

EOS MODELS APPLIED TO MIXTURES

- For pure component EOS calculation, physical properties needed are

$$\left. \begin{array}{l} \circ T_c \\ \circ P_c \\ \circ \omega \text{ (acentric factor)} \end{array} \right\} \begin{array}{l} a = f(T_c, P_c, \omega) \\ b = f(T_c, P_c) \end{array}$$

- Both Peng Robinson and SRK EOS are equally good in doing thermodynamic calculations of pure components/compounds.

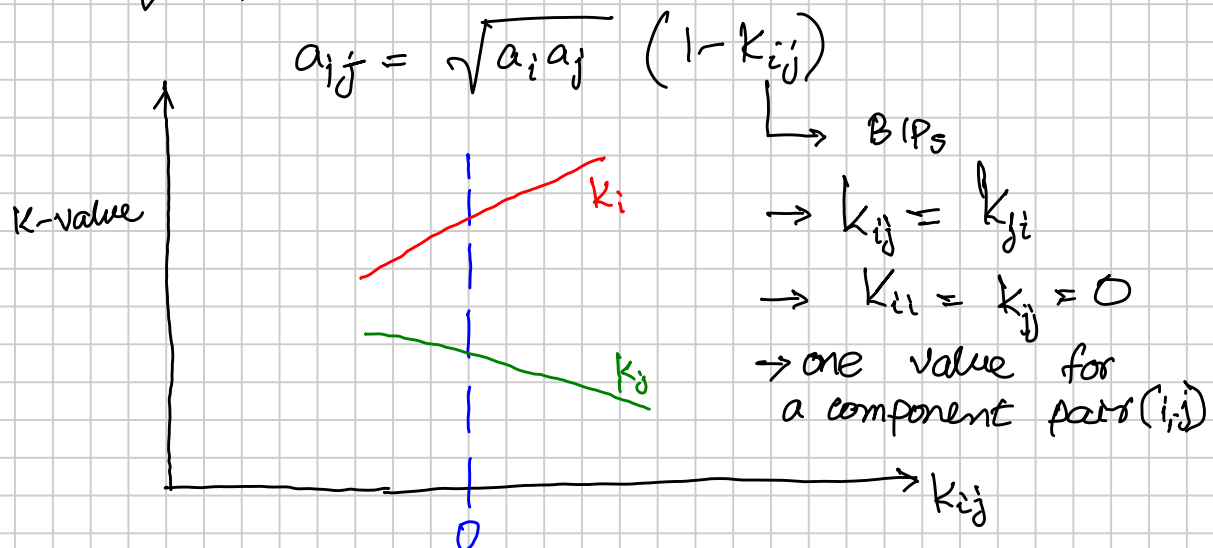
- For mixtures, average \bar{a} and \bar{b} are calculated knowing the composition u_i .

$$\bar{a} = \sum \sum u_i u_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}$$

$$\bar{b} = \sum u_i b_i$$

- EOS models for mixtures need additional correction term for improved phase behavior prediction called Binary Interaction parameters (BIPs) or (BICs) at high pressures.
- BIPs mainly affects K -values at high pressures.



Workflow for EOS Calculation:

Requirements for EOS calculations:

- (a) Component physical properties
 - (b) Binary interaction parameters
 - (c) Composition
- } EOS

Steps in EOS calculations:

- (1) Estimate of K_i (Wilson correlation, stability test)
- (2) Perform Rachford Rice flash calculation
 - x_i, y_i
 - n_v, n_l
- (3) use x_i, y_i to calculate \bar{a}_i, \bar{b}_l and \bar{a}_v, \bar{b}_v
- (4) calculate v_l & v_v from cubic EOS.
- (5) Calculate μ_{iv} & μ_{il}
- (6) check $\mu_{iv} = \mu_{il}$
- (7) if $\mu_{iv} \neq \mu_{il}$, update K_i & repeat steps 1-6
 - o Successive Substitution method
 - o GDEM (General Dominant Eigenvalue method).

⑧ If $M_{lv} = M_{vz}$ Calc. total system energy

$$g_{mix} = F_V g_V + (1-F_V) g_L \quad ; \quad F_V = \frac{n_V}{n_T}$$

$$g_L = \sum n_{Li} M_{Li}$$

$$g_V = \sum n_{Vi} M_{Vi}$$

⑨ Perform 1-8 with other sets of v_L & v_V

↳ Cubic EOS gives three roots

of v_L and v_V ($v_{L1}, v_{L2}, v_{L3}, v_{V1}, v_{V2}, v_{V3}$)

always discard v_{L2} and v_{V2} .

→ Be consistent with one root path until soln converges.

⑩ Choose v_L and v_V giving minimum

$$g_{mix}$$

⑪ Calculate total system energy as single phase

$$g_z = \sum n_i M_{zi} \quad \text{where } M_{zi} = f(z_i, \bar{a}, \bar{b})$$

⑫ If $g_{mix} < g_z$: Solution stable as two phases

$g_{mix} = g_z$: total system is at Psat

$g_{mix} > g_z$: total system exists as single phase (true flash)

⑬ Calculate :

$$V_L = n_L v_L \quad \& \quad V_V = n_V v_V$$

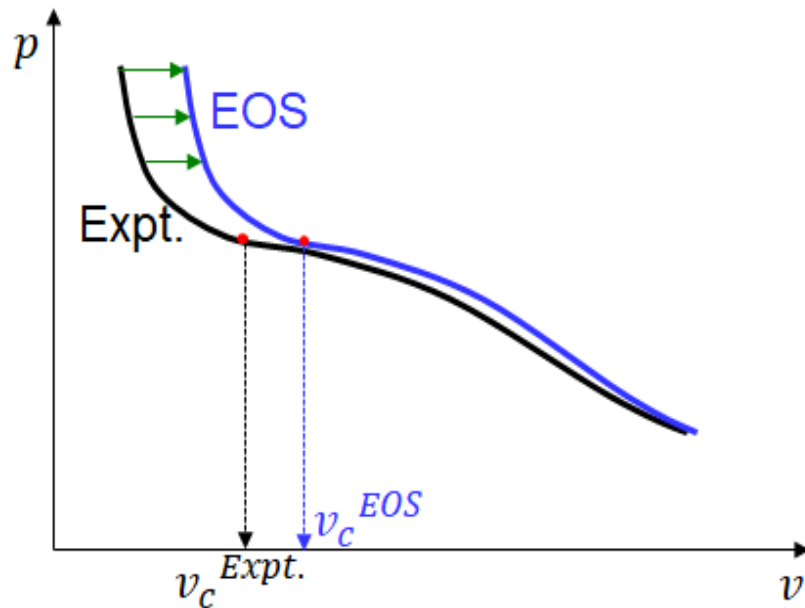
$$M_L = \sum x_i M_i \quad \& \quad M_V = \sum y_i M_i$$

$$m_L = M_L n_L \quad \& \quad m_V = M_V n_V$$

$$L_L = \frac{m_L}{V_L} \quad \& \quad L_V = \frac{m_V}{V_V}$$

→ Third parameter in cubic EOS

- liquid densities with two parameter EOS are underpredicted
- vapor liquid equilibrium calculations are all good (e.g. vapor pressure, equilibrium phase compositions, phase amounts in moles)



- Need an additional parameter in cubic EOS to provide reasonable densities (molar volumes)
- Peneloux et al provided a remarkable way to introduce third constant that only affect densities / molar volumes without affecting VLE calculation.

$$v^{(3)} = v^{(2)} - c$$

So,

$$\left. \begin{aligned} v_L^{(3)} &= v_L^{(2)} - c_L \\ v_V^{(3)} &= v_V^{(2)} - c_V \end{aligned} \right\} \begin{aligned} c_L &= \sum c_i x_i \\ c_V &= \sum c_i y_i \end{aligned}$$

CONCLUSION FROM PHAZECOMP CALCS

① SRK without BIPs & volume shifts

② Equilibrium K_i, y_i, x_i, n_v, n_l at low pressure (14.7 psia & 60°F) are similar to flash calc results from Wilson correlation K -values.

↳ K_i estimate from Wilson correlation is very good approximation at low pressure for thermodynamic equilibrium calculation i.e. $f_{li} \approx f_{vi}$. With this estimate of K_i , equilibrium condition of $f_{li} = f_{vi}$ can be reached in very small number of iterations.

→ This is usually the case because at low pressure:

- $K_i = f(P_{vi}) \rightarrow$ independent of z_i
- $P_{vi} = f(T_{bi}, T_{ci}, P_{ci}, T)$
- T_{bi}, T_{ci}, P_{ci} are well known for components upto C_6 .
- C_7+ fractions are usually negligible in gases at low pressure and K -values are small & negligible.
- properties of lighter HC are the same no matter what type of HC is there and which part of the world is
- So, K_i are mainly function of p & T at low pressure
- Therefore correlations do work at low pressures to provide very good estimate of K_i

(b) moles of each phase at low pressure are accurate from ^{two param} EOS and also x_i & y_i but k values are accurate as K_i is mainly function of p & T .

(c) Oil densities are very poor (under predicted) and so does volumes calculated from moles are wrong and thusGOR.

(d) P_{sat} prediction at $236^\circ F$ is off from given value. Also the k -values and incipient phase composition are different from Wilson K_i . P_{sat} calculation results
↳ K_i at high pressures needs to be modified in EOS to match P_{sat}
→ one should not expect K_i to be similar as Wilson K_i at high pressures.

② SRK without BIP but with volume shifts

(a) Adding volume shifts only affect densities and not vapor liquid equilibrium calculations (K_i, y_i, x_i, F_i)

(b) with volume shifts, liquid densities are accurate and so does GOR.

③ SRK with BPs and volume shifts:

→ P_{sat} match

→ Minimal effect on K_i of low pressures (similar phase compositions, phase amounts and densities compared to NO BPs)

→ High pressure K_i is altered and thus the incipient phase composition

→ Comparing K_i at 3100 psia & 226°F with and without BPs show that having positive BPs b/w C_1 and heavies (F_1, F_2 & F_3),

$$K_{C_1} \uparrow, K_{F_1} \downarrow, K_{F_2} \downarrow, K_{F_3} \downarrow$$

→ with P_{sat} match; K_i and incipient phase compositions are different from Wilson results

↳ Correlations do not provide good estimate of K_i at high pressures due to strong dependence of K_i on z_i

→ starting with Wilson K_i , we need more iterations ^{at high pressures} before K_i converges to a value and satisfy $z_i = f_i$ compared to low pressure

④ PR with BPs and VS

Ⓐ very similar results compared to SRK

Ⓑ Both SRK and PR are equally good when 'VS' and appropriate BPs are used for mixture phase behavior and

volumetric calculations