# A New Approach for Reliably Computing All Azeotropes of Multicomponent Mixtures

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# Computing Azeotropes

- Why

  - Identify limitations in distillation operations
  - Construction of residue curve maps for design and synthesis of distillation operations
  - Evaluation of thermodynamic models

- How

  - Solve system(s) of nonlinear equations derived from equifugacity condition
  - These equation system(s) have multiple trivial roots, and an unknown number of actual solutions

# Previous Work

This work is a continuation of previous efforts in our group using the Interval Newton Generalized Bisection (IN/GB) algorithm. Our work on azeotropes includes

- Homogeneous azeotropes

  - 1 liquid phase, no reactions
  - Wilson, NRTL and UNIQUAC activity coefficient models (Maier et al., 1998, 1999)
  - Cubic equations of state

- Reactive homogeneous azeotropes (Maier et al., 1999)

  - 1 liquid phase, reactions in the liquid phase
  - NRTL and ideal gas
  - NRTL with vapor phase association

- Heterogeneous azeotropes

  - 2 or more liquid phases
  - Total liquid phase composition equal to vapor phase composition

# Previous Solution Methods

- Heterogeneous azeotropes from unstable homogeneous azeotropes (Chapman and Goodman, 1993)

- Homotopy algorithms (Eckert and Kubicek, 1997; Tolsma and Barton, 1998)

- Global optimization based on branch and bound using convex underestimating functions (Harding et al., 1998)

# Formulation

$$y_i P - x_i^I \gamma_i^I P_i^{sat} = 0, \ \forall i \in \mathcal{C}$$

$$y_i P - x_i^{II} \gamma_i^{II} P_i^{sat} = 0, \ \forall i \in \mathcal{C}$$

$$y_i - x_i^I \theta + x_i^{II} (1 - \theta) = 0, \ \forall i \in \mathcal{C}$$

$$\sum_{i \in \mathcal{C}} x_i^I - 1 = 0, \ \sum_{i \in \mathcal{C}} x_i^{II} - 1 = 0$$

- $y_i$, $x_i$ are vapor and liquid phase mole fractions

- $\theta$ is the number of moles of liquid phase $I$ divided by the total number of moles of liquid

- $P_i^{sat}(T)$ are the pure component vapor pressures (Antoine equation)

- $\gamma_i(\mathbf{x}, T)$ are the activity coefficients (NRTL)

- $\mathcal{C}$ is the set of all $N$ components

- Ideal vapor phase

- Need solution method <u>guaranteed</u> to find <u>all</u> solutions

# Computation Issues

- Chosen formulation has $3N + 2$ variables, $y_i, x_i^I, x_i^{II} \forall i \in N, T, \theta$.

- An alternative formulation using $2N + 2$ variables is available, but less efficient in terms of CPU time.

- Solutions of equifugacity equations may not be stable phases (liquid may split). Interval analysis also provides guaranteed method to determine stability (Stadtherr *et al.*, 1994)

- Trivial solutions
  - Occur at $(\mathbf{x}^*, T^*)$ where a homogeneous azeotrope (stable or unstable) or a pure component at its boiling point exists
  - When $X^I = X^{II} = \mathbf{x}^*, T = T^*$, all values of $\theta$ satisfy the equations for heterogeneous azeotropy
  - Since IN/GB is not designed to handle non-discrete solutions, special procedures must be implemented to remove these areas from the search space

# Removing Trivial Roots

- We can remove boxes that contain a trivial root by examining the Hessian of the Gibbs' energy of mixing.

- If Hessian matrix is **not** positive definite

    - Indicates composition and temperature are unstable.
    - If an entire region $\mathbf{X^I}$ or $\mathbf{X^{II}}$ is not positive definite throughout, then it can be deleted.

- If Hessian matrix **is** positive definite

    - Can not determine stability.
    - Only one liquid phase can exist at equilibrium in a region that is positive definite throughout.
    - If a region which contains both $\mathbf{X^I}$ **and** $\mathbf{X^{II}}$ is positive definite throughout, then no heterogeneous azeotrope can exist since two liquid phases can not coexist.

# Constraint Propogation

- First step in the IN/GB algoritm is to determine whether or not it is **possible** for each function to contain zero. If not, the box can be deleted.

- If zero does lie within the possible range of each function, it may be possible to reduce the domain of one or more variables. We do this by solving the equations in our system for the independent variables. For example

$$X^I_{i,calc} = \frac{Y_i + X^{II}_i}{\theta} - 1$$

$$X^I_{i,new} = X^I_{i,calc} \cap X^I_{i,old}$$

- In some cases, we can eliminate a particular box because there is no intersection.

- Since these calculations are extremely fast, as many permutations as possible are used.

# 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, *with mathematical and computational certainty* either provide tight, rigorous enclosures for all solutions or prove 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), $\mathbf{X}^{(k)}$,

- Use constraint propogation algorithm.

- If $\mathbf{X}^{(k)}$ contains any trivial root, attempt to delete by examining Hessian of Gibbs energy of mixing.

- Compute the range of all functions in the system, and delete if 0 is not an element of all ranges.

- 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 $\mathbf{X}^{(k)}$.
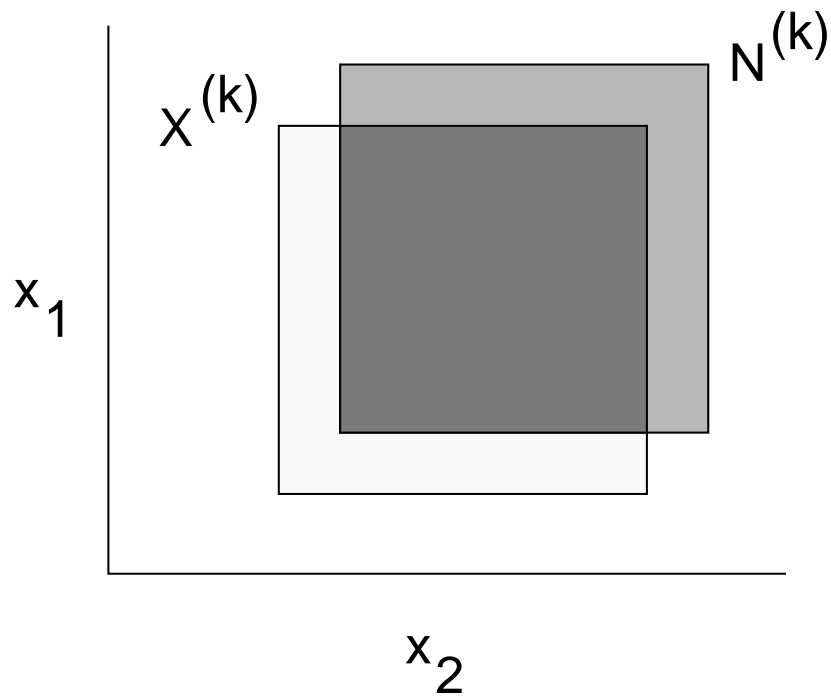
$x_1$

$x_2$
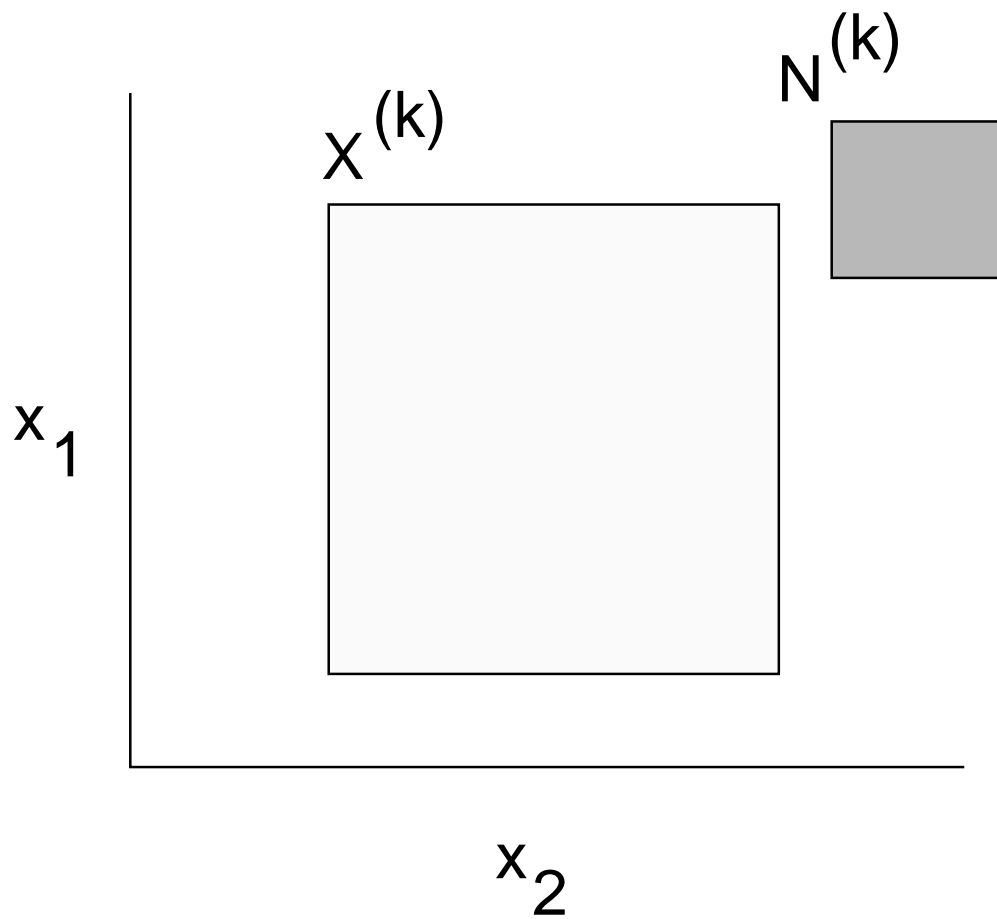
There was no solution in $X^{(k)}$

$x_1$

$X^{(k)}$

$N^{(k)}$

$x_2$
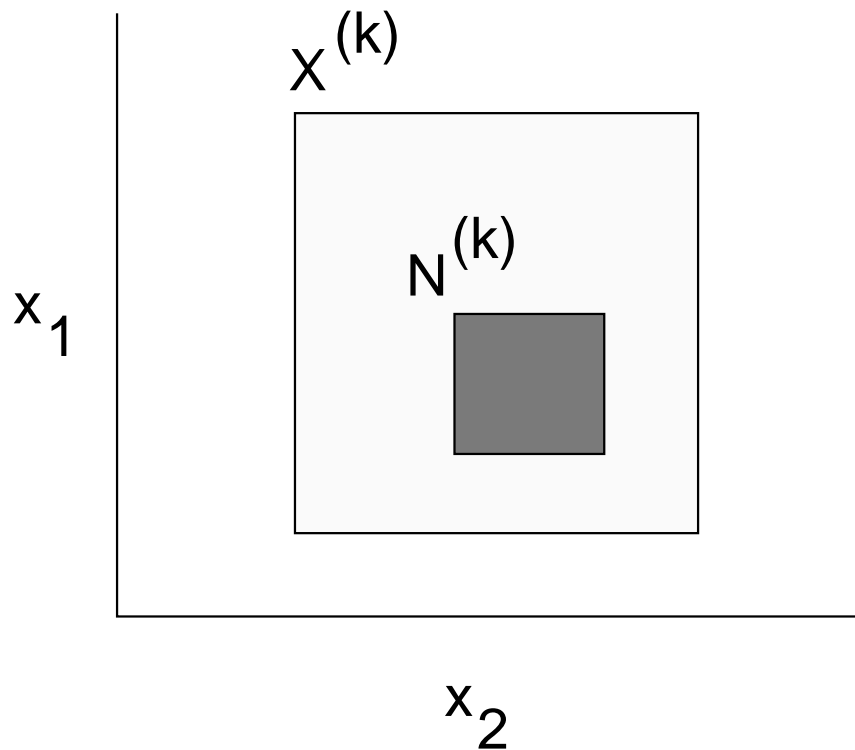
Unique solution in $X^{(k)}$

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

- NRTL model, full temperature dependence

- Ideal vapor phase, Antoine equation for vapor pressures

- CPU times for Ultra 2/1300

- Example 1 - Water $+$ Cyclohexane

- Example 2 - Water $+$ Ethanol $+$ Benzene

# Results - Problem 1

| | $x_i^I$ | $x_i^{II}$ | $y_i$ |
|---|---|---|---|
| Water | 0.0049 | 0.9996 | 0.2996 |
| Cyclohexane | 0.9951 | 0.0004 | 0.7004 |
| $T = 71.5°C$ | | $\theta = 0.7037$ | |

- 1 heterogeneous azeotrope

- 3 trivial solutions

- CPU time - 1.2 sec

# Results - Problem 2

|          | $x_i^I$ | $x_i^{II}$ | $y_i$  |
|----------|---------|------------|--------|
| Ethanol  | 0.2620  | 0.4345     | 0.3082 |
| Water    | 0.0578  | 0.5380     | 0.1864 |
| Benzene  | 0.6801  | 0.0275     | 0.5055 |
| $T = 64.3°C$ | | $\theta = 0.7324$ | |

|          | $x_i^I$ | $x_i^{II}$ | $y_i$  |
|----------|---------|------------|--------|
| Ethanol  | 0.0000  | 0.0000     | 0.0000 |
| Water    | 0.0525  | 0.9950     | 0.3069 |
| Benzene  | 0.9475  | 0.0050     | 0.6931 |
| $T = 70.1°C$ | | $\theta = 0.7301$ | |

- 2 heterogeneous azeotropes

- 7 trivial solutions

- CPU time - 270 sec

# Concluding Remarks

- Can be used with other activity coefficient models or with equation of state models

- IN/GB provides a <u>mathematical and computational guarantee</u> of reliability

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of phase behavior and in other process modeling problems

- Present method can be extended to solve for reactive heterogeneous azeotropes

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