ODE's to describe Simple Batch Distillation

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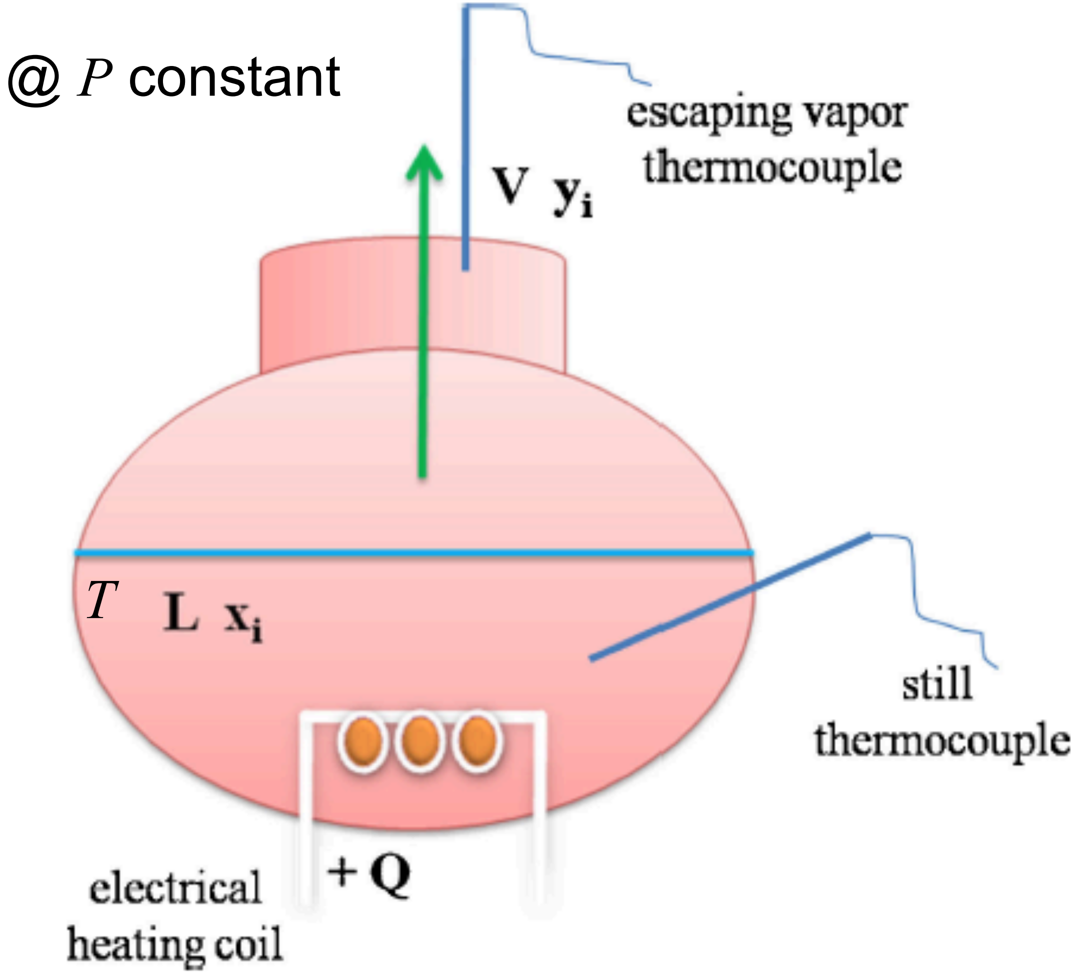
Simple batch distillation



Michael Doherty, UC Santa Barbara

Assumptions:

- LVE
- $Q(t)$ is given (driving force of the evaporation)
- n components
- Initial conditions: L_0, $\underline{x}_0$

Simple batch distillation

- Unknowns:
- $\underline{x},\ \underline{y},\ \dot{V},\ L,\ T \qquad \Rightarrow 2n+3$
- Equations:

energy balance (1)

component balance (n)

equilibrium conditions (n)

$$\sum_i x_i = 1 \quad (1)$$

$$\sum_i y_i = 1 \quad (1)$$

Simple batch distillation - Equations

- General balance: $\text{ACC} = \text{IN} - \text{OUT}$
- Component balance: $\dfrac{d\left(Lx_i\right)}{dt} = -\dot{V}y_i \qquad i = 1,\ldots,n$
- LVE: $y_i = K_i x_i = K_i\left(\underline{x}, T, p\right)x_i$
- Stoichiometric eqs.: $\sum_i x_i = 1 \quad \sum_i y_i = 1$
- Energy balance:

$$\frac{dH_L}{dt} = \boxed{\frac{d\left(Lh_L\left(\underline{x},T\right)\right)}{dt} = \dot{Q}\left(t\right) - \dot{V}h_V\left(\underline{y},T\right)}$$

Simple batch distillation - Fugacity

- Isofugacity condition: $f_i^L = f_i^V$
- Ideal gas, non-ideal liquid: $\gamma_i x_i p_i^V = y_i P$
- Solve for y_i:

$$y_i = \frac{\gamma_i p_i^V}{P} x_i = K_i\left(\underline{x}, T, P\right) x_i$$

Simple batch distillation

- Summing all component balances:

$$\sum_{i=1}^{n} \frac{d\left(Lx_i\right)}{dt} = -\sum_{i=1}^{n} \dot{V} y_i \quad \Rightarrow \frac{d\left(L\sum x_i\right)}{dt} = -\dot{V}\sum y_i$$

- → overall mass balance: $\frac{dL}{dt} = -\dot{V}$
- Transforming the component balances:

$$\frac{d\left(Lx_i\right)}{dt} = L\frac{dx_i}{dt} + x_i\frac{dL}{dt} = -\dot{V} y_i \quad = \frac{dL}{dt} y_i$$

- Component balances: $L\frac{dx_i}{dt} = -\frac{dL}{dt}\left(x_i - y_i\right)$

Simple batch distillation

- Final set of equations (ODEs + Aes):

$$L\frac{dx_i}{dt} = -\frac{dL}{dt}\left(x_i - y_i\right) \qquad (i = 1,..,n-1)$$

$$y_i = K_i x_i \qquad (i = 1,..,n)$$

$$\sum_i x_i = 1 \qquad\qquad \sum_i y_i = 1$$

$$\begin{cases} \dfrac{dL}{dt} = -\dot{V} & \rightarrow L \\ \text{energy balance} & \rightarrow \dot{V} \end{cases}$$

– Initial conditions: L_0, $\underline{x}_0$ (T_0 is B.P. of $\underline{x}_0$)

Simple batch distillation

- Problem: t does not approach infinity
- Define new variable:

$$-\frac{dL}{L} = d\xi \quad > 0$$

- ξ is a modified time, called *warped time*
- Transformation:

$$L\frac{dx_i}{-dL} = x_i - y_i = \frac{dx_i}{d\xi} \qquad i = 1, \ldots, n-1$$

Simple batch distillation

$$-\frac{dL}{L} = d\xi$$

- Using the initial conditions:

$$L = L_0 \qquad \xi = 0$$

$$L \to 0 \qquad \Rightarrow \xi = +\infty$$

$$\boxed{\Rightarrow \ln\frac{L_0}{L} = \xi}$$

- → the definition makes sense

$$\Rightarrow \xi = \left[0, +\infty\right[$$

Simple batch distillation

- Final set of nonlinear ODEs (w/o energy bal.)

$$\frac{dx_i}{d\xi} = x_i - y_i \quad \rightarrow x_i \quad (i = 1, \ .., \ n-1)$$

$$y_i = K_i(\underline{x}, T, p) x_i \quad \rightarrow y_i \quad (i = 1, \ldots, n)$$

$$\sum_i x_i = 1 \quad \rightarrow x_n$$

$$\sum_i y_i = 1 = \sum_{j=1}^{n} K_i(\underline{x}, T, P) x_i \quad \rightarrow T$$

bubble point equation

Simple batch distillation

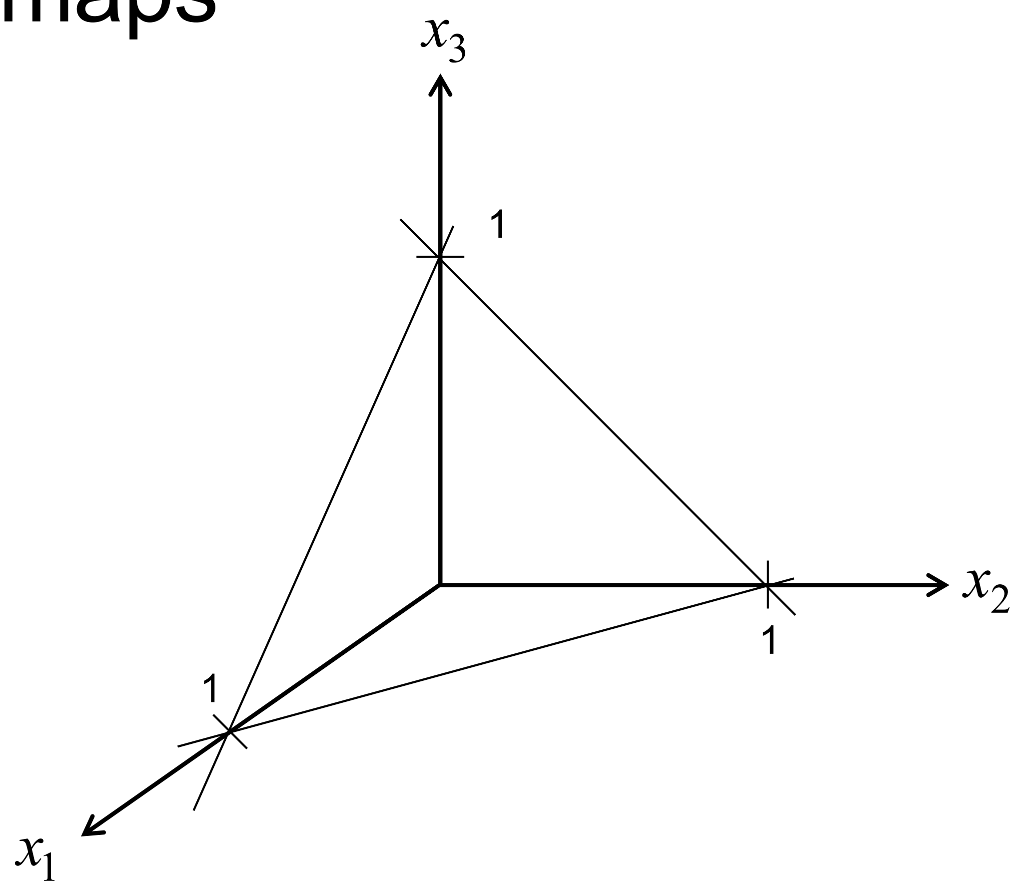
- At steady state:

$$\frac{dx_i}{dt} = 0 \qquad \Leftrightarrow x_i = y_i$$

- Mathematics: steady states calculated from a strongly nonlinear system of AEs.
- Phase equilibrium thermodynamics: the s.s. condition is fulfilled by pure species and azeotropes (only!).

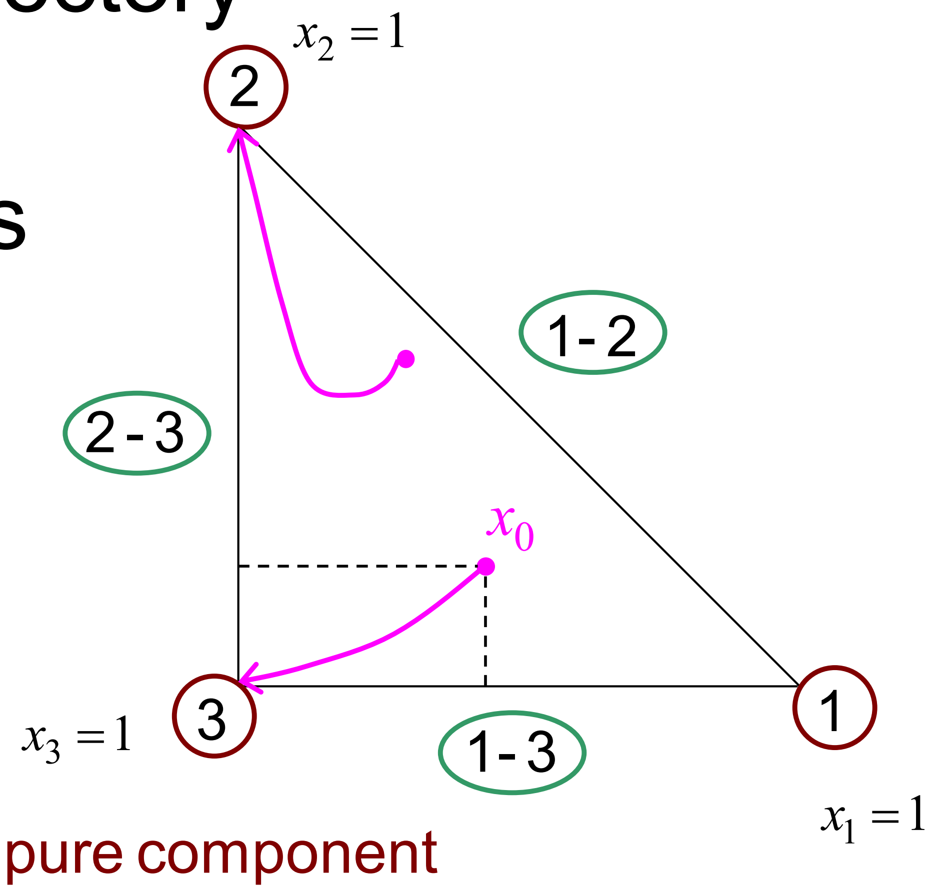
Simple batch distillation

- Residue curve maps
- $n = 3$
- $x_1 + x_2 + x_3 = 1$



Distillation – Residue curve maps

- Residue curve ≡ trajectory
- Residue curve map: map of all the curves



Distillation – Residue curve maps

- Set of equations:

$$\begin{cases} \dfrac{dx_1}{d\xi} = x_1 - y_1 \\ \dfrac{dx_2}{d\xi} = x_2 - y_2 \end{cases}$$

$$x_3 = 1 - x_1 - x_2$$

$$\sum_i y_i = 1$$

$$y_i = K_i(\underline{x}, T, p)\, x_i$$

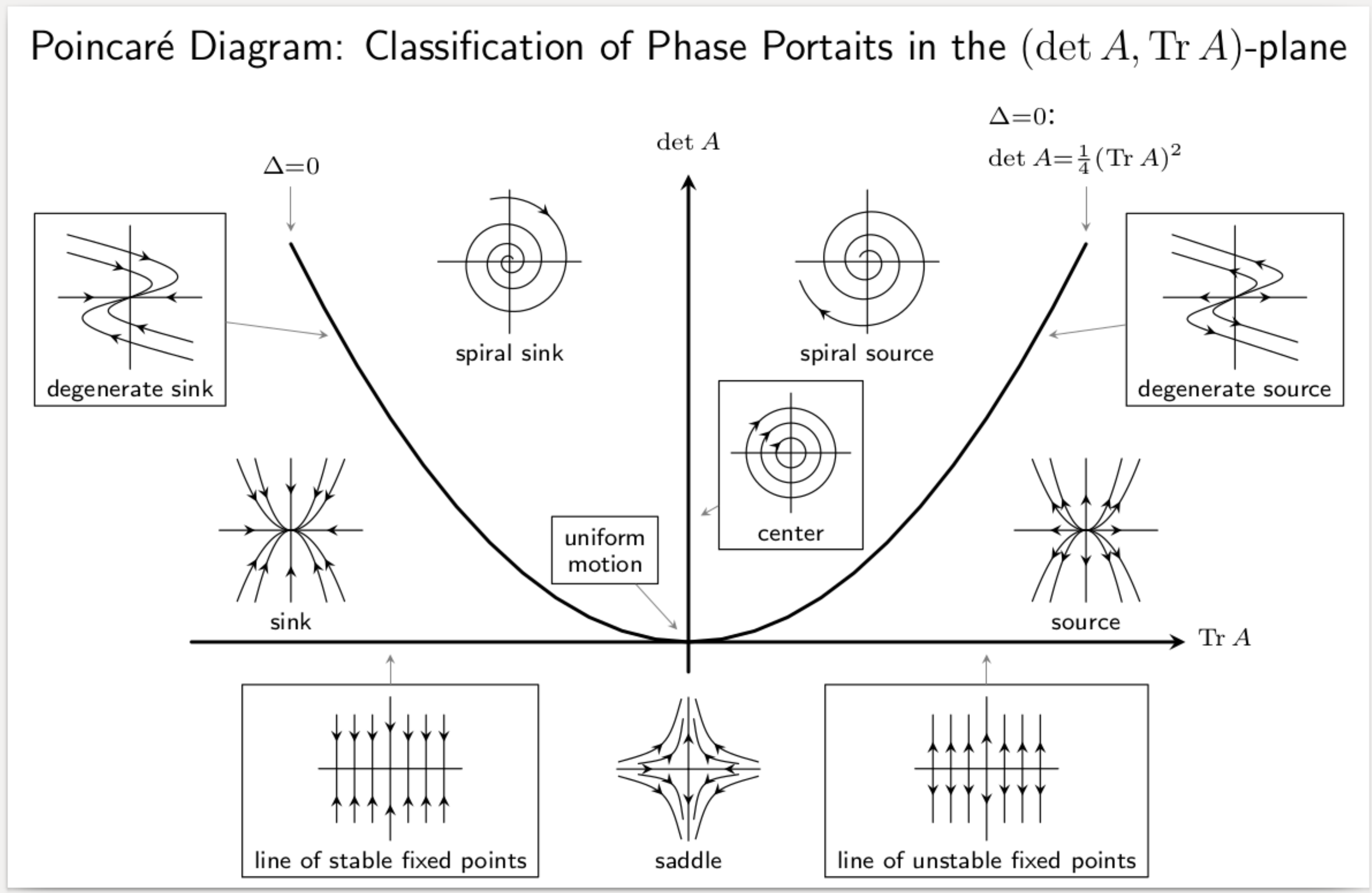
Distillation – Residue curve maps

- Procedure on how to create a residue curve map:
  - identify the pure species (and their b.p.)
  - identify the azeotropes (and their b.p.)
  - indicate the direction of movement of the trajectories
  - the temperature increases along the residue curves
  - neither limit cycles nor oscillations can exist

Distillation – Residue curve maps

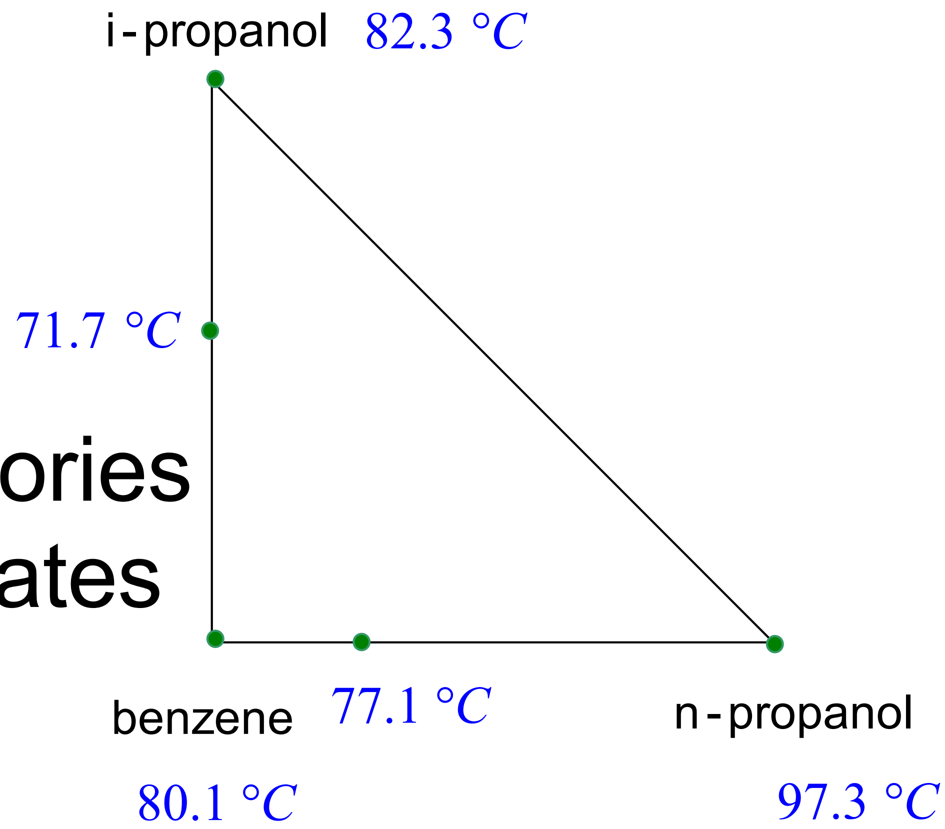
- Some important details to characterise the steady states
  - the point with the highest boiling temperature is a stable node
  - the point with the lowest boiling temperature is an unstable node
  - steady states can only be nodes or saddles, focus‘ would leave the triangle!

Classification of steady-states



Residue curve map

- pure components
- azeotropes
- b.p. temperatures
- directions of trajectories between steady states
- draw trajectories



Residue curve maps – Example

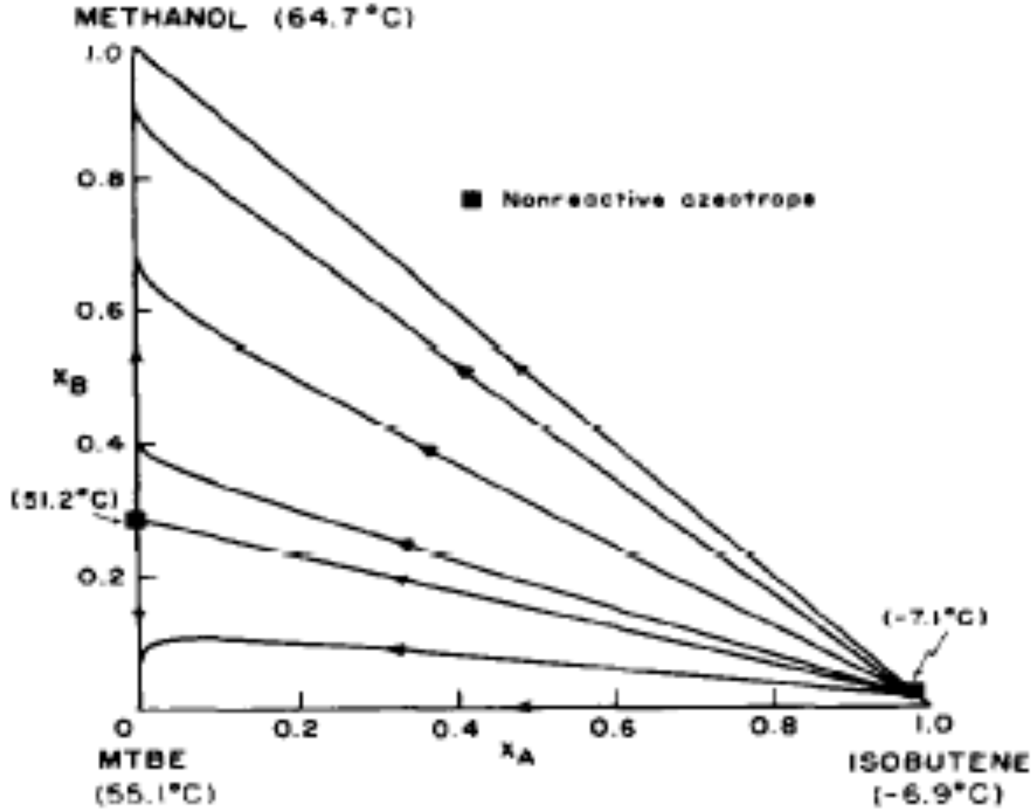


Fig. 5. Residue curve map for the non-reactive system isobutene–methanol–MTBE.

Barbosa, D., Doherty, M. F., The Simple Distillation of Homogeneous Reactive Mixtures

Residue curve maps – Example

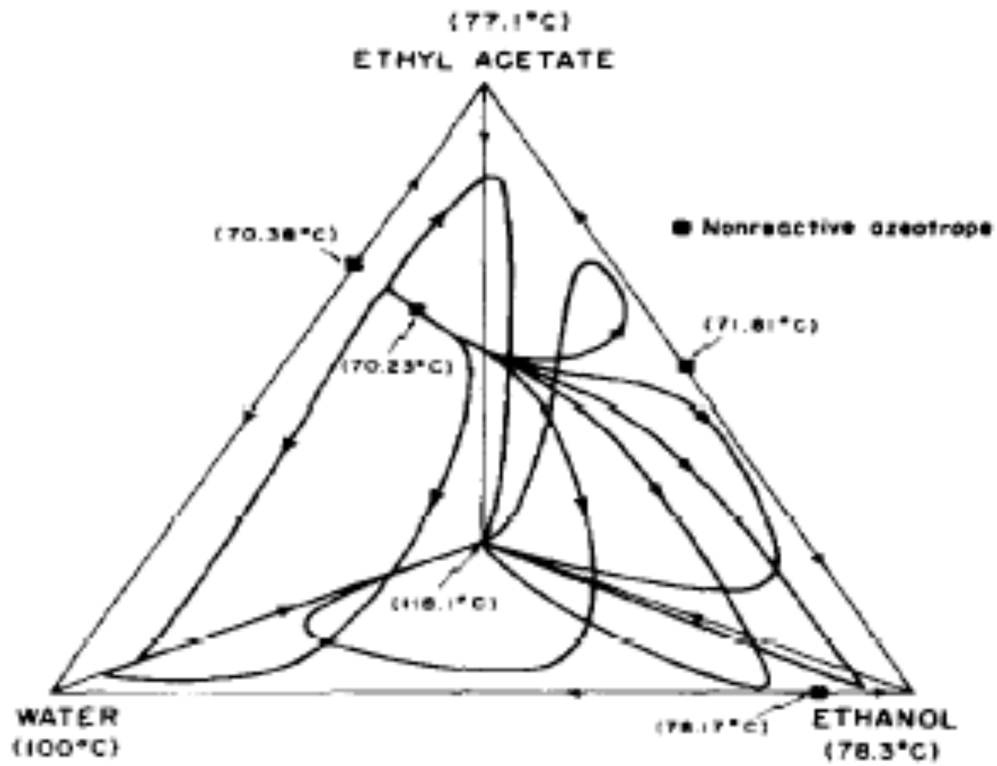


Fig. 9. Three-dimensional representation of the residue curve map for the non-reactive system acetic acid–ethanol–ethyl acetate–water.

Barbosa, D., Doherty, M. F., The Simple Distillation of Homogeneous Reactive Mixtures

Residue curve maps - Example

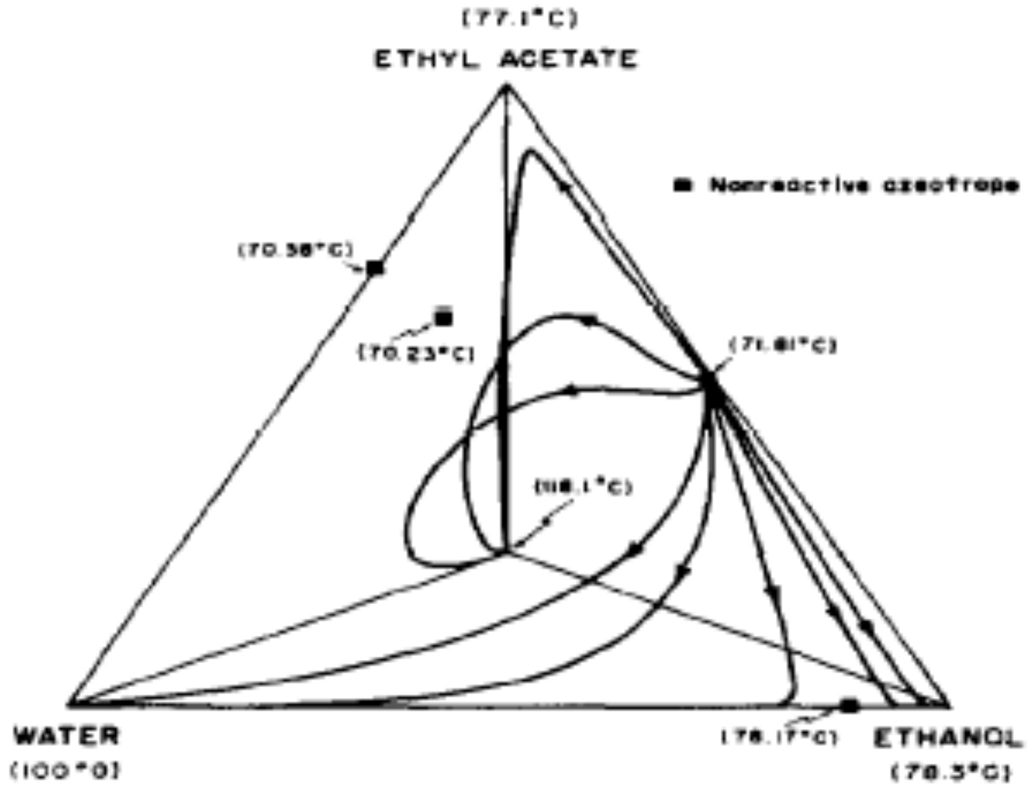


Fig. 10. Three-dimensional representation of the residue curve map for the reactive system acetic acid–ethanol–ethyl acetate–water in terms of the liquid mole fractions.

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Residue curve maps - Example

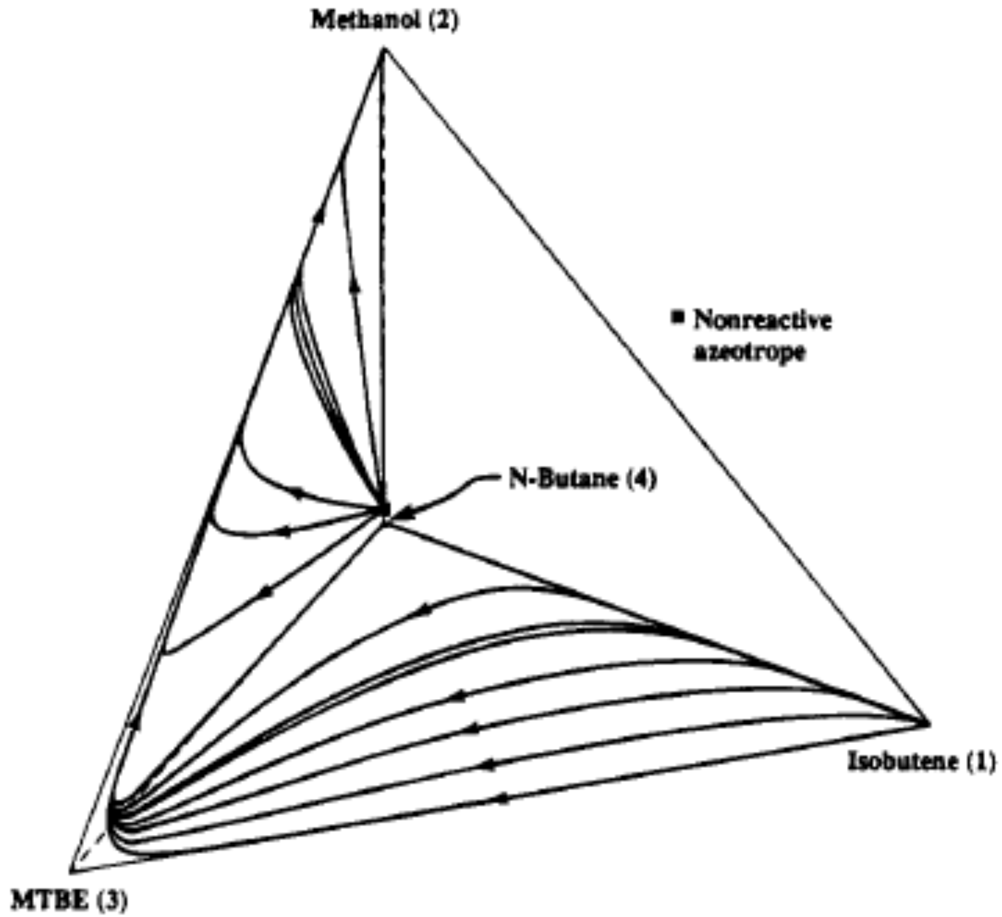

Figure 2. Residue curves in the mole fraction tetrahedron for the reactive mixture isobutene (1) + methanol (2) ⇌ MTBE (3) with n-butane (4) as inert. P = 11 atm.

Ung, S., Doherty, M.F., Calculation of Residue Curve Maps for Mixtures with Multiple Equilibrium Chemical Reactions