

# Increased Chemical Reactivity of the Surface Compared With That in the Bulk Volume of Britton-Robinson Universal Buffers

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A direct comparison of the chemical reactivity at the surface with that in the bulk volume of buffer solutions over the range  $pH$  7 to  $pH$  11.8 was made, using Corning 015 glass as the indicator. By observing interferometrically the surface alterations of optically flat specimens brought about by exposures to aqueous buffer solutions under controlled conditions of time, temperature, and  $pH$  it was possible to evaluate, at least semiquantitatively, the difference between the chemical reactivity of the surface and the bulk volume of the solutions. For the buffer at  $pH$  7 the surface reactivity appeared to correspond to a hydrogen ion activity of  $pH$  9.4. The apparent concentration differential between the surface and bulk volume falls off sharply for buffers of increased  $pH$ , amounting to only 0.2  $pH$  unit for the buffer at  $pH$  11.0, and becomes nondetectable at  $pH$  11.8. Unfortunately the chemical durability characteristics of the glass were such that no differentiation could be made between the hydrogen ion activity of the surface and the bulk volume in solutions more acid than  $pH$  7.

## 1. Introduction

Although direct experimental verification is often difficult, there is abundant theoretical evidence that the concentration at the surface of a solution may differ considerably from the bulk-volume concentration. J. Willard Gibbs emphasized this point when he derived his mathematical relation between surface concentration and surface tension [1].<sup>1</sup> This relation, as simplified and expanded by Wolfgang Ostwald is  $u = -c/RT \cdot d\gamma/dc$ , where  $u$  is excess solute in unit surface,  $c$  is concentration or activity, and  $\gamma$  is surface tension [2].

Inspection of this equation reveals that if the surface tension  $\gamma$  increases with the concentration then  $u$  is negative and the surface concentration is less than the concentration of the bulk of the solution. However, if  $\gamma$  decreases as the concentration increases,  $u$  is positive and the surface concentration is greater than the concentration of the bulk volume. Finally, if the surface tension is independent of the concentration, then the concentration of the solute in both the surface layer and the bulk of the solution will be the same.<sup>2</sup>

In a previous investigation into the relation between chemical durability of glass and the voltage anomalies of the glass electrode, a pronounced increased reactivity on optical glass flats by the surface of Britton-Robinson universal buffer solutions had been noted [5]. The present investigation was undertaken to study these effects systematically over an extended  $pH$  range.

## 2. Experimental Procedure

Instead of using surface tension as an uncertain and uninterpretable indicator of concentration difference in the complex buffers used, the increased

chemical activity at the surface compared with that in the interior of the solution (bulk volume) was studied on a glass of known durability characteristics in order to obtain direct comparison of the hydrogen ion activity  $[H^+]$  at the surface and in the bulk volume. A glass sensitive to attack in alkaline solutions and having a composition near the lowest melting eutectic of the soda-lime-silica ternary phase equilibrium diagram, viz., 23% of  $Na_2O$ , 5% of  $CaO$ , and 72% of  $SiO_2$  (Corning 015 glass) was selected as the indicator in this study [6, 7, 8]. Glass was chosen primarily because its use eliminated oxygen as a possible contributing factor in the interpretation of the results.

Small specimens of this glass having surfaces sufficiently flat and well polished to give satisfactory interference bands when placed beneath a fused silica optical flat, were exposed by partial immersion in a series of buffer solutions under controlled conditions of time, temperature, and  $pH$ . This procedure leaves a portion of the specimen unexposed to either the surface or the bulk volume of the test solution. The excess chemical activity of the surface (attack on the glass) compared with that of the bulk volume of the solution was obtained from the alteration of the interference pattern caused by exposures of 6 hours at 80° C.

The solutions employed were Britton-Robinson universal buffers, because with these a controlled  $pH$  range from  $pH$  2 to  $pH$  11.8 could be obtained without introducing any new ionic species [9]. Basically, these buffers consist of a mixture of phosphoric, acetic, and boric acids in which the desired  $pH$  is obtained by adding the proper amount of sodium hydroxide.

The experiments were performed with a thin layer of liquid petrolatum on the surface of the buffers to minimize evaporation during the period of the test. This simplified procedure was accepted and adopted only after ascertaining that exposure in a closed

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.  
<sup>2</sup> Gibbs' equation has been verified experimentally [3] and the difference in concentration between the bulk of the liquid and the surface determined for different substances by several methods [4].

system without an oil layer did not give appreciably different results.

### 3. Results and Discussion

Figure 1 shows typical examples of interference patterns obtained for specimens of Corning 015 after partial immersion in buffers of different  $pH$  values for 6 hours at  $80^{\circ}C$ . In each of the photographs the lower part of the field is that of the immersed portion of the specimen, which when compared with the unexposed portion of the field gives the surface alterations of the specimen brought about in the main bulk and at the surface of the buffer. For the portion of the specimen exposed to the buffer at  $pH$  4 (fig. 1,A) the displacement of the fringes to the left indicate a swelling of about 2/10 fringes. Such swelling is characteristic of many glasses in acid buffers [10, 11]. At  $pH$  7 (fig. 1,B) and at  $pH$  9 (fig. 1,C) a perceptible swelling for the portion of the specimen exposed is evident in the bulk solution, but a distinct attack or surface cut (i. e., a displacement of the fringes to the right) appears at the surface of the solution. Such surface cuts were noted and briefly discussed in an earlier publication [5]. At  $pH$  10 (fig. 1,D) the specimen exhibits attack for the immersed portion with additional attack at the buffer surface.

Figure 2 shows the composite curve obtained when these and additional data from table 1 were plotted with surface alterations as the ordinates and  $pH$  as the abscissa. The closed circles represent the values found for alteration of the specimen occurring in the bulk volume of the solution. The open circles give the accompanying attack (surface cut) attributable to the chemical activity of the surface of the solution. Inspection of figure 2 reveals that these surface cuts may be interpreted directly in terms of the effective  $pH$  for the surface of the buffer solutions. For example, for the buffer at  $pH$  7 the alkalinity of its surface has caused an attack on the glass equal to the bulk-volume attack caused by a buffer at

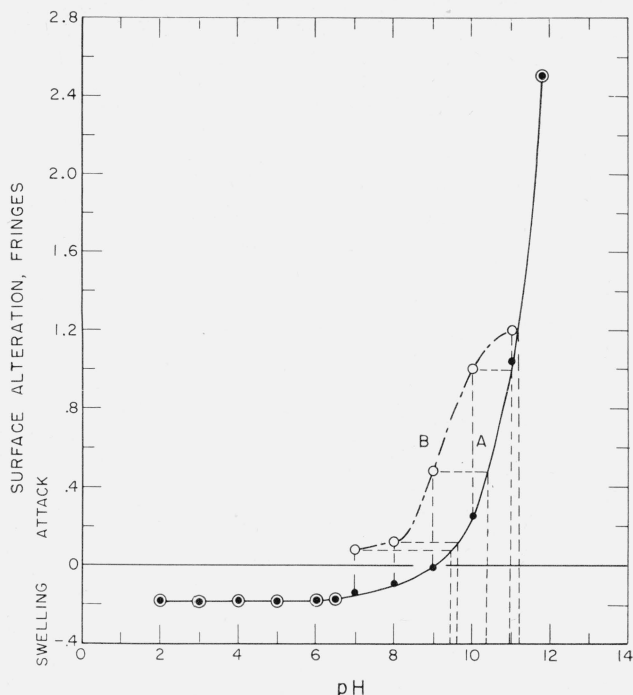


FIGURE 2. Chemical durability characteristics of Corning 015 glass over the range  $pH$  2 to  $pH$  11.8

Exposure 6 hours at  $80^{\circ}C$ . A, Surface alteration of the specimens in the bulk volume of the buffers; B, surface alteration of the specimens brought about by the increased surface reactivity of the buffers.

$pH$  9.4. In other words the surface of the buffer at  $pH$  7 appears to be more alkaline than the bulk-volume value by at least 2.4  $pH$  units. Similarly for the buffers at  $pH$  8 to  $pH$  11.8, the observed differences are given in table 2.

At  $pH$  11.8 the effective reactivity of the buffer and that of its surface either approach the same value, or the use of this glass as an indicator loses its effectiveness. This latter suggestion can be dismissed, because from the ascending shape of the chemical durability curve it is evident that the glass

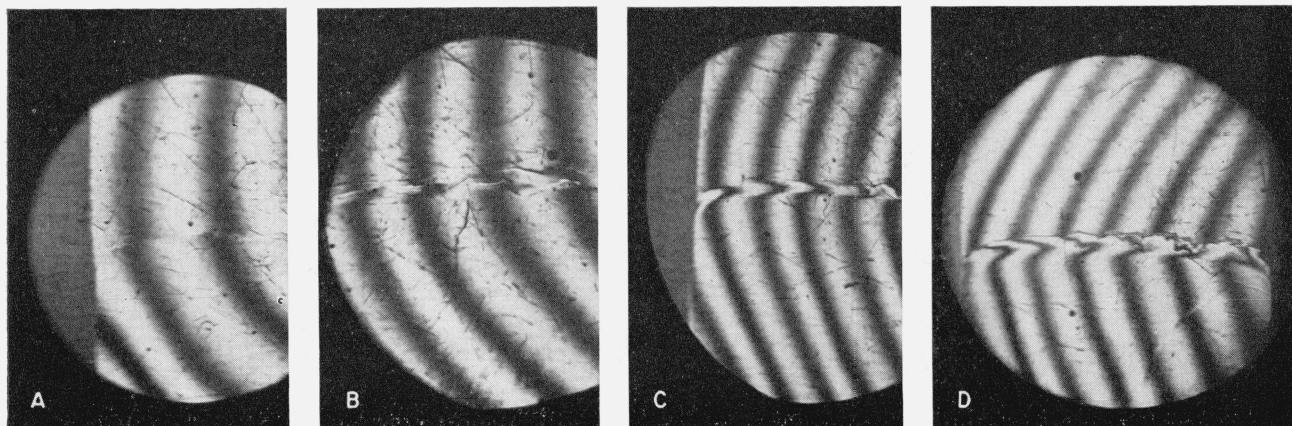


FIGURE 1. Interferometric patterns illustrating the chemical durability characteristics of Corning 015 glass for exposures of 6 hours at  $80^{\circ}C$ .

A, Pattern for  $pH$  4, illustrating the swelling generally initiated by acid buffers; B, pattern for  $pH$  7 showing slight attack at the buffer surface and swelling below; C, pattern for  $pH$  9 illustrating liberal attack at the buffer surface and swelling below; D, pattern for  $pH$  10 exhibiting attack for the immersed portion with additional attack at the buffer surface.

TABLE 1. Chemical durability of Corning 015 glass over an extended pH range

Buffers	Alteration of the specimens after exposure to the following buffers for 6 hours at 80° C		
	Swelling	Attack	Surface cut
pH	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>
2.0	<.2	-----	-----
3.0	<.2	-----	-----
4.0	<.2	-----	-----
5.0	<.2	-----	-----
6.0	<.2	-----	-----
6.5	<.2	-----	-----
7.0	<.1	-----	<.1
8.0	.1	-----	>.1
9.0	(*)	-----	<.5
10.0	-----	0.25	1
11.0	-----	>1	1.2
11.8	-----	2.5	2.5

\* Detectable swelling.

TABLE 2. Indicated surface pH of various buffers in the alkaline range

Compiled from figure 2

Bulk-volume alkalinity	Surface alkalinity	Difference
pH	pH	pH
7	9.4	2.4
8	9.6	1.6
9	10.4	1.4
10	10.9	0.9
11	11.2	.2
11.8	11.8	.0

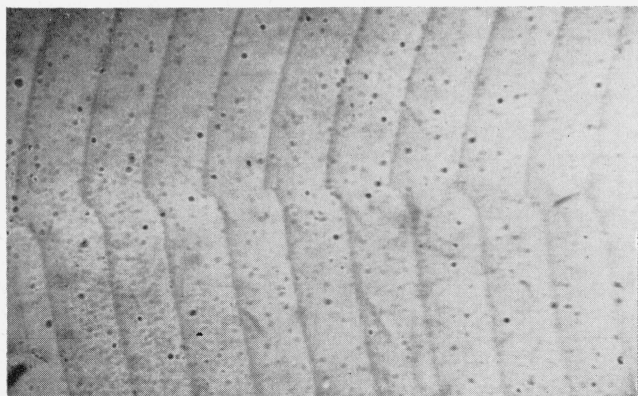


FIGURE 3. Fabry-Perot interferometric pattern for specimens exposed at pH 11.8 for 1 hour at 80° C, showing the absence of any excess surface reactivity at this high alkalinity.

should be a very sensitive indicator at this high alkalinity. The attack by the bulk volume for 6 hours at pH 11.8 was so large, it was feared that any accompanying surface cut might have been obscured. To ascertain for sure if such a cut did or did not exist another specimen was given a 1-hour exposure at pH 11.8. Inspection of figure 3 obtained with the Fabry-Perot interferometric technique [12] reveals no indication of an excess surface attack. The reason for the surface and the bulk volume of the

buffers exhibiting equal activities at high alkalinities may be (a) that the surface approaches saturation or (b) that the same molar change for the surface at pH 11.8 that appeared at pH 7 would be a very small pH change indeed at the higher concentration.

Unfortunately no data were obtainable in the acid range because this glass gives a small uniform swelling over the range pH 2 to pH 6.5, making any differentiation of activity between the surface and bulk volume impossible.

#### 4. Concluding Remarks

The difference in chemical reactivity at the surface and in the bulk volume of buffer solutions has been examined over a broad pH range using Corning 015 glass as the indicator. This glass served as an acceptable indicator over the range pH 7 to pH 11.8, but was ineffective for buffers more acid than pH 6.5. The increased chemical reactivity of the surface of buffers may be interpreted in terms of an increase in the effective pH at the surface of the buffer solution. This difference in effective pH between the surface and bulk volume was greatest near pH 7 where it was to be expected, and decreased with increasing pH.

Liquid-line corrosion has been observed on many substances other than glass. Examples are calcite in hydrochloric acid, sucrose and sodium carbonate in water [13], and metals in aqueous solutions [14]. Several theories have been advanced to account for the surface cuts in the cases cited, but none of these theories alone are compatible with the data obtained in the present study. For example: (1) Increased oxygen content at the surface of the liquid can be eliminated from consideration because a material was used that was already oxidized; (2) increased diffusion rate of active ions, increased reaction at the surface, or protection of the main body of the specimen by the downward streaming of reaction products might explain the increased surface attack in some systems, but for the Corning 015 glass a change from swelling in the body of the solution to attack at the surface (as shown at pH 7) can be accounted for only by a change in alkalinity at the surface of the liquid.

In analyzing these results, it is important to point out that knowledge of the value of the pH of a solution is not sufficient to predict its chemical reactivity. The attacking ions must be of a type that will form soluble compounds with the constituents of the glass network. For example, most glasses are inert to an aqueous solution of NH<sub>4</sub>OH at pH 13.3 [15]; yet these same glasses will be attacked rapidly by NaOH prepared at an equivalent pH. Thus, the results obtained in the present study do not apply to all alkaline solutions of varying pH but only to the particular series of buffers used.

From inspection of the photographs it can be seen that some gain in accuracy and increase in sensitivity of the method can be obtained by improving the quality of the polish and optical flatness of the surfaces of the specimens. It was shown that further refinement could be brought about by increasing the

sensitivity of the interferometer by employing the Fabry-Perot [12] or the Saunders' multiple reflection techniques [16].

There is at least one other particularly interesting observation from these data that is not primarily concerned with the surface versus bulk-volume concentration of buffer solutions, but should not be overlooked. For example, inspection of the interference patterns of figure 1 shows at a glance why glass specimens partially immersed in aqueous solutions should be mechanically weakened at the liquid-air interface.

## 5. References

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