction parameters. In this investigation a novel technique was used to obtain first-order ternary interaction parameters. This isopiestic distribution technique involves bringing a Cu-Bi-M ternary alloy, where M represents either Fe, As or Sb, into pseudo equilibrium with a binary alloy containing only Cu and Bi.

The isopiestic distribution technique has many advantages. Primarily, the technique is simple, involving a small and easily assembled cell which is equilibrated at one temperature. The exposure time and initial Bi concentration must be experimentally established; they depend on the temperature and partial pressure of Bi associated with the alloys, the kinetics of vapor transport and the analytical methods available for quantitative analysis of the alloys. In addition,

the isopiestic distribution technique can be used with simple instrumentation and is relatively quick and inexpensive.

The system employed is shown in Figure (3.1) and consists of two melts separated by a crucible and sealed under vacuum in a silica tube. In order to prevent contamination of the binary melt by Fe, As or Sb, Cu-Fe, Cu-As and Cu-Sb alloys were prepared separately. A portion of these alloys was added to Cu and Bi to achieve the desired ternary alloys. Bismuth, copper and the Cu-M alloy were mixed to give a total weight of two grams which was placed in a 8 mm O.D. silica crucible which was, in turn, placed in a 10 mm O.D. silica tube containing two grams of a Cu-Bi alloy. The silica tube was sealed under a vacuum of 0.067 Pa with a hydrogen-oxygen flame.

Four sealed assemblies were placed into a refractory brick, as shown in Figure (3.2). The refractory brick was then inserted in a furnace and heated simultaneously to either 1398 K, 1448 K or 1473 K for equilibration. The experimental results, as noted later, indicate that 48 hours was adequate to achieve a pseudo equilibrium distribution of Bi at the concentrations employed in this study. The vapor pressure data in Figures (3.3), (3.4) and (3.5) reveals that Bi in copper has a substantially greater vapor pressure than pure copper and Fe, As and Sb alloyed with copper. Therefore, the Bi distributes itself between the two melts under an isopiestic equilibrium condition. During an experiment the furnace was

maintained within  $\pm 2\text{K}$  using a PDI controller. The temperature was monitored using a Pt/6%Rh-Pt/30%Rh thermocouple. Upon completion of an experiment the specimens were quenched in water and recovered.

Atomic absorption spectrophotometry was used to provide quantitative analysis of the alloys recovered from the isopiestic experiments. Prior to analysis the alloy buttons were dipped in a dilute HCL-HNO<sub>3</sub> acid mixture and rinsed to remove any impurities adhering to the buttons. The method used for digestion of alloys is given below:

1. Weigh precisely 0.50 g of a sample and place in a 150 ml beaker.
2. Add 2 ml of 1:1 (v/v) HNO<sub>3</sub> nitric acid and 10 ml of 1:1 (v/v) HCL hydrochloric acid to the beaker.
3. Cover the beaker and let sit for 24 hours.
4. Upon completion of digestion, pour the contents into an acid-rinsed volumetric flask (50 ml).
5. Dilute the digested solution with distilled water to the 50 ml mark, then transfer the contents to an acid rinsed plastic bottle for analysis. The source of chemicals used for digestion are identified in Table (3.5)

## II. Vapor Pressure Calculation

The essential condition for the application of the isopiestic distribution thermodynamic equilibrium technique is the pressure difference. The vapor pressure of bismuth should be two orders of magnitude higher than that of the ternary element M or Cu. Later calculations show that for Bi, Fe, As, Sb and Cu only bismuth has a significant vapor pressure. In this investigation bismuth vapor was equilibrated between melts of Cu-Bi-Fe / Cu-Bi, Cu-Bi-As / Cu-Bi and Cu-Bi-Sb / Cu-Bi. The total vapor pressures of Bi, Fe, As, and Sb associated with the alloys were calculated as indicated in the following sections.

### 1. Bismuth

The total vapor pressure of bismuth associated with the alloys can be estimated by examining the Cu-Bi alloy. The chemical reaction involved are



$$\Delta G^0 = 195125 - 101.7T \text{ (J/mole)} \quad (3.1b)$$

and



$$\Delta G^0 = -97833 + 5.21T \text{ (J/mole)} \quad (3.2b)$$

for which the equilibrium constants are

$$K_{q3.1} = \frac{P_{Bi}}{a_{Bi}} \quad (3.3)$$

and

$$K_{q3.2} = \frac{P_{Bi_2}^{\frac{1}{2}}}{P_{Bi}} \quad (3.4)$$

The activity of bismuth in the alloy can be represented in the usual manner as follows:

$$\begin{aligned} \ln a_{Bi} &= \ln X_{Bi} + \ln \gamma_{Bi} \\ &= \ln X_{Bi} + \ln \gamma_{Bi}^{\infty} + \epsilon_{Bi}^{Bi} X_{Bi} + \dots \end{aligned} \quad (3.5)$$

Since values of  $\gamma_{Bi}^{\infty}$  and  $\epsilon_{Bi}^{Bi}$  are known, specifying a value for  $X_{Bi}$  leaves three unknown,  $a_{Bi}$ ,  $P_{Bi}$  and  $P_{Bi_2}$ , which then can be determined by solving equations (3.3), (3.4) and (3.5) simultaneously. Table (3.1) shows the calculated vapor pressure of Bi at 1423 K.

Table (3.1) shows that the vapor pressure of Bi was approximately  $10^{-4}$  atm for the Bi concentration (0.5 to 3.0 wt.%) employed in this investigation.

Table (3.1) Vapor pressure of Bi (atm)

wt.%Bi	$P_{Bi} \times 10^4$	$P_{Bi_2} \times 10^6$	$P_{total} \times 10^4$
0.5	0.656	0.295	0.659
1.0	1.30	1.16	1.31
1.5	1.91	2.51	1.94
2.0	2.49	4.25	2.53
2.5	3.01	6.21	3.07
3.0	3.47	8.24	3.55

## 2. Iron

Iron was considered as a solute in the binary Cu-Fe alloy and its activity can be represented using the following equation,

$$a_{Fe(g)} = \frac{P_{Fe}}{P_{Fe}^0} \quad (3.6)$$

where  $P_{Fe}^0$  is the vapor pressure associated with pure liquid iron at the temperature of interest and  $P_{Fe}$  is the actual pressure of iron expected over the melt.

$P_{Fe}^0$  can be calculated using the published vapor pressure equation (Hultgren, et al., 1973),

$$\log P_{Fe}^0 = -\frac{21080}{T} - 2.14 \log T + 16.89 \quad (3.7)$$

since the activity of Fe in the melt is also equal to  $\gamma_{Fe}X_{Fe}$ , the partial pressure of Fe over the melt can be represented as follows:

$$P_{Fe} = \gamma_{Fe}X_{Fe}P_{Fe}^0 \quad (3.8)$$

where  $\gamma_{Fe}$  is obtained from

$$\ln \gamma_{Fe} = \ln \gamma_{Fe}^{\infty} + \epsilon_{Fe}^{Fe}X_{Fe} \quad (3.9)$$

The values of  $\gamma_{Fe}^{\infty}$ ,  $\epsilon_{Fe}^{Fe}$  and  $P_{Fe}^0$  at 1473 K are 19.5, -8 and  $2.8 \times 10^{-8}$  atm, respectively.

Table (3.2) shows the vapor pressure of Fe as a function of weight percent of Fe in the Cu-Fe alloy at 1423 K.

Table (3.2) Vapor pressure of Fe (atm)

wt.%Fe	0.25	0.5	1.0	1.5	2.0	2.5
$P_{Fe} \times 10^8$	0.27	0.53	1.00	1.44	1.83	2.18

Figure (3.3) shows that at the experimental temperature 1423 K, the vapor pressure of Fe is  $10^{-8}$  atm, which is four orders of magnitude smaller than that of bismuth in the experimental range.

### 3. Arsenic

The vapor pressure associated with arsenic was calculated assuming a Cu-As binary alloy. The vapor pressure of arsenic over the liquid phase was calculated using the same method as that employed for the bismuth vapor pressure calculations. Arsenic vapor exists in several forms which can be represented by the following equations:



and



for which the standard Gibbs free energies (J/mole) are

$$\Delta G^0 = 3.30 \times 10^{-3}T^2 - 46.9T + 38900 \quad (3.10b)$$

$$\Delta G^0 = 3.41 \times 10^{-3}T^2 - 39.1T + 56500 \quad (3.11b)$$

$$\Delta G^0 = -2.93 \times 10^{-3}T^2 - 52.3T + 191600 \quad (3.12b)$$

and

$$\Delta G^0 = -21.6T + 33100 \quad (3.13b)$$

respectively.

For the above equations the equilibrium constants are:

$$K_{q3.10} = \frac{P_{As_4}^{\frac{1}{4}}}{a_{As}} \quad (3.14)$$

$$K_{q3.11} = \frac{P_{As_2}^{\frac{1}{2}}}{P_{As_4}^{\frac{1}{4}}} \quad (3.15)$$

$$K_{q3.12} = \frac{P_{As}}{P_{As_2}^{\frac{1}{2}}} \quad (3.16)$$

and

$$K_{q3.13} = \frac{P_{As_3}^{\frac{1}{3}}}{P_{As_4}^{\frac{1}{4}}} \quad (3.17)$$

The activity of arsenic in the alloy can be represented by the following equation,

$$\begin{aligned} \ln a_{As} &= \ln X_{As} + \ln \gamma_{As} \\ &= \ln X_{As} + \ln \gamma_{As}^{\infty} + \epsilon_{As}^{As} X_{As} + \dots \end{aligned} \quad (3.18)$$

The values for  $\gamma_{As}^{\infty}$  and  $\epsilon_{As}^{As}$  at 1423 K were, as noted earlier, taken as 0.0049 and 6.1 respectively. Specifying a specific value for  $X_{As}$  leaves five unknown,  $a_{As}$ ,  $P_{As}$ ,  $P_{As_2}$ ,  $P_{As_3}$  and  $P_{As_4}$  which can be calculated by solving equations (3.14), (3.15), (3.16), (3.17) and (3.18) simultaneously. The vapor pressures of the multi-vapor species of As, as a function of weight percentage of As in the melt, are presented in Table (3.3).

Table (3.3) Vapor pressure of As (atm)

wt.%As	$P_{As} \times 10^8$	$P_{As_2} \times 10^7$	$P_{As_3} \times 10^{11}$	$P_{As_4} \times 10^{14}$	$P_{total} \times 10^7$
1.0	1.12	0.184	0.989	0.472	0.297
1.5	1.73	0.439	3.615	2.666	0.612
2.0	2.37	0.823	9.30	9.35	1.06
2.5	3.04	1.37	19.7	25.4	1.66
3.0	3.74	2.06	36.8	58.7	2.44
3.5	4.48	2.96	63.4	121	3.42

Figure (3.4) presents the vapor pressures of As, Bi and Cu in the experimental range. From Figure (3.4) it can be seen that the total vapor pressure of As is three orders of magnitude lower than that of Bi in the alloy.

#### 4. Antimony

For the system Cu-Bi-Sb, a similar calculation of the vapor pressure for the multi-vapor species of antimony was computed. Again, the calculations are based on a binary system (Cu-Sb), which is represented by the following equilibria:



and

$$\frac{1}{2}Sb_2(g) = \frac{1}{4}Sb_4(g) \quad (3.21)$$

for which the equilibrium constants are

$$K_{q3.19} = \frac{P_{Sb}}{a_{Sb}} \quad (3.22)$$

$$K_{q3.20} = \frac{P_{Sb_2}^{\frac{1}{2}}}{P_{Sb}} \quad (3.23)$$

and

$$K_{q3.21} = \frac{P_{Sb_4}^{\frac{1}{4}}}{P_{Sb_2}^{\frac{1}{2}}} \quad (3.24)$$

The activity of antimony in the melt can be calculated by the following equation,

$$\begin{aligned} \ln a_{Sb} &= \ln X_{Sb} + \ln \gamma_{Sb} \\ &= \ln X_{Sb} + \ln \gamma_{Sb}^{\infty} + \epsilon_{Sb}^{Sb} X_{Sb} + \dots \end{aligned} \quad (3.25)$$

where the values for  $\gamma_{Sb}^{\infty}$  and  $\epsilon_{Sb}^{Sb}$  at 1423 K are 0.013 and 10.7 respectively. By solving the equations (3.22), (3.23), (3.24) and (3.25), the multi-vapor pressures of Sb are calculated and presented in Table (3.4) and Figure (3.5).

According to the calculations, it can be seen that the total vapor pressure of Sb is much smaller than that of Bi. Therefore, only the vapor pressure of bismuth will be significant during this investigation.

Table (3.4) Vapor pressure of Sb (atm)

wt.% Sb	$P_{Sb} \times 10^7$	$P_{Sb_2} \times 10^{10}$	$P_{Sb_4} \times 10^{17}$	$P_{total} \times 10^7$
0.5	0.13	0.43	0.065	0.129
1.0	0.27	1.89	0.122	0.270
1.5	0.42	4.63	0.732	0.424
2.0	0.58	8.95	2.740	0.592
2.5	0.76	15.22	7.92	0.776
3.0	0.95	23.86	19.5	0.976
3.5	11.6	35.4	42.8	1.2

### III. Materials

Three ternary alloy systems Cu-Bi-Fe, Cu-Bi-As and Cu-Bi-Sb have been investigated. For each system, three sets of experiments were conducted, each at a different temperature: 1398 K, 1448 K and 1473 K. In the investigation the experiments were designed to vary the compositions of Bi, Fe, As and Sb. The purity and source of chemicals used in this investigation are identified in Table (3.5).

Table (3.5) Purity and source of materials

Materials	Purity	Supplier
Cu	5N, shot 2-8 mm,	Alfa
Bi	6N, shot 2.5 mm,	Alfa
Fe	5N, sponge,	Johnson Mathey Chemicals
As	4N, lumps	Alfa
Sb	5N, lumps	Alfa
HNO <sub>3</sub>	37% AR	Mallinckrodt
HCL	reagent	MCB

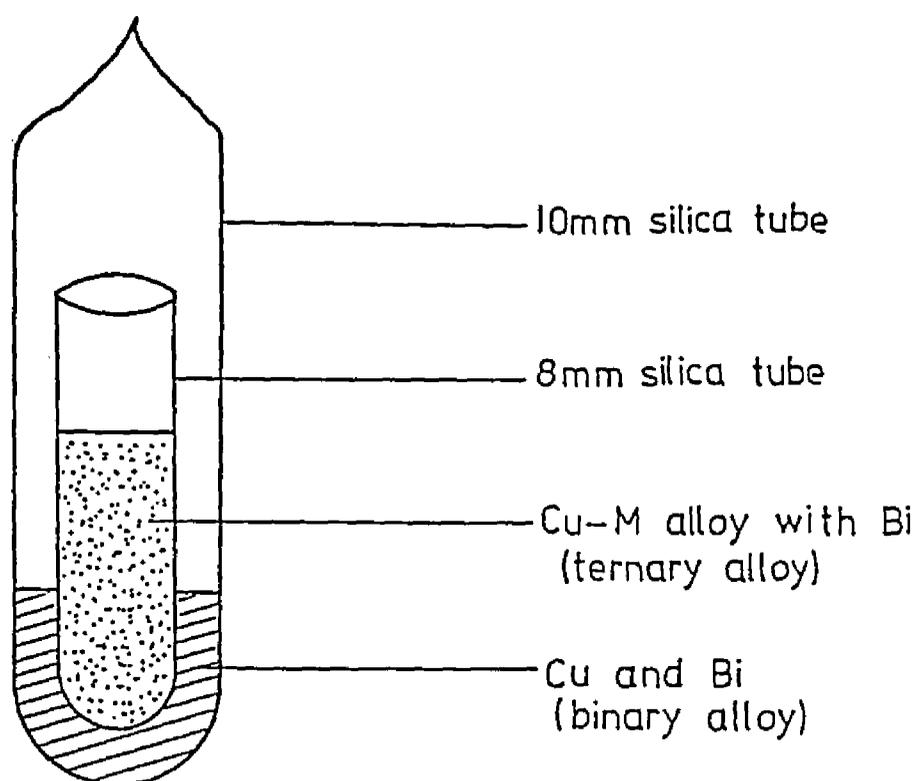


Figure 3.1 Cell used in distribution experiments

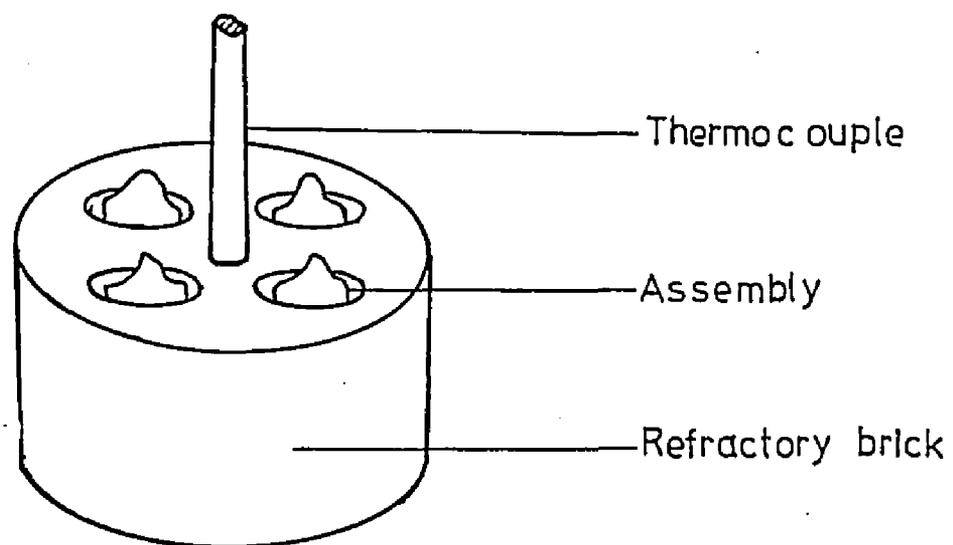


Figure 3.2 Apparatus used in experiments

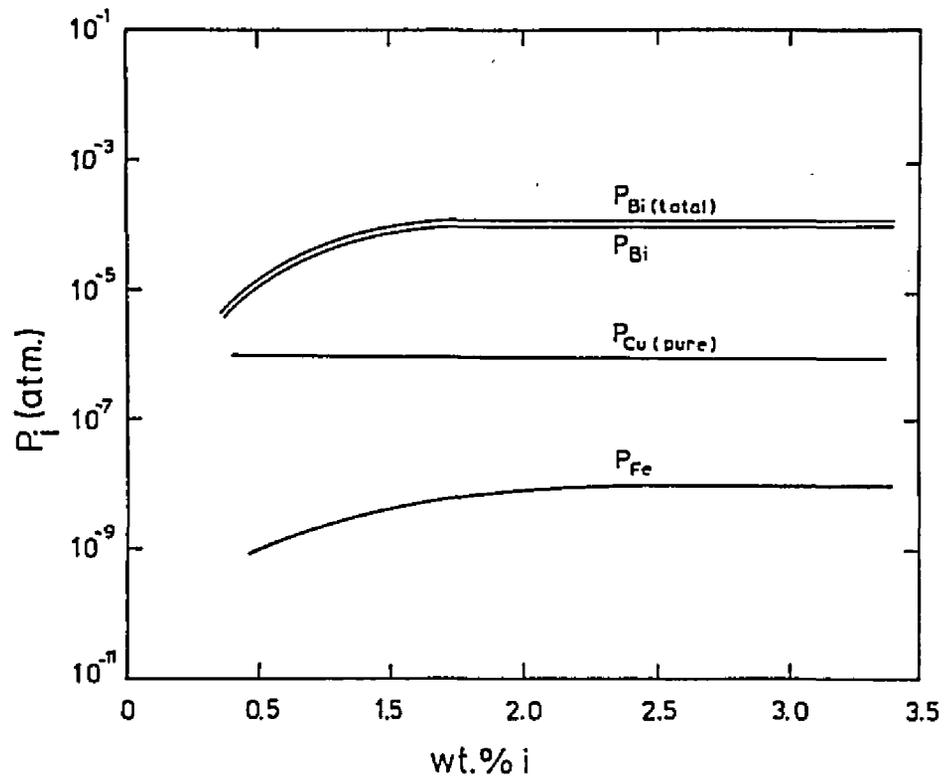


Figure 3.3 Comparison of vapor pressures of Bi and Fe in molten copper to that of pure molten copper

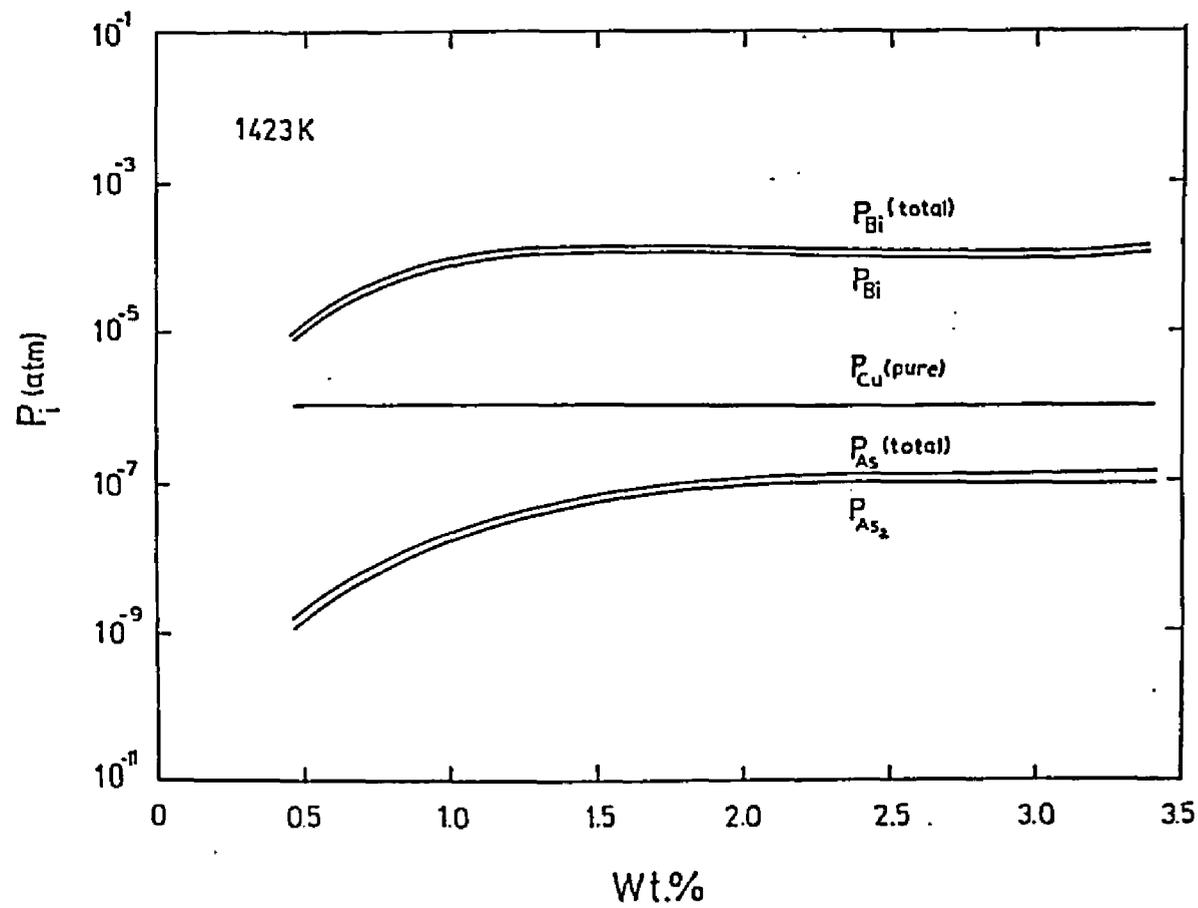


Figure 3.4 Comparison of vapor pressures of Bi and As in molten copper to that of pure molten copper

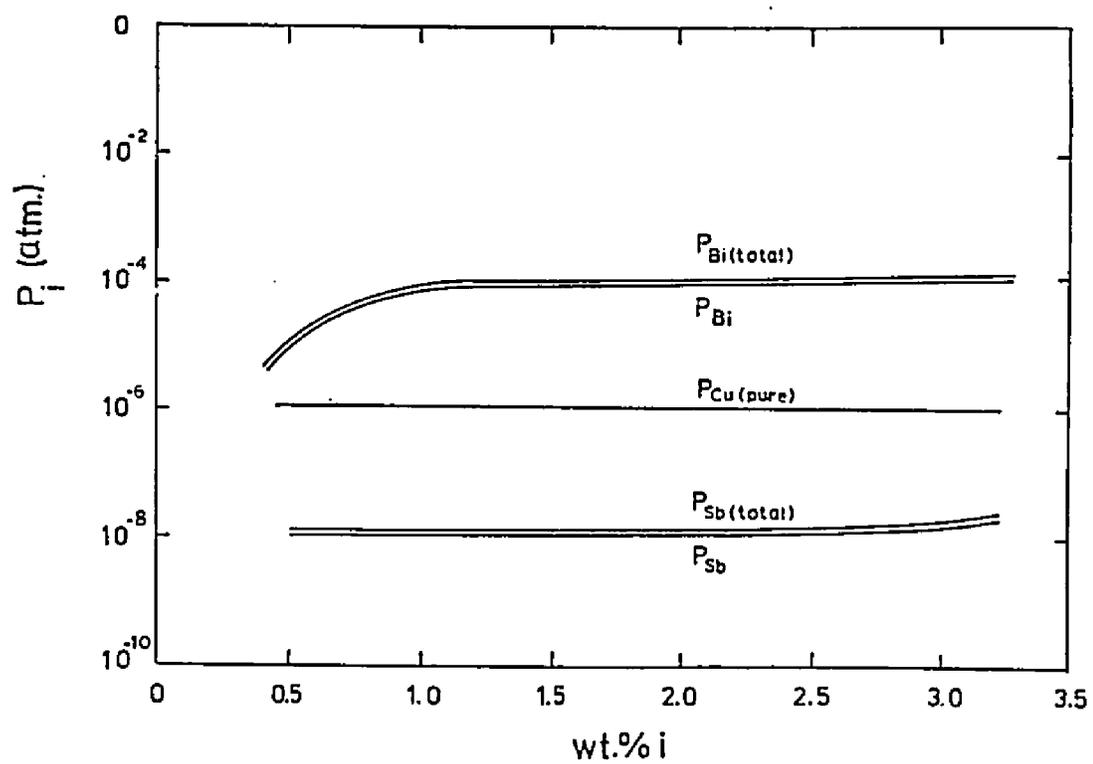


Figure 3.5 Comparison of vapor pressures of Bi and Sb in molten copper to that of pure molten copper

## Chapter 4

### RESULTS

Three systems Cu-Bi-Fe, Cu-Bi-As and Cu-Bi-Sb were investigated in this study. The initial concentration of bismuth in both the binary and ternary melts was identical in each experiment. The final results in Tables (4.1), (4.2) and (4.3) indicate that bismuth was only preferentially dissolved in the ternary alloys containing antimony.

#### I. Cu-Bi-Fe System

For Cu-Bi-Fe system, three sets of experiments with Bi at different temperatures were investigated. The compositional range for Bi was 0.5–3.0 wt.% and for Fe, 0.5–1.0 wt.%. The first set was investigated at 1398 K; the second was at 1448 K; and the third at 1473 K. The results of these experiments are presented in Table (4.1).

The results in Table (4.1) indicated that the binary melt, which initially contained only copper and bismuth, picked up some iron from the ternary melt during the experimental process. It is not likely that the presence of iron in the binary melt is due to vapor transport, but more likely due to the diffusion of

iron through the silica crucible wall. The iron reacted with residual oxygen in the metal to form fayalite at the crucible wall. This reaction is beneficial in that it reduces the overall oxygen content in the melts and thereby minimizes the influences of oxygen on the activity of Bi.

## II. Cu-Bi-As System

Like the Cu-Bi-Fe system, three sets of experiments with Cu-Bi-As alloys were also investigated. For Cu-Bi-As system, the wt.% of As varied from 0.75–3.5 and for Bi the wt.% varied from 0.5–2.5. The experimental results are presented in Table (4.2).

The results in Table (4.2) indicated that the binary melt, which initially contained only copper and bismuth, picked up very little As during the experimental process. As might be expected from vapor pressure data, the most probable form of transport of As between the melts involves  $\text{As}_4\text{O}_6$  vapor which could form by the reaction between arsenic and residual oxygen. The results in Table (4.2) indicated that bismuth was preferentially dissolved in those alloys with lower As concentration.

## III. Cu-Bi-Sb System

For the Cu-Bi-Sb system, the experimental composition range was from 0.75 wt.% Sb and 0.5 wt.% Bi to 3.0 wt.% Sb and 2.25 wt.% Bi; and the chemical

analysis results for these experiments are presented in Table (4.3). The results in Table (4.3) indicated that the binary melt, which initially contained only copper and bismuth, picked up very little Sb during the experimental process, as was the case with arsenic. The results further indicated that bismuth was preferentially dissolved in those alloys containing antimony.

Table (4.1) Results for Cu-Bi-Fe System

Ternary Melts		Binary Melts		Time	Temp
Bi wt.%	Fe wt.%	Bi wt.%	Fe wt.%	hrs	K
0.910	0.460	1.20	0.022	24	1398
2.60	0.360	3.10	0.054	36	1398
1.00	0.440	1.20	0.043	48	1398
1.70	0.470	2.00	0.022	48	1398
2.50	0.430	2.80	0.097	48	1398
1.87	0.160	1.90	0.006	24	1398
0.500	0.130	0.530	0.040	48	1398
1.10	0.130	1.30	0.026	48	1398
2.60	0.160	2.90	0.020	48	1398
1.00	0.520	1.10	0.024	48	1448
1.50	0.520	1.60	0.024	48	1448
2.10	0.530	2.30	0.023	48	1448
1.60	0.670	1.60	0.012	48	1448
2.00	0.690	2.20	0.0072	48	1448
0.520	0.530	0.550	0.010	48	1448
0.980	0.510	1.00	0.034	48	1448
2.10	0.530	2.20	0.015	48	1448
1.00	0.320	0.960	0.092	48	1473
1.60	0.440	1.50	0.036	48	1473
0.460	0.430	0.500	0.019	48	1473

Table (4.2) Results for Cu-Bi-As System

Ternary Melts		Binary Melts		Time	Temp
Bi wt.%	As wt.%	Bi wt.%	As wt.%	hrs	K
1.46	1.50	1.60	0.116	48	1398
1.61	2.46	1.84	0.0305	48	1398
2.04	2.53	2.62	0.0016	48	1398
0.480	3.26	0.550	0.103	48	1398
1.47	2.77	1.76	0.0715	48	1398
2.13	2.54	2.39	0.0230	48	1448
2.06	2.18	2.43	0.0050	48	1448
1.54	2.56	1.81	0.0092	48	1448
2.10	2.46	2.35	0.0288	48	1473
1.04	3.28	1.25	0.0626	48	1473
1.83	2.45	2.14	0.0526	48	1473
1.01	2.96	1.08	0.150	48	1473

Table (4.3) Results for Cu-Bi-Sb System

Ternary Melts		Binary Melts		Time	Temp
Bi wt.%	Sb wt.%	Bi wt.%	Sb wt.%	hrs	K
2.12	1.62	1.95	0.000	48	1398
1.62	1.52	1.55	0.000	48	1398
1.10	1.68	1.00	0.020	48	1398
0.570	1.46	0.48	0.050	48	1398
0.580	2.01	0.51	0.000	48	1398
2.11	1.91	1.98	0.060	48	1398
2.27	2.83	2.00	0.040	48	1398
2.14	1.57	2.08	0.000	48	1448
1.72	1.52	1.55	0.070	48	1448
1.17	1.74	1.06	0.040	48	1448
0.570	2.20	0.510	0.000	48	1448
1.12	2.12	0.990	0.000	48	1448
1.63	2.00	1.45	0.060	48	1448
1.01	1.56	0.920	0.020	48	1473
1.55	1.54	1.49	0.080	48	1473
0.590	2.28	0.520	0.000	48	1473
1.55	2.13	1.50	0.090	48	1473
1.67	2.57	1.45	0.050	48	1473
2.16	2.70	2.05	0.040	48	1473

## Chapter 5

### DISCUSSION

#### I. Interaction Parameter Calculation

In order to evaluate the behavior of minor elements in the smelting of copper concentrates it is necessary to understand the role that each minor element has on the activity of the solute in question, in molten copper. Bismuth, because of its volatility and the positive deviation from ideality it displays, in molten copper, is ideally suited for analysis. The influence of other solutes on the activity of bismuth in copper are evaluated in terms of interaction parameters.

##### 1. First-order self interaction parameter of Bi, $\epsilon_{Bi}^{Bi}$ .

The activity of bismuth in molten copper can be written as:

$$a_{Bi} = \left( \frac{P_{Bi}}{P_{Bi}^0} \right) = \left( \frac{P_{Bi_2}}{P_{Bi_2}^0} \right)^{1/2} \quad (5.1)$$

where  $P_{Bi}^0$  and  $P_{Bi_2}^0$  are the saturation pressures of pure liquid bismuth, and  $P_{Bi}$  and  $P_{Bi_2}$  are the partial pressures over the melt at equilibrium and the temperature of interest.

According to the definition of activity, the activity coefficient of Bi is given by:

$$\gamma_{Bi} = \frac{a_{Bi}}{X_{Bi}} = \frac{(P_{Bi}/P_{Bi}^0)}{X_{Bi}} \quad (5.2)$$

where  $P_{Bi}^0 = 8.054 \times 10^{-3}$  atm at 1373 K. Using Sibanda and Baker's data, values of  $\gamma_{Bi}$  have been calculated. Those values are listed in Table (5.1).

Table (5.1) Reevaluation of Sibanda and Baker's Data

$X_{Bi}$	$P_{Bi}$ (atm.)	$a_{Bi}$	$\gamma_{Bi}$
0.00993	$2.27 \times 10^{-4}$	0.02820	2.8390
0.01333	$2.84 \times 10^{-4}$	0.03524	2.6437
0.01433	$2.71 \times 10^{-4}$	0.03364	2.3475
0.01742	$2.97 \times 10^{-4}$	0.03685	2.1153
0.02081	$4.14 \times 10^{-4}$	0.05143	2.4714
0.02081	$4.39 \times 10^{-4}$	0.05448	2.6925
0.02179	$4.72 \times 10^{-4}$	0.05864	2.6925
0.02536	$4.52 \times 10^{-4}$	0.05570	2.1959
0.02959	$5.16 \times 10^{-4}$	0.06408	2.1656
0.03480	$5.29 \times 10^{-4}$	0.08827	2.5366
0.04000	$8.00 \times 10^{-4}$	0.09933	2.4830

At dilute concentrations of bismuth in molten copper, the activity coefficient of Bi can be described as:

$$\ln \gamma_{Bi} = \ln \gamma_{Bi}^{\infty} + \epsilon_{Bi}^{Bi} X_{Bi} + \text{higher order terms} \quad (5.3)$$

Ignoring the higher order terms and plotting the values of  $\ln \gamma_{Bi}$  versus  $X_{Bi}$  should yield a line with a slope equal to  $\epsilon_{Bi}^{Bi}$ . Such an analysis is presented in Figure (5.1). A least squares analysis of the Bi data in that figure yields values of  $\gamma_{Bi}^{\infty}$  and  $\epsilon_{Bi}^{Bi}$  of 2.6 and  $-2.5$  respectively. The former number is in agreement with the value of 2.5 reported in the original paper for  $\gamma_{Bi}^{\infty}$  (Sibanda and Baker, 1979). The value of  $-2.5$  for  $\epsilon_{Bi}^{Bi}$  is similar to the value of  $-2.3$  obtained by Arac and Geiger (1981). However, the reader is cautioned that this may only be a fortuitous condition given the uncertainty in Arac's data as noted earlier.

## 2. First-order ternary interaction parameter, $\epsilon_{Bi}^M$

When the pseudo equilibrium condition was reached during the experimental process, Bi vapor was distributed between the binary and the ternary phases under an equilibrium condition. Accordingly, the chemical potential of bismuth in the binary and ternary phases must be the same,

$$\mu_{Bi}^{\beta} = \mu_{Bi}^{\tau} \quad (5.4)$$

where  $\beta$  and  $\tau$  represent the binary and ternary phases respectively. Since the chemical potential of a species is defined as:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (5.5)$$

the chemical potential of Bi in the binary phase can be represented as:

$$\mu_{Bi}^\beta = \mu_{Bi}^{0,\beta} + RT \ln a_{Bi}^\beta \quad (5.6)$$

Similarly, the chemical potential of Bi in the ternary phase can be represented as:

$$\mu_{Bi}^\tau = \mu_{Bi}^{0,\tau} + RT \ln a_{Bi}^\tau \quad (5.7)$$

where  $\mu_{Bi}^{0,\beta}$  and  $\mu_{Bi}^{0,\tau}$ , equal  $\mu_{Bi}^0$  if the same standard state is selected for the both melts.

Substituting equations (5.6) and (5.7) into equation (5.4), and replacing the standard state chemical potential in the former equations with  $\mu_{Bi}^0$  yields the following relationship:

$$\ln a_{Bi}^\beta = \ln a_{Bi}^\tau \quad (5.8)$$

Using a Taylor series expansion to represent the activity coefficient, the activity for Bi can be expressed as follows:

$$\ln a_{Bi}^\tau = \ln X_{Bi}^\tau + \ln \gamma_{Bi}^\infty + \varepsilon_{Bi}^{Bi} X_{Bi}^\tau + \varepsilon_{Bi}^M X_M^\tau + \text{higher order terms} \quad (5.9)$$

and

$$\ln a_{B_i}^\beta = \ln X_{B_i}^\beta + \ln \gamma_{B_i}^\infty + \varepsilon_{B_i}^{B_i} X_{B_i}^\beta + \varepsilon_{B_i}^M X_M^\beta + \text{higher order terms} \quad (5.10)$$

The mole fraction,  $X_M^\beta$ , should, under ideal conditions be zero.

Equating equations (5.9) and (5.10), neglecting higher order terms and rearranging the results yields:

$$\ln \frac{X_{B_i}^\beta}{X_{B_i}^r} + \varepsilon_{B_i}^{B_i} (X_{B_i}^\beta - X_{B_i}^r) = \varepsilon_{B_i}^M (X_M^r - X_M^\beta) \quad (5.11)$$

Analysis of equation (5.11) reveals that plotting  $[\ln \frac{X_{B_i}^\beta}{X_{B_i}^r} + \varepsilon_{B_i}^{B_i} (X_{B_i}^\beta - X_{B_i}^r)]$  versus  $(X_M^r - X_M^\beta)$  should yield a line with the slope equal to  $\varepsilon_{B_i}^M$ .

For use in the analysis, the value of  $\varepsilon_{B_i}^{B_i}$  has been selected as  $-2.5$ . The value of  $-2.5$  is based on the reviewed analysis of the data obtained by Sibanda and Baker (1979) as presented in the previous section. Although the value for  $\varepsilon_{B_i}^{B_i}$  is only reported for 1373 K, its use at the temperatures employed in this investigation does not pose a serious problem as only a relatively small temperature variation is involved.

## II. Experimental Results of $\varepsilon_{B_i}^M$

The values for the left-hand side of equation (5.11) were calculated using the results in Tables (4.1), (4.2) and (4.3) and plotted versus  $(X_M^r - X_M^\beta)$  in Figures (5.2) through (5.4). The experiments conducted for iron at the lowest

temperature, 1398 K, were equilibrated for periods of 24, 36 and 48 hours. The fact that there is reasonable agreement in the results obtained for the three different time periods suggests that an isopiestic equilibrium condition with regard to Bi was established. Since at the lowest temperature, the greatest segregation of bismuth occurs and kinetic processes are slowest, 48-hour equilibration time was deemed adequate for all experiments.

A least squares technique was used to fit a line to the data points at each temperature as shown in Figures (5.2) through (5.4). The slope of those lines correspond to the first-order ternary interaction parameters, yielding values for  $\epsilon_{Bi}^{Fc}$ ,  $\epsilon_{Bi}^{As}$  and  $\epsilon_{Bi}^{Sb}$  as listed in Table (5.2).

Table (5.2)

First Order Ternary Interaction Parameters  
of Cu-Bi-M system

Temperature	$\epsilon_{Bi}^{Fc}$	$\epsilon_{Bi}^{As}$	$\epsilon_{Bi}^{Sb}$
1398 K	40	7.2	-11
1448 K	8.6	6.8	-11
1473 K	0.73	5.4	-8.1

The values of the first-order ternary interaction parameters have been plotted versus inverse temperature as recommended by Chipman and Corrigan (1967) in Figures (5.5) through (5.7), according to the equation,

$$\epsilon_{Bi}^M = \frac{\eta_{Bi}^M}{RT} - \frac{\sigma_{Bi}^M}{R} \quad (5.12)$$

where  $\eta_{Bi}^M$  and  $\sigma_{Bi}^M$  are the enthalpy and entropy terms associated with the ternary interaction parameter.

Fitting the experimental results to equation (5.12) yields:

$$\epsilon_{Bi}^{Fe} = \frac{1.11 \times 10^6}{T} - 754 \quad (5.13)$$

$$\epsilon_{Bi}^{As} = \frac{4.4 \times 10^4}{T} - 24 \quad (5.14)$$

and

$$\epsilon_{Bi}^{Sb} = -\frac{6.5 \times 10^4}{T} + 35 \quad (5.15)$$

Equation (5.13) should not be applied at temperatures above 1473 K, which is the temperature at which  $\epsilon_{Bi}^{Fe}$  in equation (5.13) equals zero. It is generally accepted that an increase in temperature tends to bring a system closer to ideality and that as a result  $\epsilon_{Bi}^{Fe}$  should approach zero asymptotically as temperature increases. Accordingly,  $\epsilon_{Bi}^{Fe}$  should not switch signs as suggested in equation (5.13). Since equations (5.14) and (5.15) do not switch signs within the

applicable temperature range (1398 K to 1473 K) no problem is anticipated with those equations.

Chipman and Corrigan (1967) have shown that the ratio  $\frac{\eta_j^j}{e_j^j}$  is approximately 42 KJ. Since the value of the ratio is temperature dependent it can only serve to establish the general magnitude expected of  $\frac{\eta_j^j}{e_j^j}$ , provided that the temperature does not approach  $T'$  as defined in Figure (5.5). At the melting point for copper, the value of  $\frac{\eta_{Bi}^{Fe}}{e_{Bi}^{Fe}}$  according to equation (5.13) is approximately 3.5 times the value suggested by Chipman and Corrigan (1967). Although the value of  $\frac{\eta_{Bi}^{Fe}}{e_{Bi}^{Fe}}$  is larger than that of the suggested value it is within the right magnitude. Furthermore, it should be noted that the value of 42 KJ for  $\frac{\eta_j^j}{e_j^j}$  was evaluated at temperatures such that the ratio  $T/T'$  was less than 0.76. That ratio for the present system corresponds to a temperature of 1119 K. Utilizing that temperature and equation (5.13), the ratio of  $\frac{\eta_{Bi}^{Fe}}{e_{Bi}^{Fe}}$  is approximately 39 KJ which compares very favorably with the values reported by Chipman and Corrigan (1967).

A similar evaluation for Cu-Bi-As system, based on equation (5.14), reveals  $T'$  to have a value of 1833 K. At 1398 K the ratio,  $\frac{T}{T'}$ , has a value of 0.76 and  $\frac{\eta_{Bi}^{As}}{e_{Bi}^{As}}$  is found to have a value of 48 KJ which also compares favorably with the value suggested by Chipman and Corrigan.

Unlike the Cu-Bi-Fe system or Cu-Bi-As system, the tightly grouped data with Cu-Bi-Sb system at 1398 K and 1448 K, and the scatter in the data at

1473 K suggests that any attempt to fit the data to equation (5.12) would yield results with a stronger temperature dependence than actually exists. This can be seen in equation (5.15). Deletion of the three smaller negative values for  $\ln\left(\frac{X_{Bi}^\beta}{X_{Bi}^\tau}\right) + \varepsilon_{Bi}^{Bi}(X_{Bi}^\beta - X_{Bi}^\tau)$  at 1473 K would yield a value of  $\varepsilon_{Bi}^{Sb}$  approaching that obtained at the other temperatures. The experimental evidence suggests that  $\varepsilon_{Bi}^{Sb}$  is, over the temperature range investigated, independent of temperature and has a value of  $-11$ . That  $\varepsilon_{Bi}^{Sb}$  is independent of temperature implies that the enthalpy term,  $\eta_{Bi}^{Sb}$ , has a value of zero. Antimony and bismuth form a lens shaped binary phase diagram which is typical of ideal solution behavior (Hultgren et al, 1973). The heat of mixing for such solution is zero. A value of  $\eta_{Bi}^{Sb}$  approaching zero is, thus, consistent with binary phase diagram information.

A caveat regarding the experimental technique and its impact on the values of  $\varepsilon_{Bi}^M$  merits discussion. Analysis of equation (5.11) reveals that as the value of  $X_{Bi}^\beta$  approaches the value of  $X_{Bi}^\tau$ , the first term on the left side of the equation (5.11) is dominant. The distribution of Bi between the two alloys is dependent on the amount of minor element (M) in each phase. The difference in the amount of M in each melt must be large enough such that the difference between  $X_{Bi}^\beta$  and  $X_{Bi}^\tau$  is larger than the uncertainty in the chemical analysis for Bi. If not, the dominant term on the left side of equation (5.11) can switch signs leading to a large scatter in the data as the value of  $(X_M^\tau - X_M^\beta)$  is reduced. In

this investigation, data from all specimens were discarded when the difference in the concentration of Bi in the ternary and binary alloys did not surpass the uncertainty in the analysis. This procedure not only eliminated scatter in the results, but probably also has contributed to larger values for the interaction coefficient. This problem is particularly serious for iron at 1473 K, where the influence of Fe on the distribution of Bi is minimal, resulting in the rejection of over 75% of all data points. The same problem for Cu-Bi-As system was overcome by increasing the concentration of As in the ternary melt. Unfortunately, that practice can lead to the necessity of including second-order interaction parameters in the analysis. Given that consideration the concentration of As in the ternary melts were confined to a maximum of 3.5 wt.%.

The results indicate that  $\epsilon_{Bi}^{Fe}$  is approximately zero at temperatures above 1473 K, but increases rapidly as temperature is decreased. This behavior is consistent with the fact that upon cooling an alloy, through the liquidus surface for copper, both iron and bismuth are rejected from the solid copper matrix.

The experimentally determined values for  $\epsilon_{Bi}^{As}$  suggests that arsenic has a similar effect on bismuth except in a less dramatic manner. Antimony, on the other hand, has been found to promote Bi solubility in molten copper.

### III. Isoactivity Curves

From examination of Figure (5.8), the binary systems which constitute the ternary Cu-Bi-Fe system, it can be concluded that Bi is not compatible with iron or copper. Both the Fe-Bi and Cu-Bi phase diagrams indicate that bismuth is insoluble in both copper and iron in the solid phase, and that no intermetallic compounds are formed between Bi and Cu, and Bi and Fe. A similar situation exists with the Cu-Fe system, except, as shown in Figure (5.8), there is some solid solubility. Again there are no intermetallics. The broad and almost horizontal character of the liquidus curve in the three binary diagrams indicates that near immiscibility exists in the liquid phase. That conclusion is supported in part by the large positive values for the infinitely dilute activity coefficients for constituents in the molten alloys as shown in Table (2.2).

The positive deviation from ideality for both Fe and Bi in molten copper coupled with a repulsion between Bi and Fe (as demonstrated in the Bi-Fe phase diagram) suggests that a first-order ternary interaction parameter may have a dominante effect on activities.

As shown in Figure (5.9), isoactivity curves have been added to the copper rich corner of the ternary Cu-Bi-Fe system. Similary, the isoactivity curves at the copper rich corner of the ternary Cu-Bi-As and Cu-Bi-Sb systems are shown in

Figures (5.10) and (5.11) respectively. The activities have been calculated using the standard analytical expressions for the activity coefficients listed below:

$$\ln \gamma_{B_i} = \ln \gamma_{B_i}^{\infty} + \epsilon_{B_i}^{B_i} X_{B_i} + \epsilon_{B_i}^M X_M \quad (5.16)$$

$$\ln \gamma_M = \ln \gamma_M^{\infty} + \epsilon_M^M X_M + \epsilon_M^{B_i} X_{B_i} \quad (5.17)$$

and

$$\ln \gamma_{Cu} = -\frac{1}{2} \epsilon_{B_i}^{B_i} X_{B_i}^2 - \frac{1}{2} \epsilon_M^M X_M^2 - \epsilon_{B_i}^M X_{B_i} X_M \quad (5.18)$$

The values and sources for the interaction parameters used above are identified in Table (2.2). The values of  $\gamma_{F_e}^{\infty}$  and  $\epsilon_{F_e}^{F_e}$  were taken from the works of Sigworth and Elliott (1974) and Honig, Kirchner and Hillent (1972) as being 19.5 and  $-8$  respectively. The values of  $\gamma_{A_s}^{\infty}$  and  $\epsilon_{A_s}^{A_s}$  were taken from the works of Lynch (1980) and Hino and Azakami (1985) as being 0.0049 and 6.1. The values of  $\gamma_{S_b}^{\infty}$  and  $\epsilon_{S_b}^{S_b}$  were taken from the work of Hino and Toguri (1987) as being 0.013 and 10.7 respectively. The value of  $\epsilon_{B_i}^{B_i}$  was taken as  $-2.5$  as noted earlier and  $\gamma_{B_i}^{\infty}$  was obtained from the following equation:

$$\log \gamma_{B_i}^{\infty} = \frac{1686}{T} - 0.76$$

which was developed from analysis of the results in Figure (2.1).

For molten copper alloys, values of the first-order ternary interaction parameters,  $\epsilon_{Bi}^{Fc}$ ,  $\epsilon_{Bi}^{As}$  and  $\epsilon_{Bi}^{Sb}$ , have been evaluated in this investigation at temperatures between 1398 K and 1473 K. The results indicate the values for  $\epsilon_{Bi}^{Fc}$  range from 40 to 0.73, that values for  $\epsilon_{Bi}^{As}$  range from 7.2 to 5.4, and that  $\epsilon_{Bi}^{Sb}$  is approximately constant at  $-11$  over the stated temperature range.

The isoactivity curves in Figure (5.9) indicate that as the temperature is decreased, the interaction between iron and bismuth has a pronounced effect on the activity of Bi in the alloy. The isoactivity curves for Bi at 1398 K reveal a strong dependence on the concentration of iron. If bismuth behaved ideally the isoactivity curves for that species would be vertical. Instead, at 1398 K and 1448 K the curves are drawn to the left, indicating that the presence of iron in copper increases the activity of bismuth. The effect is nearly gone at 1473 K.

The activity curves in Figure (5.11) are consistent with the negative value of  $\epsilon_{Bi}^{Sb}$ . Activity data for Bi in molten copper reveals positive deviation from ideality, while Sb exhibits the opposite behavior (Hino and Toguri, 1987). The fact that Bi and Sb readily substitute for each other, as suggested by the Bi-Sb phase diagram, implies that antimony in molten copper should draw bismuth into solution with it.

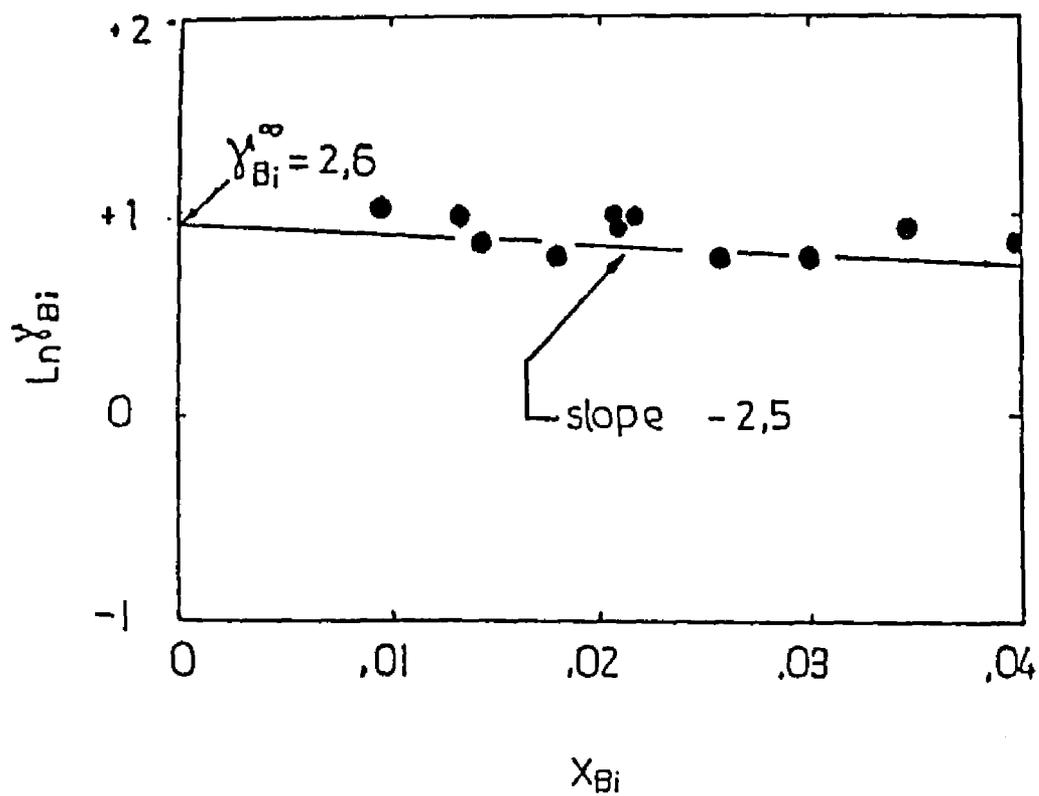


Figure 5.1 Reevaluation from Sibanda and Baker's data for  $\gamma_{Bi}^\infty$  and  $\epsilon_{Bi}^B$

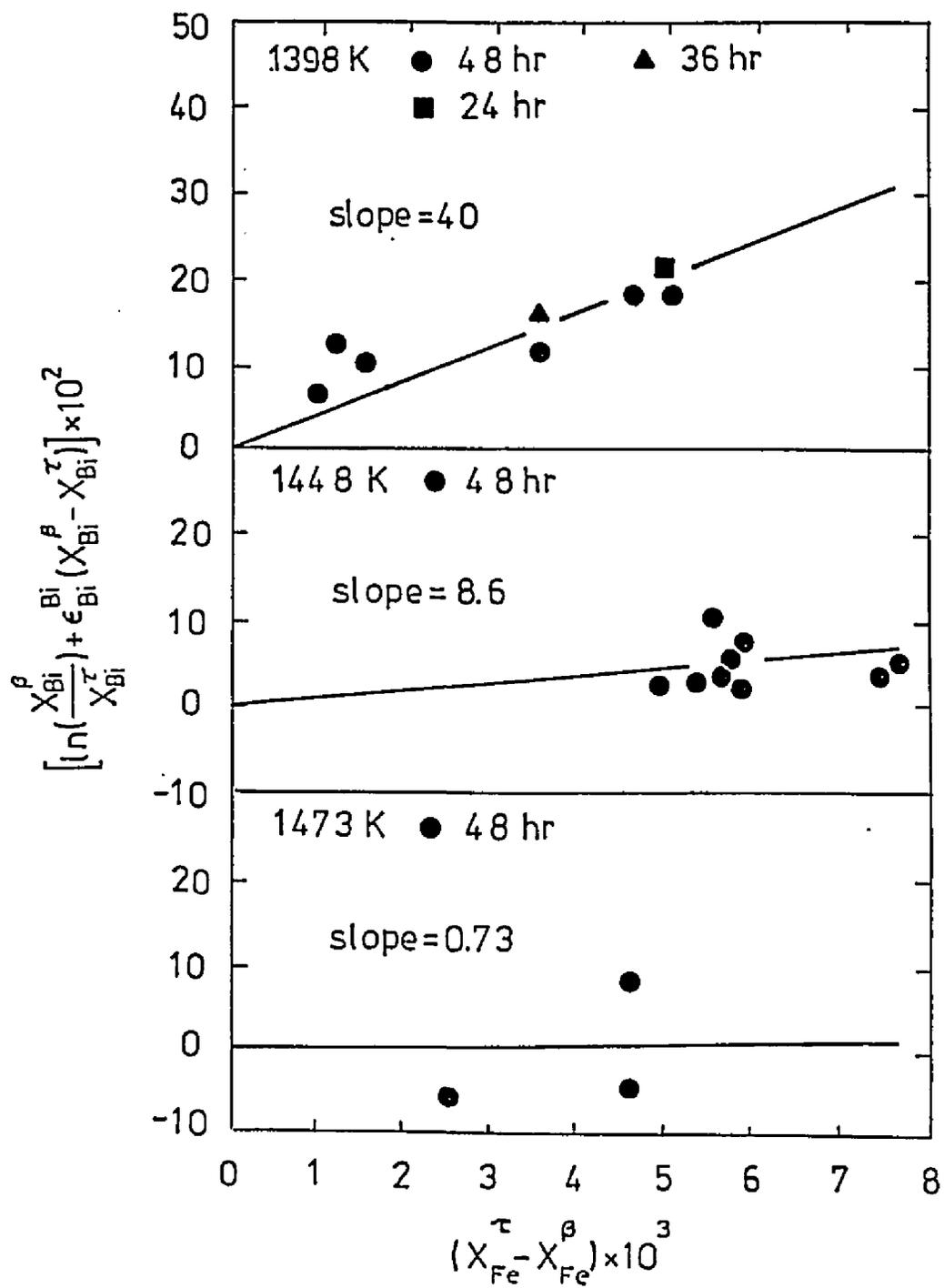


Figure 5.2 Evaluation of data for  $\epsilon_{Bi}^{Fe}$

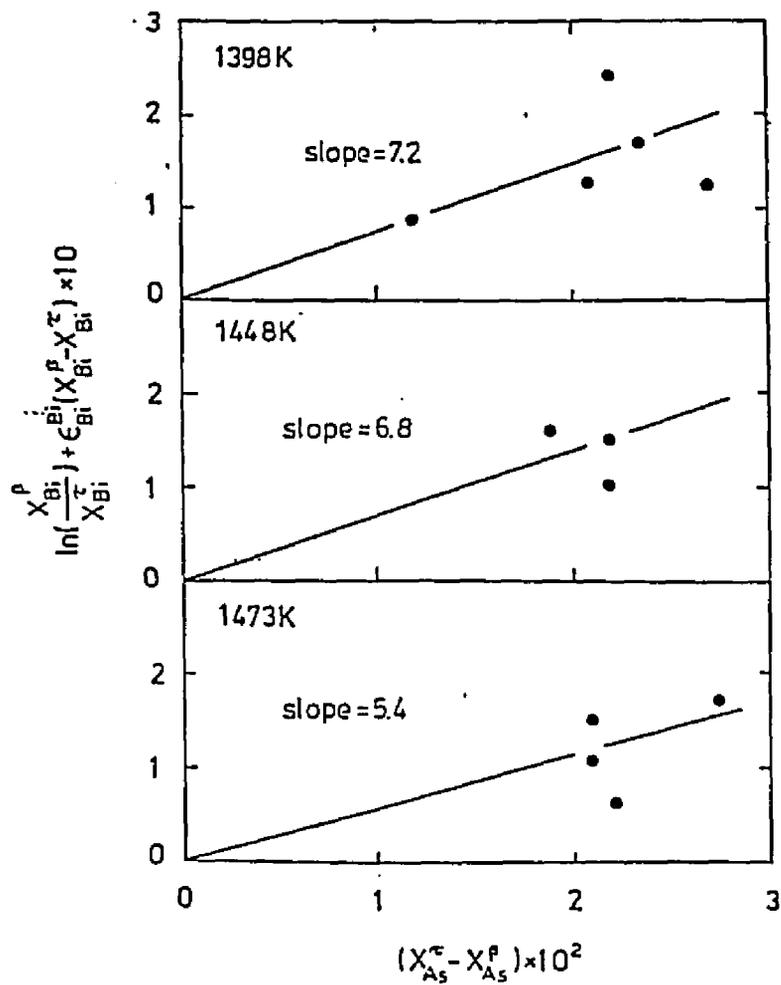


Figure 5.3 Evaluation of data for  $\epsilon_{Bi}^{As}$

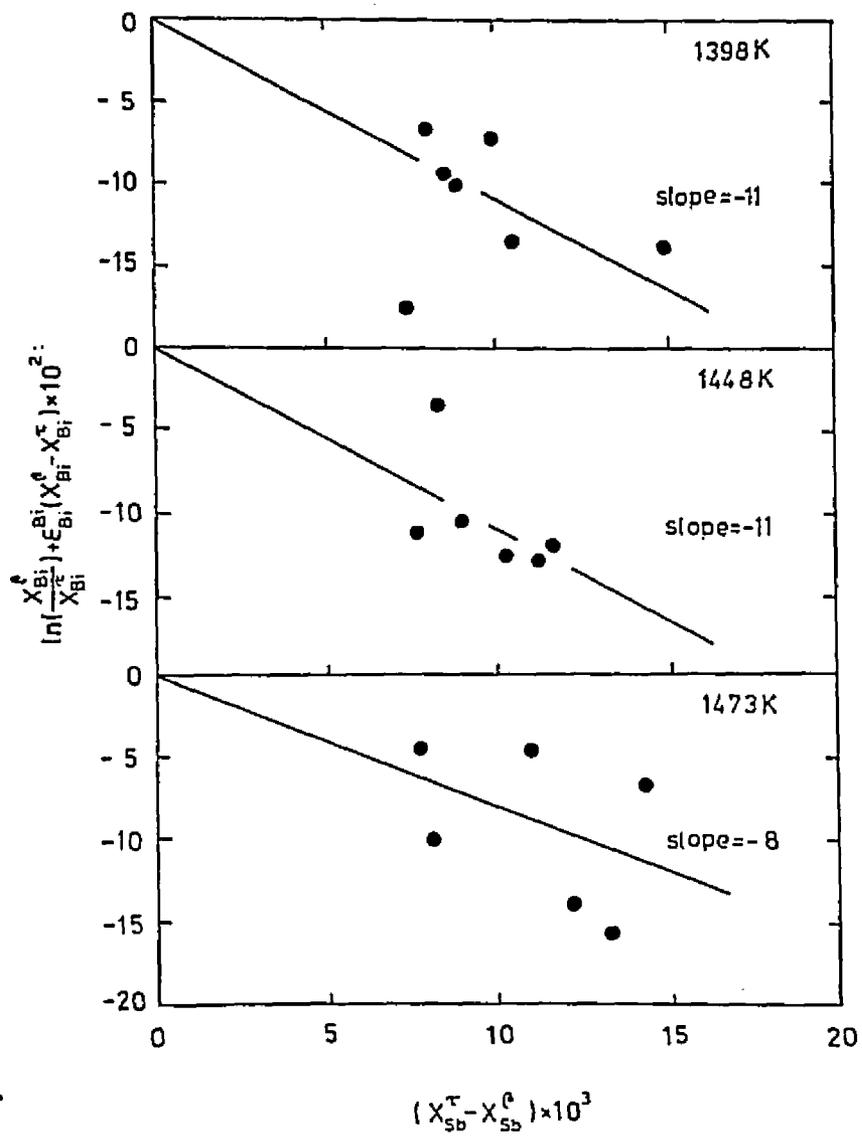


Figure 5.4 Evaluation of data for  $\epsilon_{Bi}^{Sb}$

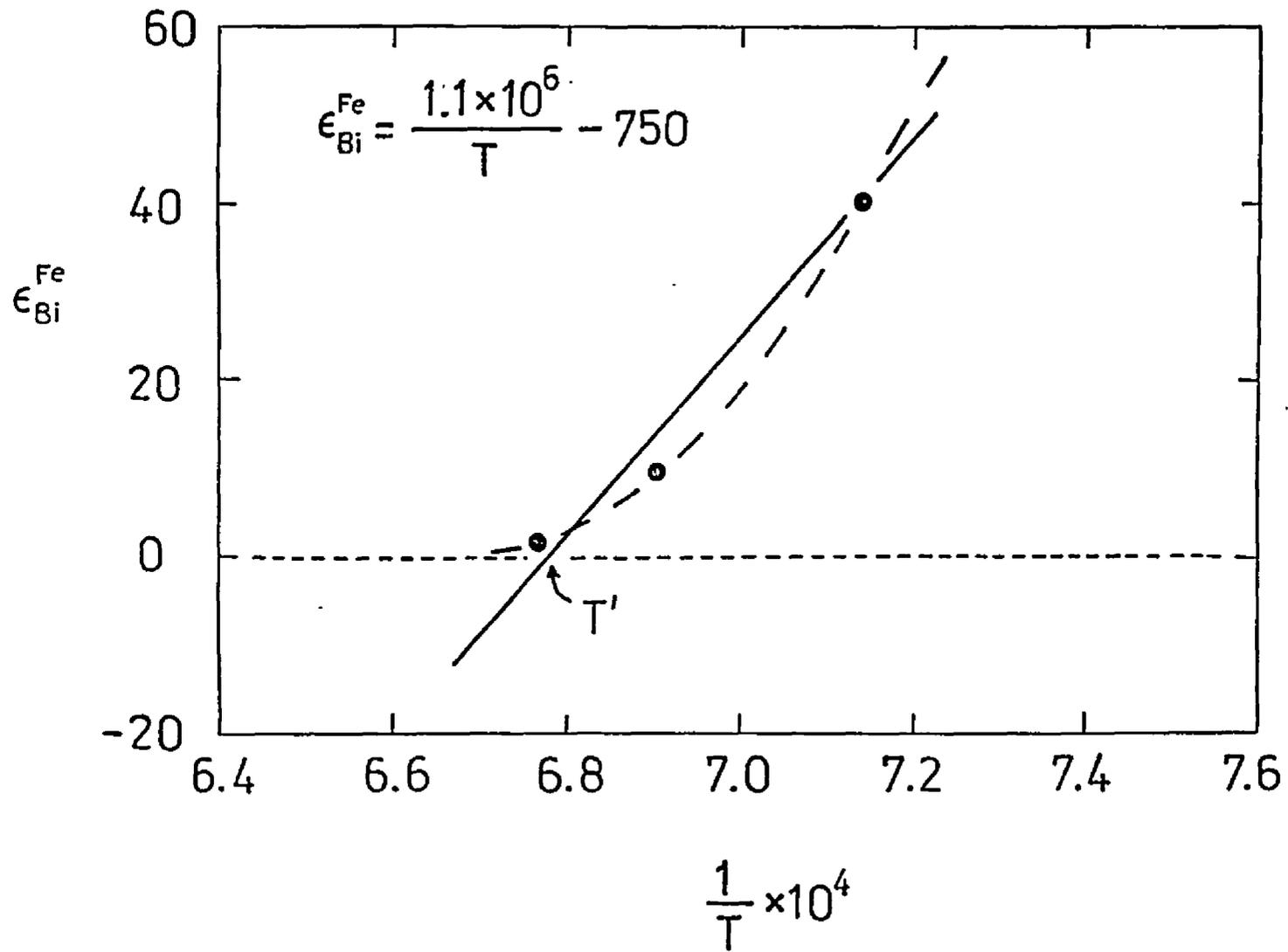


Figure 5.5 Temperature dependence of  $\epsilon_{Bi}^{Fe}$

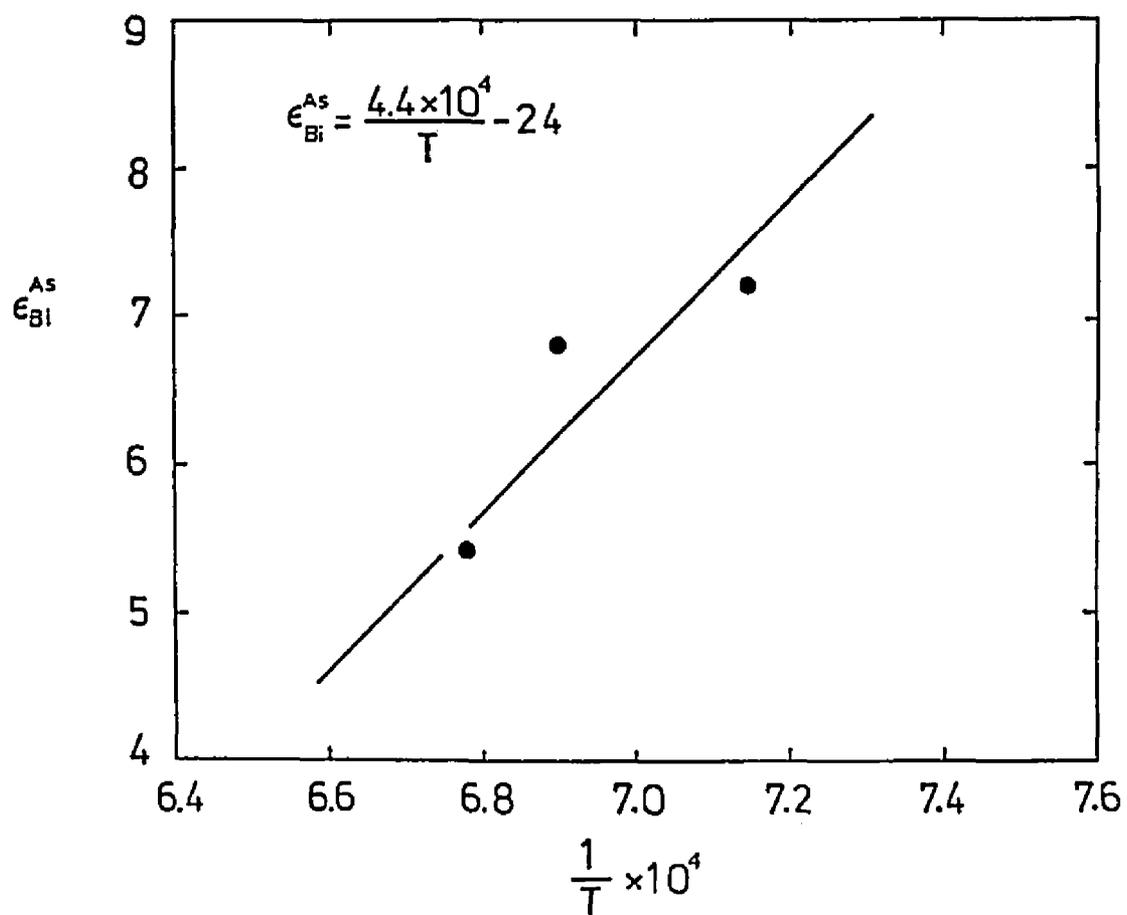


Figure 5.6 Temperature dependence of  $\epsilon_{Bi}^{As}$ .

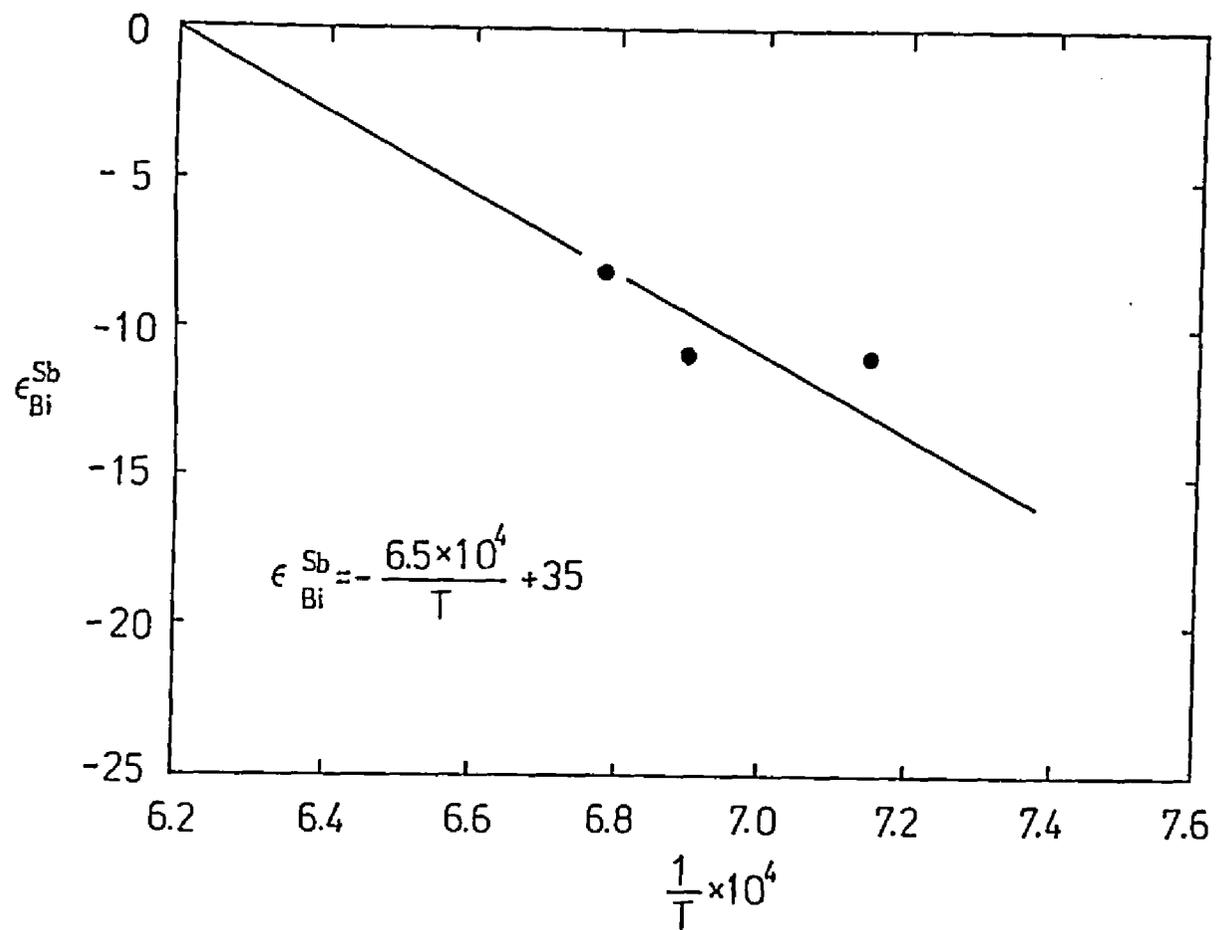


Figure 5.7 Temperature dependence of  $\epsilon_{Bi}^{Sb}$

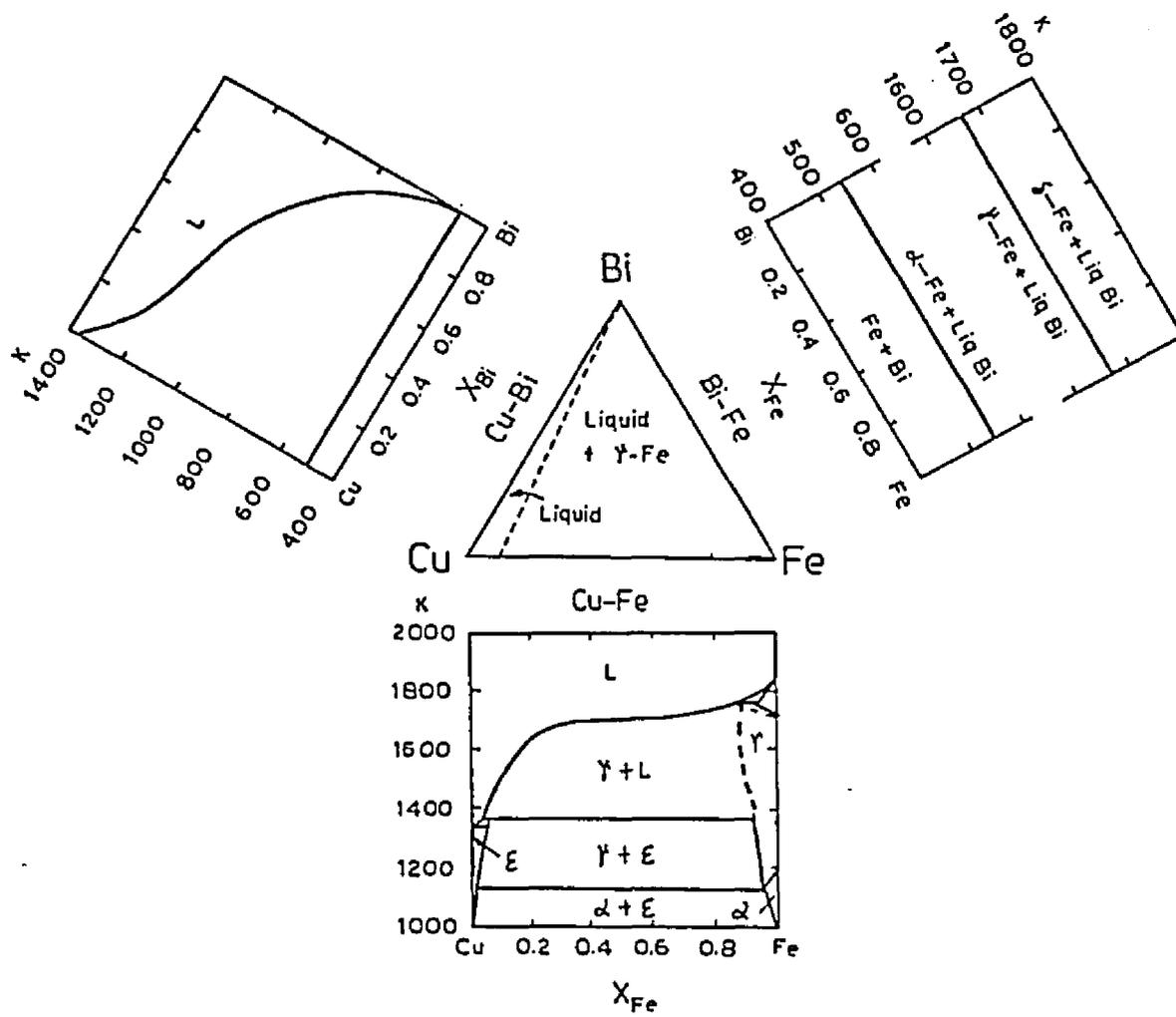


Figure 5.8 Binary phase diagrams for Cu-Bi-Fe system

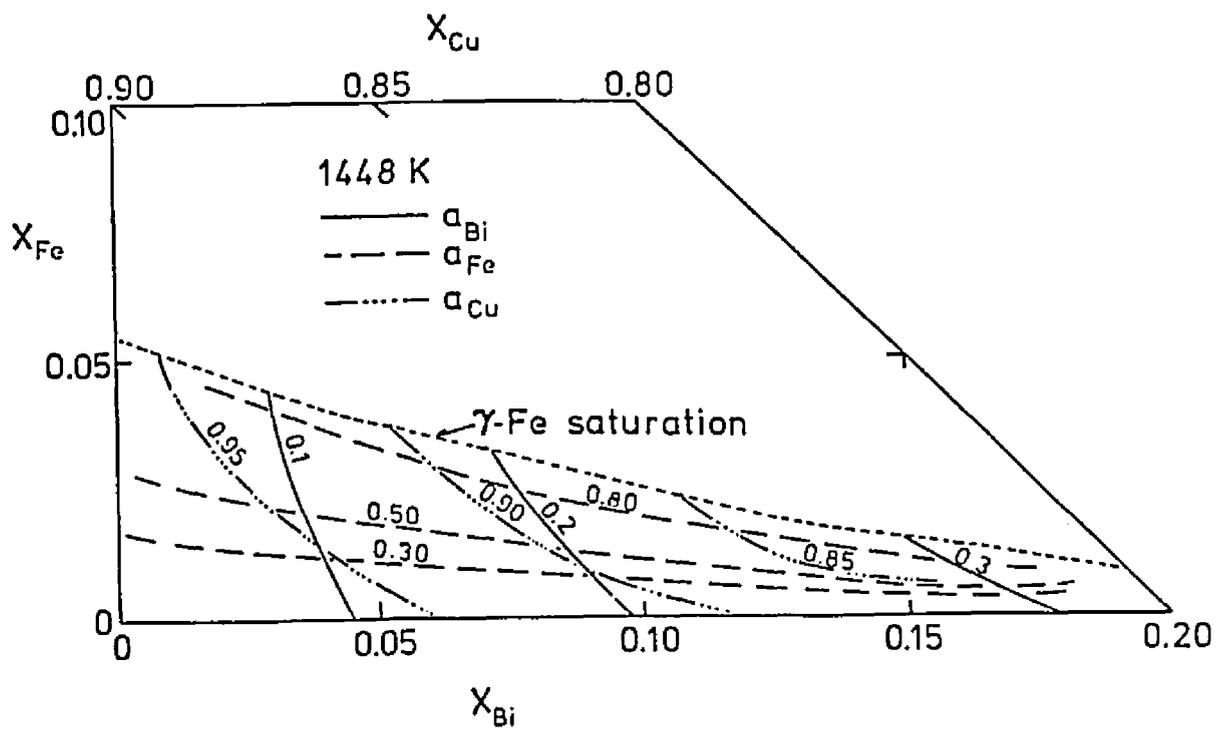
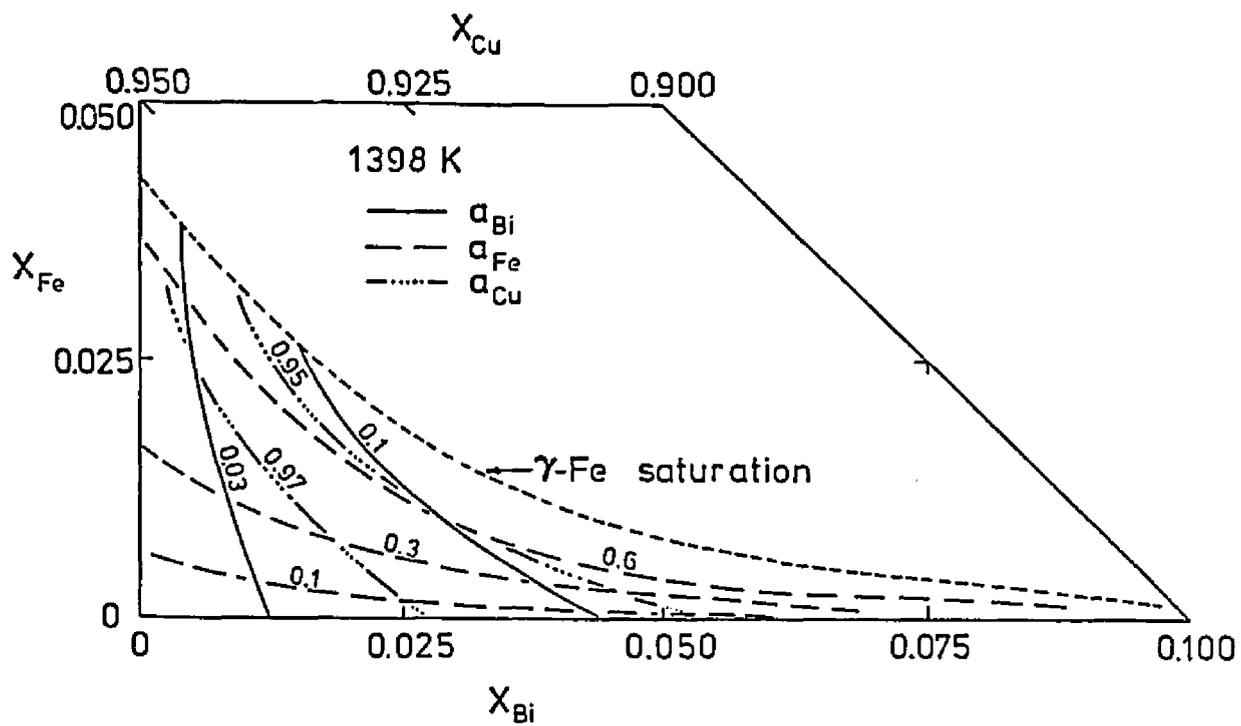


Figure 5.9 Isoactivity curves for Cu-Bi-Fe system

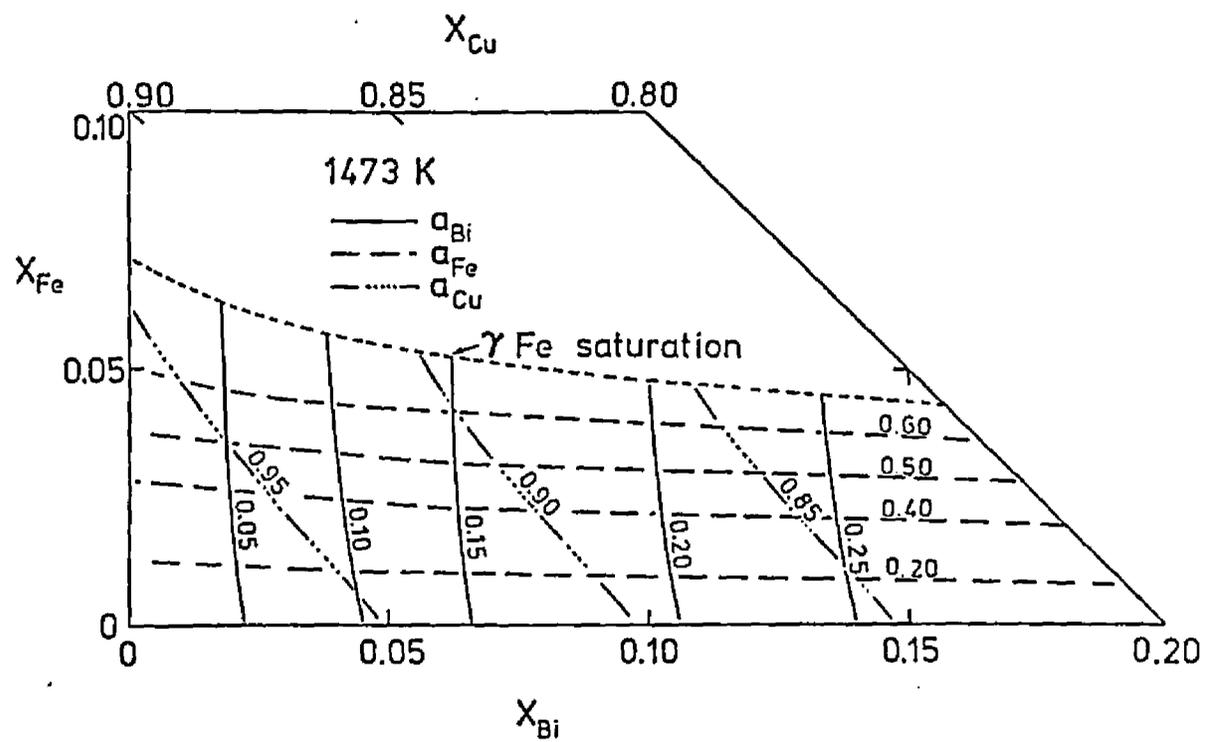


Figure 5.9 Isoactivity curves for Cu-Bi-Fe system

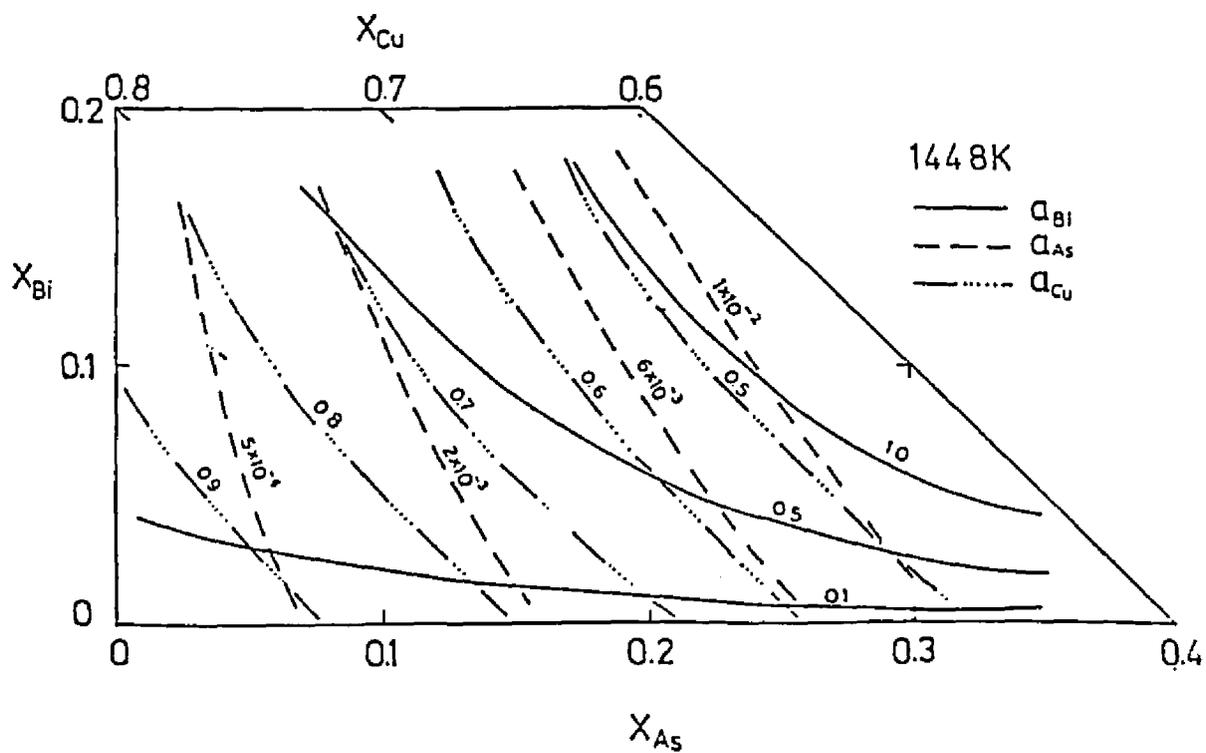
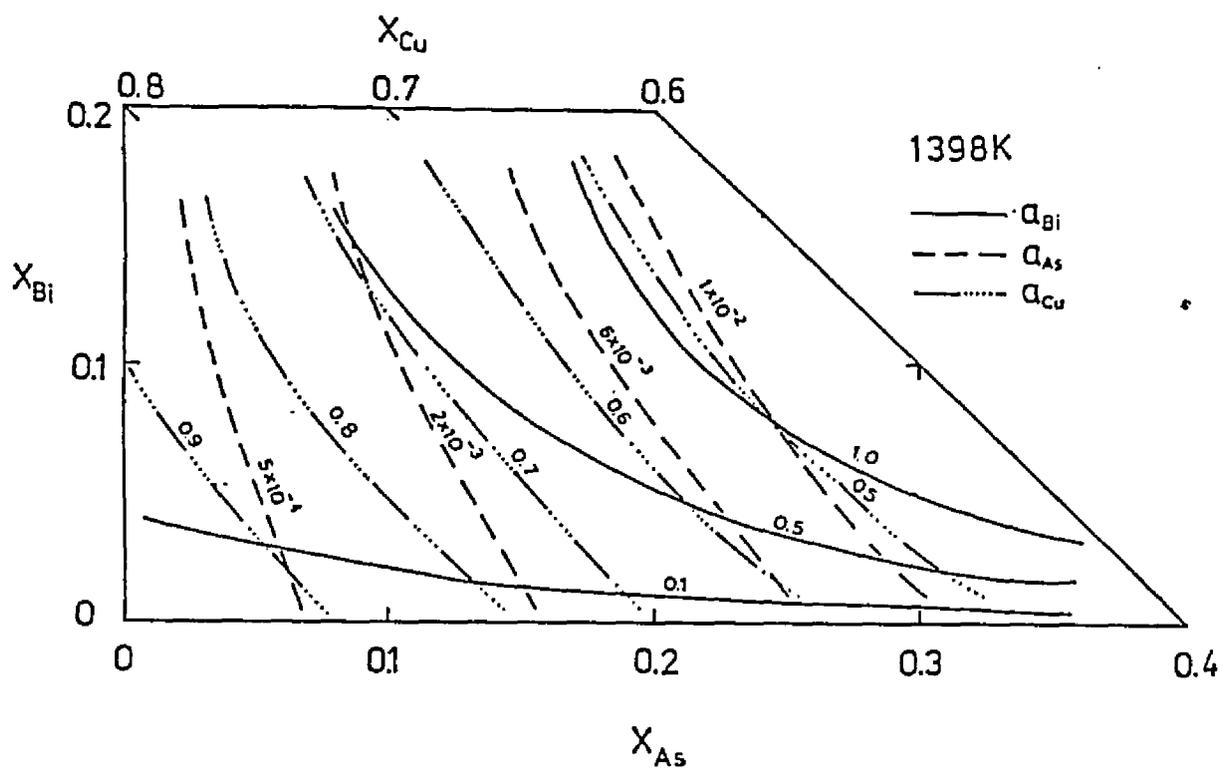


Figure 5.10 Isoactivity curves for Cu-Bi-As system

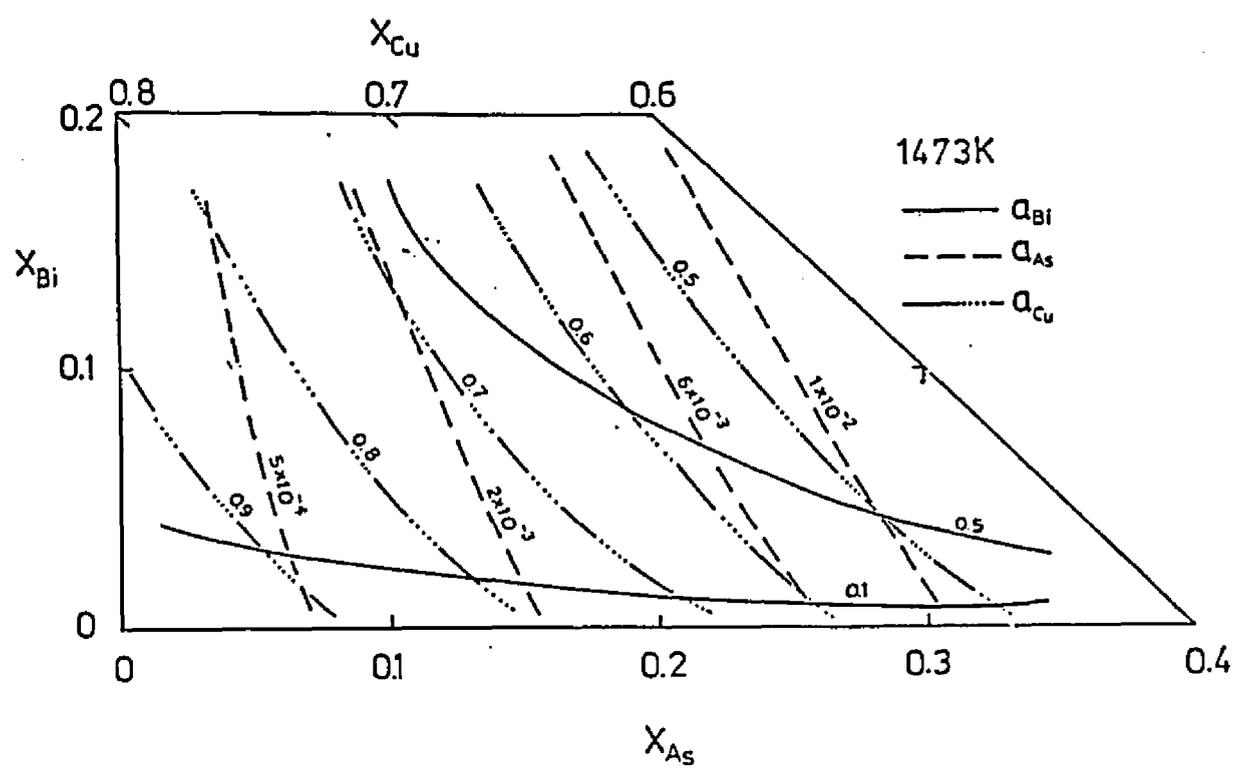


Figure 5.10 Isoactivity curves for Cu-Bi-As system

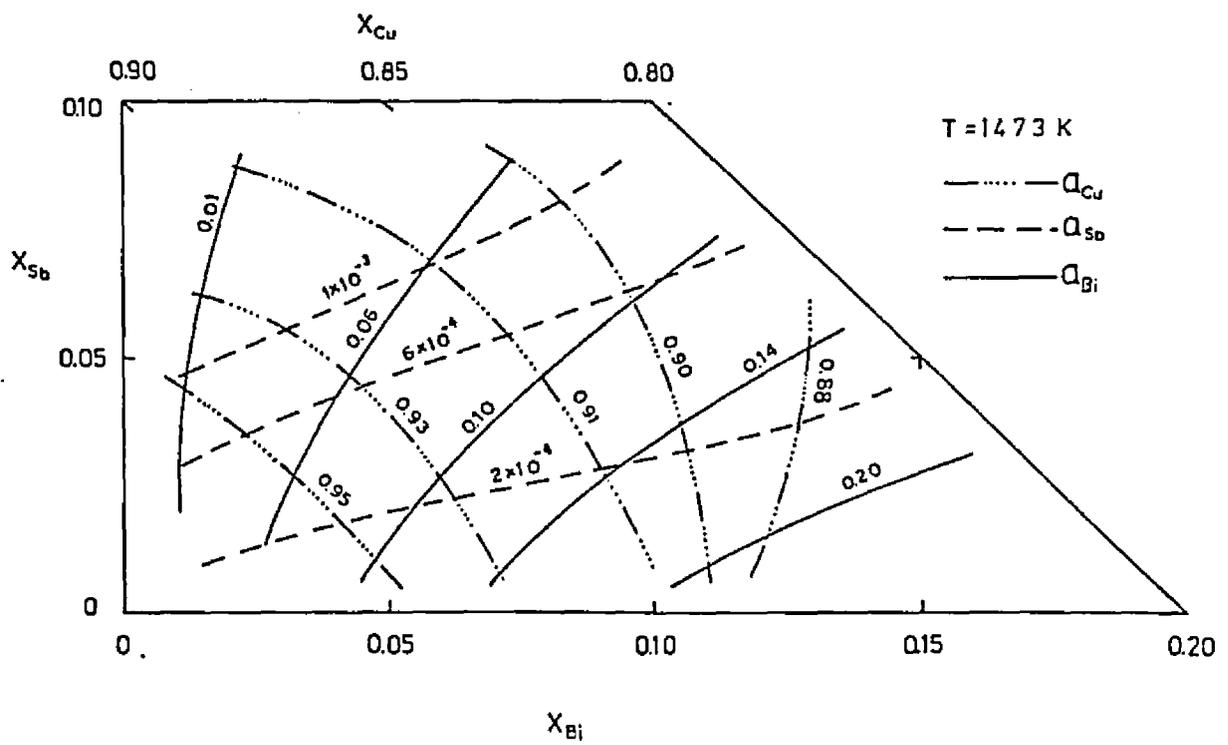


Figure 5.11 Isoactivity curves for Cu-Bi-Sb system

## Chapter 6

### CONCLUSION

To clarify the behavior of impurities in molten copper thermodynamic studies on the behavior of Bi have been carried out utilizing an isopiestic distribution technique in this investigation. The interaction parameters for Bi in liquid copper ternary alloys containing bismuth with iron, arsenic and antimony were evaluated and applied to isoactivity calculations. The following conclusions are made:

1. Generally speaking, the experimental and analytical procedures used in this study produced satisfactory results. The isopiestic distribution technique discussed in chapter Three does require two orders of magnitude of vapor pressure difference between the volatile metal (Bi) and other components (Cu, Fe, As, Sb) in the solutions.
2. The activity coefficient for Bi in Cu have been re-evaluated. The infinite activity coefficient for Bi is summarized as:

$$\log \gamma_{Bi}^{\infty} = \frac{1686}{T} - 0.76$$

and the first-order self interaction parameter,  $\epsilon_{Bi}^{Bi}$ , is  $-2.5$  at  $1423$  K.

3. The first-order ternary interaction parameters,  $\epsilon_{Bi}^{Fe}$ ,  $\epsilon_{Bi}^{As}$  and  $\epsilon_{Bi}^{Sb}$  for bismuth in molten copper have been evaluated at the temperatures between 1398 K and 1473 K. The interaction parameters can be represented by the following equations:

$$\epsilon_{Bi}^{Fe} = \frac{1.11 \times 10^6}{T} - 754 \quad (1398K \leq T \leq 1473K)$$

$$\epsilon_{Bi}^{As} = \frac{4.4 \times 10^4}{T} - 24 \quad (1398K \leq T \leq 1473K)$$

and

$$\epsilon_{Bi}^{Sb} = -11 \quad (1398K \leq T \leq 1473K)$$

4. The experimental results are used to calculate the isoactivity curves for each constituent in the copper rich corner of each ternary system. The experimental results indicate that for the Cu-Bi-Fe system, the first-order ternary interaction parameter strongly affects the activity curves as temperature is decreased, which makes the activity of bismuth much more dependents on the concentration of Fe than that of Bi. For the Cu-Bi-As system, the presence of arsenic increases the activity of bismuth in molten copper. For the Cu-Bi-Sb system, antimony in molten copper should draw bismuth into solution with it.

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