

Bioelectronics

Some Physicochemical Aspects of Bio-electronic Coordinates



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By József ORSZÁGH (adapted and translated by André Leguerrier)

SUMMARY

Three bioelectronic coordinates, pH, rH_2 and ρ (resistivity) are discussed in relation with the molecular structure of aqueous solutions. In order to clarify a number of inadequacies in the definition of rH_2 (related to Clark's rH-term), this concept is analyzed in terms of electronic activity. A thermodynamical formulation of L-C. Vincent's quantifying number W is proposed.

1 How Bioelectronics Fit In

Bioelectronics is one possible means of quantitatively characterizing an aqueous medium. The relative simplicity of the measures it provides contrasts with the wealth of information that can be learned. Bearing in mind its practical and theoretical limitations, it is a valuable analytical and research tool in a great many fields such as chemistry, biology, medicine, metallurgy and corrosion.

With the state of present-day theoretical knowledge, only bio-electronic measurements taken in aqueous media can be strictly interpreted, although the temptation is great to extend it to non-aqueous media or dispersed systems. Short of outright excluding this possibility, we restrict our study to that of aqueous solutions in which the levels of intermolecular transfer of electrically positive (protons) and negative (electrons) charges can be measured. In addition, the very high ionizing power and electrical polarity of these media facilitate electrostatic interactions and transport phenomena, other components of bioelectronics. This theory's microscopic features of course relate to the structure of aqueous solutions.

Our present-day perception of water at the molecular level consists of a more or less mobile network of electric charges whose structure may contain a large number of « data » in the form of specific configurations of variable stability.

Incapable of providing a microscopic spatial image of these configurations, bioelectronics is likely to define the macroscopic physicochemical conditions for the existence of each type of molecular configuration or polarization. As vital phenomena are sensitive to these conditions, bio-electronic coordinates define a mathematical space in which to locate any biological activity including disease. Thus, thanks to bioelectronics, the concept of *biological terrain* (diathesis) becomes strictly significant.



2 The Nature of Water – Medium of Life

Life as we know it occurs in aqueous media to such an extent that it is no exaggeration to say that every living being is primarily composed of water structured by a series of other substances. In light of its chemical composition, water is related to the mineral kingdom, while its molecular, and especially supramolecular structure makes it a welcome harbour for the exuberance of life. So we can say that water borders on the mineral and the living ¹.

Among the thousands of known liquids, water has particularities which fall into a distinct category. Even if we disregard the fact that vital phenomena are closely linked to water, it presents physicochemical anomalies ², when compared to other known liquids, such as abnormal fluctuations in density with respect to temperature or in viscosity with respect to pressure, or the boiling and freezing points too high given the molecular weight, or the lowering of the melting point under pressure, or behaviours in a state of supercooling and superheating, surface tension too high, etc. Add to this the fact that water can act both as an acid or base and as a reducing or oxidizing agent, can be insulating or electrically conductive depending on the experimental conditions.

All these properties result from its molecular structure, most especially its high density cohesive energy due to hydrogen bonds ³.

In the water molecule, the oxygen atom is bonded to two hydrogen atoms by polarized covalent bonds. The molecule's eight valence electrons (two from hydrogen atoms and six from the oxygen atom) are distributed around the oxygen nucleus into four electron pairs, two of which are involved in oxygen-hydrogen linkages, while the other two are on nonbonding molecular orbitals. The four electron pairs repel each other, and according to Gillespie's theory ⁴, they form a regular tetrahedron centered on the oxygen atom. On two tetrahedron vertices are found the two hydrogen atoms: the other two vertices with two pairs of nonbonding electrons become privileged places for positive electrical charges from outside of the molecule. Isolated from others, the water molecule appears as a symmetrical V-shaped atomic formation whose apex is occupied by the oxygen atom.

The two O-H bonds form an angle of 105°. The uneven distribution of electron density due to oxygen's higher electro-negativity causes oxygen, with its two pairs of nonbonding electrons carries a partial negative electrical charge, while the two hydrogens are positively charged. Thus, each water molecule is a tiny electric dipole that will tend to align itself in an external electric field, which explains its very high dielectric constant (approx. 80). However, given the spatial distribution of charges in the case of the water molecule, it is more correct to speak of tetrahedral quadrupole.

When two water molecules are in close proximity, they preferentially place themselves with opposing electric charges. The first oxygen molecule's nonbonding electronic orbital will attract the partial positive charge of one of the hydrogens from the second molecule. This hydrogen atom will then place itself on the axis that links the two molecules' oxygen atoms, a little closer to « its oxygen », while remaining connected to the other. Thus formed, the *hydrogen bond* mobilizes energy of about 20 kilojoules per mole. At room temperature this energy is greater than the energy

¹ André Faussurier, *Triades*, winter 1976, p.187-195

² C. Auten Abgell, *Les anomalies de l'eau (Water Anomalies)*. La Recherche, n°133, May 1982
also read : D.V. Luu et C. Luu, *Sciences du Vivant*, vol.3, p. 90-139 (1991)

³ Y. Maréchal, *La liaison d'hydrogène (The Hydrogen Bond)*. La Recherche, n°209, April 1989

⁴ J. Gillespie, *L'actualité chimique*. n°4, p.27 (1973)



of thermal agitation. As a result, such linked water molecules have many chances of staying together despite the thermal agitation which tends to disperse them.

In liquid water, each molecule is engaged in one to four hydrogen bonds. This more or less loosely bonded network of hydrogen bonds formally appears as a crosslinked polymeric structure, while retaining a degree of mobility by rotation about the bonds, and by the constant breaks and reforming of hydrogen bonds that are successively made and unmade between neighbouring molecules. Through the hydrogen bonds, water is so far the known liquid medium whose cohesive energy density is highest: 2440 joules per cm³ or 24.4 kilobars. By comparison, most liquids have a density of cohesive energy between 2 and 6 kbar ⁵.

But back to quadrupolar molecules with which one can construct an infinitely large variety of spatial structures like a huge molecular scale puzzle. It is easy to show that three neighbouring molecules can place themselves in three different positions, each with respect to the other two. The addition of a fourth molecule increases to 48 the number of potential spatial combinations, and so on. In the absence of other types of molecules (solutes) and an external electromagnetic field, water molecules form clusters whose internal configuration and size are determined by the balance between the structuring power of hydrogen bonds and the scattering power of thermal agitation. The higher the temperature, the more the cluster size decreases and vice versa ⁶.

The introduction of a foreign molecule, whatever its nature, causes a dramatic disruption of this configuration. The random nature gives way to ordered structures induced by the molecule introduced (dissolved). At the macroscopic level, this fact leads to negative entropy and volume dissolution ⁷. In the case of electrolyte solutions, this phenomenon is what is called *electrostriction* by electrochemists. The solute (the dissolved molecule) is immediately surrounded by a number of water molecules which remain attached and form the solvation layer or ring (hydration). Thanks to the water molecules' polar nature, the energy released by the formation of this layer is greater than the energy needed to break up the solid solute's array, even if it is an ionic array, hence water's quite exceptional solvent power.

The solute's solvation shell or eventual electric field in turn induces molecular rearrangements in water, whose quadrupole character ensures the rapid spread of electric signals, even over a great distance. Because of this property – quantitatively characterized by bioelectronics – any solute, even at very weak concentration, induces a residual structure due to the stability of hydrogen bonds, a structure that can be considered the solute's « digital footprint ». This persistence is responsible for many unexpected properties of very dilute aqueous solutions ⁸. Without it, water could not support life.

3 Bioelectronics at the Molecular Scale

a) Proton exchanges

Hydrogen (or more precisely its nucleus: the proton) engaged in a hydrogen bond is « shared » unequally between two water molecules ⁹. This positively charged proton which we designate by

⁵ J.H. Hildebrand, J.M. Prausnitz, & R.L. Scott, *Regular and Related Solutions*. Van Nostrand (1970)

⁶ J-P. Hansen, I.R. McDonald, *Theory of Simple Liquids*. Academic Press, (1976)

⁷ G.A. Krestov, *Thermodynamics of Solvation*. p. 98, Ellis Horwood Ltd., (1991)

⁸ J. Livage, *Approche théorique globale de l'interaction soluté – solvant (Global Theoretical Approach to solute-solvent interactions)*, in « L'eau, vecteur d'information ». Colloque à Lyon-Charbonnières, 9-10 December 1988

⁹ R. P. Bell, *The Proton in Chemistry*. Meuthen, Londres, (1961)



the symbol H^+ , can leave its original molecule and join the neighbouring molecule by sliding along the hydrogen bond. This tiny movement of a few tenths of Angstroms ($1 \text{ \AA} = 10^{-10} \text{ m}$) creates a new situation that can be written schematically as follows:



This is a typical case of «small cause - big effect» because from two neighbouring water molecules, through a tiny displacement, is formed an ion pair – a hydronium ion H_3O^+ and a hydroxide ion OH^- - which in turn hydrolyse ¹⁰, and their electric field induces new structures. This phenomenon of proton transfer is spontaneous even in pure water where, at room temperature, it affects on average one molecule in two billion. Despite its seemingly marginal character, this transfer occurs experimentally by electrical conductivity ¹¹ and the creation of a measurable potential. But the biggest impact is the restructuring of pseudo-polymeric clusters due to the electrostatic fields of the ions formed.

The proton exchange can occur in reverse: when a hydronium ion encounters a hydroxide ion, there is neutralization of electric charges and formation of two water molecules. In fact, there are as many proton transfers in the sense of formation of H_3O^+ and OH^- as there are in the sense of their neutralization ¹². These transfers are in a dynamic balance, and ensure a constant concentration of ions in water. The dynamic balance between formation and neutralization of these ions leads to another: the balance between the pseudo-polymeric clusters of different size, shape and geometry. These forms are ephemeral in space, but remarkably constant over time. They move and are transformed into one another like the ripples from a wheat field in the wind. In living beings (intracellular water), outside thermodynamic balance ¹³, the binding of these structures in space requires a constant energy supply. In this sense, intracellular water forms very pronounced dissipative structures. Outside of living matter, at isothermal equilibrium and supramolecular scale, the aqueous medium may be likened to a micro-adiabatic system. The conservation of the entropy is only possible as long as the volume of each type of configuration is *quantitatively* maintained. This fact is reflected by the constant ratio of different O-H lines (vertices) in the spectra of Raman laser. This ratio obviously varies with temperature, and the solutes' nature and concentration. For example, an acid capable of providing protons to water increases the concentration of hydronium ions. It obviously entails a decrease in the concentration of hydroxide ions in the same proportion as the quantity of anions (negative ions) released by the acid having lost protons; all solvent-solute to remain electrically neutral. The resulting molecular restructuring induces a higher electrical potential at a metal conductor immersed in the solution. That is what the experimenter measures when he acidifies an aqueous solution.

Like water, the molecules of other bodies may possess nonbonding electron pairs: this is the case of HN_3 (ammonia) for example. These pairs have a tendency to bind a proton when contacted with water. They produce OH^- hydroxide ions in excess. The increase in hydroxide ion concentration restructures water to cause a decrease in the solution's electrical potential. We observe this phenomenon when making a solution more alkaline.

¹⁰ H.L. Clever, *The Hydrated Hydronium Ion*. J. Chem. Education, vol.40, p.637 (1963)

¹¹ A. Iverson, *J.Phys.Chem.*, vol.68, p.515 (1964)

¹² The reaction between these 2 ions is precisely called « acido-basic neutralization ».

¹³ F.A. Popp, *Sciences du Vivant*, vol.3, p.145 (1991)



When there is proton exchange between solutes and water, the electric fields of the ions formed cause a restructuring of the entire solution at the molecular level. This re-structuring is reflected among others by the variations in measured electrical potential ¹⁴.

An acidic or alkaline solution's water (solvent) does not have the same microscopic characteristics as pure water. In an acidic solution, the triangular-base pyramid-shaped H₃O⁺ ions induce compact structures in the solution's cybotactic region ¹⁵. In a basic solution, a fragmented structure of water molecules is formed around the OH⁻ ions, retaining a certain mobility where one of the consequences is the lowering of the cohesive energy density and of the surface tension.

In summary, the first bio-electronic coordinate – the pH – represents a measure of proton exchange levels between water and solutes, and globally quantifies these phenomena.

b) Electronic exchanges

Under certain conditions, neighbouring water molecules can exchange electrons. One or more electrons lost or gained destabilize the molecule. In fact, we must transfer two electron pairs to dismantle two water molecules and generate two hydrogen H₂ molecules and an oxygen O₂ molecule



The resulting overall reaction is none other than the electrolysis of water. When this occurs without an electric field or other external influence, we speak of *self-electrolysis*. This phenomenon, while providing start-up for other electron transfers, is quite marginal at room temperature. Thermodynamic calculations show that under such conditions, there is, on average, one molecule of hydrogen per twenty thousand litres of water, formed spontaneously. Thus, the level of electronic exchanges by self-electrolysis is virtually zero in pure water. It is nonetheless true that *tiny electron exchanges have well measurable impacts on the solution's potential*. A reducer will, upon dissolution, tend to « enrich » water with electrons. Water readily accepts these additional charges which are distributed among a large number of molecules. The structural consequences of this input are difficult to analyze because when the reducer is dissolved, the electrolytic dissociation generates cations that are often acid, following the Lewis structure. In these cases, it is thus virtually impossible to isolate the electron exchanges and proton exchanges, making it difficult to interpret the thermodynamic quantities of dissolution ¹⁶, although correlations of these quantities with rH₂ still await systematic studies to clarify our vision. Yet one datum is acquired: *the addition of electrons to water has the effect of reducing the potential of the solution*.

This shows that the electric potential and the intramolecular structure are essentially determined by the number of H⁺ protons and e⁻ electrons exchanged with dissolved substances. The first is expressed by means of the bio-electronic variable pH, the second being the variable rH₂.

¹⁴ In the present case, we did not consider the existence of *electron* exchanges with water. There is therefore no redox reaction, only an acid-base reaction. Contrary to established and largely diffused viewpoints, the variation in a solution's electric potential thus *has no bearing whatsoever with any so called modification of a solution's redox state*. To eliminate this false notion about a solution's potential, we must insist on the fact that the *measured redox potential does not characterize the redox state*.

¹⁵ This sensible term was introduced by J. Kosower, in *Physical Organic Chemistry*, p.284 John Wiley, (1968)

¹⁶ G.A. Krestov, *Thermodynamics of Solvation*. p.229, Ellis Horwood Ltd., (1991)

c) Transport phenomena

The third bio-electronic coordinate, electrical resistivity ρ (pronounced ro) is no longer an equilibrium size as the first two. Its reciprocal value, conductivity κ (pronounced kappa) expresses the ease with which an electrical current can flow through the aqueous medium. This current is either carried by moving electric charges (ions in solution) or by cascading intermolecular charge transfer (as per the Grotthuss mechanism). The resistivity thus depends on the concentration (ionic strength) of the species present and their mobility. The latter depends on the size of the ions (Stokes-Einstein law) and the structure of their solvation shell, which in turn depends on the pH and rH_2 .

Outside the equilibrium position, the chemical reactions of charge transfer (including those that occur in the living environment) are facilitated by the ionic strength increase as measured overall by the resistivity.

4 The Bio-electronic Coordinates

There are three bio-electronic coordinates: acidity-alkalinity or pH; oxidation-reduction (redox) or rH_2 and electric resistivity designated by the symbol ρ . Our intention is *not* to describe in detail the concepts widely known and well described in general works ¹⁷, but to draw attention to some of their lesser known properties.

The first point concerns the concept of *concentration* which is widely used in chemistry to characterize the composition of the system. This concept is often encountered in the physicochemical relationships where it is used instead of the *thermodynamic activities*. Thus the pH is usually defined as the logarithm of the reciprocal of the « hydronium ion concentration (or hydroxonium) »:

$$pH = \log \frac{1}{[H_3O^+]} \quad (3)$$

Strictly speaking, $[H_3O^+]$ is *not a concentration*, but a *thermodynamic activity*, a dimensionless number. The numerical value of the activity is equal to the concentration if the solution is « ideal » ¹⁷. An aqueous solution containing electrolytes (acids, bases, salts, oxidants, reducers) is never ideal, even at low concentrations due to electrostatic interactions. To consider the activity as a concentration is a simplification of writing probably introduced for educational reasons. This has no impact when it comes to pH, because in the case of hydronium, ion concentration barely differs from the activities ¹⁸. That is not the case for rH_2 whose concept, contrary to widespread use, can in no way be linked to a « hydrogen concentration » or worse, to a « hydrogen pressure » ¹⁹. The strict definition of rH_2 is related to hydrogen's thermodynamic activity which we designate by the symbol $[H_2]$ never to be confused with a concentration:

$$rH_2 = \log \frac{1}{[H_2]} \quad (4)$$

¹⁷ P.W. Atkins, *Physical Chemistry*, 3rd edition, Oxford Univ. Press, (1989)

¹⁸ R.G. Bates, *Determination of pH*. John Wiley (1973)

¹⁹ The totally inadmissible equality $[H_2] = P_{H_2}$ is explicitly detailed in countless and excellent works : Among these, see : D.R. Crow, *Principles and Applications of Electrochemistry*, Chapman & Hall, 2nd edition, p. 102 (1979)



where the term $[H_2]$ is a *thermodynamic activity* related to the amount of electrons exchanged between the solutes and water ²⁰ likely to shift the self-electrolytic balance. The rH introduced by Clark in 1920 was linked to a « hydrogen pressure » that does not exist in aqueous solutions. This conceptual error led to the rejection by the scientific world of this very convenient concept, and despite subsequent works by Vles, Déribéré, Huyberchts ²¹ and Vincent - father of bioelectronics - and many other researchers, the notion of rH₂ is struggling to establish itself as a *concept equivalent and complementary to pH*.

The second point concerns the highly controversial correlation between pH, rH₂ and the potential redox E. Mathematically, this correlation is written (at 25° C):

$$rH_2 = 33,8 E + 2 pH \quad (5)$$

where E is expressed in Volts. There are in fact only two independent variables: the rH₂ and pH. *The redox potential E is an experimental quantity whose numerical value is determined by both the protonation (pH) and electronification (rH₂) of the solution*, hence the ambiguity about redox potential measurements. The fact that you can or cannot experimentally change the pH without changing the rH₂ or vice versa, does not alter the conceptually independent natures of these two quantities: the first relates to the exchange of protons, the second to electron exchanges. Some acids or bases are virtually *indifferent* from a redox perspective, whereas some redox systems are *neutral* from an acid-base perspective. Yet, there are many bodies which affect both water's pH and rH₂.

In the same vein, one of the common objections raised against the use of rH₂ is that the pH and potential E are experimental quantities, while rH₂ is the « linear combination of these two quantities ». According to this objection, rH₂ would be an « empirical variable », without theoretical interest. In fact the pH (as well as the potential E) is determined by measuring a difference potential between two electrodes and is *calculated* from this experimental measurement. The pH is directly proportional to the difference potential measured between a reference electrode and a glass electrode ²² that is sensitive to the presence of hydronium ions ; the redox potential E is the difference in potential between the standard electrode and a hydrogen platinum (or gold) electrode immersed in the solution studied. From these two difference potentials, we calculate the pH and rH₂. Moreover, this calculation is executed by the measuring instrument's microprocessor. In this sense, rH₂ is no more « empirical » than the pH, and they are complementary in disambiguating the redox potential. It remains nonetheless true that the redox potential

$$E = \frac{1}{33,8} (rH_2 - 2pH) \quad (6)$$

is proportional to the free enthalpy (i.e. Gibbs energy) of the reaction that can take place between the redox system studied and the redox system of reference: H₃O⁺/H₂. Being the « motor » of any physicochemical transformation, this free enthalpy is therefore the sum of the two terms (taking into account the algebraic sign): one depends on the solution's rH₂, the other on its pH. Thus, if we disregard the rH₂, we are faced with an inability to interpret the influence of pH on redox reactions whenever the activity of hydronium H₃O⁺/ ions doesn't appear explicitly in the expression

²⁰ J. Országh, *Sciences du Vivant*, vol.1, p.23-34 (1990)

²¹ M. Huybrechts, *Le pH et sa mesure, les potentiels d'oxydo-réduction, le rH*. Ed. Masson, (1939)

²² G. Eisenman, *Glass Electrodes for Hydrogen and their Cations*. Ed. Arnold, Londres (1967)

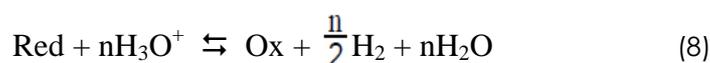
of the equilibrium constant. In this sense, the rigorous study of incomplete redox systems ²³ is one of the fundamental contributions of bioelectronics in the field of electrochemistry.

The third point concerns the reference system of acid-base and oxidation-reduction reactions. Beside the well-known concept of acid-base *neutrality* in aqueous solutions, the concept of *redox indifference* ²⁴ was introduced thanks to the notion of rH_2 . An aqueous solution is indifferent when, at 25°C, its rH_2 is equal to 27.6. This corresponds to chemically pure water whose $pH = 7$. According to this view, the reference system of these two types of reactions is water that naturally contains the acid-base couple H_3O^+/OH^- and the H_3O^+/H_2 redox couple. Choosing the hydrogen electrode for point zero on the potential scale flows logically from this reference system based on the notion of active solvent, whereas in the classic description of redox systems, the choice of this reference electrode appears to be quite arbitrary.

« Nernstian » reasoning ²⁵ leads to deny the existence of the couple H_3O^+/H_2 in pure water, by asserting that hydrogen « concentrations » corresponding to $rH_2 = 28$, for example, « have no physical significance »" since the amount of molecular hydrogen produced by the equilibrium displacement of water's self-electrolytic reaction can in no way determine the potential of a platinum electrode ²⁶. In fact, in aqueous solutions, especially dilute ones, the electrode is essentially in contact with water and very little with the solutes. The mechanism by which the electrochemical double layer is formed, thus determining the potential, is not well known. The generally accepted theories are based on the existence of a solution layer chemisorbed on the electrode. Although theoretical investigations do not appear to have been made in this sense, one could also admit the idea by which the potential is generated by electric charges that the water exchanges with the solutes. Such a hypothesis is as equally plausible as the double layer theory, especially in very dilute solutions. Admitting this hypothesis which is in fact experimentally well verified, the potential of an inert electrode immersed in *any aqueous solution* depends only on the activities $[H_3O^+]$ and $[H_2]$ of the following relationship

$$E = \frac{RT}{2F} \ln \frac{[H_3O^+]^2}{[H_2]} \quad (7)$$

where the activity of hydrogen $[H_2]$ is related to the amount of electrons exchanged between the solutes and water as per the following reaction



This is another way of saying that the potential of any redox couple is measured against the couple H_3O^+/H_2 whose standard reduction potential is zero, by convention. We therefore remain consistent with existing conventions concerning the potential scale, giving it more consistent and less arbitrary content.

The balance of the reaction (8) is generally shifted to the left, especially for an incomplete redox system by only involving the oxidized form. Yet it remains that any change in solute concentration, whether oxidizing or reducing leads to a quite measurable potential variation ²⁷ according to the

²³ J. Országh, *Sciences du vivant*, vol.2, p.81-97 (1991)

²⁴ Voir Réf. 20, ainsi que M. Déribéré, *Les applications industrielles du rH*. 2^d édition, Dunod, (1949)

²⁵ J. O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol.2, Plenum, New York, p.906-907 (1977)

²⁶ This denies the experimental fact that anyone can take measurements of water with a simple galvanometer.

²⁷ In the absence of solvent – solute reactions, as suggested by rH_2 detractors at constant pH , the potential should also

rH₂ theory of incomplete systems. Arguing on the absence of reactions between the redox solutes and water is equivalent to ignoring this experimental fact, whereas by measuring the rH₂ of incomplete redox systems, we can determine the *true* responsiveness of redox couples that don't react according to forecasts that have been based on the accepted values of standard reduction potentials²³. This is another fundamental consequence of bioelectronics.

The third bio-electronic coordinate, electrical resistivity ρ , poses no conceptual problem. However, given the Arrhenius theory of electrolytic dissociation²⁸, it would have been wiser to choose the electrical conductivity as coordinate, the reciprocal of resistivity. The conductivity is directly proportional to the concentration of charge carriers (ionic strength and mobility) of the solution. Thus in very dilute solutions, a small change in concentration leads to excessive variations in the value of ρ . These variations are not like those which arise at the molecular level in solution. It would therefore be wiser to use the conductivity.

$$\kappa = \frac{1}{\rho}$$

or even the equivalent conductivity to characterize electrolyte solutions.

Moreover, within certain limits²⁹, conductivity is proportional to the hydrotimetric hardness and osmotic pressure. In addition, virtually all marketed laboratory devices display conductivity (in microSiemens/cm [$\mu\text{S}/\text{cm}$]) or concentrations (salinity), and not the resistivity.

5 The L-C. Vincent Quantization

Using bio-electronic coordinates, L-C. Vincent put forth a calculation method to measure the energy level «stored» in an organism with respect to the energy that is «eliminated» from it. To do so, he applied classical electricity to potential redox and to a living medium's resistivity.

We can attempt a thermodynamic analysis of the LC Vincent quantization value W .

All redox systems can be diagrammed using a battery consisting of a normal hydrogen electrode, with an electrode in solution containing the redox system studied. This battery's electromotive force (or free enthalpy (i.e. Gibbs) to a constant) is obviously equal to the potential E . By convention, we can put forth that an inert electrode $s = 1 \text{ cm}^2$ is immersed in a ratio of 1 cm^3 of this electrolyte having a resistivity of ρ . The maximum power W of this battery will therefore be

$$W = k \frac{E^2}{\rho} \quad (9)$$

where k is a constant which's numerical value equals $1 \text{ cm}^2/\text{cm}$. If E is expressed in millivolts and ρ in ohm.cm, you get W in microwatts (μW). In fact this constant is the ratio of surface s of the electrode and the distance l traveled by the current through the battery:

remain constant within the concentrations' wider limits. This is absolutely not the case confirmed by laboratory observations.

²⁸ D.R. Crow, *Principles and Applications of Electrochemistry*, Chapman & Hall, 2nd edition, p.102 (1979)

²⁹ J. Rodier, *L'analyse de l'eau*, Dunod, (1978)

$$k = s/\ell$$

The W term expresses the maximum speed of dissipation of energy by a chemical or biochemical charge transfer in the broadest sense of that term, since the potential E depends on both pH and the middle rH_2 .

Taking into account the bio-electronic coordinates and the fact that $k = 1 \text{ cm}^2/\text{cm}$ by convention, we can calculate W using the practical relationship:

$$W = A \frac{(rH_2 - 2pH)^2}{\rho} \quad (10)$$

where A is a constant with a numerical value of 875 at 25°C. Constant A increases proportionately to the square of the absolute temperature:

$$A = \left(\frac{RT}{2F} \ln 10 \right)^2 = \left(\frac{8,314 \times 298}{2 \times 96500} \ln 10 \right)^2 = 8,75 \cdot 10^{-4}$$

whereas $A = 875$, if we wish to express W in microwatts. At 37°C (or 310 °K), $A = 946$. Before comparing the W values published by various authors, it is best to adjust the calculations to the same reference temperature.

The power of W is thus higher as the system is more oxidizing (high rH_2), more acidic (lower pH) and loaded with mineral salts (weak ρ). In living systems, W increases proportionately to T^2 , thus quantifying the impact of fever on redox and acid-base reactions. In this case, the chemical energy contained in the fluids of the living is dissipated at a faster speed.

Since the term ρ appears in the expression of W , this becomes a variable measuring a state of electrochemical potentiality to dissipate energy, and not to characterize the state of thermodynamic equilibrium. A W difference between two electrolytic media that are in contact becomes a factor of kinetic energy intake necessary to maintain the given structure that could be dissipative or macroscopic.

6 A Few Experimental Aspects

With bio-electronic measurements, we touch one of the portals between knowledge of the phenomena described by laws of classical thermodynamics (including irreversible phenomena) and that of the more subtle phenomena governing the maintenance and flow of life in matter. On first approach, these portals lead on to random phenomena that are difficult to interpret. For example, something as commonplace as the pH holds its own surprises when it is measured in rainwater ³⁰ or seawater over a period of time ³¹.

When measuring rH_2 , ones fully enters a field of research that lies outside the main pathways of experimental research. It would be fascinating to analyze the subjective and objective reasons this field was abandoned. The difficulty in reproducing redox potential measurements probably

³⁰ S.Y. Tyree, *Rainwater Acidity Measurement Problems*, in *Atmospheric Environment*, vol.5, p.57-60, Pergamon Press Ltd. (1981)

³¹ J. Rousseau, *Sciences du Vivant*, vol.1, p.55-93 (1990)



explains why the extension of bioelectronics has been hampered. It is undeniable that the significant measurement of rH_2 , requires a certain experimental tact with most devices designed up to now, despite its apparent simplicity ³².

The source of some gross mistakes lies in the sometimes rough surface conditions of the redox electrodes used, determined by the history of each electrode. Proper depolarization is a measurement's key to success. Fortunately, all technical requirements are present for a real breakthrough in the development and manufacture of reliable user-friendly bio-electronimeters, even for non-specialized experimenters. The greatest obstacle seems to be the disregard or rejection of the rH_2 notion by most scientists. The development of a triple combined electrode²⁰ with automatic temperature compensation, connected to a compact measuring instrument that displays the bio-electronic coordinates would greatly facilitate the acquisition of data that could be used and analyzed by appropriate computer software.

Recent advances in the manufacture of redox electrodes have now removed the obstacles on the reproducibility of rH_2 measurements.

Given its sensitivity, especially because of rH_2 measurements, bioelectronics is an interesting experimental tool, notably to study the influence of electromagnetic or hydrodynamic factors (turbulence and flow potentials ³³) that don't affect the chemical composition of water, and thus escape conventional analytical methods.

7 Limitations of Bioelectronics

Bio-electronic coordinates only give a *global* measure of the « biological terrain » (called diathesis: the body's constitutional predisposition to certain maladies). Where the chemical composition of the system studied is globally known, a brief bio-electronic study provides an excellent basis for comparison, such as for drinking water, where good coordinates constitute the necessary condition to potability, but they are not a substitute for a chemical and microbiological analysis.

The medical applications fit well in all the techniques of diagnosis and monitoring of changes in the evolution of conditions of sickness.

From simple, fast and above all inexpensive measurements, the practitioner can learn a lot of very useful information for his healing arts.

Bio-electronic measurements can obviously not replace a chemical analysis when one needs to know the composition of the studied system. Very different solutions may have the same bio-electronic coordinates. On the other hand, for a type of given solution (blood, urine, saliva, etc.), bio-electronic coordinates always reveal any significant change.

The usefulness and possibilities of this technique were already recognized more than thirty years ago, although it has had as of yet limited expansion. Professor Pourbaix ³⁴ spoke thus in his letter of 20 May 1957 addressed to Louis-Claude Vincent, the father of bioelectronics: « *It seems to me that*

³² Comment from the author (2013-04-06) : With current electrodes and apparatus, measurements are much easier.

³³ These potentials are measured in the famous « baignoire de Jeanne Rousseau », but also in many springs and rivers that are reputed for their therapeutic virtues.

³⁴ Former professor at the Université Libre de Bruxelles and Secretary General of the *Comité International de Thermodynamique et de Cinétique Electrochimique*. He was a recognized scholar in the field of modern electrochemistry: he invented the E – pH diagrams that bears his name, on corrosion of metals, well known by specialists.



a systematic study of areas of electrode tension pH or rH_2 - pH stability of various substances in living nature, as well as areas of life or existence of microbes, viruses and hormones would be at this point of view of an absolutely vital interest, it being understood that such determinations need to be done, partly by considerations of balance, and partly by experimental kinetic considerations. » Is not this a beautiful definition of bioelectronics? Pourbaix continues his letter by saying: « A final word regarding the issue of nomenclature. You speak of rH_2 : I assume that this is what we call in Belgium rH where rH is defined by the relation $= - \log H_2$? Is this really the meaning you give to rH_2 ? I tell you right away that I prefer your symbol rH_2 to our symbol rH . » In the famous so-called Pourbaix diagrams on the corrosion of metals, there are quite many oblique lines E - pH, which are placed in rH_2 constant.