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Chemical durability of glasses; a thermodynamic approach

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The various hypotheses regarding corrosion of oxide glass surface by aqueous solutions have been reviewed. It has been shown that the long-term chemical resistance of a glass is mainly determined by the thermodynamic activity and stability of its component oxides in aqueous solutions. The stability of different oxides commonly used in glass-making like SiO_2, ZnO, PbO, Al_2O_3, ZrO_2 etc. in aqueous solutions of different pH has been calculated with available thermodynamic data, and these have been discussed in relation to the corrosion behaviour of glasses (prepared with these oxides) in aqueous solutions of various pH range. Suitable experimental results have been furnished to justify the importance of thermodynamic stability of component oxides of a glass on its corrosion behaviour in aqueous solutions.

1. Introduction

The term "Chemical Durability" has been conventionally used to express the resistance offered by a glass towards attack by aqueous solutions and atmospheric agents. There is no absolute or explicit measure for the chemical durability and glasses are usually graded relative to one another after subjecting them to similar experimental conditions; the nature of the experiment usually determines the relative order. Interferometry and weight loss measurements on the attacked glass as well as alkalimetric titration, pH and electrical conductivity measurements on the extracts have been in common use in the past. In recent years a complete analysis of the leached solutions for all the glass components and a detailed analysis of the leached glass surface have provided useful information for insight into the various factors involved in the decomposition of glass. For example, changes in the near corroded surface of glass (1 to 20 Å) can be monitored with Auger electron spectroscopy (AES) [1], electron spectroscopy for chemical analysis (ESCA) [2], ion-scattering spectroscopy (ISS) [3] or secondary ion mass spectroscopy (SIMS) [4]. Coupling these methods with ion-beam milling yields highly detailed compositional profiles of the intermediate glass surface (20 to 2000 Å) [5]. Measurement of the average composition of the far surface can easily be made with electron microprobe analysis (EMP), energy-dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM), or infrared reflection spectroscopy (IRRS) [6].

Various durability tests have been devised to compare the rates of attack on different glass compositions under standard conditions. These tests are usually performed on carefully prepared graded glass grains [7], or on a worked glass surface, such as a bottle. The choice would normally depend upon whether information is required on the intrinsic durability of a certain composition, or on how a finished product will stand up to attack.

The chemical durability of a formed glass article can be improved by lowering the alkali content of the surface of the article before use. Such reduction can be achieved by heating the articles in an atmosphere of SO_2 [8], or by adding various chemicals to the glass surface which react with alkali diffusing to the surface at high temperature (~ 650° C), forming alkali compounds such as Na_2SO_4 [9]. The sulphate can then be rinsed off, thus reducing the concentration of alkali at the glass surface.

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2. Mechanism of reactions of glasses with aqueous solution

When a piece of ordinary glass is brought in contact with aqueous solution, alkali ions are extracted into the solution in preference to silica and an alkali-deficient leached layer is formed on the surface of the virgin glass. The formation of this layer usually reduces the rate of alkali extraction by forming a barrier through which further alkali ions must diffuse before they can be brought into solution. Recent X-ray diffraction analysis, using pair function and disorder distribution function analysis, has shown that the silica-rich films formed during the corrosion process are more closely equivalent to vitreous silica produced from the molten state, than to a hydrated silica structure [10]. The thickness of the silica-rich films and probably their compactness also vary with the composition of the glass, and for the same glass depends on the test conditions; time, temperature and pH of the solution. Under identical conditions of corrosion, a low durability glass usually produces a thicker film than a high-durability glass.

According to Charles [11] the corrosion of alkali–silicate and alkali–lime–silicate glasses by aqueous solutions can be described in terms of three chemical reactions: (a) the penetration of a "proton" from water into the glassy network, replacing an alkali ion into soluton;

$$\equiv \mathrm{Si}-\mathrm{OR}+\mathrm{H_2O} \rightleftharpoons \equiv \mathrm{Si}-\mathrm{OH}+\mathrm{R}^+ + \mathrm{OH}^- \quad (1)$$

(b) the hydroxyl ion in solution disrupts siloxane bond in glass;

$$\equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv + \mathrm{OH}^- \rightleftharpoons \equiv \mathrm{Si}-\mathrm{OH} + \equiv \mathrm{Si}-\mathrm{O}^- \quad (2)$$

(c) the non-bridging oxygen formed in reaction 2 interacts with a further molecule of water producing a hydroxyl ion, which is free to repeat reaction 2 over again;

$$\equiv \mathrm{Si}-\mathrm{O}^- + \mathrm{H_2O} \rightleftharpoons \equiv \mathrm{Si}-\mathrm{OH}+\mathrm{OH}^- \quad (3)$$

Penetration of a bare proton, as suggested in reaction 1, is energetically improbable for the hydration energy of H^+ to H_3O^+ is very large and negative ($\sim -367\,\mathrm{kcal\,mol^{-1}}$). In a recent infrared study on corroded thin films of glass, Scholze *et al.* [12] has reported the existence of free water molecules inside the leached layer; the ratio of entrant protons to H_2O molecules inside the leacher layer was found to vary with the temperature of leaching and the nature of replaceable alkali ion, but apparently seems to be independent of the alkali content of the glass. However, it is not clear from this study whether the H_2O molecules estimated with IR spectroscopy in the leached layer have really diffused from the solution phase as H_2O or H_3O^+ species, or formed *in situ* inside the leached layer due to an auto-condensation reaction of the type

$$\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{HO}-\mathrm{Si}\equiv \rightleftharpoons \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv + \mathrm{H_2O} \quad (4)$$

It should be pointed out that a condensation reaction of this type is fairly well known on hydrated silica surfaces [13] and, indeed, is the reaction converting soluble silicic acid to insoluble silica in gravimetric estimation of silica in silicate materials.

Douglas and Isard [14] studied the extraction of alkali from a commercial silicate glass (SiO_2 69.9%, Al_2O_3 2.6%, CaO 5.4%, MgO 3.6%, Na_2O 16.8%) and found that the amount of sodium removed from the glass surface by the action of distilled water varied as the square root of time. From the observation they concluded that the rate-controlling process involved is one of diffusion, and that the rate of extraction of the sodium should be related to the electrical conductivity of the glass. They assumed that below the softening temperature of the glass, the atoms of the network are in fixed positions, whereas the Na^+ ions can move from one site to a neighbouring site if they acquire a definite energy E, and that the passage of electric current through the glass takes place exclusively by migration of Na^+ ions. During the diffusion of Na^+ ions to the glass surface, the electrical neutrality of the glass must be maintained by the contra-diffusion of other ions; otherwise an electric double layer would be set up at the glass surface which would prevent further removal of sodium ions. The amount of sodium that could be removed before the double layer stopped the process was estimated to be of the order of 100 times less than the amount of sodium actually extracted. On the assumption of simple diffusion, the following relation between Q, the quantity of Na^+ ions removed D the diffusion coefficient and σ the electrical conductivity of the glass, can be derived.

$$Q = \frac{2N_0}{\sqrt{(\pi)}}\sqrt{(Dt)} \quad (5)$$

and

$$\frac{Q}{\sqrt{(t)}} = \frac{2N_0}{\sqrt{(\pi)}}\frac{\sigma kT}{N_0 \epsilon^2} \tag{6}$$

where N_0 is the initial concentration of Na^+ in the glass, t is the time, k is the Boltzman's constant, T is the absolute temperature, and ϵ is the electronic charge.

Douglas and Isard observed that when the experimental values are inserted in Equation 6, the equation balanced expect for a factor of about 3. However, further work from the same laboratory [15] has shown that a marked difference between the diffusion coefficient, D_R calculated from the leaching experiments and the diffusion coefficient, D_c estimated from the electrical conductivity measurements occur particularly when the chemical composition of the glass changes. This discrepancy, according to these authors may be due to any, or a combination, of the following factors: (a) the diffusion medium in the leaching experiments is different from that of the conductivity experiments, (b) no account was taken in the above treatment of the amount of silica removed from the glass surface during leaching, (c) it has been assumed that the diffusion coefficient is not concentration-dependent, which is not necessarily true, and (d) it has been assumed that all the Na^+ ions in the glass take part in the leaching and in the conductivity and this also may not be true.

Numerous other workers have also studied the extraction of alkali from different types of glasses as a function of time, and nearly all the available data can be summarized into two main forms of rate equation: the rate of alkali extraction varies linearly with the square root of time at short times and low temperatures, then linearly with time after sufficiently long times and/or at high temperatures. As an example the results of water-leaching of 15 Na_2O, 85 SiO_2 glass at various temperatures are shown in Figs. 1 and 2. Fig. 1 shows a plot of the weight (mg) of Na_2O extracted from 1 g of glass against the square root of time for the early stages of the extraction, while Fig. 2 represents a plot of the weight of Na_2O extracted against the time for longer periods of extraction. This sort of extraction behaviour can be represented by an empirical relationship of the following form

$$Q = a\sqrt{(t)} + bt \tag{7}$$

where t is time, and a and b are empirical constants. From Equation 7

$$\frac{\mathrm{d}\log Q}{\mathrm{d}\log t} = \left[\frac{a}{2\sqrt{(t)}} + b\right]\left[\frac{1}{a\sqrt{(t)} + b}\right] \tag{8}$$

The gradient of Equation 8 has the limiting values $\frac{1}{2}$ as $t \to 0$, and 1 as $t \to \infty$, and increases slowly with time at intermediate values. Over limited times approximately linear plots of log Q versus log t would be expected, and the slopes of these plots would vary between $\frac{1}{2}$ and 1 as time and temperature increase.

In the case of leaching of silicate glasses by aqueous solutions, sodium and silicon (in the form of soluble silicate groups) are extracted simultaneously. Hlavàč *et al.* [16] have developed a mathematical model with which it is possible to explain the whole course of the decomposition of glass in aqueous solutions including the period of constant rate. They assumed that during corrosion of glass in aqueous solution, the following two processes occur simultaneously:

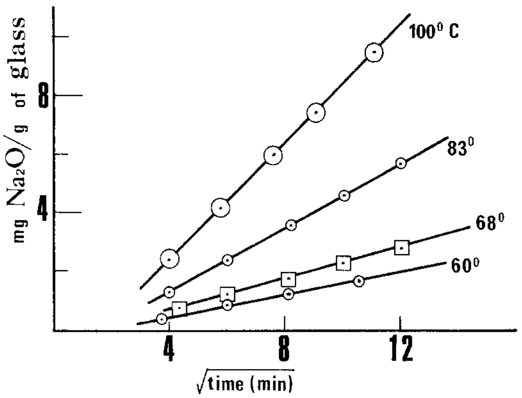

Figure 1 Short-time water leaching of 15 Na_2O, 85 SiO_2 glass grains at different temperatures.

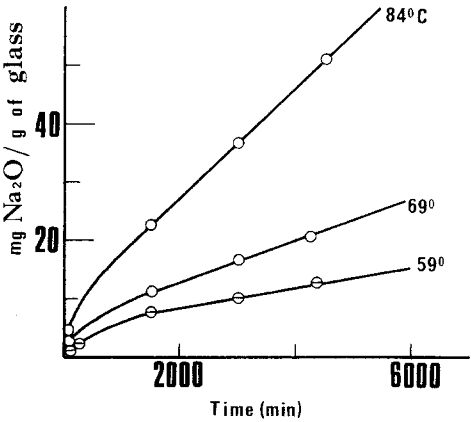

Figure 2 Long-time water leaching of 15 Na_2O, 85 SiO_2 glass grains at different temperatures.

Process I; Exchange of glass cations for H_3O^+ cations of solution controlled by the diffusion of the ions involved through the thus formed destroyed (leached) layer,

Process II; Dissolution of the leached layer controlled by a surface reaction. Process II continuously diminishes the thickness of the leached layer, thus increasing the concentration gradient and affecting also process I.

To give a mathematical formalism to such a complex process, they made the following simplifying assumptions; (a) a linear concentration gradient in the destroyed layer whose thickness is thus also determined*, (b) the rate of process II is constant, (c) corrosion products are being removed from the solution, and therefore do not affect the further course of corrosion, (d) corrosion takes place on a planar interface or on particles whose radii are sufficiently large in relation to the rate of the process, and (e) the presence of one kind of alkali ion is considered. With the above assumptions, the derivation is based on the relation

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = D\frac{C_\mathrm{A}}{x(t)}F \tag{9}$$

where D is the apparent diffusion coefficient, C_A the concentration of alkali ion in the original glass, x the thickness of the destroyed layer, and F the reaction area.

The total amount of alkali transferred into solution in time t by diffusion according to Equation 9 consists of two parts: of the amount that corresponds to a fully destroyed portion of glass, Q_2, and of the amount that corresponds to the thickness of the remaining layers, Q_AV:

$$Q_\mathrm{AV} = FC_\mathrm{A}\,x(t)/2 \tag{10}$$

$$Q_2 = BFC_\mathrm{A}t \tag{11}$$

where B is a constant giving the rate of heterogenous reactions as the rate of progress to the depth. The total amount, Q, is then given by:

$$Q = Q_2 + Q_\mathrm{AV} = FC_\mathrm{A}\,[x(t)/2 + Bt] \tag{12}$$

Differentiating Equation 12 yields

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = FC_\mathrm{A}\left[\frac{1}{2}\frac{\mathrm{d}x}{\mathrm{d}t} + B\right] \tag{13}$$

By substituting into Equation 9, the velocity equation for x is obtained.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 2\left[\frac{D}{x} - B\right] = \frac{A}{x} - 2B \tag{14}$$

where $A = 2D$. With the initial conditions $t = 0$, $x = 0$, the integration of Equation 14 leads to the relation

$$t = \frac{1}{(2B)^2}\left[A\ln\frac{1}{1-\dfrac{2Bx}{A}} - 2Bx\right] = f(x) \tag{15}$$

For $t \to \infty$ the thickness of the layer tends to the value $A/2B$.

Hlaváč *et al.* have shown that, with two adjustable parameters A and B, Equation 15 describes the leaching behaviour of alkali oxides from binary and ternary silicate glasses satisfactorily. Lyle [18] has reported an extensive amount of leaching data in which plots of log Q against log t can be represented by straight lines over two decades of log t; the slope of the lines varied between 1.107 to 0.500.

3. Factors affecting chemical durability measurements of a glass

Factors effecting Chemical durability measurements of glass are (a) weight of glass grains used and the surface area exposed, (b) ratio of the weight of the glass to the volume of the leaching solution, (c) nature of the leaching solution and the frequency of replenishing it, and (d) temperature of leaching.

3.1. Surface area

Surface area is an important factor and the amounts of various constituents released by a glass under certain conditions are proportional to the surface area exposed. In most of the investigation it is assumed that carefully prepared grains of a definite size range have a surface area which is proportional to their weight. The validity of this assumption can be checked from the results of an experiment in which the weight of glass grains was varied while other factors were kept constant. Fig. 3 represents a plot of the weight of K_2O extracted from a 25 K_2O, 75 SiO_2 glass against the

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*It should be pointed out that this assumption is not correct for concentration gradients in the leached layer have been found to be non-linear [17].

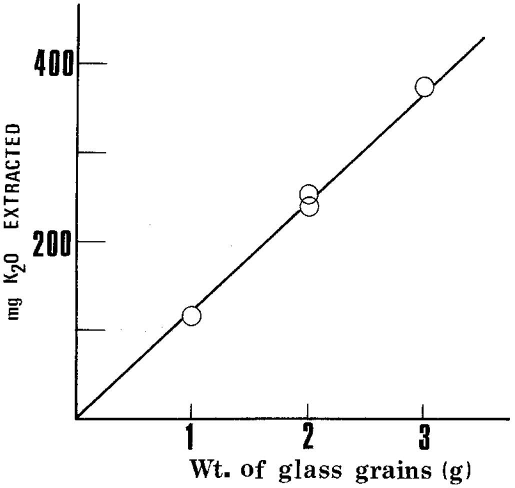


Figure 3 Relationship between weight of glass grains and quantity of alkali extracted from a $25\,K_2O$, $75\,SiO_2$ glass at 40° C.

weight of grains used. The relation is linear and the straight line passes through the origin, suggesting the validity of the assumption adopted.

3.2. Surface area of the glass: volume of the leaching solution

Dimbleby and Turner [19] found that the percentage weight loss of an $Na_2O–MgO–SiO_2$ glass increased by a factor of 2 with a four-fold increase in the amount of grains tested in a given volume of solution. This suggests that the quantity of material extracted from a silicate glass varies with the ratio surface area of glass to the volume of the leaching solution. An investigation was carried out by Shamy [20] to determine the effect of variation of this ratio on the amount of the individual constituents extracted from binary alkali oxide silicate glasses. Three leaching experiments were carried out on a $25\,K_2O$, $75\,SiO_2$ glass. In these experiments the volume of the leaching solution was kept at 100 ml while the weight of the glass grains was increased systematically. The quantity of alkali and silica extracted after various time intervals was determined in every case. It has been found that the quantity of silica extracted per gram of glass after a given time increased as the ratio of the surface area of the glass to the volume of the leaching solution increased. The ratio of alkali to silica in the extracts is higher than that in the glass. Final pH of the leaching solution increased slightly when the ratio of the surface area of the glass to the volume of the solution is increased. As will be shown later, the rate of silica extraction from a glass increased with the pH of the solution after pH 9. The rise in the amount of silica extracted from this glass when the ratio of the surface area to the volume of the solution is increased can be attributed to the accompanying increase in the pH of the solution.

The quantity of alkali removed in a given time did not vary appreciably with the ratio of the surface area of the glass to volume of the solution. The results show that the pH of the solution increases when the ratio of the surface area of the glass to the volume of the solution is increased. The increase in the pH would be expected to suppress the exchange of alkali ions of the glass with protons from the solution. However, increasing the pH of the solution also favours the dissolution of silica and this has the opposite effect on the removal of alkali from the glass, because it causes alkali to pass into solution through breakdown of the silica network and reduces the thickness of the leached layer. It is, therefore, probable that the apparent independence of alkali extraction on the ratio of th surface area of the glass to volume of the solution is due to these two factors counterbalancing one another.

Limitations on the ratio of the surface area of glass to the volume of the leaching solution to be used in any experiment are usually imposed by the sensitivity of the analytical methods as well as the size of the sample to be used. Yet the choice of this ratio remains arbitrary over a relatively wide range depending on the details of the experiment.

3.3. The leaching solution and the frequency of replenishing it

An experiment was carried out by Shamy [20] to study the effect of frequency of replenishing on the amount of alkali and silica extracted from a glass under certain conditions. 2.00 g of grains of $25\,K_2O$, $75\,SiO_2$ glass were leached in water with initial pH ~ 6.0 at 40°C. The experiment continued for 45 min during which the leaching solution was renewed 18 times. The experiment was repeated under nearly identical conditions except that the number of replenishing times was decreased to 8, 4 and 2 times. The results, shown in Fig. 4, show a marked increase in the amount of silica extracted as the number of replenishing times is decreased. This can be attributed to the

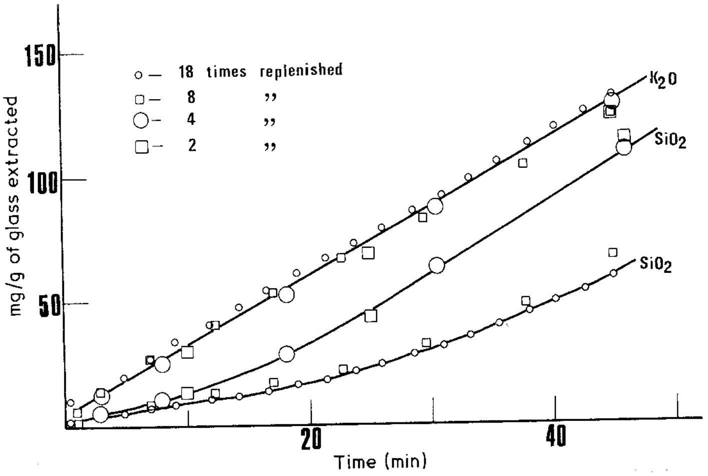


Figure 4 Effect of the frequency of replenishing the leach solution on the extraction rate from a 25 K_2O, 75 SiO_2 glass at 40° C.

accompanying rise in the pH of the attacking solution.

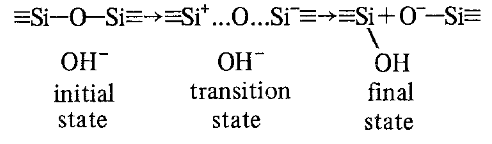
Silica is severely attacked by fluorine, hydrofluoric acid and alkaline solution. The resistance of silica towards attack appears to depend on the form in which silica exists. Quartz was found to be less susceptible to attack by alkaline solution than fused silica. The depolymerization reactions of silica can be represented by

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{Na^+\,OH^-} = \equiv\mathrm{Si{-}OH} \quad + \equiv\mathrm{Si{-}O^-Na^+} \tag{16}$$

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H^+\,F^-} = \equiv\mathrm{SiOH} \quad + \equiv\mathrm{SiF} \tag{17}$$

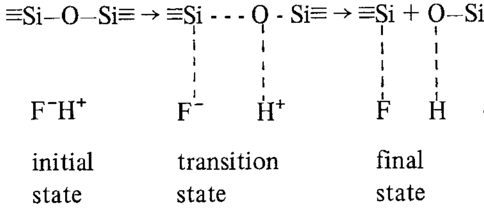
$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{Na^+\,F^-} = \equiv\mathrm{Si{-}O\,Na} \quad + \equiv\mathrm{SiF}. \tag{18}$$

These equations imply that the essential step in the depolymerization process is the breaking of a siloxane bond $\equiv\mathrm{Si{-}O{-}Si}\equiv$. The siloxane bond, though strong, is polar. It may be represented as $(\mathrm{Si}^{\delta+}\ldots{}^{\delta-}\mathrm{O})$. The incremental positive charge on the silicon atom makes it susceptible to attack by nucleophilic reagents such as OH^- and F^- ions. The high rate of depolymerization appears to be specific to solutions containing these two particular ions. Budd [21] has suggested that reaction 16 proceeds through the nucleophilic attack on the silicon atom according to



$$\begin{array}{ccc} \equiv\mathrm{Si{-}O{-}Si}\equiv\rightarrow & \equiv\mathrm{Si^+\ldots O\ldots Si^-}\equiv\rightarrow & \equiv\mathrm{Si}+\mathrm{O^-{-}Si}\equiv \\ \mathrm{OH^-} & \mathrm{OH^-} & \mathrm{OH} \\ \text{initial} & \text{transition} & \text{final} \\ \text{state} & \text{state} & \text{state} \end{array}$$

As for the reaction 17, it was suggested that it proceeds through the simultaneous nucleophilic and electrophilic attack on the network silicon and oxygen atoms respectively according to



$$\begin{array}{cccc} \equiv\mathrm{Si{-}O{-}Si}\equiv\rightarrow & \equiv\mathrm{Si}\;\text{- - -}\;\mathrm{O}\text{ - }\mathrm{Si}\equiv\rightarrow & \equiv\mathrm{Si}+\mathrm{O{-}Si}\equiv & \\ \mathrm{F^-H^+} & \mathrm{F^-}\quad\mathrm{H^+} & \mathrm{F}\quad\mathrm{H} & (19) \\ \text{initial} & \text{transition} & \text{final} & \\ \text{state} & \text{state} & \text{state} & \end{array}$$

Budd pointed out that "the bridging oxygen atoms" of the network, although subject to electrophilic attack, are rarely affected, because hydrogen ions are not sufficiently powerful to cause disruption of the O–Si bond. Hwever, if the nucleophilic attack on the silicon atom is proceeding simultaneously, then it should be possible for electrophilic attack on the oxygen atom to occur and this will reinforce the nucleophilic attack on silicon. This type of reaction would occur when the reagent comprises both a strong nucleophilic agent and a strong electrophilic reagent. Normally, this is a stringent requirement; for instance H^+ and OH^- cannot exist together in any substantial quantity (for the dissociation constant of water, K_w at 25°C must be 10^{-4}). These conditions, however, are met in the case of hydrofluoric acid. The fluoride ion is a moderately strong nucleophilic reagent. In the presence of H^+ ions, simultaneous nucleophilic and electrophilic attack on the network can occur in the manner represented by Equation 19.

Although acids like hydrochloric and hydroiodic satisfy the requirements for a simultaneous nucleophilic–electrophilic attack as put forward by Budd better than hydrofluoric acid, yet their degrading effect on silica is almost negligible.

It seems that the problem of the depolymerization of silica requires more sophisticated atomistic interpretation than the simple one presented by Budd.

3.4. Temperature of leaching

The quantity of alkali extracted from a glass in a given period of time increases with increasing temperature. For most silicate glasses the quantity leached in a given time is nearly double for every 8 to 15°C rise in temperature depending on the composition of the glass and the type of alkali ion. Some workers have attempted to express the temperature dependence of alkali extraction in terms of Arrhenius equation

$$A = B\,e^{-E/RT} \tag{20}$$

where A is the specific reaction rate changing with temperature, B is a constant, R the gas constant, T the absolute temperature, and E the activation energy, defined as the minimum energy a system must acquire for a reaction to occur. Apparent activation energies were obtained for the process of alkali removal from the glass and these were different from those obtained from electrical conductivity measurements. In cases where Equation 20 applies it is difficult to express the results in terms of the Arrhenius equation, because the two reaction constants α and K in the relation $Q = Kt^{\alpha}$ both vary with the temperature. In glass alkali extraction is always associated with pH changes and these depend not only on the quantity of alkali released but also on that of silica so that it is not possible to eradicate the effect of temperature on either alkali or silica extraction. Great care should, therefore, be taken before any physical meaning is ascribed to such apparent activation energies.

4. Effect of glass composition

The rate of alkali extraction from glass by aqueous solution is largely determined by the composition of the glass. Generally, the rate decreases with decreasing alkali content of the glass, with decreasing ionic radius of the alkali ion, or when part of the silica is replaced by almost any other divalent oxide.

Dubrovo and Shmidt [22] made a systematic study of the reaction of vitreous sodium silicates with water and with hydrochloric acid solutions. Nine glasses having Na_2O/SiO_2 ratio equal to 1:1, 1;1.4, 1:1.7, 1:2, 1:2.3, 1:2.6, 1:3, 1:4, and 1:6, were studied. Glasses in the form of discs having a known surface area were subjected to the action of water and hydrochloric acid at two or three different temperatures. Samples of the leaching solution were removed after certain periods of time; these were analysed for soda and silica. The amounts of alkali and silicic acid found in the solution were calculated as moles of the corresponding oxides (Na_2O and SiO_2) going into solution from 1 cm² of surface and were denoted n_{Na_2O} and n_{SiO_2}. In order to characterize the process of interaction the authors used some other quantities. If the composition of the glass is expressed in the form $Na_2O.mSiO_2$ then the amount of SiO_2 in the layer of the glass that has undergone reaction corresponding to n_{Na_2O} would be $m \times n_{Na_2O}$ and the fraction of this (α) which has passed from this layer to the solution will be $(n_{SiO_2})/(m \times n_{Na_2O})$. Thus α is the fraction of silicic acid which has passed into solution from the layer of the glass that has undergone reaction; its value gives an idea of the nature of the process that is taking place. When $\alpha = 1$, the components are passing into solution in the same proportion as those in which they occur in the glass i.e. dissolution is occurring. On the other hand when $\alpha = 0$, leaching occurs with the result that a layer of silicic acid remains on the surface of the glass.

The conclusions of Dubrovo and Shmidt can be summarized as follows:

(1) The process of interaction of sodium silicate with water can be divided into two stages: exchange of sodium ions of the glasses for hydrogen ions of the solution, resulting in the formation of a residual layer of silicic acid, which, together with the silica of the original glass, comprises a protective film on the surface; and reaction of the protective layer with the alkaline solution that has been formed, resulting in removal of silicic acid from the surface by the solution.

(2) In the case of sodium silicates having a low silica content, a kinetic equilibrium is established between the primary and secondary reactions, so that dissolution of the glass appears to take place. In the case of sodium silicates of high silica content, the main process is the leaching of Na_2O from the glass.

(3) When sodium silicates are treated with hydrochloric acid solution, transfer to the solution of SiO_2 lags behind that of Na_2O to a greater extent than in the case of water treatments. In

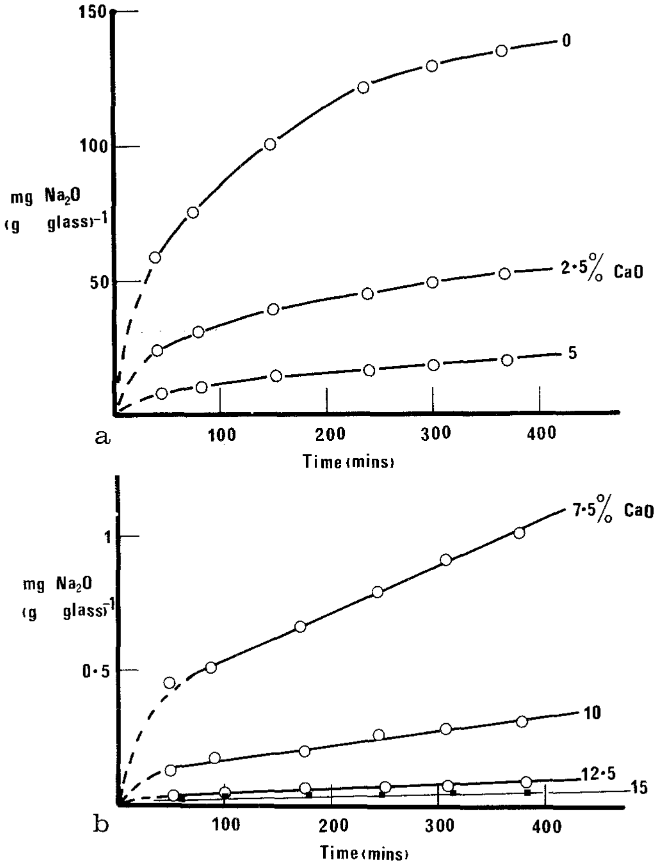


Figure 5 Extraction of Na_2O from (25-x) Na_2O, xCaO, 75 SiO_2 glass grains at 75° C, pH = 1.

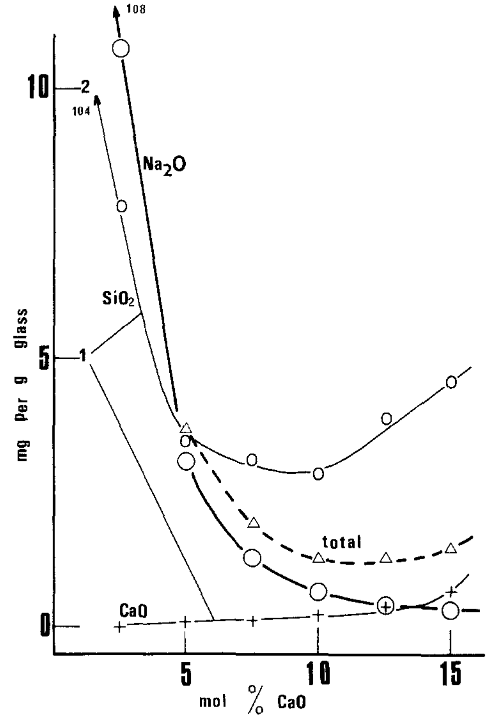


Figure 6 Extraction of Na_2O, CaO and SiO_2 from (25-x) Na_2O, x CaO, 75 SiO_2 glass grains at 75° C, pH = 10 in 5 h.

the case of glasses having a silica content greater than that of the disilicate, no SiO_2 could be detected in the solution.

(4) The relation between the logarithms of the amounts of components passing into solution and the molecular percentage of silica in the glass is represented over the range of compositions examined by smooth curves or by straight lines.

(5) With rise in temperature the amounts of the components passing into solution increase considerably, and at the same time the boundary of the region of soluble silicates moves in the direction of glasses of higher original silica content.

(6) Alkali removed by hydrochloric acid treatment is higher than that removed by water and does not vary with the concentration of the acid in the range from 1.0 to 0.01 M HCl i.e. in the pH range from about 0 to 2.

4.1. Effect of lime in silicate glasses

Addition of CaO to binary alkali silicate glass is known to increase durability. Some typical results of a series of (25-x) Na_2O, x CaO, 75 SiO_2 (where $x = 0$ to 15 mol % at 2.5 mol % intervals) are shown in Figs. 5 and 6. It can be seen from Fig. 5

that extraction of Na_2O decreases sharply as it is partially replaced by equivalent amount of CaO in the glass. Increasing the CaO content from 0 to 10 mol % caused a rapid decline in soda extraction. However, with an increase of more than 10% CaO, the Na_2O extraction is virtually the same and the rate of change of soda extraction with lime content is negligible.

Extraction of CaO: (i) The lime extraction from these glasses in the buffer solution of $pH = 1$ is less than 0.1 ppm i.e. below the detection limit. (ii) CaO passes into the solution at $pH = 10$, but the amount of extraction is very small. Fig. 6 shows that the extraction of lime increases with increasing CaO content of the glass.

Extraction of SiO_2: (i) Silica extraction at $pH = 1$ is extremely small, and below the limit of measurement (~ 0.1 ppm). (ii) At $pH = 10$, the silica extraction is very high for low lime glasses (1.57 mg from the glass containing 2.5 mol % CaO).

Under identical conditions, the silica extraction goes through a minimum around 10 mol % CaO, and increases again with further increase of CaO in the glass. Similar behaviour has also been reported by Budd and Frackiewiez [23] in different Na_2O–CaO–SiO_2 glasses. This enhanced silica extraction with high CaO–containing glasses may be either due to microphase separation or/and activity of CaO in these glasses, containing more than 10 mol % CaO, may be disproportionately higher than other glasses of this series.

Gastev [24] has calculated the depth to which various oxides are leached from a series of glass of the composition: 18% Na_2O, $(82\text{-}x)\%$ SiO_2, $x\%$ MO where M represents an alkaline earth metal The depth to which CaO (and oxides of other alkaline earth metals) is leached was found to increase gradually with increasing content of it in the glass, but remained less than the depth of leaching of soda and silica. This is shown in Fig. 7. The results of Das [25] also suggest that in 15 Na_2O, 5 MO, 80 SiO_2 glasses the amount of MO extracted by water from a glass is less than that expected if it had been removed as a result of network breakdown of the silica structure. Possible explanations for this phenomenon are that calcium, released by the glass through a network breakdown, is partly retained by adsorption on the surface, or that silica is preferentially extracted from the bulk of the leached layer formed on the surface of the glass leaving it with an alkaline earth oxide/silica ratio higher than that of the original glass.

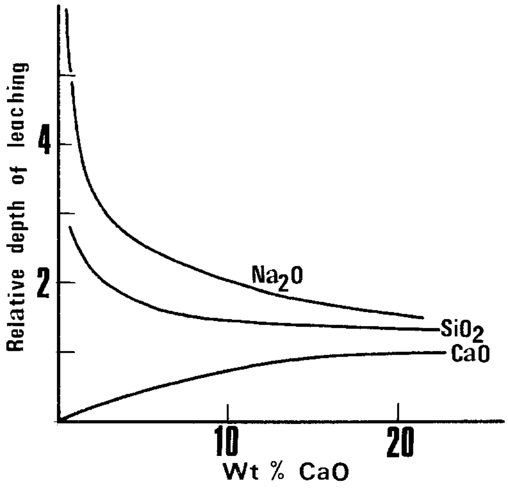


Figure 7 Effect of CaO content on the water resistance of glass.

5. Thermodynamic stability and the effect of pH of the solution

Chemical durability of silicate glasses is critically dependent on the pH and the nature of the attacking solution. When an alkali silicate glass is placed in pure water, the water instantaneously becomes a solution of alkali oxide and silica. The pH of this solution depends on the concentration (activity), as well as on the relative ratio of alkali oxide to silica. Both the centration and ratio change with time and so the pH of the attacking solution would also be expected to change correspondingly.

The effect of the solutions having different pH values on the decomposition of simple glasses and

TABLE I Standard free energy and formation constants of different silicate anions in aqueous solution at 25° C

Reaction	ΔG^0 (cal mol^{-1})	log *K*
SiO_2 (quartz) + H_2O (liq) $\rightleftharpoons H_2SiO_3$	+ 7,090	$-5.198 = \log {}^a(H_2SiO_3)$
$H_2SiO_3 \rightleftharpoons HSiO_3^- + H^+$	+ 13,640	$-10.000 = \log {}^a(HSiO_3^-) - pH$
$H_2SiO_3 \rightleftharpoons SiO_3^= + 2H^+$	+ 30,000	$-21.994 = \log {}^a(SiO_3^=) - 2pH$
SiO_2 (quartz) + 6HF(liq) $\rightleftharpoons SiF_6^= + 2H_2O + 2H^+$	− 11,020	$+8.079 = \log {}^aSiF_6^= - 2pH$

the rate at which the constitutents of the glass go into solution have been studied by a number of investigators [26] and their results showed that all the silicate glasses become particularly susceptible to decomposition above pH 9 to 10. This may be easily inferred from Table I, which gives the thermodynamic equilibrium constants for the formation of different silicate and silico–fluoride ions. The formation of silicate and silico–fluoride ions is pH-dependent; activity of $HSiO_3^-$ becomes important around $\mathrm{pH} \sim 10$, and thus even vitreous silica will decompose at $\mathrm{pH} \geqslant 10$. This thermodynamic prediction has been found to be true by Shamy *et al.* [27]; some of their results are shown in Fig. 8. In the presence of HF or fluoride ions, a silico–fluoride anion will be formed. Although this reaction is also pH-dependent, the equilibrium constant is so large and positive that almost quantitative reaction will take place in all practically attainable acid and alkaline media. Indeed the very corrosive action of fluoride on silicate glasses is well known.

Before going any further in discussing thermodynamic stability of different glasses in aqueous solutions, let us first define the term "stability". A system is stable if it does not change with time. There are two types of stability: thermodynamic stability and kinetic stability, however, in common usage, these are sometimes intermixed in a confusing way. With thermodynamic stability the system is in equilibrium corresponding to minimum possible free energy; the system is stable in the strict sense, that is, none of the conceivable changes in the system can occur spontaneously. On the other hand, in the case of apparent or kinetic stability, the system is not in a state of equilibrium; some changes can occur spontaneously but at an immeasurably slow rate. The best possible example of kinetic stability is the existence of glass itself!

There may be some argument as to whether chemical durability of glass is a matter of thermodynamic equilibrium (true stability) or apparent stability involving high activation barrier for various diffusion processes involved during decomposition of glass in aqueous solutions.

The work of Morey and co-workers [28] showed that vitreous silica or quartz grains continuously rotated in water at a speed of 0.5 rpm produces less than 1 ppm soluble silica even after 1 year. At the same time the use of glass electrodes for measuring activities of H^+ ion and other ionic species in solution is a fairly common practice. In the case of glass electrodes a major part of the observed potential originates from the differences of chemical potential of the species in the solution and that exchanged on the glass surface. A reproducible steady potential with glass electrodes is possible with establishment of ion-exchange equilibrium at least at the surface of the glass. Since with conventional glass electrodes steady potentials are obtained within a short time, the kinetic barrier does not seem to play any important part, at least at the surface of the glass.

In fact, the durability of glass may be expressed as a function of both the thermodynamic and kinetic stability of its component oxides:

$$\text{Durability} = f(\text{kinetic stability}) \times f(\text{thermodynamic stability}).$$

The relative influence of either of these two fac-

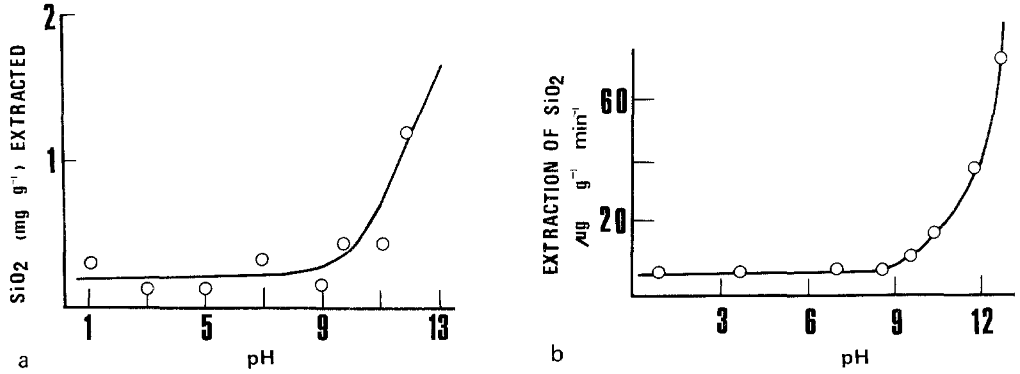


Figure 8 Effect of pH on the rate of extraction of SiO_2 from (a) fused silica power at 90° C; (b) 25 Na_2O, 75 SiO_2 glass grains at 35° C.

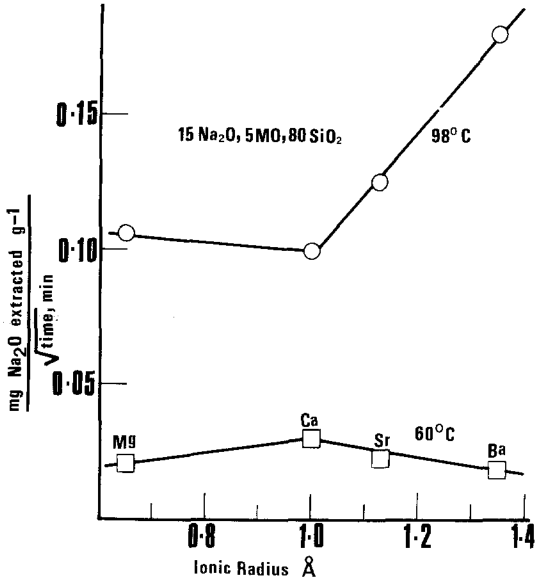


Figure 9 Rate of extraction of Na_2O from $15Na_2O$, 5MO, 80 SiO_2 glass grains at different temperatures.

tors on durability will depend on the nature of test. If the test is carried out at low temperature, the system will have little thermal energy to overcome the activation barrier, and the kinetic part will be predominant. On the other hand, if the surface area of the glass sample exposed to the corroding medium is high, and/or the experiment is carried out at a relatively high temperature the thermodynamic part will be more important. For example, Fig. 9 shows the rate of Na_2O extracted (mg Na_2O extracted from 50 cm^2 of glass surface/(time in minutes)$^{1/2}$) by distilled water from a series of 15 Na_2O, 5 MO, 80 SiO_2 glasses (where M refers to Mg, Ca, Sr and Ba) at different temperatures. At the higher temperature, 98° C, the glass containing BaO was least durable, and the durability increased with decreasing ionic size of M^{2+}. As may be seen from Table II, this behaviour is in accordance with the thermodynamic stability of different binary alkaline earth silicates in water. However, although the reaction of all the divalent oxides under present discussion with water is exothermic (ΔH can be calculated from values given in Table III), the leaching behaviour of the same glasses at 60° C indicates the apparent stability of the BaO-containing glass over even the MgO containing glass. This is probably due to the fact that at lower temperatures the diffusion of the large Ba^{++} ion becomes energetically restricted, while the smaller Mg^{++} ion can move through the leached layer relatively easily, and thus can be extracted giving way to the leaching of mobile Na^+ ion from the glass.

From the above discussion, it is clear that a large increase of either thermodynamic or kinetic stability will make the glass more durable. In the limiting case, it can be argued that in the case of thermodynamic stability (equilibrium), the chemical potentials of the species on the glass surface and that in solution are equal and thus no net mass transfer will take place and the glass will be durable in the strict sense.

The relationship between the equilibrium constant K and the standard free energy change of the reaction, ΔG^0 is

$$\Delta G^0 = -RT \ln K \tag{21}$$

where R is the gas constant (1.987 cal deg^{-1} mol^{-1}), and T the absolute temperature. At 298.15 K (room temperature) therefore

$$\Delta G^0 = -1364 \log K$$

thus

$$\log K = -\frac{\Delta G^0}{1364} \tag{22}$$

5.1 Equilibrium solubility of silica in aqueous solution

The low solubility of silica in water is one of the main factors in the corrosion resistance of glass. When silica (quartz) is brought in contact with

TABLE II Ion exchange equilibrium constant of different binary silicates in water at 25° C

Reaction	ΔG^0 (cal mol^{-1})	$\log K$
Li_2SiO_3 (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + $2Li^+$ (aq)	−22,740	16.67
Na_2SiO_3 (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + $2Na^+$ (aq)	−28,815	21.125
K_2SiO_3 (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + $2K^+$ (aq)	−72,830	53.395
Rb_2SiO_3 (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + $2Rb^+$ (aq)	−46,500	34.091
Cs_2SiO_3 (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + $2Cs^+$ (aq)	−46,820	34.325
$MgSiO_3$ (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + Mg^{++} (aq)	−13,888	10.182
$CaSiO_3$ (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + Ca^{++} (aq)	−16,116	11.815
$SrSiO_3$ (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + Sr^{++} (aq)	−!24,400	17.889
$BaSiO_3$ (cryst) + $2H^+$ (aq) $\rightleftharpoons$ H_2SiO_3 + Ba^{++} (aq)	−30,570	22.412

TABLE III The standard free energies of formation, the standard heats of formation, and the standard entropies of some selected species at 25° C

Formula	Description	state	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	S^0 (cal mol^{-1} deg^{-1})
Hydrogen					
H_2		gas	0	0	31.211
H^+		aq.	0	0	0
H_2O		liq.	−56.690	−68.317	16.716
H_2O		gas	−54.636	− 57.798	45.206
OH^-		aq.	−36.595	−54.957	−2.519
Lithium					
Li	Metal	cryst.	0	0	6.70
Li^+		aq.	−70.22	−66.554	3.4
Li_2O		cryst.	−133.9	−142.4	9.06
LiOH		cryst.	−106.1	−116.45	12.0
LiOH		aq.	−107.82	−121.51	0.9
LiCl		aq.	−101.57	−206.577	16.6
Li_2SO_4		aq.	−317.78	−350.01	10.9
$LiNO_3$		aq.	−96.63	−115.926	38.4
Li_2CO_3		aq.	−266.66	−294.74	−5.9
$Li_2O, 2SiO_2$		cryst.		−586.8	28.5
Li_2O, SiO_2		cryst.		−381.2	19.2
$2Li_2O, SiO_2$		cryst.		−543.2	29.0
$Li_2O, Al_2O_3, 2SiO_2$	β-Eucryptite	cryst.		−984.49	49.6
$Li_2O, Al_2O_3, 4SiO_2$	α-Spodumene	cryst.		−1638.36	61.9
$Li_2O, Al_2O_3, 4SiO_2$	β-Spodumene	cryst.		−1624.96	73.8
Sodium					
Na	Metal	cryst.	0	0	12.2
Na^+		aq.	−62.589	−57.279	14.4
Na_2O		cryst.	−90.0	−99.4	17.4
NaOH		cryst.	−99.23	−101.99	12.5
NaOH	un-ionized	aq.	−90.1		
NaCl		aq.	−93.939	−97.302	27.6
Na_2CO_3		aq.	−251.4		
$NaHCO_3$	un-ionized	aq.	−202.89	−222.5	37.1
$NaHCO_3$		aq.	−202.56		
$NaCO_3$		aq.	−190.54		
$NaSO_4$		aq.	−240.91		
Na_2O, SiO_2		cryst.		−360.4	27.2
$2Na_2O, SiO_2$		cryst.		−490.3	46.8
$Na_2O, Al_2O_3, 2SiO_2$·	Nepheline	cryst.		−949.3	29.7
$Na_2O, Al_2O_3, 4SiO_2$	Jadeite	cryst.		−1356.6	31.9
Potassium					
K	Metal	cryst.	0	0	15.2
K^+		aq.	−67.466	−60.04	25.5
K_2O		cryst.	−46.2	−86.4	20.8
KOH		cryst.	−89.5	−101.78	14.2
KCl		cryst.	−97.592	−104.175	19.76
K_2CO_3		cryst.	−255.5	−273.93	33.6
KOH		aq.	−105.061	−115.00	22.0
$K_2O, 2SiO_2$		cryst.		−547.7	43.5
K_2O, SiO_2		cryst.		−357.1	34.9
$K_2O, 4SiO_2$		cryst.		−981.9	63.5
$K_2O, Al_2O_3, 2SiO_2$	kaliphilite	cryst.		−981.5	63.6
K_2O, Al_2O_3, SiO_2	leucite	cryst.		−1399.5	88.0
$K_2O, Al_2O_3, 6SiO_2$	orthoclase	cryst.		−1819.89	
$K_2O, Al_2O_3, 6SiO_2$	microcline	cryst.		−1815.9	105
$K_2O, Al_2O_3, 6SiO_2$	andularia	cryst.		−1814.5	112

TABLE III Continued.

Formula	Description	state	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	S^0 (cal mol^{-1} deg^{-1})
$K_2O, Al_2O_3, 6SiO_2$	sanidine	cryst.		−1813.3	113.8
$K_2O, 3Al_2O_3, 6SiO_2, 2H_2O$	muscovite	cryst.		−1965.5	138
Rubidium					
Rb	metal	cryst.	0	0	16.6
Rb^+	aq.	aq.	−67.45	−58.9	29.7
Rb_2O		cryst.	−69.5	−78.9	26.2
RbOH		cryst.	−87.1	−98.9	16.9
RbOH		aq.	−105.05	−113.9	27.2
Rb_2CO_3		cryst.	−249.3	−269.6	23.3
$Rb_2O, 4SiO_2$		cryst.		−980.8	66.5
$Rb_2O, 2SiO_2$		cryst.		−564.7	46.5
Rb_2O, SiO_2		cryst.		−352.8	38.5
Cesium					
Cs	metal	cryst.	0	0	19.8
Cs^+		aq.	−67.41	−59.2	31.8
Cs_2O		cryst.	−65.6	−75.9	29.6
CsOH		cryst.	−84.9	−97.2	18.6
$Cs_2O, 4SiO_2$		cryst.		−977.8	70
$Cs_2O, 2SiO_2$		cryst.		−564.2	50
Cs_2O, SiO_2		cryst.		−353.3	42
Magnesium					
Mg	Metal	cryst.	0	0	7.77
Mg^{++}		aq.	−108.99	−110.41	−28.2
MgO		cryst.	−136.13	−143.84	6.4
$Mg(OH)_2$		cryst.	−199.27	−221.00	15.09
$MgOH^+$		aq.	−150.10		
$MgCl_2$		cryst.	−141.57	−153.40	21.4
$MgCO_3$		cryst.	−246	−266	15.7
$MgHCO_3^+$		aq.	−250.88		
$MgSO_4$		cryst.	−280.5	−305.5	21,9
$MgSO_4$	unionized	aq.	−289.55		
$MgCO_3$	unionized	aq.	−239.55		
MgO, SiO_2	clinoenstatite	cryst.		−357.9	162
$2MgO, SiO_2$	forsterite	cryst.		−508.1	22.75
$3MgO, 2SiO_2, 2H_2O$	serpentine	cryst.		−1018.8	53.1
$3MgO, 4SiO_2, H_2O$	talc	cryst.		−1365.0	62.3
$7MgO, 8SiO_2, H_2O$	anthophyllite	cryst.		−2791.3	133.6
$2MgO, 2Al_2O_3, 5SiO_2$	cordierite	cryst.		−2114.0	97.3
Calcium					
Ca	Metal	cryst.	0	0	9.95
Ca^{++}		aq.	−132.18	−129.77	−13.2
CaO	Cubic	cryst.	−144.4	−151.9	9.5
$Ca(OH)_2$	Rhombic	cryst.	−214.22	−235.8	18.2
$CaOH^+$		aq.	−171.55		
$CaCO_3$	Calcite	cryst.	−269.78	−288.45	22.2
$CaSO_4$	Anhydrite	cryst.	−135.56	−342.42	25.5
$CaSO_4$	Soluble	cryst.	−313.52	−340.27	25.9
$CaSO_4$	Soluble	cryst.	−312.46	−339.21	25.9
$CaSO_4$	unionized	aq.	−312.67		
$CaCO_3$	unionized	aq.	−312.76		
$CaHCO_3^+$		aq.	−273.67		
CaO, SiO_2	Wollastonite	cryst.	−358.2	−378.6	19.6
CaO, SiO_2	pseudowollastonite	cryst.	−357.4	−377.4	20.9

TABLE III Continued.

Formula	Description	state	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	S^0 (cal mol^{-1} deg^{-1})
$2CaO, SiO_2$	β	cryst.	−512.7	−538.0	37.6
$2CaO, SiO_2$	γ	cryst.	−513.7	−539.0	37.6
$3CaO, SiO_2$		cryst.		−688.1	40.3
$CaO, MgO, 2SiO_2$	diopside	cryst.		−741.2	34.2
CaO, MgO, SiO_2	monticellite	cryst.		−528.7	26.4
$2CaO, MgO, 2SiO_2$	akermanite	cryst.		−902.3	50.0
$2CaO, 5MgO, 8SiO_2, H_2O$	termolite	cryst.		−1144.5	131.2
$3CaO, MgO, 2SiO_2$	merwinite	cryst.		−1067.3	60.5
$CaO, Al_2O_3, 2SiO_2$	anorthite	cryst.		−983.6	48.4
Strontium					
Sr	Metal	cryst.	0	0	13.0
Sr^{++}		aq.	−133.2	−130.38	−9.4
SrO		cryst.	−133.8	−141.1	13.0
$Sr(OH)_2$		cryst.	−207.8	−229.3	21
$SrCO_3$	strontianite	cryst.	−271.9	−291.2	23.2
$SrSO_4$		cryst.	−218.9	−345.3	29.1
SrO, SiO_2		cryst.	−350.8	−371.2	22.5
$2SrO, SiO_2$		cryst.	−495.7	−520.6	43
$2SrO, Al_2O_3, SiO_2$		cryst.		−928.09	
Barium					
Ba	Metal	cryst.	0	0	16
Ba^{++}		aq.	−134.0	−128.67	3
BaO		cryst.	−126.3	−133.4	16.8
$Ba(OH)_2$		cryst.	−204.7	−226.2	22.7
$BaCO_3$	witherite	cryst.	−272.2	−291.3	26.8
$BaSO_4$		cryst.	−323.4	−350.2	31.6
BaO, SiO_2		cryst.	−338.7	−359.5	24.2
$2BaO, SiO_2$		cryst.	−470.6	−496.8	46.4
$BaO, 2SiO_2$		cryst.		−585.5	
$2BaO, 3SiO_2$		cryst.		−965.4	
Zinc					
Zn	Metal	cryst.	0	0	9.95
Zn^{++}		aq.	−35.184	−36.43	−25.45
ZnO	orthorhombic	cryst.	−76.88		
$Zn(OH)_2$	white	cryst.	−133.31		
$Zn(OH)_2$	amorphous		−131.85		
$HZnO_2^-$		aq.	−110.9		
$ZnCO_3$		cryst.	−208.31	−233.88	29.8
$ZnSO_4$		cryst.	−88.255	−99.40	19.7
$ZnCl_2$		cryst.	−174.8	−194.2	25.9
ZnO, SiO_2		cryst.	−274.8	−294.6	21.4
$2ZnO, SiO_2$	willmite	cryst.	−7.8	31.4	
Cadmium					
Cd	Metal	cryst.	0	0	12.3
Cd^{++}		aq.	−18.58	−17.30	−14.6
CdO	cubic	cryst.	−53.79	−60.86	13.1
$Cd(OH)_2$	active	cryst.	−112.46	−133.26	22.8
$HCdO_2^-$		aq.	−86.5		
$CdCl_2$		cryst.	−81.88	−93.00	28.3
$CdCl^+$		aq.	−51.8		5.6
$CdCl_2$	unionized	aq.	−84.3		17
$CdCO_3$		cryst.	−160.2	−178.7	25.2
$CdSO_4$		cryst.	−195.99	−221.36	32.8
CdO, SiO_2		cryst.		−271.06	23.3

TABLE III Continued.

Formula	Description	state	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	S^0 (cal mol^{-1} deg^{-1})
Lead					
Pb	Metal	cryst.	0	0	15.51
Pb^{++}		aq.	−5.81	0.39	5.1
PbO	yellow	cryst.	−45.05	−52.07	16.6
PbO	red	cryst.	−100.6	−123.0	21
$Pb(OH)_2$		cryst.	−81.0		
$HPbO_2^-$		aq.	−45.25	−52.40	16.2
$PbSO_4$		cryst.	−193.89	−219.50	35.2
$PbCl_2$		cryst.	−75.04	−85.85	32.6
$PbCO_3$		cryst.	−149.7	−167.3	31.3
$PbO, PbCO_3$		cryst.	−195.6	−220.0	48.5
$2PbO, PbCO_3$		cryst.	−242	−273	65
$Pb_3(OH)_2(CO_3)_2$		cryst.	−406.0		
PbO, SiO_2		cryst.	−239.0	−258.9	27
$2PbO, SiO_2$		cryst.	−285.7	−312.7	43
$4PbO, SiO_2$		cryst.		−417.68	
Boron					
B		cryst.	0	0	1.56
B_2O_3		glass	−280.4	−297.6	18.8
H_3BO_3		cryst.	−230.2	−260.2	21.41
H_3BO_3		aq.	−230.16		
$B_4O_7^=$		aq.	−616		
H_2BO_3		aq.	−217.63	−251.8	7.3
HBO_3		aq.	−200.29		
BO_3^{3-}		aq.8	−181.48		
BF_3		gas.	−261.3	−265.4	60.70
BF_4^-		aq.	−343	−365	40
Al	Metal	cryst.	0	0	6.769
Al^{+++}		aq.	−155.0	−125.4	−74.9
Al_2O_3	corundum	cryst.	−376.77	−399.09	12.186
Al_2O_3, H_2O	boehmite	cryst.	−435.0	−471.0	23.15
$Al(OH)_3$	amorph.	amorph.	−271.4	−304.9	17
$H_2AlO_3^-$		aq.	−257.4		
AlO_2^-		aq.	−200.7		
$Al_2Si_2O_5(OH)_4$	kaolinite	cryst.	−884.5		
Silicon					
Si	Metal	cryst.	0	0	4.47
SiO_2	quartz II	cryst.	−192.4	−205.4	10.00
SiO_2	cristobalite II	cryst.	−192.1	−205.0	10.19
SiO_2	tridymite IV	cryst.	−191.9	−204.8	10.36
SiO_2		vitreous	−190.9	−202.5	112
$SiF_6^=$		aq.	−511	−558.5	−12
H_4SiO_4		aq.	−300.3		
$H_3SiO_4^-$		aq.	−286.8		
SiF_4		gas	−360	−370	68.0
$SiCl_4$		gas	−136.2	−145.7	79.2
H_2SiO_3		aq.	−242		
$HSiO_3^-$		aq.	−228.36		
$SiO_3^=$		aq.	−212.0		
Germanium					
Ge	Metal	cryst.	0	0	10.14
GeO_2		cryst.	−1361		
H_2GeO_3		aq.	−186.8		
$HGeO_3^-$		aq.	−175.2		
$GeO_3^=$		aq.	−157.9		

TABLE III Continued.

Formula	Description		state	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1}	S^0 (cal mol^{-1} deg^{-1})
Titanium						
Ti	Metal		cryst.	0	0	7.24
TiO_2	Rutile		cryst.	−212.3		
TiO^{++}			aq.	−138.0		
$TiO(OH)_2$			cryst.	−253.0		
$HTiO_3^-$			aq.	−111.7		
Zirconium						
Zr	Metal		cryst.II	0	0	9.18
Zr^{4+}			aq.	−142.0		
ZrO^{++}			aq.	−201.5		
ZrO_2			cryst.	−247.7		
$ZrO(OH)_2$			cryst.	−311.5	−338.0	22
$HZrO_3^-$			aq.	−287.7		
$Zr(OH)_4$			cryst.	−370.0	−411.2	31
Phosphorus						
P	Metal	white	cryst. III	0	0	10.6
		red	cryst.II	−3.3	−4.4	7.0
		black	cryst. I	−10.3		
H_3PO_4			aq.	−274.2	−308.2	42.1
$H_2PO_4^-$			aq.	−271.3	−311.3	21.3
$HPO_4^=$			aq.	−261.5	−310.4	−8.6
PO_4^{3-}			aq.	−245.1	−306.9	−52.0
P_2O_5			cryst.		−356.6	27.35

water at ordinary temperatures the value of the equilibrium solubility is very low (~6 ppm for quartz), but it is the extremely slow rate of hydration that is responsible for the glass having a high resistance to the attacking water.

In principle the thermodynamic stability of a glass may considered to be the stability of its component oxides which in turn is a function of activity (chemical potential) (for $\mu_i = \mu_i^0 + RT \ln a_i$) of that particular oxide in glass and the equilibrium constants of hydration, ionization and complexation. With the available thermodynamic data it is possible to calculate the various energy changes associated with these processes, and there from the stability of the glass under various conditions can be estimated. Standard chemical potentials of some selected species relevant to common glass compositions are given in Table III. Since this data is commonly available only for 25° C and one atmosphere pressure, the following discussion will refer to that temperature and pressure only.

5.1.1 Effect of pH of the solution on the solubility of SiO_2

The reaction between water and silica may be presented as

$$SiO_2 \text{ (quartz)} + H_2O \rightleftharpoons H_2SiO_3 \qquad (23)$$

$$K = \frac{a_{H_2SiO_3}}{a_{SiO_2} a_{H_2O}} \qquad (24)$$

ΔG^0 of reaction 23 is $+7090 \text{ cal mol}^{-1}$, and therefore $\log K = -5.198$. In this particular case, pure quartz is reacting with pure water, with very little formation of H_2SiO_3, thus

$$a_{SiO_2} = a_{H_2O} = 1 \qquad (25)$$

Therefore

$$a_{H_2SiO_3} = K = 10^{-5.198} \sim c_{H_2SiO_3}.$$

From Equation 25 it would appear that the solubility of SiO_2 in terms of H_2SiO_3 in solution is independent of pH, but in the presence of alkali, additional silica passes into solution as silicate ions. The dissociation of silicic acid can be written as

$$H_2SiO_3 \overset{K_1}{\rightleftharpoons} H^+ + HSiO_3^- \qquad (26)$$

$$HSiO_3^- \overset{K_2}{\rightleftharpoons} H^+ + SiO_3^= \qquad (27)$$

For reaction 26, $\Delta G^0 = +13\,640 \text{ cals mol}^{-1}$ and $\log K_1 = -10$

$$K_1 = \frac{a_{H^+}\, a_{HSiO_3^-}}{a_{H_2SiO_3}}$$

so

$$\log K_1 = \log a_{HSiO_3^-} - \log a_{H_2SiO_3} - \mathrm{pH}$$

and

$$\log a_{HSiO_3^-} = -15.198 + \mathrm{pH} \qquad (28)$$

This shows that although the solubility of silica near the neutral point ($\mathrm{pH} \sim 7$) is not greatly affected by pH, the solubility increases rapidly with alkalinity at $\mathrm{pH} \geqslant 9$. Similarly for reaction 27, $\Delta G^0 = +16\,360$ cals mol^{-1} and $\log K_2 = -11.994$. Thus

$$\log a_{SiO_3^=} = -11.994 + \log a_{HSiO_3^-} + \mathrm{pH} \quad (29)$$

Using Equations 25, 28 and 29 the equilibrium activity (or loosely, the concentration in moles per litre) of different species of silica in aqueous solution has been calculated at various pH, and these are shown in Fig. 10, along with the corresponding solubility values for vitreous silica.

One can divide Fig. 10 into three distinctly different pH zones based on the predominance of each particular silica species. For example, in the first zone ($\mathrm{pH} \leqslant 10$), the minimum solubility is represented by the undissociated but soluble portion of H_2SiO_3, reaching about $10^{-5.2}$ M; this species predominates up to $\mathrm{pH} = 9$ (independent of pH). In the second zone (pH 10 to 12) most of the silica which passes into the solution is due to the formation of $HSiO_3^-$ species. In the third zone ($\mathrm{pH} \geqslant 12$) $SiO_3^=$ predominates. It is evident that the quantity of silica extracted from both quartz and vitreous silica follows the same pattern but the solubility of silica from the glassy form is more than that from quartz. This is because chemical potential of quartz is more negative than that of vitreous silica; in other words quartz is thermodynamically more stable than vitreous silica.

From Fig. 10 and the preceeding discussions it is now obvious that all silica base glasses follow the same trend with respect to pH changes of the solution; the absolute magnitude on Y-axis of Fig. 10, however, would vary with $\log a_{SiO_2}$, where a_{SiO_2} denotes activity of silica in the respective glass with fused silica as the standard state.

Let us now consider the effect of pH of the solution on the stability of binary sodium silicate glasses. The reaction between a sodium silicate glass, for simplicity say $Na_2O \cdot SiO_2$, and water may be typically written as:

$$Na_2SiO_3(\text{glass}) + 2H^+(aq) \rightleftharpoons H_2SiO_3(\text{glass}) + 2Na^+(aq)$$

$$K = \frac{a_{H_2SiO_3}\, a^2_{Na^+(aq)}}{a_{Na_2SiO_3}\, a^2_{H^+(aq)}} \qquad (30)$$

ΔG^0 for the reaction 30 is $-28\,880$ cal mol^{-1} and $\log K = +21.44$. Therefore

$$\log H_2SiO_3(\text{glass}) = 21.44 - 2 \log a_{Na^+(aq)} - 2\mathrm{pH} \qquad (31)$$

From Equation 31 it is clear that unlike pure silica in the case of sodium silicate glass, the activity of H_2SiO_3 (glass) or the extent of ion exchange represented by reaction 30 will depend on the pH, as well as on the activity of Na^+(aq) in the leach solution. According to this equation, when a sodium silicate glass is brought in contact with an aqueous solution in which the activity of Na^+ is very small (say 1 ppm) e.g. distilled water;

$$a_{Na^+(aq)} = 10^{-6} \text{ and } 2\log Na^+(aq) = -12. \qquad (32)$$

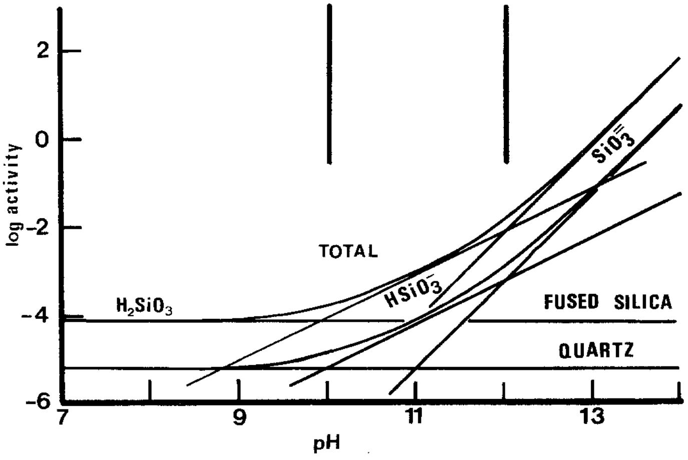


Figure 10 Stability of SiO_2 in aqueous solutions at different pH (25° C).

Substituting Equation 32 into Equation 31 we have

$$\log a_{H_2SiO_3}(\text{glass}) = 33.44 - 2\text{pH} \quad (33)$$

This means that if the $Na^+(aq)$ ions are not allowed to build up in the leach solution, almost a complete removal of Na^+ (glass) is possible even up to a pH ~ 16.7. As we have seen before, H_2SiO_3(glass) becomes unstable, due to ionization and consequent solution, at pH $\geqslant$ 9 to 10; that is why binary sodium silicate glasses are not durable in water. In fact, as can be seen from Table II, none of the binary alkali silicate glasses should be durable in water; and from thermodynamic point of view absolute stability should increase in the order: $K_2SiO_3 < Na_2SiO_3 < Li_2SiO_3$. Indeed the better durability of lithium silicate glass over sodium or potassium silicate glasses of same molar composition is well known [29].

Comparing the standard free energy of formation of Na_2SiO_3 ($-1338\,\text{kcal mol}^{-1}$) with that of H_2SiO_3 ($-242\,\text{kcal mol}^{-1}$), sodium silicate appears to be more stable, which in reality is not the case. The reason for this is that Na_2SiO_3 when in contact with aqueous solutions, releases an Na^+ ion into solution which gets hydrated, and causes a lot of free energy difference. The effect of hydration of Na^+ ion on the decomposition of sodium silicate glass can be examined; if Na_2SiO_3 is brought in contact with a solvent such as dioxan doped with an anhydrous proton (this can be achieved by dissolving organic carboxylic acids like adipic acid in dioxan, in which the acid ionizes producing H^+) in which Na^+ cannot be hydrated, the glass is expected to be durable. Under such anhydrous conditions, binary alkali silicate glasses have been found to release very little alkali into the solution phase [30]. Some typical results are shown in Fig. 11.

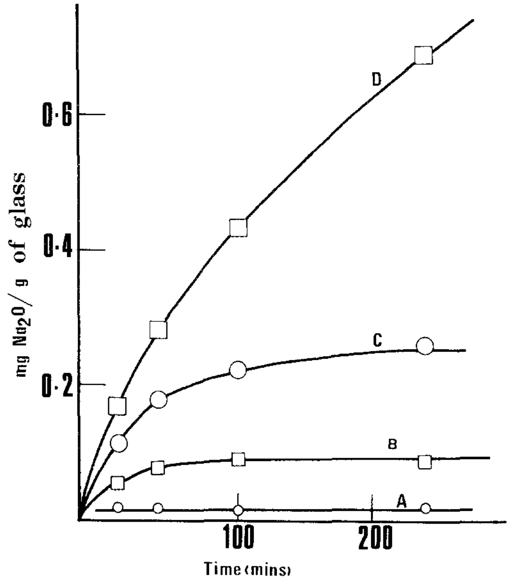


Figure 11 Rate of extraction of Na_2O from 25 Na_2O, 75 SiO_2 glass grains in water-dioxan-adipic acid mixtures at 65° C: Curve A 1 wt% adipic acid + 0.0 vol% water + Dioxan; Curve B, 1 wt% adipic acid + 2.0 vol% water + Dioxan; Curve C, 1 wt% adipic acid + 4.0 vol% water + Dioxan; Curve D, 1 wt% adipic acid + 10.0 vol% water + Dioxan.

5.1.2. Effect of CaO on the durability of silicate glasses at different pH

When $CaSiO_3$ glass is brought in contact with an aqueous solution the ion exchange reaction may be written as

$$CaSiO_3\,(\text{glass}) + 2H^+(aq) \rightleftharpoons H_2SiO_3\,(\text{glass}) + 2H^{++}(aq) \quad (34)$$

ΔG^0 of (34) is $-16\,780\,\text{cal mol}^{-1}$, thus $\log K = 12.30$

$$K = \frac{a_{H_2SiO_3}\, a_{Ca^{++}}}{a_{CaSiO_3}\, a^2_{H^+}}$$

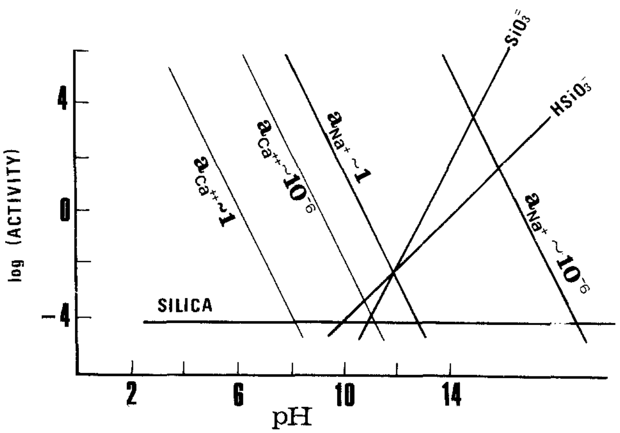
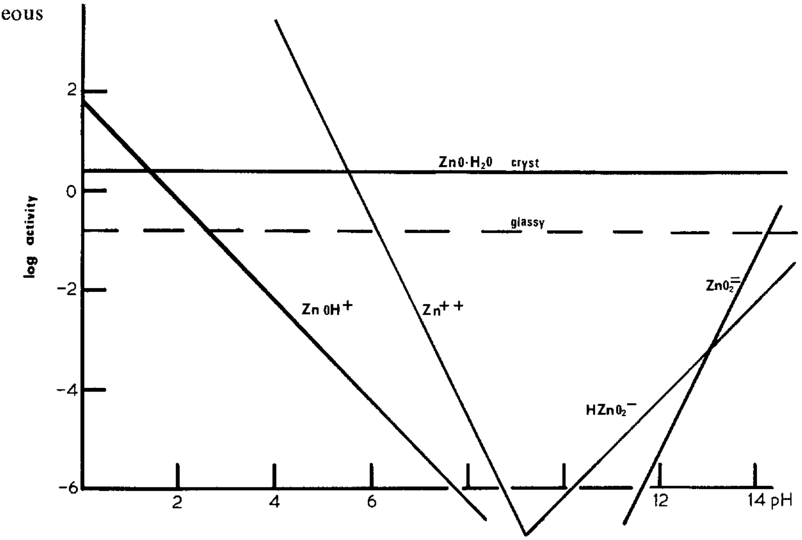


Figure 12 Relative stability of Na_2SiO_3 and $CaSiO_3$ crystal at different pH (25° C).

Figure 13 Stability of ZnO in aqueous solutions at different pH (25° C).



and $\log K = \log a_{H_2SiO_3} + \log a_{Ca^{++}(aq)} + 2pH$

or $$\log a_{H_2SiO_3} = 12.3 - \log a_{Ca^{++}(aq)} - 2pH \quad (35)$$

From Equation 35 it is clear that the exchange of Ca^{++} (glass) for H^+(aq) or "hydration" of calcium silicate glass is dependent on the pH and on the activity of Ca^{++} ion of the leach solution. It should be pointed out that unlike NaOH, the solubility of $Ca(OH)_2$ in water is low. Thus even a small concentration of Ca^{++}(aq) ions will produce a significant activity in the solution.

In Fig. 12 is plotted the ion exchange behaviour of Na_2SiO_3 and $CaSiO_3$ glasses for two activities of Na^+(aq) and Ca^{++}(aq) in the leach solution at different pH. Fig. 12 also contains the decomposition behaviour of vitreous silica at different pH. From this figure it may be seen that even for $a_{Ca^{++}(aq)}$ as low as 10^{-6} in the solution,

$$a_{Ca^{++}(solution)} = a_{SiO_3^=} \sim 0.0005 \text{ at pH} = 10.8$$

This corresponds to about 0.05% of calcium exchange from the $CaSiO_3$ glass. At lower pH, although exchange of calcium from the glass is favoured (about 2% calcium exchange at pH = 10) in acidic solutions, the silicic acid does not ionize and probably offers a very high activation barrier for the idffusion of calcium ions through it. Thus calcium containing glasses should appear durable up to pH ⩽ 10.

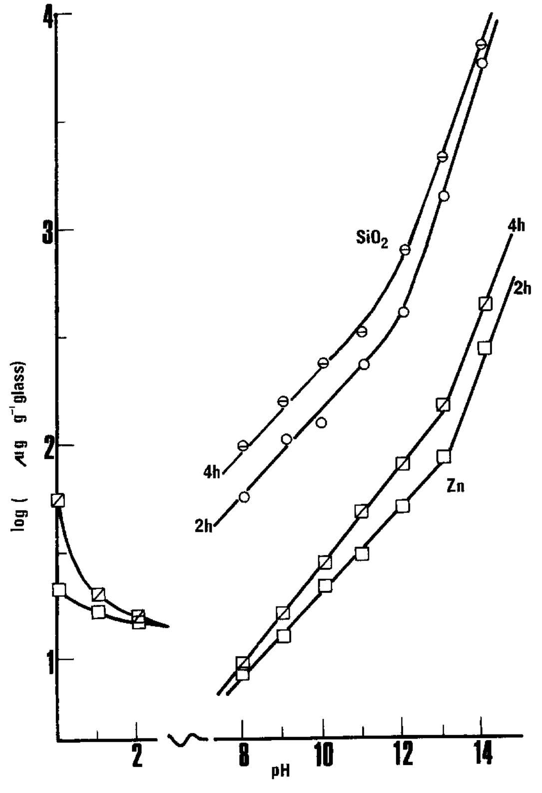


Figure 14 Extraction of zinc and silica from 15 Na_2O, 10 ZnO, 75 SiO_2 glass grains at different pH (70° C).

5.1.3. Durability of glasses containing ZnO

ZnO though costly relative to CaO has been used in the past in making chemically resistant scientific glasses; a typical example is JENA glass, containing about 7 wt % ZnO. The stability of ZnO in aqueous solutions of different pH is shown in Fig. 13. It is clear that hydration of ZnO is easier than that of vitreous silica. Below the pH range 6.1 to 5.5 (depending on the type of hydrated ZnO formed) the activity of Zn^{++}(aq) will exceed that of hydrated ZnO, and zinc will be extracted into the solution as Zn^{++}(aq). Thus zinc-containing glasses will be susceptible to acid attack up to a pH ~ 5.5. In the alkaline range ZnO forms $HZnO_2^-$ and $ZnO_2^=$ ions; the activity of either of these species is smaller than that of hydrated ZnO. The iso-activity point corresponding to $HZnO_2^-$ and $ZnO_2^=$ species occurs at pH = 13.1. This means that zinc-containing glasses will be susceptible to vigorous alkaline attack above pH ~ 13. It may be recalled that the corresponding critical pH for the predominance of $SiO_3^=$ is ~12. Thus addition of ZnO to a silicate glass is expected to increase its chemical durability in the alkaline range up to a pH ~ 13, and it can be seen that this expectation is nicely followed from Fig. 14, where the leaching behaviour of a 15 Na_2O, 10 ZnO, 75 SiO_2 glass is shown at different pH from 0 to 14.

5.1.4. Durability of glasses containing PbO

PbO is used in many commercial glasses, the most important being crystal glass. Lead is a poison; even small amounts of lead cause health hazards. Recently a lot of attention has been focussed on the leaching behaviour of lead from glass surfaces, particularly those coated with low-melting lead borosilicate enamels. The stability diagram of PbO in aqueous solutions of different pH is shown in Fig. 15. Hydration of PbO is small. In the acidic

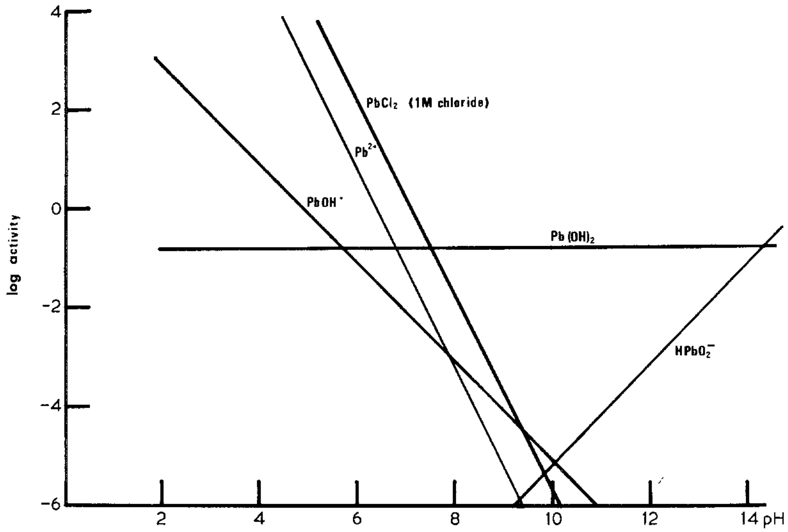


Figure 15 Stability of PbO in aqueous solutions at different pH (25° C).

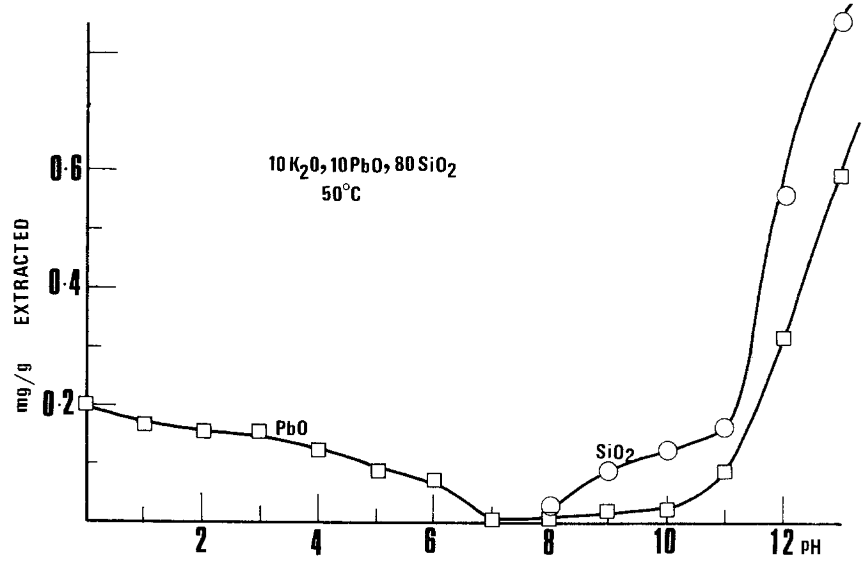


Figure 16 Extraction of lead and silica from a 10 K_2O, 10 PbO, 80 SiO_2 glass grains at different pH (50° C).

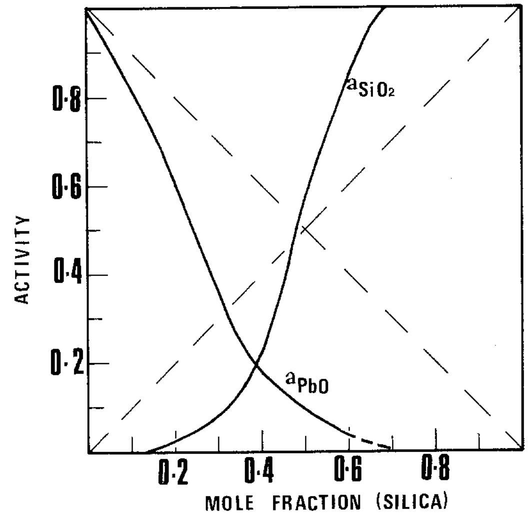


Figure 17 Activity of PbO and SiO_2 in $PbO–SiO_2$ melts at 1200° C.

range ($pH \leqslant 6.8$), lead dissolves as Pb^{2+} and $PbOH^+$, the activity of the former being always much greater than that of $PbOH^+$. In the alkaline range, lead forms $HPbO_2^-$ and the activity of $HPbO_2^-$ becomes greater than that of $Pb(OH)_2$ only above pH 14.5. Thus PbO in a silicate glass is expected to increase the alkaline durability, whereas the acidic durability should decrease. This can be seen from Fig. 16 where leaching behaviour of a typical lead crystal glass is shown. Recently Shamy and Taki-Eldin [31] has reported the durability of binary $PbO–SiO_2$ glasses in different acidic media and observed a sharp increase in lead extraction when PbO content was increased from 35 to 40 mol %. Fig. 17 shows the activity of PbO and SiO_2 in the $PbO–SiO_2$ system at 1200° C. It is clear that in this system, silica saturation occurs around 66 mol % SiO_2; activity of PbO in binary lead-silicates containing less than 34 mol % PbO is very low and increases sharply above this critical concentration. Although the activity of PbO and SiO_2 in the binary $PbO–SiO_2$ system will change with temperature, the qualitative nature of activity–concentration relationship of PbO at room temperature is virtually the same as that at 1200° C. Thus the silica unsaturation is probably related with the enhaced lead extraction from glasses containing more than 35 mol % PbO.

5.1.5. *Durability of glasses containing Al_2O_3*

Al_2O_3 is added in many commercial glasses. Small amounts of Al_2O_3 are known to accelerate the glass batch reaction [32]. Al_2O_3 is also known to improve the chemical durability of silicate glasses. The stability diagram of Al_2O_3 in aqueous solution of different pH is shown in Fig. 18. In the acid range of $pH \leqslant 3.2$ the predominant species is Al^{3+} and is expected to be leached out from the glass surface. In the alkaline range AlO_2^- is formed and becomes significant around $pH \geqslant 10.7$. Thus Al_2O_3 in glass is expected to slightly increase the alkaline durability of glass. It is well known that cation-sensitive glasses containing Al_2O_3 become H^+-sensitive below pH ~ 4. This is presumably

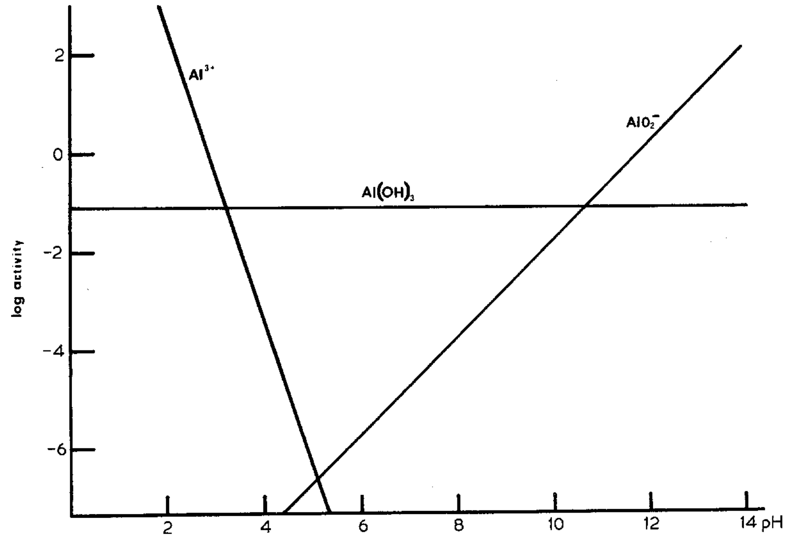


Figure 18 Stability of Al_2O_3 in aqueous solutions at different pH (25° C).

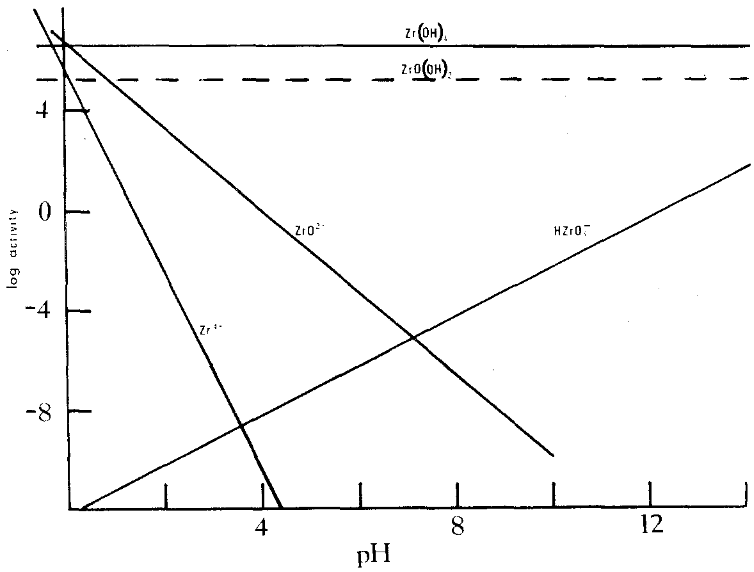


Figure 19 Stability of ZrO_2 in aqueous solutions at different pH (25° C).

due to the fact that the alkali cations get absorbed on the hydrated alumina sites on the glass surface; below a pH ~ 4 these sites are leached into the solution as Al^{3+}(aq) and the cation sensitivity of the surface is lost.

5.1.6. Durability of glasses containing ZrO_2

ZrO_2 is known to increase the chemical durability of silicate glasses. Even a small amount of ZrO_2 (about 2 wt%) increases acid and alkaline durability of a glass significantly [33]. This is the reason why commercial glass fibres for cement reinforcement, where a very high alkaline durability is desired, contain about 16 wt% ZrO_2 [34]. The extreme durability of ZrO_2-containing glasses is apparent from the stability diagram of ZrO_2 in aqueous solution as shown in Fig. 19. Although hydration of ZrO_2 is energetically very favourable, the predominance of ionic species like ZrO^{2+}, Zr^{4+} and $HZrO_3^-$ will only occur below pH ~ 0 and above pH ~ 17 respectively. Thus hydrated ZrO_2 surface is stable at all conceivable pH ranges of the solution and probably offers a very high activation barrier for diffusion of other ionic species through it.

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