RAND-based Chemical and Phase Equilibrium Calculation

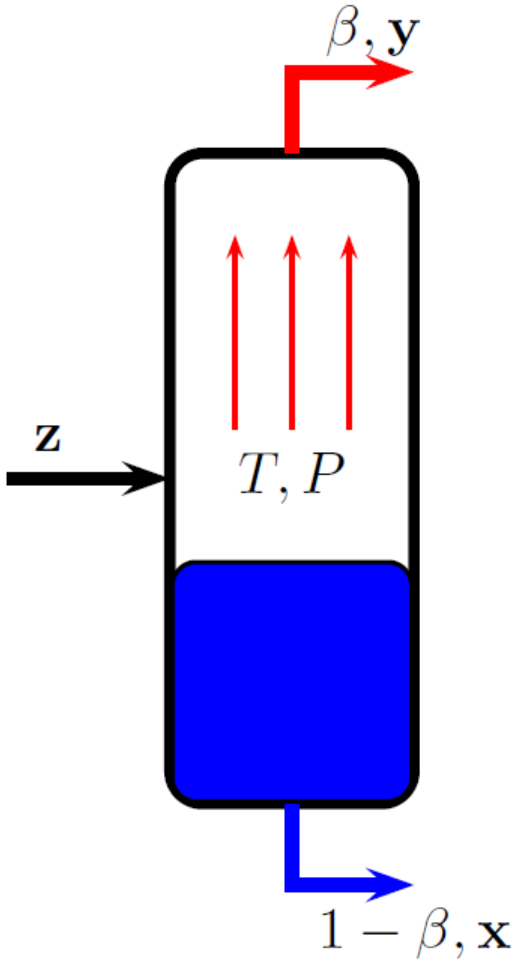
Wei Yan
Center for Energy Resources Engineering, DTU Chemistry
Email: weya@kemi.dtu.dk

November 12, 2024

Outline

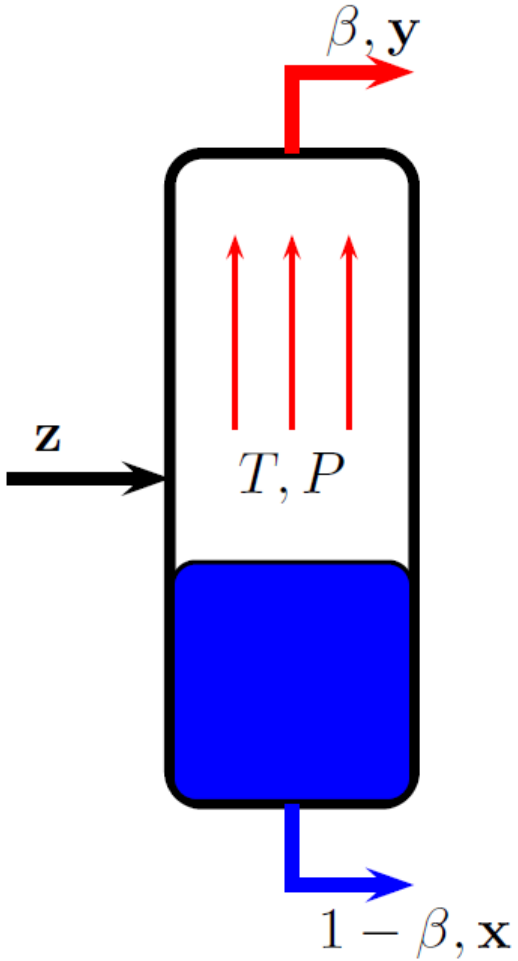
- General discussion about phase equilibrium calculation
- RAND formulation and its derivation
- Examples of RAND-based calculations
  - Modified RAND
  - Vol-RAND
  - Other flash specifications
  - Chemical and phase equilibrium (CPE)
  - “Open” systems
  - Saturation point and phase envelope
  - Geochemical calculations
- Summary

Phase equilibrium calculation (PEC)



- Single-stage phase equilibrium calculation (PEC)
  - To determine equilibrium phase compositions and amounts at certain conditions
  - In general, it covers multiphase and chemical reactions as well
- PEC: An essential and recurrent element in the simulation of chemical processes
  - Standalone equilibrium calculations
  - Multistage—coupled with material and energy balances…
    - Chemical engineering: distillation, adsorption, and extraction
    - Subsurface processes: reservoir simulation, CO_2 sequestration…
- Examples
  - Two-phase TP-Flash: $(\mathbf{z}, T, P) \rightarrow (\beta, \mathbf{x}, \mathbf{y})$
  - Bubble point pressure: $(\mathbf{x}=\mathbf{z}, \beta=1, T) \rightarrow (P, \mathbf{y})$
  - …

Michelsen's PEC classification

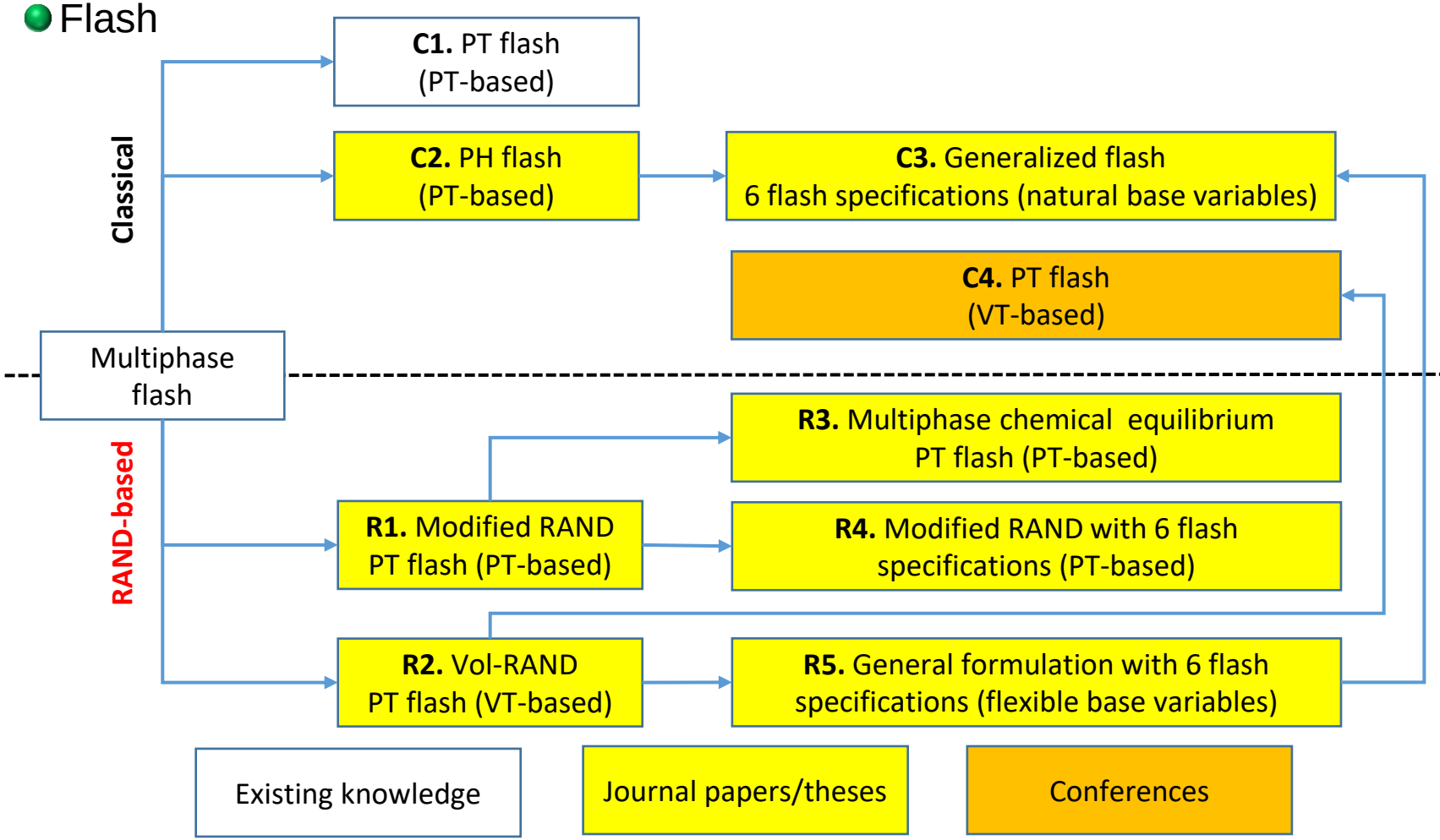


- Flash specifications—Minimization of a thermodynamic state function
  - In addition to *TP*-flash, (*P*, *H*), (*P*, *S*), (*T*, *V*), and (*U*, *V*) flash
  - Extension to multiphase and to reactive systems (Paterson et al.)
  - Extension to open systems: "Open system" flash (Medeiros et al.)
- Phase fraction specifications (*β* specifications)
  - Bubble P, Bubble T, Dew P, Dew T
  - *β* specifications not equal to 0 or 1
  - Phase envelope construction—a series of saturation points
- Others
  - Indirect specifications: Critical points, cricondentherm, cricondenbar
  - (P, V), (T, H) … of minor importance

Michelsen, M.L. Phase equilibrium calculations. What is easy and what is difficult? Computers Chem. Engng. 17 (1993)

PEC-related research in our group since 2014

- Flash



Highlights (academic)

- RAND formulation
- Thermodynamics based on VT or other variables
- Various flash specifications
- "Flash" for open systems

"Flash" for open systems

Highlights (application)

- Multiphase reactions
- Multiphase PH flash…
- Faster flash for advanced models
- Geochemical reactions

- Saturation pressure for reactive mixtures (RAND-based)
- PEC in porous media (involving capillarity/adsorption)

Conventional multiphase flash formulation

- For a non-reacting system with C components and F phases , the classical second-order approach uses the following formulation:

$$\left(\frac{\partial \boldsymbol{\mu}_j}{\partial \mathbf{n}_j} - \frac{\partial \boldsymbol{\mu}_{\text{ref}}}{\partial \mathbf{n}_j}\right)\Delta \mathbf{n}_j = \boldsymbol{\mu}_j - \boldsymbol{\mu}_{\text{ref}} \qquad j \neq \text{ref}$$

  - It solves $C(F\text{-}1)$ equations where the independent variables $\mathbf{n}_j$ ($j \neq \text{ref}$) are updated iteratively.

Pros:

- Abundant implementation experiences
- Works well particularly for two-phase flash

Cons:

- Hessian for multiphase flash not well scaled for Trust Region—Empirical modifications used instead.
- Dependent phase “ref” should be component dependent to handle round off errors—Complex Hessian for multiphase flash and significant bookkeeping.
- Extension to reacting systems is challenging.

RAND-based multiphase flash formulation

- From RAND to modified RAND:
  - RAND is a non-stoichiometric method for chemical reaction equilibrium
  - Named after the affiliation of White et al. (the RAND corporation), who proposed the original RAND in 1958
  - Original RAND is for single-phase chemical equilibrium of an ideal mixture
  - Modified RAND and its variations are for multiphase non-ideal mixtures
  - Key ideas:
    - Use (elemental) chemical potentials to express mole fractions/numbers
    - Second order convergent algorithms

Paterson et al., SPE J. **2018**, 23(2), 535-549; Tsanas et al., Ind. Eng. Chem. Res. **2017**, 56, 11983-11995.

Modified RAND multiphase flash formulation

- Derivation in brief: A reacting system with C components, F phases, R reactions, E elements ($E = C - R$)

Gibbs energy minimization using Lagrange multipliers:

$$\mathcal{L}(\mathbf{n},\boldsymbol{\lambda}) = \sum_{j=1}^{F} \mathbf{n}_j^T \frac{\boldsymbol{\mu}_j}{RT} - \boldsymbol{\lambda}^T \left(\mathbf{A} \sum_{j=1}^{F} \mathbf{n}_j - \mathbf{b} \right)$$

- $\mathbf{A}$ $E \times C$ formula matrix
- $\mathbf{b}$ moles of elements in feed
- $\boldsymbol{\mu}_j$ chemical potentials in phase j
- $\boldsymbol{\lambda}$ Lagrange multipliers/elemental potentials

Equilibrium: $$\frac{\partial \mathcal{L}}{\partial n_{i,j}} = \frac{\mu_{i,j}}{RT} - \sum_{j=1}^{E} A_{ki}\lambda_k = 0$$ CF equations

Mass balance: $$\frac{\partial \mathcal{L}}{\partial \lambda_k} = -\sum_{i=1}^{C} A_{ik} \sum_{j=1}^{F} n_{i,j} + b_k = 0$$ E equations (C equations if no reactions)

- Linearization of chemical potential $\boldsymbol{\mu}$ in terms of mole numbers $\mathbf{n}$ (and T & P if T & P vary)

$$\frac{1}{RT}\left(\boldsymbol{\mu}_j + \frac{\partial \boldsymbol{\mu}_j}{\partial \mathbf{n}_j} \Delta \mathbf{n}_j + \boldsymbol{\mu}_{T,j} \Delta T + \boldsymbol{\mu}_{P,j} \Delta P \right) - \mathbf{A}^T \boldsymbol{\lambda} = 0$$

with $\boldsymbol{\mu}_{T,j} = \frac{\partial \boldsymbol{\mu}_j}{\partial T}$ and $\boldsymbol{\mu}_{P,j} = \frac{\partial \boldsymbol{\mu}_j}{\partial P}$

Modified RAND multiphase flash formulation

- Derivation in brief:
  - Expression of $\Delta\mathbf{n}_j$ using elemental chemical potentials $\boldsymbol{\lambda}$

$$\Delta\mathbf{n}_j = \mathbf{x}_j\Delta\beta_j + \beta_j\mathbf{M}_j\left[\mathbf{A}^T\boldsymbol{\lambda} - \frac{1}{RT}\left(\boldsymbol{\mu}_j + \boldsymbol{\mu}_{T,j}\Delta T + \boldsymbol{\mu}_{P,j}\Delta P\right)\right]$$

$$\text{where } \mathbf{M}_j = \mathbf{m}_j^{-1} \text{ and } \quad m_{p,q,j} = \beta_j\left(\frac{1}{RT}\frac{\partial\mu_{p,j}}{\partial n_{q,j}} + 1\right) = \frac{\delta_{p,q}}{x_{p,j}} + \beta_j\frac{\partial \ln\phi_{p,j}}{\partial n_{q,j}}$$

  - The first E equations: Substitution of $\Delta\mathbf{n}_j$ into the E linearized mass balance equations $\mathbf{A}\sum_{j=1}^{F}\Delta\mathbf{n}_j = 0$ gives

$$\mathbf{A}\left(\sum_{j=1}^{F}\beta_j\mathbf{M}_j\right)\mathbf{A}^T\boldsymbol{\lambda} + \mathbf{A}\mathbf{X}\Delta\boldsymbol{\beta} = \mathbf{A}\left(\sum_{j=1}^{F}\beta_j\mathbf{M}_j\frac{\boldsymbol{\mu}_j}{RT}\right)$$

$\mathbf{X}$ $C\times F$ matrix of phase mole fractions $x_{i,j}$

Modified RAND multiphase flash formulation

- Derivation in brief:
  - The last F equations: Multiply the $\Delta\mathbf{n}_j$ expression by $\mathbf{1}^{\mathrm{T}}$ and utilize the Gibbs-Duhem equation

$$\mathbf{X}^T\mathbf{A}^T\boldsymbol{\lambda}=\mathbf{g} \qquad \text{where } g_j=\frac{1}{RT}\sum_{i=1}^{C}x_{i,j}\mu_{i,j}$$

  - Final modified RAND equations:
    - E+F equations for reacting mixtures

$$\begin{pmatrix}\mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\mathbf{A}^T & \mathbf{AX}\\ (\mathbf{AX})^T & \mathbf{0}\end{pmatrix}\begin{pmatrix}\boldsymbol{\lambda}\\ \Delta\boldsymbol{\beta}\end{pmatrix}=\begin{pmatrix}\mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\dfrac{\boldsymbol{\mu}_j}{RT}\\ \mathbf{g}\end{pmatrix}$$

    - C+F equations for non-reacting mixtures

$$\begin{pmatrix}\sum_{j=1}^{F}\beta_j\mathbf{M}_j & \mathbf{X}\\ \mathbf{X}^T & \mathbf{0}\end{pmatrix}\begin{pmatrix}\boldsymbol{\lambda}\\ \Delta\boldsymbol{\beta}\end{pmatrix}=\begin{pmatrix}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\ln\mathbf{f}_j\\ \mathbf{g}\end{pmatrix} \qquad \text{where } g_j=\sum_{i=1}^{C}x_{i,j}\ln f_{i,j}$$

Modified RAND multiphase flash formulation

$$\begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\mathbf{A}^T & \mathbf{AX} \\ (\mathbf{AX})^T & \mathbf{0} \end{pmatrix}\begin{pmatrix} \boldsymbol{\lambda} \\ \Delta\boldsymbol{\beta} \end{pmatrix}=\begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\dfrac{\boldsymbol{\mu}_j}{RT} \\ \mathbf{g} \end{pmatrix}$$

- Advantages:
  - Quadratically convergent
  - Material balance satisfied at each step
  - Gibbs energy can be monitored
  - No singularity close to the phase boundary
  - All phases and all components are treated equally, simple to implement, no book-keeping
  - For non-reacting flash, it solves $C+F$ equations instead of $C(F-1)$ equations (conventional method).
  - Most attractive feature: Same formulation for phase & chemical equilibrium
    - It has $E+F$ equations for reacting systems—A “classical” stoichiometric formulation needs $CF-E$ equations.
    - RAND particularly suitable with many phases and many reactions.

Variation I: Using volume-based thermodynamics

- Vol-RAND using volume-based thermodynamics

  Linearization of chemical potentials: $\boldsymbol{\mu}_j + \mathbf{A}_{nn,j}\Delta\mathbf{n}_j + \mathbf{A}_{nV,j}\Delta V_j - \mathbf{A}^T\hat{\boldsymbol{\lambda}} = 0$ $\quad \hat{\boldsymbol{\lambda}} = \boldsymbol{\lambda}RT$

  Linearization of pressure: $-P_j + \mathbf{A}^T_{nV,j}\Delta\mathbf{n}_j + \mathbf{A}_{VV,j}\Delta V_j + P^{spec} = 0$

  - Expression of $\Delta\mathbf{n}_j$ is straight forward: $\Delta\mathbf{n}_j = \mathbf{A}^{-1}_{nn,j}\left(\mathbf{A}^T\boldsymbol{\lambda} - \boldsymbol{\mu}_j\right) + \boldsymbol{\rho}_j\Delta V_j$ $\quad \boldsymbol{\rho}_j = \mathbf{n}_j / V_j$

  - Final formulation: *E+F* equations in ($\boldsymbol{\lambda}$, $\Delta\boldsymbol{V}$), where $\Delta\boldsymbol{V}$ is the change in phase volumes.

$$\begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\mathbf{A}^{-1}_{nn,j}\mathbf{A}^T & \mathbf{AR} \\ (\mathbf{AR})^T & \mathbf{0} \end{pmatrix}\begin{pmatrix} \hat{\boldsymbol{\lambda}} \\ \Delta\mathbf{V} \end{pmatrix} = \begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\dfrac{\boldsymbol{\mu}_j}{RT} \\ \boldsymbol{\rho}_j^T\boldsymbol{\mu}_j + \mathbf{A}_{V,j} + P^{spec} \end{pmatrix}$$

$\mathbf{R}_j$ $C \times F$ matrix $(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, ..., \boldsymbol{\rho}_F)$

Note: **A** in **black** color for the vector/matrix of Helmholtz energy derivatives

A in **red** color for the formula matrix

Variation II: Extension to other specifications

- RAND for (V,T), (P,H), (P,S), (U,V) and (V,S) flash
  - Additional constraints (one or two): $S - S^{spec} = 0,\ H - H^{spec} = 0,\ V - V^{spec} = 0,\ U - U^{spec} = 0$
  - Linearization of these constraints and simplifications result in two additional equations:

$$\frac{C_p}{RT^2}\Delta T - \frac{1}{RT}\frac{\partial V}{\partial T}\Delta P - \sum_{j=1}^{F}\mathbf{e}_j^T \Delta n_j = r_T$$

$$-\frac{1}{RT}\frac{\partial V}{\partial T}\Delta T - \frac{1}{RT}\frac{\partial V}{\partial P}\Delta P - \sum_{j=1}^{F}\boldsymbol{\gamma}_j^T \Delta n_j = r_P$$

where $\mathbf{e}_j = \boldsymbol{\mu}_{T,j} / RT$, $\boldsymbol{\gamma}_j = \boldsymbol{\mu}_{P,j} / RT$, and r_T and r_P depend on specifications.

  - Final formulation: A common Jacobian of size $E+F+1$ or $E+F+2$ (E replaced by C for non-reacting systems).

$$\begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\mathbf{A}^T & \mathbf{AX} & -\mathbf{t} & -\mathbf{q} \\ (\mathbf{AX})^T & \mathbf{0} & \mathbf{s}_1 & \mathbf{s}_2 \\ -\mathbf{t}^T & \mathbf{s}_1^T & C_x & \Omega \\ -\mathbf{q}^T & \mathbf{s}_2^T & \Omega & \Psi \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta\boldsymbol{\beta} \\ \Delta T \\ \Delta P \end{pmatrix} = \begin{pmatrix} \mathbf{A}\sum_{j=1}^{F}\beta_j\mathbf{M}_j\frac{\boldsymbol{\mu}_j}{RT} \\ \mathbf{g} \\ r_T - \sum_{j=1}^{F}\beta_j\mathbf{e}_j^T\mathbf{M}_j\frac{\boldsymbol{\mu}_j}{RT} \\ r_p - \sum_{j=1}^{F}\beta_j\boldsymbol{\gamma}_j^T\mathbf{M}_j\frac{\boldsymbol{\mu}_j}{RT} \end{pmatrix}$$

Performance of modified-RAND and vol-RAND

- 17-component containing H_2O, CO_2, and H_2S (up to 3 phases)

Equation of state	Two-phase flash		
	Conventional method	Modified RAND	Vol-RAND
SRK	1	2.03	2.00
CPA1	2.47	4.05	2.11
CPA2	4.63	6.62	2.38
	Three-phase flash		
SRK	2.98	2.89	2.88
CPA1	5.41	5.40	3.08
CPA2	8.65	8.45	3.50

CPA1: 2 types of sites for H_2O

CPA2: 5 types of sites for H_2O, H_2S and CO_2 (solvating)

- 5-componet mixture: C_1, C_2, C_3, H_2S, CO_2 (up to 4 phases)

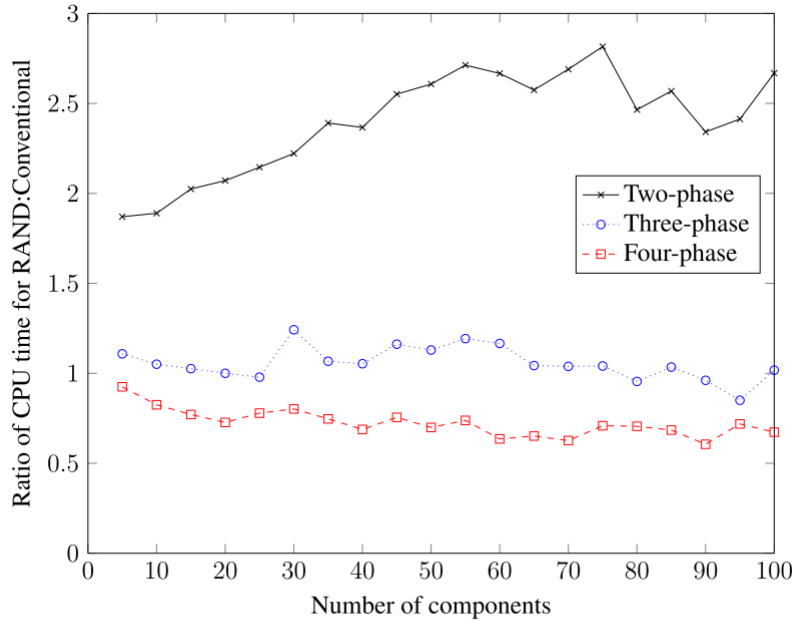
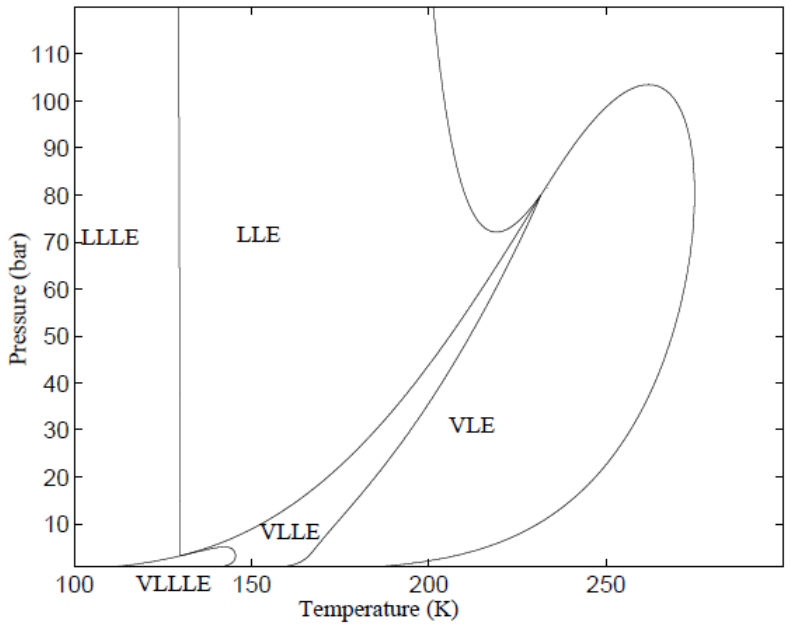


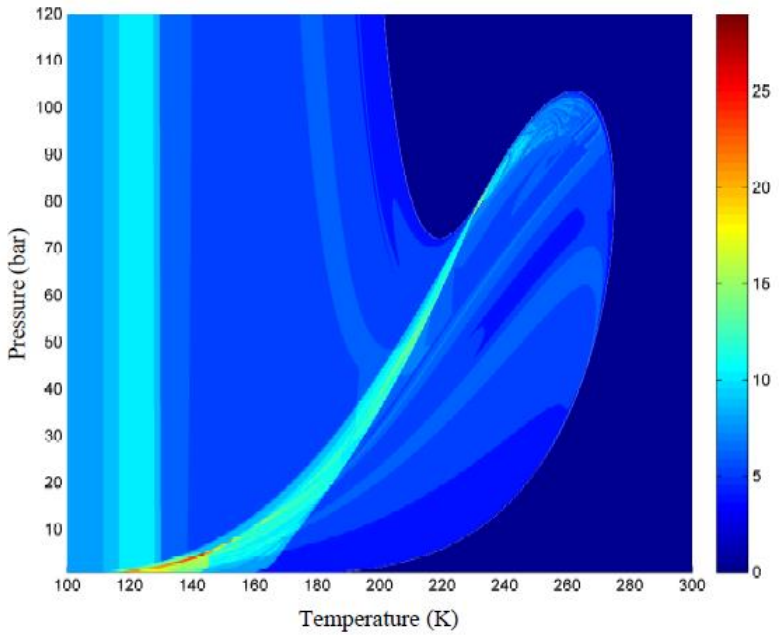
Fig. 4.3 Ratio of CPU time for the RAND method against the conventional method. The RAND method scales better as the number of phases increases.

Paterson, PhD thesis (2017)

Multiphase flash with different specifications

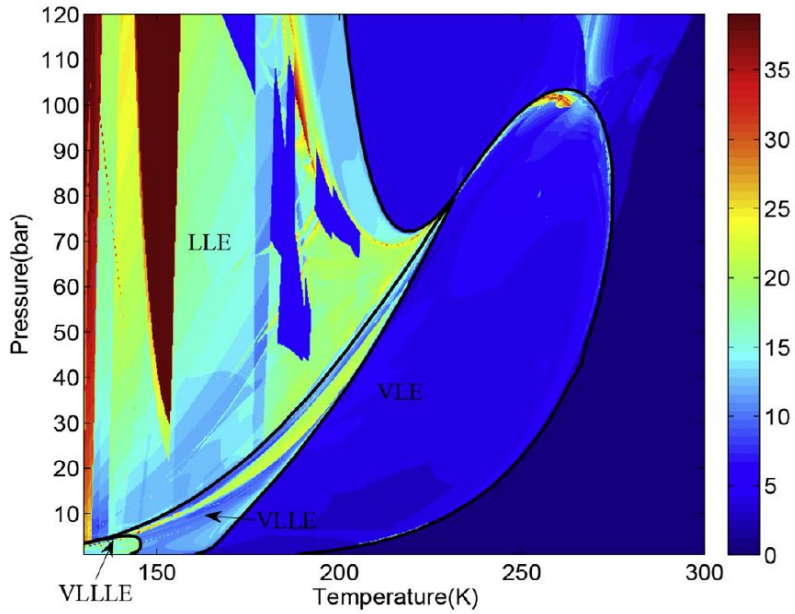
- Modified RAND used for 5-component mixture (C_1, C_2, C_3, H_2S, CO_2, up to 4 phases)





PT flash

(Average 6 iterations)



UV flash

Overall: 2.3x time, 3% needs Q-function maximization

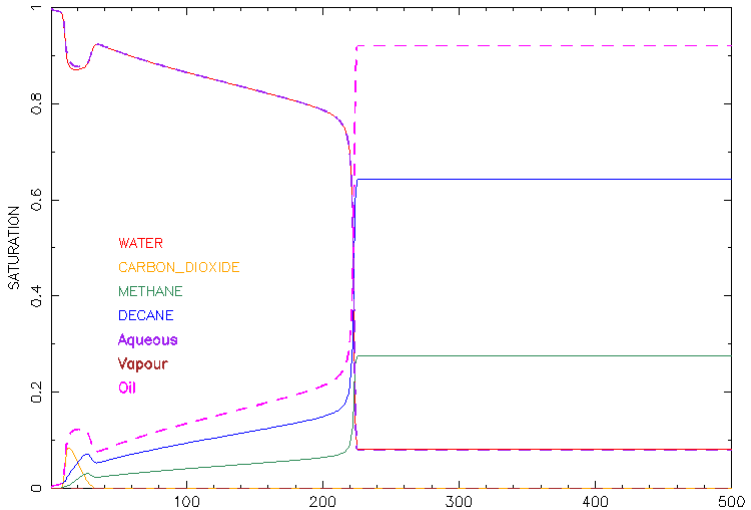
Four-phase region: 2.3x time, 8% needs Q-function

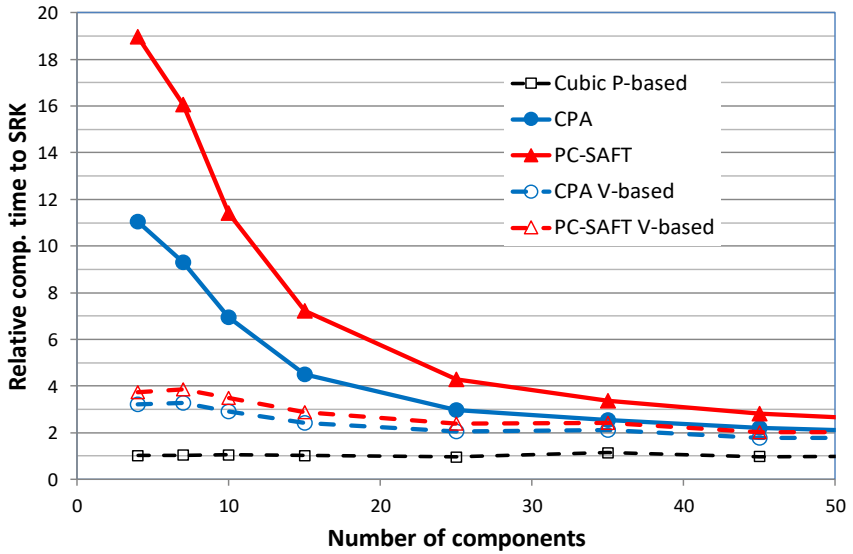
Paterson et al., FPE **2018**, 458, 288-299

Vol-RAND in slimtube simulation

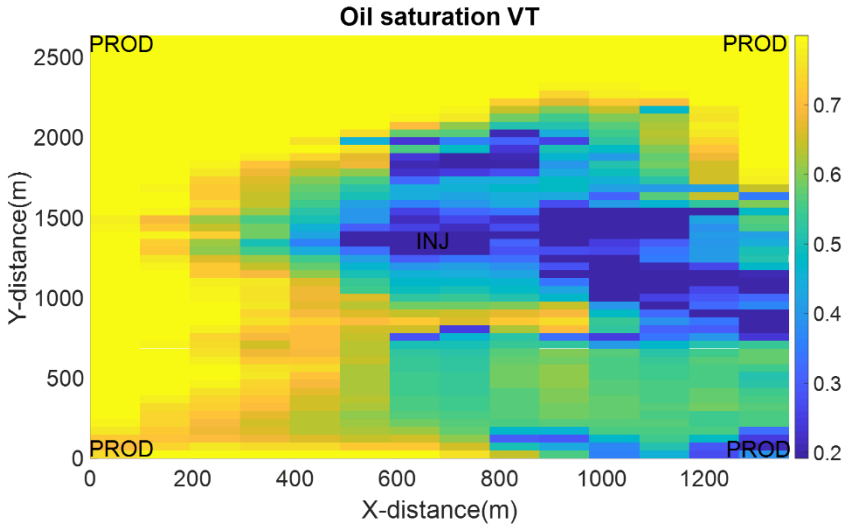
- It avoids solving the density roots and is particularly suitable to complex equation of state.

3-phase slimtube, 4C scheme water





3D reservoir simulation



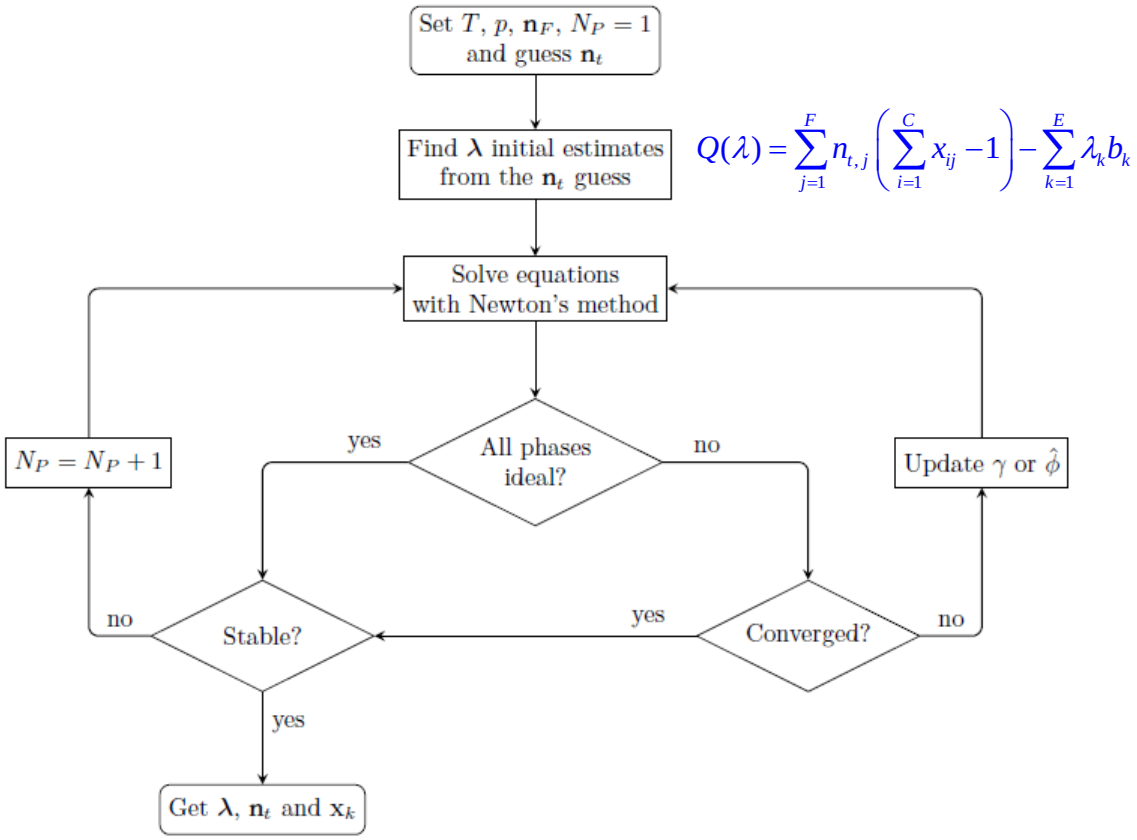
Computation time	TP-based (s)	TV-based (s)
Full simulation	136.5	108.6
Flash	54.1	36.5
System of equations	37.5	45.9

Paterson et al. (2018) ECMOR

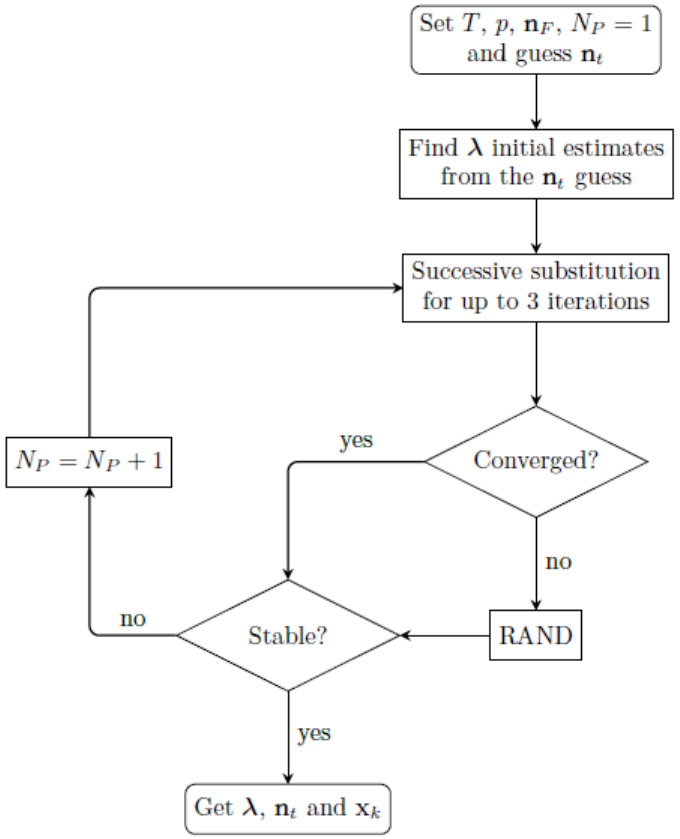
Chemical and phase equilibrium (CPE) calculation

- A combined non-stoichiometric algorithm: A “successive substitution” algorithm + RAND

Successive substitution algorithm



Combined algorithm

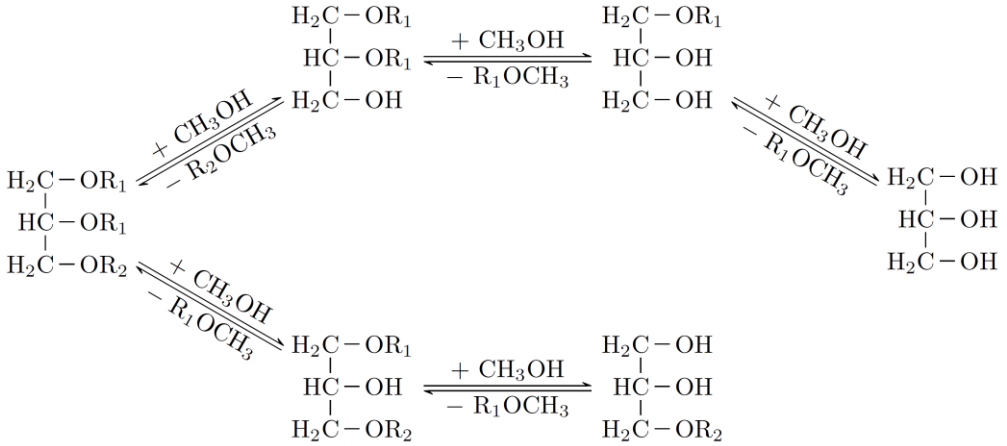


Tsanas et al., Chem. Eng. Sci. **2017**, 174, 112-126.

Tsanas et al., Ind. Eng. Chem. Res. **2017**, 56, 11983-11995

RAND-based CPE calculation

System	C	R	F
Esterification of acetic acid/ethanol	4	1	2
Esterification of acetic acid/1-butanol	4	1	2
MTBE synthesis	4	1	2
TAME synthesis	5	1	2
Propene hydration	3	1	2
Cyclohexane synthesis	3	1	2
Formaldehyde/water	4	2	2
p- and *m*-xylene separation	6	2	2
Methanol synthesis	7	2	2
Transesterification of triglycerides with methanol	9	5	≤3



Transesterification of triglycerides with methanol

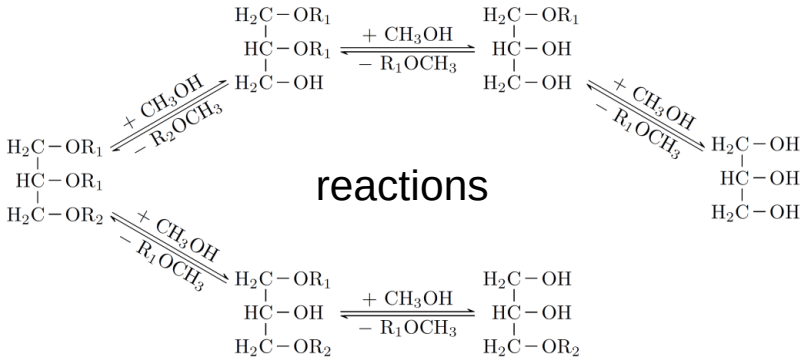
Tsanas et al., Chem. Eng. Sci. **2017**, 174, 112-126.

Tsanas et al., Ind. Eng. Chem. Res. **2017**, 56, 11983-11995

RAND-based CPE calculation

- Transesterification of PPOFAG (Palmitic-Palmitic-Oleic Fatty Acid Glyceride)

	Component	Element	
1	CH_4O	CHO	
2	$C_3H_5O_3(R_1)_2R_2$	H	
3	$C_3H_6O_3(R_1)_2$	R_1	$C_{16}H_{31}O$
4	$C_3H_6O_3R_1R_2$	R_2	$C_{18}H_{31}O$
5	$C_3H_7O_3R_1$		
6	$C_3H_7O_3R_2$		
7	$C_3H_8O_3$		
8	CH_3OR_1		
9	CH_3OR_2		



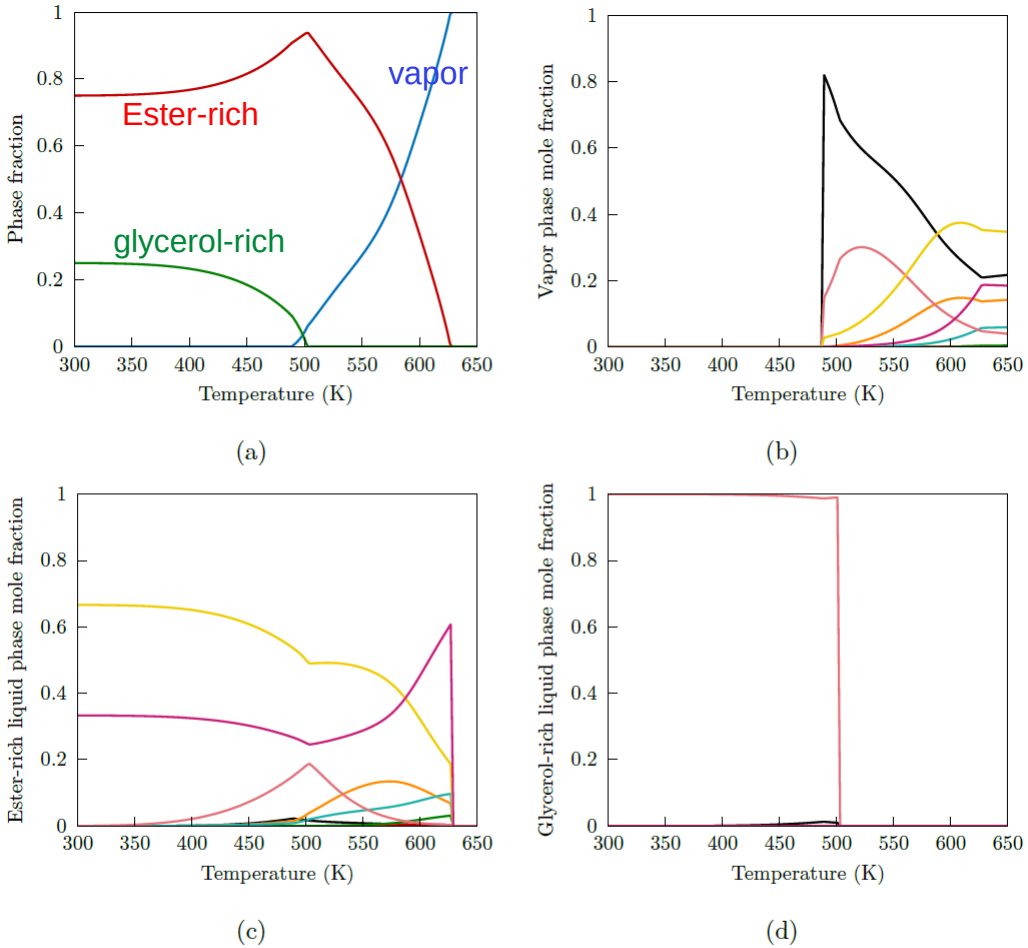


Figure 4.15: Equilibrium in PPOFAG transesterification with methanol and PPOFAG/methanol ratio equal to 1:3 at 1 atm: (a) phase fractions [vapor (—), ester-rich liquid (—), glycerol-rich liquid (—)], (b, c, d) mole fractions [methanol (—), PPOFAG (—), PPFADIG (—), POFADIG (—), PFAMONOG (—), OFAMONOG (—), glycerol (—), PFAME (—), OFAME (—)].

RAND and CPE involving electrolytes

- Speciation and some mineral reactions lead to many equilibrium reactions
- Electroneutrality not a problem—Implicitly satisfied*
- Geochemical reaction with multiple mineral phases ($R = 11, C = 21, F \leq 5$)
  - Same results as PHREEQC's
  - But much faster

Table 4
CPU time to obtain the equilibrium solution of the systems examined (SSA: successive substitution algorithm, CA: combined algorithm, processor: Intel®Core™ i7-7600U CPU@ 2.80 GHz).

System	T (K)	p (atm)	SSA (ms)	CA (ms)
NH_3/CO_2	373	10	0.398	0.391
$CO_2/CaCl_2/CaCO_3$	393.15	250	1.223	1.305
Three-mineral system	298.15	1	0.916	4.650

Three-mineral system PHREEQC 179 ms (195x slower)

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$
$$CO_3^{2-} + 2H^+ \rightleftharpoons CO_2 + H_2O$$
$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$$
$$H_2O + Mg^{2+} \rightleftharpoons H^+ + MgOH^+$$
$$CO_3^{2-} + Mg^{2+} \rightleftharpoons MgCO_3$$
$$H_4SiO_4 \rightleftharpoons H^+ + H_3SiO_4^-$$
$$H_4SiO_4 \rightleftharpoons 2H^+ + H_2SiO_4^{2-}$$
$$Calcite \rightleftharpoons CO_3^{2-} + Ca^{2+}$$
$$Dolomite \rightleftharpoons 2CO_3^{2-} + Ca^{2+} + Mg^{2+}$$
$$2H_2O + Quartz \rightleftharpoons H_4SiO_4$$

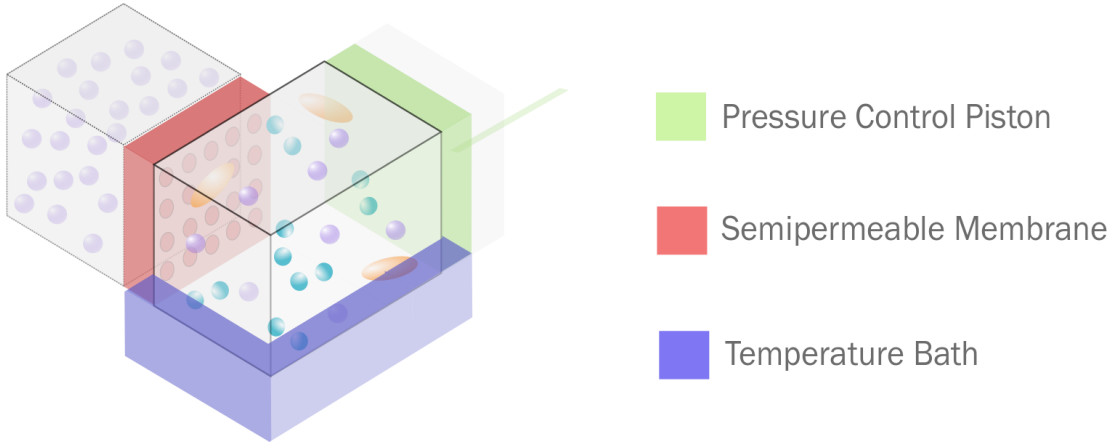
- Possibility for including gas-oil equilibrium

Tsanas et al., Fluid Phase Equilibria **2019**, 482, 81-98.

* For more than one phase w/ electrolytes, see Tsanas, Mougin & de Hemptinne, CES (2021)

Flash for “open” systems—not just for RAND

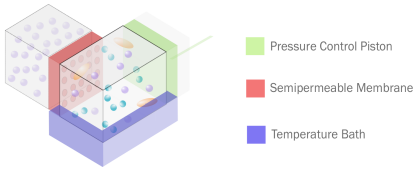
- Do we need flash for an open system?
  - Equilibrium where one or several chemical potentials are fixed: “membrane” flash
  - Geochemical calculations at constant partial pressure or at constant pH



- How to solve the problem?
  - Legendre transform—to define new state function for the problem
  - Michelsen’s Q-function—to solve state function based “flash”

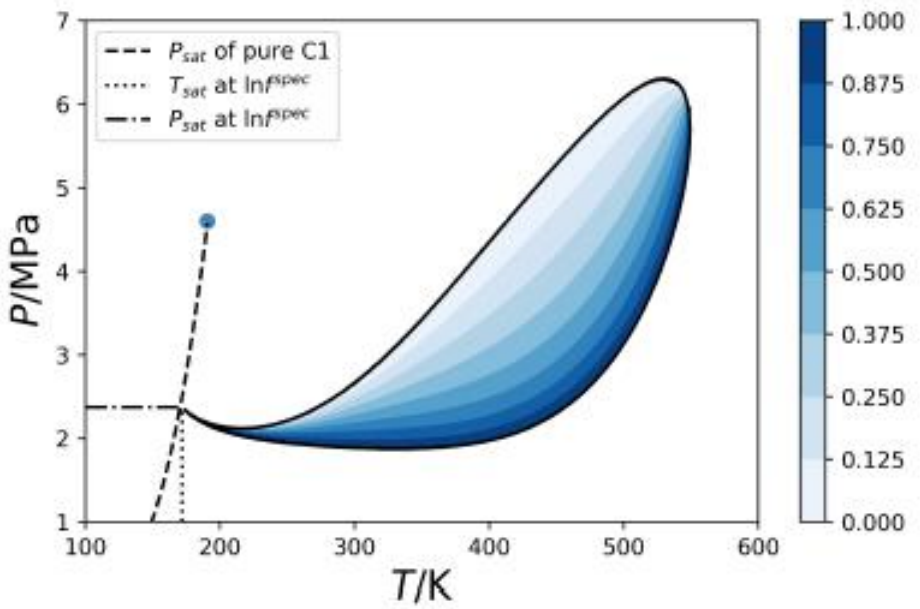
Essentially, a further extension of Michelsen's PH, PS, TV, UV, VS flash (1999) to “open” systems and to reactive systems (e.g., using RAND). The algorithm ensures convergence to a unique solution.

Examples for flash for open systems



- Phase equilibrium

5-comp. hydrocarbon mixture phase diagram at methane fugacity=0.6 MPa

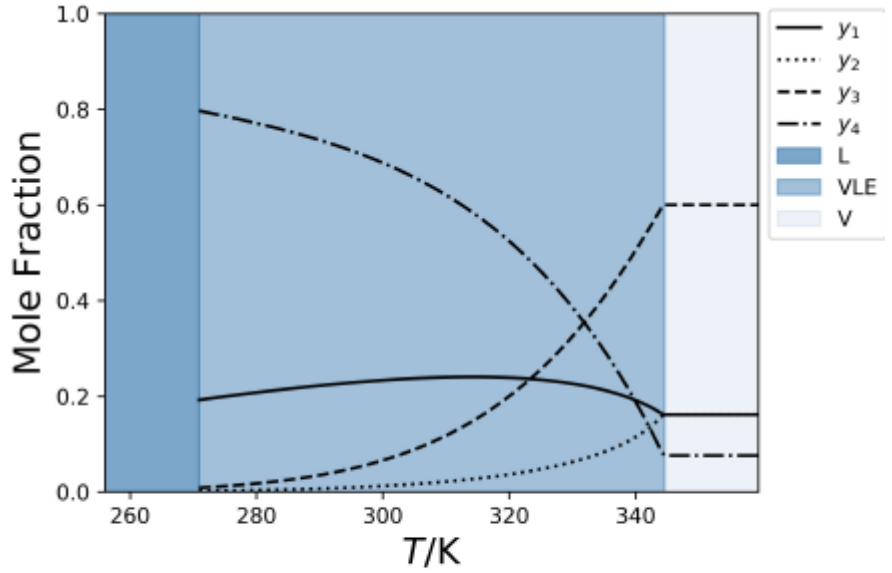


(a) β^V

Medeiros et al. AIChE J. **2021**, 67, e17050

- Propene hydration reaction

4-comp. (water, propene, propanol, and inert propane) 2-phase reaction at fixed water chemical potential



(c) Vapor Mole Fraction

$$H_2O + C_3H_6 \rightleftharpoons C_3H_7OH$$

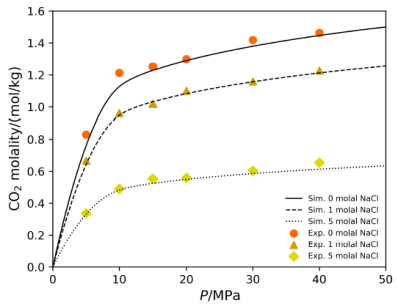
Saturation point and phase envelope for reactive systems

- Important to get an overview of reactive systems' phase boundaries: CCS systems, electrolyte and geochemical systems, production of chemicals
- Solution method: Michelsen's phase line tracing (1980) + RAND formulation + Element K-values ($\ln\mathbf{K}^e$)

$$\mathbf{J}_{(E+4)\times(E+4)}\left(\Delta\boldsymbol{\lambda}, \Delta\beta_1, \Delta\beta_2, \Delta T, \Delta P\right)^T = \mathbf{R}_{(E+4)\times 1}$$

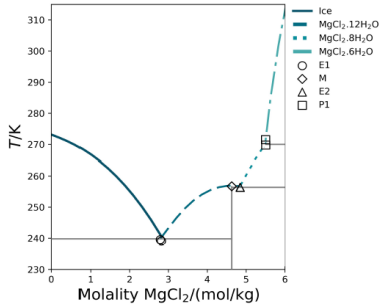
  - β_j not conserved—use $\beta^r{}_j = \beta_j / \sum \beta_j$ and $\alpha^r{}_j = \alpha_j / \sum \alpha_j$, α_j is total moles of elements in phase j
  - Use $\ln\mathbf{K}^e$ in the specification equation, and estimate its change using the RAND vector $\mathbf{X}^{RAND}$

1 Px Diagram: CO_2 Solubility



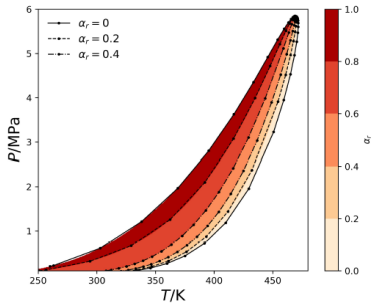
CO_2 in Brine
VLE + $\gamma\phi$ approach

2 Tx Diagram: Salt Solubility



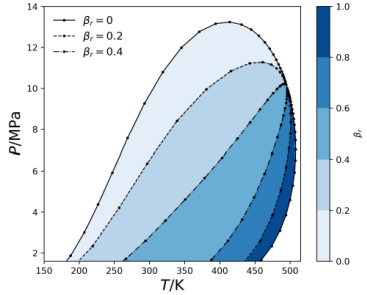
Electrolyte Systems
SLE + $\gamma\phi$ approach

3 Phase Envelope: Reactive Mixture



Hydration Reaction
VLE + $\phi\phi$ approach

4 Phase Envelope: Non Reactive



Hydrocarbon Mixture
VLE + $\phi\phi$ approach

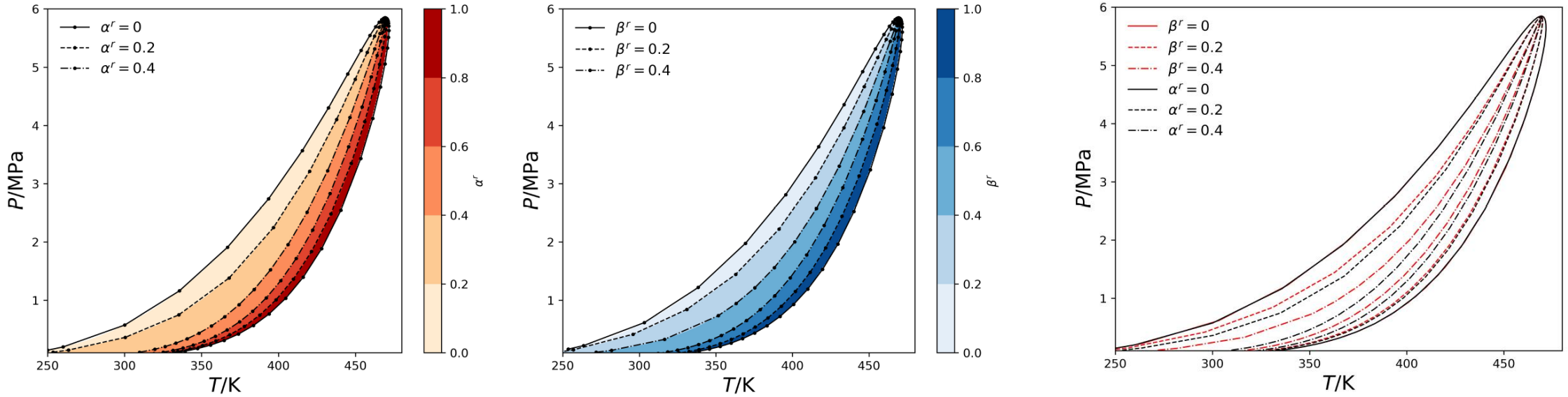
Medeiros et al. CES **2022**, 247, 116911

Example 3. Phase envelope: Alkene hydration

- PT phase envelope for the alkene hydration system
  - 4 components: water, propene, 1-propanol, propane (inert)
  - Reaction:

$$H_2O + C_3H_6 \rightleftharpoons C_3H_7OH$$

  - 3 elements: propene, water, and propane
  - Phase envelope at different α and β^r specifications at initial load of (1, 1, 0, 0.8) moles

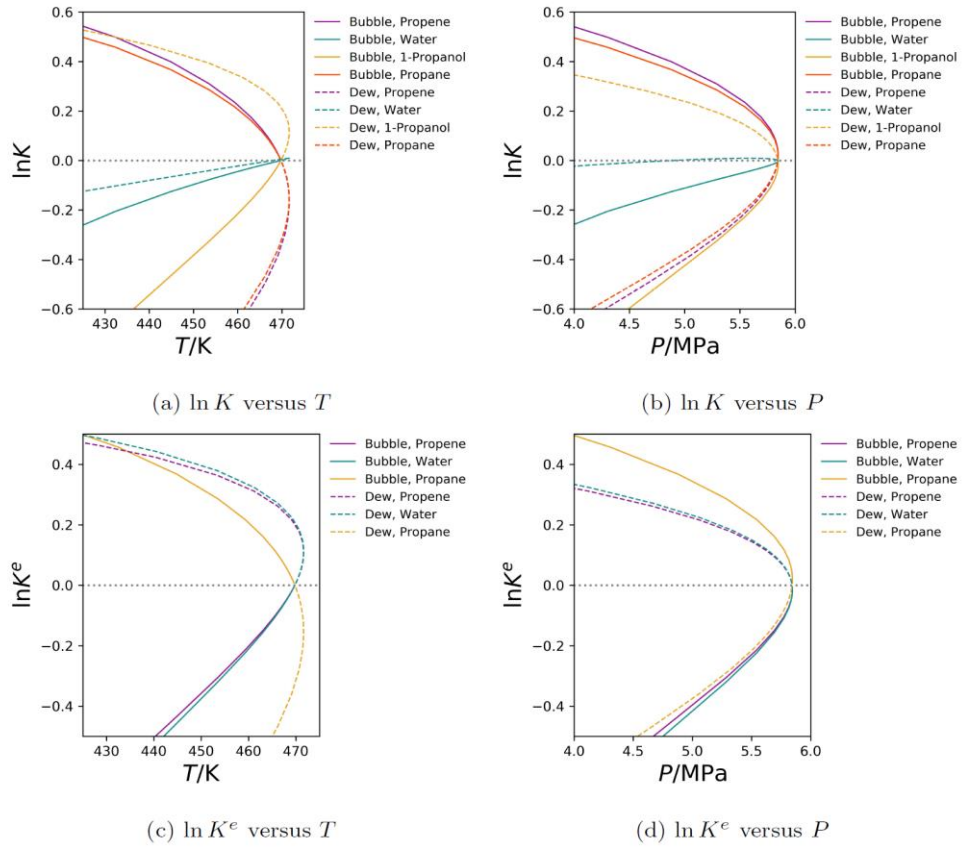


(a) Specified α (b) Specified β^r

Medeiros et al. CES **2022**, 247, 116911

Example 3. Phase envelope: Alkene hydration

- PT phase envelope for the alkene hydration system
  - A detailed look at "*K*-factors"



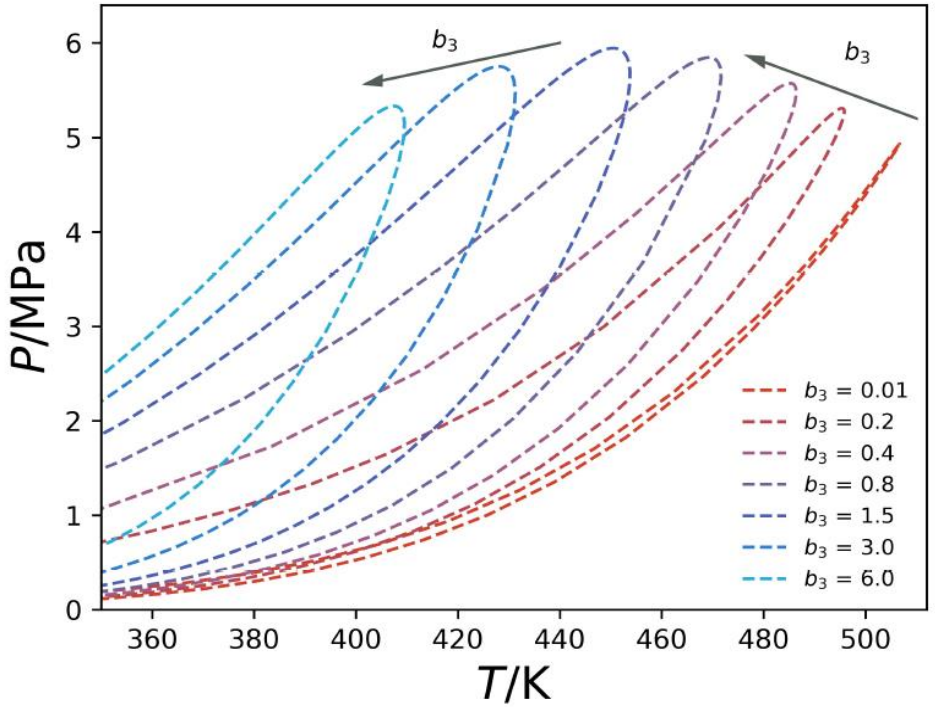
(a) $\ln K$ versus T (b) $\ln K$ versus P

(c) $\ln K^e$ versus T (d) $\ln K^e$ versus P

$$H_2O + C_3H_6 \rightleftharpoons C_3H_7OH$$

- Influence of the inert component:

  b_3 = 0.01, 0.2, 0.4, 0.8, 1.5, 3.0, 6.0



Medeiros et al. CES **2022**, 247, 116911

Example 2. Tx diagram for $MgCl_2$-water

- SLE diagram for electrolyte $MgCl_2$-water
  - Many possible solid phases: Ice, $MgCl_2{\cdot}12H_2O$, $MgCl_2{\cdot}8H_2O$, $MgCl_2{\cdot}6H_2O$
  - Pitzer model in PHREEQC
  - Precipitation and speciation reactions:

$$MgCl_2(H_2O)_6(s) \rightleftharpoons Mg^{2+}_{(aq)} + 2Cl^-_{(aq)} + 6H_2O_{(l)}$$

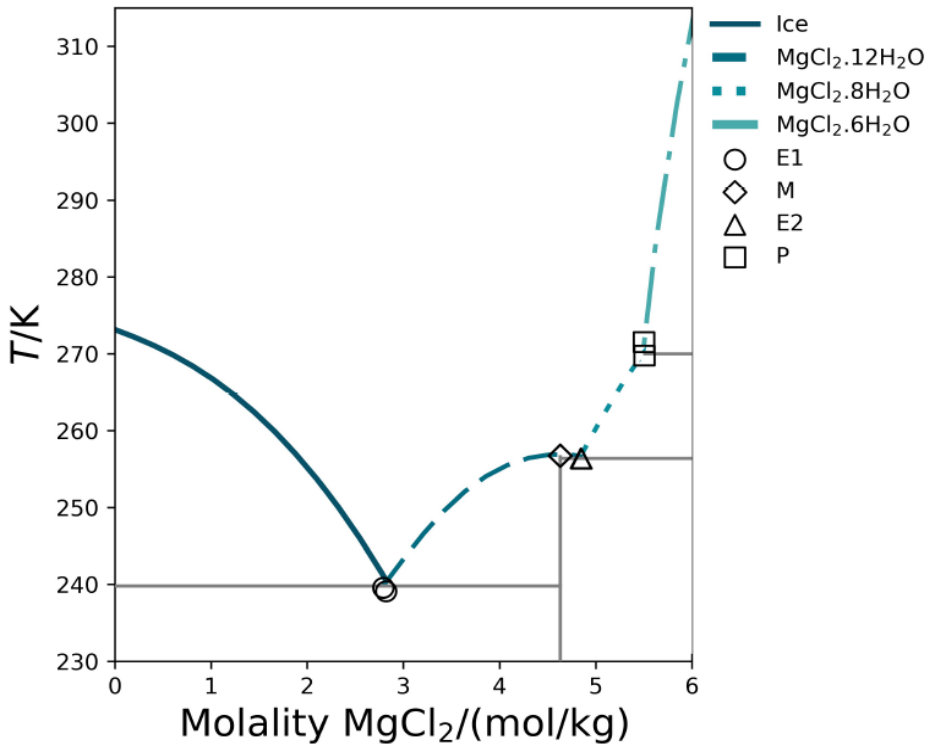
$$MgCl_2(H_2O)_8(s) \rightleftharpoons Mg^{2+}_{(aq)} + 2Cl^-_{(aq)} + 8H_2O_{(l)}$$

$$MgCl_2(H_2O)_{12}(s) \rightleftharpoons Mg^{2+}_{(aq)} + 2Cl^-_{(aq)} + 12H_2O_{(l)}$$

$$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)}$$

$$Mg^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons MgOH^+_{(aq)} + H^+_{(aq)}$$

  - Four elements: OH^-, H^+, Mg^{2+}, Cl^-
  - Saturation point calculation: $\alpha_g = \alpha_g^r = 0$

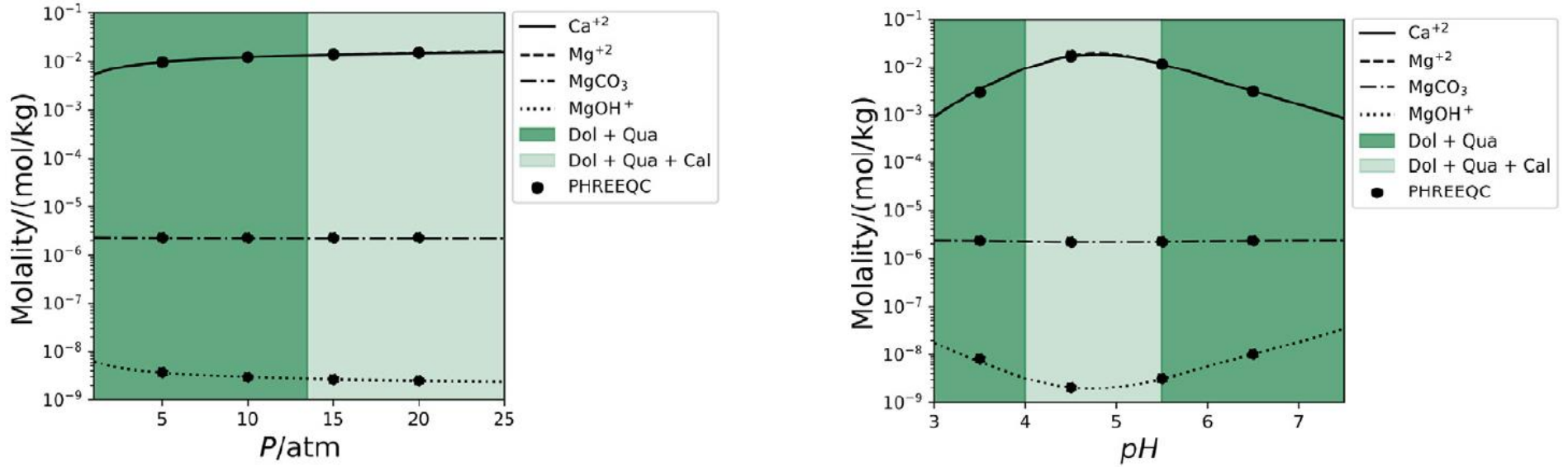


Medeiros et al. CES **2022**, 247, 116911

RAND-based geochemical calculation

- Similar functions to PHREEQC, but more robust and efficient
  - PT flash / Flash at constant P_{CO2} / Flash at constant pH

A system with silicon-containing minerals: 22 components (13 aqueous species and 9 possible solid species) and 16 reactions (7 in brine and 9 mineral formation)

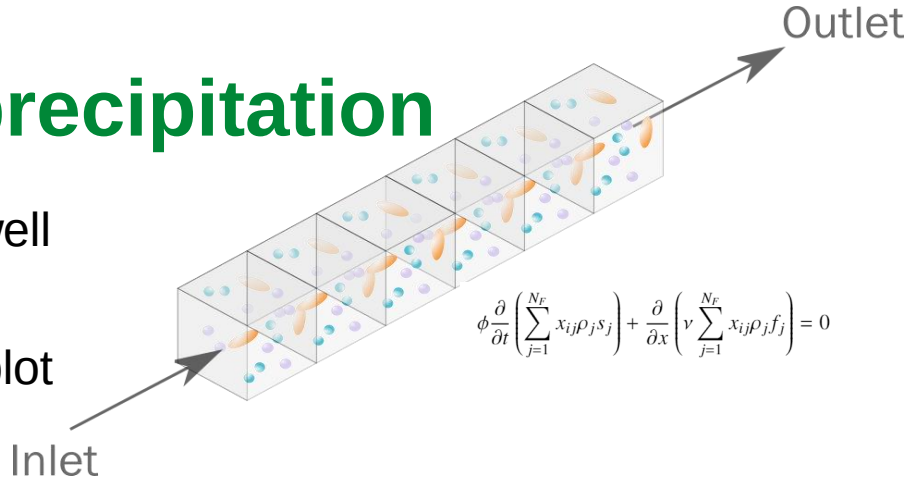


Metal containing species varies with P_{CO2} (left) and pH (right)

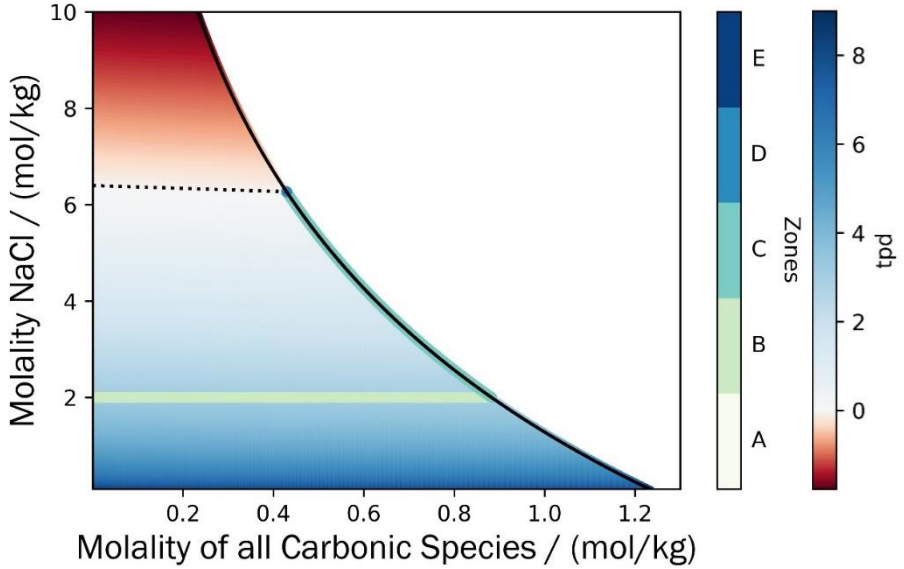
Medeiros et al., ADWR **2021**, 152, 103918

Thermodynamic analysis of salt precipitation

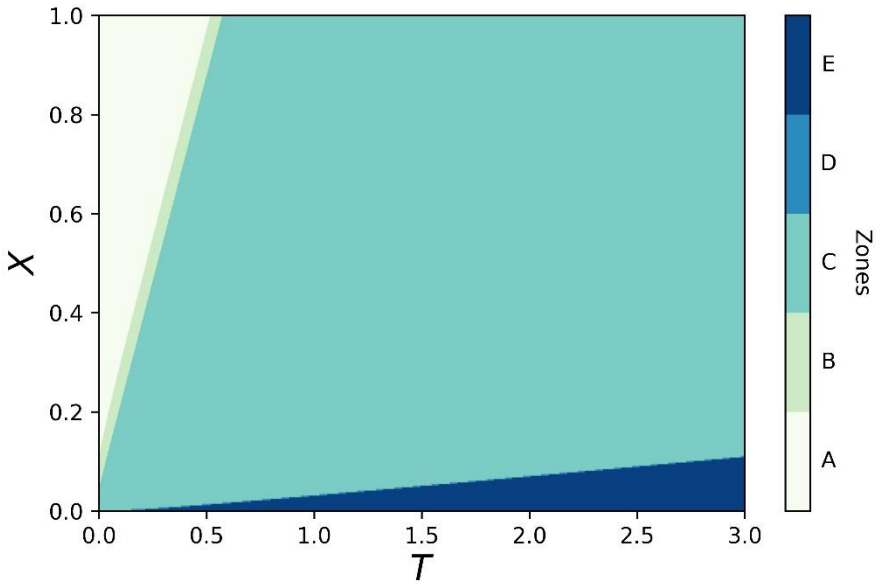
- Long-time injection of dry CO_2 can result in salt precipitation near the well
  - A “ternary” diagram to represent CO_2+water+salt
  - 1D slimtube simulation: The composition path can be shown in the plot



- NaCl brine



CO_2-NaCl-H_2O diagram (brine & solid) and composition path



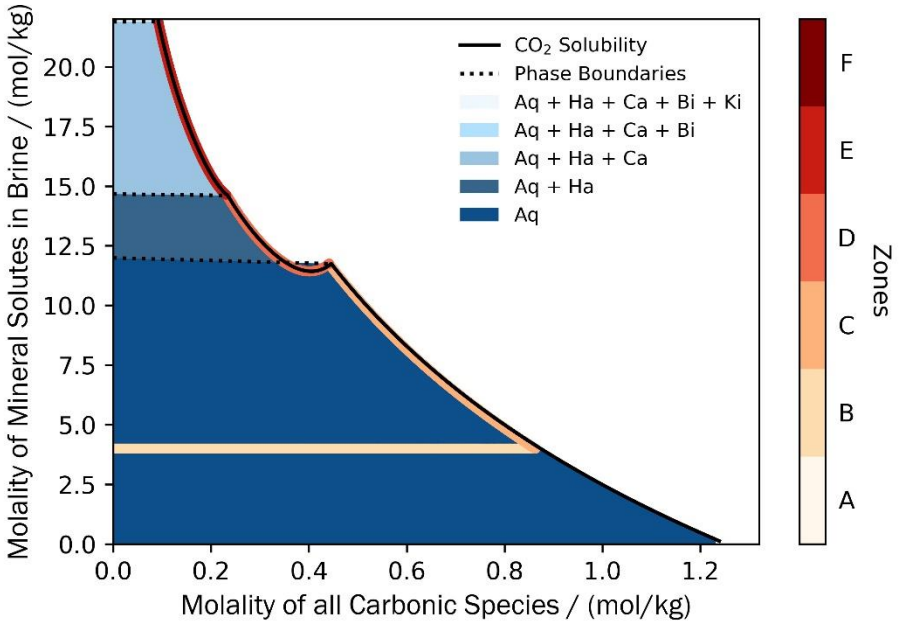
Propagation of different zones from 1-D sim.

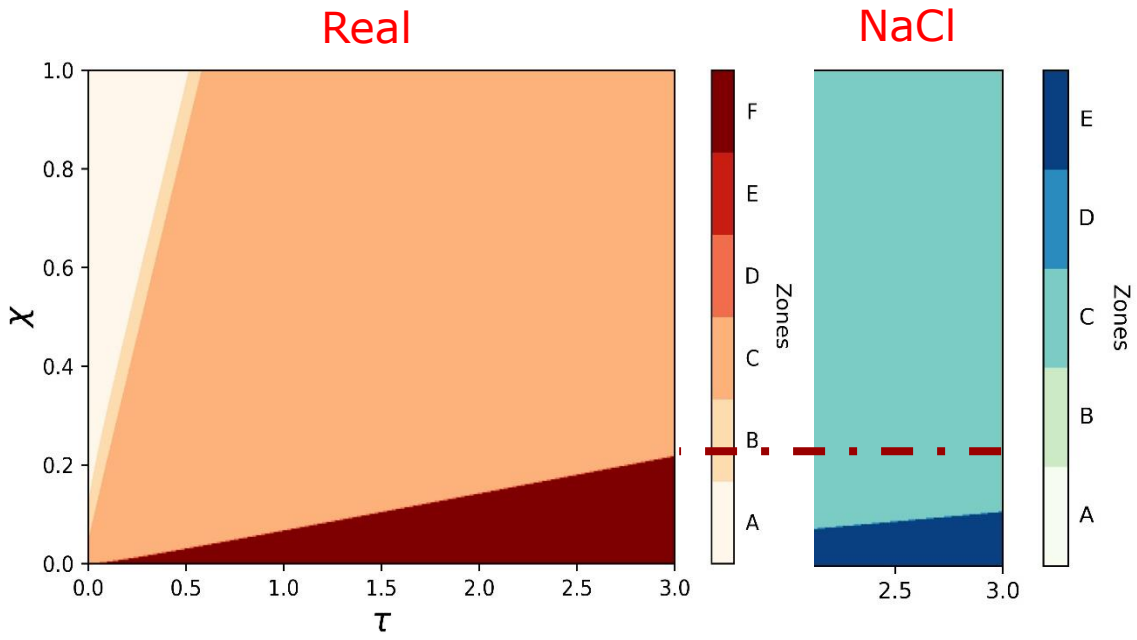
A,B: initial and undersaturated; C: two-phase; D: 3-phase halite; E: dry-out

Medeiros et al., TCCS (2021)

Thermodynamic analysis of salt precipitation

- Real brine





CO_2-Salts-H_2O diagram (brine phase) and composition path

Minerals: **Ha**lite, **Ca**rnallite, **Bi**schoffite, **Ki**eserite

Propagation of different zones from 1-D sim.

A,B: initial and undersaturated; C: two-phase; D, E: V+L+solids; F: dry-out

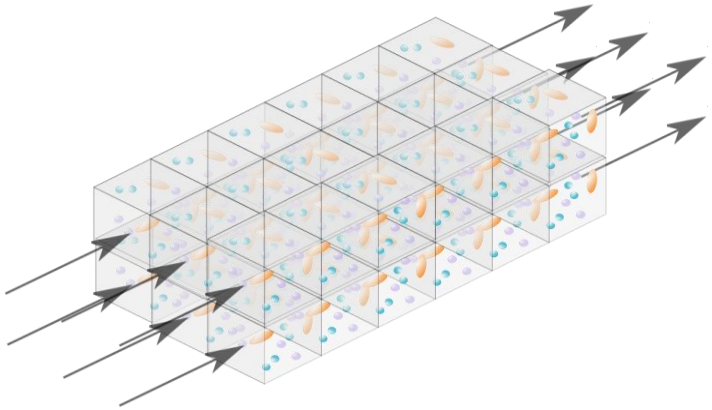
Medeiros et al. TCCS (2021)

General non-isothermal compositional simulator

- Mass balance

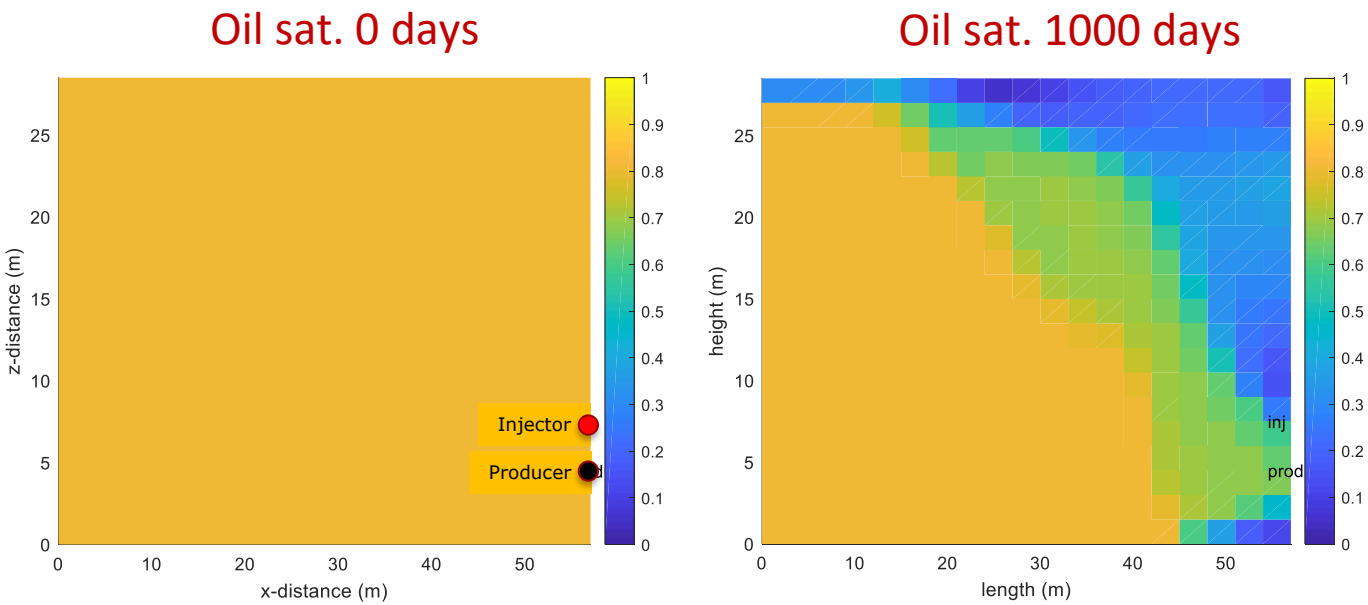
$$\frac{\partial}{\partial t}\left(\phi\sum_{j=1}^{N_P} x_{i,j}\rho_j S_j\right)+\nabla\cdot\left(\sum_{j=1}^{N_P} x_{i,j}\rho_j \mathbf{u}_j\right)+q_j-\sum_{q=1}^{N_P}\nu_{i,q}r_q^{\mathrm{eq}}-\sum_{w=1}^{N_K}\nu_{i,w}r_w^{\mathrm{kin}}=0$$

- Energy balance
- Phase (and chemical) equilibrium
- Other constitutive relations



General non-isothermal compositional simulator

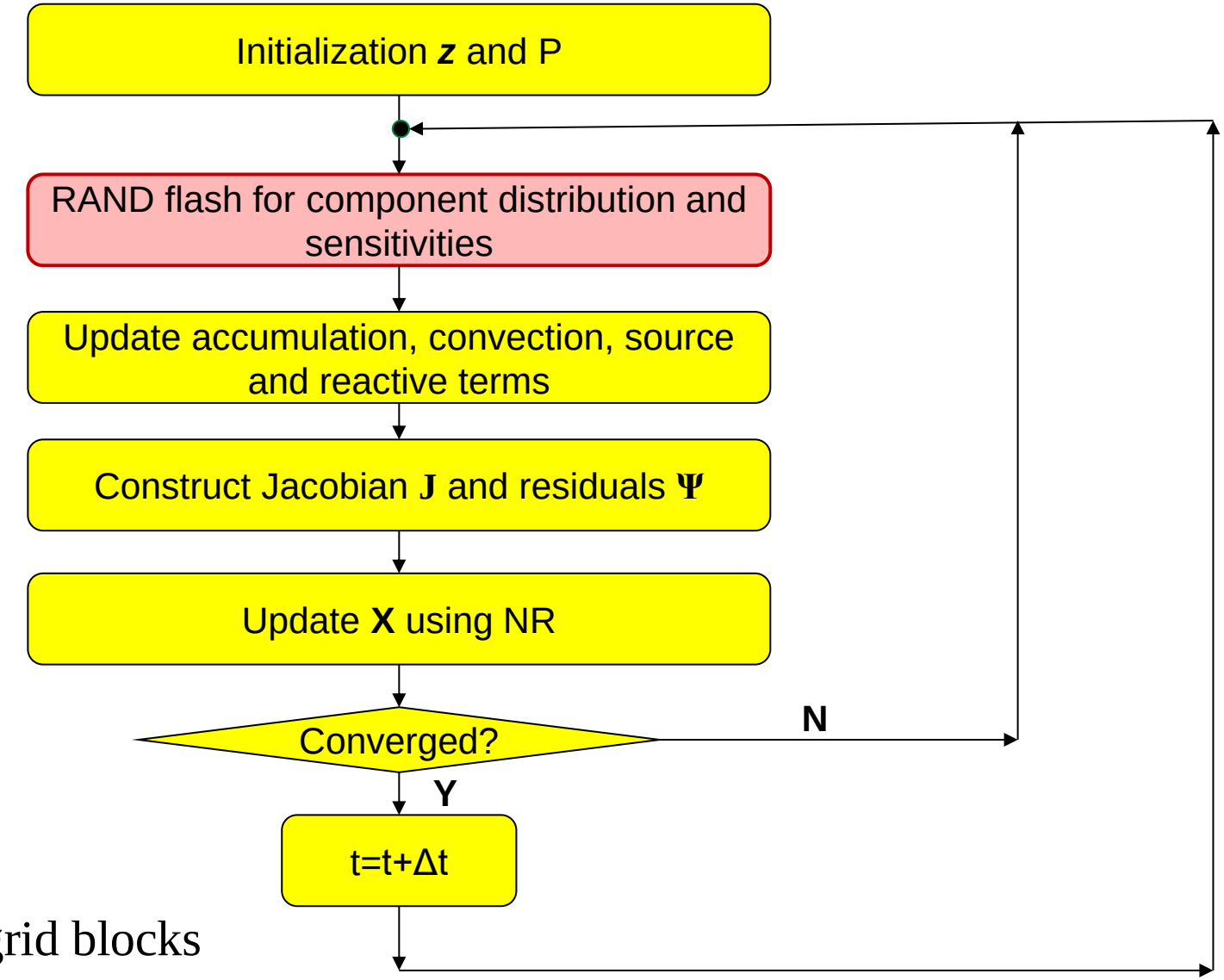
- RAND-based compositional simulator developed by Paterson et al.
  - RAND-based flash
  - Multiphase equilibrium
  - Advanced EoS models (e.g., CPA)
  - Example simulations
    - Gas injection
    - Depletion
    - Water flooding
    - SAGD (non isothermal)



SAGD (Steam Assisted Gravity Drainage) simulation

- A platform for future development, e.g., for CO_2 sequestration simulation with multiple phases (gas, oil, water, mineral phases) and geochemical reactions, and for geothermal simulation.

Flowchart for comp. simulation with reaction



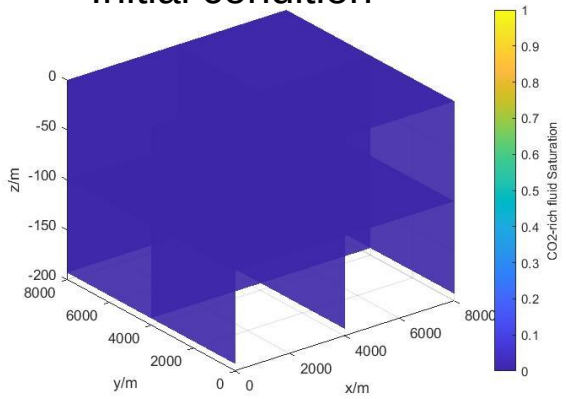
$$\mathbf{J}\Delta\mathbf{X} + \boldsymbol{\psi} = 0$$

$\mathbf{X}$ includes $\mathbf{z}$ and P for all grid blocks

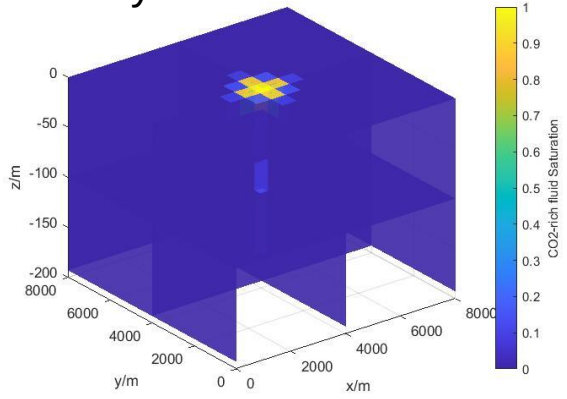
3D simulation of CO_2 sequestration

- 8000 m x 8000 m x 200 m, loosely based on Ghanbari et al. (2006)

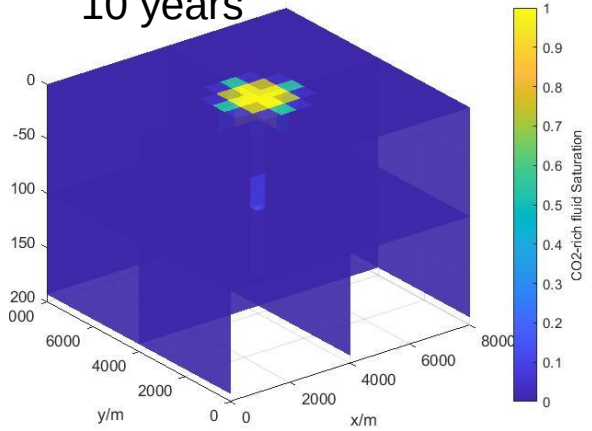
Initial condition



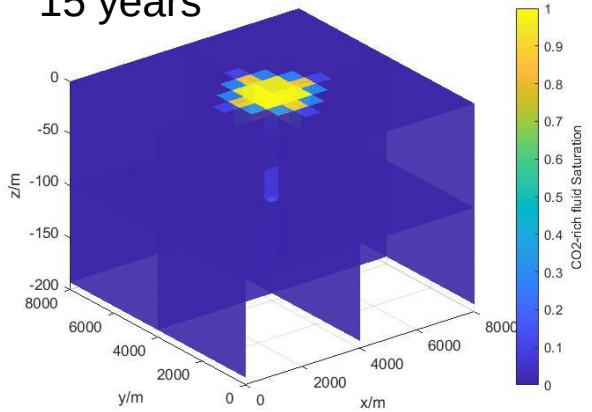
5 years



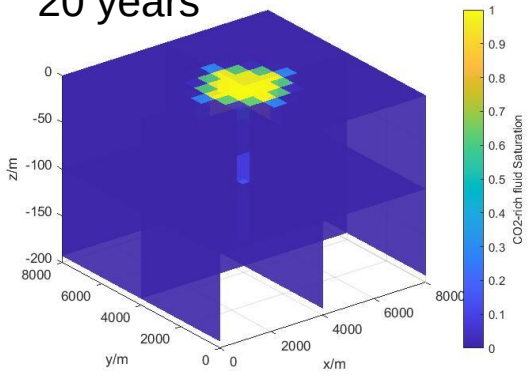
10 years



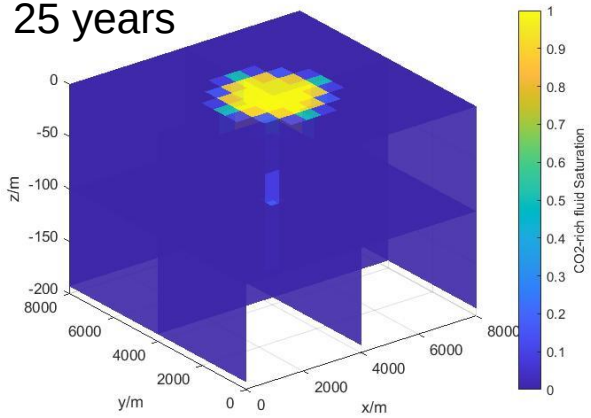
15 years



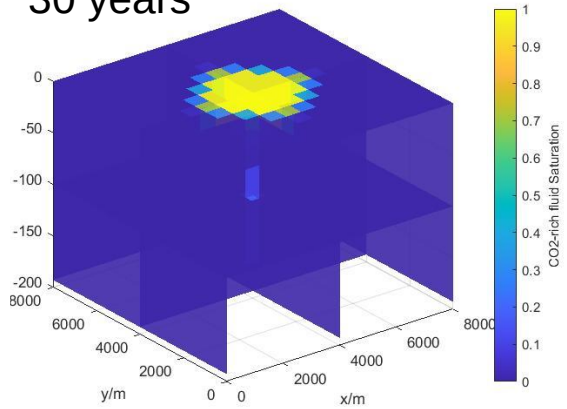
20 years



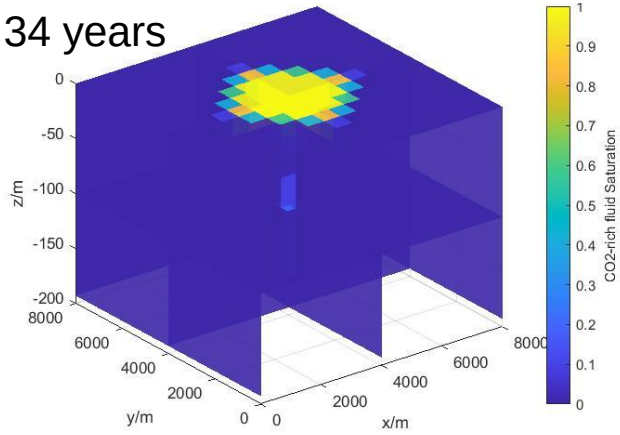
25 years



30 years



34 years



Summary

- Chemical reactions are important, interesting, but challenging to describe—A PEC area not fully explored.
- RAND provides a framework that can replace the classical formulation for PEC. The new framework is especially advantageous in multiphase equilibrium involving many reactions.
- RAND can provide an engine for future simulation in the CCS-related area and other areas involving reactions.
- Classical formulation will still be used, especially in PEC without reactions—The choice of solution algorithms depend on many factors in practice.