# Electrochemical Determination of the Solubility of Copper in Mercury

FINN GRØNLUND and BJARNE KRISTENSEN

Chemical Laboratory IV, University of Copenhagen, Universitetsparken 5,
DK-2100 Copenhagen Ø, Denmark

The solubility of copper in mercury was measured in the range 10 to 25 °C by monitoring the potential of a copper amalgam whose copper content could be varied at will from zero to past saturation by coulometric electrolysis. Measurements were performed in a vacuum cell with a saturated copper amalgam as reference electrode. Saturation concentrations in the range examined are $(1.61+0.209t/{}^\circ C) \cdot 10^{-4}$ mol (kg Hg)$^{-1}$ giving $6.84 \cdot 10^{-4}$ mol kg$^{-1}$ at 25 °C.

Copper amalgams are extensively used, particularly in electrochemical measurements, since they are known to respond better than electrodes made from pure copper. In spite of this, no general agreement has been reached with respect to the nature of components and phases present, and solubility values given at room temperature range from $3.1 \cdot 10^{-4}$ to $6.2 \cdot 10^{-4}$ mol/(kg Hg).[1-6] Such small concentrations are difficult to measure, and the measurements may be perturbed in several ways. In the first place, traces of oxygen present in the electrolyte may remove copper from the amalgam by oxidation:

$$Cu+2H^{+}+\tfrac{1}{2}O_2 \rightarrow Cu^{2+}(aq)+H_2O$$
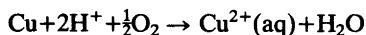
Second, copper may be transported from one metallic electrode A to another B through the solution by the reactions

$$Cu(A)+Cu^{2+}(aq) \rightarrow 2Cu^{+}(aq) \rightarrow Cu(B)+Cu^{2+}(aq)$$
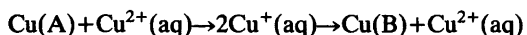
provided that $\mu_{Cu}^{A} > \mu_{Cu}^{B}$. This process, often overlooked, may take place even in the absence of current. Finally, formation of intermetallic compounds and (in case of excess) crystallization are relatively slow processes so that metastable systems may exist for considerable lengths of time.

We have used a cell in which known amounts of copper could be deposited into a pool of mercury by electrolysis from a solid copper electrode, and where the potential of the mercury phase was followed relative to that of a saturated copper amalgam reference electrode. To avoid side reactions, the cell was filled and operated in vacuum, the copper electrode was raised when not in use, and a capillary separated the reference electrode from the electrolyte.

## EXPERIMENTAL

With a few exceptions the thermostatted vacuum cell and filling procedures are identical to those described previously.[7]

Fig. 1 shows the cell and the three electrodes which it contains: a measuring amalgam electrode (test electrode), a copper electrode which serves as a source of copper for making up the amalgam, and a saturated amalgam reference electrode. Three such cells were run from a common vacuum system and thermostat.

The test electrode in the bottom of the cell is a weighed quantity (about 25 g) of mercury (Mercure-Industrie, 99.99999 %), stirred magnetically, to which known amounts of copper may be added by electrolysis. By reversing the current, the copper may later be removed, and the cell be used again. A platinum wire, insulated from the
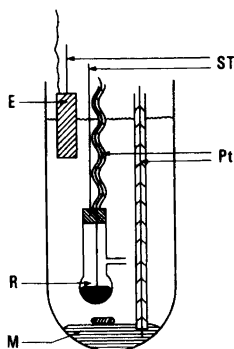
*Fig. 1.* Electrode compartment of vacuum cell. E, copper electrolysis electrode; R, reference amalgam electrode with side capillary; M, test electrode with magnet stirrer; ST, suspension threads; Pt, insulated platinum wire.

electrolyte solution, ensures the electrical connection.

The electrolysis electrode which serves as a copper source is a solid cylindrical copper rod (ASARCO, 99.999 %). When first immersed into a freshly prepared solution, it serves to equilibrate the latter with respect to $Cu^+$ ions by the reaction $Cu+Cu^{2+}\rightarrow2Cu^+$. If it is kept immersed for longer periods of time, however, and if the solution is also in contact with an undersaturated amalgam the latter may act as a drain for copper supplied by the rod. This has been shown to happen even in the absence of current. To prevent this, the copper rod is kept above the solution when not in use. A constant current source of 5 mA was used for electrolysis, giving a c.d. of about 1 mA $cm^{-2}$ at the test electrode. The current was measured on a $4\frac{1}{2}$ digit DVM, and the time on a stopwatch.

The reference electrode is a saturated, aged copper amalgam electrode with great excess of copper. It communicates via a capillary with the electrolyte when immersed.

The electrolyte was made from low-conductivity water which was added to $CuSO_4$ (Merck, *anal. pur.*) and $H_2SO_4$ (BDH, *anal. pur.*) in the cell to obtain a concentration of 0.7 M and a pH of 2. Temperature measurements were made using a thermistor checked against a calibrated platinum resistance thermometer. The potential difference between the test and reference electrodes was recorded during 6 to 12 h and then measured with a Keithley 610 B electrometer.

Once assembled, each cell was used in a number of experiments since copper could be removed from the measuring electrode or titrated

into it at will by anodic or cathodic electrolysis without demounting the cell.

Apart from obvious advantages this ensures permanent equilibration of the electrolyte with respect to $Cu^+$ ions.

The leak rate of the cell was estimated by following the cell voltage at low copper concentrations over several days. In this way a decrease of copper molality in the test electrode of about $5 \cdot 10^{-6}$ mol $kg^{-1}$ $(24h)^{-1}$ was observed, corresponding to an oxygen supply of about $7 \cdot 10^{-13}$ mol $s^{-1}$ to 25 g amalgam. This would indicate a leak rate of at most $3.5 \cdot 10^{-12}$ mol air $s^{-1}$ or, in vacuum terminology, about $9 \cdot 10^{-11}$ atm l $s^{-1}$. It would be quite difficult to exclude oxygen to the same extent in a conventional cell filled with inert gas.

## RESULTS

The voltage of the cell

$$Cu(Hg), \; a_{Cu(Hg)sat}|Cu^{2+}(aq)|Cu(Hg), \; a_{Cu(Hg)}$$
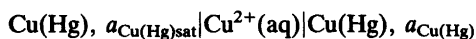
in which the right-hand electrode is the amalgam under study while the left-hand reference electrode is a saturated and equilibrated copper amalgam, is given by

$$E= -\; \frac{RT}{2F} \ln \frac{a_{Cu(Hg)}}{a_{Cu(Hg)sat}} \qquad (1)$$

independent of the electrolyte composition. It is positive if the test electrode is dilute with respect to copper, zero at saturation, and negative for slightly supersaturated amalgams which are relatively stable. As the amalgams in question are very dilute, activity may be replaced by the molality $m$, and the desired saturation concentration may then be found as that value of $m$ at which $E=0$.

In each experiment $m$ was determined as follows. Initially the test electrode had a high positive potential $E'$ (35−50 mV) due to a small residual molality $m'$ of copper remaining from previous experiments (typically about 5 % of the saturation value). By coulometric addition of copper this molality was increased by a known amount $\Delta m$ so adjusted as to bring the final value $m=m'+\Delta m$ close to the saturation value, as testified by the corresponding final equilibrium voltage $E$ in the range −2 to 2 mV. Applying
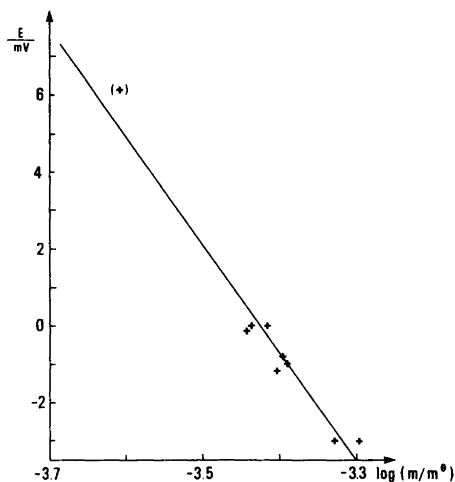
*Fig. 2.* Plot of equilibrium EMF *vs.* logarithm (base 10) of Cu molality in test electrode at 10.2 °C. Points in parentheses are disregarded and a line with slope −28.11 mV/decade has been fitted numerically.

eqn. (1) before and after addition of Cu one obtains

$$m'=m_{sat} \exp{(-2FE'/RT)} \qquad (2a)$$

$$m=m'+\Delta m=m_{sat} \exp{(-2FE/RT)} \qquad (2b)$$

which combine to give the required expression

$$m=\Delta m/[1-\exp(2F(E-E')/RT)] \qquad (3)$$

At each of four temperatures in the range 10 to 25 °C, a series of nine measurements were made. In each case the voltage after addition of Cu first decreased to −5 to −10 mV but then increased over a few hours to a value near 0 mV where it remained constant for days; this was taken to be the equilibrium value $E$ of the cell. Each series was analyzed by plotting $E$ *vs.* log $m$ as shown in Fig. 2 which contains the data at 10.2 °C. In all cases the observations grouped closely around a line with a slope close to the theoretical value $-(RT/2F)$ ln 10.

In the calculation of $m_{sat}$ only those points were retained which lay within a few millivolts from the saturation value (6−8 measurements in each series). A line of slope $-(RT/2F)$ ln 10 was fitted numerically to these; its intersection with

$E=0$ gives $m_{sat}$. The four saturation concentrations thus obtained, with estimated deviations, are given in Table 1 along with the corresponding temperatures. They conform to the linear expression

$$m_{sat}=(1.61+0.209t/°C) \cdot 10^{-4} \text{ mol Cu/(kg Hg)} \qquad (4)$$

with $m_{sat}=6.84 \cdot 10^{-4}$ mol Cu/(kg Hg) at 25°C.

These figures are valid at the vapour pressure of the test solution but the change in passing to one atmosphere is negligible as may be inferred from the thermodynamic relation

$$\left( \frac{\partial \text{ n } K}{\partial P} \right)_T = -\frac{\Delta V^\theta}{RT} \qquad (5)$$

The volume change $\Delta V^\theta$ on dissolving one mol of $CuHg_y$ in Hg at infinite dilution is not known, but

*Table 1.* Solubility of Cu in Hg from 10 to 25 °C.

| $t/°C$ | $\dfrac{m_{Cu}}{10^{-4} \text{mol kg}^{-1}}$ | $\dfrac{\sigma_m}{10^{-4} \text{mol kg}^{-1}}$ |
|---|---|---|
| 10.2 | 3.72 | 0.05 |
| 15.8 | 5.00 | 0.10 |
| 22.1 | 6.08 | 0.07 |
| 25.1 | 6.95 | 0.05 |

*Table 2.* Survey of copper solubility values in Hg at 25 °C.

| Ref. | Method of Cu detn. | Reference electrode | Solubility $10^{-4}$ mol Cu/kg Hg |
|---|---|---|---|
| 2 | coulometric | calomel | 3.0−4.8[a] |
| 5 | coulometric | calomel | 4.4[b] |
| 6 | coulometric | calomel | 3.2 |
| 1 | gravimetric | Cu | 4.3 |
| 4 | coulometric | Cu(Hg) | 6.2 |
| Pres. work | coulometric | Cu(Hg) | 6.8 |
| 3 | not specified | | 3.1[c] |

[a] Valid at 15 °C. [b] Temperature not cited. [c] Analysis of saturated amalgams after heat treatment and filtration (25−550 °C).

its numerical value is probably smaller than 10 $cm^3$ $mol^{-1}$. This would correspond to a relative change in $K=m_{sat}/m^\theta$ of $4 \cdot 10^{-4}$ $atm^{-1}$ which is well below the accuracy of measurement.

## DISCUSSION

Available values of the solubility of copper in mercury expressed in mol Cu/kg Hg are listed in Table 2. Unless otherwise specified they are valid at 25 °C (the figures of Ref. (2) should be multiplied by about 1.4 to apply to 25 °C).

In all cases but the last one[3] the state of the amalgam was monitored by EMF measurement at varying copper concentration. The use of a calomel reference electrode[2,5,6] implies a salt bridge, makes the cell voltage dependent on electrolyte concentration, and may introduce other errors unless precautions are taken. It is difficult to estimate the magnitude of these from the sparse information given but a value of 0.5 to 5 mV might be a reasonable guess. In contrast to this, if the calomel electrode is replaced by a reference electrode of the same kind as the test electrode[1,4] one may expect a considerable reduction in both random and systematic errors. The data of Levitskaya and Zebreva[4] suggest errors in the range 0.2–0.5 mV, and we are inclined to think that the same applies to our work. Schupp et al.[1] used a copper reference electrode treated with $Hg(NO_3)_2$ but unfortunately their paper, having a different aim, is not sufficiently informative to permit an analysis. Finally, the last paper[3] cited in Table 2 describes a different technique: filtration and analysis of the liquid phase resulting from the interaction of copper and mercury over a large range of temperature; it gives a rather low value at room temperature.

It is interesting that the temperature coefficient of the solubility found by Levitskaya and Zebreva coincides closely with ours. Taking their data at 20 and 40 °C (but neglecting those at 50 °C which appear to be less reliable, see their Fig. 1) one finds $0.202 \cdot 10^{-4}$ mol Cu/(kg Hg) $K$ or almost the same as our value, $0.209 \cdot 10^{-4}$ mol/(kg·K). Both give $\Delta H^\theta=28$ kJ/mol for the reaction

$$CuHg_y \text{ (s)} \rightarrow Cu(Hg)+y \text{ Hg}$$
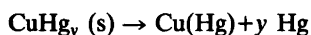
with $y=6/7$.[8] By contrast, Jangg and Palman[3] present a plot of $1/T$ vs. $\log x_{Cu}$ which is linear in the range 25–400 °C; its slope gives a $\Delta H^\theta$ value of only 22 kJ/mol. However, most of their measurements were taken above 100 °C where the solid intermetallic compound is unstable,[8] and therefore apply to the dissolution of Cu, not $CuHg_y$, in Hg.

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