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Anion distribution in alkaline silicates

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Alkaline sodium silicates have been prepared by heating sodium carbonate and silica mixtures in the mole ratio of 2·5:1.

The silicates have been examined by chronopotentiometric and thermogravimetric methods. The electro-analytical technique has allowed the identification of the oxy-anions SiO_4^{4-}, $Si_2O_7^{6-}$ and $Si_3O_{10}^{8-}$ by their electro-reduction at cathodic potentials with reference to a graphite anode of approximately −1·0, −1·6, −2·0 V respectively.

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1. Introduction

Although it has been possible to obtain quantitative data of chain length distribution in phosphate glasses by chromatography [1, 2], the examination of silicates has proved more difficult. Recently, gas chromatographic methods have been developed for silicate glasses, using trimethylsilyl derivatives of silicate anions [3, 4]. Molten phosphates have been examined by electro-analytical techniques [5, 6] and it was decided to apply this method to a molten silicate system. The present paper deals with the examination of sodium silicates with metal oxide contents in excess of 60%. In this region it would be expected that the majority of anions present would be SiO_4^{4-} and $Si_2O_7^{6-}$.

2. Experimental

2.1. *Preparation of sodium silicates*

Anhydrous Analar sodium carbonate was mixed with precipitated silica in the molar proportions of 2·5:1 [7]. The mixture was placed in a platinum crucible and heated in a furnace under normal atmospheric conditions. For initial experiments the mixture was heated for 4 h at 900°C. Further samples were prepared at 1100°C and the heating time varied between 1 and 28 h. After the reaction, the molten mixture was quenched by pouring on to an aluminium plate and then stored in a desiccator over magnesium perchlorate.

2.2. *Chronopotentiometry of silicate solutions*

The silicates were added to an equimolar mixture of sodium chloride and potassium chloride to the extent of 4–10% by weight. The mixture was placed in a graphite crucible which acted as the macro-anode; a 1 mm tungsten rod was used as the micro-cathode. Using this enclosed electrolysis cell (Fig. 1), constant current electrolysis was carried out using a stabilized voltage supply and a standard high resistance box in series with the cell.

In chronopotentiometry, the changing potential of the micro-electrode (in this case the cathode) at constant current density is plotted as a function of time. For linear diffusion of electro-active species, the transition time (τ) is related to the other variables in the system by the relationship

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}nF\pi^{\frac{1}{2}}D^{\frac{1}{2}}C \qquad (1)$$

where i is the current density; C is the initial concentration of reducible species; D is the diffusion coefficient of the reducible species; and n is the number of electrons involved in the unit electrode reaction.

At a fixed temperature, the value of $i\tau^{\frac{1}{2}}$ varies with the concentration only. The changing potential was displayed on a Tektronix Oscilloscope 564.

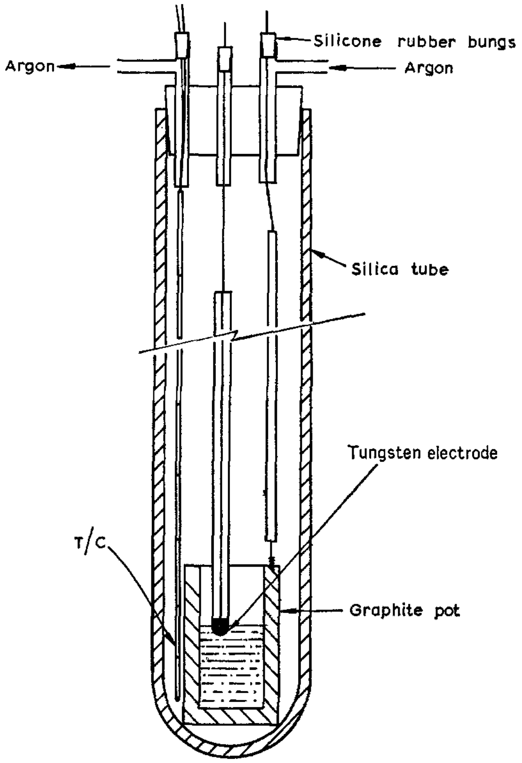

Fig. 1. Electrolysis cell.

2.3. *Thermogravimetric measurements*

The weight losses occurring in the reaction between the sodium carbonate and silica were examined by two methods. In one series of measurements, the reaction mixture was heated in a Stanton Redcroft Thermobalance and the weight changes determined over the temperature range, ambient to 1000°C.

In the other series of experiments, the sodium carbonate was heated in the furnace at 1100°C to determine the decomposition occurring in the absence of silica. Samples were then made up in the 2·5 : 1 ratio as above and heated at 1100°C for times between 1 h and 6 h. The weight changes were determined for each sample.

3. Results and discussion

3.1. *Chronopotentiometry in molten halides*

The sodium silicate prepared by heat treatment at 900°C was made into a 10% solution in the halides and the electrolysis examined over the temperature range 660–800°C.

At 660°, three transitions occurred at potentials with reference to the graphite anode of about −1·0, −1·6, and −2·0 V. When the temperature of the melt was raised, the transition time due to the third process was reduced and at 780°C only the first two transitions were found.

Comparing these results with those for the phosphate system [5, 6], it was considered that the two processes corresponded to the reduction of the oxy-anions $\mathrm{SiO_4}^{4-}$, $\mathrm{Si_2O_7}^{6-}$ respectively. Excess sodium carbonate could lead to the removal of the trisilicate by the process

$$\mathrm{Si_3O_{10}}^{8-}+\mathrm{CO_3}^{2-} = \mathrm{SiO_4}^{4-}+\mathrm{Si_2O_7}^{6-}+\mathrm{CO_2} \tag{2}$$

When the sodium silicates prepared at 1100°C were examined, only the first two transitions were observed, even at the lowest halide melt

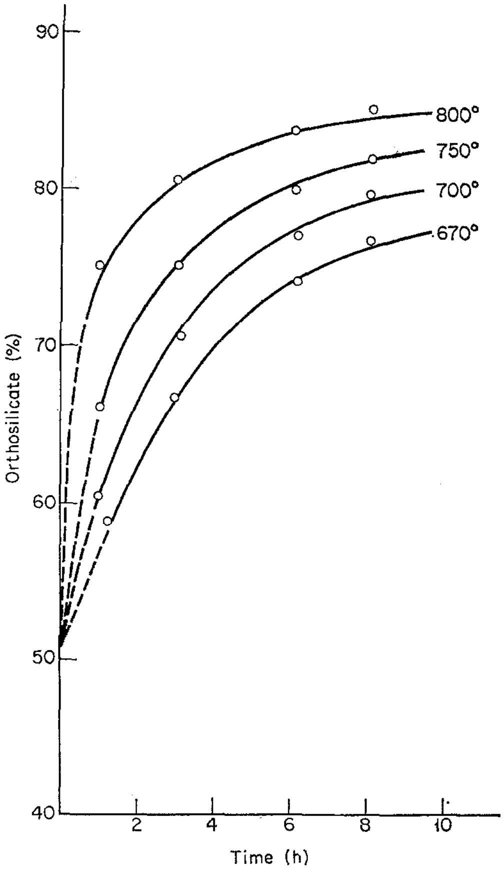

Fig. 2. Variation of the percentage orthosilicate with time in NaCl–KCl solvent.

temperatures employed. In addition, it was found that the ratio between the transition times varied as the experiments continued. If the silicate was left in the melt for a few hours at a fixed temperature, the first transition time increased. Consequently, for each sample, transitions were determined at fixed time intervals and the composition of the initial silicate solution was estimated by extrapolation to zero time. Typical values are shown in Fig. 2. The increase in orthosilicate would be expected from a reaction similar to that shown in Equation (2) above. That is,

$$Si_2O_7{}^{6-} + CO_3{}^{2-} = 2SiO_4{}^{4-} + CO_2 \qquad (3)$$

On the basis of the temperature effect, the reaction should be endothermic.

Using heats of formation [8] of the compounds involved, a value of +27 kcal is obtained, whereas for a reaction of the type

$$O^{2-} + Si_2O_7{}^{6-} = 2SiO_4{}^{4-} \qquad (4)$$

a value of -49 kcal would be expected.

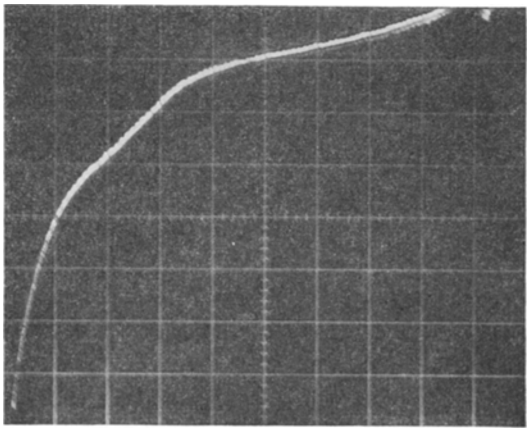

Fig. 3. Chronopotentiogram for two electro-active species heated at 1100°C for 4 h and dissolved in NaCl–KCl at 870°C. (Vertical axis 0·2 V cm^{-1}.)

When silicate heated for 28 h was examined, it only gave the first transition at a cathodic potential of $-1{\cdot}0$ V. Typical chronopotentiograms are shown in Figs. 3 and 4.

3.2. *Electrode reactions*

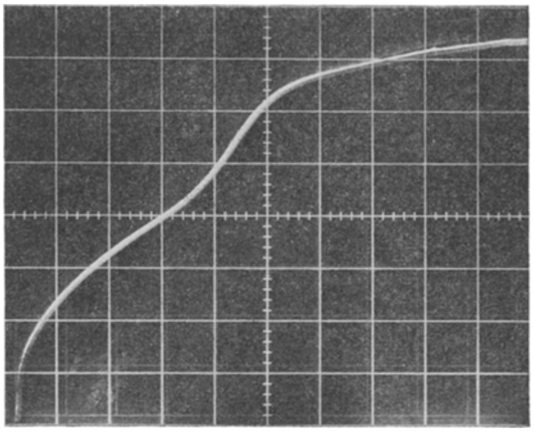

Fig. 4. Chronopotentiogram for a sample heated at 1100°C for 28 h and dissolved in NaCl–KCl at 870°C. (Vertical axis 0·2 V cm^{-1}.)

In order to estimate the respective concentrations of the ortho- and pyrosilicate ions, it is necessary to obtain the value of the number of electrons exchanged in the reduction reaction (n in Equation (1) above). This can be determined for the first transition by examining the change in electrode potential E_t with time t. For a reversible process involving soluble products and soluble reactants, the relationship obtained is

$$E_t = E_{\tau/4} - \frac{RT}{nF} \log_e \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \qquad (5)$$

A reversible process involving insoluble products gives the relationship

$$E_t = \text{constant} - \frac{RT}{nF} \log_e \tau^{\frac{1}{2}} - t^{\frac{1}{2}}$$

and an irreversible process gives the relationship

$$E_t = \text{constant} - \frac{RT}{\alpha nF} \log_e \tau^{\frac{1}{2}} - t^{\frac{1}{2}}$$

Where $E_{\tau/4}$ is the quarter-wave potential (E_t at $t = \tau/4$) and α is less than unity.

The results are plotted in Fig. 5 and indicate a reversible reaction with two electrons transferred. It is known that electro-reduction of silicates produces silicon as a cathode product and this was confirmed in the present work using molten sodium disilicate. The current was adjusted to maintain the cathode potential between $-1{\cdot}0$ V and $-1{\cdot}3$ V with respect to the graphite anode i.e. so that only the process corresponding to the first transition would occur.

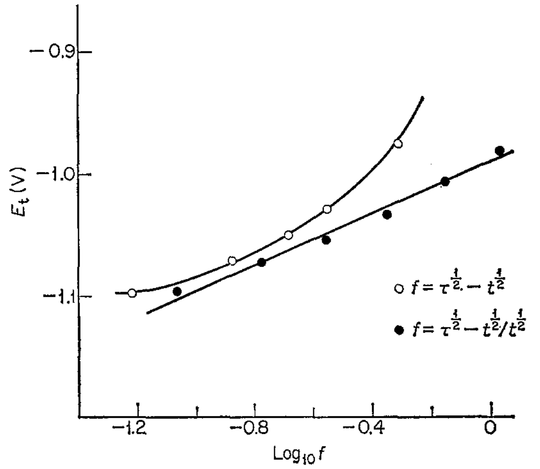

Fig. 5. Plots of E_t versus $\log_{10}\tau^{\frac{1}{2}}-t^{\frac{1}{2}}/t^{\frac{1}{2}}$ and $\log_{10}\tau^{\frac{1}{2}}-t^{\frac{1}{2}}$

Thus for the reduction of the orthosilicate ion, silicon production would correspond to the overall reduction process

$$SiO_4{}^{4-}+4e = Si+4O^{2-} \qquad (6)$$

On the basis of the above chronopotentiometric considerations, the oxidation state of the product arising during the chronopotentiometric current pulse is two. This oxidation state is known in silicon monoxide. The following reduction mechanism is therefore suggested

(i) Electroreduction $SiO_4{}^{4-}+2e = SiO_2{}^{2-}+2O^{2-}$

(ii) Decomposition $2SiO_2{}^{2-} = SiO_4{}^{4-}+Si$

which corresponds to the overall reaction (Equation 6).

If it is assumed that in the chronopotentiometric reduction of the pyrosilicate ion, the silicon oxidation state likewise changes from four to two; the n value for the pyrosilicate would be four as there are two silicon atoms in this ion. The concentrations of the two electroactive species can then be determined from the transition times τ_1 and τ_2^* (1 = orthosilicate, 2 = pyrosilicate) using the equations,

$$i\tau_1{}^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}}n_1FD_1{}^{\frac{1}{2}}C_1 \qquad (7)$$

and

$$i(\tau_2{}^{\frac{1}{2}}-\tau_1{}^{\frac{1}{2}}) = \tfrac{1}{2}\pi^{\frac{1}{2}}n_2FD_2{}^{\frac{1}{2}}C_2 \qquad (8)$$

Using the values $n_1 = 2$ and $n_2 = 4$ and assuming D_1 and D_2 are similar, the ratios of C_1 to C_2, can be determined from the transition times. The metal oxide to silica ratio (R) can then be calculated for the silicate since C_1 is equivalent to $2Na_2O.SiO_2$ and C_2 is equivalent to $3Na_2O.2SiO_2$. Thus R would be given by $(2C_1+3C_2)/(C_1+2C_2)$. By extrapolating to zero time, the R values were obtained for the series of samples heated in the furnace at 1100°C. The results are shown in Fig. 6.

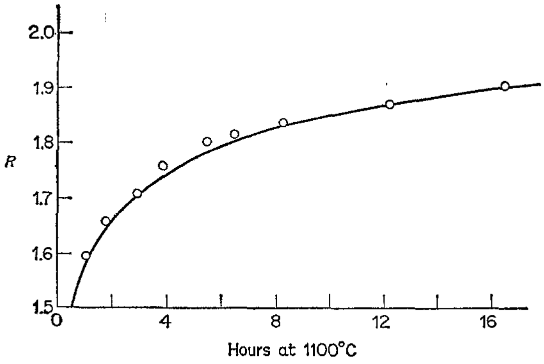

Fig. 6. Silicate composition–variation with time in the furnace at 1100°C.

3.3. *Thermogravimetric results*

Using the thermobalance, it was found that the reaction between the sodium carbonate and silica did not start until the temperature reached

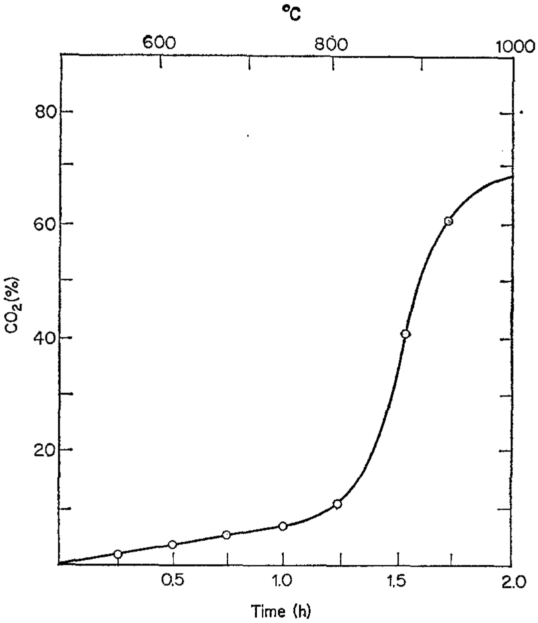

Fig. 7. Thermobalance results.

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* Measured from the *start* of the charging cycle.

500°C. In the temperature range 500–800°C, a slow reaction occurred; this became rapid after about 820°, corresponding to the formation of a molten phase. The weight changes are illustrated in Fig. 7.

When the sodium carbonate was heated alone at 1100°C, a loss of about 1% per hour occurred. This was taken into account when determining the weight loss due to reaction in the mixed sodium carbonate and silica samples. For a final silicate composition of $R\mathrm{Na_2O.SiO_2}$, the reaction can be expressed as

$$2{\cdot}5\mathrm{Na_2CO_3}+\mathrm{SiO_2} = R\mathrm{Na_2O}\,.\,\mathrm{SiO_2}+R\mathrm{CO_2}+(2{\cdot}5-R)\,\mathrm{Na_2CO_3} \qquad (9)$$

Table 1. Variation of R value with time of heating at 1100°C

Heating time (hours)	*R values* Chronopotentiometric	Thermogravimetric
1	1·58	1·55
2	1·67	1·65
3	1·70	1·70
4	1·74	1·75
5	1·78	1·80
6	1·80	1·81

The results obtained, for samples heated between 1 and 6 h, are shown, together with those calculated by chronopotentiometry, in Table 1. The close agreement between these results gives us confidence in the calculations based on transition times.

3.4. *Reaction in molten halides*

The increase in R value of the silicate with time and temperature in the molten halides can be compared with that for the reaction occurring in the furnace (Equation (9)). Using the values shown in Fig. 2, the variations can be indicated (Table 2). The reaction rate is increased in the molten halides despite the lower temperature. This would be expected on the basis of the much lower viscosity of the molten halides compared with that of the sodium carbonate-silicate mixture in the furnace. Increases in the velocity constant with temperature in the halide mixture can be estimated from the initial slopes of the curves in Fig. 2 and an activation energy for the reaction calculated. Results are shown in Table 3 and Fig. 8. These give an activation energy of 23 kcal mole^{-1}.

Table 2. Variation of R value with temperature of molten halide. (Initial R value = 1·67)

Temperature (°C)	*R value after 6 h*
670	1·80
700	1·82
750	1·85
800	1·87

Table 3. Variation of velocity constant with temperature

Temperature (°C)	$\frac{1000}{T}$	*Relative slope (k)*	$\log_{10} k$
670	1·06	5·0	0·699
700	1·03	6·4	0·806
750	0·98	11·0	1·041
800	0·93	21·5	1·332

4. Conclusions

Alkaline silicates have been dissolved in molten chloride–potassium chloride and ortho-, pyro-

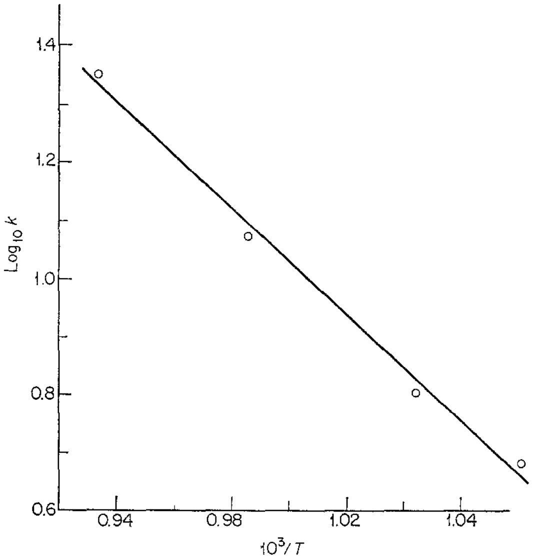

Fig. 8. Plot of $\log_{10}k$ versus the reciprocal temperature.

and trisilicate ions identified by means of chronopotentiometry. This method of examination should also apply to the more acid glassy silicates and it is proposed to use the method both for halide solutions and for the molten glass themselves.

The reduction of the orthosilicate oxy-anion was found to be a two-electron process. On the basis of the agreement between the chronopotentiometric and thermogravimetric measurements, it is suggested that in the electro-reduction of the pyrosilicate the oxidation state of the silicon is likewise reduced from four to two.

In preparing the sodium orthosilicate from a mixture of sodium carbonate and silica, the *R* values increased with time of heating at 1100°C. The increase occurred at a faster rate when the silicate—sodium carbonate mixture was dissolved in molten sodium chloride—potassium chloride, even when the temperatures were as low as 700°C.

Acknowledgments

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