615° calcium bentonite and 595° hydrogen Putnam membranes are probably usable. For the potassium determinations alone, membranes insensitive to calcium, such as the 490° hydrogen bentonite membranes previously described, are required.

(3) **Calcium-Sodium Mobility Ratios.**—Only the 615° calcium bentonite and 615° calcium Putnam membranes were examined. As would be expected, the ratios U_{Ca}/U_{Na} were somewhat greater than the corresponding U_{Ca}/U_K values. They showed also more variability with concentration.

(4) **Calcium-Magnesium Mobility Ratios.**—A limited series was determined using high temperature membranes. Much greater constancy was found than with the monovalent-divalent series. These results will be discussed in the succeeding paper, which deals with the determination of magnesium.

Summary

Membranes prepared from hydrogen and calcium bentonite (montmorillonite) and hydrogen and calcium Putnam clay (beidellite), preheated to various temperatures, were examined as to their suitability for the determination of calcium. Hydrogen bentonite membranes heated to 300–415° are suitable; at 450° and higher these are insensitive to divalent cations, but sensitive to monovalent. Calcium bentonite membranes are suitable and are improved only slightly by pretreatment between 300° and 550°. Hydrogen Putnam clay membranes showed great improvement with increasing temperature of pretreatment, but even the 600° membranes were somewhat inferior to the 600° calcium bentonite membranes. The calcium Putnam membranes throughout were better than the hydrogen Putnam, but in the range 500–600° were still slightly inferior to the 500–600° calcium bentonite membranes.

Mobility ratios for calcium–hydrogen, and calcium–potassium were also determined. In many cases this ratio varied greatly with concentration. However, the 350–415° hydrogen bentonite and the 615° calcium bentonite membranes showed reasonable constancy for U_{Ca}/U_H and could be employed for the analysis of mixtures containing calcium and hydrogen ions. For calcium–potassium the 615° calcium Putnam membranes were the most favorable.

COLUMBIA, MISSOURI RECEIVED SEPTEMBER 29, 1947

[CONTRIBUTION FROM COLLEGE OF AGRICULTURE, UNIVERSITY OF MISSOURI]

The Electrochemical Properties of Mineral Membranes. VII. Clay Membranes for the Determination of Magnesium[1]

BY C. E. MARSHALL[2a] AND L. O. EIME[2b]

The theoretical and experimental considerations which have been discussed in the preceding paper of this series[3,4] apply in large measure to the determination of magnesium. The same membrane materials were under investigation and no change was needed in the experimental techniques.

The magnesium chloride solutions employed were arranged in a series according to the calculated magnesium ion activities, adjacent members being in the fixed ratio 3.00. The calculations employed for this purpose were precisely similar to those described for calcium. The basic data were taken from Landolt–Börnstein,[5] and because the activity coefficients of magnesium chloride solutions only extend down to 0.05 molal, a more extensive extrapolation to low concentrations was required than for calcium chloride. Table I gives the activities and concentrations employed. The latter were checked by gravimetric determination of the magnesium as pyrophosphate.

TABLE I

Magnesium ion activity, $a_{Mg^{++}}$	Magnesium chloride molality, m	Grams $MgCl_2$ per 1000 g. water
0.0001	0.000106	0.0101
.0003	.000330	.0314
.0009	.001152	.1098
0027	.00398	.379
.0081	.01490	1.419
.0243	.05600	5.340

The Effects of Heat Treatments upon Membrane Potentials.—Figures 1–4 illustrate the general situation for the four clays hydrogen bentonite, calcium bentonite (montmorillonite), hydrogen Putnam clay, and calcium Putnam clay (beidellite). One marked difference is apparent in all cases between these curves for magnesium and those previously given for calcium. In the case of magnesium the curves fall off more or less sharply after attaining the maximum value. This greatly restricts the range over which accurate determinations of magnesium ion activities can be made.

(a) **Hydrogen Bentonite.**—As in the case of calcium, the three curves for 300, 350 and 400° membranes lie very close together. They attain the theoretical e.m.f. at a slightly lower activity of magnesium than of calcium. Down to 0.0003 $a_{Mg^{++}}$ they give good values, but beyond it the

---

[1] This work was aided by a research grant made by the International Minerals & Chemical Corporation to the Department of Soils, for which the authors wish to express their appreciation.

[2a] Professor of Soils, University of Missouri.

[2b] Research assistant and graduate student in Soils and Chemistry, respectively.

[3] C. E. Marshall and A. D. Ayers, THIS JOURNAL, **70**, 1297 (1948).

[4] Journal series No. 1065 of the Agricultural Experiment Station, University of Missouri.

[5] Landolt–Börnstein, Physikalisch-Chemische Tabellen, 5 Auflage, 2 Ergänzungsband, 2 Teil, 1931.

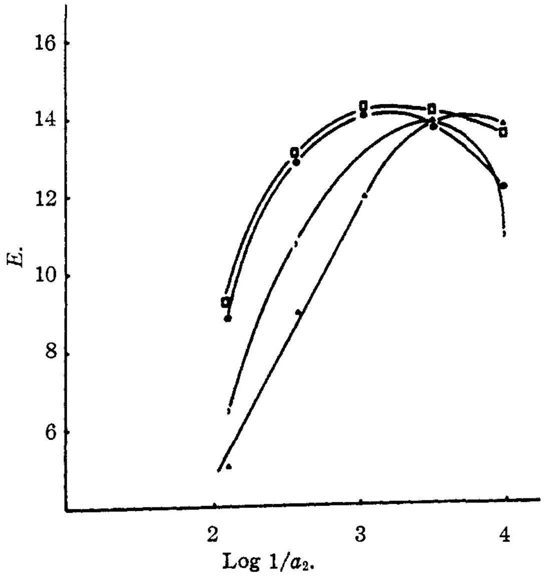

Fig. 1.—Characteristic curves for hydrogen bentonite (montmorillonite) membranes in magnesium chloride solutions: △, 400°; •, 465°; ●, 500°; □, 600°.

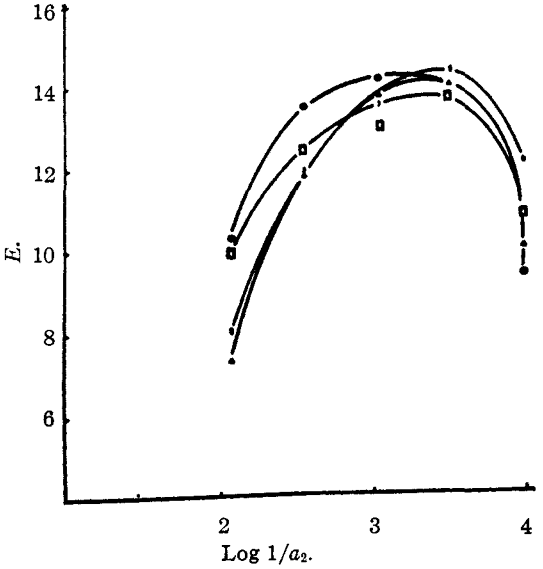

Fig. 2.—Characteristic curves for calcium bentonite (montmorillonite) membranes in magnesium chloride solutions: △, 405°; •, 455°; ●, 500°; □, 550°.

potential shows a rapid falling off. The pair of solutions 0.0003/0.0001 gives only about 10 millivolts instead of 14.1. Thus the range where good accuracy can be secured runs only from about 0.003 to 0.0003.

(b) **Calcium Bentonite.**—These membranes showed considerable improvement with increasing temperature of pretreatment. The 500 and 550° membranes were distinctly superior to the hydrogen bentonite membranes and the usable range of magnesium activities extended from about 0.008 to 0.0003.

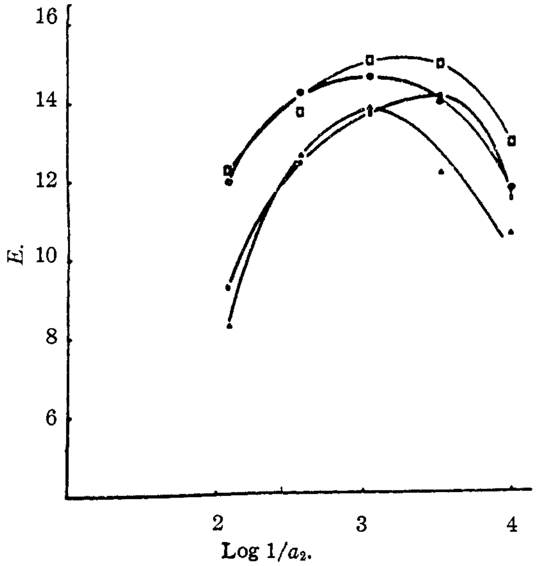

Fig. 3.—Characteristic curves for hydrogen Putnam clay (beidellite) membranes in magnesium chloride solutions: ■, 405°; •, 455°; ●, 500°; □, 550°.

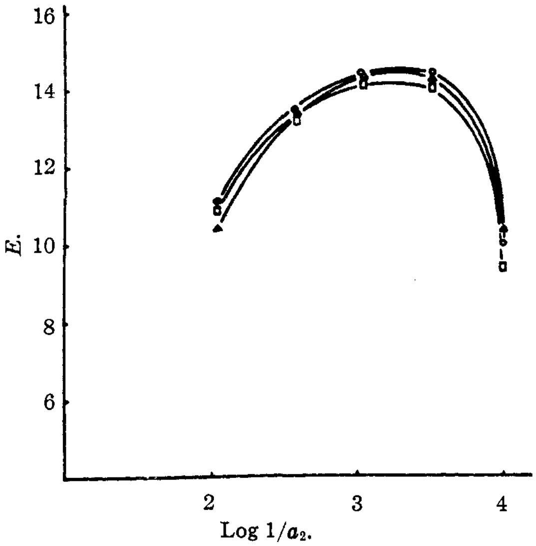

Fig. 4.—Characteristic curves for calcium Putnam clay (beidellite) membranes in magnesium chloride solutions: □, 300°; △, 350°; ○, 400°.

(c) **Hydrogen Putnam Clay.**—The properties were considerably improved by higher temperatures of pretreatment. The 600° membranes showed a less marked falling off in potential beyond 0.0003 $a_{Mg^{++}}$ than any of the bentonite membranes. However, the curves were less favorably placed with regard to the higher activities and the usable range runs from about 0.004 to 0.0001.

(d) **Calcium Putnam Clay.**—These membranes were very similar to the corresponding hydrogen Putnam series at the higher activities, but their potentials fell off more below 0.0003.

It can be seen from the curves that the final decline in potential with increasing dilution is general, but that it varies greatly in extent. The basic cause would seem to be hydrolysis, with production of ions such as $(MgOH)^+$. These ions would also affect the membrane potentials, and the preliminary heat treatments would presumably determine to what extent they are potential determining. Unfortunately, the data in the literature on the activity coefficients and equivalent conductivity of magnesium chloride solutions do not extend to sufficiently high dilutions to throw any clear light on their hydrolysis. The same membranes, it should be noted, gave only a very slight indication of a falling off in potential at high dilutions when calcium chloride was used.

One further slight irregularity should be mentioned. There is a tendency for somewhat high potentials to arise at intermediate concentrations, generally with the 0.0027/0.0009 $a_{Mg^{++}}$ pair of solutions. The departure from the theoretical is always less than 1 millivolt, generally around 0.1–0.4 millivolt, but it appears to be real with a given set of membranes. Some of the results with sodium showed similarly high potentials, whereas with potassium and calcium the results were very close to the theoretical.

In consequence, the conditions for the accurate determination of magnesium are distinctly less favorable than for calcium. In the restricted range of magnesium ion activities from 0.008 to 0.0003 using 550° calcium bentonite and 400° hydrogen bentonite membranes, and from 0.004 to 0.0001 using 600° hydrogen Putnam membranes an over-all accuracy of 5% could be relied upon with selected membranes. Comparisons of closely similar magnesium ion activities could be made with greater precision than this.

Cationic Mobility Ratios in Relation to Pretreatment.—The conditions under which divalent–divalent and monovalent–divalent mobility ratios may be determined have been examined in the preceding paper dealing with calcium. The experimental details were essentially the same both for calcium and magnesium.

(1) **Calcium–Magnesium Mobility Ratios.**—When ions of the same valence are employed, the equilibrium potentials are more quickly established and there is less individual variation amongst membranes than for the monovalent–divalent series. Table II gives typical experiments for a series of concentrations; these may be compared with Table II of the preceding paper.

TABLE II[a]

Membrane material	$a_{Ca^{++}}$	$a_{Mg^{++}}$	Mean mobility ratio U_{Ca}/U_{Mg}
615° Calcium Putnam	0.0081	0.0081	1.54
	.0027	.0081	1.59
	.0027	.0027	1.54
	.0009	.0027	1.52
	.0009	.0009	1.33
	.0003	.0003	1.26
	.0001	.0003	1.26
615° Calcium bentonite	.0081	.0081	1.52
	.0027	.0081	1.51
	.0027	.0027	1.40
	.0009	.0009	1.29
	.0003	.0009	1.34
	.0003	.0003	1.24

[a] Determinations by A. D. Ayers.

The complete results are summarized in Table III. The variation is much less than for monovalent–divalent ratios. In almost every case where the calcium ion activity is kept constant and the magnesium ion activity decreased, a perceptible fall in the mobility ratio U_{Ca}/U_{Mg} is found. It may be seen that the range of variation is narrow, except for the calcium bentonite and the hydrogen and calcium Putnam membranes heated to around 400°. Excluding these, the range covered is surprisingly similar for the different clays, exchange cations and temperatures of pretreatment. It would not be possible to select from these two sets of membranes with widely different U_{Ca}/U_{Mg} values, which might be used to determine both calcium and magnesium in a mixture by solving two simultaneous equations.

TABLE III

THE RANGE OF CALCIUM-MAGNESIUM MOBILITY RATIOS OF MEMBRANES PREHEATED TO VARIOUS TEMPERATURES

Membrane material	U_{Ca}/U_{Mg}			
	300°	360°		400°
H bentonite	1.22–1.37	1.36–1.54		1.55–1.66
	405°	455°	500°	615°
Ca bentonite	0.92–1.41	1.08–1.44	1.12–1.45	1.24–1.52[a]
	415°	510°		595°
H Putnam	0.55–1.27 0.64–2.05[a]	1.31–1.45		1.34–1.51 1.38–1.55[a]
	405°	500°	550°	615°
Ca Putnam	0.37–1.18	1.17–1.46	1.38–1.55	1.26–1.59

[a] Determinatons by A. D. Ayers.

(2) **Magnesium–Hydrogen Mobility Ratios.**—Table IV summarizes the range of values obtained with magnesium chloride and hydrochloric acid solutions. The activity of the magnesium ion was held constant at 0.0027 and that of the hydrogen ion ranged downwards from 0.00069. The simplified equation which presupposes that a_H is small compared with a_{Mg} was employed in calculating U_H/U_{Mg} (equation similar to 3b of the preceding paper). Some membranes gave reasonably constant values. In general, the higher temperatures of pretreatment gave the more consistent results. By comparing with Table III of the preceding paper it is apparent that the membranes showing the greatest constancy in U_{Ca}/U_H values are the best also in respect of U_{Mg}/U_H. The actual values of U_{Mg}/U_H are slightly higher than for U_{Ca}/U_H in most cases. The best membranes for use with mixtures of magnesium and hydrogen ions are evidently the

TABLE IV

THE RANGE OF MAGNESIUM–HYDROGEN AND MAGNESIUM–POTASSIUM MOBILITY RATIOS FOR VARIOUS TEMPERATURES OF PRETREATMENT

Membrane material				
H bentonite	Pretreatment at	300°	360°	400°
	U_{Mg}/U_H	0.137–0.201	0.70–0.85	0.81–0.99
Ca bentonite	Pretreatment at	405°	455°	
	U_{Mg}/U_H	0.063–0.262	0.250–0.266	
H Putnam	Pretreatment at	415°	510°	595°
	U_{Mg}/U_H	0.065–0.139	0.142–0.203	0.126–0.216
Ca Putnam	Pretreatment at	550°		
	U_{Mg}/U_H	0.067–0.24		
H bentonite	Pretreatment at	300°	360°	400°
	U_{Mg}/U_K	0.061–0.602	0.174–0.920	1.60–2.97
Ca bentonite	Pretreatment at	405°	455°	
	U_{Mg}/U_K	0.021–0.236	0.012–0.185	
H Putnam	Pretreatment at	415°	510°	595°
	U_{Mg}/U_K	0.036–0.128	0.239–0.285	0.185–0.201
Ca Putnam	Pretreatment at	500°		
	U_{Mg}/U_K	0.333–0.389		

hydrogen bentonites pretreated at 360 and 400° since these gives ratios of good constancy relatively close to unity. The high temperature calcium bentonite membranes also give good constancy.

(3) **Magnesium–Potassium Mobility Ratios.**—These were also determined under conditions such that a_{K^+} was small compared with $a_{Mg^{++}}$. The latter comprised two values, 0.0081 and 0.0027, and a_K varied from 0.001 to 0.00011. From Table IV it can be seen that U_{Mg}/U_K can be either greater or less than U_{Mg}/U_H for the same membrane, the greater values predominating. On comparing with the ratios U_{Ca}/U_K in Table III of the preceding paper, almost without exception U_{Mg}/U_K is less than U_{Ca}/U_K for the same membrane material. Those showing the greatest constancy in U_{Mg}/U_K are 510° and 595° hydrogen-Putnam, and the 500° calcium-Putnam membranes.

Summary

Using membranes of hydrogen and calcium bentonite (montmorillonite) and hydrogen and calcium Putnam clay (beidellite) preheated over a range of temperatures from 300–600° the conditions most favorable for the determination of the magnesium ion activity have been examined.

Owing probably to the hydrolysis of highly dilute magnesium salt solutions the range was somewhat restricted as compared with calcium. Where magnesium ions alone were concerned, the 400° hydrogen bentonite and 550° calcium bentonite membranes could be used from 0.008 to 0.0003, and the 600° hydrogen Putnam membranes from 0.004 to 0.0001.

Good constancy of the mobility ratio U_{Ca}/U_{Mg} was found with a variety of pretreatments and with the two clays and two exchange cations employed. It was not possible to select membranes with sufficiently widely different values of U_{Ca}/U_{Mg} to make a potentiometric determination of both Mg and Ca in a mixture feasible.

The magnesium–hydrogen and magnesium–potassium mobility ratios were generally variable with concentration. Fortunately, the 400° hydrogen bentonite and 455° calcium bentonite membranes showed reasonable constancy, so that magnesium ions may be determined in the presence of hydrogen ions. The 595° hydrogen Putnam membranes showed the greatest constancy in the magnesium–potassium mobility ratio.

COLUMBIA, MISSOURI RECEIVED SEPTEMBER 28, 1947