

Fig.2. The average radius of the crystals as a function of time.

continued for a longer time this deviation is found to diminish. Hence, Eqn. (10) gives the rate of change of the radii of the particles if the experiment is carried out for a sufficiently long time.

Todes¹ obtained the following asymptotic expression for the change in the average concentration with time:

$$\bar{c} - c_{\infty} = a \sqrt[3]{\frac{Dn c_{\infty}}{\rho}} t \quad (11)$$

where a is a dimensionless constant equal to ~ 0.9 . A comparison of (11) with (9) shows how the average radius varies with time, viz.,

$$\bar{R}(t) = \frac{1}{a} \sqrt[3]{\frac{Dn c_{\infty}}{\rho}} t \quad (12)$$

Values of $\bar{R}$ as a function of $t^{1/3}$, calculated from the data used in drawing the curve in Fig. 1, are shown in Fig. 2, and it is seen that they exhibit a good linear relationship.

Todes¹ showed that $\bar{R}^3 \propto t$. For this reason, it is found that $\bar{R}^3$ and $(\bar{R}^3)$ vary with time in the same way in the growth process under investigation. Experimental confirmation of this could justify to a certain extent the hypothesis put forward by Todes¹ that the function for the distribution of particles according to size remains similar throughout the process.

SUMMARY

1. During the recrystallisation of particles suspended in a stationary medium and evenly distributed, crystals, for which $R = \bar{R}$ at any given time, do not alter in size, while those for which $R = 2\bar{R}$ have the maximum rate of growth.
2. The average radius of the particles is proportional to the cube root of the time. These results agree well with experimental data.

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THEORY OF THE GLASS ELECTRODE

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The first version (simple theory) of the ion-exchange theory of the glass electrode postulates constancy of the activity coefficients and the same strength of bonding in the glass for cations of each type regardless of the degree of their exchange for cations of another type¹. With these assumptions, the theory leads to the following expression relating the glass electrode potential to the activities of H^+ and M^+ ions in solution:

$$\varphi = \varphi_0 + \theta \log(a_H + K a_M), \quad (1)$$

where $\theta = 2.303 RT/F$. In Eqn. (1) the constant K is defined by

$$K = \frac{a_H N_M}{a_M N_H}, \quad (2)$$

which expresses the ion-exchange equilibrium between the glass and the solution¹. Eqn. (1) reflects the fact that under appropriate conditions the glass electrode is reversible with respect to the hydrogen ions ($\varphi = \varphi_0 + \theta \log a_{H^+}$) or to metal ions ($\varphi = \varphi_0' + \theta \log a_{M^+}$), and also gives the potential in the transition region between the two types of electrode function (Figure, curves 1a and 1b). However, the transition in reality takes place more smoothly (over a wider pH range) than would appear from this equation.

To explain the discrepancy between the theory and experiment, it was suggested that the bonds involving cations in the glass structure are inhomogeneous (generalised theory). Some consequences of this hypothesis were examined in Ref. 2 and led to the following expression for the glass electrode potential:

$$\varphi = \varphi_0 - \theta \log \sum_i \frac{\alpha_i \beta_i}{a_{H^+} + \alpha_i K a_M} \quad (3)$$

In the derivation of Eqn. (3) it was assumed that the activities of the ions in the glass (a_H and a_M) are additive functions of their "partial activities" corresponding to structural units of the glass with different bond strengths, and that each partial cationic activity can be represented by a product of the concentration N_i of these ions and a constant α_i characterising the bond strength of the ion in the i -th group:

$$a_H = \sum_i \alpha_i^H N_i^H; \quad a_M = \sum_i \alpha_i^M N_i^M = \sum_i \alpha_i^H (N_i^H - N_i^H) \quad (4)$$

In Eqn. (4) N_i^0 denotes the total number of cationic sites in the i -th bond group. Obviously, $N_i^0 = N_i^H + N_i^M$. In Eqn. (3) $\beta_i = N_i^0/N_i^H$.

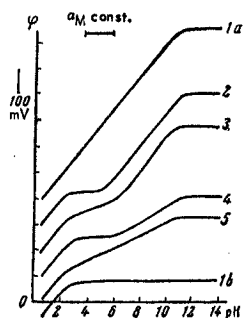
The generalised glass electrode theory, expressed by Eqn. (3), led to satisfactory agreement with experiment over the entire pH range investigated, including the transition region where the glass electrode ceases to be reversible with respect to hydrogen ions and becomes reversible with respect to sodium ions. Furthermore, this theory predicts the possible existence of electrode glasses which would yield a "stepwise" variation of the potential with pH. We were in fact able to observe such variation experimentally for a number of glasses³ (Figure, curve 2).

In recent years many experimental data have accumulated, permitting a more profound analysis of the postulates of the theory. Experiment shows, for example, that one may expect the formation in the glass structure of various anionic groups, differing by many powers of ten as regards their strength of bonding with hydrogen ions (strongly acid and weakly acid anions). It was therefore desirable to derive new equations based on the idea of different degrees of dissociation of the ionogenic groups ("acids" and "salts") in the glass structure, which are in ion-exchange equilibrium with the solution. In particular, we may reject the earlier arbitrary hypothesis about the ionic activities in the glass phase [Eqns. (4)], and replace it by postulates based on the Law of Mass Action.

We shall assume that there are n groups of anions (R_i^-) in the glass structure, differing in their strength of bonding with H^+ and M^+ ions. As in the simple theory, we obtain the initial expression for the glass electrode potential:

$$\varphi = \varphi^0 + 0.059 \log \frac{a_H}{N_H} = \varphi^0 - 0.059 \log \frac{N_{R-}}{a_H + K a_M} \quad (5)$$

In the simple theory it was assumed that the concentration of the free anions in the glass is constant: $N_{R-} = N_H + N_M = \text{const}$, which leads to Eqn. (1). However, if the ionogenic groups are incompletely dissociated, the concentration of the anions in the glass will depend on the relative content of the H^+ and M^+ ions in the glass and consequently, in view of Eqn. (2), the concentration N_{R-} will be a function of the activities of these ions (a_{H^+} and a_{M^+}) in solution.



Variation of the glass electrode potential with the pH for various special cases of the theory:

1) complete dissociation of the ionogenic groups in the glass — Eqn. (1) [(a) $K \approx 10^{-10}$; (b) $K \approx 10$]; 2), 3), and 4) two ionogenic groups — Eqns. (3) and (14) with various combinations of the constants α_1 , α_2 , β , and K ; 5) one incompletely dissociated ionogenic group with a large difference between k^H and k^M — Eqn. (16).

Thus the problem reduces to finding an explicit function of the concentration N_{R-} in terms of a_{H^+} and a_{M^+} . This function can be deduced if it is remembered that part of the H^+ and M^+ ions are firmly combined with anions in the glass, the others being present in the dissociated state ("solvated" ions in the glass phase). For each group of anions we can write the following dissociation equilibria of the ionogenic groups of the glass (HR_i and MR_i):

$$k_i^H = \frac{N_H N_{R_i^-}}{N_{HR_i}}, \quad k_i^M = \frac{N_M N_{R_i^-}}{N_{MR_i}}, \quad (6)$$

where $N_{R_i^-}$ and N_{HR_i} , N_{MR_i} are the concentrations of the free and bound anions of the i -th group in the glass, and N_H and N_M are the concentrations of the "free" H^+ and M^+ ions in the glass phase, which we took to be equal to their activities a_H and a_M . Taking into account Eqn. (2), we obtain from (6)

$$\frac{N_M}{N_H} = \frac{N_{MR_i}}{\alpha_i N_{HR_i}} = \frac{K a_M}{a_H}, \quad (7)$$

where $\alpha_i = k_i^H/k_i^M$ is the equilibrium constant of the homogeneous double-decomposition reaction in the glass: $M^+ R_i^{g1} + H^+ R_i^{g1} = H^+ R_i^{g1} + M^+ R_i^{g1}$. Rearrangement of Eqn. (7) leads to the following expression for the ratio of the ionic activities in the glass and in the solution:

$$\frac{N_H}{a_H} = \frac{N_M}{K a_M} = \frac{N_{R-}}{a_H + K a_M}, \quad (8)$$

where $N_{R-} = \sum_{i=1}^n N_{R_i^-}$ is the total concentration of all the free anions in the glass, equal to the sum of the concentrations of the free (dissociated) H^+ and M^+ ions:

$$N_{R-} = N_H + N_M.$$

For the total concentration of free anions in the glass, we can write

$$N_{R-} = \sum_{i=1}^n N_{R_i^-} = \frac{1}{N_H} \sum_{i=1}^n k_i^H N_{HR_i}. \quad (9)$$

Remembering that the total concentration of the i -th group of anions in the glass is given by $N_i^0 = N_{HR_i} + N_{MR_i} + N_{R_i^-}$, we obtain, taking into account Eqns. (6), (7), and (8), the following equation for the concentration of H^+ ions in the glass combined with R_i^- :

$$N_{HR_i} = \frac{(N_i^0 - N_{R_i^-}) a_H}{a_H + \alpha_i K a_M} = \frac{N_i^0 N_{R-} a_H}{(A_i N_{R-} + A) k_i^H}, \quad (10)$$

where

$$A_i = (a_H + \alpha_i K a_M) \frac{1}{k_i^H}$$

and

$$A = a_H + K a_M. \quad (11)$$

Substitution of Eqn. (10) in (9), with allowance for (8), yields the expression

$$\frac{N_H}{a_H} = \frac{N_{R-}}{A} = \sum_{i=1}^n \frac{N_i^0}{A_i N_{R-} + A}. \quad (12)$$

whose solution in principle yields N_{R-} as a function of the ionic activities in the solution. Substitution of this in (5) gives the final expression for the glass electrode potential. Since it is impossible to solve the problem in a general form, we shall confine ourselves to certain special cases which have fairly wide application.

1. Complete dissociation of all ionogenic groups. As already stated, Eqn. (1) applies here. It can be readily derived from the general equations (5) and (12), putting $N_{R^-}/k_i^H \ll 1$ and $N_{R^-}/k_i^M \ll 1$, *i.e.* assumptions which have the physical significance of the case under discussion (dissociation constants k_i^H and k_i^M are large) and show the limits of its applicability.

2. Low dissociation of all ionogenic groups. Within the limits of applicability of the conditions $N_{R^-}/k_i^H \gg 1$ and $N_{R^-}/k_i^M \gg 1$, we obtain from Eqns. (5) and (12) the following expression for the glass electrode potential:

$$\varphi = \varphi^0 + \frac{1}{2} \theta \log(a_H + K a_M) - \frac{1}{2} \theta \log \sum_i \frac{N_i^0 k_i^H}{a_H + \alpha_i K a_M}. \quad (13)$$

Investigations of the properties of glasses by different methods show that the hypothesis of the low dissociation of the ionogenic groups is quite likely⁴. In this connection it is of interest to analyse certain consequences of Eqn. (13) for glasses with two groups of anions. Eqn. (13) then takes the following form:

$$\varphi = \varphi^0 + \frac{1}{2} \theta \log(a_H + K a_M) - \frac{1}{2} \theta \log \left(\frac{1}{a_H + \alpha_1 K a_M} + \frac{\beta}{a_H + \alpha_2 K a_M} \right), \quad (14)$$

where

$$\varphi^0 = \varphi^0 - \frac{1}{2} \theta \log N_1^0 \frac{k_1^H}{k_1^M}$$

and

$$\beta = \frac{N_2^0 k_2^H}{N_1^0 k_1^H}.$$

Depending on the numerical values of the constants, K , β , α_1 , and α_2 , defining the properties of the glass, Eqn. (14) can yield different theoretical curves for the variation of the potential with the pH; some of these curves are given in the Figure (curves 3 and 4). The experimental curves which we obtained recently for three-component glasses containing, apart from silica and an alkali metal, a second glass-forming oxide (B_2O_3 , Al_2O_3 , Ga_2O_3 , Fe_2O_3 , ZrO_2 , P_2O_5 , etc) proved in many cases to be similar to curves 3, 4, and 5 in the Figure³.

3. Only one group of anions present in the glass. This corresponds to the simple theory. Eqns. (5) and (12) then give

$$\varphi = \varphi^0 - \theta \log \frac{(A^2 + 4N^0 A A_1)^{1/2} - A}{2A_1 A}, \quad (15)$$

where

$$A_1 = (a_H + \alpha_1 K a_M) \frac{1}{k_1^H},$$

$$A = a_H + K a_M,$$

and

$$\alpha_1 = k_1^H / k_1^M.$$

In the case of complete dissociation ($k^H \gg N_{R^-}$ and $k^M \gg N_{R^-}$) Eqn. (15) reduces to Eqn. (1). For weak dissociation, we have

$$\varphi = \varphi^0 + \frac{1}{2} \theta \log(a_H + K a_M) + \frac{1}{2} \theta \log(a_H + \alpha K a_M), \quad (16)$$

where

$$\varphi^0 = \varphi^0 - \frac{1}{2} \theta \log N^0 \frac{k_1^H}{k_1^M}$$

and

$$\alpha = \frac{k_1^H}{k_1^M}.$$

In agreement with experiment, Eqn. (15) predicts a smooth transition from complete hydrogen ion response to complete metal ion response[†]. When the difference between k^H and k^M is large, the equation yields, for solutions with a constant activity of M^+ ions, φ -pH curves with three linear sections: one with a slope of θ , another with a slope of $\frac{1}{2}\theta$, and a third horizontal (Figure, curve 5). The experimental curves for certain types of glass are indeed of this type.

Application of Eqn. (16) or the most general expressions (5) and (12) to the case where two similar cations ($k^{M'} \approx k^{M''}$) are exchanged in the glass yields a particular solution, expressed by Eqn. (1), which agrees with experiment⁶.

Thus the old and the new generalised theories lead to a variation of the glass electrode potential with the solution composition which is essentially similar in both cases, and which agrees with experiment. However, the details of the new equation are substantially different from those of the old theory. Experiment will establish the limits and conditions of applicability of the various versions of the old and new theories and will suggest further theoretical development.

SUMMARY

New equations for the variation of the glass electrode potential with the activities of ions in solution (H^+ and M^+) have been derived on the assumption of different degrees of dissociation of ionogenic groups in the glass (compounds of H^+ and M^+ cations with various anions in the glass structure), which are in ion-exchange equilibrium with the solution.

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COMBUSTION OF MODEL BINARY OXIDANT-FUEL MIXTURES

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When Ballistite powders burn in a vacuum, the main stages of combustion may be practically completely isolated¹. Depending on the pressure (*in vacuo*, *i.e.* at low pressures) the powder burns without a flame, with a cold

[†] A recent paper⁶ develops a theory of the glass electrode for homogeneous bonding of the cations of the glass, which yields an equation analogous to Eqn. (15). The author of this theory started from the postulates similar to ours for the case where only one group of anions is present in the glass.