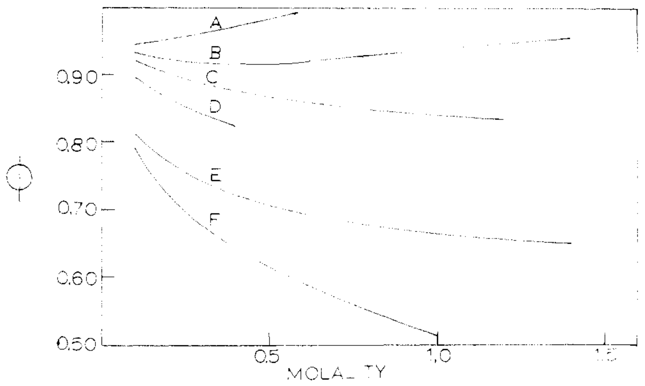

Figure 2. Osmotic coefficients at 25 °C: (A) methanesulfonic acid, (B) sodium methanesulfonate, (C) sodium sulfamate, (D) sodium iodate, (E) sulfamic acid, (F) iodic acid.

that of the salts (about 0.1%).

Stoichiometric activity coefficient data are plotted in Figure 1 for the sodium salts of methanesulfonic, sulfamic, *p*-toluenesulfonic, and sulfanilic acids, and the behavior is rather unexpected. The methanesulfonate curve lies far above the sulfamate curve. This is not surprising when one realizes that the replacement of the CH_3 group by a NH_2 group permits the linear association of the sulfamate anions especially if resonance structures of the type $H_2N^+ = SO_3^{2-}$ are at all important. The surprising relationship is that between the aromatic compounds where the sulfanilate curve lies above the *p*-toluenesulfonate curve. Similar relationships also hold true for the potassium salts of these acids.

The order of osmotic coefficients for a strong acid and its salts at any concentration is $H^+ > Li^+ > Na^+ > K^+$, an order due primarily to the differing degrees of hydration of the cations. Incomplete ionization causes the coefficient of an acid to be smaller than that of its salts. The ratio of the coefficients of an acid and its sodium salt at any concentration gives a rough idea of the degree of ionization since the solvation effect of the anion is largely compensated, especially in the case of fairly large anions (*6*). The coefficients of the sulfamates and iodates of Figure 2 suggest that the ionization constants of the two acids are probably not too different with sulfamic acid being a slightly stronger acid than iodic acid rather than a slightly weaker acid as was calculated from emf and conductance measurements. Methanesulfonic acid, which contains the CH_3 rather than the NH_2 group, is a strong acid, as is shown by the coefficients of the acid and the sodium salt (*7*, *8*).

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Equilibrium Distribution Coefficients of Lead, Copper, and Cadmium in Tin

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The equilibrium distribution coefficients of lead, copper, and cadmium in tin were obtained by using a modified zone refiner. This refiner is characterized by alternating high-speed clockwise and anticlockwise rotations (0–3000 rpm) of the containing tube at short intervals (0.5–10 s) resulting in a thin diffusion layer thickness. The equilibrium distribution coefficients k_0 of these impurities in tin were 0.14 (Pb), 2.0 × 10^{-2} (Cu), and 0.48 (Cd), and these values showed good correspondence to those estimated from the phase diagram.

It is important to know the distribution coefficient of a solute in planning a zone refining experiment or process. The methods of determining the equilibrium distribution coefficient are generally classified into three groups: (a) use of a phase diagram, (b) a thermodynamic method based on the laws of dilute solution, and (c) calculation from an effective distribution coefficient obtained by experiment (*1*). In method a, it is inevitable that the phase equilibrium in a desired binary system near the end composition should be accurately and clearly known. An accurate phase diagram, however, is not available at the desired concentration, especially for very dilute solutions. In method b, solutions would be assumed to be ideal solutions. In general, however, solutions are not ideal enough to permit more than a rough estimate of the equilibrium distribution coefficient. Therefore, in the present paper, the equilibrium distribution coefficient was obtained by method c, and these values were compared with those estimated from phase diagrams.

According to Burton et al. (*2*), if the zone travel rate is constant and the diffusion of the impurity in the solid is negligible, the effective distribution coefficient can be expressed by eq 1. By rearranging eq 1, one obtains eq 2a and 2b.

$$k_0/k = k_0 + (1 - k_0)\exp[-f\delta/D] \qquad (1)$$

$$\ln(1/k - 1) = \ln(1/k_0 - 1) - f\delta/D \qquad \text{for } k < 1 \qquad (2a)$$

$$\ln(1 - 1/k) = \ln(1 - 1/k_0) - f\delta/D \qquad \text{for } k > 1 \qquad (2b)$$

Therefore, by measuring the effective distribution coefficient in the material refined at different zone travel rates with identical stirring conditions, one can obtain the value of the equilibrium distribution coefficient from the intercept of the line plotting ln $(1/k - 1)$ or ln $(1 - 1/k)$ against the zone travel rate.

The zone refining apparatus used in this work is especially intended to make the diffusion layer thickness a minimum and has a characteristic of high-speed clockwise and anticlockwise

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Table I. Effective Distribution Coefficients of Lead, Copper, and Cadmium in Tin[a]

	effective distribution coefficient k									
impurity f^b	0.26	0.29	0.33	0.53	0.74	1.00	1.18	1.22	1.79	2.00
Cu	0.038	0.035	0.046				0.26	0.30	0.64	0.67
Pb	0.19	0.21		0.35		0.49	0.56	0.54	0.64	
Cd	0.56		0.56		0.71	0.78	0.80			0.92

[a] Experimental conditions: sample size, 6 mm in diameter, 10 cm long; zone length, 3 cm; alternating period, 1.0 s; rotation velocity, 500 rpm. [b] f = zone travel rate (mm/min).

Table II. Equilibrium Distribution Coefficients of Lead, Copper, and Cadmium in Tin

	this study	phase diagram
Pb	0.14 ± 0.03	≈0.1
Cu	0.02 ± 0.004	0.01-0.001[a]
Cd	0.48 ± 0.02	≈0.3

[a] General value in the case of binary eutectic.

rotations (0–3000 rpm) of the container which is made of a Pyrex glass tube of 8-mm o.d. and 45 cm long and placed vertically. The apparatus is composed of three main parts: (a) heaters and heater control unit, (b) clockwise and anticlockwise rotation mechanism of the container, and (c) heater driving unit. The mechanism of zone travel is simple. As an Archmedes cam rotates, a brass pole which is connected to the heaters goes up at a constant speed. Five resistance heaters are placed around the container at 5-cm intervals. The heaters currently in use are helical coils of Nichrome wire bent into about 25-mm i.d. circular configuration. The heaters are temperature controlled independently. In this work, however, only the bottom heater was used to obtain the effective distribution coefficient. The container is cooled by compressed air streaming from sets of orifices which protrude from the brass pole. Heaters gradually move 5 cm upward and fall rapidly to the initial position, thus transferring each zone to the upper heater. The details of the experimental setup are reported elsewhere (*3*).

Experimental Section and Results

The samples for the determination of the equilibrium distribution coefficient were prepared by adding 1000 ppm lead, copper, and cadmium to 99.99% pure tin shot from Wako Pure Chemical Industries. After the tin shot was melted in a high-purity graphite crucible under vacuum and made homogeneous, it was then transferred to a glass tube and sealed at about 0.1 Pa. Before the tin bar was purified, the homogeneity of impurities was ascertained by means of graphite furnace atomic absorption spectrometry (GFAAS). The concentration of each impurity was 1000 ± 50 ppm. This fact indicates that the homogeneity of impurity is well assured by this method of sample preparation within the precision of analysis. The effective distribution coefficient was obtained in the following manner in this work. When the mean concentration of impurity in the charge is C_0, the initial concentration to freeze at $x/L = 0$ is kC_0 by definition. Therefore, the effective distribution coefficient is obtained by taking the ratio of the concentration of the initially purified charge to that of the original charge.

The concentration of impurities in the sample was determined by GFAAS after approximately 100 mg of filings was taken from near the starting point of zoning (about 2–3 mm) and dissolved in mixed acid of 10 mL of 10% tartaric acid, 2 mL of hydrochloric acid, and 1 mL of nitric acid as directed by Varian-Techtron (*4*).

Table I shows the effective distribution coefficient obtained at various zone travel rates. These values were fitted to eq 2a by using the method of least squares. The results are shown in Figure 1. The coefficient of determination for the calculated lines is in the range of 0.998–0.999. The calculated values of the equilibrium distribution coefficient obtained from the intercept of the line in Figure 1 are listed in Table II together with the estimated values from the phase diagram (*5–7*). The error in determining the equilibrium distribution coefficient by this method is mainly due to slightly scattered values of the effective distribution coefficient. The error in Table II was estimated from the extrapolation lines in Figure 1. As the correspondence of both values is fairly good, this method would be applicable to the determination of the equilibrium distribution coefficient for various binary systems for which phase diagrams have not been accurately constructed yet.

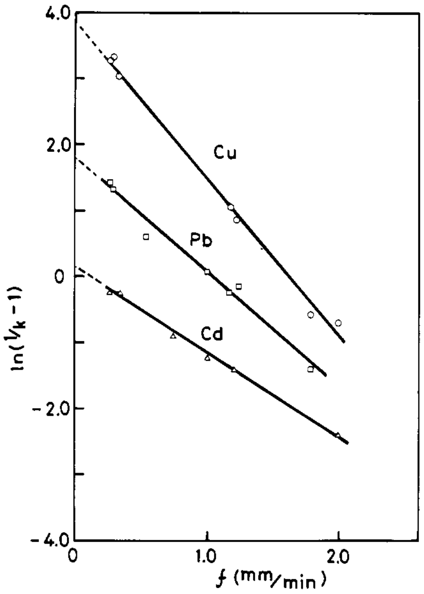

Figure 1. Relation between ln ($1/k - 1$) and the zone travel rate in zone refining of tin. Impurity: (□) Pb, (○) Cu, (△) Cd.

Glossary

k_0	equilibrium distribution coefficient
k	effective distribution coefficient
f	zone travel rate
δ	diffusion layer thickness
D	diffusion coefficient of the solute

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