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An Improved Molten Salt EMF Cell.
Studies Using SnCl_2 and Tin
Alloyed with Cu, Ag, or Au
to Test for Raoult's Law Behavior

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AN IMPROVED MOLTEN SALT EMF CELL. STUDIES USING SnCl_2 AND TIN ALLOYED WITH
Cu, Ag, OR Au TO TEST FOR RAOULT'S LAW BEHAVIOR

By

G. R. B. Elliott and J. F. Lemons

ABSTRACT

An H-cell of new design provides for stirring and solute addition in a sealed, isolated, and heated system. Measurements at 535°K have been made using dilute solute, X, and cells of the type

The cell voltages were constant at any time to a few tenths of a micro-volt with day-to-day variations generally less than $1\text{ }\mu\text{v}$. Unlike many precise vapor pressure measurements which have failed to indicate approach to the slope of Raoult's law in similar composition regions, these measurements for copper, silver, and gold solutions lie very close to Raoult's law at their dilute limit. For tin with silver, the data deviate from Raoult's law by following a term in the square of the solute mole fraction; with gold, the deviations are more complex and are interpreted in terms of solution structure. Possible inaccuracies in thermodynamic prediction are discussed.

INTRODUCTION

If the pure solvent is used as the standard state of a solution, all solvent activities must approach the value of one as the solution becomes very dilute. By definition, then, the Raoult's law value ($a_1 = N_1 = 1$) is approached by any solution. Whether all very dilute solutions approach the unit slope associated with Raoult's law is a question which requires an experimental answer, and here the answer is less clear.

The validity of Raoult's law and, indeed, of the thermodynamic application of the Duhem relationship to Henry's law to deduce Raoult's law, has been questioned;^(1,2) cases are pointed out where the slope of Raoult's law was apparently not being approached even in fairly dilute solutions. Other

aspects of thermodynamics prediction have also been discussed.⁽³⁾

Since marked deviations from Raoult's law were demonstrated in many of the above cases, it became of interest to learn how closely the behavior of solutions might follow Raoult's law in other cases. Quite possibly the best experimental evidence for ideal asymptotic approaches to the slope of Raoult's law lies in the work of Yanko et al.,⁽⁴⁾ where tin concentration cells were used with silver, gold, and antimony solutes. However, certain questions existed regarding the Yanko measurements as compared with other similar measurements.^(5,6) Furthermore, it appeared that some aspects of the Yanko technique could be improved with regard to stirring, solute addition, exclusion of air, temperature uniformity, and

chemical purity. Finally, the data did not meet all theoretical tests.

The Raoult's law value for the ratio of emf divided by absolute temperature should depend only on the concentration ratio at the two electrodes and the value of n for the electrons per atom of metal transferred,

$$\frac{E - E_0}{T} = - \frac{R}{nF} \ln \frac{N}{N_0} \quad (1)$$

The Raoult's law value takes no cognisance of materials used for solvent, solute, or electrolyte. Since a rather small but fairly systematic variation from Eq. 1 may be observed in the Yanko data, it appeared desirable to check the measurements and to try to improve upon them.

The electrochemical systems were similar to those used by Yanko,

where both alloy and electrolyte were molten.

EXPERIMENTAL

Material Purification

Commercial hydrated stannous chloride contained in Pyrex was fused under rough vacuum to produce $SnCl_2$ with considerable quantities of tin oxides and presumably higher chlorides. This first crude anhydrous stannous chloride was transferred to a new container, placed under vacuum, and vaporized by gentle flaming into a second clean container. After cooling, the container was broken open and the partially purified $SnCl_2$ was removed. This material was introduced, along with a small piece of pure tin, into another container which was part of the electrochemical cell assembly. (These containers were larger than the size indicated at the left of Fig. 1.)

After sealing and evacuating, the $SnCl_2$ was boiled to bring about contact between the molten salt and the molten tin; this was to reduce hydroxides and higher chlorides and to replace and extract the metal from any salts less stable than tin. (Salts more stable than $SnCl_2$ should not influence the cell emf in the Raoult's law region.) A second distillation left behind the tin and any oxide traces. These tails were isolated by collapsing the crossarm connection and were removed. Finally, a

Fig. 1. The H-cell design (tubes drawn slightly oversize).

third evaporation introduced the $SnCl_2$ into the electrochemical cell and the tails were removed.

To prepare electrochemically satisfactory tin, reagent grade tin was melted in Pyrex under good vacuum with a small amount of purified $SnCl_2$. The $SnCl_2$ was boiled to assure contact with the tin. The $SnCl_2$ -washed tin was then poured into sidearms of the tube, and the arms were flamed to bring any trapped electrolyte to the surface. This procedure was undertaken to remove any metals more chemically active than tin and to remove volatile impurities and oxide (which is soluble in $SnCl_2$). The arms were then removed and the glass was crushed. $SnCl_2$ was washed off the tin rods with water.

The silver and gold were of 99.98% purity by supplier's specifications; the copper was sheeting of electrolytic purity. The impurities introduced by the solute were negligible. Cut marks were examined under a microscope for stains or for steel fragments. All these materials and tools were washed with petroleum ether and acetone before use.

The tungsten electrodes were cleaned by being

dipped into NaOH solution and by passing an intermittent AC current using a variable autotransformer operating from zero to 15 v. They were then washed with water and acetone.

The Pyrex H-cell, pictured in Fig. 1, was evacuated, flamed, and loaded with argon. Weighed tin was loaded beside the stirrers and weighed solute pieces were added to one or both arms. The standard taper joints were regreased, using Apiezon N in the turning regions, with an excess amount applied above the joint. The SnCl_2 was introduced as described earlier.

The tin was melted into position and allowed to freeze. (The freezing sometimes broke the seal at the smaller standard taper joints, but the excess grease around these joints kept them hermetically sealed and vacuum was not lost.) The final evaporation put the SnCl_2 onto the tin and across the bar of the H-cell. The connection between the secondary leg and the H-cell was then collapsed and the leg was removed.

The cell, still under vacuum, was placed in the furnace and reconnected to the vacuum system. The system was occasionally stirred and periodically evacuated to remove any gases which might be evolved while minimizing contamination from oxygen traces in the vacuum. The cell potential for tin vs tin gradually dropped to near zero emf and became stable. This took hours and sometimes days.

The vacuum system was then isolated at the stopcock which was not reopened during a run. By tilting the cell support slightly and tapping the cell sidearm, single pieces of solute could be added while the cell remained hot. The cell could then return easily to its original position to be stirred until the emf results became stable. Another solute addition could then be made.

Measurement of Electromotive Force

The emf was measured by Leeds and Northrup K-2 potentiometer. The furnace was isolated by partial Faraday cages to keep out stray voltages from other electrical apparatus: one cage was made of copper screening, and a nickel-plated copper cylinder around the cell inside the furnace served as the other cage. Both were attached to a ground independent of that used for working electrical equipment. A grounded stainless tube around the temperature control thermocouple (except for the exposed

tip) helped prevent stray emf effects from the heater. Cell temperature was measured by a Pt/Pt-10% Rh thermocouple glass-taped to the cell just outside one metal-salt interface.

Temperature Control

The heater was outside four nesting nickel-plated copper cylinders separated by air gaps. (These were similar to those used with the isopiestic balance.⁽⁷⁾) The massive copper served as a heat ballast, and also conducted heat around each cylinder much faster than across the air gap. Therefore each cylinder was of more uniform temperature than the cylinder outside it. Furnace temperatures were necessarily less uniform in this arrangement than in the isopiestic balance because the emf cell had to protrude vertically from the furnace; however, considering the small bias which might be ascribed to the thermocell effects (0.0, 5.0, or 7.0 μv) and the small (1 or 2 μv) emf effect on stirring, the temperature gradients must have been very small. A Pyrovane temperature regulator was adequate when coupled with the copper heat ballast.

When a cell was broken open and the salt and alloy dissolved, there was no indication of attack on either the Pyrex or the tungsten.

RESULTS

The results are indicated in Table I. Once a cell had been adequately stirred, any measurement was stable (without rapid shifts of emf) in the $\pm 0.1 \mu\text{v}$ range. However, after stirring intermittently for many hours, the cell did not always return to the identical voltage of the previous measurements. The range of this long-term variation, when several measurements had been taken, set the uncertainty indicated in Table I. Within that uncertainty the potential was in some cases followed and observed to be constant for a day or two.

In Fig. 2, the dilute solution data are plotted with the Raoult's law value shown as the solid line and the results of Yanko et al. shown by the solid dots. (Note the offset of the abscissa for the different solutes.)

For the corrections we used the emf for measurements of "pure" tin vs "pure" tin except when a piece of copper fell in prematurely. In this case we corrected the first emf to the Raoult's law value. Several factors could require this correction --

there could be small differences in impurities in the purified tin as added, or trace impurities in the electrolyte could be scavenged more by one tin bath than by the other. Also, a temperature difference of 0.01°K between the cell legs could account for $\sim 6 \mu\text{V}$, if the temperature effect for our cell is not greatly different from the thermocell

However, this much difference seems to be ruled out since stirring (which tends to bring cooler material from the upper portions of the cell), as noted earlier, caused only one or two microvolts change of

* Reinhold(8) has made extensive measurements of such thermocells, and these measurements have been used for theoretical treatments.(9,10) We were unable to find a measured absolute entropy for $\text{SnCl}_2(l)$ to use for a theoretical calculation. However, Kubaschewski and Evans' technique of estimation(11) would lead to the same difference in entropy between $\text{Sn}(s)$ and $\text{SnCl}_2(s)$ as exists between $\text{Pb}(s)$ and $\text{PbCl}_2(s)$. Further calculation would lead to predicted thermocell effects for the tin cells which are not greatly different from those for the lead thermocells.

Fig. 2. Dilute solution emf measurements as compared with Raoult's law.

emf once the cell had become stable.

CONCLUSIONS

The activity of tin containing copper approaches Raoult's law asymptotically as well as the data can show.**

In Fig. 3 the tin with silver vs tin data are plotted on a Dundee type plot which examines the change of solvent (tin) activity with solute mole fraction. The data very closely approach the limiting Raoult's law slope with a correction term in the square of the solute mole fraction. Whether the limit is exactly approached is not experimentally clear.

Fig. 3. Dundee plot of the data for tin with silver. (Shows linearity if $a_{\text{Sn}} = 1 - k_1 N_{\text{Ag}} + b N_{\text{Ag}}^2$ and unit intercept if $k_1 = 1$.)

** This calculation assumes that all the tin added is still present in the alloy and that $\bar{n} = 2$ in $\Delta G = -nRT$. With considerable discrepancy the solubility of tin in SnCl_2 at 773°K is reported to be 3.2×10^{-5} mole fraction(12) or 2.6×10^{-2} mole fraction; (13) at 573°K the value is reported as 8.3×10^{-3} mole fraction.(13) Use of the larger values, and calculation for the amounts of material and the temperature used, would result in alloy solute concentrations $\sim 0.3\%$ larger than reported. (In the equation forms used in the figures, $a_{\text{Sn}} = c - k_1 N_{\text{solute}} + b N_{\text{solute}}^2$, the value for k_1 is decreased by ~ 0.003 .) There is a larger possible effect on $\bar{n}$. A 7×10^{-3} mole fraction solubility of tin in SnCl_2 at 525°K might (by one theory of the soluble species) change $\bar{n}$ to $2.000/1.007$. These two corrections would move the gold data to the other side of Raoult's law and would lead to $k_1 \approx 0.99$ for copper and silver solutions.

TABLE I
Sn/SnCl₂/Sn,X Concentration Cells

Solute Mole Fraction ^a	emf, μ v (measured)	Temperature °K	emf, μ v (corrected) ^b	Raoult's Law Prediction	Activity Coefficient
(Gold)					
0.001098	25.9 $\pm$ 0.5	540.8		25.6	0.99990
0.003243	76.0 $\pm$ 0.5	540.9		75.7	0.99998
0.004194	98.3 $\pm$ 0.7	540.7		97.9	0.99998
0.007744	182.1 $\pm$ 1.2	540.6		181.0	0.99995
0.015517	370.2 $\pm$ 1.2	540.4		364.0	0.99973
0.024243	593.9 $\pm$ 2.0	540.3		571.2	0.99903
0.036336	924.0 $\pm$ 2.0	541.3		862.9	0.99740
0.046890	1224.0 $\pm$ 1.0	541.5		1120.1	0.99557
0.063830	1754.5 $\pm$ 1.5	542.0		1539.7	0.99087
0.093873	2784.5 $\pm$ 0.5	542.1		2301.1	0.97954
(Silver)					
0.000000	5.0 $\pm$ 0.8	531.0	(0.0)		
0.000484	5.8 $\pm$ 0.5	531.2	10.8	11.1	1.00001
0.002570	53.5 $\pm$ 0.5	534.0	58.5	59.2	1.00003
0.004314	94.3 $\pm$ 0.5	534.4	99.3	99.5	1.00001
0.010042	223.6 $\pm$ 0.2	534.7	228.6	232.4	1.00017
0.025193	557.9 $\pm$ 0.2	534.1	562.9	587.0	1.00106
0.033933	745.0 $\pm$ 0.2	534.7	750.0	795.0	1.00196
(Copper)					
0.000716	9.2 $\pm$ 0.2	534.7	(16.2)	16.5	
0.002243	44.9	534.2	51.9	51.7	0.99999
0.003866	82.2 $\pm$ 0.1	534.0	89.2	89.1	1.00000
0.008225	182.2 $\pm$ 0.1	533.9	189.2	189.9	1.00003

^a Approximately 20 g of tin in each leg.

^b Corrections: Gold - none, Silver - add 5.0 μ v, Copper - add 7.0 μ v.

In Fig. 4 the data for tin with gold vs tin are treated similarly. Here a change in behavior at about 0.01 mole fraction gold is indicated. As discussed above, the uncertainty indicated by the bars

was set by the scatter in several emf readings. The compositional uncertainty seems extremely small since all the weights involved had at least four significant figures.

Fig. 4. Dundee plot of the data for tin with gold.

Accepting the data at face value, we would interpret the effect as resulting from changes in highly ordered atomic arrangements as the composition is shifted. This implies an extreme level of short-range order, a perhaps almost microcrystalline arrangement. Similar effects have been noted in vapor pressure studies of cadmium alloys with gold, lead, and copper. (14,15)

The data below 0.01 mole fraction gold have been described by the most experimentally satisfactory equation, which, however, agrees with Raoult's law within the experimental error. As with the silver, whether the limit is exactly approached is not experimentally clear.

As noted earlier, the use of thermodynamic prediction as an exact description of physical reality has been questioned. (1-3) It is clear that the above emf values lead to activities lying much closer to Raoult's law than have been observed (1,15) for the activities from precise vapor pressure measurements. Whether this difference results from coincidentally ideal tin alloy behavior, or whether the activities as measured by vapor pressure do not agree with the activities as measured by emf, is not clear from the data presented.

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