

Supplemental Material: The COVID-19 Pandemic, Part 2: Understanding the Efficacy of Oxidized Copper Compounds in Suppressing Infectious Aerosol-Based Virus Transmission

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DATA AVAILABILITY

All thermodynamic data was taken from Lange’s Handbook of Chemistry¹ (L), with the exception of the equilibrium constant of the copper compound, atacamite $\text{Cu}_4(\text{OH})_6\text{Cl}_2$, which was taken from Barton and Bethke² (B.B.) and the stability constants for Cu(II)-carbonate complexation, which was taken from Benjamin (Ben.).³ The following tables report all thermodynamic data used in this analysis (and more).

Table S1.

	Valence	Chemical Potential (kJ/mole)	Source
Cu	0	0	L
Cu ⁺	1	50	L
Cu ²⁺	2	65.52	L
CuCl _(s)	1	-119.9	L
CuCl _{2 (s)}	2	-175.7	L
Cu ₂ O	1	-149	L
CuO	2	-129.7	L
Cu(OH) _{2 (s)}	2	-373	L
CuSO _{4 (s)}	2	-662.2	L
CuSO _{4 (aq)}	2	-679.11	L
CuSO ₄ ·5H ₂ O	2	-1,880.04	L
H ₂ O		-237.140	L
OH ⁻		-157.280	L
Cl ⁻		-131.3	L
SO ₄ ²⁻		-744.5	L

Table S2.

	Valence	Log(β)	Source
Cu(NH ₃) ⁺	1	5.93	L
Cu(NH ₃) ²⁺	1	10.86	L
Cu(NH ₃) ₂ ⁺	2	4.31	L
Cu(NH ₃) ₂ ²⁺	2	7.98	L
Cu(NH ₃) ₂ ²⁺	2	11.02	L

(continued)

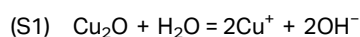
	Valence	Log(β)	Source
Cu(NH ₃) ₄ ²⁺	2	13.32	L
Cu(NH ₃) ₅ ²⁺	2	12.86	L
CuCl ₂	1	5.5	L
CuCl ₃ ²⁻	1	5.7	L
CuCl ⁺	2	0.1	L
CuCl ₂ ⁰	2	-0.6	L
Cu(OH) ⁺	2	7	L
Cu(OH) ₂ ⁰	2	13.68	L
Cu(OH) ₃ ⁻	2	17	L
Cu(OH) ₄ ²⁻	2	18.5	L
Cu(Lact) ²⁺	2	3.02	L
Cu(Lact) ₂ ²⁺	2	4.85	L
Cu(CO ₃) ⁰	2	6.7	Ben.
Cu(CO ₃) ₂ ²⁻	2	10.2	Ben.

Table S3.

Compound	Equilibrium	Log(K)	Source
Cu ₄ (OH) ₆ Cl ₂	$K = \frac{[\text{Cu}^{2+}]^4 [\text{OH}^-]^6 [\text{Cl}^-]^2}{1}$	-69.4	B.B.
H ₂ O	$K = \frac{[\text{H}^+][\text{OH}^-]}{1}$	-14	L
Carbonate	$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$	-6.35	L
	$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$	-10.33	L
Ammonium	$K_{a1} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$	-9.25	L
Lactate	$K_{a1} = \frac{[\text{Lactate}][\text{H}^+]}{[\text{Lactic Acid}]}$	-3.86	L

EQUILIBRIUM EXPRESSIONS

Cu₂O



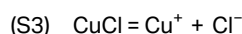
$$\text{Log}\left(\frac{[\text{Cu}^+]^2 [\text{OH}^-]^2}{1}\right) = -\frac{(2 * 50,000 + 2 * -157,280) - (-149,000 + -237,140)}{2.303 * 8.314 * 298}$$

$$2\text{Log}([\text{Cu}^+]) + 2\text{log}([\text{OH}^-]) = -\frac{171,580}{2.303 * 8.314 * 298} = -30.07$$

$$\text{Log}([\text{Cu}^+]) = -15.04 - \text{log}([\text{OH}^-]) = -15.04 + (14 - \text{pH})$$

(S2) **Log([Cu⁺]) = -1.04 - pH**

CuCl

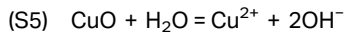


$$\text{Log}\left(\frac{[\text{Cu}^+][\text{Cl}^-]}{1}\right) = -\frac{(50,000 + -131,300) - (-119,900)}{2.303 * 8.314 * 298}$$

$$\text{Log}([\text{Cu}^+]) + \text{log}([\text{Cl}^-]) = -\frac{38,600}{2.303 * 8.314 * 298} = -6.76$$

(S4) $\text{Log}([\text{Cu}^+]) = -6.76 - \text{log}([\text{Cl}^-])$

CuO



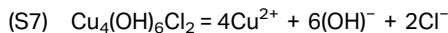
$$\text{Log}\left(\frac{[\text{Cu}^{2+}][\text{OH}^-]^2}{1}\right) = -\frac{(65,520 + 2 \cdot -157,280) - (-129,700 + -237,140)}{2.303 \cdot 8.314 \cdot 298}$$

$$\text{Log}([\text{Cu}^{2+}]) + 2 \text{log}([\text{OH}^-]) = -\frac{117,800}{2.303 \cdot 8.314 \cdot 298} = -20.65$$

$$\text{Log}([\text{Cu}^{2+}]) = -20.65 - 2 \text{log}([\text{OH}^-]) = -20.65 + 2(14 - \text{pH})$$

(S6) $\text{Log}([\text{Cu}^{2+}]) = 7.35 - 2\text{pH}$

Cu₄(OH)₆Cl₂



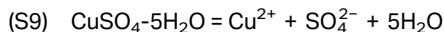
$$-69.4 = \text{log}\left(\frac{[\text{Cu}^{2+}]^4[\text{OH}^-]^6[\text{Cl}^-]^2}{1}\right)$$

$$4\text{log}(\text{Cu}^{2+}) = -69.4 - 6\text{log}(\text{OH}^-) - 2\text{log}(\text{Cl}^-)$$

$$\text{log}(\text{Cu}^{2+}) = -17.35 + 1.5(14 - \text{pH}) - .5\text{log}(\text{Cl}^-)$$

(S8) $\text{log}([\text{Cu}^{2+}]) = 3.65 - 1.5\text{pH} - .5 \text{log}(\text{Cl}^-)$

CuSO₄-5H₂O



$$\text{Log}\left(\frac{[\text{Cu}^{2+}][\text{SO}_4^{2-}]}{1}\right) = -\frac{(65,520 + -744,500 + 5 \cdot -237,140) - (-1,880,040)}{2.303 \cdot 8.314 \cdot 298}$$

$$\text{Log}([\text{Cu}^{2+}]) + \text{log}([\text{SO}_4^{2-}]) = -\frac{15,360}{2.303 \cdot 8.314 \cdot 298} = -2.69$$

(S10) $\text{Log}([\text{Cu}^{2+}]) = -2.69 - \text{log}([\text{SO}_4^{2-}])$

Assuming that the initial starting concentration of sulfate is negligible, the only source of sulfate in solution comes from the dissolution of this copper sulfate compound. In this case, the concentration of sulfate will be equal to the concentration of the cupric cation (Cu²⁺) and this expression reduces to:

(S11) $\text{Log}([\text{Cu}^{2+}]) = -1.35$

MASTER EXPRESSIONS FOR TOTAL AQUEOUS COPPER

Cu(I)

$$[\text{Cu(I)}]_{\text{aq}}^{\text{Tot}} = [\text{Cu}^+] + [\text{Cu}(\text{NH}_3)^+] + [\text{Cu}(\text{NH}_3)_2^+] + [\text{CuCl}_2] + [\text{CuCl}_2^{2-}]$$

$$\text{Cu(I)}_{\text{aq}}^{\text{Tot}} = [\text{Cu}^+] + 10^{5.93}[\text{Cu}^+][\text{NH}_3] + 10^{10.86}[\text{Cu}^+][\text{NH}_3]^2 + 10^{5.5}[\text{Cu}^+][\text{Cl}^-]^2 + 10^{5.7}[\text{Cu}^+][\text{Cl}^-]^3$$

(S12) $\text{Cu(I)}_{\text{aq}}^{\text{Tot}} = [\text{Cu}^+](1 + 10^{5.93}[\text{NH}_3] + 10^{10.86}[\text{NH}_3]^2 + 10^{5.5}[\text{Cl}^-]^2 + 10^{5.7}[\text{Cl}^-]^3)$

Cu(II)

$$[\text{Cu(II)}]_{\text{aq}}^{\text{Tot}} = [\text{Cu}^{2+}] + [\text{Cu}(\text{OH})^+] + [\text{Cu}(\text{OH})_2^0] + [\text{Cu}(\text{OH})_3^-] + [\text{Cu}(\text{OH})_4^{2-}] + [\text{CuCl}^+] + [\text{CuCl}_2^0] + [\text{Cu}(\text{NH}_3)^{2+}] + [\text{Cu}(\text{NH}_3)_2^{2+}] + [\text{Cu}(\text{NH}_3)_3^{2+}] + [\text{Cu}(\text{NH}_3)_4^{2+}] + [\text{Cu}(\text{NH}_3)_5^{2+}] + [\text{Cu}(\text{Lact.})^+] + [\text{Cu}(\text{Lact.})_2^0] + [\text{Cu}(\text{Cu}_3)^0] + [\text{Cu}(\text{CO}_3)_2^{2-}]$$

$$[\text{Cu(II)}]_{\text{aq}}^{\text{Tot}} = [\text{Cu}^{2+}] + 10^7[\text{Cu}^{2+}][\text{OH}^-] + 10^{13.68}[\text{Cu}^{2+}][\text{OH}^-]^2 + 10^{17}[\text{Cu}^{2+}][\text{OH}^-]^3 + 10^{18.5}[\text{Cu}^{2+}][\text{OH}^-]^4 + 10^{0.1}[\text{Cu}^{2+}][\text{Cl}^-] + 10^{-0.6}[\text{Cu}^{2+}][\text{Cl}^-]^2 + 10^{4.31}[\text{Cu}^{2+}][\text{NH}_3] + 10^{7.98}[\text{Cu}^{2+}][\text{NH}_3]^2 + 10^{11.02}[\text{Cu}^{2+}][\text{NH}_3]^3 + 10^{13.32}[\text{Cu}^{2+}][\text{NH}_3]^4 + 10^{12.86}[\text{Cu}^{2+}][\text{NH}_3]^5 + 10^{3.02}[\text{Cu}^{2+}][\text{Lact.}] + 10^{4.85}[\text{Cu}^{2+}][\text{Lact.}]^2 + 10^{6.7}[\text{Cu}^{2+}][\text{CO}_3^{2-}] + 10^{10.2}[\text{Cu}^{2+}][\text{CO}_3^{2-}]^2$$

$$(S13) \quad [\text{Cu(II)}_{\text{aq}}^{\text{Tot}}] = [\text{Cu}^{2+}](1 + 10^7[\text{OH}^-] + 10^{13.68}[\text{OH}^-]^2 + 10^{17}[\text{OH}^-]^3 + 10^{18.5}[\text{OH}^-]^4 \\ + 10^{0.1}[\text{Cl}^-] + 10^{-0.6}[\text{Cl}^-]^2 + 10^{4.31}[\text{NH}_3] + 10^{7.98}[\text{NH}_3]^2 + 10^{11.02}[\text{NH}_3]^3 \\ + 10^{13.32}[\text{NH}_3]^4 + 10^{12.86}[\text{NH}_3]^5 + 10^{3.02}[\text{Lact.}] + 10^{4.85}[\text{Lact.}]^2 + 10^{6.7}[\text{CO}_3^{2-}] + 10^{10.2}[\text{CO}_3^{2-}]^2)$$

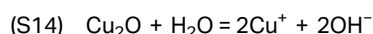
FINAL EQUILIBRIUM EXPRESSION TO GRAPH⁴⁻⁵

The master expression for total aqueous copper concentration was derived for both valence states of copper (I [S12] and II [S13]), assuming electrode potentials at which each valence state dominates, respectively. For the Cu(I) compounds, the $[\text{Cu}^+]$ concentration is isolated from the equilibrium expression ([S2] or [S4]) and plugged into the master expression for total aqueous Cu (I) ([S12]) in the place of the $[\text{Cu}^+]$ term. This renders a final expression which can be graphed as a function of pH, if the concentration of all of the other ligands is known (as for an artificial sweat solution, for example).

The same procedure is carried out regarding the equilibrium expression for the Cu(II) compounds ([S6], [S8], or [S11]) and the master expression for total aqueous Cu(II) ([S13]).

TRAJECTORY EXPRESSIONS TO CORRELATE CU RELEASE TO PH CHANGE

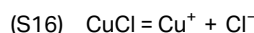
Cu₂O



For every 2 cuprous cations (Cu^+) released, two hydroxyl anions (OH^-) are also released (a 1:1 ratio).

$$(S15) \quad \text{Log}(\text{Cu(I)}_{\text{aq}}^{\text{Tot}}) = \text{Log}([\text{Cu}^+]_{\text{initial}} + \left(\frac{1}{4}(10^{-\text{pH}_{\text{initial}}} - 10^{-\text{pH}_{\text{instantaneous}}})\right) + \left(\frac{1}{4}(10^{\text{pH}_{\text{instantaneous}}-14} - 10^{\text{pH}_{\text{initial}}-14})\right))$$

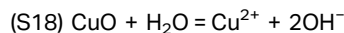
CuCl



For every cuprous cation (Cu^+) released, there is no change in $[\text{OH}^-]$ concentration.

$$(S17) \quad \text{pH}_{\text{instantaneous}} = \text{pH}_{\text{initial}}$$

CuO

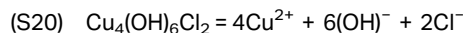


For every cupric cation (Cu^{2+}) released, two hydroxyl anions (OH^-) are also released (a 1:2 ratio).

The cupric cation may continue to complex with hydroxyl to adjust the net release of hydroxyl with respect to total aqueous copper released (hydroxyl complexation is dependent on pH). The f_{OH^-} function describes how many OH^- anions are complexed by the cupric cation as a function of pH.

$$(S19) \quad \text{Log}(\text{Cu(II)}_{\text{aq}}^{\text{Tot}}) = \text{Log}\left([\text{Cu}^{2+}]_{\text{initial}} + \left(\frac{1}{2 - f_{\text{OH}^-}}(10^{-\text{pH}_{\text{initial}}} - 10^{-\text{pH}_{\text{instantaneous}}})\right) + \left(\frac{1}{2 - f_{\text{OH}^-}}(10^{\text{pH}_{\text{instantaneous}}-14} - 10^{\text{pH}_{\text{initial}}-14})\right)\right)$$

Cu₄(OH)₆Cl₂

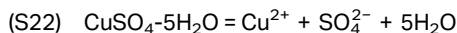


For every four cupric cations (Cu^{2+}) released, six hydroxyl anions (OH^-) are also released (a 2:3 ratio).

The cupric cation may continue to complex with hydroxyl to adjust the net release of hydroxyl with respect to total aqueous copper released (hydroxyl complexation is dependent on pH). The f_{OH^-} function describes how many OH^- anions are complexed by the cupric cation as a function of pH.

$$(S21) \quad \text{Log}(\text{Cu(II)}_{\text{aq}}^{\text{Tot}}) = \text{Log}\left([\text{Cu}^{2+}]_{\text{initial}} + \left(\frac{2}{3 - 2f_{\text{OH}^-}}(10^{-\text{pH}_{\text{initial}}} - 10^{-\text{pH}_{\text{instantaneous}}})\right) + \left(\frac{2}{3 - 2f_{\text{OH}^-}}(10^{\text{pH}_{\text{instantaneous}}-14} - 10^{\text{pH}_{\text{initial}}-14})\right)\right)$$

CuSO₄·5H₂O



For every cupric cation (Cu^{2+}) released, there is no change in $[\text{OH}^-]$ concentration.

The cupric cation may continue to complex with hydroxyl to adjust the net release of hydroxyl with respect to total aqueous copper released (hydroxyl complexation is dependent on pH). The f_{OH^-} function describes how many OH^- anions are complexed by the cupric cation as a function of pH.

$$(S23) \quad \text{Log}(\text{Cu(II)}_{\text{aq}}^{\text{Tot}}) = \text{log} \left([\text{Cu}^{2+}]_{\text{initial}} + \left(\frac{1}{0 - f_{\text{OH}^-}} (10^{-\text{pH}_{\text{initial}}} - 10^{-\text{pH}_{\text{instantaneous}}}) \right) \right. \\ \left. + \left(\frac{1}{0 - f_{\text{OH}^-}} (10^{\text{pH}_{\text{instantaneous}} - 14} - 10^{\text{pH}_{\text{initial}} - 14}) \right) \right)$$

References

1. P.D. James Speight, *Lange's Handbook of Chemistry*, 16th ed. (New York, NY: McGraw-Hill Education, 2005).
2. P.B. Barton, P.M. Bethke, *Am. J. Science Bradley Volume 258-A* (1960): p. 21-34.
3. M.M. Benjamin, *Water Chemistry*, 6th ed. (Long Grove, IL: Waveland Press, 2014).
4. M.E. McMahon, R.J. Santucci, J.R. Scully, *RSC Advances* 9, 35 (2019): p. 19905-19916.
5. R.J. Santucci, M.E. McMahon, J.R. Scully, *npj Mater. Degradation* 2, 1 (2018): article 1.