Residue Curve maps (ODE)

Batch Distillation

How the composition in the pot evolves over time?

(Doherty M.F. Perkins J.D., Chem. Eng. Sci. 1978 (33))

@ $p = \text{const}$

C: # of component

L: [mol] liquid

$\underline{x}$: liq. mole fraction

$\dot{V}\left[\frac{mol}{s}\right]$: vapor flow rate

$\dot{Q}(t)$: heat input $\left[\frac{J}{s}\right]$

y: vapor mole fraction

Assump: - thermodynam. equil. (does not imply constant T)

Mat. Bal:

$$\underbrace{\frac{dL}{dt} = -\dot{V}} \quad \boxed{1}$$

$$\rightarrow \frac{d(x_i L)}{dt} = -y_i \dot{V} \quad \boxed{C-1}$$

stoch. equations

$$\sum_{i=1}^{C} x_i = 1 \quad \boxed{1}$$

$$\sum_{i=1}^{C} y_i = 1 \quad \boxed{1}$$

# of equations:
Select a subset:
$2(C+1)+1$ equation
$C+1$ ODE, $C+2$ AE

# of var: $2C+3$

Thermodyn. equil:

$$y_i = \boxed{K_i(T,p,x)} \cdot x_i \quad \boxed{C}$$

$\rightarrow$ isofugacity condition

$$y_i = \frac{f_i^L(x_i) \cdot \gamma_i(T,p,\underline{x})}{P}$$

complic function!

Energy balance:

$$\frac{d(L\,h_L)}{dt} = \underbrace{\dot{Q}(t)}_{\text{makes the system non-autonom.!}} - \dot{V} H_V \quad \boxed{1}$$

Init. Cond:

$t = 0: \quad L = L_0, \quad \underline{x} = \underline{x}_0 \quad (T = T_0(x)$: bubble point temp$)$

Issues: (1) $\dot{Q}(t) \Leftrightarrow$ non-auton.

(2) Energy bal. coupled with MBs

(3) $t \to +\infty$ is phys. not possible

Model is give, but not in a form in which we can apply the ~~ODE~~ that we have studied.

Idea: transform the problem into one that we can analyze more easily.

Here: change of the indep. var.

$$\frac{d(x_i L)}{dt} = -y_i \cdot \dot{V}$$

plug in (1)st Equa. $\frac{dL}{dt} = -\dot{V}$

$$\frac{dx_i}{dt} \cdot L + \underbrace{x_i \cdot \frac{dL}{dt}}_{} = \frac{dL}{dt} \cdot y_i \quad / \text{ rearr}$$

$$L \cdot \frac{dx_i}{dt} = (y_i - x_i) \frac{dL}{dt} \quad / : \left(\frac{dL}{dt}\right)$$

$$L \cdot \frac{dx_i}{\cancel{dt}} \frac{\cancel{dt}}{dL} = y_i - x_i$$

$$\frac{dx_i}{\ominus \frac{dL}{L}} = x_i - y_i \xrightarrow{\xi} \boxed{\frac{dx_i}{d\xi} = x_i - y_i}$$

ξ: $\underbrace{d\xi := -\frac{dL}{L}}_{} \quad / \int$

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

'warped time' (from $0 \to \infty$!)

Need to have an initial value:

$L: \; L_0 \to 0$

$t: \; 0 \to t_{END}$

$C\xi: \; \underset{L=L_0}{0} \to \underset{L=0}{+\infty}$? solves issue #3

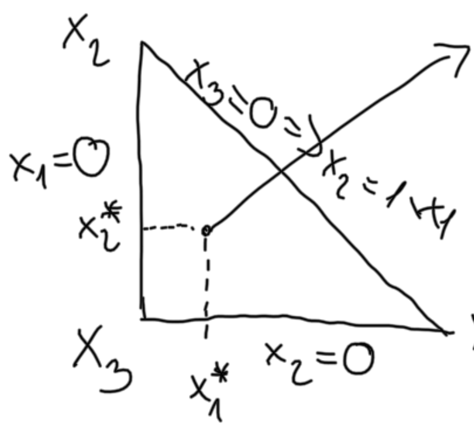
$$\left[\begin{array}{l} \bullet \; \dfrac{dx_i}{d\xi} = x_i - y_i = x_i - y_i(T, P, \underline{x}) \\ \bullet \; y_i = K_i(T, P, \underline{x}) \cdot x_i \\ \bullet \; \sum_{i=1}^{C} y_i = \boxed{\sum_{i=1}^{C} K_i(T, P, \underline{x}) \cdot x_i = 1} \\ \bullet \; x_C = 1 - \sum_{i=1}^{C-1} x_i \end{array}\right] \begin{array}{l} C-1 \\ \\ 1 \\ 1 \end{array}$$

Bubble point calculation
Only T is unknown, since x_i comes from the ODE

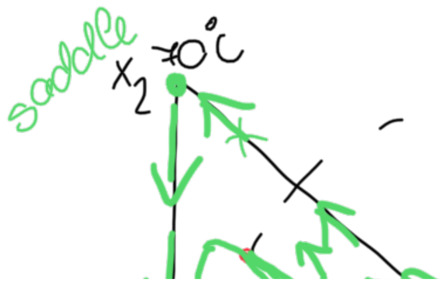
we got: DAE with C-1 ODEs and 2 AE, autonom.
C AEs for y_i (thermody. eq) (solves issue #1) $\Rightarrow$

$\Rightarrow x_i, y_i, T$

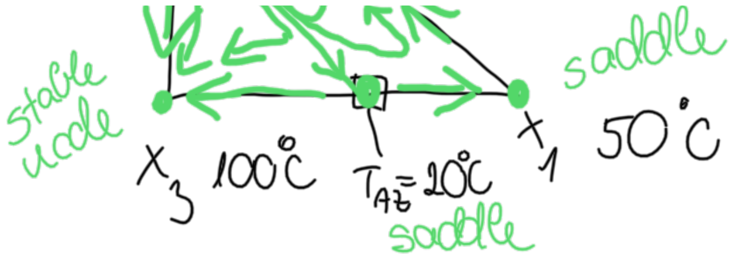
3 component case



$\to x_3^* = 1 - x_1^* - x_2^*$



$\to T_{Az,123} = 10°C$
unstable node



$$\begin{cases} x_1 + x_2 + x_3 = 1 \rightarrow x_3 = 1 - x_2 - x_1 \quad \boxed{1} \\ \left.\begin{array}{l} \dfrac{dx_1}{d\xi} = x_1 - y_1 \\ \dfrac{dx_2}{d\xi} = x_2 - y_2 \end{array}\right\} c-1 = \boxed{2} \\ y_i = \boxed{K_i(T,P,x)} \cdot x_i \\ \sum_i K_i(T,P,x) \cdot x_i = 1 \end{cases}$$

Let's start by looking at the SSs!

(1) SS: nonlinear system

$$\left.\begin{array}{l} x_1 - y_1 = 0 \\ x_2 - y_2 = 0 \end{array}\right\} \rightarrow x_1 = y_1$$

nonlinearity!

Mathem. we are stuck but physically: 2 possibilities:

a) azeotropes

b) pure compounds

(2) Trajectories will be the sides of the triangle!

(if one component is not present initially, can't appear)

(3) type of SS: node: stable or unstable

saddle

(stable) node

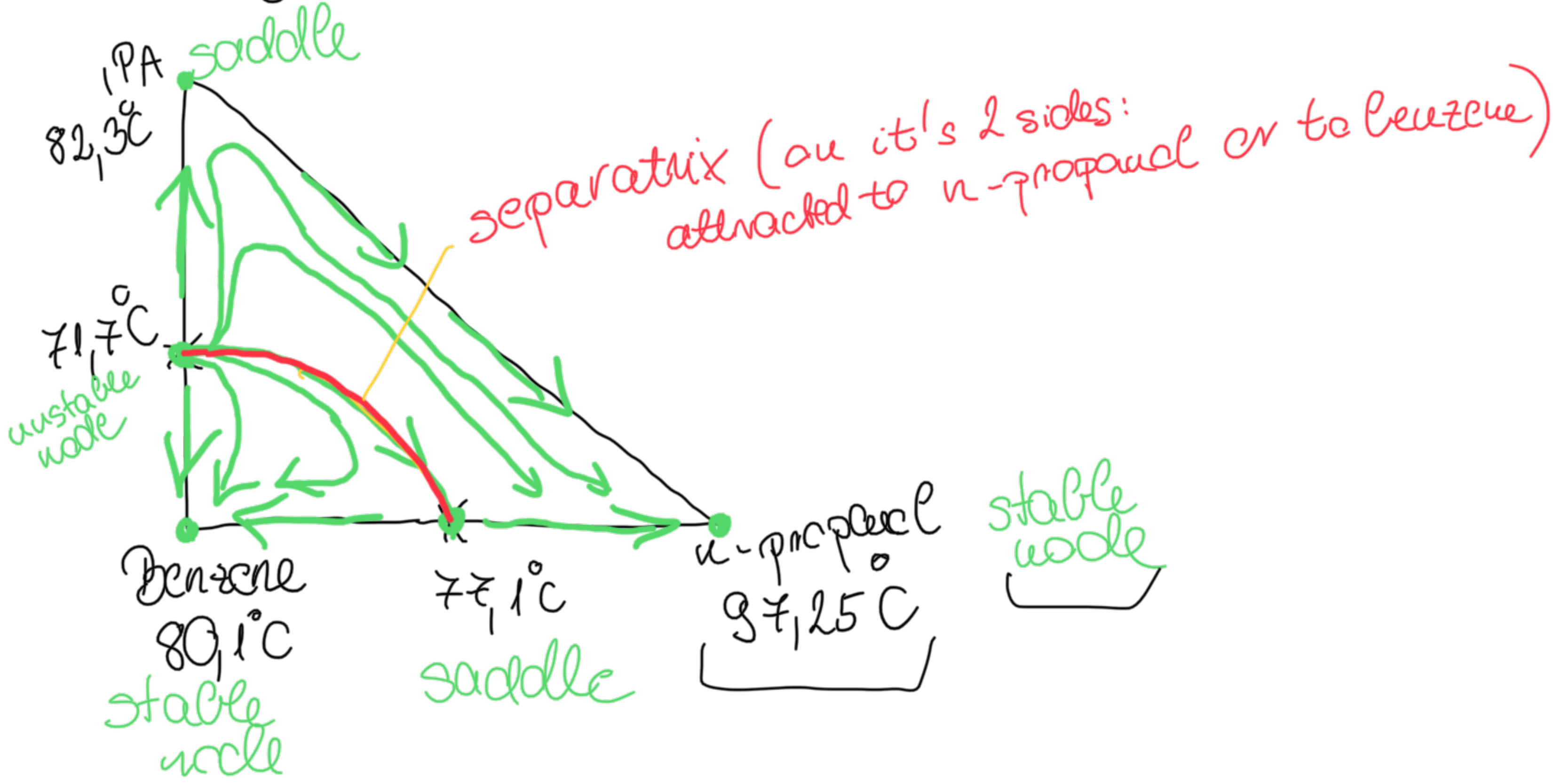
saddle

(4) Physically, the T can only increase! => No periodic solutions!

Know the directions of the trajectories on the axes when we know the magnitude of T_b!

Example 1:

Real system: 3 species: IPA, benzene, n-propanol



Steady state with the highest T_b will always be a stable node!

The steady state with the lowest T_b will always be an unstable node!

Example 2: