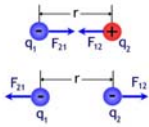


Chemistry BC3254y:
Methods and Applications in Physical Chemistry
Topic III.C Ions in Motion

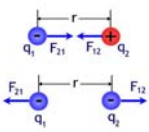
Some review



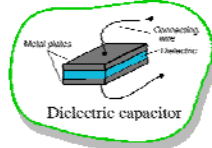
Coulomb's Law:

- | | | |
|---|----------|-----------------------------|
| SI | | cgs (old system) |
| $V = -Q_1Q_2/(4\pi\epsilon_0\epsilon r)$ | | $V = -Q_1Q_2/(\epsilon r)$ |
| $F = Q_1Q_2/(4\pi\epsilon_0\epsilon r^2)$ | | $F = Q_1Q_2/(\epsilon r^2)$ |
| V | Joules | ergs |
| F | Newtons | dynes |
| r | meters | cm |
| Q | Coulombs | esu |
- $e = -$ charge on electron = 1.602177×10^{-19} C, $Q_k = Z_k e$
 ϵ Dielectric constant of medium, no units.
 ϵ_0 Permittivity of vacuum = 8.854×10^{-12} C²/J-m

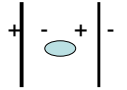
Some review



\mathcal{E} = electric potential difference (in Volts) = $(\Delta\phi)$
 old nomenclature: electromotive force, emf
 E = electric field strength between plates separated by ℓ : $E = \mathcal{E}/\ell$
 ϵ **Dielectric constant of medium**, no units.
 Measures the ability of the medium to permit the electrical field.
 Also called relative permittivity: $\epsilon = \mathcal{E}_0/\mathcal{E} = E_0/E$
 ratio of the electric field between two parallel plates
 (in vacuum)/(in specified medium)
 = ratio of potential difference between two parallel plates
 (in vacuum)/(in specified medium)



ϵ Dielectric constant



Measures the ability of the medium to permit the electrical field.
 Always > 1 : medium inhibits field
 ϵ (H_2O) = 78.54 at 25°C, 80.37 at 20°C
 ϵ (CH_3OH) = 32.63 at 25°C
 ϵ (C_6H_6) = 2.274 at 25°C
 Why is water so large?
dipoles align in the field
 higher T, more disorder, so $\epsilon \downarrow$
 also some polarization, induced dipole
 Dielectric constant depends both on
 polarizability and dipole moment.

TABLE 7-1. Dielectric Constants for Common Materials.

| MATERIAL | CONSTANT |
|------------------|-----------|
| Vacuum | 1.0000 |
| Air | 1.0006 |
| Paraffin paper | 2.5 - 3.5 |
| Transformer oil | 4 |
| Glass | 5 - 10 |
| Mica | 3 - 6 |
| Rubber | 2.5 - 35 |
| Wood | 2.5 - 8 |
| Porcelain | 6 |
| Glycerine (15 C) | 56 |
| Petroleum | 2 |
| Pure water | 81 |



More review: Ohm's Law



$$I = \mathcal{E}/R$$

I current ampere (A) = Coulomb/sec
 \mathcal{E} electric potential difference Volts (V) = Joules/Coulomb
 R resistance ohm (Ω) = V/A

R is a property of the material: wire, solution, etc.

Experimentally, observed that

R proportional to ℓ , length of wire, object...

R proportional to $1/A$, where A = area of wire, object...

Define ρ = "specific resistance" so $R = \rho \ell/A$

units: ohm-cm.

ρ is R for a cube of material 1 cm on each edge.

More review: Ohm's Law

$$I = \mathcal{E}/R$$

R resistance ohm (Ω) = V/A
 useful to define **conductance** $G = 1/R$

units 1/ohm (once called "mho") = Sieman = $1/\Omega$
specific conductance (κ or σ) = $1/[\text{specific resistance } (\rho)]$
 also called **conductivity**

SI unit: S/m, but often reported in S/cm.

For pure substances, G, R depend only on material and shape

For solutions, added factor of **concentration**.

conductance and conductivity

Conductance $G = 1/R$ units: Sieman = S = $1/\Omega$
specific conductance (κ) = $1/[\text{specific resistance } (\rho)]$
 also called **conductivity** units: Sieman/m

| Material | T | κ or σ (S/m) |
|------------|----|----------------------------|
| silver | 20 | 63.01×10^6 |
| copper | 20 | 59.6×10^6 |
| aluminum | 20 | 37.8×10^6 |
| seawater | 23 | 5 |
| tap water | 20 | 0.0005 to 0.05 |
| pure water | 20 | 5.5×10^{-6} |

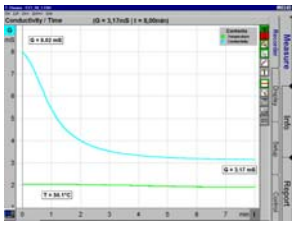
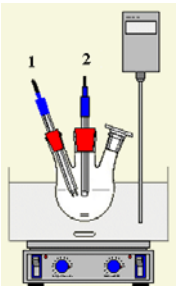
ref: Wikipedia (3/31/08)

Measuring conductance

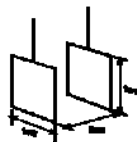


Conductance $G = 1/R$ units: Sieman = $1/\Omega$
specific conductance (κ) = $1/[\text{specific resistance } (\rho)]$
 Conductance or conductivity cell

parallel plates large enough to give uniform field,
 small enough to manage; geometry determined by calibration.



conductance



Conductance, G , of an ionic solution will depend on

1) concentrations of ions

2) charges on ions

3) mobilities of ions (to be defined)

one equivalent of electrolyte = amount with one \mathcal{F} of (+, -) charge

one \mathcal{F} is -(charge on one mole of electrons)

Let c = moles/L (molarity), and c^* = equivalents/L (normality)

| | | |
|----------------------------------|------------------------|------------|
| for 1:1 electrolyte (KCl), | 1 mole = 1 equivalent | $c^* = c$ |
| 1:2 electrolyte (K_2SO_4) | 1 mole = 2 equivalents | $c^* = 2c$ |
| 2:2 electrolyte ($MgSO_4$) | 1 mole = 2 equivalents | $c^* = 2c$ |
| 3:1 electrolyte ($Al(NO_3)_3$) | 1 mole = 3 equivalents | $c^* = 3c$ |

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conductance of ionic solutions

Conductance depends on **concentrations, charges, mobilities**

c = moles/L (molarity), and c^* = equivalents/L (normality)

Define **equivalent conductance** $\Lambda = \kappa/c^*$

if κ in S/cm and c^* in eq/L, multiply by 1000 cm^3/L to get

Λ (in S-cm²/eq) = 1000 κ/c^*

Atkins (strict re SI) uses units mS-m²/eq

Alternatively, define **molar conductance** $\Lambda_m = \kappa/c$

(two will be same for 1:1 electrolytes)

Because this includes the concentration, Λ varies slowly with c .

for strong electrolytes, as c increases, Λ tends to decrease.

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conductance of ionic solutions

equivalent conductance $\Lambda = \kappa/c^*$ **molar conductance** $\Lambda_m = \kappa/c$

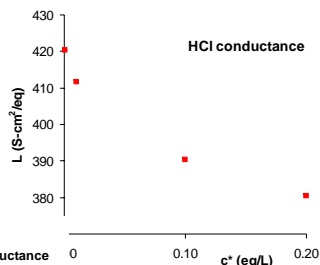
if κ in S/cm and c^* in eq/L, multiply by 1000 cm^3/L to get

Λ (in S-cm²/eq) = 1000 κ/c^*

Data:

| c | κ (S/cm) | Λ (S-cm ² /eq) |
|--------|-----------------|-----------------------------------|
| 0.0010 | 0.0004204 | 420.4 |
| 0.0100 | 0.004116 | 411.6 |
| 0.100 | 0.03904 | 390.4 |
| 0.200 | 0.07608 | 380.4 |

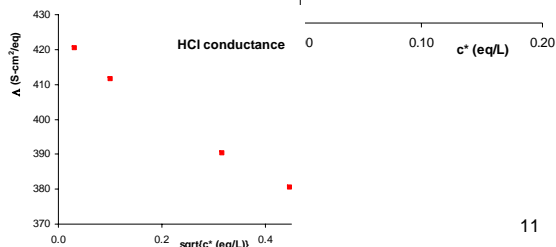
HCl solutions



curved:
try $\sqrt{c^*}$ x-axis
more nearly linear...

Kohlrausch's Law:

$$\Lambda = \Lambda_m^\circ - Kc$$



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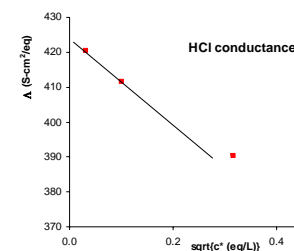
conductance of ionic solutions

equivalent conductance $\Lambda = \kappa/c^*$

Let $\Lambda^\circ = \lim_{c \rightarrow 0} \Lambda$

$\Lambda = \Lambda_m^\circ - Kc$ ($K = -\text{slope}$; not K_{eq})

| Electrolyte | Λ° (S-cm ² /eq) |
|------------------|---|
| HCl | 426.16 |
| NaCl | 126.45 |
| NaI | 126.94 |
| KCl | 149.86 |
| KI | 150.38 |
| KNO ₃ | 126.50 |



These remove the effect of concentration and charge
values differ due to different mobilities of the ions
as they move through solvent and other ions

Patterns: Λ° generally smaller when ions are larger

HCl anomalously large (same for other strong acids): protons fast!

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conductance of ionic solutions



Kohlrausch observed

$$\Lambda^0(\text{KCl}) - \Lambda^0(\text{NaCl}) = \Lambda^0(\text{KI}) - \Lambda^0(\text{NaI}) \text{ etc.}$$

proposed *law of independent migration of ions*

i.e. $\Lambda^0(\text{KCl}) = \lambda^0(\text{K}^+) + \lambda^0(\text{Cl}^-)$

cannot measure cations/anions independently, but if value for one taken arbitrarily, all others may be determined

| cation | λ^0 (S-cm ² /eq) | anion | λ^0 (S-cm ² /eq) |
|------------------|-------------------------------------|-------------------------------|-------------------------------------|
| H ⁺ | 349.82 | Cl ⁻ | 76.34 |
| Na ⁺ | 50.11 | Br ⁻ | 78.4 |
| K ⁺ | 73.52 | I ⁻ | 76.8 |
| Ag ⁺ | 61.92 | OH ⁻ | 198 |
| Ca ²⁺ | 59.50 | SO ₄ ²⁻ | 79.8 |

OH⁻ also anomalously large (in aqueous solution)

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conductance of ionic solutions



$$\Lambda^0(\text{salt}) = \sum_k \lambda_k^0 \quad \text{or} \quad \Lambda_m^0(\text{salt}) = \sum_k \nu_k \lambda_{k,m}^0$$

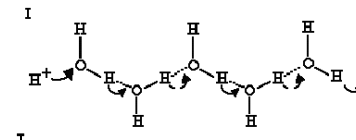
λ_k^0 are per equivalent, $\lambda_{k,m}^0$ per mole

Why are λ^0 's for H⁺ and OH⁻ anomalously large?

(in aqueous solution)

one ion does not actually have to move all the way through the solution!

"Grotthuss mechanism"



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current and velocity

The current is carried by cations and anions: $\mathbf{I} = \mathbf{I}_+ + \mathbf{I}_-$

$$I_k = dQ_k/dt = |z_k|e \, dN_k/dt$$

If the parallel plates have area A, and the ions move at speed v_k

$$\Delta N_k = (N_k/V)(A v_k \Delta t)$$

$$dN_k/dt = (N_k/V) A v_k$$

$$I_k = |z_k|e (N_k/V) A v_k = |z_k|e N_A (n_k/V) A v = |z_k| \mathcal{F} c_k A v_k$$

where c_k is the moles/L of ion k

The current is proportional to the **concentration** and proportional to the **velocity** of the ions.

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conductance and mobility

Electric field strength between plates separated by ℓ is $\mathbf{E} = \mathcal{E}/\ell$

$$I = \mathcal{E}/R, \quad G = 1/R = A\kappa/\ell \rightarrow I = \mathcal{E}A\kappa/\ell = EA\kappa$$

$$\kappa_k = c_k \lambda_m \rightarrow I_k = EA c_k \lambda_m$$

but (previous slide) $I_k = |z_k| \mathcal{F} c_k A v_k$

$$\rightarrow EA c_k \lambda_m = |z_k| \mathcal{F} c_k A v_k \quad \lambda_m = |z_k| \mathcal{F} v_k / E$$

Define **ionic mobility**, $\mathbf{u} = \mathbf{v}/\mathbf{E}$ units: m²/s-V

$$\lambda_m = |z_k| \mathcal{F} u_k$$

Mobility-Conductivity relationship: $\lambda = z u \mathcal{F} = z u N_A e$

conductivity λ_k is a macroscopic observable

mobility u_k is the underlying microscopic property.

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conductance and mobility

ionic mobility $\mathbf{u = v/E}$ and $\mathbf{u_k = \lambda_k / |z_k|}$ \mathcal{F}

Consider Cl^- at 25 C: $\lambda^\circ = 76.34 \text{ cm}^2\text{-S/eq}$

$$u = (76.34 \text{ cm}^2\text{-S/mole}) / (96484 \text{ C/mole}) = 7.912 \times 10^{-4} \text{ cm}^2\text{-S/C}$$

units: $S = \text{A/V}$ and $\text{A} = \text{C/s}$, so $\text{S/C} = 1/\text{V-s}$

$$u = \mathbf{7.912 \times 10^{-4} \text{ cm}^2/\text{V-s}}$$

Consider $\mathcal{E} = 1 \text{ Volt}$, and $\ell = 1 \text{ cm}$: then $E = \mathcal{E}/\ell = 1 \text{ V/cm}$

$$v = uE = (7.912 \times 10^{-4} \text{ cm}^2/\text{V-s})(1 \text{ V/cm}) = \mathbf{7.912 \times 10^{-4} \text{ cm/s}}$$

i.e. it takes $1264 \text{ s} = 21 \text{ minutes}$ to move 1 cm

Nernst related **diffusion** to mobility: $\mathbf{D_k = u_k RT / |z_k|}$ \mathcal{F}

gives $D(\text{Cl}^-) = 2.03 \times 10^{-5} \text{ cm}^2/\text{s}$; in 1264 s : $\Delta x = \sqrt{2Dt} = 0.23 \text{ cm}$

motion of ion driven by 1 V is ~ 4 times faster than diffusion.

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conductance and mobility

Electrical force, F , on ion of charge ze : $F_{el} = zeE = ze\mathcal{E}/\ell$

cations go to negative electrode, anions to positive

F_{fric} for particle moving at speed, v : $F_{fric} = v\mathbf{f}$

Steady state velocity (drift speed): $F_{el} = F_{fric} \rightarrow \mathbf{v = zeE/f}$

velocity is proportional to electric field strength

ionic mobility $\mathbf{u = v/E}$ so $\mathbf{u = ze / f}$

Sources of friction?

hydrodynamic friction: Stokes Law $f = 6\pi\eta r$

larger ions would be expected to have less mobility, smaller λ

viscosity of the solvent affects u and λ

electrophoretic effect: ions swim against counterions

relaxation effect: ion dragged by its ionic atmosphere

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conductance and mobility

Ionic mobility, $\mathbf{u = v/E}$

$$\mathbf{\lambda = zu} \mathcal{F} = \mathbf{zu N_A e}$$

Effect of ionic size on mobility:

For bulky ions,

larger ions have lower conductivity.

But radius $r =$ hydrodynamic radius (Stokes radius):

small ions carry (labile) hydration sphere so mobilities

and molar conductivities increase from Li^+ to Rb^+

even while the bare ionic radii increase.

small ions have higher charge density than large ions

and larger hydration sphere

Ionic Mobilities
(Water 25°C)

| Ion | u ($\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}$) | Ionic Radius (pm) |
|------------------|---|---------------------------------|
| H^+ | 36.23×10^{-8} | |
| Li^+ | 4.01×10^{-8} | 59 |
| Na^+ | 5.19×10^{-8} | 102 |
| K^+ | 7.62×10^{-8} | 138 |
| Rb^+ | 7.92×10^{-8} | 149 |
| Zn^{2+} | 5.47×10^{-8} | |



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conductance: weak electrolytes

Data above for strong electrolytes;

Kohlrausch also studied weak

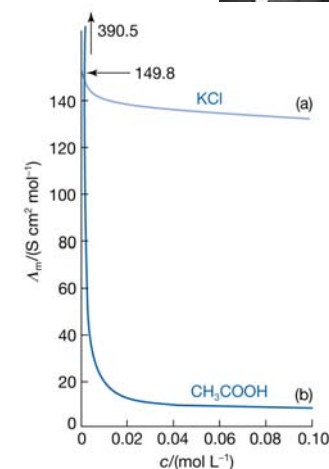
Λ values typically much less.

$\Lambda = \Lambda_m^\circ - Kc$ no longer applies.

This was early confirmation that weak electrolytes ionize partially.

Conductivity measurements

can be used to learn about the degree of ionization.

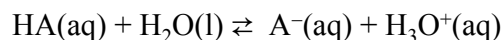


20

conductance: weak electrolytes

Not fully ionized in solution. Let $[HA]_0 = c$

for weak Brønsted acids (e.g., acetic acid)



Conductivity depends on degree of ionization, α :

$$[H_3O^+] = \alpha c \quad [A^-] = \alpha c \quad [HA] = (1-\alpha)c$$

$$K_a = [H_3O^+][A^-]/[HA] = (\alpha c)(\alpha c)/(1-\alpha)c = c \{\alpha^2 / (1-\alpha)\}$$

As c decreases, α increases ("Ostwald dilution law").

Assume that molar conductivity, Λ_m , is $\Lambda_m = \alpha \Lambda_m^\circ$

Can use conductance measurements to study α , K_a

two approximations: (1) neglecting activity coefficients

(2) assuming that $\Lambda_m = \Lambda_m^\circ$ when $\alpha = 1$

both become more reliable when solutions are very dilute.

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conductance: weak electrolytes

$$K_a = c \{\alpha^2 / (1-\alpha)\}$$

$$K_a/\alpha = c \{\alpha / (1-\alpha)\}$$

$$1/\alpha = (c/K_a) \{\alpha / (1-\alpha)\}$$

$$(1-\alpha)/\alpha = (c\alpha/K_a)$$

$$1/\alpha = 1 + (c\alpha/K_a)$$

$$\alpha = \Lambda_m / \Lambda_m^\circ$$

$$\Lambda_m^\circ / \Lambda_m = 1 + (c/K_a)(\Lambda_m / \Lambda_m^\circ)$$

$$\Lambda_m^\circ / \Lambda_m = 1 + (c\Lambda_m / (K_a \Lambda_m^\circ))$$

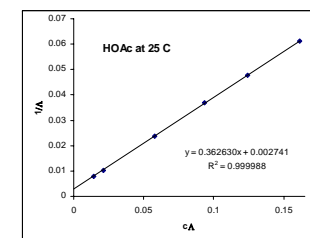
$$1/\Lambda_m = 1/\Lambda_m^\circ + c\Lambda_m / (K_a \Lambda_m^\circ)$$

Measure Λ_m vs. c : **Ostwald plot** $1/\Lambda_m$ vs. $(c\Lambda_m)$

line with intercept = $(1/\Lambda_m^\circ)$ slope = $1/(K_a \Lambda_m^\circ)$

HOAc at 25 C (Noggle, p 416)

| c | L | cΛ | 1/Λ |
|------------|--------|-------------|----------|
| 0.00011135 | 127.75 | 0.014224963 | 0.007828 |
| 0.00021844 | 96.493 | 0.021077931 | 0.010363 |
| 0.0013634 | 42.227 | 0.057572292 | 0.023682 |
| 0.00344065 | 27.199 | 0.093582239 | 0.036766 |
| 0.00591153 | 20.962 | 0.123917492 | 0.047705 |
| 0.0098421 | 16.371 | 0.161125019 | 0.061084 |



| m | b | Λ° | Ka |
|---------|-----------|---------|-----------|
| 0.36263 | 0.0027413 | 364.790 | 2.072E-05 |
| 0.00062 | 0.0000584 | 7.774 | |

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conductance: weak electrolytes

HOAc at 25°C, data from Noggle, page 416

$$\alpha = \Lambda_m / \Lambda_m^\circ$$

$$\Lambda_m^\circ = 390.7 \text{ (from } \lambda_k \text{'s)}$$

$$K_a' = c \{\alpha^2 / (1-\alpha)\}$$

plot $\ln K_a'$ vs. \sqrt{c}

intercept $\ln K_a = -10.947$

$$K_a = 1.76 \times 10^{-5}$$

more basic method,

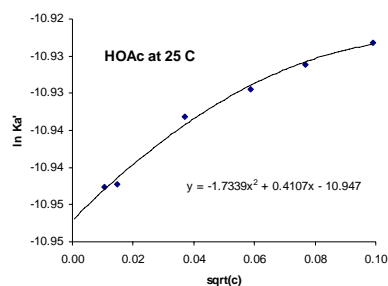
probably better...

accounts for activities.

but requires Λ_m°

done first by Arrhenius

| c | Λ | α | sqrt(c) | K _a ' | ln K _a ' |
|------------|--------|----------|----------|------------------|---------------------|
| 0.00011135 | 127.75 | 0.326977 | 0.010552 | 1.769E-05 | -10.9426 |
| 0.00021844 | 96.493 | 0.246975 | 0.014780 | 1.769E-05 | -10.9423 |
| 0.00136340 | 42.227 | 0.108080 | 0.036924 | 1.786E-05 | -10.9332 |
| 0.00344065 | 27.199 | 0.069616 | 0.058657 | 1.792E-05 | -10.9295 |
| 0.00591153 | 20.962 | 0.053652 | 0.076886 | 1.798E-05 | -10.9262 |
| 0.00984210 | 16.371 | 0.041902 | 0.099207 | 1.804E-05 | -10.9231 |



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conductance and solubility



Measure κ of a saturated solution of a salt in a conductance cell (must be dissolved in very pure water!)

e.g. Silver chloride in water

$$\kappa (\text{AgCl in water at } 25^\circ\text{C}) = 1.92 \times 10^{-7} \text{ S/cm}$$

$$\kappa (\text{water at } 25^\circ\text{C}) = 0.92 \times 10^{-7} \text{ S/cm}$$

$$\kappa (\text{due to ions}) = 1.00 \times 10^{-7} \text{ S/cm}$$

Assume that $\Lambda = \Lambda^\circ = 1000 \kappa/c$ where c is the ionic concentration

$$\Lambda^\circ = \lambda^\circ(\text{Ag}^+) + \lambda^\circ(\text{Cl}^-) = 140.3 \text{ S-cm}^2/\text{mole}$$

$$c = 1000 \kappa / \Lambda = (1000 \text{ cm}^3/\text{L})(1.00 \times 10^{-7} \text{ S/cm}) / (140.3 \text{ S-cm}^2/\text{mole})$$

$$= 7.13 \times 10^{-7} \text{ mole/L}$$

$$K_{sp} = c^2 = 5.1 \times 10^{-13}$$

approximate, but still useful.

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