# 'Universal' curve of ionic conductivities in glasses

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Glass composition can be varied continuously as compared to crystal, and so does an ionic conductivity, $\sigma$. This difference arises from the flexibility glass has by its disordered structure. At room temperature, $\sigma$ can range from $10^{-1}$ S/cm to less than $10^{-15}$ S/cm with compositions.

Usually, $\sigma$ satisfies the relation

$$\sigma = \sigma_o \exp(-E_a/kT), \qquad (1)$$

where $\sigma_o$ is the pre-exponential factor and $E_a$ is the activation energy for conduction. Many glasses show linearities in the plots of log $\sigma$ versus $1/T$, to give $E_a$. Fig. 1 shows the Arrhenius plots of $\sigma$ for 17 glasses of different compositions, ranging from the so-called 'superionic' glasses to the low-conducting glasses [1–10]. The magnitudes and the slopes are widely dispersed.

Provided the scattered data by glasses of different compositions are unified by a single 'universal' equation or 'universal' curve, we can gain further insight into the nature of ion dynamics in glass. Several trials have been done towards this goal. Swenson and Börjesson [11], for example, proposed the relation

$$\sigma(d)/\sigma(m) \approx ![(V_d - V_m)/V_m]^3 \qquad (2)$$

for superionic (metal halide salt-doped) glasses, where $V_m$ and $V_d$ are the volumes the network forming units (e.g., $B_2O_3$, $P_2O_5$, etc.) span in the salt-undoped and salt-doped glasses, respectively, and $\sigma$ $(d)$ and $\sigma$ $(m)$ are the corresponding ionic conductivities.

For example, consider the $x\mathrm{AgI}(1-x)\mathrm{AgPO}_3$ glasses [12]. By salt doping, the volume which a single $P_2O_5$ unit (or equivalently a single $P$ atom) spans expands from $V_m$ to $V_d$. The ratio $R$ $(=(V_d - V_m)/V_m)$ which characterizes expansion amounts to 120% at $x = 0.55$. The authors claimed that an increase in $\sigma$ by salt doping is caused by 'excess free volume,' originating from expansion of the glass network skeleton.

The present author defined the free volume by [13]

$$V_f = 1 - \pi p n_i (2r_i)^3, \qquad (3)$$

as the volume, in 1 cm$^3$ of a glass, in which no atoms exist, where $n_i$ is the number within 1 cm$^3$ of a glass of atomic species $i$, and $r_i$ is its atomic radius. This is quite a rough approximation, by neglecting ionicity of the glass constituents and the glass structure. Moreover, it varies, depending on the values of $r_i$

chosen. Nevertheless, because of simplicity, it can be a measure of the free volume, at least in the first approximation.

When Equation 3 is used to the alkali borate and silicate glasses, $V_f$ decreases almost linearly with an increase in alkali content. Besides, the concentration of the network forming atoms (i.e., boron and silicon) decreases in near parallel [13]. This suggests that alkali addition causes disruption and accompanying expansion of the network structure, and that added alkali oxide enters into the voids which the network provides and decrease $V_f$. That is, the (macroscopically defined) free volume decreases while $\sigma$ increases with an increase in alkali content.

For the $x\mathrm{AgI}(1-x)\mathrm{AgPO}_3$ glasses, on the other hand, no drastic change in $V_f$ is seen with salt doping (Fig. 2). Similar indifference of $V_f$ to salt doping was already reported for the $x\mathrm{AgI}(1-x)\mathrm{Ag}_4\mathrm{P}_2\mathrm{O}_7$ glasses [13]. These data imply that the doped salt, in contrast to doped alkali oxide into borate and silicate glasses, does not disturb the composition and structure of the mother glass, but enters into glass as another phase having a similar free volume. (This does not necessarily mean that the doped salt composes the microdomains [14]. There have been oppositions [15, 16] against the microdomain model.) In other words, although the $\mathrm{AgPO}_3$-rich phase expands and the ratio $R$ increases by salt doping, the free volume does not expand. Therefore, Equation 2 should be explained not in terms of 'excess free volume,' but by other (unknown) mechanism.

More recently, Adams and Swenson [17] presented the relation

$$\log(\sigma T) \approx \& F^{1/3} \qquad (4)$$

which they claimed would be held by any ionic conductors including crystals and molten salts, where $F$ is the volume fraction of infinite pathway clusters as estimated from the reverse Monte Carlo produced structural model using the bond-valence sum calculation technique. Equation 4 can be the 'universal' relation provided it is verified at different temperatures other than the room temperature used. Also, they should explain why the ordinate is $\log(\sigma T)$, not log $\sigma$, and why the abscissa is $F^{1/3}$, not $F$.

As discussed above, extensive studies have recently been made for obtaining a 'universal' equation from the standpoint of the glass structure, but the goal seems still out of sight. Formally, however, a 'universal' curve could be drawn quite simply. Fig. 3 shows the plots of
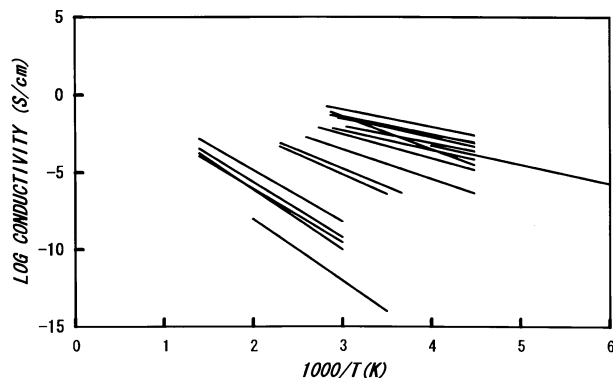
Figure 1 Arrhenius plots of ionic conductivities for 17 different glasses. The data were taken from [1–10].
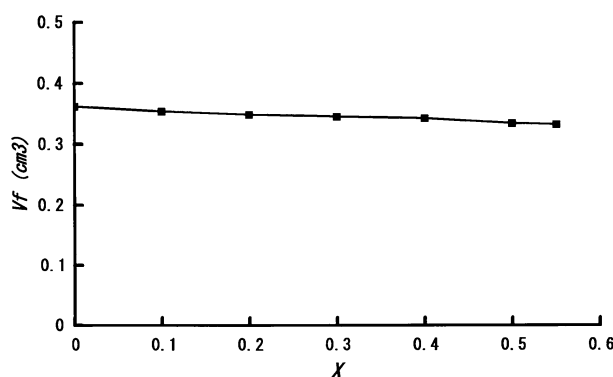


Figure 2 Free volume, $V_f$, as a function of AgI content, $x$, in the $x$AgI$(1 − x)$AgPO$_3$ glasses, as estimated using the densities reported [12].
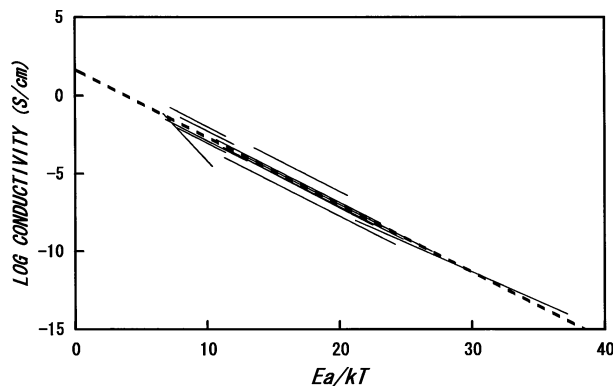


Figure 3 Arrhenius plots of ionic conductivities for 17 different glasses of Fig. 1, where the abscissa is given by $E_a/kT$ in place of $1/T$. The dashed line is a 'universal' curve, Equation 5.

log àè for 17 different glasses of Fig. 1 as a function of $E_a/kT$, not as a function of $1/T$. The data fit an 'universal' relation

$$\text{àè}(S/cm) = 50 \exp(-E_a/kT) \qquad (5)$$

within one order of magnitude of dispersion.

Ionic conduction in glass is the thermally activated process of the mobile ions by surmounting a potential barrier $E_a$. The pre-exponential factor is usually given by [18]

$$\text{àè}_o = ne^2 \text{àã}^2 \text{àç}/\text{àã}kT, \qquad (6)$$

where $n$ is the number density of the mobile ions, àã is the average jump distance, àç is the local vibrational frequency of the ions, and àã is the number of possible jump directions. It is plausible, therefore, that àè$_o$ varies with glass compositions and àè deviates a little from Equation 5. Equation 5 implies that àè has an upper limit, 50 S/cm. Truly, the ionic conductivities of many ion-conducting glasses as well as their super-cooled liquids seem to converge to 100 S/cm or less with increasing temperatures to infinity [19]. For e.g., the Na$_2$O-2B$_2$O$_3$ glass, àè$_o$, calculated from Equation 6 using the nominal density of the sodium ions of $1.4 \times 10^{22}$ cm$^{-3}$, àç of $7.0 \times 10^{12}$ Hz [20], and on the assumption of homogeneous distribution of the mobile sodium ions, is $3.5 \times 10^2$ S/cm which is a little larger than the observed, 38.3 S/cm [9] or 110 S/cm [21]. As far as Equation 6 is correct, this difference infers that the fraction of overall sodium ions which can contribute to àè is only 3æS or less.

Statistical-mechanically, the conductivity should be given in the form like Equation 1, provided ionic conduction is the thermally activated process [22]. The fact that àè lies on the single 'universal' curve (within scatters of one order of magnitude) for many ion-conducting glasses means that àè is governed mainly by $E_a$. Therefore, if we measure àè at some temperature, we can estimate $E_a$ from Equation 5, and we can have a rough sketch of àè at different temperatures. Or, if $E_a$ is obtained by some experimental or theoretical technique, ionic conductivity can be calculated. Theoretical estimation of $E_a$ was done first by Anderson and Stuart [23].

## References

1. D. KUNZE, in "Fast Ion Transport in Solids," edited by W. van Gool (North-Holland Publ., Amsterdam, 1973) p. 405.
2. T. MINAMI, H. NAMBU and M. TANAKA, J. Amer. Ceram. Soc. **60** (1977) 467.
3. R. J. GRANT, M. D. INGRAM, L. D. S. TURNER and C. A. VINCENT, J. Phys. Chem. **82** (1978) 2838.
4. J. P. MALUGANI, A. WASNIEWSKI, M. DOREAU and G. ROBERT, Mater. Res. Bull. **13** (1978) 1517.
5. C. LIU, H. G. K. SUNDAR and C. A. ANGELL, ibid. **20** (1985) 525.
6. A. DOI and S. MARUNO, J. Mater. Sci. **21** (1986) 1863.
7. J. KAWAMURA and M. SHIMOJI, J. Non-Cryst. Solids **88** (1986) 281.
8. A. DOI, J. Mater. Sci. **24** (1989) 749.
9. A. DOI and K. WATANABE, Solid St. Ion. **104** (1997) 215.
10. A. DOI, J. Appl. Phys. **86** (1999) 2655.
11. J. SWENSON and L. BÖRJESSON, Phys. Rev. Lett. **77** (1996) 3569.
12. J. P. MALUGANI and R. MERCIER, Solid St. Ion. **13** (1984) 293.
13. A. DOI, J. Non-Cryst. Solids **246** (1999) 155.
14. R. MERCIER, M. TACHEZ, J. P. MALUGANI and C. ROUSSELOT, Mater. Chem. Phys. **23** (1989) 13.
15. S. ADAMS and J. MAIER, Solid St. Ioni. **105** (1998) 67.
16. J. SWENSON, R. J. McGREEVY, L. BÖRJESSON and J. D. WICKS, ibid. **105** (1998) 55.
17. S. ADAMS and J. SWENSON, Phys. Rev. Lett. **84** (2000) 4144.
18. A. E. OWEN, in "Progress in Ceramic Science," Vol. 3, edited by J. E. Burke (Pergamon, New York, 1963) p. 84.

19. A. DOI, *Solid St. Ion.* **107** (1998) 81.
20. E. I. KAMITSOS, G. D. CHRYSSIKOS and M. A. KARAKASSIDES, *Phys. Chem. Glasses* **29** (1988) 121.
21. A. DOI, *Solid State Ion.* **109** (1998) 279.
22. A. B. LIDIARD, in "Handbuch der Physik," Vol. 20 (Springer, Berlin, 1957) p. 275.
23. O. L. ANDERSON and D. A. STUART, *J. Amer. Ceram. Soc.* **37** (1954) 573.