

TECHNICAL REPORT

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**The rH index in aqueous
and aqueous-organic media**

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AQUEOUS-ORGANIC MEDIA**
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IEC 62432, which is a technical report, has been prepared by subcommittee 65D: Analyzing equipment, of IEC technical committee 65: Industrial-process measurement and control.

The text of this technical report is based on the following documents:

Enquiry draft	Report on voting
65D/120/DTR	65D/123/RVC

Full information on the voting for the approval of this technical report can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "<http://webstore.iec.ch>" in the data related to the specific publication. At this date, the publication will be

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- replaced by a revised edition, or
- amended.

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INTRODUCTION

The fundamental rationale for the rH index, extended to cover the pure aqueous and the aqueous-organic media, has been recently described critically [1]¹, but for the user's convenience, the essentials will be recalled in the present Technical Report together with the application domains, the recommended procedures and operational details.

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¹ Numbers in square brackets refer to the bibliography.

THE rH INDEX IN AQUEOUS AND AQUEOUS-ORGANIC MEDIA

1 Scope

This Technical Report concerns analyzers, sensor units and electronic units used for the determinations of the rH index in aqueous and aqueous organic media.

This Technical Report identifies the terminology, definitions, theory and methodology used for the determination of rH values or redox systems in aqueous solvent or aqueous-organic solvent mixtures.

2 General principles

2.1 Redox couples, redox equilibria, redox potentials, redox systems

An oxidation/reduction couple ("redox" couple) O|R, present in water or in an aqueous-organic solvent mixture involves the concurrence of an oxidant species O (ionic or uncharged) and a reductant species R (ionic or uncharged) of the same chemical element, thereby establishing an oxidation/reduction equilibrium (redox equilibrium) $O + ne = R$, and an electrochemical oxidation/reduction potential (redox potential) $E_{O|R}$ which is transmitted to the meter by an inert metal electrode (usually platinum or gold). This metal participates in the specific charge transfer which is going on throughout the solution and is called upon only to act as a donor or acceptor of electrons. When both the O and R species are at unit activity (standard state) the redox potential $E_{O|R}$ becomes the standard redox potential, symbolized as $E_{O|R}^{\circ}$.

In the environmental, hydrological, biomedical, winery, dairy-farming, and corrosion domains of interest for rH measurements, only seldom is a single O|R couple present alone in the solvent medium. Instead, an undefined number of redox couples O|R, O'|R', O''|R'',...Oⁿ|Rⁿ overlap, thus determining a mixed redox potential of very complex (not to say impossible) interpretation: therefore it is better to speak of a "redox system", but this latter term is also legitimately applicable to a single redox couple.

NOTE Some examples of familiar redox couples with related reaction equilibria and redox potential expressions, are given in Table 1.

Table 1 - Examples of familiar redox couples with related reaction equilibria and redox potential expressions

Redox couple	Redox equilibrium	Redox potential
ferric ferrous	$Fe^{3+} + e = Fe^{2+}$	$E_{Fe^{3+} Fe^{2+}} = E_{Fe^{3+} Fe^{2+}}^{\circ} + k \log(a_{Fe^{3+}}/a_{Fe^{2+}})$
H ⁺ H ₂ (hydrogen electrode)	$2H^{+} + 2e = H_2$	$E_{H^{+} H_2} = E_{H^{+} H_2}^{\circ} + k \log a_{H^{+}} - (k/2)\log p_{H_2}$
Cl ₂ Cl ⁻ (chlorine electrode)	$Cl_2 + 2e = 2Cl^{-}$	$E_{Cl_2 Cl^{-}} = E_{Cl_2 Cl^{-}}^{\circ} - k \log a_{Cl^{-}} + (k/2)\log p_{Cl_2}$
O ₂ H ₂ O (oxygen electrode)	$O_2 + 4e + 4H^{+} = 2 H_2O$	$E_{O_2 H_2O} = E_{O_2 H_2O}^{\circ} + k \log a_{H^{+}} + (k/4)\log p_{O_2} - (k/2)\log a_{H_2O}$
MnO ₄ ⁻ Mn ²⁺ (permanganate electrode)	$MnO_4^{-} + 5e + 8H^{+} = Mn^{2+} + 4H_2O$	$E_{MnO_4 Mn^{2+}} = E_{MnO_4 Mn^{2+}}^{\circ} + (k/5)\log(a_{MnO_4 Mn^{2+}}/a_{Mn^{2+}}) + (8k/5)\log a_{H^{+}} - (4k/5)\log a_{H_2O}$

Symbols: e = the electron; k = Nernstian coefficient = 2,303RT/F ; a = activity; p = pressure.

2.2 The rH value

The notional definition of the rH index [2,3] for a given redox system in a given (aqueous or aqueous-organic) medium is

$$rH = -\log p_{H_2} \quad (1)$$

where p_{H_2} is that pressure of hydrogen gas that would equalize the potential $E_{H+|H_2}$ of the hydrogen gas electrode to the redox potential $E_{O|R}$ of the system being studied (thus zeroing the pd of the cell resulting from the combination of these two electrodes). **rH is an index of the reducing power of the redox system under consideration.** The Nernstian expression for $E_{H+|H_2}$ is (with $k = 2,303RT/F$):

$$E_{H+|H_2} = E_{H+|H_2} - k \text{pH} + (k/2) rH \quad (2)$$

where $E_{H+|H_2}$ is the standard electrode potential (which varies with the solvent but it is conventionally put equal to zero at any temperature in pure aqueous medium [4, 5]). If the hydrogen gas electrode works at $p_{H_2} = 1$ bar (i.e. under standard state conditions), then $rH = 0$ at any pH of the solution (see Figure 1, which describes the pertinent Pourbaix's E_{Redox} vs. pH diagram), and this is **the nominal zero of the rH-metric scale** to which corresponds **the nominal maximum reducing power** of a redox system

One redox system of paramount importance is the **equimolal (quinone[Q] + hydroquinone[H₂Q]) system**, commonly called the "quinhydrone", of symbol QHY, whose electrode potential is expressed by

$$E_{\text{QHY}} = E_{\text{QHY}} - k \text{pH} \quad (3)$$

On consideration of equations (2) and (3), the potential difference E_4 of the cell (4) below, where the quinhydrone electrode is combined with the hydrogen electrode and the two solutions are at equal activity of the H^+ ion:



is clearly independent of pH. (In common practice, the two electrode compartments are kept separated by a porous glass frit or a closed stopcock, as indicated by the | symbol, to avoid the mutual diffusion of hydrogen gas and quinhydrone which would produce an irreversible chemical reaction and formation of a useless mixed electrode potential). Therefore, equating $E_{H+|H_2}$ to E_{QHY} in accord with the equation (1), i.e. putting $E_4 = 0$, gives the related rH_{QHY} value:

$$E_4 = E_{\text{QHY}} - E_{H+|H_2} = E_{\text{QHY}} - E_{H+|H_2} - (k/2) rH_{\text{QHY}} = 0 \quad (5)$$

from which

$$rH_{\text{QHY}} = 2 (E_{\text{QHY}} - E_{H+|H_2}) / k = rH_S \quad (6)$$

As equation (6) shows, since the difference ($E_{\text{QHY}} - E_{H+|H_2}$) is a well defined and accurately known quantity which is a function of temperature but is **invariant upon passing from pure water medium to most water-rich aqueous-organic media** [1], the **quinhydrone redox system constitutes the key standard rH_S** for reference in rH measurements, according to the operational equation (27) described later on. In the context of this invariancy, at 298,15 K, ($E_{\text{QHY}} - E_{H+|H_2}$) = 0,699 75 V [6] and, therefore:

$$(rH)_{\text{QHY}} = rH_S = 2 \times 0,699 75 / 0,059 159 7 = 23,66 \quad (7)$$

For this reason, the cell (4) can be considered the archetype of the rH-metric **calibration cell**. Another important redox system for which it is important to know the rH value is that of the oxygen gas electrode, of reaction $O_2 + 4H^+ + 4e = 2H_2O$. Thus, its redox potential $E_{O_2|H_2O}$ will, assuming unit H_2O activity, be given by

$$E_{O_2|H_2O} = E_{O_2|H_2O} - k \text{ pH} - (k/4) \text{ rO} \quad (8)$$

where we use the further definition

$$\text{rO} = -\log p_{O_2} \quad (9)$$

The rO index, which is a quantity complementary to rH, is an **index of the oxidizing power of the given redox system** in the same medium (analogously, the pOH index of alkalinity is a complementary quantity to the pH index of acidity: see the comparative Table 2). In this context, p_{O_2} is that pressure of oxygen gas that would equalize the potential $E_{O_2|H_2O}$ of the oxygen gas electrode to the redox potential of the system being studied.

The related cell (10)



at $p_{O_2} = 1$ bar (which means $\text{rO} = 0$, at any pH of the solution, and **maximum oxidizing power**, see Table 2 and the pertinent Pourbaix's diagram in Figure 1 has a pd E_{10} given by

$$E_{10} = E_{O_2|H_2O} - E_{H + |H_2} = E^\circ_{O_2|H_2O} - E^\circ_{H + |H_2} - (k/2) \text{ rH} \quad (11)$$

Therefore, putting $E_{10} = 0$, in water (where $E_{O_2|H_2O} - E_{H + |H_2} = 1,229$ V at 298,15 K), one obtains the $(\text{rH})_{O_2|H_2O}$ value (i.e. the **measurand unknown rH_x value**) of the specific $O_2|H_2O$ redox system:

$$(\text{rH})_{O_2|H_2O} = \text{rH}_x = 2 (E_{O_2|H_2O} - E_{H + |H_2}) / k = 2 \times 1,229 / 0,059 159 7 = 41,6 \quad (12)$$

(at any pH of the solution)

Now, the values **rH = 0** and **rH = 41,6** mark the **rated (nominal) limits of the rH scale** (analogously, pH = 0 and pH = 14 mark the limits of the pH scale in water). The cell (10) is the archetype of an **rH-metric measuring cell**.

To establish the general operational equation for the rH determination, which requires measuring one cell pd (E_{13}) on the selected standard rH_S (QHY) and one (E_{14}) on the sample solution of unknown rH_X , a few steps are still necessary. The generalized pair of the *ad hoc* cells would be:



Putting E_{13} and E_{14} to zero, one gets, respectively:

$$E_{13} = E_{QHY} - E_{H + |H_2} = E_{QHY} - (k/2) rH_S + k \text{ pH}_S = 0, \quad (15)$$

from which

$$rH_S = 2 E_{QHY} / k + 2 \text{ pH}_S \quad (16)$$

and

$$E_{14} = E_{\text{SAMPLE}} - E_{\text{H} + \text{H}_2} = E_{\text{SAMPLE}} - (k/2) r\text{H}_X + k \text{pH}_X = 0, \quad (17)$$

from which

$$r\text{H}_X = 2 E_{\text{SAMPLE}} / k + 2 \text{pH}_X \quad (18)$$

Now, to avoid the above mentioned inconveniences caused by the cumbersome use of the H^+ -reversible hydrogen gas electrodes in cells (13) and (14), these electrodes are replaced by two H^+ -selective glass electrodes, which are totally insensitive to the effects of a diffusion of any redox system on their surfaces. Therefore, no electrode compartment separation by a porous glass frit is now necessary. The standard potential of the glass electrode at a given temperature obviously differs from that of the hydrogen electrode by a constant, which can be determined, if necessary, by one pd E_{19} measurement on the cell (19):

$$\text{Pt}|\text{H}_2 (p_{\text{H}_2} = 1 \text{ bar}) | \text{H}^+ \text{ solution} | \text{Glass electrode} \quad (19)$$

$$E_{19} = E_{\text{GLASS}} - E_{\text{H} + \text{H}_2} \quad (20)$$

Thus, the cells (13) and (14) take their respective final operational configurations (17) and (18):

$$\text{Pt}|\text{Glass electrode}|\text{QHY Standard at } r\text{H}_S|\text{Pt (for calibration)} \quad (21)$$

$$\text{Pt}|\text{Glass electrode}|\text{Sample at } r\text{H}_X|\text{Pt (for measure)} \quad (22)$$

whose pd's are:

$$E_S = E_{\text{QHY}} - E_{\text{GLASS}} + k \text{pH}_S \quad (23)$$

$$E_X = E_{\text{SAMPLE}} - E_{\text{GLASS}} + k \text{pH}_X \quad (24)$$

Of course, the cell diagrams (21) and (22) can be unified in the form:

$$\text{Pt}|\text{Glass electrode}|\text{QHY Standard at } r\text{H}_S, \text{ or Sample at } r\text{H}_X|\text{Pt} \quad (25)$$

Combining equations (16), (18), (20), (23), and (24) one obtains:

$$E_X - E_S = (k/2) r\text{H}_X - (k/2) r\text{H}_S \quad (26)$$

from which the final operational equation for the rH measurements [7] is attained:

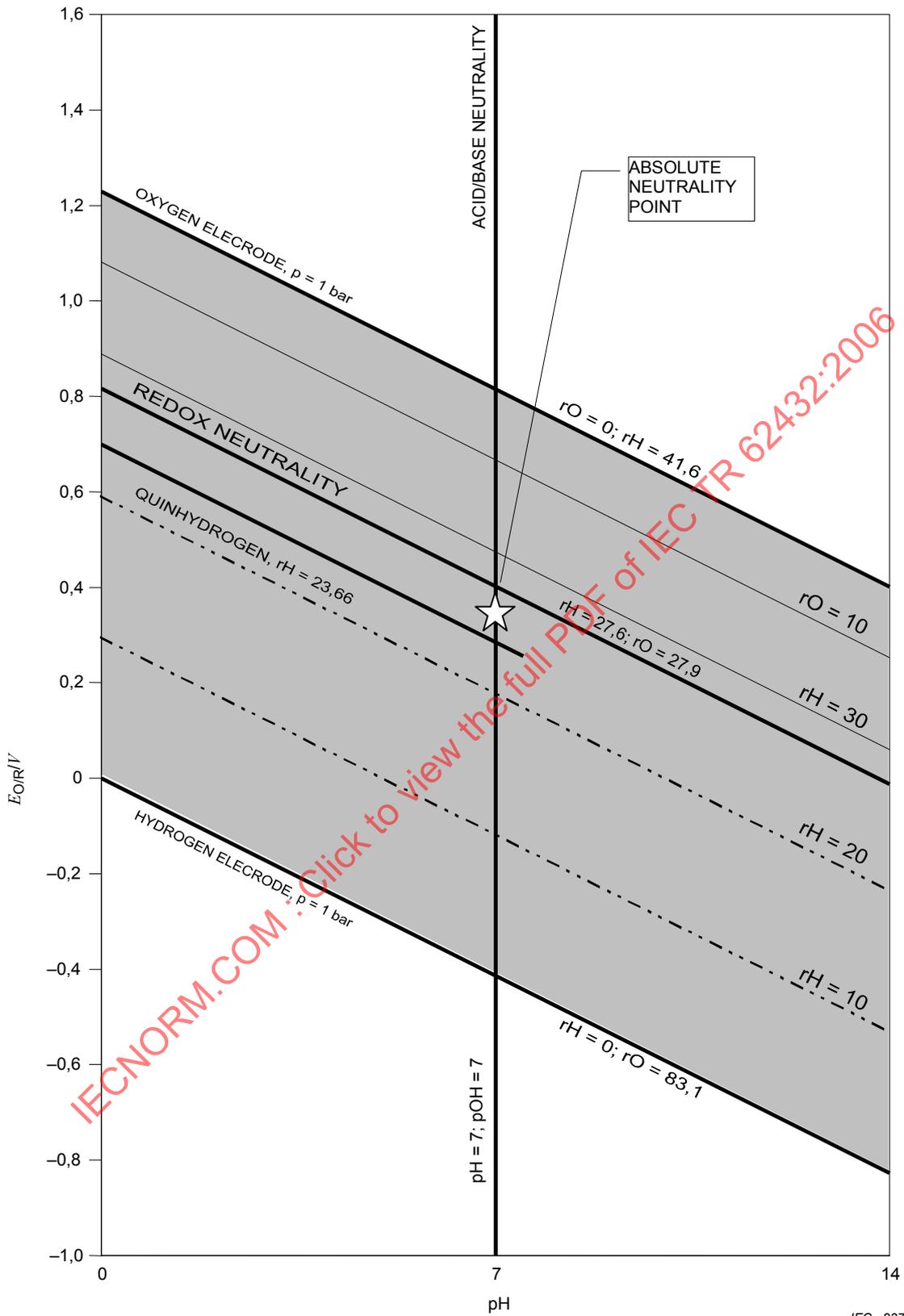
$$r\text{H}_X = r\text{H}_S + (2/k) (E_X - E_S) \quad (27)$$

NOTE 1 Measuring the rH along with the above cell scheme (25) does NOT involve liquid junction potentials (unlike in the pH measurement), *i.e.* no need of salt bridges.

NOTE 2 The glass electrode should anyway be periodically controlled by means of the "bracketting pH standards technique" to verify that its "slope factor" k does not significantly deviate from the theoretical Nernstian slope ($= 2,303 RT/F$).

NOTE 3 Of course, measuring the rH by means of cells of the types (21) and (22) requires using the electrometric voltmeter of highest input impedance ($>10^{13} \Omega$), because both cells contain the glass electrode thus featuring high inner resistances ($10^9 \Omega$).

NOTE 4 The QHY-saturated solution in the calibration cell should be acidic or neutral, because the component hydroquinone of the QHY undergoes a chemical reaction in alkaline solution.



NOTE The shaded area is the band of thermodynamic stability of water.

Figure 1 – Pourbaix's diagram for the triad rH – pH – $E_{O|R}$ for some key redox systems

Table 2 – Parallelisms between the aqueous pH-metric and rH-metric scales

Quantity	pH (Sørensen) [10, 11]	rH (Clark) [2, 3]
Notional definitions	$\text{pH} = -\log a_{\text{H}^+}$ $\text{pOH} = -\log a_{\text{OH}^-}$ (a = adimensional activity)	$\text{rH} = -\log p_{\text{H}_2}$ $\text{rO} = -\log p_{\text{O}_2}$ (p = adimensional pressure)
Type of H ₂ O dissociation equilibrium implied	IONIC: H ₂ O (liq.) = H ⁺ (aq.) + OH ⁻ (aq.)	GASEOUS: 2H ₂ O (liq.) = 2H ₂ (gas) + O ₂ (gas)
Equilibrium constant at 25 °C	$K_{\text{W}} = a_{\text{H}^+} a_{\text{OH}^-} = 1,008 \times 10^{-14}$ $\text{p}K_{\text{W}} = \text{pH} + \text{pOH} = 14,0$	$K_{\text{WG}} = p_{\text{H}_2}^2 p_{\text{O}_2} = 8,318 \times 10^{-84}$ $\text{p}K_{\text{WG}} = 2 \text{rH} + \text{rO} = 83,1$
Neutrality conditions	<i>Acid/Base Neutrality:</i> $a_{\text{H}^+} = a_{\text{OH}^-}$ <i>viz.:</i> $\text{pH} = \text{pOH} = \frac{1}{2} \text{p}K_{\text{W}} = 7,0$	<i>Redox Neutrality:</i> $p_{\text{H}_2} = 2 p_{\text{O}_2}$, <i>viz.:</i> $\text{rH} = \text{rO} - \log 2$, therefore: $\text{rH} = (\text{p}K_{\text{WG}} - \log 2)/3 = 27,6$ and: $\text{rO} = (\text{p}K_{\text{WG}} + 2 \log 2)/3 = 27,9$
Conventional zeroes in respective scale ranges	$\text{pH} = 0$ (maximum acidity), <i>viz.:</i> $a_{\text{H}^+} = 1$ (<i>standard state</i>)	$\text{rH} = 0$ (maximum reducing power), <i>viz.:</i> $p_{\text{H}_2} = 1$ (<i>standard state</i>)
	$\text{pOH} = 0$ (maximum alcalinity), <i>viz.:</i> $a_{\text{OH}^-} = 1$ (<i>standard state</i>)	$\text{rO} = 0$ (maximum oxidizing power), <i>viz.:</i> $p_{\text{O}_2} = 1$ (<i>standard state</i>)
Conventional scale ranges	$0 < \text{pH} < 14$	$0 < \text{rH} < 41,6$
	$14 > \text{pOH} > 0$	$83,1 > \text{rO} > 0$
NOTE All rH-metric standards made of aqueous buffers at pH < 7,5 saturated with "quinhydrone" at 25 °C yield rH _S = 23,66, viz. at about mid rH scale (41,6 / 2 = 20,8) and also near to redox neutrality (rH = 27,6).		

2.3 rH Standards for use in water and aqueous-organic solvent mixtures

Some rH-metric standards rH_S [7 to 9] based on buffered acidic solutions saturated with quinhydrone and required by the operational equation (27) for rH_X measurements at 25 °C are quoted in Table 3. Data at temperatures other than 25 °C can be obtained from Ives and Janz's ($E_{\text{QH}_2} - E_{\text{H}^+|\text{H}_2}$) values [6] quoted in Table 4. Some other rH_S standards were characterized recently [7].

Table 3 – Some reference aqueous solutions proposed as rH-metric standards rH_S [8, 9] at 25 °C and for the calibration of the redox electrode at E_{OIR}

Standard Redox Solution	rH _S	pH _S	E _{OIR} /V
0,05 m Potassium Tetroxalate buffer solution, saturated with Quinhydrone	23,66	1,65	0,602 1
0,01 M HCl + KCl 0,09 M solution ("Veibel's solution" [10]) saturated with Quinhydrone	23,66	2,07	0,583 1
0,05 m Potassium Hydrogen Phthalate buffer solution, saturated with Quinhydrone	23,66	4,01	0,462 5
0,014 42 M Na ₂ HPO ₄ + 0,026 44 M NaH ₂ PO ₄ buffer solution, saturated with Quinhydrone	23,66	7,00	0,285 6

Table 4 – Values of ($E_{\text{QHY}} - E_{\text{H} + / \text{H}_2}$) [6] with corresponding $r\text{H}_\text{S}$ values, at various temperatures, valid for any solvent (water W, or aquo-organic mixture $Z = W + S$ compatible with Quinhydrone) in non-alkaline solution

Temperature		$E_{\text{QUINH}} - E_{\text{H} + / \text{H}_2}$	$r\text{H}_\text{S}$
/ K	/ °C		
273,15	0	0,717 98	26,57
278,15	5	0,714 37	25,91
283,15	10	0,710 73	25,28
288,15	15	0,707 09	24,66
293,15	20	0,703 43	24,19
298,15	25	0,699 76	23,66
303,15	30	0,696 07	23,11
308,15	35	0,692 37	22,57
313,15	40	0,688 65	22,21

2.4 Electrodes for the operational rH cell

2.4.1 General

The electrodes required by the cell pair (21) and (22) are the well-known H^+ -selective glass electrode and an inert noble-metal electrode (usually platinum or gold). They should be submitted to the preliminary verifications described below.

2.4.2 The glass electrode

The glass electrode is the classical H^+ -selective electrode used for pH measurements, and it should be submitted to all pretreatments and cares of the pH praxis. In particular, the decay of its performance should be checked frequently by the "bracketing standards" technique.

2.4.3 The inert noble-metal electrode (Pt or Au)

After prolonged use, the platinum or gold electrode may have undergone fouling or filming thus becoming unreliable. Therefore, they should be frequently cleaned by appropriate procedures, possibly of self-cleaning type.

2.5 rH Scales in diverse solvents

A comparative summary, such as that shown in Table 2, may be helpful to the reader to better understand the problem of the intercomparison between rH scales in different solvents.

There are some parallelisms, but also some significant differences, between the range of rH scale and the range of the familiar pH scale. In fact, the pH range is defined as $-\log pK_{\text{W}} = \text{pH} + \text{pOH} = 14,0$, where $K_{\text{W}} = 1,008 \times 10^{-14}$ is the self-ionisation equilibrium constant of water, and $\text{pH} = 7,0$, whereas the rH range is defined [12] as $-\log pK_{\text{WG}} = \text{rH} + \text{rO} = 83,1$, where $K_{\text{WG}} = 8,318 \times 10^{-84}$ is the gaseous-dissociation equilibrium constant of water, and $\text{rH} = 27,6$ together with $\text{rO} = (pK_{\text{WG}} + 2 \log 2) / 3 = 27,9$. Therefore, the nominal scale ranges are: for pH, $0 < \text{pH} < 14$, and for pOH, $14 > \text{pOH} > 0$; but for rH, $0 < \text{rH} < (83,1 / 2 = 41,6)$, and for rO, $83,1 > \text{rO} > 0$. Thus, for the conventional zeroes of the respective scales one has: $\text{pH} = 0$ for the maximum acidity, and pOH for the maximum alkalinity; parallelly, $\text{rH} = 0$ for the maximum reducing power, and $\text{rO} = 0$ for the maximum oxidizing power. Finally, it is evident that the recommended saturated-quinhydrone-based standard $r\text{H}_\text{S} = 23,66$ is close to both the mid rH scale ($41,6 / 2 = 20,8$) and the redox neutrality $\text{rH} = 27,6$. It is interesting to note that *any* redox electrode