Ion Transport in Electrolyte Solutions

Craig E. Nelson - Consultant Engineer

Nelson Research, Inc. 2142 – N. 88th St. Seattle, WA. 98103 USA 206-498-9447 Craigmail @ aol.com

Charge Mobility – Absolute – any Kind of Force

From Bockris and Reddy Vol 1 pages 370 - 371

Absolute Mobility = ua = drift velocity / force

Let z = # charges per particle
e = charge of an electron = 4.8 * 10 ^ -10 {statcoulomb}
X = electric field {volts/cm}
1/300 = electrostatic unit conversion factor

Force = F = z*e*X*(1/300) {dynes}

1 dyne = 10^ -5 Newton

Force = F = z*e*X*(1/300)*(10^ -5) {Newtons}

Example: X = .05 volt/cm Vdrift = 2*10^ -5 cm/sec

Force = 8 * 10 ^ -14 {dynes} Force = 8 * 10 ^ -19 {Newtons}

Uabs = 2.5*10^ 8 { cm / (sec * dyne) } Uabs = 2.5*10^ 13 { cm / (sec * Newtons) }

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Charge Mobility – Conventional – Electric Force Only

From Bockris and Reddy Vol 1 pages 370 -371

Conventional Mobility = Uc = Vd / X = (1/300) * z * e * Uabs {cm^2 / (volt * sec)

Absolute Mobility = Uabs = Vd / F = (300 * Uc) / (z*e) {cm / (sec*dyne)

Example:

X = .05 volt/cm Vdrift = 2*10^ -5 cm/sec

Uconv = 4*10^ -4 { cm^2 / (volt*sec) }

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Ion Conductivity – Electric Force Only

From Bockris and Reddy Vol 1 pages 373

Particle Flux Density = J = concentration * velocity { moles/(cm^2 * sec }

Current Density = I = z* F * Conc * Vel { amperes / cm^2 }

F = 9.48 * 10 ^ 4 { coulomb / mole } Conc = {moles / cm^2 }

Note : Conc = {moles / cm^2 } = (1/1000) * Conc {moles/liter}

Conductivity = sigma = I / X { siemens / cm }

Sigma = z * F * Conc * Uconv

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Absolute Mobility and Diffusion Coefficient – Einstein Relation

From Bockris and Reddy Vol 1 pages 374

Particle Flux Density = Jd = concentration * velocity = - D* dC/dx { moles/(cm^2 * sec }

Vdrift = Uabs * Force { cm/sec }

Current Density = I = z*F*Conc* Vd { amps / cm^2 }

Conduction Flux Density = Jc = I / (z*F) = Conc * Vd = {moles / (cm^2 * sec)}

Jc = Conc * Uabs * Force

Particle Flux Density Total = Jtot = Jdiff + Jcond

D = Diff Coef = Uabs * K * T { cm^2 / sec }

D = Diff Coef = (300 * Uc) / (z*e) * K * T { cm^2 / sec }

K * T = .0257 eV = 4.12 * 10 ^ -21 { Joules } =
RT/F = .0257 eV

dC/dx = (C * Uabs * F) / D

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Joules, Ergs and Electron Volts

1 joul = 1 * 10 ^ 7 ergs

1 electron volt = 1 eV = 1.6 * 10^ -19 joul = 1.6 * 10^ -12 ergs

Boltzman's constant = Kb = 1.3807 x 10 -23 joule / K = 1.3807 x 10 -16 erg per k

T0 = 273 K   T27 = 300

K*T = 1.3807 x 10 -16 * 300 = 3.9e-14 ergs

1 erg = 1 dyne * cm

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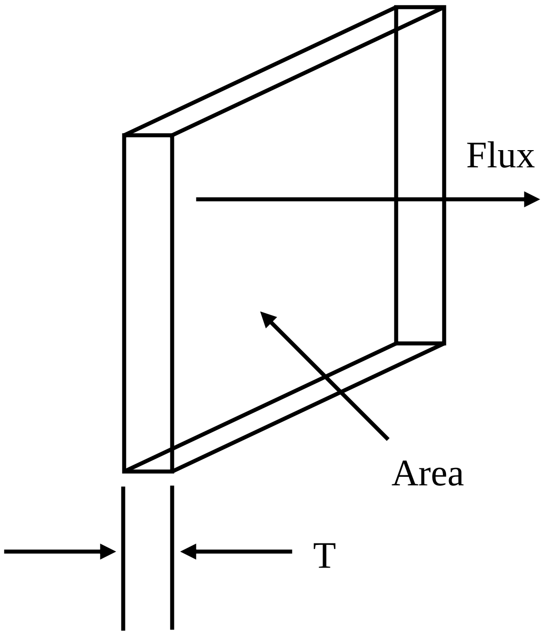
Example - Ionic Conduction in 4 Molar H2SO4 – 1 Amp / cm^2



D = Uabs * K*T = Uabs * (R*T/F) { cm^2 / sec }

T = .2 cm A = 1 cm^2 I = 1 amp/cm^2

Conc = 4 moles/liter = .004 moles / cm^3

Specific Conductivity = sigma = .75 Siemens / cm

Uproton_conv = 3 * 10 ^ -3 cm^2 / (sec*volt)
Usulfate_conv = .5 * 10 ^ -3 cm^2 / (sec*volt)
Bockris & Reddy p471

Uproton_abs = (300 / z*e) * Uc
= (300 / 4.8 * 10 ^ -10) * .003
= 1.875 * 10 ^ 9 cm/(sec*dyne)

Dproton = Uabs * KT
= 1.875 * 10 ^ 9 * 3.9e-14
= 7.3 *10^ -5 cm^2/sec

V = T / sigma = T /.75 = .267 Volts

X = electric field = .267 / .2 = 1.34 volts / cm

Vdrift_proton = Uc * X = .003 * 1.34 = .004 cm/sec

= .04 mm/sec = 40 microns/sec

or 100 seconds to cross the 2 mm channel

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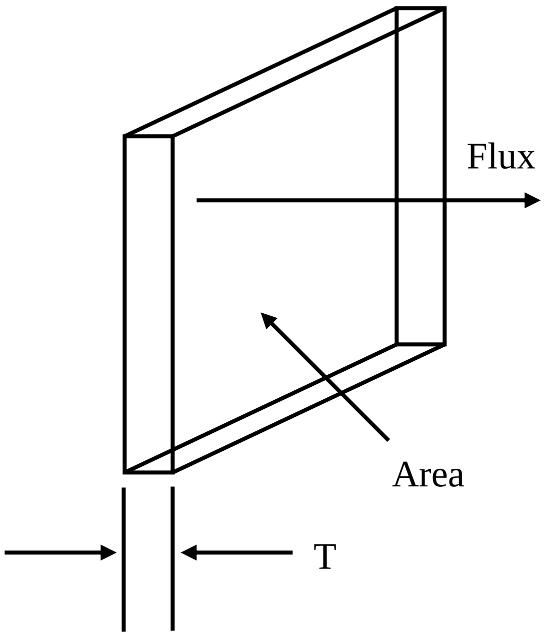
Example - Diffusion Current Density of 1 Amp/cm^2



Dproton = 7.3 * 10 ^ -5 { cm^2 / sec } Bockris – p 471

T = .2 cm A = 1 cm^2 I = 1 amp/cm^2

Specific Conductivity = sigma = .75 Siemens / cm

Electric Field = E = dV/dx = 1.34 Volts/cm (for 1 amp/cm^2)

Assume 2 molar MeOH at the anode inlet is half reacted then the concentration of newly created protons at the cathode facing surface of the anode must be 1*6 m/liter = .006 mole/cm^3
In the steady state all of this must be reacted.in the surface region

Current Density = i = - F^2 * dE/dx * z^2 * Uconv* C