Kinetics of solid state reactions with a positive feedback between the reaction and fracture

2.* The kinetics of ion exchange in an alkaline-silicate glass

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The kinetics of ion exchange of Na^+ for Li^+ in an alkaline-silicate glass in a salt melt containing Li^+ were studied in the temperature range from 180 to 250 °C. The results obtained (the reaction front rate and the fragment size of the fractured product) were compared with the predictions of the previously suggested quantitative model. Theoretical predictions differ from the experimental data by less than 30%.

Key words: alkaline-silicate glass, ion exchange, kinetics of ion exchange, product morphology, fracture front, quantitative model.

Chemical reactions occurring in solid phases are often accompanied by mechanical fracture of the reagents. This phenomenon is caused by the relaxation of mechanical stress, which generally appears during reactions in solid phases due to the mismatch between the structures or molar volumes of the products and reagents. The consequences of stress relaxation, in the general case manifested as structural defects (point defects, dislocations, pores, cracks), change the physicochemical properties of reagents and probably affect the reactivity of solids in the reactions.[2] This phenomenon may be the major factor governing the spatial organization of a process and its macrokinetics.[3,4]

Solid phase reactions involving liquid or gas phases are accelerated as the specific surface of the solid reagent increases, which occurs upon fracture. Such reactions differ according to the type of changes in the volume or in the structure of the solid phase. The most favorable conditions for nucleation and propagation of cracks are created in reactions which cause stretching stress in the reaction zone.[5] Hindrance to the formation of cracks in the reaction zone with compressing stress can bring about a complete change in the relaxation mode to plastic deformation or give rise to specific fracture, which results from nonuniformities of the reaction zone or commensurability of the sizes of the reaction zone and the reacting solid. In this case, fracture does not give rise to such definite feedback localized in the reaction zone as that appearing upon fracture caused by stretching stress in the reaction zone. Therefore, at this stage we are considering reactions occurring with a decrease in the solid phase volume.

Previously,[1] we suggested a model of steady-state kinetics of the decomposition of a solid compound to solid and gaseous products with a decrease in the solid phase volume. The assumptions used in the model included the infinitness and isotropy of the reacting specimen, the equality of the mechanical characteristics of the solid reagent and the product, the absence of structural transformations in the solid phase, and the planar geometry of the reaction front.

In the present work aimed at the experimental verification of the model mentioned above, we studied the ion exchange of Na^+ for Li^+ in an alkaline-silicate glass, which occurs upon immersion of the glass into a salt melt containing Li^+ ions at temperatures below the beginning of glass softening. It is known[6] that an alkaline-silicate glass is a three-dimensional polymer formed by the SiO_2 and CaO oxides. An alkali metal oxide modifies the polymer structure by introducing $—O^-$ "tails" at which the alkaline metal ions are localized. It is also known that the reaction under consideration is accompanied by a decrease in the glass volume, which occurs only due to the shrinkage of the polymer network formed by SiO_2 and CaO. The mechanical properties of the glass virtually do not change upon ion exchange, since they are determined by the polymer network. The condition of glass electroneutrality during the exchange makes it sufficient to consider only one of the two metals for the description of their mutual diffusion in the glass and their surface exchange, as their concentrations supplement each other to a constant value. Given the absence of the Na^+ ions in the melt and a constant melt composition, the surface reaction can be represented as desorption similar to the process considered in the model[1]

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* For Part 1, see Ref. 1.

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$Na^+(glass) \rightarrow Na^+(melt)$

with an effective rate constant *k*.

This process totally complies with the conditions of the model:[1] the reaction scheme is analogous to that considered in the model, the solid phase volume decreases as the reaction proceeds, stress relaxation occurs by brittle fracture, the reagent is isotropic and has almost constant mechanical characteristics, and structural transformations are absent. In addition, the crack geometry in this reaction is very similar to that described in the model: the fragments of the fractured product have the form of plates (Fig. 1).

Experimental

Glass of the mass composition ~77% SiO_2, ~8% CaO, and ~15% Na_2O was used as 1.2 mm-thick plates. The exchange reaction was carried out in a melt of a mixture whose composition was close to the eutectic (~60 mol.% of $LiNO_3$ and ~40 mol.% of $CsNO_3$). It was found preliminarily that the participation of Cs^+ ions in ion exchange can be neglected in the temperature range studied.

The change in glass volume on complete exchange of Na^+ for Li^+ was found by hydrostatic weighing of the specimens in CCl_4 before and after the reaction.

The reaction kinetics were studied in the temperature range from 180 to 250 °C. The degree of conversion was determined from the mass change of specimens exposed to the salt melt for various periods of time. In addition, the position of the fracture front was monitored by optical microscopy.

The size of fragments of the exchange product was determined by measurement of the specific surface and from electron microphotographs of the exchange product.

Results and Discussion

Our experiments showed that the mass change of the specimens when the reaction goes to the end (~75 mg per 1 g of the starting specimen mass) corresponds to total replacement of the Na^+ ions in the glass by Li^+.

The reaction involves an induction period, during which no fracture occurs, while the exchange rate gradually decreases. A comparison of the specimen mass during the induction period with the effective depth reached by the exchange reaction shows that the reaction depth is ~1 μm at all temperatures studied. When fracture starts, the reaction accelerates and reaches a steady-state mode, in which the fracture front moves at a constant rate, and its position visible through an optical microscope is related to the degree of conversion.

Let us focus on the process which occurs during the induction period. According to the model described in Ref. 1, the relative concentration of Li^+ ions in the glass, $C(x,t)$, obeys the diffusion equation

$$C_t = DC_{xx}$$

with the boundary condition describing a surface reaction (an infinite semi-space is considered),

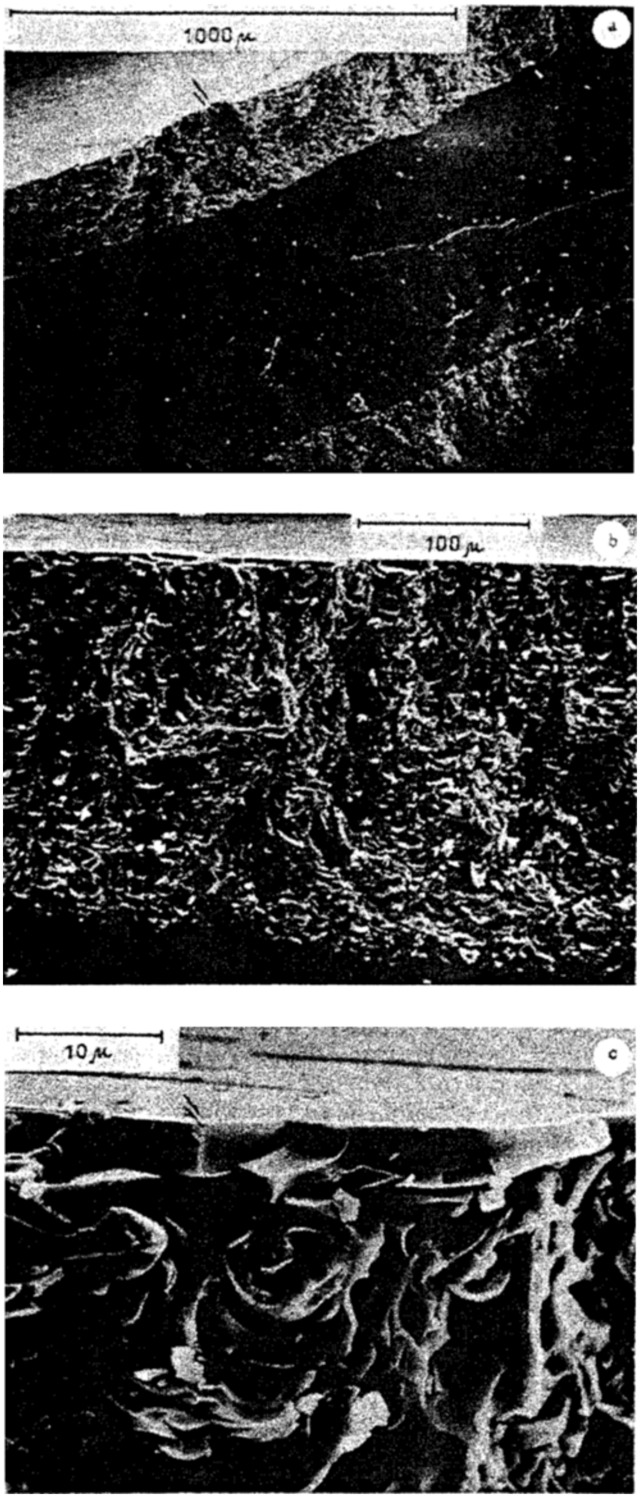

Fig. 1. Morphology of an ion exchange reaction product: *a*, position of the reaction front in a glass specimen subjected to ion exchange; *b*, *c*, detailed picture of the morphology of the ion exchange reaction product.

$$DC_x = k(C-1) \text{ (at } x = 0)$$

and the starting condition

$$C(x) = 0 \text{ (at } t = 0).$$

The solution of this problem has the form

$$C(x,t) = erfc(x/2(Dt)^{1/2}) - \exp(k^2t/D + kx/D)erfc(x/2(Dt)^{1/2} + k(t/D)^{1/2}). \qquad (1)$$

The mass change of the specimen corresponding to this profile (taking the two reacting sides of a plane specimen into account) can be obtained by integrating Eq. (1) over x:

$$M = (2M_0D/kd)(erfc(k(t/D)^{1/2})\exp(k^2t/D) - 1 + 2k(t/\pi D)^{1/2}), \qquad (2)$$

where M_0 is the change in the specimen mass upon reaction completion, and d is the specimen thickness. Let us analyze Eq. (2) in two limiting cases. At $k(t/D)^{1/2} << 1$, one obtains a linear time dependence

$$M = 2M_0kt/d. \qquad (3)$$

This is the case when the process is limited by a surface reaction.

At $k(t/D)^{1/2} >> 1$, diffusion is the limiting stage, and the time dependence of mass assumes the form

$$M = (4M_0/d)(Dt/\pi)^{1/2}. \qquad (4)$$

It is easy to find the relation between these limits and those considered in the model. In both cases, their meaning is to determine the limiting stage of the reaction. The similar meaning of the corresponding limits is clear if one notices that $k(t/D)^{1/2} = k(Dt)^{1/2}/D$ and that $(Dt)^{1/2}$ is the characteristic width of the diffusion profile. It is evident that the induction period corresponds to the first cycle of diffusion, stress accumulation in the near-the-surface glass layer, and its relaxation through fracture. This cycle does not differ essentially from the subsequent cycles, which constitute the observed steady-state reaction mode and are described in the model. Hence, if the reaction kinetics during the induction period are described by Eq.s (3) or (4), the kinetics during the steady-state period should be described by Eq.s (5) or (6), respectively.

According to the model,[1] the kinetics have two characteristic modes determined by the dimensionless quantity kh_0/D, where $h_0 = 36(1-\nu)\gamma\alpha/(1+\nu)E\beta^2$ is the characteristic size of the system, $\alpha = 1 + 2h/L$ is a correction factor which accounts for the finite longitudinal size of the specimens, and L is the characteristic size of the plates that are splitting off. In the limit $kh_0/D >> 1$

$$h = 3.6h_0, \; Vh/D = 5.6, \qquad (5)$$

where $V = h/\tau$ is the mean rate of fracture front movement. Evidently, in this mode $kh/D >> 1$, *i.e.*, the reaction in a split-off plate is limited by diffusion.

In the limit $kh_0/D << 1$

$$h = 2.2h_0^{1/3}(D/k)^{2/3}, \; Vh/D = 3.9. \qquad (6)$$

In this mode we have $kh/D << 1$. This means, on the contrary, that the reaction in the plate is limited by the surface stage.

It is seen in electron microphotographs (see Fig. 1) that the product fragments split off after the induction period (a distinct surface layer) are shaped as perfect plates. Moreover, we calculated (similarly to the calculation performed in the model) the critical moment of time after which splitting-off is possible, and the corresponding critical fragment thickness for stress distribution determined by concentration profile (1). It was found that the results differed from those obtained in the model by no more than a few percent. Thus, the induction period should almost not differ from the subsequent reaction and fracture cycles, and the study of its kinetics should give unambiguous information about the subsequent reaction.

However, one of the conditions for the induction period is not fulfilled. The original glass surface does not contain a sufficient number of stress concentrators, so fracture cannot start instantly on reaching the critical state; it is necessary that cracks be nucleated. This implies that fracture will occur after a delay. This delay will cause thickening of the stressed layer, and hence thicker plates will be split off, this effect being considerable for short delays. It is evident in the photographs (see Fig. 1) that the plates close to the surface are about twice as thick as those that are deeper. We calculated the thickness of plates split off after various delays (the calculation is not presented here). According to the calculation, such thickening can be caused by a delay by ~20% of the critical time, while the diffusion profile becomes longer by only ~10%. Despite the complication due to an undetermined fracture delay during the induction period, its analysis can still provide some information on the mode of the reaction and fracture; at least, the D and k values can be obtained.

Studying the reaction kinetics during the induction period showed that a linear dependence of the degree of conversion (mass change) on the time to the power 1/2 is observed in the entire temperature range (Fig. 2). This result corresponds to limit (4) ($k(t/D)^{1/2} >> 1$). This made it possible to determine the diffusion coefficient at various temperatures and its activation energy, which was found to be ~95±6 kJ mol^{-1} (Fig. 3).

In addition, according to the above considerations, the kinetics during the induction period implies the limit $kh_0/D >> 1$, which has been considered in the model and which corresponds to the situation in which diffusion is the limiting step of a reaction in the bulk with characteristic size h_0. This limit is characterized by the

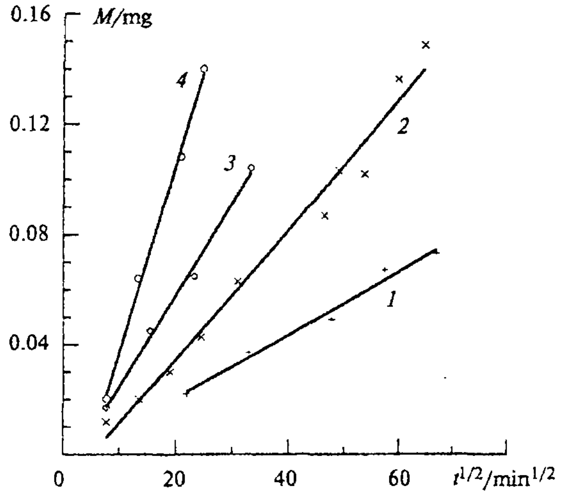

Fig. 2. Reaction kinetics during the induction period at 180 (*1*), 200 (*2*), 225 (*3*), and 250 (*4*) °C.

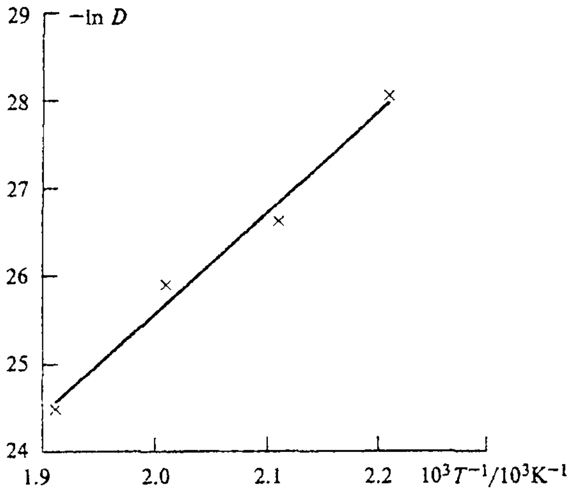

Fig. 3. Temperature dependence of the diffusion coefficient of ions in the glass.

temperature-independent thickness of split-off plates, which is $h = 3.6h_0$. Microscopic observations and specific surface measurements show that the fracture pattern is the same in the entire temperature range studied, namely, the shape of the fragments is close to plates with a thickness of $h \approx 1.5$—2 μm. This fact agrees qualitatively with model predictions in the case $kh_0/D >> 1$. A quantitative comparison of the experimental data with the theory will be based on the literature data:[6] Young's modulus of alkaline-silicate glass is $E = 6.5 \cdot 10^{11}$ dyne cm^{-2}, the Poisson modulus is $\nu = 0.23$, and the surface energy of fracture for quasisteady-state cracks in the glass (in the absence of the Rebinder effect) is γ = 2000—3000 erg cm^{-2}. Measurement of the change in glass volume after reaction completion gave the value of bulk shrinkage, $\beta = 0.05$. The photographs allow one to estimate the correction factor α. It is seen that the ratio of the longitudinal plate size to its thickness is $h/L \approx 5$, hence $\alpha = (1 + 2h/L) \approx 1.4$. On the other hand, $h_0 \approx$ 0.4—0.6 μm. Thus, taking the mean values of h and h_0 into account, we obtain $h \approx 3.5h_0$ with an error within 30%. Evidently, the thickness of the plates split off in the course of the reaction is fairly well described by the model.[1]

Let us now consider the steady-state reaction regime, which starts from the onset of fracture. The steady-state rates of the fracture front at various temperatures were determined on the basis of the slopes of linear time dependences of the specimen mass (Fig. 4). The activation energy of the movement rate (Fig. 5) was found to be ~90±6 kJ mol^{-1}. One can see that the activation energy of the front movement rate and that of

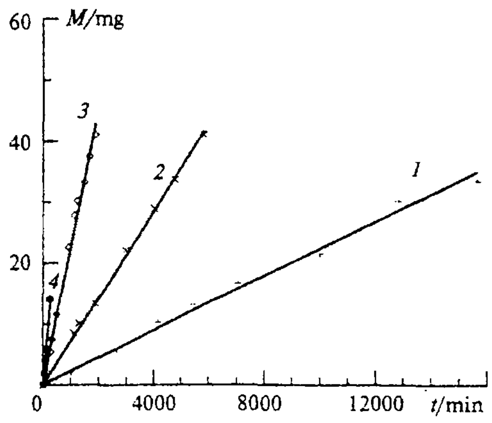

Fig. 4. Steady-state kinetics of the ion exchange reaction at 180 (*1*), 200 (*2*), 225 (*3*), and 250 (*4*) °C.

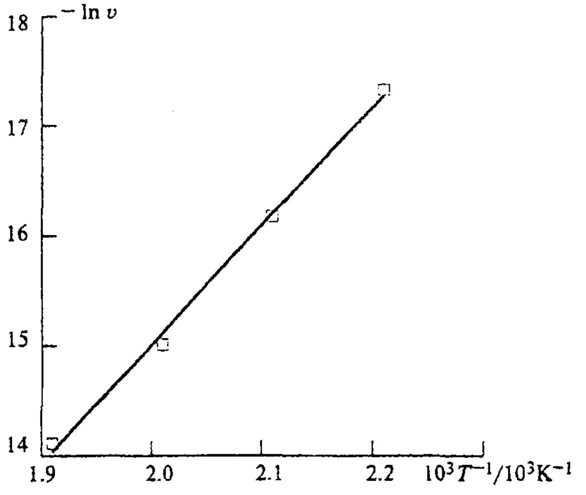

Fig. 5. Temperature dependence of the reaction front movement rate.

ion diffusion in the glass are in fair agreement, which is qualitatively confirmed by the expression $v = 5.6D/h \approx 1.6D/h_0$ given by the model for the $kh_0/D >> 1$ case. The D/v ratio for the temperature range used in the experiment was found to be ~0.25±0.05 μm. Thus, the experiments gave $vh/D = 7\pm2.4$. This result demonstrates a good quantitative agreement between the model and experiment (see Eq. (5)).

Thus, the reaction studied made it possible to conclude that the model is adequate in one of the two limiting cases. To consider the same reaction in the other limit ($kh_0/D << 1$), one can use the method which involves decreasing the effective rate constant of a surface reaction, k. This can be achieved by decreasing the Li^+ concentration in the melt, since k is proportional to it. With this purpose, we conducted qualitative experiments, in which a molten mixture of $Ca(NO_3)_2$ (~40 mol.%) and $CsNO_3$ (~60 mol.%) was doped with a small amount of $LiNO_3$ (~1%) and the reaction was carried out at 300 °C. The size of the product fragments that formed due to fracture was ~50 μm. This agrees qualitatively with the model, since it predicts an increase in the fragment size with decreasing kh_0/D. According to the model, $h/h_0 \sim 1/(kh_0/D)^{2/3}$ at $kh_0/D << 1$ (see Eq. (6)). Thus, the kinetics of the reaction studied agrees with the model of the feedback between the reaction and fracture.

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