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Can the redox conditions in natural waters be predicted by a single parameter?

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ABSTRACT

The thermodynamic pε (redox potential) is the theoretical master variable of the ultimate redox conditions in aqueous solutions. Real multicomponent redox processes, however, cannot be predicted by pε considerations alone. In such cases a detectable notion, the operational parameter pe, has to be introduced which is defined by the response of an adequate sensor to redoxchemical changes in natural extracellular systems. The solution/sensor interaction is described by the general theory of stationary states and, in case of Pt metal as sensor, by the electronic equilibrium of Pt in aqueous solutions. Examples of pe/D.O. feedback control experiments with sediment-water systems from L. Kinneret indicate that pe is dependent on the electon donator and the electron acceptor, thus being predictive to the real electron transfer reactions.

1. Introduction

Chemical and biological processes in waters are mainly interconnected by redox reactions. Such reactions can simply be described as an electron transfer from reductants (red) to oxidants (ox) where the reductants are oxidized and the oxidants reduced,

$$\mathrm{red}_1 + \mathrm{ox}_2 \rightleftarrows \mathrm{ox}_1 + \mathrm{red}_2.$$

Analogous to Brønsted's theory where $[H_3O^+] \cdot [OH^-] = K_W$* is defined as the acid-base reference equilibrium, redox equilibria in aqueous solutions are refered to the Standard Hydrogen Electrode (SHE), i.e. a blank platinum metal electrode immersed into 1 N HCl and coated with H_2 gas at $P_{H_2} = 1$ atm and 25 °C. The SHE is thus defined by the thermodynamic equilibrium between $[H_3O^+]$, $[e^-]$ (the electron concentration) and P_{H_2} (the partial pressure of H_2),

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* For simplicity no differentiation between activity and concentration will be made in the forthcoming text.

$$2\ H_3O^+ + 2\ e^- \rightleftarrows H_2 + 2\ H_2O;\ K_{SHE} = 1$$

In p-notation (p means the $-\log_{10}$ operator)

$$2\ pH + 2\ p\varepsilon = rH$$

($rH \equiv -\log_{10} P_{H_2}$ in order to prevent confusion with $-\log_{10}[H_3O^+]$)

The graphical representation of the SHE is shwon in Fig. 1. The diagram shows that equilibria between the redox or acid-base components in the solution can comprehensively be described by the 'master' variables

- pε, if stoichiometrically due to a perpendicular line on the pε axis (y-axis) i.e. the considered reaction is pH independent;
- rH, if stoichiometrically due to a perpendicular line on the rH axis (z-axis), i.e. the considered reaction obeys $\Delta p\varepsilon + \Delta pH = 0$;
- pH, if stoichiometrically due to a perpendicular line on the pH axis (x-axis), i.e. the considered reaction is pε independent (acid-base reactions);
- pε and pH, if the considered reaction does *not* obey $\Delta p\varepsilon + \Delta pH = 0$ (the most common situation in natural freshwaters, see (1)).

pε and redox equilibria are interrelated by the Nernst equation,

$$p\varepsilon = p\varepsilon^\circ + \frac{1}{n}\log_{10}\frac{[ox]}{[red]};$$

where pε corresponds to the traditional redox potential Eh as

$$p\varepsilon = \frac{Eh}{2303 \cdot RT \cdot F^{-1}};\ (Eh\ in\ mV).$$

pH and acid-base equilibria are interrelated by the Henderson-Hasselbalch equation

$$pH = pK + \log_{10}\frac{[base]}{[acid]}.$$

Analogous to Brønsted's definition of pH in neutral water we can calculate a corresponding pε value for 'redox-neutral' water where $[H_2]$ and $[O_2]$ correspond to the autolysis of H_2O; it follows

$$2\ H_3O^+ + 2\ e^- \rightleftarrows H_2 + 2\ H_2O;\ K_{SHE} = 1$$

and

$$O_2 + 4\ H_3O^+ + 4\ e^- \rightleftarrows 6\ H_2O;\ K_{O_2}^{25^\circ C} = 10^{83.1}$$

in p-notation

$$p\varepsilon(P_{O_2} = 1 \text{ atm}) = 20.8 - pH \text{ (upper boundary line in Fig. 1)}$$
$$p\varepsilon(P_{H_2} = 1 \text{ atm}) = -pH \text{ (lower boundary line in Fig. 1)}$$

Since $P_{H_2}/P_{O_2} = 2/1$, we obtain

$$6\ pH + 6\ p\varepsilon = 82.8$$
$$p\varepsilon = 13.8 - pH$$

For neutral pH (= 7)
$$p\varepsilon = 6.8$$

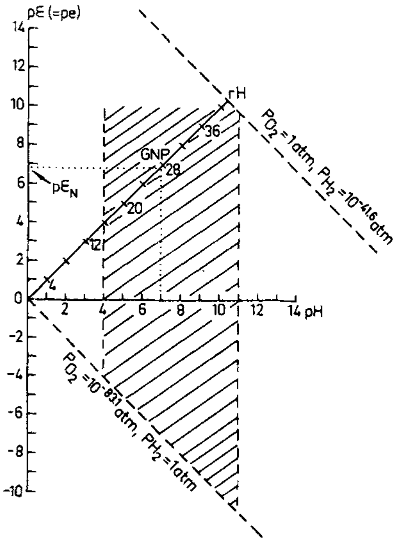

Fig. 1: pε/pH stability diagram of the Standard Hydrogen Electrode (SHE) where pε = pe by definition; hatched area = pε(pe)/pH ranges of natural freshwater systems, GNP = general neutral point (pH 7; $p\varepsilon_N = 6.8$), upper and lower dotted lines signify the thermodynamic boundaries where H_2O is oxidized and reduced, respectively (from (1)).

Thus, the general neutral point with standard conditions (25 °C) will be at pH = 7 and pε = 6.8 or rH = 27.6.

Problems arise when pε, pH or rH shall be confirmed by measurements in real systems. In a strict sense this is impossible since even most refined measurement techniques will uncontrollably disturb the chemical equilibrium.

However, considering potentiometric pH measurements with glass electrodes we know that the measured data will highly reflect equilibria since acid-base reactions belong to the most rapid chemical reactions so that equilibria are the normal case. Furthermore, the glass electrode can easily be proved to be an ion-sensitive membrane with extreme high selectivity and sensitivity to H_3O^+ and OH^-, respectively. (There are operational difficulties, e.g. with pH measurements in milk or colloidal systems, which however cannot be discussed here.) There are no basic problems to verify the concept of the (conventional) pH scale in multicomponent acid-base solutions.

This is not the case with redox measurements. Neither pε nor rH can operationally be verified due to (conventional) scales except for a narrow range alongside the lower boundary line in Fig. 1. For example, at the general neutral point the electron concentration should be $[e^-] = 10^{-p\varepsilon} = 10^{-6.8}$ M, a fully hypothetical order of magnitude as free electrons of such high concentrations have never been detected in aqueous solutions (2). The same refers to rH; no means exists to detect a H_2 partial pressure of $10^{-27.6}$ atm! Even if we could detect corresponding rH values they would only refer to redox reactions with stoichiometric ratios of $H_3O^+/e^- = 1$; as many redox reactions deviate from that stoichiometry rH comes out to be conceptually as well as operationally a useless parameter. Unlike pH, redox intensities of multicomponent systems corresponding to $p\varepsilon \gg -7$ (pH = 7) cannot be defined by the concentration of the conventional reference components, i.e. the electron concentration $10^{-p\varepsilon}$ M or the H_2 partial pressure 10^{-rH} atm.

Consequently, in order to determine the redox conditions in aerated natural waters redox models have been put forward refering to the redox-controlling impact of the concentrations of D.O. or H_2O_2 as the predominant oxidants, e.g.

(a) The water is considered to be in contact to the atmosphere with $P_{O_2} = 0.21$ atm (3),

$$\frac{1}{2} O_2 + 2\ H_3O^+ + 2\ e^- \leftrightarrows 3\ H_2O;\ K_{D.O.}^{25^\circ C} = 10^{41.6}$$

or

$$p\varepsilon = \frac{1}{2} \cdot \log K_{D.O.} + \frac{1}{4} \log P_{O_2} - pH.$$

For pH = 7 follows

$$p\varepsilon_a = 13.6.$$

(b) The same conditions as with (a), however, the redox couple H_2O/H_2O_2 is controlling the redox conditions

$$H_2O_2 + 2\ H_3O^+ + 2\ e^- \leftrightarrows 4\ H_2O \text{ with } K_{H_2O_2}^{25^\circ C} = 10^{60}$$

analogous to (a) $p\varepsilon_b$ is given as

$$p\varepsilon_b = \frac{1}{2} \log K_{H_2O_2} - pH + \frac{1}{2} \log p[H_2O_2].$$

It is difficult to estimate the natural H_2O_2 concentrations. However, considering available data, mean concentrations of 10^{-7} M may be assumed (4). For pH = 7, follows

$$p\varepsilon_b = 19.5.$$

(c) The same conditions as with (a), however, H_2O_2/O_2 is considered as redox controlling (5)

$$O_2 + 2\ H_3O^+ + 2\ e^- \leftrightarrows H_2O_2 + 2\ H_2O;\ K^{25^\circ C}_{O_2/H_2O_2} = 10^{23.4}$$

or

$$p\varepsilon = \frac{1}{2}\log K_{O_2/H_2O_2} - pH + \frac{1}{2}\log P_{O_2} - \frac{1}{2}\log [H_2O_2].$$

At pH = 7, $P_{O_2} = 0.21$ atm and $[H_2O_2] = 10^{-7}$ M,
$p\varepsilon_c = 7.9$.

The significant deviations between $p\varepsilon_a$, $p\varepsilon_b$ and $p\varepsilon_c$ indicate the stoichiometric sensitivity of such redox models.

Measurements in aerated natural waters using the SHE analogous Pt metal electrode as a sensor (Table 1.1 (a) for the definition of pe see part 3) confirm the redox controlling predominance of H_2O_2/O_2 (model (c)) or the redox-inert behaviour of D.O., respectively (condition of the general neutral point). They deviate remarkably from pε values as calculated from the models (a) and (b).

In very pure waters Bockris and Huq (6) measured, nevertheless, residual potentials with Pt metal electrodes similar to $p\varepsilon_a$ corresponding to the redox potential (Eh) of the O_2/H_2O redox couple. Furthermore, Wang and Brinigar (7) and Parsons (8) suggested that the biochemical (intracellular) O_2 reduction is rather a four electron (model (a)) than a two electron transfer (model (c)) supporting again model (a). Summarizing these findings Stumm (9) concluded that aerated natural waters correspond to model (a) irrespective of the results of measurements with Pt metal electrodes. In anoxic systems pε is thus computed due to the sequence of different free energy levels of anoxic electron acceptors (e.g. Mn (IV), NO_3^--N, Fe(III) etc.).

2. Oxidation state diagrams

Oxidation state diagrams have been introduced in order to elucidate natural redox components by their oxidation numbers (10, 11). Due to this conception the volt-equivalent (VE_A) of redox reactants are plotted versus their oxidation numbers (n). In well-aerated waters the relative stability of distinct oxidation numbers versus D.O. is calculated as (pH = 7, 1 atm., 25 °C) $[VE(O_2/H_2O)] = (VE^\circ_A) - n(0.80)$

where E°_A = redox potential of the considered redox couple (e.g. NH_4^+/NO_3^-), and n(0.80) = the product of the oxidation number of the considered oxidant and the redox potential of O_2/H_2O in Volts. The oxidation state leading to the lowest volt-equivalents [$VE(O_2/H_2O)$] belongs to the most stable species.

Although normalizing the redox potentials Eh° (pε°) of terminal electron acceptors on their free energy levels (per volume) the volt-equivalent conception seems not to overcome the redox indicator problem in natural systems since

— taking Eh's for calculating (VE_A) implies thermodynamic equilibria between the redox reactants;

— $VE(O_2/H_2O)$ as a reference supports a certain redox model (model (a)); using different models will lead to different stability coefficients for the same oxidation numbers.

3. The pe concept

The bias of Stumm's conclusion or of model (a) is that it is not necessarily the only one describing oxic redox processes. Further, natural waters are often open systems which do not necessarily approach thermodynamic equilibrium (only stationary states)*.

As long as one-directional biogeochemical electron (energy) transfer continues the assumption of redox equilibria or Nernstian conditions is unrealistic, even in microenvironments (12). Additionally, many natural redox reactions are slow. The majority of them depends on the presence and mediating impact of microorganisms (13); thus they have to be considered as interactions between the intracellular and the extracellular medium.

If rigorously described by thermodynamic notions natural systems have to be reduced to numerous partial equilibria whose significances are unpredictable and which nullifies the conception of one pε as a "master" variable for all redox couples. Further, our knowledge about the stoichiometries of enzyme controlled redox reactions is still insufficient. It is worthwhile to remind that, in a strict thermodynamic sense, the pertinent respiratory redox reactions (i.e. oxidation of $C^{\pm 0}$ by O_2, Mn(IV), NO_3^-, Fe(III), SO_4^{2-} etc.) could occur simultaneously as they are all bound to losses in free enthalpy ($-\Delta G_R$), and that thus the stoichiometries and kinetics of such multi-step redox processes can hardly be discussed only thermodynamically.

What we may assume, however, is that the intracellular microbial metabolism reflects the extracellular conditions (12, 13, 15), i.e. certain intracellular redox processes can only occur (and influence the extracellular environment) if the extracellular redox conditions are adequate (establishment of a certain "biogeocenosis").

Unlike pε, the pe conception is an operational approach for defining the extracellular redox condition; it correlates the mixture of certain redox components to their elec-

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* Indeed, the (calculated) pε/(measured) pe discrepancy as reported from groundwaters by Lindberg and Runnells (cf. comment of W. Stumm) may be due to the usually non-stationary redox conditions, the almost impossibility to obtain reliable mV readings in such waters, and the neglect of relevant redox couples when calculating the pε values (e.g. the authors do not consider the dissolved organic carbon concentrations which may be highly relevant at least in surface groundwaters).

troactivity versus a sensor irrespective of existing redox equilibria; thus, pe is defined as

$$pe \equiv -\log_{10} a_e \text{ (sensor)}$$

(the sensor may be "electron selective" analogous to "ion selective" electrodes (14)). Redoxchemically a_e (sensor) corresponds to the control of electroactive compounds by microbial mediators (i.e. to the "bioelectrocenosis").

For brevity we call a_e (sensor) a_e. The total process of electron transfer may be described in two (fictive) partial processes:

1. Metabolic activation of organic matter will lead to increasing concentrations of electroactive electron donators in solution exchanging electrons with the sensor,

$$\frac{d\,a_e}{dt} = \vec{k}$$

where $\vec{k}$ means the sensor-detected kinetic coefficient of the electron donator release.

2. Since redox reactions involve electron transfer, there must exist an electron acceptor acting as a sink for the electrons; thus

$$-\frac{d\,a_e}{dt} = \overleftarrow{k}\,(a_e)_t$$

where $(a_e)_t$ means the concentration of the electron donator in solution at time t.

A stationary state will be reached when $t \rightarrow \infty$ or

$\left|\frac{d\,a_e}{dt}\right| = 0$, and the residence time exceeds the reaction time.

Consequently, we obtain

$$(a_e)_t = (a_e)_{t=\infty} + [(a_e)_{t=0} - (a_e)_{t=\infty}] \cdot \exp - \vec{k} \cdot t$$

where $(a_e)_{t=0}$ means the initial non-stationary concentration in the solution.

It follows that

$$(a_e)_{t=\infty} = \frac{\vec{k}}{\overleftarrow{k}} = \tilde{K}_{sensor}$$

As long as the electron donators or acceptors do not change, $\tilde{K}_{sensor}$ is given as

$$\tilde{K}_{sensor} = \frac{\Sigma\,[\text{electron donator}]}{\Sigma\,[\text{electron acceptor}]}$$

i.e. as the ratio between the stationary concentrations of the electroactive electron donator and acceptor. If one of them or both are changed $\tilde{K}_{sensor}$ (or the "bioelectrocenosis") must also change. We, therefore, can write

$$pe \equiv -\log_{10}\tilde{K}_{sensor}$$

or

$$pe = pe_{redox} - \log_{10}\frac{\Sigma[\text{electron donator}]}{\Sigma[\text{electron acceptor}]}$$

where [electron donator] and [electron acceptor] are given in equiv. $\cdot\, l^{-1}$.
Electron acceptors, (e.g. D.O., NO_3^-–N, Mn(IV), Fe(III), SO_4^{2-}–S, org. C) are usually limited in natural waters. Where D.O. is predominant and the composition of the electron donator fixed one may simplify (pH = const., °C)

$$pe = pe_{D.O.} - \log_{10}\frac{[\text{equiv. } e^- \cdot l^{-1}]}{[\text{equiv. D.O.} \cdot l^{-1}]}$$

for [equiv. e^-] = const., and in p-notation

$$pe'_{D.O.} = pe + p[\text{equiv.D.O.}].$$

The pe'_{redox} values refer to an operational "electron concentration" scale analogous to pX or pMe concentration scales with ion-selective electrode methods. In contrast to pε models pe is not contradictory to thermodynamic implications and defines the redox condition as due to the sensor response on the present electron donators and acceptors in extracellular solution. From experiments we know that D.O., NO_3^-–N, NO_2^-–N, Mn(IV), Fe(III) etc. are sequentially depleted, i.e. due to the optimum metabolic energy yield (12). We know further that a change from one to another predominant electron acceptor will usually not be followed by a breakdown but by a change of the microbial biocenosis (15).
Considering the extreme case where almost no energetic difference exists between electron donator and acceptor ($pe \leqq -5$ at pH 7, e.g. under conditions where CO_2 and/or H_3O^+ is reduced) redox equilibria become thus more likely. That means that pe values should resemble pε values. If finally H_3O^+ will be reduced to H_2 and the sensor is Pt metal, the (measured) pe value *must* be identical to pε since SHE conditions are verified (see Fig. 1). Extreme low pe's may represent thus equilibrium, i.e. metabolic "death". On the other hand, the ubiquitous presence of organic matter, metabolizing microorganisms and electron acceptors different from H_3O^+ make higher pe's representative for "life" or for conditions far from overall redox equilibria. The SHE can, therefore, operationally be regarded as a reference for pe and pε.

4. Using Pt metal as the pe sensor

Stationary electrode response means, however, electrochemical equilibrium between the test solution and the sensor. As was pointed out by Frumkin and Damaskin (16) metal electrodes (including Pt) have to be regarded as in "electronic equilibrium" with the solution as long as no potential drift occurs. As metals contain removable electrons (17) they will be "electron-sensitive". Consequently, De Battisti and Trasatti (18) suggested to consider the metal/solution equilibrium as

$$\mathrm{Me} + \mathrm{H_2O} \leftrightharpoons \mathrm{Me(aq)} \leftrightharpoons \mathrm{Me^{+}(aq)} + \mathrm{e(aq)}$$

i.e. as given by the solubility of the metal itself. The origin of the single equilibrium components, including e(aq), has no significance; thus e(aq) will determine the response of the electrode to the solution or the electroactivity of the solution versus the metal electrode, i.e. e(aq) will be identical to $a_e(\mathrm{Pt})$. In the (most common) case of $\mathrm{Pt(aq)} \leftrightharpoons \mathrm{Pt^{2+}(aq)} + 2\ \mathrm{e(aq)}$ we obtain due to the Nernst equation (19)

$$\mathrm{pPt^{2+}(aq)} = 2\left(\mathrm{E^{\circ}_{Pt/Pt^{2+}}} \cdot \frac{0.4343 \cdot \mathrm{F}}{\mathrm{RT}} - \mathrm{p}\varepsilon_{\mathrm{Pt/Pt^{2+}}}\right)$$

or, for 25 °C and $\mathrm{E^{\circ}_{Pt/Pt^{2+}}} = 1600$ mV (pH = 0)

$$0.5\ \mathrm{pPt^{2+}(aq)} = 27.03 - \mathrm{p}\varepsilon_{\mathrm{Pt/Pt^{2+}}}$$

$\mathrm{p}\varepsilon_{\mathrm{Pt/Pt^{2+}}}$ must be identical to pe. The lower limit of the electrode response is given by $0.5\ \mathrm{pPt^{2+}} = \mathrm{p}\varepsilon_{\mathrm{Pt/Pt^{2+}}}$ corresponding to pe = 13.5. Consequently, changes of the composition of the redox components in solution correlated to $a_e(\mathrm{Pt}) \geqq 10^{-13.5}$M (pH O) will change the electroactivity of the solution, i.e. will lead to an electrode response. Indeed, pe values > 13.5 have never been reported even in well-aerated waters.

Inversely, if we consider pe = 10 as the most positive value in natural waters we obtain (pH O)

$$\mathrm{pPt^{2+}} = 54.1 - 2\ \mathrm{pe}$$

or

$$\mathrm{pPt^{2+}} = 34.1$$

i.e. the equilibrium activity of $\mathrm{Pt^{2+}}$ will be 10^{-34}M, an order of magnitude which in any case (including $\mathrm{Pt^{2+}}$ complexation) should be verified near the electrode surface i.e. at pe ≦ 10 the $\mathrm{Pt^{2+}}$ will decrease and the Pt electrode be only responsive to $a_e(\mathrm{Pt})$.

Electrochemically, the metal/solution interaction is described by the anodic (i_{an}) and cathodic (i_{cat}) interphase currents between the electrode and the dissolved components. If metal or other solid state electrodes are used as the pe detector the electrical response of the sensor is given by the Butler-Volmer equation;

$$i_{an} = \mathrm{F}\ k_{sensor}[\mathrm{A}]\ \exp\left(-\mathrm{F}\Delta \mathrm{E_A}/2\mathrm{RT}\right)$$

and

$$i_{cat} = \mathrm{F}\ k'_{sensor}[\mathrm{D}]\ \exp\left(\mathrm{F}\Delta \mathrm{E_D}/2\mathrm{RT}\right)$$

where the symmetry coefficient β of the interfacial electron transfer may equal 0.5, [A] and [D] are the bulk concentrations of the electrode electronizing and de-electronizing components in the solution, k_{sensor} and k'_{sensor} are the kinetic coefficients of the interfacial electron transfer, and i_{an} and i_{cat} are the interfacial electronizing and de-electronizing current densities.

As ΔE_A and ΔE_D are the current-driving potential differences between the inner phase of the sensor and the bulk solution we can write,

$$i_{an} = F\, k_{sensor}[A] \cdot 10^{-\frac{2.3\Delta E_A \cdot F}{2RT}}$$

and

$$i_{cat} = F\, k'_{sensor}[D] \cdot 10^{\frac{2.3\Delta E_D \cdot F}{2RT}}$$

or, since $pe = \dfrac{2.3 \cdot E \cdot F}{RT}$,

$$i_{an} = F\, k_{sensor}[A] \cdot 10^{-0.5\,\Delta pe_{an}}$$

and

$$i_{cat} = F\, k'_{sensor}[D] \cdot 10^{0.5\,\Delta pe_{cat}}$$

If electrochemical equilibrium between solution and sensor is established (i.e. $i_o = i_{an} = i_{cat}$, we may conclude

$$k_{sensor}[A] \cdot 10^{-0.5\,\Delta pe_{an}} = k'_{sensor}[D] \cdot 10^{0.5\,\Delta pe_{cat}}$$

or

$$\tilde{K}_{sensor} = \frac{k_{sensor}[A]}{k'_{sensor}[D]} = \frac{10^{0.5\,\Delta pe_{cat}}}{10^{-0.5\,\Delta pe_{an}}} = 10^{-pe},$$

i.e. $k_{sensor} \cdot [A]$ and $k'_{sensor} \cdot [D]$ correspond to [electron donator] and [electron acceptor] as given above (part 4.). The ratio k_{sensor}/k'_{sensor} will thus determine the electroactivities of the electrode electronizing or de-electronizing components in solution.

From the Butler-Volmer equation it cannot be deduced whether the pe corresponding electrode potentials are mixed potentials or not. Mixed potentials imply

$$A + D \not\rightleftharpoons A' + D'$$

i.e. the electronizing and de-electronizing components in solution are inert to each other.

As we mentioned previously the ubiquitous occurrence of redox-catalyzing microorganism ("biogeocenosis") is the normal case; at least for the majority of natural respiratory redox reactions we may, therefore, assume

$$A + D \xrightarrow{\text{enzyme}} A' + D'.$$

Consequently, although the electronizing and de-electronizing components may be different the corresponding pe value will be significant due to the redox mediating impact of microorganisms ("bioelectrocenosis").

Whitfield (20) reported for oxic freshwaters and for anoxic sediments a mean steady state current density of $i_o = 1.95 \pm 1.45 \cdot 10^{-7}\ A \cdot cm^{-2}$ using Pt metal sheet electrodes; this value is sufficient to lead to stable mV readings (cf. part 5.1). Spiro (21) and Tanaka and Tamamushi (22) reported exchange current densities of inorganic electron acceptors $\leqq 10^{-7}\ A \cdot cm^{-2}$ (except for Fe(II)/(III)) as refered to their natural concentration range ($\leqq 10^{-4}$M). In most natural freshwaters DOC averages at 15 $mg \cdot l^{-1}$, i.e. $10^{-2.8}$ M (average of 500 Wisconsin lakes, see (23)).

The electro-catalyzing effect of Pt metal is well known (24). If, by surface catalysis, the molar steady state current densities of the DOM is similar to the steady state current densities of mineral electron acceptors, the relative high concentrations of organic compounds make a response of Pt metal due to the DOM (i.e.A) and the predominant electron acceptor (i.e. D) very likely.

5. Potentiometric pe measurements with Pt electrodes

Whitfield (25) suggested that oxygen may directly be absorbed at the Pt metal surface when Pt is immersed into oxic waters; he assumed the following interphasic equilibrium,

$$Pt^{\circ} + H_2O \leftrightarrows Pt\text{-}O + 2\ H_3O^+ + 2\ e^- \text{ with } K_{Pt\text{-}O}^{25^{\circ}C} = 10^{-29.7}$$

The activities of Pt° and Pt-O (solid phases) can be set unity; thus

$$p\varepsilon_{Pt\text{-}O} = \frac{1}{2} pK_{Pt\text{-}O}^{25^{\circ}C} - pH$$

or, at pH = 7

$$p\varepsilon_{Pt\text{-}O} = 7.9$$

This result is noteworthy since it fits to the oxic pe's given in Table 1(a). The Pt-O coating is conductive and not inhibiting interphasic electron exchange (25); it probably confines the positive pe scale in aerated waters although not preventing the equilibration of the electrode to more oxidative solutions if the latters are well redox buffered (poised). The equilibration between Pt metal and D.O. allows an accurate pH correction of pe data due to the following pH dependence (25);

$$pe = pe_{Pt\text{-}O} - pH$$

or

$$pe_7 = (pH_{meas.} - 7) + pe.$$

In H_2S-bearing waters Pt metal was assumed to react with S^{2-} ions (25);

$Pt^{\circ} + S^{2-} \leftrightarrows PtS + 2\ e^{-}$ with $K_{PtS} = 10^{32.05}$

and $[S^{2-}] = \alpha_2 [S_{tot}]$, follows

$p\varepsilon_{PtS} = \frac{1}{2} pK_{PtS} + p\alpha_2 + p[S_{tot}]$

at $pH = 7$ and $[S_{tot}] = 10^{-4}M$

$p\varepsilon_{PtS} = 11.2$

This order of magnitude was never confirmed by pe measurements (Table 1.1(b)) which makes a direct sulfide "poisoning" doubtful (26). Pt metal is easily wetted by water (27); in spite of that hydrophobic organics may be absorbed during longterm measurements. It is well known that such coatings diminish the wetting degree, but it is still an open question whether they also affect $a_e(Pt)$.

5.1 Calibration

The pe measurement cell is described as Ag, AgCl/3 M KCl//sol./Pt(Ag). Amplifiers adequate for direct-potentiometric measurements (input impedance > 10^{13} Ohm, current drain < 0.1 pA) have been developed only recently. There is no doubt that older "redox potential" measurements suffered from the electronical drain of the meters.

Many authors overlook the influence of the reference half cell, particularly with respect to the state of the liquid junction. Reactions between internal electrolyte and components of the solution can create deviations until 60 mV (28). It cannot be excluded that reports on "galvanic poisoning" of the Pt metal are due to damaged liquid junctions or inadequate meters.

In Fig. 2 the potentiometric pe and pH measurement cells are schematically shown (in cases where pH is known and well-buffered the "rH" measurement cell is optimum for pe detections since the glass half cell functions as reference electrode). It is useful to calibrate the pe measurement cell with regard to irreversible changes of the Pt metal surface and the reference electrode. The calibration is usually carried out with well-poised mixtures of electroactive redox couples (quinhydrone solutions at pH 0...7, see (1)). For such solutions $p\varepsilon$ is known and equals the measured pe. For unknown solutions pe can then be calculated (diffusion potential E_j neglected),

$$pe = pe^{\circ} + \frac{(mV - mV^{\circ})}{S}$$

where pe°, mV° refer to the used calibration standard and S to the slope mV/pe.

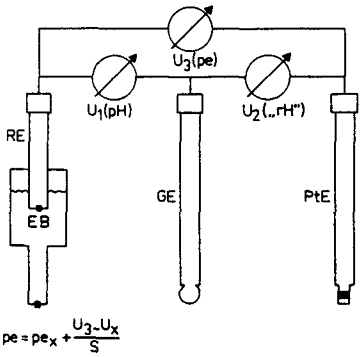

Fig. 2: Electrode combinations for pe/pH measurements. PtE–Pt metal half cell; GE-glass half cell; RE-reference half cell with inert-electrolyte bridge (EB). U_1, U_2, U_3-residual potentials of the possible half cell combinations (from (1)).

The Pt-O coating of the metal surface may create longterm potential drifts in weakly buffered solutions (as many natural waters are). Treating the electrode with 0.1 N Na_2SO_3 solution will destroy the coating and thus accelerate the equilibration between the metal and the solution (24).

6. Experimental determination of pe_{redox} levels

The majority of reported "redox potential" detections follow the operational sequence:
redox state→sensor response*
reflecting the idea that redox equilibria represented by a pε value do exist and can simply be confirmed by an appropriate sensor response.
For the pe (or pe_{redox}) detection the opposite sequence is necessary:
sensor state→redox response
i. e. the redox state of the system is defined by the sensor's behaviour.
Following the preceding considerations we regard the Pt electrode as an appropriate sensor and pe as the master parameter of the redox intensity in the test solution; S_{redox} is the slope coefficient between $a_e(Pt)$ and the proportions of redox components. The problem is that we cannot predict S_{redox} by thermodynamic calculations as we do with pε's. S_{redox} must be detected experimentally. For the macroscopic interrelationship between $a_e(Pt)$ and [redox] we may write (pH = const.)

$$a_e(Pt) = S_{redox} \cdot [redox]$$

or

$$\log_{10} S_{redox} = p[redox] - pe$$

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* Probably, this sequence is also due to all field data used by Lindberg and Runnells (cf. comment of W. Stumm).

where [redox] stands for the redox component under consideration. For D.O. as predominant electron acceptor,

$$\log_{10} S_{redox} = p[\text{equiv. D.O.}] + p[\text{redox}] - pe_{D.O.}$$

If S_{redox} is known, changes of [redox] can be predicted by pe measurements. In order to determine S_{redox} the most precise results will come from pe feedback control procedures. In this case certain pe (pH = const.) values are chosen as set points, and the subsequent redoxchemical response of the system is observed. In Fig. 3(a) the block diagram of a pe/pH regulation loop for the feedback control of a sediment-water interface is shown (1). As long as $S_{redox} \neq O$(i.e. $\Delta a_e(Pt) > 10^{-13.5}$M (pH O)) pe is the appropriate control parameter for ongoing redox processes.

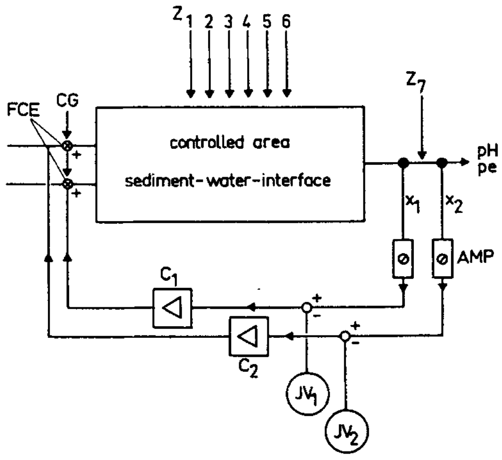

Fig. 3(a): Block diagram of the pe/pH feedback control loop in sediment-water systems: X_1, X_2-pH, pe signal output; AMP-amplifier; JV_1, JV_2-index values (pH, pe set points); C_1, C_2-controller; FCE-final control elements (magnetic valves); CG-control gases (N_2, CO_2, air).

Z_{1-7}-interferences: 1 dilution by overlying water exchange; 2, 3 electroactive oxidants, reductants input; 4, 5 release of electroactive reductants from the sediment and by the reduction of oxidants in the overlying water; 6 acid-base shift due to redox reactions in the overlying water and sediment; 7 selectivities and stabilities of the sensors (from (1)).

The regulation accuracy depends on $d\log_{10}[\text{redox}]/d\text{pe}$. The pe buffer intensity $\beta_{(pe)}$ is thus defined (pH = const.)

$$\beta_{(pe)} = \frac{1}{V_s} \cdot \frac{d[\text{redox}]}{d\text{pe}} \text{ in equiv.} \cdot l^{-1}.$$

Follows for [redox] = [equiv. D.O.]

$$\beta_{(pe)} = \frac{1}{V_s} \cdot \frac{d[\text{equiv. D.O.}]}{d\text{pe}}$$

with V_s = volume (liter) of the considered solution. The lower $\beta_{(pe)}$ the more precise will be the regulation; however, the more difficult it will be to avoid overshoots by the reset action of the controller. Thus, the regulation accuracy (α) due to frequency and amplitude of the controller's reset action will be in the most simple case,
α = frequency/amplitude,
or reset pulses per hour and Δpe.
Sediment-water systems should be suitable for determining pe/redox dependences, at least for oxic/suboxic redox levels. Firstly, the organic carbon content of the sediment upper layer should create a strong buffering (poising) of the electron donator. Secondly, D.O. as electron acceptor can easily be provided to the system by the reset action. According to the feedback loop as shown in Fig. 3(a) the regulation works by O_2 additions into the overlying water due to the pe set point, thus, counterbalancing the pe drop due to the metabolic oxygen uptake in the sediment upper layer and in the overlying water (one-sided regulation).

7. Experiments

pe feedback control experiments have been carried out with sediment-water systems from maximum depth of Lake Kinneret (biblical Sea of Galilee). The results allow first insights into the Δpe/ΔD.O. interrelationship in the overlying water.

7.1 Materials and Methods

Lake Kinneret is a warm-monomictic lake (max. depth: 43 m) whose sediments are rich in $CaCO_3$ (20–70% d.wt.). From May until December it is stratified with hypolim-

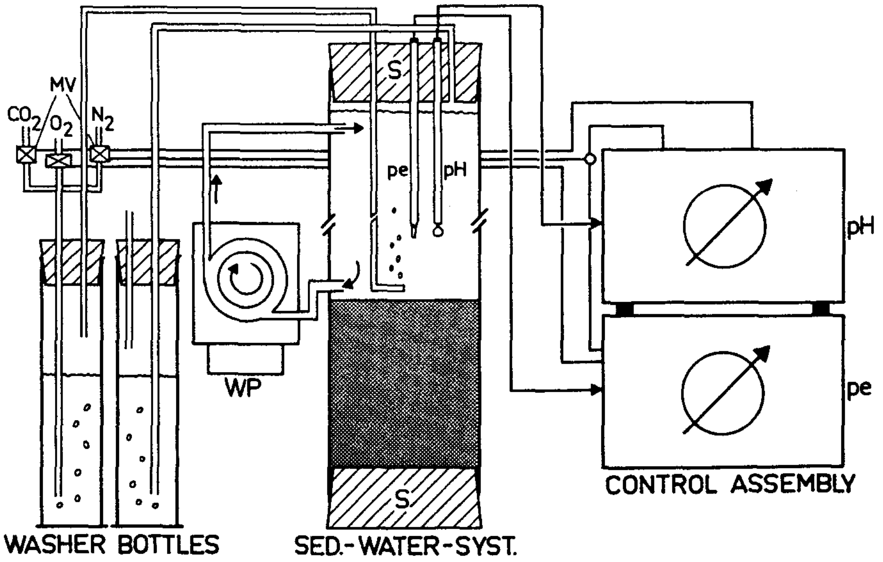

Fig. 3(b): Experimental mounting for the pe/pH feedback control experiments in the overlying water with sediment-water systems. S-stopper; WP-water pump; MV-magnetic valves (the symbol "O_2" holds for air supply).

netic H_2S-sulfur concentrations of $2 \cdot 10^{-4}$ M; the water is enriched with NaCl by submerse thermomineral springs ($[Cl^-]$averages at $10^{-2.2}$ M (29)).

Undisturbed sediment-water systems from maximum depth were taken (30) and darkly incubated under standard temperature (25±1 °C). The systems were connected to a feedback controlling device as schematically shown in Fig. 3(b); pe and pH were one – or double – sided regulated by N_2/air and CO_2/N_2 bubbling into the overlying water. D.O. was monitored in the well overturned overlying water, H_2S in the 0–0.5 cm sediment upper layer (ORBISPHERE D.O. detector model 2115, pH_2S microelectrode INGOLD Ltd., see (31)).

The regulation program was a stepwise pe (pH) increase or decrease observing the pe/D.O. balance in the overlying water; pe set points < 0 have been avoided in order to prevent the occurrence of H_2S in the overlying water (Table 1(b)).

Table 1. Some pe values ("redox potentials") as measured in natural freshwaters (pe's were either directly reported or approximately calculated due to pe = e.m.f. (vs. SHE)/59)

a) well-aerated waters

Compartment	pe	pH	pe_7	authors
about 400 surface waters			7.6	Baas-Becking et al. (32)
well-aerated soil suspension	7.5	6.16	6.7	Bohn (33)
mixolimnion of meromictic lakes			8.0...9.0	Kjensmo (34)
Par Pond, surface	7.9	7.1	8.0	Zimmermann (35)
Lake Kyrkfjörden, surface	3.7	8.5	5.2	Manheim (36)
Lake George sediment-water interface			5.9	Viner (37)
Lake Constance (Obersee, surface)			6.5...7.0	Frevert (1)
Tarawa freshwater ponds	4.0..6.2	7.44..9.39	4.5..7.9	Frevert (38)
Aldabra freshwater ponds	4.5	6.0...10.2		Potts and Whitton (39)
Kinneret surface (epilimnetic waters)	6.2..6.4	8.4..8.9	7.1..7.9	Frevert (unpubl.)

b) anoxic (mostly H_2S-bearing) waters

Compartment	pe	pH	pe_7	authors
Lake George			−1.5	Viner (37)
Lake Kyrkfjörden, bottom	−3.2	6.9	−3.3	Manheim (36)
Fish pond, bottom water	−4.2			Schindler and Honick (40)
anoxic interstitial water from Lake Greifensee	−4.0	7.1	−3.9	Emerson (41)
Tarawa freshwater ponds (anoxic interstitial water)	−5.3	7.29	−5.0	Frevert (38)
Aldabra freshwater ponds (anoxic)	−2.4	6.0	−3.4	Potts and Whitton (39)
Kinneret (H_2S-bearing hypolimnetic waters)	−2.6	7.24	−2.4	Frevert (unpubl.)

Table 2. D.O. concentrations of the suboxic-oxic transition state and corresponding pe_7 in artificial Kinneret water (TOC $\leqq$ 2 ppm)

D.O. ppm	pe	pH	pe_7	$pe'_{D.O.}$ (pH 7)
.015	3.2	8.62	4.8	10.5
.055	3.2	8.58	4.8	10.0
.102	3.3	8.50	4.8	9.7
.159	3.5	8.41	4.9	9.6
.208	3.7	8.31	5.0	9.6
.302	3.9	8.19	5.1	9.5
.433	4.2	8.01	5.2	9.5
.513	4.3	7.91	5.3	9.5
.617	4.6	7.76	5.3	9.4
.713	4.7	7.64	5.4	9.5
.811	4.9	7.53	5.4	9.4
1.127	5.4	7.16	5.6	9.5
1.678	5.8	6.81	5.6	9.3
1.826	5.9	6.49	5.4	9.0

$\Delta pe/\Delta p[\text{equiv. D.O.}] = 0.426$

7.2 Results and Discussion

In Table 2 results of an experiment with artificial Kinneret water are summarized. They show that pe is only slightly dependent on D.O. concentrations when > 0.01 ppm, and that $pe'_{D.O.}$ in artificial Kinneret water (i.e. not being influenced by sediments) remains constant at $pe'_{D.O.} = 9.5 \pm 0.2$ irrespective of dropping D.O. concentrations ($\leqq$ 2 ppm).

Further, with two sediment-water systems from max. depth the same pe_7 set points have been regulated but in one system (core A) at once after sampling and in the other system (core B) after 1 month of intensive aeration of the overlying water.

The results in Table 3 indicate clearly the pe dependence on D.O. and the electron donator since the pe dependent D.O. concentration response in core B was about 1/10 of the concentration response in core A. As $pe'_{D.O.}$ differs from core B to A about one unit there is evidence that the electron donator was depleted in B by the oxygen bubbling prior to the regulation experiment. This is also confirmed by the differences of pe's at the sediment surface (pH ~ const.) and in the overlying water. The reset intervals (mean duration of one reset action of the controller) have been larger with core A than with core B due to the one- and double-sided regulation mode.

In order to differentiate between pe_{redox} values being significant for the pe levels of certain redox processes we, therefore, have also to consider the release of the electroactive electron donator by the metabolic activity in the system, not only the electron acceptor.

Unfortunately, only few authors have investigated redox system/sensor response relationships which may compete to feedback control experiments. Nevertheless, in Tab. 4 some literature results are summarized; the pe values have been calculated from "Eh measurements" as pe = Eh(mV)/58. These results and our experiments indicate that it should be possible to scale natural redox processes due to the response of an electrochemical sensor (or due to the "bioelectrocenosis").

Table 3. pe/D.O. feedback ratios in sediment-water systems from maximum depth of Lake Kinneret (43 m) at 26±1 °C and pH = 7.00±0.03, no exchange of the overlying waters

Sediment core A, sampled: 11.03.83, one-sided reset action by air injection into the overlying water

pe set point	pe at sed. surf.	Δpe	mean D.O. (ppm)	ΔD.O.	Δpe/Δp [equiv. D.O.]	$pe'_{D.O.}$	reset intervals (hours)
6.8 (init.)	4.9	7.3...6.6	.82	1.1...0.54	2.3	10.8	1.9
5.8	4.2	6.1...5.6	.66	0.92...0.39	1.3	9.9	1.4
4.8	3.1	5.8...4.5	.50	0.72...0.27	1.6	9.0	1.6
3.8	2.8	4.3...3.7	.29	0.38...0.19	2.0	8.2	1.9
2.8	2.2	3.2...2.8	.10	0.11...0.08	2.9	7.7	≪ 1.0
8.8 (final)		6.8...6.6	2.40	3.2...1.6	0.7	10.3	2.9

Sediment core B, sampled: 11.03.83; one-sided reset action by N_2 or air injection into the overlying water

pe set point	pe at sed. surf.	Δpe	mean D.O. (ppm)	ΔD.O.	Δpe/Δp [equiv. D.O.]	$pe'_{D.O.}$	reset intervals (hours)
6.8 (init.)	4.2	6.9...6.3	.09	0.13...0.04	1.2	11.6	1.2
5.8	3.5	5.9...5.4	.06	0.09...0.03	1.1	10.9	0.9
4.8	3.8	5.1...4.4	.04	0.06...0.02	1.5	10.1	0.7
3.8	3.3	4.2...3.6	.03	0.04...0.01	1.0	9.3	0.7
2.8	2.8	3.1...2.6	.03	0.04...0.01	0.8	8.2	0.9
7.3 (final)		7.5...7.2	.50			11.5	

Table 4.

redox process	pe	pH	author
hydrogenase activity E. coli K_{12} culture	< 2.6	7	Wimpenny (15)
$SO_4^{2-} \rightarrow H_2S$ reduction (Huron silty clay loam)	$pe \leqq -3.4$	7	Bailey and Beauchamp (42)
$NO_3^- \rightarrow NO_2^-$ reduction (Huron silty clay loam)	$pe \leqq 3.5$		
D.O. below detection limit (L. Esrom)	$pe \leqq 1.7$	7	Hargrave (43)
Fe(III)→Fe(II) (sediment-water system L. Constance)	3.8–3.1	7	Frevert (1)
Mn(IV)→Mn(II) (sediment-water system L. Constance)	$3.9 < pe < 5.0$	7.1	Ostendorp and Frevert (44)
H_2S-H_2O and H_2S-S_8-H_20 system	$pe \simeq p\varepsilon$	4–10	Boulègue and Michard (26)
degradation kinetics of octadecane and naphtalene in Gulf Coast wetland sediment	$pe = 8.6$ $pe = -3.5$	4.5 7.6	Delaune et al. (45)

8. Conclusions

In summary it is concluded:

- pε (incl. $p\varepsilon_{A/A}$, representing partial equilibria) is the master variable in order to compute redox equilibria or the maximum free enthalpies (max. energy gain) of redox reactions in a closed, but otherwise undefined system.
- Unlike pH, pε cannot operationally be defined in most natural waters neither by an electrode response nor by conventional reference component ($[H_2]$) which will usually be much below any detection limit (whereas 10^{-pH} ranges at $\geqq 10^{-14}$M). The postulate of a predominant redox equilibrium determining the conditions of redox processes in multicomponent systems is theoretically possible but stoichiometrically and kinetically vague.
- pe ($\equiv -\lg a_e$ (sensor)) represents an operational approach to describe redox conditions under stationary states. The redox condition is defined by the response of a sensor which allows the prediction and control of real redox processes; corresponding pe values are evaluated from (feedback control) experiments.

Summary

It is shown, that the pε conception, with pε as the redox-chemical "master variable", is correct but not adequate to predict and control real redox processes in biohydrochemical systems. The pε concept (including the conception of partial equilibria) does

not provide a detectable notion enabling the investigator to experimentally reconfirm conceptually deduced pε values.

In view of the general kinetics of natural electron transfer reactions an operational notion, pe, is suggested in order to define the condition of a stationary (not necessarily equilibrated) redox state in the test solution. Unlike pε, the pe values are independent of the internal redox equilibrium in the test solution (only a stationary state has to be established) but depend on the equilibration between the test solution and an appropriate sensor. The latter provides the possibility to detect pe values experimentally and to identify and control natural redox processes by use of regulation techniques.

Preliminary results of pe feedback control experiments in sediment-water systems from L. Kinneret (Sea of Galilee) indicate that pe defined redox conditions depend not only on the predominant electron acceptor (here the D.O. concentration) but also on the electron donator in the system (here most likely the dissolved and particulate organic matter).

ZUSAMMENFASSUNG

Es wird gezeigt, dass die Konzeption des pε-Wertes als redox-chemische «master variable» in natürlichen Wässern zwar korrekt, aber nicht hinreichend ist, um tatsächliche Redoxumsetzungen bzw. extrazelluläre «Redoxbedingungen» im biohydrochemischen System vorherzusagen oder zu kontrollieren. Das pε-Konzept (auch unter der Annahme partieller Redoxgleichgewichte) liefert keine eindeutige Messvorschrift, um konzeptionell deduzierte pε-Werte im tatsächlichen Einzelfall experimentell zu überprüfen.

Aus der Kinetik natürlicher Elektronentransferreaktionen wird eine operationale Redoxkenngrösse, pe-Wert, für stationäre Redoxzustände (nicht notwendigerweise Gleichgewichte) abgeleitet, die jedoch nicht (wie pε) durch Gleichgewicht zwischen allen Redoxkomponenten einer Messlösung, sondern lediglich durch das Gleichgewicht, das sich zwischen einem geeigneten Sensor und der Messlösung unter stationären Redoxbedingungen einstellt, definiert ist.

Die Bezugnahme auf einen bestimmten Sensor macht pe-Werte messbar und ermöglicht somit (etwa unter Anwendung von Mess- und Regeltechniken mit Rückkopplung) Identifikation und Kontrolle natürlicher Redoxprozesse. Erste Ergebnisse von pe-Regelversuchen in Sediment-Wasser-Systemen des See Genezareths mit gelöstem Sauerstoff als Stellgrösse zeigen, dass pe indizierte Redoxbedingungen nicht allein durch den vorherrschenden Elektronenakzeptor (hier: gelöst. Sauerstoff), sondern gleichfalls vom vorherrschenden Elektronendonator (hier sehr wahrscheinlich gelöster und partikulärer organischer Kohlenstoff) geprägt werden.

RÉSUMÉ

Le concept du pε, variable gouvernant les processus d'oxydoréduction, est correct mais il ne suffit pas pour prévoir et contrôler les processus d'oxydoréduction dans les systèmes biohydrochimiques. Le concept de pε (y compris le concept de l'équilibre partiel) ne fournit pas un cadre conceptuel qui permettrait de reconfirmer expérimentalement les valeurs ainsi déduites.

La notion opérationnelle de pe, dérivée de la cinétique générale des réactions de transfert des électrons, est proposée. Elle permet de définir la condition d'un état d'oxydoréduction stationnaire, mais pas nécessairement équilibré, dans la solution test. Les valeurs du pe, contrairement à celles du pε, sont indépendantes de l'équilibre d'oxydoréduction au sein de la solution test: il suffit d'établir un état stationnaire. Les valeurs du pe dépendent de l'équilibre existant entre la solution test et un détecteur approprié. Celui-ci permet de déterminer expérimentalement les valeurs du pe et d'identifier et de contrôler les processus d'oxydoréduction naturels au moyen de techniques de régulation.

Les premiers résultats d'expériences avec contrôle rétroactif du pe dans les systèmes eau-sédiment du lac Kinneret (lac de Tibériade) indiquent que les conditions d'oxydoréduction ainsi définies ne dépendent pas seulement de l'accepteur d'électrons principal (dans ce cas, l'oxygène dissous) mais aussi du donneur d'électrons (dans ce cas, probablement la matière organique dissoute et particulaire).

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