Computation of Reactive Azeotropes Using Interval Analysis

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Computing Reactive Azeotropes

- Why?
  - Identify limitations/benefits for reactive distillation operations
  - Evaluate thermodynamic models
  - Reduce time required for costly experimentation

- How?
  - Solve a system of nonlinear equations derived from equifugacity and chemical equilibrium conditions
  - This equation system has an unknown number of solutions

Reactive Azeotropy

- Equality of Transformed Mole Fractions (Ung and Doherty, 1995)

$$Y_i = X_i, \ \forall i \in C_N$$

$$Y_i = \left(\frac{y_i - \nu_i^T \mathcal{V}^{-1} y_{Ref}}{1 - \nu_{TOT}^T \mathcal{V}^{-1} y_{Ref}} \right)$$

$$X_i = \left(\frac{x_i - \nu_i^T \mathcal{V}^{-1} x_{Ref}}{1 - \nu_{TOT}^T \mathcal{V}^{-1} x_{Ref}} \right)$$

  - C_N is the set of non-reference components
  - $\mathcal{V}$ is the matrix of stoichiometric coefficients for the reference components
  - ν_i is the vector of stoichiometric coefficients for component i
  - ν_{TOT} is the vector of total mole generation for each non-reference component over all reactions

Reactive Azeotropy (Cont'd)

- Phase Equilibrium

$$y_i P = x_i \gamma_i^L (T) P_i^{sat} (T), \ \forall i \in C$$

  - C is the set of all components

- Chemical Equilibrium

$$K_r (T) = \prod_{i \in C} a_i^{\nu_{ri}}, \ \forall r \in R$$

  - R is the set of independent chemical reactions

- Summation Constraints

$$\sum_{i \in C_N} X_i = \sum_{i \in C_N} Y_i = 1$$

$$\sum_{i \in C} x_i = \sum_{i \in C} y_i = 1$$

Formulation

- Need to choose a set of independent variables and equations
- Solve phase equilibrium relations for y_i, and substitute into equations for Y_i
- Independent variables are the liquid phase mole fractions and temperature
- Formulation is

$$X_i\left(\underline{x},T\right) = Y_i\left(\underline{x},T\right),\ \forall i \in C_N$$

$$K_r\left(T\right) = \prod_{i\in C} a_i^{\nu_{ri}}\left(\underline{x},T\right),\ \forall r \in R$$

$$\sum_{i\in C} x_i = 1$$

Formulation (cont'd)

- All homogeneous reactive azeotropes are solutions
- Stability of solutions solved for separately, using the same solution technique
- Need solution method guaranteed to find all solutions, or to determine with certainty that there are none.

Some Current Solution Methods

- Various local methods — Fast, but initialization dependent and hard to find all roots

- Ung and Doherty (1995) derived transformed composition variables
  - Reduced the number of degrees of freedom
  - Convenient statement of reactive azeotropy ($X_i = Y_i$)

- Okasinski and Doherty (1997) used arc-length continuation with the equilibrium constant as the homotopy parameter

Interval Approach

- Interval Newton/Generalized Bisection (IN/GB)
  - Given a system of equations to solve, an initial interval (bounds on all variables), and a solution tolerance
  - IN/GB can find (enclose)

    with mathematical and computational certainty

    either all solutions or that no solutions exist. (e.g., Kearfott 1987,1996; Neumaier 1990)

- A general purpose approach : requires no simplifying assumptions or problem reformulations

- Details of algorithm given by Schnepper and Stadtherr (1996)

- Implementation based on modifications of routines from INTBIS and INTLIB packages (Kearfott and coworkers)

Interval Approach (Cont'd)

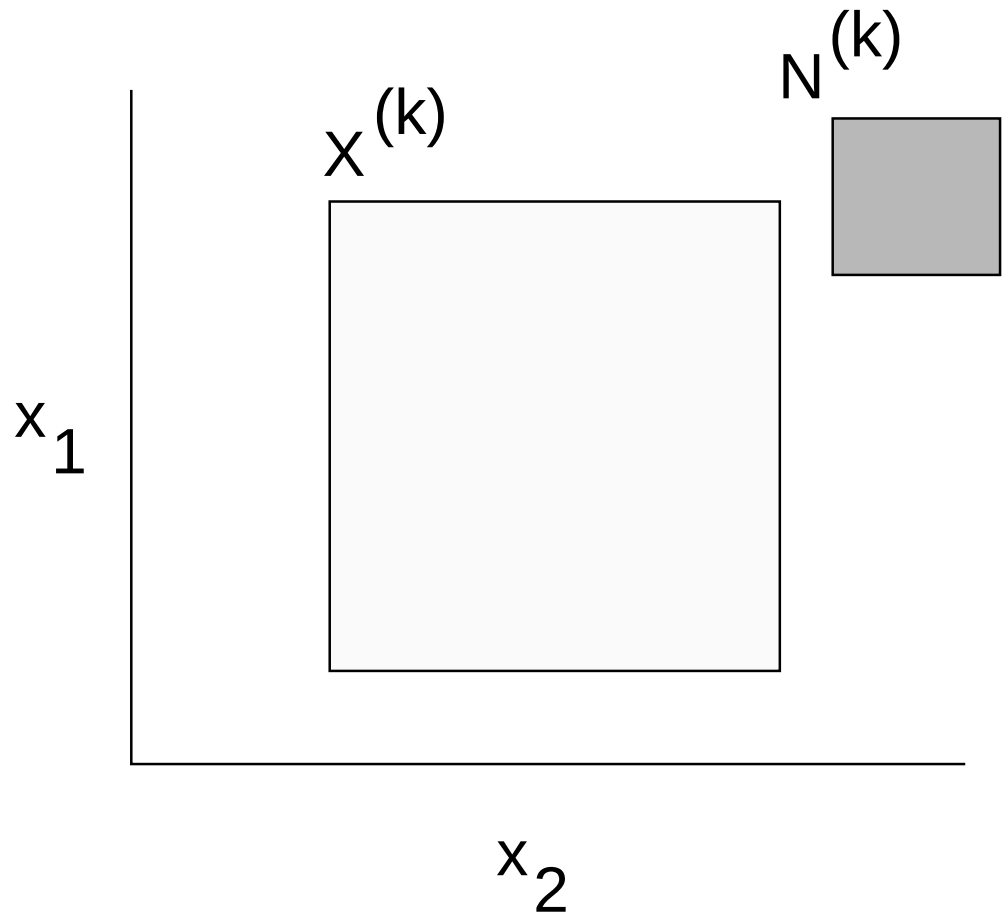
Problem: Solve $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ for all roots in interval $\mathbf{X}^{(0)}$.

Basic iteration scheme: For a particular subinterval (box), $\mathbf{X}^{(k)}$, perform root inclusion test:

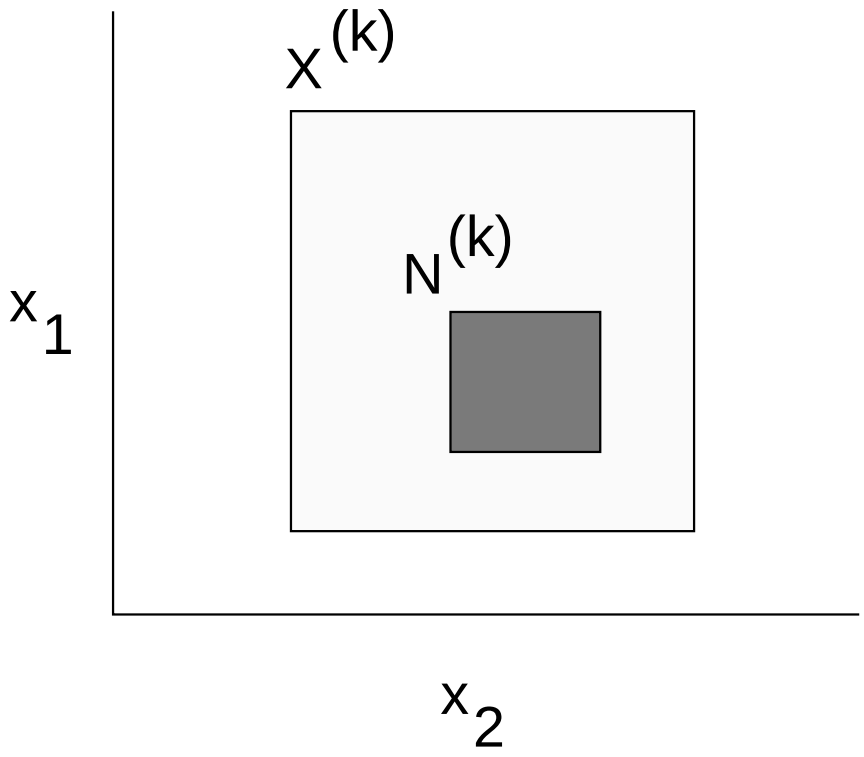
- Compute the range of each function in the system.
- If 0 is not an element of each range, delete the box.
- If 0 is an element of each range, then compute the $image$, $\mathbf{N}^{(k)}$, of the box by solving

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)})$$

- $\mathbf{x}^{(k)}$ is some point in the interior of $\mathbf{X}^{(k)}$.
- $F'\left(\mathbf{X}^{(k)}\right)$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$.



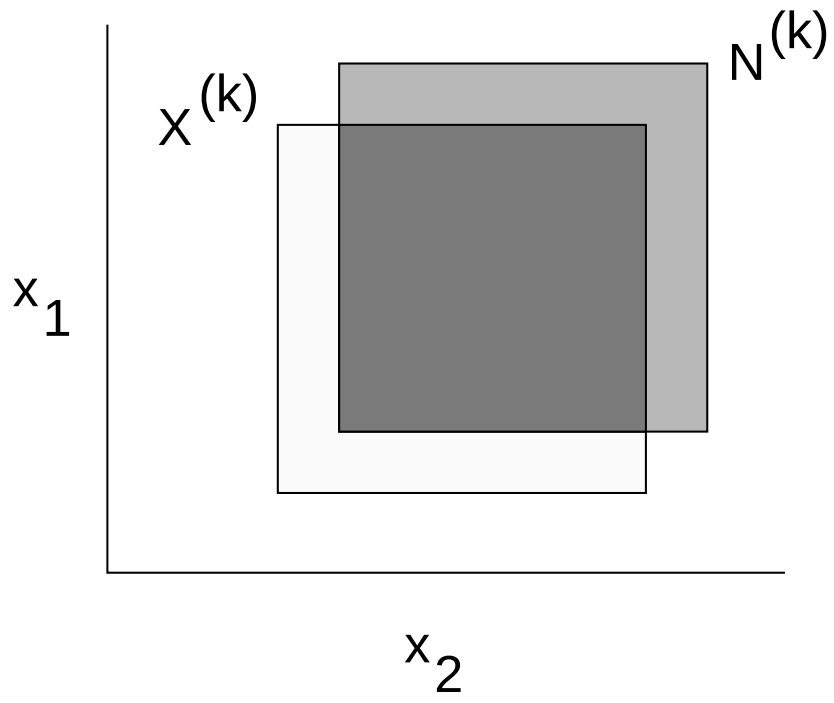
There was no solution in $X^{(k)}$



Unique solution in $X^{(k)}$

This solution is in $N^{(k)}$

Point Newton method will converge to it



Any solutions in $X^{(k)}$ are in intersection of $X^{(k)}$ and $N^{(k)}$

If intersection is sufficiently small, repeat root inclusion test; otherwise bisect the result of the intersection and apply root inclusion test to each resulting subinterval.

Example Problems

- First 2 examples previously solved by Barbosa and Doherty (1988)
- Third example previously solved by Okasinski and Doherty (1997)
- Vapor phase modeled as ideal
- Full temperature dependence of γ_i is included
- Times reported for Sun Ultra 30 workstation

Results - Problem 1

- $A + B \leftrightarrow C$
- 1 atm, 10-200 °C
- $\Delta G_f^\circ = -8314 J/mol$, ideal liquid phase

Reactive Azeotrope

	x_i	y_i
A	0.07	0.17
B	0.50	0.55
C	0.43	0.28
	$T = 121.7°C$	

- $X_A = Y_A = 0.35$
- $X_B = Y_B = 0.65$
- CPU time = 2.1 sec

Results - Problem 2

- $A + B \leftrightarrow C + D$
- 1 atm, 10-200 °C
- $\Delta G_f^\circ = -831.4 J/mol$, ideal liquid phase

Reactive Azeotrope

	x_i	y_i
A	0.19	0.07
B	0.36	0.24
C	0.21	0.33
D	0.24	0.36
	$T = 89.5°C$	

- $X_A = Y_A = 0.43$
- $X_B = Y_B = 0.60$
- $X_C = Y_C = -0.03$
- CPU time = 12.2 sec

Results - Problem 3

- $Isobutene + Methanol \leftrightarrow MTBE$
- 8 atm, 10-200 °C
- $K_{eq} = 49.0$, Wilson Activity Coefficient Model

Reactive Azeotropes

	x_i	y_i	x_i	y_i
$i-C4$	0.01	0.07	0.04	0.17
MeOH	0.40	0.44	0.12	0.24
MTBE	0.59	0.49	0.84	0.59
	$T = 118.0°C$		$T = 119.1°C$	

- $X_{I1} = Y_{I1} = 0.38$
- $X_{Me1} = Y_{Me1} = 0.62$
- $X_{I2} = Y_{I2} = 0.48$
- $X_{Me2} = Y_{Me2} = 0.52$
- CPU time (total) = 5.6 sec

Concluding Remarks

- Interval analysis provides a general-purpose approach for solving reactive azeotrope problems, providing a mathematical and computational guarantee of reliability

- Can be used in conjunction with other activity coefficient models and EOS.

- Can also be used with multiple reactions and in the presence of inerts.

- Interval analysis is also a general-purpose approach for solving other types of azeotrope problems: nonreactive, homogeneous (Maier *et al.*, 1998) or heterogeneous.

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of phase behavior and in other process modeling problems (e.g., Schnepper and Stadtherr, 1996; Hua *et al.*, 1998)

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