References

1. H. FUJIMORI, T. MASUMOTO, *Suppl. to Sci. Rep. Research Institutes Tohoku University (RITU) A* June (1978) 181.
2. R. C. SHERWOOD, *Amer. Inst. Phys. Conference Proceedings* **24** (1975) 745.
3. H. FUJIMORI, M. KIKUCHI, Y. OBI, T. MASUMOTO, *Sci. Rep. Research Institutes Tohoku University (RITU)* **A26** (1976) 36.
4. R. C. O'HANDLEY, L. I. MENDELSOHN, E. A. NESBITT, *IEEE Trans. Magn.* **MAG-12** (1976) 942.
5. T. EGAMI, P. J. FLANDERS, C. D. GRAHAM Jr., *Amer. Inst. Phys. Conference Proceedings* **24** (1975) 697.
6. N. FUNAKOSHI, T. KANAMORI, T. MANABE, *Jap. J. Appl. Phys.* **15** (1976) 1833.
7. H. E. KISSINGER, *J. Res. Nat. Bur. Stan.* **57** (1956) 217.
8. A. INOUE, T. MASUMOTO, M. KIKUCHI, T. MINEMURA, *J. Jap. Inst. Metals* **42** (1978) 294.
9. S. OMORI, Y. HASHIMOTO, *Trans. Jap. Inst. Metals* **18** (1977) 347.

Received 10 January
and accepted 30 January 1980.

J. LATUSZKIEWICZ
T. KULIK
H. MATYJA
Institute of Materials Science and Engineering
Warsaw Technical University
Narbutta 85, 02-524 Warszawa
Poland

Comment on "Influence of surface potential on the kinetics of glass reactions with aqueous solutions"

The amount of alkali ion extracted from a unit area of glass sample on the effect of an aqeous solution is a function of time. Namely, a square root dependence prevails at the beginning of the attack while after a certain time a linear function can be observed provided that the rate of network dissolution is sufficiently fast. The network dissolution moderates and finally can stop the thickening of the surface layer formed by the ion exchange and interdiffusion of alkali ion and hydrogen ion. Thus the dissolution of network leads or may lead to a steady state in which the phase boundary is shifted toward the glass bulk with a constant velocity and the rates of all processes are constant. Consequently, the amounts of the products of both the ion exchange and network vary linearly with time.

Recently Mularie, Furth and Westwood [1] attributed the deviation from the square root dependence and the transition to the linear regime to the effect of an electric field present in the "near surface region" of the glass. These authors disregarded the fact of network dissolution [2] and the related explanation of the time dependence of alkali extraction [3]. (However, the respective publications are cited in their reference list.) Nevertheless their final conclusion is in accordance with the experimental observation. This contradiction is the reason for discussing the treatment presented in the authors' paper.

The extended Fick's equation given by the authors are

$$J(x, t) = -D\frac{\partial N(x, t)}{\partial x} + vN(x, t) \qquad (1)$$

and

$$\frac{\partial N(x, t)}{\partial t} = D\frac{\partial^2 N(x, t)}{\partial x^2} - v\frac{\partial N(x, t)}{\partial x} \qquad (2)$$

where N is the mobile charge carrier concentration, J the flux of this ion, D the diffusion coefficient and v denotes the alkali ion velocity which is equal to mobility μ times the field strength E

$$v = \mu E \qquad (3)$$

By attributing a constant value to E, a solution for Equation 2 and a formula for amount, Q, of extracted alkali have been obtained. Limiting cases of the latter are

$$\lim_{t \to 0} Q(t) \propto \sqrt{t} \qquad (4)$$

and

$$\lim_{t \to \infty} Q(t) \propto t \qquad (5)$$

in agreement with experiments.

Equations 1 and 2 apply, of course, when interstitial mechanism prevails. In this case the rate of an interdiffusion depends on self diffusion coefficients of both types of ion involved. Accordingly, the flux and the diffusion coefficient of hydrogen

0022–2461/80/092398–02$02.20/0

ion should be also considered besides those for alkali ion. Inserting Equation 3 into Equation 2 and labelling the symbols for alkali ion by 1 and those for hydrogen ion by 2 we have

$$J_1(x, t) = -D_1 \frac{\partial N_1(x, t)}{\partial x} + \mu_1 N_1(x, t)E \qquad (6)$$

and

$$J_2(x, t) = -D_2 \frac{\partial N_2(x, t)}{\partial x} + \mu_2 N_2(x, t)E \qquad (7)$$

Considering that

$$J_1(x, t) = -J_2(x, t), \qquad (8)$$

the fluxes in Equation 6 and 7 can be eliminated and an expression for E can be obtained. For the sake of brevity, it is only noted here that this expression is identical with that of the gradient of diffusion potential. Thus the field strength is defined by the parameters and the ion distribution, consequently, no arbitrary value or function may be attributed to E. Eliminating E we finally obtain a formula for the flux of ions (cf. [4])

$$J_1 = -J_2 = D_1 D_2 \frac{N_1 + N_2}{N_1 D_1 + N_2 D_2} \frac{\partial^2 N_1}{\partial x^2} \qquad (9)$$

where the coefficient corresponds to the interdiffusion coefficient. This formula and a comparison with Equations 6 and 7 indicate that *E exerts no effect on the ionic interdiffusion except for balancing the fluxes of the diffusates.*

The astonishingly correct result expressed by Equations 4 and 5 can be explained by a formal similarity. The form of Fick's second law for a moving co-ordinate system fixed to the actual surface of dissolving glass [3] is

$$\left(\frac{\partial c}{\partial t}\right)_y = D\left(\frac{\partial^2 c}{\partial y^2}\right)_t + a\left(\frac{\partial c}{\partial y}\right)_t \qquad (10)$$

where y denotes the distance coordinate in the system moving at a rate a, c is the concentration of alkali ions and D the interdiffusion coefficient. Since the time dependence of alkali extraction has been explained on the basis of this differential equation, Equation 2 of the same forms leads to an apparently perfect solution.

Summarizing the relation disclosed we may say that the authors have obtained reasonable correlations although a crucial process was disregarded and a misleading hypothesis was introduced. This interesting paradox recalls a statement of Aristotle (Organon, First Analysis, Book 2, Chapters 2 and 3) that erroneous premises of a certain kind may give a correct conclusion.

References

1. W. M. MULARIE, W. F. FURTH, A. R. C. WESTWOOD, *J. Mater. Sci.* **14** (1979) 2659.
2. M. A. RANA, R. W. DOUGLAS, *Phys. Chem. Glasses* **2** (161) 179.
3. Z. BOKSAY, G. BOUQUET, S. DOBOS, *Phys. Chem. Glasses* **9** (1968) 69.
4. R. W. DOUGLAS, J. O. ISARD, *J. Glass Technol* **33** (1949) 289.

Received 10 January
and accepted 30 January 1980.

Z. BOKSAY
Dept. of General and Inorganic Chemistry
Eötvös L. University, Budapest, Hungary
H-1445 Budapest, P.O.B. 323
Hungary

Reply to 'Comment on "Influence of surface potential on the kinetics of glass reactions with aqueous solutions".'

In the preceding letter [1], Professor Boksay summarizes the classical "inter-diffusion model" for glass corrosion, in which the driving force is derived solely from concentration gradients. Explicit in our paper [2], however, is the view that this model is incomplete, because it does not provide either qualitative or quantitative agreement with experimental observations on the kinetics of dissolution.

Boksay's note [1] raises a number of questions regarding our suggestion that the existence of a surface potential can substantially influence near-surface diffusion behaviour and account for much of the discrepancy between theory and observation. In the recent review article on the glass/electrolyte interface by Stein [3], the potential we refer to is termed ψ_0. Important to our model is the spatial variation of this potential *inside* the solid (the shaded region in Fig. 7 of [3]). A tacit assumption of the diffusion model, on the other hand, is that this gradient, the electric field, is zero. This assumes that glass is a carrier-free, perfect insulator. In fact, alkali-containing silica glasses are extrinsic insulators, and one can calculate, as has Charles [4], the distance into the solid over which the surface potential decays effectively to zero. In the glasses we have considered, this distance is a few micrometres. The resultant fields are large (see Tables I, II [2]) and thus, we believe, greatly influence local diffusion kinetics.

Regarding the explicit objections raised in Boksay's comment:

(a) Dissolution: The claim is made that we have disregarded network dissolution in our model. Actually, we have chosen a co-ordinate system consistent with the parameter we wish to measure. Our stated intent was to show that inclusion of the electrostatic interaction yields an analytical expression for the ion concentration in solution, $Q(t)$, which agrees satisfactorily with experimental observations. Accordingly, our co-ordinate system was chosen such that it was stationary with respect to the solid/liquid interface, as our boundary condition $N(0, t) = N_0$ indicates. Thus $Q(t)$ can be calculated without the need for arbitrary assumptions regarding the rate of dissolution. In effect, we rejected the *a priori* assumption of Boksay *et al.* [5], (see Equation 10 in [1]), that network dissolution occurs at a *constant rate* because this assumption does not correlate with experimental observations [6]. More seriously, we question the validity of a kinetics approach in which linear behaviour is imposed as an initial condition. Such an approach does not permit a prediction to be made from a knowledge of basic, measurable parameters.

(b) Linear kinetics: As noted above, linear kinetics result from the basic assumption of a linearly moving interface. Contrary to Boksay's suggestion, it is not necessary for us to attribute a constant value to the field strength, E, in order to reach our result. The appropriate value of E in our analysis is simply the value at the interface, or more exactly, the value of the spatial gradient of the potential as the limit of x tends to zero. In a one-dimensional model this cannot be other than constant and single-valued. A concern one might have here is the constancy of E with time due to, for example, network dissolution, but experimental evidence from electrokinetic measurements [7] indicates that the interface potential does remain stable during dissolution. However, confusion could arise regarding our method of estimating the magnitude of the surface fields used in Tables I and II of [2] by a simple linear (capacitor) approximation, in which a 100 mV potential drop over 1 μm yields an average field of 1000 V cm^{-1}. The important point is to realize the large magnitude of the field involved; exact calculations of its strength could be made [8] if such information were needed.

(c) Interdiffusion: Charge neutrality obviously must be preserved as alkali ions are extracted from the solid. Interdiffusion (the exchange of hydrogen ions with the ejected alkali ions) may fulfill the neutralization requirement since this exchange is not affected by the presence of an electric field in the liquid double layer [7], as Boksay points out (see Equations 6–9 of [1]). Interdiffusion is not, however, necessary to our model, and other charge neutralization mechanisms could be formulated. The point is that whatever the charge neutralization mechanism is, it is *not* rate-determining in the kinetics of extraction of alkali ions from glass into aqueous solution. Rather, it is field-enhanced diffusion in the surface region of the solid which

0022–2461/80/092400–02$02.20/0

determines these kinetics. Boksay's equations (Equations 6–8 in [1]) are valid in the liquid double layer, but cannot be applied to the surface region of the solid unless we assume that a hydrogen-ion defect coexists with the interstitial alkali in the solid. Then Equation 8 of [1] would be invalidated because the separate ion fluxes would be in the same direction, and generally not equal in magnitude unless their defect densities, activation energies and diffusion coefficients were fortuitously equal.

Boksay did not comment on the necessity for any model proposed to achieve quantitative agreement with experimental results. The model we have proposed yields reasonable "numbers" without invoking a variety of other contributing factors. Adherence to the diffusion model, however, produces difficulties in this respect. One such problem is the observation that the diffusion coefficient of alkali ions in the surface region of a glass can be three orders of magnitude larger than that for the bulk. Diffusion model proponents attribute this to the presence of a "swollen" surface layer, in which, ostensibly, the barrier to diffusion is lowered. From simple diffusion theory [9] one can calculate that the lattice would have to "swell" by a factor of more than thirty in order to account for such an increase in diffusion coefficient. On the other hand, the large electric fields present in the surface region can readily induce ion drift velocities ($v = \mu E$) corresponding to those observed experimentally.

Models are useful in that they allow us to conceptualize and test hypotheses related to physical phenomena. However, they cannot be held inviolate when they cease to provide the right answers. Professor Boksay quotes Aristotle to the effect that a true conclusion may be drawn from a false premise. With respect to the simple diffusion model, we believe, following Euripides (Aeolus, fragment 32), that a bad beginning makes a bad ending.

References

1. Z. BOKSAY, *J. Mater. Sci.* **15** (1980) 2398.
2. W. M. MULARIE, W. F. FURTH and A. R. C. WESTWOOD, *J. Mater. Sci.* **14** (1979) 2659.
3. H. N. STEIN, *Adv. Coll. Int. Sci.* **11** (1979) 76, 95.
4. R. J. CHARLES, *J. Electrochem. Soc.* **116** (1969) 1514.
5. Z. BOKSAY, G. BOUQUET and S. DOBOS, *Phys. Chem. Glasses* **9** (1968) 69.
6. R. W. DOUGLAS and T. M. M. EL-SHAMY, *J. Amer. Ceram. Soc.* **50** (1967) 1.
7. J. M. HORN, Jr. and G. Y. ONODA, Jr., *J. Amer. Ceram. Soc.* **61** (1978) 523.
8. A. MANY, Y. GOLDSTEIN and N. B. GROVER, "Semiconductor Surfaces" (North Holland Publishing Company, Amsterdam, 1965) Ch. 4.
9. B. I. BOLTAKS, "Diffusion in Semiconductors" (Academic Press, New York and London, 1963) ch. II.

Received 30 April
and accepted 9 May 1980

W. M. MULARIE
Central Research Laboratories,
3M Company,
St. Paul, Minnesota, 55101, USA
W. F. FURTH
A. R. C. WESTWOOD
Martin Marietta Laboratories,
Baltimore, Maryland, 21227, USA

On the region I in superplasticity

In several investigations of superplasticity at low strain rates, a region (region I) characterized by high n value and diffusivity equal to that for lattice self-diffusion, was reported [1–3]. The deformation in region I is accompanied by lower elongation to fracture [4, 5] and grain boundary sliding contribution to the total strain [6] than in region II.

Microstructural investigations reveal [7] that all the features characteristic to region II are also present during deformation in region I with the addition that more grain growth occurs. More grain growth in this region is understandable considering the longer test times involved at these low strain rates.

Arieli and Mukherjee [8] have shown for a Zn–22% Al eutectoid alloy that the high n and diffusivity values in region I are only apparent

0022–2461/80/092401–02$02.20/0