Computational Prediction and Electrochemical Simulation of the Benzoquinone/Hydroquinone Redox Couple in Water at pH 9 (vs SHE)

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Executive summary

This report documents a practical workflow to obtain electrode-referenced redox potentials and to generate cyclic voltammograms (CVs) for the 1,4-benzoquinone/ hydroquinone (BQ/HQ) couple in water at pH 9. The computational protocol computes solution-phase Gibbs free energies with a continuum solvent model, transforms the standard potential to the target pH for a 2e■/2H■ proton-coupled electron transfer (PCET), references the potential to the standard hydrogen electrode (SHE), and simulates CVs using a 1D diffusion + Butler–Volmer model. The workflow is easily extensible to other quinones and pH values.

1. Thermodynamic protocol (DFT in solution)

We recommend optimizing oxidized (BQ) and reduced (HQ) forms directly in water using a continuum model (e.g., IEF-PCM/COSMO/SMD) with a modern hybrid functional (e.g., B3LYP-D3BJ) and at least a double-ζ basis (def2-SVP; def2-TZVP preferred for production). A harmonic frequency calculation provides thermal and entropic corrections to obtain Gibbs free energies G°. The reaction free energy for the 2e■/2H■ PCET is converted to an absolute potential via $E\_abs = -\Delta G°/(nF)$, then referenced to SHE and shifted to the target pH using a Legendre (Pourbaix) transform for PCET.

Equations: $E\_abs = -\Delta G°/(nF)$; $E\_vs\_SHE(pH=0) = E\_abs - E\_abs(SHE)$; $E\_vs\_SHE(pH) = E\_vs\_SHE(pH=0) - (m/n)\cdot 0.05916 \cdot pH$ (25 °C)

Notes. (i) Use a consistent value for the absolute SHE potential. The IUPAC-recommended value is 4.44 ± 0.02 V at 298 K; alternative thermodynamic cycles report 4.281 V. (ii) For broader pH ranges and possible changes in dominant protonation, the Alberty–Legendre transform should be applied using microstates and pK■ values. (iii) Calibration to a reference couple (e.g., ferro/ferricyanide) in the same medium can reduce systematic solvation/entropy errors via a constant shift.

2. Implementation details (updates to the Python/Psi4 workflow)

• Solvent switched to water in the PCM block.
• Geometry optimization + frequency in solvent to obtain G (J/mol).
• pH transform for m = 2, n = 2 at pH 9: $\Delta E\_pH \approx -0.05916 \times 9 \approx -0.533$ V.
• Referencing to SHE with E_abs(SHE) = 4.44 V by default (user-settable).
• Error bars estimated by varying PCM cavity area (0.05–0.10 Å² grid).
• Optional calibration step: shift all computed potentials so a known reference matches experiment.

3. Cyclic voltammetry (CV) simulation

CVs are simulated with a triangular potential sweep applied to a planar electrode, coupling 1D semi-infinite diffusion (Fick's second law) to Butler–Volmer interfacial kinetics. The simulator returns current–potential traces that reproduce reversible (Randles–Ševčík) and quasi-reversible behaviour depending on the heterogeneous rate constant k^0. Peak currents scale with $v^{1/2}$ in the reversible limit, providing a diagnostic and a route to estimate diffusion coefficients.

Parameter	Symbol	Default
Electrons	n	2
Transfer coefficient	α	0.5
Std. rate constant	k^0	0.02 cm s^{-1} (tunable)
Diffusion (O/R)	D_O/D_R	7×10^{-6} cm² s^{-1}
Concentration	C	0.7 M (can downscale to 5–20 mM for instrumentation)
Area (3 mm disk)	A	0.07 cm²
Scan rates	v	10–500 mV s^{-1}

4. Code excerpts (as implemented)

Below are condensed snippets illustrating the key updates. Use the full script to run calculations and generate CV plots.

```
# pH transform and referencing
def pH_transform_and_reference(E_abs, m_protons=2, n_electrons=2, pH=9.0,
Eabs_SHE=4.44):
E_vs_SHE_pH0 = E_abs - Eabs_SHE
return E_vs_SHE_pH0 - (m_protons/n_electrons)*0.05916*pH

# Gibbs free energy in water (opt + freq)
def psi4_free_energy_in_water(geom, area=0.10, method="B3LYP-D3BJ",
basis="def2-SVP"):
# Build PCM block for water and run optimize + frequency
# Return G in J/mol (fallback to electronic energy if G unavailable)
...

# CV simulation (diffusion + Butler-Volmer)
# Returns potential E (V) and current i (A) at chosen scan rates.
def simulate_cv(E0, n=2, alpha=0.5, k0=0.02, D_O=7e-6, D_R=7e-6, C_bulk=0.0007,
A=0.07, scan_rate=0.1, ...):
...
```

5. Practical guidance and validation

• **Calibration**: compute a reference couple in the same electrolyte and apply a constant shift.

• **Speciation**: at pH 9, hydroquinone is largely neutral (pKa ≈ 10); using m = 2 is reasonable for the acid-form PCET. If including deprotonated forms, use a pKa-aware Legendre transform.

• **Convergence**: verify that peak current scales $\propto v^{1/2}$ for reversible settings (Randles–Ševčík) and adjust k^0 when peak separation indicates kinetic limitations.

• **Numerics**: ensure spatial domain (L) and grid (Nx) are large/fine enough so the diffusion layer does not reach the boundary during the scan.

6. References

IUPAC Gold Book: Standard hydrogen electrode (SHE) and absolute potential (E_abs(SHE) ≈ 4.44 V at 298 K). doi:10.1351/goldbook.S05917

Fornari, R. P.; de Silva, P. (2021) A Computational Protocol Combining DFT and Cheminformatics for Prediction of pH-Dependent Redox Potentials. Molecules 26, 3978. doi:10.3390/molecules26133978

Pine Research: Randles–Šev■ík Equation (peak current scaling with v^{1/2}).

IUPAC Gold Book: Randles–Šev■ík equations. doi:10.1351/goldbook.09143

Isse, A. A.; Gennaro, A. (2010) Absolute Potential of the SHE and Interconversion Between Solvents. J. Phys. Chem. B 114, 7894–7899. doi:10.1021/jp100402x