THE POTENTIAL OF LEAD–LEAD ION

BY MERLE RANDALL AND JESSIE Y. CANN

The potential of the lead–lead ion electrode was taken as 0.122 volt by Lewis and Randall,[1] who based their calculations largely upon measurements of the lead–lead chloride electrode and a fairly satisfactory guess of the activity coefficient of lead chloride in the saturated solution. New methods of evaluating the activity coefficients, new values of the reference electrodes and the results of the solubility measurements of Randall and Vietti[2] make it desirable to restudy the older measurements and to determine the potential by an independent method.

The Cell: Pb (in sat. amalg.), $Pb(NO_3)_2$ (aq) | KNO_3 (aq) | KCl (aq), AgCl (s), Ag (s).—The activity coefficient of lead nitrate was measured by Randall and Scott[3] by the freezing point method, and since the uncertainty in the potential of the flowing liquid junction with a common ion at the same equivalent concentration of salts is not large, we have measured the cell Pb (in sat. amalg.), $Pb(NO_3)_2$ (aq) | KNO_3 (aq) | KCl (aq), AgCl (s), Ag (s).

The Cell.—The electrode vessels were of the usual form. The flowing junctions were an all-glass modification of the type described by Randall and Langford.[4] The complete cell of pyrex glass is shown in Fig. 1. The dropping funnels A, B and C contained the solutions of lead nitrate, potassium nitrate and potassium chloride. The reservoirs D, E and F were filled with the corresponding solutions and served to bring the temperature of the solutions to the temperature of the thermostat. During measurements Stopcocks G and H were open and I and J were adjusted so that there would be the same flow from the tips K and L. The flow was regulated by means of the stopcocks of the dropping funnels. The rods M and N were raised, the flow from tips K and L regulated, then the rods were lowered and contact was made through the film of solution around the rods. Waste solutions were continuously removed by means of suction applied to small tubes inserted nearly to the bottom of O and P.

The warmed lead amalgam was poured rapidly in succession through a series of clean, dry, pyrex glass test-tubes, which removed all traces of the slight surface film of oxides, and was immediately introduced into the

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

[2] (a) Randall and Vietti, THIS JOURNAL, 50, 1526 (1928); (b) "International Critical Tables," McGraw-Hill Book Co., New York, Vol. VII, Section on Free Energy of Chemical Substances (in press).

[3] Randall and Scott, THIS JOURNAL, 49, 636 (1927).

[4] Randall and Langford, unpublished.

cell, Q, and covered quickly with the solution that was to be used. This was done after the whole apparatus had been flushed with hydrogen. The surface of the amalgam was just below the tip of the connecting tube. The cell was placed in the usual oil thermostat, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

Materials.—The solutions were made up by weight (moles per 1000 g. of water in vacuum) from high grade "analyzed" salts and conductivity water. Pure hydrogen was bubbled through the solutions to remove traces of oxygen.
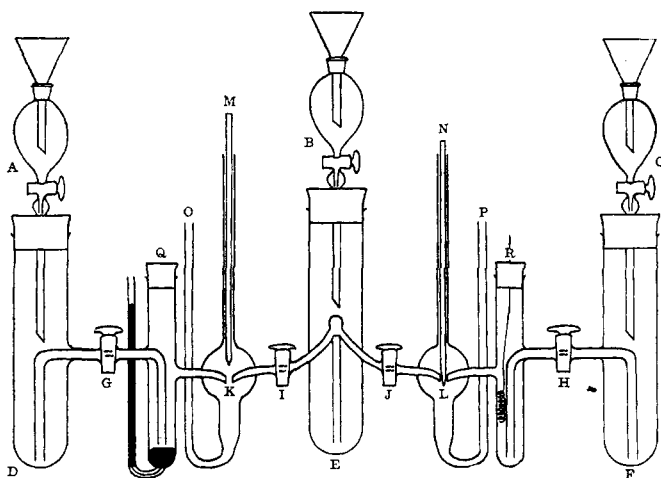

Fig. 1.—Cell with two flowing junctions.

The saturated two-phase lead amalgam was made by heating together in vacuum 5 g. of "analyzed" test lead and 100 g. of distilled mercury according to the method of Gerke.[5] This amalgam had a slight film of oxide which was removed as described above.

The silver–silver chloride spiral electrodes were made in the same way as those used by Randall and Young.[6] Before introducing into the electrode vessel, the spirals were placed in the solution to be used and evacuated for about thirty minutes with gentle heating, or until all bubbles ceased to appear at the surface of the spiral. Complete removal of oxygen by the above means and by flushing the solutions and apparatus with hydrogen was found to be necessary in order to obtain steady and concordant potentials.

The Standard Potential of the Lead–Lead Ion Electrode.—The molality of the solutions used and the potentials obtained are shown in the first four columns of Table I.

[5] Gerke, THIS JOURNAL, **44**, 1684 (1922).
[6] Randall and Young, *ibid.*, **50**, 989 (1928).

TABLE I

Pb (IN SAT. AMAL.), Pb(NO₃)₂ (AQ.) | KNO₃ (AQ.) | KCl (AQ.), AgCl(s), Ag(s) AT 25°

m Pb-(NO₃)₂	m KNO₃	m KCl	E volt	E Pb(NO₃)₂ | KNO₃	E KNO₃ | KCl	E less liquid	$E^0_{298.1}$	$\mu^{1/2}$	log γ + const.
0.025	0.05	0.05	0.4760	−0.0062	0.0013	0.4809	0.3361	0.2738	−4.0188
.05	.10	.10	.4545	− .0078	.0017	.4606	.3367	.3873	−4.0910
.10	.20	.20	.4327	− .0098	.0023	.4402	.3368	.5477	−4.1621

The values of the potential given in Col. 4 represent the average of several hundred measurements with various rates of flow of the solutions in the liquid junctions, with several solutions and different electrodes for each series. The flowing liquid junctions proved quite reproducible, the principal error being introduced by alteration of the temperature of the solutions when the rate of flow was great. About forty drops per minute was found to be the best rate. The potentials of the liquid junctions were calculated by means of the Lewis and Sargent[7] formula, the conductivities being taken from the compilation by Holborn[8] from the work of Kohlrausch and others at 18°. The ratio of the conductivities at 18 and 25° was assumed to be the same.

The cell reaction after elimination of liquid potentials may be written

Pb(in sat. amalg.) + 2AgCl(s) = 2Ag(s) + Pb⁺⁺ (in Pb(NO₃)₂ (aq.) +
2Cl⁻ (in KCl (aq.))   (1)

in which, formally, aqueous lead chloride is produced, not with an activity coefficient which is that of lead chloride, but one which is the geometric mean of the activity coefficients of lead and chloride ions in lead nitrate and potassium chloride, respectively. As an approximation, which is not wholly justified, we may assume the hypothesis of the independent activity coefficient of the ions,[9] whence the activity coefficient of this hypothetical lead chloride is given by

$$\gamma_\pm (\text{Pb}^{++} \text{ (in Pb(NO}_3)_2 \text{ (aq.))}) \; 2\text{Cl}^- \text{ (in KCl (aq.))} = [\gamma^3(\text{Pb(NO}_3)_2) \; \gamma^4\text{KCl}/\gamma^4\text{KNO}_3]^{1/3}$$
(2)

Whence, substituting the values of the activity coefficients taken from the work of Randall and Scott,[3] for lead nitrate, of Randall and White[10] for potassium chloride, and of an unpublished summary of activity coefficients, we find by the usual equation[11] the values of **E**° given in the eighth column of Table I, from which we choose the average value

$$\mathbf{E}° = 0.3367 \text{ v.}; \quad \Delta F°_{298.1} = -15{,}538 \text{ cal.}$$

[7] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[8] Landolt, Börnstein, Roth, Scheel, "Tabellen," Springer, Berlin, **1923**, Vol. II, pp. 1079–1080.

[9] Ref. 1, p. 380.

[10] Randall and White, THIS JOURNAL, **48**, 2514 (1926).

[11] (a) (Ref. 1, p. 396); (b) Randall, *Trans. Faraday Soc.*, **23**, 505 (1927).

We may make an independent extrapolation of the activity coefficient of this hypothetical aqueous lead chloride by means of the equation[11b]
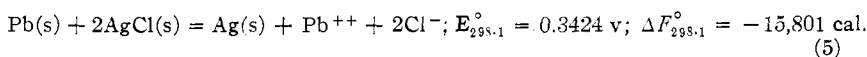
$$\log \gamma + \text{const.} = -\mathbf{E}/0.088725 - \log m \pm \tag{3}$$

The values of the square root of the ionic strength and of $\log \gamma$ +const. in Equation 3 are given in the last two columns of Table I. Plotting on transparent paper, $\log \gamma$ +const. on the standard scale against $\mu^{1/2}$ and referring to the standard plot of activity coefficients as was done by Randall and Vietti,[2] we obtain constant $= -3.8000$ or $\mathbf{E}^{\circ} = 0.3372$ v.; but the value 3.7938, corresponding to $\mathbf{E}^{\circ} = 0.3366$ seems from the plot to be a reasonable value.

For the potential of saturated lead amalgam we take[12]

$$Pb(s) = Pb(\text{in sat. amalg.}); \quad \mathbf{E}^{\circ}_{298.1} = 0.00586; \quad \Delta F^{\circ}_{298.1} = -270 \text{ cal.} \tag{4}$$

whence

$$Pb(s) + 2AgCl(s) = Ag(s) + Pb^{++} + 2Cl^-; \mathbf{E}^{\circ}_{298.1} = 0.3424 \text{ v}; \Delta F^{\circ}_{298.1} = -15,801 \text{ cal.} \tag{5}$$

and combining with Gerke's value for the free energy of formation of silver chloride $(\Delta F^{\circ}_{298.1} = -26,220)$, and the new value of the chloride ion of Randall and Young[7] $(\Delta F^{\circ}_{298.1} = -31,345)$ we find

$$Pb = Pb^{++} + 2E^-; \quad \mathbf{E}^{\circ}_{298.1} = 0.1203 \text{ v}; \quad \Delta F^{\circ}_{298.1} = -5551 \text{ cal.} \tag{6}$$

The relation of this potential to that determined from the potential of lead–lead halide electrodes will be discussed in another place.

Summary

The potential of the lead–lead ion electrode has been determined by measurements of the lead amalgam–lead nitrate electrode, combined through flowing junctions, with a silver–silver chloride electrode. The standard potential of lead ion is found to be 0.1203 v., and the free energy of formation to be -5551 cal. at $25°$.

BERKELEY, CALIFORNIA

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[12] Randall and Spencer, unpublished, see Ref. 2 b.