Activities in Liquid In-Hg Alloys*

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An attempt was made to apply the TIE method at room temperature to measurement of the activities in liquid In-Hg alloys.

The accuracy in the present study cannot be assumed better than the studies at the elevated temperatures contrary to our expectation, but the measured activities of both components seem to be reasonable compared with the literature values.

It is to be noted that there appeared constant activities in the concentration range of $N_{\text{In}}=0.3$ to 0.4.

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I. Introduction

In the past decade, a series of investigations has been made to know the availability of the TIE method at the elevated temperatures^{(1)~(9)†}. A problem still remains to determine the activity more precisely in the case that a reaction occurs between the liquid alloy and the electrolyte⁽¹⁾⁽²⁾⁽⁸⁾. Another approach to study this problem is to make an attempt to apply the TIE method at room temperature.

Since a rapid decrease in the reaction rate is, in general, expected with decreasing tempera-

ture, the TIE study at the room temperature can be expected to become a key to the understanding of the reaction rates in a more direct manner than has heretofore been done, together with measuring of reliable activities. One of the advantages in the present study lies in that the injection of the electrolyte may become visible.

To attack these problems, the activities of two components in the liquid In-Hg alloy were at first measured by employing aqueous solutions as the electrolyte and subsequently the application of the present method was extended to the investigation of the reaction rate between the liquid alloy and the electrolyte. The measurements of the reaction rate will be reported separately.

II. Experimental Apparatus

Indium of 99.9+ % purity and mercury of the highest commercial grade were employed for alloying and the standard electrodes, and $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ of 99+ % and HgCl_2 of the highest reagent grade for the electrolytes.

Figure 1 illustrates the two different cell types employed for measuring the activities. The *H*-shaped cell container was made of the first-class hard glass, having an injection side tube for the electrolyte. The cell having the side tube in the middle is called type (*A*). The cell in which the left tube has the side tube, called type (*B*), and this shape cell was adopted to measure the activities of the component mercury.

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† The e.m.f. values of the concentration cells were measured under the experimental conditions of uniform temperatures and homogenized molten electrolyte and alloy concentrations. Furthermore, the e.m.f. measurements by the TIE method had no effect of the dissolution of the metals into their molten salts. It must be emphasized that there was passage of nearly zero current in the concentration cell because the synchroscope has impedance above 1 megohm and the determined component activities have been verified to be highly reliable.^{(1)~(3)(6)~(8)} Consequently, the experimentally determined e.m.f. may be regarded as being equal to the reversible e.m.f. of the concentration cell, and the maximum work efficiency of the cell can thus be obtained corresponding to the equilibrium potential of the cell reaction.

† Measure d is varied in reaction rate study.

Fig. 1 Cells for e.m.f. measurements.

Since the temperature fluctuations in the laboratory ranged from 12 to 24° during the experiments covering a period of several months, the cell was positioned in an air thermostat maintained at 25°C, which was constituted from a nichrome-winding glass container covered with an asbestos plate, in particular, without using a liquid bath. It was inevitable to cut the electric power as described already⁽¹⁾.

The cell design is illustrated in Fig. 1 (A), the mercury thermometer marked at intervals of 0.2 degree being used. The solid indium electrode 50 mm long was prepared by the procedure similar to that reported in an earlier publication⁽⁷⁾.

The concentration of $\text{In}_2(\text{SO}_4)_3$ aqueous solution for the electrolyte was chosen to be 0.075 mol/l as a result of the experiments

which were made to clarify how the e.m.f. of the cell depends on the concentration. On the basis of similar evidence the HgCl_2 aqueous solution was chosen to be 0.1 mol/l. About 5 cc of the electrolyte was needed each run and it was injected into the cell by a syringe with a rubber ball 4.5 cm in diameter.

III. Experimental Procedure

In order to determine the activities of the component indium in the alloys, the standard electrode of pure solid indium was employed following the experimental method described previously⁽⁷⁾. At the moment the electrolyte came in contact with both electrodes, the cell for the In-Hg alloy was constituted as follows:

To examine the influence of changes in the concentration of aqueous solution on the e.m.f., additional preliminary experiments were carried out using the cell (1) and the concentration of $\text{In}_2(\text{SO}_4)_3$ was chosen to be 0.075 mol/l. Then, selecting the alloy of $N_{\text{In}}=0.10$ for the reference electrode to raise the accuracy in the measurement, almost all the experiments of this kind were carried out and the e.m.f. values obtained were converted to the values relative to pure liquid indium using data by the cell (1). The values of E_s , the e.m.f. measured relative to the standard of the pure solid indium by the cell (1), must be converted to E_l the e.m.f. of pure liquid indium and this conversion was carried out in a similar way to the Ag-Bi system described previously⁽⁷⁾. That is, if the corrective e.m.f. is E_c ,

$$E_l = E_s - E_c \quad (2)$$

$$E_c = -\Delta F^\circ/nF \quad (3)$$

where ΔF° , n and F denote the free energy of fusion for indium, the valence of ion ($n=3$) and the Faraday constant, respectively.

The activity of the component indium, a_{In} , can be obtained by virtue of the following equation:

$$-nE_lF = RT \ln a_{\text{In}}. \quad (4)$$

The free energy of fusion for indium was calculated thermodynamically using the fol-

lowing atomic heats⁽¹⁰⁾:

$$\text{In (s)} \quad C_p = 5.81 + 2.50 \times 10^{-3} T \quad (5)$$

$$\text{In (l)} \quad C_p = 7.24 - 0.33 \times 10^{-3} T. \quad (6)$$

Since the temperature and the heat of fusion for indium are 157°C and 780 cal/mol⁽¹⁰⁾, respectively, the following free energy of fusion ΔF° can be obtained:

$$\Delta F^\circ = 427 - 1.43 T \ln T + 1.42 \times 10^{-3} T^2 + 7.07 T. \quad (7)$$

The results for the cell of the solid indium electrode were somewhat contrary to our expectation, which is believed to be due to the oxidation of the solid indium electrode.

Thus the use of the following liquid-liquid cell was desired. Therefore, most of the runs were carried out on the basis of the following cell:

The cell design employed in the activity measurements for the component indium is illustrated in Fig. 1(A).

In the measurements of the activities of the component mercury, a_{Hg} , the cell type shown in Fig. 1(B) was required, and the following cell was constituted at the moment the electrolyte came in contact with both electrodes:

The activities were calculated from an equation similar to eq. (4) as $n=2$. Seven g of indium and mercury, weighed out accurately in a desired proportion, was put in the right electrode tube in Fig. 1(B), while 7 g of mercury was put in the left tube. The alloy electrode was agitated thoroughly with a tungsten wire possessing a glass bead at its end for homogenization. In this operation, care has to be taken to avoid error arising from the sticking of the alloy to the glass tube wall.

In the cell (8), indium and mercury for alloying were put in both electrode tubes as shown in Fig. 1(A). The cell was then positioned in the thermostat maintained at 25°C. At the start of the measurements, the power was cut off, and as soon as the synchroscope was swept, the electrolyte was injected into the cell

with the syringe. Produced sweep curves were photographed.

Note that this procedure was applied similarly in the case of the cell (1).

The activity measurements of the component mercury by the cell (9), were performed in a similar way to the aforementioned method. Immediately after the sweep curve was photographed, the post-reaction e.m.f.⁽¹¹⁾ of the cell was measured on the potentiometer, which will be reported separately to discuss the reaction rate.

IV. Experimental Results

Figure 2 shows the influence of concentration of $\text{In}_2(\text{SO}_4)_3$ on the e.m.f. of the cell in the concentration range of 0.01 to 0.30 mol/l, but the concentration outside the range was avoided because somewhat unusual form of the sweep curve appeared. For this reason, the concentration of $\text{In}_2(\text{SO}_4)_3$ in aqueous solution was chosen to be 0.075 mol/l during all the experiments that followed. In addition, although the InCl_3 aqueous solution was used in a preliminary experiment, the experimental evidence supported that the $\text{In}_2(\text{SO}_4)_3$ aqueous solution was more suitable.

Table 1 gives the experimental results for the cell employing the solid indium as the standard electrodes. The measurements employing the solid indium electrodes seem somewhat less accurate than that of the liquid metal standard electrodes. This is understandable in consideration of the fact that indium is oxydized more easily than silver⁽⁷⁾. There-

Fig. 2 Relationship between e.m.f. of the cell and concentration of $\text{In}_2(\text{SO}_4)_3$ aq. soln. ($N_{\text{In}}=0.300$)

Table 1 Experimental results for the activities of the component indium.

(A) $\text{In(s)} | \text{In}^{++} | \text{In-Hg} (l, N_{\text{In}}=0.100)$

N_{In}	E_s (mV)	$\bar{E}_s$ (mV)	E_l^* (mV)	a_{In}
0.100	36.3			
0.100	36.6			
0.100	37.4	37.1	40.4	0.0089
0.100	37.4			
0.100	37.9			

(B) $\text{In-Hg} (l, N_{\text{In}}=0.100) | \text{In}^{++} | \text{In-Hg} (l, N_{\text{In}}=X)$

N_{In}	$E_{l(0.1)}$ (mV)	E_l^{**} (mV)	a_{In}
0.150	6.3	34.1	0.019
0.179	6.9	33.5	0.020
0.200	9.4	31.0	0.027
0.248	9.3	31.1	0.026
0.263	11.6	28.8	0.035
0.300	18.5	21.9	0.077
0.325	20.3	20.1	0.095
0.350	21.8	18.6	0.11
0.372	20.6	19.8	0.099
0.400	19.7	20.7	0.089
0.400	20.6	19.8	0.099
0.446	24.3	16.1	0.15
0.477	26.2	14.2	0.19
0.521	27.6	12.8	0.22
0.551	30.1	10.3	0.30
0.572	33.2	7.2	0.43
0.600	33.4	7.0	0.44
0.642	35.5	4.9	0.56
0.649	35.6	4.8	0.57

* $E_l = E_s + 3.3$ ** $E_l = 40.4 - E_{l(0.1)}$

fore, the indium electrode must be prepared carefully. For the experiments for $N_{\text{In}}=0.10$ which were carried out by employing three different electrodes of the solid indium, the values in five runs were averaged as shown in Table 1(A).

Table 1(B) gives the experimental results for the cell measured relative to a $N_{\text{In}}=0.10$ liquid alloy, the activities of indium being converted relative to pure liquid indium by employing the value 40.4 mV obtained from both the value 37.1 mV in the standard electrode of the solid indium and $E_c=3.3$ mV at 25°C.

Figure 3 illustrates typical examples of the sweep curves. There are two types of the sweep curves drawn before the contact of the alloy with the electrolyte: one sweeps downward

and the other sweeps upward, though they do not give any effect on the results. When the solid indium electrode was unsatisfactory, a wide spread of the curvature as shown in Fig. 3 appeared deteriorating the accuracy of the result.

Figure 4 illustrates the typical sweep curves in the measurement of the activities of the component mercury in which remarkable reactions between the electrolyte and the electrode occurred. Figure 4(c) in the high sensitivity was photographed distinctly, but unfortunately, the other cases were not greatly different from the previously reported cases at elevated temperatures, in which the photographing of the activity potential point was apt to become obscure due to a large reaction rate and subsequently the film photographed had to be observed carefully. This reason is probably attributed to that the sweep line in the moment the electrolyte comes in the contact with the alloy is considered to become darker due to the brightness of the sweep line drawn before the contact of the electrolyte. Therefore an attempt to place the bright spot out of sight was made as shown in Fig. 4(d). In this case, the location 1 mV above the spot position was photographed applying the voltage generated from outside. Although the initial sweep line could not be observed on the scale, the time of reaction occurrence, that is, the location of an activity potential point could be known without difficulty because of favorable shadowing. Thus, the objective line like the spot could be read near this part though darkness still remains.

There was the evidence that such darkness depends on the alloy concentration.

The DC triggered method is found to be difficult for the reason that a positive impulse voltage produces before the contact of the electrolyte with the alloy electrode as shown in Fig. 4(a) or (b).

Figure 5 shows the activities of the component indium together with the data⁽¹²⁾⁽¹³⁾ available for comparison. Good agreement is seen to exist among the three sets of data, except for the presence of a horizontal activity line, i.e. the constancy of the present activity data in the concentration range of $N_{\text{In}}=$

Fig. 3 Sweep curves in the activity measurements for the component indium. (1 sec/cm)
 (a) $N_{\text{In}}=0.263$ (St. $N_{\text{In}}=0.100$), 5 mV/cm. (b) $N_{\text{In}}=0.372$ (St. $N_{\text{In}}=0.100$), 10 mV/cm.
 (c) $N_{\text{In}}=0.551$ (St. $N_{\text{In}}=0.100$), 10 mV/cm. (d) $N_{\text{In}}=0.649$ (St. $N_{\text{In}}=0.100$), 20 mV/cm.
 (e) $N_{\text{In}}=0.100$ (Pure solid In), 20 mV/cm. (f) $N_{\text{In}}=0.100$ (Pure solid In), 20 mV/cm.

Fig. 4 Sweep curves in the activity measurements for the component mercury. (0.5 sec/cm)
 (a) $N_{\text{In}}=0.600$ ($N_{\text{Hg}}=0.400$), 20 mV/cm. (b) $N_{\text{In}}=0.400$ ($N_{\text{Hg}}=0.600$), 10 mV/cm.
 (c) $N_{\text{In}}=0.200$ ($N_{\text{Hg}}=0.800$), 2 mV/cm. (d) $N_{\text{In}}=0.151$ ($N_{\text{Hg}}=0.849$), 1 mV/cm.

0.3 to 0.4.

The experimental results of the activities for the component mercury are listed in Table 2

and illustrated in Fig. 6. The extrapolated values of vapor pressure over a temperature range 284 to 423°C, by Predel *et al.*⁽¹⁴⁾ are

Fig. 5 Activities of indium in liquid In-Hg alloys. (25°C)

Table 2 Experimental results for the activities of the component mercury.

N_{In}	N_{Hg}	E (mV)	a_{Hg}	Sensitivity (mV/cm)
0.100	0.900	1.7	0.88	1
0.151	0.849	2.7	0.81	1
0.200	0.800	3.9	0.74	2
0.250	0.750	6.9	0.58	2
0.300	0.700	13.5	0.35	5
0.330	0.670	13.4	0.35	2
0.350	0.650	13.4	0.35	2
0.400	0.600	15.1	0.31	10
0.500	0.500	22.8	0.17	10
0.545	0.455	28.9	0.11	10
0.600	0.400	33.7	0.072	20

Fig. 6 Activities of mercury in liquid Hg-In alloys. (25°C)

given in Fig. 6 for an approximate comparison⁽¹⁵⁾. The agreement can be said to be good except for a part in view of the error by a considerable extrapolation. A relatively horizontal portion of the activity curve for the component mercury in the concentration range of $N_{\text{In}}=0.3$ to 0.4 was very similar to the case of the component indium. A similar trend has frequently been noted in the activity behavior⁽¹⁶⁾.

Now, a strong similarity between the two curves in this concentration range is compared with the phase diagram⁽¹⁷⁾ of the considered system as shown in Fig. 7. It is of interest to note that the horizontal portions of the activity curves are corresponding to the eutectic region in the phase diagram, the position being marked by the arrow. Careful inspection of the phase diagram indicates that the phase diagram consists of similar two adjacent regions lying

Fig. 7 Relationship between the activities and the phase diagram.

at the right or left of the eutectic point, and this tendency seems to reflect the activity curves separating into two curves. The previous paper⁽¹⁶⁾ has provided the evidence that the eutectic composition can be related to the horizontal activity curve.

V. Discussion

Recently, marked progress has been made in the investigation of the TIE method at elevated temperatures above 400°C using the electrolyte of molten salts. In the present study an aqueous solution was employed in an attempt to investigate this method at room temperature.

It seems most likely that the accuracy of the present study is better than that at the elevated temperatures, but the results obtained were somewhat contrary to our expectation.

The molten salt dissolves the metal or alloy but the error can be minimized by addition of a third salt. At present, the problem is complicated by the fact that the dissolution of indium metal into the aqueous solution is accompanied by an exchange reaction⁽¹⁸⁾.

The measurements of the cell (1) by the potentiometer proved that dissolution of the metal into the aqueous solution can be observed distinctly from the change of e.m.f. in which the e.m.f. increases for several minutes to reach a maximum and then decreases. This fact suggests that the measurement becomes more difficult at the higher concentration of the aqueous solution.

In the activity measurements of the component mercury which causes the displacement reaction between the electrolyte and the alloy, it is very interesting to know how the experimental condition at room temperature differs from that at the elevated temperatures. In consequence, the difficulty in photographing in the present study did not differ significantly from that at the elevated temperatures though the large difference between single electrode potentials of mercury and indium becomes important as already pointed out⁽¹¹⁾⁽¹⁹⁾⁽²⁰⁾.

It seems important in understanding the reaction rate that more distinct photographing has been obtained at higher sensitivity and

mercury concentration.

VI. Summary

The TIE method was applied to the measurement of the activities in liquid In-Hg alloys at room temperature, 25°C.

The activities measured of both components were in good agreement with the literature values but there appeared constant activities in the concentration range of $N_{\text{In}}=0.3$ to 0.4.

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