Dissolution Phenomenon of Some Optical Glass in an Acid

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Introduction

Many studies have been made concerning the effect of acid on optical glass from the standpoint of the scientific research or the practical use. There are numerous reports(1,2,3,4,5) on the relation between the amount of the alkali dissolved and the time of dissolution. In most of these experiments powdered glass was used and the alkali dissolved in an acid solution after immersing the sample in it was titrated. In such cases, as pointed out by Tieze(1), it happens frequently that the metal ions present near the surface may dissolve at first without being peeled off of the SiO_2 film formed on the surface sloughs, therefore the reaction velocity is hard to measure.

The author adopted the method of measuring the apparent velocity through the change of interference color which was caused by the thickness of the SiO_2 film formed after the escape of metal ions from glass. In this method the SiO_2 film is not peeled off, so it is very advantageous to the observation of the erosive action of an acid for the polished surface of glass.

Experimental Method

The apparatus is shown in Fig. 1. A polished sample of optical glass, b, supported by a Terex glass holder, d, was washed with alcohol, immersed for 1 minute in a 0.5 *N* solution of caustic soda, and washed again thoroughly with distilled water. Immediately after this treatment, it was immersed in a nitric acid solution kept at a constant temperature. After that, with much attention to the change of the temperature, the reflection of the light radiated from the light source, a, was caught on a screen, c, and the change of the interference color with the time was observed at a desired temperature.

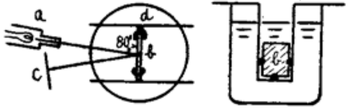

Fig. 1.—Experimental apparatus.

The change thus observed was examined from the relation between the interference color in the case of Newton's ring and the thickness of a film (SiO_2 film; $n=1.46$), and graphically shown in Fig. 2 as the relation between the thickness of a film and the time. A number of plates (24×20×2 mm. in size) of Flint glass (F-1, F-2, F-3, SF-2, KF-2 glass) were examined, each of which has been cut from the lump glass and polished under the same condition.

Their components are shown in Table 1.

Table 1

Composition of Glass

	Component, %					
Glass	SiO_2	PbO	Na_2O	K_2O	Al_2O_3	ZnO
F-1	45.0	45.1	1.5	7.7		
F-2	44.7	46.2	0.2	8.8	0.02	
F-3	45.6	43.4	1.7	8.6		
SF-2	40.99	51.1	0.6	6.9	0.04	
KF-2	66.8	11.6	16.0	0.1	1.5	3.8

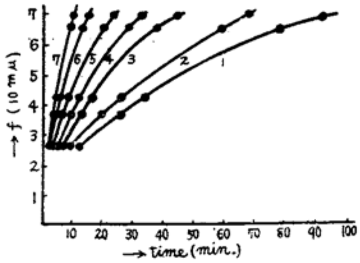

Fig. 2.—*f*-*t* curve of the F-2 glass: 1, 60°C.; 2, 63°C.; 3, 66.5°C.; 4, 70°C.; 5, 75°C.; 6, 80°C.; 7, 84.5°C.

Experimental Results and Discussion

(1) On the Concentration Change of the Acid through the Experiment.—The change of the concentration of the 1 *N* nitric acid was examined by the volumetric analysis, and it was almost negligible for the present investigation.

(2) On the Reaction Velocity.— When

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(1) P. Tieze, *Sprechsaal*, **61**, 809 (1928); *Glastech. Ber.*, **6**, 716 (1928-29).

(2) G. Keppeler, *Glastech. Ber.*, **12**, 366 (1934); *Chem. Centr. Bl.*, 2026 (1935).

(3) E. Berger, *Glastech. Ber.*, **14**, 351 (1936); **16**, 296 (1938).

(4) T. Moriya, *J. Soc. Chem. Ind. Japan*, **43**, 884, 886 (1940).

(5) S. Nagaeda, *J. Japan. Cer. Assoc.*, **49**, 140 (1941).

optical glass is immersed in an acid, the reflection from its surface gradually changes. This is ascribed to the formation of a film on the glass surface which differs from the base glass in the index of refraction and the film formed is a SiO_2 film, as clearly known from the studies of Blodgett and others[6,7,8], so the refractive index of the film is considered to be 1.46.

In the case of ordinary soda-lime glass, the immersion in an acid solution does not cause the variation in the interference color, but alkali is dissolved in the solution. In the case of KF-2 glass, after showing a certain interference color, it becomes colorless. This indicates that the film remains without being peeled off to a certain thickness and then all was peeled off. In the case of F-2 glass, the interference color was gradually changed, which indicates that the SiO_2 film is not removed.

Therefore, it is phenomenologically inferred that PbO and K_2O present in the glass, reacting with nitric acid to be $Pb(NO_3)_2$ and KNO_3, are removed and then the skeleton of SiO_2 remains with the water included.

The relation between the amount of reaction and time, as shown in Fig. 2, is generally parabolic. If the diffusion of something is supposed to be the factor for this reaction, the following equation is to be established.

$$\frac{df}{dt} = k\frac{1}{f} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where f is the thickness of the film. By integrating equation (1), it becomes (2),

$$f^2 = 2kt + k' \quad \ldots\ldots\ldots\ldots (2)$$

and the relation between f^2 and t (time) should be linear. From this point of view, the relation between f and t given in Fig. 2 was revised as that between f^2 and t, then it was represented as a straight line. This justifies the above presumption. It is concluded that the dissolution phenomenon of optical glass in an acid is parabolic at its initial stage, and its reaction velocity is dominated by the diffusion of some substance.

In Fig. 3 the relation between the reaction velocity k and the temperature is shown; the relation log k and $1/T$ is linear and there holds the following equation:

$$K = Ae^{-\frac{E}{RT}} \quad \ldots\ldots\ldots\ldots (3)$$

This may properly show that the reaction velocity is dominated with the diffusion of some substance.

(3) Influence of the Additive Ion in the Solution.—It is considered possible that the escaped ions from the glass may have some influence on the formation of this film.[9,10] For the purpose of full discussion, we have traced the influence of the K^+ Pb^{++} on the SF-2 glass in the nitric acid. We have adopted the 100 cc. solution of 1 N nitric acid, in which 0.1 mg., 0.5 mg., 1 mg., 5 mg., 10 mg. of KNO_3 and $Pb(NO_3)_2$ were dissolved respectively at 50° and 80°.

It may be concluded from this experiment that the K^+, Pb^{++} in the nitric acid give no influence on the reaction velocity described above.

(4) Influence of Stirring on the Dissolution.—When the solid dissolves in the liquid, it is well-known fact that the diffused layer, formed between the rubbing faces of the solid and the liquid, is very strong and does not come off easily, and that the diffusion of the ions or others through this layer generally determines the reaction velocity.

Dissolution phenomenon of the optical glass in an acid is not considered so simple as above mentioned, but it may be considered to contain that this phenomenon is found in one part of the diffused systems, then the possible existence of the diffused layer may be taken up for consideration.

For experimental convenience the author did not circulate the solution, on the other hand shaked up and down the test pieces of the optical glass (SF-2) in the solution. The distance of the movement in the solution was about 6 cm., and the number of times to move up and down 90 to 100 for one minute.

The observation of the reaction velocity was made by the optical method as similar to that mentioned above. The results showed that the reaction velocity becomes a little faster by the stirring but its amount is so small that the stirring gives no influence on the reaction velocity.

As it is unnecessary to consider the diffused layer which exists at the boundary between glass and liquid, it may be concluded that the diffusion which determines the reaction velocity is in the glass itself.

(5) On the Peculiarity of the SiO_2 Film.—As mentioned above, the author adopted

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(6) K. B. Blodgett, *Phys. Rev.*, **55**, 391 (1939).

(7) I. Sawai, J. Tashiro and K. Umeya, *J. Japan. Cer. Assoc.*, **52**, 109, 198, 200 (1944).

(8) I. Sawai, J. Tashiro, K. Umeya, and S. Kozaki, *J. Japan. Cer. Assoc.*, **52**, 258 (1944).

(9) Geffeker, *Kolloid Z.*, **86**, 11 (1939).

(10) D. Hubbard and F. H. Hamilton, *J. Res. Nat. Bur. Stands.*, **27**, 143 (1941).

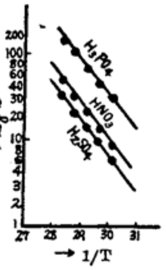

Fig. 3.—SF-2 glass.

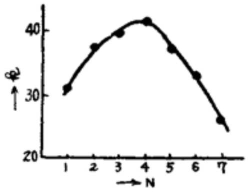

Fig. 4.—F-2 glass at 80°C.

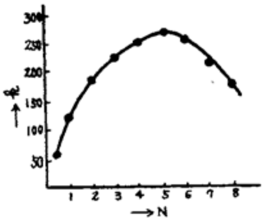

Fig. 5.—SF-2 glass at 80°C.

the method of measuring the apparent velocity through the change of interference color.

It means the safe existence of the skeleton of the SiO_2 retaining the binding force by hydrogen ions or water molecules which got into the hole formed after the escape of metal ions. The phenomenon in proof of this fact is that the interference color glides off into the one which is produced when the film seems to have decreased in thickness, if the glass is taken out into the air and decomposed by heat.⁽¹¹⁾

It is considered that the water included in SiO_2 skeleton run out by the the heat treatment and the film shrinks a little. In the case of KF-2 glass mentioned above, the intimate relations might be thought to exist between the inner constitution of the glass and the thickness of SiO_2 film capable of maintaing the SiO_2 linkage.

So it is surmised that the SiO_2 film is not peeled off but stays on the glass surface at the Flint glass, but the binding force acts in various ways in relation to the change of the glass component and inner constitution.

The author considered that the refractive index of the film is uniformly 1.46. But Schröder⁽¹²⁾ reported that the erosive film has not a simple refractive index as fused quarts, but some gradient along the depth of the film. He also reported that it has no objection to use the average refractive index $\bar{n}$. (actually it is a serious question what value is to be used for n.)

When the initial stage of these reactions come into question, *i. e.*, the film is very thin, it may be considered that as if Na^+, $K,^+$ Pb^{++} etc. are stayed in the SiO_2 film, and refractive index of the film grows larger corresponding to go into the inner part of the film. But this difference is very small, and it has no objection to think the refractive index of the film is almost 1.46.

(6) Experiment in the Sulfuric Acid and Phosphoric Acid.—The initial dissolution phenomenon in an acid with 1 N sulfuric acid and 1 N phosphoric acid besides 1 N nitric acid was studied, and it is found to proceed parabolically.

Fig. 3 shows the relation between log k and $1/T$ in the case of SF-2 glass. These linear lines only get loose in parallel and it is considered that the rate determining stage of this reaction is not caused by the diffusion of the anions (NO_3^-, SO_4^{--}, PO_4^{---}) in the glass.

(7) The Relation between the Reaction Velocity Constant and the Concentration of the Solution.—In the curve expressing the relation between the reaction velocity constant and the initial concentration of the solution there appears a maximum point in Fig. 4 and Fig. 5 in the case of F-2 and SF-2 glass and the position of the maximum points in two curves are not coincident.

This disparity of the maximum points is due to the amount of PbO contained in each optical glass, so it is considered that for the rate determining stage of this reaction the amount of PbO in the glass play an important part.

Conclusion (Reaction Mechanism)

It is surmised from the facts mentioned above that the mechanism of these reactions is as follows.

At first Na^+, K^+ and Pb^{++} that existed combined with the tetrahedron of the SiO_2 in the glass are brought out, *i. e.*, diffused to the glass surface and thrown up into the solution leaving holes. Thus the skeleton layer of SiO_2 is formed. Then H^+, H_3O^+ etc. enter into the holes of the skeleton layer and Na^+, K^+ and Pb^{++} are diffused out further from the more inner part of the glass for the lack of the positive charge.

It is considered that the reaction is advanced by these courses, and that, therefore these reactions are the exchange reaction between

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(11) S. Tsuchihashi, unpublished.

(12) H. Schröder, *Ann. Phys.* **39**, 55 (1941).

Na^+, K^+, Pb^{++} and H^+, H_3O^+.

As mentioned above, the diffusion of the Pb^{++} carry out the important role in these steps.

It may also be considered that this mechanism is not unreasonable in consideration of the relation between the reaction velocity constant k (or diffused constant) and the component of the glass.

In conclusion the author wishes to express his thanks to the director of this institute Dr. K. Fuwa, and also to Professor S. Horiba (Kyoto University) for their stimulating interest in the author's work.

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