

PRE-EXPONENTIAL TERM IN THE ARRHENIUS EQUATION FOR ELECTRICAL CONDUCTIVITY OF GLASS

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Résumé. - Des résultats très précis pour la conductivité électrique pour une série de six verres de composition molaire $25(xNa_2O + (1-x)K_2O) - 5Al_2O_3 - 70SiO_2$ pour $0,95 \leq x \leq 1$ ont été obtenus pour un assez grand intervalle de température ($\sim 310^\circ C$). L'analyse de ces résultats suggère que le terme pré-exponentiel dans l'équation d'Arrhenius pour la conductivité ne dépend pas de la température.

Abstract. - Very precise electrical conductivity data on a series of six glasses of molar composition $25(xNa_2O + (1-x)K_2O) - 5Al_2O_3 - 70SiO_2$ with $0.95 \leq x < 1$ have been obtained over a large temperature range ($\sim 310^\circ C$). Analysis of this data suggests that the pre-exponential term in the Arrhenius conductivity equation is temperature independent.

1. **Introduction.** - Ionic diffusion in glass and ceramics is an activated process usually visualized as jumping of ions over energy barriers.^{1,2} The temperature dependence of the microscopic, mobile species diffusion coefficient D is generally represented by an Arrhenius equation of the form

$$D = (v_0 d^2 / 6) \exp(\Delta S^\ddagger / k) \exp(-\Delta H^\ddagger / kT) \tag{1}$$

where ΔS^\ddagger and ΔH^\ddagger are the activation entropy and enthalpy for the jump of a mobile ion, v_0 the attempt frequency, d the jump distance and k the Boltzmann constant. The electrical conductivity due to an ion of charge e is related to the diffusion coefficient by the Nerst-Einstein equation:

$$\sigma = ne^2 D / kT \tag{2}$$

where n is the concentration of mobile species. These might be, for instance, interstitial ions or ion pairs or vacancies. (The microscopic diffusion coefficient D is related to the experimental ionic self diffusion coefficient D_b by the expression³:

$$nD = n_b D_b / f \tag{3}$$

where n_b is the bulk ionic concentration and f a correlation factor.) The mobile species concentration is given by^{1,2,4}

$$n = n_b \exp(\Delta S_d / 2k) \exp(-\Delta H_d / 2kT) \tag{4}$$

where ΔS_d and ΔH_d are the entropy and enthalpy changes for mobile species formation. Combination of eqs. (1), (2) and (4) gives

$$\sigma = (n_b e^2 d^2 v_0 / 6kT) \exp(\Delta S^* / k) \exp(-\Delta H^* / kT) \tag{5}$$

where $\Delta S^* (= \Delta S^\ddagger + \Delta S_d / 2)$ and $\Delta H^* (= \Delta H^\ddagger + \Delta H_d / 2)$ are the apparent activation entropy and enthalpy.

A number of expressions have been proposed for the attempt frequency v_0 . In the simplest case, which we shall term the simple jump theory, v_0 is assumed to be temperature dependent, so that

$$v_0 = \text{constant} \quad (6a)$$

In the transition state theory of Eyring and coworkers⁵ it is presumed that the attempt frequency represents a fully excited vibrational degree of freedom, so that

$$v_0 = kT/h \quad (6b)$$

where h is Planck's constant. Finally, following the approach of Cohen and Turnbull⁶, one might imagine that the ion moved about its cage of neighboring atoms with the velocity of an ideal gas molecule. This kinetic theory then gives

$$v_0 = \bar{c}/2d = (8kT/\pi M)^{1/2}/2d \quad (6c)$$

where \bar{c} is the mean velocity of a gas particle of mass M and d the diameter of the cage (presumably approximately the same as the jump distance). Substituting eqs. (6) into eq. (5) gives the functional form of the temperature dependent conductivity:

$$\sigma = (B/T^m)\exp(-\Delta H^*/kT) \quad (7)$$

where B is a constant, and m is 1, 0 or 1/2 for respectively the simple jump, transition state and kinetic theory expressions for v_0 .

Equation (7) predicts that an Arrhenius plot of $\ln(\sigma T^m)$ (or, via eqs. (2) and (3), a plot of $\ln(D_b T^{m-1})$) should be linear in $1/T$. The temperature dependence of σ is dominated by the exponential term in eq. (7), and the influence of the pre-exponential T^{-m} term is extremely weak. The claim is usually made^{7,8} that, given limitations in the range and precision of the σ vs. T (or D_b vs. T) data, one cannot tell what value of m gives the most linear Arrhenius plot. We ourselves were unable to find any ceramic or glass ionic diffusion or conduction data of sufficient precision to allow accurate assessment of the value of m in eq. (7). One case is known of diffusion of an inert gas, He, in vitreous SiO_2 in which the data do allow an assessment of m ; in this instance a value of $m=0$ (corresponding to an attempt frequency v_0 proportional to T , as in Eq. (6b)) gives the best description of the temperature dependence of D_b .^{9,10} We report here some recent glass electrical conductivity results which appear to be of sufficient precision to allow accurate assessment of the pre-exponential temperature term in eq. (7).

2. Experimental Results and Discussion. - Electrical conductivity measurements over the temperature range -11 to 300°C were carried out on a series of six glasses of molar composition $25(x\text{Na}_2\text{O} + (1-x)\text{K}_2\text{O}) - 5\text{Al}_2\text{O}_3 - 70\text{SiO}_2$ with $0.95 \leq x < 1$. In this temperature-composition range the concentration and mobility of K^+ ions is extremely low, so that these glasses are Na^+ ion conductors. The real parts of the complex conductivity σ' and dielectric constant ϵ' of the glasses were measured as a function of frequency. The bulk glass d.c. electrical resistivity $\rho (=1/\sigma)$ was obtained by casting the data into the form of complex resistivity ρ^* and extrapolating the bulk glass ρ^* arc to zero frequency.^{11,12} More complete details on experimental procedure are published elsewhere.^{12,13} The overall precision of our σ vs. T results is 2% or better.

To assess the contribution of the pre-exponential temperature term to the overall temperature dependence of σ , we wrote eq. (7) in logarithmic form:

$$\ln \sigma = \ln B - m \ln T - \Delta H^*/kT \quad (8)$$

Two parameter linear least squares fits of the data to eq. (8) were carried out for fixed values of $m = -1, -1/2, 0, 1/2$ and 1. In addition a three parameter fit (to determine the best fit values of $\ln B$, m and ΔH^*) was carried out in each case. The goodness of the fit was expressed in terms of the standard deviation $SD \ln \sigma$ from the least squares line:

$$SD \ln \sigma = [\sum (\Delta \ln \sigma)^2 / N]^{1/2} \quad (9)$$

where $\Delta \ln \sigma$ is the deviation of a data point from the line and N the number of data

points.

In Fig. 1 Arrhenius plots of $\log \sigma$ and $\log(\sigma T)$ are shown along with the least squares lines for, respectively, $m = 0$ and 1 for one of our glasses. When the data are plotted on this scale no differences in the linearity of the $\ln \sigma$ and the $\ln(\sigma T)$ plots are apparent. The situation becomes clearer in Fig. 2, where we have plotted the deviations $\Delta \ln \sigma$ from the least squares lines versus temperature for m values of $1, 0$ and -1 for two of our glasses. For the single alkali glass ($x = 1.00$) the deviations from the best fit line are small and random for $m = 0$, while they are considerably larger and systematic for $m = -1$ and 1 . For the mixed alkali glass ($x = 0.95$) the fit using $m = 0$ gives more scatter than for the single alkali glass $m = 0$ fit, but the $m = 0$ fit is still markedly better than the $m = 1$ fit and marginally better than that for $m = -1$.

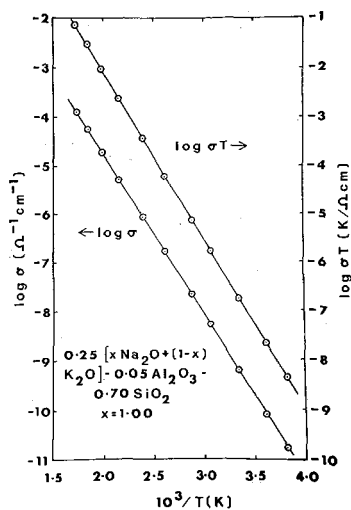


Fig. 1: Arrhenius plots of $\log \sigma$ and $\log(\sigma T)$ vs. $1/T$ for alkali aluminosilicate glass.

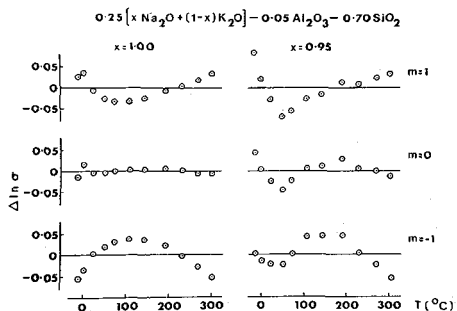


Fig. 2: Deviations as a function of temperature of $\ln \sigma$ from least squares lines obtained from fits to eq. (8) for $m = -1, 0$ and 1 .

In Table I we have summarized the standard deviations for all our computer fits. The m values which give the best fits lie in the range -0.34 to 0.11 , and $100 \text{SD} \ln \sigma$ for the best fit m is generally consistent with our estimate of a precision of 2% or better in the σ vs. T data. (Note that since $d \ln \sigma = d\sigma/\sigma$, $100 \text{SD} \ln \sigma$ is the root mean square percentage deviation of the points from the least squares line.) Of the m values for which there is a theoretical basis ($m = 0, 1/2$ and 1) the fit for $m = 0$ is the best in all cases, and $100 \text{SD} \ln \sigma$ for $m = 0$ differs negligibly from that for the best fit m . The sensitivity of $100 \text{SD} \ln \sigma$ to the choice of m is sufficient that we may say with confidence that the value $m = 1$ is definitely inconsistent with the data for all of the glasses and that the value $m = 1/2$ is inconsistent with the data for the first three glasses ($x = 1.00, 0.99$ and 0.98).

TABLE I. Root mean square percentage deviations of electrical conductivity of $25(x\text{Na}_2\text{O}+(1-x)\text{K}_2\text{O})-5\text{Al}_2\text{O}_3-70\text{SiO}_2$ glasses from least squares fits to eq. (8) for different values of m .

x	100SD% σ					Best fit
	$m = -1$	$m = -1/2$	$m = 0$	$m = 1/2$	$m = 1$	
1.00	3.2	1.8	0.8	1.3	2.6	0.7($m=0.11$)
0.99	2.6	1.5	1.2	2.2	3.5	1.2($m=-0.17$)
0.98	2.6	1.8	2.0	2.9	4.2	1.8($m=-0.34$)
0.97	2.9	2.1	2.2	2.9	4.1	2.0($m=-0.27$)
0.96 (Run 1)	3.3	2.6	2.6	3.3	4.3	2.5($m=-0.25$)
0.96 (Run 2)	3.5	2.7	2.5	3.1	4.0	2.5($m=-0.13$)
0.95 (Run 1)	3.1	2.5	2.6	3.4	4.5	2.5($m=-0.33$)
0.95 (Run 2)	3.1	2.4	2.4	3.1	4.2	2.3($m=-0.24$)

These results thus support the view that the pre-exponential term in the Arrhenius equation for electrical conductivity of glass is temperature independent. This requires in turn, via the Nernst-Einstein equation, a T^1 dependence of the pre-exponential term for the ionic diffusion coefficient, as was also found to be the case for diffusion of He in fused silica. While this result is consistent with the prediction of the transition state theory of an attempt frequency ν_0 proportional to T , its theoretical significance is difficult to judge. The jump model of diffusion, not to speak of the transition state theory, probably considerably oversimplifies the ionic or molecular transport process in glass. Certainly, the present results go no way to answering the criticisms of the transition state theory. An alternative explanation for the non-linearity of the $\ln(\sigma T)$ vs. $1/T$ plots is that there are two ionic transport processes operative in the glass, e.g., a vacancy and an interstitialcy mechanism, as suggested by Lim and Day.¹⁴ If the contribution of each mechanism to $\ln(\sigma T)$ were linear in $1/T$ and if one mechanism dominated the low temperature conductivity while the other was dominant at high temperatures, curvature in the $\ln(\sigma T)$ vs. $1/T$ plots would result. However, it does seem that highly accurate ionic conductivity data for glass should be fitted to an Arrhenius equation with no temperature dependence in the pre-exponential term.

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