

although these experiments were done at concentrations where the Brønsted-Christiansen-Scatchard equation does not apply. However, the slope of the graph of  $\log R$  vs.  $\mu^{1/2}$  is not the same when the ionic strength is adjusted with sodium chloride as when it is adjusted with sodium sulfate. The two slopes are 0.646 and 0.431, respectively.

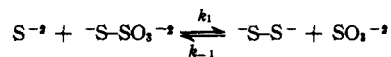
A graph of  $\log R$  vs. the square root of the sodium ion concentration is also linear, with slopes of 0.582 and 0.537 when the adjustment is made with sodium chloride and sodium sulfate, respectively. It is clear that the concentration of sodium ions correlates the rates better than does the ionic strength. At the same value of the ionic strength, the rate constant may differ by as much as 60% for runs in which sodium chloride or sodium sulfate is used; at the same sodium ion concentration, however, the rates do not differ by more than 15%. It is not unexpected that the rate is correlated better by the concentration of positive ions than by the ionic strength in a reaction between two negative ions.<sup>12</sup>

One further feature of the rate behavior in the presence of inert salts is worth pointing out. The order of the exchange in thiosulfate was measured with both sodium sulfate and sodium chloride as the inert salt. In the former case, the sodium ion concentration as well as the ionic strength could be held constant; however, when sodium chloride was used, the ionic strength was held constant but the sodium ion concentration varied (last five lines of Table I). Nevertheless, the order in thiosulfate was observed to be almost the same regardless of which inert salt was used. The orders were 1.14 and 1.13 for sodium chloride and sodium sulfate runs, respectively.

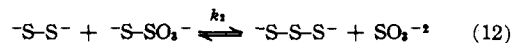
### Conclusions

It has been shown that sulfide attacks thiosulfate on the outer sulfur atom.

(12) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).



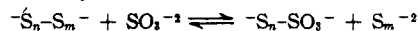
We suggest that the the mechanism of eq. 4 also involves attack on the outer sulfur atom.



It is reasonable to postulate that this reaction is a general one for polysulfides



and that the rate for any given polysulfide species is governed by its concentration and its thiophilicity towards thiosulfate. Attack by all of the polysulfides probably occurs, but the concentration of the higher polysulfides is small and their reactions are not measurable here. In addition, the reaction of the higher polysulfides is complicated by the fact that polythionates can be formed by an attack on an inner sulfur atom.



There is positive evidence for the attack of sulfide on the outer sulfur of thiosulfate. However, since the attack on either sulfur atom would give the same rate law, there is the possibility that a fraction of the exchange which is represented by the first term of eq. 6 could be an attack on the inner sulfur atom of the thiosulfate. Since  $K_{eq}$  is known, a direct measurement of the rate constant for the reaction between disulfide and sulfite ( $k_{-1}$ ) would allow the calculation of  $k_1$ . The value obtained in this way should agree with that found above. A smaller value of  $k_1$  would indicate that the  $k_1$  found above is a composite, containing some contribution from attack on the inner sulfur. We believe that this possibility is unlikely since this mechanism would be expected to have a much higher activation energy than obtained here. The reaction of hydroxide with thiosulfate, which may involve attack on the inner sulfur of thiosulfate, has an activation energy of 57 kcal./mole.<sup>6</sup>

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## Multilayer Membrane Electrodes. V. Biionic Potentials across Nonpressurized Membranes

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Nonpressurized calcium stearate electrodes have been used to measure the biionic potentials of mixed calcium and sodium chloride solutions. The results showed that sodium ions can enter the membrane and set up a diffusion potential,  $E_{Na}$ . By applying the Nernst-Planck diffusion equation, it was possible to derive the following relationship between the diffusion potential and the activities of calcium and sodium ions in solution:  $E_{Na} = (RT/3) \ln [1 + \lambda a_{Na}/a_{Ca}^{1/2}]$ . The experimental results fitted this equation with  $\lambda = 2.0$ . Earlier results with calcium or barium and potassium chloride solutions were re-examined and found also to obey this equation with  $\lambda = 2.9$  for  $CaCl_2$ -KCl and  $\lambda = 1.2$  for  $BaCl_2$ -KCl. Provided that the sodium/calcium ratio is not too high and the sodium content of the solution is known, these nonpressurized electrodes can be used for the direct determination of calcium ion activities, by applying the above equation. For example, in the determination of the calcium ion activity in milk which has an average sodium plus potassium content of 0.06  $M$  and a calcium content of 0.03  $M$ , a variation in the alkali metal content of  $\pm 5\%$  leads to a calcium ion activity error of  $\pm 5\%$ .

### Introduction

The preparation and properties of multilayer membrane electrodes composed of alkaline earth stearates have been described in earlier papers.<sup>1-3</sup> As prepared

or "unprotected" these electrodes are reversible to the cationic species only in the presence of the corresponding alkaline earth salts. They are not reversible to the alkaline earth cations only when used in mixed electrolytic solutions containing appreciable amounts of alkali metal cations. These membranes can be pressurized or "protected" by containing the multi-

- (1) H. P. Gregor and H. Schonhorn, *J. Am. Chem. Soc.*, **79**, 1507 (1957).
- (2) H. P. Gregor and H. Schonhorn, *ibid.*, **81**, 3911 (1959).
- (3) H. Schonhorn and H. P. Gregor, *ibid.*, **83**, 3576 (1961).

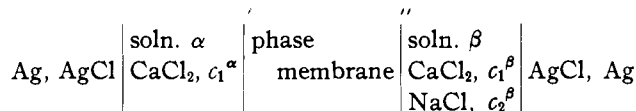
layer between conventional cation-permeable membranes under high pressure; under certain conditions, pressurized electrodes appear to be completely specific for the alkaline earth cation only, as at a molar ratio of potassium to barium or calcium of 100:1.<sup>3</sup>

Nonpressurized electrodes are simpler to prepare than pressurized electrodes and respond more rapidly to changes in ambient solution concentrations. In solutions of relatively low alkali metal:alkaline earth ion concentration ratios, they may be useful for measurements of the activity of alkaline earth cations, given a reproducible and reasonably low alkali metal "leak" and corresponding electrode response. This is a report of an experimental and theoretical investigation of these unpressurized electrode systems.

### Experimental

Calcium stearate multilayer membranes were prepared by the method described in earlier papers.<sup>1,2</sup> Certain refinements in the technique of their preparation were observed. The water of the plating substrate must be particularly pure, both with regard to foreign cations and to organic matter, particularly that which is surface active. Carefully distilled water was satisfactory, but deionized water was not. Also, the two halves of the electrodes were assembled between optical flats to ensure that the plated surfaces were aligned as perfectly as possible.

The following solution chain was examined



where the molar concentrations ( $c$ ) are designated by their appropriate superscripts, the superscript bar denoting quantities in the membrane phase. The two solution-membrane phase boundaries are designated by primes, with ionic concentrations at the boundary designated  $\bar{c}_2', \bar{c}_1'$ , etc. Subscripts 1 and 2 refer to calcium and sodium in their ionic forms only. The chloride ion is designated by a subscript 3, so that the mean practical (molar) activity coefficient of calcium chloride is  $\gamma_{13}$ . The molar ratio of sodium chloride to calcium chloride in solution  $\beta$  was varied from 1:1 to 60:1 and its total ionic strength  $\mu_T$  from 0.0325 to 0.539. Potential measurements were made with a Keithley vacuum tube voltmeter and were accurate to  $\pm 2\%$ . Appropriate corrections were employed for the asymmetry of the reference electrodes and the asymmetry potential of the multilayer electrode itself (usually  $\pm 2-3$  mv.)

### Results

The membrane electrodes were first tested without the addition of sodium chloride to solution  $\beta$ . The observed potentials were invariably within 0.5 mv. of the values calculated assuming complete ion specificity for calcium, and the response time was well within 5 min. Mixed solutions of calcium and sodium chlorides were then examined and steady potentials obtained within a few minutes after the solutions came into contact with the membrane for low sodium/calcium molar ratios; response times were less rapid (within 10 min.) at the highest ratio (60:1). After several measurements with mixed solutions, the potential in the absence of sodium chloride was again determined and found to be never more than 1-2 mv. higher than its original value, and it slowly decreased to the theoretical value.

Table I gives the results of measurements on three different membrane electrodes. The sodium diffusion potential  $E_{Na}$  will be discussed later. The lifetime of a membrane electrode in contact with solutions of calcium chloride alone was at least 100 hr. After this time the membrane ceased to function, its resistance

decreased by a factor of  $10^8$  and the free diffusion potential was observed. The lifetime of a membrane in contact with solutions containing sodium ions was considerably shorter, in some cases only 3-4 hr. In the dry state, the electrodes were stable for several months, at least.

TABLE I  
POTENTIALS OF CALCIUM STEARATE MULTILAYER ELECTRODES  
IN MIXED SOLUTIONS OF CALCIUM AND SODIUM CHLORIDES  
Chain: Ag, AgCl | soln.  $\alpha$  | membrane | soln.  $\beta$  | AgCl, Ag

Soln. $\alpha$ CaCl <sub>2</sub> , $m$	Soln. $\beta$		-E.m.f., mv.	- $E_{Na}$ , mv.
	CaCl <sub>2</sub> , $m$	NaCl, $m$		
Electrode A				
0.0025	0.005	0.000	23.5	..
0.0025	0.0025	0.025	61.0	24.0
0.0025	0.0025	0.050	77.0	26.8
0.0025	0.0025	0.125	108.5	41.0
0.0025	0.0025	0.150	120.0	49.0
0.005	0.0025	0.025	37.0	23.8
0.005	0.0025	0.050	52.0	24.6
0.005	0.0025	0.700	79.0	39.0
0.005	0.0025	0.725	85.5	41.8
0.005	0.0025	0.750	95.0	47.9
0.005	0.0025	0.000	-25.4	..
Electrode B				
0.005	0.0025	0.00	-23.0	..
0.005	0.0025	0.750	100.0	50.2
Electrode C				
0.113	0.226	0.000	23.0	..
0.113	0.113	0.100	27.4	18.0
0.113	0.113	0.200	43.4	23.1
0.0113	0.0226	0.000	24.0	..
0.0113	0.0113	0.010	18.4	9.0
0.0113	0.0113	0.020	28.0	14.1

### Theoretical

The membrane itself is a mixed crystal of calcium stearate, stearic acid, and, when sodium ions are present in solution  $\beta$ , sodium stearate. It is assumed that the acid does not participate in the exchange processes, that the stearate ions are fixed, and that chloride ions do not enter the membrane phase.

At the interface ', a state of equilibrium exists between calcium ions in the solution phase and in the membrane phase. Employing the practical (molar) system of denoting concentrations and activities ( $a$ ), the following relation exists between the chemical potential of calcium ions in solution  $\mu_1^\alpha$  and in the surface  $\bar{\mu}_1'$

$$\mu_1^\alpha = \bar{\mu}_1' + 2E'\mathfrak{F}$$

$$\mu_1^\circ + RT \ln a_1^\alpha = \bar{\mu}_1^\circ + RT \ln \bar{a}_1' + 2E'\mathfrak{F} \quad (1)$$

where  $\bar{a}_1'$  is the activity of calcium ions in the membrane and  $E'$  is the phase boundary potential. With only calcium ions present in solution  $\alpha$ , the activity of calcium ions in the solid phase at the boundary is constant and

$$E' = E^\circ + \frac{RT}{2\mathfrak{F}} \ln a_1^\alpha$$

where

$$2\mathfrak{F}E^\circ = \mu_1^\circ - \bar{\mu}_1^\circ - RT \ln \bar{a}_1' \quad (2)$$

Similarly, at interphase '' if either no sodium ions are present or if they do not enter the membrane phase

$$E'' = E^o + \frac{RT}{2\mathfrak{F}} \ln a_1^\beta \quad (3)$$

and the total potential of the chain with electrodes reversible to the chloride ions is<sup>2</sup>

$$E_{\text{rev}} = \frac{RT}{2\mathfrak{F}} \ln \frac{4(c_1^\alpha \gamma_{18}^\alpha)^3}{c_1^\beta (2c_1^\beta + c_2^\beta)^2 (\gamma_{18}^\beta)^3}$$

When sodium ions (for example) are present in solution 2, it is assumed that sodium ions replace calcium ions setting up a concentration gradient from interface '' to some point inside the membrane. Since the stearate ion concentration remains unchanged throughout the membrane, the following relation exists between the concentration of calcium stearate and sodium stearate throughout the membrane

$$2[\text{CaSt}_2] + [\text{NaSt}] = \text{a constant}$$

The equivalent fractions of calcium and sodium stearate are given by

$$\bar{X}_{14} = \frac{2[\text{CaSt}_2]}{2[\text{CaSt}_2] + [\text{NaSt}]}; \quad \bar{X}_{24} = \frac{[\text{NaSt}]}{2[\text{CaSt}_2] + [\text{NaSt}]}$$

and  $\bar{X}_{14} + \bar{X}_{24} = 1$ , where subscript 4 refers to the stearate ion. Throughout the membrane phase it is postulated that the molar concentration of free calcium and sodium ions is proportional to the equivalent fraction of the corresponding stearate

$$\bar{c}_1 = \bar{K}_1 \bar{X}_{14}/2; \quad \bar{c}_2 = \bar{K}_2 \bar{X}_{24} \quad (4)$$

where  $\bar{K}$  is the ionization constant of the corresponding, pure stearate. It is worth noting at this point that the degree of ionization of the stearate is quite small and that  $\bar{K}$  is also quite small. The above postulate implies the absence of significant nearest-neighbor interactions so that  $\bar{K}$  is independent of concentration.

In considering diffusive-exchange processes in the membrane phase, it is quite correct to ignore concentration polarization in the adjacent solutions because the concentration-mobility product of ions is considerably greater there.

For unidimensional diffusion at right angles to interface '', the Nernst-Planck equation leads to

$$-\frac{\bar{J}_1}{\bar{D}_1} = \frac{d\bar{c}_1}{dx} + 2\bar{c}_1 \frac{\mathfrak{F}}{RT} \cdot \frac{dE}{dx} + \bar{c}_1 \frac{d \ln \bar{\gamma}_1}{dx} \quad (5)$$

$$-\frac{\bar{J}_2}{\bar{D}_2} = \frac{d\bar{c}_2}{dx} + \bar{c}_2 \frac{\mathfrak{F}}{RT} \cdot \frac{dE}{dx} + \bar{c}_2 \frac{d \ln \bar{\gamma}_2}{dx} \quad (6)$$

where  $\bar{J}$  is the ionic flux,  $\bar{D}$  the diffusion coefficient,  $E$  the potential, and  $\bar{\gamma}$  the practical (molar) activity coefficient. At zero current,  $2\bar{J}_1 + \bar{J}_2 = 0$ ; in the quasi-stationary state,  $\bar{J}_1$  and  $\bar{J}_2$  are constant. In eq. 5 and 6, all concentrations refer to ionic concentrations and diffusion coefficients are those for the ionic species only, defined in terms of Fick's law with the ionic concentration gradient operative. Then, substituting for  $\bar{c}_1$  and  $\bar{c}_2$  from eq. 4 and neglecting any variation of  $\bar{\gamma}$  with composition

$$dE = \frac{RT}{\mathfrak{F}} \frac{\bar{K}_2 \bar{D}_2 - \bar{K}_1 \bar{D}_1}{2\bar{K}_1 \bar{D}_1 \bar{X}_{14} + \bar{K}_2 \bar{D}_2 (1 - \bar{X}_{14})} d\bar{X}_{14}$$

Integrating between the two interfaces

$$\int' dE = \frac{RT}{\mathfrak{F}} \int_1^{\bar{X}_{14}''} \frac{\bar{K}_2 \bar{D}_2 - \bar{K}_1 \bar{D}_1}{2\bar{K}_1 \bar{D}_1 \bar{X}_{14} + \bar{K}_2 \bar{D}_2 (1 - \bar{X}_{14})} d\bar{X}_{14}$$

$$E_{\text{Na}} = \frac{RT}{\mathfrak{F}} \frac{\bar{K}_2 \bar{D}_2 - \bar{K}_1 \bar{D}_1}{2\bar{K}_1 \bar{D}_1 - \bar{K}_2 \bar{D}_2} \times \ln \frac{\bar{K}_2 \bar{D}_2 + (2\bar{K}_1 \bar{D}_1 - \bar{K}_2 \bar{D}_2) \bar{X}_{14}''}{2\bar{K}_1 \bar{D}_1} \quad (7)$$

where  $E_{\text{Na}}$  is the sodium diffusion potential.

Let  $\bar{K}_1/\bar{K}_2 = \alpha$ ;  $\bar{D}_2/\bar{D}_1 = \delta$ . We now make the following assumptions which will be discussed later:  $\bar{X}_{14}'' \cong 1$ ;  $\alpha \ll 1$ ;  $\delta \geq 1$ . With these assumptions eq. 7 simplifies to the following

$$E_{\text{Na}} = \frac{RT}{\mathfrak{F}} \ln \left[ 1 + \frac{\delta}{2\alpha} (1 - \bar{X}_{14}'') \right]$$

Previously, we have assumed a state of equilibrium at the interfaces. At interface ''

$$(\bar{a}_2''/a_2^\beta)^2 (a_1^\beta/\bar{a}_1'') = K_{12}$$

where  $K_{12}$  is the distribution coefficient. Substituting for  $\bar{a}_1''$  and  $\bar{a}_2''$  from eq. 4

$$[\bar{K}_2 (1 - \bar{X}_{14}'') \bar{\gamma}_2''/a_2^\beta]^2 [2a_1^\beta/\bar{K}_1 \bar{X}_{14}'' \bar{\gamma}_1''] = K_{12}$$

$$1 - \bar{X}_{14}'' = \left[ \frac{K_{12} \bar{K}_1 \bar{\gamma}_1''}{2(\bar{K}_2 \bar{\gamma}_2'')^2} \right]^{1/2} \frac{a_2^\beta}{(a_1^\beta)^{1/2}}$$

and

$$E_{\text{Na}} = -\frac{RT}{\mathfrak{F}} \ln [1 + \lambda a_2^\beta/(a_1^\beta)^{1/2}] \quad (8)$$

where

$$\lambda = \frac{\bar{D}_2}{\bar{D}_1} \left[ \frac{K_{12} \bar{\gamma}_1''}{8\bar{K}_1 (\bar{\gamma}_2'')^2} \right]^{1/2}$$

Examination of  $\lambda$  shows that apart from  $(\bar{\gamma}_1''/(\bar{\gamma}_2'')^2)$  it contains only constants. The assumption that  $\bar{X}_{14}'' \cong 1$  means that only a very dilute solid solution of sodium stearate is formed in the membrane, and under these conditions we can assume that  $\bar{\gamma}_1''/\bar{\gamma}_2''^2$  is also constant. Equation 8, therefore, predicts a simple relation between the sodium diffusion potential and the activities of sodium and calcium ions in solution  $\beta$ . Since we have set  $\bar{X}_{14}'' \cong 1$ , it follows that the phase boundary potential  $E''$  is almost unchanged and thus the total potential of the chain is given by  $E_{\text{rev}} + E_{\text{Na}}$ .

### Discussion

Three assumptions were made in the derivation of the equation for  $E_{\text{Na}}$ , and concerned  $\bar{X}_{14}''$ ,  $\alpha$ , and  $\delta$ . The analysis of monolayers spread on substrates containing calcium and sodium ions has revealed a very high specificity for calcium over sodium.<sup>4,5</sup> Attempts to determine the sodium content of a skimmed layer on a substrate of the same composition as that used for making multilayer electrodes showed that the mole fraction of sodium was less than 1%.<sup>5</sup> Quite similar results were found when palmitic acid was spread on substrates containing calcium and sodium ions, and the

(4) E. Havinga, *Rec. Trav. Chim.*, **71**, 72 (1952).

(5) J. Bagg, *et al.*, *J. Am. Chem. Soc.*, **86**, 2759 (1964).

selectivity coefficient was found to be 1000.<sup>6</sup> All this evidence strongly supports the approximation  $\bar{X}_{14}'' \cong 1$ .

Havinga<sup>4</sup> proposed that over 90% of the calcium in the monolayer was undissociated or specifically bound and that less than 10% was present in the ionic form. From his study of the calcium/sodium ratio in palmitic acid monolayers, Danielli<sup>6</sup> also concluded that calcium was bound by specific forces, forming a complex with the carboxyl groups. The formation of complexes between calcium and carboxyl groups is well known and illustrated by the complexes formed with oxalic acid and polyacrylic acid<sup>7</sup>; in both cases, the stability constant is  $10^8$ . Sodium, on the other hand, forms almost completely ionic compounds and rarely forms complexes. The greater solubility of sodium stearate compared to calcium stearate is another indication of the greater ionic character of the sodium salt. The ratio of the ionization constants,  $K_1/K_2$  should, therefore, be much less than unity.

No measurements have been made of the ionic diffusion coefficients in sodium or calcium stearate. However, in view of the close similarity in the values of the unhydrated ionic radii (Ca, 0.99 Å.; Na, 0.96 Å.), it seems unlikely that the diffusion coefficients differ greatly, *i.e.*,  $\bar{D}_2/\bar{D}_1 \geq 1$ .

The sodium diffusion potential,  $E_{Na}$ , is given by the difference between the observed potential and the calculated, reversible potential; this value is reported in Table I. In calculating  $E_{rev}$  the value of  $\gamma_{18}^\beta$  was taken as the mean molar activity coefficient of a calcium chloride solution of the same ionic strength as solution  $\beta$ , using the values given by Harned and Owen.<sup>8</sup> In solutions of high ionic strength, the activity of one electrolyte in the presence of another usually obeys Harned's rule. The results of Gregor and Schonhorn<sup>3</sup> for mixed calcium and potassium chlorides showed that even at the highest ionic strength used ( $\mu_T = 0.539$ ) the Harned's rule correction was small, and none was made here.

To compare the experimental results with the theory,  $\exp(E_{Na,K} \mathcal{F}/RT)$  vs.  $a_2^\beta/(a_1^\beta)^{1/2}$  was plotted (see Fig. 1). The results show some scatter but may be considered to show a linear relationship with slope  $\lambda = 2.0$ . There are two effects which might contribute to the observed scatter. Single-ion activities were taken from Conway<sup>9</sup> for solutions of the same ionic strength as solution  $\beta$ . The extrapolation of values calculated for solutions containing a single cation to mixed electrolytic solutions may introduce error. Further, the multilayer is eroded by solutions containing sodium, with the result that penetration of sodium ions into the crystal itself is always quite shallow. However, this erosion in the crack will establish a small diffusion potential in the adjacent solution.

Earlier work<sup>3,10</sup> had shown that in measurements of mixed solutions of calcium or barium and potassium

(6) J. F. Danielli, "Surface Chemistry," Butterworth and Co., Ltd., London, 1949, pp. 87-93.

(7) H. P. Gregor, *et al.*, *J. Phys. Chem.*, **59**, 990 (1955).

(8) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958.

(9) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., 1952.

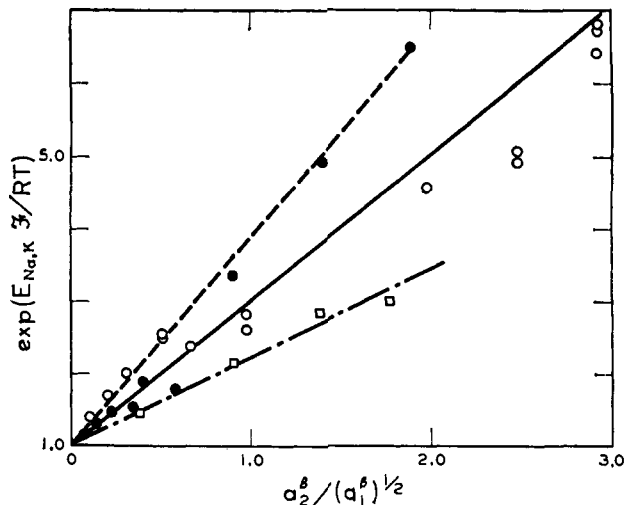


Fig. 1.—Plots of data for calcium chloride-sodium chloride-calcium stearate electrode systems (O —); for calcium chloride-potassium chloride-calcium stearate electrode systems (● - -); for barium chloride-potassium chloride-barium stearate electrode systems (□ - -).

chlorides with calcium or barium stearate multilayer electrodes, potassium ions interfered in much the same way as sodium ions. The assumptions we have described above would be expected to hold also for potassium ions. The values of  $E_K$  are shown in Fig. 1 also, and were derived and tested in exactly the same way as described for sodium. The value of  $\lambda$  was 2.9 for potassium and calcium and was 1.2 for potassium and barium. It is clear that the experimental results for potassium ions obey the diffusion equation quite satisfactorily. It is of interest that the lifetime of multilayers in contact with potassium ions appears to be longer than in contact with sodium, so that presumably less erosion occurs. The scatter of the results for potassium interference is less than for sodium, supporting the suggestion made earlier that erosion plays a part in the observed potential variations. Within experimental error, potassium and sodium ions interfere with a calcium stearate multilayer electrode to almost the same extent. Barium stearate multilayer electrodes are less sensitive to potassium ions than are calcium stearate electrodes.

This theory has led to a greater understanding of the nature of the interference by sodium and potassium ions with calcium and barium stearate multilayer electrodes. The expression for the diffusion potential allows nonpressurized electrodes to be used to determine calcium ion activities in solutions of known sodium or potassium ion content, for example, in systems of biological interest.

Work is in progress to study the interference by other metal ions and so to extend the applicability of these electrodes.

**Acknowledgments.**—This study was supported by a grant from the Atomic Energy Commission, Contract AT (30-1)-2279, for which the authors wish to express their thanks.

(10) H. Schonhorn, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1959.