Information on redox voltage measurement

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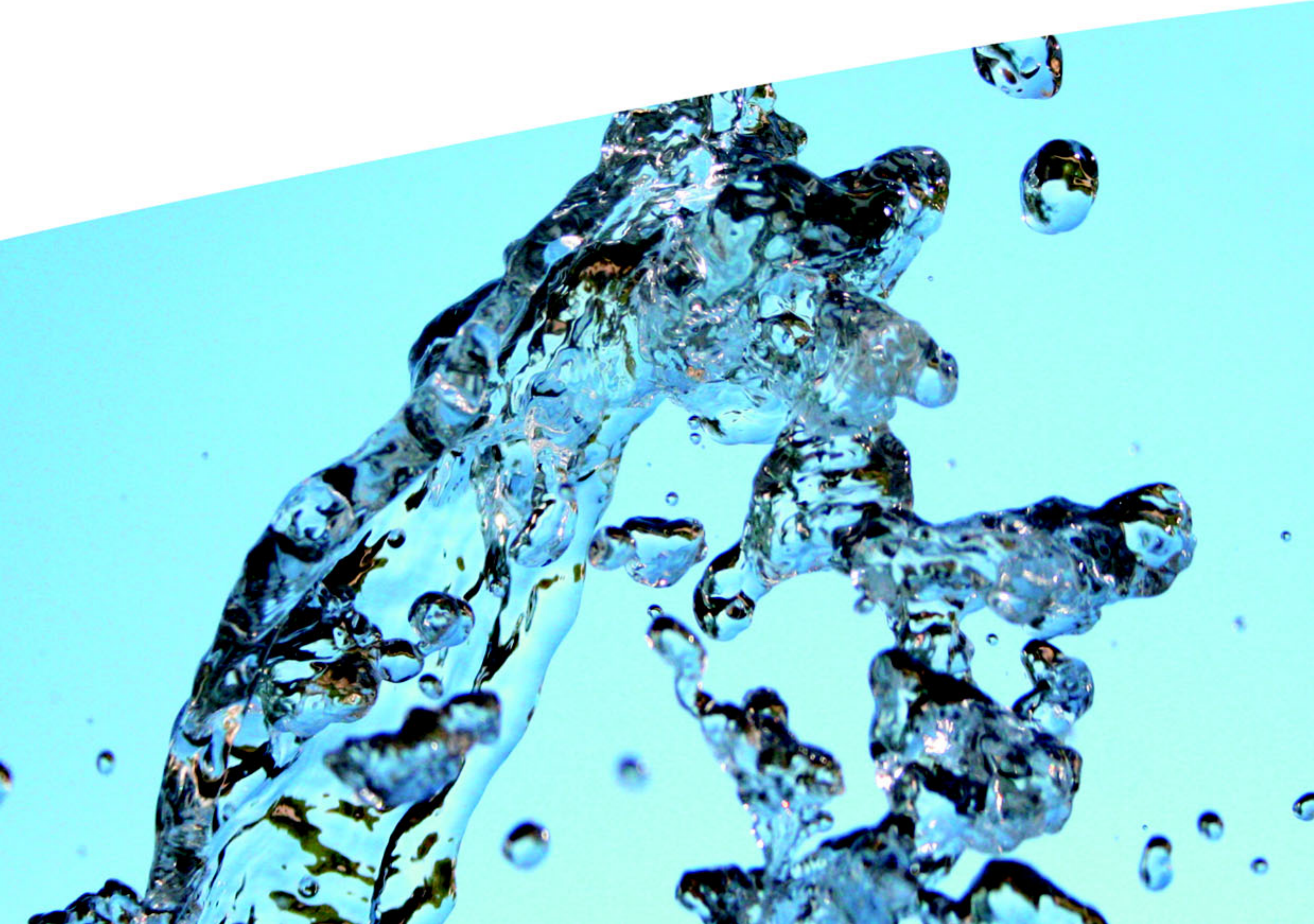

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Preface

Together with the pH value, the redox voltage is one of the most frequent process variables in industrial and municipal effluent plants, as well as in installations for monitoring drinking water and bathing (swimming pool) water.

This technical publication presents the basic electrochemical relationships and typical applications in a general, easily understood form. In addition, information is given on the current state of the technology with transmitters, controllers and sensors for this process variable.

We are trying to keep this “Information on redox voltage measurement” fully up to date, and call upon our readers to collaborate in an active exchange of experience and knowledge. We would very much like to receive your suggestions and contributions to the discussion.

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Contents

1.1 General

1.1.1 Reduction - Oxidation

The name *redox reaction* is derived from the two terms:

- reduction and
- oxidation.

Originally, every reaction of a substance with oxygen was called oxidation (from the Latin oxygenium = oxygen). The return to the original state was referred to as reduction.

On the basis of detailed tests made possible by modern technology, a different definition has been found for these two terms.

oxidation = donation of electrons
reduction = acceptance of electrons

However, since free electrons never occur in aqueous solutions, reduction and oxidation processes can only occur coupled to one another, such that one reaction supplies exactly as many electrons as are used by the other partner. These coupled reduction and oxidation processes that take place simultaneously are described as

redox reactions.

We come across redox reactions every day without paying any attention to them however, or consciously noticing them. Examples of them are:

- Rusting of iron
- Copper forming a verdigris coating
- Silver turning black

But how do these electron transfers take place ?
Electrons are negatively charged elementary particles. In metals, the electrons are present in a freely mobile form, known as an “electron gas”. Supplying energy (through impact, friction, electric fields and the like), permits the electrons to be detached from their fixed bonding. Electrically charged particles called ions remain behind.

If an iron plate is placed in water, no reaction is observed. However, if the water is mixed with acid (e. g. hydrochloric acid), then gas bubbles will be seen rising from the iron plate. The gas formed is hydrogen. But electrons are needed for the production of hydrogen. The hydrochloric acid is completely dissociated as hydrogen ions and chloride ions. The hydrogen ions accept the electrons from the iron, leading to the formation of hydrogen. The chloride ions are not involved in the reaction, and remain unchanged. The driving force for the ion transfer is the “electrical force” of the system. This electrical force can be measured in the form of a voltage (potential). How this takes place will be explained later in the course of this section. The iron atoms are forced to give up their electrons. The iron is said to be oxidized. The hydrogen atoms accept the released electrons and form hydrogen. The hydrogen ions are said to be reduced.

1.2 Origin of the voltage

1.2.1 Character of metals

The character of a metal is largely determined by how easily it can be oxidized, i. e. converted into positively charged ions.

Metals that can be easily oxidized are referred to as base metals.

Examples of these are:

- Sodium
- Aluminium
- Iron

Metals which are difficult to oxidize are referred to as noble metals.

Examples of these are:

- Copper
- Silver
- Gold

If the metals are arranged according to their oxidizability i. e. according to their efforts to form positively charged ions, the result is the voltage series of the metals.

1.2.2 Electrochemical voltage series

Reduction potential increases	**Metal**	**Standard potential in V**	**Redox system**	Oxidation potential increases
↑	Lithium	-3.05	$Li \Leftrightarrow Li^{+} + e^{-}$	↓
	Potassium	-2.92	$K \Leftrightarrow K^{+} + e^{-}$	
	Calcium	-2.76	$Ca \Leftrightarrow Ca^{2+} + 2\ e^{-}$	
	Sodium	-2.71	$Na \Leftrightarrow Na^{+} + e^{-}$	
	Magnesium	-2.34	$Mg \Leftrightarrow Mg^{2+} + 2\ e^{-}$	
	Aluminium	-1.67	$Al \Leftrightarrow Al^{3+} + 3\ e^{-}$	
	Manganese	-1.05	$Mn \Leftrightarrow Mn^{2+} + 2\ e^{-}$	
	Zinc	-0.76	$Zn \Leftrightarrow Zn^{2+} + 2\ e^{-}$	
	Chromium	-0.56	$Cr \Leftrightarrow Cr^{3+} + 3\ e^{-}$	
	Iron	-0.44	$Fe \Leftrightarrow Fe^{2+} + 2\ e^{-}$	
	Cobalt	-0.28	$Co \Leftrightarrow Co^{2+} + 2\ e^{-}$	
	Nickel	-0.23	$Ni \Leftrightarrow Ni^{2+} + 2\ e^{-}$	
	Tin	-0.14	$Sn \Leftrightarrow Sn^{2+} + 2\ e^{-}$	
	Lead	-0.12	$Pb \Leftrightarrow Pb^{2+} + 2\ e^{-}$	
	Hydrogen	**0.00**	**1/2H2 ⇔ H+ + e^{-}**	
	Copper	+0.35	$Cu \Leftrightarrow Cu^{2+} + 2\ e^{-}$	
	Silver	+0.80	$Ag \Leftrightarrow Ag^{+} + e^{-}$	
	Mercury	+0.85	$Hg \Leftrightarrow Hg^{2+} + 2\ e^{-}$	
	Platinum	+1.2	$Pt \Leftrightarrow Pt^{2+} + 2\ e^{-}$	
	Gold	+1.36	$Au \Leftrightarrow Au^{3+} + 3\ e^{-}$	

Table 1: Electrochemical voltage series

The effort to change over to the ionic state decreases from top to bottom. Each metal displaces the metals standing below it in the voltage series from their salt solutions. Such redox reactions then always occur when a base metal is immersed in the solution of a noble metal i.e. when the base metal is present in elementary form, and the noble metal, on the other hand, is present in ionized form. The base metal is oxidized, the noble metal is reduced. Whether a particular metal behaves as an oxidizing agent or as a reducing agent depends on the reaction partner.

Example 1
Copper acts as a reducing agent against silver ions:

$$Cu + 2\ Ag^{+} \Leftrightarrow Cu^{2+} + 2\ Ag\downarrow \tag{1}$$

Copper ions act as an oxidizing agent against zinc:

$$Zn + Cu^{2+} \Leftrightarrow Zn^{2+} + Cu\downarrow \tag{2}$$

Generally, the following statements hold true:
Every metal acts as a reducing agent against the ions of all metals that stand further below it in the voltage series. The ions of a metal act as an oxidizing agent against all metals that stand further above it in the voltage series.

From a pair of metals, the metal in the higher position strives to achieve the ionic state each time, and the one in the lower position strives to achieve the elementary state. If the baser of the two metals is already in ionic form and the nobler metal already in elementary form, no such redox reaction occurs.

Example 2
A copper plate does not react with a $ZnSO_4$ solution.

Hydrogen is included with the metals in the voltage series as, like the metals, it also forms cations. Nevertheless, hydrogen occupies a special position in the voltage series. Everything that was said above about metals also applies to hydrogen.

All metals above hydrogen displace hydrogen from dilute acids..

Example 3

$$Zn + 2\,H^+ \Leftrightarrow Zn^{2+} + H_2\uparrow \tag{3}$$

$$Fe + 2\,H^+ \Leftrightarrow Fe^{2+} + H_2\uparrow \tag{4}$$

On the other hand, copper does not react with dilute acids.

The standard potential is a measure of the effort made by a metal to form ions dissolved in water. If a metal is immersed in water or in an aqueous salt solution, metal atoms can pass into solution as cations, or cations are separated from the metal. In the first case, the released electrons cause a surplus of electrons, in the second case a shortage of electrons. The metal is therefore negatively or positively charged. An electrical voltage (a potential difference) then exists at the boundary layer between metal and liquid. The magnitude of the voltage depends firstly on the type of metal, and secondly on the concentration of the solution. Such a combination of metal and salt solution is referred to as a half-element.

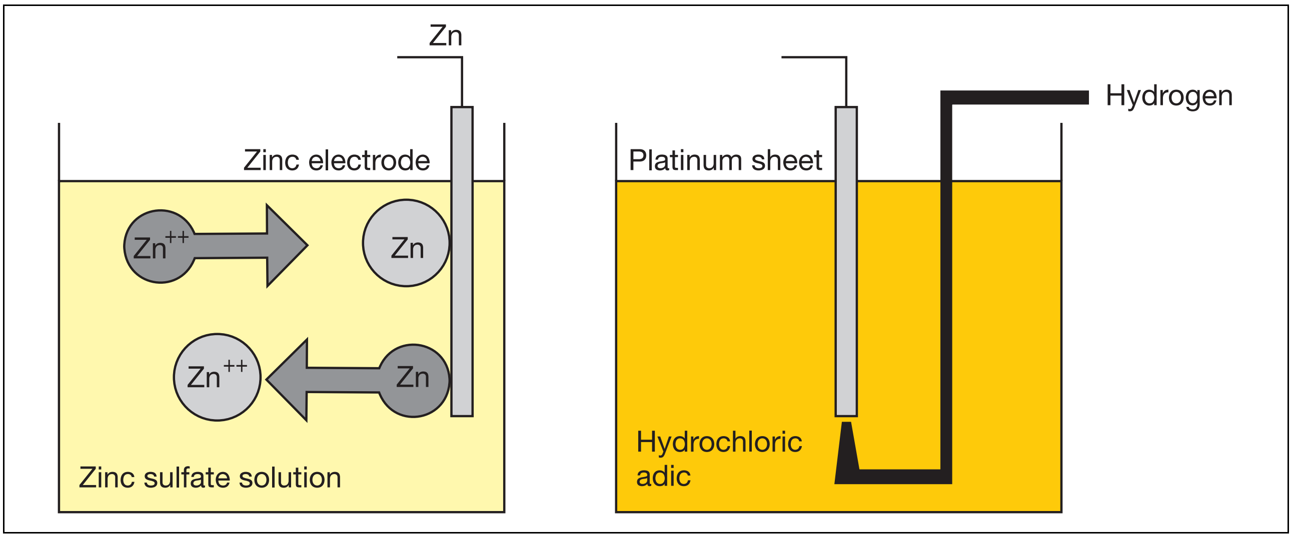

Fig. 1: **Half-element (left) and Standard hydrogen electrode (right)**

The potential that occurs in such a half-element cannot be measured directly. A reference system is needed for this.

One such reference system consists of an additional half-element, e.g. the hydrogen/hydrochloric acid system in the form of the standard hydrogen electrode (SHE). Here, a platinum sheet is immersed in a hydrochloric acid solution and continuously surrounded by hydrogen. The two half-elements are now connected by a conductive agent - in most cases an electrolyte bridge made from KCl. The potential difference between a metal and the SHE is referred to as the standard potential of the metal. This value is recorded in the voltage series.

If two different metals are immersed in a salt solution, then a voltage (potential difference) develops. Such a combination is referred to as a galvanic element or a galvanic chain. The voltage of a galvanic element is higher, the greater the separation of the two standard potentials from each other in the table.

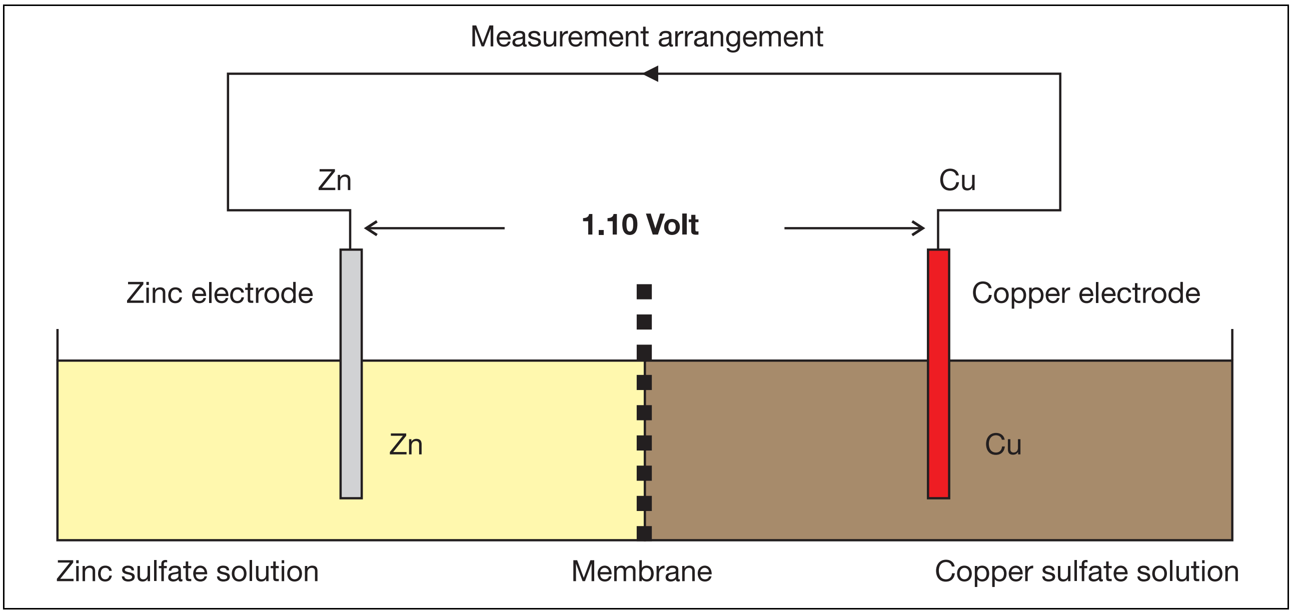

Fig. 2: **Galvanic element**

1.2.3 Equations

This is expressed numerically by means of the Nernst equation, familiar from pH measurement:

$$\Delta E = E_0 - \frac{RT}{nF} \bullet \ln K \qquad (5)$$

At 25°C and using the logarithm to the base 10, this gives us:

$$\Delta E = E_0 - \frac{0.059}{nF} \bullet \lg K \qquad K = \frac{[C] \bullet [D]}{[A] \bullet [B]} \qquad (6)$$

K = equilibrium constant of the reaction
n = number of electrons

With the aid of the Nernst equation, the value at different concentrations[1] can now be determined arithmetically. The effect of temperature on the redox potential follows from the Nernst equation. In addition, the state of equilibrium of a redox reaction can be influenced by the temperature and the pH value. For this reason, temperature and pH value are also stated together with the redox potential.

Example
Galvanic Zn/Cu element, c = 1 mol/liter for both solutions

Reaction equation:

$$Zn + Cu^{++} \Rightarrow Zn^{++} + Cu \tag{7}$$

$$A + B \Rightarrow C + D$$

The concentration of solids is constant and the value is set equal to 1. Zn and Cu drop out. As a result of this, we obtain the following formula for the above equation:

$$\Delta E = E_0 - \frac{0.059}{n} \bullet \lg\frac{[Zn^{++}] \bullet [Cu]}{[Zn] \bullet [Cu^{++}]} \Rightarrow \Delta E = E_0 - \frac{0.059}{n} \bullet \lg\frac{c[Zn^{++}]}{c[Cu^{++}]} \tag{8}$$

$$\Delta E = E_0 - \frac{0.059}{n} \bullet \lg\frac{1}{1} \Rightarrow \Delta E = 1.10V - \frac{0.059}{2} \bullet 0 = 1.10V$$

If we now change the concentration of the copper sulfate solution to a value of c = 0.01 mol/liter, the value for the Galvani potential obtained changes as follows:

$$\Delta E = 1.10V - \frac{0.059}{2} \bullet \lg\frac{1}{0.01} \tag{9}$$

$$\Delta E = 1.10V - \frac{0.059}{2} \bullet \lg 100$$

$$\Delta E = 1.10V - 0.059 = 1.04V$$

The voltage has become smaller. The reaction no longer has as large a value of driving force as was present at the start, with the concentrated solution. It is obvious from this that the voltage of the particular redox system can also be determined arithmetically with the aid of the standard potential and the concentration of the solutions involved. The voltage generated here is also called the electromotive force (EMF).

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[1] The concentration is used as an approximation here, instead of the activity of the components.

2.1 Construction of a redox measuring circuit

The following items of equipment are required to construct a redox measuring circuit:

- immersion or flow-through fitting
- metal electrode and
- reference electrode or
- combination metal electrode
- screened measuring cable
- transmitter/controller (mV meter)

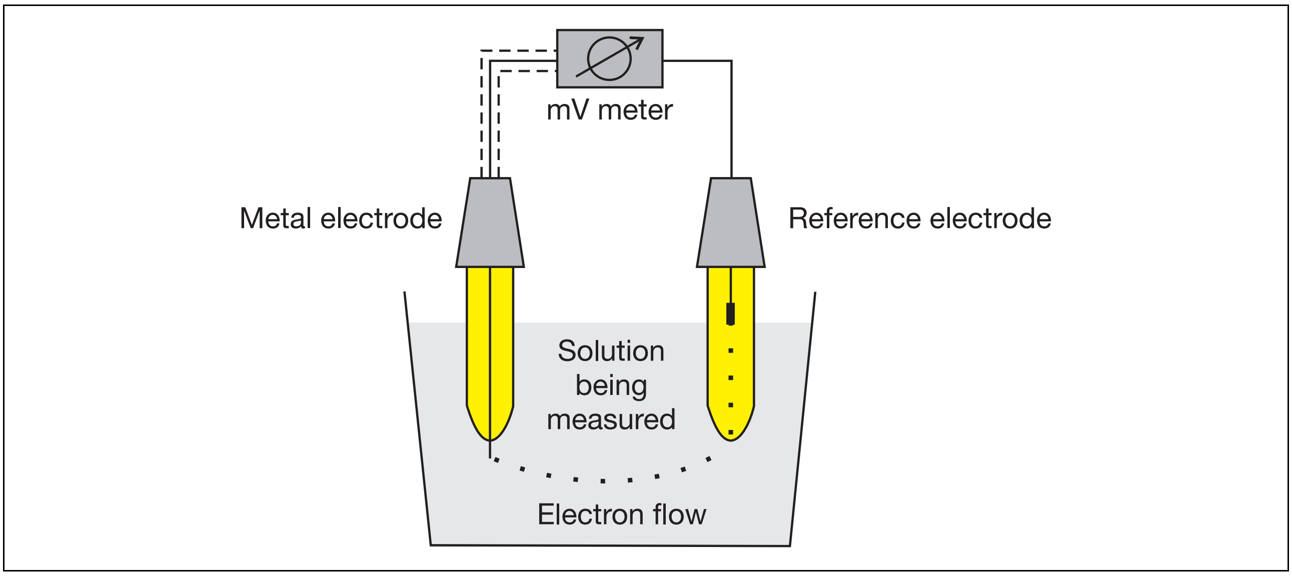

Fig. 3: **Redox measuring circuit**

2.2 Construction of the individual components

2.2.1 Immersion/flow-through fittings

Fittings are used for holding and protecting sensors (metal electrode, reference electrode, redox combination electrode).

Immersion fittings permit measurement not only at the surface of the liquid but also deep inside it. A wide range of mounting elements and accessories permit mounting on almost all containers. The immersion fittings are normally manufactured from polypropylene (PP) and are supplied in immersion lengths up to 2000 mm. However, other materials (e. g. V4A) are also available for special purposes.

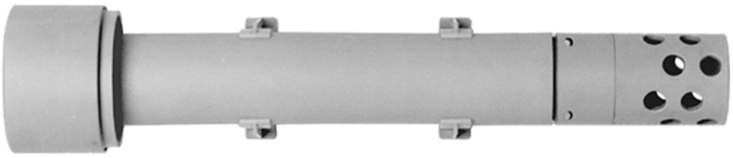

Fig. 4: **Immersion fitting**

Flow-through fittings permit measurement directly in the liquid flow lines or in a bypass of these lines. The sensor reacts immediately to changes in the medium, so that the dead times of the control loop can be kept short.

It is essential that all fittings are situated in an easily accessible position, to permit regular servicing and examination of the sensors.

Fig. 5: Flow-through fitting

2.2.2 Metal electrodes

Metal electrodes consist of a glass or plastic tube, at the lower end of which is sealed a piece of metal (Pt tip, Pt or gold pin) of a specific form. Used in conjunction with a reference electrode, this forms a complete measuring circuit.

Fig. 6: Metal electrode

2.2.3 Reference electrodes

The reference electrode has the job of supplying a constant potential during potentiometric measurements, against which the potential of the metal electrode is measured. It consists of a glass or plastic tube that is filled with the reference electrolyte (3-molar potassium chloride solution in liquid or gel form) and equipped with a filler system. A membrane (ceramic, glass silk or PTFE) in the wall of the tube sets up the conducting path between the electrolyte and the measuring medium.

Fig. 7: Bezugselektrode

2.2.4 Redox combination electrode

A redox combination electrode contains both metal and reference electrodes in a single tube, and hence represents a complete measuring circuit.

Fig. 8: **Redox combination electrode**

2.2.5 Screened measuring cable

In order to maintain perfect transmission of the measurement signal, only screened coaxial cables are used for the measurement. They establish the electrical connection between the sensor and the transmitter.

Fig. 9: **Measuring cable**

2.2.6 Transmitter/Controller

Control
The transmitter has the job of preparing the signal of the redox electrode. In the simplest case, this is implemented with a 2-wire transmitter, where the electrode signal is converted into a 4 — 20mA signal and can then be relayed to a subsequent PLC for indication and control of the redox value. If an on-site indication is required, suitable panel mounting instruments are used. Surface mounting housings or special instruments with cases for site mounting can also be supplied. Most of the instruments available nowadays are microprocessor instruments that can be individually matched to the particular measurement loop. The measurement range is in the region of ±1200mV. Limit controllers are used for the control of a redox reaction. In most cases, a precise dosing of the chemicals used is not necessary. An overshoot of the redox value is not as problematical as with pH measurement, because, for example, an excess of decontaminating agent is generally used in decontamination reactions.

Normally, it is not necessary to use an impedance converter. However, an impedance converter can be used, particularly with long cables, in order to stabilize the measurement signal.

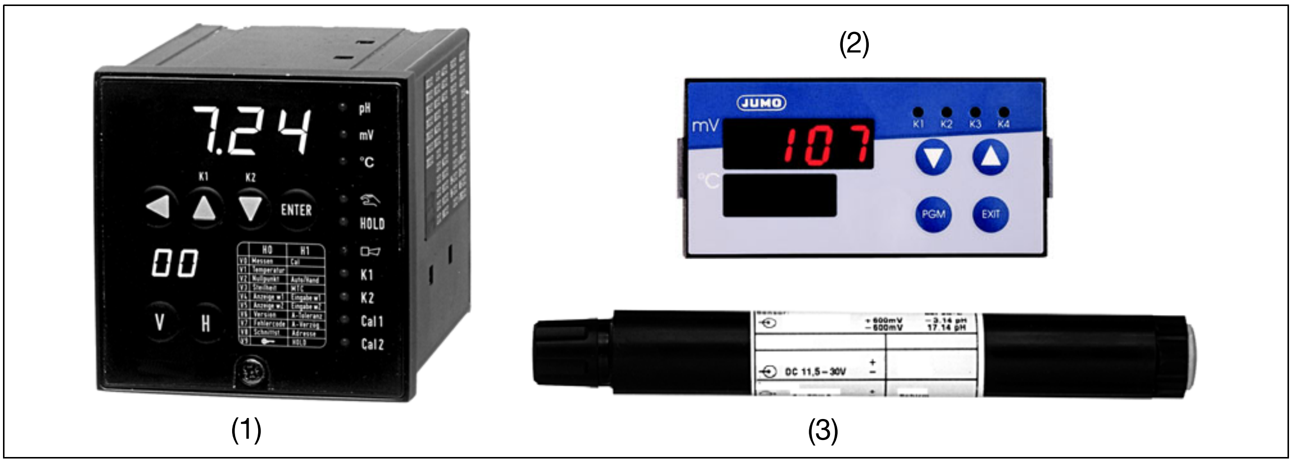

Fig. 10: **(1) JUMO redox transmitter, Type 262510,**
(2) JUMO redox transmitter, Type dTRANS Rd01,
(3) JUMO 2-wire transmitter for redox

2.3 Commissioning a measurement channel

Care should also be taken to choose the correct electrode, according to the particular application. For strongly oxidizing media such as chromate reduction or cyanide decontamination, for instance, gold electrodes and combination electrodes with gold tips are suitable. Electrodes with platinum as the electrode metal are used for applications in swimming pools or with nitrite oxidation. The electrolyte and the membrane constitute another important criterion. For media temperatures up to 90°C, gel-filled electrodes can be used. Liquid KCl electrodes are recommended for use at temperatures higher than this. If the measuring medium is affected by heavy contamination, electrodes with dirt-repellent PTFE membranes are used. Where there is a risk of blockage due to precipitations or similar, the electrode can be equipped with a ceramic membrane.

Once the suitable electrode has been chosen, care should be taken during installation of the electrode to ensure that the metal part and the membrane are well immersed in the measuring solution, as otherwise the measurement will not function. With industrial applications (e. g. decontamination reactions), the use of a cleaning spray head is recommended to remove any accumulated contamination.

A calibration at the beginning of the measurement, as is normal with pH measurements, is not necessary. The electrodes are ready for immediate use. If the measured value only adjusts slowly, the cause of this can be a passivation of the surface of the metal. This can be remedied by suitable preparatory treatment of the surface of the electrodes.

Advice on this is given, for instance, in DIN 38 404, Part 6:

- degrease and clean with cleaning agent
- rinse with water
- treat with hydrochloric acid
- rinse with water

Further preparatory treatment is arranged to suit the magnitude of the expected redox voltage and the metal electrode used. When gold electrodes are used, no further preparatory treatment is required.

Platinum electrodes require additional treatment as follows:

- for measurement in an oxidizing medium
  rinse with an ammonia solution, $w(NH_3) = 25\,\%$
- for measurement in a reducing medium:
  rinse with iron(II) sulfate or iron(III) citrate solution,
  rinse with water in both cases

If this advice is heeded, there is now nothing to stop a correct redox measurement.

2.4 Causes of error

2.4.1 Reference electrode error

Changes of slope do not occur with redox electrodes. If false measurements do crop up, this is most often caused by a dirty (contaminated) surface of the electrode. This can be easily remedied in this case by cleaning the electrode (distilled water, rub over the electrode metal with a fine scouring powder that does not contain a chlorine- or acid-based bleaching agent).

The response behavior of gold and platinum electrode metals depends on their previous history and preparatory treatment. If there is a change from a medium with oxidizing properties to a medium with reducing properties, or vice versa, a longer settling time before a constant potential is reached may possibly have to be tolerated. This also applies, for instance, to the JUMO 468mV buffer solution.

An oxidizing medium can lead to a change of the surface (formation of an oxide layer) even with gold and platinum, supposedly inert metals. Platinum can form hydrides in strongly reducing solutions. The surface of redox electrodes only adjusts gradually to a new medium. In order to reduce this time, it is possible to use the preparatory treatments for oxidizing and reducing media recommended in DIN 38 404, Part 6 (see Section 2.3 *„Commissioning a measurement channel“*).

It is not possible to give universally applicable advice here, as the preparatory treatment depends on the measuring medium present. If necessary, a suitable preparatory treatment must be determined by means of the user’s own tests. The preparatory treatment that has shown itself to be the best possible, should then always be carried out in the same way.

The surface phenomena described above can lead to a situation where the reproducibility of the redox potentials is poor. Deviations of ±25mV are acceptable. Well-reproducible results are only obtained in heavily weighted redox systems with good reversibility. The term “weighting” with redox systems is analogous to “buffering” with acid/base systems. With maximally weighted systems $c_{red} = c_{ox}$ applies, and this also includes, for instance, redox buffers.

2.4.2 Calibration

Where there is a shift of the measured value, a single point calibration can be carried out. With the single point calibration, the electrode zero point is determined afresh using a buffer solution (e.g. Jumo 468 mV buffer solution). The adjustment to the new zero point takes place automatically in the transmitter, after the start of the calibration process.

2.4.3 Critical influences on the reference system

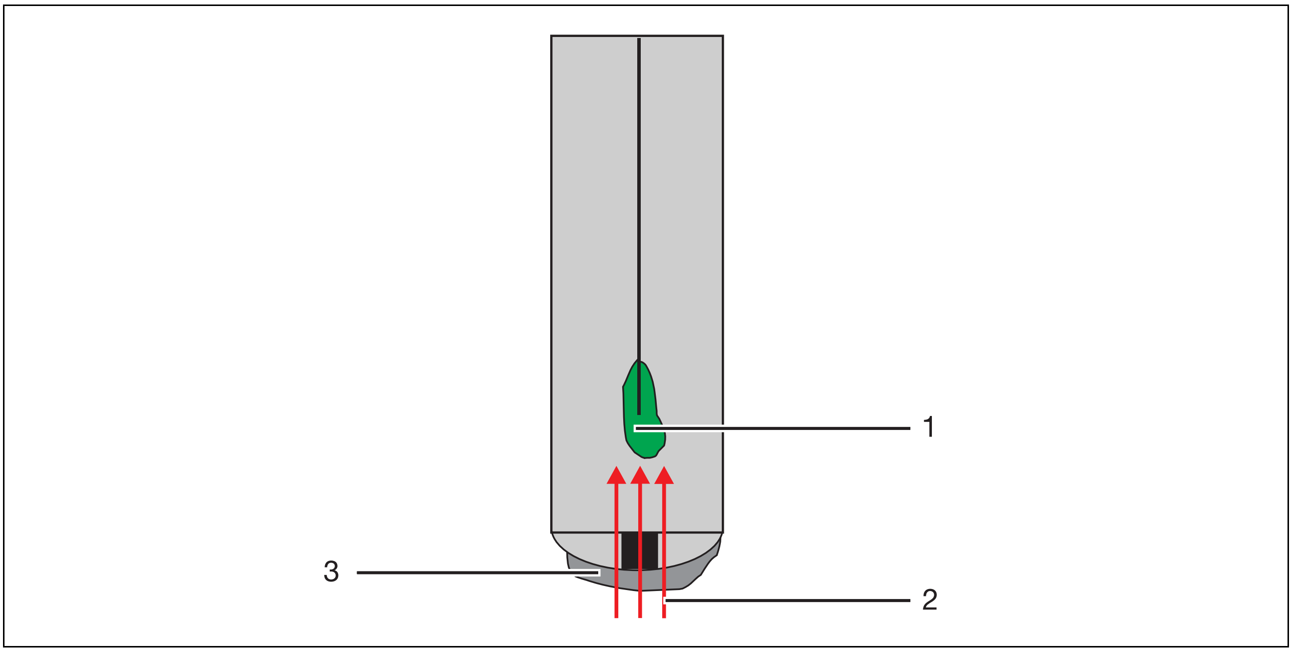

Fig. 11: **Critical influences on the reference system**

Malfunction on the reference system, caused by:

- moisture in the cable
- faulty contacts
- semiconducting layer not removed
- short-circuit in connector

1 **Poisoned reference sstem, caused by:**
2
- electrode poisons (e. g. sulfides, cyanides)
- heavy metals

3 **Blocked membrane, caused by:**
- formation of deposits (e. g. lime)
- blockage through fats and proteins
- organic substances

The following typical applications will be examined in a little more detail below:

- cyanide decontamination
- chromate reduction
- nitrite oxidation
- monitoring of swimming pool water

The legal aspects are dealt with in Section 4 *„Legal aspects“*.

3.1 Cyanide decontamination with sodium bisulfite

3.1.1 Removal of cyanides

An example of the industrial application of a redox measurement is the removal of cyanides from effluents. Cyanide-containing effluent is cleaned in continuous treatment plants. These consist of the following components:

- reactor (container)
- mixer (stirrer)
- measurement and control installation (recording of various parameters)
- dosing section (valves and pumps)
- chemical store (storage bunker) and
- concentrate store (intermediate storage)

Cyanides in effluent results from:

- galvanizing plants
- heat-treatment plants
- printed circuit board manufacture and
- mechanical workshops

Cyanides and the stem compound hydrogen cyanide (HCN) are highly toxic substances. The reason for the toxicity is that both substances form very stable complexes with heavy-metal-containing ferments (enzymes) of the human organism, and hence block the normal operation of the ferments. For this reason, the removal of cyanides from effluent is an absolute necessity. The aqueous solution of hydrogen cyanide is generally known under the name prussic acid.

The decontamination of the effluent occurs in partial reactions that are described below:

- oxidation of the cyanide to cyanogen chloride
- hydrolysis of the cyanogen chloride to cyanate
- oxidation of the cyanate to carbonic acid and nitrogen

3.1.2 Decontamination

As already explained at the beginning, the decontamination is carried out in continuous treatment plants. Here, the effluent is first of all fed into the reactor. For the decontamination, a pH value of ≥ pH 10 is required and this is set here. A pH value in the acidic range would otherwise lead to the formation of hydrogen cyanide. By the addition of sodium hypochlorite solution (NaOCl), the cyanide is converted to cyanogen chloride (ClCN) (reaction 1). Cyanogen chloride is a similarly toxic gas with a high dissolvability in water (25 liter ClCN gas/liter water).

Conversion to the non-toxic cyanate (CNO^-) takes place in the next stage of the reaction (reaction 2). This reaction only occurs at high pH values. Because the first partial reaction is not pH dependent, the high pH value is already set at the beginning of the decontamination. Generally, the complete reaction is conducted with a 20% excess of NaOCl.

Under the conditions described at the beginning, the decontamination is completed within a maximum of 20 minutes. In order to ensure that all the cyanide is converted, the sanctioning authorities insist on durations between 40 and 60 minutes.

In the final partial reaction, the cyanide obtained above is oxidized to carbonic acid and nitrogen at pH values around 7-8. This reaction runs its course within 30 minutes (reaction 3).

Once the decontamination is completed, additional stages follow, i.e. neutralization, sedimentation, filter press and final inspection, before the purified effluent is fed back into the drainage system.

Reaction 1

$$2\ CN^- + 2\ OCl^- + 2\ H_2O \Rightarrow \underset{\text{canogen chloride}}{2\ ClCN} + 4\ OH^- \qquad (10)$$

Reaction 2

$$2\ ClCN + 4\ OH^- \Rightarrow \underset{\text{cyanate}}{2\ CNO^-} + 2\ Cl^- + 2\ H_2O \qquad (11)$$

Reaction 3

$$2\ CNO^- + 3\ OCl^- + H_2O \Rightarrow N_2 + 2\ CO_3^{2-} + 3\ Cl^- + 2\ H^+ \qquad (12)$$

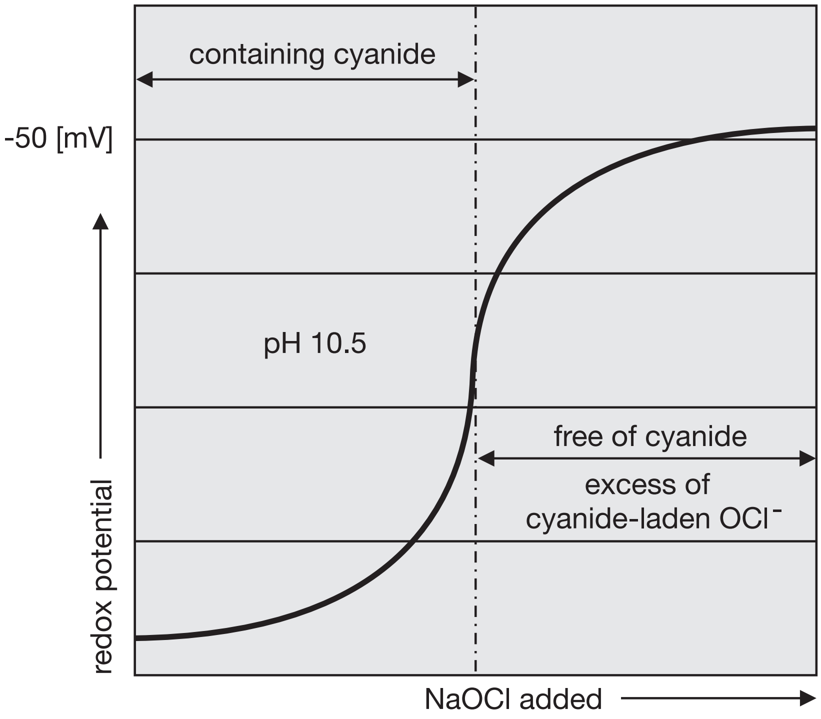

Fig. 12: **Course of the cyanide decontamination reaction**

3.2 Chromate reduction

With chromate reduction, the toxic Cr^{6+} is converted into Cr^{3+}. umgesetzt. Chromat fällt an bei:

- electrolysis (burnished and hardened chromium)
- pickling and etching baths
- production of aluminium
- chromating baths

3.2.1 Chromat-Entgiftung

Chromate is removed from the effluent in the acidic range. Depending on the concentration of H^+ ions, chromate (CrO_4^{2-}) is formed in the alkaline range; dichromate ($Cr_2O_7^{2-}$) is formed in the acidic range.

The pH value and the redox voltage are measured in the reactor with a pH combination electrode and a gold redox combination electrode respectively. If the pH value is above 2.5, it is adjusted to 2.5 using either dilute sulfuric acid or hydrochloric acid. A constant pH value is required for the quantitative changes of the reaction. The conversion of chromium(VI) into chromium(III) takes place spontaneously, and manifests itself by a step change in potential of several 100mV in a negative direction. Care should be taken during the chromate decontamination to ensure that no other acidic effluents are fed into the plant. These can form additional redox systems as a result of contained metals, leading ultimately to the step change in potential being only distinguishable as a drift. This can be remedied here by the addition of a strong reducing agent (e.g. sodium dithionite). This will neutralize the other redox systems. Even small quantities are sufficient in this case.

The conversion of the toxic chromium(VI) compounds into the non-toxic chromium(III) compounds takes place in accordance with the following reaction equation:

$$\underset{\text{chromate}}{CrO_4^{2-}} + 4\ H_2O + 3\ e^- \Rightarrow Cr(OH)_3 + 5\ OH^- \quad \text{(alkaline} \tag{13}$$

$$\underset{\text{dichromate}}{Cr_2O_7^{2-}} + 14\ H^+ + 6\ e^- \Rightarrow 2\ Cr^{3+} + 7\ H_2O \quad \text{(acidic)} \tag{14}$$

Sulfur dioxide ($SO_{2)}$, sulfite or iron(III) compounds can be used as possible decontaminating agents. If sulfur dioxide (SO_2) is used, the plant must be covered and equipped with an extraction system.

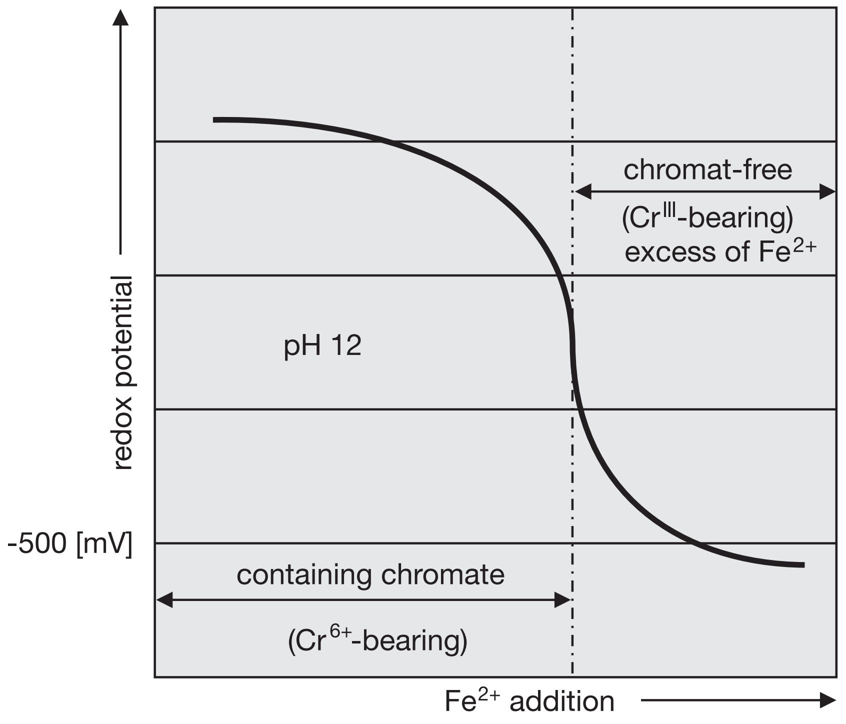

Fig. 13: **Course of the cromate decontamination reaction**

As there would normally be a requirement to remove chromium (a heavy metal) from the effluent, the Cr^{3+}, which is soluble in the acidic pH range, is precipitated out as $Cr(OH)_3$ by neutralization.

3.3 Nitrite oxidation

Nitrites are the salts of nitrous acid HNO_2. Nitrites also occur as intermediate products during nitrification and denitrification These intermediate products must be removed from the effluent by suitable treatment measures. In the course of this, the nitrite is oxidized to nitrate. The most common variant of nitrite oxidation processes is the treatment of the effluent with sodium hypochlorite solution. The reaction takes place quickest in a weak acid medium with pH values of 3-4. The standard potential of the reaction is around +0.94V. Indication of the reaction is monitored by a redox measurement (step change in potential).

3.3.1 Reaction equation

$$\underset{\text{nitrous acid}}{HNO_2} + \underset{\text{hypochlorite}}{HClO} \rightarrow \underset{\text{nitrate}}{NO_3^-} + 2H^+ + Cl^- \tag{15}$$

However, because of the presence of organic compounds in the effluent, there is a danger that chlorinated hydrocarbons may be formed here. This can be avoided by the use of hydrogen peroxide instead of sodium hypochlorite. Here again, nitrate is obtained as the end product of the conversion.

The course of the reaction is as follows:

$$\underset{\text{nitrous acid}}{HNO_2} + \underset{\text{hydrogen peroxide}}{H_2O_2} \rightarrow \underset{\text{nitrate}}{NO_3^-} + H^+ + H_2O \tag{16}$$

To prevent the formation of nitrous gases in the weak acid medium, it is recommended that the right quantity of hydrogen peroxide is added first, and then the correct pH value adjusted.

In this case too, because oxides of nitrogen are also formed during the oxidation, the plant must be covered and equipped with an extraction system.

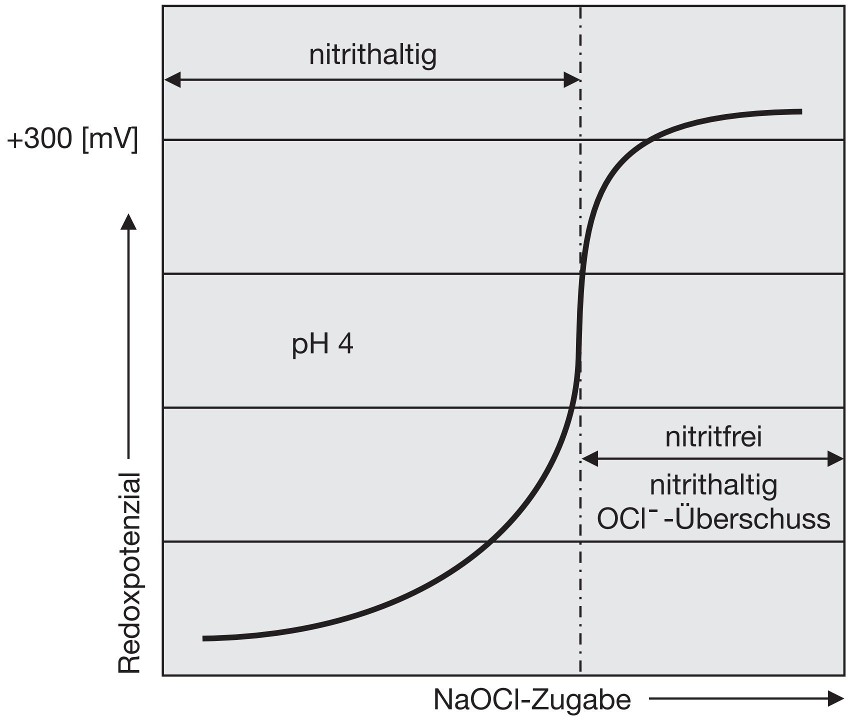

Fig. 14: **Course of the nitrite decontamination reaction**

3.4 Monitoring of pool water in swimming baths

In the German federal law concerning epidemics, § 11 prescribes that swimming pool or bathing pool water must be provided in such a way that there is no risk of damage to the human organism.

For this reason, a special treatment must be provided for swimming pool water. The pH value and the redox voltage play an important role here. The pH value is important for the flocculation, filtration and disinfection of the water. For instance, too high a pH value reduces the disinfecting effect of hypochlorite.

The redox voltage can be used to make a statement about the bactericidal effect of the swimming pool water. In an ideal case, the redox voltage should be in the region of around 700 mV. If the actual value falls below or exceeds this figure by an appreciable amount, appropriate action with the chlorine dosing must be taken.

DIN 34 408, Part 6 recommends a flow-through fitting for redox measurement in water, in order to eliminate the disturbing influence of the atmospheric oxygen.

3.5 Constructing an electrolyte bridge

3.5.1 General

pH and redox measurements are subject to a number of disturbing influences. If the liquid being analyzed disturbs, contaminates or corrodes the measuring electrodes, the only remedy is to use specially selected electrodes, condition the sample or construct an electrolyte bridge.

Such disturbing influences may be:

- Oiling up - blockage of the diaphragm function
- Poisoning - chemical reaction of the conductive system with the sample liquid
- Pressure fluctuations - ingress of the sample liquid into the electrode
- Blocking up - blockage of the diaphragm function

The reference electrode is removed from the sample liquid and installed in a safe place with the help of the electrolyte bridge.

The following describes the construction of an electrolyte bridge when applied in the flow or in containers.

3.5.2 Example of construction in the flow

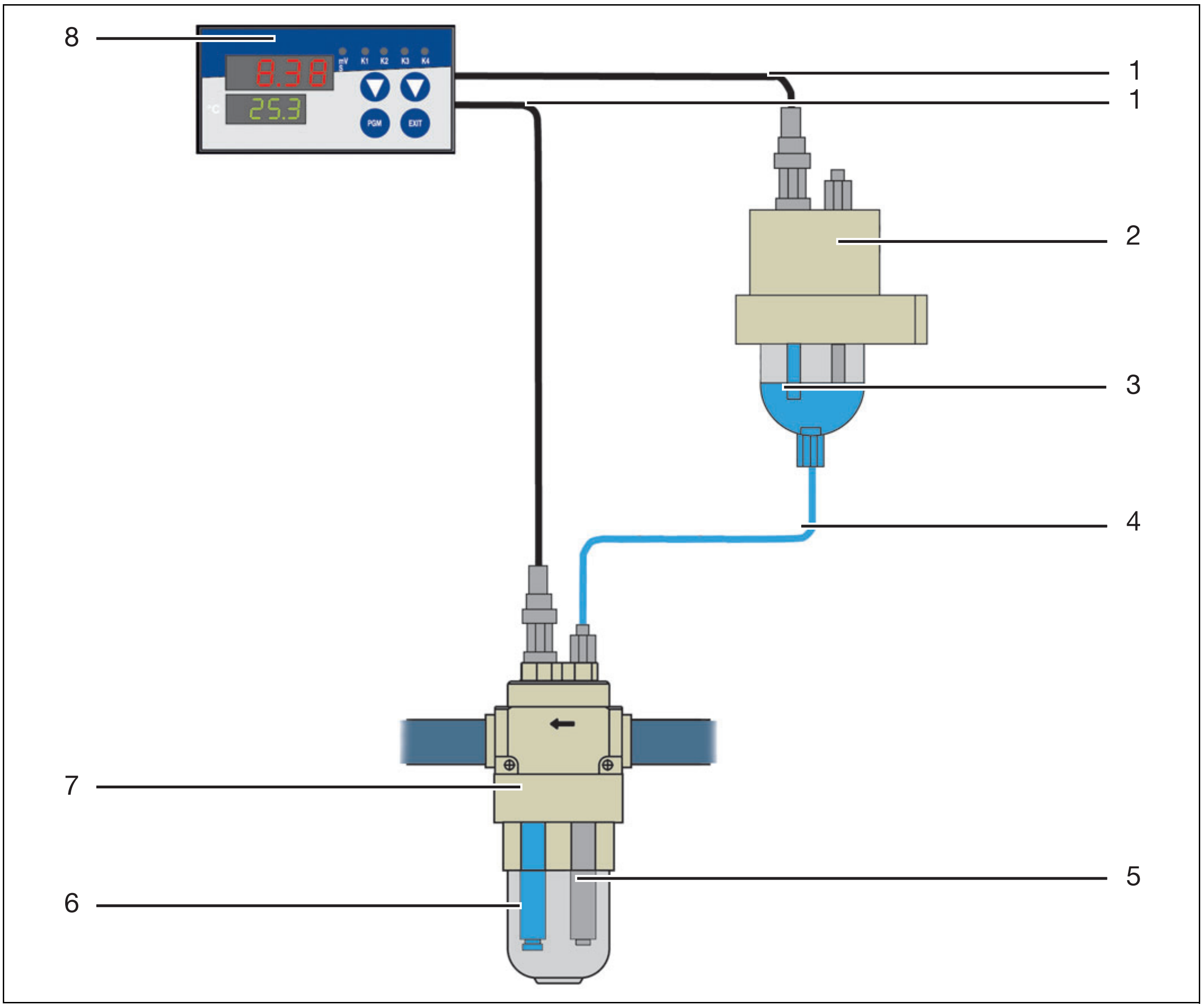

Fig. 15: **Example of construction in the flow**

1 Electrode connection cable,
e. g. 2992-2(10)-0

2 KCl reservoir,
e. g. Sales No. 20/00060254

3 Reference electrode,
e. g. 201080/11-89-04-07-22-120

4 Hose connection
to the KCl reservoir

5 Diaphragm tube,
e. g. 201080/15-87-04-22-120

6 pH glass electrode,
e. g. 201080/10-89-10-22-120

7 Flow-through fitting,
e. g. 202810/03-104-87-80/000

8 JUMO dTRANS pH 01 pH transmitter,
e. g. 202530/10-888,000-23-00/000

3.5.3 Example of construction in the container

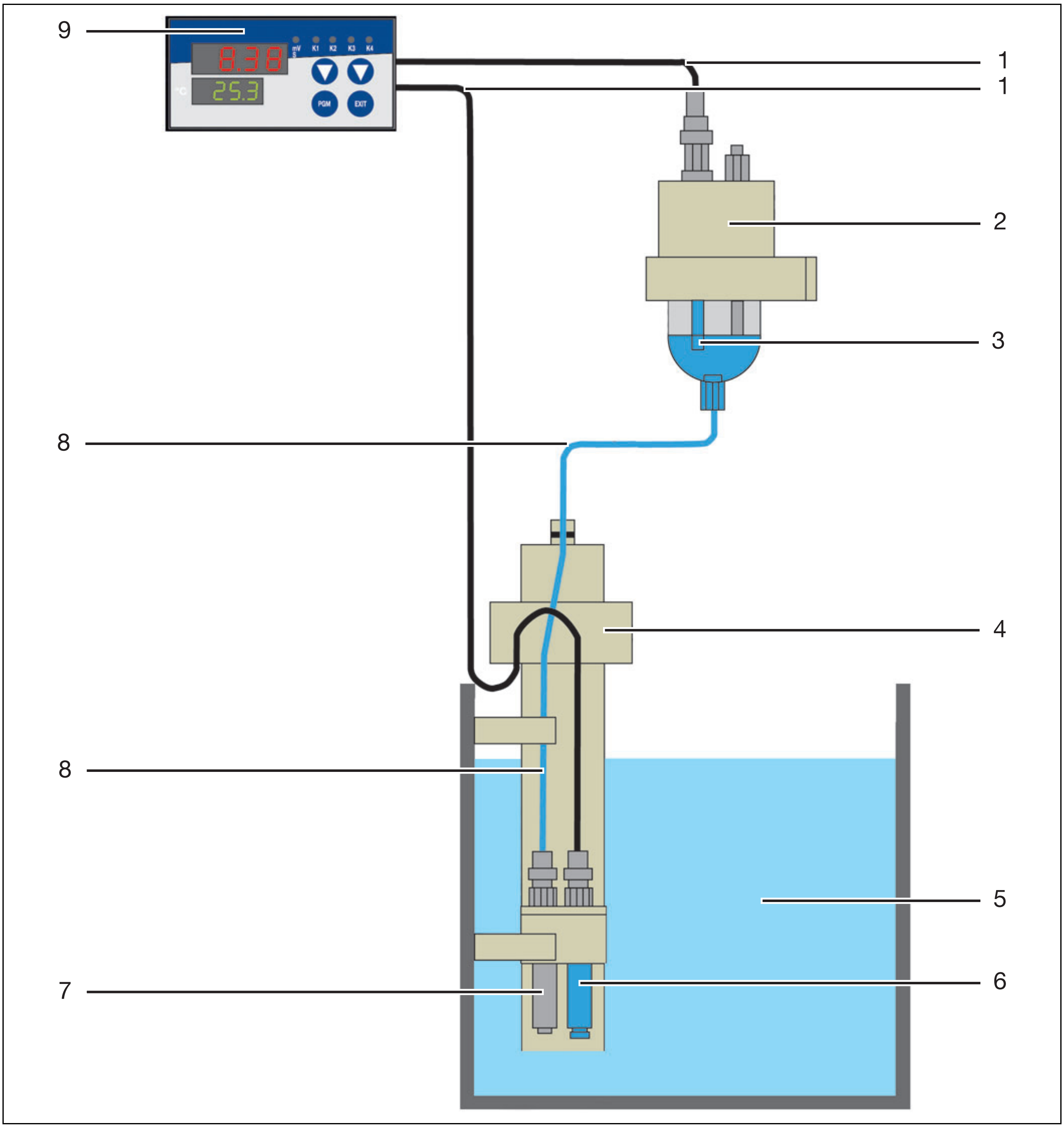

Fig. 16: **Example of construction in the container**

1 Electrode connection cable,
e. g. 2992-2(10)-0
2 KCl reservoir,
e. g. Sales No. 20/00060254
3 Reference electrode,
e. g. 201080/11-89-04-07-22-120
4 Immersion fitting,
e. g. 202820/63-0500-87/000
5 Tank/container
6 pH glass electrode,
e. g. 201080/10-89-10-22-120
7 Diaphragm tube,
e. g. 201080/15-87-04-22-120
8 Hose connection to the KCl reservoir
or to the diaphragm tube
9 JUMO dTRANS pH 01 pH transmitter,
e. g. 202530/10-888,000-23-00/000

Effluent treatment plants require official approval. This results in a whole list of duties arising for the operator of such a plant. Among others, these include:

- the local authority's discharge licence must be available
- where new works or modification to sections of the plant are carried out, a new application for a discharge licence must be submitted.
- prescribed limit values must be observed
- if demanded, effluent is to be tested and monitored in line with the requirements.

The legal principles are prescribed in appropriate EU directives, German federal laws, state laws and municipal regulations. In the short to medium term, the EU directives quoted in the overview will be translated into national law. From the following tables, it will be clear that the planning, construction and commissioning of effluent treatment plants is no easy task, and that a multitude of clauses and regulations must be observed.

4.1 EU directives

- 98/83/EC
  Drinking water directive
- 91/271/EEC
  Urban waste water treatment
- 87/217/EEC
  Prevention and reduction of environmental pollution from asbestos
- 86/280/EEC
  Limit values and quality objectives for discharge of certain dangerous substances
- 84/491/EEC
  Limit values and quality objectives for discharge of hexachlorocyclohexane
- 84/156/EEC
  Limit values and quality objectives for mercury discharge
  other than from chlor-alkali electrolysis
- 83/513/EEC
  Limit values and quality objectives for cadmium discharge
- 82/176/EEC
  Limit values and quality objectives for mercury discharge from chlor-alkali electrolysis
- 80/778/EEC
  Quality of water intended for human consumption
- 80/68/EEC
  Protection of ground water against pollution
- 79/869/EEC
  Methods of measurement, frequency of sampling and analysis of surface water intended
  for the abstraction of drinking water
- 76/464/EEC
  Pollution caused by discharge of certain dangerous substances
- 76/160/EEC
  Bathing water quality
- 75/440/EEC
  Quality required of surface water intended for the abstraction of drinking water

4.2 Overview of German federal law

Water usage law WHL

- Basic principles
- Permission and approval requirements for water usage
- Definition of water usage
- Permission: revocable authority
- Requirements for the discharge of effluent („effluent regulations“)
- Approval: right to use a body of water
- Approval procedure
- Duties and plans for effluent removal
- Construction and operation of effluent plants
- Acceptance of effluent treatment plants
- Authorization of pipework systems for conveyance of substances hazardous to water
- Systems for dealing with substances hazardous to water
- Building permission for plants
- Operator duties: specialized operations, monitoring
- Specialized operations: quality mark of a monitoring or quality association recognized in building regulations
- Monitoring by authorities
- Appointment of operator’s representative for water protection with more than 750 m³ effluent per day
- Duties of the operator’s representative: monitoring, measurement, advice, instruction and making reports
- User’s duties: written appointment, reporting to the authorities

Water pollution control levy law

- Calculation of the levy for discharge of effluent into a body of water

Effluent regulations

- Gradually replacing the current effluent regulations and the outline specification for effluent management

Management specification

- Concerns the minimum requirements for discharge of effluent, particularly the outline specification for effluent management (insofar as it is not yet transferred into the effluent regulations)

Ground water regulations

Drinking water realugations

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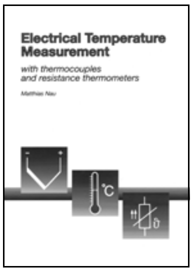

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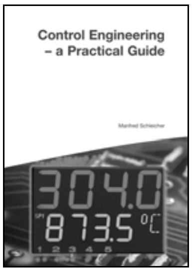

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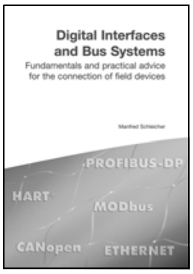

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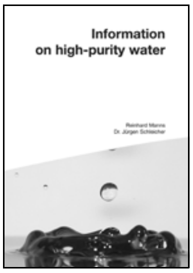

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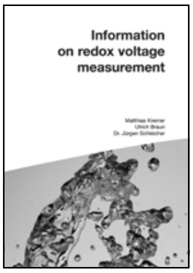

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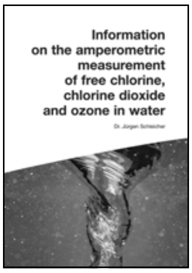

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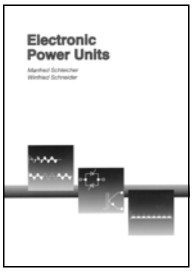

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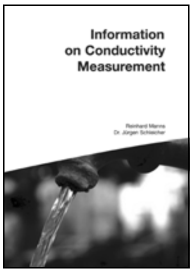

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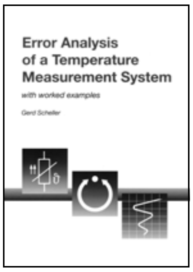

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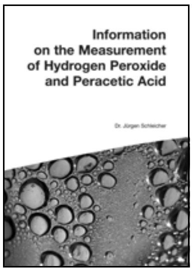

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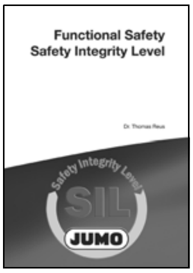

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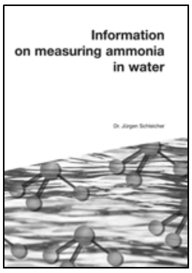

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