Molar Conductivity

Molar and Equivalent Conductivities

The electrical conductivity EC is an easy-to-measure parameter; its *exact* calculation, however, is rather non-trivial. Today exist a variety of approaches 1, but all of them are no more than approximations (especially for waters of arbitrary composition). In any case, physical-based approaches to EC start always from the concept of *molar* or *equivalent* conductivities:

(1a)	electrical conductivity (specific conductance)	EC 2'3	in S/m (or μS/c
(1b)	molar conductivity	$\Lambda_m = EC / c$	in S cm^2 mol^{-1}
(1c)	equivalent conductivity	$\Lambda_{eq} = \Lambda_m / \lvert z \rvert$	in S cm^2 eq^{-1}

Here *c* symbolizes the molar concentration of the electrolyte (in mol/L) and *z* refers to the electrical charge. The molar conductivity Λ_m is defined as the conductivity of a 1 molar aqueous solution placed between two plates (electrodes) 1 cm apart.
The *equivalent* conductivity refers to the *normality* of the solution (rather than molarity). It accounts for the obvious fact that ions with higher *z* are able to transport more charge. Introducing the

(2) equivalent concentration: $c_{eq} = |z|\, c$

the equivalent conductivity in Eq.(1c) becomes

(3) $\Lambda_{eq} = EC / c_{eq}$

Kohlrausch's Law for Strong Electrolytes (Limiting Conductivities)

Strong electrolytes (in contrast to *weak* electrolytes) are salts, acids and bases that dissociate completely. For strong electrolytes one might expect a linear relationship between EC and the concentration, i.e. EC = const · c, where the molar conductivity $\Lambda_m$acts as proportionality constant. Unfortunately, nature is not so simple: Λ_m is not constant and diminishes when c raises. About 100 years ago F. Kohlrausch deduced from experimental data the "Square-Root Law":

(4a) $\Lambda eq = \Lambda 0eq - Kceq−−√\Lambda eq = \Lambda eq0 - Kceq$

or, equivalently,

(4b) $\Lambda m = \Lambda 0m - K'c√\Lambda m = \Lambda m0 - K'c$ with $K' = K / |z|^{1.5}$

It is valid for *strong electrolytes*4 at low concentrations, c ≤ 10 mM. The Kohlrausch parameter K depends on the type of electrolyte. A theoretical explanation of the square-root dependence of *c* was provided by Debey, Hückel and Onsager about 50 years later.
Limiting Conductivities. In the very special case of zero concentration, c → 0 (infinite dilution), the above equations collapse to the

(5a) equivalent limiting conductivity Λ^0_{eq} in S cm^2 eq^{-1}

(5b) molar limiting conductivity Λ^0_m in S cm^2 mol^{-1}

These are the only experimentally accessible, basic electrotransport properties of a given ion.

Kohlrausch's Law of the Independent Migration of Ions

According to the Law of independent migration the limiting molar conductivity can be expressed as a sum of cation and anion contributions:

(6) $$\Lambda^0_m = \nu_+\Lambda^+_m + \nu_-\Lambda^-_m$$

where ν_+ and ν_- label the stoichiometric coefficients. Some typical values of limiting molar conductivities[5] at 25°C are:

	cation	Λ^+_m **[S cm^2 mol^{-1}]**		**anion**	Λ^-_m **[S cm^2 mol^{-1}]**

Given the composition of an aqueos solution, Eq.(6) allows us to compute its electrical conductivity EC as a sum over all dissolved ions *i*:

(7a) ideal solution (c → 0): $$EC^{(0)} = \sum_i \Lambda^0_{m,i} c_i = \sum_i \Lambda^0_{eq,i} |z_i| c_i$$

(7b) real solution: $$EC = \sum_i \Lambda_{m,i} c_i = \sum_i \Lambda_{eq,i} |z_i| c_i$$