Multicomponent Geochemical Computations in TOUGHREACT

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TOUGHREACT

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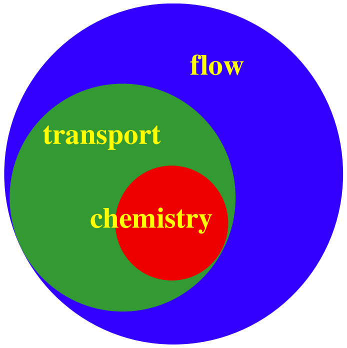
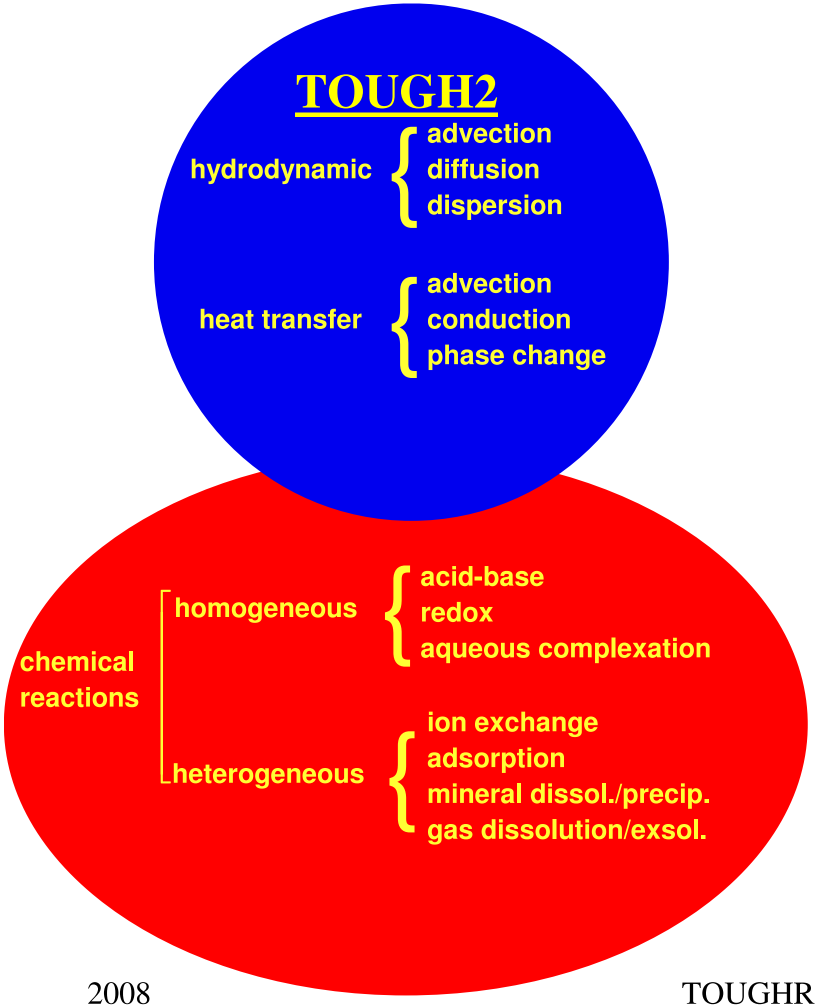


Processes



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.

- 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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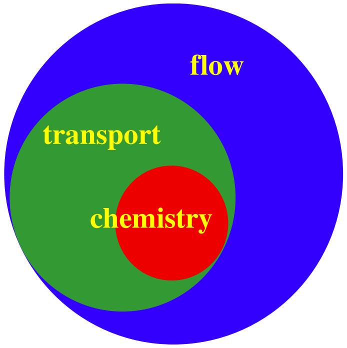

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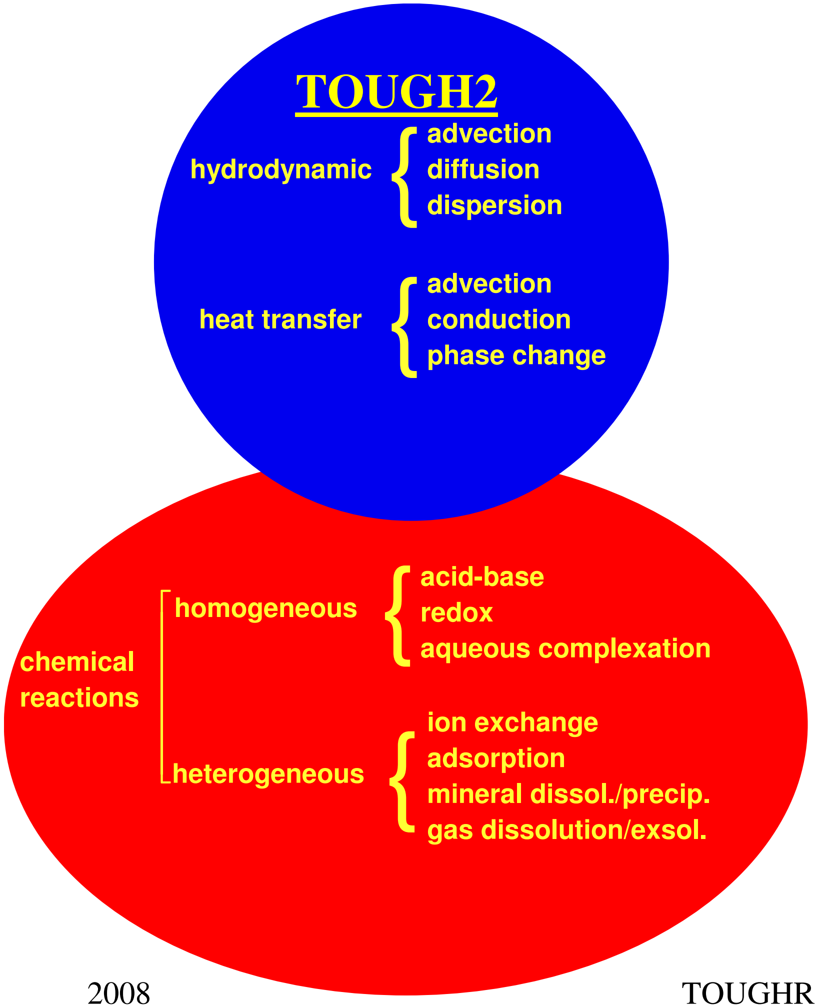

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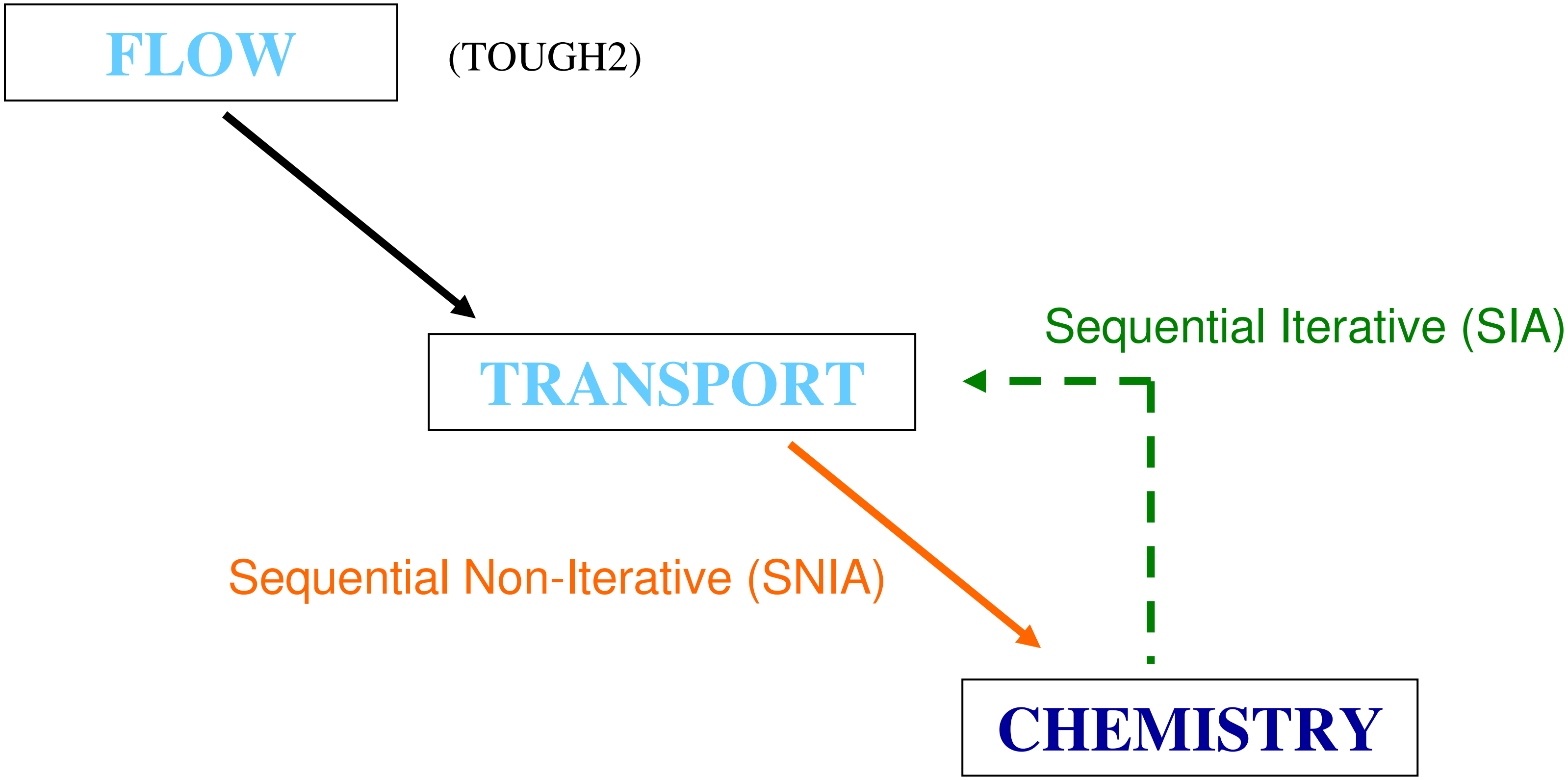
Focus

Reactive Transport Computational Approach



FLOW

(TOUGH2)

TRANSPORT

Sequential Iterative (SIA)

Sequential Non-Iterative (SNIA)

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:
  - H_2O, H^+, Cl^-, Ca^{+2}, Na^+, SO_4^{-2}, HCO_3^-
    - Best to use primary species representing dominant species
    - H_2O and H^+ always primary species in TOUGHREACT
- Secondary aqueous species
  - OH^-, CO_3^{-2}, HSO_4^-, $CaHCO_3^+$ etc... (automatic selection or specified)
- Minerals (specified input)
  - Calcite ($CaCO_3$), Gypsum ($CaSO_4$) etc...
- Gases (specified input)
  - $CO_{2(g)}$, $HCl_{(g)}$ (Note, $H_2O_{(g)}$ is handled by flow EOS modules!)

Mass-Action Equations

- Expressions in terms of primary species only
- Secondary aqueous species ($a_i = \gamma_i \times m_i$)

$OH^- + H+ = H_2O$ $\quad K_{OH-} = a_{H2O} / (a_{H+} \times a_{OH-})$

$HSO_4^- = H^+ + SO_4^{-2}$ $\quad K_{HSO4-} = (a_{H+} \times a_{SO4--}) / a_{HSO4-}$

$CO_3^{-2} + H^+ = HCO_3^-$ $\quad K_{CO3--} = a_{HCO3-} / (a_{H+} \times a_{CO3--})$

$CaHCO_3^+ = Ca^{+2} + HCO_3^-$ $\quad K_{CaHCO3} = (a_{Ca++} \times a_{HCO3-}) / a_{CaHCO3}$

- Minerals

$CaCO_{3(s)} + H^+ = Ca^{+2} + HCO_3^-$ $\quad K_{calcite} = (a_{Ca++} \times a_{HCO3-}) / a_{H+}$

$CaSO_{4(s)} = Ca^{+2} + SO_4^{-2}$ $\quad K_{gypsum} = a_{Ca++} \times a_{HCO3-}$

- Gases ($f_i = \phi_i \times P_i$)

$CO_{2(g)} + H_2O = HCO_3^- + H^+$ $\quad K_{CO2} = (a_{H+} \times a_{HCO3-}) / (f_{CO2} \times a_{H2O})$

Mass-Balance Equations

- Total moles (M^t) in terms of molal concentrations (mol/kg_w)
  - Solutes

substitute mass action (in terms of γ and m)

$$M^t_C = \{[HCO_3^-] + [CO_3^{-2}] + [CaHCO_3] \ldots\} \times kg_w + \Delta n_{calcite} + n_{CO2(g)} + \ldots$$

$$M^t_{H+} = \{[H^+] - [OH^-] - [CO_3^{-2}] + [HSO_4^-] + \ldots\} \times kg_w - \Delta n_{calcite} + n_{CO2(g)} + \ldots$$

$$M^t_{Ca} = \{[Ca^{+2}] + [CaHCO_3^+] + \ldots \} \times kg_w + \Delta n_{calcite} + \Delta n_{gypsum} + \ldots$$

  - Solvent (water, after Reed 1982 GCA)

$$M^t_w = \{55.505 + [\ldots] + \ldots\} \times kg_w + \Delta n_{\ldots} - n_{CO2(g)} + \ldots$$

- Minerals – incremental change Δn_m (in moles)

Kinetics: $\Delta n_m = R \times \Delta t$ R = kinetic rate (positive = dissolve)

Equilibrium: solve for Δn_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 <u>pure</u> 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 γ values are set to one
  - Dissolved gases: Drummond (1981 – unpubl. Ph.D. Penn State)
- 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:
    - H_2O and O_2 (preferable if dealing with mostly oxidized systems)
    - SO_4 and 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: Fe^{+3}, H_2O, $O_{2(aq)}$, etc... (with Fe^{+2} as secondary species)

$$Fe^{+2} + 0.25O_{2(aq)} + H^+ = Fe^{+3} + 0.5H_2O$$

  - Primary species: Fe^{+2}, SO_4 and HS^- , etc... (with Fe^{+3} as secondary species)

$$8Fe^{+3} + HS^- + 4H_2O = 8Fe^{+2} + SO_4^{--} + 9H^+$$

- 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

$$Rate = \pm k A_m \prod_i a_i^{p} \left| \left[\left(Q/K \right)^{m} - 1 \right] \right|^{n}$$

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

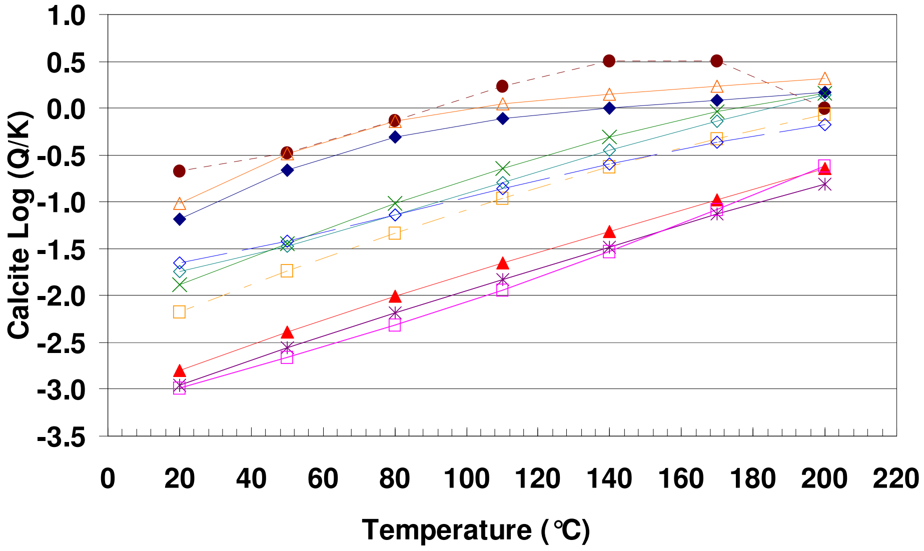
$$k = k_0 \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right]$$

- Rate constant k
- Surface area A_m
- Equilibrium constant K

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

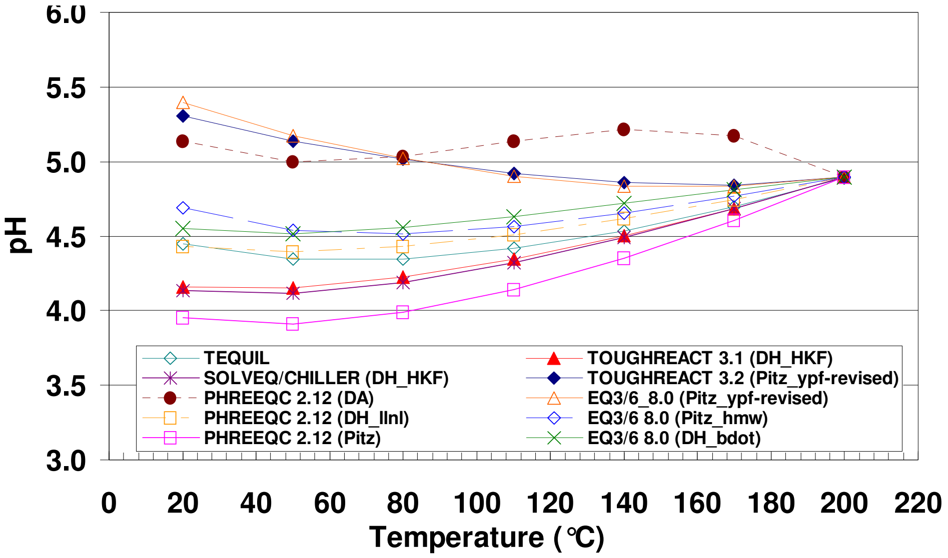
Large uncertainty in A_m and k !!

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)

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