SUPPORTING INFORMATION

First-Principles-Based Prediction of Copper Electrochemical Oxidation and Corrosion under Multiple Environmental Factors

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1 Density Functional Theory Calculations

1.1 Functional Assessment

The formation energy, volume, electronic band gap, and magnetic moments were determined and compared to experimental sources to assess how well each functional accurately captured the behavior of each phase (Table S1). Formation energies were found to be relatively similar to experiment. Electronic band gaps were underestimated by local and semilocal functionals, except in the case of hybrid HSE06, which is common and well documented. Overall, DFT at the HSE06 level was found to give the best description of all properties considered.

Table S1: Properties calculated with DFT using different functionals. Free energy of formation, conventional unit cell volume, electronic band gap, and any magnetic moments stabilized are included. Experimental data on each solid is provided for comparison from the NIST Janaf Tables¹ and a variety of other sources. Energetically, small deviations were seen between experimental and DFT data.

SOLID-STATE COMPOUNDS							
Cu, Cubic							
Functional	Energy (eV/f.u.)	Volume (Å ³)	Band Gap (eV)	Magnetic Moment (μ_B)			
Experimental	0.000	47.1633	0.00	0.000			
LDA	0.000	43.7453	0.00	0.000			
PBE	0.000	47.9865	0.00	0.000			
PBEsol	0.000	45.4433	0.00	0.000			
SCAN	0.000	45.0705	0.00	0.000			
HSE06	0.000	48.0609	0.00	0.000			
Cu ₂ O, Cubic							
Functional	Energy (eV/f.u)	Volume (Å ³)	Band Gap (eV)	Magnetic Moment (μ_B)			
Experimental	-1.5327^{1}	77.7725	$2.1^{2,3}$	0.000			
LDA	-1.6777	72.8722	0.73	0.000			
PBE	-1.2788	79.8630	0.48	0.000			
PBEsol	-1.2597	75.7100	0.57	0.000			
SCAN	-1.5951	76.4457	0.48	0.000			
HSE06	-1.5277	77.7725	1.30	0.000			
Cu(OH) ₂ , Orth	orhombic						
Cu(OH) ₂ , Orth Functional	orhombic Energy (eV/f.u.)	Volume (Å ³)	Band Gap (eV)	Magnetic Moment (μ_B)			
Cu(OH) ₂ , Orth Functional Experimental	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5}	Volume (Å ³) 164.0976	Band Gap (eV) 0.00 ^{6–8}	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9}			
Cu(OH) ₂ , Orth Functional Experimental LDA	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031	Volume (Å ³) 164.0976 143.3151	Band Gap (eV) 0.00 ^{6–8} 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995	Volume (Å ³) 164.0976 143.3151 171.0463	Band Gap (eV) 0.00 ⁶⁻⁸ 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.)	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³)	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 Band Gap (eV)	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 Magnetic Moment (μ_B)			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional Experimental	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.) -1.3297 ¹	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³) 81.4014	Band Gap (eV) 0.00 ⁶⁻⁸ 0.00 0.00 0.00 0.00 0.00 Band Gap (eV) 1.4 ^{10,11}	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional Experimental LDA	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.) -1.3297 ¹ -1.5311	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³) 81.4014 82.4583	Band Gap (eV) 0.00 ⁶⁻⁸ 0.00 0.00 0.00 0.00 0.00 Band Gap (eV) 1.4 ^{10,11} 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional Experimental LDA PBE	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.) -1.3297 ¹ -1.5311 -1.0536	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³) 81.4014 82.4583 89.8508	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 0.00 1.4 ^{10,11} 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.001 0.002			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional Experimental LDA PBE PBEsol	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.) -1.3297 ¹ -1.5311 -1.0536 -1.1494	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³) 81.4014 82.4583 89.8508 85.5860	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 Band Gap (eV) 1.4 ^{10,11} 0.00 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.001 0.002 0.003			
Cu(OH) ₂ , Orth Functional Experimental LDA PBE PBEsol SCAN HSE06 CuO, Monocli Functional Experimental LDA PBE PBEsol SCAN	norhombic Energy (eV/f.u.) -3.7303 ^{1,4,5} -4.9031 -3.4995 -3.8374 -3.6525 -5.4102 nic Energy (eV/f.u.) -1.3297 ¹ -1.5311 -1.0536 -1.1494 -1.5448	Volume (Å ³) 164.0976 143.3151 171.0463 152.1084 181.2558 159.6701 Volume (Å ³) 81.4014 82.4583 89.8508 85.5860 84.9546	Band Gap (eV) 0.00 ^{6–8} 0.00 0.00 0.00 0.00 0.00 Band Gap (eV) 1.4 ^{10,11} 0.00 0.00 0.00 0.00 0.00 0.00	Magnetic Moment (μ_B) 0.000 (weakly AFM/FM) ^{8,9} 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.001 0.002 0.003 0.586			

1.2 Diatomic Oxygen and Hydrogen

The electronic energies E_e of elemental oxygen and hydrogen gas have a significant impact on the $\Delta_f G$ reported for each solid oxide and hydroxide. Systematic errors associated with ab initio calculations of gaseous molecules are well reported.^{13–16} The magnetic moment for oxygen is consistently determined to be 2.00 μ_B for each functional, which is in agreement with experiment.¹⁷ The binding energies reported from different functionals for gaseous hydrogen and oxygen are fairly consistent (Figure S1). The exception is SCAN, which predicts the binding energy to be around ≈ 1.5 eV greater for O_{2(g)} than what is predicted for HSE06. On the other hand, HSE06 gives an O_{2(g)} binding energy that is closest to the experimental binding energy of -2.56 eV/atom.^{16,18} Other GGA functionals and LDA have larger binding energies, consistent with documented problems associated with overbinding.^{15,16}



Figure S1: Binding energies and magnetic moments for hydrogen and oxygen gas with various exchange-correlation functionals to DFT. No zero point corrections are added. (a) The binding energies of the diamagnetic hydrogen molecule show small variations with functional. (b) The binding energies and magnetic moments of the oxygen molecule. All functionals predict the triplet ground state (magnetic moment of $2.0 \mu_B$. The DFT energy per atom is consistently predicted to be $\approx -3 \text{ eV}$.¹⁹ SCAN severely overestimates the binding energy of $O_{2(g)}$, while HSE06 most closely matches the experimental binding energy.

2 Parent Formation Reactions

Thermodynamic stability regions can be connected through their formation reactions. For the Pourbaix and probability diagrams, formation reactions were defined as oxidation-reduction reactions or chemical reactions from elemental copper. The chemical potential of each reaction ($\Delta \mu_{rxn}$) was dependent on many environmental and thermodynamic variables, including the Gibbs free energy of formation, temperature, pressure, solution activity, pH, and applied potential.

1.
$$Cu_{(s)} + H_2O \rightarrow CuO_{(s)} + 2e^- + 2H^+$$

2. $2Cu_{(s)} + H_2O \rightarrow Cu_2O_{(s)} + 2e^- + 2H^+$
3. $Cu_{(s)} + 2H_2O \rightarrow Cu(OH)_{2(s)} + 2e^- + 2H^+$
4. $Cu_{(s)} \rightarrow Cu^+ + e^-$
5. $Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$
6. $Cu_{(s)} + H_2O \rightarrow Cu(OH) + e^- + H^+$

- 7. $Cu_{(s)} + 2H_2O \rightarrow Cu(OH)_2^- + e^- + 2H^+$
- 8. $Cu_{(s)} + H_2O \rightarrow Cu(OH)^+ + 2e^- + H^+$
- 9. $Cu_{(s)} + 2H_2O \rightarrow Cu(OH)_2 + 2e^- + 2H^+$
- 10. $Cu_{(s)} + 3H_2O \rightarrow Cu(OH)_3^- + 2e^- + 3H^+$
- 11. $Cu_{(s)} + 4H_2O \rightarrow Cu(OH)_4^{2-} + 2e^- + 4H^+$

12.
$$2Cu_{(s)} + 2H_2O \rightarrow Cu_2(OH)_2^{2+} + 4e^- + 2H_2^{-}$$

13. $3Cu_{(s)} + 4H_2O \rightarrow Cu_3(OH)_4^{2+} + 6e^- + 4H^+$

3 Inclusion of the Hydrated Cu(OH)_{2(s)} Phase

Traditionally, due to experimental formation energies, $Cu(OH)_{2(s)}$ was not present in published copper Pourbaix diagrams. The hydrated phase exhibits limited solubility in water, which increases substantially over pH \approx 9.6.²⁰ There is little experimental observation of the formation for copper hydroxide as a passivating phase. However, computationally, some DFT functionals like LDA estimate a much higher free energy of formation for Cu(OH)_{2(s)} than experimental sources report.^{1,21} We here show the standard state Pourbaix diagrams calculated from $\Delta_f G$ values (in Table S2) where Cu(OH)_{2(s)} is considered (Figure S2).

Table S2: The free energies of formation for $Cu(OH)_{2(s)}$ at different levels of theory and from two different experimental sources. We note that van der Waals (VDW) interactions are included for all functionals except SCAN, where specified.

Functional	$\Delta_f G$ (eV/f.u.)
Experimental (NIST-Janaf Tables ¹)	-3.8623
Experimental (Puigdomenech ²¹)	-3.7303
LDA	-4.8798
PBE	-3.4995
PBEsol	-3.8374
SCAN with VDW	-1.8177
SCAN without VDW	-3.6544
HSE06	-3.8215

PBEsol, HSE06, and the experimentally-sourced diagrams allow for corrosion to occur at low and high pHs (approximately pH≤6 and pH≥14). The passivisation regime only allows for copper (II) hydroxide and Cu₂O_(s) to form, and the protection region itself is much larger than it is when Cu(OH)_{2(s)} is suppressed. We note that the Cu₂O_(s) region is not observed for PBEsol. SCAN will not show the Cu(OH)_{2(s)} phase with or without the van der Waals correction included because the CuO_(s) solid has such a low formation energy. We note that with the rVV10 energy correction, the free energy of formation is much lower than experiment (by nearly 2 eV/f.u.), necessitating future benchmarking of the use of van der Waals corrections for transition metal hydroxides with SCAN. The LDA-sourced Pourbaix diagram shows overestimated Cu(OH)_{2(s)} domains. In this case, the presence of copper hydroxide greatly increases the passivisation regions, and does not allow for well known corrosion or passivisation behavior at extreme pHs. The only Pourbaix diagram without a stable copper hydroxide domain is that sourced from the PBE functional, as the Cu(OH)_{2(s)} free energy of formation is low (about 0.2 eV/f.u. below the experimentally-sourced range).

Pourbaix originally published two copper diagrams, one with only $\text{CuO}_{(s)}$ and one with the hydroxide passivisation phase also considered.⁵ Both experimentally sourced diagrams presented in this study are consistent with his work.⁵ However, we note that experimental $\Delta_f G$ value for $\text{Cu}(\text{OH})_{2(s)}$ varies by as much as 0.2 eV/f.u.^{1,5,21} Past studies do not identify $\text{Cu}(\text{OH})_{2(s)}$ as a primary product formed on copper in solution, and identify $\text{CuO}_{(s)}$ as the most stable passive product in most cases. Other experiments specify that while the initial solubility constant of $\text{Cu}(\text{OH})_2$ is small, over a large amount of time the solid breaks down and dissolves in solution or transitions into CuO, pointing to instability of the solid.^{20,22,23}



Figure S2: Copper Pourbaix diagrams shown at standard state and the typical corrosion limit $(\eta_I = 10^{-6})$, where Cu(OH)_{2(s)} is included. No energy corrections (E_c) are included. Experimental solid free energies of formation were sourced from the NIST-Janaf Tables,¹ as other experimental sources do not allow for a Cu(OH)_{2(s)} predominance region. The LDA Pourbaix diagram demonstrates large Cu(OH)_{2(s)} passivation regions, and does not allow for stable corrosion regions at extreme pH values. Additionally, the passivation impedes the immunity region of elemental copper. The inclusion of copper hydroxide does not change the PBE Pourbaix diagram, as the free energy of formation of the hydrated phase is 0.2 eV/f.u. lower than experiment. The SCAN Pourbaix diagram does not change as well, even when the higher $\Delta_f G$ obtained without including the van der Waals correction, because the CuO_(s) phase dominates. Pourbaix diagrams calculated using experimental energies, PBEsol and HSE06 demonstrate passivation regions at ranges of intermediate pHs, and corrosion at highly acidic or basic conditiuons. The immunity region in all cases is preserved except with use of LDA. Cu₂O_(s) occurs in the experimentally and DFT-sourced diagrams, except for those computed at the LDA and PBEsol level.

4 Activity Dependence

The activity, or concentration, dependence of corrosion behavior is well documented. Figure S3 shows that in high purity water, corrosion behavior is dominated by aqueous ions ($\eta_I = 10^{-8}$). In contrast, Figure S4 shows protective solid oxides form at wider pH ranges at higher concentrations ($\eta_I = 10^{-2}$). The behavior varies greatly depending on the formation energy source. The experimental and LDA diagrams are in relatively good agreement, and predict large passivation near neutral and basic pHs. On the other hand, PBE, PBEsol, and HSE06 do not predict CuO_(s) to be a stable phase at low copper concentrations. SCAN drastically over predicts the stability of solid phases, and does not allow for any stability regions for aqueous ions.



Figure S3: Copper Pourbaix diagrams at standard state for low solute activity ($\eta_I = 10^{-8}$). No energy corrections are added. Functional dependence follows similar trends to diagrams created at the typical corrosion limit. SCAN and LDA overestimate the stability range of the solid copper compounds. Conversely, PBE and PBEsol do not allow for stability of solid species. HSE06 does not predict CuO_(s) to be stable, but does allow for a small region of Cu₂O_(s) stability around neutral pHs. Diagrams shown here are applicable to standard state conditions for relatively pure water, with approximate copper concentrations at 10^{-8} mol/L copper.



Figure S4: Copper Pourbaix diagrams at standard state for high solute activity ($\eta_I = 10^{-2}$). No energy corrections are added. Functional dependence follows similar trends to diagrams created at the typical corrosion limit. SCAN and LDA overestimate the size of the CuO_(s) region, and do not predict corrosion to occur at high pHs. PBE and PBEsol underestimate the passivation region. The GGA functionals also allow for the formation of additional aqueous ions at intermediate pHs. Cu₃(OH)²⁺₄ occurs in acidic conditions for diagrams based on PBE and PBEsol energies. PBE also stabilizes Cu(OH)⁻₃ at around pH = 12. HSE06 and the experimentally derived diagrams are in good agreement. Both show large copper oxide passivation regions, and predict immunity of elemental copper at neutral pHs and potentials. These diagrams are relevant for situations where copper activity is large, corresponding to approximate concentrations of 10⁻² mol/L copper.

5 CRCP Method Pourbaix Diagram

The CRCP is used to reproduce the dissolution boundaries of Pourbaix diagrams created from experimental $\Delta_f Gs$.²⁴ The CuO_(s) regions for all computational sources are found to be very similar to the experimentally derived diagrams (Figure S5). Only the HSE06 $\Delta_f G$ values reproduce nearly exactly the experimental Pourbaix diagram.



Figure S5: The CRCP method implemented from experimentally sourced E_c at standard state. The typical corrosion limit was used. E_c was based on the $\Delta_f G$ of CuO_(s) from experiment.

6 Synopsis of the Revised Helgeson-Kirkham-Flowers Method

The Helgeson-Kirkham-Flowers (HKF) method encompasses a collection of works published from the 1970s through the 1990s, including the select works highlighted herein.^{25–31} Several studies use the revised HKF method to account for different thermodynamic behavior of solutions at nonstandard state, including to construct Pourbaix Diagrams.^{21,32} The method is founded on the basis that the change in behavior of a solution can be derived from the sum of its solvated and nonsolvated contributions, and approximates the size of the ion radius and its subsequent Born coefficient through experimental observations and fitted data. Further dependence of solution structure based upon changes to the dielectric constant and effective volume are documented with temperature and pressure changes. Several parameters and functions, including the *g*-function and the dielectric constant of water, have been well documented. The entropy, enthalpy, heat capacity, and therefore formation energies of solutions can be calculated at nonstandard state. We utilized the following equations, similar to those those used by Puigdomenech and Binter,^{32,33} to find the entropy and heat capacity at elevated temperatures.

We start with the equation for the molal formation energy of a species at nonstandard state:

$$\Delta \bar{G}^{\circ} = \Delta \bar{G}_{f}^{\circ} + (\bar{G}_{P,T}^{\circ} - \bar{G}_{P_{r},T_{r}}^{\circ})$$
(S1)

where the difference $(\bar{G}_{P,T}^{\circ} - \bar{G}_{P_r,T_r}^{\circ})$ is related to our definition of the Gibbs formation energy, which is dependent on the entropy, heat capacity, volume, and pressure:

$$\bar{G}_{P,T}^{\circ} - \bar{G}_{P,T_r}^{\circ} = -\bar{S}_{P_r,T_r}^{\circ}(T - T_r) + \int_{T_r}^T \bar{C}_{P_r}^{\circ} dT - T \int_{T_r}^T \bar{C}_{P_r}^{\circ} d\ln(T) + \int_{P_r}^P \bar{V}_T^{\circ} dP \,.$$
(S2)

In this study we assumed the $\int_{P_r}^{P} \bar{V}_T^{\circ} dP$ term, describing the change in volume in the system at different pressure, is negligible. We therefore need the nonstandard state heat capacity in order to calculate the change in formation energy. We also assume that the integrated heat capacity can be approximated by the average temperature of the heat capacity at the given temperature range. The equation for partial molal heat capacity, \bar{C}_P^0 , is shown below as a sum of its solvated and nonsolvated contributions.

$$\bar{C}_P^0 = \Delta \bar{C}_{P,n}^0 + \Delta \bar{C}_{P,s}^0 \tag{S3}$$

This ultimately gives us the final equation for the standard partial molal heat capacity as:

$$\begin{split} \bar{C}_{P}^{0} &= c_{1} + \frac{c_{2}}{\left(T - \Theta\right)^{2}} - \left(\frac{2T}{\left(T - \Theta\right)^{3}}\right) \times \left(a_{3}(P - P_{r}) + a_{4}\ln\left(\frac{\Psi + P}{\Psi + P_{r}}\right)\right) \\ &+ \omega T X + 2T Y \left(\frac{\partial \omega}{\partial T}\right)_{P} - T \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial^{2} \omega}{\partial T^{2}}\right)_{P}, \end{split}$$
(S4)

where \bar{C}_P^0 is given as a function of temperature and pressure. It accounts for changes in temperature and pressure through the inclusion of the dielectric constant and its dependent terms, the Born coefficient, and the coefficients of equations of state. The nonstandard state temperature and pressure are given by *T* and *P* respectively. Θ and Ψ are solvent parameters equal to 228 K and 2800 bar. Implementation of these equations yields the standard molal heat capacity at elevated temperatures and pressures. We show the $\Delta \bar{C}_p^0$ is dependent upon parameters c_1 , c_2 , a_3 , a_4 , Z, and ω . Additional equationsof-state coefficients a_1 and a_2 are used for the approximation of other properties like nonstandard state entropy, but are not needed for this study. The values for the equations-of-state coefficients are derived from experiment, and are given in a variety of works.^{26,27,34} In the case where parameters were not given, the coefficients were approximated by the coefficients provided for structurally and electronically similar ions found in works by Shock and Helgeson, particularly when modeling anionic copper complexes.^{26,27,30} We point out that the cuprite and cuprous hydrolysis series found to be stable in largely basic conditions, such as Cu(OH)²₃ and Cu(OH)²⁻₄, can also be written as the HCuO²₂ and CuO²⁻₂.

The series of the conventional Born coefficient ω_j and its partial derivatives with respect to temperature are given below, which exhibit a dependence on the *g*-function (within the radii terms, $r_{e,j}$):

$$\omega_j = \omega_j^{abs} - Z_j \omega_{H^+}^{abs} \tag{S5}$$

$$\omega_j^{abs} = \frac{N^0 e^2 Z_j^2}{2r_{e,j}} = \frac{\eta_j^2 Z_j^2}{r_{e,j}}$$
(S6)

$$\omega_j^{abs} = \frac{\eta Z_{e,j}^2}{r_{e,j}} \tag{S7}$$

where Z is the formal charge on the ion, N^0 is Avagadro's number, *e* is the absolute electronic charge equal to 4.80298×10^{-10} esu, and $\eta = 1.66027 \times 10^5$ Åcal/mol. An important point to note is that neutral ions are often found to still behave as a charged ion in solution, but the revised HKF method for neutral atoms does not define a formal charge for these species. Values in the original works were found from experimental extrapolation exclusively. In this work, we define Z = 0 for electronically neutral ions, and extrapolate reported values for structurally similar ions to our own species. The value $\omega_{H_{+}}^{abs}$ is the Born coefficient of the H^+ ion, equal to approximately 5.387×10⁴ cal/mol (225.4 kJ/mol) at standard state.²⁷ The effective radii of the j^{th} ion, $r_{e,j}$ is defined as

$$r_{e,j} = r_{x,j} + |Z_j|(k_z + g)$$
(S8)

where $r_{x,j}$ is the crystallographic radius of the ion, k_z is a charge dependent constant defined as 0.94 for cations and 0.0 for anions,²⁶ and g is the g function characterized in Tanger and Helgeson (1988).³⁰ The values of the g function are reported in Shock et al. (1992) and further in this section.³⁴

To calculate the \bar{C}_{P}^{0} value, we find the partial derivatives of the Born coefficient with respect to temperature. These are defined below, where each partial derivative similarly relies on the *g*-function and its partial derivatives.

$$\left(\frac{\partial\omega}{\partial T}\right)_{P} = -\eta \left[\frac{abs(Z^{3})}{r_{e}^{2}} - \left(\frac{Z}{(3.082+g)^{2}}\right)\right] \left(\frac{\partial g}{\partial T}\right)_{P}$$
(S9)

$$\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P = 2\eta \left[\frac{Z^4}{r_e^3} - \left(\frac{Z}{(3.082+g)^3}\right)\right] \left(\frac{\partial g}{\partial T}\right)_P^2 - \eta \left[\frac{abs(Z^3)}{r_e^2} - \left(\frac{Z}{(3.082+g)^2}\right)\right] \left(\frac{\partial^2 g}{\partial T^2}\right)_P \quad (S10)$$

We highlight that the *g*-function, while defined elsewhere, was defined and then fit with a power series in Tanger and Helgeson (1988),³⁰ and later Shock et al.³⁴ As discussed in Shock et al. (1992),³⁴ the *g*-function is a solvent function that describes the effective electrostatic radii of pressure and temperature dependence of the solvent, in this case water.³⁰ We define it below.

$$g = a_g (1 - \hat{\rho})^{b_g} \tag{S11}$$

$$a_g = a'_g + a''_g T + a'''_g T^2$$
(S12)

$$b_g = b'_g + b''_g T + b'''_g T^2$$
(S13)

Here, a_i and b_j are parameters given in a variety of texts, *T* is temperature, and $\hat{\rho}$ is the density of water divided by 1 $\frac{g}{cm^3}$.³³ Qualitative trends and descriptions of the *g*-function can be found in Shock et al.³⁴

The partial derivatives of the *g*-function with respect to temperature, at constant pressure, are necessary to find the final temperature-dependence of the Born coefficient as shown below. Explicit values of the partial derivatives at different pressures and temperatures are found in Shock et al.³⁴

$$\left(\frac{\partial g}{\partial T}\right)_p = g \left[\frac{\hat{\rho}\alpha b_g}{1-\hat{\rho}} + (b_g^{''} + 2b_g^{'''}T)\ln(1-\hat{\rho}) + \frac{a_g^{''} + a_g^{'''}T}{a_g}\right]$$
(S14)

$$\begin{pmatrix} \frac{\partial^2 g}{\partial T^2} \end{pmatrix}_P = g \left[\frac{\hat{\rho} \alpha b_g}{1 - \hat{\rho}} \left[\frac{2(b_g^{''} + 2b_g^{'''}T)}{b_g} + \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_P - \alpha - \frac{\hat{\rho} \alpha}{(1 - \hat{\rho})} \right] \right. \\ \left. + 2b_g^{'''} \ln(1 - \hat{\rho}) + \frac{2a_g a_g^{'''} - (a_g^{''} + 2a_g^{'''}T)^2}{a_g^2} \right] + \frac{1}{g} \left(\frac{\partial g}{\partial T} \right)_P^2$$
(S15)

where α is the coefficient of thermal expansion for water.

Also necessary for the calculation of \bar{C}_p^0 are X, Y, and Z, which allow for the changes in the dielectric behavior of water, including its ability to stabilize solvents with temperature and pressure. We note that the Z in this case is dependent upon the dielectric constant of water, and is not the ion's formal charge. The definitions of X, Y, and Z are below, where ϵ is the dielectric constant of water:

$$Z = -\frac{1}{\epsilon}$$
(S16)

$$Y = \left(\frac{\partial Z}{\partial T}\right)_P = \left(\frac{1}{\epsilon^2}\right) \left(\frac{\partial \epsilon}{\partial T}\right)_P \tag{S17}$$

$$X = \left(\frac{\partial Y}{\partial T}\right)_{P} = \left(\frac{1}{\epsilon^{2}}\right) \left[\left(\frac{\partial^{2}\epsilon}{\partial T^{2}}\right)_{P} - \frac{2}{\epsilon} \left(\frac{\partial\epsilon}{\partial T}\right)_{P}^{2} \right]$$
(S18)

The values of X, Y, and Z at a range of pressures and temperatures are documented in Shock et al.³⁴ The variation of the dielectric constant of water is based on temperature, pressure and density has been well documented.^{33,35}

$$\epsilon = \sum_{i=0}^{4} k_i(\tau)\hat{\rho}^i \tag{S19}$$

where $k_i(\tau)$ are fitting parameters for the density of water, given as $\hat{\rho}$ divided by 1 g cm⁻³. Therefore, the first and second partial derivatives with respect to temperature of Z used to calculate the Y and X functions are:

$$\left(\frac{\partial\epsilon}{\partial T}\right)_{P} = \sum_{i=0}^{4} \hat{\rho} \left[\left(\frac{\partial k_{i}(\tau)}{\partial T}\right)_{P} - i\alpha k_{i}(\tau) \right]$$
(S20)

$$\left(\frac{\partial^{2}\epsilon}{\partial T^{2}}\right)_{P} = \sum_{i=0}^{4} \hat{\rho}^{i} \left[\left(\frac{\partial^{2}k_{i}(\tau)}{\partial T^{2}}\right)_{P} - i \left(\alpha \left(\frac{\partial k_{i}(\tau)}{\partial T}\right)_{P} + k_{i}(\tau) \left(\frac{\partial \alpha}{\partial T}\right)_{P}\right) - i \alpha \left(\left(\frac{\partial k_{i}(\tau)}{\partial T}\right)_{P} - i \alpha k_{i}(\tau)\right) \right]$$
(S21)

These equations are founded on established changes in the dielectric constant of water with respect to temperature and pressure. To implement these equations we require the coefficient of thermal expansion, α , and its respective derivatives, which can be found in a variety of sources.^{25,26,29}

In summary, the follow general steps are necessary to calculate the Gibbs free energy of formation for aqueous ions at elevated temperatures with the revised HKF model:

- 1. Enumerate ion independent parameters in the methodology, such as Ψ and Θ .
- 2. Establish known and desired thermodynamic data and properties for the given ion. This includes the desired nonstandard state pressure and temperature, charge, and standard state values of $\Delta_f G$, S and C.
- 3. Find temperature and pressure independent parameters for the ion including c₁, c₂, a₁, a₂, etc. These should be experimentally given or approximated.
- 4. Calculate or find from the literature the volume and volume derivatives of water, its dielectric coefficient and its derivatives, and the *g*-function and its derivatives.
- 5. Calculate or find from literature the born functions of water, such as Z, Y, X.
- 6. Enumerate the ionic radii and effective ionic radii of the ion.
- 7. Calculate the Born coefficient and its derivatives.
- 8. Calculate the heat capacity and entropy of the ion. Utilize use the (non-)standard state thermodynamic properties to approximate the extrapolated $\Delta_f G$ at nonstandard state.

The thermodynamic behavior found in this study should be viewed as correctly capturing the trends for the aqueous ions considered, and is not claimed to give exact values of the formation energies of these species at higher temperatures. Future experimental work could focus on identifying the nonstandard state thermodynamic properties of copper aqueous ions. To that end, we find agreement between our calculated entropies and heat capacities to those calculated by Puigdomenech.²¹ Furthermore, these approximations for the temperature and pressure dependence of the formation energies have been used successfully before.³¹

7 Temperature and Pressure Dependence of Water Stability Region

The water stability region is defined as the region between the reduction and oxidation potentials of water. This region varies with pH, temperature, and pressure. The potential is reported in reference to the standard hydrogen electrode (E_{SHE}), which is 0 V at 0 pH at all temperatures. The temperature *T* and pressure *P* dependencies of E_{SHE} are described through the Nernst equation:

$$E = -\frac{RT}{2F} \ln \frac{p_{\rm H_2}}{p^0} - \frac{2.303RT}{F} \text{pH} = E^0 - \frac{2.303RT}{F} \text{pH}$$
(S22)

where E is the potential (in V), and p^0 and p_{H_2} are the standard pressure and partial pressure of hydrogen (in Pa), respectively. We calculate E^0 as 0 and $\Delta_f G(H_2O)/2F$ for water reduction and oxidation, respectively.

Figure S6 presents two-dimensional heat maps of how the potential *E* approximately varies with temperature and pressure at pH = 0, 7, and 14. Gibbs free energies of formation for water at specific temperature and pressure points are sourced from H. Halbach, et al.³⁶ Potentials were found as interpolations from the previously calculated $\Delta_f G$. We see that temperature has the most substantial effect on *E*. As temperature and pressure increases, *E* decreases.



Figure S6: The oxidation potential of water *E* calculated for temperatures from 373.15 K to 573.15 K (100°C to 300°C) and 0.5 kbar to 5 kbar. *E* depends on the $\Delta_f G$ of water, which was interpolated between calculated values.³⁶

8 Species Temperature and Pressure Dependence

We use the above revised HKF method to calculate the temperature and pressure dependence of all considered aqueous ions. We compare the data with formation energies found using only the room temperature heat capacity. When we plot the relative change in $\Delta_f G$ as a function of temperature for select ions (Figure S7), we find good agreement between the changes in free energies of formation calculated with constant heat capacities and temperature-dependent heat capacities calculated from the revised HKF method.²⁶ Figure S7 shows the formation energy dependence for the Cu⁺ and Cu²⁺ hydrolysis series.



Figure S7: Change in aqueous ions $\Delta_f G$ as a function of temperature for the a) Cu¹⁺ and b) Cu²⁺ hydrolysis series. We see the largest change in the $Z = 2^+$ series (e.g., Cu(OH)₄²⁻ as part of the Cu²⁺ series) at elevated temperatures. We observe charged species generally become less favorable at higher temperatures, consistent with the smaller dielectric constant and decreased structure of water. This effect is more pronounced with larger species, particularly with the Cu(OH)₃⁻ and Cu(OH)₄²⁻ ions. The neutral species in each series, Cu(OH)₂ and CuOH, both show small increases in stability at high temperatures.

All aqueous ions are found to change at around the same magnitude or less than the formation energies of other aqueous ions reported in revised HKF works.^{26,27} The only exception are the $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ ions, whose formation energies increased by over 0.4 and 0.6 eV per formula unit (f.u.) at 300° when compared to their standard state $\Delta_f G$ values. We attribute these changes to the large size of these ions in comparison to the smaller, single atom ions typically reported in these works. Additionally, we note that while this change in formation energy is large, it only relates to an 8.6% and 10.4% change from the standard formation energy. The largest percentage change in formation energy changes came from the Cu^{2+} ion, whose $\Delta_f G$ value changed by 18% at 150°C and 52% by 300°C. This is large when compared to other aqueous ions, whose formation energies varied by less than 2% at temperatures below 150°C.

We also plot the temperature dependent $\Delta_f G$ at two different pressure points for Cu⁺ and Cu²⁺ (Figure S8). We explore the ions' behavior at the saturation pressure (P_{sat}) and 500 bar. We find that both species change approximately linearly at low temperatures, where the most substantial changes



Figure S8: Change in $\Delta_f G$ as a function of temperature and pressure for cationic copper ions (e.g. Cu⁺ and Cu²⁺). The room temperature free energy of formation is sourced from experiment.^{37–39} The thermodynamic behavior is approximated using the revised HKF method. We observe a small decrease in the free energy of formation for Cu⁺ as temperature increases, while the free energy of formation for Cu²⁺ decreases. At high pressures, $\Delta_f G$ for both ions matches the free energy of formation at saturation pressure for T < 150 K. At high temperatures, increased pressure stabilizes both ions, and the free energy of formation is less than it would be at saturation pressure.

occur above 150°C. Cu²⁺ increases in formation energy, while $\Delta_f G$ of Cu⁺ decreases. At higher pressures, we find that the formation energies in fact decrease and become more stable relative to the P_{sat} set. The increase in formation energy of Cu²⁺ is attributed to the larger atomic radius, which is more difficult to stabilize at elevated temperatures as the structure of water deteriorates. Additionally, as its dielectric constant decreases with increasing temperature, larger charges become increasingly difficult to stabilize. We note the coefficients for equations-of-state for these species were sourced from the original HKF works.²⁶

We plot the temperature dependence of the $\Delta_f G$ values for the solid species of copper in Figure S9. We see that all species become more stable as the temperature increases. Temperature dependence was calculated as stated in the Methods Section following the method by Grabowski et al.⁴⁰ Excellent agreement is found between PBE and PBEsol, although for this study we use the PBEsol functional for the Pourbaix diagram calculations. At 300°C, which is the highest temperature explored in the study, we find that the largest change in $\Delta_f G$ only accounts for about a 24% difference.

We note that many of the $\Delta_f G$ changes in the aqueous ions were relatively small. In fact, the largest contribution at high temperatures to μ is the $RT\ln(\eta_I)$, with the exception of Cu(OH)₄²⁻. At 300°C, the solvation term $RT\ln(\eta_I)$ decreases μ by around 0.6 eV. Therefore, the small changes seen in Figure S9 are assumed to be relatively negligible for this study for temperatures below 150°C. This is attributed to the zero value of the *g*-function at $T < 150^{\circ}$ C, such that water's structure and dielectric properties are fairly consistent below this value.³⁰ Above this temperature, it is suggested



Figure S9: Change in the $\Delta_f G$ with temperature changes for the prominent solid oxides (Cu_(s), Cu₂O_(s), CuO_(s)). The vibrational energy decreases as temperature increases, leading to larger stability for all solid species. There is close agreement between PBE and PBEsol.

that the HKF method is used to estimate the formation energy change of ions at varying temperatures and pressures.

We show the pressure dependence on $\Delta_f G$ of the two copper oxides considered at nonstandard state. Table S3 shows the difference (Δ) of the $\Delta_f G$ values at no pressure and 5 kbar applied pressure for three different functionals. The largest difference was found for Cu₂O with PBEsol, which demonstrates a 13.4% difference at the maximum applied pressure in the system. We note that HSE06 calculations were not explicitly relaxed due to computational cost, and the volume change was approximated with PBEsol.

Table S3: The free energies of formation differences for $Cu_2O_{(s)}$ and $CuO_{(s)}$ at different levels of theory. Δ represents the difference in Gibbs free energy of formation between the relaxed 5 kbar structure and that without an applied pressure.

Functional	Cu ₂ O Δ (eV/f.u.)	CuO Δ (eV/f.u.)
PBEsol SCAN HSE06	0.1689 0.1770 0.1620	-0.0216 -0.0162

Finally, to explore driving forces in the aqueous copper system at higher temperatures, we plot the change in reaction chemical potential $(\Delta \mu_{rxn})$ at selected temperatures and pHs, shown in Figure S10. At high temperatures, we find the Cu²⁺ and Cu(OH)₂⁻ ions increase in stability at the expense of protective CuO_(s) and Cu₂O_(s) regions. The driving forces to create these passive layers are not substantial at higher temperatures. Moreover, the change in $\Delta \mu_{rxn}$ plummets between elemental copper and aqueous ions as the temperature increases. At $T > 50^{\circ}$ C, we see Cu₂O_(s)



Figure S10: Changes in the chemical potentials of the system produced with formation energies calculated with HSE06 (no energy correction added). No applied potential is considered (U = 0 V). Temperature increases from left to right, undermining protection for elemental copper. At $T \le 50^{\circ}$ C, there is a small passivation region at pH≈8. The driving force for Cu₂O_(s) in this case is small as there are other phases whose change in chemical potential are quite close to those of copper(I) oxide. $T = 100^{\circ}$ C shows reduced driving forces for Cu_(s) at acidic pHs, and the stabilization of aqueous ions and pH ≥ 6. By $T = 200^{\circ}$ C the immunity region has disappeared.

disappear as the most stable phase. $CuOH^+$ in particular becomes more stable at acidic and neutral pHs, blocking the formation of copper oxide. With increasing temperature there is relatively little increase in stability for Cu^{2+} relative to the $Cu_{(s)}$ with no applied potential, implying that no increase in temperature will allow for Cu^{2+} to be stable instead of $Cu_{(s)}$. Instead, at higher temperature the immunity region is infringed upon by through the increased stability of Cu^+ , CuOH, and CuOH⁺ ions. Information within Figure S10 indicates care should be taken when solid copper is exposed to elevated temperatures. To help prevent corrosion at elevated temperatures, manipulation of other variables within the system (i.e., increased copper concentration, under potentials, low pHs) could increase protection of elemental copper.

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