Equilibria in electrolytes solutions and water hardness

by Urszula Lelek-Borkowska

Electrolytes

When the substance dissolved in water or other solvent exhibits electrical conductivity it is called an **electrolyte.** solvent

The unique properties of water arise mainly from its molecular structure. The molecule of water is composed of one oxygen and two hydrogen atoms. Due to the difference in electronegativity each hydrogen atom is linked to an oxygen atom with an polarized atomic bound. That means that connecting pair of electrons is shifted to the oxygen.

Electronegativity - the power of an atom to attract electrons to itself. The presence of two lone electron pairs on the oxygen atom and polar nature of the O-H bonds combine to make water molecule highly polar. The interaction between the polar water molecules and the solute plays a major role in processes of dissolution.
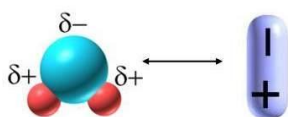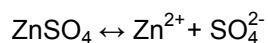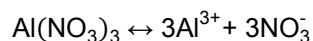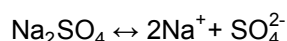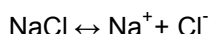

Fig.1. Water molecule as a dipole.

Fig.2. Hydration of the ions in water.

Dissociation, hydration, conductivity of ions

Ionic dissociation concept was developed by Arrhenius. According to his theory **ionic dissociation** is the process of splitting the chemical compound into ions (electrically charged particles) caused by interaction with molecules of solvent.

The electrolytic dissociation undergoes compounds in which are present ionic or strongly polarized covalent bonds. Almost all water-soluble salts, all acids and bases dissociate.

The dissociation process is always reversible. Below are examples of dissociation reactions:

$$NaCl \leftrightarrow Na^+ + Cl^-$$
$$Na_2SO_4 \leftrightarrow 2Na^+ + SO_4^{2-}$$
$$Al(NO_3)_3 \leftrightarrow 3Al^{3+} + 3NO_3^-$$
$$ZnSO_4 \leftrightarrow Zn^{2+} + SO_4^{2-}$$

Dissolved ions stays in the solution surrounded by solvent molecules. Such a phenomenon is called **solvatation**. In case when the solvent is water - this process is called **hydration**.

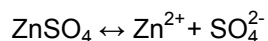The electrolytic dissociation undergoes compounds in which are present ionic or strongly polarized covalent bonds. Almost all water-soluble salts,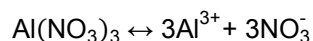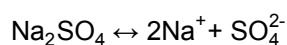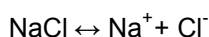 all acids and bases dissociate. The dissociation process is always reversible. Below are examples of dissociation reactions:

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Degree of dissociation, strength of the electrolytes

The electrolyte can dissociate completely or partially. Electrolytes dissociating completely are called strong electrolytes. Electrolytes dissociating slightly are called week electrolytes. The power of electrolytes determines the dissociation degree. The **dissociation degree** is the fraction of original solute molecules that have dissociated. It is usually indicated by the Greek symbol α.

$$\alpha = \frac{n_{diss}}{n_0}$$

where: n_{diss} - number of moles of the dissociated reactant,

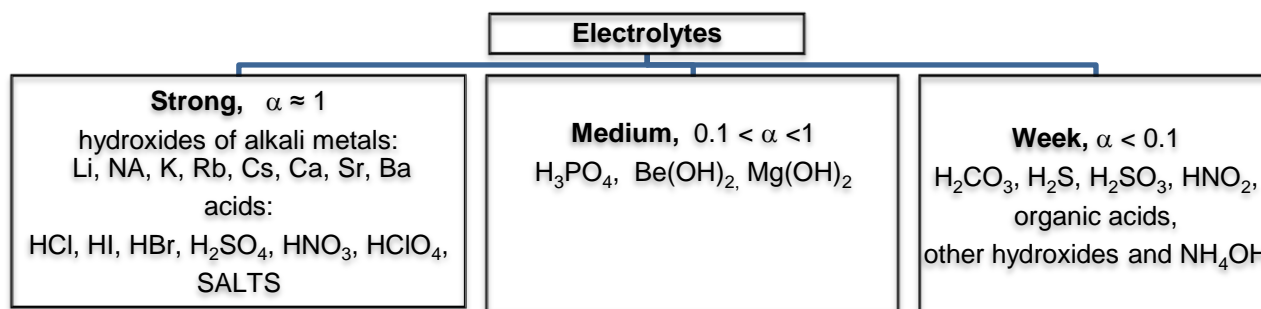n_0 - number of moles of the reactant present initially.

When all of molecules of solute are split into ions – the dissociation degree is equal unity ($\alpha = 1$), when no molecule dissolves – the dissociation degree is equal zero.

$$0 < \alpha < 1$$

Sometimes it can be expressed in %:

$$0\% < \alpha < 100\%$$

For strong electrolytes $\alpha \approx 1$, for week electrolytes $\alpha < 0.1$, what means that less than 10 % of solute molecules are dissolved and the majority stays in undissolved form.
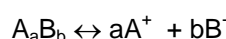
Electrolytes		
Strong, $\alpha \approx 1$ hydroxides of alkali metals: Li, NA, K, Rb, Cs, Ca, Sr, Ba acids: HCl, HI, HBr, H_2SO_4, HNO_3, $HClO_4$, SALTS	**Medium,** $0.1 < \alpha < 1$ H_3PO_4, $Be(OH)_2$, $Mg(OH)_2$	**Week,** $\alpha < 0.1$ H_2CO_3, H_2S, H_2SO_3, HNO_2, organic acids, other hydroxides and NH_4OH

The degree of dissociation depends on:

1) the nature of the electrolyte,

2) concentration of the solution (increasing with dilution solution, $C\downarrow \rightarrow \alpha\uparrow$),

3) temperature (increasing slightly with increasing temperature, $t\uparrow \rightarrow \alpha\uparrow$),

4) the presence of other substances in the solution.

Dissociation constant

The undissociated weak electrolytes molecules are in equilibrium with dissociation products, or ions. Consider the following equation of dissociation:

$$A_aB_b \leftrightarrow aA^+ + bB^-$$

The equilibrium constant of this reaction can be expressed as follows:

$$K_d = \frac{[A^+]^a \cdot [B^-]^b}{[A_aB_b]} \qquad \text{or} \qquad K_d = \frac{c_{A^+}^a \cdot c_{B^-}^b}{c_{A_aB_b}}$$

where: $[A^+]$, $[B^-]$, c_{A^+}, c_{B^-} - molar concentration of ions,

$[A_aB_b]$ - molar concentration of undissociated part of electrolyte,

a, b – stoichiometric coefficients.

(4.3)

The **dissociation constant** is the ratio of the product of the concentration of ions to the concentration of undissociated molecules.

The dissociation constant K is a characteristic for a given electrolyte. In contrast to the degree of dissociation is not dependent on the concentration of the electrolyte, but only on the temperature – increases with increasing temperature. he dissociation constant determined only for the weak or medium strength electrolytes. For the strong dissociation of the solid electrolyte generally is not defined (the concentration of undissociated molecules is close to zero).

Multi-protonated acids, containing in its molecule more than one hydrogen atoms dissociate more gradually.

For example, carbonic acid:

1st step: $$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

2nd step: $$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

or phosphoric acid:

1st step: $$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$$

2nd step: $$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$$

3rd step: $$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$$

So, for acids with more than one hydrogen molecule we must write the dissociation constant for every dissociation step:

$$K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]}$$

$$K_2 = \frac{[H^+] \cdot [CO_3^{2-}]}{[H_2CO_3]}$$

Summing up the constants for each steps gives the total dissociation constant:

$$K = \frac{[H^+]^2 \cdot [CO_3^{2-}]}{[H_2CO_3]}$$

Ostwald dilution law

Wilhelm Ostwald's dilution law is a relationship between the dissociation constant K_d and the degree of dissociation α can be expressed:

$$K = \frac{c \cdot \alpha^2}{1 - \alpha} \qquad (4.4)$$

This law is true only for week electrolytes. When $\alpha \ll 1$, the denominator is equal to one and the above equation can be simplified as follows:

$$K = c \cdot \alpha^2 \qquad (4.5)$$

Solubility product

In the case of a saturated solution of the slightly soluble substance the dissolving substance remains, for the most part, in the solid phase. It can be assumed that concentration of undissociated part of the solute is constant:

$$[A_aB_b] = const. \qquad (4.6)$$

The equilibrium constant of dissociation reaction of such solution takes the form of solubility product:

$$K_{sp} = [A^+]^a \cdot [B^-]^b$$

Example:

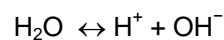Solubility product of strontium carbonate:

$$SrCO_3 \leftrightarrow Sr^{2+} + CO_3^{2-} \qquad K_{sp} = [Sr^{2+}] \cdot [CO_3^{2-}]$$

Solubility product of ferric chloride:

$$FeCl_3 \leftrightarrow Fe^{3+} + 3\ Cl^- \qquad K_{sp} = [Fe^{3+}] \cdot [Cl^-]^3$$

Autodissociation of water

Water dissociate in course of the reaction:

$$H_2O \leftrightarrow H^+ + OH^-$$

(it should be kept in mind that it is a simplification, since the hydrogen cation is always accompanied by water molecules as hydronium ion H_3O^+).

The dissociation constant for water has a form:

$$K = \frac{[H^+] \cdot [OH^-]}{[H_2O]}$$

Knowing that water is only slightly dissociated and assuming that concentration of water in water is almost constant there can be written the formula of ionic product of water:

$$K_w = [H^+] \cdot [OH^-]$$

At 25 °C K_w is equal to $1.0 \cdot 10^{-14}$, so:

$$[H^+] \cdot [OH^-] = 10^{-14}$$

pH is the negative logarithm of the activity of the hydrogen ion in an aqueous solution:

$$pH = -\log [H^+] \quad \text{or} \quad pH = -\log c_{H^+}$$

The value of the water ionic product is equal:

$$c_{H^+} \cdot c_{OH^-} = 10^{-14}, \quad \text{that means in pure water} \qquad c_{H^+} = c_{OH^-} = 10^{-7}$$

so, the pH of pure water: $pH = -\log c_{H^+} = 7$, $pOH = -\log c_{OH^-} = 7$, so $pH + pOH = 14$

The full scale of pH is then $0 < pH < 14$.

0 < pH < 7 – acidic solution

pH = 7 – neutral solution

7 < pH < 14 – alkaline solution

To determine the value of pH there can be used indicators - the chemical compounds, mostly organic, that react with hydrogen ions and change colour depending on the pH. The most accurate measurements of the pH is carried out using a pH-meter measurement based on the use of a pH sensitive electrode, a reference electrode, and a temperature element to provide a temperature.

Example 1: Calculate pH of 0.005 M H_2SO_4, assuming it's full dissociation ($\alpha = 1$)

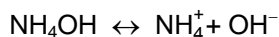Calculating the concentration of hydrogen ions from the equation: $\quad C_j = C_M \cdot \alpha \cdot n$

where: C_M - molar concentration of an electrolyte, α- dissociation constant n - number of H^+ ions origin from 1 molecule of electrolyte.

$$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-}$$
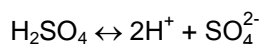
$$[H^+] = 0.005 \cdot 1 \cdot 2 = 10^{-2}\ mol/dm^3, \qquad pH = -\log 10^{-2} = 2$$

Answer: pH of 0.005 M H_2SO_4 is equal 2.

Example 2. Calculate pH of 0.1 M NH_4OH, $\alpha = 1\%$

$$NH_4OH \leftrightarrow NH_4^+ + OH^-$$

$C_M = 0.1\ mol/dm^3$, $\alpha = 1\% = 0.01$, n = 1 (1 OH^- ion origin from 1 molecule of NH_4OH)

$[OH^-] = 0.1 \cdot 0,01 \cdot 1 = 10^{-3}\ mol/dm^3$, $pOH = -\log 10^{-3} = 3$, $pH = 14 - 3 = 11$

*Answer:* pH of 0.1 M NH_4OH is equal 11.

Hydrolysis

All of the salts are strong electrolytes, that means they are completely dissociated. The salt ions can react with the molecules of water. Reaction of the salt ions with water is called hydrolysis.

Hydrolysis – reaction of the salt ions with the molecules of water yielding hydroxide and acid, the reaction reverse of the neutralization reaction.
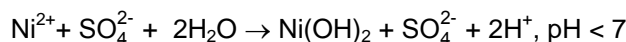
salt + water = acid + base
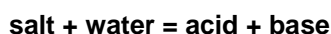
The resulting compounds, depending on their strength will be present in the dissociated or the undissociated form.

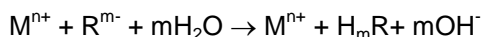Hydrolysis of the salts of <u>strong acids</u> and <u>weak hydroxides</u>:

$$M^{n+} + R^{m-} + nH_2O \rightarrow M(OH)_n + R^{m-} + nH^+$$
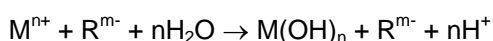
after hydrolysis there are present hydrogen ions - the solution is <u>acidic</u>

Example: nickel (II) sulphate $NiSO_4$

$$Ni^{2+} + SO_4^{2-} + 2H_2O \rightarrow Ni(OH)_2 + SO_4^{2-} + 2H^+, pH < 7$$

Hydrolysis of the salts of <u>weak acids</u> and <u>strong hydroxides</u>:

$$M^{n+} + R^{m-} + mH_2O \rightarrow M^{n+} + H_mR + mOH^-$$

after hydrolysis there are present hydroxide ions - the solution is <u>alkaline</u>

Example: potassium carbonate K_2CO_3

$$2K^+ + CO_3^{2-} + 2H_2O \rightarrow 2K^+ + H_2CO_3 + 2OH^-, pH > 7$$

Hydrolysis of the salts of <u>weak acids</u> and <u>weak hydroxides</u>:

$$M^{n+} + R^{m-} + xH_2O \rightarrow M(OH)_n + H_mR$$
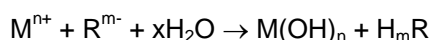
after hydrolysis there is no hydrogen or hydroxide ions - the solution is <u>neutral</u>

Example: ferrous sulfide FeS

$$Fe^{2+} + S^{2-} + 2H_2O \rightarrow Fe(OH)_2 + H_2S, pH = 7$$

The salts of strong acids and strong hydroxides do not undergo hydrolysis!

Proof: sodium chloride NaCl

$$\cancel{Na^+} + \cancel{Cl^-} + H_2O \rightarrow \cancel{Na^+} + \cancel{Cl^-} + H^+ + OH^-$$

finally: $\qquad\qquad\qquad\qquad H_2O \rightarrow H^+ + OH^-$ - dissociation of the water molecule
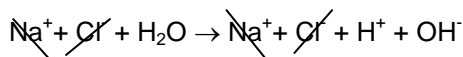
Hardness of water

Hard water is formed when through deposits of limestone and. The presence of soluble calcium and magnesium salts in water cause so called **water hardness**. Calcium and magnesium salts enter the water percolates the soils and rocks containing limestone and chalk-containing minerals

such as calcium and magnesium. During this process the sparingly soluble in water salts converts into a well water-soluble calcium and magnesium bicarbonates. This reaction is called chemical weathering of limestone and occurs due to the following reactions:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

$$MgCO_3 + CO_2 + H_2O = Mg(HCO_3)_2$$
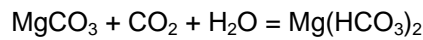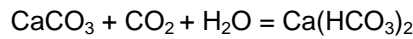
Calcium and magnesium bicarbonates ($Ca(HCO_3)_2$, $Mg(HCO_3)_2$) cause so called carbonate hardness, also called temporary hardness T_T. Sulphates and chlorides of calcium and magnesium ($CaSO_4$, $MgSO_4$, $CaCl_2$, $MgCl_2$) cause permanent hardness of water T_P. The sum of the temporary and permanent hardness of water is a general hardness T_G.
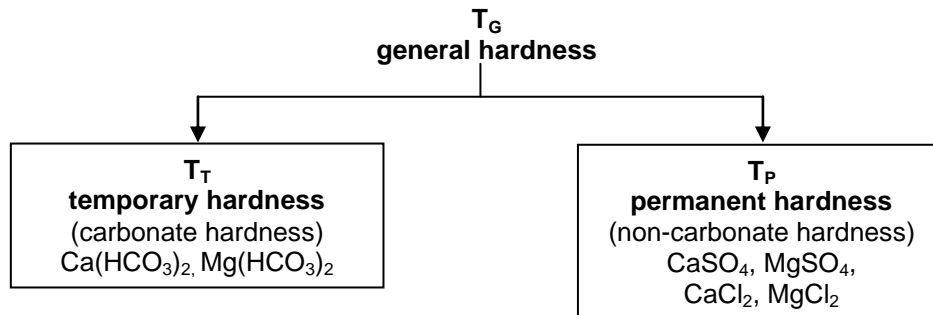
Expressions of the water hardness

Water hardness is expressed in various units, such as: **degrees of general hardness (dGH), German degrees (°dH, deutsche Härte), parts per million (ppm or American degree), French degrees (°fH or °f) or English degrees (°e or °Clark).**

1 ppm = 1 mg $CaCO_3/dm^3$ H_2O (parts per million or American degree)

dGH = °dH = 10mg CaO/dm^3 H_2O or 17.848 ppm.

°fH = 10mg $CaCO_3/dm^3$ H_2O = 10 ppm

°e = 1 grain $CaCO_3$ /imperial gallon = 64.8 mg $CaCO_3$ /4.55 dm^3 H_2O= 14.254 ppm.

Table 1. *The conversion factors between the various units.*

	ppm, mg/dm^3	dGH, °dH	°e, °Clark	°fH
ppm, mg/dm^3	1	17.85	14.25	10
dGH, °dH	0.05603	1	0.7986	0.5603
°e, °Clark	0.07016	1.252	1	0.7016
°fH	0.1	1.785	1.425	1

Table 2. *Classification of water in terms of hardness[1]*

Classification	hardness in ppm	hardness in mg/dm^3	hardness in dGH/°dH
Soft	less than 60	0–60	0-3.37
Moderately hard	60-120	61–120	3.38-6.74
Hard	120-180	121–180	6.75–10.11
Very hard	> 180	≥ 181	≥ 10.12

[1] USGS - U.S. Geological Survey Office of Water Quality. "USGS Water-Quality Information: Water Hardness and Alkalinity". *usgs.gov.*

Removal of hardness (softening of water)

Water for industrial purposes, in particular for supplying boilers and refrigeration systems must be soft , ie. free from ingredients that cause the formation of lime. The water scale would cause damage or even rupture of the boiler following a crack of the limescale layer, when water comes into contact with the hot wall of the boiler. Limescale can also cause fuel losses due to bad thermal conductivity. Generally, water softening is the removal of the ions that cause hardness: Ca^{2+}, Mg^{2+} and other metal ions as Fe^{2+}, Mn^{2+}, Al^{3+}. Water softening may be carried out using:

1. distillation,
2. thermal methods,
3. chemical methods
4. physico-chemical methods.

Distillation

The distillation is a physical process of evaporation and condensation of pure water removing all impurities with leaving. Distillation gives an ideal softened water, however the costs of softening the water by this method are high and it is not the industry greater use.

Thermal method

Bicarbonate temporary hardness can be easily removed from the water by boiling. There occurs the decomposition of the bicarbonate according to the reactions:
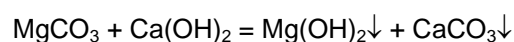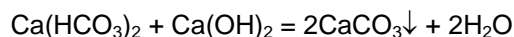
$$Ca(HCO_3)_2 = CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 = MgCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$MgCO_3 + H_2O = Mg(OH)_2 \downarrow + CO_2 \uparrow$$
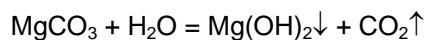
This method of removing temporary hardness is not favourable for water for industrial purposes, because the precipitation of sparingly soluble $CaCO_3$ is the cause of limescale. Scale is a mixture of different substances: calcium carbonate, magnesium carbonate, magnesium hydroxide, magnesium sulfate, dehydrated silicate acid - silica and iron oxides. Depending on which type of the compound is predominantly, the limescale can be classified into carbonate, sulfate or silicate scale.
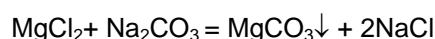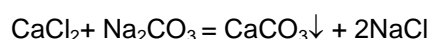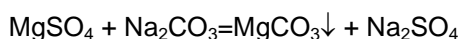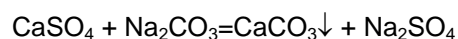
Chemical methods

Chemical methods for removal of water hardness (softener) are based on precipitation of insoluble deposits, which include insoluble calcium and magnesium salts.

One way is to use the **method of soda-lime**. Lime remove hardness temporary according to the reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 \downarrow + CaCO_3 \downarrow + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$

While soda removes permanent hardness:

$$CaSO_4 + Na_2CO_3 = CaCO_3 \downarrow + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 = MgCO_3 \downarrow + Na_2SO_4$$

$$CaCl_2 + Na_2CO_3 = CaCO_3 \downarrow + 2NaCl$$
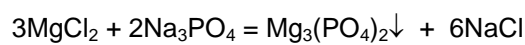
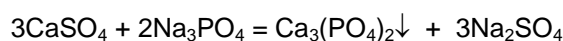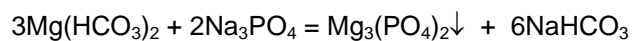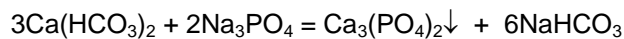$$MgCl_2 + Na_2CO_3 = MgCO_3 \downarrow + 2NaCl$$

Insoluble calcium and magnesium salts are filtered off or settles on the bottom of container in the form of sluggish precipitate. This method is widely used because it is cheap and simple.

Another chemical method of removing water hardness is **addition of a strong acid**. As a result, there is decomposition of calcium and magnesium bicarbonates in the following reactions:

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2H_2O + 2CO_2\uparrow$$

$$Mg(HCO_3)_2 + 2HCl = MgCl_2 + 2H_2O + 2CO_2\uparrow$$
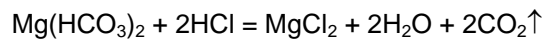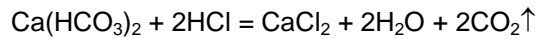
This method of removing hardness prevents the creation of scale, but unfortunately increases the corrosive properties of the water.

Phosphate softening is the removal of calcium and magnesium ions in the form of insoluble phosphate deposits. The cost of phosphate softening is higher than other chemical methods, and therefore this method is used for softening water with a low hardness or in addition to other methods.

$$3Ca(HCO_3)_2 + 2Na_3PO_4 = Ca_3(PO_4)_2\downarrow + 6NaHCO_3$$

$$3Mg(HCO_3)_2 + 2Na_3PO_4 = Mg_3(PO_4)_2\downarrow + 6NaHCO_3$$

$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2\downarrow + 3Na_2SO_4$$

$$3MgCl_2 + 2Na_3PO_4 = Mg_3(PO_4)_2\downarrow + 6NaCl$$

Phosphates do not cause corrosion of iron, prevent limescale and dissolution of already existing one

Physico-chemical methods

Physico-chemical methods of water hardness removal include the use of ion exchangers. Ion exchangers they are the substances with the ability to exchange cations (cation) or anions (anion exchangers). Ion exchangers are not soluble in water, but react at their surface with the compounds contained in water. Historically, water softening was carried out using natural zeolite - inorganic compounds as alumina-silicates eg. $Na_2Al_2Si_4O_{12}$. Recently, zeolites have been replaced by synthetic ion exchange resins of high molar mass. Purified water is first passed through the cation exchanger which exchanges the cations contained in the water to the hydrogen ions according to the scheme:
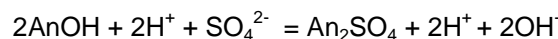
$$2HKt + Ca^{2+} + CO_3^{2-} = CaKt_2 + 2H^+ + CO_3^{2-}$$

or $\qquad 2HKt + Ca^{2+} + SO_4^{2-} = CaKt_2 + 2H^+ + SO_4^{2-}$
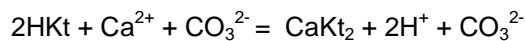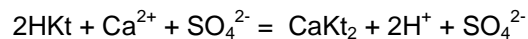
this process is followed by passage through the anion exchanger resin which exchanges sulfates, chlorides or other anions for hydroxide ions present in the pure water.

$$2AnOH + 2H^+ + CO_3^{2-} = An_2CO_3 + 2H^+ + 2OH^-$$

or $\qquad 2AnOH + 2H^+ + SO_4^{2-} = An_2SO_4 + 2H^+ + 2OH^-$
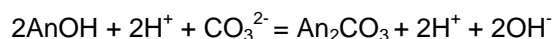
Proper running water demineralization on ion-exchangers allows to obtain as clean water as after the distillation process. The resulting water is used to power industrial steam boilers.