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

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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.

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[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).

Kamienski[4] used in technical electrometric determinations, especially of metals, a copper electrode in saturated copper sulfate as reference and a carborundum electrode against gold or platinum electrodes. Ball[5] proposed as a standard electrode a platinum wire immersed in a 3 N sulfuric acid solution (for oxidation–reduction work) or in N hydrochloric acid (for acidimetry), the electrical connection with the solution titrated being established through a wet asbestos fiber sealed securely in the end of a small glass tube. Müller[6] used in oxidation–reduction titrations an electrode system consisting of a platinum wire sealed inside of a capillary containing a very small volume of the original solution, the other electrode being a platinum wire wound around the capillary.

A very convenient and accurate method for differential potentiometric titrations has been described by MacInnes and Jones[7] and by MacInnes.[8] Modified procedures for this method are found in the papers of Roth,[9] Heckzo[10] and Hall.[11]

Among other recent methods avoiding the use of a standard half-cell in potentiometric titrations, but based on different principles than those noted above, might be mentioned those of Sandved and Backer,[12] Reissaus,[13] Foulk and Bawden[14] and Furman and Wilson.[15]

The electrode described here eliminates the use of the standard half-cell in all types of potentiometric titrations. The principle involved is extremely simple. A clean, bright platinum wire, immersed in any standard solution (oxidizing or reducing agent, acid or alkali, or a precipitating agent) will rapidly assume a perfectly definite potential.

Therefore, a very satisfactory reference electrode can be obtained by sealing a piece of smooth platinum wire into the tip of the buret (below the stopcock). It is thus in contact with the standard solution used in the titration. By dipping the tip of the buret into the solution titrated, an electrical connection is established with the indicator electrode. This "buret electrode" is shown in Fig. 1.

The tip of the buret is bent and drawn out to keep the buret out of the way and to minimize the diffusion at the point of contact of the solutions. The error due to diffusion is negligible as far as reaction inside and at the

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[4] Kamienski, *Przemysl Chemiczny*, 11, 769 (1927).

[5] Ball, *Ind. Eng. Chem.*, 19, 370 (1927).

[6] Müller, *Z. physik. Chem.*, **135**, 102 (1928).

[7] MacInnes and Jones, This Journal, **48**, 2831 (1926).

[8] MacInnes, *Z. physik. Chem.*, **130**, 217 (1927).

[9] Roth, *Z. Elektrochem.*, **33**, 127 (1927).

[10] Heckzo, *Z. anal. Chem.*, **73**, 404 (1928).

[11] Hall, Jensen and Baeckström, This Journal, **50**, 2217 (1928).

[12] Sandved and Backer, *Tids. Kemi Bergv.*, **5**, 224 (1925).

[13] Reissaus, *Z. anal. Chem.*, **69**, 450 (1926).

[14] Foulk and Bawden, This Journal, **48**, 2045 (1926).

[15] Furman and Wilson, *ibid.*, **50**, 277 (1928).

tip of the buret is concerned because the tip is flushed out during each successive addition of the reagent, and because the concentration of the ion titrated is being constantly diminished and becomes vanishingly small near the end-point. As far as the change in potential due to diffusion is concerned, it has been shown in a control experiment that during the time between two successive additions of the titrating agent this is less than the error in measurement. The buret was filled with 0.1 *N* potassium bromate and the tip dipped into a solution *N*/40 with respect to arsenite. The potential between a smooth platinum wire in this solution and the buret electrode was measured every minute; the deviation from the initial value during five minutes did not exceed 0.2 mv.

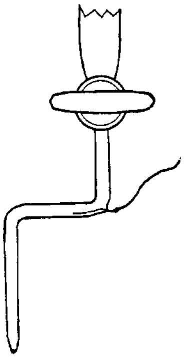

Fig. 1.

To demonstrate the usefulness of such an electrode and the constancy of its potential, a titration was made of 0.1 *N* potassium dichromate with 0.1 *N* ferrous sulfate in a solution containing 25 cc. of concd. sulfuric acid in 100 cc. of solution. Three electrodes dipped into the solution: a silver chloride electrode, a bright platinum wire and a "buret electrode." The potential between any two of them could be measured. The results are shown in Table I.

TABLE I

POTENTIALS BETWEEN DIFFERENT ELECTRODES

Titration of approx. 0.1 *N* $K_2Cr_2O_7$ with 0.1 *N* $FeSO_4$.

	Potential between		
$FeSO_4$ added, cc.	Pt. AgCl, mv.	Pt/buret electrode, mv.	Buret electrode/AgCl, mv.
0.0	0.8813	0.6610	0.220
4.0	.8896	.6695	.220
8.0	.8911	.6714	.220
12.0	.8930	.6724	.221
16.0	.8935	.6739	.220
20.0	.8905	.6697	.220
24.0	.8994	.6802	.219
24.5	.9000	.6801	.220
24.7	.8969	.6771	.220
24.9	.8946	.6752	.220
25.0	.8812	.6598	.221
25.1	.8418	.6243	.218
25.2	.4594	.2393	.220
25.3	.4344	.2124	.222
25.5	.4123	.1940	.218

The curves obtained by plotting potential against volume have obviously the same shape regardless of which electrode is used, but are displaced vertically from each other by an amount equal to the potential difference between the "buret electrode" and the standard half-cell. A change from the mean value of a few millivolts in the potential of the "buret electrode" is due to polarization in the process of balancing the potentiometer circuit. In some solutions (particularly 0.1 *N* sodium hydroxide) this polarization can become appreciable unless sufficient care is taken in balancing. A control experiment showed that this was concentration polarization.

A summary of the tests to which this method was subjected is shown in Table II. All solutions were carefully standardized and were approximately 0.1 *N*. The figures given represent the results of individual titrations.

In the case of permanganate, a trace of manganese dioxide forms on the platinum wire and at the tip of the buret, but the error is negligible.

Table II

Comparison of "Buret Electrode" and AgCl Electrode

Subs. titrated	Titrating soln.	$\Delta E/\Delta v$ at e.-pt. mv./cc. "Buret electrode"	$\Delta E/\Delta v$ at e.-pt. mv./cc. AgCl electrode	Calcd., cc.	Found, cc.
$K_2Cr_2O_7$	$FeSO_4$	3850	3820	25.18	25.15
$FeSO_4$	$KMnO_4$	4270	4240	24.93	24.90
H_3AsO_3	$KBrO_3$	2900	2500	25.00	24.95
HCl	NaOH	1680	1820	18.55	18.55
HCl	$AgNO_3$	490	510	25.08	25.10

Summary

1. A simple reference electrode has been devised, consisting of a platinum wire fused into the tip of a buret.
2. The constancy of the potential of this electrode has been shown by titrations involving oxidation–reduction, neutralization and precipitation reactions.

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NOTES

A Micro Extraction Method.—For the extraction of very small amounts of material the following method may prove helpful.

A capillary of about 1–2 mm. in inner diameter and 8–10 cm. in length is filled with the liquid material (1 drop) to be extracted and an equal amount of the non-miscible extraction medium. It is then sealed at both ends and centrifuged in such a manner, that the liquid layer with the higher specific gravity is forced through the liquid layer having the lower specific gravity by having the first one at the top in the centrifugal tube and the latter on the bottom. This operation is repeated several times.

The closed capillary is then cut apart under the microscope at the zone of contact. By opening the ends both liquids, the solvent and the extraction medium, become available for examination.