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Posted Date: 23 March 2026

doi: 10.20944/preprints202603.1577.v2

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Hypothesis

Water as a Counterion-Deficient Charge Reservoir

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Abstract

Water can support counterion-deficient aqueous charge states when one dissolved charge is generated selectively and the compensating opposite charge is not co-stored in the same phase. We formulate a water-specific chemistry-first framework in which the positive branch is written as $\text{He}^{2+} + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{He}(\text{g}) + 2\text{H}^+(\text{aq}) + \frac{1}{2}\text{O}_2(\text{g})$ and the negative branch as $2\text{e}^- + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$. Unlike the nonaqueous case, the aqueous treatment emphasizes protonic and hydroxidic defect chemistry, oxygen lone-pair participation in low-energy helium-ion electron scavenging, and the strong thermal load of the positive branch. Maxwell relaxation and interfacial electrostatics explain how the liquid remains near-neutral in the bulk while sustaining counterion deficiency chemically. The framework yields stoichiometric, transport, and stability relations, a conservative aqueous entry criterion of $E_{\text{entry}} \leq 0.515 \text{ eV}$, and an explicit heat-release constraint for practical realization.

Keywords: counterion-deficient states; aqueous charge defects; proton transport; hydroxide transport; hydrogenbond network; electrochemical charge balance; Maxwell relaxation; interfacial charge localization; water oxidation; Rayleigh limit; theoretical physical chemistry

1. Introduction

Conventional aqueous chemistry is usually discussed in terms of dissolved ionic countercharge, buffering equilibria, and local acid-base compensation. The present work examines a narrower regime in which selective stoichiometric generation or removal of one dissolved charge may create a liquid phase that is chemically deficient in conventional counterions while overall charge balance is maintained by the interface and the surrounding environment rather than solely by dissolved ionic partners. In this sense, the manuscript is concerned with how electroneutrality is enforced, not with whether electroneutrality applies.

Water is used here as the anchor medium because it is simultaneously a high-permittivity liquid, a hydrogen-bond network, and a medium for unusually rapid protonic and hydroxidic defect transport. The positive and negative aqueous charges are therefore written as $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ as bookkeeping labels for excess positive and negative aqueous charge carried by hydrated structures rather than by isolated vacuum-like bare ions. The resulting logic is the water-specific analog of the first reservoir framework: the chemistry defines the state, and the physics only determines whether that state is consistent with charge conservation, transport theory, electrostatics, and capillary stability [1,2,6–9].

The paper is organized into a chemical part and a physical part. The main claim is chemical: a dissolved aqueous phase can be deficient in ordinary ionic counterions. The role of the physics is explanatory rather than constitutive. It is used to test whether that chemical state is compatible with Maxwell relaxation, Poisson electrostatics, environmental leakage, and the Rayleigh stability bound, and to derive falsifiable predictions by which the claim can be disproved.

A key clarification is required at the outset. The proposed state is not one of persistent macroscopic bulk space charge. When water is sufficiently conductive, Maxwell relaxation drives the interior toward approximate electroneutrality, while any finite net charge is localized at the phase boundary and balanced by induced or environmental countercharge. The electric field discussed below is therefore

not treated as an externally imposed starting point; it is the electrostatic consequence of chemically generated charge imbalance.

This framing also clarifies why the chemical state itself is not restricted by a single vessel radius or sample size. Geometry controls interfacial field strength, capacitance, and stability bounds, but the existence of a counterion-deficient dissolved phase is determined primarily by chemistry, transport, and environmental charge balance. The same framework can therefore be formulated for laboratory cells, flow systems, and larger-volume reactors so long as the corresponding admissibility criteria remain satisfied.

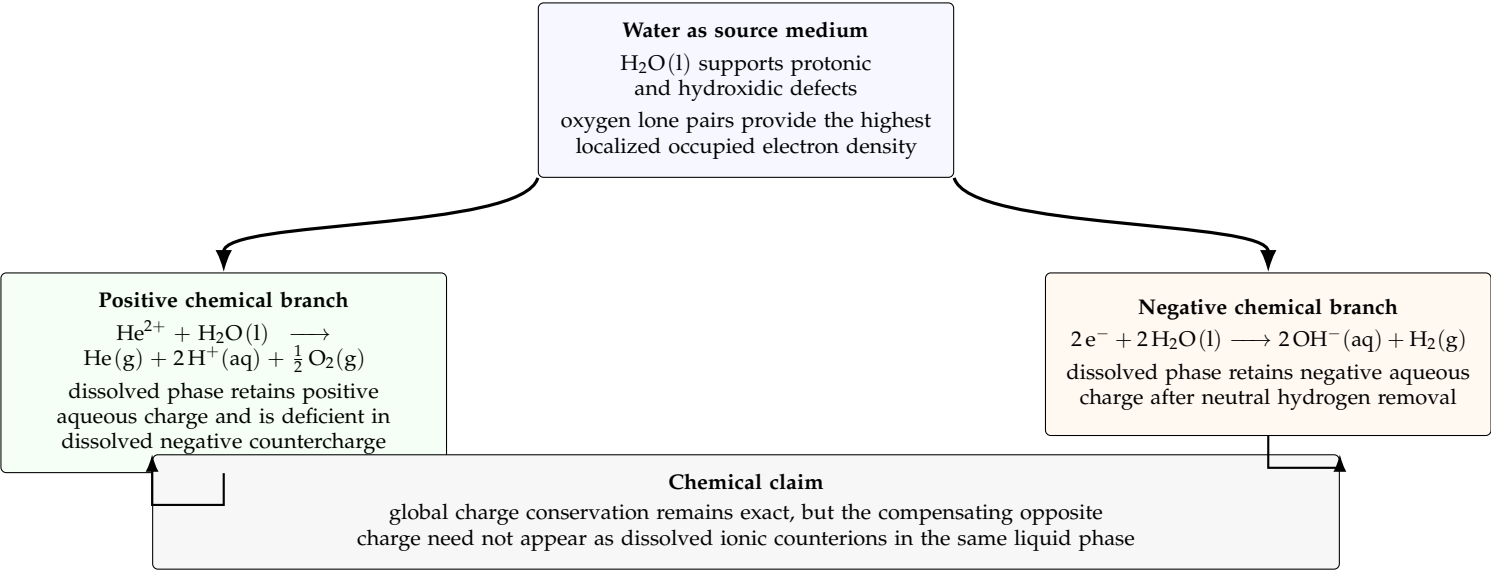
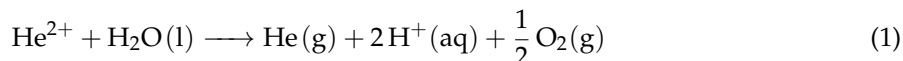


Figure 1. Chemistry -first logic of the aqueous framework written with explicit species and stoichiometric equations. The central proposition is the absence of conventional dissolved counterions in the liquid phase, not any violation of global charge conservation.

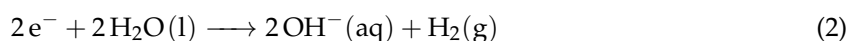
2. Chemical Framework and Theoretical Methods

2.1. Water-Specific Source Relations and Exact Charge Conservation

The aqueous framework does not begin from metal dissolution. It begins directly from globally balanced positive and negative source relations in water. The positive-source channel is



and the negative-source channel is



Equation (1) is the positive aqueous analog of selective electron removal, whereas Eq. (2) is the negative aqueous analog of selective negative-charge generation. Both are used as globally balanced bookkeeping relations that define the net stoichiometric connection between the entering species and the retained aqueous charge.

Charge conservation at the point of formation remains exact. For the positive branch,

$$Q_+ = Fn_{\text{H}^+(\text{aq})}, \quad Q_{\text{He}} = 2Fn_{\text{He}^{2+}}, \quad n_{\text{H}^+(\text{aq})} = 2n_{\text{He}^{2+}} \quad (3)$$

whereas for the negative branch,

$$Q_- = -Fn_{\text{OH}^-(\text{aq})}, \quad n_{\text{OH}^-(\text{aq})} = n_{\text{e}^-} \quad (4)$$

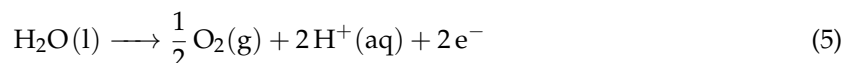
The dissolved state therefore constitutes an aqueous charge reservoir from which one dissolved charge may be selectively generated or retained without requiring immediate appearance of a conventional ionic countercharge partner in the same phase.

2.2. Positive and Negative Aqueous Reservoir Forms

A positive aqueous reservoir is obtained when proton-equivalent positive aqueous charge is generated more rapidly than it is chemically neutralized or environmentally discharged. In that regime, positive aqueous charge is retained while the corresponding negative aqueous countercharge is not co-stored in the same liquid phase. A negative aqueous reservoir is obtained when hydroxide-equivalent negative aqueous charge is generated while positive aqueous countercharge is not reintroduced into the same phase. The instantaneous reservoir charge is not the full Faradaic quantity associated with cumulative throughput because generation occurs through a rate-limited process and is continuously opposed by environmental leakage or discharge. The electrostatic state is therefore dynamical rather than static.

2.3. Explicit Selective Reactions for Helium Ions and Electrons in Water

The chemistry is written directly in its operative stoichiometric form. The positive water-specific sequence is conveniently decomposed into the water oxidation step



and the helium neutralization step



whose sum is Eq. (1). The precise local electron-scavenging step is therefore Eq. (6). The negative branch is represented by direct electron delivery to water through Eq. (2). These are the exact positive and negative water-branch steps used throughout the manuscript.

2.4. Lone-Pair Interpretation of the Positive Branch

The positive branch becomes chemically more interpretable if the oxygen lone pairs of water are treated explicitly. The water molecule contains two O–H bonds and two nonbonding lone-pair regions. These lone-pair regions are the highest localized occupied electron density in water and therefore provide the most natural local electronic doorway for low-energy cationic capture. In this sense, oxygen-centered lone-pair density is the chemically relevant local resource from which positive aqueous charge may be generated when electrons are removed and neutral helium is formed.

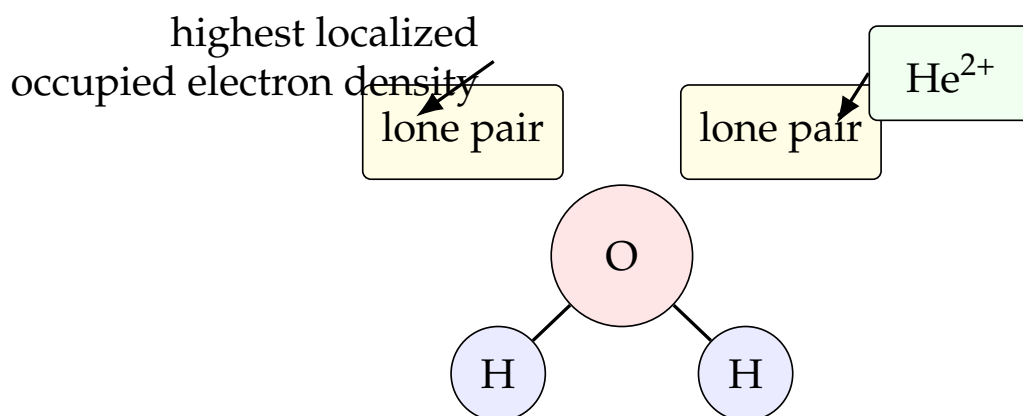


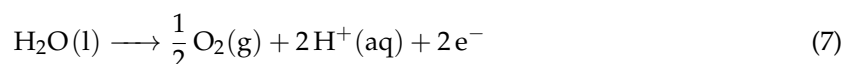
Figure 2. Interpretive lone-pair picture used in the manuscript. The oxygen lone-pair regions are treated as the highest localized occupied electron density in water and therefore as the most natural entrance site for low-energy helium-ion electron scavenging.

2.5. Thermodynamic Cycles and Heat Removal

The positive and negative aqueous branches can be written as explicit Hess cycles. In what follows, the individual steps are used as thermodynamic bookkeeping relations that make the enthalpy partition transparent; they are not intended as claims about single elementary collisions.

2.5.1. Positive Branch Hess Cycle

For the positive branch, the water-specific oxidation step is



which is assigned the liquid-water formation enthalpy in reverse,

$$\Delta H_{\text{pos,ox}} \approx +286 \text{ kJmol}^{-1}. \quad (8)$$

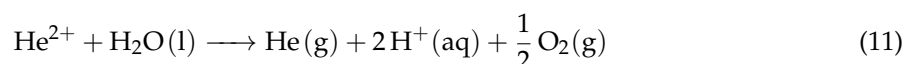
The helium neutralization step is



with the helium double-ionization energy written in molar form as

$$\Delta H_{\text{He,neut}} \approx -7623 \text{ kJmol}^{-1}. \quad (10)$$

Adding Eqs. (7) and (9) gives the net positive branch,



with the direct Hess-cycle enthalpy estimate

$$\Delta H_{\text{pos,net}} \approx -7337 \text{ kJmol}^{-1}. \quad (12)$$

In the paired branch bookkeeping used in the present manuscript, it is convenient to allocate an additional 400 kJmol^{-1} to the complementary negative water-reduction branch. Under that partitioning, the positive branch is carried in the manuscript as

$$\Delta H_{\text{pos,book}} \approx -6823 \text{ kJmol}^{-1}. \quad (13)$$

Regardless of whether Eq. (12) or Eq. (13) is used for the final bookkeeping split, the helium neutralization step itself releases approximately 7623 kJ for each mole of He^{2+} converted to neutral helium. Any practical realization of the positive branch would therefore require active cooling and heat removal sufficient to prevent local overheating, boiling, gas-driven geometry changes, or breakdown of the bounded-reservoir assumptions.

2.5.2. Negative BRANCH HESS CYcle

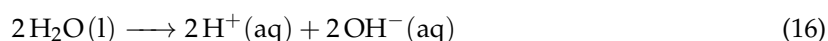
For the negative branch, a convenient cycle begins with the reverse of liquid-water formation,



with

$$\Delta H_{\text{neg,revwater}} \approx +572 \text{ kJmol}^{-1}. \quad (15)$$

A second bookkeeping step is the reverse of neutralization,



with

$$\Delta H_{\text{neg,auto}} \approx +114 \text{ kJmol}^{-1}. \quad (17)$$

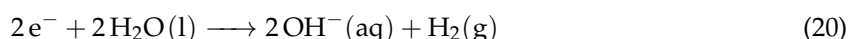
Finally, hydrogen formation from aqueous protons is written as the reference relation



with

$$\Delta H_{\text{neg,h2}} \approx 0 \text{ kJmol}^{-1}. \quad (19)$$

After algebraic cancellation, the net negative branch is



which is carried in the paired-branch bookkeeping of the manuscript as

$$\Delta H_{\text{neg,book}} \approx -400 \text{ kJmol}^{-1}. \quad (21)$$

The sign and magnitude in Eq. (21) are therefore not introduced independently; they are the complementary thermodynamic allocation used alongside Eq. (13) so that the two branches can be compared on the same manuscript bookkeeping scale.

2.5.3. Summary Thermodynamic Split

The branch-wise Hess-cycle values used in the manuscript are collected in Table 1.

Table 1. Hess-cycle thermodynamic split adopted for the two aqueous branches.

Branch reaction	Assigned ΔH
$\text{He}^{2+} + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{He}(\text{g}) + 2 \text{H}^+(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g})$	-6823 kJmol^{-1}
$2 \text{e}^- + 2 \text{H}_2\text{O}(\text{l}) \longrightarrow 2 \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	-400 kJmol^{-1}

2.6. Entry-Energy Admissibility in Water

A chemically useful counterion-deficient reservoir requires not only charge generation, but also survival of the retained aqueous charge on timescales long compared with redistribution and discharge. The energy relevant to charge-mediated chemistry is the kinetic energy of the incoming species at the point of entry into the liquid. To suppress direct solvent bond cleavage, the entry energy is constrained to be at most one-tenth of the energy required to cleave the weakest bond in water,

$$E_{\text{entry}} \leq \eta E_{\text{weakest}}, \quad \eta = 0.1 \quad (22)$$

Taking the O–H bond as the weakest bond relevant to the present aqueous framework, with an energy of approximately 5.15 eV, the conservative entry criterion becomes

$$E_{\text{entry}} \leq 0.515 \text{ eV} \quad (23)$$

Under Eqs. (22) and (23), the entering helium ions and electrons are treated as chemically operative charges rather than as sources of indiscriminate solvent fragmentation.

2.7. Injection Current and Stoichiometric Scaling

The electrical current associated with selective charge-transfer chemistry follows directly from Faraday's law. If dn_{tr}/dt denotes the molar rate of charge-transfer events and z_{tr} the number of electronic charges transferred per event, then

$$I = z_{\text{tr}} F \frac{dn_{\text{tr}}}{dt} \quad (24)$$

For the positive branch,

$$\frac{dn_{\text{H}^+(aq)}}{dt} = 2 \frac{dn_{\text{He}^{2+}}}{dt} \quad (25)$$

so the charging current is

$$I_{\text{He}} = F \frac{dn_{\text{H}^+(aq)}}{dt} = 2F \frac{dn_{\text{He}^{2+}}}{dt} \quad (26)$$

For the negative branch,

$$\frac{dn_{\text{OH}^-(aq)}}{dt} = \frac{dn_{e^-}}{dt} \quad (27)$$

so the charging current is

$$I_{e^-} = -F \frac{dn_{\text{OH}^-(aq)}}{dt} = -F \frac{dn_{e^-}}{dt} \quad (28)$$

The sign convention is chosen such that positive current charges the water positively and negative current charges it negatively.

2.8. Environmental Charge Balance and Throughflow Operation

The surrounding environment is not electrically inert. Countercharge may be supplied or removed through induced polarization, controlled grounding, air-ion conduction, finite wall conductivity, or surface leakage. A minimal dynamical law for the net charge $Q(t)$ is therefore

$$\frac{dQ}{dt} = I - \frac{Q}{\tau_{\text{leak}}} \quad (29)$$

with

$$\tau_{\text{leak}} = R_{\text{env}} C \quad (30)$$

and the corresponding steady state

$$Q_{\text{ss}} = I \tau_{\text{leak}} \quad (31)$$

This linear form is used as a leading-order environmental relaxation model. The chemical counterion-deficient state does not require large stored charge; it requires only that selective charge generation be balanced by environmental or interfacial countercharge rather than by dissolved counterions within the liquid phase.

2.9. Dimensionless Admissibility Parameters

A compact way to compare systems of different size and operating mode is to organize the theory through dimensionless admissibility parameters:

$$\Lambda_R = \frac{Q_{ss}^2}{64\pi^2\epsilon\gamma R^3} \quad (32)$$

$$\Lambda_B = \frac{E(R)}{E_{crit}} \quad (33)$$

$$\Lambda_K = \frac{E_{entry}}{E_{weakest}} \quad (34)$$

$$\Lambda_M = \frac{\tau_M}{t_{experiment}} \quad (35)$$

A physically admissible regime requires

$$\Lambda_R < 1, \quad \Lambda_B < 1, \quad \Lambda_K \leq 0.1, \quad \Lambda_M \ll 1 \quad (36)$$

2.10. Solvent-General Admissibility Window Specialized to Water

Collecting the principal constraints, a chemically and physically admissible aqueous operating regime is defined by

$$|Q_{ss}| < Q_R \quad (37)$$

$$E(R) < E_{crit} \quad (38)$$

$$E_{entry} \leq 0.1E_{weakest} \quad (39)$$

$$\tau_M \ll t_{experiment} \quad (40)$$

$$\text{Re}(\lambda_j) < 0 \quad \text{for all eigenvalues of } M \quad (41)$$

The last condition ensures dynamical stability of any coupled charge-reaction steady state introduced below.

2.11. Maxwell Relaxation and Bulk Neutrality

Bulk charge redistribution is governed by the Maxwell relaxation time,

$$\tau_M = \frac{\epsilon}{\sigma} \quad (42)$$

with

$$\epsilon = \epsilon_r \epsilon_0 \quad (43)$$

At 25 °C, the aqueous benchmark uses

$$\epsilon_r \approx 78.5, \quad \epsilon \approx 6.95 \times 10^{-10} \text{ Fm}^{-1} \quad (44)$$

for water and

$$\sigma \approx 5.5 \times 10^{-6} \text{ Sm}^{-1} \quad (45)$$

for ultrapure water. Hence

$$\tau_M \approx \frac{6.95 \times 10^{-10}}{5.5 \times 10^{-6}} \approx 1.26 \times 10^{-4} \text{ s} \quad (46)$$

When τ_M is short compared with the experimental timescale, any bulk charge imbalance relaxes rapidly toward the boundary. The framework therefore does not assume that bulk space charge persists indefinitely. Rather, it assumes that the physically sustainable electrostatic state is boundary-localized while the liquid interior approaches electroneutrality.

2.12. Charge Continuity and Drift-Diffusion Transport

Let $\rho(\mathbf{r}, t)$ denote bulk charge density. Gauss's law and charge continuity require

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon} \quad (47)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (48)$$

For positive aqueous charge,

$$\rho(\mathbf{r}, t) = F c_{\text{H}^+(aq)}(\mathbf{r}, t) \quad (49)$$

and for negative aqueous charge,

$$\rho(\mathbf{r}, t) = -F c_{\text{OH}^-(aq)}(\mathbf{r}, t) \quad (50)$$

For a mobile charge with mobility μ , a simplified drift current is

$$\mathbf{J} = \rho \mu \mathbf{E} \quad (51)$$

A more general transport law uses the Nernst–Planck form,

$$\mathbf{J}_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \Phi \quad (52)$$

where D_i is a diffusion coefficient, u_i the ionic mobility, and Φ the electric potential. The associated continuity equation is

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i + R_i \quad (53)$$

where R_i contains reaction source or sink terms.

2.13. Boundary Localization and Electrostatic Geometry

The electric potential obeys Poisson's equation,

$$\nabla^2 \Phi = -\frac{\rho}{\epsilon} \quad (54)$$

with electric field

$$\mathbf{E} = -\nabla \Phi \quad (55)$$

If the bulk has already relaxed such that $\rho_{\text{bulk}} \rightarrow 0$, then the nontrivial solution is carried by the boundary conditions. For a reservoir of surface area A_s , the surface charge density is

$$\sigma_s = \frac{Q}{A_s} \quad (56)$$

For a sphere of radius R this becomes

$$\sigma_s = \frac{Q}{4\pi R^2} \quad (57)$$

For spherical symmetry and $r \geq R$, Gauss's law gives

$$\oint \mathbf{E} \cdot d\mathbf{A} = \frac{Q}{\epsilon} \quad (58)$$

so that

$$E(r)(4\pi r^2) = \frac{Q}{\epsilon} \quad (59)$$

and hence

$$E(r) = \frac{Q}{4\pi\epsilon r^2} \quad (60)$$

The interfacial potential is

$$\Phi = \frac{Q}{4\pi\epsilon R} \quad (61)$$

The spherical capacitance is

$$C = 4\pi\epsilon R \quad (62)$$

The stored electrostatic energy may be written either as

$$U_{\text{el}} = \frac{Q^2}{2C} \quad (63)$$

or, equivalently,

$$U_{\text{el}} = \frac{Q^2}{8\pi\epsilon R} \quad (64)$$

The field-energy density is

$$u = \frac{1}{2}\epsilon E^2 \quad (65)$$

2.14. Mechanical and Dielectric Limits

If the charge reservoir is associated with a liquid body of effective surface tension γ , electrostatic stability requires that charge remain below the Rayleigh limit,

$$Q_R^2 = 64\pi^2\epsilon\gamma R^3 \quad (66)$$

The corresponding maximum stable potential is

$$\Phi_R = \frac{Q_R}{4\pi\epsilon R} \quad (67)$$

The criterion for electrohydrodynamic stability is therefore

$$|Q_{\text{ss}}| < Q_R \quad (68)$$

The interfacial field must also remain below the dielectric breakdown threshold of the liquid and the surrounding medium,

$$E(R) < E_{\text{crit}} \quad (69)$$

with

$$E(R) = \frac{|Q_{\text{ss}}|}{4\pi\epsilon R^2} \quad (70)$$

Electrostatic stress at the interface scales as

$$P_{\text{el}} \sim \frac{1}{2}\epsilon E^2 \quad (71)$$

Whenever the instantaneous interfacial charge exceeds the Rayleigh limit,

$$|Q| > Q_R \quad (72)$$

that excess charge is not treated as stably stored. Instead, electrohydrodynamic instability and environmental discharge drive leakage or emission until the remaining interfacial charge returns to the admissible regime,

$$|Q| \leq Q_R \quad (73)$$

This discharge interpretation is central because the chemistry of a counterion-deficient aqueous phase does not require sustained storage of super-Rayleigh charge.

2.15. Aqueous Reservoir-Electrolyte Interactions and Reaction Bookkeeping

This subsection is retained because it gives the strongest formal statement of why ordinary reaction chemistry does not automatically restore local counterions. A generic electrolyte dissociation may be written as



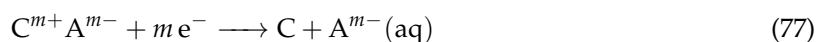
In a negatively charged aqueous reservoir the reduction step is



The anion remains solvated while the aqueous reservoir supplies the reducing charge. For example,



More generally,



A representative cation-reduction step is



and, for a cation of charge m ,



In every case, charge is conserved, but local counterion symmetry is not automatically restored. This is precisely why reaction chemistry does not invalidate the main claim of the manuscript.

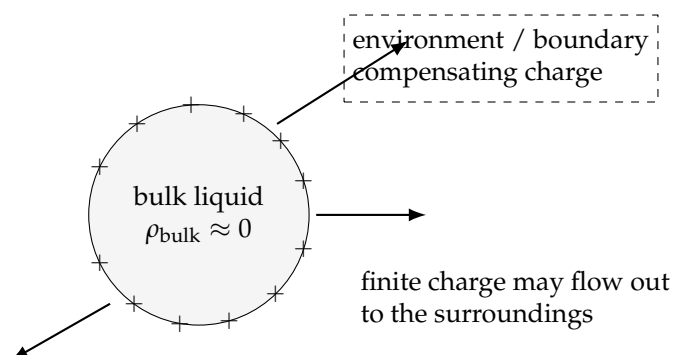


Figure 3. Minimal physical picture needed to explain the chemistry. The bulk liquid relaxes toward electroneutrality, any finite net charge is localized at the boundary, and compensating opposite charge is realized in the surrounding environment rather than as dissolved counterions inside the same phase.

3. Results and Discussion

3.1. Primary Anchor System: Water

3.1.1. Positive Aqueous Reservoir

The positive aqueous construction begins from Eq. (1). The stoichiometric relation is

$$n_{\text{H}^+(aq)} = 2n_{\text{He}^{2+}} \quad (80)$$

The total theoretical integrated positive charge throughput is therefore

$$Q_{\text{inj},+} = F n_{\text{H}^+(aq)} = 2F n_{\text{He}^{2+}} \quad (81)$$

The water entry-energy condition is written as

$$E_{\text{entry}} \leq 0.1 E_{\text{weakest}}(\text{H}_2\text{O}) \leq 0.515 \text{ eV} \quad (82)$$

The charging current is

$$I_{\text{He}} = 2F \frac{dn_{\text{He}^{2+}}}{dt} \quad (83)$$

with dynamical evolution

$$\frac{dQ}{dt} = I_{\text{He}} - \frac{Q}{\tau_{\text{leak}}} \quad (84)$$

and steady state

$$Q_{\text{ss}} = I_{\text{He}} \tau_{\text{leak}} \quad (85)$$

The electrostatic relations are

$$\varepsilon = \varepsilon_r \varepsilon_0 \quad (86)$$

$$\rho(\mathbf{r}, t) = F c_{\text{H}^+(aq)}(\mathbf{r}, t) \quad (87)$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon} \quad (88)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (89)$$

$$\mathbf{J} = \rho \mu \mathbf{E} \quad (90)$$

$$\tau_M^{(\text{H}_2\text{O})} = \frac{\varepsilon_{\text{H}_2\text{O}}}{\sigma_{\text{H}_2\text{O}}} \approx 1.26 \times 10^{-4} \text{ s} \quad (91)$$

Accordingly,

$$\rho_{\text{bulk}} \rightarrow 0 \quad (92)$$

$$E_{\text{bulk}} \rightarrow 0 \quad (93)$$

For a spherical reservoir of radius R ,

$$\sigma_s = \frac{Q}{4\pi R^2} \quad (94)$$

$$\oint \mathbf{E} \cdot d\mathbf{A} = \frac{Q_{\text{ss}}}{\varepsilon} \quad (95)$$

$$E(r)(4\pi r^2) = \frac{Q_{\text{ss}}}{\varepsilon} \quad (96)$$

$$E(r) = \frac{Q_{\text{ss}}}{4\pi \varepsilon r^2} \quad (97)$$

$$\Phi = \frac{Q}{4\pi \varepsilon R} \quad (98)$$

The admissibility window is therefore

$$Q_{ss} < Q_R \quad (99)$$

$$E(R) < E_{crit} \quad (100)$$

$$E_{entry} \leq 0.515 \text{ eV} \quad (101)$$

$$\tau_M^{(H_2O)} \ll t_{experiment} \quad (102)$$

3.1.2. Negative Aqueous Reservoir

The negative aqueous construction begins from Eq. (2). The stoichiometric relation is

$$n_{OH^-(aq)} = n_{e^-} \quad (103)$$

The total negative charge throughput is therefore

$$Q_{inj,-} = -Fn_{e^-} \quad (104)$$

The negative charging current is

$$I_{e^-} = -F \frac{dn_{e^-}}{dt} \quad (105)$$

with

$$\frac{dQ}{dt} = I_{e^-} - \frac{Q}{\tau_{leak}} \quad (106)$$

$$Q_{ss} = I_{e^-} \tau_{leak} \quad (107)$$

The charge density is now

$$\rho(\mathbf{r}, t) = -Fc_{OH^-(aq)}(\mathbf{r}, t) \quad (108)$$

while all of the same Maxwell-relaxation and field-localization relations apply. The boundary and dielectric conditions remain

$$|Q_{ss}| < Q_R \quad (109)$$

$$E(R) < E_{crit} \quad (110)$$

$$E_{entry} \leq 0.515 \text{ eV} \quad (111)$$

$$\tau_M^{(H_2O)} \ll t_{experiment} \quad (112)$$

Table 2. Explicit chemical bookkeeping for the water anchor system. Full stoichiometric equations are retained, while the retained aqueous charges are understood microscopically as hydrated protonic and hydroxidic defects.

Case	Explicit equation	Dissolved species retained	Interpretation
Positive branch	$\text{He}^{2+} + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{He}(\text{g}) + 2\text{H}^+(\text{aq}) + \frac{1}{2}\text{O}_2(\text{g})$	Positive aqueous charge written as $\text{H}^+(\text{aq})$	Selective helium-ion electron scavenging yields a dissolved phase deficient in dissolved negative countercharge.
Negative branch	$2\text{e}^- + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	Negative aqueous charge written as $\text{OH}^-(\text{aq})$	Electron delivery yields a dissolved phase deficient in dissolved positive countercharge after neutral hydrogen removal.
Helium-ion step	$\text{He}^{2+} + 2\text{e}^- \longrightarrow \text{He}$	—	Exact local scavenging step used in the positive branch.
Electrolyte reduction example	$\text{NaCl} + \text{e}^- \longrightarrow \text{Na} + \text{Cl}^-(\text{aq})$	$\text{Cl}^-(\text{aq})$ coproduct	Reaction conserves charge but does not automatically restore a counterion-free product unless coproducts are removed.
Water-specific microscopic motif	Oxygen lone pairs hold the highest localized occupied electron density	Lone-pair density and hydrated defects	Connects explicit chemistry to the aqueous electronic structure without changing the continuum balance laws.

3.2. Scale, Geometry, and Interpretation of Electroneutrality

The framework developed here is scale-general in the same precise sense as the first manuscript. The existence of a counterion-deficient aqueous phase is set by selective chemistry and environmental charge balance, not by a single prescribed vessel radius or sample amount. What does depend on geometry are electrostatic observables such as field strength, capacitance, and interfacial energy. For spherical symmetry,

$$E(R) = \frac{Q}{4\pi\epsilon R^2}, \quad \Phi(R) = \frac{Q}{4\pi\epsilon R}, \quad C = 4\pi\epsilon R$$

(113)

Thus larger systems generally produce smaller interfacial fields for the same stored charge, while larger capacitance permits the same potential at larger Q . None of these geometric facts, however, determines whether the liquid phase can be chemically counterion-deficient.

The theory does not require that macroscopic charge remain stored in the liquid at all times. In one limit, finite charge is sustained at the interface and the system behaves as a bounded electrostatic reservoir. In another limit, excess charge is transferred rapidly to the environment and the system behaves as a charge-throughflow reactor with minimal net storage. Both limits remain compatible with counterion-deficient chemistry in the dissolved phase.

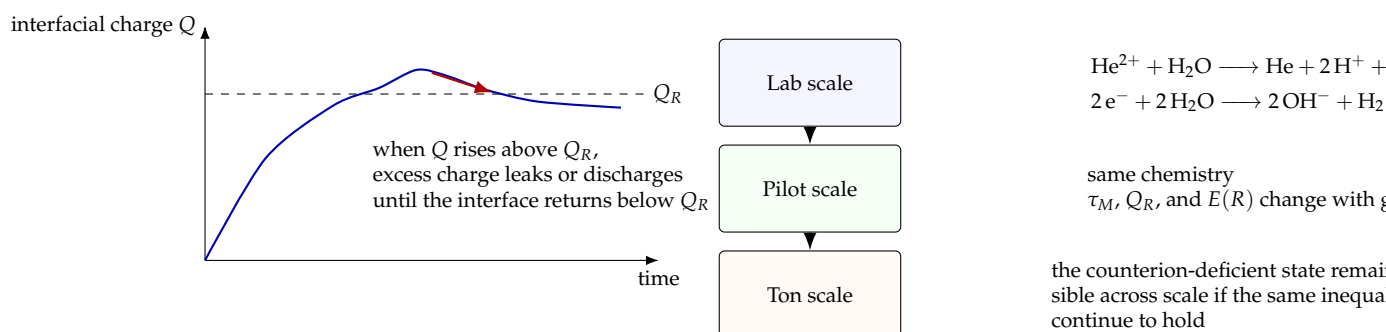
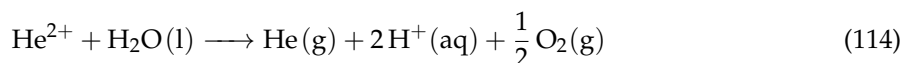


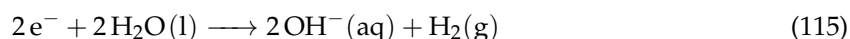
Figure 4. Left: qualitative charge evolution in the bounded regime. The interfacial charge may transiently cross the Rayleigh threshold Q_R , after which excess charge leaks or discharges until the interface returns below the admissible limit. Right: scale-general interpretation. The chemical logic is the same from laboratory to ton scale; geometry changes observables and limits, not the existence of the counterion-deficient state itself.

3.3. Falsifiable Predictions and Experimental Signatures

Because the manuscript is purely theoretical, its value depends on explicit observables that could support or disprove the framework. For the positive water benchmark channel,



and the negative benchmark channel,



the first falsifiable prediction is chemical rather than electrical: positive forcing should correlate with proton-equivalent aqueous charge and the neutral gas products He and O_2 , whereas negative forcing should correlate with hydroxide-equivalent aqueous charge and the neutral gas product H_2 . A wrong-sign field relative to the observed gas product would contradict the bookkeeping chemistry.

Second, because Maxwell relaxation remains much faster than the overall charge-processing time,

$$\tau_M = \frac{\varepsilon}{\sigma} \quad (116)$$

the theory requires

$$\rho_{\text{bulk}} \rightarrow 0 \quad (117)$$

while any finite residual net charge is carried at the boundary through

$$\sigma_s = \frac{Q}{4\pi R^2} \quad (118)$$

Thus the theory is contradicted if the central liquid volume develops and sustains a field comparable to the boundary field on timescales long compared with τ_M .

Third, the Rayleigh condition remains a direct stability test. If

$$Q_R^2 = 64\pi^2\varepsilon\gamma R^3 \quad (119)$$

then observed operation above Q_R should not remain stable; charge should leak or discharge to the surroundings until $|Q| \leq Q_R$. If instead a reproducible super-Rayleigh steady state were observed under the assumptions of the present theory, the framework would require revision.

Fourth, geometry should alter measurable quantities such as $E(R)$, $\Phi(R)$, C , and Q_R without changing the underlying chemical claim. The same counterion-deficient logic should therefore remain admissible from laboratory vessels to industrial reactors provided the inequalities in Eqs. (36)–41 continue to hold.

3.4. Why Only a Small Physical Subset Is Required

Only a limited part of the physical formalism is essential to explain the chemistry developed here. The required ingredients are: exact stoichiometric charge conservation at the chemical step; rapid Maxwell relaxation that restores near-neutrality in the bulk; Poisson and Gauss relations that define the existence of an interfacial field once finite charge is present; and the Rayleigh condition that forces excess charge to leak away when the interface becomes capillarily unstable. More elaborate field-polarization or field-activated-kinetics constructions are not needed for the central claim of the manuscript, which is simply that the dissolved liquid phase may be chemically deficient in ordinary counterions while global charge neutrality is enforced at the boundary and through the environment.

4. Conclusions

A chemistry-first framework has been developed for counterion-deficient states in liquid water. The principal conclusion is that a dissolved aqueous phase can be chemically deficient in conventional ionic countercharge without violating global charge neutrality. In the present formulation, the compensating opposite charge is carried predominantly by the boundary and the surrounding environment rather than by dissolved counterions within the same phase.

Only the portion of the physics needed to explain that chemistry is retained. Maxwell relaxation explains why the bulk need not remain space-charged, Poisson and Gauss relations define the existence of any interfacial field once finite charge is present, and the Rayleigh condition provides the capillary limit: if the interfacial charge rises above Q_R , excess charge leaks or discharges until the interface returns below the admissible threshold. The theory therefore does not require sustained macroscopic charge storage.

The positive helium-neutralization branch also carries a thermal load of approximately 7623 kJmol^{-1} per mole of He^{2+} neutralized, so any implementation would require active cooling and heat removal. The same chemical logic is scale-general. Laboratory cells, pilot systems, and ton-scale reactors differ in geometry, capacitance, field magnitude, and stability thresholds, but not in the governing bookkeeping: whenever the admissibility conditions remain satisfied, dissolved counterions are not the only possible mechanism by which electroneutrality can be maintained. That proposition is experimentally falsifiable, and the framework given here specifies the equations and signatures by which it can be confirmed or disproved.

Conflicts of Interest: The author declares no competing financial interest.

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