

Laue data, and, considering both, the value of the F-H-F distance may be given as 2.26 Å. with a probable error of not more than 0.01 Å.

Discussion

In going from the HF_2^- ion in crystalline potassium bifluoride to the $(\text{HF})_n$ polymers in gaseous hydrogen fluoride there is a lengthening of 0.29 ± 0.06 Å. in the F-H-F distance. This shows that formation of additional hydrogen bonds lengthens the F-H-F distance. While the value 2.37 ± 0.1 Å. for the F-H-F distance in ammonium bifluoride leaves some doubt as to a lengthening, it is strongly indicated that the formation of two additional N-H . . . F bonds causes a weak-

ening of the F-H-F bond and a probable lengthening of about 0.1 Å. The theoretical value calculated by Pauling⁵ for this distance is 2.32 Å. with a symmetrical linear configuration for F-H-F.

Summary

A redetermination of the parameter in potassium bifluoride has been carried out using Laue and oscillation photographs. The value $u = 0.1408 \pm 0.003$ leads to the fluorine-fluorine distance 2.26 ± 0.01 Å. in $\{\text{F-H-F}\}^-$. A comparison is made with other reported values.

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 277.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY AND THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Silver and Mercurous Iodide Electrodes

BY WARREN C. VOSBURGH, PAUL F. DERR, GERALD R. COOPER AND ROGER G. BATES¹

The silver and mercurous iodide electrodes have both been shown to be reproducible under favorable conditions,² and it seemed desirable to attempt a direct comparison of the two. This was found surprisingly difficult, and the result can be considered only approximate. Some of the observations made in the course of the study are of value, however.

Silver Iodide Electrode.—All of the silver iodide electrodes were prepared by the thermal method; some from silver oxide and iodate^{2a} and some from oxide and iodide.^{2b} In the preparation of some, the platinum wire was electroplated with silver before application of the paste, but this was found unnecessary and was omitted in the later electrodes.

Silver iodide electrodes agreed within 0.02 mv. when compared in the same vessel with oxygen-free potassium iodide solution (about 0.02 *m*) as the electrolyte. The agreement was better on the second day than on the first, and continued good indefinitely. The agreement was not as good when the electrolyte was saturated with lead iodide or when 0.01 *m* cadmium iodide was used as the electrolyte. When air was admitted to a cell consisting of two silver iodide electrodes

in the same vessel, it caused disagreement of the electrodes.³ A trace of mercurous iodide also caused disagreement.

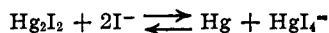
Mercurous Iodide Electrodes.—While the mercurous iodide electrode is highly reproducible when the electrolyte is a saturated cadmium iodide solution,^{2c,d} it was found much less reproducible when the electrolyte was a potassium iodide solution. Two mercurous iodide electrode systems in a single H-vessel prepared with nitrogen-vacuum technique gave a cell with an electromotive force anywhere from zero to well over a millivolt in spite of considerable care to avoid errors. When one electrode had a thick (1 to 2 cm.) layer of mercurous iodide paste covering the mercury and the other a thin (0.5 cm.) layer, the thick-layer electrode was always positive, and the electromotive force varied from 0.3 mv. to nearly 2 mv. in different cells and at different times. When both layers of mercurous iodide were thin, the electromotive force varied from zero to 0.3 mv. When the electrolyte was a 0.01 or 0.02 *m* cadmium iodide solution, the effect of thick and thin layers was not as pronounced. Solid lead iodide at both electrodes, with a potassium iodide electrolyte, reduced the effect of thick and thin layers, also.

(1) Sterling Fellow at Yale University, 1937-39.

(2) (a) Owen, *THIS JOURNAL*, **57**, 1526 (1935); (b) Bates, *ibid.*, **60**, 2934 (1938); (c) Vosburgh, *ibid.*, **50**, 2391 (1928); (d) Bates and Vosburgh, *ibid.*, **59**, 1584 (1937).

(3) (a) Smith and Taylor, *Rozsniki Chem.*, **18**, 762 (1938); (b) Taylor and Smith, *J. Research Natl. Bur. Standards*, **22**, 307 (1939).

The effect of thick and thin layers may possibly be explained on the basis of the reaction



This reaction takes place when mercurous iodide and sufficient iodide ion come together, and therefore the iodide ion concentration at a mercurous iodide electrode is not the same as in the main body of the electrolyte. If the reaction is slow, diffusion would be able to keep the iodide ion concentration at the thin-layer electrode larger than at the thick-layer electrode. A larger iodide ion concentration means a smaller mercurous ion concentration and consequently a more negative electrode. Mercurous iodide electrodes are reproducible in saturated cadmium iodide solutions because the small iodide ion concentration⁴ is held practically constant by the various equilibria in the solution. If this theory is correct, the value assigned to the normal potential of the mercurous iodide electrode⁴ must be considered less certain than the precision of the measurements would indicate.

Cells.—A large number of cells were made, each with one silver iodide and one mercurous iodide electrode. When made in ordinary H-shaped vessels the constancy was not satisfactory. Diffusion of the mercurous iodide to the silver iodide electrode was probably responsible. A plug of glass wool to retard diffusion helped, but did not overcome the trouble, and the special cell vessel illustrated in Fig. 1 was designed. The electrode systems were placed in parts A and B, with the use of nitrogen-vacuum technique. The tube C was not filled with electrolyte until a measurement was to be made. It was then filled through tube D with air-free solution from a flask like that described by Brown and MacInnes.⁵ After a measurement, the solution in C was expelled through F by nitrogen pressure. Some of the vessels used had interchangeable ground-glass joints at C. This allowed an interchange of electrodes between cells. A few vessels had two legs at A and two at B, allowing the preparation of duplicate electrodes of each kind. Cells made in the vessels having the joints at C were maintained at constant temperature in an air-bath and the others in an oil-bath.

Of a large number of cells made with 0.02 *m* potassium iodide solution as the electrolyte, 48 were selected as the most satisfactory. The

electromotive forces of these on the first day varied between 0.1119 and 0.1141 v. at 30°, the silver iodide electrode being negative.

The highest cells decreased during the next few days and most of the lower ones increased. For 18 cells that varied less than 0.2 mv. during the first four days the range was 0.1127 to 0.1136 v. This is within the range of variability of mercurous iodide electrodes with different thicknesses of the mercurous iodide layer. Three of the cells were measured over a period of twenty-four to forty days. One of these started at 0.1141 v. and decreased to 0.1131 v. On shaking the mercurous iodide electrode, the value dropped to 0.1128 v. and remained constant thereafter for twenty-five days. Another cell started at 0.1130 v., decreased in four days to 0.1128 v. and remained constant for thirty-six days. Its electromotive force was not affected by shaking. The third was like the first, except that its initial electromotive force was not as high. All three cells gave the value 0.1128 v. after shaking.

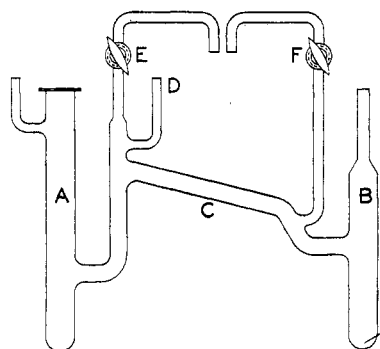


Fig. 1.

If the differences between cells is ascribed in part to differences in thickness (or denseness of packing) of the mercurous iodide layer, the lower electromotive forces should correspond to cells in which the layer is thin. The effect of shaking is probably to aid diffusion, and this lowers the electromotive force to the thin-layer value of 0.1128 v.

A group of cells made with 0.01 *m* potassium iodide solution was less satisfactory, but the best ten varied between 0.1124 and 0.1130 v. between the second and fourth days, with an average of 0.1127 v. A number of cells made with an electrolyte of 0.02 *m* potassium iodide solution saturated with lead iodide were variable and unsatisfactory, except for one cell that was constant at 0.1128 v. The use of a dilute cadmium iodide

(4) Bates and Vosburgh, *THIS JOURNAL*, **59**, 1189 (1937).

(5) Brown and MacInnes, *ibid.*, **57**, 1358 (1935).

solution as the electrolyte gave cells that were rather variable and lower than 0.1128 v. Saturated cadmium iodide gave cells that started very high and decreased continuously. The bad effect of cadmium iodide is undoubtedly on the silver iodide electrode.

In connection with a study of the thermodynamics of zinc iodide in aqueous solution by means of zinc-silver iodide cells,^{2b} some cells with mercurous iodide electrodes were made from which the electromotive force of the silver-mercurous iodide cell could be calculated. The calculated values are given in Table I. The results are in

TABLE I
CALCULATED ELECTROMOTIVE FORCE OF THE CELL
Ag/AgI, ZnI₂(m)/ZnI₂(m), Hg₂I₂/Hg

ZnI ₂ , m	E ₁₅	E ₂₀	E ₂₅	E ₃₀	E ₃₅
0.01075	0.1076	0.1091	0.1106	0.1122	0.1139
.01474	.1081	.1096	.1112	.1127	.1144
.01801	.1086	.1102	.1117	.1134	.1150
.033731125	.1141	...
.06068	.1117	.1132	.1147	.1163	.1179

approximate agreement with those described above. They show that the electromotive force depends on the electrolyte concentration, which is in agreement with the theory proposed above for the variability of the mercurous iodide electrode. Table I and also some measurements of the previously described cells show that the temperature coefficient is about 0.00030 v. per degree; 0.1127 v. at 30° corresponds to 0.1112 v. at 25°.

Bates and Vosburgh⁴ found for the normal potential of the mercurous iodide electrode the value 0.0405 v. at 25°. They used rather thin layers of mercurous iodide and a molality of potassium iodide of about 0.01 and their value can be combined with 0.1112 v. to give the approximate value 0.1517 v. at 25° for the normal potential of the silver iodide electrode. Owen^{2a} found 0.1522 v. and Cann and Taylor⁶ found 0.1510 v. In view of the uncertainty of the value 0.1517 v., it cannot be considered to be in serious disagreement with either of these. Some recent measurements by Gould and Vosburgh of the silver iodide electrode against a hydrogen electrode are in as good agreement with 0.1517 v. as could be expected.

Summary

The cell Ag/AgI, I⁻/I⁻, Hg₂I₂/Hg was found to be not as reproducible or constant as experience with the two electrode systems in other cells would lead one to expect, but the most probable value based on a large number of cells leads to an approximate value for the silver iodide electrode.

The trouble with the silver-mercurous iodide cell may be summarized by saying that while each of the electrode systems is highly reproducible under favorable conditions, no single electrolyte was found that did not affect one or the other of the electrodes unfavorably.

(6) Cann and Taylor, *THIS JOURNAL*, **59**, 1484 (1937).

DURHAM, N. C.

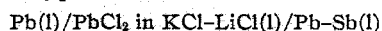
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

A Thermodynamic Study of the Lead-Antimony System

BY HARRY SELTZ AND BERNARD J. DEWITT

In the hope that the accumulation of data on the thermodynamic properties of binary liquid metal solutions may lead eventually to a better understanding of the nature of such systems, investigations along these lines are being continued in this Laboratory. In this paper the results of a study of the lead-antimony system are described. The electromotive force values of cells of the type



were measured, using the purified metals and technique described in previous publications.^{1,2}

(1) Strickler and Seltz, *THIS JOURNAL*, **58**, 2084 (1936).

(2) Seltz and DeWitt, *ibid.*, **60**, 1305 (1938).

In this work it was found possible to extend the e. m. f. readings in rather thick-walled Pyrex H-cells under vacuum up to 630° without collapse of the cells. This permitted measurements to a mole fraction of lead of 0.1 and eliminated any difficulty in the extrapolation of the activity and partial molal relative heat content curves.

Experimental Data

In Table I, the experimental results are tabulated, along with the calculated activities and relative heat contents for lead at the various mole fractions. (The subscript 1 will be used to designate values for the lead component.) At the