Multicomponent Geochemical Computations in TOUGHREACT

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TOUGHREACT
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Processes

- Introduction of reactive chemistry into TOUGH2
- Reactions between gas - aqueous - solid phases, equilibrium or kinetics
- General database for minerals, aqueous and gaseous species
- Porosity and permeability change
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Processes

TOUGH2
- hydrodynamic
  - advection
  - diffusion
  - dispersion
- heat transfer
  - advection
  - conduction
  - phase change

chemical reactions
- homogeneous
  - acid-base
  - redox
  - aqueous complexation
- heterogeneous
  - ion exchange
  - adsorption
  - mineral dissol./precip.
  - gas dissolution/exsol.

flow
transport
chemistry

Focus

- Introduction of reactive chemistry into TOUGH2
- Reactions between gas - aqueous solid phases, equilibrium or kinetics
- General database for minerals, aqueous and gaseous species
- Porosity and permeability change
Reactive Transport Computational Approach

FLOW (TOUGH2)

TRANSPORT

Sequential Non-Iterative (SNIA)

Sequential Iterative (SIA)

CHEMISTRY
Multicomponent Chemical System

- Multicomponent Reactions (water must be present)
  - Aqueous Species
  - Minerals
  - Gases
  - Exchange Species
  - Surface Complexes (v2.0 beta)

- Aqueous Speciation: equilibrium (v2.0 beta with kinetics)
- Surface Complexation/Exchange: equilibrium

- Mass Transfer:
  - Minerals: equilibrium or kinetic constraints
  - Gases: equilibrium

- External Thermodynamic Database: reaction stoichiometries, equilibrium constants, activity coefficient data, etc.
Geochemical Computations - General

- Chemical system definition
  - Temperature and Pressure
  - Total aqueous concentrations (e.g., analytical)
  - Mineral amounts (0 for potential secondary phases)
  - Gas partial pressures (optional, unsaturated medium)

- Numerical approach: mass balance/mass action
  - Primary aqueous species (actual unknowns)
  - Derived species (functions of primary species – mass action)
    - Secondary aqueous species (ion pairs, complexes)
    - Minerals
    - Gases
  - Newton-Raphson iterative procedure
    - Solve for concentrations of primary species and kg water
    - Derive all other concentrations, mineral amounts, and gas partial pressures from mass action laws involving primary species
Example Chemical System

• Components of interest:
  – O, H, Na, Cl, Ca, S, C

• Primary species reflecting the components:
  – H₂O, H⁺, Cl⁻, Ca²⁺, Na⁺, SO₄⁻², HCO₃⁻
    • Best to use primary species representing dominant species
    • H₂O and H⁺ always primary species in TOUGHREACT

• Secondary aqueous species
  – OH⁻, CO₃⁻², HSO₄⁻, CaHCO₃⁺ etc... (automatic selection or specified)

• Minerals (specified input)
  – Calcite (CaCO₃), Gypsum (CaSO₄) etc...

• Gases (specified input)
  – CO₂(g), HCl(g) (Note, H₂O(g) is handled by flow EOS modules!)
Mass-Action Equations

• Expressions in terms of primary species only

• Secondary aqueous species ($a_i = \gamma_i \times m_i$)
  
  \[
  \begin{align*}
  \text{OH}^- + \text{H}^+ &= \text{H}_2\text{O} & K_{\text{OH}^-} &= a_{\text{H}_2\text{O}} / (a_{\text{H}^+} \times a_{\text{OH}^-}) \\
  \text{HSO}_4^- &= \text{H}^+ + \text{SO}_4^{2-} & K_{\text{HSO}_4^-} &= (a_{\text{H}^+} \times a_{\text{SO}_4^{2-}}) / a_{\text{HSO}_4^-} \\
  \text{CO}_3^{2-} + \text{H}^+ &= \text{HCO}_3^- & K_{\text{CO}_3^{2-}} &= a_{\text{HCO}_3^-} / (a_{\text{H}^+} \times a_{\text{CO}_3^{2-}}) \\
  \text{CaHCO}_3^+ &= \text{Ca}^{2+} + \text{HCO}_3^- & K_{\text{CaHCO}_3} &= (a_{\text{Ca}^{2+}} \times a_{\text{HCO}_3^-}) / a_{\text{CaHCO}_3} \\
  \end{align*}
  \]

• Minerals
  
  \[
  \begin{align*}
  \text{CaCO}_3(s) + \text{H}^+ &= \text{Ca}^{2+} + \text{HCO}_3^- & K_{\text{calcite}} &= (a_{\text{Ca}^{2+}} \times a_{\text{HCO}_3^-}) / a_{\text{H}^+} \\
  \text{CaSO}_4(s) &= \text{Ca}^{2+} + \text{SO}_4^{2-} & K_{\text{gypsum}} &= a_{\text{Ca}^{2+}} \times a_{\text{HCO}_3^-} \\
  \end{align*}
  \]

• Gases ($f_i = \phi_i \times P_i$)
  
  \[
  \begin{align*}
  \text{CO}_2(g) + \text{H}_2\text{O} &= \text{HCO}_3^- + \text{H}^+ & K_{\text{CO}_2} &= (a_{\text{H}^+} \times a_{\text{HCO}_3^-}) / (f_{\text{CO}_2} \times a_{\text{H}_2\text{O}}) \\
  \end{align*}
  \]
Mass-Balance Equations

• Total moles ($M^t$) in terms of molal concentrations (mol/kg$_w$)
  - Solutes
    $M^t_C = \{[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CaHCO}_3] \ldots \} \times kg_w + \Delta n_{\text{calcite}} + n_{\text{CO}_2(g)} + \ldots$
    $M^t_{\text{H}^+} = \{[\text{H}^+] - [\text{OH}^-] - [\text{CO}_3^{2-}] + [\text{HSO}_4^-] + \ldots \} \times kg_w - \Delta n_{\text{calcite}} + n_{\text{CO}_2(g)} + \ldots$
    $M^t_{\text{Ca}} = \{[\text{Ca}^{2+}] + [\text{CaHCO}_3^+] + \ldots \} \times kg_w + \Delta n_{\text{calcite}} + \Delta n_{\text{gypsum}} + \ldots$
  - Solvent (water, after Reed 1982 GCA)
    $M^t_w = \{55.505 + \ldots + \ldots \} \times kg_w + \Delta n_{\ldots} - n_{\text{CO}_2(g)} + \ldots$

• Minerals – incremental change $\Delta n_m$ (in moles)
  Kinetics: $\Delta n_m = R \times \Delta t$  \hspace{1cm} $R =$ kinetic rate (positive = dissolve)
  Equilibrium: solve for $\Delta n_m$ by adding mass action eqn (negative = dissolve)

• Gases, at equilibrium – total moles $n_i$ (change + initial)
  From gas law: $P_i V = n_i RT$ with gas concentration $= n_i/V$ and $P_i$ from mass-action law (ideal, $P = f$, except with ECO2 module)
Activity Coefficients Calculations

• Charged species and water:
  
  Extended Debye-Hückel (Helgeson et al., 1981 AJS)
  
  – Assumes predominant ions are Na\(^+\) and Cl\(^-\)
  – Careful above ionic strength 1 molal for non Na-Cl dominant waters!
  – Not bad to ~ 6 m for pure NaCl solution
  – Remove NaCl\(_{aq}\) (derived species) in the database!
  – Watch! D-H \(a_0\) values are calculated from input effective radii in database (different from more standard “b-dot” equation)

• Neutral species:
  
  – Optional Setchenow equation: \(\log(\gamma) = (\text{const}) \times \text{(ionic strength)}\), otherwise \(\gamma\) values are set to one

• Unreleased beta-version with Pitzer ion-interaction model for concentrated solutions (Zhang et al., 2006)
Redox Reactions

• Same approach as non-redox reactions if:
  – Unique redox couple (i.e., donor and acceptor) is defined with two primary species. For example:
    • \( \text{H}_2\text{O} \) and \( \text{O}_2 \) (preferable if dealing with mostly oxidized systems)
    • \( \text{SO}_4 \) and \( \text{HS}^- \) (preferable if dealing with mostly reduced systems)
  – Electron transfer is balanced using the specific redox couple in all reactions of the database (i.e., no free electrons!).

• Example:
  – Primary species: \( \text{Fe}^{+3}, \text{H}_2\text{O}, \text{O}_2(\text{aq}), \text{etc...} \) (with \( \text{Fe}^{+2} \) as secondary species)
    \[ \text{Fe}^{+2} + 0.25\text{O}_2(\text{aq}) + \text{H}^+ = \text{Fe}^{+3} + 0.5\text{H}_2\text{O} \]
  – Primary species: \( \text{Fe}^{+2}, \text{SO}_4 \) and \( \text{HS}^- \), etc... (with \( \text{Fe}^{+3} \) as secondary species)
    \[ 8\text{Fe}^{+3} + \text{HS}^- + 4\text{H}_2\text{O} = 8\text{Fe}^{+2} + \text{SO}_4^{--} + 9\text{H}^+ \]

• Utility provided to “switch” the redox couple in the database
• Unreleased v2.0 beta with redox disequilibrium (Xu, 2006)
Thermodynamic Data

- \( \log(K) \) values for mass-action equations and D-H parameters for activity coefficients are calculated as functions of temperature (\( T_K \), Kelvin) from coefficients read in external database for given reaction stoichiometries
  \[ a + \ln(T_K) + b + cT_K + d/T_K + e/T_K^2 \]

- **Watch!!!! Crucial for confidence in results!**
  - Quality/consistency of \( \log(K) \) data
  - Applicability of activity coefficient model
  - Consistency between activity coefficient model and types of secondary aqueous species and their \( \log(K) \) values

- **DO NOT use supplied database as black box!**
- **Understand the data you are using (trash in = trash out)**
Kinetic Data

\[ Rate = \pm kA_m \prod_i a_i^p \left[ \left( \frac{Q}{K} \right)^m - 1 \right]^n \]

(e.g., Steefel and Lasaga, AJS, 1994)

- Rate constant \( k \)
- Surface area \( A_m \)
- Equilibrium constant \( K \)

\[ k = k_0 \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] \]

\( Q \) is ion activity product, \( a_i \) are individual activities (e.g., \( H^+ \))
Equilibrium at \( Q/K = 1 \), dissolution at \( Q/K < 1 \), precipitation at \( Q/K > 1 \)

Large uncertainty in \( A_m \) and \( k \) !!
Beware of Data/Model Limits (!)

Cool same geothermal brine from 200°C (pH 4.9, ionic strength 1.8)

This is mostly an effect of activity coefficient uncertainty at elevated temperature when dealing with concentrated solutions.
Useful General References
(not related to TOUGHREACT)


