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14. Deuteronomy 6:22.

INSTRUMENTS AND TECHNIQUES

Glass Electrodes Sensitive to Divalent Cations

Ion exchange models for new electrode glasses simplify analyses for calcium and other ions.

R. M. Garrels, M. Sato, M. E. Thompson, A. H. Truesdell

Glass electrodes, whose electrode response is analogous to that of *p*H glass electrodes, have been prepared and used to measure the concentrations of divalent cations, such as Ca^{++}, Mg^{++}, Ba^{++}, Sr^{++}, Mn^{++}, and Zn^{++}. Certain electrodes or combinations of electrodes can be used to determine the activities of individual divalent cations or the sum of the activities of two or more divalent cations in solutions that may contain moderate concentrations of monovalent cations. The electrode response apparently is not affected by the nature of the anions.

These electrodes may be used for measuring the hardness of drinking water, the calcium and magnesium in sea water, and the calcium in urine. It is anticipated that with some further development it will be possible to measure the activities of calcium and magnesium in whole blood or serum. Measurement of one divalent cation in the presence of others may also soon become practical.

Glass electrodes for measuring *p*H have been used during much of the last half century. The change in potential of the best of these electrodes in solutions of varying *p*H is found to be nearly identical to the change in potential measured by the standard hydrogen electrode in the same solutions. For this reason, with appropriate safeguards, it is customary *formally* to equate *p*H, as measured by the glass electrode, with $-\log a_{H^+}$ (*1*).

The extent of the "alkali error" of *p*H glass electrodes is known to be a function of the composition of the glass. Advantage was taken of this fact by Eisenman and his co-workers (*2*), who developed practical sodium- and potassium-sensitive glass electrodes. The response of these electrodes to monovalent cations is sufficiently close to that predicted by the Nernst equation to permit postulation of a formal relation between measured potential and $-\log a_{\mathrm{ion}}$, as defined by the relation

$$E = E^0 + (2.303\,RT/\mathrm{F})\log(a_{\mathrm{ion}})$$

where R is the gas constant, T is the absolute temperature, and F is the faraday.

Sensitivity of some glass electrodes to divalent cations has been noted before (*3*), but these glasses have strong *p*H functions and unreproducible responses and therefore never came into general use. In other attempts to measure divalent cation activities, particularly of calcium, use has been made of the electrical properties of other types of membrane surfaces—for example, clay membranes (*4*), ion-exchange resin membranes (*5*), and multilayer stearate membranes (*6*).

We chose the glasses that we tested for several reasons. Because the ion selectivity of glass electrodes is related to the differential strength of bonding of cations to the glass structure, we tried glasses close in composition to insoluble crystalline silicates—that is, natural glasses, such as obsidians or tektites.

We tested Pyrex, because it is a borosilicate glass and alkaline earth borates are much less soluble than alkali borates. We made and tested the potassium barium aluminum silicate because it was thought that a glass containing large cations might more easily accommodate divalent cations.

The experimental electrodes are glass tubes; they contain an inner solution of potassium chloride or hydrogen chloride and a chloridized silver wire that is connected by a shielded lead to an amplifier. The sensitive glass, in the form of a membrane, is at the lower end

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Table 1. Compositions of some of the divalent-cation-sensitive glasses (in mole percent).

Component	Samples					Pyrex
	NG-1	NG-3	NG-5	NG-6	KBA-1	
SiO_2	80.7	79.	82.7	76.	50.	84.
Al_2O_3	7.7	9.	7.8	8.	25.	1.2
B_2O_3						10.6+
Fe_2O_3	2.3	0.2	0.3	0.2		
FeO	1.0	1.6	0.8	4.0		
As_2O_3						0.9
MgO	0.2	2.2	0.3	4.4		
CaO	0.4	0.3	0.7	4.0		
BaO					12.5	
Na_2O	4.0	4.2	3.7	1.7		2.17
K_2O	3.7	3.5	3.7	1.7	12.5	

of the tube. The membrane is made either by blowing a bubble of the molten glass or by grinding a slice of the glass to a convenient thickness (about 0.03 mm). This is then glued to the end of a glass tube with a thermoplastic cement.

Because the experimental electrodes have very high resistances, a high input impedance electrometer (Keithley 610A) was used to measure the electromotive forces.

The development of sensitivity to divalent cations is apparently dependent upon the ratios of the monovalent, divalent, and trivalent oxides in the glass, rather than upon their specific nature, and the proportion of silica is important chiefly for glass-making reasons. The proportions of monovalent, divalent, and trivalent oxides in our electrode glasses are shown in Fig. 1. Some other oxide ratios of electrode glass are also shown in Fig. 1—for example, ratios for several *p*H glasses and for some of Eisenman's sodium- and potassium-sensitive glasses.

The selectivity of the glasses for different cations may depend upon the specific nature of the oxides added to the glass. Chemical compositions of some of the tested glasses are given in Table 1. Samples NG-1 and NG-3 are obsidians, NG-5 is a welded tuff, and NG-6 is a tektite (*7*). The other glasses are synthetic.

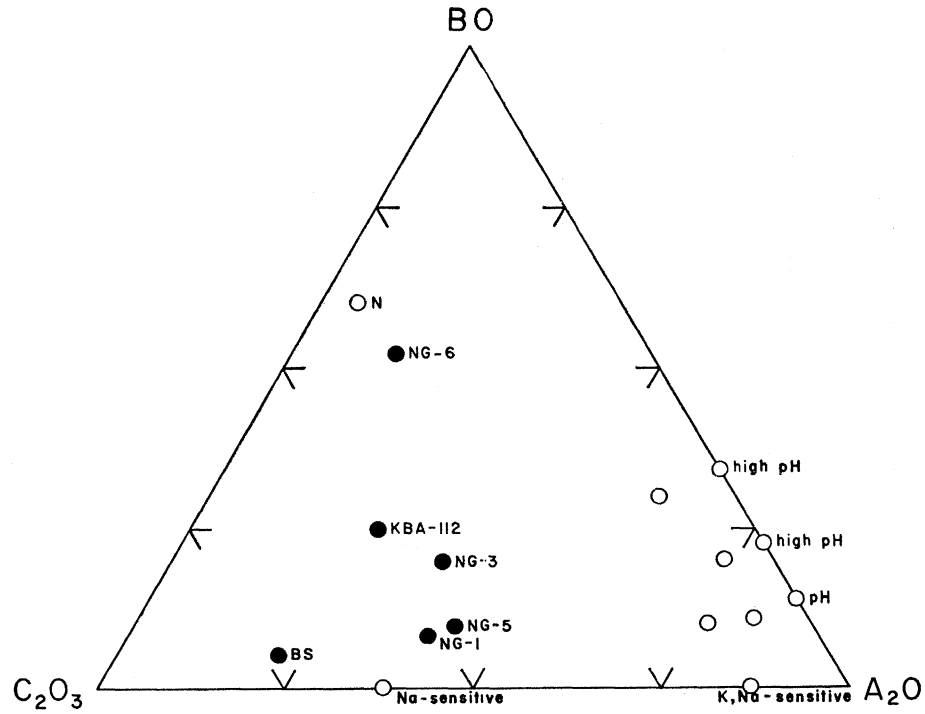

Fig. 1. Compositions of electrode glasses (exclusive of silica or other tetravalent oxides) in mole percent of monovalent oxides, A_2O; divalent oxides, BO; and trivalent oxides, C_2O_3. The silica content of the glasses ranges from 40 to 90 mole percent. Solid circles, glasses that show divalent cation sensitivity; open circles, glass of unsuitable composition for measuring such ions.

Electrode Response to Cations

The potential of the test electrodes was measured against that of a saturated calomel electrode in a cell of the following type: Ag | AgCl | 0.1*M* KCl | glass | test solns | KCl(satd) | Hg_2Cl_2| Hg.

Figure 2 shows the electromotive-force response of electrodes of several glass compositions to $MgCl_2$ alone, and to $MgCl_2$ in solutions with various initial concentrations of KCl. Similar curves are obtained by using other divalent salts (for example, $CaCl_2$, $BaCl_2$, and $SrCl_2$) and other monovalent salts (for example, NaCl and HCl). The direct-current resistance of the circuit including the electrodes is of the order of 10^6 to 10^{10} ohms. By using a null-balance method with a high impedance electrometer, we are able to measure electromotive forces reproducibly to ±0.2 millivolt. In a solution containing only Ca^{++} this electromotive-force range corresponds at 25°C to ±2 percent of the activity of the Ca^{++} present.

The response of some electrodes of high resistance is slow, and achievement of a constant potential is best observed through use of a recorder. Response of these electrodes is reproducible, however, and furthermore, the asymmetry potentials of electrodes prepared from a given glass are the same within a few millivolts. As with all glass electrodes, conditioning of the membrane in water lowers their resistances and improves the rate of response.

Empirical Electrode Equations

Equations 1 through 4, below, describe the observed behavior of cation-sensitive glass electrodes.

$$E = C_A + (RT/\mathrm{F})\ln([A^+]^{1/n} + k^{1/n}[B^+]^{1/n})^n \quad (1)$$

$$E = C_A + (RT/2\mathrm{F})\ln([A^{++}]^{1/n} + k^{1/n}[B^{++}]^{1/n})^n \quad (2)$$

$$E = C_A + (RT/2\mathrm{F})\ln([A^{++}]^{1/n} + k^{1/n}[B^+]^{2/n})^n \quad (3)$$

$$E = C_A + (RT/2\mathrm{F})\ln([A^{++}]^{1/n} + k^{1/n}[B^+]^{2r/n})^n \quad (4)$$

C_A is a constant dependent upon the particular electrode, *R* is the gas constant, *T* is the absolute temperature, and F is the faraday. The square brackets are used to denote activities; *A* and *B* represent ions of indicated charges. The constants n and k are dependent upon the particular electrode and pair of cations being measured and might more properly be written with subscripts—for example, n_{AB}. The exponent n represents a modification of the basic Nernst electrode equation; for many electrodes n is near enough to unity to be disregarded. Some electrodes that are sensitive to divalent cations show less than the predicted electromotive-force changes for monovalent cations; for these electrodes the exponent r in Eq. 4 must be introduced.

Figure 3 shows experimental versus calculated relationships for the response of electrode NG-6 to Mg^{++} in a solution with an initial pCa^{++} of 5.07. This electrode follows Eq. 2, with $n = 1$, within the limits of experimental error.

Theoretical Considerations

Eisenman (*2*) indicated that the empirical electrode equation involving two monovalent cations could be derived from the law of mass action. We made and extended the derivation to include divalent as well as monovalent cations (*8*). The derivation is based upon the assumption that an ion-exchange equilibrium is established between the glass surface and the aqueous solution and that the electrode potential originates from the distribution of cations between the two. For example, the electrode equation for two monovalent cations can be derived from the following reaction:

$$AX + B^{+} = BX + A^{+} \qquad (5)$$

where AX and BX represent the fixed species of cations A^{+} and B^{+} in the exchangeable phase that exists in and near the surface of the glass electrode. The symbol X denotes the framework of the glass. From the law of mass action, at equilibrium, we derive

$$\frac{[A^{+}]}{[B^{+}]} = K\frac{[AX]}{[BX]}$$

$$= K\frac{\lambda_{AX}(AX)/\{(AX)+(BX)\}}{\lambda_{BX}(BX)/\{(AX)+(BX)\}} \qquad (6)$$

where the square brackets are used to denote activities, K is the equilibrium constant, and λ is the activity coefficient when concentrations are expressed in mole fractions.

Movement of a cation from the glass to the solution leaves a negative site behind: $AX = A^{+} + X^{-}$. By analogy

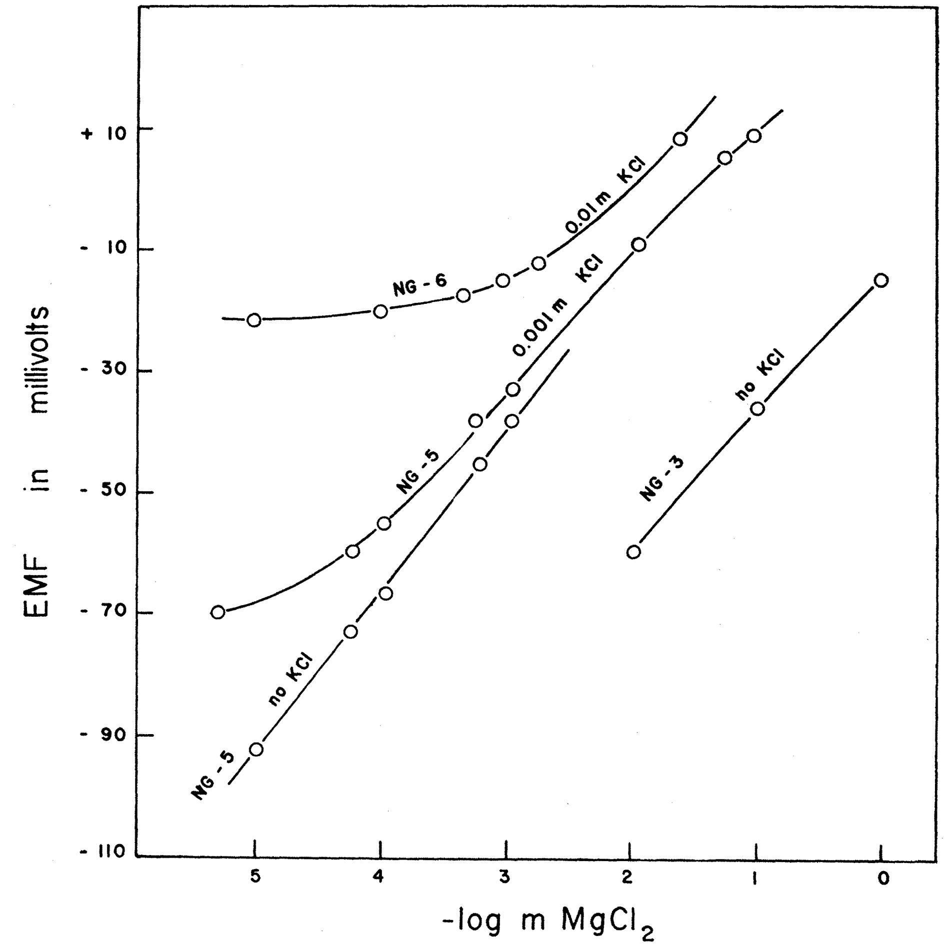

Fig. 2. Changes in electromotive force (EMF) of several glass-electrode and saturated-calomel-electrode pairs as a function of $MgCl_2$ concentration, in the presence and absence of KCl. Symbols on the curves refer to the glass compositions of Fig. 1.

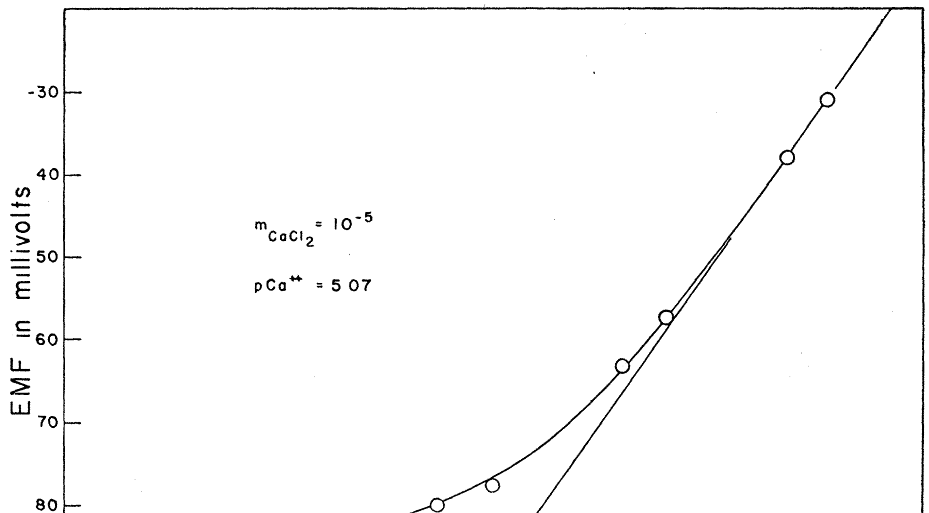

Fig. 3. Change in electromotive force (EMF), at 25°C, of electrode number NG-6 with additions of Mg^{++} to a solution initially 10^{-5} molal in $CaCl_2$ (pCa^{++} = 5.07). Open circles, measured EMF values. The curve is a plot of the equation $E_{CaMg} = C_{Ca} + 0.0296 \log ([Ca^{++}] + K[Mg^{++}])$, where $C_{Ca} = 0.0646$, $[Ca^{++}] = 10^{-5.07}$, and $K = 0.645$.

Table 2. Measured and calculated electromotive-force (EMF) values (in millivolts) for K^+-Ca^{++} exchange on a glass electrode. Initial $pK^+ = 3.016$; $C_{Ca} = 0.0646$.

pCa^{++}	Measured EMF, electrode NG-6	Empirical electrode equation*	Regular solution model†	Ideal solution model‡
	−67.3	−67.3	−67.3	−67.3
5.36	−65.0	−64.5	−64.8	−66.0
5.06	−62.9	−62.6	−62.9	−64.8
4.28	−54.0	−53.8	−53.8	−56.7
4.03	−49.0	−49.2	−49.3	−52.2
3.30	−32.5	−32.6	−32.7	−34.0
3.07	−26.5	−26.4	−26.6	−28.0
2.83	−20.4	−19.9	−20.5	−20.9

*$E_{CaK} = 0.0646 + \frac{RT}{2F} \ln([Ca^{++}]^{1/1.33} + 42.8^{1/1.33} [K^+]^{2/1.33})^{1.33}$

†$E_{CaK} = 0.0646 + \frac{RT}{2F} \ln \left(\frac{[Ca^{++}]}{e^{-0.9N^2} K_2X_2} + 42.8 \frac{[K^+]^2}{e^{-0.9N^2} CaX_2} \right)$

‡$E_{CaK} = 0.0646 + \frac{RT}{2F} \ln([Ca^{++}] + 42.8 [K^+]^2)$

to the ionization of a metal, a half-cell potential equation can be written:

$$E = C_A + (RT/F)\ln([A^+]/[AX]) \quad (7)$$

The activity of A^+ in the glass phase can be expressed in terms of an activity coefficient and a mole fraction, and substitutions can be made from Eq. 6 to obtain a general electrode equation for two monovalent cations (*9*):

$$E = C_A + (RT/F)\ln\left(\frac{[A^+]}{\lambda_{AX}} + K\frac{[B^+]}{\lambda_{BX}}\right) \quad (8)$$

The general electrode equation involving any number of monovalent and divalent cations takes the form:

$$E = C_A + (RT/2F)\ln\left(\sum_{J=A}^{u} K_{AJ} \frac{[J^{z+}]^{2/z}}{\lambda_{J2/zX2}}\right) \quad (9)$$

Where J is any cation A to u, z indicates the magnitude of the charge, and the other symbols are as given in the earlier equations.

It can be shown that the empirical electrode equations for which n equals 1 correspond to theoretical systems in which the glass-surface phase behaves like an ideal solid solution (for example, $\lambda_{JX} = 1$).

Empirical electrode equations involving two cations in which n is not unity can be derived from the theory of "regular solutions" (*10*), for which

$$\lambda_{AX} = \exp\left(\frac{B}{RT}(1 - N_{AX})^2\right)$$

where B is a constant and N indicates mole fraction. In these equations an approximate solution is obtained: $n \cong 1 - B/(2RT)$. In the limit, as the ratio of the mole fractions of the adsorbed species in the glass-surface phase approaches 1, n becomes equal to $1 - B/(2RT)$.

Table 2 shows the electromotive-force response of electrode NG-6 in a solution containing, initially, $pK^+ = 3.018$ with varying pCa^{++}. The data are fitted within the limits of experimental error by the empirical electrode equation in which $n = 1.33$, and by a theoretical equation in which $B/RT = -0.9$. We predict that electrode equations based on regular solution theory will in general fit observed electromotive-force values better than the empirical equation involving n in the range of glass-surface-phase compositions where the ratio of mole fractions is markedly different from unity.

Summary

Glass electrodes suitable for measurement of divalent cations have been made and tested. Empirical and theoretical electrode equations have been presented to describe electrode behavior in a variety of aqueous solutions. Most electrodes show response interpretable as showing nearly ideal solid-solution behavior of the cations in the glass surface. The electrodes should be useful in the measurement of divalent-cation activities in natural waters and biological fluids, and useful in general analytical chemistry.

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