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The Equilibrium between Lead, Lead Iodide, and Iodine.

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May 1924.

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The Equilibrium between Lead, Lead Iodide, and Iodine.

The fact of the instability of lead iodide at moderately high temperatures is well known.^{1,2} This work was undertaken in order to discover, if possible, the degree of dissociation, its change with the temperature, and to collect any other important facts connected with the equilibrium.

The problem was attacked in two ways, the second mode being undertaken after it was plain that no progress could at that time be made on the first. The original attempt was to discover at what temperatures the first noticeable break-up occurred and to measure the progress of the thermal decomposition with increasing temperature. Later it seemed advisable to investigate, by means of the electromotive force measurements of a galvanic cell, the energy change involved in the formation of lead iodide from its elements and its change over a necessarily limited range of temperatures.

In both of these investigations progress was impeded by the lack of necessary apparatus. The delay involved in repairs to a vacuum pump and due to trouble with a potentiometer - both instruments vital to the work - served

(¹ Abegg & Auerbach - Handbuch der Anorg. Chem.

(² Helfenstein - Zeit. Anorg. Chem. 23, 255, (1900)

to slow down, and in one case, to cause abandonment of the project.

The lead iodide used was prepared by precipitation from lead nitrate solution with potassium iodide. It was carefully washed and part - that used in cell electrodes - purified by recrystallization from hot water.

(I)

Lead iodide, when heated in contact with air is oxidized with the formation of an oxide and the liberation of free iodine¹. A stream of nitrogen to exclude oxygen was tried at first but was found to be unsatisfactory. Lead iodide was then heated in an inclosed tube in as perfect a vacuum as could be obtained with the pump and aspirator available. Iodine vapor became visible at temperatures above 200°C and below the melting point of the solid (around 300°C) became very dense and condensed on the cooler portions of the tube. Certainly some of this decomposition, possibly that at lower temperatures, was due to the remaining oxygen in the tube. This, however, could account for only a small part of the liberated iodine. It would seem, then, that under reduced pressures the decomposition begins and reaches a comparatively advanced stage at temperatures below the melting point.

It was planned to continue this line of work and, with a vibrating quartz fibre manometer^{3,4}, to study the progress of the decomposition by measuring the pressure exerted by

(3) Haber & Kerschbaum - Zeit. Elektrochem. 20, 296 (1914)

(4) Dushman - Gen. Electric Rev. 23, 738 (1920)

the evolved iodine. The activity of iodine vapor in attacking mercury and other metals⁵ precluded the use of a McLeod gauge or other more easily manipulated device. It was thought advisable to abandon this plan and turn to electrochemical methods.

(II)

Thermodynamics is now so generally applied to physical chemistry that no explanation of its applicability to this problem is necessary. The notation and system is that of Lewis and Randall's "Thermodynamics", and the calculations of free energy follow those of Chapters XIV, XV, XXIX, XXX, and XXXVII. The data concerning reference potentials and the convention of signs of electromotive forces was taken from Chapters XXIX and XXX of that work.

There has been considerable work done on the lead iodide equilibrium in determining by means of reversible galvanic cells its heat of formation and free energy of formation. Gerke⁶, Taylor⁷, and Taylor⁸ and Parrott have measured the E.M.F. of cells depending on the reaction of the formation of lead iodide from its elements, and have calculated the free energy and entropy changes involved. None of these investigators used cells of exactly the same construction and constitution so this partial duplication of their work was undertaken.

- (⁵) Shenstone - Trans. Chemical Soc. 71, 471, (1897)
- (⁶) Jr. Am. Chem. Soc. 44, 1684, (1922)
- (⁷) Jr. Am. Chem. Soc. 38, 2295, (1916)
- (⁸) Jr. Am. Chem. Soc. 43, 489, (1921)

The cells used were of the usual separate-electrode type with a solution containing a common ion between. The chemicals used were purified and precautions were taken that no current should be drawn from the cell. All measurements were made with a Leeds and Northrup precision potentiometer. This instrument was not in perfect condition and, consequently, the accuracy of the fourth figure is in considerable doubt.

One electrode consisted of an amalgam of lead (approx. 1%), solid lead iodide, and N/10 potassium iodide solution, dipping into N/10 potassium iodide solution. This was measured against a Decinormal Calomel Electrode - mercury, mercurous chloride, N/10 potassium chloride solution, and dipping in the intermediate N/10 chloride solution. Both electrodes were fitted with stopcocks to prevent diffusion and mixing of solutions.

A cell of this nature does not lend itself to measurements over any large range of temperatures. The tendency to evaporation at higher temperatures affects the accuracy of readings and the very different heat capacities of the various units makes some kind of thermostatic control imperative. At temperatures near that prevailing in the laboratory fair reproducibility of results was obtained, but the values of the E.M.F. at temperatures higher than this were decidedly erratic. Their value as data - except for one or two isolated points - is very doubtful. This is due largely to the lack of a thermostat where equilibrium

conditions could be secured. Recourse was had to measurements taken while heating and cooling and the non-correspondence of these values points to this as an important source of error.

The E.M.F. of the cell -
- Pb(amalgam), PbI_2 (sol.), N/10 KI, N/10 KCl, HgCl(sol.), Hg⁺
was measured directly and correction then made for the Decinormal electrode and the amalgam. Both the amalgam used and pure sheet lead were measured against the calomel electrode in a solution of lead nitrate and the difference in the E.M.F. taken as the potential difference between the lead and the amalgam. The lead electrode coated quickly in solution causing a rapid shift in potential and a consequent uncertainty as to the accuracy of the figures obtained. It was found that the amalgam was at approximately 0.01 volt higher potential than the pure lead.

All potential readings were reduced so as to be measured from that of the Standard Hydrogen electrode. The value taken for the Decinormal electrode was E.M.F. -.3351 volt, as given by Lewis and Randall^{9,10}. No correction was made for the liquid potential between the potassium chloride and iodide solutions due to the lead ion present in the latter".

Table I gives values of the E.M.F. at varying temperatures. Only those figures that check within reasonable limits are included.

(⁹ Lewis and Randall's "Thermo." Chap. XXX, Pages 405-406

(¹⁰ Lewis, Brighton, Sebastian. Jr. Am. Ch. Soc. 39, 2245 (1917)

(" Gerke - same as note 6.

Table I.

E.M.F. of cell $\text{Pb}(\text{amalg.}), \text{PbI}_2(\text{s}), \text{N}/10 \text{ KI}, \text{D.E.}^+$

<u>Temperature (in degrees Centigrade.)</u>	<u>E.M.F. (in volts)</u>
25.0	.6219 *
25.025.0	.6219 *
25.5	.6221 *
25.8	.6217 *
26.2	.6215
27.0	.6202
27.3	.6213
28.0	.6200
28.3	.6208
29.0	.6195
31.0	.6193
31.0	.6193
32.0	.6191
33.0	.6184
33.5	.6184
34.5	.6179
35.0	.6181
35.5	.6175
36.0	.6175
37.5	.6170

These values, when plotted, do not fall on a line or curve, but rather lie along two lines nearly parallel. Only in the neighborhood of 25°C the points are clustered, and reproducible results were obtained. The accuracy of the

location of the other points is much in doubt. There is not enough reliable data to attempt to determine the temperature coefficient of the cell.

If the first four values in the list are averaged, the E.M.F. value for 25.3° C is 0.6219 volt. Adding to this the correction for the amalgam and subtracting the potential of the calomel electrode, the E.M.F. for the half-cell -

Pb, PbI₂, I⁻ - is 0.2968 volt.

$$(0.6219 + 0.01 - 0.3351 = 0.2968)$$

This means that the lead is at a lower potential than its solution.

We have the equation $\Delta F = -NFE$ where ΔF is the free energy change in the reaction, N the number of chemical equivalents taking part, F the Faraday Equivalent, and E the E.M.F.

$$\Delta F = -NFE = -2 \times 96540 \times 0.2968$$

$$\Delta F = -57306 \text{ calories.}$$

This value of the E.M.F. of the cell for 25.3° C checks very well with that found by Gerke at 25.0 C. He used the cell - Pb, PbI₂, N/10 KI, N.E. - where N.E. is the Normal Calomel electrode. Assuming, as we have, that for the Standard Hydrogen electrode $E = 0$, the E.M.F. for his half-cell - Pb, PbI₂, I⁻ - , E is 0.2990 .

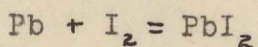
This verification shows that the E.M.F. of 0.2968 volt and consequently the free energy value: $\Delta F = -57306$ calories must be at least approximately correct. Comparison with the free energy data for various kindred solids shows for

lead chloride, $\Delta F = -74990$ and for lead oxide, $\Delta F = -41000$ cal. This would indicate that the stability of lead iodide in the neighborhood of 25°C was less than that of lead chloride and greater than that of lead oxide. Much more adequate data is needed before any attempt can be made to calculate the dissociation of lead iodide with temperature, other than by direct chemical and physical measurements.

Summary:

An attempt was made to measure the thermal dissociation of lead iodide by a measurement of the pressure of the iodine evolved. This was abandoned.

E.M.F. measurements were made on the cell -
(Pb, PbI_2 , N/10 KI, N/10 KCl, HgCl, Hg) -
over a range of temperatures. The values obtained were, in general, unsatisfactory, but those found for 25°C checked well with similar data available. No attempt was made to apply the figures for higher temperatures. The figures pointed to the following values for the reaction :



$$E = 0.2968 \text{ volt,}$$

$$\Delta F = -57306 \text{ calories.}$$