Title

VAPOR PRESSURE OF THALLIUM AND ACTIVITY MEASUREMENTS ON LIQUID SILVER-THALLIUM ALLOYS BY THE TORSION EFFUSION METHOD

Authors

Desre, Pierre J.
Hawkins, Donald T.
Hultgren, Ralph.

Publication Date

1968-05-01

UCRL-17828

eg. 7

University of California

Ernest O. Lawrence Radiation Laboratory

VAPOR PRESSURE OF THALLIUM AND ACTIVITY MEASUREMENTS ON LIQUID SILVER-THALLIUM ALLOYS BY THE TORSION EFFUSION METHOD

Pierre J. Desré, Donald T. Hawkins and Ralph Hultgren

May 1968

Berkeley, California

UCRL-17828
eg. 2

DISCLAIMER

UCRL-17828
Preprint

Submitted to:
Transaction of Metallurgical Society of AIME

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

VAPOR PRESSURE OF THALLIUM AND ACTIVITY MEASUREMENTS ON LIQUID SILVER-THALLIUM ALLOYS BY THE TORSION EFFUSION METHOD

Pierre J. Desré, Donald T. Hawkins and Ralph Hultgren

May 1968

Vapor Pressure of Thallium and Activity Measurements on Liquid Silver-Thallium Alloys by the Torsion Effusion Method

Pierre J. Desré, Donald T. Hawkins, and Ralph Hultgren

This paper reports the results of a study of the liquid Ag-Tl system by the torsion effusion method. The method has been discussed in detail previously[1] and will be only briefly summarized here. The sample is contained in a cell which is suspended on a torsion wire. Vapors effusing from orifices on opposite sides of the cell exert a torque on the wire. The torque is related to the vapor pressure by the following relation:

$$P = \frac{2D\phi}{f_1 a_1 q_1 + f_2 a_2 q_2}$$

where D is the torsion constant of the wire, ϕ the angle of torque, f_1 and f_2 the correction factors determined by Freeman and Searcy[2] to account for orifice length, a_1 and a_2 the areas of the orifices, and q_1 and q_2 the distances of the orifices from the axis of rotation. By using the same cell for pure thallium and the alloy, it follows that

$$a_{Tl} = \frac{P_{Tl,\,alloy}}{P_{Tl,\,pure}} = \frac{\phi_{Tl,\,alloy}}{\phi_{Tl,\,pure}}$$

so that most systematic errors are eliminated in determining the activities.

Pierre J. Desré is Maître des Conférences, Faculté des Sciences, Métallurgie et Électrométallurgie, Université de Grenoble, Grenoble, France. Donald T. Hawkins and Ralph Hultgren, Member AIME, are Graduate Research Assistant and Professor of Metallurgy, respectively, Department of Mineral Technology, College of Engineering and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California.

EXPERIMENTAL

99.999+% Tl was obtained from the American Smelting and Refining Co, and 99.999% Ag was obtained from Cominco American, Inc. Seven Ag-Tl alloys, ranging in composition from $x_{Tl} = 0.33$ to 0.90, were prepared by melting together weighed amounts of the pure metals in sealed, evacuated Vycor tubes and quenching the melts in water.

The apparatus and graphite cells were the same as those used by Hawkins and Hultgren[3] in their study of the Pb-Sn system.

RESULTS

Ten measurements were made on pure Tl in the temperature range 931°- 996°K, and the results are presented in Table I. Values of $\Delta H^{\circ}_{v,298}$ were calculated using tabulated Gibbs (free) energy functions.[4] No dependence of $\Delta H^{\circ}_{v,298}$ on temperature or orifice size was found, indicating that equilibrium was attained.

Data for the Ag-Tl alloys are shown in Table II. Values were smoothed with respect to composition by a plot of $\frac{\Delta \bar{G}^{xs}_{Tl}}{x^2_{Ag}}$ vs x_{Tl}, where $\Delta \bar{G}^{xs}_{Tl} = RT \ln \frac{a_{Tl}}{x_{Tl}}$.

DISCUSSION

The value $\Delta H^{\circ}_{v,298} = 43520 \pm 100$ calories per g-atom for pure thallium (95% uncertainty limit) is in excellent agreement with previous investigations.[4]

In the Ag-Tl system, this study shows positive deviations from Raoult's Law at all compositions. Figure 1 gives the phase diagram

according to Hansen,[5] and Figure 2 presents the activity values measured in this study as well as those from emf measurements at 950°K by Terpilowski, Kundys and Slaby.[6] The emf data were extrapolated to 975°K from their temperature coefficient measurements. Values of this investigation scatter less than the emf values and show, on the average, greater deviations from ideality.

Values of $\Delta\bar{G}^{xs}_{Ag}$ were calculated by Gibbs-Duhem integration. The constant of integration was calculated from the phase diagram and the assumption of Raoult's Law in the small (7 at. -%) solid solution range. The standard state has been taken to be supercooled liquid silver, for which it is assumed that ΔS_m = 2.31 calories per degree per g-atom, independent of temperature. Table III gives the resulting smoothed values. It is interesting to note that a_{Ag} approaches the Raoult's Law value approximately at the liquidus boundary. Terpilowski, Kundys, and Slaby[6] found a similar behavior.

ACKNOWLEDGMENT

This work was conducted under the auspices of the U.S. Atomic Energy Commission.

REFERENCES

1. P. Roy and R. Hultgren: Trans. TMS-AIME, 1965, vol. 233, pp. 1811-15.

2. R. D. Freeman and A. W. Searcy: J. Chem. Phys., 1954, vol. 22, pp. 762-63 and 1137-38.

3. D. T. Hawkins and R. Hultgren: Trans. TMS-AIME, 1967, vol. 239, pp. 1046-49.

4. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley: Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, Inc., New York, 1963.

5. M. Hansen: Constitution of Binary Alloys, 2nd ed., McGraw-Hill, New York, 1958.

6. J. Terpilowski, E. Kundys, and H. H. Slaby: Archiwum Hutnictwa, 1961, vol. 6, pp. 137-46.

TABLE I.

Vapor Pressure of Thallium

T, °K	P, 10^{-6} atm.	$\Delta H^{\circ}_{V,298}$ cal per g-atom
931	34.341	43521
938	40.584	43519
943	43.394	43616
954	58.379	43533
962	72.740	43459
974	90.535	43548
976	99.276	43449
980	102.71	43551
990	133.93	43454
996	146.73	43517
Average $\Delta H^{\circ}_{V,298}$ = 43520(±100) (95% uncertainty limit)		

TABLE II.

Vapor Pressure of Ag-Tl Alloys at 975°K

x_{Tl}	$P_{Tl,alloy}$, 10^{-6} atm.	$\Delta \bar{G}^{xs}_{Tl}$, cal per g-atom
0.33	53.07	1041
0.4	58.50	857
0.5	67.80	711
0.6	73.35	510
0.7	77.39	315
0.8	81.65	160
0.9	86.33	40

TABLE III.

Properties of Liquid Alloys at 975°K

$$(1-x)Ag_{(\ell)} + xTl_{(\ell)} = Ag_{1-x}Tl_{x(\ell)}$$

$$Ag_{(\ell)} = Ag(\text{in alloy})_{(\ell)}$$

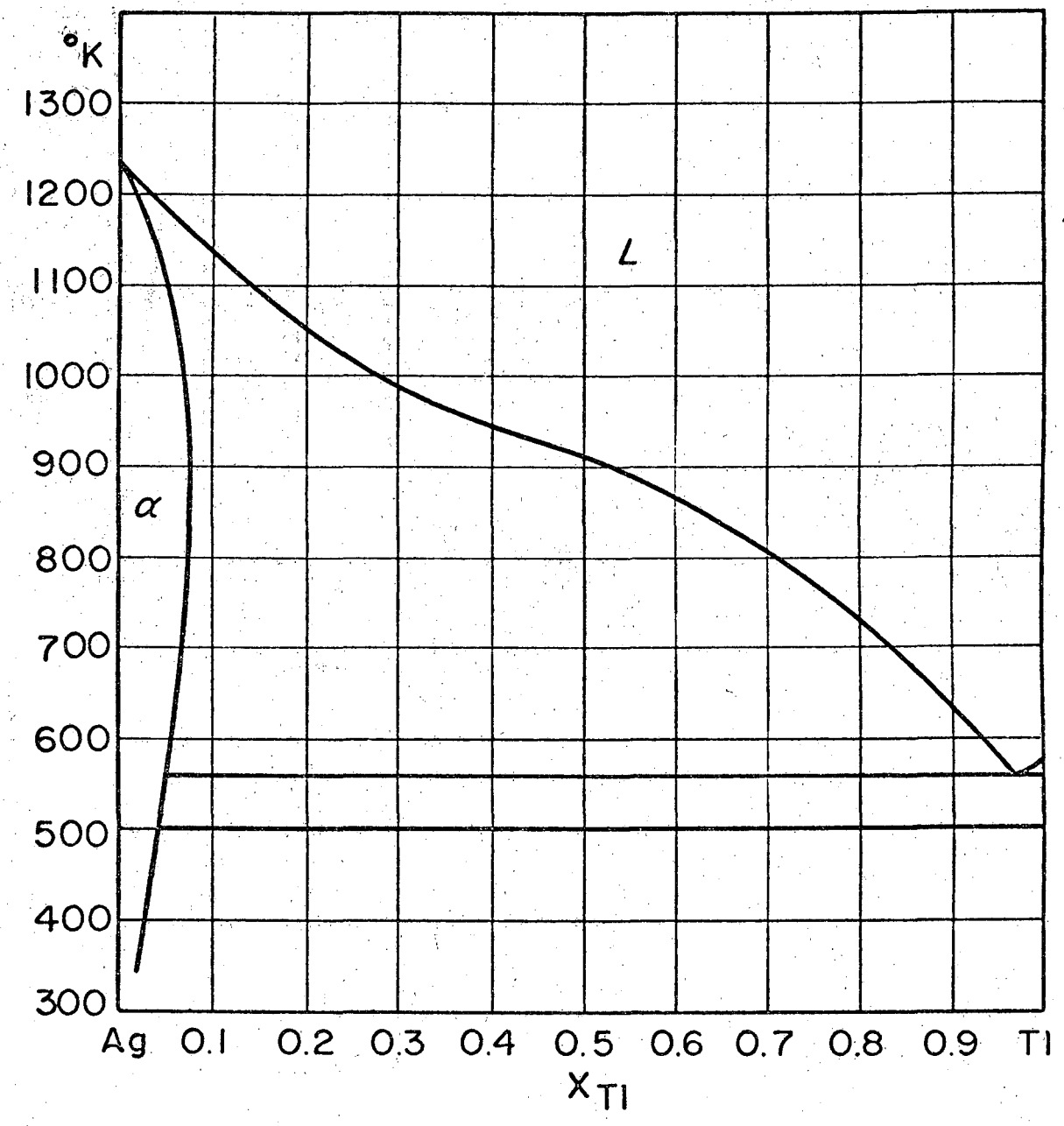
$$Tl_{(\ell)} = Tl(\text{in alloy})_{(\ell)}$$

x_{Tl}	ΔG cal per g-atom	$\Delta \bar{G}_{Ag}$ cal per g-atom	$\Delta \bar{G}_{Tl}$ cal per g-atom	a_{Ag}	γ_{Ag}	a_{Tl}	γ_{Tl}
0.35	- 899	- 816	- 1052	0.657	1.010	0.581	1.660
0.4	- 921	- 920	- 922	0.622	1.037	0.621	1.553
0.5	- 875	- 1117	- 633	0.562	1.124	0.722	1.443
	(± 100)	(± 100)	(± 100)	(±0.03)	(±0.06)	(±0.04)	(±0.08)
0.6	- 809	- 1302	- 480	0.511	1.277	0.781	1.301
0.7	- 714	- 1501	- 376	0.461	1.536	0.823	1.176
0.8	- 577	- 1796	- 272	0.396	1.979	0.869	1.086
0.9	- 397	- 2497	- 164	0.276	2.756	0.919	1.021
1.0	0	- ∞	0	0.000	4.242	1.000	1.000

List of Figure Captions

Figure 1. Ag-Tl Phase Diagram.

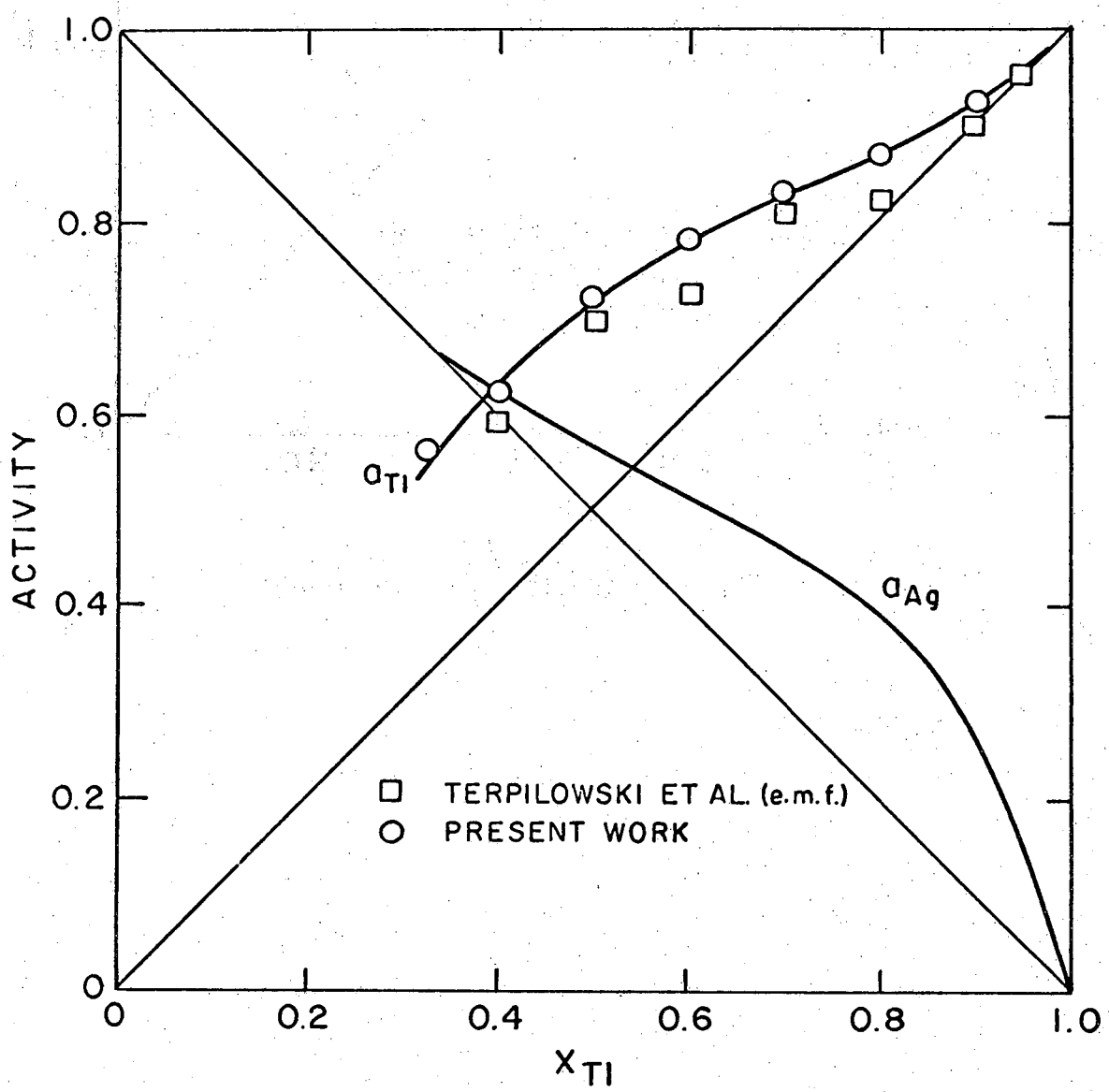
Figure 2. Activity Values for Liquid Ag-Tl Alloys at 975°K with Respect to Liquid Thallium and Supercooled Liquid Silver.



Ag-Tl Phase Diagram

XBL 687-1316

Fig. 1



Activity Values for Liquid Ag-Tl Alloys at 975°K

XBL 687-1317

Fig. 2