Phase Behavior

THREE-PHASE CALCULATIONS & APPLICATION TO VAPOR-LIQUID-ADSORPTION EQUILIBRIUM

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Phase behavior is pore-size dependent

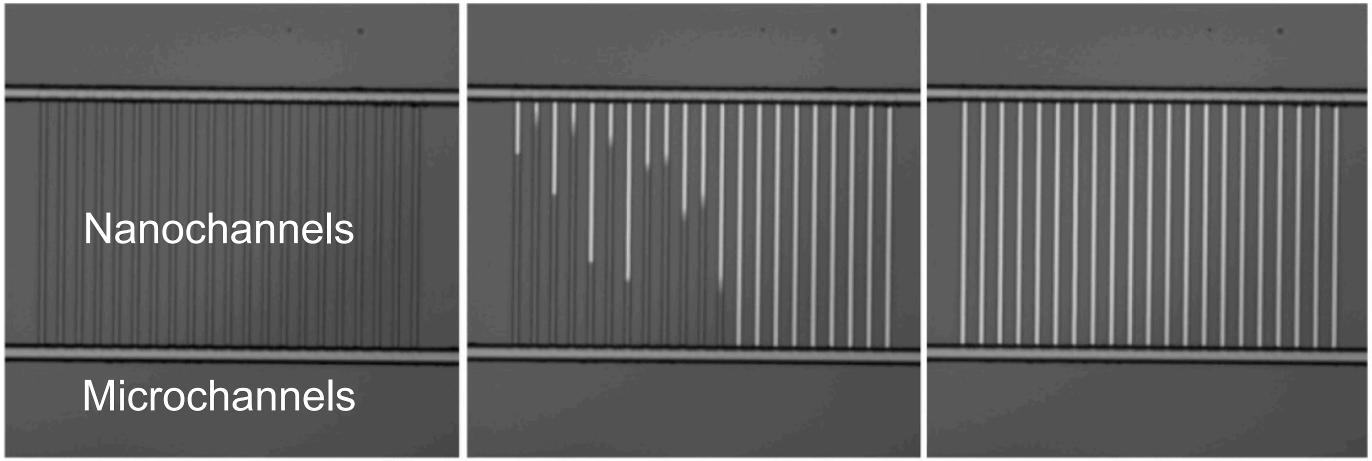


Fig.4—Three consecutive images during the vaporization of pure n-pentane in the chip.

Liquid nC_5 first evaporated in microchannels, then nanochannels

SPE 169581
Wang et al. 2014

$$P_V = P_{V0} \exp\left(-\frac{V_{L0}}{RT} \frac{2\sigma \cos\theta}{r} \right)$$

Capillary pressure causes the reduction in the vapor pressure

Kelvin equation

The smaller the pore size, the lower the equilibrium vapor pressure

Modeling phase behavior in a single pore

The following equations are solved

- Input – z_i, P_L, T, r, θ, $P_{\sigma i}$ *Pore size, contact angle, parachor*
- Output – n_L, x_i, y_i, K_i, V_L, V_G, σ, P_G
- Composition equations

$$\sum_{i=1}^{n_c}\left(x_i - y_i\right) = 0 \qquad x_i = \frac{z_i}{n_L + K_i\left(1 - n_L\right)} \qquad y_i = K_i x_i$$

- Equation of states for liquid and vapor

$$P_L = \frac{RT}{V_L - b_L(\mathbf{x})} - \frac{a_L(\mathbf{x})}{V_L^2 + 2b_L(\mathbf{x})V_L - b_L^2(\mathbf{x})}$$

$$P_G = \frac{RT}{V_G - b_G(\mathbf{y})} - \frac{a_G(\mathbf{y})}{V_G^2 + 2b_G(\mathbf{y})V_L - b_G^2(\mathbf{y})}$$

- Capillary pressure

$$\sigma^{1/4} = \sum_{i=1}^{n_c} x_i P_{\sigma i} \Big/ V_L - \sum_{i=1}^{n_c} y_i P_{\sigma i} \Big/ V_G$$

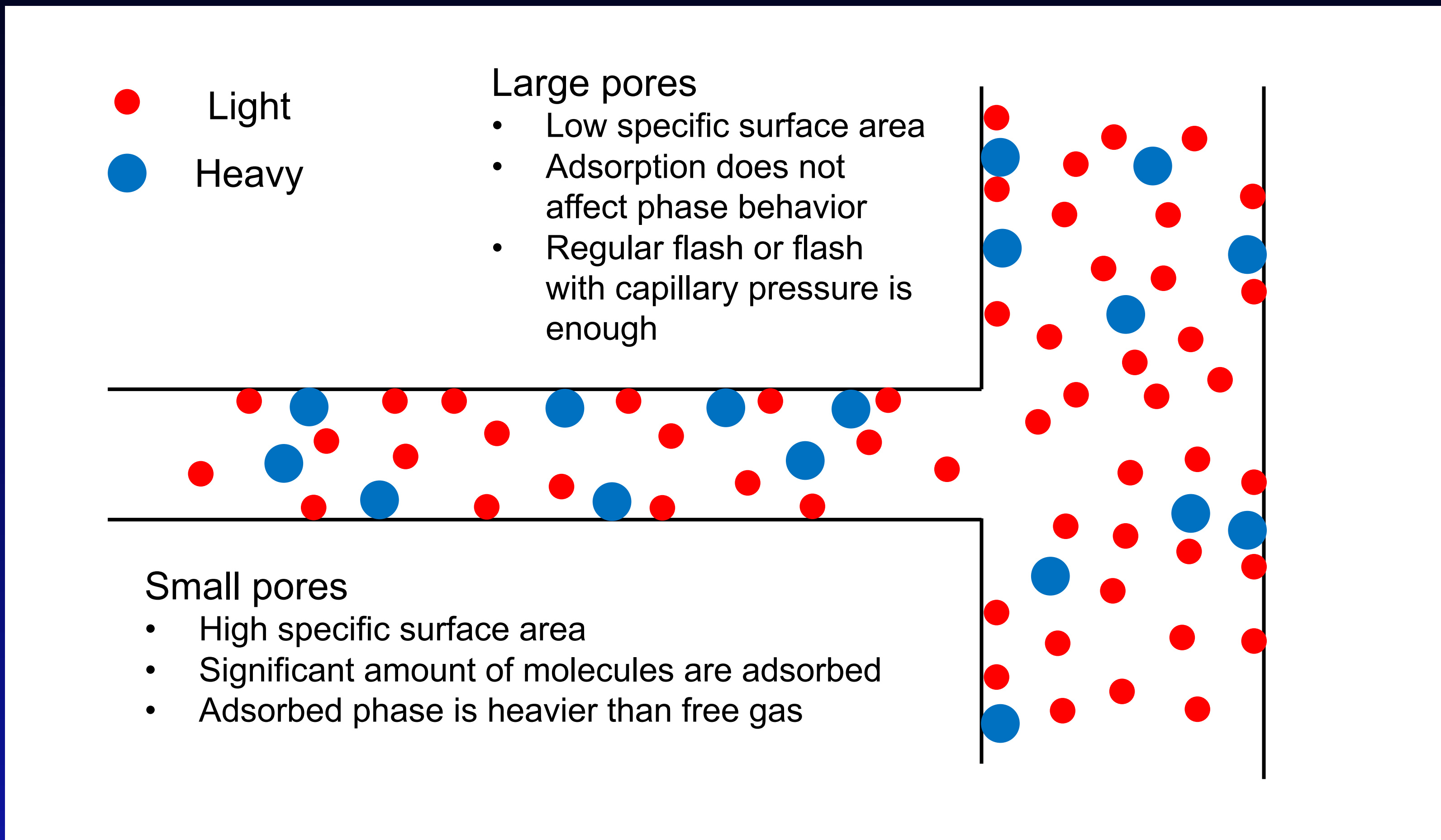
$$P_G - P_L = 2\sigma\cos\theta / r$$

- Equilibrium ratios

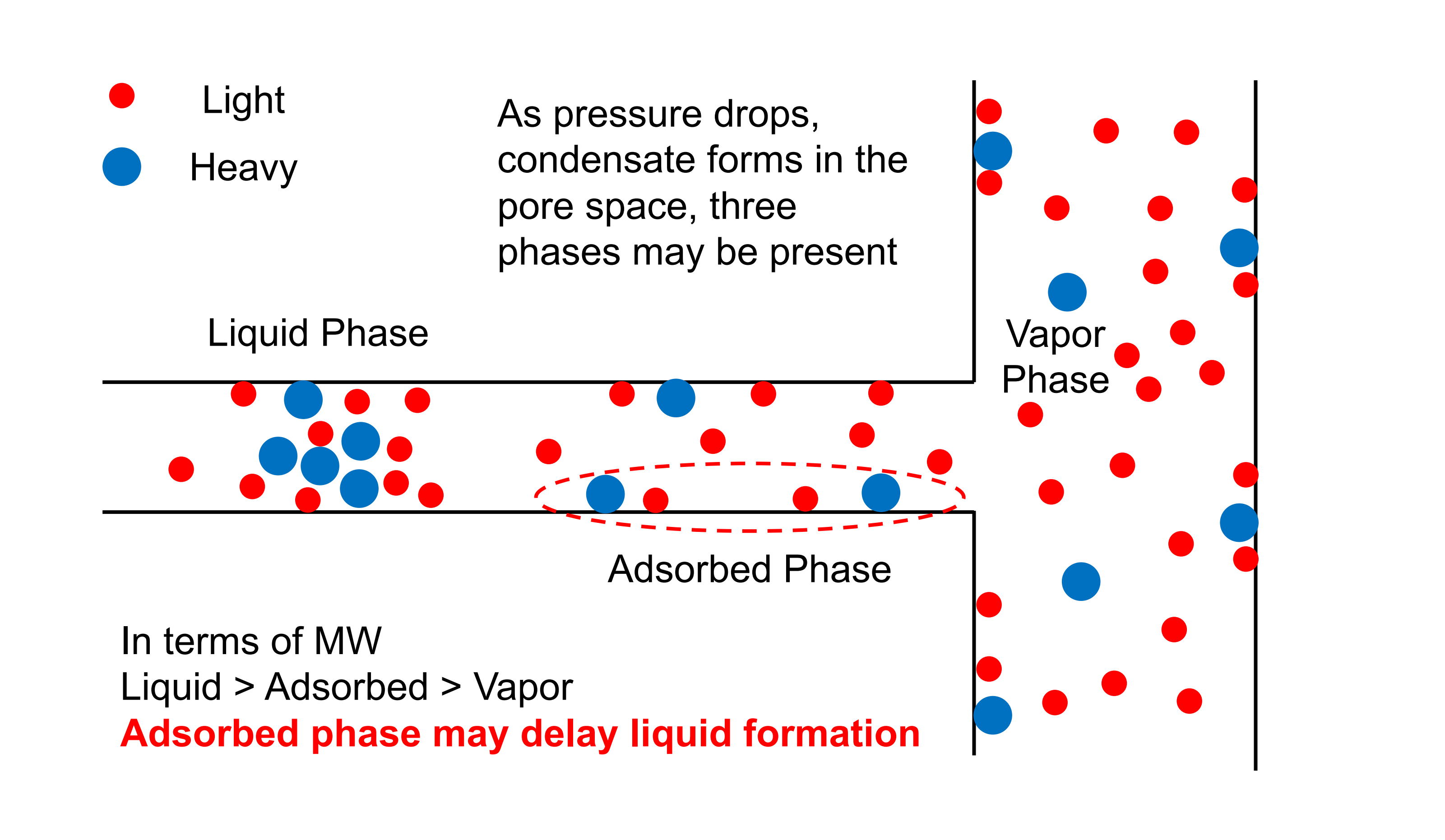
$$K_i = \frac{\Phi_i^L\left(V_L, \mathbf{x}, P_L, T\right)}{\Phi_i^G\left(V_G, \mathbf{y}, P_G, T\right)}\frac{P_L}{P_G}$$

$3n_c$ + 5 equations; $3n_c$ + 5 unknowns
Brusilovsky 1992; Shapiro and Stenby 2001

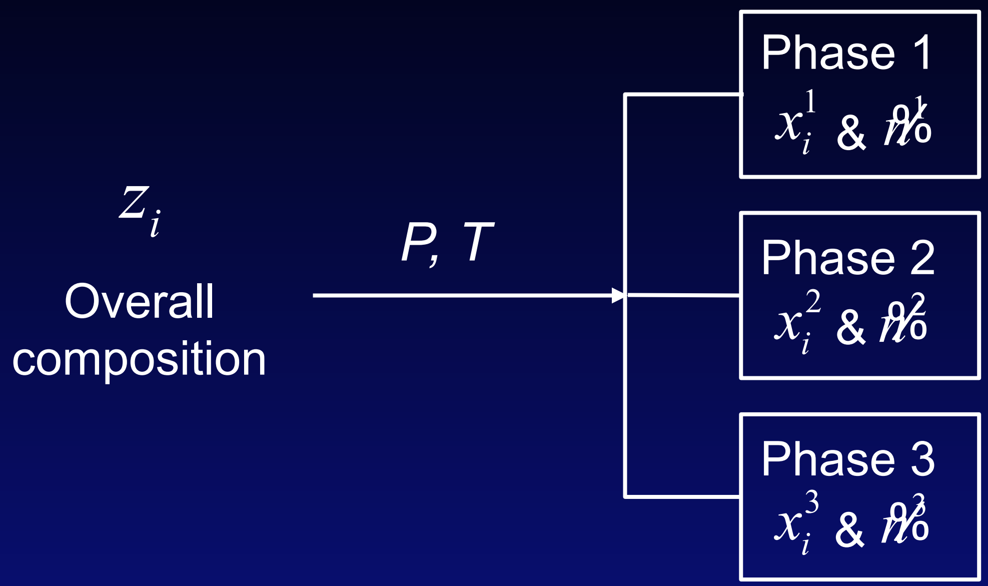
Only vapor-liquid equilibrium?



Vapor-liquid-adsorption equilibrium (VLAE)



Three-phase flash (w/o capillary pressure)



x_i^α Fraction of component *i* in phase *α*

ν^α Mole fraction of phase *α* in the mixture

- $3n_c - 1$ unknowns
- $n_c - 1$ parameters
- Need $2n_c$ equilibrium ratios to achieve unique solution

$$K_i^{\alpha\beta} = x_i^\alpha / x_i^\beta$$

Fraction of component *i* in phase *α* over fraction of component *i* in phase *β*

Properties of $K_i^{\alpha\beta}$ and Rachford-Rice equation

For a three-phase system, there are $6n_c$ equilibrium ratios however only $2n_c$ of them are *independent* because

$$K_i^{\alpha\beta} = 1 \big/ K_i^{\beta\alpha} \qquad K_i^{\alpha\beta} = K_i^{\alpha\gamma} K_i^{\gamma\beta} \qquad \alpha, \beta, \gamma = 1, 2, 3$$

Using the equilibrium ratios, x_i^{α} can be eliminated, leading to three-phase Rachford-Rice equation

$$\sum_{i=1}^{n_c} \frac{(1-K_i^{12})z_i}{K_i^{12} + \left(1-K_i^{12}\right)\tilde{n}\%^{2} - K_i^{12}\left(1-\frac{1}{K_i^{13}}\right)\tilde{n}\%^{3}} = 0 \quad (1)$$

$$\sum_{i=1}^{n_c} \frac{(1-K_i^{13})z_i}{K_i^{13} + \left(1-K_i^{13}\right)\tilde{n}\%^{3} - K_i^{13}\left(1-\frac{1}{K_i^{12}}\right)\tilde{n}\%^{2}} = 0 \quad (2)$$

Solve $\tilde{n}\%^{2}$ and $\tilde{n}\%^{3}$ from these two equations

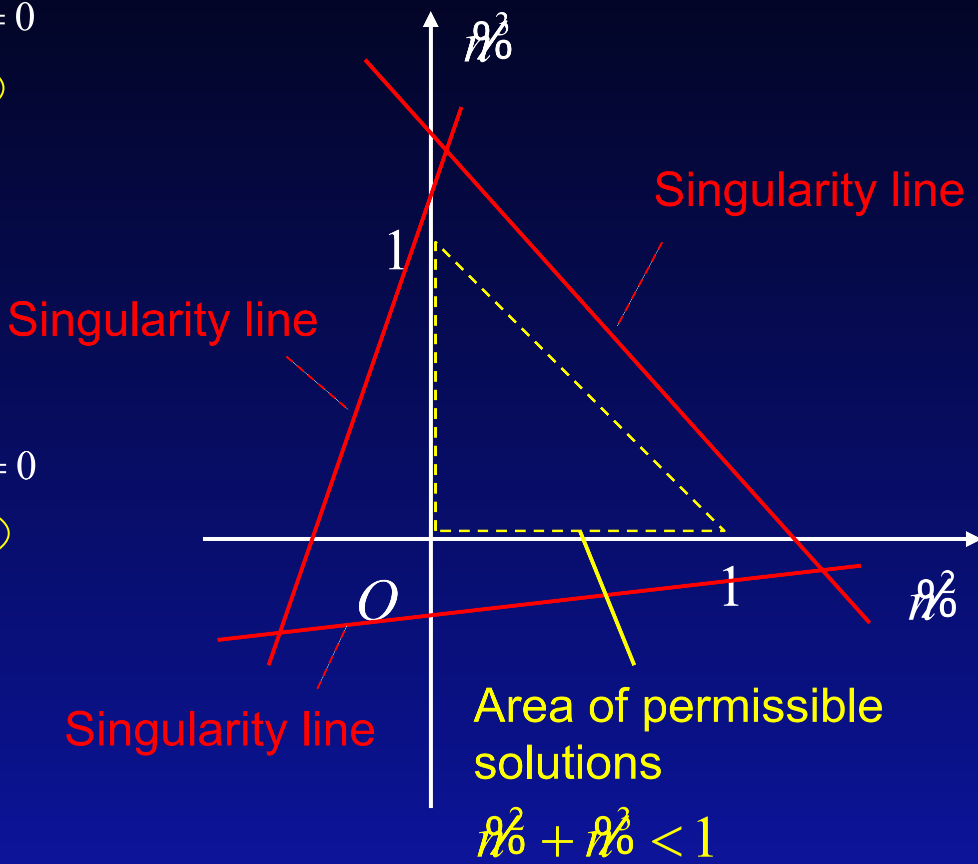
Properties of 3-phase Rachford-Rice equation

$$\sum_{i=1}^{n_c} \frac{(1-K_i^{12})z_i}{K_i^{12} + \left(1-K_i^{12}\right)\tilde{\nu}^{2} - K_i^{12}\left(1-\frac{1}{K_i^{13}}\right)\tilde{\nu}^{3}} = 0$$

Condition that the denominator = 0 gives a set of lines on which ① → ± ∞

$$\sum_{i=1}^{n_c} \frac{(1-K_i^{13})z_i}{K_i^{13} + \left(1-K_i^{13}\right)\tilde{\nu}^{3} - K_i^{13}\left(1-\frac{1}{K_i^{12}}\right)\tilde{\nu}^{2}} = 0$$

Eq. ② also has a set of singularity lines



Solution procedure

Identify the singularity lines surrounding the area of permissible solutions

↓

Use successive substitution to solve Eq. (1) and (2) iteratively

↓

Converged $\tilde{n}^2$ and $\tilde{n}^3$ are used to compute the compositions of the phases x_i^1 through x_i^3

- *This solution procedure is robust and can be extended to N-phase flash*
- *Solution is sought in an Euclidean space with dimension N – 1*
- *Singularities are Euclidean sub-spaces with dimension N – 2*

Sample calculation – Case I

- The solver is tested against an gas-oil-water system

Composition = methane (0.6), n-butane (0.35), water (0.05)

Condition and equilibrium ratios:

$$K_{C1}^{go} = 2.18 \qquad K_{nC4}^{go} = 0.35 \qquad K_{H_2O}^{go} = 1.447$$

$$K_{C1}^{gw} = 467.5 \qquad K_{nC4}^{gw} = 1487 \qquad K_{H_2O}^{gw} = 0.029$$

Solution:

Gas phase	Oil phase	Water phase
$\tilde{n}_g = 0.6546$	$\tilde{n}_o = 0.3207$	$\tilde{n}_w = 0.0247$

Sample calculation – Case II

- The solver is tested against an gas-oil-water system

Composition = methane (0.6), n-butane (0.35), water (0.05)

Condition and equilibrium ratios:

$$K_{C1}^{go} = 2.137 \qquad K_{nC4}^{go} = 0.343 \qquad K_{H_2O}^{go} = \infty$$

← Water does not dissolve in oil

$$K_{C1}^{gw} = 467.5 \qquad K_{nC4}^{gw} = 1487 \qquad K_{H_2O}^{gw} = 0.029$$

Solution:

Gas phase

$$\tilde{n}_g = 0.6551$$

Oil phase

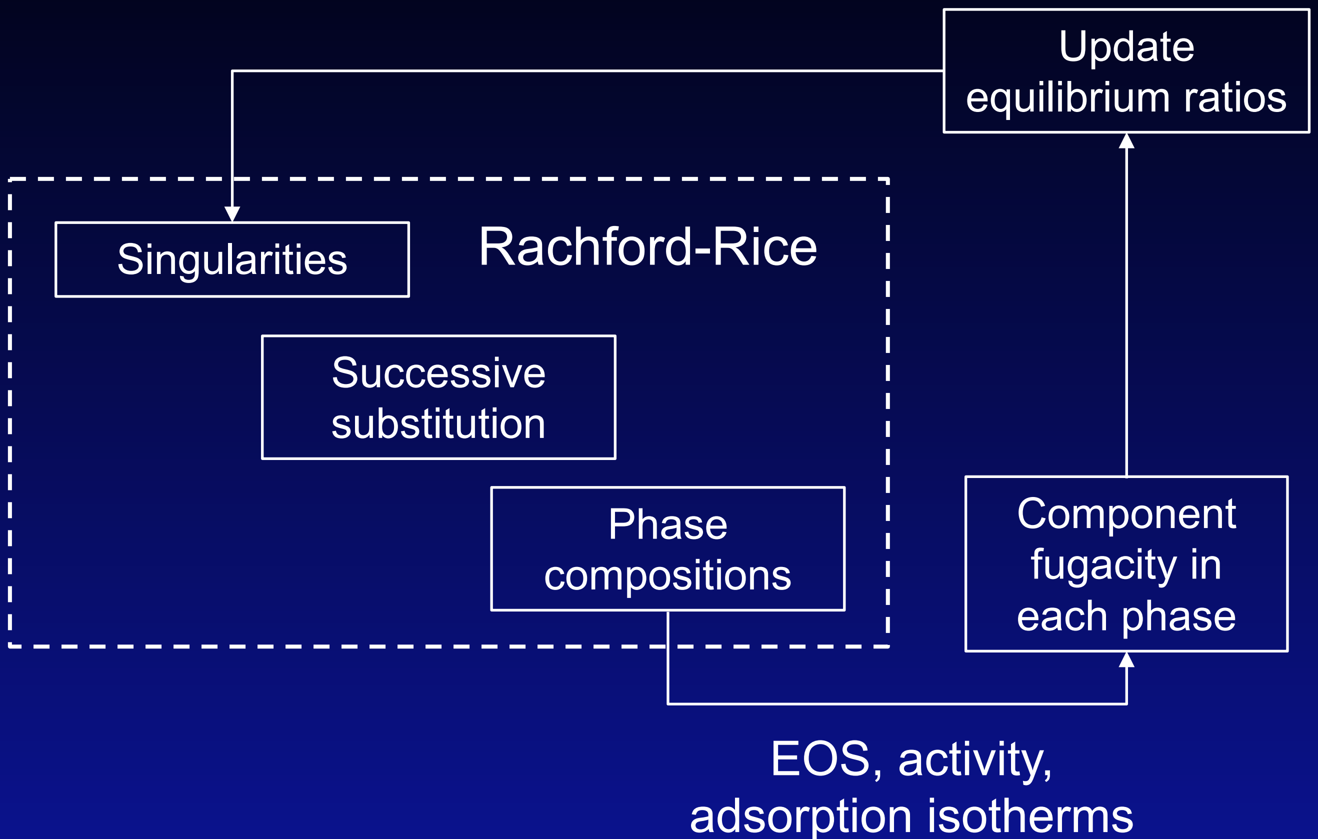
$$\tilde{n}_o = 0.3138$$

Water phase

$$\tilde{n}_w = 0.0331$$

← Water phase fraction increased

Incorporation of fugacity models



Work to do

- Look for a multi-component adsorption model
- Program and test the VLAE model

Some useful references

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