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Self-Electrified Water is a Powerful Toolbox for the Production of Chemicals and Energy

Fernando Galembeck, *[*,a,b] ***Leandra P. Santos,*** [b] ***Thiago A. L. Burgo*** [c] ***and Andre Galembeck*** [d]

[a] *Instituto de Química, Universidade de Campinas, 13083-872 Campinas-SP, Brazil*

[b] *Galembetech Consultores e Tecnologia, 13080-661 Campinas-SP, Brazil*

[c] *Departamento de Química e Ciências Ambientais, Universidade Estadual Paulista (Unesp), 15054-000 São José do Rio Preto-SP, Brazil*

[d] *Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50740-560 Recife-PE, Brazil*

Three groups of unexpected experimental findings were published in the past twenty years in different research areas, opposing current paradigms, and supporting the following statements: (*i*) water is becoming the ideal medium for chemical synthesis; (*ii*) water is an electrifying agent of most materials; (*iii*) macroscopic matter is formed by charge mosaics that are often the outcomes of surface processes at the aqueous interfaces. These statements provoke major changes in chemical thinking that have a common feature: the behavior of chemicals in aqueous electrified interfaces may largely differ from their behavior in bulk and theoretical predictions. This review discusses eight widely accepted statements familiar to chemists, students, professors, and teachers, but challenged by many experimental findings obtained in systems having aqueous interfaces. A broader statement that is being used in this context is that the thermodynamic properties of ionic species change depending on the local electric potential, modifying their reactivity, mass transfer, and other properties. Beyond synthetic applications, atmospheric moisture is becoming a promising source of electricity. These new views create huge opportunities for chemical research and development, based on the most abundant and environmentally compatible chemical. Aqueous interfaces are thus a powerful toolbox for building a sustainable economy.

Keywords: self-electrification, interfaces, contact charging, Maxwell-Wagner-Sillars effect, “on-water” reactions

1. Introduction

Safety and sustainability concerns provoke deep changes in chemical practice, restricting the use of many substances and processes, and increasing the running costs of laboratories and plants. This situation is faced by increasing R&D (Research and Development) activity whose successful outcomes are quickly incorporated into the goods required to improve the quality of life of billions of humans.

The contribution to decarbonization[1] and the independence from non-sustainable raw materials are now decisive for the adoption of a new product or process, as much as its technical and economic viability. Processes that do not require high temperatures or pressure to transform abundant and inexpensive raw materials, producing valuable chemicals and minimal amounts of waste are in high demand, fueling the adoption of biotechnology processes.

A new fact is the growing number of surprising water-based processes that are appearing in the literature under various keywords: “on-water” chemistry,[2] droplets,[3-6] hydrovoltaics,[7] hygroelectricity,[8] electro-crystallization,[9] electro-wetting,[10] -condensation, and -adhesion. These findings challenge established experimental guidelines and were not also predicted by theoretical or computational approaches, thus requiring new ideas for their interpretation.[11]

The chemical knowledge expressed in textbooks and the current literature largely refers to single molecules and bulk matter. The myriad interfaces found everywhere are specialized topics treated in colloid and surface science, catalysis, and electrochemistry, but they are

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*e-mail: fernagal@unicamp.br

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In celebration of Professor Oswaldo Luiz Alves’ lifelong dedication to science.

neglected in other disciplines. This situation is supported by the assumption that macroscopic matter is normally electroneutral, stated as the Principle of Electroneutrality.[12]

However, abandoning the idea of electroneutrality is providing new explanations for challenging experimental results.

In this work, we discuss some statements that are currently widely accepted, recognizing their fundamental limitations and negative consequences:

(*i*) Macroscopic matter is electroneutral.
(*ii*) Electrostatic phenomena are not observed under high relative humidity.
(*iii*) The large electric polarization of water is a consequence of the realignment of its large molecular dipoles within a field.
(*iv*) The change in the Gibbs energy calculated from standard thermodynamic tables shows whether a chemical reaction occurs spontaneously and to what extent.
(*v*) The chemical properties of a substance depend only on the molecular energy states given by quantum-mechanical calculations combined with the Boltzmann distribution.
(*vi*) Chemical reactions progress faster when the reagent molecules are within a homogeneous medium where they can move and collide.
(*vii*) Avoiding the catastrophic consequences of metastability in phase transitions is only achieved by heterogeneous nucleation.
(*viii*) The interfacial tensions of the crystal surfaces in the crystallization environment determine crystal habits.

The following sections present new views for each statement, in the same order. Section headings are updated statements, supported by strong recent experimental evidence.

2. Electroneutrality is Seldom Observed in Macroscopic Matter

Electroneutrality[13] appears in scientific literature in different ways and in different contexts. In the IUPAC (International Union of Pure and Applied Chemistry) Gold Book, the definition for the electroneutrality principle is "The principle expresses the fact that all pure substances carry a net charge of zero".[12] Here, the properties of a substance refer to its bulk, with no reference for surface properties. Moreover, the substance is not under the action of any external energy source or field and pure substances are hardly found on Earth's surface.

Pauling's Electroneutrality Principle of molecular structure postulates "that the electron distribution in stable molecules and crystals is such that the electrical charge associated with each atom is close to zero and in all cases less than ±1, in electronic units".[14] This principle was stated for individual molecules but is often unduly extrapolated to bulk multicomponent and multiphase systems.

Another related concept is the electroneutrality approximation[15] introduced by Nernst, discussed by Planck, and widely used in treating chemical equilibria, potential junctions, voltammetry, and other electrochemical dynamic experiments. Its success supported the "electroneutrality law" or "electroneutrality principle" designations frequently found in the literature. However, it also produced paradoxes that led to a critical conclusion by Dickinson *et al.*:[15] "The avoidance of electroneutrality prevents the introduction of troubling paradoxes... more complete physical interpretations are available for simulations without electroneutrality. We expect this useful and insightful but now perhaps superfluous approximation to steadily cease to be a cornerstone of the analysis of coupled diffusion and migration in electrochemistry. … By avoiding its use, wider possibilities may be opened for the future".

Still, electroneutrality seems consistent with the everyday experience of humans because we do not sense environmental electrostatic fields. For instance, the potential gradient at the Earth's surface changes with weather and location, reaching 1 kV *per* meter. However, humans are not equipped with sensors for electric fields analogous to our light, sound, pressure, temperature, and chemical sensors.[16] We do not sense the presence of the growing cloud-to-Earth fields until a thunderstorm sets on, producing light flashes and explosion-like sounds. The previous paragraphs show that electroneutrality should not be expected in the polyphasic and multicomponent matter that makes anything on Earth's surface and beyond.

Direct experimental evidence showing charge mosaics in dielectrics and metal surfaces has been obtained since the late 1990s. Electric mapping techniques derived from atomic force microscopy (AFM), like Kelvin force microscopy (KFM), associated with electron spectroscopy imaging in transmission electron microscopes (ESI-TEM), allowed the chemical identification of surface charge in polymer latex films[17] (Figure 1). Macroscopic practical Kelvin electrodes also contributed, showing macroscopic mosaics in dielectrics.[18]

Most importantly, electroneutrality is implicit in the majority of current chemical literature, in textbooks of all disciplines and review articles published by distinguished authors in prestigious journals. As an example, an outstanding review[19] on molecular reactions at aqueous interfaces covers more than 260 references but it does not discuss excess charge at interfaces, although it pays

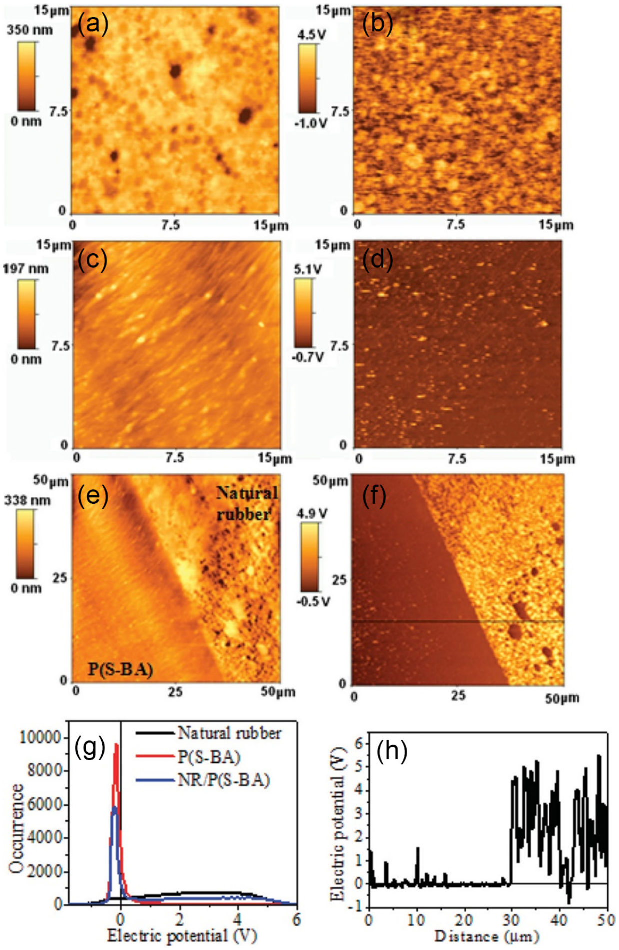

Figure 1. Electric potential mosaics on the cut surfaces of films cast from natural rubber (NR) and polystyrene (PS). Topography (a, c, e) and electric potential images (b, d, f) of the cast surface of the natural rubber film (a, b) and poly (styrene-butyl acrylate) P(S-BA) film (c, d). Topography and electric potential images (e, f) of the interface between NR and P(S-BA) films that were cast separately. Histograms (g) are shown for all electric potential images. Line profile (h) of the cut surface of the interface of NR and P(S-BA) films, which were dried separately and juxtaposed (figure from reference 17 with permission from American Chemical Society, Copyright 2024).

attention to interfacial thermodynamics and solvation. Nevertheless, the Concluding Remarks contain the phrase "In this regard, it is definitely essential to clarify and quantify the effect of dangling -OH groups and surface electrostatic potentials…".[19] The present review shows that surface electrostatic potential and interfacial electrification of bulk matter are theoretically expected and experimentally verified, causing impressive effects on chemical reactivity and other relevant chemical phenomena.

3. High Humidity has a Dual Role in Electrostatic Charging

There has been great debate on the agents of electrostatic charging: electrons, ions or mass transfer. Electrons prevail in metals and semiconductors, but ions and material fragments are the main agents in soft matter and liquid/liquid junctions. Electrons have also been considered in liquid-solid interfaces.[20-22] Electrostatic charging is often observed under dry air, and humidity is generally considered to oppose static electrification. Schrodinger's doctoral thesis[23] described charge dissipation from electrified insulators as the result of charge conduction to the ground.

Yet, experimental results from the past two decades show that water is also an active electrifying agent,[8,24] evidenced in the extensive literature on energy harvesting from moist air.[25,26] There is yet no consensus on the mechanism of power production from moisture, but the proposed mechanisms assume charge separation during water adsorption on solid surfaces.[27] Water acquires excess charge in controlled ways and stores it,[28,29] as shown in Figure 2. Charged water shows lower surface tension than neutral water, but bulk properties like viscosity and density are unaltered.[29] This is expected, considering that the charge is located at the surface of water due to Coulomb repulsion, with little or no effect on the bulk liquid.

The same experiments also showed charge transfer at the water-air interface. More recently, that was rigorously verified by measuring the decrease of excess charge in levitated water that could not contact any other liquid or

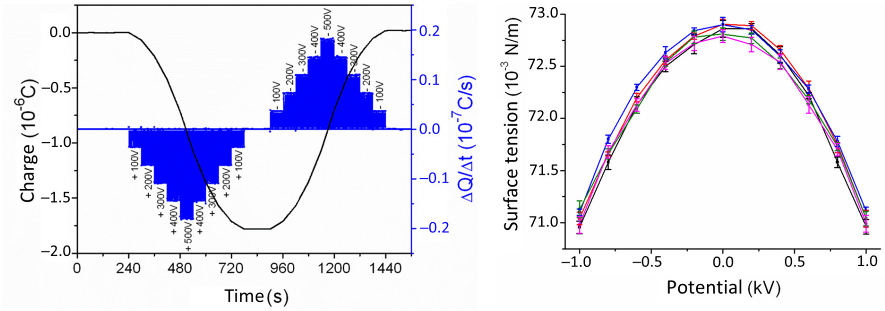

Figure 2. (left) Charge storage in water dropping from a grounded needle that fell through the center of a biased metal ring before reaching a Faraday cup. Water drops did not contact any surface other than the grounded needle and the Faraday cup. The stored charge increases with the potential applied to the needle. (right) Surface tension of water drops hanging from a biased needle (adapted from reference 29).

solid.[20] Then, charge conduction from water to the ground necessarily passes through the air. Yet, charge transfer through the gas phase is still hardly considered in textbooks or scientific literature.

Charged water undergoes shape changes and Coulomb explosion, shown in Figure 3.

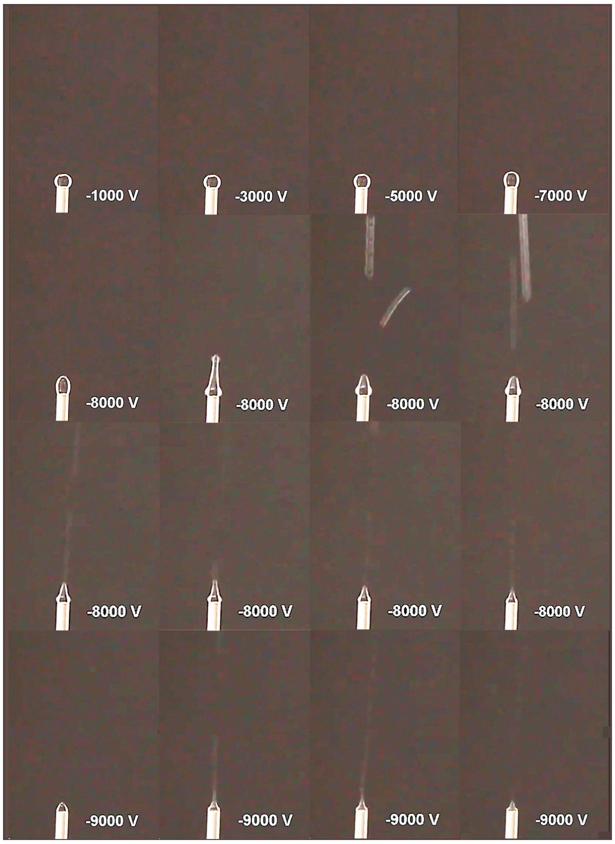

Figure 3. Successive frames extracted from a video showing a water drop sitting on top of a biased steel needle. Increasing the potential elongates the drop until it emits water jets perceived as the faint streaks in some frames. This shows that Coulomb repulsion at the drop surface decreases its surface tension.

Electrification by water phase change has been considered a main contributor to atmospheric electrification and lightning.[30] Again, there is no consensus on the relevant mechanisms, but the laboratory and field observations demonstrate electrification concurrent with water vapor condensation.[31] Thus, water also contributes to charge accumulation, depending on the system under consideration.[32] The ability of water to play opposite roles is certainly a main contributor to the difficulty experienced by many researchers attempting to explain their experimental observations. For example, Figure 4 illustrates the dual roles of water. While charge dissipation is faster under high humidity, playing a unique role under steady-state conditions: low-density polyethylene (LDPE) exhibits a negative equilibrium potential assigned to the strong adsorption of hydroxide ions. The potential is higher under low humidity but it levels off with increasing humidity which causes higher surface conductance. This shows the dual role of water in the electrification of dielectrics.

Applying a voltage to water-containing systems produces dramatic effects, as the polymer electret formation described by Chudleigh,[33] the bubble electrets, and probably the explosions of grain and electrified powders like flour or sugar.

4. High Relative Permittivity and Electric Polarization of Water Depend on Dipole Orientation but also on the Maxwell-Wagner-Sillars Effect and Ion Migration

Applying an electric field to a substance produces a macroscopic dipole moment resulting from dipole orientation, molecular deformation, and ion displacement within the sample. The molar polarization (P) is the total dipole moment *per* mol of the substance under an electric field E. It is calculated using the permittivity given by ε_0 (permittivity of vacuum), ε_r (relative permittivity), and E, the electric field applied, following equation 1. Thus, a bulk solid or liquid having a large relative permittivity also shows high polarization when placed between two

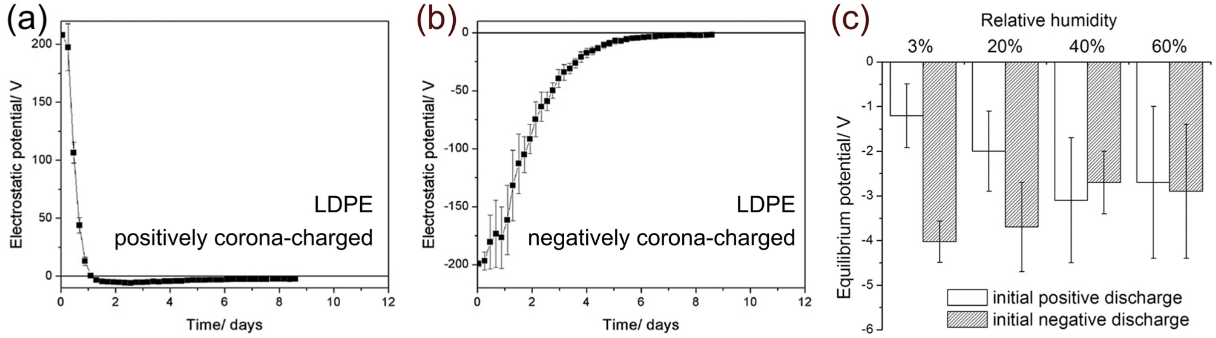

Figure 4. Electric potential decay over time in low-density polyethylene (LDPE) samples: at 60% relative humidity (RH) for (a) positively and (b) negatively corona-charged LDPE. Averaged values with error bars were calculated from 10 measurements. (c) Average equilibrium potential for each LDPE piece as a function of the RH (adapted from reference 32).

electrodes. Table 1 shows relative permittivity for relevant or illustrative chemicals.

$$P = \varepsilon_0 \times \varepsilon_r \times E/(\varepsilon_0 + \varepsilon_r) \quad (1)$$

Table 1 shows accepted values for the relative permittivities and dipole moments of some fluids and solids. The higher values are from substances whose molecules are large dipoles and show self-ionization properties, like water.

Table 1. The relative permittivity (ε_r) and dipole moment (p) for some chemicals and common materials[34]

Substance	ε_r (p / (C m))
Starch	1.7 (2.3)
Ethanol[a]	16.2 (1.66)
Methanol	33.0 (2.87)
Hydrogen cyanide	158 (2.9)
Hydrazine	58.9 (1.8)
Hydrogen fluoride	83.6 (1.83)
PVC powder	1.4
Sulfuric acid[b]	31.0
Sulfuric acid[c]	8.6
Titanium tetrachloride	2.8
Toluene	2.4
Transformer oil	2.1
Water[d]	78.2
Water[e]	10.0

[a]Concentration of 97%; [b]concentration of 17%; [c]concentration of 97%; [d]temperature of 25 °C; [e]temperature of 360 °C. PVC: polyvinyl chloride.

Large dipoles oriented and aligned under a strong field are often presented as the main contributor to water polarization. However, placing water under a field produces the migration of hydronium (H^+) and hydroxide (OH^-) ions around the electrodes, contributing significantly to polarization. Relative permittivity and electrical conductivity measurements typically use 1 kHz AC (alternating current) frequency, when the ion displacement is negligible. The experimental detection of ion motion contribution under lower frequency and the resulting Maxwell-Wagner-Sillars effect are discussed in the next section.

At higher frequencies beyond the microwave range, dipole orientation also ceases to contribute, leaving only the atomic and molecular polarization due to intramolecular charge displacement. Refractive indices (n) at the infrared and visible regions yield the relative permittivity following the Lorenz-Lorenz relationship, $\varepsilon = n^2$. Interestingly, water vapor contribution to the refractive index of air is lower than observed for other common gases, like air, nitrogen, oxygen, argon, and CO_2, showing that separated water molecules are less polarizable than these common gases.[35]

The Stern layer is an important component of the electric double-layer at water-solid and water-liquid interfaces.[36] Its pictorial representations usually show strongly aligned water molecules, neglecting the excess concentration of hydronium (hydroxide) ions adjacent to a negative (positive) surface. However, this is required by the electrochemical potential (μ_i) equation under equilibrium:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F V \quad (2)$$

where μ_i^0 is the electrochemical potential under standard conditions, a_i is the activity of ion i, z_i is its charge, F is Faraday electrochemical equivalent, and V is the local potential. When V is positive, the activity of hydronium ions decreases but increases when V is negative. This has a powerful effect on single-ion activity, represented in Table 2.

Table 2. The effect of electric potential on the chemical activity of a monovalent cation

V / V	$z_i F/RTV$	ln a_i	a_i
0.00	0.00	−7.00	1.00×10^{-7}
+0.10	3.90	−5.31	4.90×10^{-6}
−0.10	−3.90	−8.39	2.00×10^{-9}
+0.20	7.80	−3.61	2.40×10^{-4}
−0.20	−7.80	−10.39	4.10×10^{-11}
+0.30	11.70	−1.92	1.20×10^{-2}
+0.40	15.60	−0.22	6.00×10^{-1}

a_i: activity of ion I; z_i: charge; F: Faraday electrochemical equivalent; V: local potential.

Thus, the water ions concentration reaches high values adjacent to the electrified surface, comparable to the concentrations of ions from solutes. The Debye-Hückel theory for the activity of dissolved electrolytes also neglects water ion imbalance under non-zero electric potential observed around single solute ions and the aqueous interfaces of micelles, polyelectrolytes, and any colloids. A significant excess of water ion concentrations is thus expected at any water interface, modifying the electrochemical potential and thus triggering further ion-dependent events. Thermodynamic treatments are not frequently found in interfacial electrification, but a previous successful example is a detailed study of the water-PTFE (polytetrafluoroethylene) system.[37]

An associated assumption is the absence of charge transfer across water-gas interfaces, but recent determinations of charge loss from a levitating water droplet proved in an elegant experiment that water evaporation is coupled with charge transfer.[38]

Thus, realistic water polarization models should include the participation of water ions in addition to the water dipole orientation and alignment.

5. The Maxwell-Wagner-Sillars Effect, Charge Migration, and Molecular Dipoles

The study of matter polarization under an electric field received great attention during the first decades of the 20th century due to its relevance to radio transmission. The equations derived by Wagner and Sillars[39] account for interfacial electrification in any multiphase material under an electric field, thus on any material on Earth's surface. It depends on the differences between the conductivities and the relative permittivity of any phases in contact, provoking net charge accumulation and contributing to interfacial electrification everywhere.[40] The ratio between the relative permittivity ε and the conductivity σ is the relaxation time $\tau = \varepsilon/\sigma$. Thus, electric current j across any interface induces interfacial polarization, as schematically shown in Figure 5. Unfortunately, this effect was almost generally ignored for many decades, as evidenced by the number of papers citing this effect *per* year. Data in the Web of Science has less than 10 annual citations since the publication of the seminal papers in the early 20th century until 1990, then growing and reaching the 200 level by 2020.

The lack of attention to the Maxwell-Wagner-Sillars effect is explained by considering the important role of matter polarization in determining molecular structures, a frontier research problem in the early 20th century, producing many Nobel Prizes. The Nobel Lecture of Peter Debye[41] in 1936 reads: "Since Faraday had introduced the measurement of this disturbance by the aid of the dielectric constant, it was usual to consider the reason for the polarization occurring in every insulator on which the dielectric effect is based to be the displacement of the charges produced in the molecule by the field and which disappears again as the field disappears. This concept is still valid today". This phrase converges with the Maxwell-Wagner-Sillars effect. Still, a few pages later, it is followed by "I, therefore, conjectured that molecules in the state of equilibrium can also be carriers of a permanent electric moment and so the electric polarization, in general, must be attributed to two simultaneously effective causes, a deformation, and an orientation."

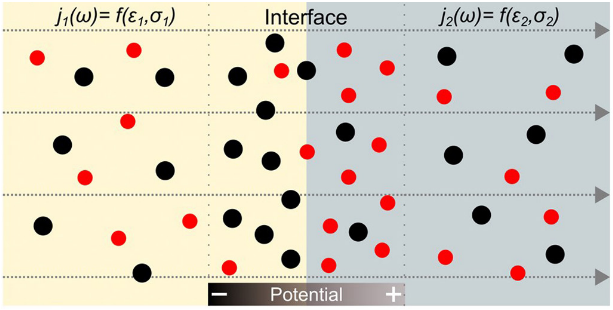

Figure 5. Schematic description of Maxwell-Wagner-Sillars interfacial polarization. Space charges migrate under an electric field, depending on the mobility of each charged entity in each phase. Black circles are the negative charges, red circles are positive. Anions moving faster than cations accumulate on the left side of the barrier but are depleted on the right side. Since ion concentration in the left is higher than in the right side, the interface acquires a negative charge.

Debye and his contemporaries realized that the determination of the dipole moment of polar molecules should be done using vapors or dilute solutions in non-polar solvents, thus eliminating the contributions of strong intermolecular interactions and self-ionization.

6. Excess Potential at Interfaces Modifies Predictions Based on Standard Thermodynamic Tables

The Gibbs energy of a chemical system decreases when it undergoes a spontaneous chemical reaction under constant T and in contact with a pressure reservoir. This is the basis for predicting whether any given reaction is spontaneous using Chemical Thermodynamics data tables-these present data for the standard conditions (for pure substances, solutions, polyphasic systems). Calculations assume ideal behavior as a first approximation, but realistic calculations use activity coefficients and related parameters. Electroneutrality is uniformly adopted, and the widely used chemical potentials do not include the effect of non-zero potential that appears in the equation for the electrochemical potential (equation 2).

Electrochemical reactions are usually provoked by applying a potential difference between two electrodes mounted within a system. However, the potential difference is also achieved by water ion partition in the electrodes, as in the hygroelectric power generators. Exposing an asymmetric capacitor formed by two plates of different metals to moist air electrifies the two plates to different extents, depending on the acid-base properties of the metal oxides at the surfaces.[8] Connecting the asymmetric capacitor plates to a simple ceramic capacitor charges the latter, proving that power can be collected from the moist atmosphere. Many pairs of conductive materials have already shown the ability to deliver energy from moisture, depending on the differences in the adsorption of water ions. Energy harvesting from atmospheric moisture is now demonstrated in the literature, and other agents often assist it.[42]

The potential difference between the electrodes triggers redox reactions of the adsorbed ions that release electrons in the negative electrode, consuming them at the positive electrode, and maintaining an electronic current outside the cell. In an aluminum-stainless steel or ERG (exfoliated and reassembled graphite)[43] cell, the detected reaction products are hydrogen and hydrogen peroxide, explained by the water dehydrogenation reaction. Figure 6 shows the working principle of a hygroelectric cell. Electrified compartments in a hygroelectric cell consist of parallel plates made from conductive materials, such as exfoliated and reassembled graphite (ERG)[44] and aluminum (Al) electrodes. The oxide layer on the Al electrode is acidic, adsorbing OH^- and acquiring a negative potential, repelling negative charge from the adjacent atmosphere. On the other hand, the ERG electrode is basic, adsorbing H^+ and generating a positive potential, surrounded by negative layers in the adjoining fluid and metal phases.

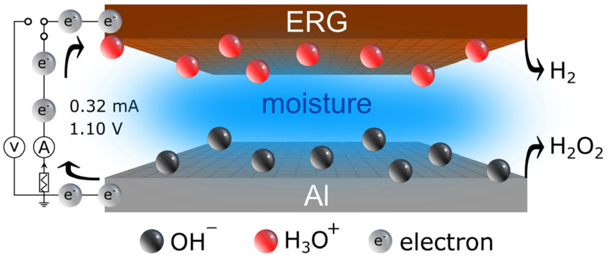

Figure 6. Hygroelectric cells generate hydrogen, hydrogen peroxide, and electric current simultaneously from water or vapor at room temperature. Thermodynamic analysis reveals non-spontaneous water dehydrogenation under standard conditions, aligning with experimental results. This illustrates a unique example of modifying chemical reactivity in charged interfaces.[25,26,45]

The same reaction products (hydrogen and hydrogen peroxide) found in hygroelectric cells were detected in aerosols carrying a negative charge and in water-oil emulsions. Thus, spontaneous electrification in multiphase systems creates conditions for advancing reactions normally seen as non-spontaneous. Many publications from the past few years have shown unexpected reactions proceeding in aerosols and other systems containing electrified interfaces.[45]

Electrified interfaces have not yet been extensively explored in mechanochemistry, but they can contribute new explanations for the differences in the products obtained in thermal or mechanochemical reactions.[46]

7. Surprising Reactivity: Organic Reactions May Progress Faster in the Presence of Non-Solvent Water than in Solution, Hydrogen is Spontaneously Formed from Water, and What Else?

Sharpless and co-workers[47] used the term "on-water" to describe the surprising rate acceleration that is observed when some insoluble organic reactants are stirred in aqueous suspension.

Many review articles[48] covered this topic, whose interest is demonstrated by their large numbers of citations. Phrases extracted from these articles show how much "on-water" reactions depart from synthetic chemistry practice:

From Lindstrom,[49] in 2002: "Many organic chemists, myself included, will remember being told in early undergraduate years: in organic synthesis water is a contaminant".

From Chanda and Fokin,[48] in 2009: "Performing organic reactions in water with substrates that are not soluble seems counterintuitive at first. We hope that this survey convinced the reader that attempting such heterogeneous reactions in water is a worthwhile endeavor." and "Perhaps one day water will become the most used solvent in synthesis, and the ones that are considered common and conventional today will take an honorable place on the rare chemicals shelf".

From Simon and Li,[50] in 2012: "The use of water as a solvent features many benefits, such as improving reactivities and selectivities, simplifying the workup procedures, enabling the recycling of the catalyst, and allowing mild reaction conditions."

From Cortes-Clerget *et al.*,[51] in 2021: "Water as the reaction medium in organic chemistry: from our worst enemy to our best friend."

Although "on-water" reactions occur in aqueous interfaces, the participation of the excess interfacial charge in these reactions is not widely recognized. They have been explained considering the hydrophobic effect and the singular properties of –OH dangling bonds at aqueous interfaces compared to water bulk.[52] High-quality theoretical work uses contemporary methods but within the electroneutrality paradigm,[19] but Beattie[53] proposed that they depend on acid catalysis triggered by OH^- adsorption at the water-hydrophobic solid interface.

A comprehensive assessment of experimental work on the effects of electric fields in chemical transformations, structure, and reactivity was recently published.[54]

8. Electric Fields Substitute Heterogeneous Nucleation in a Phase Transition

A common statement is: "When pure water is heated, it starts boiling at its boiling temperature."[55] However, water boiling within a beaker only starts when heated above the equilibrium boiling temperature unless the system contains bubble nucleation aids. The same situation appears in vapor condensation, solute crystallization, ice formation from water, and other phase transition phenomena. For instance, pure water may be cooled down to –40 ºC without freezing.[56]

The difference between the equilibrium boiling temperature and the variable temperature where boiling starts in various systems is explained by the classical nucleation theory. Shortly, bubble formation produces a positive contribution to Gibbs energy due to the formation of an interface. On the other hand, the change of the Gibbs energy in the bulk liquid-vapor transition is zero at the equilibrium boiling temperature but negative at higher temperatures. The positive interfacial contribution increases with the square of the bubble radius, while the negative bulk contribution increases with its cube, represented in equation 3 following the Classical Nucleation theory:

$$R = N_S\, Z_j \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{3}$$

where N_S is the number density of nuclei, Z_j is the probability that a nucleus at the top of the energy barrier will grow further, forming a stable particle, and ΔG* is the energy barrier to the formation of nuclei, given by equation 4:

$$\Delta G^* = \frac{4}{3}\pi r^3 \Delta g_v + 4\pi r^2 \gamma \tag{4}$$

where ΔG* the summation of two terms dependent on the particle radius, r. The first is the bulk contribution to Gibbs' energy change, below 0 ºC, for ice formation, which is < 0. The second is the surface contribution that reaches large positive values per mol when is in the nanometric size range.

For this reason, homogeneous vapor nucleation can only occur above boiling temperature, but the bubbles grow fast once it happens. The result is the release of a burst of energy, which may be a destructive explosion.

Superheated water is metastable: it looks stable until its apparent stability is suddenly broken. Water vapor may reach high supersaturation in the atmosphere, followed by fast ice or water condensation that may proceed to a thunderstorm. Phase transitions occur by non-classical mechanisms, but only in a few cases, like the spinodal phase separation in metals and polymer solutions.

Electric fields affect water crystallization, and electro-crystallization is used in industrial processes. The authors explained that water vapor metastability during condensation breaks down under an electric field, considering that electrified ice nuclei have lower surface tension due to the charge repulsion at their surfaces.[31] Thus, applying a high voltage to an electrode rapidly leads to the formation of electrified ice needles, which may subsequently give rise to dendrites, as shown in Figure 7.

9. Electric Fields Change Crystal Habit

Ice crystals formed under an electric field are shaped like needles and dendrites aligned with the field, forming beautiful displays. Shutting off the applied field is followed by dendrite collapse, which changes to porous ice blocks.[57] The elongated crystals carry a net charge, evidenced by their levitation or flight along the field lines. Calculations based on the minimum force for crystal detachment from its bed or the flight speed yield 0.62-1.25 × 10^{-6} C m^{-2} surface charge density, producing 73-147 kV m^{-1} electric fields, reaching the range measured within thunderstorms. Dendrite tree tops grow 1 mm in 4-6 s, but their lower parts do not show budding or branching activity, as expected, due to the shielding effect exerted by water.

Beyond crystal growth on existing nuclei, crystals also appear floating in the gas phase, starting as tenuous elongated structures that grow by densification with little change in their dimensions, following the same pattern observed in spinodal phase separation. Thus, electric fields trigger a non-classical phase transition mechanism with zero activation energy and avoid metastability and the ensuing problems discussed in the previous section as shown in Figure 8.[58]

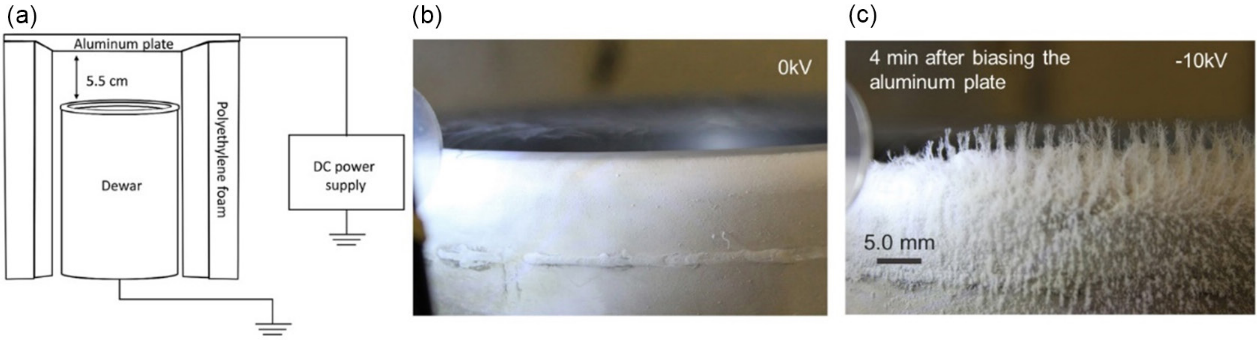

Figure 7. Electrified ice formation from moist air under an electric field and a temperature gradient. (a) Schematic drawing of the experimental arrangement showing a grounded Dewar filled with liquid nitrogen and an aluminum plate electrode placed above the Dewar. (b-c) Frames from the same area, showing the rapid growth of needles and dentrites observed when the aluminum plate is biased at –10 kV.

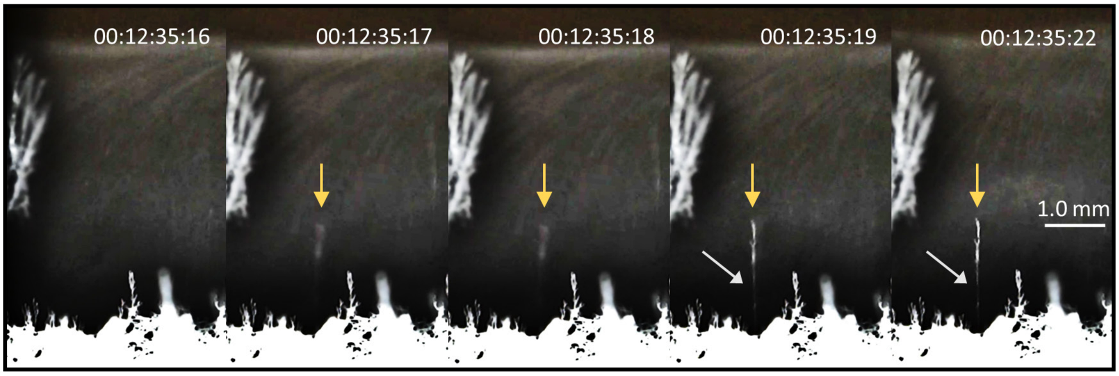

Figure 8. Frames extracted from a video capturing the formation of an ice needle through a non-classical crystallization mechanism.[57] The needle is not visible in the first frame but becomes faintly apparent in the subsequent frames. The contrast and thickness of the needle increase from second to fifth frame. The time difference between consecutive frames is 0.04 s.

Needles and dendrites also appear in young ice in natural settings. This observation is consistent with their formation's low or zero activation energy, allowing these shapes to precede the more familiar, more isometric ice shapes. Elongated crystals also appear in other events when a crystal grows under a field, like the damaging dendrite formation in batteries and chemical gardens.[59]

10. Emergent Properties of Water are not Predicted by Molecular Structure Theories

The extensive networks formed by solid and liquid water show emergent properties that are not predicted from the knowledge acquired from the isolated molecules. The connections between the properties of a system and its parts are an important problem in philosophy, dating back to Aristoteles. Following O'Connor, "The general notion of emergence is meant to conjoin these twin characteristics of dependence and autonomy. It mediates between extreme forms of dualism, which rejects the micro-dependence of some entities, and reductionism, which rejects macro-autonomy".[60]

Reductionism prevailed during the 20th century and it is implicit in Dirac's statement: "The underlying laws necessary for the mathematical theory of a larger part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations much too complicated to be soluble."[61] A strong current opposes this perspective. Those interested in chemical and overall material properties continue to largely rely on information from experiments opposing Dirac's statement.

It is thus not surprising that quantum mechanics and computational chemistry work continues to concentrate on electroneutral systems. Thus, this work did not yet contribute significantly to current knowledge of matter electrification. The former does not yet have powerful tools to handle molecular structure under an external field, while molecular mechanics is limited by the number of entities it can treat. This prevents realistic simulation of systems and events where the relevant component concentration is just parts *per* million mol, as water ions in pure water.

There are now great hopes that quantum computing and artificial intelligence will create new, powerful procedures for treating complex chemical problems. If this happens, they will contribute to the knowledge of electrified matter. However, we should not forget Debye's statement:[41] "It is, in fact, impossible to predict the dielectric behavior of liquids, such as water, alcohols, nitrobenzene, etc., based on the theory valid for gases. The molecules behave throughout these cases as if their moment is smaller than that observed for free particles". Thus, liquid water properties cannot be deduced from a single molecule or a macroscopic population of non-contacting molecules. His singularities emerge when water molecules gather in the huge populations determined by the Avogadro number, forming a bonded network that is seldom electroneutral and electrifies the majority of other substances in any environment.

11. Conclusions

Water participates in many important, unpredicted, and unexpected phenomena discovered during the past three decades, diverging from widespread ideas on the most relevant topics in chemical research, practice, and applications. The fast pace of discovery increases, revealing a new Chemistry that was not even suspected a few decades ago and is providing suitable tools for the current human search for sustainability.

The new water properties and roles derive from its ability to acquire charge during trivial transformations like evaporation, condensation, spraying, splashing, crystallization, sliding, and crystal melting. Thus, water charges any surface coated with a water film or materials where it is absorbed.

This process required reexamining the origin and validity of the widespread electroneutrality paradigm and freeing ourselves from its limitations. Extending this paradigm change to other scientific disciplines will greatly impact our understanding of natural or human-made matter.

Self-electrified interfaces everywhere change the electrochemical potentials of ions and charged particles, modifying their chemical reactivity, phase change kinetics, and crystallization pattern. This opens exciting opportunities for discovery and creates technology fully compatible with the current demand for sustainability. Spontaneously generated electrons in water microdroplets strongly suggest that the role of water microdroplet chemistry has been underestimated in atmospheric chemistry.

Wolfgang Pauli said,[62] "God made solids, but surfaces were the work of the devil." What would he say, knowing that surfaces (or interfaces) are always electrified? Electrification has been known for more than 2600 years, even before the devil was invented, but a clear picture is only emerging in this century.

Water plays a central role in Nature, but this is not only due to the properties of bulk water or individual water molecules. It is also the result of water ionization on interfaces, a property resulting from the encounter between water and an insoluble solid, liquid, or gas. A better understanding of charge separation is allowing us to improve how we see our world and driving the emergence of a new and sustainable chemistry.

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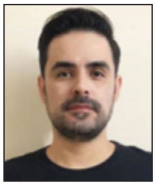
Fernando Galembeck *FRSC (Fellow of the Royal Society of Chemistry) was educated at the University of São Paulo and was a post-doc at the University of Colorado Medical Center and the University of California Davis. He became an assistant professor at University of São Paulo (USP) in 1970, moved to the University of Campinas in 1980, retired as a professor of chemistry in 2011 to become director of the National Laboratory of Nanotechnology in Campinas, until 2015. He then founded the Galembetech consulting and R&D company and continued to lecture as a volunteer at Unicamp. He is a member of the Brazilian Academy of Sciences and TWAS (The World Academy of Sciences) and an Emeritus Researcher of CNPq. Holding prizes for his scientific, educational, and technological contributions. Current research interests are matter electrification processes and consequences, and nanostructured materials.*

Leandra Pereira dos Santos *holds a PhD in Chemistry from the University of Campinas, focusing on the production, storage, and properties of electrified water. In her postdoctoral research at Unicamp and USP, she participated in projects on hygroelectricity. elastoelectricity, optoelectrochemical materials, and environmentally friendly multifunctional materials development. She is currently a researcher in the Galembetech company, working on materials and processes for energy production from water. Leandra received the Abrafati Award in Coating Science in 2020.*



Thiago Augusto de Lima Burgo *obtained his PhD from the University of Campinas, specializing in the triboelectrification of dielectric polymers. Following this, he conducted postdoctoral research at the Argonne National Laboratory in Chicago, USA, where his focus was on studying the exchange of electric charge at metal-insulator interfaces during fluctuations in frictional forces. Dr Burgo was an Assistant Professor in the Department of Physics at the Federal University of Santa Maria. In 2022, he moved to the State University of São Paulo (UNESP), where he currently serves as an Associate Professor. In 2020, he was honored with the Rising Star Award by the Electrostatics Society of America.*

Andre Galembeck *finished his PhD in Chemistry in 1998, at the University of Campinas, Brazil. Full Professor at University Federal de Pernambuco, former Director of the Center of Strategic Technologies of the Northeast (2011-2018), and member of the National Advisory Council in Nanotechnology of the Ministry of Science and Technology. CNPq fellow in Technological Development & Innovation. Develops research activities on Colloid Chemistry and Materials Science focused on the development of hybrid compounds and nanostructures based on inorganic nanoparticles, conducting polymers,* *self-healable supramolecular structures, and latex. The applications are energy generation and storage, hygroelectricity, and antibacterial activity of silver nanoparticles. Filed more than 10 patents and founded a deep tech startup in 2020.*

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