Heterogeneous Equilibria at the Glass Electrode-Solution Interface

Donald Hubbard and Richard G. Goldman

Heterogeneous equilibria at the glass-solution interface were investigated in connection with the pH response of glasses. The preferential leaching of alkali and other cations from the glass surface by acid aqueous solutions, leaving a silica-rich layer to act as a nonmigratable negatively charged ion, caused an uneven distribution of the migratable ions of the system in accordance with the dictates of the Donnan membrane equilibria and the "equation of products." The uneven distribution of $Ag(NH_3)_2^+$, and Br^- ions for various experimental conditions was readily followed potentiometrically for Corning 015, a series of Na_2O-CaO-SiO_2, and a series of Na_2O-SiO_2 glasses. The Donnan membrane theory is compatible with the various experimentally observed phenomena such as the swelling of the glass surface, repression of swelling by high concentrations of electrolytes, voltage departures in alkaline and hydrofluoric-acid solutions, voltage departures in the "superacid" region, and asymmetry potentials. However, the Donnan membrane considerations do not account for the preferential voltage response of the glass electrode to hydrogen ions with the complete or partial exclusion of other ions.

1. Introduction

Silicate glasses upon immersion in most acid aqueous solutions exhibit a preferential leaching of alkali and other cations from the more durable framework. This remaining silica-rich layer acting as negatively charged nonmigratable ions must necessarily cause an uneven distribution of all migratable ions in the system in accord with the distribution law and Donnan membrane equilibrium [1, 2].[1] Thus, a glass surface, which is generally looked upon as chemically inert and static, turns out to be transient for every solution and seething with activity. However, the framework of the silica-rich layer for many glasses is frequently sufficiently resistant to the attack of a large number of aqueous solutions to establish conditions that are adequately stable to be studied and discussed in terms of equilibria [3, p. 276]. The present investigation was undertaken to ascertain what experimental evidence could be obtained demonstrating the nature of the heterogeneous equilibria at glass-aqueous solution interfaces and to determine what part these equilibra play in the preferential electrical response of many glasses to hydrogen ions with the complete or partial exclusion of the effects of many other ions [3].

2. Theoretical Considerations

Two gases separated by a membrane that is permeable to each will diffuse through this membrane in both directions until at equilibrium both sides of the partition contain mixtures of identical composition. Such a condition also holds true for a membrane separating two solutions of different composition, if the membrane is permeable to both the solute and the solvent. However, for a case in which the membrane is impermeable to one of the ions, these simple conditions no longer prevail. In the case of the leached surface of many silicate glasses there exists an ionogen with one ion, namely, the negatively charged silica-rich layer, which cannot migrate across the glass-solution interface, while all the other ions of the system are free to do so.

For the simple case in which a leached glass surface is placed in an aqueous hydrochloric acid solution, the initial state of the system may be represented as follows: [2]

$$
\begin{array}{c|c}
H^+ & H^+ \\
\hline
Gel^- & Cl^- \\
\hline
(1) & (2)
\end{array}
$$
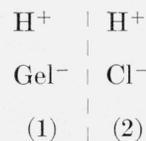
As the H^+ and Cl^- ions are free to pass across the interface, but the gel^- ions are not, the equilibrium state may be represented as

$$
\begin{array}{c|c}
H^+ & H^+ \\
\hline
Gel^- & Cl^- \\
\hline
Cl^- & \\
\hline
(1) & (2)
\end{array}
$$
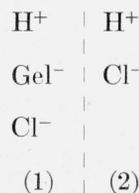
To visualize the distribution of H^+ and Cl^- ions at equilibrium, it is only necessary to remember that the oppositely charged ions must pass through the interface in pairs, otherwise electrostatic forces will be immediately set up which would prevent further diffusion. Therefore, the rate of migration of these ions across the interface depends upon the frequency with which they chance to arrive in pairs, which in turn is determined by the product of their concentration. Thus at equilibrium, when

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] In the present derivation no attempt will be made to clarify the confused silicate chemistry for glasses of varied composition. One is merely concerned with the facts that the silica-rich layer has a negative charge, adheres to the glass surface, and is permeable to the ions present in the aqueous solution. In the absence of more specific knowledge concerning the valence of the anions of this silica-rich layer, it will merely be represented by a single negative charge. However, any other negative valence ascribed to it will not alter the conclusions.

the transfer of H^+ and Cl^- ions from the outer solution to the silica-rich layer is equal to that from the glass surface to the outer solution, the product of the concentration of these ions must have the same value on either side of the interface.

$$[H^+]_2 \times [Cl^-]_2 = [H^+]_1 \times [Cl^-]_1.$$

The addition of other monomonovalent electrolytes to the system does not destroy the validity of the "equation of products." Further, the addition of polyvalent ions does not greatly complicate the situation. If a polyvalent ion arrives at the interface, it will pass across only when an equivalent number of oppositely charged ions appear there at the same time.

At equilibrium, since silica gel^- as well as H^+ and Cl^- ions are in the silica-rich layer, the hydrogen-ion concentration, $[H^+]_1$, in the gel must be greater than the chloride-ion concentration, $[Cl^-]_1$. The nature of this unequal distribution of ions may well be emphasized and rationalized further. For the outer solution, let $x = [H^+]_2 = [Cl^-]_2$, and for the silica-rich layer, let $y = [Cl^-]_1$, and $z = [gel]_1$. Hence, $y + z = [H^+]_1$. As the equation of products must be fulfilled, $x^2 = y(y + z)$. In this relation the product of equals has been equated to the product of unequals. From inspection it is obvious that the sum of the unequals is greater than the sum of the equals, that is, $2y + z > 2x$. The validity of this is readily illustrated by the following simple numerical example chosen at random.

$$x^2 = y(y + z) \quad 15 \times 15 = 3(3 + 72) = 225.$$

$$2y + z > 2x \quad 3 + 3 + 72 > 15 + 15, \text{ or } 78 > 30.$$

From this it becomes evident that the concentration of ions in the silica-rich layer at equilibrium is greater than in the outer solution. This unequal distribution of ions gives rise to an appreciable osmotic pressure across the glass-solution interface. If this excess concentration is represented by e, $2y + z = 2x + e$. If z is eliminated by solving simultaneously the equations $2y + z = 2x + e$ and $x^2 = y(y + z)$, then $x = y + \sqrt{ex}$. This relation shows at a glance that x is greater than y, that is, the concentration of Cl^- ions is greater in the outer solution than in the silica-rich layer. It is evident from this that there should be not only a difference in osmotic pressure, but also a difference in electrical potential, $E = RT/F \log_e x/y$ volts, across the glass-solution interface.

Without continuing further into the derivation of the more complicated thermodynamic aspects of the heterogeneous equilibria to be expected at the glass-solution interface, the above considerations suggest pertinent experiments for partially confirming or wholly disproving the validity of the above conclusions. For example, the osmotic pressure predicted across the glass-solution interface should give rise to persistent forces which would tend to cause swelling of the glass surface, the extent of which would be partially determined by the mechanical strength of the silica framework and its chemical durability. Any such swelling or other surface alterations can be readily followed by means of the interferometer [4, 5].

Another set of experiments which can be readily followed potentiometrically is the uneven distribution of $Ag(NH_3)_2^+$ and Br^- ions between the outer solution and the silica-rich surface of leached glasses.

3. Experimental Procedures

Surface alterations of the glasses brought about by exposure to the various solutions were followed on polished specimens by means of the interferometric procedure previously used in determining the chemical durability of optical and other glasses [4, 5]. The exposures were made at 80° C by partial immersion of rectangular glass specimens having at least one surface sufficiently flat to give interference bands when placed under a fused-silica optical flat. This procedure leaves one portion of the specimen unexposed for use as the reference plane. In all cases, swelling was plotted in the figures as negative attack.

The titration of Ag^+ and Br^- ions was made potentiometrically, using the Ag, AgBr electrode and the glass half-cell as the indicator and reference electrode, respectively. The glass electrode was adopted as the reference electrode in order to eliminate the possibility of contamination of the experimental solutions with chloride ions from the conventional salt bridge of the saturated calomel half-cell. Further, it served as a reliable indicator in the neutralization of excess NH_4OH with sulfuric acid immediately prior to the titration of silver or bromide ions. The use of the glass electrode as the reference cell allows the potentiometric readings to be obtained without transference [6]. However, this latter feature is an unnecessary refinement, and contributes no particular scientific advantage to the present investigation other than operational simplicity. By using the potentiometric procedure it was possible to titrate the solutions in the presence of powdered glass samples and the AgBr precipitated during neutralization, thereby eliminating the use of color indicators and the need for filtration, washing, and evaporation. All potentiometric measurements were made at room temperature, using a Beckman pH meter, model G.

The saturated solution of silver-ammonium bromide, $Ag(NH_3)_2Br$, was prepared by dissolving silver bromide in full-strength aqueous-ammonia solution. Full-strength ammonia was used in every case because of its minimal attack on the silica-rich layer as indicated by previous experiments on voltage departures of the glass electrode [7] and the chemical durability of glasses [5, 8]. By taking advantage of the differences in solubility products of silver iodide, silver bromide, and silver chloride (approximate values 10^{-16}, 8×10^{-13}, and 10^{-10}, respectively), the silver bromide was precipitated and purified by the addition of silver nitrate to a solution containing an excess of potassium bromide. The initial portion of the precipitate was discarded in order to remove any iodide in the potassium bromide, while all

chlorides remained in solution after the addition of the AgNO₃ and were eliminated. The silver bromide was washed repeatedly in hot distilled water with vigorous agitation with a centrifugal stirrer to remove K^+, NO_3^-, and excess Br^- ions.

All powdered glass samples were prepared by crushing the experimental glasses in a steel mortar, and that portion was used that fell between the limits of U.S. Standard sieves Nos. 50 and 150.

4. Results and Discussions

4.1. Surface alterations

a. Swelling of Glass Surfaces in Acid Solution

The derivations presented in the section on theoretical considerations pointed out that the concentrations of ions in the silica-rich layer at equilibrium are greater than in the outer solution, and that such unequal distribution must result in an osmotic pressure across the glass-solution interface. This osmotic pressure must in turn tend to cause swelling of the glass surface in all solutions in which the silica-rich layer is formed, and the framework is chemically durable. Table 1 and figure 1 illustrate typical examples of the surface alterations of several glasses upon exposure for 6 hours at 80° C to a series of buffer solutions covering the range from pH2 to pH12. Swelling is exhibited by four of these glasses in the acid buffer solutions in which silicate ions are not readily soluble. However, for the alkaline range in which soluble silicates are formed, the rate of solution of all the glasses exceeds the rate of swelling. Glasses having superior chemical durability, namely, fused silica, Pyrex chemical glassware 774, and a Na_2O-CaO-SiO_2 (18:10:72) glass, showed no detectable swelling in the acid buffers during the period of the test. Such superior glasses are known to show relatively little leaching of alkali by acid solutions [9], and thus the mechanism for initiating the uneven distribution of migratable ions with the attendant swelling is minimized. However, it must not be assumed that these effects are completely absent. Such an assumption would be incorrect, as will be demonstrated by the data presented later on the

uneven distribution of migratable ions at the glass-solution interface for chemical Pyrex and fused silica (table 2). Thus, in the present experiments we find surface alterations in the acid solutions ranging from vigorous to not detectable swelling, depending on the nature of the glasses. Such results are at least compatible with the predictions based on Donnan membrane equilibria. Swelling has been found to occur for so many silicate glasses in acid buffers that one is inclined to conclude that swelling always takes place in the earlier stages of attack except for solutions forming soluble silicate or other soluble silicon compounds [5, 8].
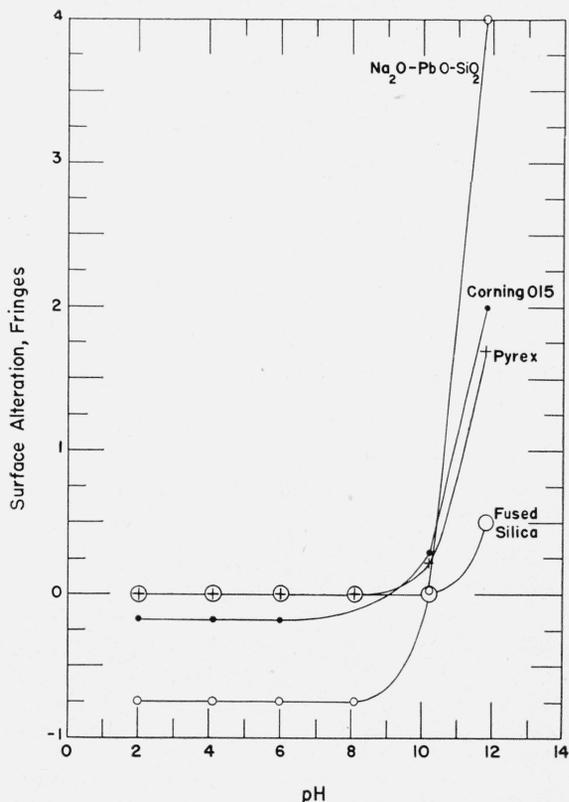

FIGURE 1. *Surface alteration-*pH *curves for typical silicate glasses for exposures of 6 hours at 80° C.*

TABLE 1. *Typical surface alterations exhibited by various silicate glasses upon exposure for 6 hours at 80° C to Britton Universal buffer mixtures covering the range* pH *2 to* pH *11.8*

Glasses							Surface alteration at pH					
Na₂O	K₂O	PbO	CaO	R₂O₃	B₂O₃	SiO₂	2.0	4.1	6.0	8.1	10.2	11.8
%	%	%	%	%	%	%	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
28	----	----	----	----	----	72	36 swell____	36 swell____	36 swell____	36 swell____	1/10 swell___	120 attack.
18	10	----	----	----	----	72	36 swell____	36 swell____	36 swell____	36 swell____	Pitted_____	193 attack.
18	----	10	----	----	----	72	3/4 swell____	3/4 swell____	3/4 swell____	3/4 swell____	D attack___	4 attack.
22 [a]	----	----	6	----	----	72	2/10—swell__	2/10—swell__	2/10—swell__	SC [e]	1/4—attack__	2 attack.
18	----	----	10	----	----	72	ND [d]	ND	ND	D [f]	1/2 attack__	3 attack.
3.6 [b]	0.2	----	----	2.2	13	81	ND	ND	ND	D	1/4—attack__	1 3/4—attack.
(c)	----	----	----	----	----	100	ND	ND	ND	ND	ND	1/2—attack.

[a] Corning 015; [b] Pyrex chemical glassware 774; [c] Fused silica; [d] ND, not detectable; [e] SC, surface cut; [f] D, detectable.

430

Glass			Surface alteration after 6 hr at pH2		Excess Ag(NH$_3$)$_2^+$
Na$_2$O	CaO	SiO$_2$			
%	%	%	*Fringes*		*M-eq/g*
10	20	70	ND		3.1×10^{-4}
15	15	70	ND		5.3
20	10	70	ND		7.2
25	5	70	1/2+swell		42
26	4	70	2 swell		63
27	3	70	6 swell		109
29	1	70	50 swell[b]		660
29.5	0.5	70	75 swell[b]		480
29.75	.25	70	120 swell[b]		310
30	--------	70	72 swell		<2
			Minimum exposure	*Excessive exposure*	
32	--------	68	180 swell[b]		<2
30	--------	70	72 swell[b]		<2
29.4	--------	70.6		72 attack[c]	
28	--------	72	36 swell[b]		6
26.7	--------	73.3		22 attack[c]	
26	--------	74	18 swell[b]		982
24	--------	76	12 swell[b]		448
22	--------	78	6—swell[b]		87.2
21.9	--------	78.1		3 1/2+attack[c]	
20	--------	80	2 swell		68
18	--------	82	3/4 swell		43.7
17.4	--------	82.6		1/2+swell	
16	--------	84	1/4+swell		12.5
14	--------	86	2/10 swell		6
13.6	--------	86.4		2/10+swell	
12	--------	88	D[d] swell		2
10.5	--------	89.5		D+ swell	
9	--------	91			2.3
0	--------	100[a]	ND[e]		1.5
Pyrex (774)			ND		1.4

[a] Fused silica.
[b] Values calculated from exposures of 5 minutes or less.
[c] Values calculated from exposures of 15 minutes.
[d] D, detectable.
[e] ND, not detectable.

b. Repression of Swelling of Corning 015 Glass in Acid Solutions

(1) *Effect of Concentration.* In the section on theoretical considerations the relation $x^2=y(y+z)$ expressed the distribution of ions on both sides of the interface. The potential difference across the interface resulting from this uneven distribution was given as $E=RT/F \log_e x/y$ volts. This relation is true even if other ionogens are added to the system, including neutral salts or other electrolytes having polyvalent ions [2]. The addition of any electrolyte must necessarily produce a change in the potential difference by disturbing the equilibrium, yet all ions present when equilibrium is again established are producing the same potential difference regardless of valence. This latter condition may be difficult to visualize, but appears directly in the derivation involving polyvalent ions [2] (see p. 435 on the effect of valence).

If the equation $x^2=y(y+z)$ is solved for y and then substituted in $E=RT/F \log_e x/y$, the relation for the potential between the silica-rich layer and the outer solution becomes

$$E=RT/F \log_e \frac{2x}{-z+\sqrt{4x^2+z^2}}$$

From this it is obvious that upon increasing the value of x while z (the negatively charged silica layer) remains almost constant, E must decrease (along with the osmotic pressure and resulting swelling), approaching zero as a limit, that is,

$$\lim_{x=\infty} E=RT/F \log_e \frac{2x}{4x^2}=0.$$

To test the validity of this reasoning as applied to glasses, Corning 015 electrode glass which exhibited a moderate rate of swelling, table 1 and figure 1, was exposed to various concentrations of organic and mineral acids. In order to emphasize the effects, the exposure time was increased to 48 hours at 80° C. The results are plotted in figure 2. In every case, the rate of swelling was decreased by the higher concentrations and approached zero for the concentrations above 50 percent.[3] According to the theory for swelling as applied to gelatin, the swelling should go through a maximum in passing from very dilute to higher concentrations of electrolytes [2,10]. This same reasoning also holds true for silicate glasses. However, earlier experiment with the swelling of Corning 015 had not revealed such a maximum for a concentration series 10^{-3} N, 10^{-2} N, 10^{-1} N, and N [5].

(2) *Effect of valence upon swelling.* Although the data plotted in figure 2, A, were obtained on solutions prepared only on an approximate percentage basis, they indicate that the acids differ in their capacity to repress the swelling of glass. A more carefully controlled set of experiments was carried out with solutions prepared on a molar basis. The results are plotted in figure 2, B. The values for swelling brought about by the monobasic mineral acid, HCl, and the monobasic organic acid, CH$_3$COOH, fall essentially on the same curve, whereas the swelling in the case of the dibasic acid, H$_2$SO$_4$, is appreciably less. The effect of the tribasic acid, H$_3$PO$_4$, follows in a general way the monobasic acids. All of these results can be rationalized, provided it is assumed that the silica-rich layer is not dissolved by any of the acids.

If the heterogeneous equilibrium at a glass-solution interface is a characteristic Donnan membrane equilibrium established by a nondiffusible negative charged gelatinous silica, the repression of swelling of the glass surface brought about by monobasic acids, such as HCl and CH$_3$COOH, should be essentially the same. On the other hand, strong dibasic acids should repress the swelling more strongly. The present procedure is not sufficiently exact to give a quantitative verification of these predictions, but the results are generally in accord with them. The tribasic acid, H$_3$PO$_4$, dissociates as a monobasic acid below pH 4.7 [11] and has been shown in the case of gelatin to influence the membrane potential as well as the osmotic pressure and swelling the same as the monobasic acids [2].

---

[3] From these observations it is evident that the commercial practice of storing concentrated acids in glass containers is preferable to storing more dilute solutions.
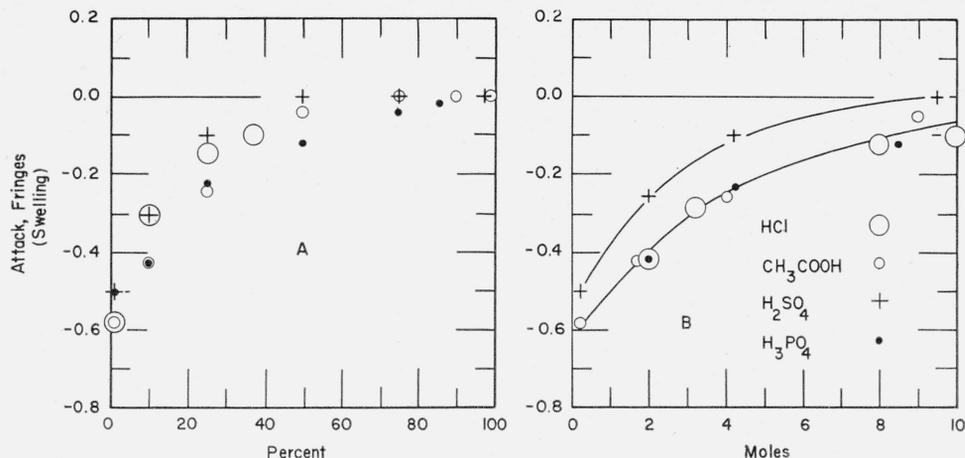
FIGURE 2. *Repression of swelling of Corning 015 glass brought about by increased concentrations of monobasic, dibasic, and tribasic acids.*

Concentrations: A, percent; B, moles; exposure, 48 hours at 80° C.

4.2. Uneven distribution of $Ag(NH_3)_2^+$ and Br^- Ions Between the Silica-Rich Layer of the Glass Surface and the Outer Solution

In the previous sections the uneven distribution of ions at the glass-solution interface has been assumed, but not actually demonstrated. As neither the concentration of ions within the glass surface nor the voltage differential existing across the glass-solution interface is readily obtainable by direct measurement, it was necessary to design experiments that would demonstrate the excess of the migratable positive ions appearing in the swollen glass surface or the excess negative ions appearing in the outer phase. $Ag(NH_3)_2Br$ dissolved in full-strength aqueous NH_3 provided very satisfactory indicator ions for such experiments. Full-strength NH_3 was used because of its low attack upon the silica-rich layer, although the pH is high [5,7].

Glass samples (approximately 10 g) which passed a U. S. Standard 50-mesh sieve and were retained on a 150-mesh screen were leached at pH 2 for 6 hours at 80°C, with occasional stirring. They were then decanted and rinsed twice in full-strength aqueous-ammonia solution, followed by 5 minutes in 50 ml of saturated $Ag(NH_3)_2Br$ solution with intermittent agitation. The glass samples were then separated from the liquid phase by decantation. The glass and liquid phases were acidified with concentrated H_2SO_4 and titrated potentiometrically for excess Ag^+ remaining in the gelatinous silica-rich surface and the excess Br^- ions appearing in the outer solution. For these determinations the solutions were made strongly acid to insure that little change in pH takes place during the titration, and also to bring about ready coagulation of the AgBr precipitated.

a. Na_2O-CaO-SiO_2 Glasses

Potentiometric titrations were made of the $Ag(NH_3)_2^+$ ions appearing in the glass surface in excess of the Br^- ions for a series of Na_2O-CaO-SiO_2 glasses containing 70 percent of SiO_2 and various percentages of Na_2O and CaO. The data are given in table 2 and summarized in figure 3, where the swelling of the glasses at pH2, and the excess $Ag(NH_3)_2^+$ ions appearing at the glass surface are plotted against the composition (percentage of CaO) of the glasses. The results are interesting because of the low titration values obtained on the glasses of superior durability as compared with the glasses of inferior durability. Another interesting feature of these data is the fact that for the two glasses of maximum swelling (29.5 and 29.75 percent of Na_2O, respectively), the excess silver appearing in the glass surface decreased, falling essentially to zero for the end member of the series, 30 percent Na_2O. This apparent anomaly will be discussed and clarified by the data obtained on the Na_2O-SiO_2 glasses (section 4.2, b).

b. Na_2O-SiO_2 Glasses

A similar set of data were obtained for a series of soda-silica glasses, table 2 and figure 4. The excess $Ag(NH_3)_2^+$ ions appearing in the negatively charged silica-rich phase increased for the glass compositions showing increased swelling down to the composition of 74 percent of SiO_2. Below this percentage of silica, the $Ag(NH_3)_2^+$ ions retained at the interface fell sharply toward zero, as in the Na_2O-CaO-SiO_2 series, because the swollen silica-rich surface of the specimens was decreased by solution and by sloughing off of the mechanically weak gel. These data illustrate well the difficulty encountered in obtaining consistent durability data by the interferometer procedure in studying the behavior of very poor glasses in acid solutions. Specimens of these glasses given 15-minute exposures suffered attack as shown in figure 4, whereas exposure of the same glasses for 5 minutes or less resulted in liberal swelling [12, 13].

c. Effect of pH

The data for the excess $Ag(NH_3)_2^+$ appearing at the glass-solution interface after samples of Corning 015 were leached in buffer solutions of different pH
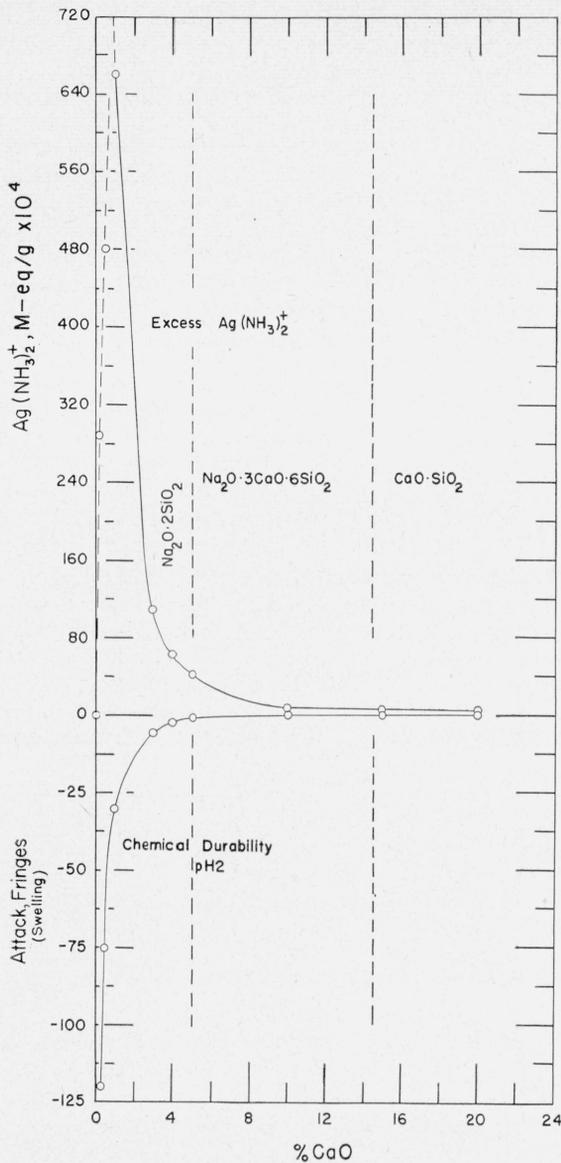
432

FIGURE 3. *Comparison of the excess* $Ag(NH_3)_2^+$ *ions appearing in the glass surface, with the chemical durability (swelling) of the glass for a series of* Na_2O-CaO-SiO_2 *glasses containing 70 percent of* SiO_2.

Exposure 6 hours at 80° C.

are listed in table 3. The resulting curve [4] is compared in figure 5 with the silicic-acid titration curve [14], the chemical-durability [5] and voltage-departure [3, 15] curves of this glass over the same pH range. A set of chemical-durability data that is representative of the "superacid" region is included. It was obtained with sulfuric-acid solutions and reported as $\log 1/[H_2SO_4]$. From inspection of these curves it is evident that as the negatively charged silica-rich layer is carried away as soluble silicates by alkaline solutions, the magnitude of the uneven distribution

[4] How well the curve represents the correct relative shape is uncertain because at times very large unexpected values for the excess $Ag(NH_3^+)$ have been obtained after leaching in solutions of high alkalinity.
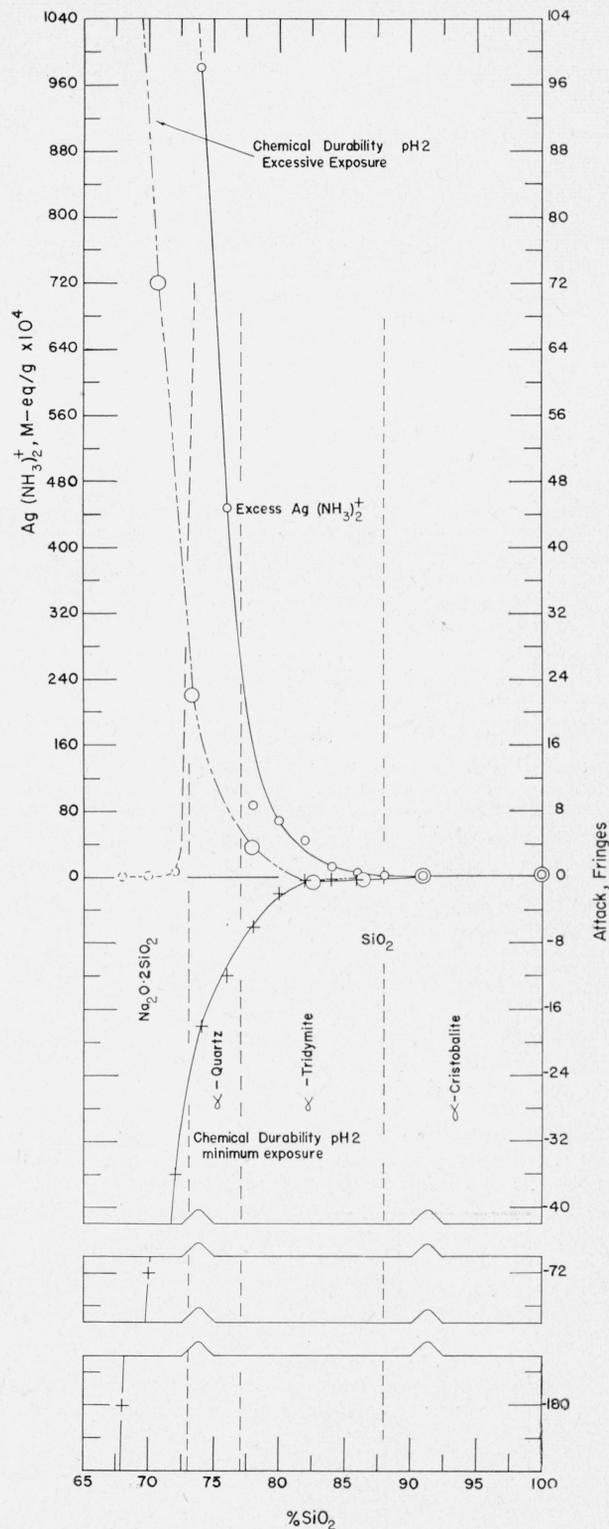

FIGURE 4. *Comparison of the excess* $Ag(NH_3)_2^+$ *ions appearing in the glass surface, with the chemical durability of the glass for a series of* Na_2O-SiO_2 *glasses.*

$\bigcirc$, apparent attack for 6 hours at 80° C calculated from observations on specimens given excessive exposure (15 minutes).

$+$, apparent swelling for 6 hours at 80° C calculated from observations on specimens given minimum exposure (5 minutes or less for the glasses of very poor chemical durability).
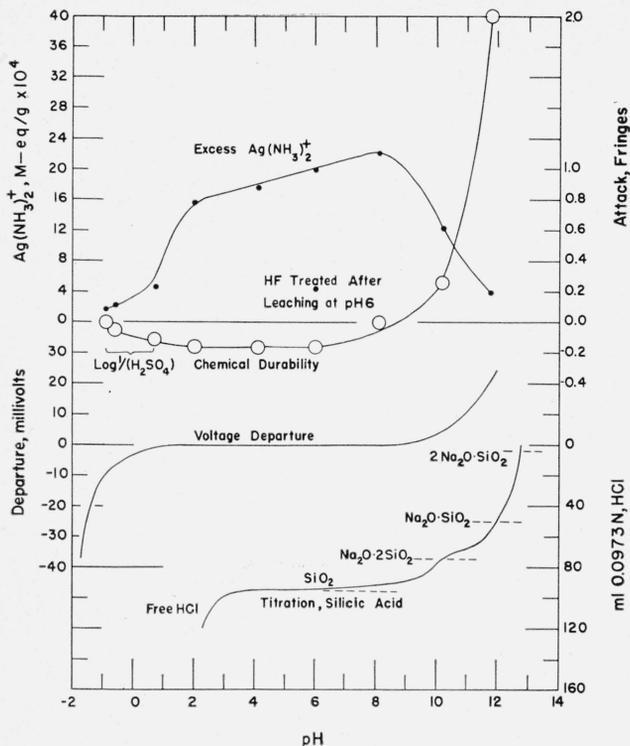
433

FIGURE 5. *Effect of the pH of the buffer solutions on the chemical durability, voltage departure, and the excess $Ag(NH_3)_2^+$ ions appearing in the glass-solution interface, compared with a titration curve of sodium silicate* [14].

of migratable ions at the interface decreases. This condition readily rationalizes the controversial, so-called "nonreversibility" of the glass electrode [3, 16, 17, 18]. The removal or partial removal of the silica-rich layer by alkaline solutions must necessarily cause a voltage shift as the nonmigratable member of the interfacial system is changed. The silica-rich surface is not wholly regenerated until the electrode is immersed again in an acid solution.

TABLE 3. *Effect of the pH of the leaching solution upon the surface alteration and upon the uneven distribution of migratable ions appearing at the surface of Corning 015 glass*

Solution	Surface alteration	Excess $Ag(NH_3)_2^+$ for specimens	
		As leached	HF-treated after leaching
pH	Fringes	M-eq/g	M-eq/g
2.0	>2/10 swell	15.7×10^{-4}	
4.1	>2/10 swell	17.6	
6.0	>2/10 swell	20	4.3×10^{-4}
8.1	SC[a]	22.1	
10.2	1/4+attack	12.3	
11.8	2 attack	4.0	
log $1/M$ H$_2$SO$_4$			
0.7	1/10 swell	4.7	
—.6	D[b] swell	2.1	
—.95	ND[c]	1.7	

[a] SC, surface cut; [b] D, detectable; [c] ND, not detectable.

In the low pH range, the correspondence of the repression of swelling and the uneven distribution of

migratable ions in H$_2$SO$_4$ solutions (table 4 and fig. 6) with the voltage departures reported for the "super-acid" region, is entirely logical. However, there are several other considerations that must not be overlooked. First, it must be borne in mind that the decrease in the water activity of the solutions at the increased concentrations also parallels the performance of the glass electrode and strongly supports the theory that the glass-electrode functions as a "water electrode" [3, 19, 20]. This theory is also strongly supported by the general correspondence of the hygroscopicity of experimental glasses with their electrode function (pH response) [13, 21].

However, as pointed out in the present investigation, there should be a lowering of the interfacial voltage with increased acid concentration in accord with the equation

$$\lim_{x=\infty} E = RT/F \log_e \frac{2x}{-z+\sqrt{4x^2+z^2}} = 0.$$

This voltage shift should theoretically be independent of any water activity interpretation, but obviously for aqueous solutions it would be accompanied by a decrease in the water activity of the solutions, and the two theories would have this same feature in common. Yet the source of the voltage departure in the first theory would be internal, whereas in the
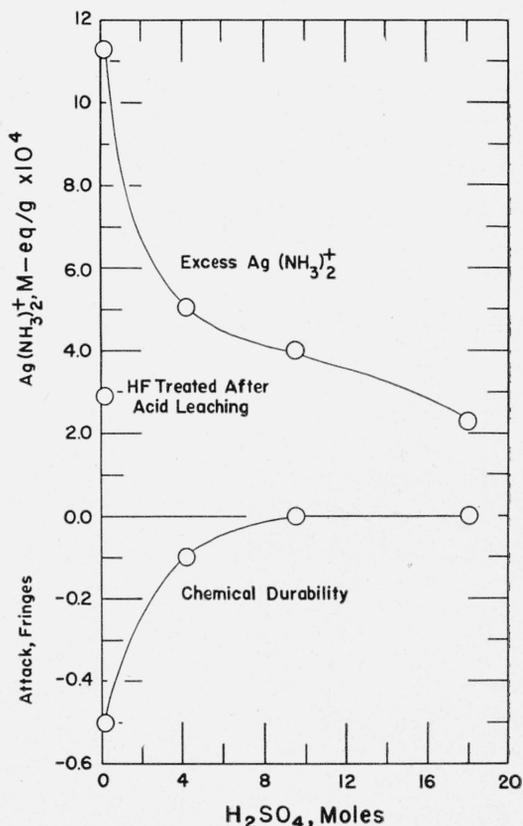

FIGURE 6. *Surface alterations (swelling) of Corning 015 glass in the "superacid" region and the accompanying uneven distribution of migratable ions.*

434

second, the postulated cause of the voltage departure would be at the interface.

TABLE 4. *Typical surface alterations (swelling) exhibited by Corning 015 glass upon exposure for 48 hours at 80° C to various concentrations of aqueous H_2SO_4, and the uneven distribution of migratable ions appearing in the glass surface*

H_2SO_4 solutions	Surface alterations	Excess $Ag(NH_3)_2^+$ for specimens	
		As leached	HF-treated after leaching
M	*Fringes*	*M-eq/g*	*M-cq/g*
0.2	0.5 swell	11.3×10^{-4}	2.9×10^{-4}
4.2	1/10 swell	5.1	
9.5	Not detectable	4.0	
18.1	do	2.3	

A further consideration, the repression of swelling with the accompanying decrease in the formation of nonmigratable ions and the attendant displacement of the heterogeneous equilibria at the glass-solution interface, is essentially a byproduct of the conditions postulated by the equation.

In selecting a theory that adequately accounts for the voltage departures of the glass electrode in the "superacid" region there is a liberal list from which to choose, namely, (1) Dehydration of the electrode glass [3, 8, 18], (2) alteration of the physical and chemical nature of the surface of the electrode [5, 8], (3) operation of the glass as a "water electrode" [3, 19, 20, 22], and (4) alteration of the interfacial voltage in accord with the above equation [1, 2]. If any one of them is correct, any disagreement as to which it is can merely center about agreement on which member of the list is the cause and which ones are the effects. Probably, as is so prevalent throughout nature, any ultimate explanation will be faced with an anomaly or contradiction.

4.3. Surface Equilibria and Glass Electrode Voltage

Although Donnan membrane phenomena occupy such a dramatic role in the glass-solution interface equilibria, they apparently can play little or no part in the preferential response of the glass electrode to the hydrogen-ion activity of aqueous solutions and the partial or complete exclusion of the effects of the other ions in the system [23]. This conclusion can be reached by an inspection of the basic equations of the equilibrium state.

The equation for the voltage appearing across the glass-solution interface due to the uneven distribution of a migratable monovalent ion is $E = RT/F \log_e x/y$ volts. If an ionogen yielding an ion of any other valency, M^{n+} is added to this system, the voltage contributed by this ion at equilibrium will be

$$E = RT/nF \log_e \frac{[M^{n+}]_{\text{solution}}{}^5}{[M^{n+}]_{\text{glass surface}}{}^5}.$$

---
[5] Hereafter abbreviated "sol" and "g".

From the equation of products $[M^{n+}]_g \times [Cl^-]_g^n = [M^{n+}]_{\text{sol}} \times [Cl^-]_{\text{sol}}^n$ and $[H^+]_g^n \times [Cl^-]_g^n = [H^+]_{\text{sol}}^n \times [Cl^-]_{\text{sol}}^n$, from which it follows that

$$\frac{[M^{n+}]_{\text{sol}}}{[M^{n+}]_g} = \frac{[H^+]_{\text{sol}}^n}{[H^+]_g^n} = \frac{x^n}{y^n}.$$

Therefore, $E = RT/nF \log_e x^n/y^n = RT/F \log_e x/y$.

It is evident from this derivation that at equilibrium all ions in the system, regardless of their valence, are contributing identical voltages across the glass solution interface. Thus, as far as this particular type of heterogeneous equilibria is concerned, the glass electrode should respond equally well as an indicator of any ion in the aqueous solution [24, 22], provided all other positive ions were held constant except the one under consideration. As this latter conclusion is so conspicuously contrary to the generally observed voltage performance of the glass electrode as used, it is obviously necessary to look elsewhere for an explanation of the selective voltage response of the glass electrode to hydrogen-ion activity. This does not imply that the voltage across the glass-solution interface due to the uneven distribution of the migratable ions is negligible or that it plays no part in the observed voltage of the glass electrode.

In reality, this interfacial voltage seems to be of considerable magnitude. For example, consider the large voltage shift (so-called "soda error") that appears when the silica-rich surface is partially or completely removed by alkaline solutions [3, 5, 19, 20] that form soluble silicates. From similar evidence obtained on the voltage shift in hydrofluoric-acid solutions, it appears that the interfacial voltage caused by the presence of the gelatinous silica-rich layer must often be greater than 250 mv, figure 7. These data were obtained with a well-conditioned glass electrode of Corning 015 compared against the hydrogen electrode [3, p. 124; 25]. The observed voltage departure cannot be attributed to hydrogen ions, because both electrodes when unattacked respond equally well to hydrogen-ion activity. Furthermore, the voltage shift cannot be attributed to an equilibrative response of either electrode to fluoride ions, because in neutral solutions no such response to fluoride ions is observed [3, p. 131]. The complete or partial removal of the silica-rich layer with its interfacial distribution of migratable ions is apparently the main contributing variable.

The surface equilibria also play an important role in the origin of the asymmetry potential of the glass electrode. The inner and outer surface of a glass-electrode bulb of the Cremer-Haber type [25, 26] are known to be very different, as shown by their capacity to sorb dyes [17]. With different heterogeneous equilibria and accompanying voltages of different magnitudes on the two surfaces an asymmetry potential for the glass electrode is inevitable. Further, upon taking appropriate steps to make the two surfaces identical, the asymmetry potential
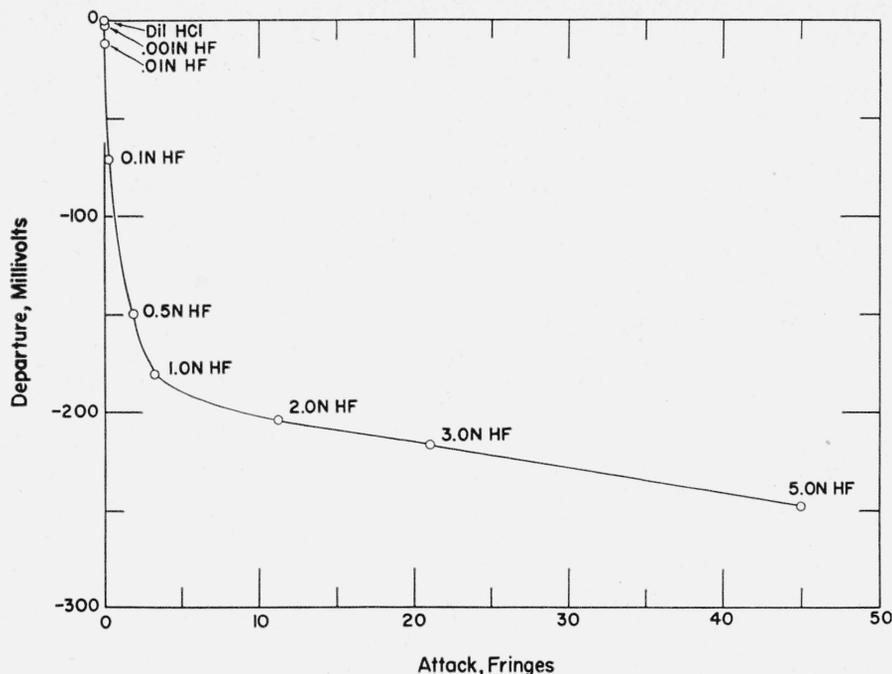
FIGURE 7. *Voltage departure of the glass electrode brought about by the partial removal of the silica-rich surface.*

Any voltage response to the hydrogen ions and fluoride ions is eliminated by the experimental techniques.

should theoretically disappear and actually does [27, 28].

5. Conclusions

Application of the Donnan membrane equations and the "Equation of Products" to the heterogeneous equilibria at the glass-electrode–solution interface accounts qualitatively for the observed uneven distribution of $Ag(NH_3)_2^-$ and Br^- ions between the glass surface and the ambient solution, the swelling of the glass surface in solutions of low and intermediate concentrations, the repression of swelling by high concentrations of electrolytes, voltage departures in alkaline and hydrofluoric-acid solutions, voltage departures in the "superacid" region, and asymmetry potentials. However, the Donnan membrane considerations do not account for the preferential voltage response of the glass electrode to the hydrogen ions.

6. References

[1] F. G. Donnan, The theory of membrane equilibrium in the presence of a non-dialyzable electrolyte, Z. Elektrochem. **17**, 572 (1911).
[2] John Arthur Wilson, Application of the thermodynamics of heterogeneous equilibria to the theory of colloidal phenomena, Colloidal Behavior, **I**, Robert Herman Bogue (McGraw-Hill Book Co., Inc., New York, N. Y.).
[3] M. Dole, Glass electrode (John Wiley & Sons, Inc., New York, N. Y.); Theory of the glass electrode, J. Am. Chem. Soc. **53**, 4260 (1931).
[4] E. Berger, Grundsätzliches über die chemische Angreifbarkeit von Gläsern I., Glastech Ber. **14**, 351 (1936).
[5] Donald Hubbard, Edgar H. Hamilton, and Alfred N. Finn, Effect of the solubility of glass on the behavior of the glass electrode, J. Research NBS **22**, 339 (1939) RP1187.

[6] Roger G. Bates and S. F. Acree, pH of aqueous mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate at 0° to 60° C, J. Research NBS **34**, 373 (1945) RP1648.
[7] S. E. Hill, The validity of the glass electrode in ammonium chloride buffers, J. Gen. Physiol. **12**, 813 (1929).
[8] Donald Hubbard and Gerald F. Rynders, Voltage anomalies of the glass electrode and the chemical durability of the glass, J. Research NBS **39**, 561 (1947) RP1848.
[9] D. E. Sharp, et al., Report of the committee on the chemical durability of glass, Bul. Am. Ceram. Soc. **14**, 181 (1935).
[10] H. R. Procter, The equilibrium of dilute hydrochloric acid and gelatin, J. Chem. Soc. **105**, 313 (1914).
[11] W. Mansfield Clark, The determination of hydrogen ions, (Williams & Wilkins Co., Baltimore, Md.).
[12] Gerald F. Rynders, Oscar H. Grauer, and Donald Hubbard, Electrode function (pH response) of the soda-silica glasses, J. Research NBS **41**, 273 (1948) RP1923.
[13] Donald Hubbard, Mason H. Black, Sylvanus F. Holley, and Gerald F. Rynders, Electrode function (pH response), hygroscopicity and chemical durability of soda-potash-silica glasses, J. Research NBS **46**, 168 (1951) RP2189.
[14] H. T. S. Britton, Hydrogen ions, D. Van Nostrand Co., Inc., New York, N. Y.; J. Chem. Soc. **425** (1927).
[15] D. A. MacInnes and D. Belcher, Further studies on the glass electrode, J. Am. Chem. Soc. **53**, 3315 (1931).
[16] H. F. Launer, Determination of the pH values of papers, J. Research NBS **22**, 553 (1939) RP1205.
[17] Edgar H. Hamilton and Donald Hubbard, Effect of the chemical durability of glass on the asymmetry potential and reversibility of the glass electrode, J. Research NBS **27**, 27 (1941) RP1400.
[18] M. Dole, Recent advances in the theory of the glass electrode for pH determinations, ASTM Symposium on pH Measurement (June 24–28, 1946).
[19] M. Dole, The relation between the activity of the water and the potentials of the glass electrode, J. Am. Chem. Soc. **54**, 2120 (1932).

[20] M. Dole, The theory of the glass electrode. II. The glass as a water electrode, J. Am. Chem. Soc. **54,** 3095 (1932).

[21] Donald Hubbard, Given W. Cleek, and Gerald F. Rynders, Electrode function (pH response), hygroscopicity and chemical durability of Na_2O-CaO-SiO_2 glasses, J. Research NBS **44,** 247 (1950) RP2076.

[22] Theodore Shedlovsky, Electromotive force from proton exchange reactions, Nat. Acad. Sci., Annual Meeting 1951; Symposium on Electrochemical Constants, National Bureau of Standards, Sept. 1951 (publication pending).

[23] Ludwig Kratz, Wirkungsweise und Theorie der Glaselektrode, Glastech. Ber. **23,** 35 (1950).

[24] B. Lengyel and E. Blum, The behavior of the glass electrode in connection with the chemical composition, Trans. Faraday Soc. **30,** 461 (1934).

[25] F. Haber and Z. Klemensiewicz, On electrical interfacial potentials, Z. physik, Chem., **67,** 385 (1909).

[26] M. Cremer, On the causes of the electromotive properties of tissue and a discussion of polyphase electric cells, Z. Biol. **47,** 562 (1906).

[27] W. Brauer, The cause of asymmetric potentials of the glass electrode, Z. Electrochem. **47,** 638 (1941).

[28] Henry H. Carey and Warren P. Baxter, Glass electrode and method, U. S. Patent 2,366,489.

WASHINGTON, February 12, 1952.