Monatshefte für Chemie 136, 1847–1852 (2005)
DOI 10.1007/s00706-005-0394-8

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Activity of Arsenic in Liquid Cu–Fe Base Alloys

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Received September 12, 2004; accepted March 3, 2005

Summary. The activity of arsenic in liquid Cu–Fe base alloys was determined by isopiestic and *Knudsen* cell-mass spectrometer methods. Based on the activity data, the volatilization of arsenic in the extraction and recycling of copper was thermodynamically evaluated.

Keywords. Data base; Activity; Mass spectrometry; Vaporization.

Introduction

The presence of arsenic in copper causes a deleterious effect on the electrical and mechanical properties of the product. Hence the elimination of arsenic should be taken at the appropriate stages in smelting the sulfide minerals or recycling the copper wastes, most of which are composed of Cu–Fe mixed sulfides and Cu–Fe base alloys, respectively.

The thermodynamic data for arsenic in these liquid substances are of practical importance for evaluating the possibility to eliminate arsenic by means of volatilization as discussed in the work of *Itagaki* [1]. Since very few data have been reported on the thermodynamic properties [2, 3] the activity and activity coefficient of arsenic in the liquid Cu–Fe–As, Cu–Fe–S–As, and Cu–Fe–C–As systems were determined at 1423 or 1473 K.

Results and Discussions

The iso-acivity lines of arsenic in the liquid Cu–Fe–As ternary system at 1423 K, which were determined with an isothermal isopiestic method, are shown in Fig. 1

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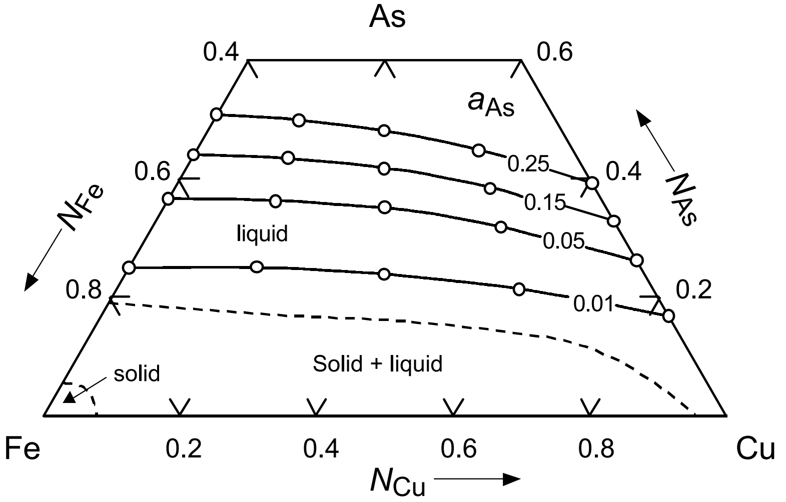

Fig. 1. Iso-activity lines of arsenic in the Fe–Cu–As system at 1423 K

against mol fractions of the alloy. The standard state of activity is pure liquid arsenic.

It is found that the activity in the investigated composition range presents a considerably large negative deviation from *Raoult*'s law, indicating a strong chemical affinity between arsenic and copper or iron in the system. The chemical affinity of arsenic to iron may be stronger than that to copper because each iso-activity line has a fairly negative gradient against the Cu–Fe axis.

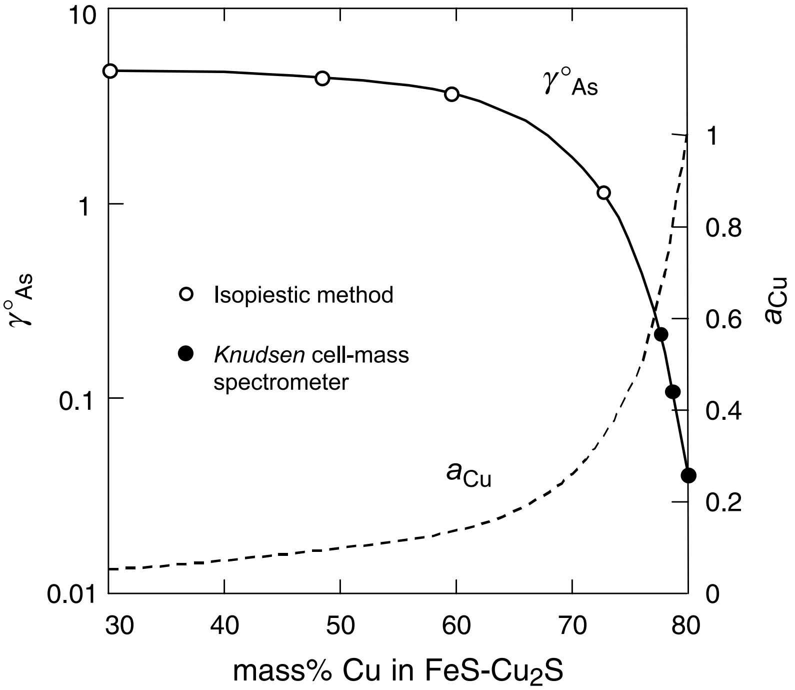

Fig. 2. Limiting activity coefficient of arsenic in FeS–Cu$_2$S matte against matte grade at 1473 K

Raoult's activity coefficient of arsenic at the infinite dilution, $\gamma^{o}{}_{As}$, in the liquid Cu_2S–FeS pseudo-binary system was determined at 1473 K by a non-isothermal isopiestic method and a double *Knudsen* cell-mass spectrometer method. It is shown in Fig. 2 against "matte grade" which is mass% Cu in the mixed sulfide. As regards the production of metallic copper from sulfide minerals, this is an important parameter for the practical smelting of copper since it expresses the degree of desulphurization.

It is found that $\gamma^{o}{}_{As}$ decreases slightly with increasing matte grade up to 65% Cu, but above 70% Cu it changes drastically. The whole change in the range between 30 and 80% Cu is very significant as it extends over two orders from about 5 to 0.04.

Since the activities of iron and copper in the Cu_2S–FeS system have a serious effect on the activity of arsenic as suggested in Fig. 1, they were evaluated according to the work of *Yazawa* [4]. It is evident from Fig. 2 (broken line) that the activity of copper increases drastically in the range of a matte above 70% Cu, whereas the activity of iron is small at about 0.01 in the whole range. This indicates that the observed very steep decrease of $\gamma^{o}{}_{As}$ in the range of higher matte grade is ascribable to the drastic increase of the copper activity in the same range.

The Cu–Fe system saturated with carbon shows a large miscibility gap consisting of a liquid iron-rich and copper-rich phase [5]. The phase relations in the Cu–Fe–As system saturated with carbon were determined at 1473 K. They are shown in Fig. 3 for the mass% ratio of mass% Cu/mass% Fe = 1/1.

It is found that, when arsenic is added to the Fe–Cu system saturated with carbon, arsenic is preferentially enriched in the copper-rich phase with a very small amount of carbon, while carbon is enriched in the iron-rich phase with a smaller amount of arsenic.

Raoult's activity coefficient of arsenic, γ_{As}, in the copper-rich and iron-rich phase of the miscibility gap of the Cu–Fe–As system (saturated with carbon at 1473 K) were derived on the basis of Eq. (1).

$$[a_{As}] = [\gamma_{As}][N_{As}] = \langle\gamma_{As}\rangle\langle N_{As}\rangle = \langle a_{As}\rangle \quad (1)$$

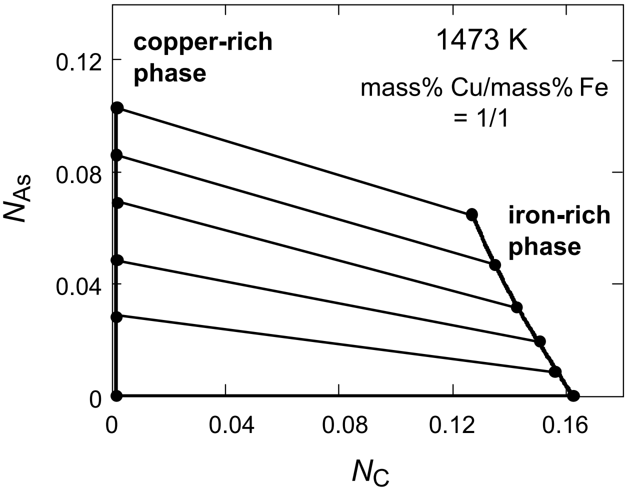

Fig. 3. Miscibility gap of the Cu–Fe–As system saturated with carbon at 1473 K (mass% Cu/mass% Fe = 1/1 in the charge)

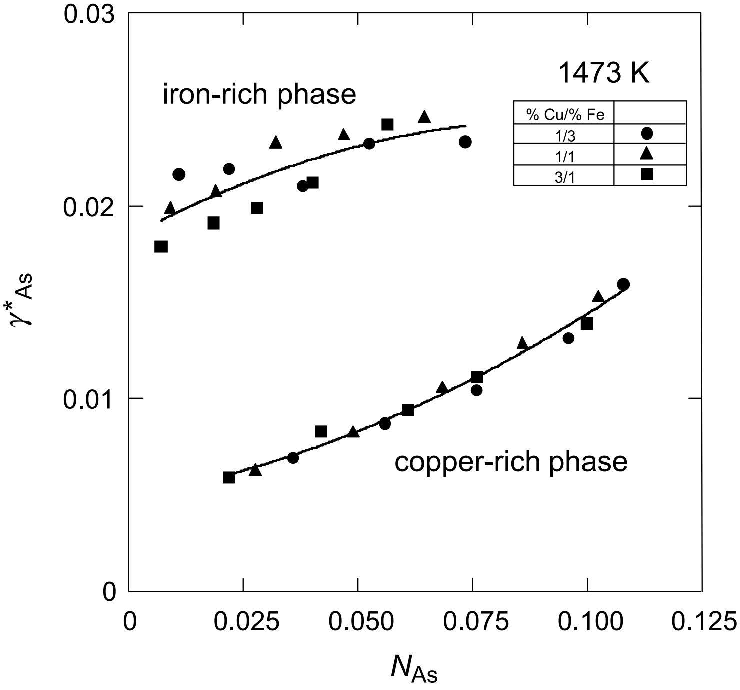

Fig. 4. γ_{As} in the miscibility gap of the Cu–Fe–As system saturated with carbon at 1473 K

where N_{As} is the mol fraction of arsenic, and [ ] and $\langle\ \rangle$ denote the iron-rich and copper-rich phases, respectively. Since the content of carbon in the copper rich phase is very small at about 0.03 mass% as shown in Fig. 3, this phase may be treated as the Cu–Fe–As ternary system. Hence, $\langle\gamma_{\mathrm{As}}\rangle$ in Eq. (1) is known by combining the activity data shown in Fig. 1 with those on the phase relations illustrated in Fig. 3. Then, γ_{As} in the iron-rich phase can be derived from Eq. (1), in relation to the arsenic content.

The activity coefficients of arsenic (the standard state of activity is pure liquid arsenic) in the iron-rich and copper-rich phase of the miscibility gap in the carbon saturated Cu–Fe–As system are shown in Fig. 4 in relation to the arsenic content in both phases. The data refer to a temperature of 1473 K and mass ratios of mass% Cu/mass% Fe = 1/3, 1/1, and 3/1.

It is noted that the activity coefficients in both phases present considerably small values of less than 0.03. It is also found that, at a given arsenic content, the activity coefficient in the iron-rich phase is about two times larger than that in the copper-rich phase. On the contrary, according to the activity data for the Fe–As and Cu–As binary systems, the activity coefficient of arsenic in the Fe–As system is smaller than that in the Cu–As system [6, 7]. This discrepancy may be ascribed to the effect of carbon in the iron-rich phase with the amount of 3–4 mass%. It is considered that the interaction between arsenic and iron may be weakened due to the strong chemical affinity of carbon to iron.

Using the data obtained in the present experiments, the possibility of eliminating arsenic in the Cu–Fe–As alloy by means of volatilization was thermodynamically evaluated as follows.

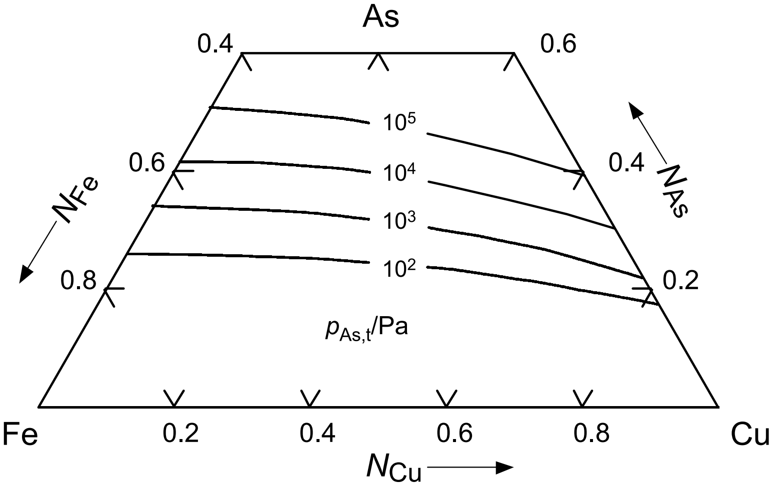

Fig. 5. Arsenic isobars (total arsenic pressure) in the Fe–Cu–As system at 1423 K

The predominant gas species over the liquid Cu–Fe–As alloy at 1423 K are As, As_2, As_3, and As_4. Hence, the total pressure of arsenic, $p_{As,t}$, is given by Eq. (2).

$$p_{As,t} = p_{As} + p_{As_2} + p_{As_3} + p_{As_4} \qquad (2)$$

On the basis of equilibrium constants for the reactions to form these gaseous species from pure liquid arsenic [1], and combining the activity values of arsenic shown in Fig. 1, the iso-total pressure lines were calculated at 1423 K and are shown in Fig. 5.

It is found that at considerably high contents of arsenic (N_{As} around 0.4) $p_{As,t}$ is of the order of 10^4 Pa, whereas it amounts to about 10^2 Pa in the composition region near the solidus line in the Cu–Fe–As system. According to the work of *Kellogg* [8] vaporization of an alloying element in a gas stream is rapid when the vapor pressure exceeds 10^4 Pa, whereas it is slow when the pressure is less than 10^2 Pa. According to this criterion, the elimination of arsenic by means of volatilization will be difficult for the Cu–Fe–As alloys with the compositions near the solidus line. Hence, use of vacuum will be required for these alloys to enhance the volatilization.

Experimental

The activity of arsenic in the liquid Cu–Fe–As system was determined by using an isothermal isopiestic method. Pre-melted and homogenized Cu–As and Fe–As binary alloys and three Cu–Fe–As ternary alloys with different mol fraction ratios, N_{Cu}/N_{Fe}, of 1/3, 1/1, and 3/1 were sealed in vacuum in a quartz isopiestic ampoule of 0.09 m length and 0.06 m *ID*. The ampoule was kept at the experimental temperature of 1423 K for 605 ks during the equilibration process. Thereafter, the ampoule was quenched in a water vessel. The copper, iron, and arsenic contents of the solidified alloys were determined by Inductively Coupled Plasma Spectrometry (ICP).

As the vapor pressures of iron and copper over the alloys were very small compared with that of arsenic, the five alloy samples were saturated with the vapor pressure of arsenic in the ampoule. The activity of arsenic in each alloy was therefore considered to be in the equilibrium condition. Thus, if the activity of arsenic in any one of the samples is known as a reference, the arsenic activity in other samples can be determined. In the present study, the Cu–As binary alloys, whose activities were reported by *Hino* and *Azakami* [7], were used as the reference.

The activity of arsenic in the liquid Cu_2S–FeS–As pseudo-ternary system was determined by using a non-isothermal isopiestic method and a double *Knudsen* cell-mass spectrometer method. Depending on the measurable range of vapor pressure, the former was used for the system with the mass% ratios of Cu_2S and FeS less than 7.1, whereas the latter was used for ratios higher than 15.4. The starting Cu_2S and FeS samples were synthesized by a pyrometallurgical method with sulfur and metal powders (99.99% purity).

In the isopiestic method, the Cu_2S–FeS sample and pure arsenic (99.99% purity) were kept in a higher temperature region (1423 K) and the minimum temperature region of a vacuum-sealed quartz container with 7×10^{-3} m *ID*, respectively. After the equilibrium time of 252 ks, the assembly was rapidly cooled in a water vessel. The arsenic content of the quenched specimen was determined by ICP. The vapor pressures of arsenic gas species were calculated by using the thermodynamic data [1]. The vapor pressures of sulfur and sulfide gas species over the Cu_2S–FeS–As system at 1423 K are very small compared with those of arsenic gas species. Hence, the activity of arsenic could be determined on the basis of a principle that the total pressure is even within a closed container. *Raoult*'s activity coefficient of arsenic at the infinite dilution was derived from the obtained relationship between the arsenic activity and the composition of arsenic in the system.

The activity of arsenic in the Cu_2S–FeS–As pseudo-ternary system was also determined by the double *Knudsen* cell-mass spectrometer method [9]. The sample under study was placed in separate alumina crucibles with 0.01 m *ID* in a cell holder, together with a reference sample with a known activity of arsenic. The unknown activity was determined from the known activity of the reference sample and the ratio of ion intensity of arsenic gas species over the unknown sample to that over the reference sample measured by the mass spectrometer. The reference samples employed in the present study were the Cu–As binary alloys with $N_{As}=0.059$ and 0.100. Their respective activities were determined by *Hino* and *Azakami* [7].

The phase relations in a miscibility gap of the Cu–Fe–As system saturated with carbon were determined by using a quenching method. The sample together with a graphite rod was charged in a magnesia crucible, and then vacuum-sealed in a quartz ampoule of 0.026 m *ID*. It was heated and kept at 1473 K for 43.2 ks when the equilibration was attained. Thereafter, it was quenched in a water vessel and the solidified samples were chemically analyzed for their components.

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