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Supplement of

HETerogeneous vectorized or Parallel (HETPv1.0): an updated inorganic heterogeneous chemistry solver for the metastable-state NH_4^+–Na^+–Ca^{2+}–K^+–Mg^{2+}–SO_4^{2-}–NO_3^-–Cl^-–H_2O system based on ISORROPIA II

Stefan J. Miller et al.

Correspondence to: Stefan J. Miller (stefan.miller@ec.gc.ca) and Paul A. Makar (paul.makar@ec.gc.ca)

Supplemental Information

Table S1: Equilibrium reactions (ER) considered in metastable state chemical subspaces. ER8 to ER25 form the basis for dry salt partitioning during the initialization of some chemical subspaces (see Table S2).

ER8	$Na_2SO_{4(s)} \rightleftharpoons 2Na^+_{(aq)} + SO_4^{2-}{}_{(aq)}$
ER9	$NH_4HSO_{4(s)} \rightleftharpoons NH_4^+{}_{(aq)} + HSO_4^-{}_{(aq)}$
ER10	$NaHSO_{4(s)} \rightleftharpoons Na^+_{(aq)} + HSO_4^-{}_{(aq)}$
ER11	$(NH_4)_3H(SO_4)_{2(s)} \rightleftharpoons 3NH_4^+{}_{(aq)} + HSO_4^-{}_{(aq)} + SO_4^{2-}{}_{(aq)}$
ER12	$(NH_4)_2SO_{4(s)} \rightleftharpoons 2NH_4^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$
ER13	$CaSO_4 2H_2O \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H_2O$
ER14	$K_2SO_{4(s)} \rightleftharpoons 2K^+_{(aq)} + SO_4^{2-}{}_{(aq)}$
ER15	$MgSO_{4(s)} \rightleftharpoons Mg^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$
ER16	$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$
ER17	$NaNO_{3(s)} \rightleftharpoons Na^+_{(aq)} + NO_3^-{}_{(aq)}$
ER18	$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$
ER19	$Ca(NO_3)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$
ER20	$CaCl_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$
ER21	$Mg(NO_3)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$
ER22	$MgCl_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$
ER23	$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$
ER24	$KNO_{3(s)} \rightleftharpoons K^+_{(aq)} + NO_3^-{}_{(aq)}$
ER25	$KHSO_{4(s)} \rightleftharpoons K^+_{(aq)} + HSO_4^-{}_{(aq)}$

Table S2. System of equations to be solved for each chemical subspace for metastable state, based on the algorithms of ISORROPIA. Note that the conditions under which a given system is solved appears in Figure 1. Activity coefficients are not included in the equations, which are assumed to be equal to unity for simplicity. Conversion factors (i.e., RT, aerosol liquid water content) are included in variables representing the equilibrium constants.

Case	**Solution: major system (solved first)**	**Solution: minor systems (solved second, after convergence of major system)**
A2	<u>The set of initial equations are:</u> (1) ER1 to ER4 (2) Mass balance for TS and TA $\mathrm{TS} = [\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}]$ $\mathrm{TA} = [\mathrm{NH_4^+}] + [\mathrm{NH_3}]$ (3) Electroneutrality $[\mathrm{NH_4^+}] + [\mathrm{H^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}]$ <u>Solution:</u> The initial step is to perform a root bracketing search for $[\mathrm{H^+}]$ within the range $[tiny, 2\mathrm{TS}]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine $[\mathrm{H^+}]$ within the identified interval, if applicable. <u>System of equations:</u> Combining (1) and (2) gives a system of equations: $[\mathrm{H^+}]$ = determined from ITP $[\mathrm{HSO_4^-}] = \frac{\mathrm{TS}}{1 + \frac{K_{\mathrm{HSO_4}}}{[\mathrm{H^+}]}}$ $[\mathrm{SO_4^{2-}}] = \mathrm{TS} - \frac{\mathrm{TS}}{1 + \frac{K_{\mathrm{HSO_4}}}{[\mathrm{H^+}]}}$ $[\mathrm{NH_4^+}] = \frac{\mathrm{TA}}{1 + \left(\frac{1}{[\mathrm{H^+}]\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}}\right)}$ $[\mathrm{NH_3}] = \mathrm{TA} - [\mathrm{NH_4^+}]$ Rearranging (3) gives the 'objective function'. The objective function is evaluated using the ion concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure. $\frac{[\mathrm{NH_4^+}]}{2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}]} + \frac{[\mathrm{H^+}]}{2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}]} - 1 = 0$ <u>For all subroutines requiring ITP</u>: The solution is solved iteratively, until the change in the bisected variable between successive iterations is less than ε (determined from a chosen tolerance) or exceeds the maximum number of allowed iterations.	**Not applicable**
B4	<u>The set of initial equations are:</u> (1) ER1 (2) Mass balance for TS and TA $\mathrm{TS} = [\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}]$	<u>The set of initial equations are:</u> (1) ER2-ER4 (2) $[\mathrm{H^+}]_i = [\mathrm{H^+}]$ and $[\mathrm{NH_4^+}]_i = [\mathrm{NH_4^+}]$ from the major system

	$TA = [NH_4^+]$ (3) Electroneutrality $[NH_4^+] + [H^+] = 2[SO_4^{2-}] + [HSO_4^-]$ <u>Solution:</u> Combining (1), (2) and (3) gives a quadratic equation in terms of $[SO_4^{2-}]$. Let $b = K_{HSO_4} + TS - TA$ and $c = -TSK_{HSO_4}$ The solution is the *positive* root of the quadratic formula: $[SO_4^{2-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ $[HSO_4^-] = TS - [SO_4^{2-}]$ $[H^+] = K_{HSO_4} \frac{[HSO_4^-]}{[SO_4^{2-}]}$	(3) Let $[NH_3] = \Delta c$ $[H^+] = [H^+]_i + \Delta c$ $[NH_4^+] = [NH_4^+]_i - \Delta c$ <u>Solution:</u> Substitution of (3) into (1) gives a quadratic equation in terms of Δc: Let $b = [H^+]_i + \frac{1}{\frac{K_{NH_3}}{K_{H_2O}}}$ and $c = -\frac{[NH_4^+]_i}{\frac{K_{NH_3}}{K_{H_2O}}}$ The solution is the *positive* root of the quadratic formula: $\Delta c = \frac{-b + \sqrt{b^2 - 4c}}{2}$
C2	Initially it is assumed: $[NH_4HSO_4] = TA$ $[SO_4]_{free} = TS - TA$ <u>The set of initial equations are:</u> (1) ER1 (2) Mass balance for TS and TA $TS = [SO_4^{2-}] + [HSO_4^-] = [NH_4HSO_4] + [SO_4]_{free}$ $TA = [NH_4^+] = [NH_4HSO_4]$ (3) Electroneutrality $[NH_4^+] + [H^+] = 2[SO_4^{2-}] + [HSO_4^-]$ <u>Solution:</u> Combining (1), (2) and (3) gives a quadratic equation in terms of $[SO_4^{2-}]$. Let $b = K_{HSO_4} + [SO_4]_{free} = K_{HSO_4} + TS - TA$ and $c = -([NH_4HSO_4] + [SO_4]_{free})K_{HSO_4} = -TSK_{HSO_4}$ The solution is the *positive* root of the quadratic formula: $[SO_4^{2-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ $[HSO_4^-] = [NH_4HSO_4] + [SO_4]_{free} - [SO_4^{2-}] = TS - [SO_4^{2-}]$ $[H^+] = [SO_4]_{free} + [SO_4^{2-}] = TS - TA + [SO_4^{2-}]$	The minor system is the same as B4.
D3	This case begins with dry salt partitioning to determine Δc, the amount of $NH_4NO_{3(s)}$ that will volatize (from ER7). Initially, all TS is assumed to be present as $(NH_4)_2SO_{4(s)}$. $[NH_4NO_3]_i = \min(TA - 2[(NH_4)_2SO_4], TN)$ $[NH_3]_{dry_i} = TA - [NH_4NO_3]_i - 2[(NH_4)_2SO_4]$ $[HNO_3]_{dry_i} = TN - [NH_4NO_3]_i$ Let	<u>The set of initial equations are:</u> (1) ER1 (2) $[H^+]_i = [H^+]$ and $[SO_4^{2-}]_i = [SO_4^{2-}]$ from the major system. (3) Let $[SO_4^{2-}] = [SO_4^{2-}]_i - \Delta c$ $[H^+] = [H^+]_i - \Delta c$

	$[\mathrm{NH_3}]_{dry} = [\mathrm{NH_3}]_{dry_i} + \Delta c$ $[\mathrm{HNO_3}]_{dry} = [\mathrm{HNO_3}]_{dry_i} + \Delta c$ $[\mathrm{NH_4NO_3}] = [\mathrm{NH_4NO_3}]_i - \Delta c$ and $b = [\mathrm{NH_3}]_{dry_i} + [\mathrm{HNO_3}]_{dry_i}$ and $c = -K_{\mathrm{NH_4NO_3}}$ The 'dry' solution is the *positive* root of the quadratic formula: $\Delta c = \frac{-b + \sqrt{b^2 - 4c}}{2}$ <u>All solids are assumed to undergo deliquescence. The set of initial equations are:</u> (1) ER2–ER5 (2) Mass balance for TS, TA and TN: $\mathrm{TS} = [\mathrm{SO_4^{2-}}] = [(\mathrm{NH_4})_2\mathrm{SO_4}]$ $\mathrm{TA} = [\mathrm{NH_4^+}] + [\mathrm{NH_3}] = 2[(\mathrm{NH_4})_2\mathrm{SO_4}] + [\mathrm{NH_4NO_3}] + [\mathrm{NH_3}]_{dry}$ $\mathrm{TN} = [\mathrm{NO_3^-}] + [\mathrm{HNO_3}] = [\mathrm{NH_4NO_3}] + [\mathrm{HNO_3}]_{dry}$ (3) Electroneutrality $[\mathrm{NH_4^+}] + [\mathrm{H^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] + [\mathrm{NO_3^-}] + [\mathrm{OH^-}]$ <u>Solution:</u> The initial step is to perform a root bracketing search the variable x (representing a change in $[\mathrm{NH_3}]_{dry}$) within the range $[tiny, [\mathrm{NH_3}]_{dry}]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine x within the identified interval, if applicable. <u>System of equations:</u> The concentration of $[\mathrm{SO_4^{2-}}]$ is constant during the iterative procedure of the major system: $[\mathrm{SO_4^{2-}}] = [(\mathrm{NH_4})_2\mathrm{SO_4}]$ $[\mathrm{HSO_4^-}] = 0$ Let: $[\mathrm{HNO_3}] = [\mathrm{HNO_3}]_{dry} - \Delta\mathrm{NO_3}$ $[\mathrm{NO_3^-}] = [\mathrm{NH_4NO_3}] + \Delta\mathrm{NO_3}$ Combining $[\mathrm{H^+}] = \frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_3}]}\frac{K_{\mathrm{H_2O}}}{K_{\mathrm{NH_3}}}$ and the expressions for $[\mathrm{HNO_3}]$ and $[\mathrm{NO_3^-}]$ with ER5 gives: $\Delta\mathrm{NO_3} = \frac{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}} K_{\mathrm{HNO_3}} [\mathrm{NH_3}][\mathrm{HNO_3}]_{dry} - [\mathrm{NH_4^+}][\mathrm{NH_4NO_3}]}{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}} K_{\mathrm{HNO_3}} [\mathrm{NH_3}] + [\mathrm{NH_4^+}]}$ Let: $[\mathrm{NH_3}] = [\mathrm{NH_3}]_{dry} - x$ $[\mathrm{NH_4^+}] = \mathrm{TA} - [\mathrm{NH_3}] = \mathrm{TA} - ([\mathrm{NH_3}]_{dry} - x) = 2[(\mathrm{NH_4})_2\mathrm{SO_4}] + [\mathrm{NH_4NO_3}] + x$ Substituting expressions for $[\mathrm{NH_3}]$ and $[\mathrm{NH_4^+}]$ into $\Delta\mathrm{NO_3}$ gives: $\Delta\mathrm{NO_3} = \frac{K_{\mathrm{HNO_3}} \frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}} [\mathrm{HNO_3}]_{\mathrm{dry}}([\mathrm{NH_3}]_{dry} - x) - [\mathrm{NH_4NO_3}](2[(\mathrm{NH_4})_2\mathrm{SO_4}] + [\mathrm{NH_4NO_3}] + x)}{K_{\mathrm{HNO3}} \frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}} ([\mathrm{NH_3}]_{dry} - x) + 2[(\mathrm{NH_4})_2\mathrm{SO_4}] + [\mathrm{NH_4NO_3}] + x}$	$[\mathrm{HSO_4^-}] = \Delta c$ Substituting (3) into (1) gives a quadratic equation to describe Δc. Let $b = -([\mathrm{H^+}]_i + [\mathrm{SO_4^{2-}}]_i + K_{\mathrm{HSO_4}})$ and $c = [\mathrm{H^+}]_i[\mathrm{SO_4^{2-}}]_i$ The solution is the *negative* root using the quadratic formula. $\Delta c = \frac{-b - \sqrt{b^2 - 4c}}{2}$

	Following the calculation of $[NO_3^-]$ and $[NH_4^+]$, $[H^+]$ is determined from the charge balance ($[OH^-]$ is replaced using ER4), giving a quadratic equation in terms of $[H^+]$: Let $b = x - \Delta NO_3$ and $c = -K_{H_2O}a_w$ The solution is the *positive* root using the quadratic formula: $[H^+] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ The objective function (from ER2-ER4) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure: $\frac{[NH_4^+]}{\frac{K_{NH_3}}{K_{H_2O}}[H^+][NH_3]} - 1 = 0$	
E4	The major system is the same as B4.	<u>The set of initial equations are:</u> (1) ER5 (2) $[H^+]_i = [H^+]$ and TN from the major system. (3) Let $[NO_3^-] = \Delta c$ $[H^+] = [H^+]_i + \Delta c$ $[HNO_3] = TN - \Delta c$ Substituting (3) into (1) gives a quadratic equation in terms of Δc: Let $b = K_{HNO_3} + [H^+]_i$ and $c = -K_{HNO_3}TN$ The solution is the *positive* root using the quadratic formula: $\Delta c = \frac{-b + \sqrt{b^2 - 4c}}{2}$
F2	The major system is the same as C2.	The minor system is the same as E4.
G5	<u>Begin with dry salt partitioning to obtain:</u> $[Na_2SO_4] = 0.5TNa$ $[SO_4]_{free} = TS - [Na_2SO_4]$ $[(NH_4)_2SO_4] = [SO_4]_{free}$ $[NH_3]_{dry} = TA - 2[(NH_4)_2SO_4]$ <u>All solids are assumed to undergo deliquescence. The set of initial equations are:</u> (1) ER2–ER6 (2) Mass balance for TS, TA, TN, TCl and TNa $TS = [SO_4^{2-}] = [(NH_4)_2SO_4] + [Na_2SO_4]$ $TA = [NH_4^+] + [NH_3] = [NH_3]_{dry} + 2[(NH_4)_2SO_4]$ $TN = [NO_3^-] + [HNO_3]$	The minor system is the same as D3.

$\mathrm{TCl} = [\mathrm{Cl^-}] + [\mathrm{HCl}]$

$\mathrm{TNa} = [\mathrm{Na^+}] = 2[\mathrm{Na_2SO_4}]$

(3) Electroneutrality

$[\mathrm{NH_4^+}] + [\mathrm{H^+}] + [\mathrm{Na^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] + [\mathrm{Cl^-}] + [\mathrm{NO_3^-}] + [\mathrm{OH^-}]$

<u>Solution:</u>

The initial step is to perform a root bracketing search the variable $[\mathrm{Cl^-}]$ within the range $[tiny, \mathrm{TCl} - tiny]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine $[\mathrm{Cl^-}]$ within the identified interval, if applicable.

<u>System of equations:</u>

The concentrations of $[\mathrm{SO_4^{2-}}]$ and $[\mathrm{Na^+}]$ are constant during the iterative procedure of the major system:

$[\mathrm{SO_4^{2-}}] = [(\mathrm{NH_4})_2\mathrm{SO_4}] + [\mathrm{Na_2SO_4}]$

$[\mathrm{HSO_4^-}] = 0$

$[\mathrm{Na^+}] = 2[\mathrm{Na_2SO_4}]$

Combining the mass balance relationships for TCl and TN with ER5 and ER6 gives:

$$[\mathrm{NO_3^-}] = \frac{[\mathrm{Cl^-}]\mathrm{TN}}{[\mathrm{Cl^-}] + \frac{K_{\mathrm{HCl}}}{K_{\mathrm{HNO_3}}}(\mathrm{TCl} - [\mathrm{Cl^-}])}$$

$[\mathrm{HNO_3}] = \mathrm{TN} - [\mathrm{NO_3^-}]$

$[\mathrm{Cl^-}] =$ determined from ITP

$[\mathrm{HCl}] = \mathrm{TCl} - [\mathrm{Cl^-}]$

Let

$[\mathrm{NH_3}] = [\mathrm{N}H_3]_{dry} - \Delta c$

$[\mathrm{NH_4^+}] = 2[(\mathrm{NH_4})_2\mathrm{SO_4}] + \Delta c$

Substituting the equations for $[\mathrm{NH_3}]$ and $[\mathrm{NH_4^+}]$ into ER2-ER4 and using (3) to eliminate $[\mathrm{H^+}]$, gives a quadratic equation in terms of Δc:

Let $b = -\left([\mathrm{N}H_3]_{dry} + [\mathrm{Cl^-}] + [\mathrm{NO_3^-}] + \frac{1}{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}}\right)$ and

$$c = [\mathrm{N}H_3]_{dry}([\mathrm{Cl^-}] + [\mathrm{NO_3^-}]) - \frac{2[(\mathrm{NH_4})_2\mathrm{SO_4}]}{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}}$$

The solution is the *negative* root using the quadratic formula:

$$\Delta c = \frac{-b - \sqrt{b^2 - 4c}}{2}$$

Following the calculation of ion concentrations, $[\mathrm{H^+}]$ is calculated from (3), with two possible cases. Let $[\mathrm{H^+}]^* = 2[\mathrm{SO_4^{2-}}] + [\mathrm{NO_3^-}] + [\mathrm{Cl^-}] - [\mathrm{Na^+}] - [\mathrm{NH_4^+}]$.

<u>Case 1: $[\mathrm{H^+}]^* > tiny$ ($[\mathrm{H^+}]$ is in excess)</u>

	Substituting $[\mathrm{OH^-}] = \frac{K_{\mathrm{H_2O}} a_w}{[\mathrm{H^+}]}$ into (3) gives a quadratic equation in terms of $[\mathrm{H^+}]$. Let $b = -[\mathrm{H^+}]^*$ and $c = -K_{\mathrm{H_2O}} a_w$ The solution is the *positive* root using the quadratic formula: $[\mathrm{H^+}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ <u>Case 2: $[\mathrm{H^+}]^* \leq tiny$ ($[\mathrm{OH^-}]$ is in excess)</u> Substituting $[\mathrm{H^+}] = \frac{K_{\mathrm{H_2O}} a_w}{[\mathrm{OH^-}]}$ into (3) results in a quadratic equation in terms of $[\mathrm{OH^-}]$. Let $b = [\mathrm{H^+}]^*$ and $c = -K_{\mathrm{H_2O}} a_w$ The solution is the *positive* root using the quadratic formula ($[\mathrm{H^+}]$ is calculated from the equation substituted initially): $[\mathrm{OH^-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ The objective function (from ER6) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure: $\frac{[\mathrm{Cl^-}][\mathrm{H^+}]}{K_{\mathrm{HCl}}[\mathrm{HCl}]} - 1 = 0$	
H6	<u>Begin with dry salt partitioning to obtain:</u> $[\mathrm{Na_2SO_4}] = \mathrm{TS}$ $[\mathrm{Na}]_{free} = \mathrm{TNa} - 2[\mathrm{Na_2SO_4}]$ $[\mathrm{NaNO_3}] = \min\left([\mathrm{Na}]_{free}, \mathrm{TN}\right)$ $[\mathrm{HNO_3}]_{dry} = \mathrm{TN} - [\mathrm{NaNO_3}]$ $[\mathrm{Na}]_{free} = [\mathrm{Na}]_{free} - [\mathrm{NaNO_3}]$ $[\mathrm{NaCl}] = \min\left([\mathrm{Na}]_{free}, \mathrm{TCl}\right)$ $[\mathrm{Na}]_{free} = [\mathrm{Na}]_{free} - [\mathrm{NaCl}]$ $[\mathrm{HCl}]_{dry} = \mathrm{TCl} - [\mathrm{NaCl}]$ $[\mathrm{NH_3}]_{dry} = \mathrm{TA}$ <u>All solids are assumed to undergo deliquescence. The set of initial equations are:</u> (1) Equilibrium reaction ER2–ER6 (2) Mass balance for TS, TA, TN, TCl and TNa $\mathrm{TS} = [\mathrm{SO_4^{2-}}] = [\mathrm{Na_2SO_4}]$ $\mathrm{TA} = [\mathrm{NH_4^+}] + [\mathrm{NH_3}] = [\mathrm{NH_3}]_{dry}$ $\mathrm{TN} = [\mathrm{NO_3^-}] + [\mathrm{HNO_3}] = [\mathrm{NaNO_3}] + [\mathrm{HNO_3}]_{dry}$ $\mathrm{TCl} = [\mathrm{Cl^-}] + [\mathrm{HCl}] = [\mathrm{NaCl}] + [\mathrm{HCl}]_{dry}$ $\mathrm{TNa} = [\mathrm{Na^+}] = [\mathrm{NaNO_3}] + [\mathrm{NaCl}] + 2[\mathrm{Na_2SO_4}]$ (3) Electroneutrality $[\mathrm{NH_4^+}] + [\mathrm{H^+}] + [\mathrm{Na^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] + [\mathrm{Cl^-}] + [\mathrm{NO_3^-}] + [\mathrm{OH^-}]$ <u>Solution:</u>	The minor system is the same as D3.

The initial step is to perform a root bracketing search for the variable x (representing a change in $[\mathrm{HCl}]_{dry}$) within the range $[tiny, [\mathrm{HCl}]_{dry} - tiny]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine x within the identified interval, if applicable.

<u>System of equations:</u>

The concentrations of $[\mathrm{SO_4^{2-}}]$ and $[\mathrm{Na^+}]$ are constants during the iterative procedure of the major system:

$[\mathrm{SO_4^{2-}}] = [\mathrm{Na_2SO_4}]$

$[\mathrm{HSO_4^-}] = 0$

$[\mathrm{Na^+}] = [\mathrm{NaNO_3}] + [\mathrm{NaCl}] + 2[\mathrm{Na_2SO_4}]$

Let

$[\mathrm{Cl^-}] = [\mathrm{NaCl}] + x$

$[\mathrm{HCl}] = [\mathrm{HCl}]_{dry} - x$

$[\mathrm{NO_3^-}] = [\mathrm{NaNO_3}] + y$

$[\mathrm{HNO_3}] = [\mathrm{HNO_3}]_{dry} - y$

Using $[\mathrm{H^+}] = \frac{K_{\mathrm{HCl}}\left([\mathrm{HCl}]_{\mathrm{dry}} - x\right)}{[\mathrm{NaCl}] + x}$ and the expressions for $[\mathrm{NO_3^-}]$ and $[\mathrm{HNO_3}]$ in ER5 and solving for y gives

$$y = \frac{[\mathrm{HNO_3}]_{dry}([\mathrm{NaCl}] + x) - \frac{K_{\mathrm{HCl}}}{K_{\mathrm{HNO_3}}}\left([\mathrm{HCl}]_{dry} - x\right)[\mathrm{NaNO_3}]}{([\mathrm{NaCl}] + x) + \frac{K_{\mathrm{HCl}}}{K_{\mathrm{HNO_3}}}\left([\mathrm{HCl}]_{dry} - x\right)}$$

Let

$[\mathrm{NH_4^+}] = \Delta c$

$[\mathrm{NH_3}] = [\mathrm{NH_3}]_{dry} - \Delta c$

Using the expressions for $[\mathrm{NH_4^+}]$ and $[\mathrm{NH_3}]$ in (3), solving for $[\mathrm{H^+}]$, and substituting the result for $[\mathrm{H^+}]$ into ER2-ER4 gives a quadratic equation for Δc:

Let $b = -\left([\mathrm{NH_3}]_{dry} + x + y + \frac{1}{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}}\right)$ and $c = [\mathrm{NH_3}]_{dry}(x + y)$

The solution is the *negative* root using the quadratic formula:

$$\Delta c = \frac{-b - \sqrt{b^2 - 4c}}{2}$$

$[\mathrm{H^+}]$ is then determined exactly as in G5, but using the ion concentrations calculated above.

The objective function (from ER2-4 and ER6) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure:

$$\frac{[\mathrm{NH_4^+}][\mathrm{Cl^-}]}{[\mathrm{HCl}][\mathrm{NH_3}]K_{HCl}\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}} - 1 = 0$$

I6

Begin with dry salt partitioning to obtain:

$[\mathrm{Na_2SO_4}] = 0.5\mathrm{TNa}$

$[\mathrm{Na}]_{free} = \mathrm{TNa} - 2[\mathrm{Na_2SO_4}]$

$[\mathrm{SO_4}]_{free} = \mathrm{TS} - [\mathrm{Na_2SO_4}]$

$[\mathrm{(NH_4)_3H(SO_4)_2}] = \min\left(\frac{1}{3}\mathrm{TA}, \frac{1}{2}[\mathrm{SO_4}]_{free}\right)$

$[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - 2[\mathrm{(NH_4)_3H(SO_4)_2}]$

$[\mathrm{NH_4}]_{free} = \mathrm{TA} - 3[\mathrm{(NH_4)_3H(SO_4)_2}]$

$[\mathrm{NH_3}]_{dry} = 0$

$[\mathrm{HNO_3}]_{dry} = \mathrm{TN}$

$[\mathrm{HCl}]_{dry} = \mathrm{TCl}$

Based on the above partitioning, there are three possible cases:

Case 1: $[\mathrm{SO_4}]_{\mathrm{free}} \le \mathrm{tiny}$

$[\mathrm{(NH_4)_3H(SO_4)_2}] = [\mathrm{(NH_4)_3H(SO_4)_2}] - [\mathrm{NH_4}]_{free}$

$[\mathrm{(NH_4)_2SO_4}] = 2[\mathrm{NH_4}]_{free}$

Case 2 (only if Case 1 = false): $[\mathrm{NH_4}]_{free} \le tiny$ and $[\mathrm{Na_2SO_4}] \le tiny$

$[\mathrm{NH_4HSO_4}] = 3\min\left([\mathrm{SO_4}]_{free}, [\mathrm{(NH_4)_3H(SO_4)_2}]\right)$

$[\mathrm{(NH_4)_3H(SO_4)_2}] = [\mathrm{(NH_4)_3H(SO_4)_2}] - [\mathrm{SO_4}]_{free}$

Case 3 (only if Case 1 and Case 2 = false): $[\mathrm{NH_4}]_{free} \le tiny$ and $[\mathrm{Na_2SO_4}] > tiny$:

$[\mathrm{NH_4HSO_4}] = 3\min\left([\mathrm{SO_4}]_{free}, [\mathrm{(NH_4)_3H(SO_4)_2}]\right)$

$[\mathrm{(NH_4)_3H(SO_4)_2}] = [\mathrm{(NH_4)_3H(SO_4)_2}] - [\mathrm{SO_4}]_{free}$

$[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - \frac{1}{3}[\mathrm{NH_4HSO_4}]$

$[\mathrm{NaHSO_4}] = 2[\mathrm{SO_4}]_{free}$

$[\mathrm{Na_2SO_4}] = [\mathrm{Na_2SO_4}] - [\mathrm{SO_4}]_{free}$

$[\mathrm{Na}]_{free} = \mathrm{TNa} - 2[\mathrm{Na_2SO_4}] - [\mathrm{NaHSO_4}]$

All solids are assumed to undergo deliquescence. The set of initial equations are:

(1) Equilibrium reaction ER2–ER6

(2) Mass balance for TS, TA, TN, TCl and TNa

$\mathrm{TS} = 2[\mathrm{(NH_4)_3H(SO_4)_2}] + [\mathrm{Na_2SO_4}] + [\mathrm{NH_4HSO_4}] + [\mathrm{(NH_4)_2SO_4}] + [\mathrm{NaHSO_4}]$

$\mathrm{TA} = 3[\mathrm{(NH_4)_3H(SO_4)_2}] + 2[\mathrm{(NH_4)_2SO_4}] + [\mathrm{NH_4HSO_4}]$

$\mathrm{TN} = [\mathrm{HNO_3}]_{dry}$

$\mathrm{TCl} = [\mathrm{HCl}]_{\mathrm{dry}}$

$\mathrm{TNa} = 2[\mathrm{Na_2SO_4}] + [\mathrm{NaHSO_4}]$

Solution:

The concentrations of $[\mathrm{Na^+}]$ and $[\mathrm{NH_4^+}]$ remain constant during the iterative procedure of the major system; $[\mathrm{Cl^-}]$ and $[\mathrm{NO_3^-}]$ are zero.

$[\mathrm{NH_4^+}] = 3[\mathrm{(NH_4)_3H(SO_4)_2}] + 2[\mathrm{(NH_4)_2SO_4}] + [\mathrm{NH_4HSO_4}]$

There are five possible cases, based on the aerosol liquid water content determined in the major system in conjunction with TCl and TN :

Case 1: $[\mathrm{H_2O}] \le tiny$

$[\mathrm{Cl^-}] = [\mathrm{Cl^-}]_i$

$[\mathrm{NO_3^-}] = [\mathrm{NO_3^-}]_i$

$[\mathrm{HCl}] = \mathrm{TCl} - [\mathrm{Cl^-}]_i$

$[\mathrm{HNO_3}] = \mathrm{TN} - [\mathrm{NO_3^-}]_i$

(Note that in I6, $[\mathrm{Cl^-}]_i = 0$ and $[\mathrm{NO_3^-}]_i = 0$ in the major system)

Case 2 (if Case 1 = false): $\mathrm{TCl} < tiny$ and $\mathrm{TN} < tiny$

$[\mathrm{Cl^-}] = 0$

$[\mathrm{NO_3^-}] = 0$

$[\mathrm{HCl}] = tiny$

$[\mathrm{HNO_3}] = tiny$

Case 3 (if Case 1 and 2 = false): $\mathrm{TCl} < tiny$ but not TN

Let $b = K_{\mathrm{HNO_3}} + [\mathrm{H^+}]_i$ and $c = -K_{\mathrm{HNO_3}}\mathrm{TN}$

The solution is the *positive* root of the quadratic formula:

$[\mathrm{NO_3^-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$

$[\mathrm{HNO_3}] = \mathrm{TN} - [\mathrm{NO_3^-}]$

$[\mathrm{H^+}] = [\mathrm{H^+}]_i + [\mathrm{NO_3^-}]$

Case 4 (if Case 1, 2 and 3 = false): $\mathrm{TN} < tiny$ but not TCl

Let $b = K_{\mathrm{HCl}} + [\mathrm{H^+}]_i$ and $c = -K_{\mathrm{HCl}}\mathrm{TCl}$

The solution is the *positive* root of the quadratic formula:

$[\mathrm{Cl^-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$

$[\mathrm{HCl}] = \mathrm{TCl} - [\mathrm{Cl^-}]$

$[\mathrm{H^+}] = [\mathrm{H^+}]_i + [\mathrm{Cl^-}]$

Case 5 (if Case1, 2, 3 and 4 = false):

Let $a = 1$,

$b = \frac{K_{\mathrm{HNO_3}}\mathrm{TN} + K_{\mathrm{HCl}}\mathrm{TCl} + ([\mathrm{H^+}]_i + K_{\mathrm{HCl}})(K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}})}{K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}}}$,

$c = \frac{([\mathrm{H^+}]_i + K_{\mathrm{HCl}})K_{\mathrm{HCl}}\mathrm{TCl} - K_{\mathrm{HCl}}\mathrm{TCl}(K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}})}{K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}}}$,

	$[\mathrm{Na^+}] = 2[\mathrm{Na_2SO_4}] + [\mathrm{NaHSO_4}]$ $[\mathrm{Cl^-}] = 0$ $[\mathrm{NO_3^-}] = 0$ Let $[\mathrm{SO_4^{2-}}] = [\mathrm{(NH_4)_3H(SO_4)_2}] + [\mathrm{Na_2SO_4}] + [\mathrm{(NH_4)_2SO_4}] + \Delta c$ $[\mathrm{HSO_4^-}] = [\mathrm{(NH_4)_3H(SO_4)_2}] + [\mathrm{NH_4HSO_4}] + [\mathrm{NaHSO_4}] - \Delta c$ $[\mathrm{H^+}] = \Delta c$ Using the expressions for $[\mathrm{SO_4^{2-}}]$, $[\mathrm{HSO_4^-}]$ and $[\mathrm{H^+}]$ in (1) gives a quadratic equation in terms of Δc. Let $b = [\mathrm{(NH_4)_3H(SO_4)_2}] + [\mathrm{Na_2SO_4}] + [\mathrm{(NH_4)_2SO_4}] + K_{\mathrm{HSO_4}}$ and $c = -K_{\mathrm{HSO_4}}([\mathrm{(NH_4)_3H(SO_4)_2}] + [\mathrm{NH_4HSO_4}] + [\mathrm{NaHSO_4}])$ The solution is the *positive* root using the quadratic formula: $\Delta c = \frac{-b + \sqrt{b^2 - 4c}}{2}$	$d = -\frac{K_{\mathrm{HCl}}^2 \mathrm{TCl}^2}{K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}}}$ The solution is the solution to a cubic equation of the form: $a\Delta c^3 + b\Delta c^2 + c\Delta c + d = 0$ Where Δc is determined from an exact analytic solution or using ITP, with $[\mathrm{Cl^-}] = \mathrm{TCl} + \Delta c$ $[\mathrm{HCl}] = \mathrm{TCl} - [\mathrm{Cl^-}]$ $[\mathrm{NO_3^-}] = \mathrm{TN} + \Delta r$ $[\mathrm{HNO_3}] = \mathrm{TN} - [\mathrm{NO_3^-}]$ $[\mathrm{H^+}] = [\mathrm{H^+}]_i + \Delta c + \Delta r$ where $\Delta r = \min\left(\frac{K_{\mathrm{HNO_3}}\mathrm{TN}\Delta c}{K_{\mathrm{HCl}}\mathrm{TCl} + \Delta c(K_{\mathrm{HNO_3}} - K_{\mathrm{HCl}})}, \mathrm{TN}\right)$ Next, TA is partitioned, following the same procedure as the minor system of Case B4, but using $[\mathrm{H^+}]$ from determined from the minor system above.
J3	<u>Begin with dry salt partitioning to obtain:</u> $[\mathrm{NH_4HSO_4}] = \mathrm{TA}$ $[\mathrm{NaHSO_4}] = \mathrm{TNa}$ $[\mathrm{SO_4}]_{free} = \mathrm{TS} - [\mathrm{NH_4HSO_4}] - [\mathrm{NaHSO_4}]$ $[\mathrm{HNO_3}]_{dry} = \mathrm{TN}$ $[\mathrm{HCl}]_{dry} = \mathrm{TCl}$ <u>The set of initial equations are:</u> (1) ER1 (2) Mass balance for TS, TA, TN, TCl and TNa $\mathrm{TS} = [\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] = [\mathrm{NH_4HSO_4}] + [\mathrm{NaHSO_4}] + [\mathrm{SO_4}]_{free}$ $\mathrm{TA} = [\mathrm{NH_4^+}] = [\mathrm{NH_4HSO_4}]$ $\mathrm{TN} = [\mathrm{HNO_3}]_{dry}$ $\mathrm{TCl} = [\mathrm{HCl}]_{dry}$ $\mathrm{TNa} = [\mathrm{Na^+}] = [\mathrm{NaHSO_4}]$ (3) Electroneutrality $[\mathrm{NH_4^+}] + [\mathrm{H^+}] + [\mathrm{Na^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] + [\mathrm{Cl^-}] + [\mathrm{NO_3^-}]$ <u>Solution:</u> The concentrations of $[\mathrm{Na^+}]$ and $[\mathrm{NH_4^+}]$ remain constant during the iterative procedure of the major system; $[\mathrm{Cl^-}]$ and $[\mathrm{NO_3^-}]$ are zero. $[\mathrm{NH_4^+}] = [\mathrm{NH_4HSO_4}]$	The minor system is the same as I6.

	$[Na^+] = [NaHSO_4]$ $[Cl^-] = 0$ $[NO_3^-] = 0$ Using (2) and (3) in (1) gives a quadratic equation in terms of $[SO_4^{2-}]$. Let $b = K_{HSO_4} + [SO_4]_{free}$ and $c = -K_{HSO_4}\left([NH_4HSO_4] + [NaHSO_4] + [SO_4]_{free}\right)$ The solution is the *positive* root using the quadratic formula: $[SO_4^{2-}] = \frac{-b + \sqrt{b^2 - 4c}}{2}$ $[HSO_4^-] = TS - [SO_4^{2-}] = [NH_4HSO_4] + [NaHSO_4] + [SO_4]_{free} - [SO_4^{2-}]$ $[H^+] = [SO_4]_{free} + [SO_4^{2-}]$	
O7	<u>Begin with dry salt partitioning to obtain:</u> $[CaSO_4] = \min(TCa, TS)$ $[SO_4]_{free} = TS - [CaSO_4]$ $[Ca]_{free} = TCa - [CaSO_4]$ $[K_2SO_4] = \min\left(\frac{1}{2}TK, [SO_4]_{free}\right)$ $[SO_4]_{free} = [SO_4]_{free} - [K_2SO_4]$ $[K]_{free} = TK - 2[K_2SO_4]$ $[Na_2SO_4] = \min\left(\frac{1}{2}TNa, [SO_4]_{free}\right)$ $[SO_4]_{free} = [SO_4]_{free} - [Na_2SO_4]$ $[Na]_{free} = TNa - 2[Na_2SO_4]$ $[MgSO_4] = \min\left(TMg, [SO_4]_{free}\right)$ $[SO_4]_{free} = [SO_4]_{free} - [MgSO_4]$ $[Mg]_{free} = TMg - [MgSO_4]$ $[(NH_4)_2SO_4] = [SO_4]_{free}$ $[HNO_3]_{dry} = TN$ $[HCl]_{dry} = TCl$ $[NH_3]_{dry} = TA - 2[(NH_4)_2SO_4]$ <u>The set of initial equations are:</u> (1) ER2–ER6 (2) Mass balance for TS, TA, TN, TCl, TNa, TCa, TMg, TK $TS = [CaSO_4] + [K_2SO_4] + [Na_2SO_4] + [MgSO_4] + [(NH_4)_2SO_4]$ $TA = [NH_3]_{dry} + 2[(NH_4)_2SO_4]$ $TN = [HNO_3]_{dry} = [NO_3^-] + [HNO_3]$ $TCl = [HCl]_{dry} = [Cl^-] + [HCl]$ $TNa = 2[Na_2SO_4] + [Na]_{free}$ $TMg = [MgSO_4] + [Mg]_{free}$ $TK = 2[K_2SO_4] + [K]_{free}$ $TCa = [CaSO_4] + [Ca]_{free}$	The minor system is the same as D3.

(3) Electroneutrality

$$[NH_4^+] + [H^+] + [Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}] = 2[SO_4^{2-}] + [HSO_4^-] + [Cl^-] + [NO_3^-] + [OH^-]$$

Solution:

The initial step is to perform a root bracketing search the variable $[Cl^-]$ within the range $[tiny, \mathrm{TCl} - tiny]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine $[Cl^-]$ within the identified interval, if applicable.

All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:

The concentrations of $[Na^+]$, $[SO_4^{2-}]$, $[Mg^{2+}]$ and $[K^+]$ remain constant during the iterative procedure of the major system.

$[SO_4^{2-}] = [K_2SO_4] + [Na_2SO_4] + [MgSO_4] + [(NH_4)_2SO_4]$

$[HSO_4^-] = 0$

$[Na^+] = 2[Na_2SO_4]$

$[Mg^{2+}] = [MgSO_4]$

$[K^+] = 2[K_2SO_4]$

$[Ca^{2+}] = 0$

Combining the mass balance relationships for TCl and TN with ER5 and ER6 gives:

$$[NO_3^-] = \frac{[Cl^-]\mathrm{TN}}{[Cl^-] + \frac{K_{HCl}}{K_{HNO_3}}(\mathrm{TCl} - [Cl^-])}$$

$[HNO_3] = \mathrm{TN} - [NO_3^-]$

$[Cl^-]$ = determined from ITP

$[HCl] = \mathrm{TCl} - [Cl^-]$

Let

$[NH_3] = [NH_3]_{dry} - \Delta c$

$[NH_4^+] = 2[(NH_4)_2SO_4] + \Delta c$

Substituting the equations for $[NH_3]$ and $[NH_4^+]$ into ER2-ER4 and using (3) to eliminate $[H^+]$, gives a quadratic equation in terms of Δc:

Let $b = -\left([NH_3]_{dry} + [Cl^-] + [NO_3^-] + \frac{1}{\frac{K_{NH_3}}{K_{H_2O}}}\right)$ and

$c = [NH_3]_{dry}([Cl^-] + [NO_3^-]) - \frac{2[(NH_4)_2SO_4]}{\frac{K_{NH_3}}{K_{H_2O}}}$

The solution is the *negative* root using the quadratic formula:

$$\Delta c = \frac{-b - \sqrt{b^2 - 4c}}{2}$$

$[H^+]$ is then calculated the same as G5, except now (3) includes $[Mg^{2+}]$ and $[K^+]$ (note $[Ca^{2+}] = 0$ and $[HSO_4^-] = 0$):

	$[H^+]^* = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+] - [NH_4^+] - 2[Mg^{2+}] - [K^+]$ The objective function (ER6) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure: $\frac{[Cl^-][H^+]}{K_{HCl}[HCl]} - 1 = 0$	
M8	<u>Begin with dry salt partitioning to obtain:</u> $[CaSO_4] = \min(TCa, TS)$ $[SO_4]_{free} = TS - [CaSO_4]$ $[Ca]_{free} = TCa - [CaSO_4]$ $[K_2SO_4] = \min\left(\frac{1}{2}TK, [SO_4]_{free}\right)$ $[SO_4]_{free} = [SO_4]_{free} - [K_2SO_4]$ $[K]_{free} = TK - 2[K_2SO_4]$ $[MgSO_4] = \min(TMg, [SO_4]_{free})$ $[SO_4]_{free} = [SO_4]_{free} - [MgSO_4]$ $[Mg]_{free} = TMg - [MgSO_4]$ $[Na_2SO_4] = [SO_4]_{free}$ $[Na]_{free} = TNa - 2[Na_2SO_4]$ $[NaNO_3] = \min(TN, [Na]_{free})$ $[Na]_{free} = [Na]_{free} - [NaNO_3]$ $[NaCl] = \min(TCl, [Na]_{free})$ $[Na]_{free} = [Na]_{free} - [NaCl]$ $[NH_3]_{dry} = TA$ $[HNO_3]_{dry} = TN - [NaNO_3]$ $[HCl]_{dry} = TCl - [NaCl]$ <u>The set of initial equations are:</u> (1) ER2–ER6 (2) Mass balance for TS, TA, TN, TCl, TNa, TCa, TMg, TK $TS = [CaSO_4] + [K_2SO_4] + [Na_2SO_4] + [MgSO_4]$ $TA = [NH_3]_{dry} = [NH_4^+] + [NH_3]$ $TN = [HNO_3]_{dry} + [NaNO_3] = [NO_3^-] + [HNO_3]$ $TCl = [HCl]_{dry} + [NaCl] = [Cl^-] + [HCl]$ $TNa = 2[Na_2SO_4] + [NaNO_3] + [NaCl] = [Na^+]$ $TMg = [MgSO_4] + [Mg]_{free}$ $TK = 2[K_2SO_4] + [K]_{free}$ $TCa = [CaSO_4] + [Ca]_{free}$ (3) Electroneutrality $[NH_4^+] + [H^+] + [Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}]$ $= 2[SO_4^{2-}] + [HSO_4^-] + [Cl^-] + [NO_3^-] + [OH^-]$	The minor system is the same as D3.

Solution:

The initial step is to perform a root bracketing search for the variable x (representing a change in $[\mathrm{HCl}]_{dry}$) within the range $[tiny, [\mathrm{HCl}]_{dry} - tiny]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine x within the identified interval, if applicable.

All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:

The concentrations of $[\mathrm{Na^+}]$, $[\mathrm{SO_4^{2-}}]$, $[\mathrm{Mg^{2+}}]$ and $[\mathrm{K^+}]$ remain constant during the iterative procedure of the major system.

$[\mathrm{SO_4^{2-}}] = [\mathrm{K_2SO_4}] + [\mathrm{Na_2SO_4}] + [\mathrm{MgSO_4}]$

$[\mathrm{HSO_4^-}] = 0$

$[\mathrm{Na^+}] = 2[\mathrm{Na_2SO_4}] + [\mathrm{NaNO_3}] + [\mathrm{NaCl}]$

$[\mathrm{Mg^{2+}}] = [\mathrm{MgSO_4}]$

$[\mathrm{K^+}] = 2[\mathrm{K_2SO_4}]$

$[\mathrm{Ca^{2+}}] = 0$

Let:

$[\mathrm{Cl^-}] = [\mathrm{NaCl}] + x$

$[\mathrm{HCl}] = [\mathrm{HCl}]_{dry} - x$

$[\mathrm{NO_3^-}] = [\mathrm{NaNO_3}] + y$

$[\mathrm{HNO_3}] = [\mathrm{HNO_3}]_{dry} - y$

Using $[\mathrm{H^+}] = \frac{K_{\mathrm{HCl}}\left([\mathrm{HCl}]_{\mathrm{dry}} - x\right)}{[\mathrm{NaCl}] + x}$ and the expressions for $[\mathrm{Cl^-}]$, $[\mathrm{HCl}]$, $[\mathrm{NO_3^-}]$ and $[\mathrm{HNO_3}]$ in ER5 and solving for y gives

$$y = \frac{[\mathrm{HNO_3}]_{dry}([\mathrm{NaCl}] + x) - \frac{K_{\mathrm{HCl}}}{K_{\mathrm{HNO_3}}}\left([\mathrm{HCl}]_{dry} - x\right)[\mathrm{NaNO_3}]}{([\mathrm{NaCl}] + x) + \frac{K_{\mathrm{HCl}}}{K_{\mathrm{HNO_3}}}\left([\mathrm{HCl}]_{dry} - x\right)}$$

Let

$[\mathrm{NH_4^+}] = \Delta c$

$[\mathrm{NH_3}] = [\mathrm{NH_3}]_{dry} - \Delta c$

Using the expressions for $[\mathrm{NH_4^+}]$ and $[\mathrm{NH_3}]$ in (3), solving for $[\mathrm{H^+}]$, and substituting the result for $[\mathrm{H^+}]$ into ER2-ER4 gives a quadratic equation for Δc:

Let $b = -\left([\mathrm{NH_3}]_{dry} + x + y + \frac{1}{\frac{K_{\mathrm{NH_3}}}{K_{\mathrm{H_2O}}}}\right)$ and $c = [\mathrm{NH_3}]_{dry}(x + y)$

The solution is the *negative* root using the quadratic formula:

$$\Delta c = \frac{-b - \sqrt{b^2 - 4c}}{2}$$

$[\mathrm{H^+}]$ is then calculated the same as G5, except now (3) includes $[\mathrm{Mg^{2+}}]$ and $[\mathrm{K^+}]$ (note $[\mathrm{Ca^{2+}}] = 0$ and $[\mathrm{HSO_4^-}] = 0$).

	$[H^+]^* = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+] - [NH_4^+] - 2[Mg^{2+}] - [K^+]$ The objective function (ER6) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure: $\frac{[Cl^-][H^+]}{K_{HCl}[HCl]} - 1 = 0$	
P13	<u>Begin with dry salt partitioning to obtain:</u> $[CaSO_4] = \min(TCa, TS)$ $[SO_4]_{free} = TS - [CaSO_4]$ $[Ca]_{free} = TCa - [CaSO_4]$ $[K_2SO_4] = \min\left(\frac{1}{2}TK, [SO_4]_{free}\right)$ $[SO_4]_{free} = [SO_4]_{free} - [K_2SO_4]$ $[K]_{free} = TK - 2[K_2SO_4]$ $[MgSO_4] = \min\ ([SO_4]_{free}, TMg)$ $[SO_4]_{free} = [SO_4]_{free} - [MgSO_4]$ $[Mg]_{free} = TMg - [MgSO_4]$ $[NaCl] = \min(TNa, TCl)$ $[Na]_{free} = TNa - [NaCl]$ $[Cl]_{free} = TCl - [NaCl]$ $[Ca(NO_3)_2] = \min\left([Ca]_{free}, \frac{1}{2}TN\right)$ $[Ca]_{free} = [Ca]_{free} - [Ca(NO_3)_2]$ $[NO_3]_{free} = TN - 2[Ca(NO_3)_2]$ $[CaCl_2] = \min\left([Ca]_{free}, \frac{1}{2}[Cl]_{free}\right)$ $[Ca]_{free} = [Ca]_{free} - [CaCl_2]$ $[Cl]_{free} = [Cl]_{free} - 2[CaCl_2]$ $[Mg(NO_3)_2] = \min\left([Mg]_{free}, \frac{1}{2}[NO_3]_{free}\right)$ $[Mg]_{free} = [Mg]_{free} - [Mg(NO_3)_2]$ $[NO_3]_{free} = [NO_3]_{free} - 2[Mg(NO_3)_2]$ $[MgCl_2] = \min\left([Mg]_{free}, \frac{1}{2}[Cl]_{free}\right)$ $[Mg]_{free} = [Mg]_{free} - [MgCl_2]$ $[Cl]_{free} = [Cl]_{free} - 2[MgCl_2]$ $[NaNO_3] = \min([Na]_{free}, [NO_3]_{free})$ $[Na]_{free} = [Na]_{free} - [NaNO_3]$ $[NO_3]_{free} = [NO_3]_{free} - [NaNO_3]$ $[KCl] = \min([K]_{free}, [Cl]_{free})$ $[K]_{free} = [K]_{free} - [KCl]$ $[Cl]_{free} = [Cl]_{free} - [KCl]$ $[KNO_3] = \min([K]_{free}, [NO_3]_{free})$	The minor system is the same as D3.

$[K]_{free} = [K]_{free} - [KNO_3]$

$[NO_3]_{free} = [NO_3]_{free} - [KNO_3]$

$[NH_3]_{dry} = TA$

$[HNO_3]_{dry} = [NO_3]_{free}$

$[HCl]_{dry} = [Cl]_{free}$

The set of initial equations are:

(1) ER2–ER6

(2) Mass balance for TS, TA, TN, TCl, TNa, TCa, TMg, TK

$TS = [CaSO_4] + [K_2SO_4] + [MgSO_4] + [SO_4]_{free}$

$TA = [NH_3]_{dry}$

$TN = [HNO_3]_{dry} + [KNO_3] + [NaNO_3] + 2[Mg(NO_3)_2] + 2[Ca(NO_3)_2]$

$TCl = [HCl]_{dry} + [NaCl] + 2[CaCl_2] + 2[MgCl_2] + [KCl]$

$TNa = [NaNO_3] + [NaCl]$

$TMg = [MgSO_4] + [MgCl_2] + [Mg(NO_3)_2] + [Mg]_{free}$

$TK = 2[K_2SO_4] + [KNO_3] + [KCl] + [K]_{free}$

$TCa = [CaSO_4] + [Ca(NO_3)_2] + [CaCl_2] + [Ca]_{free}$

(3) Electroneutrality

$$[NH_4^+] + [H^+] + [Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}] = 2[SO_4^{2-}] + [HSO_4^-] + [Cl^-] + [NO_3^-] + [OH^-]$$

Solution:

The initial step is to perform a root bracketing search for the variable x (representing a change in $[HCl]_{dry}$) within the range $[tiny, [HCl]_{dry} - tiny]$ to identify an interval where the 'objective function' contains a sign change (i.e., root), followed by an ITP search to refine x within the identified interval, if applicable.

All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:

The concentrations of $[Na^+]$, $[SO_4^{2-}]$, $[Mg^{2+}]$, $[K^+]$ and $[Ca^{2+}]$ remain constant during the iterative procedure of the major system.

$[SO_4^{2-}] = [K_2SO_4] + [MgSO_4]$

$[HSO_4^-] = 0$

$[Na^+] = [NaNO_3] + [NaCl]$

$[Mg^{2+}] = [MgSO_4] + [MgCl_2] + [Mg(NO_3)_2]$

$[K^+] = 2[K_2SO_4] + [KNO_3] + [KCl]$

$[Ca^{2+}] = [Ca(NO_3)_2] + [CaCl_2]$

Let

$P = [NaCl] + 2[CaCl_2] + 2[MgCl_2] + [KCl]$

$[Cl^-] = P + x$

$[HCl] = [HCl]_{dry} - x$

$Q = [KNO_3] + [NaNO_3] + 2[Mg(NO_3)_2] + 2[Ca(NO_3)_2]$

$[NO_3^-] = Q + y$

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$[HNO_3] = [HNO_3]_{dry} - y$

Using $[H^+] = \frac{K_{HCl}([HCl]_{dry} - x)}{P + x}$ and the expressions for $[Cl^-]$, $[HCl]$, $[NO_3^-]$ and $[HNO_3]$ in ER5 and solving for y gives

$$y = \frac{[HNO_3]_{dry}(P + x) - \frac{K_{HCl}}{K_{HNO_3}}([HCl]_{dry} - x)Q}{(P + x) + \frac{K_{HCl}}{K_{HNO_3}}([HCl]_{dry} - x)}$$

Let
$[NH_4^+] = \Delta c$
$[NH_3] = [NH_3]_{dry} - \Delta c$

Using the expressions for $[NH_4^+]$ and $[NH_3]$ in (3), solving for $[H^+]$, and substituting the result for $[H^+]$ into ER2-ER4 gives a quadratic equation for Δc:

Let $b = -\left([NH_3]_{dry} + x + y + \frac{1}{\frac{K_{NH_3}}{K_{H_2O}}}\right)$ and $c = [NH_3]_{dry}(x + y)$

The solution is the *negative* root using the quadratic formula:

$$\Delta c = [NH_4^+] = \frac{-b - \sqrt{b^2 - 4c}}{2}$$

$[H^+]$ is then calculated the same as G5, except now (3) includes $[Mg^{2+}]$, $[K^+]$ and $[Ca^{2+}]$ (note $[HSO_4^-] = 0$).
$[H^+]^* = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+] - [NH_4^+] - 2[Mg^{2+}] - [K^+] - 2[Ca^{2+}]$

The objective function (ER6) is evaluated using the ion and gas concentrations determined above, and its sign (i.e., positive or negative) is then used to initialize the next iteration of the ITP procedure:

$$\frac{[Cl^-][H^+]}{K_{HCl}[HCl]} - 1 = 0$$

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<tr><td>L9</td><td>

<u>Begin with dry salt partitioning to obtain:</u>
$[CaSO_4] = \min(TCa, TS)$
$[SO_4]_{free} = TS - [CaSO_4]$
$[Ca]_{free} = TCa - [CaSO_4]$
$[K_2SO_4] = \min\left(\frac{1}{2}TK, [SO_4]_{free}\right)$
$[SO_4]_{free} = [SO_4]_{free} - [K_2SO_4]$
$[K]_{free} = TK - 2[K_2SO_4]$
$[Na_2SO_4] = \min\left(\frac{1}{2}TNa, [SO_4]_{free}\right)$
$[SO_4]_{free} = [SO_4]_{free} - [Na_2SO_4]$
$[Na]_{free} = TNa - 2[Na_2SO_4]$
$[MgSO_4] = \min(TMg, [SO_4]_{free})$

</td><td>

Same as case I6.

Any $[NH_4]_{free}$ in the major system is added to $[NH_3]_{minor}$ after solving the minor system:
$[NH_3]_f = [NH_3]_{minor} + [NH_4]_{free}$
$[NH_4]_{free} = 0$

</td></tr>
</table>

	$[\mathrm{Mg}]_{free} = \mathrm{TMg} - [\mathrm{MgSO_4}]$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - [\mathrm{MgSO_4}]$ $[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] = \min\left(\frac{1}{3}\mathrm{TA}, \frac{1}{2}[\mathrm{SO_4}]_{free}\right)$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - 2[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}]$ $[\mathrm{NH_4}]_{free} = \mathrm{TA} - 3[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}]$ Based on the above partitioning, there are two cases: <u>Case 1:</u> $[\mathrm{SO_4}]_{free} \leq tiny$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} + 2[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - 2\left([(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - [\mathrm{NH_4}]_{free}\right)$ $[\mathrm{NH_4}]_{free_2} = [\mathrm{NH_4}]_{free} + 3[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - 3\left([(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - [\mathrm{NH_4}]_{free}\right)$ $[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] = [(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - [\mathrm{NH_4}]_{free}$ $[(\mathrm{NH_4})_2\mathrm{SO_4}] = \min\left(0.5[\mathrm{NH_4}]_{free_2}, [\mathrm{SO_4}]_{free}\right)$ $[\mathrm{NH_4}]_{free} = [\mathrm{NH_4}]_{free_2} - 2[(\mathrm{NH_4})_2\mathrm{SO_4}]$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - [(\mathrm{NH_4})_2\mathrm{SO_4}]$ <u>Case 2 (only if Case 1 = false):</u> $[\mathrm{NH_4}]_{free} \leq tiny$ $[\mathrm{NH_4HSO_4}] = 3\min\left([(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}], [\mathrm{SO_4}]_{free}\right)$ $[(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] = [(\mathrm{NH_4})_3\mathrm{H(SO_4)_2}] - [\mathrm{SO_4}]_{free}$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - \frac{1}{3}[\mathrm{NH_4HSO_4}]$ A. $[\mathrm{Na_2SO_4}] > tiny$ $[\mathrm{SO_4}]_{free_2} = [\mathrm{SO_4}]_{free}$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} + [\mathrm{Na_2SO_4}] - (\max\left([\mathrm{Na_2SO_4}] - [\mathrm{SO_4}]_{free}, 0\right)$ $[\mathrm{Na_2SO_4}] = [\mathrm{Na_2SO_4}] - [\mathrm{SO_4}]_{free_2}$ $[\mathrm{Na}]_{free} = \mathrm{TNa} - 2[\mathrm{Na_2SO_4}]$ $[\mathrm{NaHSO_4}] = \min\left([\mathrm{Na}]_{free}, [\mathrm{SO_4}]_{free}\right)$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - [\mathrm{NaHSO_4}]$ $[\mathrm{Na}]_{free} = [\mathrm{Na}]_{free} - [\mathrm{NaHSO_4}]$ B. $[\mathrm{K_2SO_4}] > tiny$ $[\mathrm{SO_4}]_{free_2} = [\mathrm{SO_4}]_{free}$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} + [\mathrm{K_2SO_4}] - (\max\left([\mathrm{K_2SO_4}] - [\mathrm{SO_4}]_{free}, 0\right)$ $[\mathrm{K_2SO_4}] = [\mathrm{K_2SO_4}] - [\mathrm{SO_4}]_{free_2}$ $[\mathrm{K}]_{free} = \mathrm{TK} - 2[\mathrm{K_2SO_4}]$ $[\mathrm{KHSO_4}] = \min\left([\mathrm{K}]_{free}, [\mathrm{SO_4}]_{free}\right)$ $[\mathrm{SO_4}]_{free} = [\mathrm{SO_4}]_{free} - [\mathrm{KHSO_4}]$ $[\mathrm{K}]_{free} = [\mathrm{K}]_{free} - [\mathrm{KHSO_4}]$ After the above partitioning, the gaseous species are: $[\mathrm{NH_3}]_{dry} = 0$	

	$[HNO_3]_{dry} = TN$ $[HCl]_{dry} = TCl$ <u>All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:</u> (1) ER1 (2) Mass balance for TS, TA, TN, TCl, TNa, TCa, TMg, TK $TS = 2[(NH_4)_3H(SO_4)_2] + [Na_2SO_4] + [NH_4HSO_4] + [(NH_4)_2SO_4] + [NaHSO_4] + [CaSO_4] + [KHSO_4] + [K_2SO_4] + [MgSO_4] + [SO_4]_{free}$ $TA = 3[(NH_4)_3H(SO_4)_2] + 2[(NH_4)_2SO_4] + [NH_4HSO_4] + [NH_4]_{free}$ $TN = [HNO_3]_{dry}$ $TCl = [HCl]_{dry}$ $TNa = 2[Na_2SO_4] + [NaHSO_4] + [Na]_{free}$ $TMg = [MgSO_4] + [Mg]_{free}$ $TCa = [CaSO_4] + [Ca]_{free}$ $TK = [KHSO_4] + 2[K_2SO_4] + [K]_{free}$ <u>All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:</u> The concentrations of $[Na^+]$, $[NH_4^+]$, $[Mg^{2+}]$ and $[K^+]$ remain constant during the iterative procedure of the major system. $[Na^+] = 2[Na_2SO_4] + [NaHSO_4]$ $[NH_4^+] = 3[(NH_4)_3H(SO_4)_2] + 2[(NH_4)_2SO_4] + [NH_4HSO_4]$ $[Mg^{2+}] = [MgSO_4]$ $[K^+] = [KHSO_4] + 2[K_2SO_4]$ $[Ca^{2+}] = 0$ $[Cl^-] = 0$ $[NO_3^-] = 0$ Let $[SO_4^{2-}] = [(NH_4)_3H(SO_4)_2] + [Na_2SO_4] + [(NH_4)_2SO_4] + [K_2SO_4] + [MgSO_4] + \Delta c$ $[HSO_4^-] = [(NH_4)_3H(SO_4)_2] + [NH_4HSO_4] + [NaHSO_4] + [KHSO_4] - \Delta c$ $[H^+] = \Delta c$ Using the expressions for $[SO_4^{2-}]$, $[HSO_4^-]$ and $[H^+]$ in (1) gives a quadratic equation in terms of Δc. Let $b = [(NH_4)_3H(SO_4)_2] + [Na_2SO_4] + [(NH_4)_2SO_4] + [K_2SO_4] + [MgSO_4] + K_{HSO_4}$ and $c = -K_{HSO_4}([(NH_4)_3H(SO_4)_2] + [NH_4HSO_4] + [NaHSO_4] + [KHSO_4])$ The solution is the *positive* root using the quadratic formula: $\Delta c = \frac{-b + \sqrt{b^2 - 4c}}{2}$	
K4	<u>Begin with dry salt partitioning to obtain:</u> $[NH_4HSO_4] = TA$ $[NaHSO_4] = TNa$	Same as case I6.

	$[KHSO_4] = TK$ $[MgSO_4] = TMg$ $[CaSO_4] = TCa$ $[SO_4]_{free} = TS - [NH_4HSO_4] + [NaHSO_4] + [KHSO_4] + [MgSO_4] + [CaSO_4]$ <u>The set of initial equations are:</u> (1) ER1 (2) Mass balance for TS, TA, TN, TCl, TNa, TCa, TMg, TK $TA = [NH_4HSO_4]$ $TNa = [NaHSO_4]$ $TK = [KHSO_4]$ $TMg = [MgSO_4]$ $TCa = [CaSO_4]$ $TCl = \left[HCl_{dry}\right]$ $TN = \left[NO_{3_{dry}}\right]$ $TS = [NH_4HSO_4] + [NaHSO_4] + [KHSO_4] + [MgSO_4] + [CaSO_4] + [SO_4]_{free}$ (3) Electroneutrality $[NH_4^+] + [H^+] + [Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}] = 2[SO_4^{2-}] + [HSO_4^-] + [Cl^-] + [NO_3^-]$ <u>All solids (except $CaSO_4$) are assumed to undergo deliquescence. System of equations:</u> $[Mg^{2+}] = [MgSO_4]$ $[K^+] = [KHSO_4]$ $[Na^+] = [NaHSO_4]$ $[NH_4^+] = [NH_4HSO_4]$ $[Ca^{2+}] = 0$ $[Cl^-] = 0$ $[NO_3^-] = 0$ Let: $[HSO_4^-] = [SO_4]_{free} + [KHSO_4] + [NH_4HSO_4] + [NaHSO_4] - x$ $[SO_4^{2-}] = [MgSO_4] + x$ $[H^+] = [SO_4]_{free} + x$ Substituting the resulting expressions for $[HSO_4^-]$, $[SO_4^{2-}]$ and $[H^+]$ into (1) gives a quadratic equation in terms of x. Let $b = K_{HSO_4} + [SO_4]_{free} + [MgSO_4]$ and $c = -K_{HSO_4}\left([SO_4]_{free} + [KHSO_4] + [NH_4HSO_4] + [NaHSO_4]\right) + [SO_4]_{free}[MgSO_4]$ The solution is the *positive* root using the quadratic formula: $x = \frac{-b + \sqrt{b^2 - 4c}}{2}$	

Table S3: The analytic solution of the quadratic formula used in HETP, as given by Press et al. (2007).

Assume a quadratic equation of the form $ax^2 + bx + c = 0$. In ISORROPIA II the quadratic equation is solved using the unmodified quadratic formula, with two possible roots

$$x_a = \frac{-b+\sqrt{b^2-4ac}}{2a}, \quad (1)$$

and

$$x_b = \frac{-b-\sqrt{b^2-4ac}}{2a}. \quad (2)$$

Press et al. (2007) gives an analytic formula to solve the quadratic equation that avoids the catastrophic cancellation experienced in (1) and (2),

$$q = -\frac{1}{2}\left(b + sign(b)\sqrt{b^2-4ac}\right) \text{ with } x_1 = \frac{c}{q} \text{ and } x_2 = \frac{q}{a}. \quad (3)$$

Expanding x_1

$$x_1 = \frac{c}{q} = \frac{-2c}{b + sign(b)\sqrt{b^2-4ac}}$$

and rationalizing the denominator gives*

$$x_1 = \frac{-2c}{b+sign(b)\sqrt{b^2-4ac}} \times \frac{b-sign(b)\sqrt{b^2-4ac}}{b-sign(b)\sqrt{b^2-4ac}} = \frac{-b+sign(b)\sqrt{b^2-4ac}}{2a}. \quad (4)$$

***(4) <u>is not</u> used in the HETP code. In the HETP code, $x_1 = c/q$, as given in (3).**

Likewise, expanding x_2 gives

$$x_2 = \frac{q}{a} = \frac{-b-sign(b)\sqrt{b^2-4ac}}{2a}. \quad (5)$$

In HETP we have updated the code so that it no longer uses (1) and (2) to solve the quadratic equation. Instead HETP uses (3), with two possible cases as shown below:

Case 1: The solution is (1).

if (b > 0) then

  $x = x_1 = c/q = \frac{-b+sign(b)\sqrt{b^2-4ac}}{2a} \equiv \frac{-b+\sqrt{b^2-4ac}}{2a}$

elseif (b < 0) then

  $x = x_2 = q/a = \frac{-b-sign(b)\sqrt{b^2-4ac}}{2a} \equiv \frac{-b+\sqrt{b^2-4ac}}{2a}$

elseif (b = 0) then

  $x = \frac{\sqrt{-4ac}}{2a}$ if $ac < 0$, otherwise undefined

end if

Case 2: The solution is (2).

if (b < 0) then

  $x = x_1 = c/q = \frac{-b+sign(b)\sqrt{b^2-4ac}}{2a} \equiv \frac{-b-\sqrt{b^2-4ac}}{2a}$

elseif (b > 0) then

  $x = x_2 = q/a = \frac{-b-sign(b)\sqrt{b^2-4ac}}{2a} \equiv \frac{-b-\sqrt{b^2-4ac}}{2a}$

elseif (b = 0) then

  $x = \frac{-\sqrt{-4ac}}{2a}$ if $ac > 0$, otherwise undefined

end if

In some instances, the sign of b is known at compile time (i.e., b always > 0), eliminating the need for a branching if statement.

Table S4: Statistics of $\boldsymbol{\xi'}$ for the summer data set containing 10,000 test cases. For the chemical subspace D3, G5, H6, O7, M8 and P13 only input conditions that require the application of bisection (ISORROPIA II) or ITP (HETP) to obtain an equilibrium solution are included. The **bolded** values denotes the smallest median error for that equilibrium constant (i.e., row) between HETP and ISORROPIA.

Case	Equilibrium Constant	ISORROPIA: $\xi' = \lvert\log(K_{true}/K_{calc})\rvert$				HETP: $\xi' = \lvert\log(K_{true}/K_{calc})\rvert$			
		Median	Q25	Q75	Maximum	Median	Q25	Q75	Maximum
D3	K_{NH_3}/K_{H_2O}	**4.59×10^{-10}**	1.73×10^{-10}	8.13×10^{-9}	22.6	5.62×10^{-10}	1.88×10^{-10}	4.27×10^{-9}	36.6
	K_{HNO_3}	**4.57×10^{-10}**	1.74×10^{-10}	8.07×10^{-9}	30.7	5.62×10^{-10}	1.88×10^{-10}	4.27×10^{-9}	49.2
	$K_{NH_4NO_3}$	**2.90**	1.51	5.39	12.0	3.00	1.54	5.39	62.4
E4	K_{HSO_4}	2.56×10^{-3}	1.47×10^{-5}	0.14	47.2	**8.88×10^{-16}**	0.00	9.02×10^{-13}	24.7
F2	K_{HSO_4}	9.65×10^{-2}	1.97×10^{-4}	0.37	1.27	**0.00**	0.00	4.44×10^{-16}	1.33×10^{-15}
G5	K_{NH_3}/K_{H_2O}	6.50×10^{-12}	2.84×10^{-14}	1.27×10^{-9}	46.1	**5.84×10^{-12}**	2.84×10^{-14}	2.89×10^{-10}	30.6
	K_{HNO_3}	**4.79×10^{-10}**	1.90×10^{-10}	3.08×10^{-4}	54.0	5.01×10^{-10}	1.83×10^{-11}	2.30×10^{-7}	29.9
	K_{HCl}	5.96×10^{-10}	1.97×10^{-10}	0.33	31.8	**5.02×10^{-10}**	1.83×10^{-11}	2.30×10^{-7}	29.9
H6	K_{NH_3}/K_{H_2O}	0.67	2.83×10^{-2}	5.16	10.5	0.67	2.83×10^{-2}	5.18	10.5
	K_{HNO_3}	**13.4**	6.72	14.5	18.9	31.8	6.72	32.9	37.4
	K_{HCl}	**0.56**	2.81×10^{-2}	5.15	10.5	0.67	2.83×10^{-2}	5.18	10.5
I6	K_{HSO_4}	0.10	9.27×10^{-3}	0.27	32.6	**0.00**	0.00	1.71×10^{-13}	6.57
	K_{HNO_3}	8.08	3.48	12.8	42.5	**3.81×10^{-10}**	1.86×10^{-10}	5.91×10^{-10}	44.1
	K_{HCl}	7.86	3.66	12.3	37.5	**3.81×10^{-10}**	1.86×10^{-10}	5.91×10^{-10}	42.5
J3	K_{HSO_4}	3.14×10^{-2}	8.03×10^{-5}	0.17	0.51	**0.00**	0.00	0.00	1.78×10^{-15}
	K_{HNO_3}	10.3	6.34	13.2	29.3	**4.83×10^{-10}**	2.44×10^{-10}	1.98×10^{-9}	29.3
	K_{HCl}	10.3	6.33	13.2	26.6	**4.83×10^{-10}**	2.44×10^{-10}	1.98×10^{-10}	29.3
O7	K_{NH_3}/K_{H_2O}	3.76×10^{-11}	7.32×10^{-13}	9.84×10^{-2}	46.1	**2.53×10^{-11}**	6.92×10^{-13}	2.94×10^{-9}	31.0
	K_{HNO_3}	1.34×10^{-8}	3.98×10^{-10}	0.28	52.7	**8.46×10^{-10}**	2.35×10^{-10}	3.18×10^{-4}	22.4
	K_{HCl}	1.34×10^{-8}	3.98×10^{-10}	0.32	48.7	**8.46×10^{-10}**	2.35×10^{-10}	3.18×10^{-4}	22.4
M8	K_{NH_3}/K_{H_2O}	**4.30×10^{-8}**	1.25×10^{-9}	5.19×10^{-3}	10.2	4.31×10^{-8}	1.24×10^{-9}	5.19×10^{-3}	10.2
	K_{HNO_3}	**0.26**	5.60×10^{-9}	12.8	27.0	0.28	3.60×10^{-9}	31.3	45.4
	K_{HCl}	2.05×10^{-9}	4.38×10^{-10}	1.55×10^{-8}	3.99	**6.98×10^{-10}**	1.30×10^{-10}	1.48×10^{-8}	1.32×10^{-2}
P13	K_{NH_3}/K_{H_2O}	**1.98×10^{-6}**	2.27×10^{-8}	1.38×10^{-4}	3.82	2.38×10^{-6}	2.42×10^{-8}	1.98×10^{-4}	13.5
	K_{HNO_3}	3.65	1.04	16.5	23.5	**3.61**	1.04	34.9	41.9
	K_{HCl}	3.01×10^{-10}	1.43×10^{-10}	1.29×10^{-9}	11.2	**8.30×10^{-11}**	1.55×10^{-11}	3.57×10^{-10}	11.7
L9	K_{HSO_4}	2.33×10^{-3}	9.93×10^{-6}	9.74×10^{-2}	62.2	**8.84×10^{-14}**	2.22×10^{-15}	3.80×10^{-11}	0.46
	K_{HNO_3}	14.7	2.53	16.9	47.7	**6.64×10^{-10}**	3.19×10^{-10}	1.42	15.0
	K_{HCl}	14.7	2.53	16.9	47.7	**6.64×10^{-10}**	3.19×10^{-10}	1.42	15.0
K4	K_{HSO_4}	2.02×10^{-2}	1.83×10^{-4}	0.11	3.32	**0.00**	0.00	8.88×10^{-16}	1.38×10^{-11}
	K_{HNO_3}	9.99	4.47	16.2	45.3	**5.00×10^{-10}**	2.40×10^{-10}	7.13×10^{-9}	45.3
	K_{HCl}	9.98	4.47	16.1	37.7	**5.00×10^{-10}**	2.40×10^{-10}	7.13×10^{-9}	45.3

Table S5: Statistics of ξ' for the winter data set containing 10,000 test cases. For the chemical subspace D3, G5, H6, O7, M8 and P13 only input conditions that require the application of bisection (ISORROPIA II) or ITP (HETP) to obtain an equilibrium solution are included. The **bolded** values denotes the smallest median error for that equilibrium constant (i.e., row) between HETP and ISORROPIA.

Case	Equilibrium Constant	ISORROPIA: $\xi' = \lvert\log(K_{true}/K_{calc})\rvert$				HETP: $\xi' = \lvert\log(K_{true}/K_{calc})\rvert$			
		Median	Q25	Q75	Maximum	Median	Q25	Q75	Maximum
D3	K_{NH_3}/K_{H_2O}	1.96×10^{-9}	3.41×10^{-10}	0.58	22.7	**6.91×10^{-10}**	1.46×10^{-10}	1.91×10^{-5}	5.95
	K_{HNO_3}	1.96×10^{-9}	3.41×10^{-10}	3.44×10^{-5}	23.7	**6.91×10^{-10}**	1.46×10^{-10}	1.91×10^{-5}	5.95
	$K_{NH_4NO_3}$	1.49	1.13	2.49	10.5	1.49	1.13	2.48	10.5
E4	K_{HSO_4}	5.77×10^{-2}	5.76×10^{-3}	5.71	46.9	**2.66×10^{-15}**	0.00	6.73×10^{-7}	26.2
F2	K_{HSO_4}	6.46×10^{-2}	2.67×10^{-4}	0.51	3.50	**0.00**	0.00	4.44×10^{-16}	1.78×10^{-15}
G5	K_{NH_3}/K_{H_2O}	2.27×10^{-12}	1.99×10^{-13}	7.35×10^{-3}	46.1	**1.21×10^{-12}**	1.42×10^{-13}	9.05×10^{-12}	29.5
	K_{HNO_3}	5.59×10^{-5}	3.62×10^{-10}	3.81	46.3	**4.60×10^{-7}**	2.03×10^{-10}	6.93×10^{-2}	29.2
	K_{HCl}	7.27×10^{-4}	3.78×10^{-10}	4.35	40.3	**4.60×10^{-7}**	2.03×10^{-10}	6.93×10^{-2}	29.2
H6	K_{NH_3}/K_{H_2O}	1.84	0.16	4.89	9.69	1.84	0.16	4.89	9.69
	K_{HNO_3}	**14.0**	12.9	14.7	22.8	32.5	31.3	33.1	41.2
	K_{HCl}	**1.83**	0.16	4.89	9.69	1.84	0.16	4.89	9.69
I6	K_{HSO_4}	1.11×10^{-3}	2.24×10^{-6}	0.32	46.7	**1.64×10^{-14}**	8.88×10^{-16}	3.52×10^{-11}	10.7
	K_{HNO_3}	5.95	2.39	13.3	46.3	**5.88×10^{-10}**	2.97×10^{-10}	3.32×10^{-4}	46.3
	K_{HCl}	5.74	2.27	13.2	38.3	**5.88×10^{-10}**	2.97×10^{-10}	3.32×10^{-4}	46.3
J3	K_{HSO_4}	7.25×10^{-2}	4.25×10^{-4}	0.52	3.50	**0.00**	0.00	4.44×10^{-16}	2.22×10^{-15}
	K_{HNO_3}	7.72	3.53	12.8	32.2	**4.99×10^{-10}**	2.52×10^{-10}	9.61×10^{-9}	32.2
	K_{HCl}	7.60	3.50	12.7	32.2	**4.99×10^{-10}**	2.52×10^{-10}	9.61×10^{-9}	32.2
O7	K_{NH_3}/K_{H_2O}	5.03×10^{-12}	3.13×10^{-13}	0.16	20.6	**1.51×10^{-12}**	1.78×10^{-13}	3.24×10^{-11}	9.39
	K_{HNO_3}	6.39×10^{-9}	4.17×10^{-10}	7.27×10^{-6}	22.0	**7.07×10^{-10}**	2.20×10^{-10}	8.08×10^{-6}	11.1
	K_{HCl}	1.05×10^{-8}	4.23×10^{-10}	1.26×10^{-3}	25.3	**7.07×10^{-10}**	2.20×10^{-10}	8.08×10^{-6}	11.1
M8	K_{NH_3}/K_{H_2O}	2.17×10^{-7}	1.58×10^{-9}	6.69×10^{-5}	7.82	2.17×10^{-7}	1.58×10^{-9}	6.57×10^{-5}	7.82
	K_{HNO_3}	**18.6**	0.73	20.8	25.9	37.0	0.73	39.2	44.3
	K_{HCl}	6.50×10^{-10}	2.69×10^{-10}	3.20×10^{-9}	3.75	**2.50×10^{-10}**	5.52×10^{-11}	7.74×10^{-10}	0.16
P13	K_{NH_3}/K_{H_2O}	3.19×10^{-9}	4.25×10^{-10}	7.18×10^{-8}	2.05	**3.18×10^{-9}**	4.26×10^{-10}	7.18×10^{-8}	2.05
	K_{HNO_3}	3.99×10^{-8}	2.38×10^{-9}	8.92×10^{-2}	23.1	**7.93×10^{-10}**	2.93×10^{-10}	8.92×10^{-2}	41.5
	K_{HCl}	2.49×10^{-9}	2.81×10^{-10}	4.04×10^{-8}	7.45×10^{-6}	**3.42×10^{-10}**	7.82×10^{-11}	8.16×10^{-10}	2.12×10^{-7}
L9	K_{HSO_4}	1.74×10^{-2}	2.93×10^{-4}	0.27	73.0	**6.66×10^{-15}**	8.88×10^{-16}	1.23×10^{-12}	12.1
	K_{HNO_3}	10.1	4.95	12.5	26.7	**4.70×10^{-10}**	2.30×10^{-10}	8.10×10^{-10}	21.0
	K_{HCl}	10.1	4.95	12.5	26.7	**4.70×10^{-10}**	2.30×10^{-10}	8.10×10^{-10}	21.0
K4	K_{HSO_4}	0.26	2.28×10^{-2}	0.84	11.9	**4.44×10^{-16}**	0.00	4.44×10^{-16}	3.52×10^{-11}
	K_{HNO_3}	7.52	3.86	11.0	29.2	**4.97×10^{-10}**	2.43×10^{-10}	2.83×10^{-9}	29.2
	K_{HCl}	7.53	3.86	11.0	29.2	**4.97×10^{-10}**	2.43×10^{-10}	2.83×10^{-9}	29.2

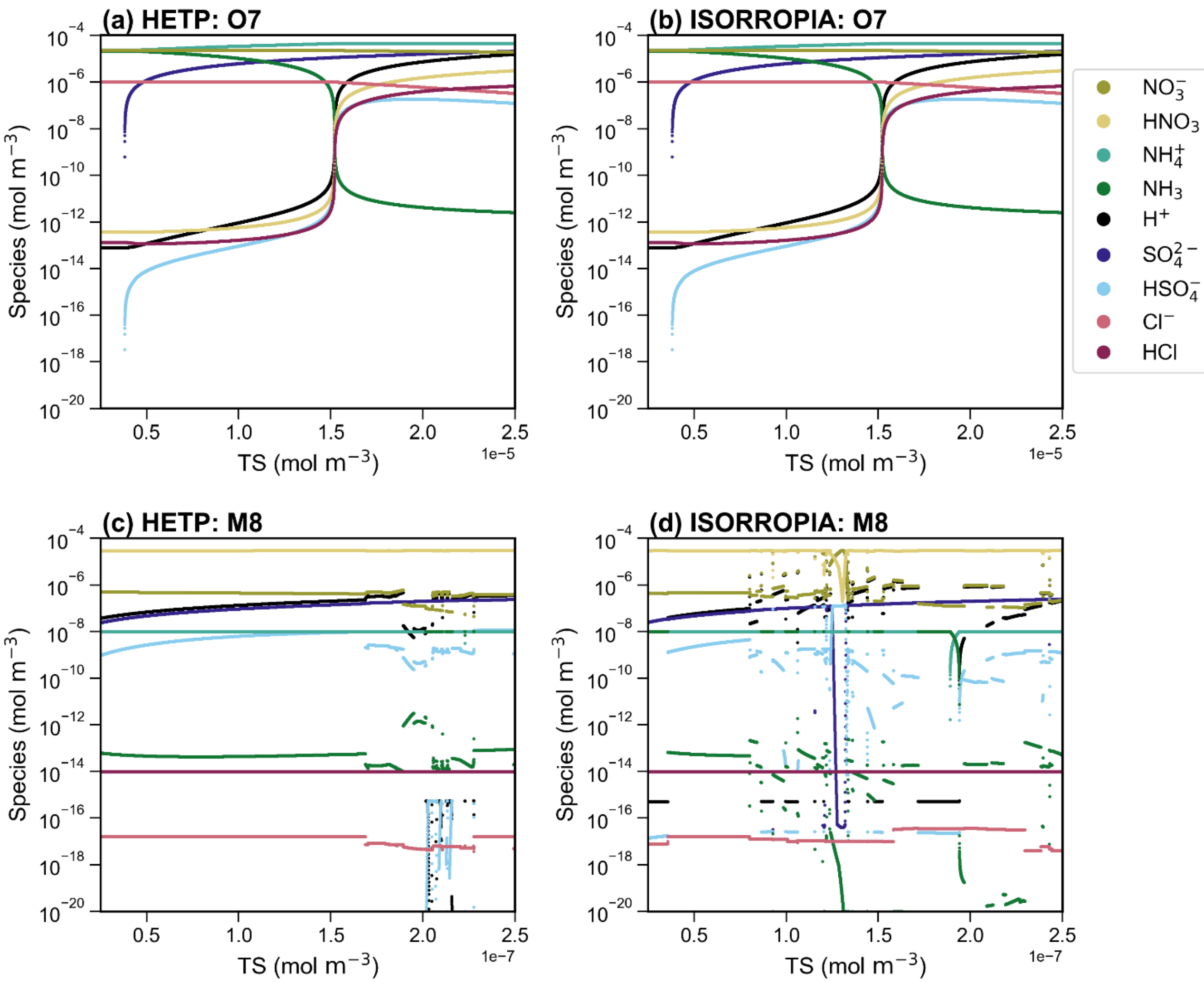

Figure S1 - A side–by–side comparison of the output from HETP (left) and ISORROPIA (right), for chemical subspace CALCO7 (a-b) and CALCM8 (c-d). All input species are held constant, except the total available sulfate (**TS)** which is varied over 10,000 sets of initial conditions. The air temperature and relative humidity are 263 K and 65% respectively, for all test cases in the figure. The convergence criteria are consistent between both solvers (see text).