

pressure was constructed. Direct measurements of the eutectic pressure, and of the freezing pressure of a 10% solution, showed a fair agreement with the indirect determinations.

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THE USE OF THE ANTIMONY ELECTRODE IN THE ELECTROMETRIC ESTIMATION OF MAGNESIUM¹

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Introduction.—Extended work on "lime" in this Department demanded determination of magnesium at frequent intervals, especially in control work. The standard methods for such determinations were long and tedious. Their precision also has been a subject of controversy in recent years. The ordinary hydrogen electrode method suggested itself but was complicated and too highly sensitive to permit of ready handling without error. The convenience and simplicity of the antimony electrode made it desirable to investigate its application to the determination of magnesium. The present paper deals with this investigation.

Literature.—Hildebrand and Harned^{1a} were the first to use the hydrogen electrode method for the determination of magnesium in the presence of calcium in dolomite and limestone. They considered their method as fairly rapid and accurate. H. S. Harned² applied the conductimetric method for the determination of magnesium in magnesium sulfate. According to him, the value "agreed with that from a gravimetric analysis." Later I. M. Kolthoff³ confirmed the above work and stated that satisfactory results were obtained by precipitating the magnesium hydroxide with excess standard alkali, filtering and titrating back with standard acid. Gilbert A. Freak,⁴ using the conductimetric method, studied the "effect of dilution in electro-titrimetric analysis." I. M. Kolthoff⁵ confirmed Pinkhoff's result (Diss., Amsterdam, 1919) and made an extensive study of this magnesium reaction, using the hydrogen electrode. He declared that the method was of little practical use.

The Use of the Antimony Electrode.—The antimony electrode has found application in recent years in electrometric work. For the most

¹ Original manuscript received February 18, 1931.

^{1a} Hildebrand and Harned, *Proc. 8th Intern. Congr. App. Chem.*, 1, 217 (1912).

² Harned, *THIS JOURNAL*, 39, 252-266 (1917).

³ Kolthoff, *Z. anorg. allgem. Chem.*, 112, 172 (1920).

⁴ Freak, *J. Chem. Soc.*, 115, 55-61 (1919).

⁵ Kolthoff, *Rec. trav. chim.*, 41 (1922), and Kolthoff and Furman in "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1926.

part, the workers starting with Uhl and Kestranek⁶ have used it for the measurement and standardization of *P_H* values or latterly for the measurement of high alkalinity in the black liquors from paper pulp cooks, where the hydrogen electrode for one reason or another failed. Among the chief workers with the antimony electrode may be mentioned E. J. Roberts and F. Fenwick,⁷ who showed the special advantages of the antimony electrode. Kolthoff and Hartong⁸ have made extensive studies of the application of the antimony electrode. K. W. Franke and J. J. Willaman⁹ studied the effect of the nature of the metal constituting the electrode and also the effect of various gases in titration work. Lucius W. Elder, Jr.,¹⁰ says "The antimony electrode shows an abnormal titration curve in acid solutions of ferric chloride, probably because of the presence of pentavalent antimony in the solutions."

However, we are not aware of any published work on the use of the antimony electrode for such estimations as that of magnesium.

Experimental

Apparatus.—The usual set-up for potentiometric titrations, using a calomel half-cell, was employed. The antimony electrode was made from commercial "stick" antimony sand-papered to a smooth surface.

Procedure.—A quantity each of standard solutions of chemically pure magnesium chloride (hexahydrated crystals) and calcium chloride was prepared such that one cc. of each contained a definite amount of MgO and CaO. The determination of MgO in the stock solution was made according to the standard gravimetric method and that of CaO by titration of the precipitated oxalate with a standard solution of potassium permanganate. From these stock solutions several mixtures of known strength of MgO and CaO were prepared. The amount of magnesium was kept constant but that of calcium was allowed to vary. The magnesium in these mixtures was then estimated. As a check several gravimetric-volumetric analyses and estimations with the hydrogen electrode were made side by side and the results compared.

To make a determination, measured amounts of magnesium and calcium solutions were diluted to 150 cc., acidified with a few drops of dilute hydrochloric acid and methyl orange indicator added. When the e. m. f. had become constant, a normal (or 0.1 *N* with dilute solutions) solution of sodium hydroxide free from carbonate was added in portions of 0.2 cc., allowing sufficient time for the e. m. f. readings to become constant, which required from two to ten minutes. The potential was plotted against volume of alkali used.

Determination of Alkali Used for Magnesium Precipitation.—The curve obtained showed two inflections corresponding to the beginning and to the end of the precipitation of magnesium hydroxide. A vertical line projected through the point of first inflection to the horizontal axis (alkali) gave the initial alkali reading to be used in calculation. The other inflection ordinarily was not quite so sharp as the first and consequently it was a little difficult to locate the exact end-point of the titration. In our method an "oscula-

⁶ Uhl and Kestranek, *Monatsh*, **44**, 29 (1923).

⁷ Roberts and Fenwick, *THIS JOURNAL*, **50**, 2126 (1928).

⁸ Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

⁹ Franke and Willaman, *J. Ind. Eng. Chem.*, **20**, 87 (1928).

¹⁰ Elder, *Trans. Am. Electrochem. Soc.*, **57**, 383 (1930).

tory" tangent between the two arms of the inflection was drawn and from a point midway between the points of contact of this tangent and the curve a vertical line was projected to the horizontal axis. The point where this line met the horizontal axis gave the final reading of the alkali. As a check, however, by plotting $\Delta E/\Delta V$ against volume a differential curve was obtained which showed two well-defined peaks. Vertical lines projected through these points to the horizontal axis (volume) gave the volume of alkali used for titration. From this the amount of magnesium present in the solution could be easily calculated.

Reagents.—All reagents and chemicals used were chemically pure. The strength of potassium permanganate used for volumetric estimation of calcium was 0.099 normal. Standard solutions of magnesium and calcium chloride contained 0.01 g. of MgO and CaO per cc., respectively (in dilute solutions 0.001 g.). Standard sodium hydroxide was 1.01 normal (0.118 normal in the case of dilute solutions).

Data

From a series of curves obtained as a result of fourteen different runs, an example is included here. The results have been summarized in the table.

The accompanying figures illustrate the curves obtained. The differential curve, Fig. 2, shows how the amount of alkali used for magnesium precipitation was ascertained. This value is the same as that obtained by the "osculation" tangent method, Fig. 1.

Runs 1-9 were made using fairly strong solutions. Runs 10-14 were with dilute solutions. The results indicate that the antimony electrode gave fairly accurate values for magnesium when it was alone

in strong or in dilute solutions. However, if the dilution was lower than 0.01 g. of MgO in 150 cc. of solution, the results were not dependable. When calcium was present, in fairly strong solutions, estimations could be made until the concentration of calcium was as much as eight times that of magnesium. The maximum error was under 3.5%. When the concentration of calcium was increased to twenty-five and fifty times that of magnesium,

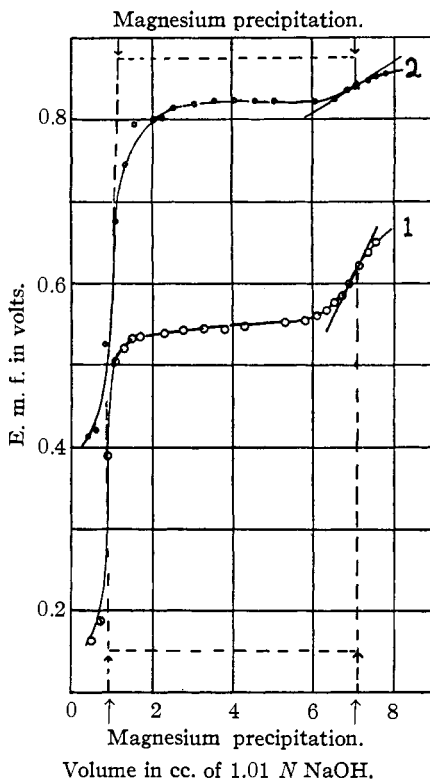


Fig. 1.—Electrometric estimation of magnesium.

	NaOH used, cc.	MgO estimated, g.	Error, %
Curve 1, hydrogen electrode	6.2	0.125	0
Curve 2, antimony electrode	6.0	0.121	-3.2

TABLE I
 COMPARATIVE RESULTS OF MAGNESIUM ESTIMATION

No.	Content of mixture		NaOH used		MgO estimated		Grav., g.	Error, %	
	MgO, g.	CaO, g.	Sb elect., cc.	H ₂ elect., cc.	Sb elect., g.	H ₂ elect., g.		Sb elect.	H ₂ elect.
1	0.125	0.000	6.2	6.0	0.125	0.121	0.125	0	-3.2
2	.125	.125	6.0	6.25	.121	.126	.125	-3.2	0.8
3	.125	.250	6.0	5.9	.121	.120	.126	-3.2	-4.0
4	.125	.500	6.2		.125			0	
5	.125	1.000	6.0		.121			-3.2	
6	.010	0.250	Not definite		Could not be estimated				
7	.010	.500	Not definite		Could not be estimated				
8	.010	.000	0.6		.118			-6.0	
9	.010	.000	4.3 ^a		.010			0	
10	.010	.000	4.25		.010			0	
11	.005	.000	1.95		.005			0	
12	.010	.010	4.55		.011			10	
13	.010	.050	4.8		.011			10	
14	.010	.100	Not definite		Could not be estimated				

^a Dilute sodium hydroxide in this and subsequent estimations.

the method failed. In dilute solutions of magnesium, if calcium was present even to the extent of equivalent proportions with magnesium, the results showed high errors and were not dependable.

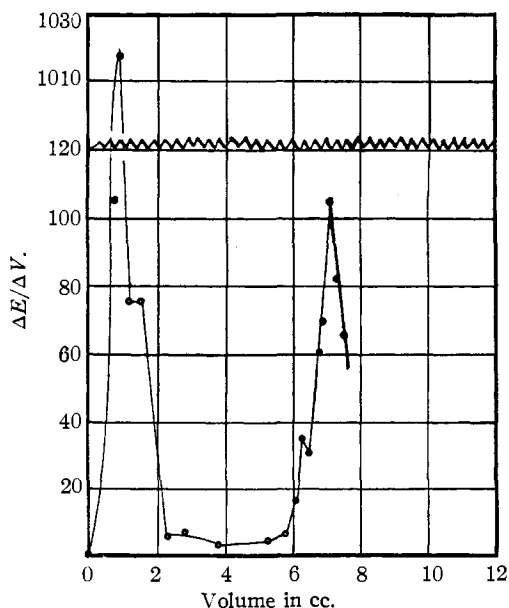


Fig. 2.—Differential curve for Curve 1; volume of alkali, ≈ 6.2 cc.

Several advantages over the hydrogen electrode characterized the antimony electrode—simplicity of construction, ease of manipulation, free-

dom from the necessity of electrodeposition of a metal, apparent absence of poisoning effect, freedom from both manipulation and control of a gas phase.

Summary

1. The antimony electrode made of commercial stick antimony was a satisfactory substitute for the hydrogen electrode in the electrometric estimation of magnesium in its salts and in mixtures of calcium and magnesium salts.

2. Calcium could be present to the extent of eight to twenty-five times the amount of magnesium.

3. The minimum concentration of MgO was 0.10 g. in 150 cc. of solution. At low dilutions the results were unsatisfactory if calcium was present in any appreciable amount, or was even equivalent in amount to the magnesium.

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THE FREE ENERGY, HEAT CONTENT AND ENTROPY OF IODINE MONOCHLORIDE

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Introduction

The absorption bands of iodine monochloride have been studied by Gibson and Ramsperger,¹ Wilson,² Curtis and Darbeyshire³ and Curtis and Patkowski;⁴ and from the results of this work the thermodynamic constants of iodine monochloride may be computed. The uncertainties in interpretation of these spectroscopic data, however, make it desirable that the thermodynamic constants be also derived from some entirely independent source. Two separate chemical studies of this problem are presented in this paper.

The combination in the vapor phase of iodine and chlorine to form iodine monochloride is not accompanied by a change in the total number of molecules. Since there is no total pressure change, the methods employed in this research for studying the reaction are necessarily indirect.

The first method used depends upon the presence of solid barium chloroplatinate which is in equilibrium with the chlorine, barium chloride and platinum, of which only the chlorine reacts with iodine. The dissocia-

¹ Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

² Wilson, *ibid.*, **32**, 611 (1928).

³ Curtis and Darbeyshire, *Trans. Faraday Soc.*, **27**, 77 (1931).

⁴ Curtis and Patkowski, *ibid.*, **25**, 725 (1929); *Nature*, **127**, 707 (1931).