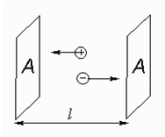
Conductimetric Determination of K_a of Weak Acids

<u>Electrical Conductance of Ionic Solutions</u>

Electrical conduction is a property of ionic solutions. Electrical conduction arises from the movement of electrical charges. Ionic conduction in solution the charges are moving as ions which is similar to electron or hole conduction through solids where electrons are moving without ion cores.

Water itself is a very poor conductor of electricity but the presence of ionic species in solution increases the conductance considerably.

The conductance in such electrolytic solutions depends on the <u>concentration of the ions</u> and also on the <u>nature of the ions</u> present (through their charges, effective sizes and mobilities). Conductance is a function of concentration is different for strong and weak electrolytes.



Resistance *R* of the body of solution is given by:

$$R = V/I$$

where *V* = the potential difference (volts) and *I* the current in amperes.

Conductance, *G* defined as the reciprocal of the resistance, of a homogeneous body of uniform cross section is proportional to the cross-sectional area *A* and inversely proportional to the length *l*.

R is directly proportional to the length and inversely proportional to area A of the conductor.

$$R \propto l/A$$

$$G = 1/R = \kappa(A/l)$$

where κ is the (***specific) conductivity*** with units Ω^{-1} m^{-1}.

$$\kappa = l/AR = C/R = CG$$

where C = cell constant = *l/A* (depends on cell geometry)

reciprocal ohm, mho; 1 Ω^{-1} = 1 Siemen = 1 S

One can think of the ***conductivity*** κ, as the conductance *G* of a cube of material, 1 m on each edge (so C = 1m^{-1}).

Any cell should be calibrated for *C* with a solution of exactly known specific conductance.

cell constant (m^{-1}); $C = l/A$

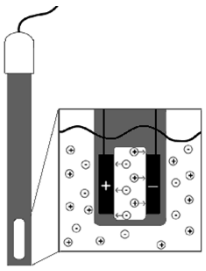
κ for an electrolyte of type $A_{\nu+}B_{\nu-}$ ($\Omega^{-1}m^{-1}$)

$$\kappa = 1000\alpha cF(\nu_+ z_+ \mu_+ + \nu_- z_- \mu_-) = l/AR = C/R$$

Conductance: $G = 1/R = \kappa A/l$

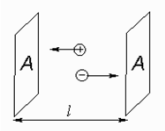
$$G = 1000\alpha cF(\nu_+|z_+|\mu_+ + \nu_-|z_-|\mu_-)C$$

Conc (equiv/L)



Conductivity Probe measures the ability of a solution to conduct an electric current between two electrodes.

Increasing concentration of ions in the solution will result in higher conductivity and vice versa.



Conceptually,

Specific *conductivity* κ : Conductivity in a cell with dimensions A = 1m and ***l*** = 1m.

Equivalent conductivity Λ: Conductivity of a cell with dimensions of area accommodating 1 *equivalent of the electrolyte* and ***l*** = 1.

Equivalent conductivity at infinite dilution Λ_o : Conductivity in a cell with dimensions of area A, accommodating 1 equivalent of the electrolyte and ***l*** = 1 at 'infinite' dilution.

Λ_o = Λ at infinite dilution.

Equivalent has a functional definition/usage as the amount (moles) of a substance which will supply or react with one mole of electrons in a redox reaction.

$$\Lambda(m^2 equiv^{-1}\Omega^{-1}) = \frac{\kappa(\Omega^{-1}m^{-1})}{1000\nu c(equiv\ L^{-1})}$$

$$\nu = \nu_+ z_+ + \nu_- |z_-| = \text{ of ions per formula}$$

For simple1:1 electrolytes (A^+B^-), there is no functional difference between equivalents and moles.

Conductivity Data for Common Aqueous Solutions

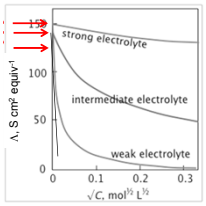
(Specific) Conductivity *(kappa)* (pS at 25°C)

ppm	NaCl	NaOH	HC1	Acetic Acid
10	21.4	61.1	116	15.1
30	64	182	340	30.6
100	210	603	1140	63.0
300	617	1780	3390	114
1000	1990	5820	11100	209
3000	5690	16900	32200	368
10000	17600	53200	103000	640

The conductivity of H^+(aq) and OH^-(aq) ions are very high.

Specific conductivity of a solution increases with concentration ***but*** the equivalent conductance with the concentration increases because ionic attraction reduces the equivalent conductance for strong,

Plotting Λ vs $\sqrt{c}$ and extrapolating to $c \rightarrow 0$ would yield Λ_0.



$$\Lambda = \Lambda_0\ (1 - \beta\sqrt{c})$$

Λ_0 0 (Onsager)

http://chemwiki.ucdavis.edu/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_Lower's_Chem1/07b._Solution_Chemistry/7b.7%3A_Ions_and_Electrolytes/1C%3A_Weak_and_Strong_Electrolytes#Not_all_Electrolytes_Totally_Dissociate_in_Solution

For an electrolyte A^+B^-, Λ_0; $\Lambda_0 = \lambda_0^+ + \lambda_0^-$

The equivalent conductance values of are additive.

Therefore for weak electrolytes such as HAc Λ_0 can be calculated as;

$$\Lambda_0(HAc) = \lambda_0(HX) + \lambda_0(MAc) - \lambda_0(MX)$$

Where MX, HX - metal halide and strong acid.

Limiting ion conductivity in water at 298 K

Cations	λ_+^0 /mS m²mol⁻¹	anions	λ_-^0 /mS m²mol⁻¹
H^+	34.96	OH^-	19.91
Li^+	3.869	Cl^-	7.634
Na^+	5.011	Br^-	7.84
K^+	7.350	I^-	7.68
Mg^{2+}	10.612	SO_4^{2-}	15.96
Ca^{2+}	11.900	NO_3^-	7.14
Ba^{2+}	12.728	$CH_3CO_2^-$	4.09

http://en.wikipedia.org/wiki/Conductivity_(electrolytic)

$$\Lambda(m^2 equiv^{-1}\Omega^{-1}) = \frac{\kappa(\Omega^{-1}m^{-1})}{1000\nu c(equiv\ L^{-1})}$$

$\nu = \nu_+ z_+ + \nu_- |z_-| =$ of ions per formula

Weak electrolytes by definition do not dissociate completely.

$$HAc \rightleftarrows H^+ + Ac^-$$

$c(1-\alpha) \quad c\alpha \quad c\alpha \quad :c =$ analytical concentration

$$\alpha = \frac{\Lambda(HAc)}{\Lambda_0(HAc)} \quad \Leftrightarrow \quad K_c = \frac{\alpha^2 c}{1-\alpha} \quad :K_c = \text{concentration}$$

$$K_a = K_c \gamma_+ \gamma_- = K_c \gamma_\pm^2 \qquad :K_a = \text{ thermodynamic K}$$

$$\log K_c = \log K_a - 2\log \gamma_\pm$$

$$\log K_c \cong \log K_a + 2A\sqrt{c_{ion}} \qquad \text{use DH Limiting Law}$$

$$\log K_c \cong \log K_a + 2A\sqrt{\alpha c}$$

Procedure

Prepare a series of acetic acid solutions of concentrations ~0.050M (= c_a), c_a/2, c_a/4, c_a/8, c_a/16, .., c_a/254 by serial dilution.

Measure the conductivity of each of the above solutions.

Measure the conductivity of water used to make the solutions.

Calculate the conductivity due to electrolyte by difference.

Generate data to plot K_c vs $\sqrt{(\alpha c)}$, extrapolate to $c \rightarrow 0$.
(use the straight line region, or fit a polynomial.)

Compare K_a to the published values at room temperature.
Verify A value of the Debye Huckel limiting law.