Glass Electrode for Measuring Sodium Ion

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In 1934, von Lengyel and Blum observed that adding the acidic oxide Al_2O_3 or B_2O_3 to sodium silicate glasses caused the glass electrode potential to become strongly dependent on the concentration of several cations besides H^+ (*1*). Their data indicated that the sensitivity probably ranked in the decreasing order H^+, Na^+, K^+ and Li^+. These observations suggested that practical glass electrodes might be developed for measuring the Na^+ activity as a continuous function of time in ionic mixtures and in biological fluids. Von Lengyel and Blum's observations have been confirmed and extended by us in a large number of electrodes made from several melts of their Du composition (SiO_2, 62 moles percent; Al_2O_3, 11 moles percent; Na_2O, 24 moles percent; CaO, 3 moles percent). In addition, we have studied the electrode potential as a function of systematic variations of glass composition in a number of simple glass systems. This article (*2*) is primarily concerned with some immediately useful consequences of the study of the ternary glass system, Na_2O-Al_2O_3-SiO_2 (*3*).

All glass electrodes containing more than a fraction of 1 mole percent of Al_2O_3 are markedly cation sensitive, and the sensitivity for different cations relative to one another is a systematic and reproducible function of glass composition (see subsequent paragraphs). In single cation solutions of H^+, Na^+, K^+, or Li^+, the glasses yield electrode potentials which are a linear function of the logarithm of cation activity with a slope of 58 millivolts for a tenfold activity change at 20° to 22°C when referred to a saturated KCl bridge calomel half-cell. When measured against a Ag-AgCl half-cell without liquid junction, the chloride salts give the expected slope of 116 millivolts. The glass electrodes are indifferent to the particular anion present (chloride, hydroxyl, bicarbonate, nitrate, acetate, carbonate, sulfate, thiosulfate, ferrocyanide, and ferricyanide were studied). They are not affected by the presence of oxidizing or reducing substances, for they have the same potential in thiosulfate as in chloride solutions, as well as in dilute solutions varying from 100-percent ferrocyanide to 100-percent ferricyanide.

Electrode Potential

A precise description of the glass electrode potential in mixtures of any two univalent cations is given by the following new empirical equation.

$$E = E^\circ + \frac{RT}{F} \ln \left[(A^+)^{1/n_{AB}} + k_{AB}^{1/n_{AB}} (B^+)^{1/n_{AB}} \right]^{n_{AB}} \qquad (1)$$

Equation 1 not only describes all of our data, but appears to be quite general, fitting representative glass electrode data (*4–6*) examined by us. Parentheses around symbols denote activity; k_{AB} and n_{AB} are empirical constants for a given glass composition and cation pair (A^+, B^+) (*7*). Figure 1 (parts *A*, *B*, and *C*) presents representative data for the electrode potential in binary mixtures of H^+ and Na^+ (part A), H^+ and K^+ (part *B*), as well as in ternary mixtures of K^+, Na^+, and H^+ [at constant *p*H and (K^+)] (part *C*). The straight dotted line drawn through the triangles in parts *A* and *B* plots the potential recorded in pure HCl solutions of varying dilution (that is, at zero Na^+ or K^+) and has the expected slope of 58 millivolts per *p*H unit. The points in Figs. 1*A* and 1*B* are experimental values recorded as a function of varying H^+ activity with Na^+ or K^+ concentration constant at 0.1 molar. (Since H^+ never exceeded 10 percent of this amount, the ionic strength and the activity of Na^+ or K^+ were effectively constant.) The curves are drawn from Eq. 1 with the indicated values of n_{AB} and k_{AB}. Changes in Na^+ or K^+ produce appropriate shifts in the curves as described by Eq. 1. In the case of H^+–Na^+ mixtures, n_{HNa} generally equals 1 for sodium glasses sensitive to sodium ion, and Eq. 1 then takes a form which is the simplest case predicted by the theories of Dole (*5*) and Nicolsky (*8*), but for H^+–K^+ mixtures n_{HK} for many glass compositions is significantly greater than 1, approaching values as high as 3.5. If Eq. 1 is expanded as a series and the terms beyond the second are neglected, then it takes the form of Dole's and Wiener's modified electrode equation (*9*).

While the importance of Eq. 1 for this article is chiefly as an empirically valid representation of the experimental data, it should be mentioned that it can be derived thermodynamically by a treatment similar to Nicolsky's (*8*). Our derivation, however, requires the assumption that the activity of the adsorbed cations is proportional to the n^{th} power of their adsorbed amount rather than to the first power. This assumption also leads to a general adsorption isotherm mass action law):

$$k_{AB} = \frac{(A^+)\,(B^+_{ads.})^{n_{AB}}}{(B^+)\,(A^+_{ads.})^{n_{AB}}} \qquad (2)$$

where (A^+) and (B^+) are the ionic activities in solution, $A^+_{ads.}$ and $B_{ads.}$ are the mole fractions of A^+ and B^+ adsorbed, and k_{AB} and n_{AB} are the same constants as in Eq. 1. Equation 2 represents satisfactorily a wide range of ion exchange equilibria extracted from the literature (for example, synthetic organic cation and anion exchangers, natural and synthetic inorganic cation exchangers, as well as the binding of univalent anions to serum albumin). An equation of this form was first described by Kornfeld and Rothmund (*10*) as an empirical description of the ion exchange of permutites; but its possible extension to glass electrodes has not been recognized.

Although a general equation for tricationic mixtures has not yet been developed and tested, Eq. 1 has been found to describe the electrode potential in Na^+-K^+-H^+ mixtures when (H^+) is held constant and A^+ and B^+ represent Na^+ and K^+ (Fig. 1C, Fig. 2). In this case n_{NaK} is constant and equals 1 over a wide *p*H range (5.6 to 10.6) for representative glasses of our series. However, k_{NaK} varies with *p*H, approaching a constant value at high *p*H. (Examine Fig. 1*B* and 1*A* in this regard.) Figure 2 illustrates how k_{NaK} varies with *p*H for NAS_{11-18} glass (Na_2O, 11 moles percent; Al_2O_3, 18 moles percent; SiO_2, 71 moles percent). At *p*H 10.6, k_{NaK} equals 3.48×10^{-3}, while at *p*H 5.6 it equals 1.06×10^{-2}.

Relative Sensitivity as a Function of Glass Composition

It is convenient and appropriate to define the "relative sensitivity" of a particular glass electrode for a given ion pair A^+, B^+ as equal to the value of k_{AB} since, above *p*H 6, n_{AB} may be taken as 1 for all ion pairs studied here, and k_{AB} does not differ greatly from its limiting value at high *p*H. (In this regard, note

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the small deviation from the asymptote above *p*H 6 in Fig. 1*B*). For *p*H greater than 6, a value of k_{AB} of 0.01 signifies that 0.01 mole (A^+) is equivalent to 1.0 mole of (B^+) in determining the electrode potential. This simplification is useful because many potential measurements are needed in evaluating n_{AB}, while two measurements (one in pure A^+ of known activity and one in pure B^+) suffice for evaluating k_{AB}.

A study of relative cation sensitivities as a function of glass composition was made by direct comparison of the electrode potentials in 0.1*N* solutions of the single alkali cations at neutral *p*H as well as in pure 0.1*N* HCl solutions. Such a simple comparison has been found sufficiently accurate for the purposes of this article. Figure 3 summarizes the systematic and reproducible relationship found between glass composition (in moles percent of the oxides as determined by chemical analysis) and cation sensitivity to Na^+, K^+, and Li^+ relative to H^+ in *A, B, C,* and Na^+ relative to K^+ sensitivity in *D*. Contours of isosensitivity are plotted in the high SiO_2 corner of the triangular composition field for the Na_2O-Al_2O_3-SiO_2 system. For example, the 100-contour line in *D* traces all those compositions wherein NAS glasses are 100 times as sensitive to Na^+ as to K^+ at *p*H 7.6 (corresponding to $k_{NaK} = 0.01$). Figure 3 illustrates the fact that sodium aluminosilicate glasses can be made whose sensitivity for the alkali cations relative to H^+ can be varied from values smaller than 10^{-10} to values approaching 1 (*11*). In addition, the differential sensitivity for Na^+ relative to K^+ at *p*H 7.6 has been maximized at about 250:1 for the glasses it has been possible to make in this ternary system to date.

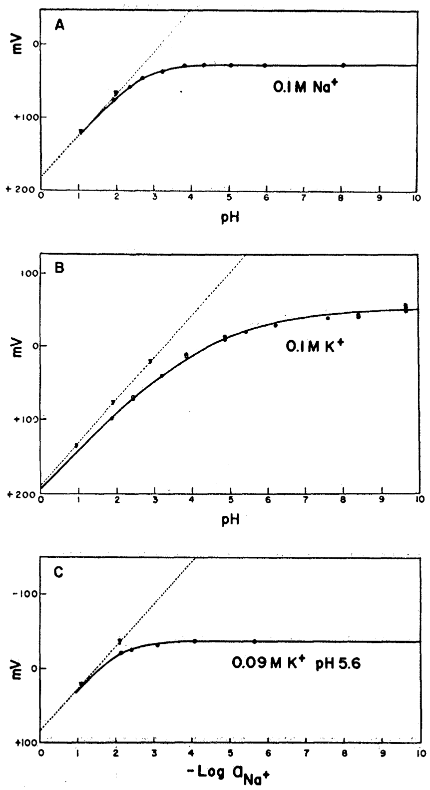

Fig. 1. Representative glass electrode potentials in ionic mixtures (Du glass). The solid curves plot the potential given by Eq. 1 for the indicated cation mixtures. The straight dotted lines plot the potential given by Eq. 1 for pure H^+ (*A* and *B*) and Na^+ (*C*) solutions. The points are experimental measurements referred to a saturated KCl-calomel half-cell. The abscissa in *A* and *B* was measured with Beckman *p*H electrodes. The abscissa in *C* was expressed as activity using 0.78 for the activity coefficient of the known Na^+ microcomponent concentration in the presence of a constant 0.09*M* K^+. The values of n_{AB} and k_{AB} used in drawing the curves were as follows: in *A*, $n_{HNa} = 1$, $k_{HNa} = 2.15 \times 10^{-2}$; in *B*, $n_{HK} = 3.5$, $k_{HK} = 8.86 \times 10^{-4}$; in *C*, $n_{NaK} = 1$, $k_{NaK} = 1.13 \times 10^{-1}$. The value of 2.303*RT/F* was taken as 58 millivolts at 22°C.

Applications

A glass having such a high selectivity for Na^+ relative to H^+ and K^+ offers an attractive device for measuring Na^+ activity in complex mixtures of ions. The best composition for many purposes is one which has the highest selectivity for Na^+ relative to K^+ and is also minimally sensitive to H^+. A comparison of Figures 3*A* and 3*D* indicates this composition to be Na_2O, 11 moles percent; Al_2O_3, 18 moles percent; and SiO_2, 71 moles percent (NAS_{11-18} in our terminology). The composition of the initial mixture from which this glass was made was Na_2O, 11 moles percent; Al_2O_3, 27 moles percent; SiO_2, 62 moles percent. The approximate relative sensitivity of this glass to the various cations at neutral *p*H is as follows: H^+, 1; Na^+, 0.08; Li^+, 0.001; NH_4^+, 0.001; K^+, 0.0003; Rb^+, < 0.00002, Cs^+, < 0.00002; Ca^{++}, < 0.000015; Mg^{++}, < 0.0000004 (*12*). In good first approximation, one may obtain the relative sensitivity for any ion pair directly from these numbers (as discussed in *7*).

In addition to the afore-mentioned measurements on the simple ternary system Na_2O-Al_2O_3-SiO_2, it has been found that adding small amounts of CaO or Fe_2O_3 to such glasses in quantities up to several moles percent does not alter significantly their electrode function. Presumably, this finding will permit the addition of small amounts of these and similar oxides to improve other physical properties of the glass. It has also been found that Na, Al, and Si per se are not needed in order that a glass may be highly cation sensitive, for Na_2O can be replaced by Li_2O or K_2O; SiO_2 can be replaced by GeO_2; and Al_2O_3 can be replaced by B_2O_3.

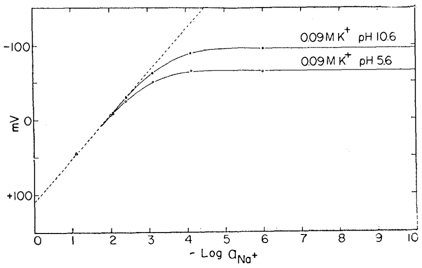

Fig. 2. Glass electrode potentials in Na^+-K^+ mixtures at *p*H 5.6 and at *p*H 10.6 (NAS_{11-18}). The solid circles are experimental points at *p*H 10.6. The open circles are experimental points at *p*H 5.6. The curves are again drawn according to Eq. 1 for $n_{NaK} = 1$, $k_{NaK} = 3.48 \times 10^{-3}$ at *p*H 10.6; and $n_{NaK} = 1$, $k_{NaK} = 10.6 \times 10^{-3}$ at *p*H 5.6

It can be calculated conservatively from the above data that, in biological fluids containing 0.15*M* Na^+ or more, an NAS_{11-18} glass electrode would measure Na^+ activity with less than 0.2 percent error owing to the presence of an unknown K^+ concentration up to 30 m*M* at any *p*H higher than 5.6. Since NAS_{11-18} glass is also relatively insensitive to Ca^{++} and Mg^{++} as well as to NH_4^+ and Li^+, these ions are also without appreciable effect on the electrode potential except when they are present in unusual concentrations.

Besides the above "ion errors," other factors may limit the precision and accuracy with which Na^+ activity can be measured in a given application. One source of error arises from electrode drift. For a representative bulb electrode, the drift measures less than 100 microvolts in any minute and less than 500 microvolts in an hour. In terms of equivalent Na^+ activity change, this amounts to less than 0.5 percent per minute and 1.3 percent per hour, respectively. Other limits to sensitivity and selectivity are amplifier sensitivity and noise, reference electrode noise, reproducibility of voltages when changing solutions, purity of reagents, the accuracy of preparing standards, stray electric fields, and temperature fluctuations of the system. Our observations have been confined chiefly to relatively gross measurements made with a standard Beckman model G *p*H meter. With this crude equipment we have been able to *detect* differences as small as 1 percent between standard NaCl solutions. With greater refinement of technique, we anticipate that one should be able to *measure* Na^+ activity to 0.1 percent with commercially available high-gain electrometers and without taking a prohibitive number of readings.

In biological applications, two other possible sources of error may exist. One is the possibility of an effect of protein on the glass. We have found no qualitative indication of poisoning by constituents of serum, cerebrospinal fluid, or brain homogenate when electrodes are soaked in these fluids for many hours; the electrodes have yielded correct potentials in standard solutions immediately upon removal. The electrodes also show the expected potentials when known concentration changes of Na^+, H^+, K^+, or Ca^{++} are produced in the aforementioned fluids and when the unknown contribution to the ionic strength due to protein is disregarded [see Northrup and Kunitz (*13*) and Scatchard *et al.* (*14*) for data supporting this assumption]. When using these electrodes in intact biological systems, one must also be able to distinguish other sources of electrical potential difference between the electrodes such as electric potential fields of membrane origin or diffusion potentials which might result from extracellular ionic concentration gradients. Methods have been developed which are capable of accomplishing this distinction (*15*) both in principle and in simple cases which have been tested.

While our primary concern has been to maximize Na^+ specificity (the limits of which are still unknown), we have also discovered that certain compositions of the Na_2O-Al_2O_3-SiO_2 system are more sensitive to K^+ than to Na^+. Thus, in Figure 3*D*, such a composition region is seen in the shaded area below the 1 contour line. The most selective glass of this system for K^+ relative to Na^+ lies below the 0.3 contour and is about 6 times as sensitive to K^+ as to Na^+. It should be noted that, by using such a glass electrode in conjunction with the highly Na^+ selective NAS_{11-18} electrode, it is possible to measure uniquely both the Na^+ and K^+ activities of an unknown mixture if one solves the two simultaneous electrode equations.

Conclusion

We conclude that a sodium aluminosilicate glass containing 11 moles percent of Na_2O, 18 moles percent of Al_2O_3, and 71 moles percent of SiO_2 offers electrodes of practical usefulness for selectively measuring the sodium ion activity as a continuous function of time in certain ionic mixtures, including extracellular biological fluids.

References and Notes

1. B. von Lengyel and E. Blum, *Trans. Faraday Soc.* 30, 461 (1934).
2. The initial part of this work was performed in the Anesthesia Laboratories of Harvard Medical School at the Massachusetts General Hospital and was aided by a grant from the National Foundation for Infantile Paralysis.
3. All but four glass compositions were made in our laboratory using a gas-oxygen furnace for 2 to 4 hours between 1300°C and 1650°C. (We thank William C. Wescott who made many glasses and Lewis E. Russell of the department of ceramics of Massachusetts Insti-

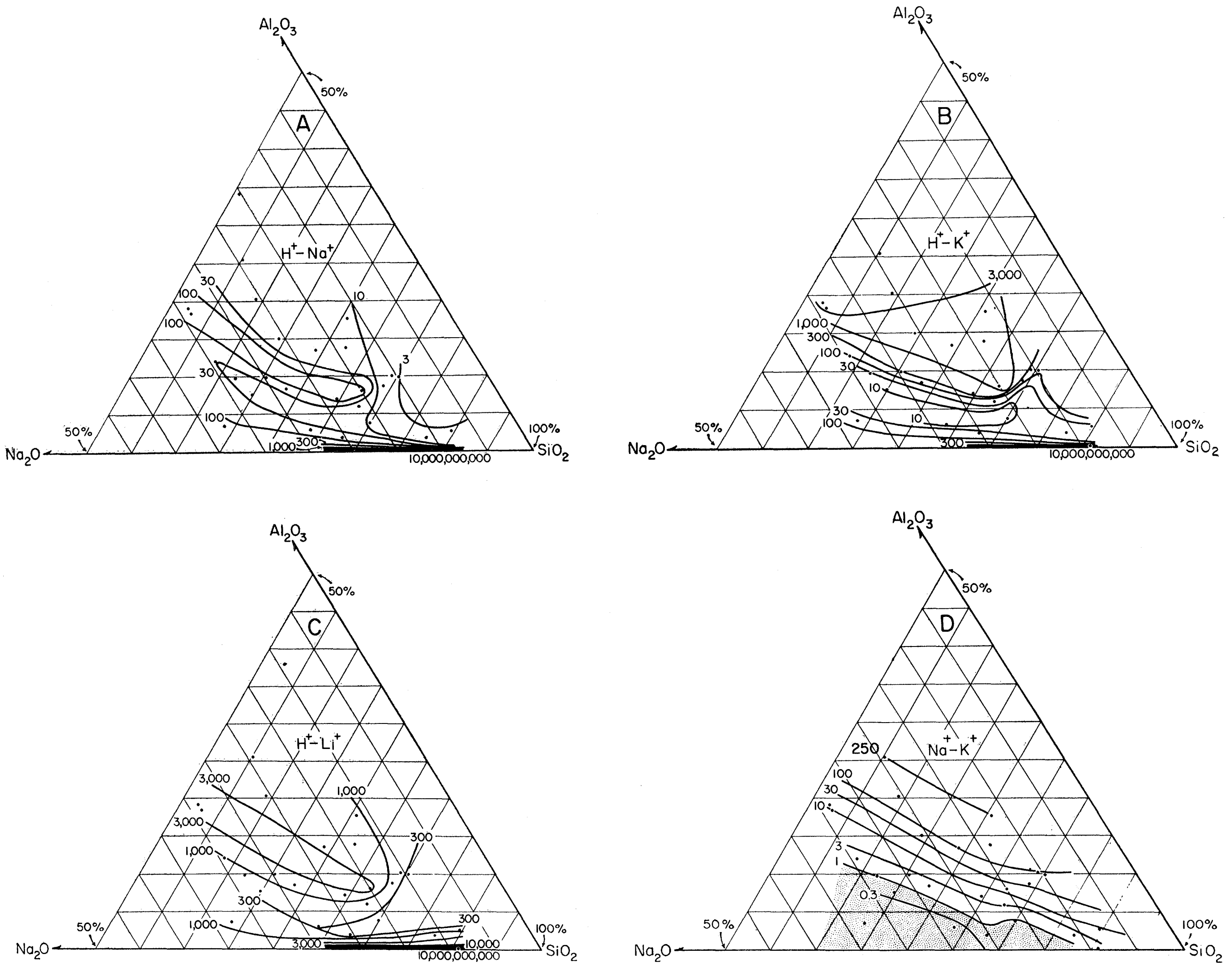

Fig. 3. Contours of isosensitivity in the high-silica corner of the Na_2O-Al_2O_3-SiO_2 composition field. Coordinate lines are given at 5 moles percent intervals. Points represent chemically analyzed glass compositions studied. The contour lines of isosensitivity are graphical interpolations from electrode potential data obtained at these composition points. The contour numbers indicate the ratio of the relative sensitivities for the specified ion pairs and are reciprocals of the k_{AB} values. Data in *A*, *B*, and *D* were obtained at *p*H 7.6; data in *C* were obtained at *p*H 6.6. In *D* note regular change in Na^+ to K^+ sensitivity and especially its reversal across the 1 contour line.

tute of Technology, who made two initial melts of Du glass.) Denver fire clay or alumina crucibles were used. SiO_2 was added as Pennsylvania Glass Sand, Na_2O as the carbonate, and Al_2O_3 as the hydroxide (both as Mallinckrodt analytical reagents). Two compositions (NAS_{10-10}, NAS_{11-18}) were made to our specifications by E. B. Shand of the Corning Glass Works. Glasses were analyzed for major constituents and trace impurities by the U.S. Testing Company. The final composition differs from that of the initial mixture in a complex manner but always has a significantly lower Na_2O and Al_2O_3 content. The losses generally take place along paths pointing toward the SiO_2 corner of the ternary diagram and are roughly proportional to the initial Na_2O or Al_2O_3 content. Data in terms of initial composition also yield systematic plots, a useful finding for surveying glasses. Haber-type bulb electrodes (3 to 10 mm in diameter) were made from small pieces of tubing blown in a gas-oxygen flame. A few small membrane electrodes (less than 300 μ in diameter) on lead glass stems were prepared by modifying the method of MacInnes and Dole. It should also be possible to prepare microelectrodes in the form of fine capillaries of sodium-sensitive glass sealed by fusing at the tip. Electrodes were filled with 0.1*M* NaCl and stored in the same solution at least 24 hours prior to study, although 0.1*M* HCl was also used without difference in results. A chlorided silver wire formed the internal electrode. Immediately prior to study, the stem of the electrode was rinsed with distilled water, dried and insulated by dipping in paraffin. The insulation proved satisfactory for several hours and could be renewed when necessary. The bulk of the measurements were made in solutions less concentrated than 0.1*M* with a Beckman model G *p*H meter and a Beckman KCl calomel fiber reference cell. Solutions were prepared directly from Baker analyzed reagents and analyzed spectrographically for impurities, which were found to be unimportant. Experiments were designed so that liquid junction potentials contributed no important error. (In Figs. 1 and 2, the liquid junction was held constant by keeping the concentration of the macrocomponent of the mixture unchanged; in Fig. 3, only the glass electrode was varied.) Single-ion activity coefficients for Na^+ and K^+ equal to the mean activity coefficients were assumed. The resistance of representative bulb electrodes lay between 10^8 and 10^{10} ohms. Most glasses respond rapidly to Na^+ change, coming to a stable value while being washed. No attempt has been made to measure the high-frequency noise (above 100 cy/sec) or to measure the response time to a rapid step in Na^+ concentration.

4. M. Dole and B. Z. Wiener, *Trans. Electrochem. Soc.* 72, 107 (1937).
5. M. Dole, *The Glass Electrode* (Wiley, New York, 1941).
6. P. Gross and O. Halpern, *J. Chem. Phys.* 2, 136 (1934); D. O. Jordan, *Trans. Faraday Soc.* 34, 1305 (1938); H. J. C. Tendeloo and A. J. Zwart Voorspuij, *Rec. trav. chim.* **62**, 793 (1943).
7. The value of k_{BC} for a particular ionic mixture B^+, C^+ can be evaluated from the k_{AB} and k_{AC} values for the ion mixtures A^+, B^+ and A^+, C^+ by the relationship $k_{BC} = k_{AC}/k_{AB}$, which has been found to be valid experimentally.
8. B. P. Nicolsky, *Acta Physicochim. U.R.S.S.* 7, 597 (1937).
9. M. Dole, personal communication.
10. G. Kornfeld and V. Rothmund, *Z. anorg. u. allgem. Chem.* 103, 129 (1918).
11. The extreme abruptness of development of alkali cation sensitivity relative to H^+ with small additions of Al_2O_3 is likely to be of practical significance in minimizing the cation error of *p*H glass electrodes since this finding suggests that even minute traces of alumina are to be avoided in preparing such glass melts.
12. For Ca^{++} and Mg^{++}, these numbers are to be taken as indicative of order of magnitude only since equations for electrode potential in mixtures of ions of unequal valence have not yet been verified.
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14. G. Scatchard, I. H. Scheinberg, S. H. Armstrong, Jr., *J. Am. Chem. Soc.* 72, 535 (1950).
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News of Science

Archeological Discoveries in Iraq

The Smithsonian Institution sponsored an archeological expedition to Shanidar Valley in the Zagros Mountains of northern Iraq during the season 1956–57 that has resulted in several important discoveries, chief of which are the finding of two adult human skeletons of premodern type in Shanidar Cave and the discovery of an early Neolithic village site nearby. Ralph S. Solecki of the Smithsonian led the expedition, his third to the area.

The discovery of the two skeletons, as well as an earlier find, that of a child's skeleton in 1953, places Shanidar Cave among the more important Early Man sites in the Old World. In western Asia it is second only to the Mount Carmel site in Palestine in upper Pleistocene skeletal remains.

Both of the adult skeletons were recovered from the top of the Mousterian layer, the bottommost of four stratigraphic layers at Shanidar Cave. One of the skeletons was found at a depth of 14.5 feet below the surface, and the other at about 23 feet. In both, the bones were in an unfossilized or natural state.

The Mousterian layer is recognized as belonging to the Middle Paleolithic period associated with Neanderthal man. The skeletal remains appear to be of Neanderthal type on preliminary observation, and their position in the upper part of the Mousterian layer, above which was found a layer containing Upper Paleolithic artifacts very similar in type to its Aurignacian counterpart in western Europe, indicates a very late type of Neanderthal man. The bottom of the Upper Paleolithic layer has been dated by the carbon-14 test to be about 34,000 years old.

The shallower of the two skeletons, by virtue of its stratigraphic depth, is possibly about 45,000 years old. Although the bones in this skeleton were broken, the skeleton is fairly complete. It measures about 5 feet 3 inches long. The skull appears to represent a "conservative" Neanderthaloid, unlike the "progressives" of Mount Carmel, which show mixed features resembling both *Homo sapiens* as well as Neanderthals. In fact, the skull of Shanidar man more closely resembles that of the Neanderthal man of the La Chapelle-aux-Saints (France) find, which is a classic or conservative type. There is one very apparent exception to the resemblance. The brow ridge in the Shanidar specimen, instead of being carried across above the eyes in a continuous bulge, or "torus," is broken between the eyes. The teeth, which show rather heavy wear, are in very good condition.

The second skeleton is not so well preserved as the first. The skull has a heavy brow ridge above the eyes, and the teeth are worn quite flat. A conservative estimate for the age of the skeleton might be 60,000 years.

Artifacts of chipped stone were found in the same strata as the skeletons, associated with remains of fire hearths, showing that the cave had been a habitation site. These artifacts are Mousterian in type.

The nearest locus of ancient skeletal or paleoanthropological finds in significant numbers is Mount Carmel, where Neanderthal skeletons of both conservative and more humanly advanced or progressive types have been recovered. One of the more interesting problems associated with the discovery of the Shanidar skeletons is that it appears that the Neanderthal progressives of Mount Carmel were earlier in time than the Shanidar remains. It would seem that Neanderthal man of a very backward or conservative type existed in the mountains of Kurdistan, while only 600 miles away in Palestine a type of man with some *Homo sapiens* characteristics lived and died some thousands of years before.

The recent excavations bring the total of skeletal finds at Shanidar Cave to six, including three skeletons of Mousterian man or Neanderthaloids, two Neolithic burials, and one Islamic age skeleton.