

The Standard Free Energy of Formation of Magnesium Bromide From Its Elements

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The ionic nature of diethyl ether, Et_2O , solutions of magnesium bromide is well known. Gillet (6) obtained a cathode deposit of elemental magnesium from a $\text{MgBr}_2\text{-Et}_2\text{O}$ solution; Evans (5) and Dessy (3) have investigated the electrochemical transport properties of this system. No reversible electrode potential for the magnesium ion in any solvent has been experimentally measured. The value of $+2.378$ volts was calculated by Coates (2) using thermochemical data coupled with solubility data for $\text{Mg}(\text{OH})_2$. This study investigates the galvanic behavior of the electrochemical cells, $\text{Mg}/\text{MgBr}_2\cdot 2\text{Et}_2\text{O}$ (s) in $\text{Et}_2\text{O}/\text{AgBr}/\text{Ag}$ and Hg-Mg (1)/ $\text{MgBr}_2\cdot 2\text{Et}_2\text{O}$ in $\text{Et}_2\text{O}/\text{AgBr}/\text{Ag}$.

Experimental

All electromotive force measurements were made at a constant temperature of $15.20 \pm 0.05^\circ \text{C}$. using a Leeds and Northrup potentiometer, type K-2. Throughout any series of measurements the system was constantly purged with helium. In unpurged systems erratic behavior of the e.m.f. was noted; the stable potentials realized in purged systems quickly dropped to 0.9 volts when either air or oxygen was admitted into the system.

The electrode materials were the purest obtainable. The Ag/AgBr electrodes were prepared electrochemically according to the procedure of Brown (1). The reproducibility of the Ag/AgBr electrodes was checked frequently. In the galvanic couple, $\text{Ag}/\text{AgBr}/\text{HBr}$ (0.01 M.)/ AgBr/Ag , the potential differences between electrodes never exceeded 0.00002 volts; for the cell, $\text{Ag}/\text{AgBr}/\text{MgBr}_2$ in $\text{Et}_2\text{O}/\text{AgBr}/\text{Ag}$, the potential differences between electrodes were always less than 0.001 volts.

Magnesium electrodes were prepared from sublimed magnesium rod (spectrographic analysis—Ca, Si, and Sn less than 0.01 per cent; Al, Cu, Fe, Mn, Pb, and Zn less than 0.001 per cent; Ni less than 0.0005 per cent). Machined magnesium slugs of $\frac{1}{2}$ inch diameter were sealed into pyrex tubing with an epoxy resin. At least a one centimeter length of magnesium rod remained exposed for contact with the solution. External contact to the electrodes was made by a platinum wire dipping into a mercury pool in contact with the magnesium slug. Preliminary to each run, the electrodes were cleaned using the Dow acetic-nitrate pickling bath (7), thoroughly rinsed with anhydrous Et_2O , and quickly transferred into the $\text{MgBr}_2\text{-Et}_2\text{O}$ electrolyte. The magnesium amalgam electrodes were prepared by weighing the proper quantities of magnesium and mercury into the cell used to hold the electrolyte; all weighings were done under a helium atmosphere.

The solid $\text{MgBr}_2\cdot 2\text{Et}_2\text{O}$ was prepared using chemically pure or reagent grade materials by the method described by Evans (4). In all measurements the electrolyte was a saturated solution of

MgBr₂·2Et₂O in Et₂O. During all determinations solvent lost through evaporation was replaced by adding electrolyte.

Results and Discussion

TABLE 1
Electromotive Force Values for the Cell, Mg/ MgBr₂·2Et₂O (s) in
Et₂O/ AgBr/ Ag.

Electrode	Run	
	1	2
I	1.425 ± 0.010 v. (5 hr.)	1.422 ± 0.001 v. (1 hr.)
II	1.427 ± 0.002 v. (1 hr.)	1.421 ± 0.002 v. (2 hr.)
III	1.417 ± 0.005 v. (3 hr.)	electrode broken
IV	1.416 ± 0.002 v. (2 hr.)	1.412 ± 0.015 v. (3 hr.)

Table 1 summarizes the e.m.f. measurements for the electrochemical cell, Mg/ MgBr₂·2Et₂O (s) in Et₂O/ AgBr/Ag. Stable values were only realized after the electrodes had been in contact with the electrolyte for from 10 to 20 hours. The tabulated values are average values observed during the time period listed in parentheses below the individual electrode. The deviation quoted is the maximum deviation of any measured value from the average. Statistically the most reliable estimate for the e.m.f. of this galvanic cell is 1.420 ± 0.008 volts at 15.20°C. Figure 1 summarizes the results obtained for the amalgam electrodes as a function of the mole fraction of magnesium in the amalgam. The experimental results are best represented by the equation,

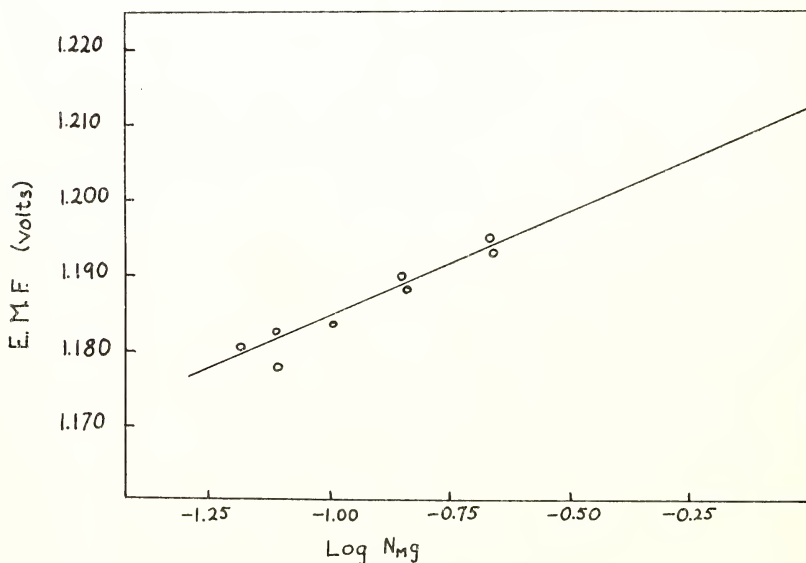
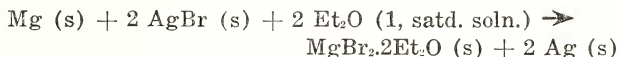


Figure 1

$$E = 1.213 + 0.0292 \log N_{\text{Mg}}$$

The predicted slope for a two electron, reversible process is 0.0286 volts at 15.20° C. The agreement between experiment and theory strongly suggests that the Ag/AgBr reference electrode behaves reversibly in the MgBr₂-Et₂O electrolyte.

From the value of 1.420 volts the free energy change for the chemical reaction at 15.20° C.,



is -65.50 kcal. mole⁻¹. Evans (4) has determined the Et₂O vapor pressures of the various MgBr₂-Et₂O systems as a function of the absolute temperature. From these results the free energy change for the reaction,



is calculated to be -63.97 kcal. mole⁻¹.

The standard free energy of formation of MgBr₂ is defined as the free energy change associated with the formation of this compound from its elements at 25° C. By means of the Gibbs-Helmholtz equation and the appropriate free energies of formation, enthalpies of formation, and molar heat capacities for Br₂, Ag, AgBr, Mg, and MgBr₂ as listed in the National Bureau of Standards tabulation of thermochemical quantities (8), a value of -109.92 ± 0.75 kcal. mole⁻¹ is obtained for the standard free energy of formation of MgBr₂. It should be pointed out that the molar heat capacity of MgBr₂ is not experimentally available; the estimated value of 19.8 cal. deg.⁻¹ mole⁻¹ has been used in the calculation (9).

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