Lecture 7.1
Independent Variables & Simple Phase Diagrams

O'Connell & Haile
Chapter 9.1-9.3

Topics:

- Independent Variables of State
- Pure component diagrams for measurables & conceptuals
- Binary VLE @ low pressure:
  - Simple & complex *Ptxy*, azeotropes
- Critical point criteria
- Binary LLE & VLLE

Note: Gives relative sizes / amounts of phases

If ignore relative sizes, get *Phase Rule*

$\mathcal{F} = \mathcal{F}' - (\mathcal{P} - 1) = C - \mathcal{P} + 2 - \mathcal{S}$

("Gibbs Phase Rule" if $\mathcal{S} = 0$) - Limitations!

Problem solving with phase diagrams

1. $\mathcal{F} \neq \mathcal{F}'$; Study Table 9.1 for $\mathcal{F}$ systems
2. Pure component cases: $\mathcal{P}$ from 1 - 3 so minimum $\mathcal{F} = 0$ via $\mathcal{P} = 3$ or via 1 critical phase & 2 mechanical stability constraints
3. Nonuniqueness from nonmonotonic behavior or "indifference" (too few variables or coupled properties like azeotrope - Study p. 371 cases)

MULTIPHASE SYSTEMS I. STATE

Like Chapter 3, extensive state of $\mathcal{C}$ components, *changed* by manipulating $\mathcal{V}_{ext}$ variables constrained by $\mathcal{S}_{ex}$ "external" constraints, that for closed system ($\mathcal{S}_{ex} = \mathcal{C}$ via MB) gives

$\mathcal{V}_{ext} = \mathcal{C} + 2 - \mathcal{S}_{ex} = \mathcal{C} + 2$

Same as for single phase! Duhem's Theorem

State *Identified* via $\mathcal{F}_{ext}$ variables with $\mathcal{S}$ "special" constraints(beyond phase, reaction equilibria)

$\mathcal{F}_{ext} = \mathcal{V}_{max} - \mathcal{S} = \mathcal{C} + 2 - \mathcal{S}$

Intensive state

Changed by manipulating $\mathcal{V} = \mathcal{V}_{ext} - 1 = C + 1$

Note: "Common" constraints do not matter

Identified via $\mathcal{F}' = \mathcal{F}_{ext} - 1 = C + 1 - \mathcal{S}$

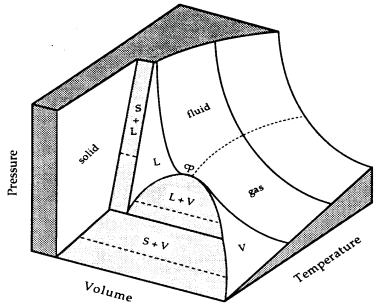
TABLE 9.1 Kinds of Geometric Objects Appearing on $\mathcal{F}$ Diagrams When Constraints Apply to Phase-Equilibrium Situations. Values of $\mathcal{F}$ from (9.1.3). This is a modified version of a table originally devised by de Loos [1].

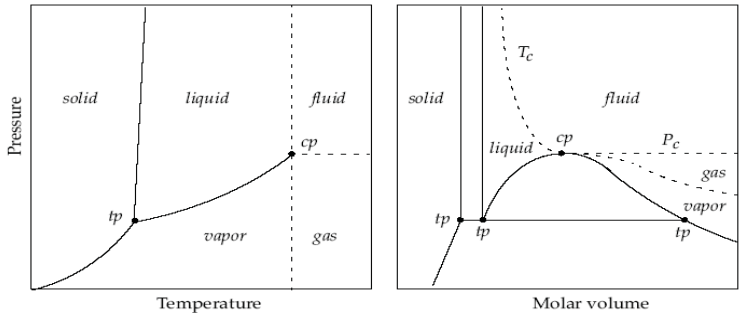
$\mathcal{C}$	$\mathcal{P}$	Constraints ($\mathcal{S}$)	Example	$\mathcal{F}$	Object
1	1	none (0)	L, S, V	2	surface
	1	mechanical stability† (2)	VL critical point	0	point
	2	none (0)	SL, SV, VL	1	line
	3	none (0)	SLV triple point	0	point
2	1	none (0)	L, S, V	3	volume
	1	diffusional stability‡ (2)	VL critical points	1	line
	1	diff. stab. (2); *Tx* extremum (1)	critical azeotrope	0	point
	2	none (0)	SL, LL, LV	2	surface
	2	*Tx* extremum (1)	azeotrope	1	line
	2	diffusional stability (2)	VLL crit. end pt.	0	point
	3	none (0)	SVL, VLL	1	line
	4	none (0)	SLLV, SSLV	0	point

† The two mechanical stability constraints are (8.2.13) and (8.2.14).
‡ The two diffusional stability constraints are (8.4.2) and (8.4.3).

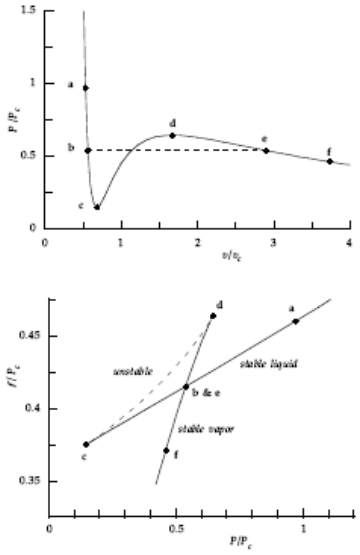
PHASE DIAGRAMS OF PURE SUBSTANCES

EoS - $f(P,T,v) = 0$; Fig 9.1 is 2D projection of
3D figure having P, T, v axes;
2D projections: Pv(T fixed), Tv(P fixed), PT
Note: Pv/Tv plots have $\mathcal{F}$' variables
(include relative amounts of phases)
PT has $\mathcal{F}$ variables
Clapeyron Equation (8.2.27) for PT slopes





Note comparisons of P & f, Figure 9.3



BINARY PHASE DIAGRAMS

EoS - $f(P,T,v,x_1)=0$ so 4D! Ignore v effects
& use PTx_1 (3D) with 2D projections
Note: Px_1, Tx_1 diagrams are $\mathcal{F}$', PT is $\mathcal{F}$
Multiphase reduces # independent variables
Table 9.1 binaries: various # phases (1-4),
set by $\mathcal{S}$
Note: min. $\mathcal{F}$ = 0 from max. Phases(4 relations)
or 2 phases (1 critical) & 2 diffusional
stability constraint relations

2-phase Px_1, Tx_1 diagrams show composition of "other phase" (y_1).

Note variations of P & T at fixed x_1

Compositions at ends of tie lines ⇒ lever rule, Figures 9.4 & 9.6

Critical points at <u>extrema</u> of 2-phase areas, Figure 9.5 & 9.7

2-phase PT have critical lines, <u>no</u> phase equil. Figure 9.8

3-D representation of Figs. 9.4-9.8

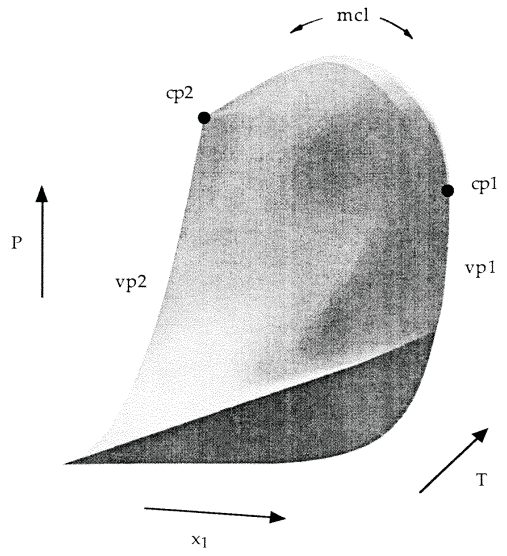


Figure 9.4

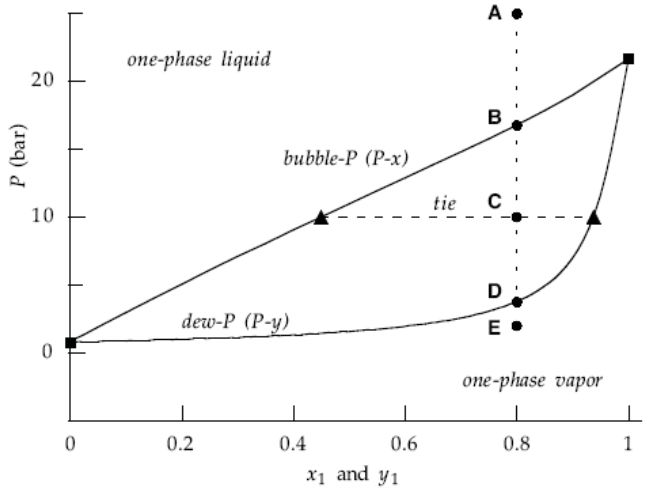


Figure 9.5

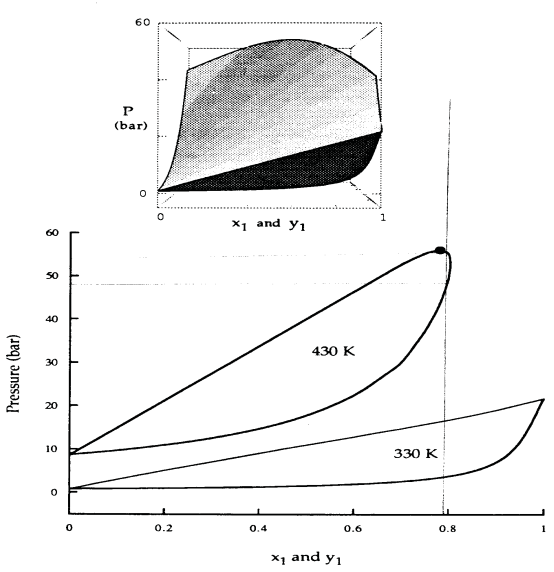


Figure 9.6

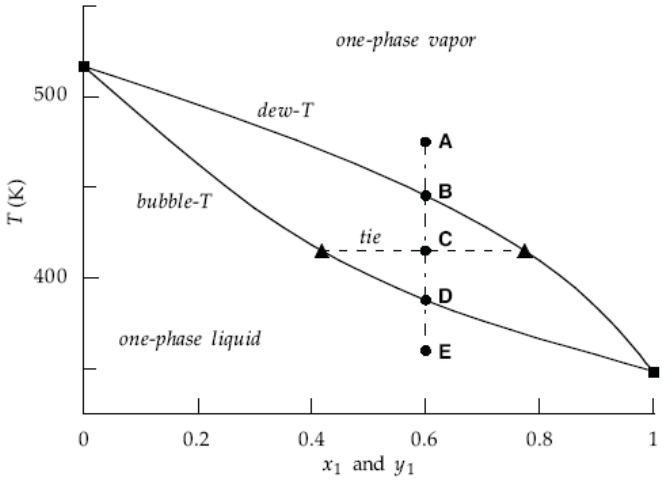


Figure 9.7

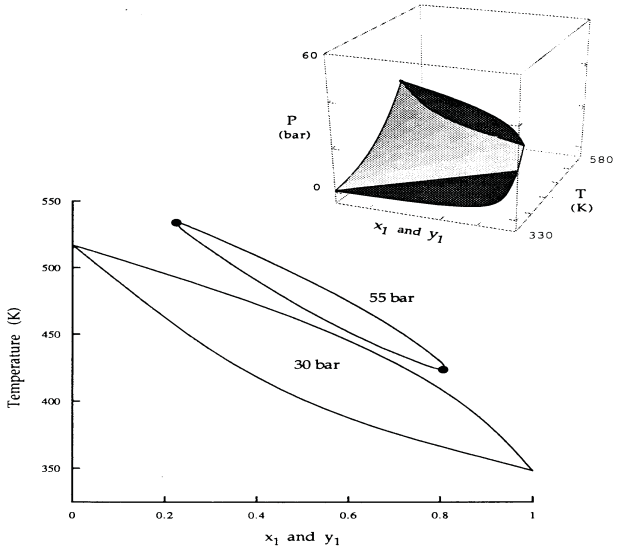
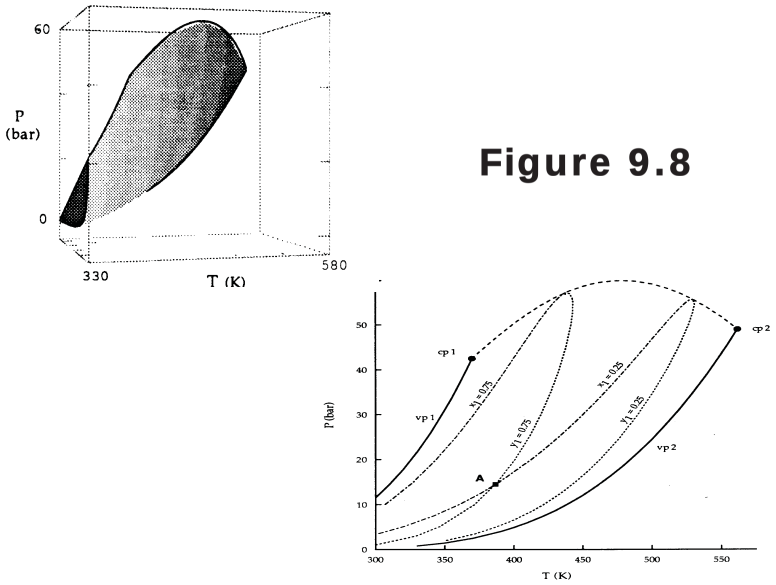


Figure 9.8



COMPLEX BINARY SYSTEMS

Extrema in Px_1y_1→azeotrope ($x_1^{az}=y_1^{az}$)-Fig 9.9,10

- **Note: 2 tie lines & Phase Rule can't distinguish**
- **Behavior complex as → VL critical (Fig 9.11)**
- **Liquid-liquid equil. usually Tx_1 diagram**
- **General shapes in Figs. 9.13, 14**
  - **(~ flat top/bottom)**
- **Vapor-liquid-liquid options; VL has azeotrope**
- **VL depends on P, LL not - Fig. 9.15, 16**

Figure 9.9

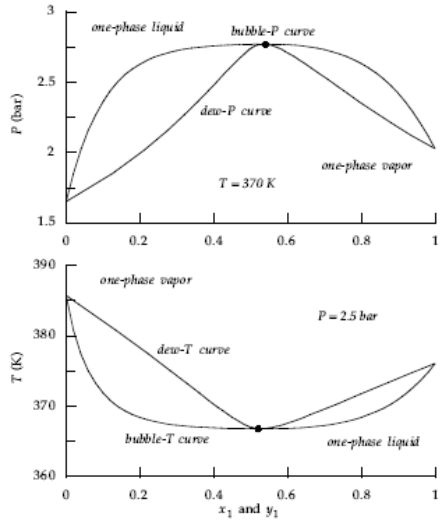
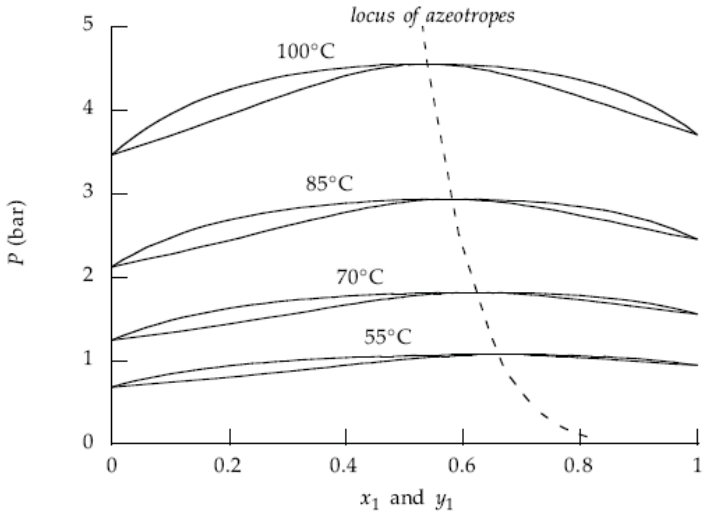
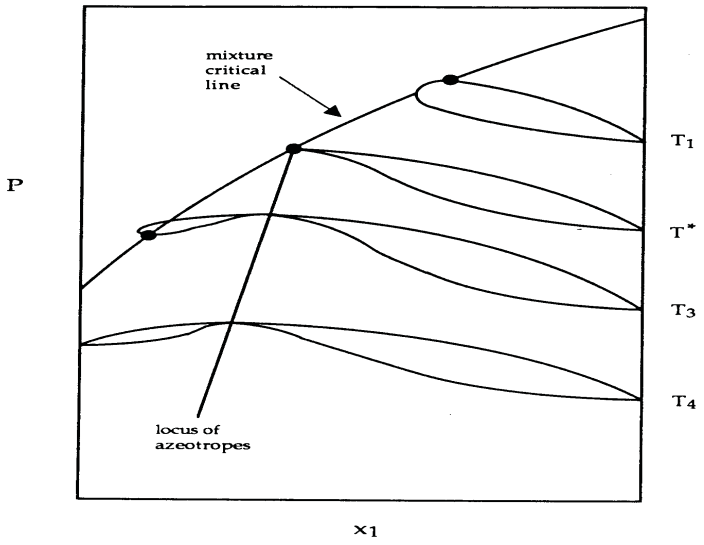


Figure 9.11





Figures 9.13, 9.14

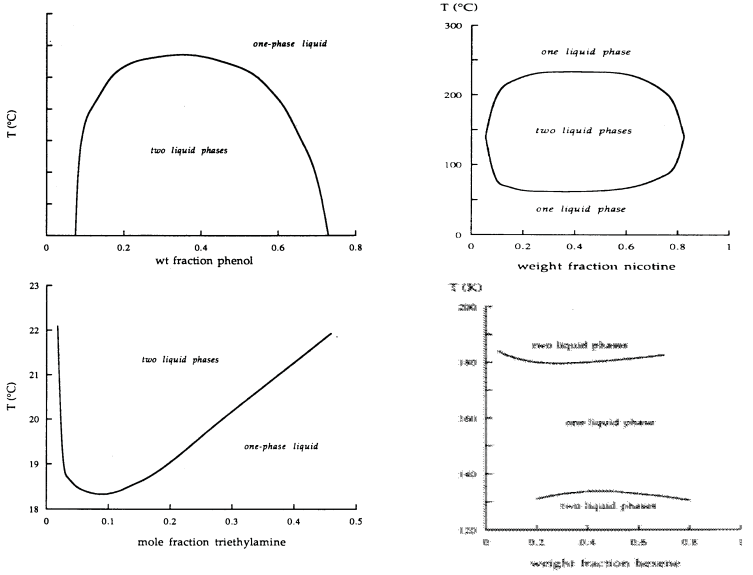


Figure 9.15

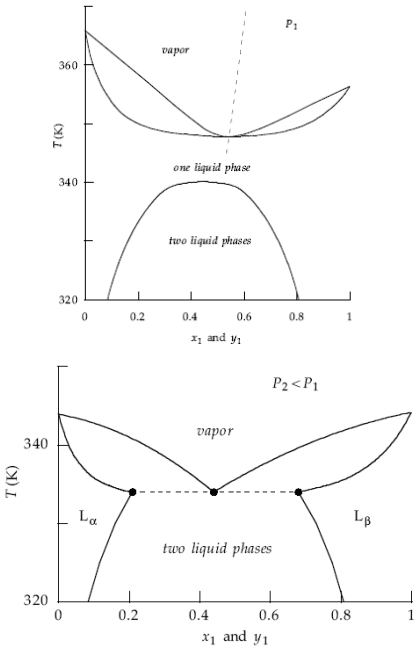


Figure 9.16

