Advanced Vitreous State - Physical Properties of Glass

Lecture 26: Charge Conduction Properties of Glass:

Ionic Conduction in Glass - Part 2

Activation Energies in Glass

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Binary Alkali Silicate Glasses

- Addition of Na_2O Increases the ionic conductivity, decreases the electrical resistivity

- Increasing the temperature increases the ionic conductivity, decreases the ionic resistivity

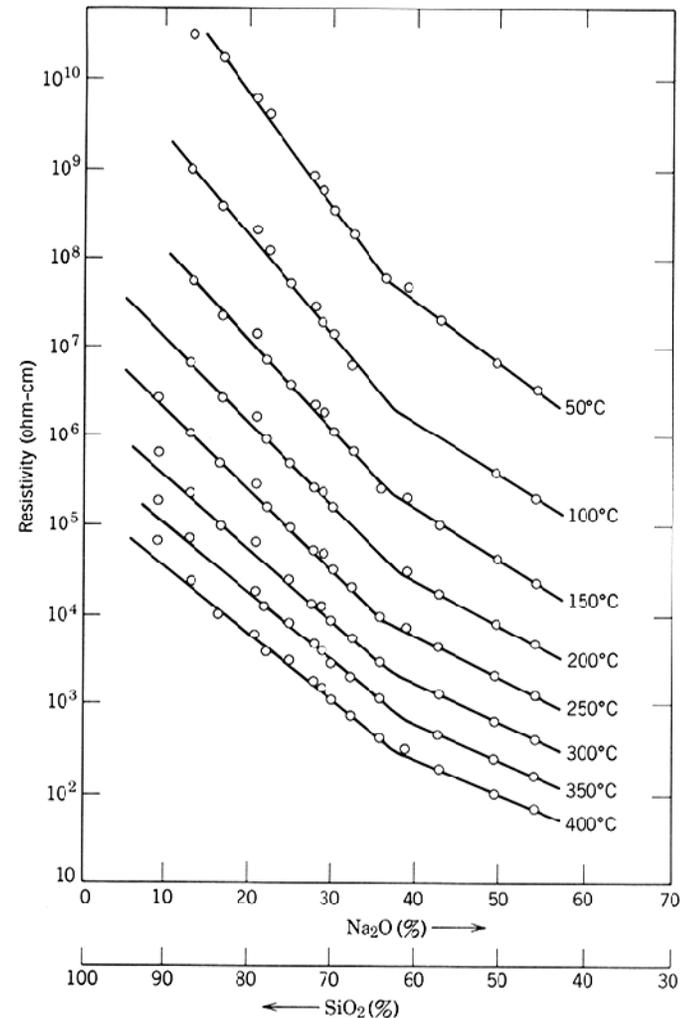- Ionic conductivity of soda glasses is still very low except for the highest temperatures

Fig. 17.17. Conductivity of glasses in the system Na_2O–SiO_2. From E. Seddon, E. J. Tippett, and W. E. S. Turner, *J. Soc. Glass Technol.*, 16, 950 (1932).

DC ion conductivity in glass

- xLi$_2$O + (1-x)P$_2$O$_5$
- Creation of non-Bridging oxygens
- "Mobile" lithium ions
- The higher the concentration of Li$_2$O, the higher the conductivity
  - Lower resistivity
- Activation energy decreases with Li$_2$O content
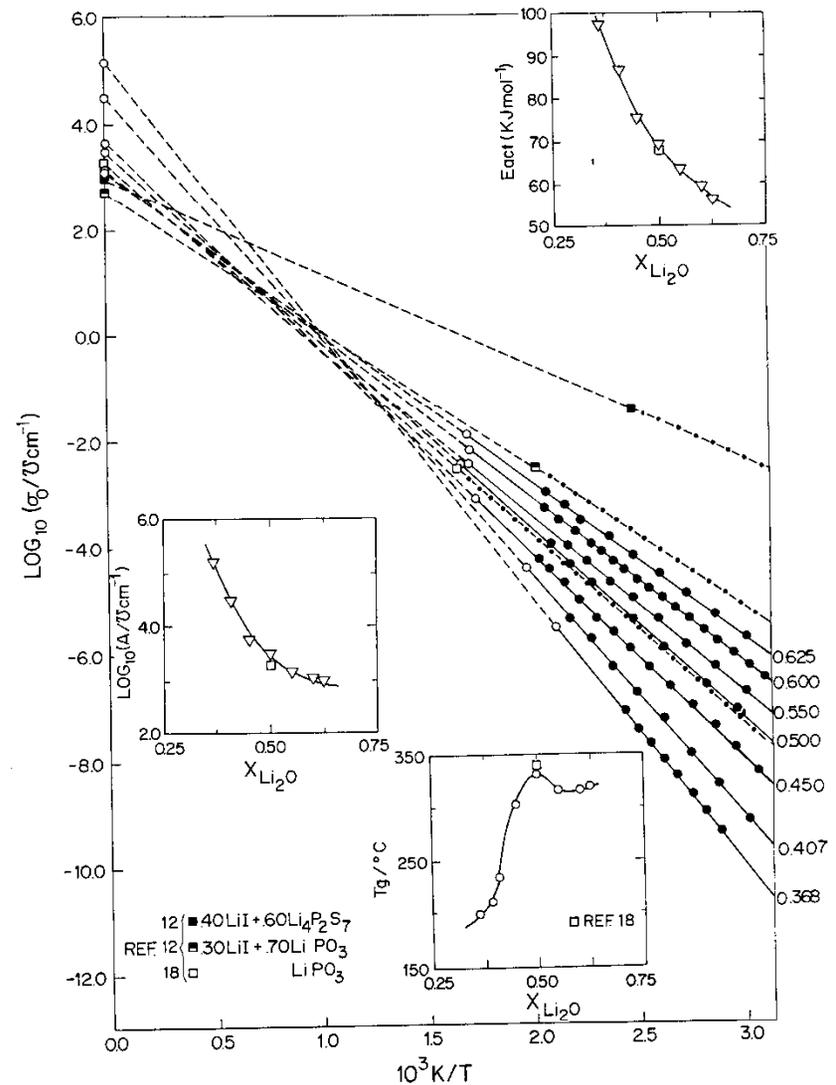
Composition Dependence of the Conductivity

- Binary lithium phosphate glasses, $Li_2O + P_2O_5$, are relative poor ion conductors

- Binary lithium borate glasses, $Li_2O + B_2O_3$, are slightly better conductors

- Binary lithium silicate glasses, $Li_2O + SiO_2$ are slightly better conductors yet.

$Li_2O:P_2O_5$

$Li_2O:B_2O_3$

$Li_2O:SiO_2$
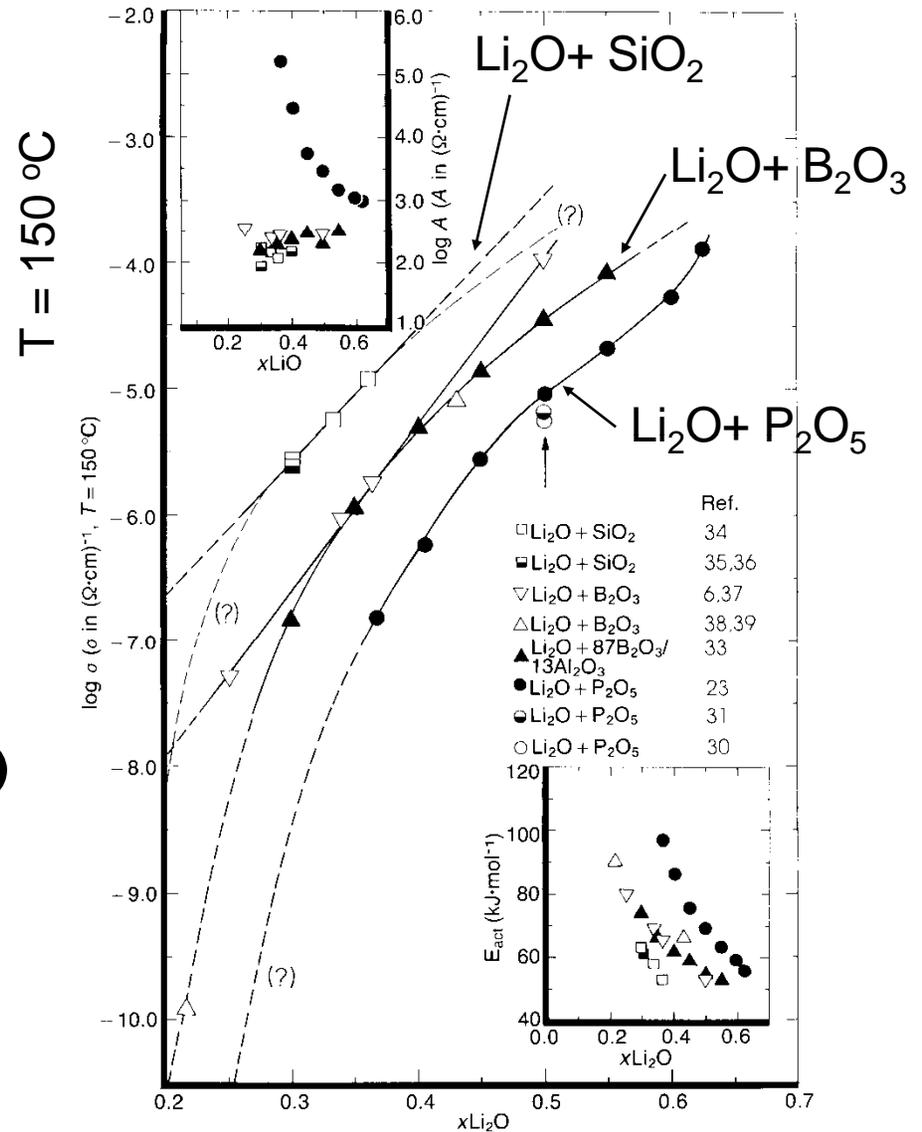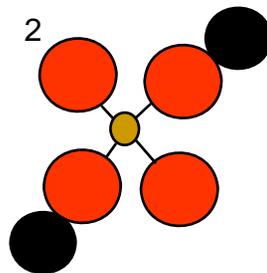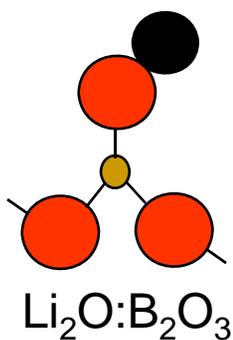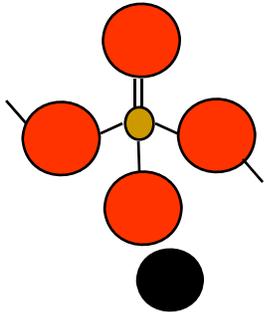
Salt doped phosphate glasses

- Halide doping strongly increases the conductivity
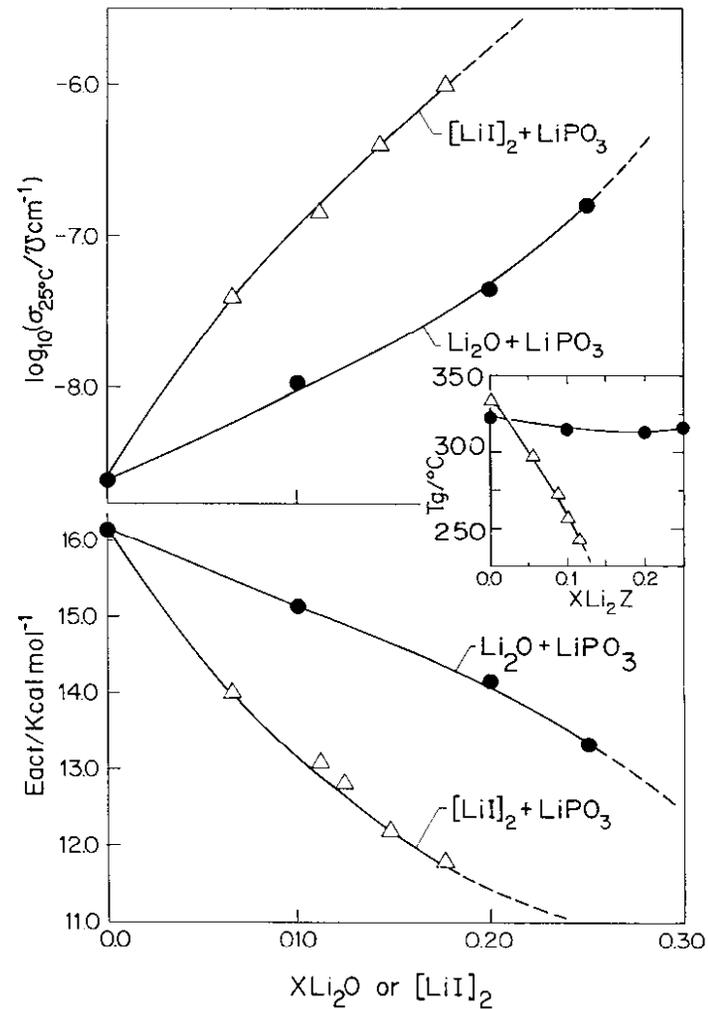
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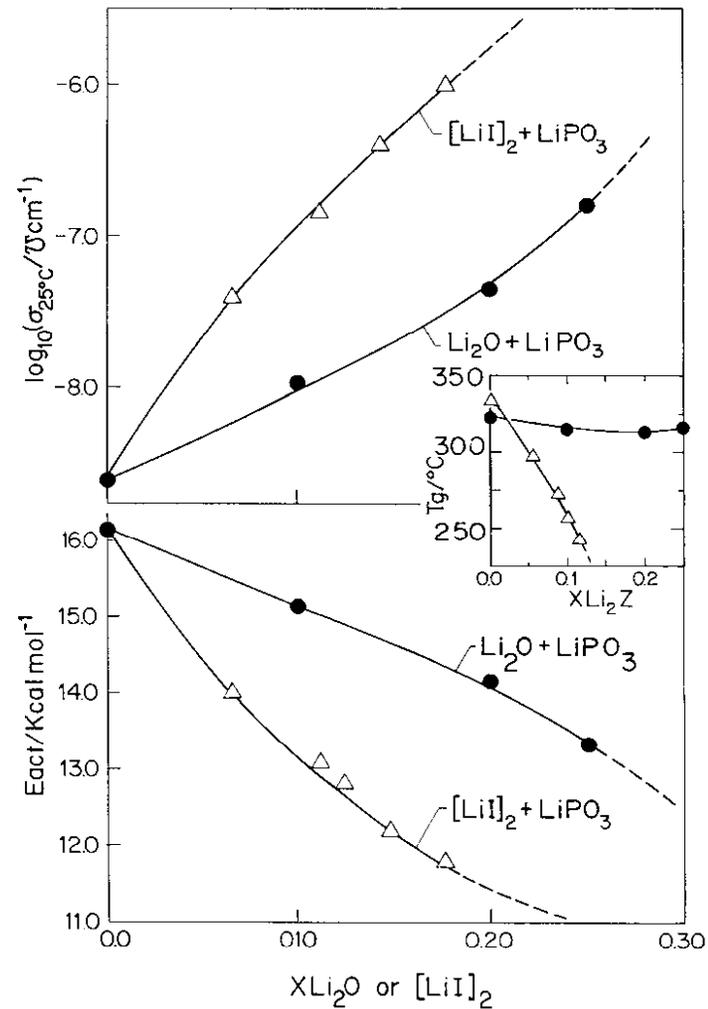
Effect of Sulfur Substitution – "Fast Ion Conductors"
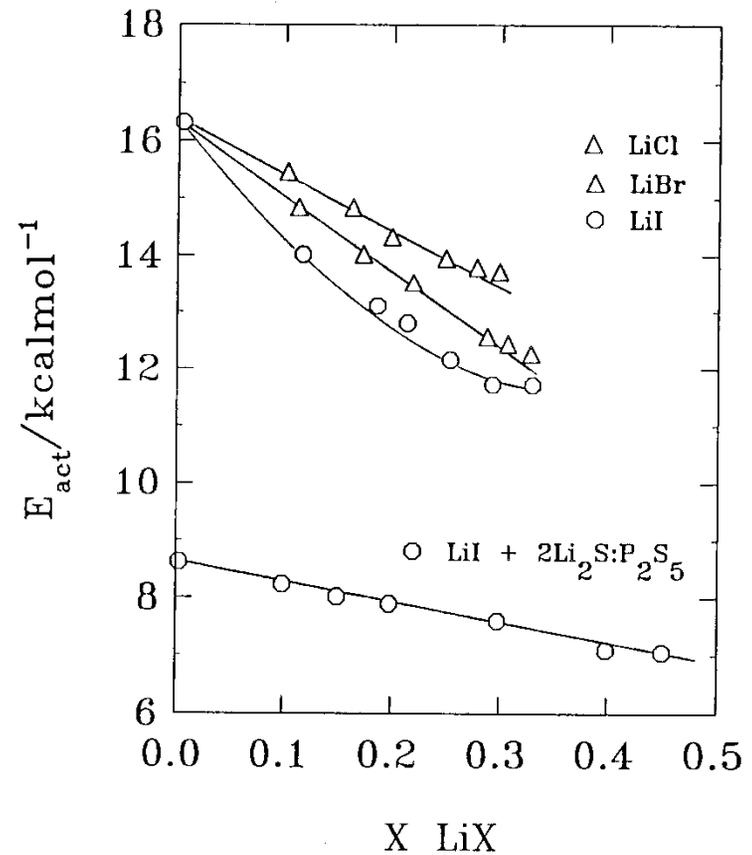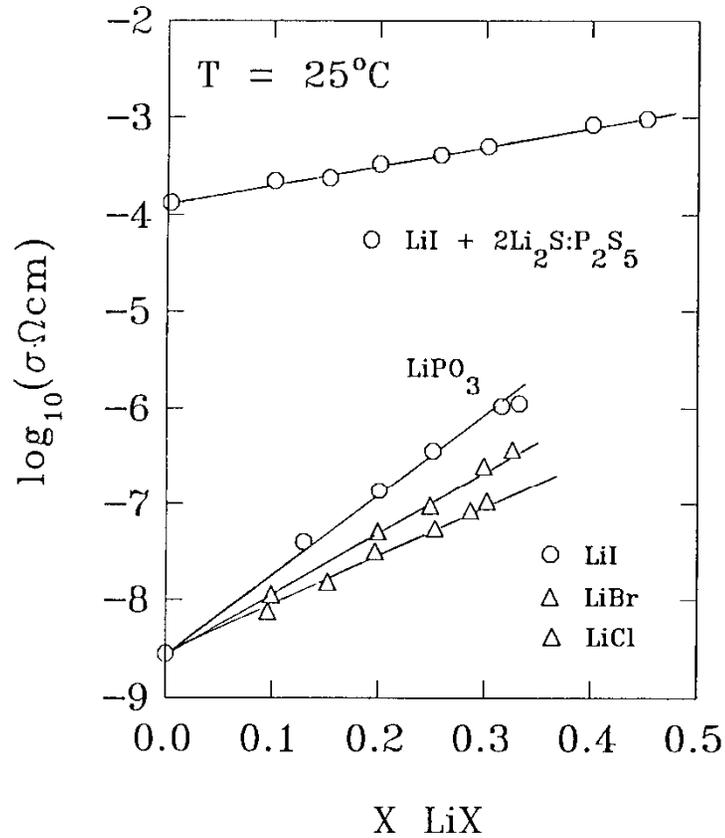
Silver Phosphate Glasses
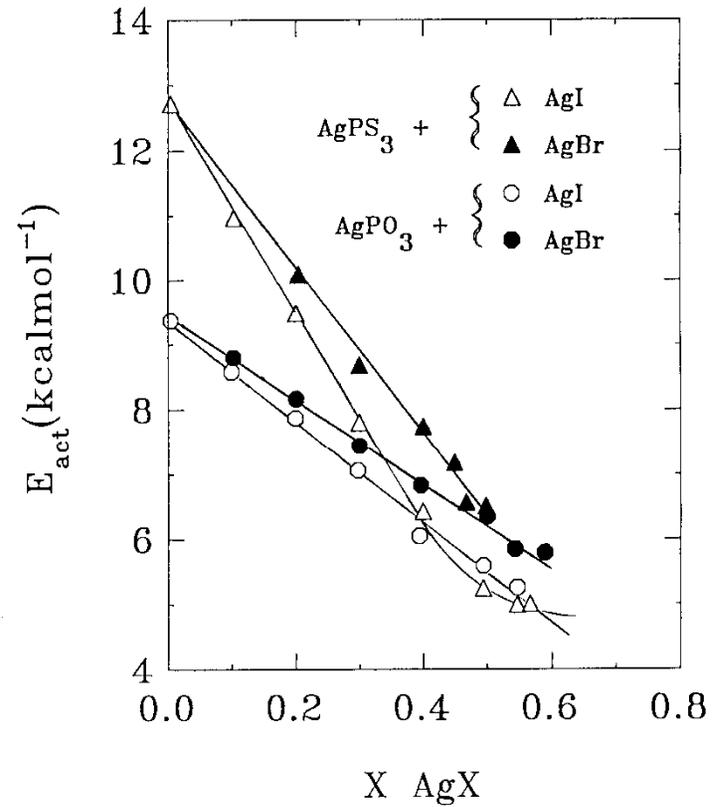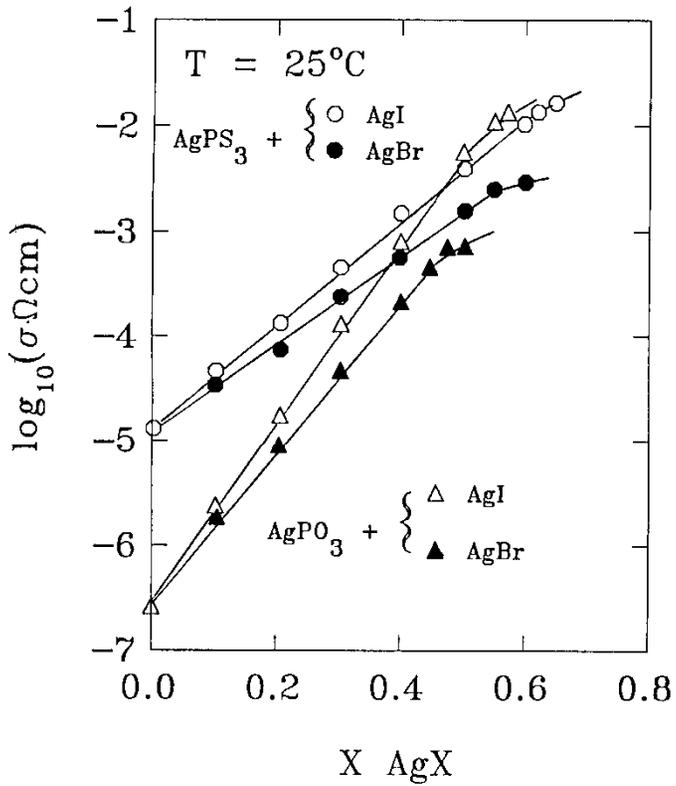
Other Silver sulfide doped glasses
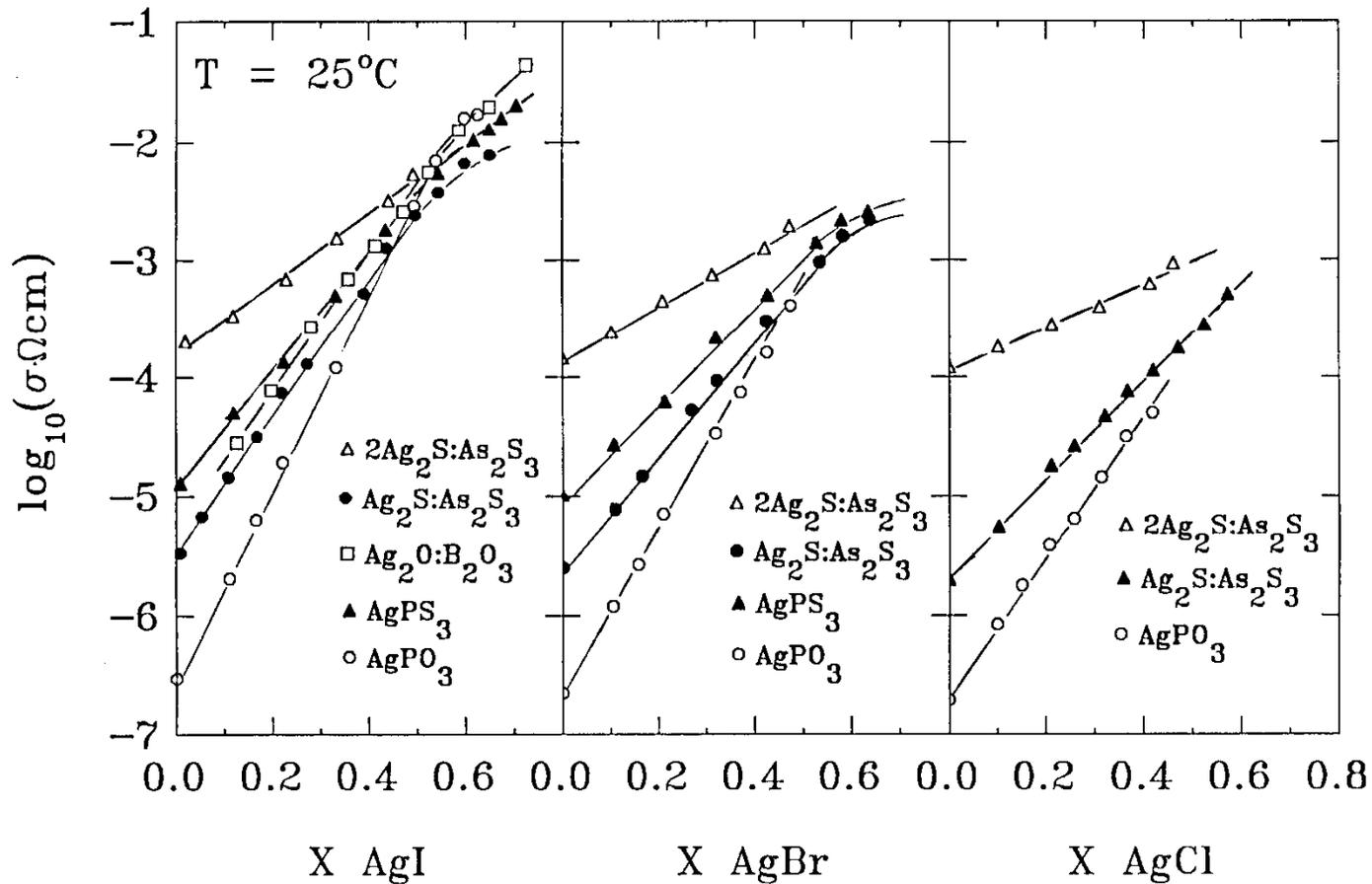
Salt doped phosphate glasses

- LiI doped $LiPO_3$ show highest conductivity and lowest activation energy among the halides
- Crystallization at the end of the glass forming limit
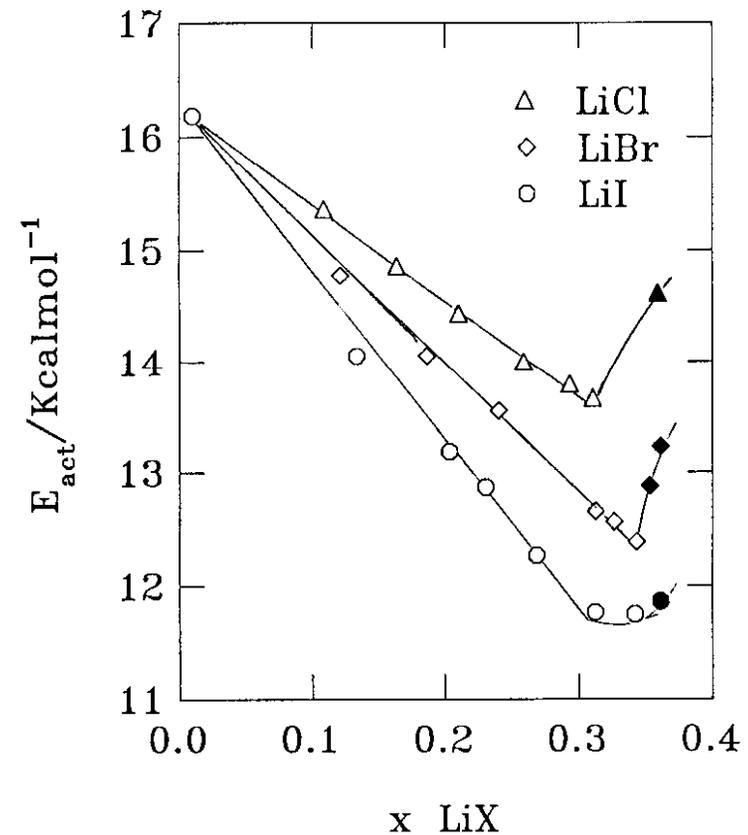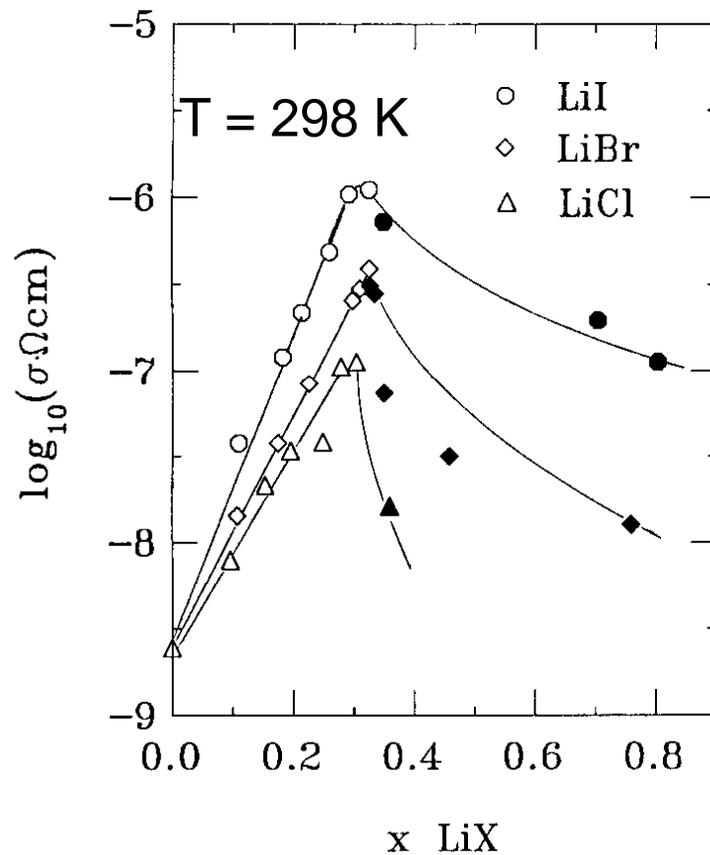
Mixed Glassformer Systems

- Phosphate and borate mixed glasses show non-linear "Mixed Glassformer" effect
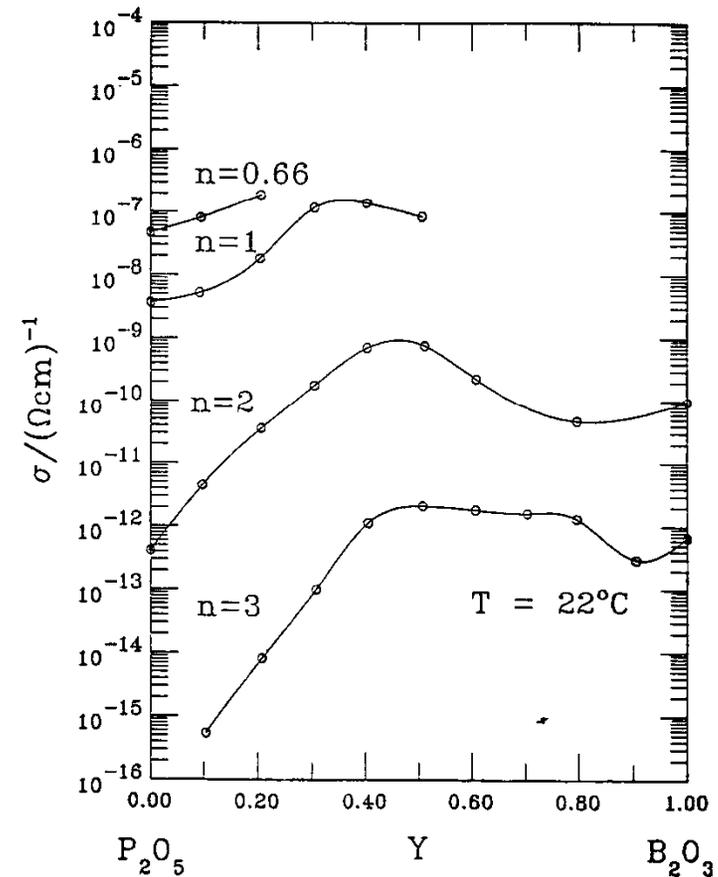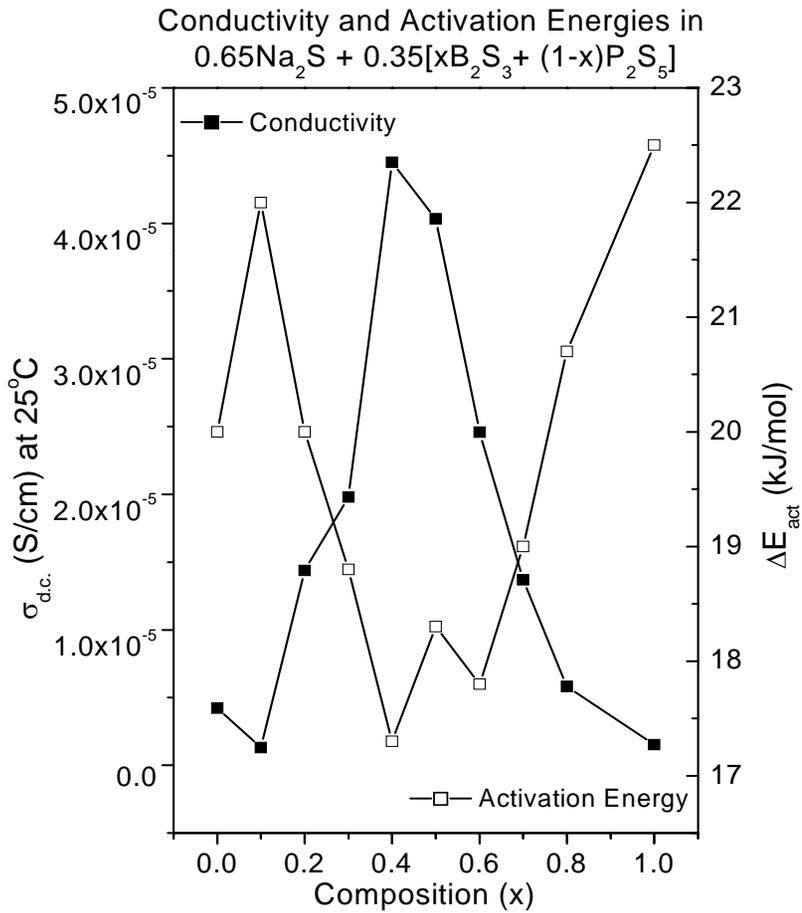
Conductivity and Activation Energies in
$0.65Na_2S + 0.35[xB_2S_3 + (1-x)P_2S_5]$

Composition Dependence of the Conductivity

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$Li_2O:P_2O_5$

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$Li_2O:SiO_2$
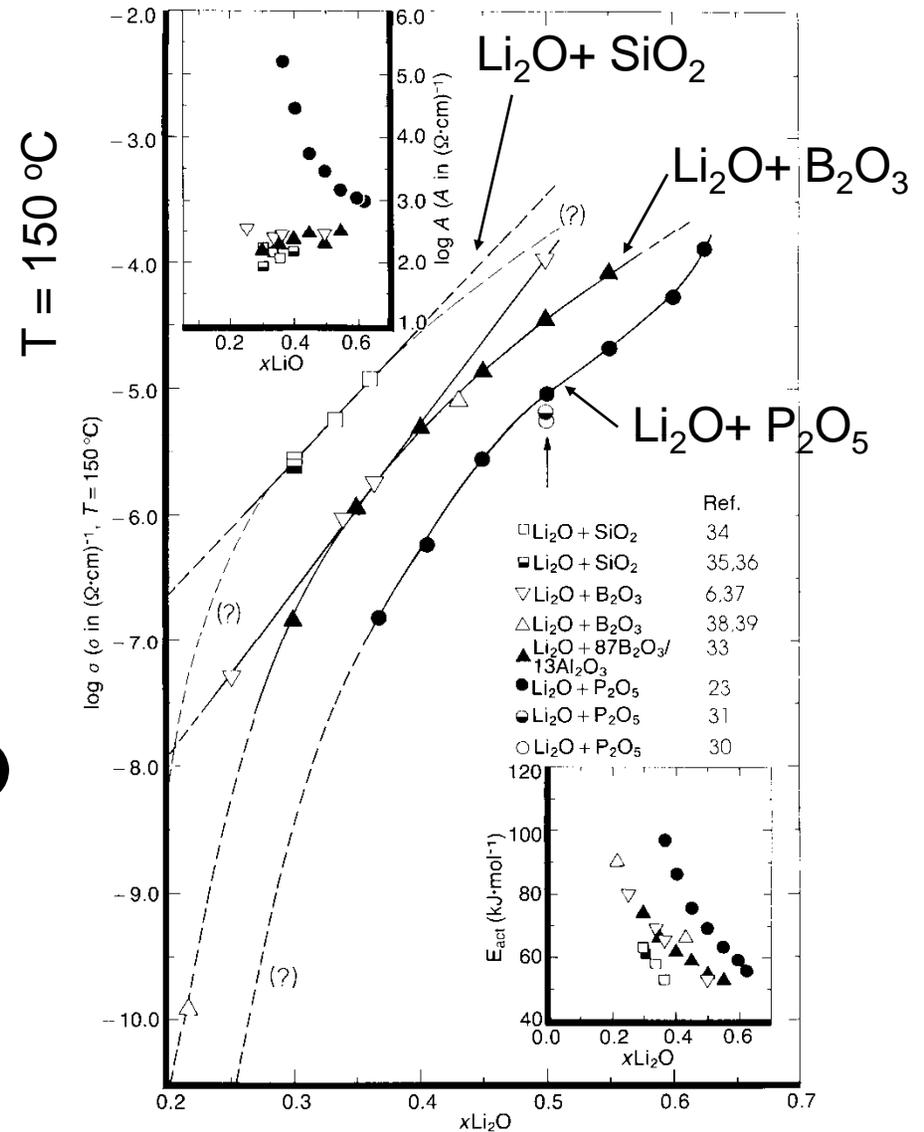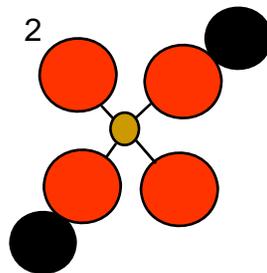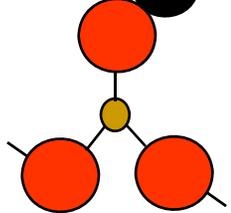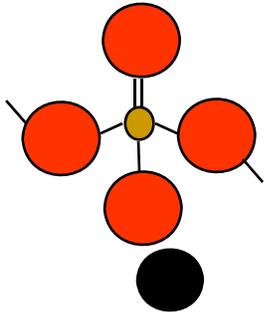
Ionic motion in glassy electrolytes

$$xNa_2O + (1-x)SiO_2$$
Glass in 2-D

$|\vec{E}|$

MD Simulations

y

BO

x

NBO   BO   NBO

Energy

$+1/r^n$

ΔE_s

ΔE_C $-e^2/r$

r   r
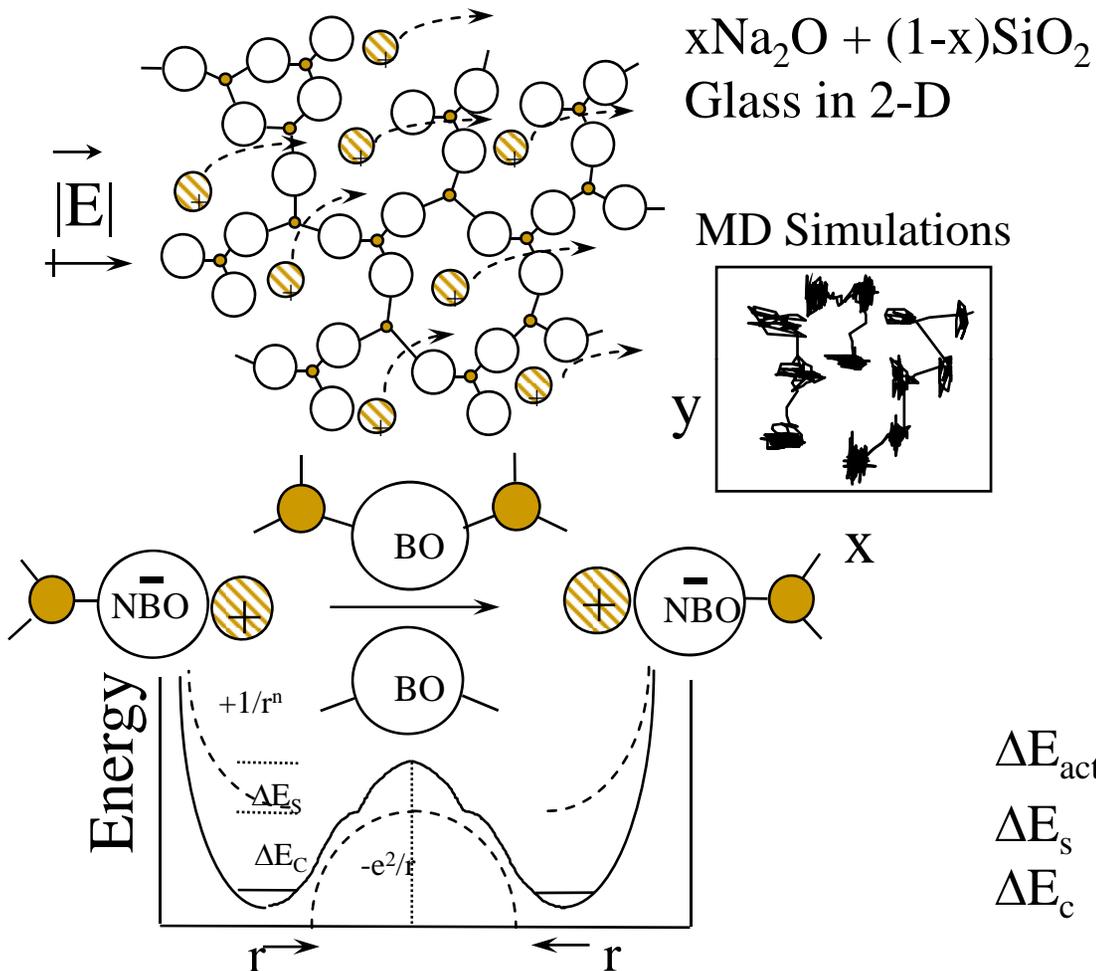
$\Delta E_{act} = \Delta E_s + \Delta E_c$

ΔE_s = Strain Energy

ΔE_c = Coulomb Energy

S.W. Martin, C.A. Angell, JNCS, 1983

Mobility and number dependence of the conductivity

$$\sigma(T) = n(T)eZ_c\mu(T) = \frac{\sigma_0}{T}\exp\left(\frac{-\Delta E_{act}}{RT}\right)$$

$$n(T) = n_o\exp\left(\frac{-\Delta E_c}{RT}\right)$$

$$\mu(T) = \frac{\mu_0}{T}\exp\left(\frac{-\Delta E_s}{RT}\right)$$

$$\sigma(T) = \frac{Z_c e n_0 \mu_0}{T}\exp\left(\frac{-\left(\Delta E_c + \Delta E_s\right)}{RT}\right)$$

Question: What are the magnitudes of $\Delta E_{S(M)}$ and ΔE_C ?

"Extreme" Models of the Activation Energy

- **Strong Electrolyte Model**
  - All cations are dissociated from their "host" anion and are available for conduction
    - Like NaCl, HCl, NaOH, H_2SO_4 dissolved in water
  - Na^+....$^-$O-Si$\equiv$
  - ΔE_C is "small" and not strongly compositionally dependent
  - $\sigma_{d.c.} \sim Zen_0\mu_0/T \exp(- \Delta E_m/RT)$
  - Migration energy dominates the d.c. conductivity

"Extreme" Models of the Activation Energy

- ## Weak Electrolyte Model
  - Only a small fraction of the cations are dissociated
    - Like HOAC, Acetic Acid, $K_a \sim 1.8 \times 10^{-5}$
  - ΔE_m is "small" and not strongly compositionally dependent
  - Most of the cations are bound with their charge compensating anion
  - $\sigma_{d.c.} \sim Ze\mu_0 n_0/T \exp(-\Delta E_c/RT)$
  - Creation energy dominates the d.c. conductivity

Strong and Weak Electrolyte models

- "Strong electrolyte" SE model suggests *all* cations are equally available for conduction.
  - *Each cation experiences an energy barrier which governs the rate at which it hops*
- "Weak electrolyte" WE model suggests only those *dissociated* cations are available for conduction
  - *Dissociation creates mobile carriers available for conduction*
- SE models suggests that $\Delta E_C + \Delta E_s$ both contribute, one could be larger or smaller than the other
- WE model suggests that ΔE_c is the dominant term
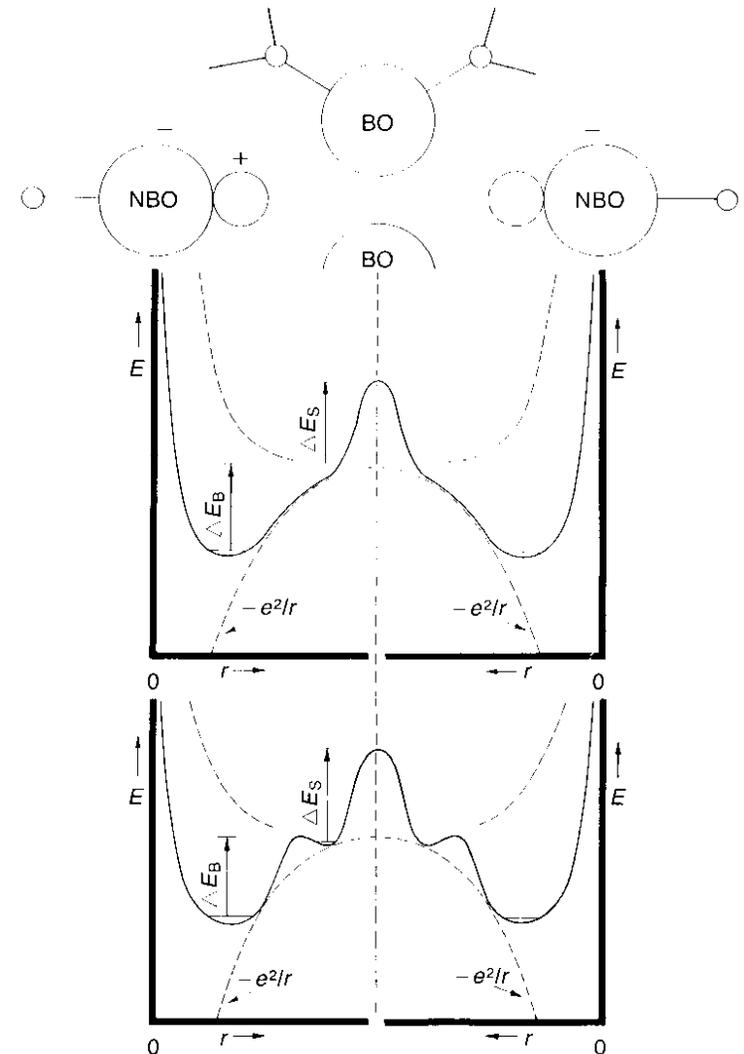
S.W. Martin, C.A. Angell, JNCS, 1983

Coulomb Energy Barrier

- Anderson-Stuart Model
- Assignment of Coulombic and Strain energy terms
  - $\Delta E_C + \Delta E_s$
- "Creation" or Concentration versus Migration energy terms, $\Delta E_C + \Delta E_m$
- Coulomb energy term, ΔE_C attractive force between cation and anion

$$\approx \frac{C_{struct\,.}}{\varepsilon_\infty}\left[\frac{-Z_c Z_a e^2}{\lambda/2} - \frac{-Z_c Z_a e^2}{(r_c + r_a)}\right] = \frac{C_{struct\,.}Z_c Z_a e^2}{\varepsilon_\infty}\left[\frac{1}{(r_c + r_a)} - \frac{2}{\lambda}\right]$$

$$\underset{\lambda \to \infty}{Lim}\ \Delta E_{act} \to \frac{C_{struct\,.}Z_c Z_a e^2}{\varepsilon_\infty(r_c + r_a)} = const\,.$$

Strain Energy Barrier

- Strain energy term - ΔE_s
- "Work" required to "dilate the network so large cations can migrate

Cation size affect on Strain Energy
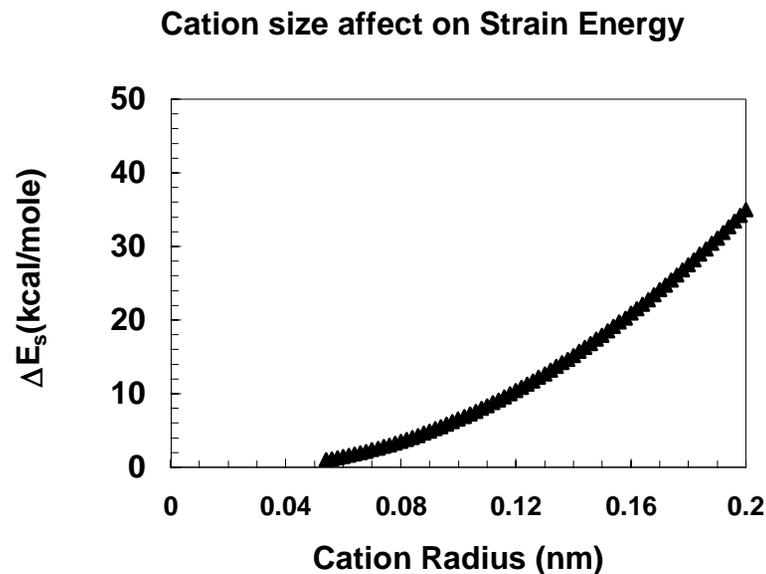
$$\Delta E_S = \pi G (r_c - r_d)^2 \lambda / 2$$

G	Shear modulus
r_c	Cation radius
r_d	Interstitial site radius
λ	Jump distance

Cation Radius Dependence of ΔE_c and ΔE_m
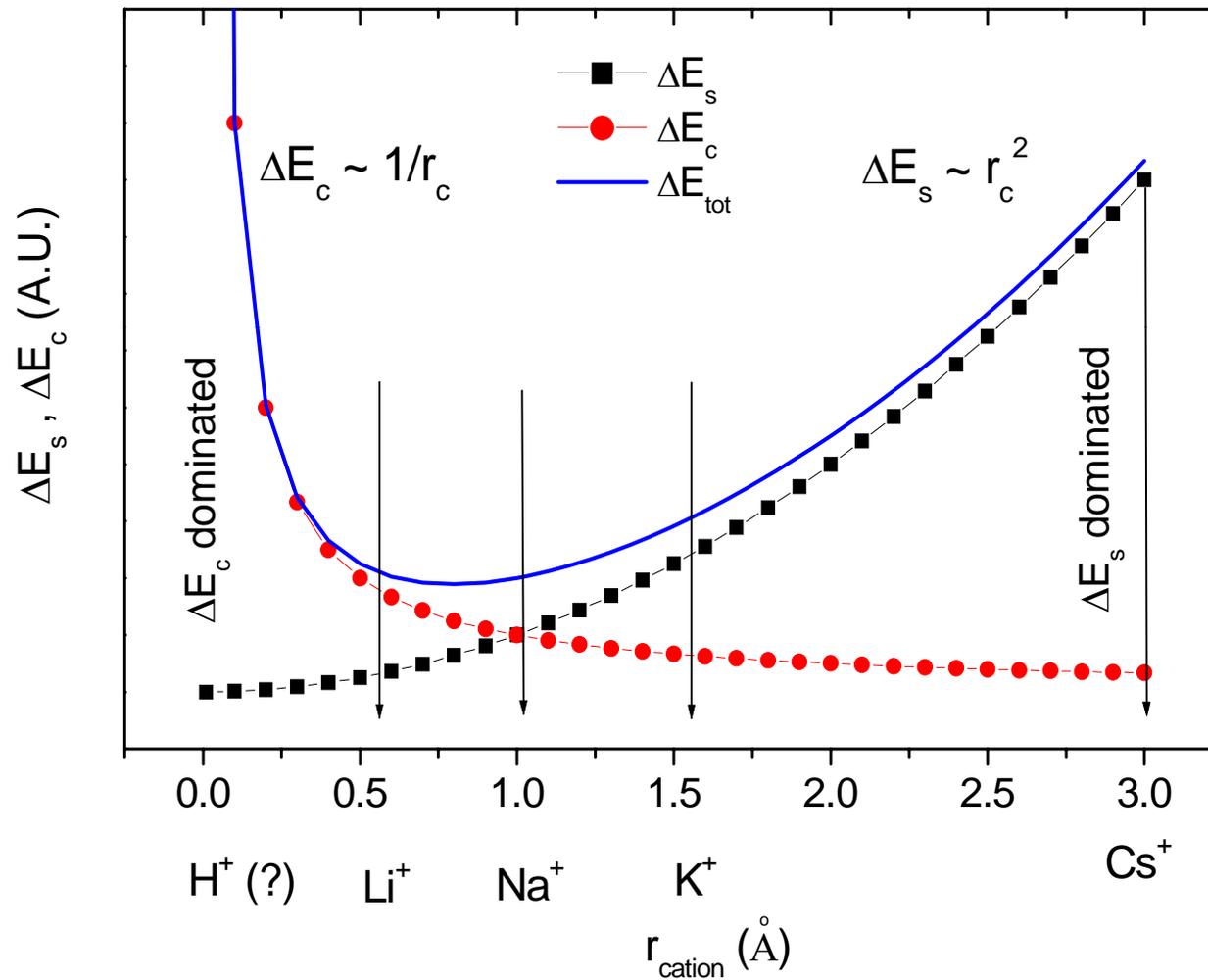
"Rational" Models of the Activation Energy

- Both activation energies are non-zero and contribute to the total activation energy
- Anderson-Stuart[1] model calculation

$$\Delta E_C = \frac{\beta_{struct.} Z_c Z_a e^2}{\varepsilon_\infty} \left[\frac{1}{(r_c + r_a)} - \frac{2}{\lambda} \right] \qquad \Delta E_s = \Delta E_m = 4\pi r_d G(r_c - r_d)^2$$

x Na$_2$O + (1-x)SiO$_2$	ΔE_s (calc)	ΔE_c (calc)	ΔE_{act}(calc)	ΔE_{act}[2]
11.8	11.7	66.9	78.6	68.1
19.2	10.9	62.3	73.2	63.7
29.7	10.0	56.1	66.1	59.7

- Calculation shows that the ΔE_c term is the larger of the two energy barriers.
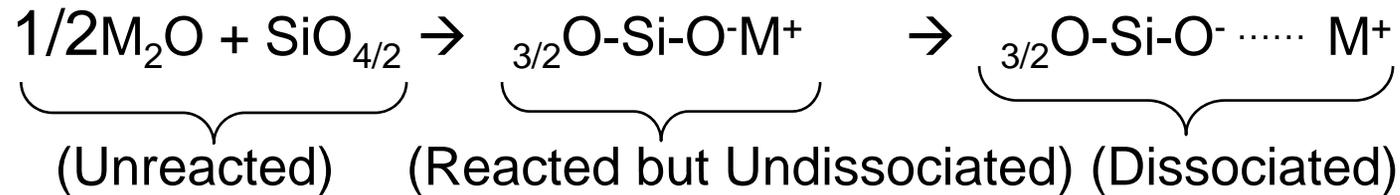- Weak-Electrolyte behavior?

[1] Anderson, Stuart, J. Amer. Cer. Soc., 1954
[2] SciGlass 5.5, Average of many glasses

Thermodynamic Models

- Glass is considered as a solvent into which salt is dissolved

- If dissolved salt dissociates strongly, then glass is considered a strong electrolyte

- If dissolved salt dissociate weakly, then glass is considered a weak electrolyte

- Coulomb energy term calculations suggest that the salts are only weakly dissociated, largest of the two energy terms

- Migration energy term is taken to be minor and weak function of composition

- Dissociation constant then determines the number of mobile cations available for conduction, dissociation limited conduction

Weak Electrolyte model, *Ravaine & Souquet '80*

$$1/2 M_2O + SiO_{4/2} \rightarrow \; _{3/2}O\text{-Si-O}^-M^+ \qquad \rightarrow \; _{3/2}O\text{-Si-O}^- \cdots\cdots M^+$$

(Unreacted)   (Reacted but Undissociated) (Dissociated)

$$K_{diss} \quad = \; a_M{+} \, a_{OM}{-} \, / \, a_{M2O}$$

$$\sim \; [M^+][OM^-]/a_{M2O} = [M^+]^2/ \, a_{M2O}$$

$$[M^+] \quad \sim \; K_{diss}^{1/2} a_{M2O}^{1/2} \equiv n$$

$$\sigma \quad = \; ze\mu n = ze\mu K_{diss}^{1/2} a_{M2O}^{1/2} \sim C \, a_{M2O}^{1/2}$$

$$\log K_{diss} \sim \; -Ne^2RT/4\pi\varepsilon_o\varepsilon_\infty \, (r_+ + r_-)$$

As r_+, r_- increase, K_{diss} increases
As ε_∞ increases, K_{diss} increases
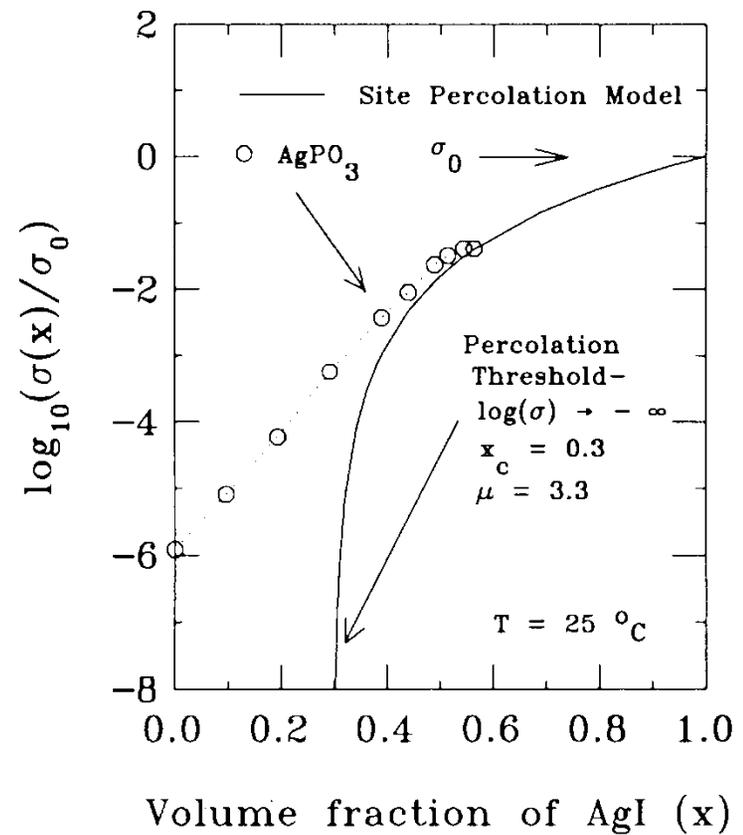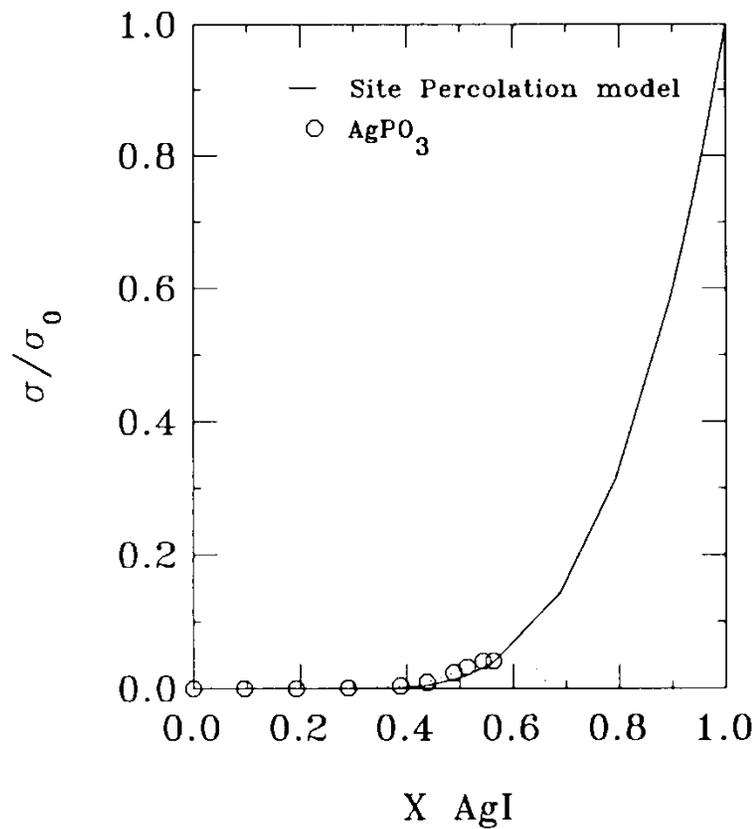
Intermediate Range Order models

- Models recognize that ion conductivity requires ion motion over relatively long length scales

- Ions must be able to move from one side of the electrolyte to the other

- Long range connectivity of the SRO structures favorable to conduction must exist

- Deep "traps" along the way must be infrequent and not severe

- Rather, low energy conduction "pathways" are thought to exist which maximize connectivity and minimize energy barriers and traps

- Cluster pathway model of Greeves '85, for example
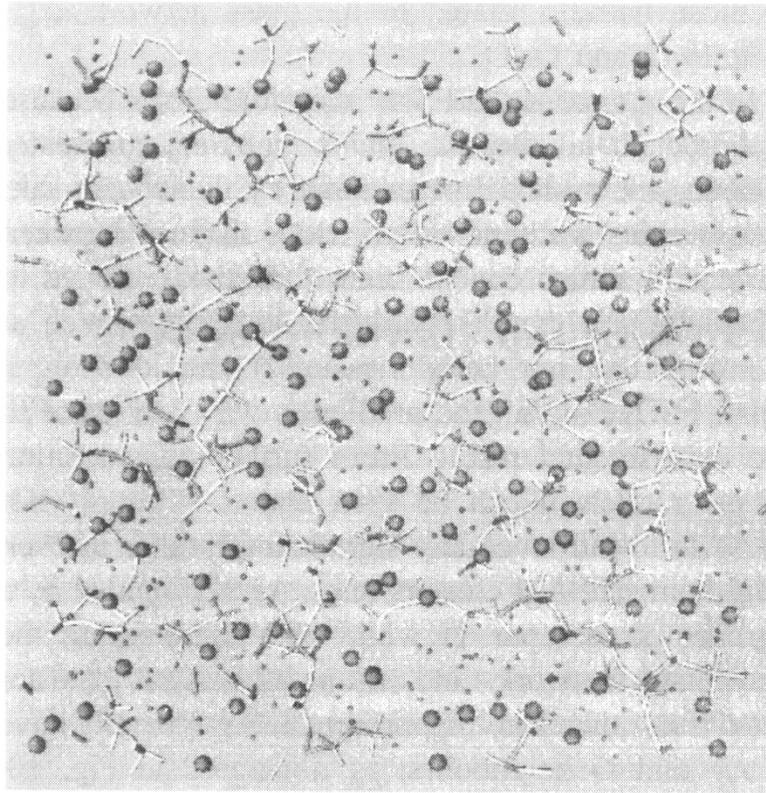
Intermediate Range Order models

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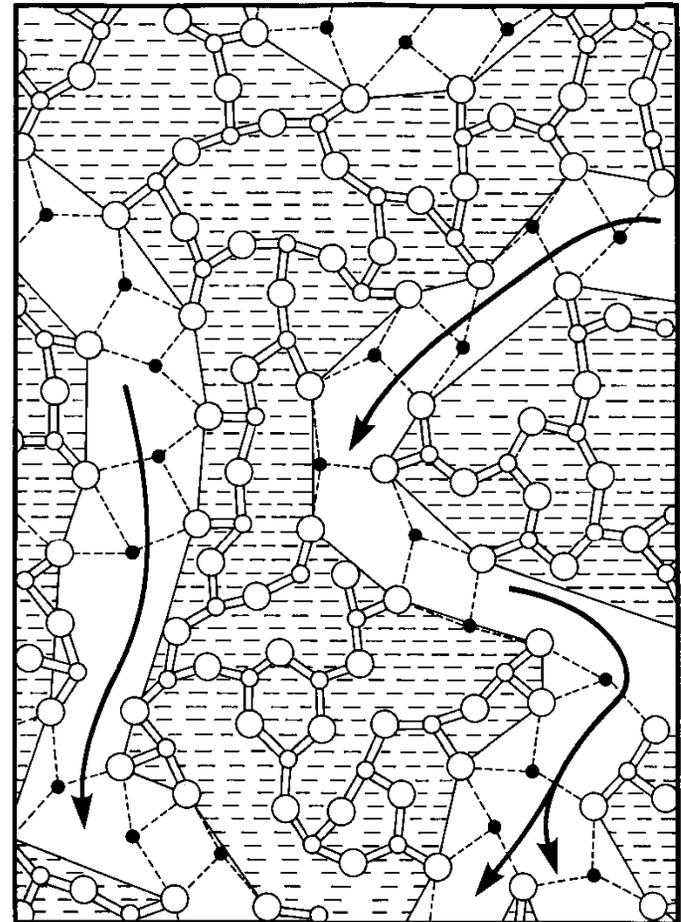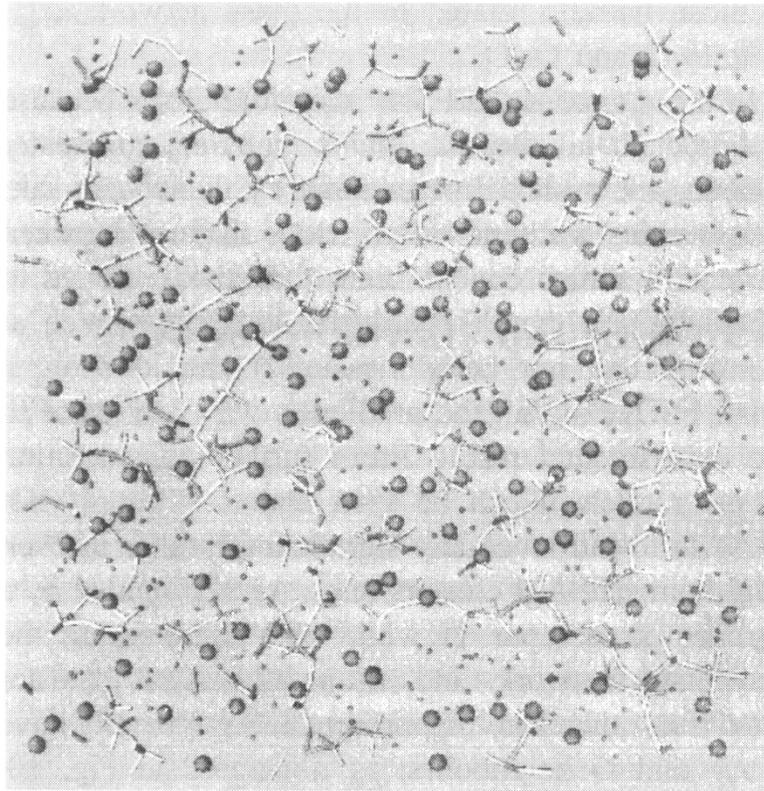
Conductivity percolation in AgI + AgPO$_3$

RMC Modeling of AgI + AgPO$_3$, *Swenson et al. '98*

4.635 nm

RMC Modeling of AgI + AgPO$_3$, *Swenson et al. '98*


4.635 nm

Intermediate Range Order models

- Microdomain models of conductivity

- Dopant salts such as AgI to oxide glasses, especially $AgPO_3$, are added to increase conductivity

- AgI is itself a FIC *crystal* above 150°C

- Extrapolations of σ to xAgI = 1 give ~ σ_{AgI}(298K)

- The question then is: Does the AgI create "microdomains" of α-AgI giving rise to the high conductivity?

AgI Microdomain model

- Most well known of all glasses is $xAgI + (1-x)AgPO_3$

- $AgPO_3$ is a long chain structure of $-O-P(O)(OAg)-O$ repeat units

- Intermediate range structure is for these long chains to intertwine and as such frustrate crystallization

- Added AgI dissolves into this liquid without disrupting the structure of the phosphate chains

- Microdomain model then suggests that this dissolved AgI creates increasingly large clusters of α-AgI between the phosphate chains

AgI Microdomain model
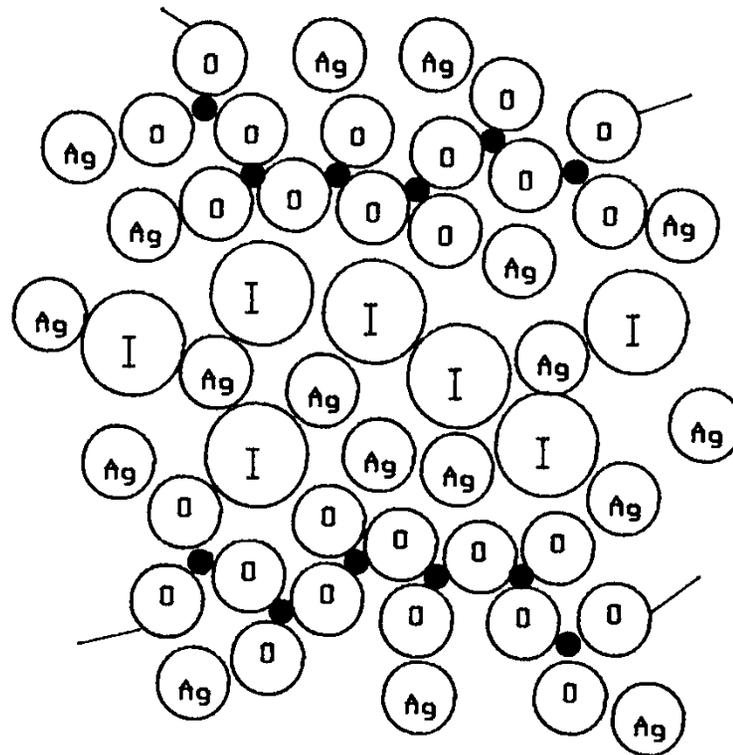
Part 2 Summary

- ## Conductivity can be increased many orders of magnitude

  - Essentially insulating values 10^{-15} $(\Omega cm)^{-1}$

  - "High Conducting" values 10^{-2} $(\Omega cm)^{-1}$

  - Activation energy appears to be dominated by coulomb potential

  - Weakening the coulomb potential between cation and anion lowers the activation energy

    - Oxide glasses lowest conducting

    - Sulfide glasses doped with ionic salts the highest conducting

AC versus DC ionic conductivity

$\omega\tau < 1$

$\omega\tau > 1$

$\log_{10}(\sigma_{a.c.})$

Energy

y

x

r →

10^3K/T

$\log_{10}(f/Hz)$

D.C. Conductivity
Conductivity

A.C.
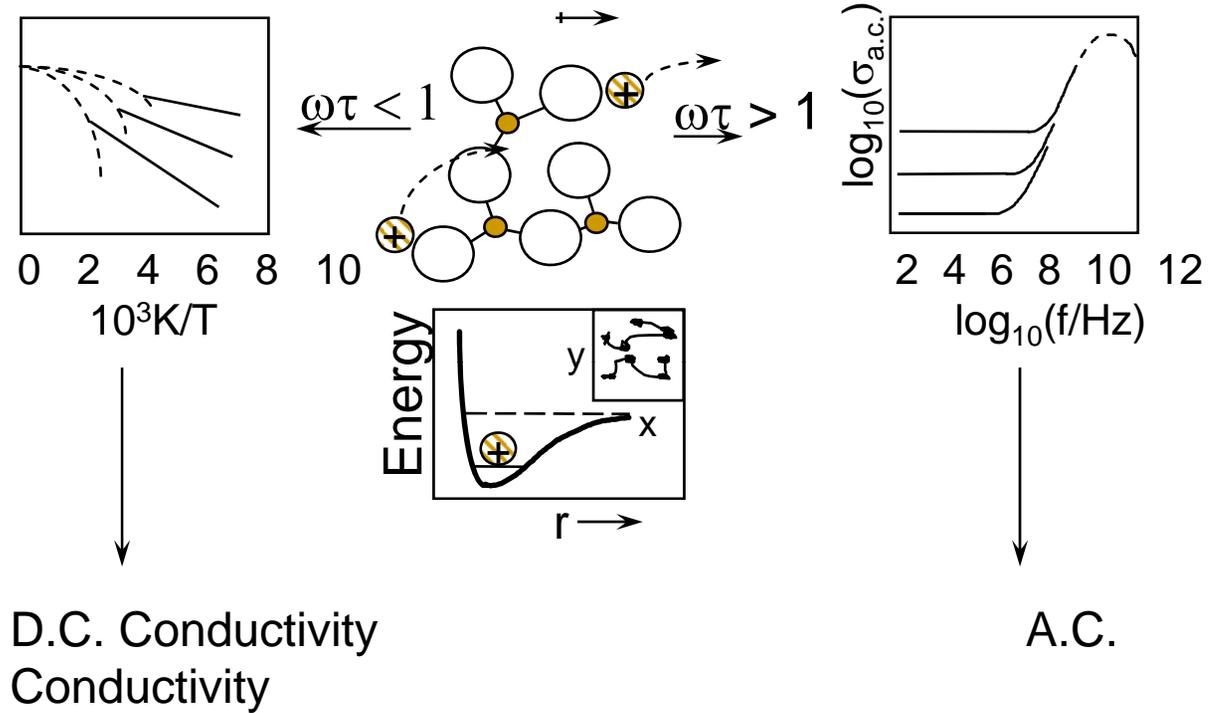
AC ionic conductivity in glass

- Connection to Far-IR vibrational modes,