Lecture 7.2
Complex Phase Diagrams

O'Connell & Haile
Chapter 9.4-9.7

Topics:

- Solids in Phase Equilibria
- Classification of high pressure diagrams
- Ternary phase diagrams

Solid-liquid analogous to VL but little *P* effect
- **Compare Fig. 9.17ab with Fig. 9.15 - SLE~VLE**
- **Fig. 9.17cd not found with VLE**
- **Full diagram is combination of simpler plots**

Note pressure dependence SL(no) & VL(yes)

Phase boundaries from *Ttt* curve(Fig. 9.19)

Figure 9.17

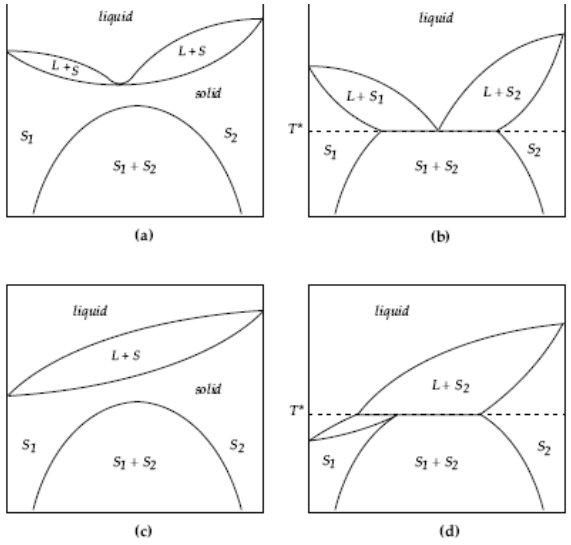
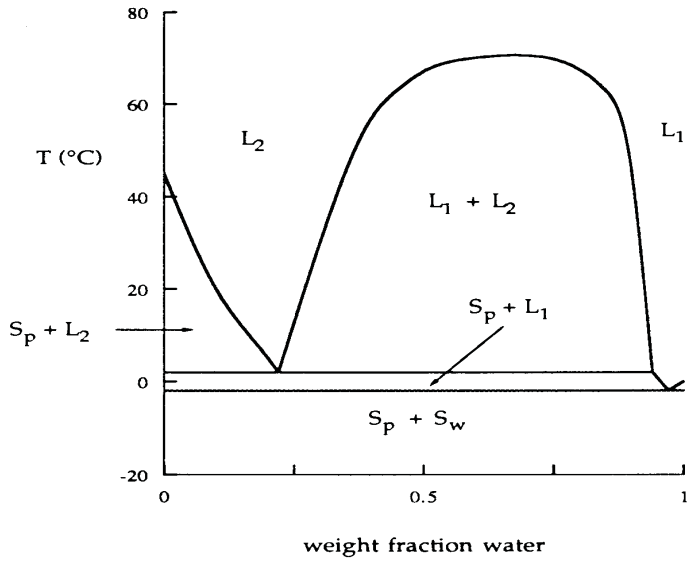


Figure 9.20



More extended example of Fig. 9.20

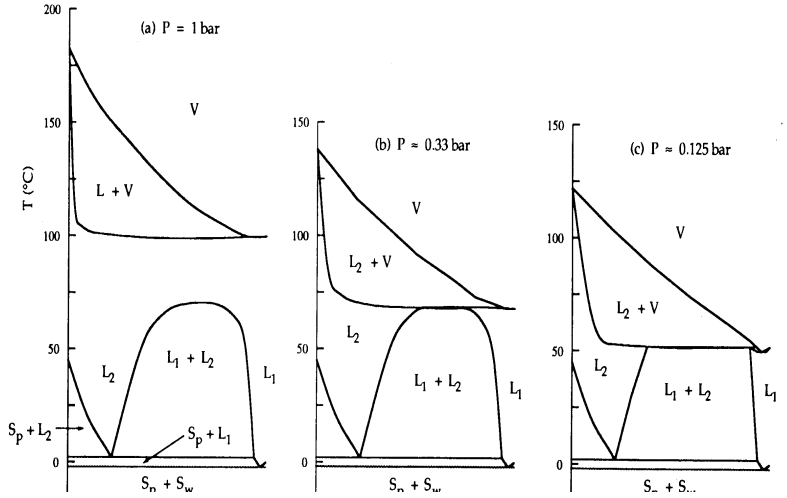
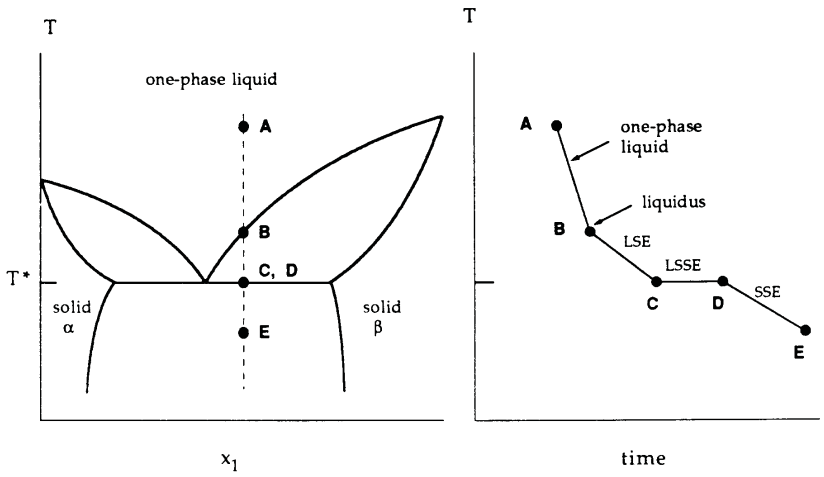


Figure 9.19



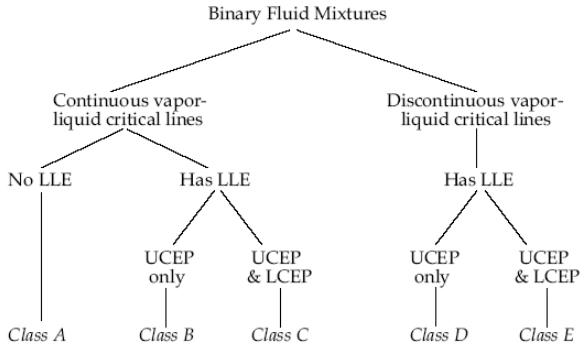
BINARY SYSTEMS AT HIGH PRESSURES I.

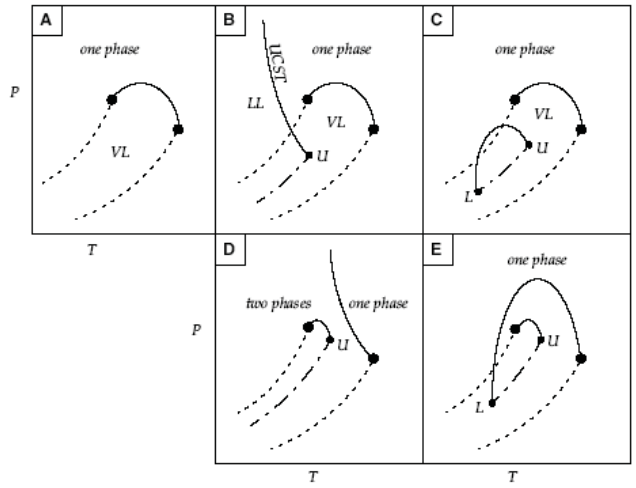
Nature's complexity requires classifications
Mostly with *PT* ($\mathcal{P}$) diagrams, especially for VLLE
Nomenclature in Fig. 9.21, cases in Fig. 9.22
Note: "discontinuous" = critical locus interrupted

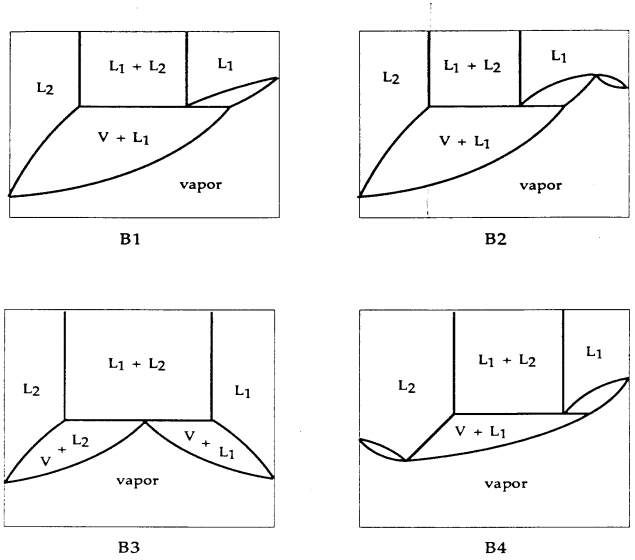
Class A - Varied critical loci & $T \gtrless T_c^{pure}$
Get "gas-gas" (GGE): 2 phases at $T > T_{c1}, T_{c2}$, $P > P_{c1}, P_{c2}$ Fig. 9.7, p. 381

Class B-VLLE-VL critical separate from LL critical

Class C-VLLE-VL critical differs-pair of LL criticals







BINARY SYSTEMS AT HIGH PRESSURES II.

Class D-VLLE-high *T* VL critical separate & low *T* VL critical "becomes" LL critical, Other GGE

Class E - VLLE - high *T* VL critical "becomes" LL critical, no low *T* VL critical

Evolution among classes by changing differences in MW (HC carbon #), polarity difference, etc. Fig.9.23

van der Waals EoS+mixing rules gets 4 classes

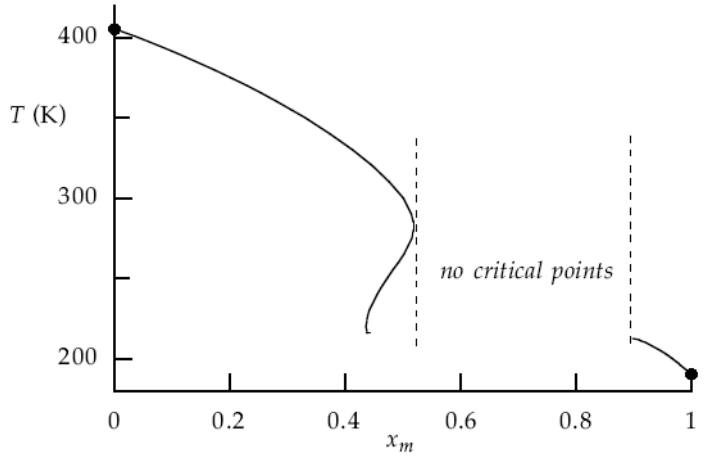
Not all compositions have critical point Fig.9.24

A → E1 → E2 → D

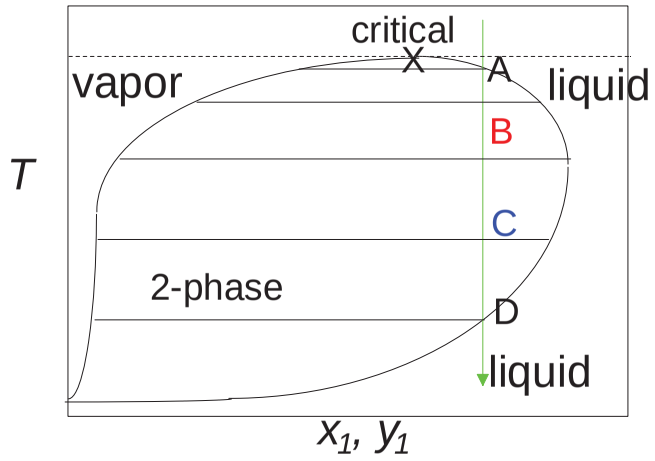
methane + propane	methane + n-hexane	methane + 1-hexene	methane + methylcyclo-pentane

A → B → D

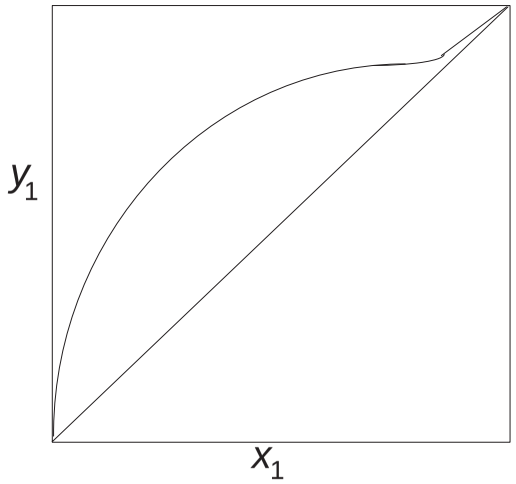
carbon dioxide + methane	carbon dioxide + n-octane	carbon dioxide + n-hexadecane
water + ethanol	water + phenol	water + benzene



Retrograde Behavior of 2-Phase Systems Near Criticals - As cool mixture, get A(bubble point), B (increasing vapor), C (decreasing vapor), D(bubble point)



Pinch Appears in *y-x* Plot Near Critical
High purity difficult to achieve



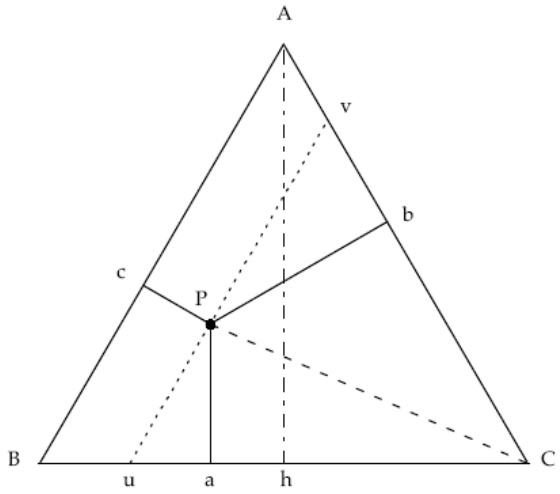
HIGHER MULTICOMPONENT SYSTEMS

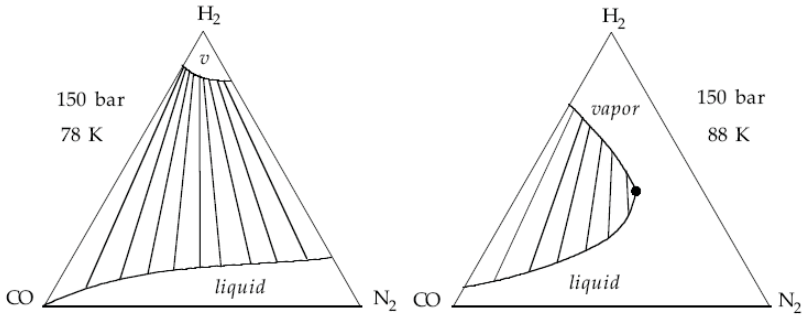
Ternaries: compositions at fixed *T*, *P* on triangle
Appendix H explains compositions
Note: Fig. 9.25ff are $\mathcal{F}$ ' diagrams, not $\mathcal{F}$

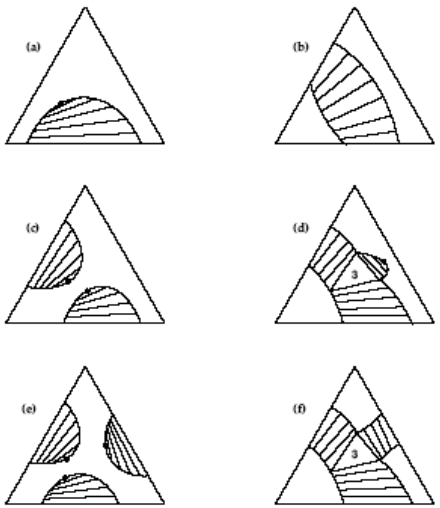
Analysis for phase behavior from vertices (pure) along edges (binaries) to interior (ternary)
Use 2-phase tie-lines, 3 phase tie-triangle
Fig. 9.26

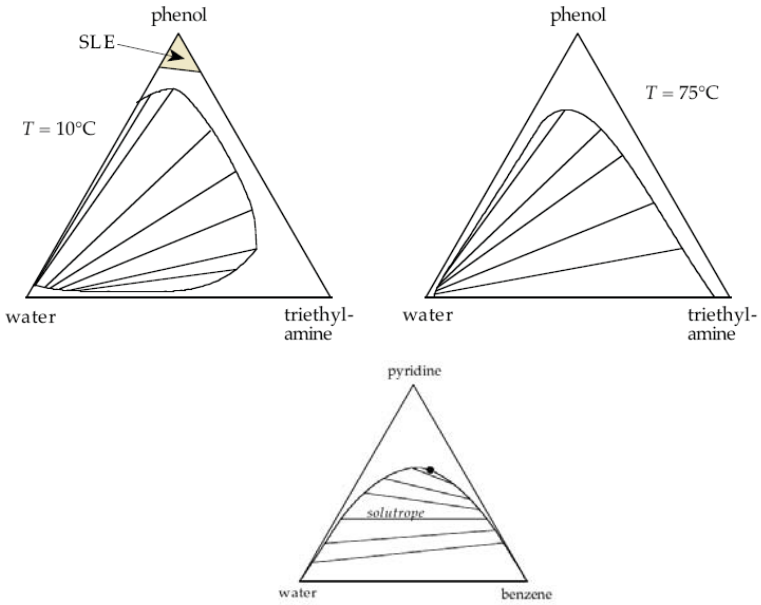
Special effects on pp. 409-10, (Fig. 9.27-8)

Study summary (Section 9.7)!!


A
v
b
c
P
B
u
a
h
C


H2
v
150 bar
78 K
liquid
CO
N2
H2
vapor
150 bar
88 K
liquid
CO
N2


(a)
(b)
(c)
(d)
3
(e)
(f)
3


phenol
SLE
T = 10°C
water
triethyl-
amine
phenol
T = 75°C
water
triethyl-
amine
pyridine
solutrope
water
benzene