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Influence of Temperature on Electrical Conductivity of Diluted Aqueous Solutions

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Influence of Temperature on Electrical Conductivity of Diluted Aqueous Solutions

Heinz Wagner

ABSTRACT

As conductivity is temperature dependent, all values reported in the major cycle chemistry guidelines are specified for a standard temperature of 25 °C. For this reason, most current conductivity monitors have an integrated temperature sensor and offer algorithms to convert measured values to the standard temperature. This article looks at the physical-chemical basics of electrical conductivity measurement and discusses the temperature dependence of specific and acid conductivity for different dissolved chemical substances. It is concluded that the conversion of a conductivity value to 25 °C can be approximated by a single equation that is applicable to samples composed of any electrolytes.

NOMENCLATURE

E_x	$V \cdot m^{-1}$	electrical field
F	$C \cdot mol^{-1}$	Faraday constant (96 493 $C \cdot mol^{-1}$)
I	A	current
$K_{W,T}$	$mol^2 \cdot L^{-2}$	temperature-dependent dissociation constant of water
$\bar{Q}$	—	averaged conversion factor
R	Ω	resistance
T	°C	temperature
V	V	voltage, electrical potential
Z	—	absolute value of the charge number of an ion
a	m	radius
c	$mg \cdot kg^{-1}$, $mol \cdot L^{-1}$	concentration of a dissolved ion or a substance
d, x	m	distance
e	C	elementary charge
f	m^2	surface area
k	—	Kohlrausch square root law constant
n_e	—	electrochemical valence
v	$m \cdot s^{-1}$	velocity
α	—	degree of dissociation
η	$P \cdot s$	dynamic viscosity
κ	$\mu S \cdot cm^{-1}$	specific conductivity
λ	$cm^2 \cdot mol^{-1} \cdot \Omega^{-1}$	equivalent ionic conductivity
Λ	$cm^2 \cdot mol^{-1} \cdot \Omega^{-1}$	equivalent conductivity
μ	$m^2 \cdot s^{-1} \cdot V^{-1}$	ion mobility

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INTRODUCTION

The electrical conductivity of a dilute aqueous solution is a measure of the total amount of ionic solutes that are present. As a sum parameter, it provides an evaluation of the quality of boiler feedwater, and of the purity of the steam and the condensate.

To ensure a safe and effective operation, the conductivity limits must be maintained. Normal operational values, as well as threshold values, are stated for the various sampling points of the water-steam-cycle (feedwater, boiler, steam, condensate, etc.) and for certain operational conditions (start-up, normal operation).

As conductivity values are dependent on temperature, the limits for standard conditions are set at 25 °C and 101.325 kPa (1 atm). With internal cooling water, the samples can usually be cooled to below 50 °C. However, for a set temperature of 25 °C an extra controlled cooling cycle is necessary, which means further expenses in purchase and maintenance.

Today most conductivity measuring instruments have an integrated temperature gauge. If the temperature dependence is known, the conductivity value at 25 °C can be calculated. However, there are differences of opinion on the usefulness of such calculations.

The following article looks at the physical-chemical basics of electrical conductivity with calculation models for different dissolved chemical substances. With these examples, we will examine in which areas these conversions function and the accuracy of the results.

ELECTRICAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS [1]

When a voltage, V, is set between two electrodes in an electrolyte solution, the result is an electric field which exerts force on the charged ions: the positively charged cations move towards the negative electrode (cathode) and the negatively charged anions towards the positive electrode (anode). The ions, by way of capture or release of electrons at the electrodes, are discharged and so a current, I, flows through this cycle and the Ohms law ($V = I \cdot R$) applies. From the total resistance of the current loop, R, only the resistance of the electrolyte solution, or its conductivity, $1/R_{el.}$ is of interest.

Space charge occurs at the electrode/electrolyte interface because of the directed flow of the ions. Therefore the potential is not linear (polarization effect). To minimize this effect, measurements are made using alternating current and not direct current. In addition, the potential difference is often measured with two other currentless electrodes in an inner area between the conducting electrodes, where there is no space charge. In this area, current I flows between two parallel electrodes, with the surface f in distance d and the electrical potential difference V

$$I = \kappa \frac{f}{d} V \tag{1}$$

where the proportionality constant κ is the specific conductivity of the electrolyte solution.

The larger the electrode surface f and the set voltage V is, the larger the current (the larger the distance d between the electrodes, the smaller the current I).

The proportionality constant κ is calculated by the electrical quantities (I and V) and the geometric dimensions (f and d) of the conductivity cell. The specific conductivity κ describes the physical-chemical properties of the sample and κ can also be expressed by the concentrations of the dissolved ions and their electrochemical characteristics,

$$\kappa = \sum_{1}^{i} c_i Z_i \lambda_i \tag{2}$$

hereby c_i is the concentration of the dissolved ion i,
Z_i the absolute value of the charge number of ion i, and
λ_i the equivalent ionic conductivity of ion i.

The equivalent ionic conductivity is a characteristic quantity for every ion type. Experimental data show that the equivalent ionic conductivity is not only dependent on the ion type, but also on the concentration and the temperature.

Dependence of the Equivalent Ionic Conductivity λ on the Ion Type

The electrical field $E_x = \partial V / \partial x$ exerts a force in a direction x on the ions with charge Ze and accelerates them. The friction resistance of the solution, which is proportional to the velocity v_x, counteracts this force. According to Stokes, this resistance for spheres with a radius a, in a solution with viscosity η equals $6\pi a \eta v_x$. In a steady state, the forces are equal and the ions flow with a constant velocity towards the electrodes:

$$6\pi a \eta v_x = ZeE_x \tag{3}$$

The quotient $\mu = v_x / E_x$ is the field strength independent ion mobility μ

$$\mu = \frac{Ze}{6\pi a \eta} \tag{4}$$

Multiplying μ by the Faraday constant F (96 493 $C \cdot mol^{-1}$) gives the equivalent ionic conductivity λ

$$\lambda = F \mu \tag{5}$$

Li^+	Na^+	K^+	NH_4^+	$½Ca^{2+}$	H^+	OH^-	Cl^-	NO_3^-	HCO_3^-	$½CO_3^{2-}$	$½SO_4^{2-}$
38.7	50.9	74.5	74.5	60	350	198	75.5	70.6	44.5	69.3	79

Table 1:
Equivalent ionic conductivity in water at 25 °C (extremely diluted solutions).

The equivalent ionic conductivity increases with the charge number and decreases with a larger radius and viscosity.

The λ values in Table 1 deviates slightly from expected values: the smaller Li^+ ion conducts less well than the more voluminous NH_4^+ ion. The difference comes from the fact that *a* is not the ion radius, but the radius of the solvated ion. A small ion or a strongly charged ion can, because of Coulomb energy, form a more substantial solvate shell than a larger ion would.

H^+ and OH^- conduct the current considerably better than the other ions. The reason is that an H^+ can readily be transferred by a H_3O^+ molecule on to a neighbouring H_2O molecule. The charge is transported more by the electrons of the molecules involved, rather than by the whole H_3O^+ and OH^- ions.

Dependence of the Equivalent Ionic Conductivity on Temperature

According to the Stokes equation, equivalent conductivity is inversely proportional to the viscosity η of the solution.

Figure 1 illustrates that the curves of the equivalent ionic conductivity follow, to a large extent, the inverse viscosity of water. This data validates the description of the steady ion flow with the Stokes equation, which means the temperature dependence is mainly determined by the viscosity of the solution.

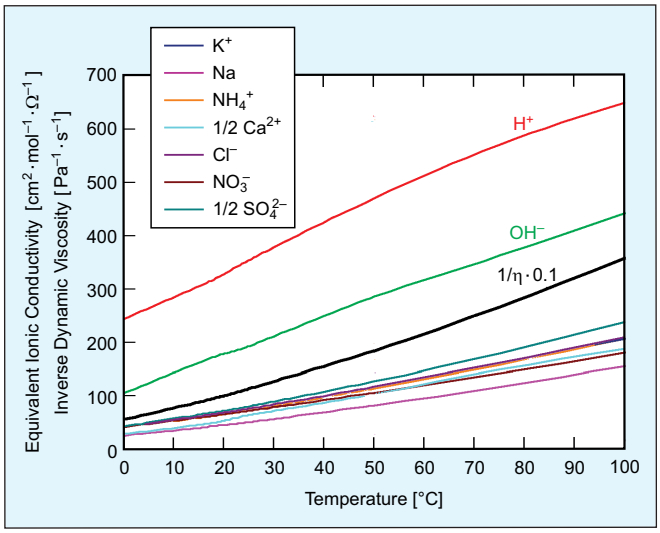

Figure 1:
Temperature dependence of equivalent ionic conductivity λ_0 [2] and the inverse viscosity $1/\eta$ of water [3].

Dependence of the Equivalent Ionic Conductivity on the Concentration of Dissolved Ions

A simple electrolyte AB dissolved in water splits at a fraction α, the degree of dissociation, into the constituent ions A^{Z+} and B^{Z-}

$$AB \xrightarrow{\alpha} A^{Z+} + B^{Z-} \tag{6}$$

Strong electrolytes ($\alpha = 1$) dissociate completely. The degree of dissociation of weak electrolytes ($\alpha < 1$) depends, according to the law of mass action, on the dissociation constant K_d and the concentrations.

$$K_d = \frac{[A^{Z+}]\cdot[B^{Z-}]}{[AB]} = \frac{(c_0\alpha)\cdot(c_0\alpha)}{c_0(1-\alpha)} = \frac{c_0\alpha^2}{1-\alpha} \tag{7}$$

hereby c_0 is the overall concentration of AB,
$[AB] = c_0(1-\alpha)$ is the concentration of dissolved but not dissociated AB,
$[A^{Z+}] = c_0\alpha$ is the concentration of the ion A^{Z+}, and
$[B^{Z-}] = c_0\alpha$ is the concentration of the ion B^{Z-}.

The dissociation constant, and as a result the degree of dissociation, is temperature dependent. Consequently, the concentrations of ions of weak electrolytes alter with temperature and so does the conductivity.

Taking into account the degree of dissociation, the equation for the conductivity is given by

$$\kappa = c_0\alpha\cdot Z^+\cdot\lambda_{A+} + c_0\alpha\cdot Z^-\cdot\lambda_{B-} \tag{8}$$

From the requirement that the solution must be overall neutral, it follows that $Z^+ = Z^- \equiv n_e$, where n_e is the electrochemical valence.

If the specific conductivity is divided by the concentration c_0 and the electrochemical valence n_e, the result is the equivalent conductivity Λ

$$\Lambda = \frac{\kappa}{c_0 n_e} = \alpha\,(\lambda_{A+} + \lambda_{B-}) \tag{9}$$

As shown in Figure 2, the equivalent conductivity Λ is not an invariable quantity [4]. It decreases with increasing concentration and therefore the equivalent ionic conductivity λ must also decrease with increasing concentration, because all electrolytes depicted in Figure 2, apart from acetic acid (HAc), are strong, i.e., completely dissociated. The degree of dissociation of acetic acid decreases explicitly with increasing concentration.

The decrease in the equivalent conductivity with higher concentration is mainly attributed to the mutual obstruction by the ions moving in the opposite direction. With increasing concentration the distance between the oppositely charged ions reduces, which leads to stronger electrostatic attraction and to Stokes friction of the hydration shell.

From experimental data, Kohlrausch empirically deduced the well-known root law for the concentration dependence on equivalent conductivity

$$\Lambda = \Lambda_0 - k \cdot \sqrt{c} \qquad (10)$$

Λ_0 is the equivalent conductivity extrapolated to high dilution, k a constant. The Kohlrausch's Law applies up to a concentration of ~ 10^{-2} mol · L^{-1}. Later it was confirmed by the theory of electrolytes by Debye, Hückel, and Onsager.

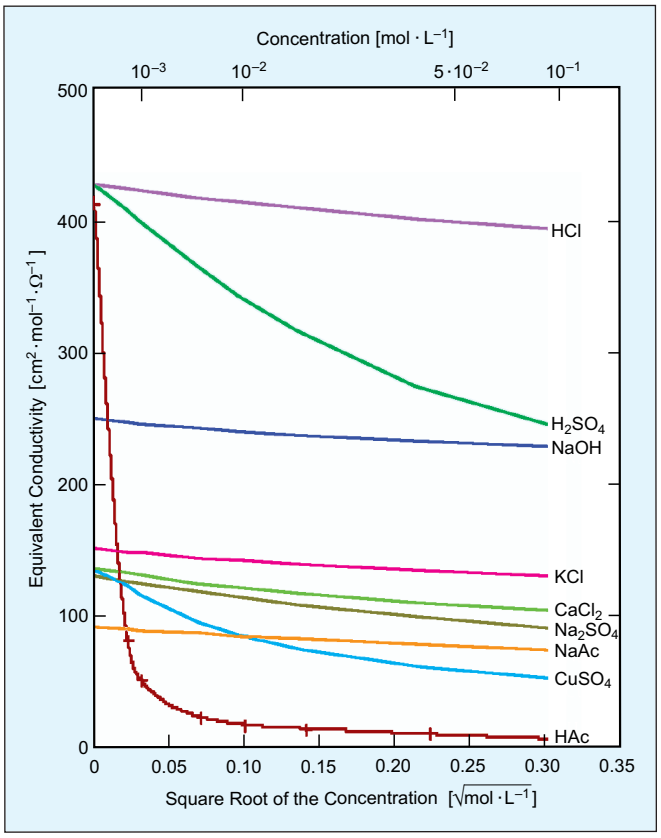

Figure 2:
Dependence of the equivalent conductivity Λ on the root of the amount-of-substance concentration at 25 °C.

APPLICATION OF CONDUCTIVITY MEASUREMENT IN THE WATER-STEAM CYCLE

For on-line monitoring of water and steam quality in the different power plant areas, samples are continually taken, pressure relieved, cooled, and then analysed.

The electric conductivity is not only directly determined as specific conductivity, but also as acid conductivity. For that, the sample must pass through an acid cation exchanger that transforms anions into the corresponding acids.

Volatile acidic components, e.g., CO_2, are removed by reboiling the sample. The result is known as degassed acid conductivity.

Table 2 illustrates which conductivity methods are applied at various sampling points of a water-steam cycle.

Depending on the kind of power plant and operation mode, limit values are set and values beyond are defined as threshold levels. These need special corrective measures.

In the section *Electrical Conductivity of Electrolyte Solutions* it was shown that the specific conductivity can be calculated from substance specific data (λ_i, K_d), ion concentrations c_i and temperature. However, neither the chemical composition of the sample, nor the concentrations can be deduced from the conductivity value. Such a

Sampling Point	Specific Conductivity	Acid Conductivity	Degassed Acid Conductivity
Condensate	x	x	
Feedwater	x	x	
Boiler water	x	x	
Superheated steam		x	x

Table 2:
Conductivity methods used at various sampling points.

conclusion is only possible if the chemical components present and their mixing ratio are known.

Significant limit values can be defined if the composition of the sample varies only within a limited extent.

CONDUCTIVITY DIAGRAMS OF WATER-STEAM CYCLE SAMPLES

In a water-steam cycle the pH is set at an alkaline range from 8.5 to 10, by adding an alkalizing agent. This agent is usually ammonia or an amine, e.g., morpholine or ethanolamine. All these substances are weak bases which only partly dissociate into ions. In comparison to the other electrolytes, these alkalizing agents are greatly in excess and they determine the conductivity to a large extent. The other electrolytes are treated as contamination. Some are carbon dioxide which enters through condenser leaks, or salt from cooling water leaks, as well as incompletely deionized make-up water, organic acids or decomposition products from amines.

The combination of the determination of the specific conductivity and the acid conductivity often makes it possible to distinguish between the content of the alkalizing agent and contamination. The strong acid cation exchanger removes the alkalizing agent and transforms salts into corresponding acids. Consequently, the acid conductivity correlates closely to the contamination.

The electrolyte concentrations of the samples are mostly at a lower $mg \cdot kg^{-1}$ level, equivalent to concentrations of 10^{-5} to 10^{-3} $mol \cdot L^{-1}$. At this level, the equivalent ionic conductivity λ varies very little from the λ_0 values and can be approximately set equal. Furthermore, the ions hardly influence each other, so that for solutions containing several electrolytes, the conductivity of the different ions can be added together.

Not only the equivalent ionic conductivity λ depends on the temperature, but also the ion concentrations for the weak electrolytes ($\alpha < 1$). The effective ion concentrations are calculated according to the law of mass action from the dissociation constant, see Eq. (7).

Below, some comments on temperature conversions for several electrolytes which are found in water-steam cycle samples.

Pure Water

The starting point of every conductivity examination in a water-steam-cycle is the water itself. The water dissociates to a minor fraction into the ions H_3O^+ and OH^-

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (11)$$

The extent of the dissociation depends on the temperature and it is determined by the dissociation constant $K_{W,T}$ [5]. [1]

$$K_{W,T} = [H_3O^+] \cdot [OH^-] \quad (12)$$

Figure 3a illustrates $[H_3O^+]$ and $[OH^-]$ for a temperature range from 0 °C to 60 °C. Figure 3b shows the specific conductivity

$$\kappa = [H_3O^+] \cdot \lambda_{H^+} + [OH^-] \cdot \lambda_{OH^-} \quad (13)$$

[1] Expressions in square brackets represent the concentrations of a chemical substance or of an ion in $mol \cdot L^{-1}$.

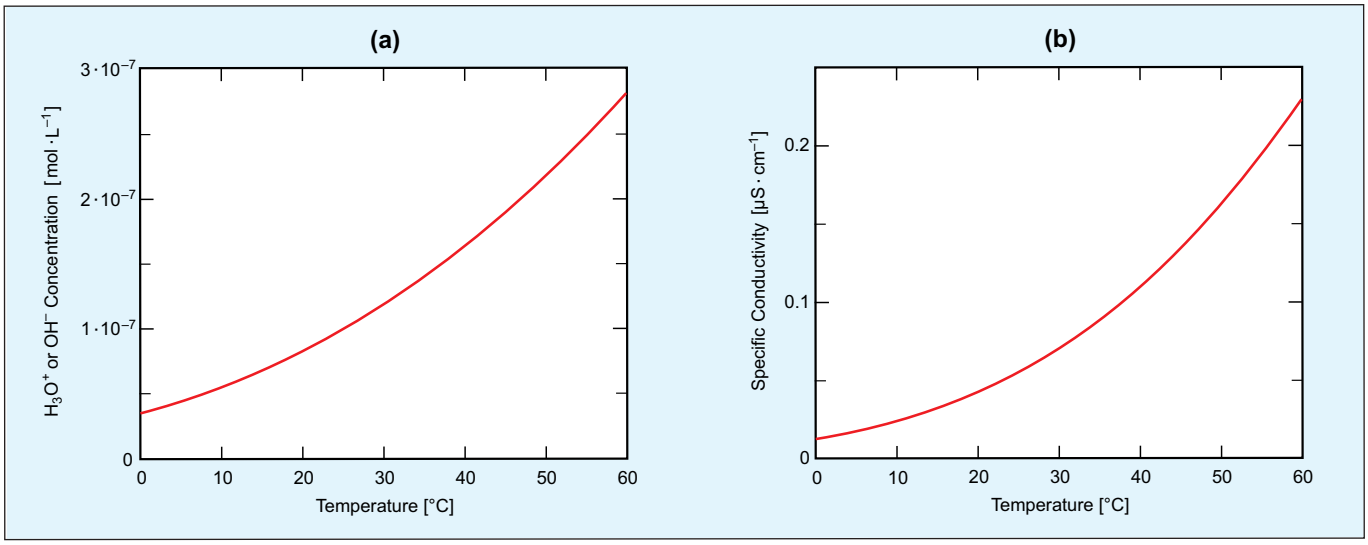

Figure 3:
Dissociation (a) and specific conductivity of water (b) in the temperature range of 0–60 °C.

The relation of conductivity and temperature is unique for pure water. A certain temperature corresponds with a certain conductivity, and vice versa.

Ammonia in Water

Ammonia is a common alkalizing agent and it is dosed so that the required pH range is maintained. Ammonia NH_3 is a weak base and dissociates in water to the degree α into ammonium NH_4^+ and OH^-

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{14}$$

Figure 4 shows the ion concentrations of NH_4^+ and OH^- for a temperature range from 0 °C to 60 °C for three different overall ammonia concentrations (0.1, 1 and 10 mg · kg^{-1}). The degree of dissociation α decreases strongly with rising concentrations, as is expected with weak electrolytes.

From 25 °C to 50 °C, the NH_4^+ and OH^- concentration curves prove to be largely temperature independent, i.e., the dissociation constant is practically non-varying in this temperature range [6].

The specific conductivity, as a function of the temperature, can be calculated from the ion concentrations $[NH_4^+]$, $[OH^-]$, and $[H^+]$ and the equivalent ionic conductivities (Figure 5a).

$$\kappa_{T[NH_3]} = [H^+]\cdot\lambda_{H^+} + [NH_4^+]\cdot\lambda_{NH_4^+} + [OH^-]\cdot\lambda_{OH^-} \tag{15}$$

At pH > 8 the H^+ concentration (< 10^{-8} mol · L^{-1}) compared to the OH^- concentration (> 10^{-6} mol · L^{-1}) can be disregarded. $[NH_4^+] \approx [OH^-]$ is valid because of the electroneutrality; in addition, as mentioned above, the concentrations $[NH_4^+]$ and $[OH^-]$ from 25 °C to 50 °C are almost invariable with changing temperature. The Eq. (15) is simplified by these approximations; $\kappa_{T,[NH_3]}$ can be shown as a product of two terms. One is only dependent on the overall NH_3 concentration and the other only on the temperature.

$$\kappa_{T,[NH_3]} = [OH^-]_{[NH_3]}\cdot(\lambda_{OH^-} + \lambda_{NH_4^+})_T \tag{16}$$

The conversion of the conductivity of temperature T to 25 °C is therefore

$$\kappa_{25\,°C} \approx \kappa_T \frac{(\lambda_{OH^-} + \lambda_{NH_4^+})_{25\,°C}}{(\lambda_{OH^-} + \lambda_{NH_4^+})_T} \tag{17}$$

The conversion factor is the ratio of both the sums of the equivalent ionic conductivities at 25 °C and at the sample temperature T. For example, if for 25 °C $(\lambda_{OH^-} + \lambda_{NH_4^+})$ = 266.5 and for 50 °C $(\lambda_{OH^-} + \lambda_{NH_4^+})_{50\,°C}$ = 399, then the result is a conversion factor of 0.668.

The projection of the conductivity curves with a constant temperature onto the κ-$[NH_3]$ cuboid surface (Figure 5b) clearly confirms that the curves differ only by a proportionality factor.

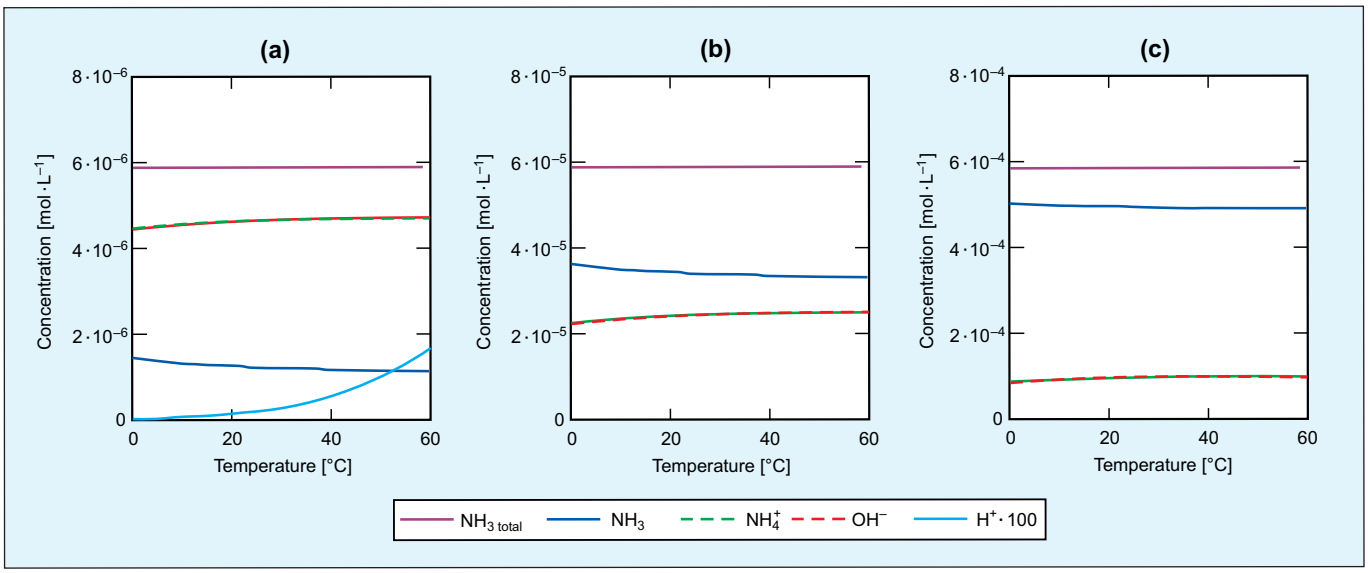

Figure 4:
Concentrations of NH_3, NH_4^+, and OH^- (and H^+) from 0 to 60 °C for NH_3 total concentrations 0.1 (a), 1 (b) and 10 mg · kg^{-1} (c).
(a) pH = 8.4
(b) pH = 9.4
(c) pH = 9.98

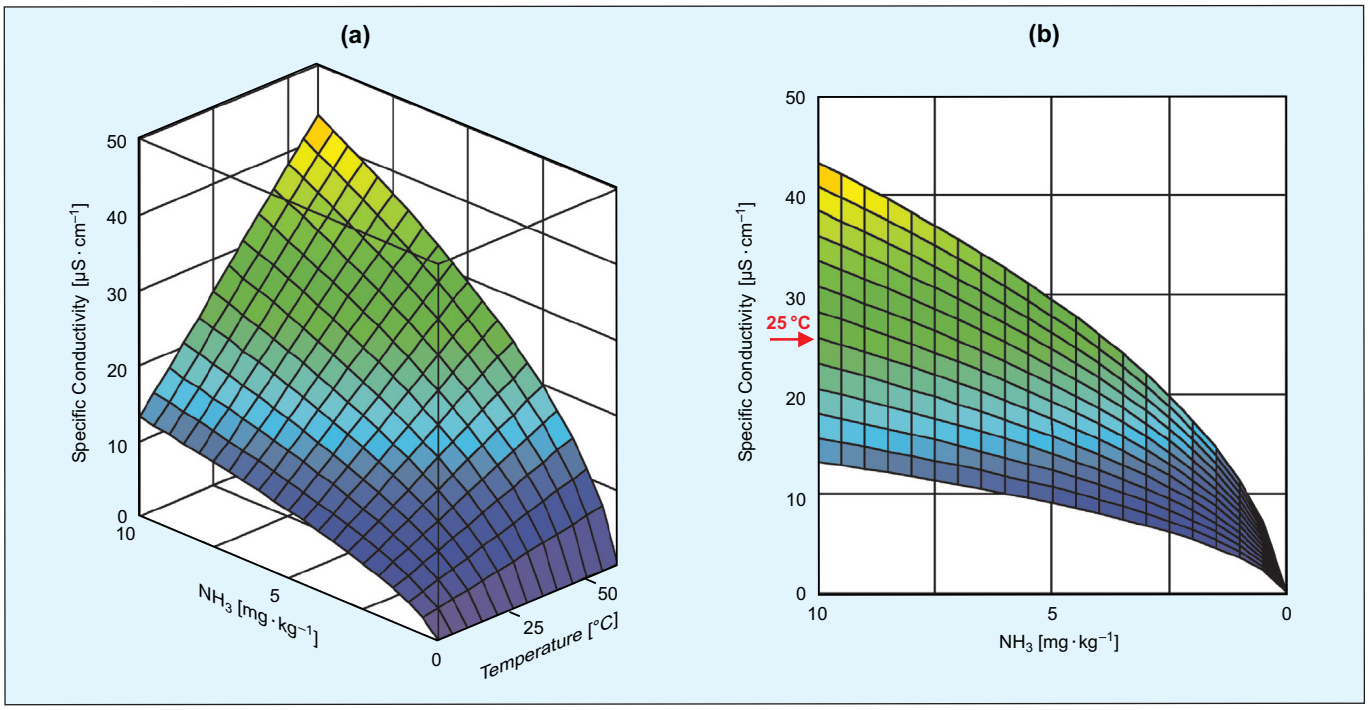

Figure 5:

Specific conductivity for NH_3 solutions with a total NH_3 concentration from 0 to 10 mg · kg^{-1} at temperatures from 0 to 60 °C (a) and the projection of the isotherm conductivity curves onto the κ-[NH_3]-surface (b).

Other volatile alkalizing agents like morpholine or ethanolamine have very similar conductivity diagrams because they are also weak bases and their dissociation constant is of a comparable size [7].

Modern conductivity measuring instruments provide models which carry out an exact (i.e., without approximations) conversion to 25 °C for temperatures from 0 °C to 90 °C and concentrations up to 10^{-2} mol · L^{-1}.

Besides the conversion models for weak bases, there are also models for other chemical substances available, CO_2, neutral salts, strong acids and strong bases.

NaCl and CO_2 after Strong Acid Cation Exchanger

The concentrations of other electrolytes are several dimensions lower in comparison to alkalizing agents, i.e., in the µg · kg^{-1} range. These are usually contaminants which enter the cycle by way of leaks or by imperfectly deionized make-up water.

Sodium chloride (NaCl) can get into the water-steam cycle through a leak in the condenser. As a strong electrolyte (α = 1) it dissociates completely into the ions Na^+ and Cl^-. For this reason the concentrations of both ions are equal to the overall concentration: [Na^+] = [Cl^-] = $[NaCl]_{total}$. NaCl is a neutral salt, which means it does not alter the pH value of a solution.

The conductivity of a NaCl solution is composed of the conductivity of water plus the conductivity of Na^+ and Cl^- ions (Figure 6):

$$\kappa_{T,[NaCl]} = [H^+]\cdot\lambda_{H^+} + [OH^-]\cdot\lambda_{OH^-} + [Na^+]\cdot\lambda_{Na^+} + [Cl^-]\cdot\lambda_{Cl^-} \quad (18)$$

which is, however, equal to

$$\kappa_{T,[NaCl]} = \kappa_{T,H_2O} + [NaCl]_{total}\cdot(\lambda_{Na^+} + \lambda_{Cl^-})_T \quad (19)$$

The conductivity Figure 6a shows a linear rise of κ with the NaCl concentration; this is typical for a strong electrolyte. Eq. (19) is a linear equation with the variable [NaCl], the slope $(\lambda_{Na^+} + \lambda_{Cl^-})_T$ and with the axis intercept $\kappa_{T,\,H_2O}$. These curves are shown in Figure 6b.

A few µg · kg^{-1} NaCl are, in the presence of several mg · kg^{-1} NH_3, difficult to detect with direct conductivity measurement because the conductivity changes of ~ 0.1 µS · cm^{-1} at a conductivity of 20 µS · cm^{-1} can hardly be measured for certain.

When a sample passes through a strong acid cation exchanger, every cation is replaced by an H^+ ion. The alkalizing agent is completely removed. According to the chemical balance reaction $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$, NH_4^+ is formed, until all the NH_3 is used up. The discharged solution contains only the anions with H^+ as counter ions, i.e., an equivalent amount of hydrochloric acid HCl is produced from a NaCl solution.

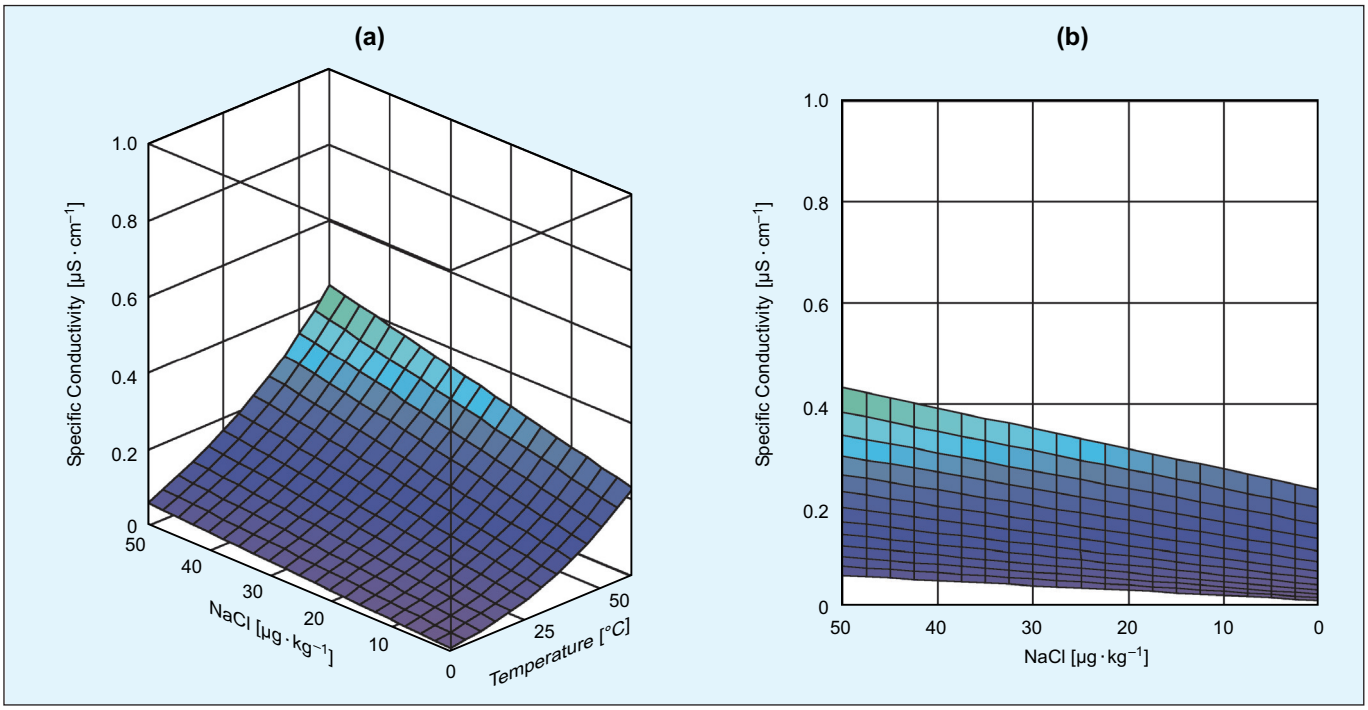

Figure 6:
Specific conductivity of 0–50 µg · kg^{-1} NaCl solutions at temperatures from 0 to 60 °C (a) and the projection of isothermic curves onto the κ-[NaCl]-surface (b).

Hydrochloric acid reacts completely together with water into H^+ and Cl^-.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \quad (20)$$

From $[H^+]$, $[OH^-]$, $[Cl^-]$ = [HCl] and the equivalent ionic conductivities, the specific conductivity as a function of the temperature can be calculated:

$$\kappa_{T,[HCl]} = [H^+]\cdot\lambda_{H^+} + [Cl^-]\cdot\lambda_{Cl^-} + [OH^-]\cdot\lambda_{OH^-} \quad (21)$$

The isotherm conductivity curves (Figure 7b) are not linear in the range with low concentrations because the OH^- concentration, in comparison with the Cl^- concentration, cannot yet be disregarded. From about 20 µg · kg^{-1}, the conductivity is linear with the HCl concentration.

Because of the higher equivalent ionic conductivity λ_{H^+}, in comparison to the other cations, the conductivity values increase with a factor 2 or 3 with equal molar concentration (compare Figure 6 and 7). For this reason, the acid conductivity is a sensitive method for tracing anionic contaminants.

At the same time, all other acids can be separated from alkalizing agents by a strong acid cation exchanger: these pass the column unchanged.

Carbon dioxide (CO_2) can enter the water-steam cycle through a leak in the vacuum part of the condenser or other equipment under vacuum.

CO_2 is a weak acid with a minor degree of dissociation. It dissociates in two steps, into hydrogen carbonate HCO_3^- and carbonate CO_3^{2-} [8]

$$CO_2 + 2H_2O \rightarrow H_3O^+ + HCO_3^- \quad K_{a1} = 10^{-6.35} \quad (22)$$

$$HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-} \quad K_{a2} = 10^{-10.33} \quad (23)$$

where
K_{a1} and K_{a2} are the acid dissociation constants.

After the acid cation exchanger, the pH is always less than 7, causing the carbonate ion to appear in negligibly small concentrations.

Even in small concentrations, CO_2 with H_2O does not completely dissociate: 1 µg · kg^{-1} CO_2 reacts at 25 °C only 80 % to HCO_3^-. The solutions are only weakly acid, which is why the $[OH^-]$ concentration cannot be disregarded in the calculation of the conductivity:

$$\kappa_{T,[CO_2]} = [H^+]\cdot\lambda_{H^+} + [HCO_3^-]\cdot\lambda_{HCO_3^-} + [OH^-]\cdot\lambda_{OH^-} \quad (24)$$

The isotherm conductivity (Figure 8b) does not depend linearly on the concentrations: with a low concentration, the conductivity is primarily determined by the ion product of the water. With a high concentration, the curves level out as a result of the decreasing dissociation grade.

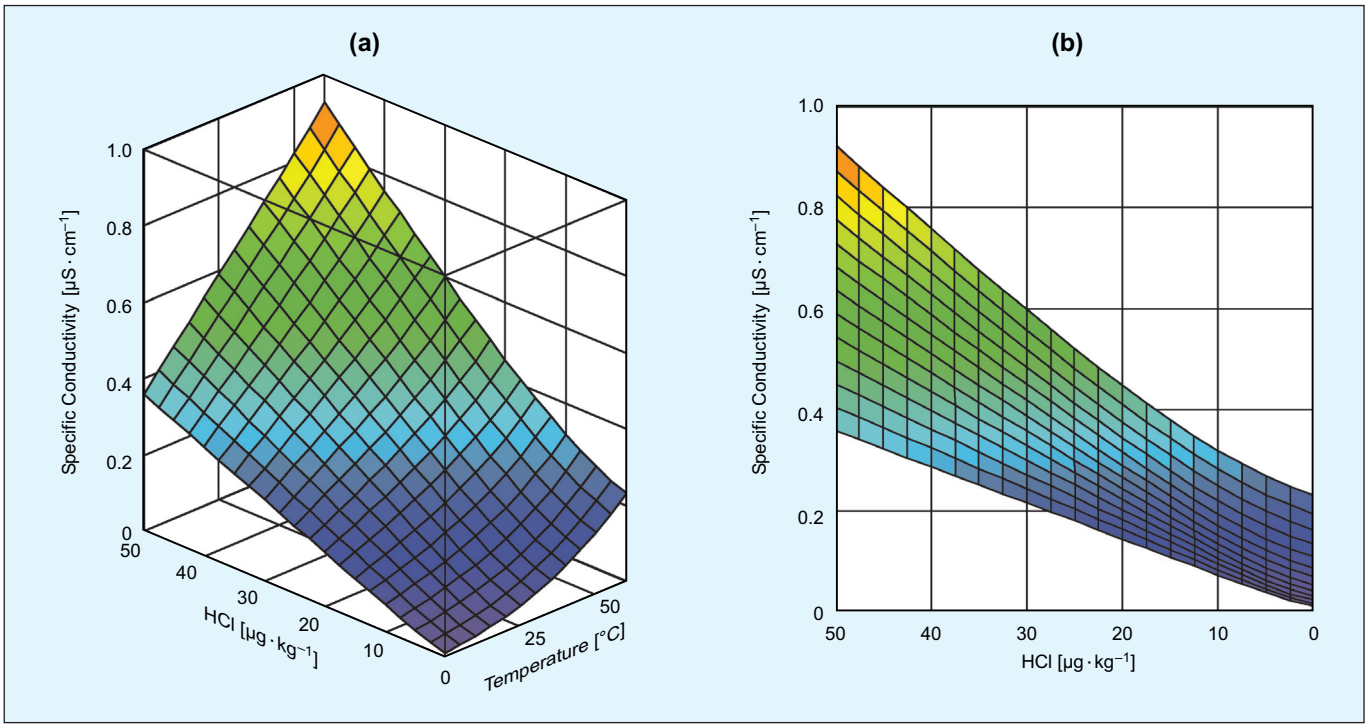

Figure 7:

Specific conductivity of 0–50 µg · kg^{-1} HCl solutions at temperatures from 0 to 60 °C (a) and the projection of isotherm conductivity curves onto the κ-[HCl]-surface (b).

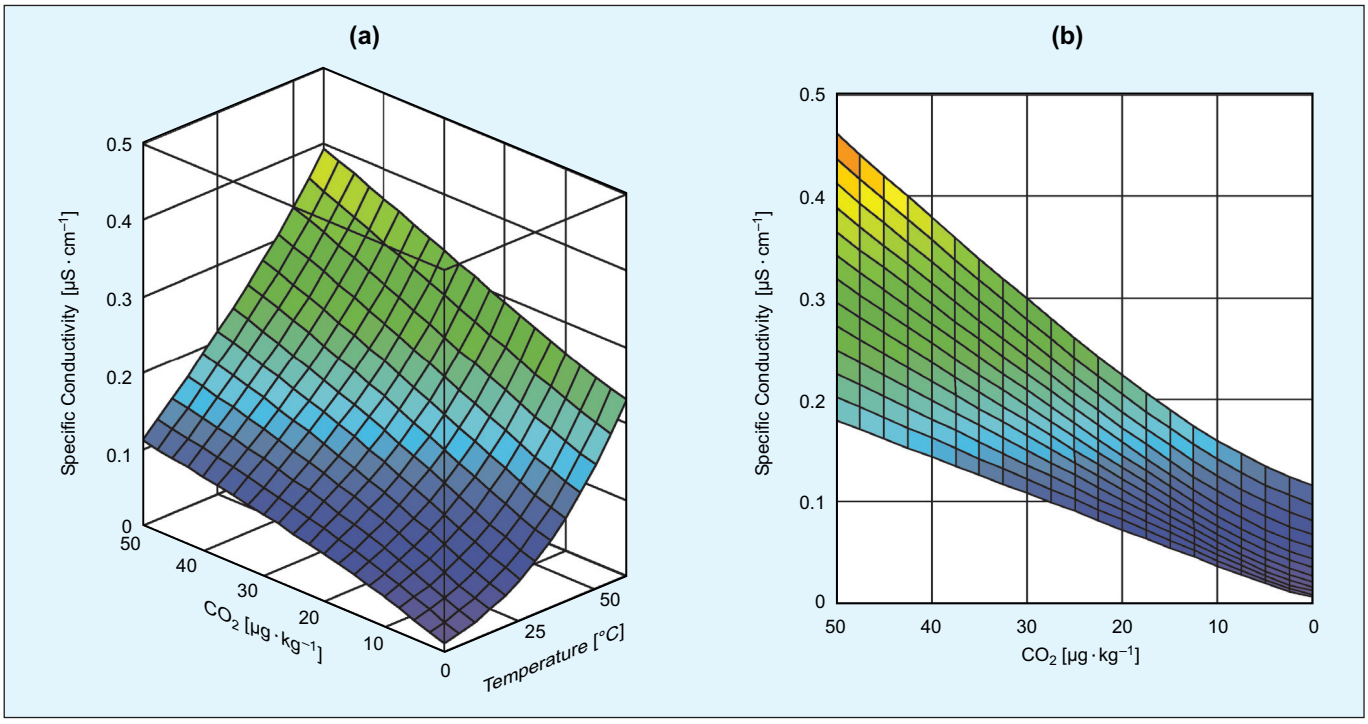

Figure 8:

Specific conductivity of 0–50 µg · kg^{-1} CO_2 at temperatures from 0 to 60 °C (a) and the projection of isotherm conductivity curves onto the κ-[CO_2]-surface (b).

CONVERSION OF CONDUCTIVITY TO 25 °C

For samples of a known composition, also with several components, the conductivity values can be exactly calculated at 25 °C as well as at sample temperature, subsequently the conversion factor is:

$$\kappa_{25\,°C} = \kappa_T \frac{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_i\right)_{25\,°C}}{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_i\right)_T} \tag{25}$$

For samples of an unknown or variable composition, conditions for an exact calculation are no longer fulfilled. The conversion can only be conducted approximately. The conductivity depends on two temperature dependent variables, on the equivalent ionic conductivity λ_i (see *Dependence of the Equivalent Ionic Conductivity on Temperature*) and on the concentration c_i with weak electrolytes (see *Dependence of Equivalent Ionic Conductivity on the Concentration of Dissolved Ions*).

According to the equation from Stokes, the equivalent ionic conductivity λ_i is roughly proportional to the inverse viscosity $1/\eta_T$. The quotients $\lambda_{i,25\,°C} / \lambda_{i,T}$ should therefore be a comparable dimension for every ion. Examples of quotients $\lambda_{i,25\,°C} / \lambda_{i,\,50\,°C}$ for various ions at a sample temperature of 50 °C are shown in Table 3.

The quotients deviate, also with a relatively high temperature of 50 °C, from the mean value $\bar{Q}_{50\,°C} \approx 0.65$ at the most by ± 5 %. The closer the sample temperature to 25 °C, the smaller the deviation. Only the quotient $Q_{H^+50\,°C}$ is somewhat larger, i.e., the temperature effect with H^+ is slightly less distinct.

The temperature conversion Eq. (25) can be approximately written with an averaged quotient $\bar{Q}_T$

$$\kappa_{25\,°C} = \kappa_T \frac{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_i\right)_{25\,°C}}{\left(\sum_1^i c_i \cdot Z_i \cdot \frac{\lambda_{i,25\,°C}}{Q_i}\right)_T} \approx \kappa_T \frac{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_i\right)_{25\,°C}}{\left(\sum_1^i c_i \cdot Z_i \cdot \frac{\lambda_{i,25\,°C}}{\bar{Q}_T}\right)_T} \tag{26a}$$

$$\kappa_{25\,°C} \approx \kappa_T \cdot \bar{Q}_T \frac{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_i\right)_{25\,°C}}{\left(\sum_1^i c_i \cdot Z_i \cdot \lambda_{i,25\,°C}\right)_T} \tag{26b}$$

The temperature dependence of the conductivity on the concentrations is determined by the last factor, the relation of both the sums in Eq. (26b).

For strong electrolytes ($\alpha = 1$) the concentrations are temperature independent and the last factor is equal to one. For weak electrolytes ($\alpha < 1$) the dissociation constant K_d, and, therefore, also the concentrations c_i in general are temperature dependent. The concentrations change in the range between 25 °C and 50 °C but only by a low percentage, for example with ammonia (compare Figure 4) or with CO_2. The last factor in (26b) is then close to one.

But the dissociation of the "weak electrolyte" water shows considerable temperature dependence (compare Figure 3a). The degree of dissociation $\alpha \approx 10^{-8}$ is so slight that the effect is only important in extremely diluted solutions. This effect is taken into account in every conductivity model because pure water is always the basis for the calculations. Every conductivity diagram (compare Figures 5a, 6a, 7a, 8a) begins with the κ_{H_2O} curve (Figure 3b) on the κ–T cuboid.

The temperature dependence of the conductivity of various electrolytes can be approximately determined by a characteristic Eq. (26b). Similarly, Handy, Greene and Tittle [9] demonstrated that for the estimation of the degassed acid conductivity a mean equivalent conductance value (MEC), for samples with different compositions of inorganic and organic acids in the $\mu g \cdot kg^{-1}$ range, can be used with close approximation.

However, conductivity instruments do not calculate with this approximation for averaged electrolytes, but with conversion models for real substances. The chemical composition of the samples is usually approximately known, so an appropriate conversion model can be chosen.

	Na^+	K^+	NH_4^+	Ag^+	½Ca^{2+}	Cl^-	NO_3^-	½CO_3^{2-}	OH^-	H^+
Equivalent ionic conductivity at 25 °C, $\lambda_{i,25\,°C}$	50.9	74.5	74.5	63.5	60	75.5	70.6	79	192	350
Equivalent ionic conductivity at 50 °C, $\lambda_{i,50\,°C}$	82	115	115	101	98	116	104	125	284	465
Quotient $\lambda_{i,25\,°C} / \lambda_{i,50\,°C}$	0.621	0.648	0.648	0.629	0.612	0.651	0.679	0.632	0.676	0.753

Table 3:
Quotients $\lambda_{i,25\,°C} / \lambda_{i,50\,°C}$.

Specific models are applied for the common alkalization agents ammonia, morpholine and ethanolamine, which not only conduct the temperature conversion accurately, but also calculate the concentration.

The following paragraph demonstrates the conversion of several examples.

EXAMPLES

Acid Conductivity after the Cation Exchanger

The starting point of this example is a sample with an acid conductivity of 0.2 µS · cm^{-1} at 40 °C, which should be converted to 25 °C. Because it is unknown which acid the sample contains, two borderline cases will be compared: on one hand, the strong acid HCl and on the other, the weak acid CO_2. The conductivity diagrams of both acids are found in the section *NaCl and CO_2 after Strong Acid Cation Exchanger*. Details of both isotherm conductivity diagrams (Figures 7b and 8b) are illustrated in the same scale in Figure 9. Each conversion (Figures 9a and 9b) of 0.2 µS · cm^{-1} from 40 °C to 25 °C is plotted.

For HCl as well as for CO_2, a reading of conductivity 0.14 µS · cm^{-1} at 25 °C is taken from the curve. This means the conversion factor from 40 °C to 25 °C is the same dimension (≈ 0.7) for both the acids. The conversion provides the correct result, irrespective of the chosen model (strong acid or CO_2). However, the acid concentration can definitely not be calculated from the conductivity: for HCl a concentration of 10.7 µg · kg^{-1} would be expected and for CO_2, 26 µg · kg^{-1}.

That both models come to the same result is no coincidence, rather it confirms the validity of the approximation Eq. (26b).

Minor errors can be expected, particularly with acids, as the conductivity of every single-stage strong and weak acid HB can be determined by the following equation:

$$\kappa_{T,[HB]} = [H^+]\cdot\lambda_{H^+} + [B^-]\cdot\lambda_{B^-} + [OH^-]\cdot\lambda_{OH^-} \qquad (27)$$

The conductivity values of various acids HB differ only in the term $[B^-] \cdot \lambda_{B^-}$. Because of the 3 or 5 times higher equivalent ionic conductivity of the OH^- or the H^+ ion respectively, the term $[B^-] \cdot \lambda_{B^-}$ contributes only a small amount to the overall conductivity. In addition the concentration $[B^-]$ is always smaller or equal $[H^+]$ because the sample must be electroneutral.

Neutral Salt NaCl in Alkalized Feedwater

The pH of the feedwater is often calculated from the difference of the specific conductivity and the acid conductivity at 25 °C (see [10]) and not measured by a glass electrode. The specific conductivity is converted to 25 °C with the algorithm of the pure alkalizing agent. The contribution of the contaminants is converted with the same factor even though it is not correct.

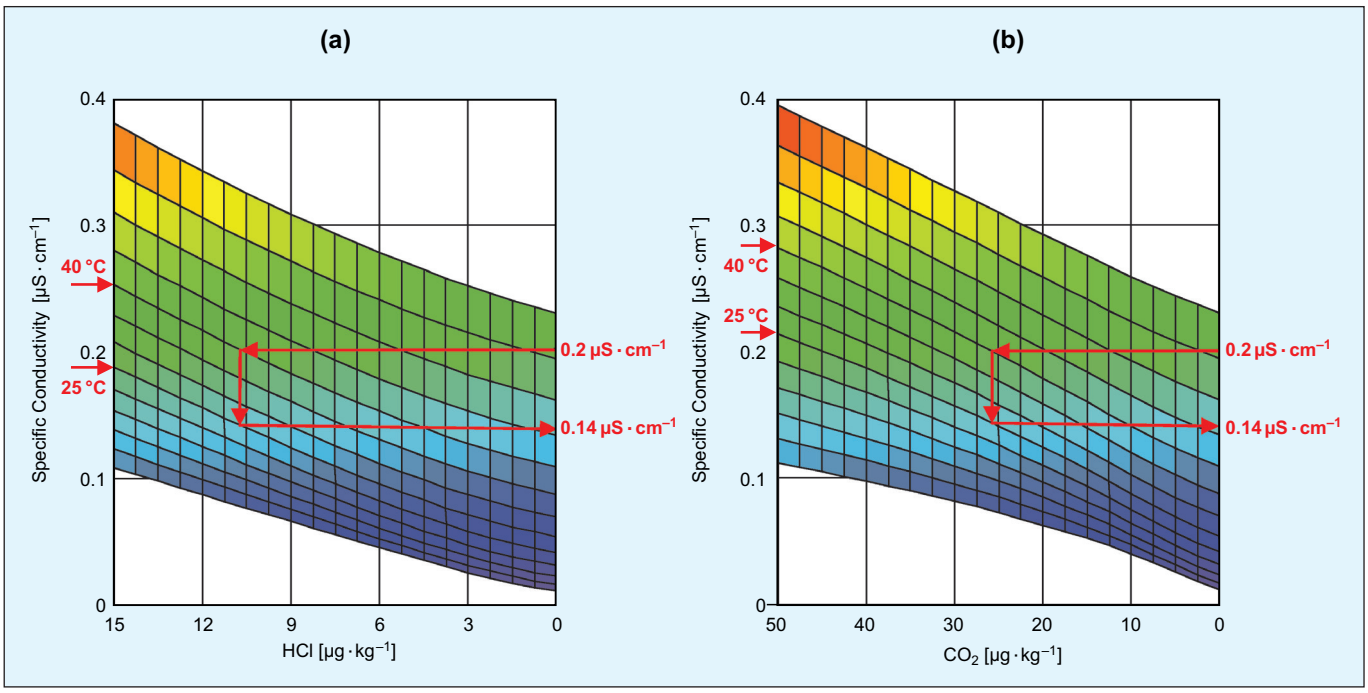

Figure 9:
Isotherm conductivities of 0–15 µg · kg^{-1} HCl solutions (a) and of 0–50 µg · kg^{-1} CO_2 solutions (b), both at temperatures from 0 to 60 °C.

Below, the effect of a contamination by NaCl of a sample with 1.5 mg · kg^{-1} NH_3, adjusted to pH 9.5, is analysed. Figure 10 illustrates the conductivity diagram with a successive addition of 0 to 1 mg · kg^{-1} NaCl.

NaCl is a neutral salt and does not change the pH of the solution. Hence the conductivity is a linear function of the NaCl concentration and the contribution to the conductivity is additive (compare Eqs. (16) and (19)).

The conversion to 25 °C is determined by the equation

$$\kappa_{25\,°C} = \kappa_T \frac{[OH^-]\cdot(\lambda_{OH^-}+\lambda_{NH_4^+})_{25\,°C} + [NaCl]\cdot(\lambda_{Na^+}+\lambda_{Cl^-})_{25\,°C}}{[OH^-]\cdot(\lambda_{OH^-}+\lambda_{NH_4^+})_T + [NaCl]\cdot(\lambda_{Na^+}+\lambda_{Cl^-})_T} \quad (28)$$

A sample containing 1.5 mg · kg^{-1} NH_3 (= 8.808 · 10^{-5} mol · L^{-1}) and 1 mg · kg^{-1} NaCl (= 1.711 · 10^{-5} mol · L^{-1}) at 50 °C is an extreme example. The true conductivity at 25 °C is compared to the incorrectly converted value. In Table 4 the ionic conductivity sums at 25 °C and 50 °C are shown for the components NH_4OH, NaCl and HCl, as well as their conversion factors $\Lambda_{25\,°C} / \Lambda_{50\,°C}$.

The true value at 25 °C is $\kappa_{25\,°C}$ = 10.8 µS · cm^{-1} and at 50 °C is $\kappa_{50\,°C}$ = 16.3 µS · cm^{-1}. If $\kappa_{50\,°C}$ is multiplied by the conversion factor for pure ammonia (0.684) the calculated result at 25 °C is 11.15 µS · cm^{-1}, that is 3 % too high.

The equation for the calculation of the pH at 25 °C given in [10] is

$$pH_{NH_3} = \log\left(\frac{\kappa_{sp,\,25\,°C} - \frac{\kappa_{acid,\,25\,°C}}{3}}{273}\right) + 11 \quad (29)$$

hereby $\kappa_{sp,\,25\,°C}$ is the specific conductivity and $\kappa_{acid,\,25\,°C}$ is the acid conductivity in µS · cm^{-1}. After the cation column, 1.711 mol · L^{-1} NaCl (1 mg · kg^{-1}) is transformed into

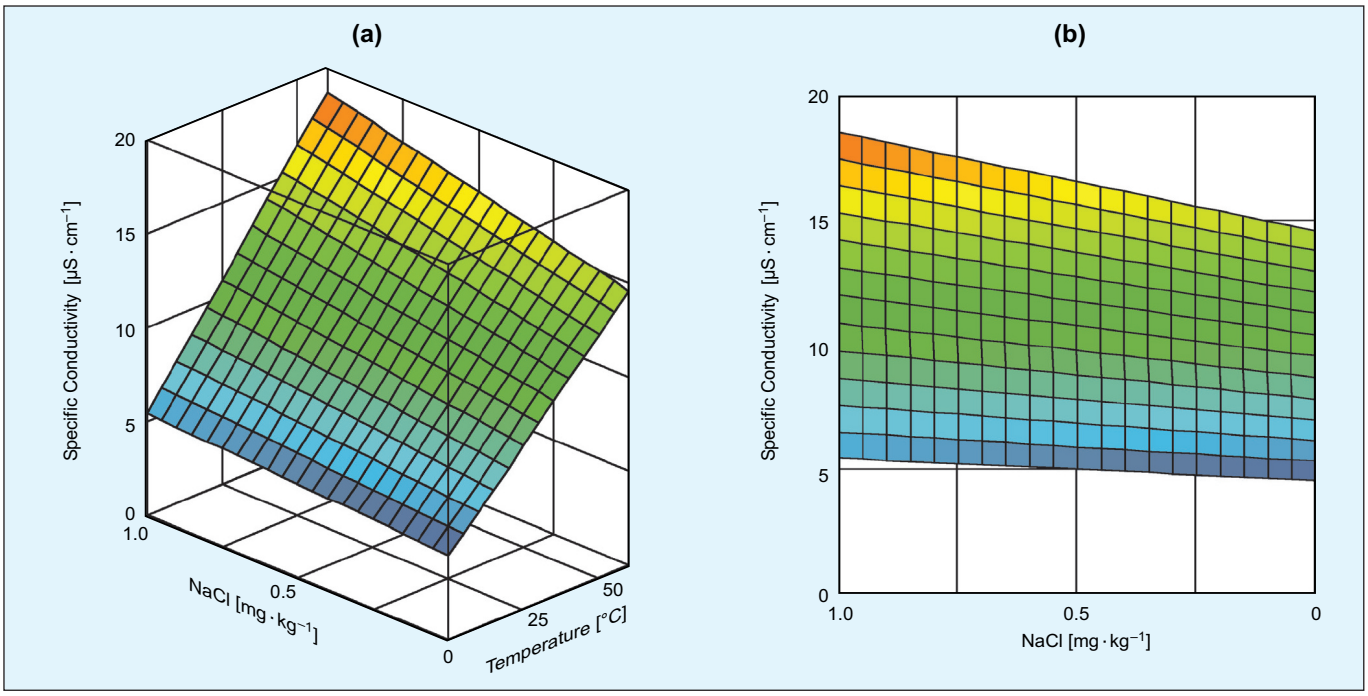

Figure 10:
Specific conductivity of 1.5 mg · kg^{-1} NH_3 solution in the presence of 0–1 mg · kg^{-1} NaCl at temperatures from 0 to 60 °C (a) and the projection of the isotherm conductivity curves onto the κ-[NaCl]-surface (b).

	$(\lambda_{OH^-} + \lambda_{NH_4^+})$	$(\lambda_{Na^+} + \lambda_{Cl^-})$	$(\lambda_{H^+} + \lambda_{Cl^-})$
Equivalent conductivity at 25 °C, $\Lambda_{25\,°C}$	198 + 75 = 273	51 + 76 = 127	350 + 76 = 426
Equivalent conductivity at 50 °C, $\Lambda_{50\,°C}$	284 + 115 = 399	82 + 116 = 198	465 + 116 = 581
Quotient $\Lambda_{25\,°C} / \Lambda_{50\,°C}$	0.684	0.641	0.733

Table 4:
Quotients $\Lambda_{25\,°C} / \Lambda_{50\,°C}$ for NH_4OH, NaCl and HCl.

1.711 mol · L^{-1} HCl with a conductivity of 7.28 µS · cm^{-1} (at 25 °C). Eq. (29) substituted with the numerical values provides the following results:

– with the true specific conductivity value $\kappa_{sp,\,25\,°C}$ = 10.8 µS · cm^{-1}, the calculated pH is 9.49

and

– with the temperature converted specific conductivity value $\kappa_{sp,\,converted\,to\,25\,°C}$ = 11.15 µS · cm^{-1}, the calculated pH is 9.50.

The close coincidence is due to the fact that the conversion factors $\lambda_{25\,°C} / \lambda_{50\,°C}$ for both components, NH_4OH and NaCl, are almost equal.

CO_2 in Alkalized Condensate

Over a period of downtime or due to a leak in the low pressure part of the condenser, air with CO_2 can enter the water-steam cycle. The sample consists of a mixture of a weak base and a weak acid. CO_2 with water reacts to hydrogen carbonate HCO_3^- as well as carbonate CO_3^{2-} because the pH is in the alkaline range (compare the section *NaCl and CO_2 after Strong Acid Cation Exchanger*, Eqs. (22) and (23)).

As an example, 5 mg · kg^{-1} CO_2 is successively added to a sample containing 1.5 mg · kg^{-1} NH_3 at pH 9.5. The conductivity diagram is illustrated in Figure 11.

The relation of the isotherm conductivity curve with the increasing CO_2 concentration is not linear. The curves at temperature above 10 °C pass through a minimum, i.e., the relation of the conductivity and the concentration is ambiguous. This complex situation is caused by the fact that 3 different chemical components are present, linked by 4 dissociation equilibria.

The concentrations (at 25 °C) of all the ions involved (NH_4^+, HCO_3^-, CO_3^{2-}, H^+, OH^-) and the neutral molecules (NH_3, CO_2) are illustrated in Figure 12a. The pH curve indicates the neutralization of the base by a change from the alkaline to the acidic range (Figure 12b).

NH_3 is transformed totally into NH_4^+ during the neutralization reaction. CO_2 is present as HCO_3^- and at a lower amount as CO_3^{2-} at the beginning of the neutralization reaction. Then with increasing concentration and decreasing pH, it is predominantly present as dissolved CO_2.

The conductivity initially falls at low CO_2 addition because the decreasing contribution of the term $[OH^-]$. (λ_{OH^-} = 198) is only incompletely compensated by the increasing terms $[NH_4^+]$. ($\lambda_{NH_4^+}$ = 75) and $[HCO_3^-]$. ($\lambda_{HCO_3^-}$ = 45).

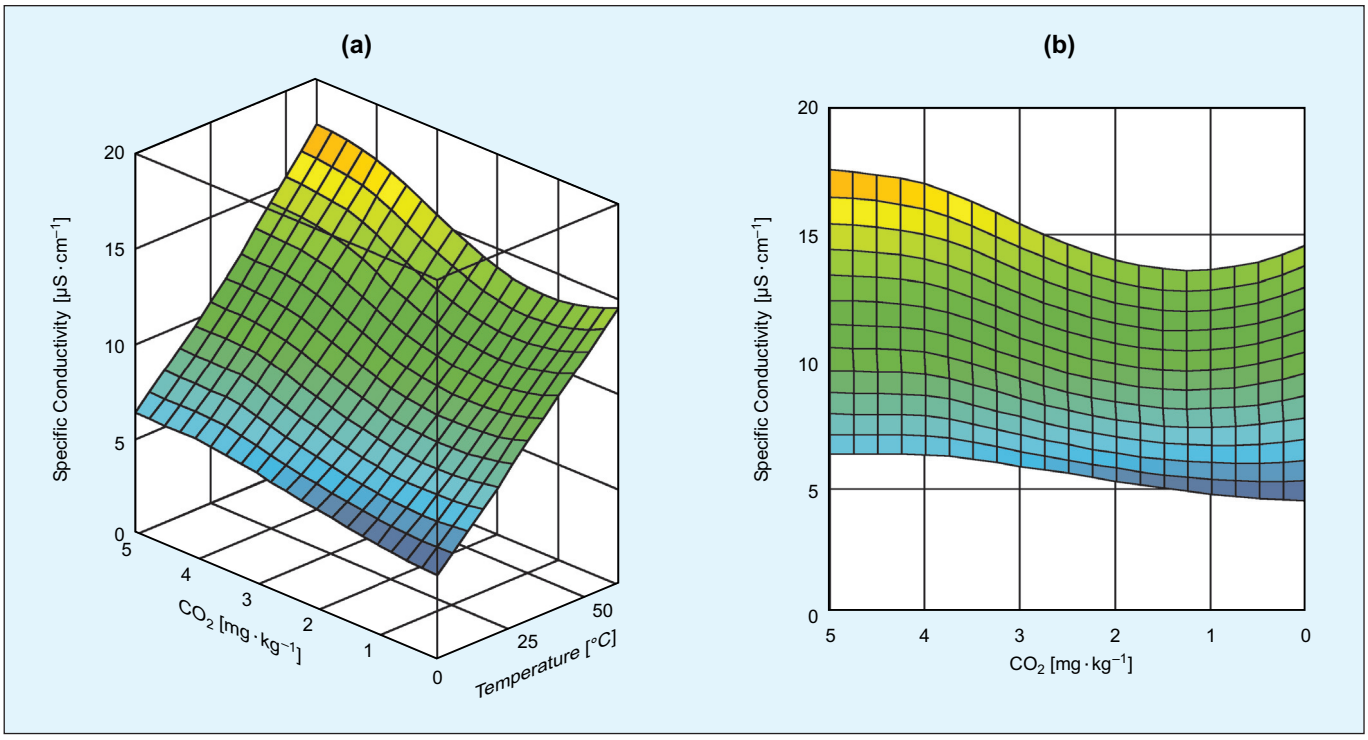

Figure 11:
Specific conductivity of 1.5 mg · kg^{-1} NH_3 solution in the presence of 0–5 mg · kg^{-1} CO_2 at temperatures from 0 to 60 °C (a) and the projection of the isotherm conductivity curves onto the κ-$[CO_2]$-surface (b).

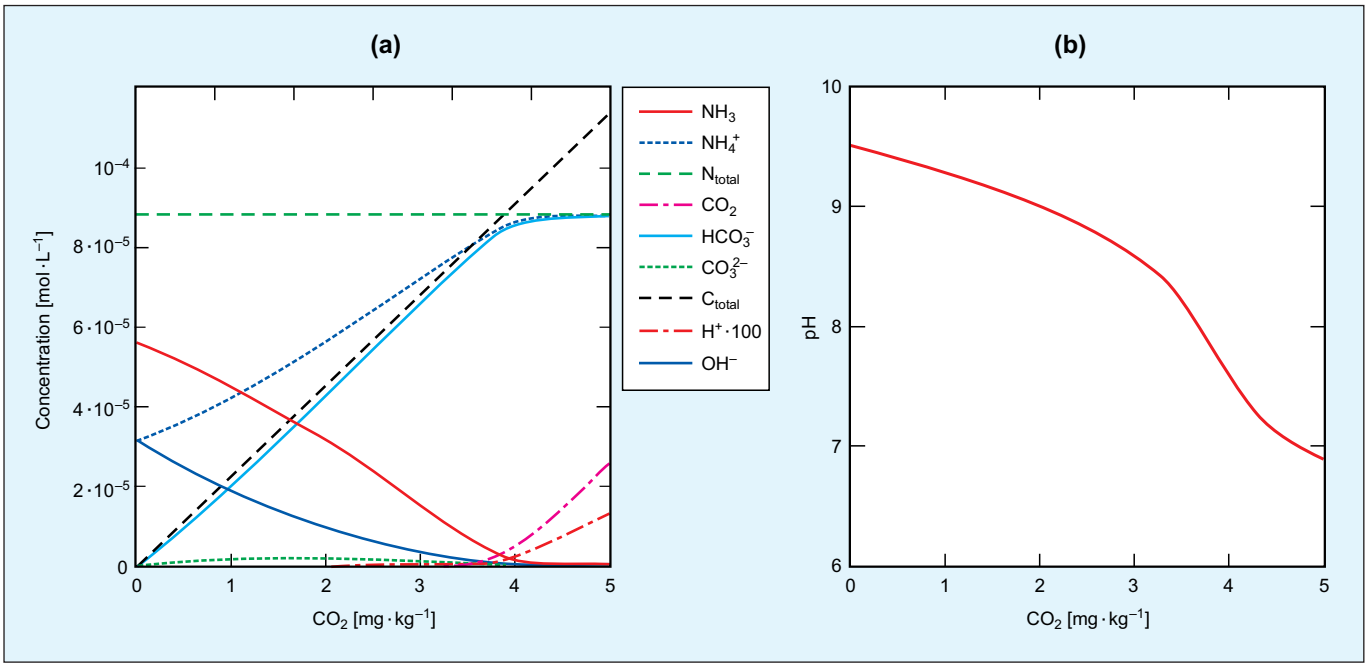

Figure 12:
Concentration of NH_3 , NH_4^+, CO_2, HCO_3^-, CO_3^{2-}, H^+, and OH^- in the solutions specified in Figure 11 at 25 °C (a) and the pH at 25 °C (b).

The conductivity rises with increasing overall CO_2 concentration.

Figure 13 is a projection of the conductivity diagram in Figure 11a onto the κ-T surface. It illustrates the temperature dependence of the conductivity. The curves for the different but fixed CO_2 concentrations are again more or less proportional to each other. The approximation in (26b) holds even for this rather complex example.

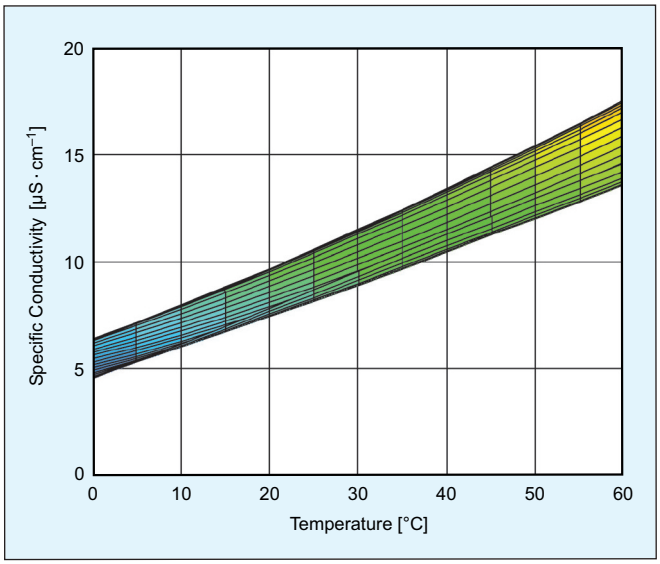

Figure 13:
Projection of the conductivity curves from Figure 11 onto the κ-T-surface.

CONCLUSION

The temperature conversion of the conductivity, within the range from 25 °C to 50 °C, depends only a little on the chemical composition of the sample. This is due to the fact that the temperature coefficients $Q_{i,T} = \frac{\lambda_{i,25\,°C}}{\lambda_{i,T}}$ of all the ions are of approximately the same dimension, which is proportional to the ratio of the reciprocal viscosity $\frac{1/\eta_{25\,°C}}{1/\eta_T}$ of water.

Consequently, the conversion of a conductivity value to 25 °C can be approximated by a single equation that is applicable to samples composed of any electrolytes.

However, concentrations can only be calculated from the conductivity when the chemical composition of the sample is known and the appropriate conversion model is chosen.

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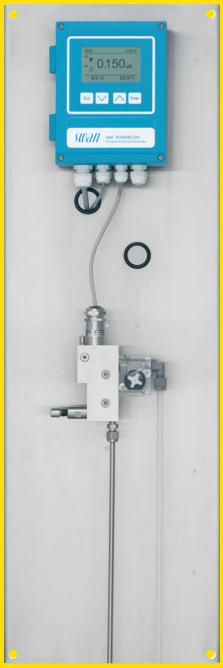

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