

Chemical Engineering Thermodynamics

A Brief Review

“Rate” vs. “State”

- Thermodynamics tells us how things “end up” (state) but not how (or how fast) they “get there” (rate)
- Limitations on getting to equilibrium:
 - Transport (mixing): diffusion, convection
 - ▶ example: why doesn't more of the ocean evaporate to make higher humidity in the deserts? (heat transfer alters dew point locally, atmospheric mixing limitations, etc.)
 - Kinetics (reaction): the rate at which reactions occur are too slow to get to equilibrium
 - ▶ example: chemical equilibrium says trees (and our bodies) should become CO_2 and H_2O (react with air)
 - ▶ example: chemical equilibrium says diamonds should be graphite (or CO_2 if in air)
- Sometimes, mixing & reaction are sufficiently fast that equilibrium assumptions are “good enough.”
 - if we assume that we can use thermodynamics to obtain the state of the system, we avoid a lot of complexity.
 - ▶ do it if it is “good enough!”
 - Most unit operations (e.g. distillation) assume phase equilibrium, ignoring transport limitations.
 - ▶ good enough if things are mixed well and have reasonable residence/contact times.

Some Terminology...

“Partial Molar” property $\bar{\mathcal{M}}_i \equiv \left(\frac{\partial N \mathcal{M}}{\partial N_i} \right)_{T,P,N_j}$

change in \mathcal{M} due to adding a differential amount of species i . For ideal mixtures, $\bar{\mathcal{M}}_i = \mathcal{M}_i$

\mathcal{M} - arbitrary thermodynamic property (per mole)

N_i - moles of species i

y_i - mole fraction of species i (liquid or gas)

$$\mathcal{M} = \sum_{i=1}^C y_i \bar{\mathcal{M}}_i$$

Gibbs-Duhem Equation: $\left(\frac{\partial \mathcal{M}}{\partial P} \right)_{T,y} dP + \left(\frac{\partial \mathcal{M}}{\partial T} \right)_{P,y} dT - \sum_{i=1}^C y_i d\bar{\mathcal{M}}_i = 0$

Note at constant T and P , $\sum_{i=1}^C y_i d\bar{\mathcal{M}}_i = 0$

“Residual” property $\mathcal{M}^R \equiv \mathcal{M} - \mathcal{M}^{ig}$

how much \mathcal{M} deviates from the ideal gas (\mathcal{M}^{ig}) behavior.

$$\mathcal{M}^{ig} = \sum_{i=1}^C y_i \mathcal{M}_i^{ig}$$

“Excess” property $\mathcal{M}^E \equiv \mathcal{M} - \mathcal{M}^{ideal}$

how much \mathcal{M} deviates from the ideal solution behavior.

$$\mathcal{M}^{ideal} = \sum_{i=1}^C y_i \mathcal{M}_i$$

Phase Equilibrium

Gibbs Energy

(thermodynamic property)

$$G = G(T, P, N_1, N_2, \dots, N_C)$$

Phase Equilibrium is achieved when G is minimized.

$$dG = -S dT + V dP + \sum_{i=1}^C \left(\frac{\partial G}{\partial N_i} \right)_{P,T,N_j} dN_i$$

Chemical Potential
(thermodynamic property,
partial molar Gibbs energy)

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i} \right)_{P,T,N_j}$$

For multiple phases in a closed system,

$$G_{\text{system}} = \sum_{p=1}^N G^{(p)}$$

$$dG_{\text{system}} = \sum_{p=1}^N dG^{(p)}$$

In phase equilibrium,

$$T^{(1)} = T^{(2)} = \dots = T^{(N)}$$

$$P^{(1)} = P^{(2)} = \dots = P^{(N)}$$

$$dG_{\text{system}} = \sum_{p=1}^N \left[\sum_{i=1}^C \mu_i^{(p)} dN_i^{(p)} \right]_{T,P}$$

For a nonreacting system, moles are conserved.

$$\sum_{p=1}^N dN_i^{(p)} = 0 \Rightarrow dN_i^{(1)} = - \sum_{p=2}^N dN_i^{(p)}$$

$$dG_{\text{system}} = \sum_{p=2}^N \left[\sum_{i=1}^C (\mu_i^{(p)} - \mu_i^{(1)}) dN_i^{(p)} \right]_{T,P}$$

To minimize G , $dG=0$. But each term in the summation for dG is independent, so each must be zero.

$$\mu_i^{(p)} = \mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(N)}$$

For phase equilibrium, the chemical potential of any species is equal in all phases.

Problem:

$$\mu_i \rightarrow -\infty \text{ as } P \rightarrow 0$$

Solution: Partial Fugacity

$$\bar{f}_i = C \exp \left(\frac{\mu_i}{RT} \right)$$

C is a temperature-dependent constant.

For phase equilibrium, the fugacity of any species is equal in all phases.

$$\bar{f}_i^{(p)} = \bar{f}_i^{(1)} = \bar{f}_i^{(2)} = \dots = \bar{f}_i^{(N)}$$

Chemical Potential, Fugacity, Activity

Thermodynamic Quantity	Definition	Description	Limiting case of ideal gas and ideal solution
Chemical potential	$\mu_i \equiv \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_j}$	Partial molar free energy, \bar{g}_i	$\mu_i = \bar{g}_i$
Partial fugacity	$\bar{f}_i = C \exp(\mu_i/(RT))$	Thermodynamic pressure	$\bar{f}_{iV} = y_i P$
Fugacity coefficient of a pure species	$\phi_i \equiv f_i/P$ $\bar{f}_i = f_i$ for a pure species	Deviation of fugacity due to pressure	$\phi_{iV} = 1.0$ $\phi_{iL} = P_i^s/P$
Fugacity coefficient of a species in a mixture	$\bar{\phi}_{iV} \equiv \bar{f}_{iV}/(y_i P)$ $\bar{\phi}_{iL} \equiv \bar{f}_{iL}/(x_i P)$	Deviations to fugacity due to pressure and composition	$\bar{\phi}_{iV} = 1.0$ $\bar{\phi}_{iL} = P_i^s/P$
Activity	$a_i \equiv \bar{f}_i/f_i^o$	Relative thermodynamic pressure	$a_{iV} = y_i$ $a_{iL} = x_i$
Activity coefficient	$\gamma_{iV} \equiv a_{iV}/y_i$ $\gamma_{iL} \equiv a_{iL}/x_i$	Deviation of fugacity due to composition.	$\gamma_{iV} = 1.0$ $\gamma_{iL} = 1.0$

For phase equilibrium, the **chemical potential, fugacity, activity** (but not activity coefficient or fugacity coefficient) of any species is equal in all phases.

P_i^s vapor pressure of species i .

y_i vapor mole fraction of species i .

x_i liquid mole fraction of species i .

$$\begin{aligned} \bar{f}_{iL} &= \bar{\phi}_{iL} x_i P & \bar{f}_{iV} &= \bar{\phi}_{iV} y_i P \\ &= \gamma_{iL} x_i f_{iL}^o & &= \gamma_{iV} y_i f_{iV}^o \end{aligned}$$

$$\bar{f}_{iL} = \bar{f}_{iV} \Rightarrow \frac{y_i}{x_i} = \frac{\bar{\phi}_{iL}}{\bar{\phi}_{iV}} \quad \text{we will use this on the next slide...}$$

Phase Equilibrium - K -Values

Phase equilibrium ratio:

How much species i is enriched in the vapor

$$K_i \equiv \frac{y_i}{x_i}$$

Relative volatility:

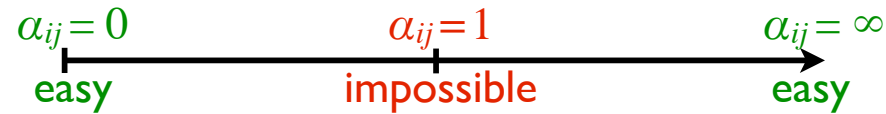
$$\alpha_{ij} \equiv \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j}$$

Note: liquid-liquid case equivalent is the “relative selectivity” β_{ij} .

$$\beta_{ij} \equiv \frac{K_{D_i}}{K_{D_j}}$$

Note: liquid-liquid case equivalent is the “partition coefficient”

$$K_{D_i} \equiv x_i^{(1)} / x_i^{(2)}$$



Solve for y_i/x_i from the previous slide:

$$K_i \equiv \frac{y_i}{x_i} = \frac{\bar{\phi}_{iL}}{\bar{\phi}_{iV}} = \frac{\gamma_{iL} f_{iL}^o}{\phi_{iV} P} = \frac{\gamma_{iL} \phi_{iL}}{\phi_{iV}}$$

Concept: determine K_i from thermodynamic models. This gives us y_i/x_i .

	Equation	Application
Rigorous forms		
Equation of state	$K_i = \bar{\phi}_{iL} / \bar{\phi}_{iV}$	Benedict-Webb-Rubin-Starling, SRK, PR equations of state, Hydrocarbon and light gas mixtures from cryogenic to critical
Activity coefficient	$K_i = \gamma_{iL} \phi_{iL} / \bar{\phi}_{iV}$	All mixtures from ambient to near critical.
Approximate forms		
Raoult's law (ideal)	$K_i = P_i^s / P$	Ideal solutions at low pressures
Modified Raoult's law	$K_i = \gamma_{iL} P_i^s / P$	Nonideal liquid solutions near ambient pressure
Poynting correction	$K_i = \gamma_{iL} \phi_{iV}^s \left(\frac{P_i^s}{P} \right) \exp \left(\frac{1}{RT} \right) \int_{P_i^s}^P v_{iL} dP$	Nonideal liquid solutions at moderate pressures and below T_c
Henry's law	$K_i = \frac{H_i}{P}$	Low to moderate pressures for species above T_c

Mix & match for different species in a mixture

Example: Raoult's Law (Ideal Mixtures)

Raoult's law: $K_i = \frac{P_i^s}{P}$

Need: P_i^s - saturation pressure for each species

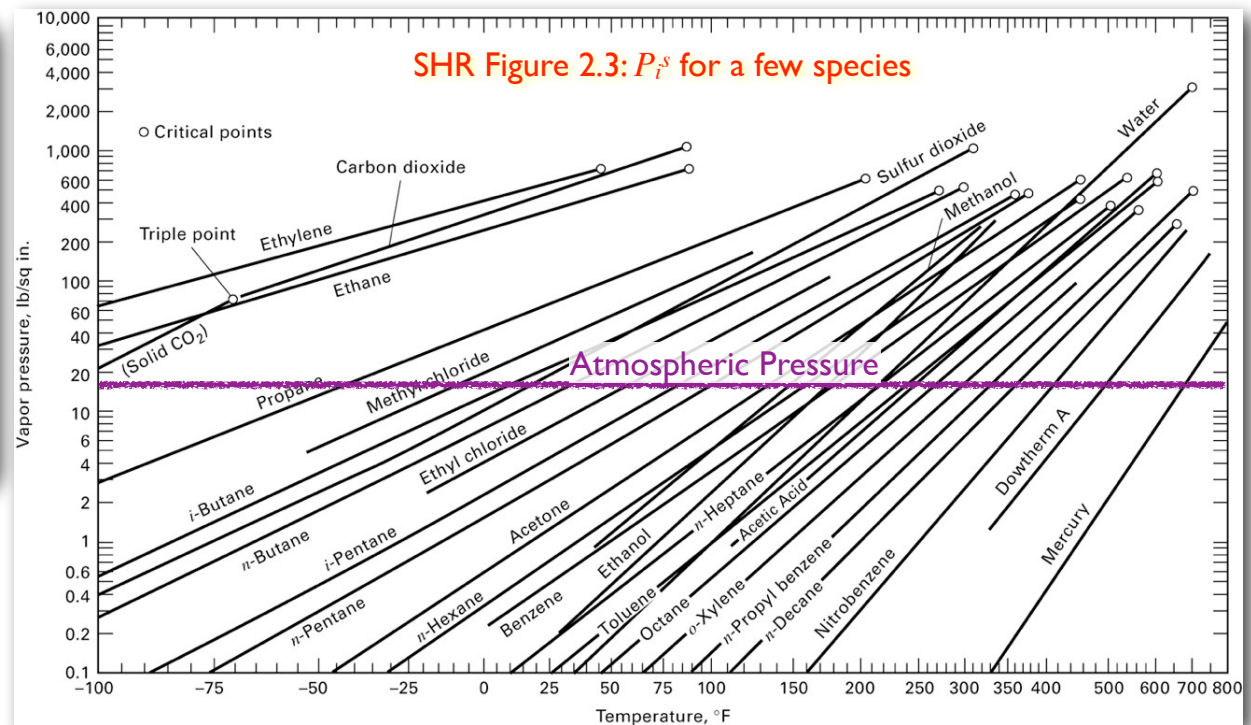
Antoine equation: $\log_{10} P_i^s = A - \frac{B}{C + T}$

Derivation of Raoult's Law:

$p_i = x_i P_i^s$ partial pressure is the weighted saturation pressure (ideal liquid mixture)

$p_i = y_i P$ Dalton's law (ideal mixture of gases)

combine to find $\frac{y_i}{x_i} = \frac{P_i^s}{P} = K_i$



Modified Raoult's law: $K_i = \gamma_i \frac{P_i^s}{P}$

For Raoult's law, K_i is independent of composition, but varies exponentially with temperature!

Liquid-Phase Activity Coefficients

Wilson 2-parameter model for mixtures:

$$\ln \gamma_k = 1 - \ln \left(\sum_{j=1}^C x_j \Lambda_{kj} \right) - \sum_{i=1}^C \left(\frac{x_i \Lambda_{ik}}{\sum_{j=1}^C x_j \Lambda_{ij}} \right)$$

For a binary system:

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} + \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right)$$

$$\Lambda_{ij} = \frac{v_{jL}}{v_{iL}} \exp \left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right]$$

$$\lambda_{ij} = \lambda_{ji} \quad \Lambda_{ij} \neq \Lambda_{ji}$$

$$\lambda_{ii} = \lambda_{jj} \quad \Lambda_{ii} = 1$$

- λ_{ij} are functions of temperature but not composition
- $\Lambda_{ij} = \Lambda_{ji} = 1$ implies ideal solution ($\gamma_i = \gamma_j = 1$)

Parameters λ_{ij} or Λ_{ij} are typically determined from experimental data via regression.

Alternatively, if we can obtain γ at infinite dilution,

$$\begin{aligned} \ln \gamma_1^\infty &= 1 - \ln \Lambda_{12} - \Lambda_{21} \\ \ln \gamma_2^\infty &= 1 - \ln \Lambda_{21} - \Lambda_{12} \end{aligned} \quad \begin{array}{l} 2 \text{ equations,} \\ 2 \text{ unknowns} \end{array}$$

Less accurate than regression.

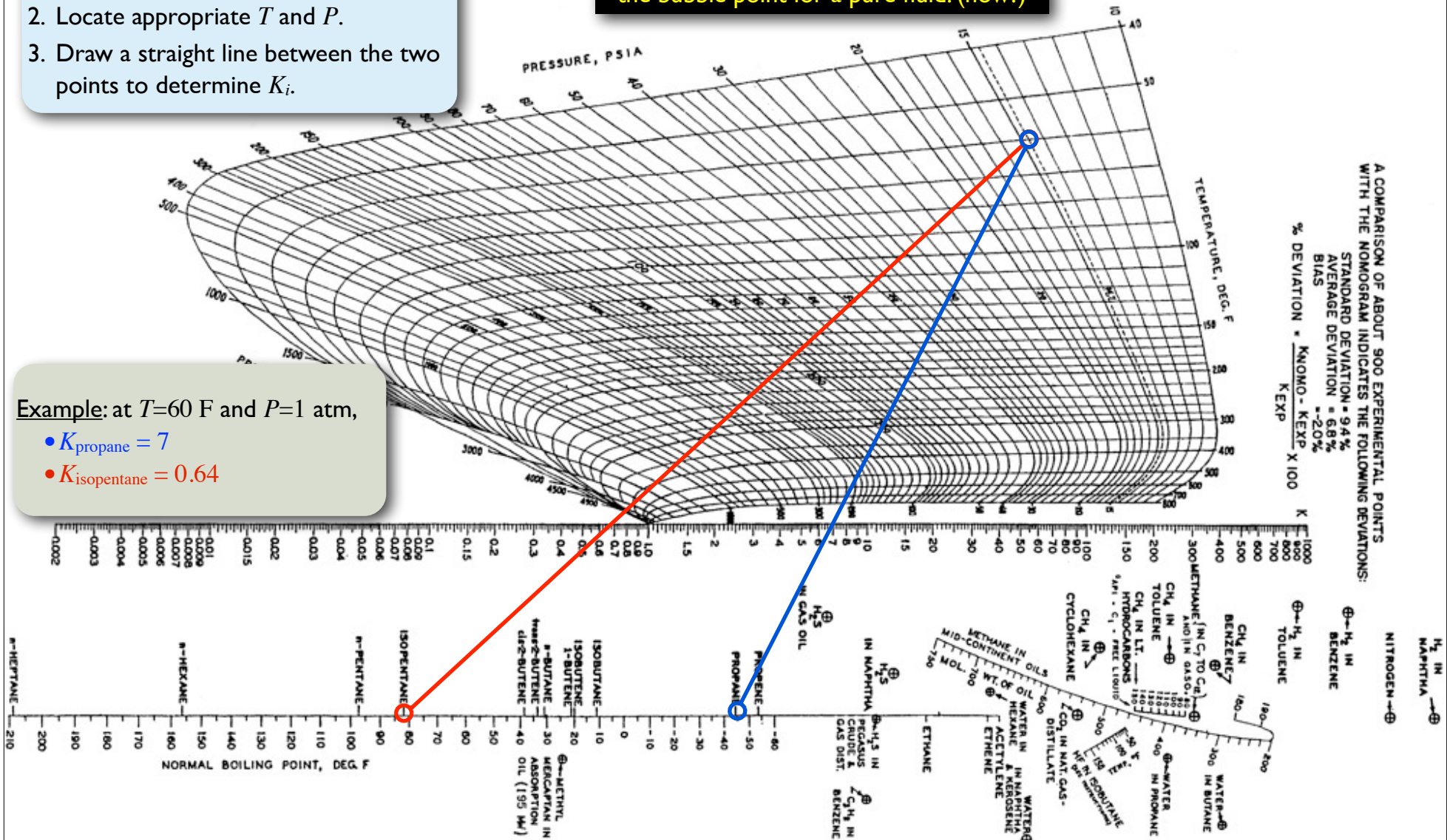
Example: Graphical Methods

1. Locate appropriate species /mixture
2. Locate appropriate T and P .
3. Draw a straight line between the two points to determine K_i .

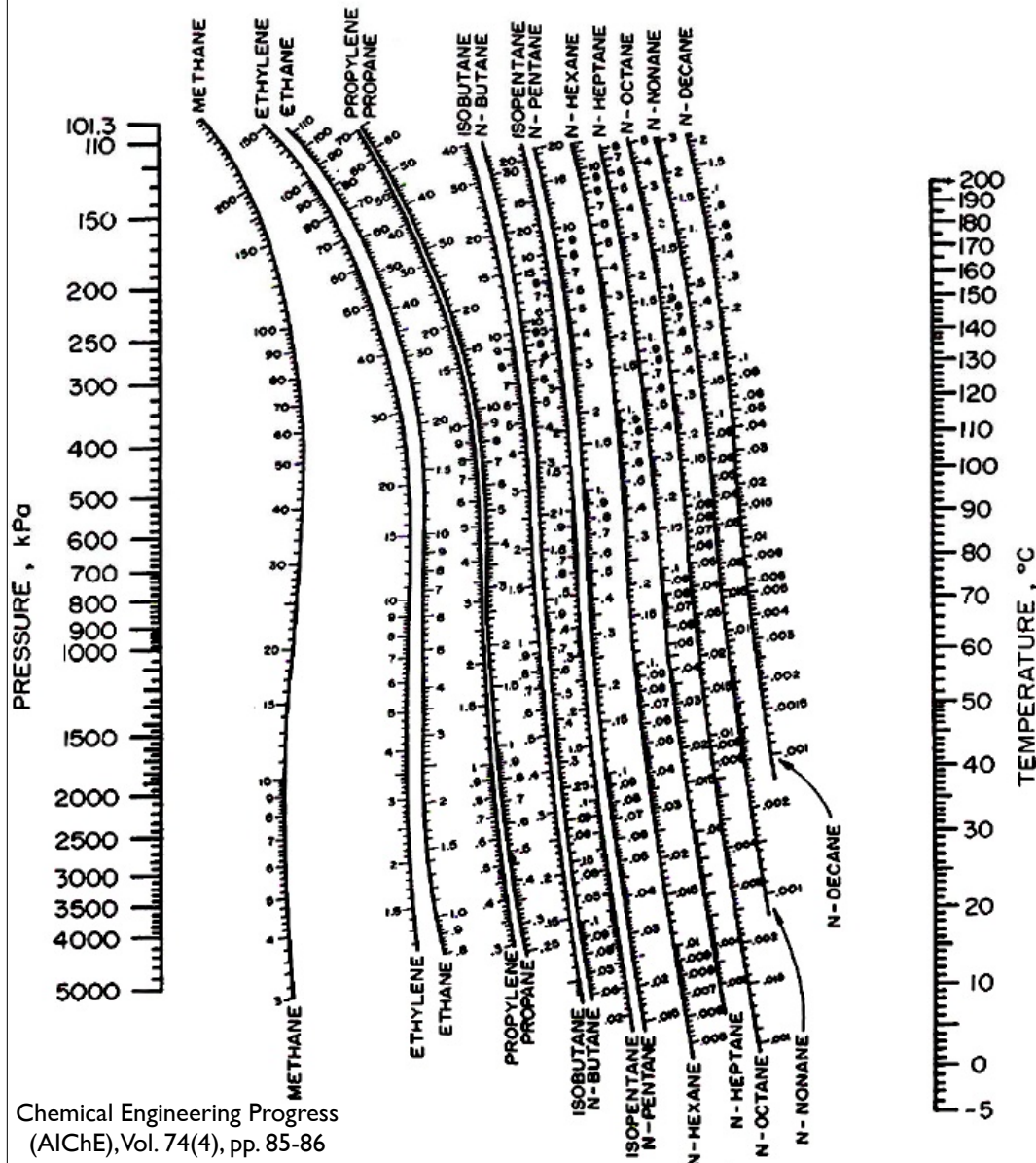
NOTE: this can also be used to estimate the bubble point for a pure fluid. (how?)

Example: at $T=60$ F and $P=1$ atm,

- $K_{\text{propane}} = 7$
- $K_{\text{isopentane}} = 0.64$



DePriester Chart



Empirical Correlation:

$$\ln K = \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + b_1 \ln p + \frac{b_2}{p^2} + \frac{b_3}{p}$$

NOTE: T in $^{\circ}R$ and p in psia!

Compound	a	a	a	b	b	b
Methane	-292,860	0	8.2445	-0.8951	59.8465	0
Ethylene	-600,076.875	0	7.90595	-0.84677	42.94594	0
Ethane	-687,248.25	0	7.90694	-0.886	49.02654	0
Propylene	-923,484.6875	0	7.71725	-0.87871	47.67624	0
Propane	-970,688.5625	0	7.15059	-0.76984	0	6.90224
Isobutane	-1,166,846	0	7.72668	-0.92213	0	0
n-Butane	-1,280,557	0	7.94986	-0.96455	0	0
Isopentane	-1,481,583	0	7.58071	-0.93159	0	0
n-Pentane	-1,524,891	0	7.33129	-0.89143	0	0
n-Hexane	-1,778,901	0	6.96783	-0.84634	0	0

M. L. McWilliams, Chemical Engineering, 80(25), 1973 p. 138.

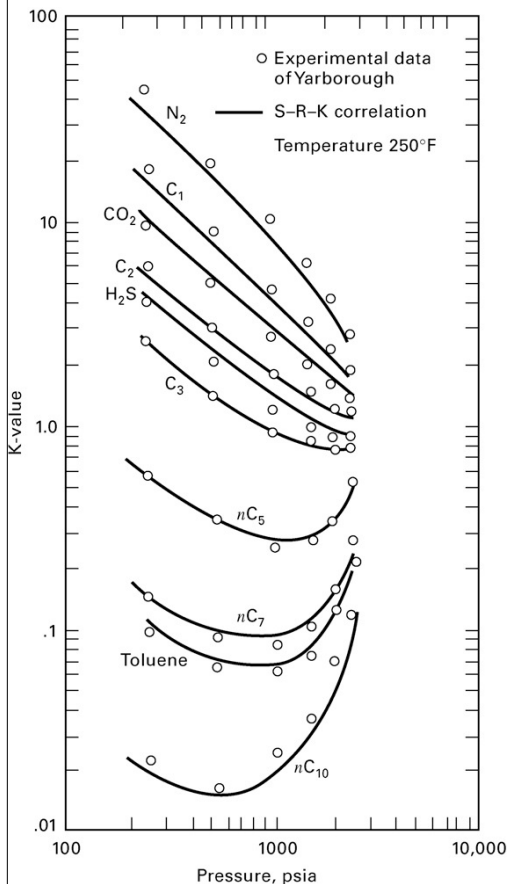
Thermo from Equations of State

fugacity coefficient $\phi_V = \exp \left[\frac{1}{RT} \int_0^P \left(v - \frac{RT}{P} \right) dP \right]$

vapor $= \exp \left[\frac{1}{RT} \int_v^\infty \left(P - \frac{RT}{v} \right) dv - \ln Z + Z - 1 \right]$

partial fugacity coefficient $\bar{\phi}_{iV} = \exp \left\{ \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_j} - \frac{RT}{V} \right] dV - \ln Z \right\}$

$V = v \sum_{i=1}^C N_i$ volume



$$K_i \equiv \frac{y_i}{x_i} = \frac{\bar{\phi}_{iL}}{\bar{\phi}_{iV}}$$

R-K:

$$b_i = 0.08664 \frac{RT_{i,c}}{P_{i,c}}$$

$$a_i = 0.42748 \frac{R^2 T_{i,c}^{2.5}}{P_{i,c} T^{0.5}}$$

For Redlich-Kwong (and S-R-K) EOS:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + bv} \quad A = \frac{aP}{R^2 T^2} \quad B = \frac{bP}{RT}$$

mixing rules: $a = \sum_{i=1}^C \left[\sum_{j=1}^C y_i y_j \sqrt{a_i a_j} \right]$ $b = \sum_{i=1}^C y_i b_i$

$$h = \sum_{i=1}^C (y_i h_i^o) + RT \left[Z - 1 - \frac{3A}{2B} \ln \left(1 + \frac{B}{Z} \right) \right]$$

$$\phi = \exp \left[Z - 1 - \ln(Z - B) - \frac{A}{B} \ln \left(1 + \frac{B}{Z} \right) \right]$$

$$\bar{\phi}_i = \exp \left[(Z - 1) \frac{B_i}{B} - \ln(Z - B) - \frac{A}{B} \left(2\sqrt{\frac{A_i}{A}} - \frac{B_i}{B} \right) \ln \left(1 + \frac{B}{Z} \right) \right]$$

Note that these can be used in vapor or liquid phases, by using appropriate values for Z , and using appropriate phase mole fractions (y_i for vapor, x_i for liquid) (because cubic EOS can approximate two-phase behavior.)

S-R-K (much better):

$$b_i = 0.08664 \frac{RT_{i,c}}{P_{i,c}}$$

$$a_i = 0.42748 \frac{R^2 T_{i,c}^2 [1 + f_\omega (1 - T_{i,r}^{0.5})]^2}{P_{i,c}}$$

$$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2 \quad \omega - \text{acentric factor}$$

Example: K -Values from SRK

Given a mixture of propane ($x=0.0166, y=0.3656$) and benzene ($x=0.9834, y=0.6344$) at 300 K & 1 atm, find the K -value using SRK.

Redlich-Kwong (&SRK) parameters

	Propane	Benzene
T	369.8	562.2
P	4250	4890
ω	0.149	0.209

Requires x_i, y_i .
This is a problem since we typically need K_i to determine this ratio!

This is typically used within another solver to determine x_i, y_i (more soon).

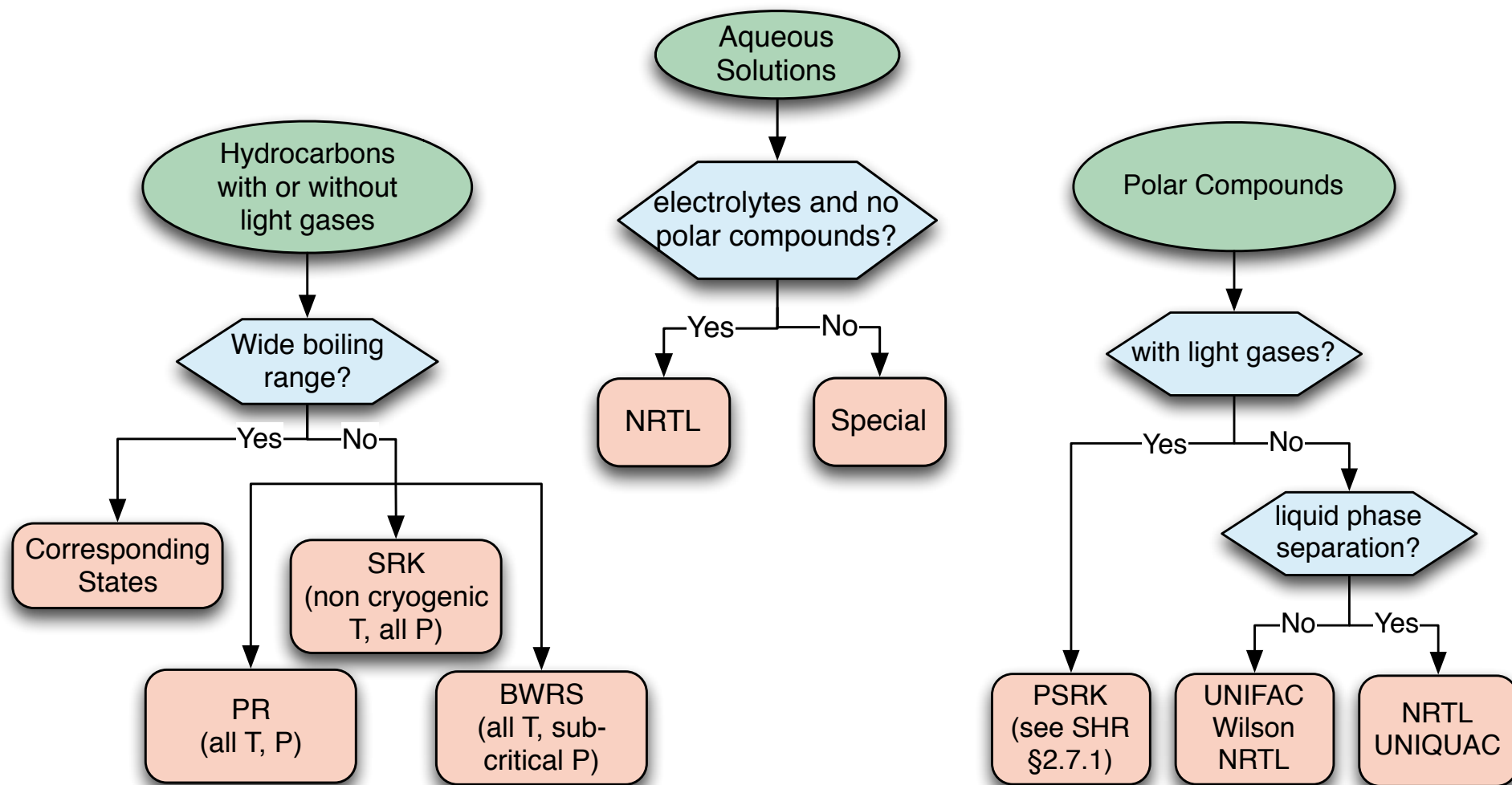
$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$\bar{\phi}_i = \exp \left[(Z - 1) \frac{B_i}{B} - \ln(Z - B) - \frac{A}{B} \left(2\sqrt{\frac{A_i}{A}} - \frac{B_i}{B} \right) \ln \left(1 + \frac{B}{Z} \right) \right]$$

$$K_i \equiv \frac{y_i}{x_i} = \frac{\bar{\phi}_{iL}}{\bar{\phi}_{iV}}$$

1. Calculate a_i, b_i and then A_i, B_i (tedious, but not difficult).
2. Calculate A and B using mixing rules.
3. Calculate Z in the vapor and liquid phases. This requires us to solve the cubic equation and pick the appropriate roots.
4. Calculate partial fugacity coefficient in vapor and liquid.
5. Calculate K_i .

Heuristics for Property Model Selection



See also <http://www.che.utah.edu/~sutherland/PropertySelection.pdf> for a much more extensive property selection flowchart from Professor Ring.