

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Magnesium Electrode in Ether Solution and the Free Energy of Formation of Magnesium Bromide¹

BY GEORGE A. SCHERER AND ROY F. NEWTON

The purpose of this investigation was to measure the reversible potential of the cell Mg(s), saturated ether solution of MgBr₂·2(C₂H₅)₂O, Hg₂Br₂(s), Hg(l) and the vapor pressure of the mono- and di-etherate of magnesium bromide at 25°, and from these data and those in the literature calculate the free energy of formation of magnesium bromide. This investigation is a step in the determination of the molal electrode potential of magnesium.

Preparation of Materials

All the ether used was of c. p. grade and was dried with clean sodium wire. Some of it was distilled from sodium just before it was used.

The magnesium powder, ribbon and rod used in the investigation were very probably all from the same basic source. A qualitative analysis of the rod according to the system of Noyes and Bray² failed to show any other element.

The mercurous bromide was prepared in connection with another investigation by Mr. M. G. Bolinger.³

The mercury was washed in a column of nitric acid and distilled under reduced pressure in a slow current of air.

The magnesium bromide di-etherate was made by passing dry hydrogen bromide into ether containing powdered magnesium. By controlling the speed of the reaction of the hydrogen bromide with the magnesium a very clear product was obtained. After boiling out the excess hydrogen bromide and cooling the mixture, white crystals separated. These were purified by several recrystallizations from ether, and when dissolved in ether gave a colorless solution which developed a pale yellowish color after several weeks.

Apparatus

Electromotive forces of the cells were measured on a Leeds and Northrup Type K potentiometer. The cells and the vapor pressure apparatus were kept in an oil thermostat maintained at a temperature of 25 ± 0.01° established with a thermometer calibrated by the United States Bureau of Standards.

E. m. f. Measurements

Metallic magnesium, like aluminum, in aqueous solutions apparently forms a film which protects it from further action and makes it inert. Amalgamating the magnesium prevents the formation of an adherent film and makes the metal so reactive that it decomposes all aqueous solutions,

making significant electrode potential measurement in aqueous solutions impossible. For this reason ethereal solutions of magnesium bromide were used in this investigation.

A two-phase saturated amalgam of magnesium was first used as an electrode because it was thought that it would give a more reproducible potential than magnesium alone. However, it was found that magnesium alone gave as constant and reproducible potential as did magnesium amalgam. Mercury-mercurous bromide was used as a reference electrode. To check the constancy of this reference electrode, measurements were made of its potential against a saturated lead amalgam-lead bromide electrode in the saturated ether solution. A constant value of 0.413 volt was found.

The first cells used were ordinary H-cells of Pyrex glass. In some of the later work 10-cm. Pyrex test-tubes with a platinum wire sealed in the bottom were used as cells. In these the mercury-mercurous bromide electrode was put in the bottom and the magnesium electrode inserted through the cork closing the tube. All of the cells were filled as rapidly as possible and sealed with corks and de Khotinsky cement. Some crystals were always put in each cell so as to be sure that the solution was saturated. The measurements of the cells are given in Table I.

TABLE I
ELECTROMOTIVE FORCE AT 25° OF THE CELL
Mg(s), MgBr₂·2(C₂H₅)₂O, Saturated Solution, Hg₂Br₂, Hg(l)

Cell no.	E. m. f.	Cell no.	E. m. f.
1	1.555 ± 0.002	6	1.567 ± 0.003
2	1.555 ± .001	7	1.563 ± .003
3	1.554 ± .003	8	1.561 ± .003
4	1.567 ± .002	9	1.560 ± .002
5	1.566 ± .002	Average 1.561 ± .004	

Cell No. 1 used a piece of magnesium ribbon which was dipped in dilute acid and then rinsed several times with ether just before being put in the cell.

Magnesium rod treated just as in cell No. 1 was used in cells Nos. 2 and 3.

In cell No. 4 the rod was treated as above and then put in a vessel and evacuated about fifteen minutes so as to remove occluded gases. Helium was bubbled through the solution in the cell to remove any dissolved gases.

Cell No. 5 was prepared in exactly the same manner as cell No. 4 except that magnesium ribbon was used in place of rod.

Magnesium rod for cells Nos. 6 and 8 was burnished with fine sand paper just before being put in the cell.

The magnesium rod in cell No. 7 was treated with dilute acid and ether and then pumped as above. Before the solution was put in the cell it was shaken for two or three days with mercurous bromide to be sure that it was satu-

(1) Based upon a thesis submitted by George A. Scherer to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1933.

(2) Noyes and Bray, "Qualitative Analysis," The Macmillan Company, New York, 1927.

(3) Newton and Bolinger, THIS JOURNAL, 52, 921 (1930).

rated. After the solution was put in the cell it was treated with helium as above.

Hydrogen was bubbled around a strip of magnesium ribbon used as an electrode in cell No. 9. The solution was untreated in this cell.

The variation of the potential of all the cells could be divided into three periods. When the cells were first prepared and put into the thermostat there was a period of gradually increasing or decreasing potential while equilibrium was being established. Following this, each gave a constant potential within the limits given in Table I. After this their behavior was erratic. The period of constancy varied from two to seven days in the different cells.

Measurements of Vapor Pressure

The vapor pressures of the etherates and of the saturated solution were measured in the apparatus shown in Fig. 1. The arrangement which is enclosed by dotted lines eliminates by a mercury trap the possibility of leakage through stopcocks C and E, which are occasionally exposed to ether vapor.

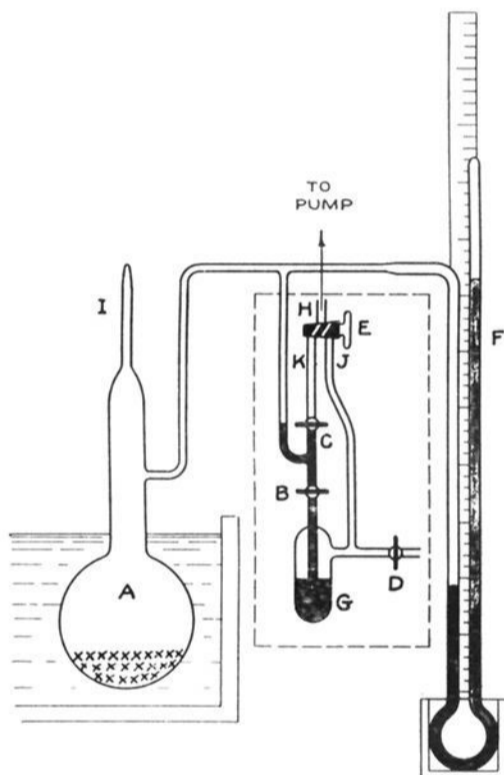


Fig. 1.—Vapor pressure apparatus.

After introducing a mixture of solid etherate and saturated solution into A, and sealing off at I, the apparatus was evacuated until the residual air was less than the error of reading the manometer, as shown by freezing out the ether vapor by means of liquid air. The bulb A was then kept at 25° until equilibrium was reached, when the pressure was recorded and the apparatus weighed. Similar observations were made after pumping out successive portions of ether.

The results are shown in Table II, and are plotted in Fig. 2. The vapor pressure of the di-etherate in equilibrium with the mono-etherate was found to be 390 mm. at 25°, and that of the mono-etherate in equilibrium with magnesium bromide, 130 mm. Similarly the vapor pressure of the saturated solution was found to be 410 mm. Interpolating from the data of Evans and Rowley⁴ 385

(4) Evans and Rowley, *THIS JOURNAL*, **52**, 3523 (1930).

TABLE II

VAPOR PRESSURE OF ETHERATES OF MgBr ₂			
Moles (C ₂ H ₅) ₂ O /mole MgBr ₂	V. p., mm.	Moles (C ₂ H ₅) ₂ O /mole MgBr ₂	V. p., mm.
1.73	387	1.00	392
1.58	387	1.00	339
1.51	392	0.99	139
1.37	387	.95	127
1.29	393	.90	130
1.18	391	.85	130
1.16	392	.82	126

mm., 94 mm. and 410 mm. are obtained for the respective vapor pressures at 25°.

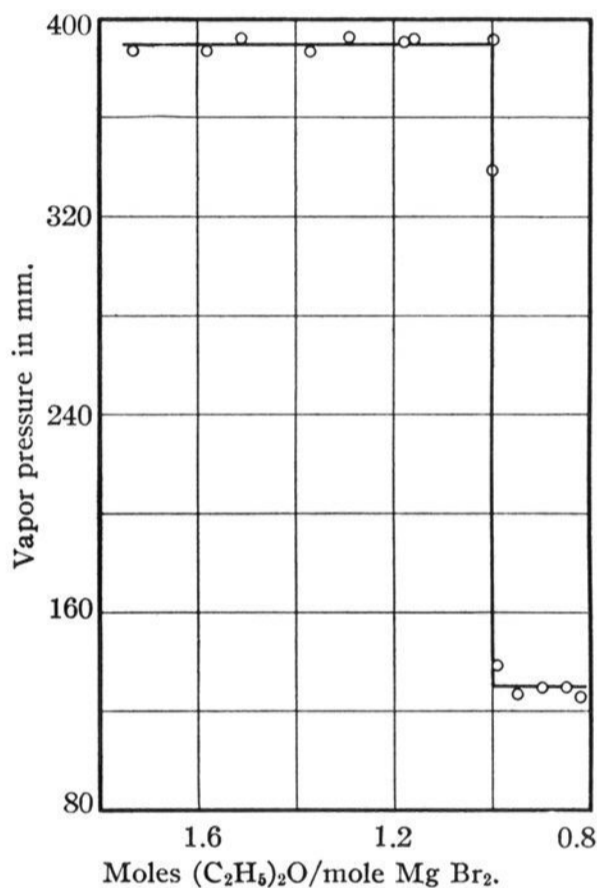
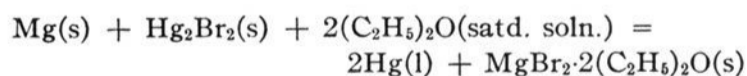


Fig. 2.—Vapor pressure of etherates of MgBr₂ at 25°.

Free Energy of MgBr₂

In the cell, Mg(s), saturated ether solution of MgBr₂·2(C₂H₅)₂O, Hg₂Br₂(s), Hg(l) the magnesium electrode is negative with respect to the mercury-mercurous bromide electrode. Thus negative current passes spontaneously through the cell from right to left and according to the convention of Lewis and Randall⁵ the e. m. f. is positive. The reaction

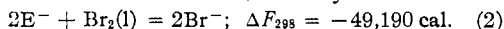


is the one which occurs when the current runs in this direction. Therefore for this reaction

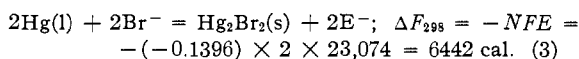
$$\Delta F_{298} = -NFE = -2 \times 1.561 \times 23,074 = -71,990 \text{ cal.} \quad (1)$$

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

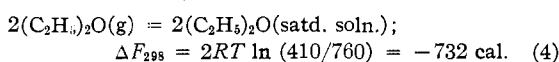
Lewis and Storch⁶ determined the potential of the bromine electrode. From this value Lewis and Randall⁵ obtain the free energy of formation of bromide ion, namely



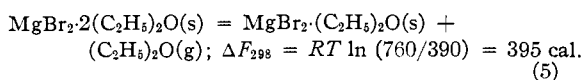
Gerke and Geddes⁷ have found the potential of the electrode, $Hg(l)$, $Hg_2Br_2(s)$, Br^- , to be -0.1369 volt. From this it follows that



The vapor pressure of a saturated ether solution of magnesium bromide at 25° has been found to be 410 mm., whence



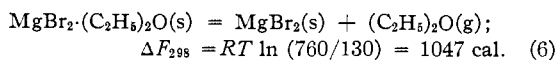
The vapor pressure of ether over a mixture of $MgBr_2 \cdot 2(C_2H_5)_2O$ and $MgBr_2 \cdot (C_2H_5)_2O$ at 25° is 390 mm. Therefore



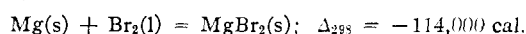
(6) Lewis and Storch, *THIS JOURNAL*, **39**, 2544 (1917).

(7) Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927).

Likewise from the vapor pressure of ether over a mixture of $MgBr_2 \cdot (C_2H_5)_2O$ and $MgBr_2$, which is 130 mm., we obtain



If equations (1), (2), (3), (4), (5) and (6) are added and the numerical result rounded off to agree with the precision of the experimental data the free energy of formation of anhydrous magnesium bromide is obtained



Summary

1. The e. m. f. of the cell, $Mg(s)$, saturated ether solution of $MgBr_2 \cdot 2(C_2H_5)_2O$, $Hg_2Br_2(s)$, $Hg(l)$ at 25° has been measured.
2. The vapor pressure at 25° of the di- and mono-etherate of magnesium bromide has been determined.
3. The free energy of formation at 25° of magnesium bromide has been calculated.

LAFAYETTE, INDIANA

RECEIVED JULY 31, 1933

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Freezing Points and Triple Points with Water

BY WALTER P. WHITE

In principle, it is easy to get a perfect freezing point for water; it needs only to mingle properly pure ice, pure water and pure air. No doubt this has often been done; rather easily for a precision of 0.002° or so. But 0.0001° has not been easy for all. One well-known worker said privately that it was impossible.¹ A very large laboratory, where thousands of ice-point determinations had been made, had come to distrust them, and was moving in the direction of triple-point apparatus. And when a carefully made ice bath of ours changed over 0.001° on slight poking, a serious investigation seemed in order.

The temperature readings were made with a thermel, which, when subjected to nearly the same temperature from end to end, is the most reliable thermometer known. Its readings are essentially differential, requiring two bodies to be read. The plan was to have, first, a triple-point bulb, as a thoroughly reliable standard

(1) For a similar opinion, coming from the Reichsanstalt, see H. Moser, *Ann. Physik*, **1**, 341 (1929).

temperature, and then to use this to test ice-points. Ultimately the ice-point apparatus which was developed was used to test two triple-point bulbs and show their errors.

The Ice-Point Apparatus

This apparatus, the "Cold Cell" (Fig. 1), was a logical development of an old device, namely, a cup, as of glass or metal, to protect the innermost part of the bath against external influences. Experiment soon led to a cup completely closed, with two small tubes for running water in and out without moving the ice.

With complete external protection, constancy—the chief object in our case—required the absence of any change originating within the cell. This means increase of impurity. Such may be introduced on thermometers, or may come, very slowly, through melting, absorption of air, or solution of glass or other material of the cell. Another important source, probably, is solution of specks of impurity imbedded in the surfaces