Advanced Vitreous State - Physical Properties of Glass

Lecture 25: Charge Conduction Properties of Glass:

Ionic Conduction in Glass - Part 1

Relationship to Glass Structure and Composition

Steve W. Martin

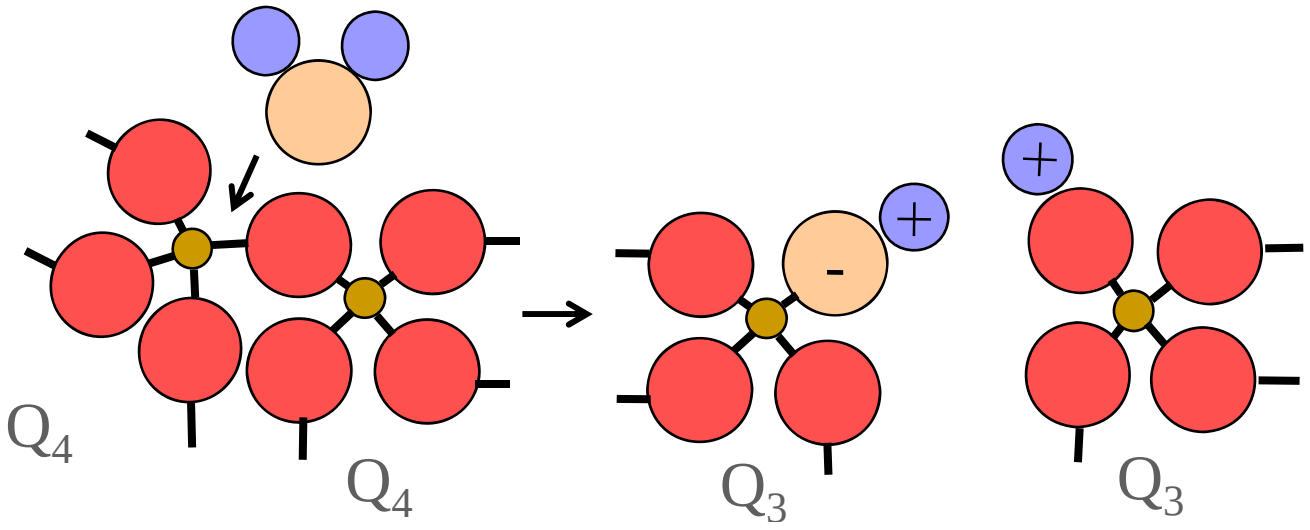
Department of Materials Science & Engineering
Iowa State University
Ames, IA
swmartin@iastate.edu

Ionic Conduction in glass

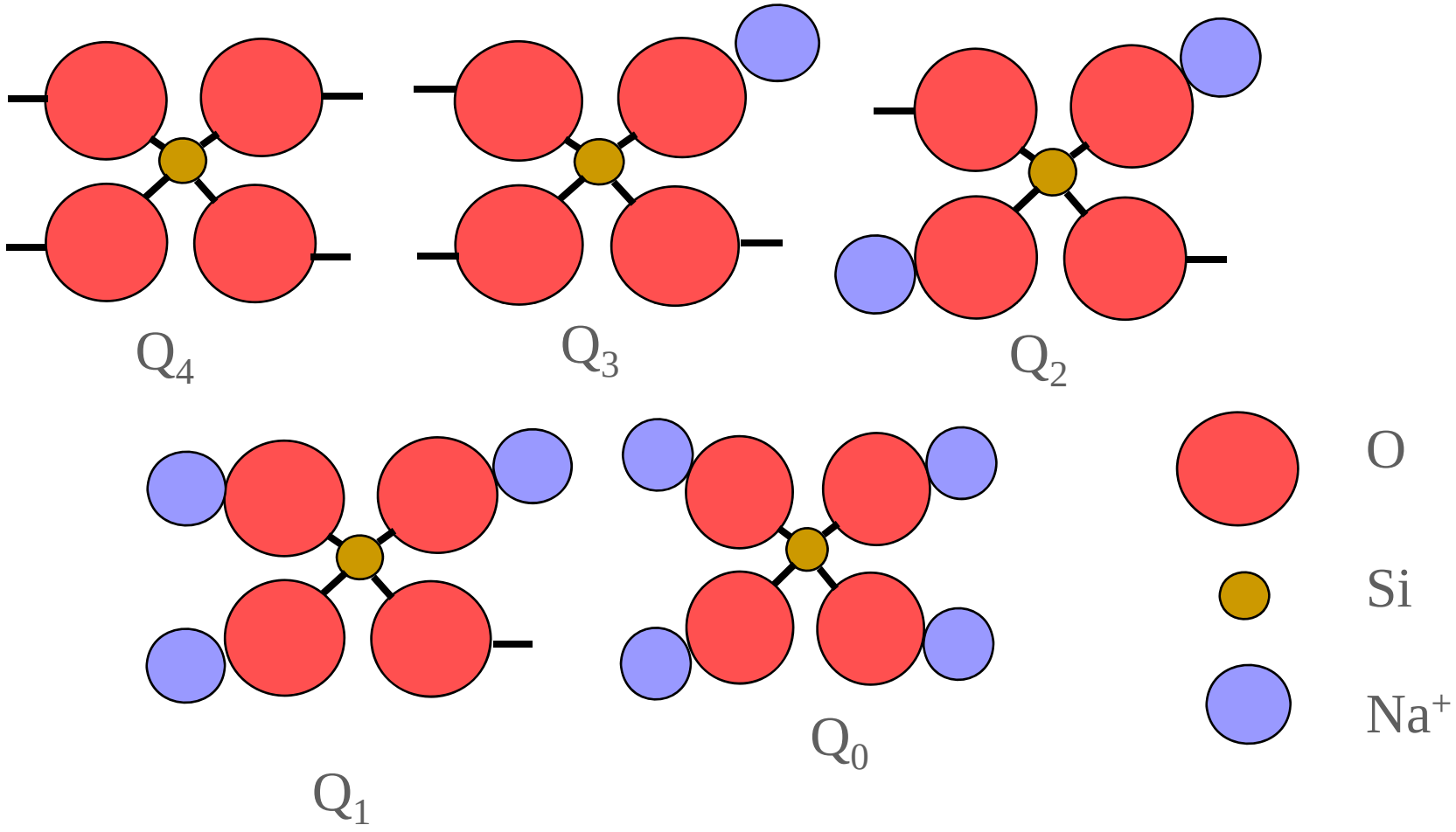
- Glasses can be systematically doped to increase conductivity
  - From near insulating values to those that rival ionic liquids
- Strong glass forming character over wide compositions ranges make them ideal for many composition studies of the ionic conductivity
- Low melting temperatures often make them compatible with many industrial processing techniques such as sputtering and evaporation to produce thin film electrolytes

Formation of Non-Bridging Oxygens

- Modifier M_2O or MO creates two NBOs per M_2O or MO added
- $xNa_2O + (1-x)SiO_2$ creates 2x NBOs
- f_{NBO} = NBOs/(NBOs + BOs)
  = 2x/(x + 2(1-x)) = 2x/(2-x)
- $f_{BO} = 1 - f_{NBO}$



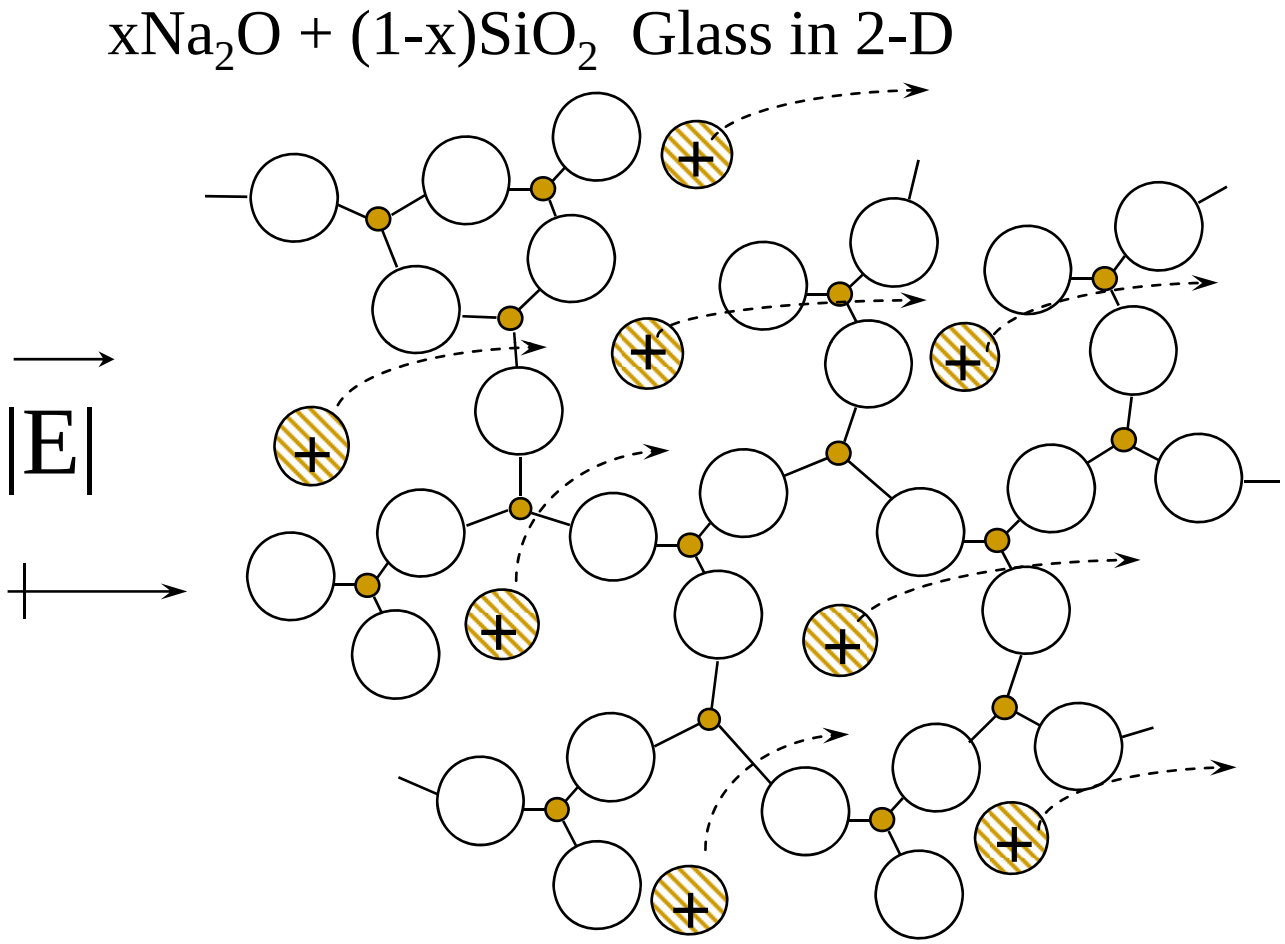
"Q_i" Units in Alkali Silicate Glasses



Alkali Ions are "weakly" bound

- "Frame work" cations, Si^{+4}, and anions, $O^{=}$
  - Covalently bonded to the network
  - "Large" bond strength, 100+ kcal/mole
- "Modifying" cations, M^{+} , and anions F^{-}
  - Ionically bonded to the network
  - "Small" bond strength, < 50 kcal/mole
- Alkali cations can be thermally activated
- To break their weak ionic bond
- And move from one alkali cation site to another
- Thermally activated ionic conduction….

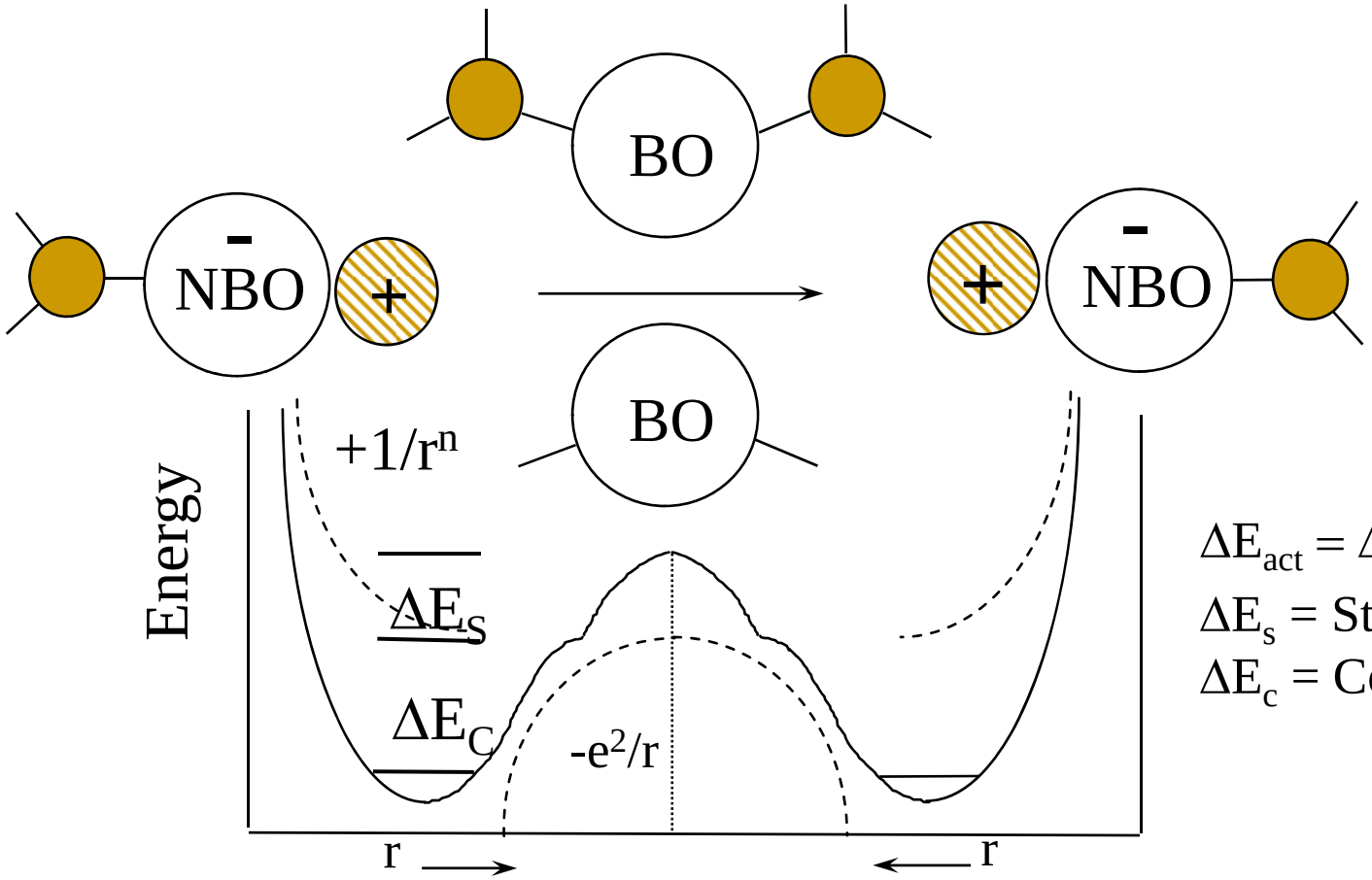
Relation of glass structure to ionic conduction



Molecular Dynamics Simulation of Ionic Conduction

- Go to Movie…..

Relation of glass structure to ionic conduction

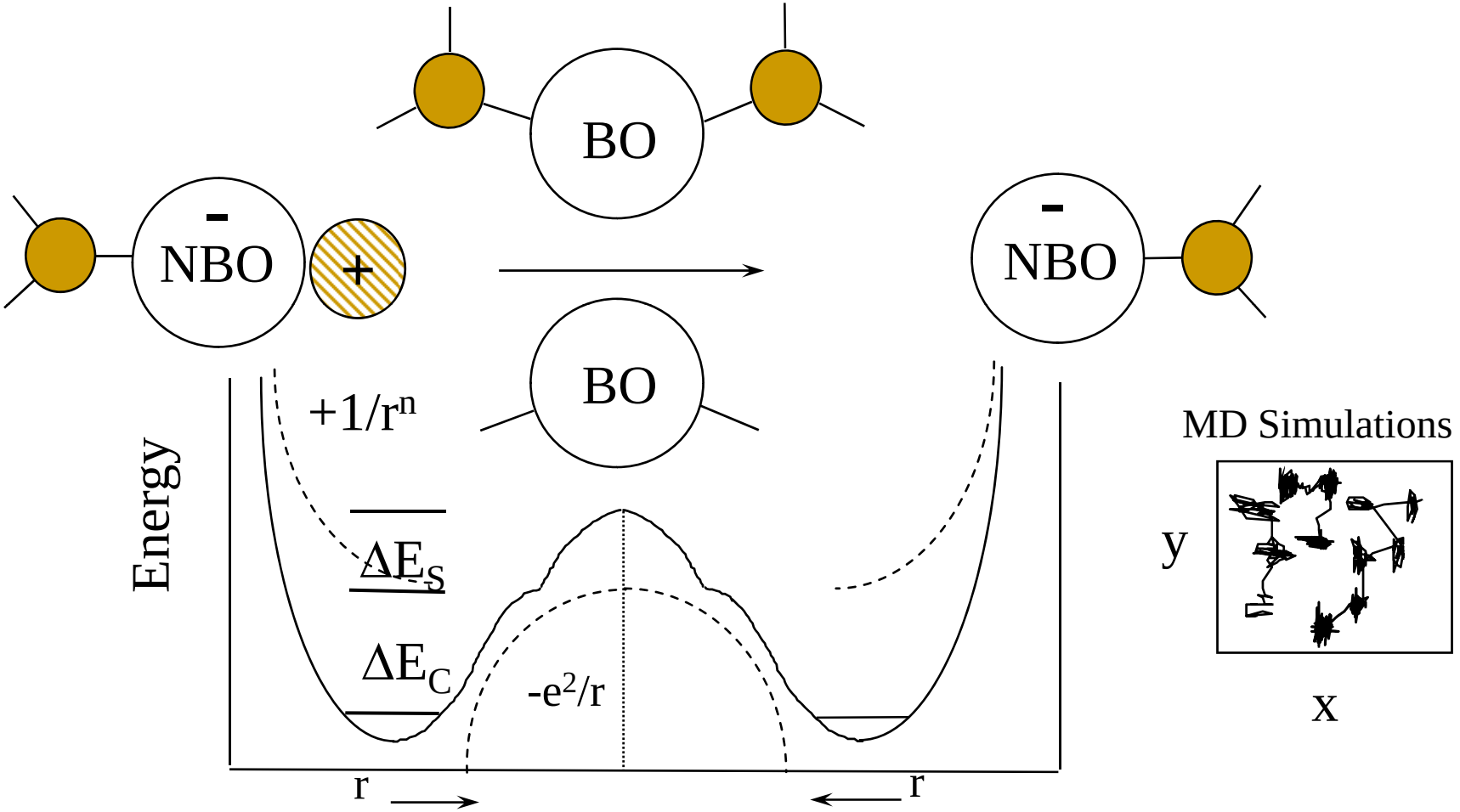


$\Delta E_{act} = \Delta E_s + \Delta E_c$

ΔE_s = Strain Energy

ΔE_c = Coulomb Energy

Cation Conduction – "Rattle and Jump"



Theory of Ionic Conduction in Glass: Simple Models

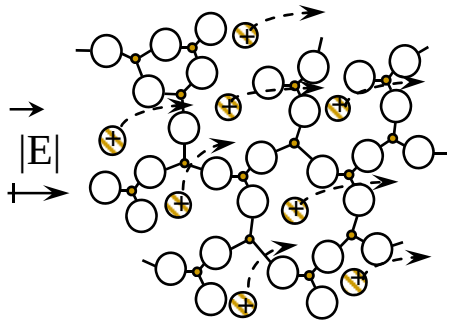
- $\sigma = 1/\rho \equiv neZ\mu$
  - n is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- What are the units of n?
  - #/cm^3
- What are the units of μ?
  - (cm/sec)/V = cm/V-sec
- What are the units of σ?
  - $(\Omega\ cm)^{-1} \equiv S/cm$

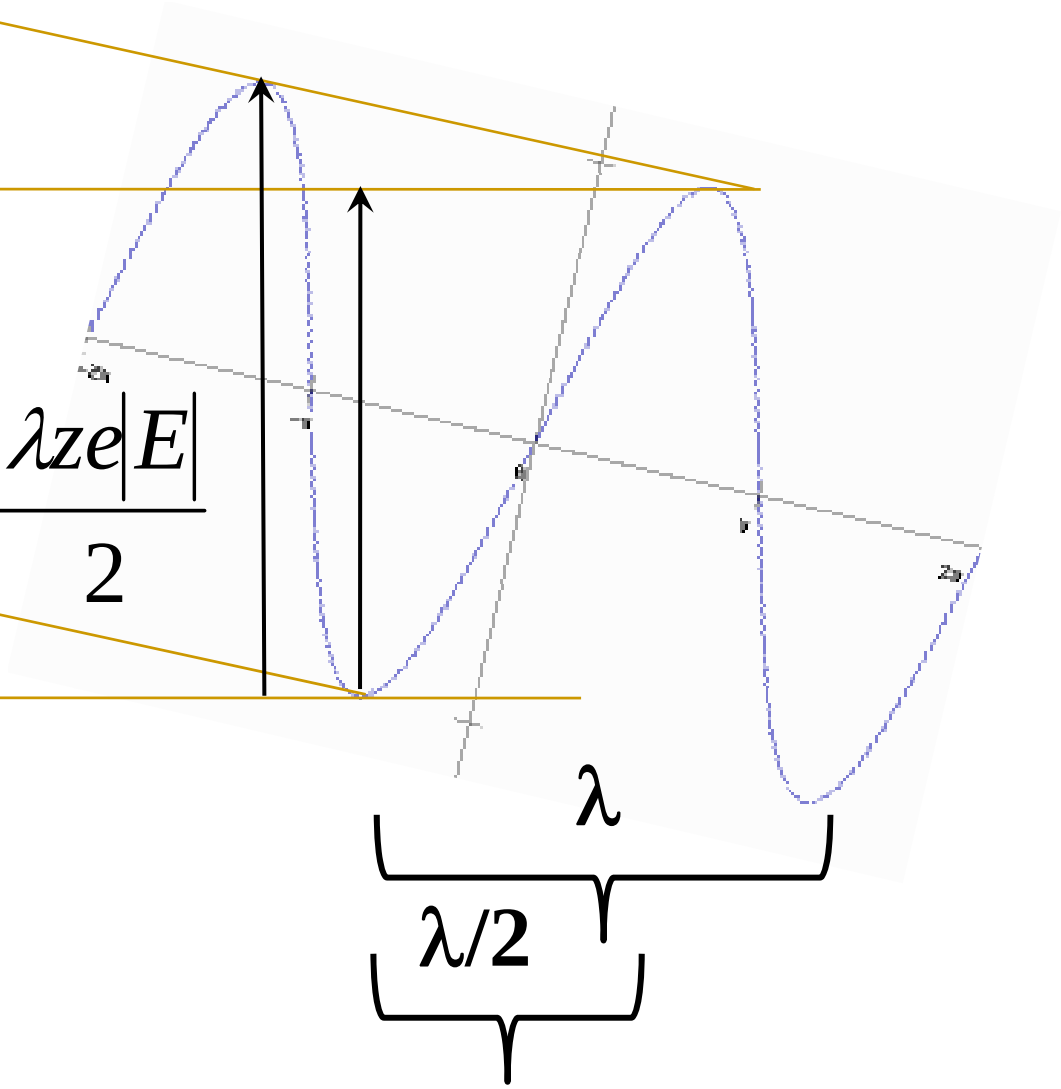
Theory of Ionic Conduction in Glass: Simple Models

$$\frac{\lambda z e |E|}{2}$$

$$|\vec{E}|$$

$$\Delta E_{act} - \frac{\lambda z e |E|}{2}$$





Theory of Ionic Conduction in Glass: Simple Models

$$\upsilon^{+}(T) = \upsilon_0 \exp\left[-\frac{\Delta E_{act} - \lambda ze|E|/2}{RT}\right]$$

$$\upsilon^{-}(T) = \upsilon_0 \exp\left[-\frac{\Delta E_{act} + \lambda ze|E|/2}{RT}\right]$$

$$\upsilon_{net} = \upsilon^{+}(T) - \upsilon^{-}(T)$$

$$\upsilon_{net} = \upsilon_0 \exp\left[-\frac{\Delta E_{act}}{RT}\right]\left(\exp\left[\frac{\lambda ze|E|}{2RT}\right] - \exp\left[-\frac{\lambda ze|E|}{2RT}\right]\right)$$

$$\upsilon_{net} = 2\upsilon_0 \exp\left[-\frac{\Delta E_{act}}{RT}\right]\sinh\left(\frac{\lambda ze|E|}{2RT}\right) \sim \frac{\upsilon_0 \lambda ze|E|}{RT}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

Theory of Ionic Conduction in Glass: Simple Models

$$\upsilon_{net} = 2\upsilon_0 \exp\left[-\frac{\Delta E_{act}}{RT}\right]\sinh\left(\frac{\lambda ze|E|}{2RT}\right) \sim \frac{\upsilon_0 \lambda ze|E|}{RT}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

$$velocity = \upsilon_{net} \times \lambda = \frac{\upsilon_0 \lambda^2 ze|E|}{RT}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

$$mobility = velocity / E = \frac{\upsilon_0 \lambda^2 ze}{RT}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

$$conductivity = mobility \times conductivity \times charge$$

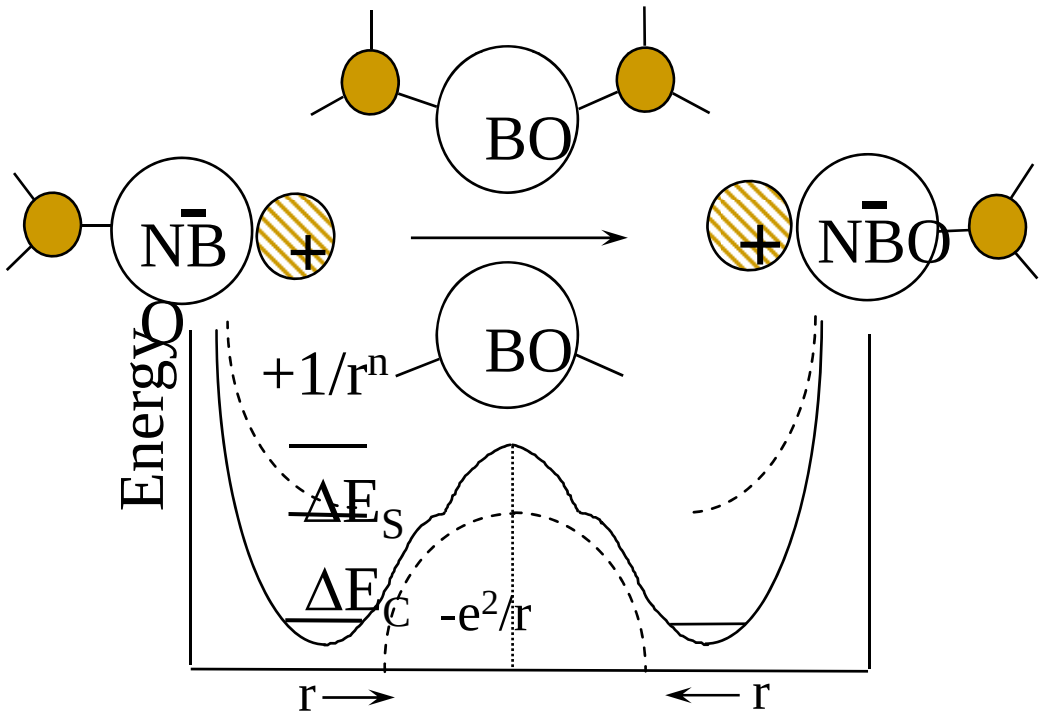
$$\sigma(T) = \frac{n\upsilon_0 \lambda^2 (ze)^2}{RT}\exp\left[-\frac{\Delta E_{act}}{RT}\right] \equiv \frac{\sigma_0}{T}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

Theory of Ionic Conduction in Glass: Simple Models

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

ΔE_s = Strain Energy

ΔE_c = Coulomb Energy



$$\sigma(T) = \frac{\sigma_0}{T}\exp\left[-\frac{\Delta E_{act}}{RT}\right]$$

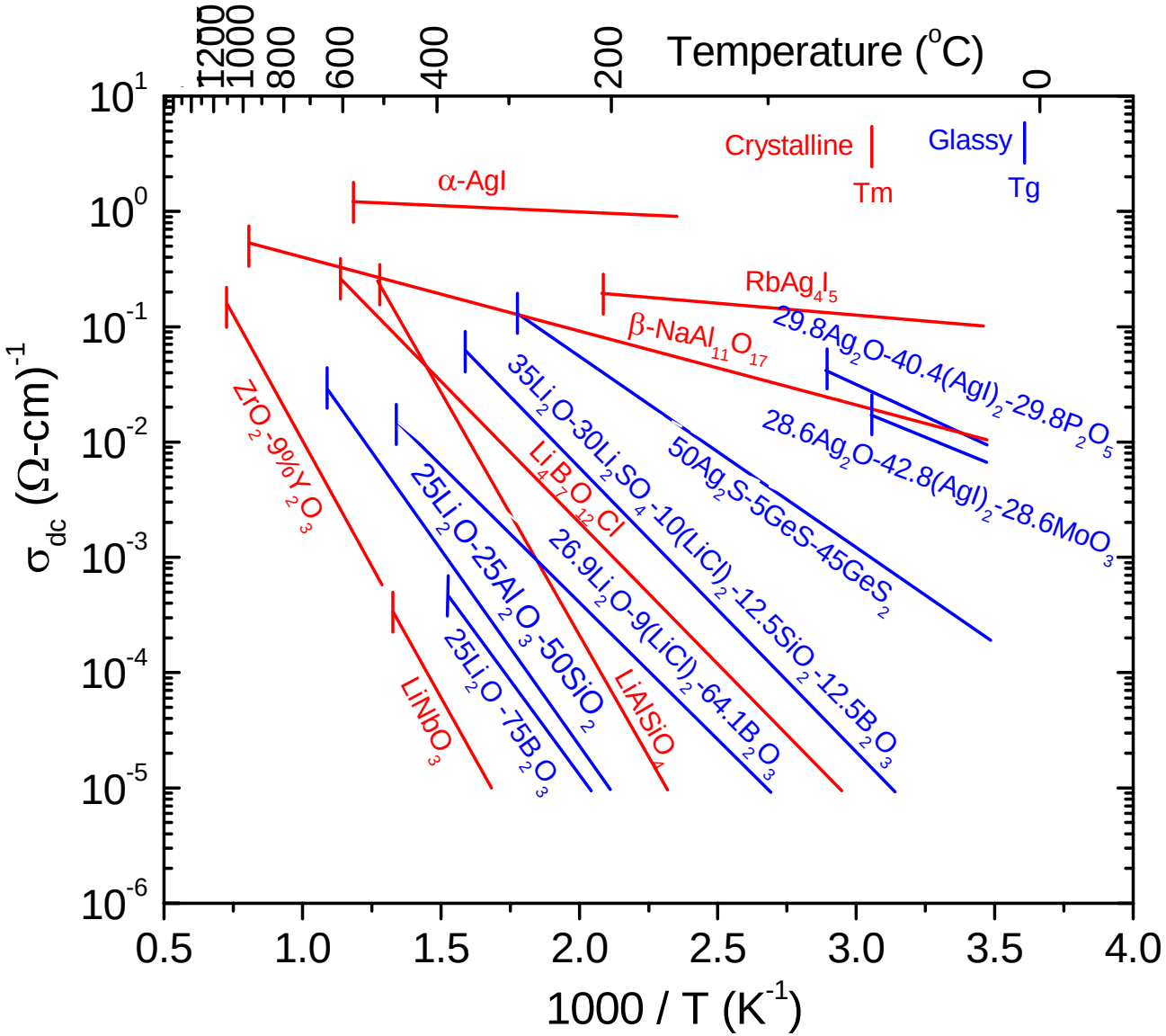
$$= \frac{\sigma_0}{T}\exp\left[-\frac{\Delta E_C + \Delta E_S}{RT}\right]$$

$$n(T) = n_0 \exp\left[-\frac{\Delta E_C}{RT}\right]$$

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

$$\frac{\nu_0 \lambda^2 (ze)^2}{RT}\exp\left[-\frac{\Delta E_S}{RT}\right]$$

Arrhenius Ionic Conductivity in Glass



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 excep for the highest temperatures

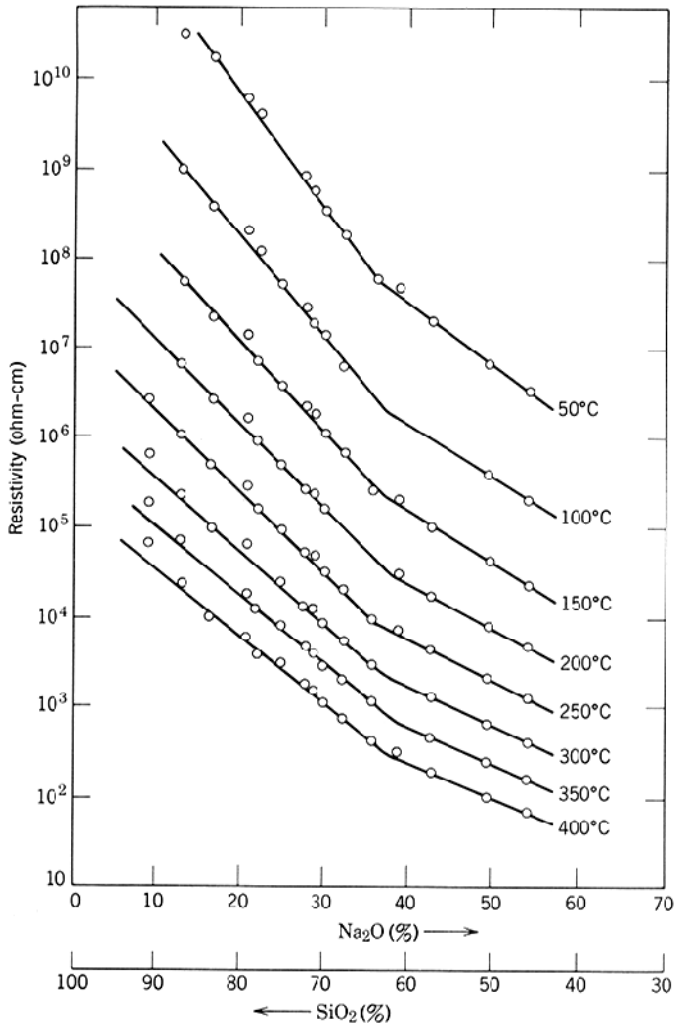
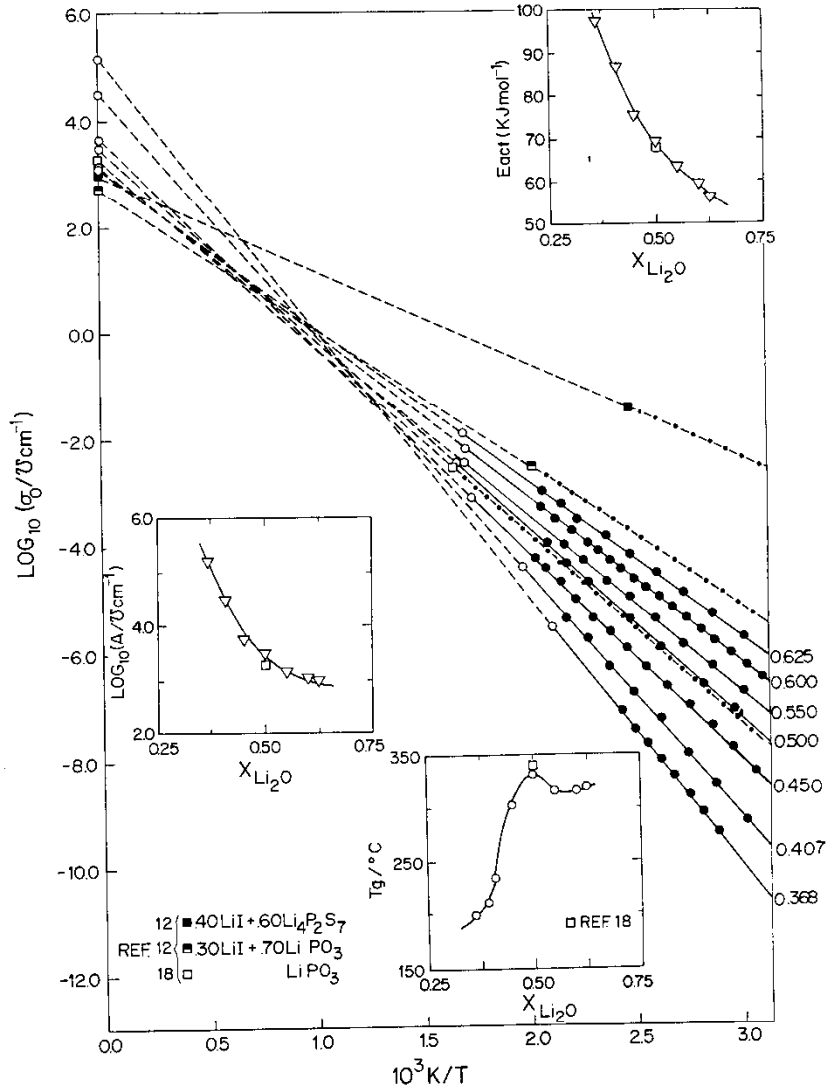


Fig. 17.17. Conductivity of glasses in the system Na_2O–SiO_2. From E. Seddon, E. J. Tippett, and W. E. S. Turner, *J. Soc. Glass Technol.*, **16**, 950 (1932).

DC ion conductivity in glass

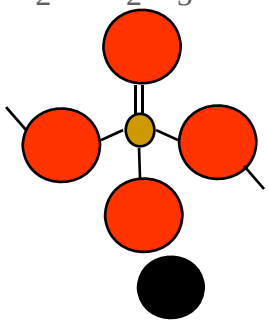
- $xLi_2O + (1-x)P_2O_5$
- Creation of non-Bridging oxygens
- "Mobile" lithium ions
- The higher the concentration of Li_2O, the higher the conductivity
  - Lower resistivity
- Activation energy decreases with Li_2O content

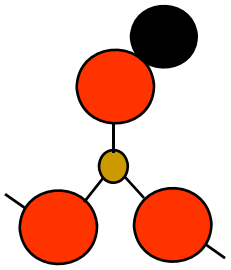


Composition Dependence of the Conductivity

- 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.

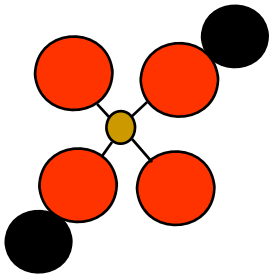
$Li_2O:P_2O_5$

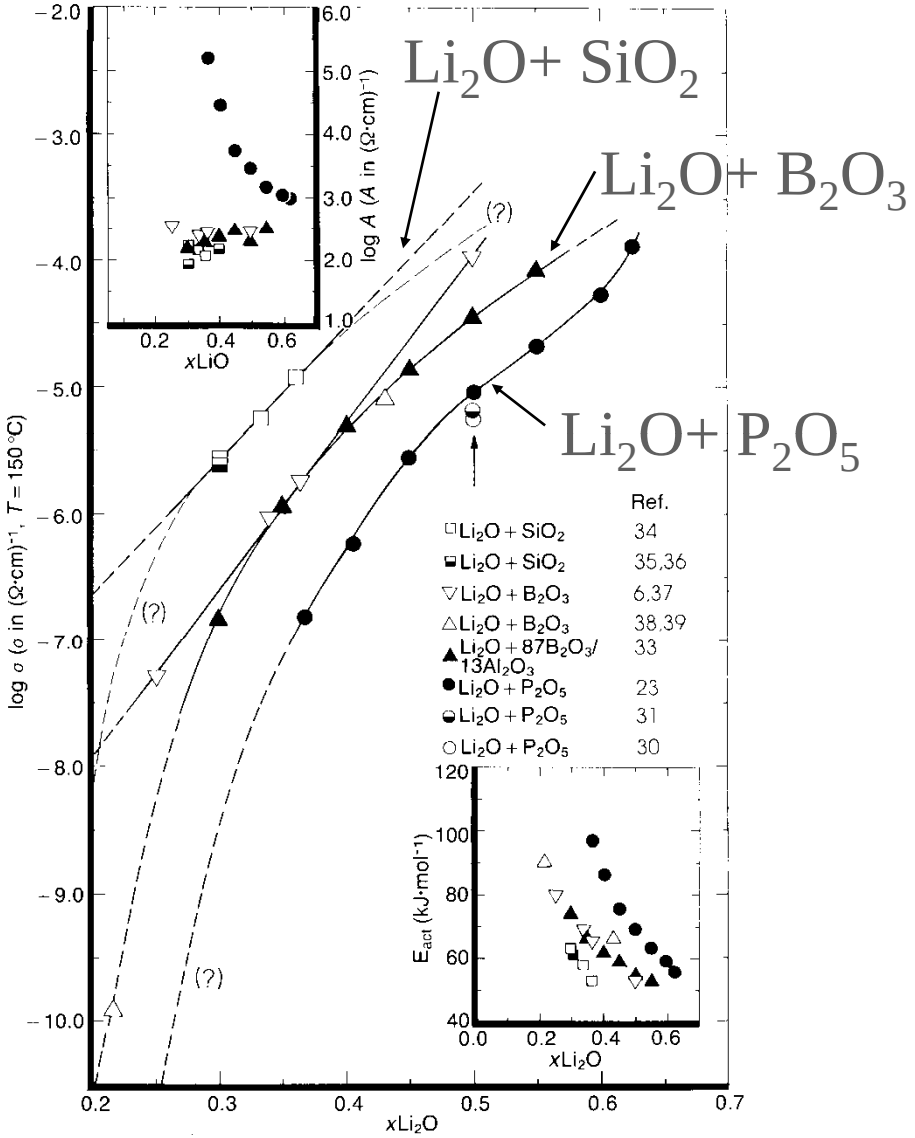




$Li_2O:B_2O_3$

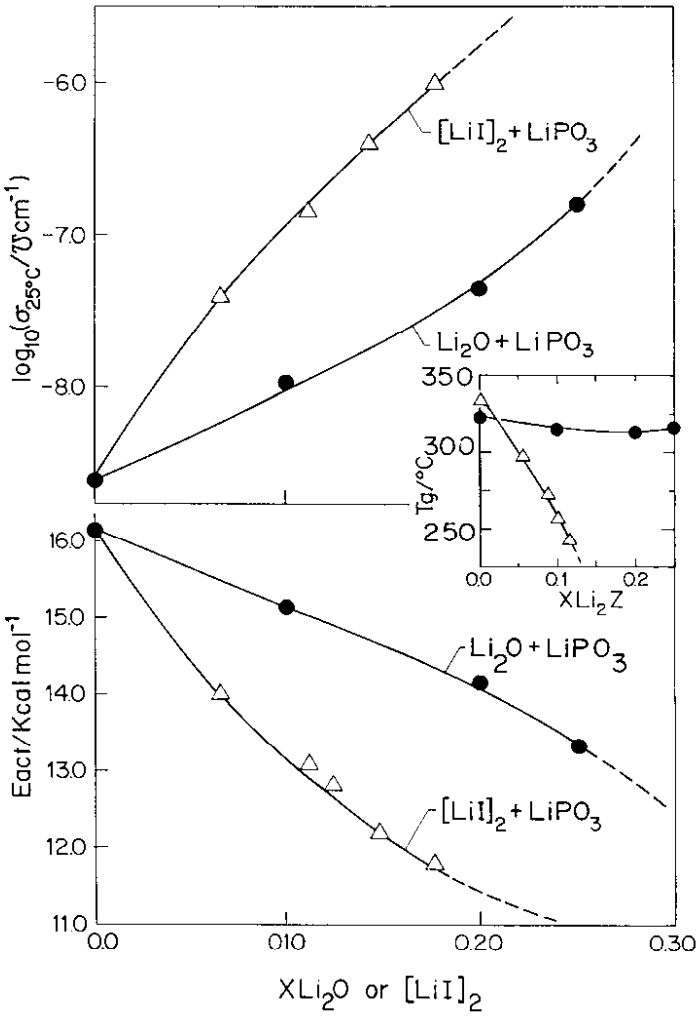
$Li_2O:SiO_2$



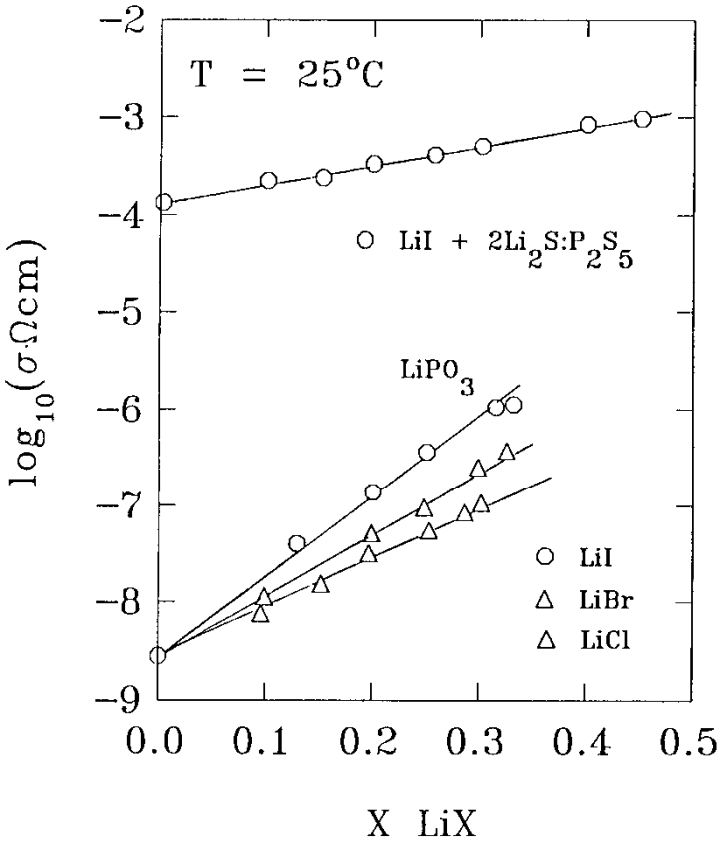


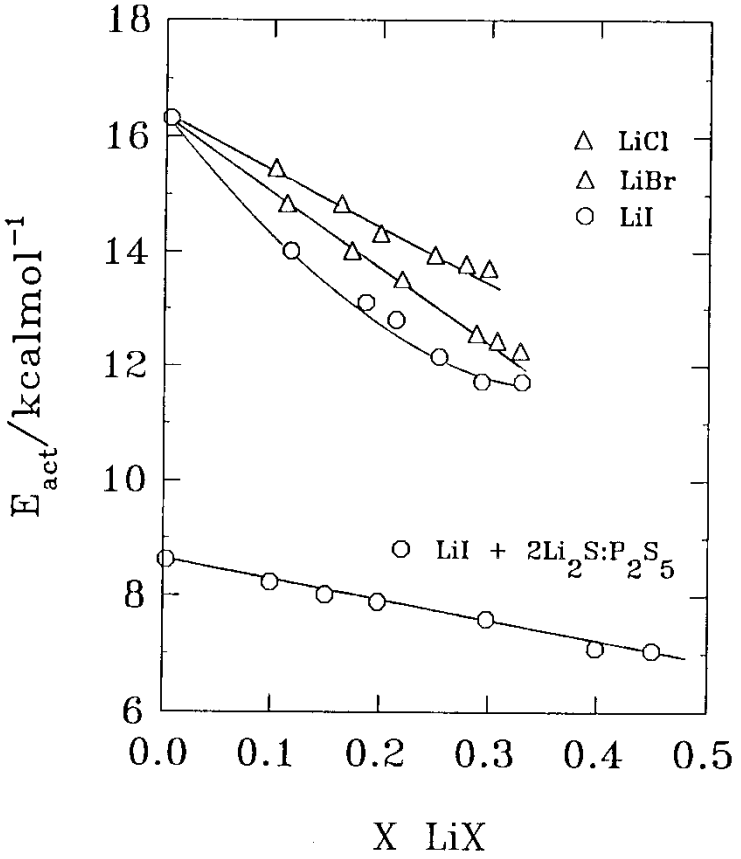
Salt doped phosphate glasses

- Halide doping strongly increases the conductivity



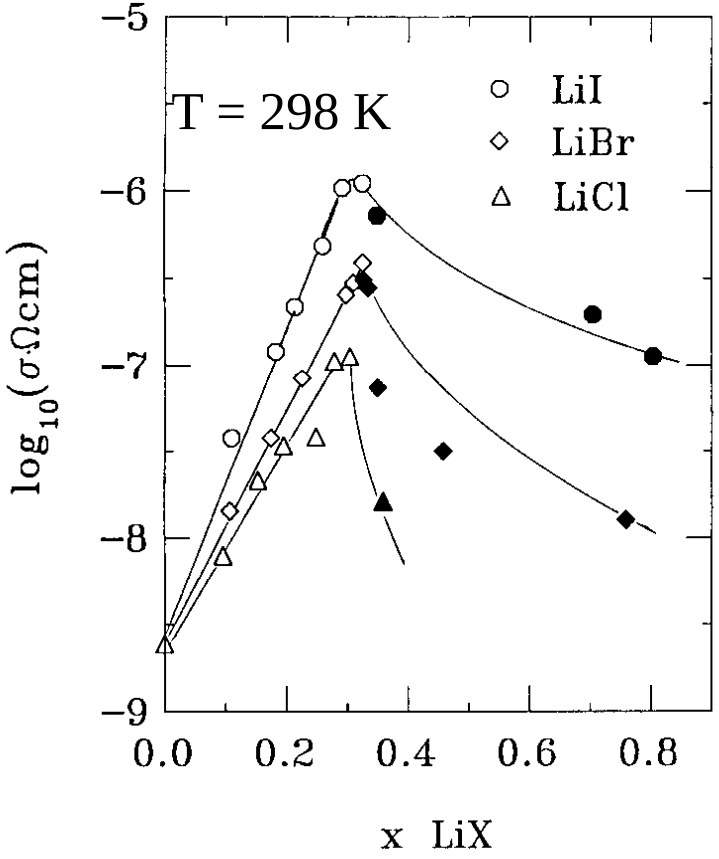
Effect of Sulfur Substitution

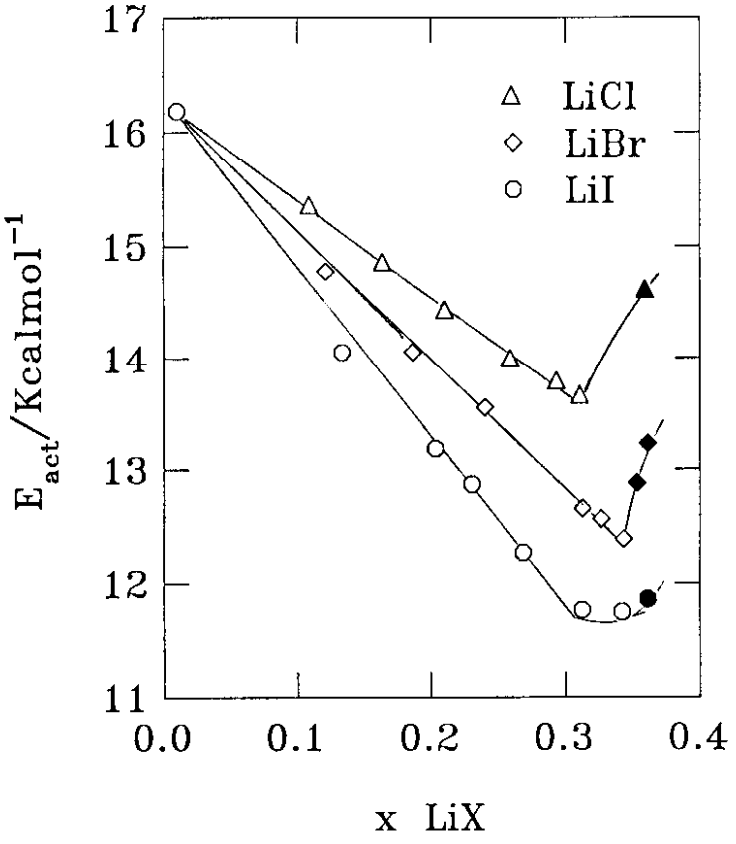




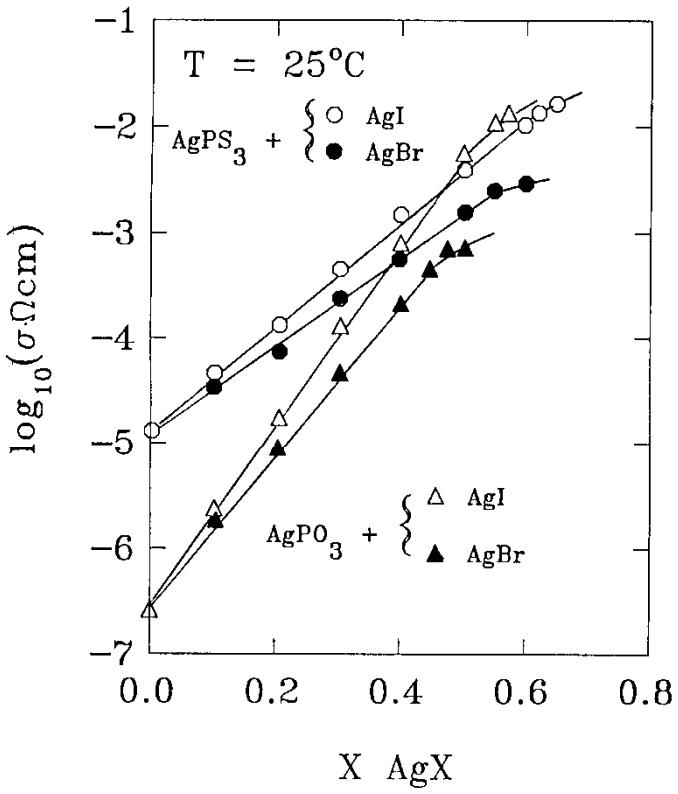
Salt doped phosphate glasses

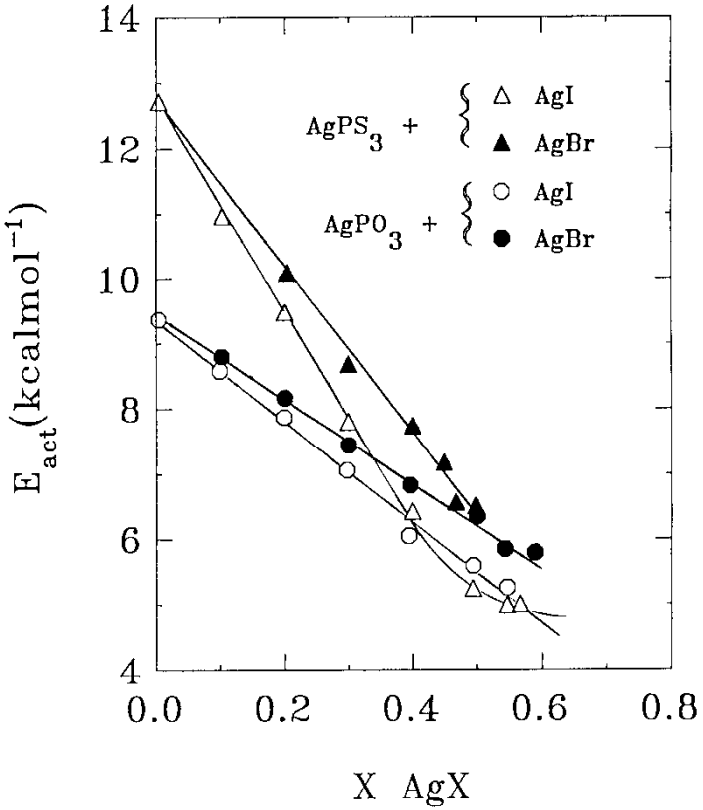
- LiI doped $LiPO_3$ show highest conductivity and lowest activation energy among the halides
- Crystallization at the end of the glass forming limit



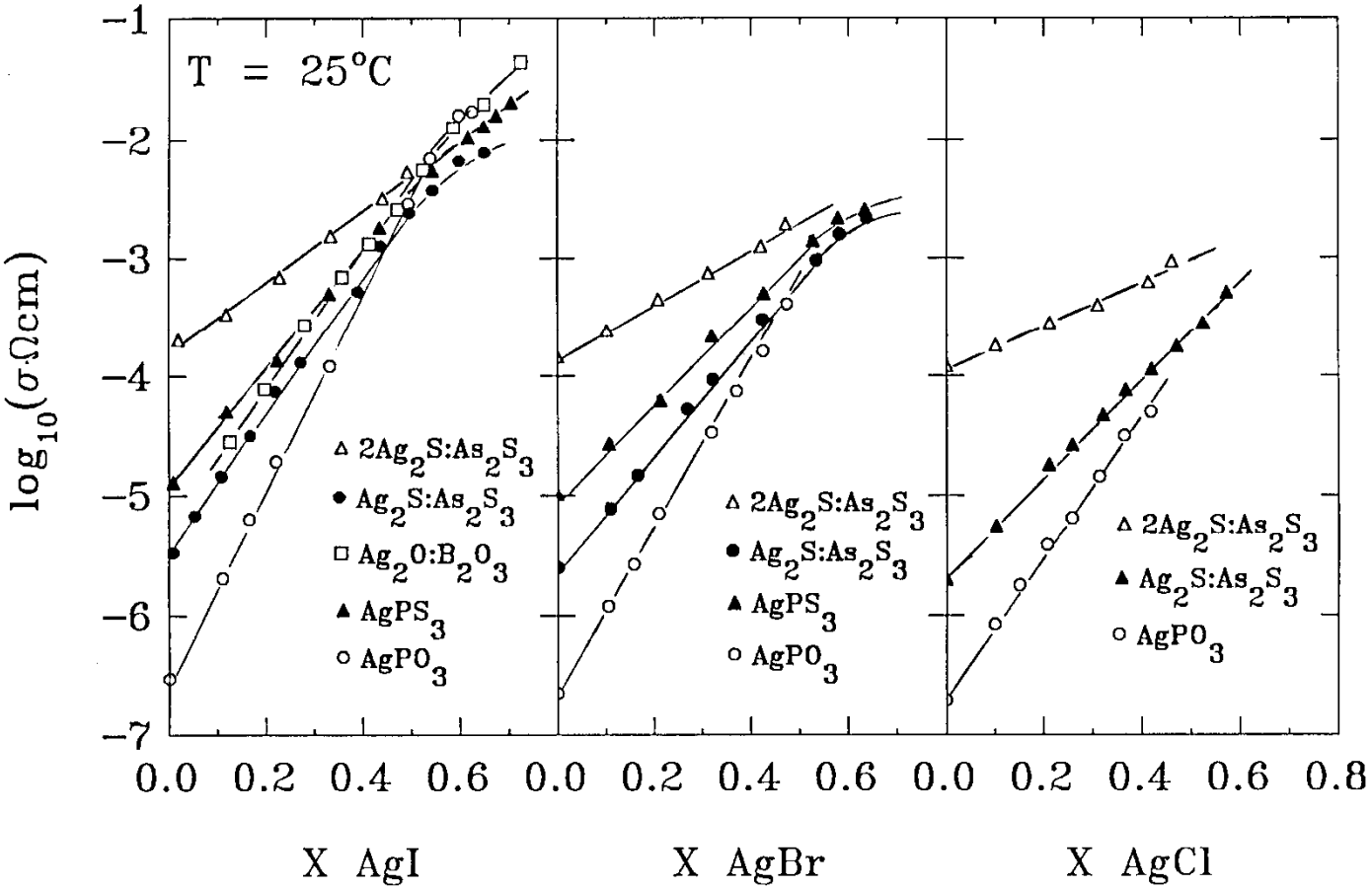


Silver Phosphate Glasses



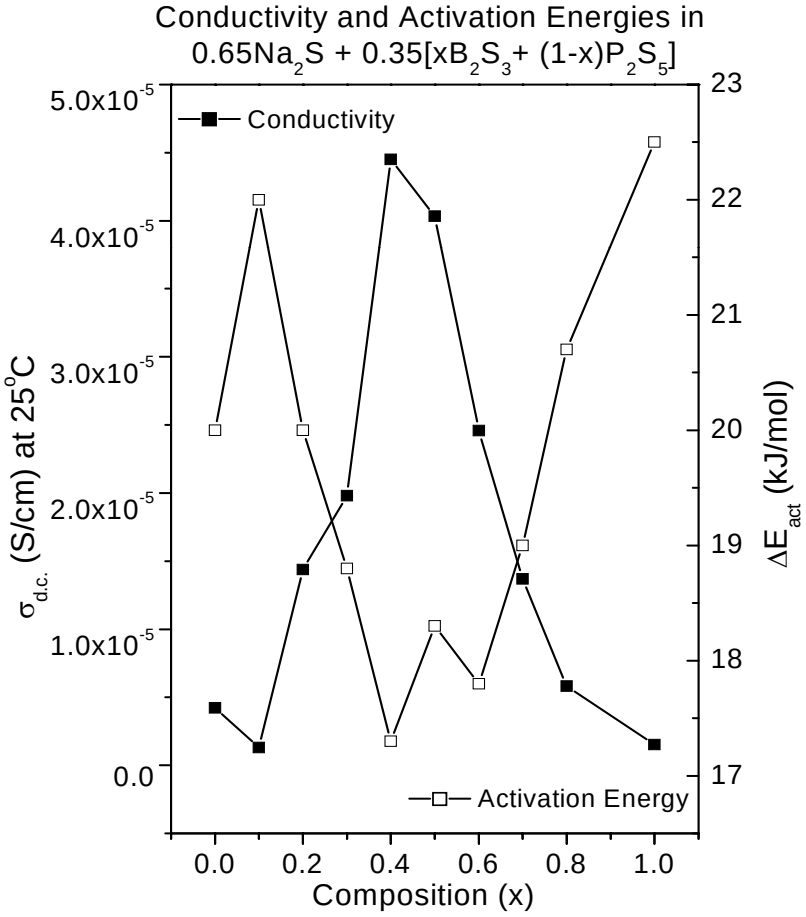


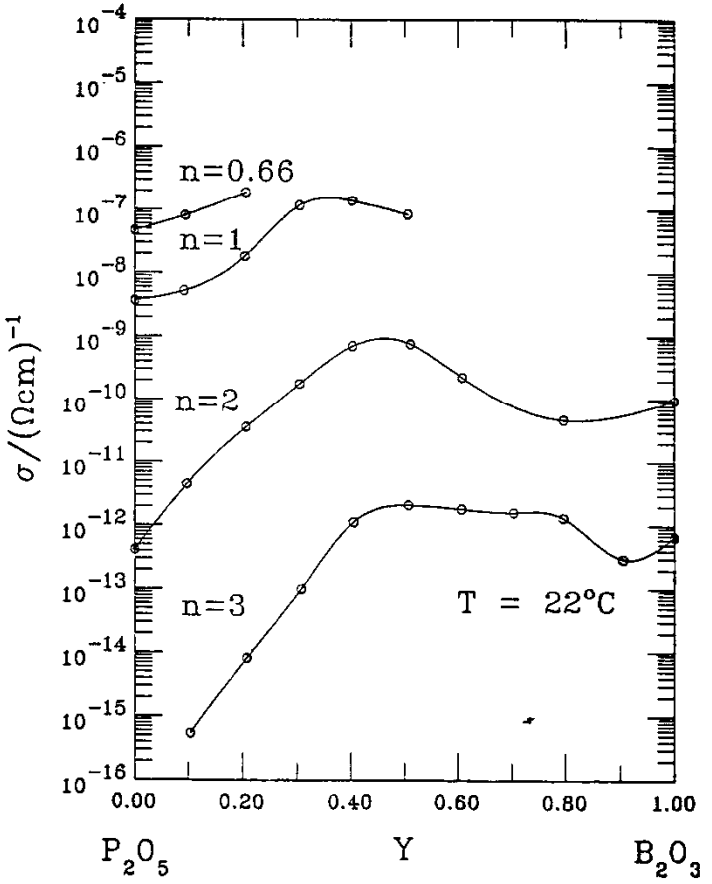
Other Silver sulfide doped glasses



Mixed Glassformer Systems

- Phosphate and borate mixed glasses show non-linear “Mixed Glassformer” effect





Short Range Order models of Conduction Energetics

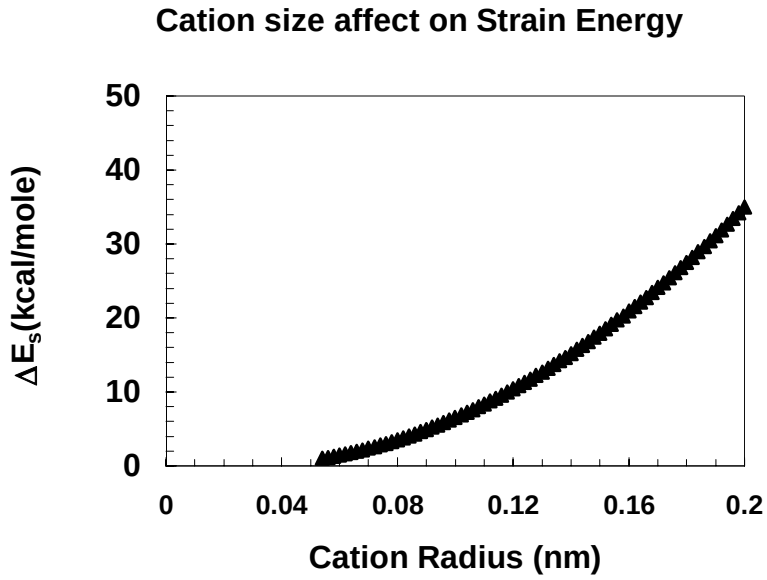
- Anderson-Stuart Model
- Assignment of Coulombic and Strain energy terms, $\Delta E_C + \Delta E_s$
- "Creation" or Concentration versus Migration energy terms, $\Delta E_C + \Delta E_m$
- Coulomb energy term, ΔE_C attractive force between cation and anion

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

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

Short Range Order models

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



$$\Delta E_S = \pi G (r_c - r_d)^2 \lambda / 2$$

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

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*

$\underbrace{1/2M_2O + SiO_{4/2}}_{\text{(Unreacted)}} \rightarrow \underbrace{{}_{3/2}O\text{-}Si\text{-}O^-M^+}_{\text{(Reacted but Undissociated)}} \rightarrow \underbrace{{}_{3/2}O\text{-}Si\text{-}O^- \cdots\cdots M^+}_{\text{(Dissociated)}}$

$K_{diss} = a_{M}{}^{+} a_{OM}{}^{-} / a_{M2O}$

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

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

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

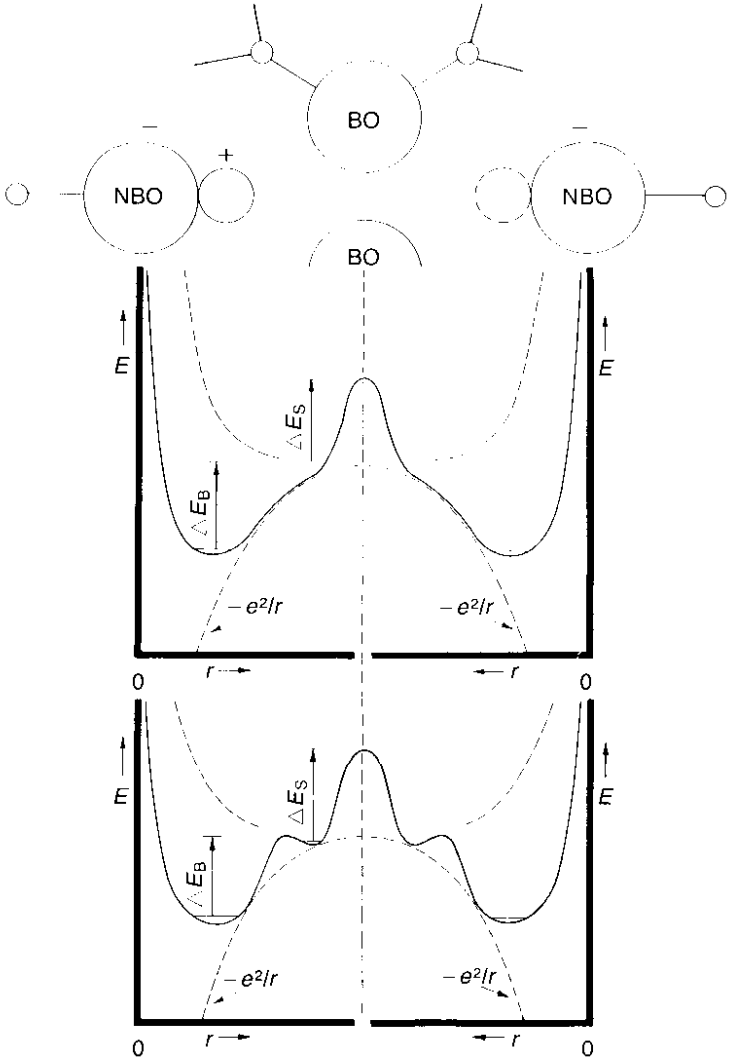
$\log K_{diss} \sim -Ne^2RT/4\pi\varepsilon_o\varepsilon_\infty (r_+ + r_-)$

As r_+, r_- increase, K_{diss} increases

As ε_∞ increases, K_{diss} increases

Strong and Weak Electrolyte models

- "Strong electrolyte" 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" 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

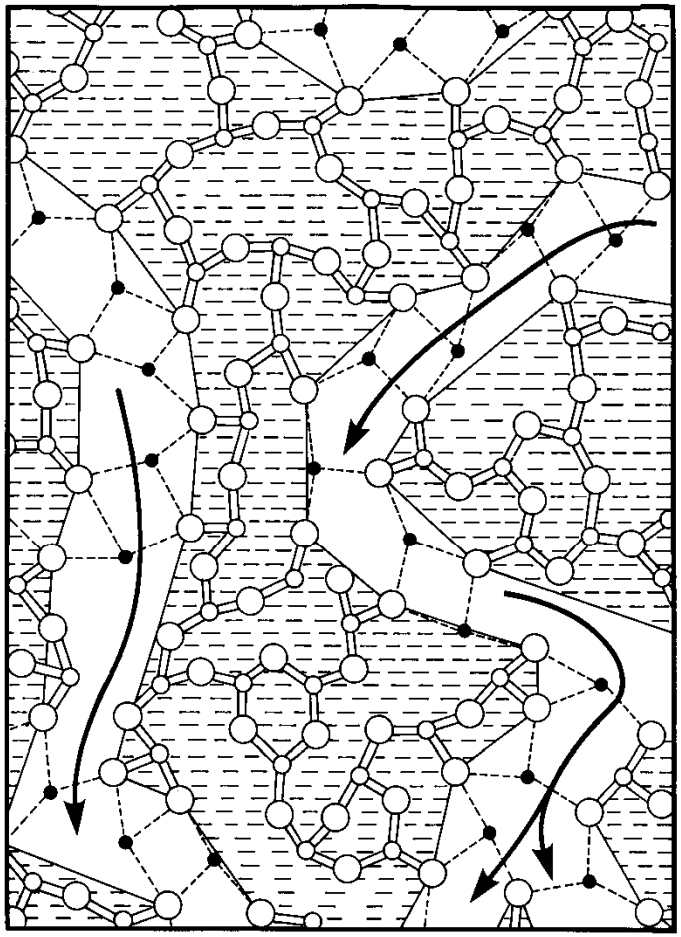


Intermediate Range Order models

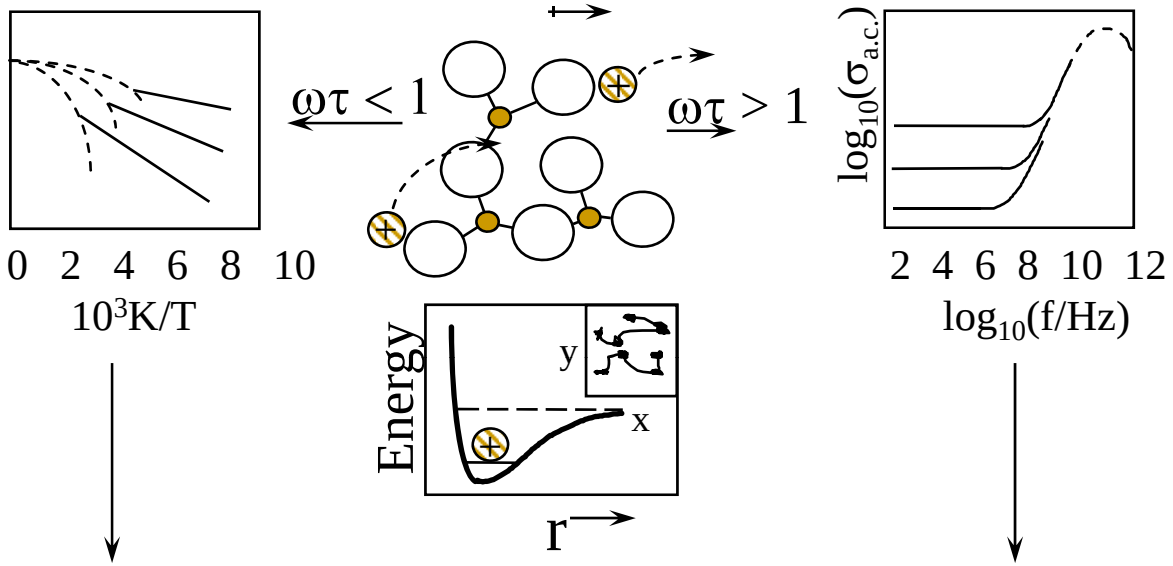
- Models recognize that ion conductivity requires ion motion over relatively long length scales
- Ions must be able to move from one side of the electrolyte to the other
- Long range connectivity of the SRO structures favorable to conduction must exist
- Deep “traps” along the way must be infrequent 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

- Cluster pathway model, *Greeves et al '85*



AC versus DC ionic conductivity

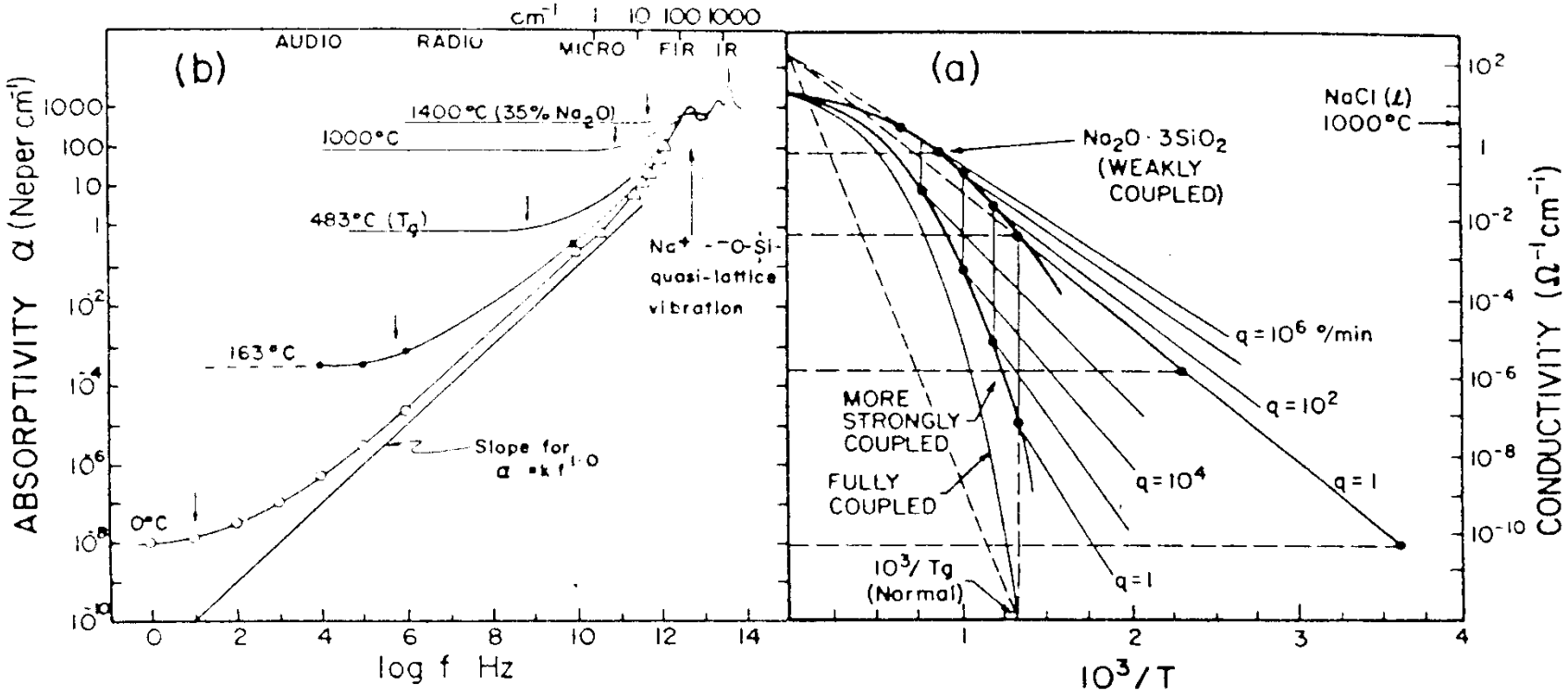


D.C. Conductivity
Conductivity

A.C.

AC ionic conductivity in glass

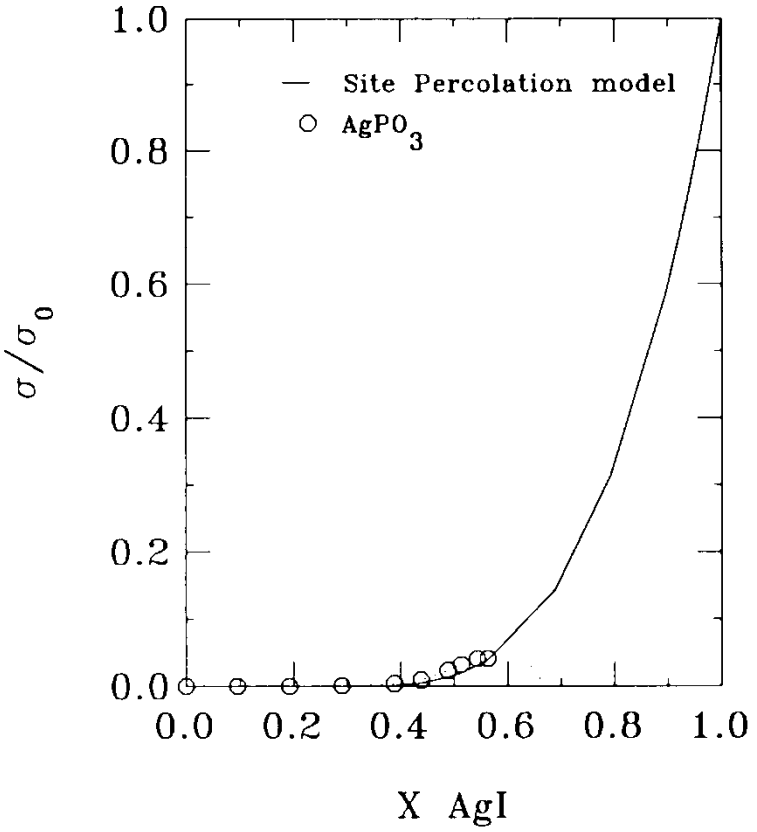
- Connection to Far-IR vibrational modes,

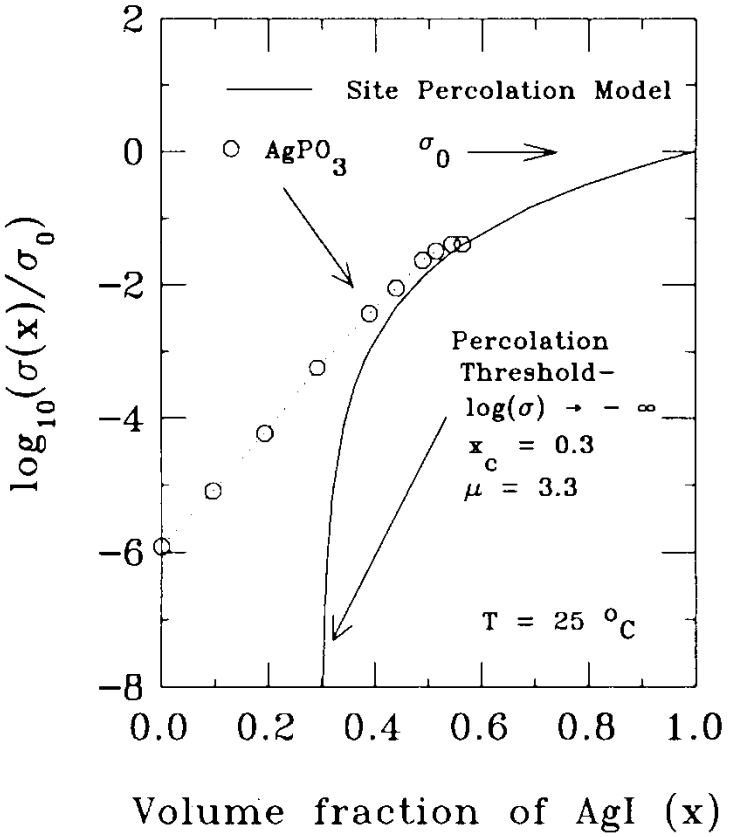


Intermediate Range Order models

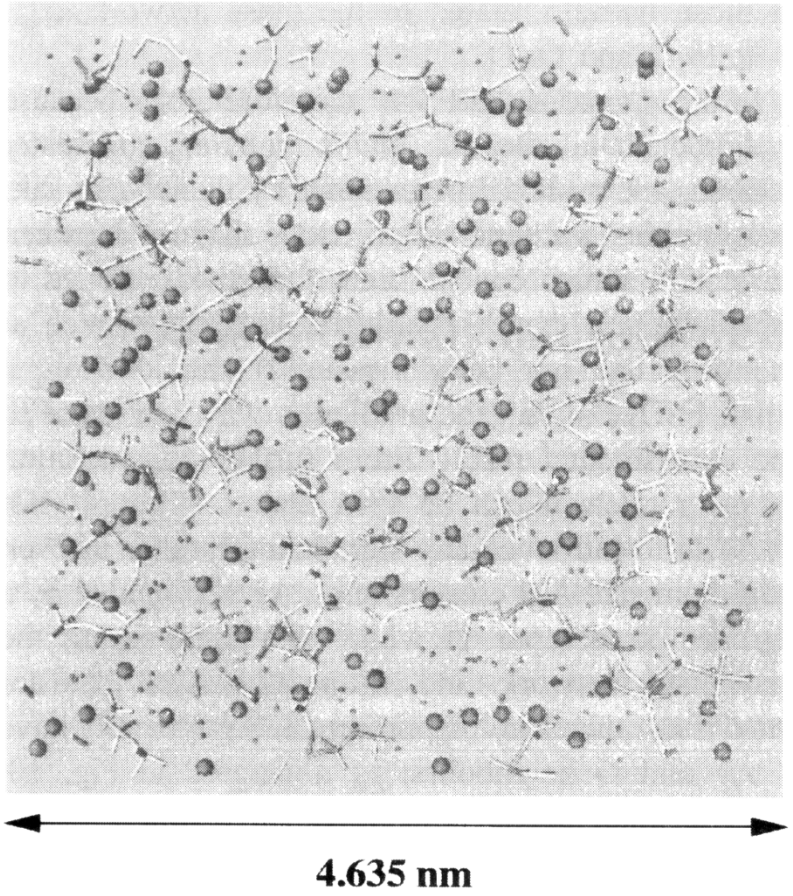
- Percolation Models - Johari *et al.* '87
  - At low dopant concentrations
    - Cations are far separated
    - Mobile species are diluted in a non-conducting host glass
  - At intermediate concentrations
    - Cations begin to approach proximity
    - Preferential conduction paths form
    - Sites percolate
  - At high concentrations
    - Cations are fully connected
    - Conduction pathways are fully developed

Conductivity percolation in AgI + $AgPO_3$





RMC Modeling of AgI + $AgPO_3$, *Swenson et al. '98*



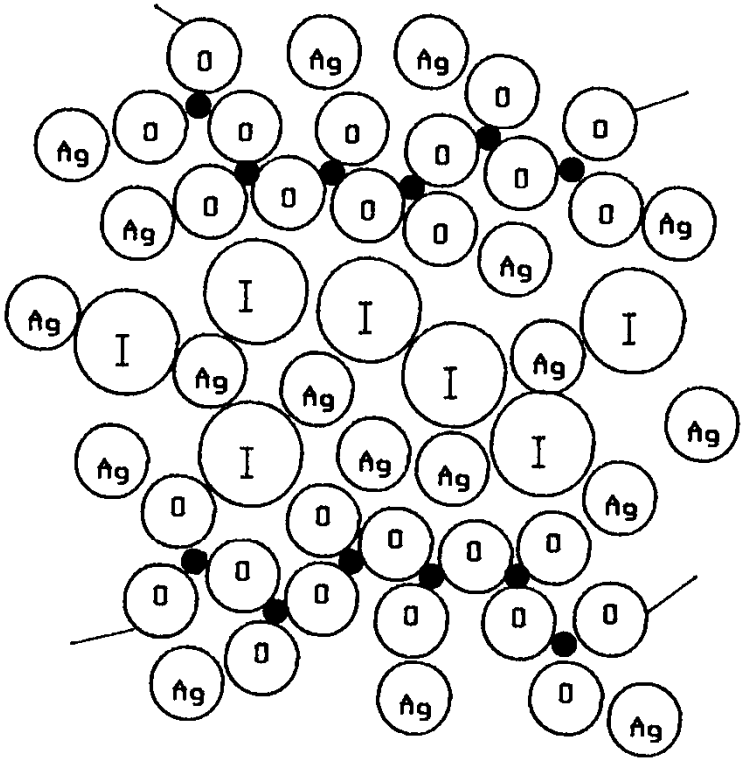
Intermediate Range Order models

- 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^{o}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



Ionic Conduction in Glass

- Ohms law
  - $V = IR$
  - $V = I \rho t/A = I \rho k$
  - $\rho = 1/\sigma$
  - $\rho(\Omega cm)$, $\sigma(\Omega cm)^{-1}$
- Calculate σ for
  - $I = 1\ \mu A$
  - $V = 1\ V$
  - $k = 1\ mm/1\ cm^2$