THE ACTIVITIES OF MOLTEN ALLOYS OF THALLIUM WITH TIN AND WITH LEAD

BY J. H. HILDEBRAND AND J. N. SHARMA

The investigation described in this paper represents a continuation of the program begun five years ago by N. W. Taylor[1] under the direction of the senior author for the determination of activities in molten alloys by a study of the e.m.f. of concentration cells. Such measurements give accurate data concerning activities over a large temperature range and are of great interest in connection with theories of solution already presented.[2] Taylor studied the alloys of cadmium with zinc, tin, bismuth and lead, and the alloy of zinc with tin. In the present investigation we have studied alloys of thallium with tin and with lead. The electrolyte used was the eutectic mixture of the fused salts of 60% lithium chloride and 40% potassium chloride, with a small amount of thallous chloride. The alloy constituted one electrode and pure thallium the other. The reaction in the cell may be represented as the transference of thallium from its pure state, where it has a unit activity, to the alloy, where its activity is a_1. The electromotive force is related to the activity by the equation $E_I = RT/N_1F \ln 1/a_1$, where R, T, N and F have the usual significance. All symbols with subscript "1" will be used in the course of this article to represent the more electropositive component of the alloy, thallium.

Materials.—The lithium chloride, potassium chloride and thallous chloride used in this research were found to be free from heavy metals. The lead was from the material purified by Hogness;[3] the tin was of known purity, and was used without further purification. About 500 g. of thallium that was at hand contained perhaps 7% of lead and small amounts of other impurities. The method used for its purification was the one used by Richards and Smyth.[4] This purified electrolytic thallium was placed in an alundum tube, which in turn was placed in a pyrex glass apparatus provided with a small inlet tube for the passage of hydrogen gas. This apparatus was heated by an electric unit and a current of hydrogen passed through. When the metal was melted, the bottom of the alundum tube was broken with the aid of a long glass rod. The pure, clean metal ran into the glass tubing provided for that purpose. Sticks of lead and tin were cast in the same manner.

Apparatus.—The cell was similar to that used by Taylor, with two cups to contain pure thallium and four other cups for alloys of varying composition. The only modification from Taylor's cell was that tungsten electrodes were soldered to heavy gold wires to lead out of the furnace and connect with the potentiometer, instead of to the

[1] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923).

[2] Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, Inc., New York, **1924**, especially Chap. XVI.

[3] Hogness, THIS JOURNAL, **43**, 1621 (1921).

[4] T. W. Richards and C. P. Smyth, *ibid.*, **44**, 524 (1922).

oxidizable copper wires previously used. These wires were insulated by short pieces of narrow pyrex glass tubing.

The furnace was the one used by Taylor. Temperatures were determined by two chromel-alumel thermocouples, which were calibrated against the melting points of tin, zinc and antimony. Each calibration was accurate to 1°, corresponding to 0.05 millivolt in e.m.f., which was within the limit of error.

Experimental Procedure.—The metals, whose surfaces were scraped clean and bright, were cut into small pieces. The pure thallium was put into two cups while weighed amounts of both the metals were placed in each of the remaining four cups to give alloys of known composition. The total weight of the alloy varied from about 7 to 8 g. All inlet tubes except two were sealed off and the cell was placed in the furnace. The current was turned on and a stream of hydrogen passed through the cell. In the meantime the electrolyte was prepared by weighing 60% lithium chloride and 40% potassium chloride, together with small amounts of thallous chloride and potassium hydroxide, the latter to insure the absence of hydrogen ion. When the metals in the cell had melted, the stream of hydrogen was shut off, the clear electrolyte was immediately poured into the cell and the two remaining inlet tubes were stoppered.

The gold leads from the several compartments were connected through mercury cups to the potentiometer. This was a Leeds and Northrup (new) K type instrument, and was used with a working battery of 2 Edison cells. The electromotive force at the beginning changed more or less rapidly, but after about six or seven hours the phases became uniform in composition and the e.m.f. became constant to 0.1 m.v. The temperature of the furnace was controlled by means of the resistance and electromotive force readings were taken at intervals of one-half hour until ten or more readings were obtained. The duration of each run was usually two or three days.

In the beginning of the experimental work measurements were made on zinc–tin systems to develop the technique. The results obtained agreed with those of Taylor within the limits of experimental error.

The System Thallium–Tin.—Four runs were made on this system. The constancy of electromotive force values is illustrated in Table I, giving observed values from Run 4. Table II summarizes the observations for each run. Each e.m.f. recorded is an average of ten or more readings taken at half-hour intervals. In each recorded run, the two compartments containing the pure thallium gave zero e.m.f. against each other.

TABLE I

SUMMARY OF TYPICAL RUN (No. 4)

Electromotive forces of thallium concentration cells in thallium–tin alloys at 414°

Thermocouple in m.v.	Temp., °C.	Cell 5–1	Cell 5–2	Cell 5–3	Cell 5–4
17.04	414	0.0857	0.1195	0.0326	0.0232
17.04	414	.0858	.1192	.0325	.0232
17.04	414	.0857	.1192	.0325	.0232
17.04	414	.0857	.1191	.0325	.0232
17.03	414	.0857	.1192	.0326	.0232
17.03	414	.0857	.1192	.0326	.0232
17.03	414	.0858	.1191	.0325	.0232
17.03	414	.0858	.1192	.0325	.0231
17.03	414	.0857	.1192	.0325	.0231
17.03	414	.0857	.1192	.0325	.0232
Average		.08573	.11921	.03253	.02318

TABLE II

SUMMARY OF OBSERVATIONS ON THALLIUM-TIN ALLOYS

Run No. 3

	N_1	0.1242	0.2107	0.3407	0.7128
414°	E	.0867	.0629	.0422	.0157
	Log γ_1	.2684	.2151	.1578	.0321
478°	E	.0979	.0712	.0507	.0194
	Log γ_1	.2544	.1917	.1272	.0170

Run No. 4

	N_1	0.05138	0.1241	0.4387	0.5645
352°	E	....	.0709	.0270	.0164
	Log γ_1	....	.3465	.1398	.0936
414°	E	.1192	.0857	.0325	.0232
	Log γ_1	.3514	.2775	.1194	.0744

Run No. 5

	N_1	0.5781	0.3944	0.15023	0.07937
353°	E	.0172	.0301	.0627	.0893
	Log γ_1	.0963	.1612	.3175	.3799
414°	E	.0225	.0374	.0756	.1047
	Log γ_1	.0731	.1300	.2701	.3325
478°	E	....	....	.0884	.1217
	Log γ_1	....	....	.2302	.2837

Run No. 6

	N_1	0.1030	0.2685	0.3722	0.6714
352°	E	.0776	.0418	.0314	.0155
	Log γ_1	.3612	.2340	.1761	.0479
414°	E	.0940	.0506	.0381	.0183
	• Log γ_1	.2985	.1998	.1507	.0388
478°	E	.1097	.0604	.0462	.0210
	Log γ_1	.2518	.1660	.1195	.0320

The table also gives values of log γ_I, where γ_I is the activity coefficient, defined as a_I/N_I, where N_I is the mole fraction of thallium, that is, the activity is taken as unity in the pure metal and not, as is customary in dealing with aqueous solutions, as the infinitely dilute solution.

The calculated values of a_1 are plotted against N_1 in Fig. 1 to show deviations from Raoult's Law. Log γ_I is plotted against N_1 in Fig. 2. This latter plot has an important physical significance for, as the senior author has stated,[5] we may regard γ_I as the ratio of the escaping tendency of a single molecule of thallium in solution to its escaping tendency from the pure liquid thallium. The logarithm of this ratio is zero when Raoult's law is obeyed by the solution, that is, when the intermolecular forces do not change with the composition. Due to the presence of the tin, these forces have become weaker, and hence there are positive deviations from Raoult's law.

[5] Ref. 2, p. 43.

The activity of the tin has been calculated by the aid of the Duhem equation, which may be expressed as follows: $N_1 \, d \log \gamma_1 = N_2 \, d \log \gamma_2$. For symmetrical curves such as these, Porter[6] has found, and the senior author has confirmed for many systems, that the relation between activity and mole fraction is often expressed by the simple equation: $\log \gamma_1 = \beta N_2^2$. The application of the Duhem equation gives for the other component: $\log \gamma_2 = \beta N_1^2$.
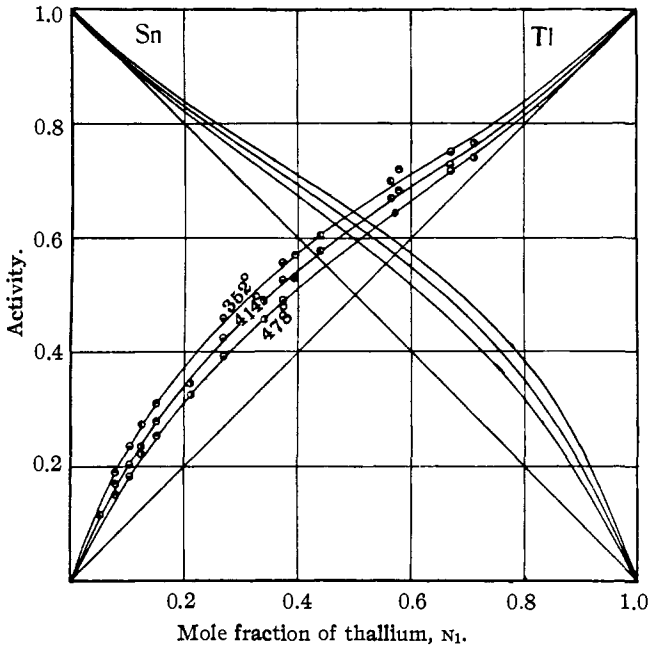
O, Run 1;   O, Run 2;   O, Run 3;   O, Run 4.
Fig. 1.—Activities for the system thallium–tin.

The values of $\log \gamma_1$ for the three temperatures are plotted against N_2^2 in Fig. 3. The slopes of the straight lines that can be drawn through the points give directly the several values of β given in Table III. The variation of β with T is linear and is given closely by the equation $\beta = 1.0763 - 0.00101 \, T$, as shown by the excellent agreement between observed and calculated values in Table III.

TABLE III
VARIATION OF β WITH T

T	Observed	Calculated	βT
625	0.4450	0.4450	278
687	.3826	.3824	263
751	.3175	.3178	239

6 A. W. Porter, *Trans. Faraday Soc.*, **16**, 336 (1921).

This justifies the calculation of a_1 in this system by the equation $\log a_1/N_1 = (1.0763 - 0.00101T)N_2^2$, and of a_2 by the same equation with subscripts interchanged. Table IV gives values of a_1 so calculated for certain values of N_1. The values of a_2 are given if N_2 and a_2 are read in place of N_1 and a_1.

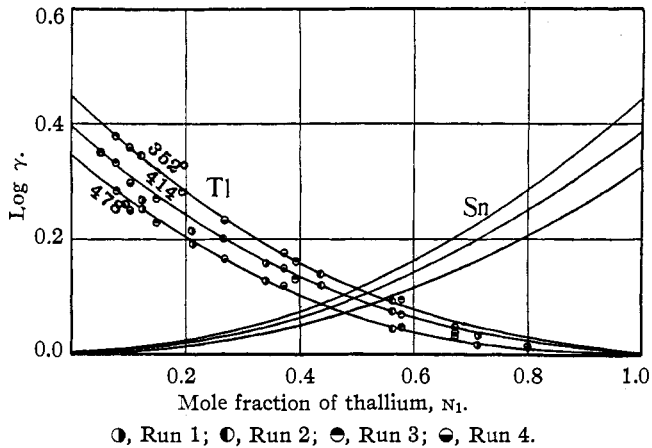◑, Run 1; ◐, Run 2; ◕, Run 3; ◔, Run 4.

Fig. 2.—Deviation of thallium–tin alloys from Raoult's law.

The table also gives the corresponding values of $\log \gamma_1$, where γ_1 is the activity coefficient, a_1/N_1, also values of the heat of transfer of thallium from pure metal to alloy, $\bar{H}_1 - H_1^\circ$, and the free energy of transfer of thal-

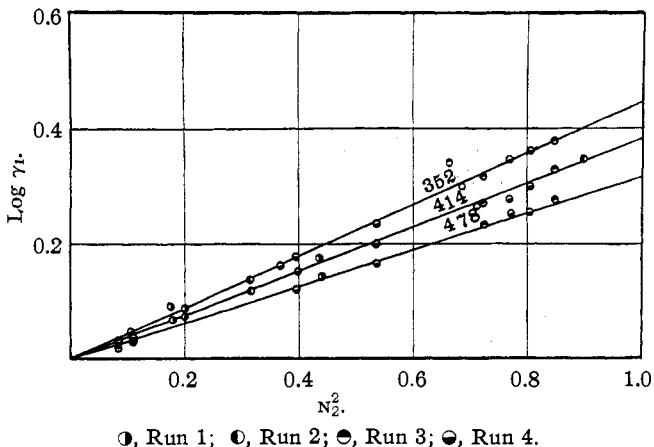◑, Run 1; ◐, Run 2; ◕, Run 3; ◔, Run 4.

Fig. 3.—Plot of logarithm of activity coefficient of thallium against square of mole fraction of tin.

lium from an ideal solution to the actual solution of the same concentration, $\bar{F}_1 - \bar{F}_1^i$. The latter is given by $RT \ln \gamma_1$, and the former by the expression $0.00101 \times 2.3026 \times RT^2N_2^2$, which is derived from the

expression for free energy and its temperature coefficient. We may recall, in this connection, that since there is no heat of solution in forming an ideal solution, the molal heat content of the liquid in the pure state, H_1°, is the same as its partial molal heat content in the ideal solution, $\bar{H}_1^i$; hence $\bar{H}_1 - H_1^{\circ} = \bar{H}_1 - \bar{H}_1^i$.

TABLE IV

THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THALLIUM AND TIN

t	N_1	$\log \gamma_1$	a_1	$\bar{F}_1 - \bar{F}_1^i$	$\bar{H}_1 - H_1^{\circ}$
352°	0.0	0.4443	0.0000	1305	1805
	.2	.2843	.2291	835	1155
	.4	.1599	.5781	470	650
	.6	.0711	.7067	209	289
	.8	.0178	.8335	52	72
	1.0	.0000	1.0000	0	0
414°	0.0	.3823	0.0000	1238	2182
	.2	.2447	.3514	792	1395
	.4	.1376	.5492	446	786
	.6	.0612	.6909	198	349
	.8	.0153	.8287	50	87
	1.0	.0000	1.0000	0	0
478°	0.0	.3183	0.0000	1128	2610
	.2	.2037	.3197	722	1670
	.4	.1146	.5207	406	940
	.6	.0509	.6746	181	418
	.8	.0127	.8238	45	104
	1.0	.0000	1.0000	0	0

So far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author.[7] The simplest equation applying to such a system is $RT \ln a_1/N_1 = bN_2^2$. This would apply to the system under consideration if βT were a constant, b/R. The values of βT given in Table III show that β decreases more rapidly than this. We may see the discrepancy in different but equivalent terms by recalling that a regular solution is defined in part as one which involves no entropy changes in the transfer of a component to it from an ideal solution of the same mole fraction. When this is true, the corresponding free energy and heat changes are identical, but the values in Table IV show that $\bar{F}_1 - \bar{F}_1^i$ is not equal to $\bar{H}_1 - \bar{H}_1^i$ in this case, although the two approach each other as the temperature is lowered.

An explanation of the discrepancy might be found, at least in part, if we knew the volume change involved in forming the mixture. It may prove necessary to consider the specific heat of the electrons in the alloy and in the pure metal. Although this is usually comparatively small, it may occasionally be very considerable. The previous studies of metallic solutions have ignored any influence of the free electrons, and it will be

[7] Hildebrand, *Proc. Nat. Acad. Sci.*, 13, 267 (1927); THIS JOURNAL, 51, 66 (1929).

interesting to determine how long this neglect can continue. We hope to make a study, in this connection, of the thermoelectric potentials of liquid alloys against pure metals.

The magnitude of the deviation from Raoult's law has been shown with other systems to correspond approximately to differences in internal pressure. We do not have the data for a close estimate of the internal pressure of thallium but the table published by the senior author shows thallium two places below tin and cadmium two above. This agrees well with the fact that the systems thallium–tin and cadmium–tin deviate to the same extent from Raoult's law, as shown by the following comparison: for the former system at 478°, when the mole fraction of tin is 0.1, its activity is 1.81; in the latter system at 483°, the activity of tin at the same mole fraction is 1.78.

TABLE V

SUMMARY OF OBSERVATIONS ON THALLIUM–LEAD ALLOYS

Run No. 1

	N_1	0.88483	0.60871	0.30793	
438°	E	.0048	.0381	.0865	
	Log γ	+ .019	− .055	− .108	
500°	E	.0056	.0408	.0914	
	Log γ	+ .017	− .051	− .085	
563°	E	.0064	.0425	.0974	
	Log γ	+ .014	− .041	− .077	

Run No. 3

	N_1	0.07271	0.2015	0.50692	0.7037
438°	E	.1711	.1152	.0520	.0245
	Log γ	− .074	− .121	− .073	− .021
500°	E	.1813	.1221	.0557	.0262
	Log γ	− .044	− .100	− .068	− .018
562°	E	.1922	.1290	.0589	.0276
	Log γ	− .024	− .084	− .061	− .015

Run No. 4

	N_1	0.04069	0.14267	0.80154
438°	E	.1936	.1356	.0142
	Log γ	+ .018	− .116	− .004
500°	E	.2193	.1457	.0142
	Log γ	− .039	− .104	+ .004

Run No. 5

	N_1	0.04541	0.0812	0.13157	0.76525
438°	E	.1840	.1660	.1413	.0180
	Log γ	− .008	− .086	− .120	− .011
500°	E	.2020	.1777	.1511	.0183
	Log γ	+ .026	− .068	− .104	− .003
563°	E	.2122	.1885	.1597	.0192
	Log γ	+ .060	− .050	− .085	− .000

The System Thallium–Lead.—Six successful runs were made on the system thallium–lead. The electromotive forces recorded in Table V are each averages of ten or more individual readings.

The activity of thallium is plotted against its mole fraction in Fig. 4, and log γ_1 is plotted against N_1 in Fig. 5. This system, although not deviating much from Raoult's law, is evidently rather complicated and strongly resembles the system lead–bismuth, investigated by Taylor,[1] showing both positive and negative deviations from Raoult's law. In

————, Observed; ————, PbCl₂ calcd.; ●, Run 1; ◐, Run 2;
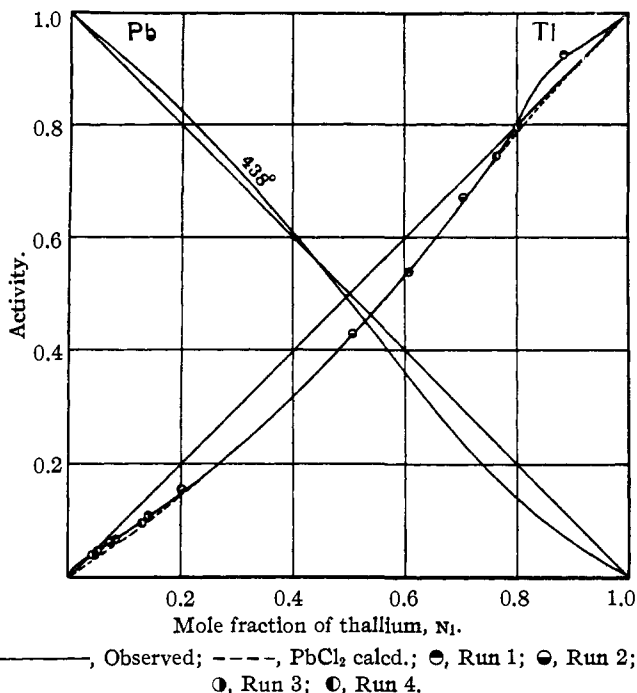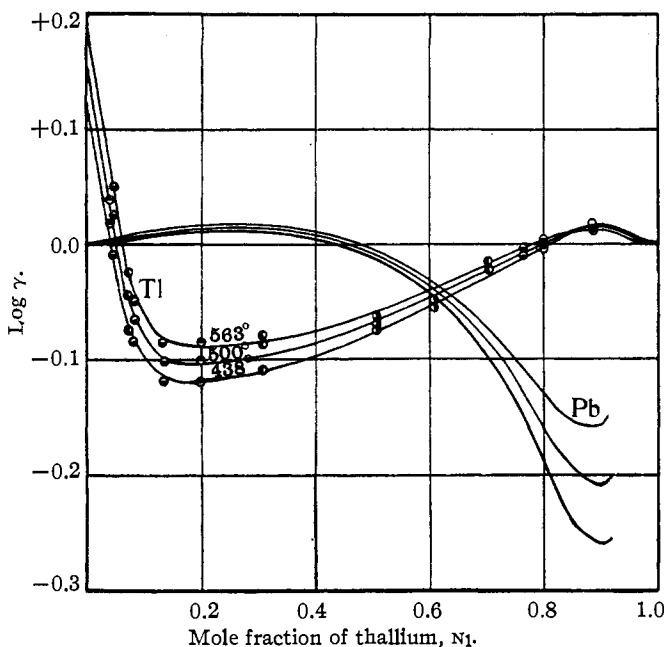◑, Run 3; ◔, Run 4.

Fig. 4.—Activities for the system thallium–lead.

order to make sure that this complication was not due to any participation of lead in the electrical process, the electrolyte was analyzed after the completion of the run. No trace of lead was found.

Taylor's investigation showed the possibility of the existence of a weak compound, Cd_3Bi_2, while the freezing-point composition diagram for the present system[8] shows the existence of the compound $PbTl_2$. It is, therefore, not surprising that both of these systems should show positive and negative deviations alike, the latter due to the formation of the compound, the former to differences in internal pressure between compound and pure components.

[8] Lewkonja, *Z. anorg. allgem. Chem.*, **52**, 454 (1907).

Neglecting the differences in internal pressure, the effect of compound formation may be calculated by methods already developed.[9] Expressing the equilibrium constant for the reaction $Pb + 2Tl = PbTl_2$ in terms of

O, Run 1; ○, Run 2; ●, Run 3; ◓, Run 4.

Fig. 5.—Deviation of thallium–lead alloys from Raoult's law.

the mole fractions of each molecular species present, we find that by assigning to it the value 2.719, we get the dotted curve shown in Fig. 4, which agrees well with the observed points except at the ends. Differ-

TABLE VI

ACTIVITIES OF THALLIUM, (a_1), AND OF LEAD, (a_2)

	438°		500°		563°	
N_1	a_1	a_2	a_1	a_2	a_1	a_2
0.0	0.000	1.000	0.000	1.000	0.000	1.000
.1	.080	.919	.084	.918	.087	.912
.2	.152	.823	.157	.828	.163	.829
.3	.232	.716	.240	.720	.247	.723
.4	.320	.604	.328	.610	.336	.611
.5	.419	.488	.428	.495	.436	.495
.6	.529	.367	.538	.373	.545	.373
.7	.656	.243	.665	.248	.672	.251
.8	.790	.132	.801	.139	.810	.148
.9	.935	.055	.929	.062	.923	.069
1.0	1.000	.000	1.000	.000	·1.000	.000

[9] *Cf.* ref. 2, p. 75.

ences in internal pressure, not taken into account in this calculation, of course diminish the quantitative significance of the above numerical value of K.

The activity of the lead in these alloys was calculated by the aid of the Duhem equation, using a graphic method of integration,[10] since no simple equation could be found to represent this system. The calculated values of a_2 are given in Table VI for certain values of N_1, together with the smoothed-out values for a_1.

Summary

1. The activities of thallium in liquid alloys with tin and with lead have been determined over a range of 125° by the aid of e.m.f. measurements and an equation is given for the activity in terms of mole fraction and temperature for the thallium–tin system.

2. The partial molal heat of transfer of thallium from an ideal solution to the tin solution of the same mole fraction has been calculated over a range of composition and temperature. Comparison with the free energy values calculated for the same process shows disagreement; hence, although the solution behaves as a regular solution with the respect to changes in composition, it is not regular with respect to changes in temperature.

3. The thallium–lead system, although not deviating much from ideality, shows a rather complicated behavior, almost identical with that of cadmium–bismuth alloys and which may be attributed, in part, to the presence in solution of some of the compound $PbTl_2$.

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A SIMPLE REFERENCE ELECTRODE FOR POTENTIOMETRIC TITRATIONS

BY H. H. WILLARD AND A. W. BOLDYREFF

The inconvenience connected with the use of the calomel or silver chloride half-cell as a reference electrode in potentiometric titration has long been recognized. Hostetter and Roberts[1] suggested the use of a palladium wire in place of the usual half-cell. Willard and Fenwick[2] studied a large number of bimetallic systems. Furman[3] proposed an amalgamated gold electrode as a suitable reference electrode in some oxidation–reduction reactions.

[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 268 ff.

[1] Hostetter and Roberts, THIS JOURNAL, 41, 1343 (1919).

[2] Willard and Fenwick, ibid., 44, 2504 (1922).

[3] Furman, ibid., 50, 268, 273 (1928).