

Keseimbangan Uap/Cair: Pendahuluan

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Kesetimbangan Fase

- Aplikasi
 - Distilasi, absorpsi, dan ekstraksi → membuat kontak antar fase-fase yg berbeda
- Sejauh mana perubahan dan kecepatan transfer massa antar fase, tergantung pada keberangkatan sistem dari kesetimbangannya.
- Perhitungan kuantitatif transfer massa; T dan P saat kesetimbangan; dan komposisi tiap fase → harus diketahui

Sifat Kesetimbangan

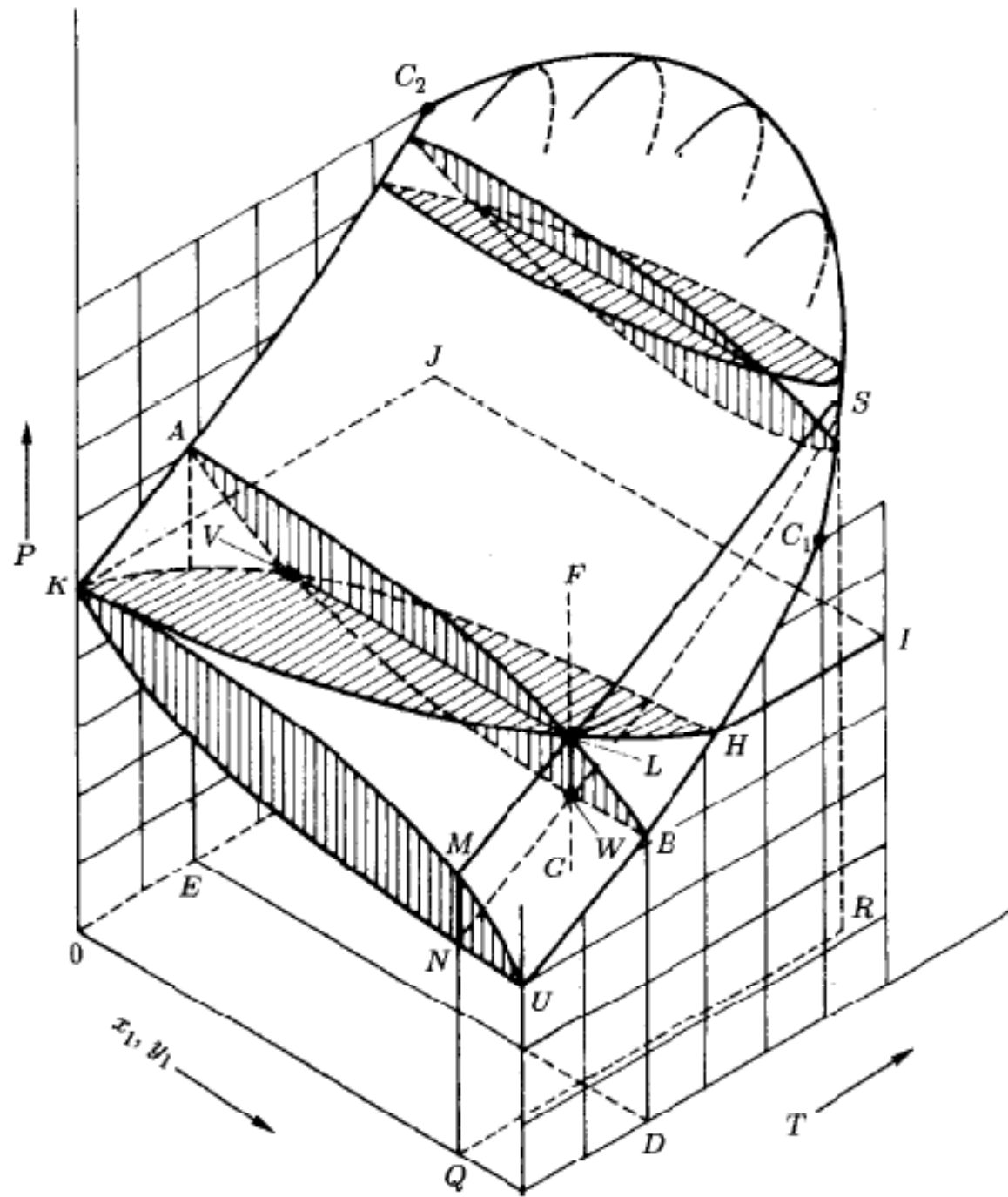
- Sebuah kondisi statis di mana tidak ada perubahan terjadi dalam sifat-sifat makroskopik sistem terhadap waktu.
- Pada tingkat mikroskopik, kondisi tidak statis.
Transfer massa molekuler adalah sama pada kedua arah, dan secara netto transfer massa antarfase sama dgn nol.
- Sistem terisolasi yg terdiri dari fase cair & uap dalam kontak yg akhirnya mencapai keadaan di mana tdk ada kecenderungan perubahan terjadi di dlm sistem.
Saat itu suhu, tekanan, dan komposisi fase tetap.

Phase rule vs. Duhem's theorem

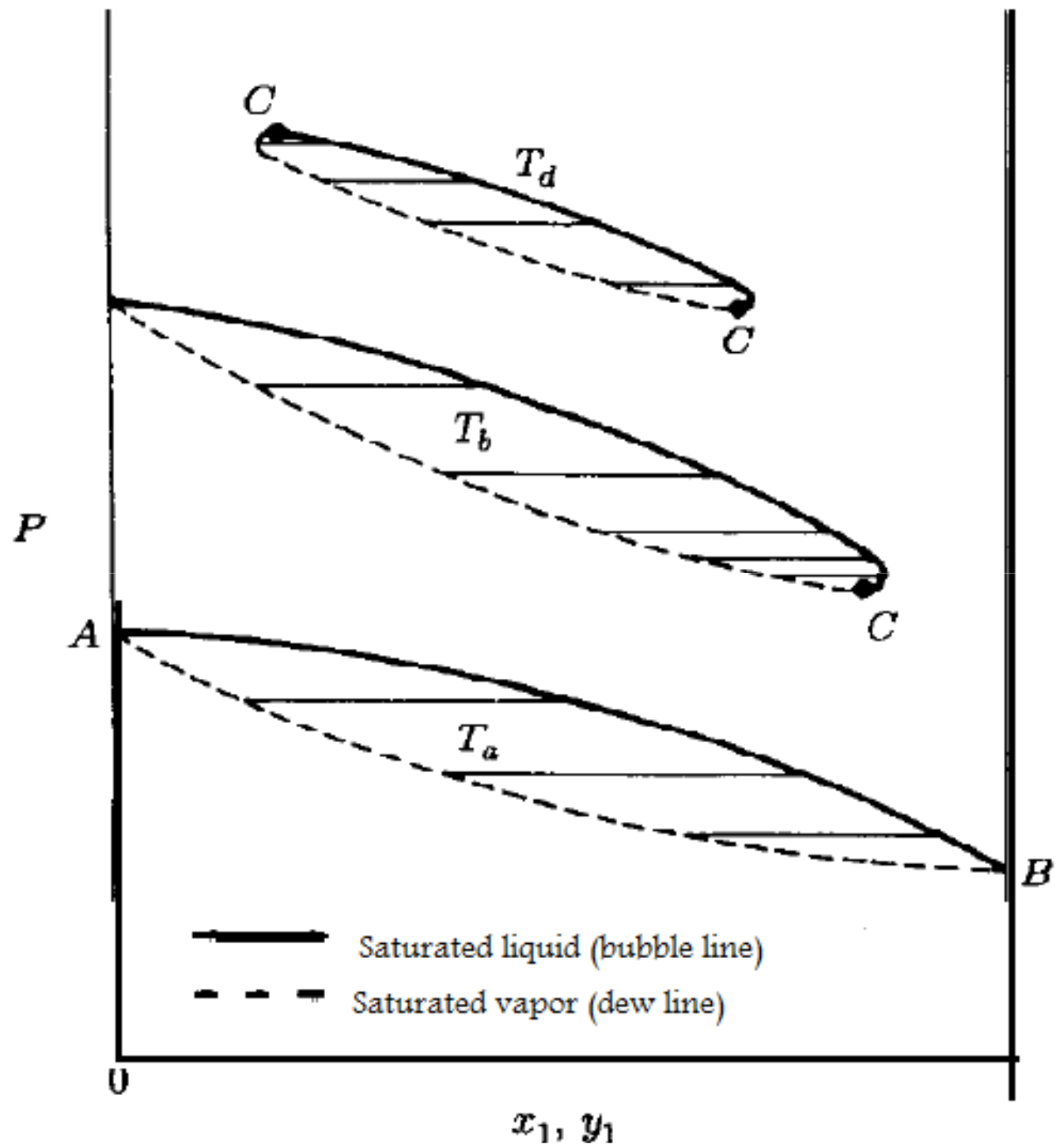
- (The number of variables that is independently fixed in a system at equilibrium) = (the number of variables that characterize the intensive state of the system) - (the number of independent equations connecting the variable):
- Phase rule: $F = 2 + (N - 1)(\pi) - (\pi - 1)(N) = 2 - \pi + N$
- Duhem's rule: $F = 2 + [(N - 1)(\pi) + \pi] - [(\pi - 1)(N) + N] = 2$
 - for any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when **any two** independent variables are fixed.
 - **Two ?** When phase rule $F = 1$, at least one of the two variables must be extensive, and when $F = 0$, both must be extensive.

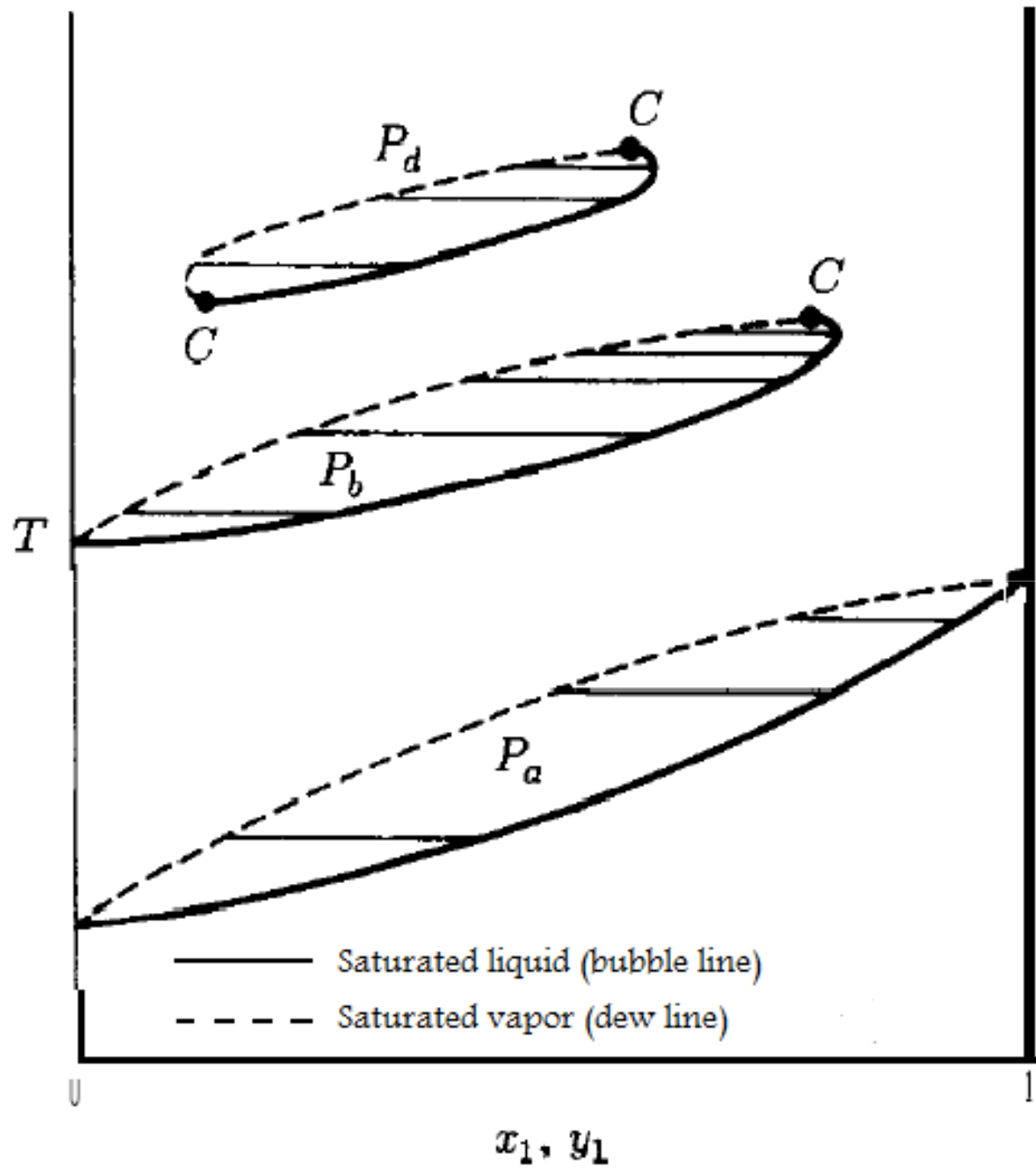
VLE: qualitative behavior

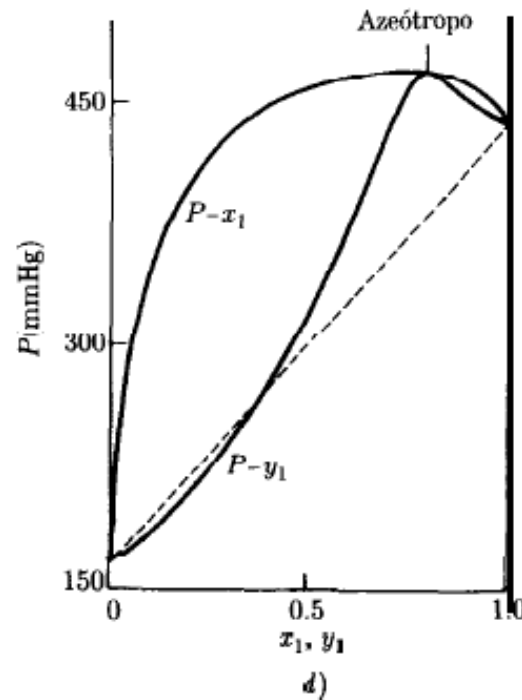
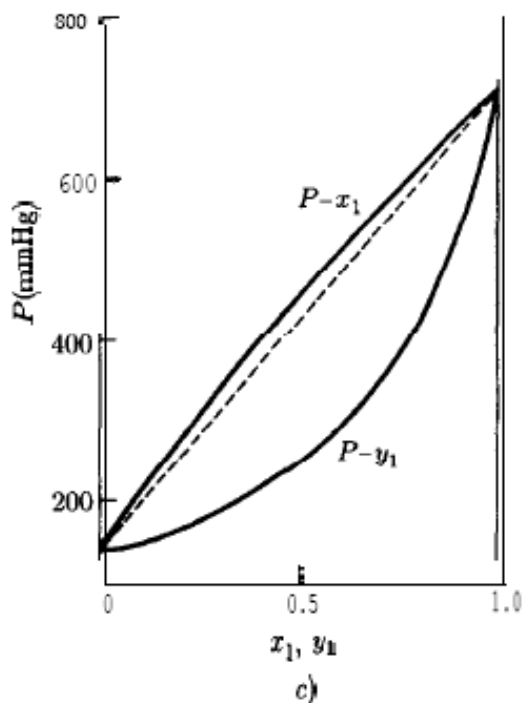
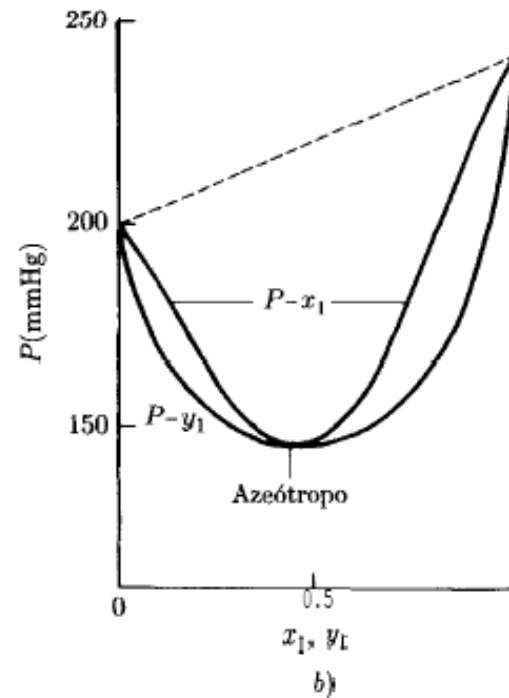
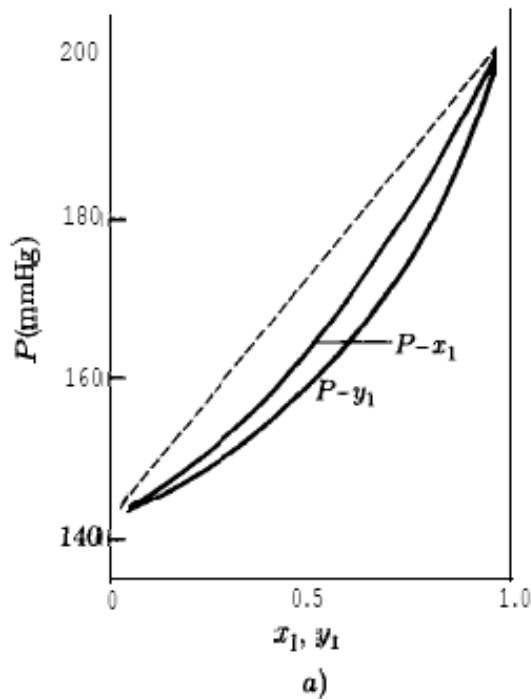
- When two chemical species: $N = 2$
 - phase rule: $F = 4 - \pi$
 - the maximum value of $F = 3$ ($\pi = 1$), namely, P, T, and one mole fraction. All equilibrium states of the system can be represented in three-dimensional P-T-composition space.



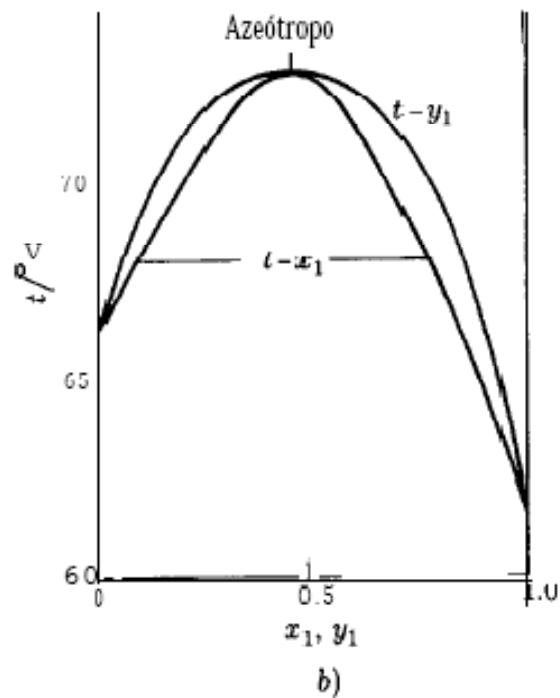
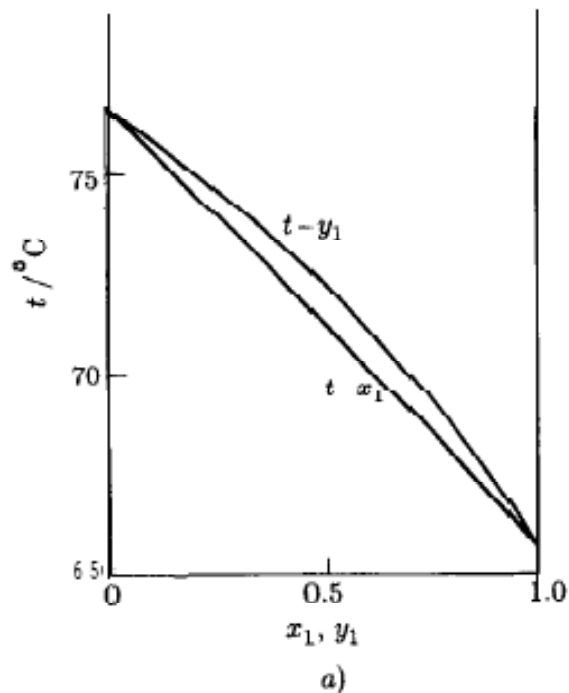
- Within this space, the states of pairs of phases coexisting at equilibrium define surfaces.
 - The subcooled-liquid region lies above the upper surface; the superheated-vapor region lies below the under surface.
 - $UBHC_1$ and KAC_2 represent the vapor pressure-vs.-T curves for pure species 1 and 2.
 - C_1 and C_2 are the critical points of pure species 1 and 2.
 - L is a bubble point and the upper surface is the bubblepoint surface.
 - Line VL is an example of a tie line, which connects points representing phases in equilibrium.
 - W is a dewpoint and the lower surface is the dewpoint surface.
- Pxy diagram at constant T
- Txy diagram at constant P
- PT diagram at constant composition







- Fig 10.8 (a)(b), Negative departures from $P-x_1$ linearity: strong liquid-phase inter-molecular attractions between unlike than between like pairs of molecules.
- Fig 10.8 (c)(d), Positive departures from $P-x_1$ linearity: strong liquid-phase inter-molecular attractions between like than between unlike pairs of molecules.
- Fig 10.8 (b)(d), the “azeotrope”: the point where $x_1 = y_1$ the dewpoint and bubblepoint curves are tangent to the same horizontal line. The liquid does not change in composition as it evaporates. No separation of such a constant-boiling solution is possible by distillation.

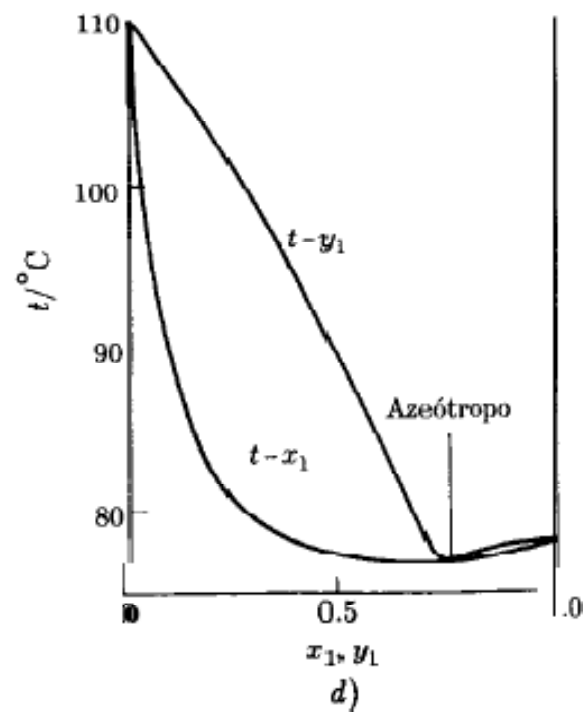
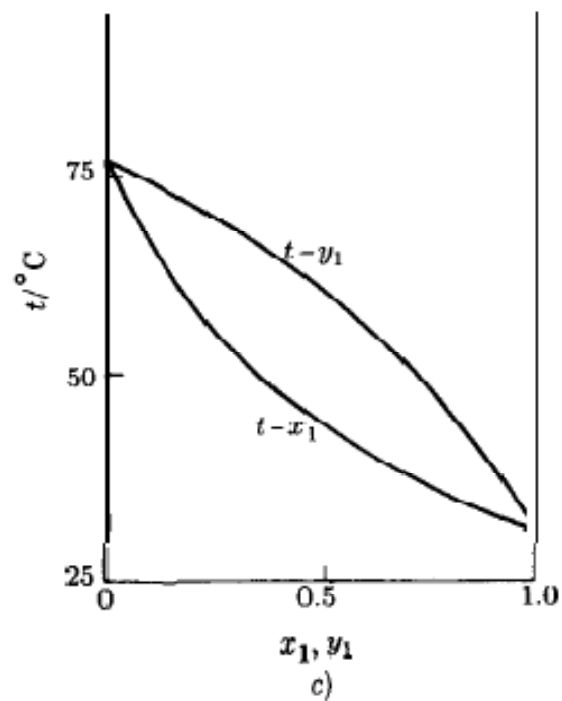


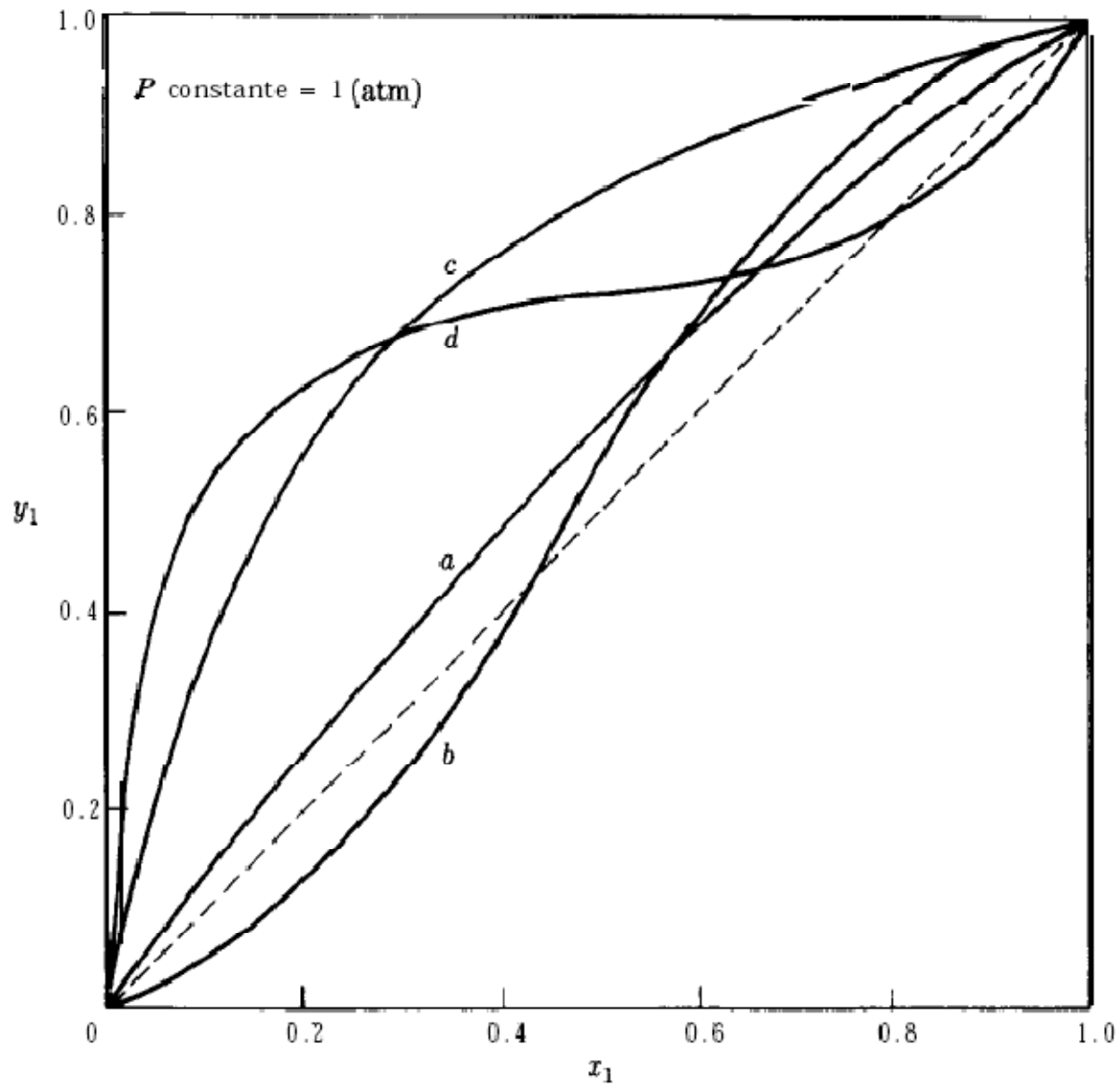
(a) tetrahydrofuran(1)/
carbon tetrachloride(2)

(b) Chloroform(1)/
tetrahydrofuran(2)

(c) Furan(1)/ carbon
tetrachloride(2)

(d) Ethanol(1)/ toluene(2)





- (a) tetrahydrofuran(1)/
carbon tetrachloride(2)
- (b) Chloroform(1)/ /
tetrahydrofuran(2)
- (c) Furan(1)/ carbon
tetrachloride(2)
- (d) Ethanol(1)/ toluene(2)

Simple models for VLE

- The simplest are Raoult's law and Henry's law.
- Raoult's law:
 - the vapor phase is an ideal gas (apply for low to moderate pressure)
 - the liquid phase is an ideal solution (apply when the species that are chemically similar)
 - $y_i P = x_i P_i^{sat} \quad (i = 1, 2, \dots, N)$
 - although it provides a realistic description of actual behavior for a small class of systems, it is valid for any species present at a mole fraction approaching unity, provided that the vapor phase is an ideal gas.

$$y_i P = x_i P_i^{sat} \quad (i = 1, 2, \dots, N)$$

$$\sum_i y_i = 1$$

$$P = \sum_i x_i P_i^{sat} \quad (i = 1, 2, \dots, N)$$

Binary system

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1$$

$$\sum_i x_i = 1$$

$$P = \frac{1}{\sum_i y_i / P_i^{sat}} \quad (i = 1, 2, \dots, N)$$

For dewpoint calculation

For bubblepoint calculation

Binary system acetonitrile (1)/nitromethane(2) conforms closely to Raoult's law.
 Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{sat} / \text{kPa} = 14.2724 - \frac{2945.47}{t / ^\circ\text{C} + 224.00} \quad \ln P_2^{sat} / \text{kPa} = 14.2043 - \frac{2972.64}{t / ^\circ\text{C} + 209.00}$$

- (a) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 75°C.
 (b) Prepare a graph showing t vs. x_1 and t vs. y_1 for a pressure of 70 kPa.
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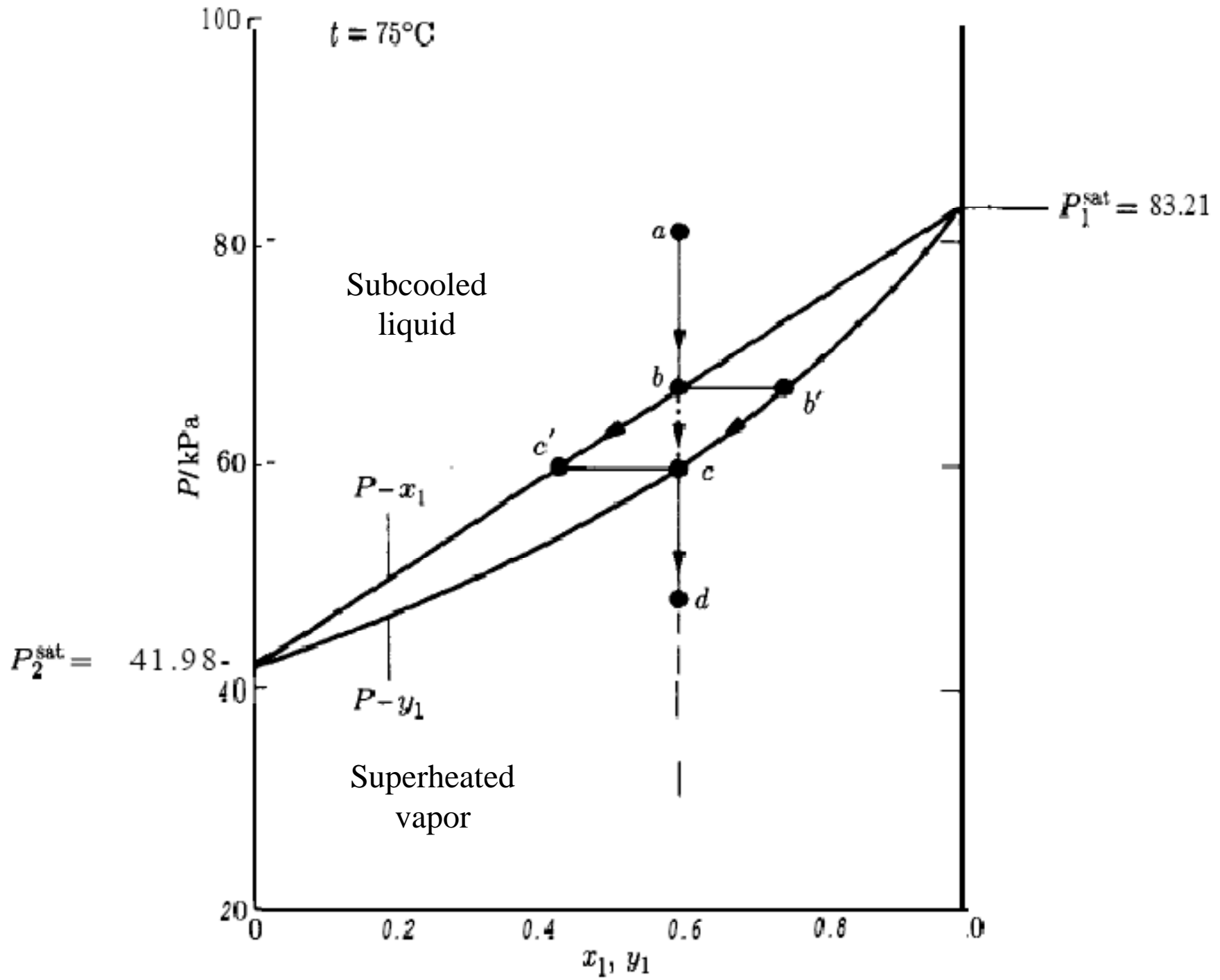
(a) *BUBL P* $P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1$

At 75°C $P_1^{sat} = 83.21$ $P_2^{sat} = 41.98$

$P = 41.98 + (83.21 - 41.98)x_1$ e.g. $x_1 = 0.6$ $P = 66.72$

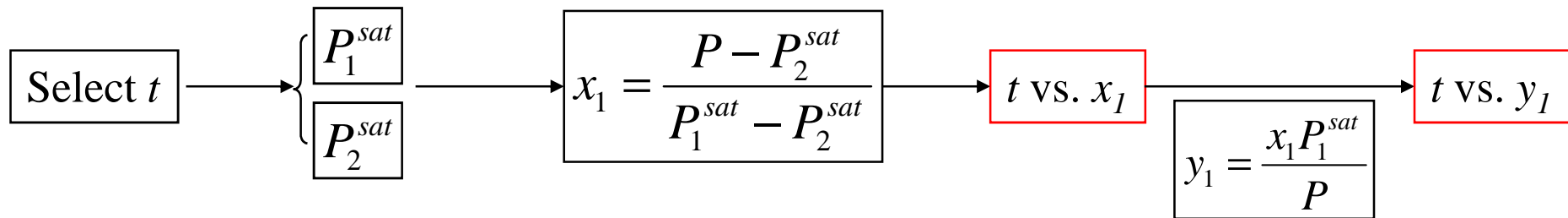
$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483$

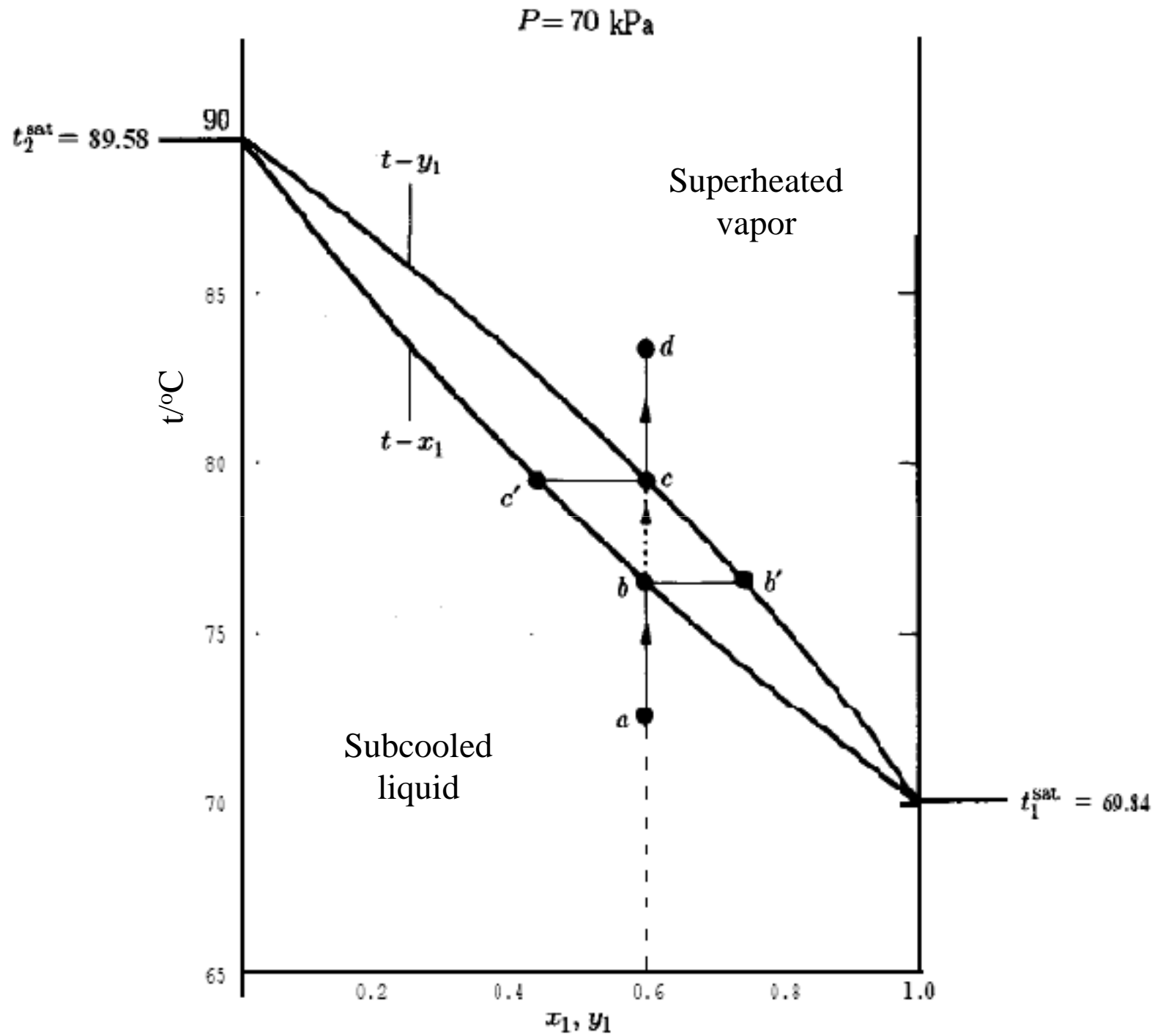
At 75°C, a liquid mixture of 60 mol-% (1) and 40 mol-% (2) is in equilibrium with a vapor containing 74.83 mol-% (1) at pressure of 66.72 kPa.



(b) *BUBL T*, having $P = 70$ kPa

$\ln P_1^{sat} / \text{kPa} = 14.2724 - \frac{2945.47}{t / ^\circ \text{C} + 224.00}$	$\ln P_2^{sat} / \text{kPa} = 14.2043 - \frac{2972.64}{t / ^\circ \text{C} + 209.00}$
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Henry's law

- For a species present as a very dilute solute in the liquid phase, the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction:

$$y_i P = x_i H_i$$

- H = Henry's Constant
- See table 10.1

Assuming that carbonated water contains only CO₂ (species 1) and H₂O (species 2), determine the compositions of the vapor and liquid phases in a sealed can of “soda” and the pressure exerted on the can at 10°C. Henry’s constant for CO₂ in water at 10°C is about 990 bar.

Henry’s law for species 1: $y_1 P = x_1 H_1$

Raoult’s law for species 2: $y_2 P = x_2 P_2^{sat}$

$$P = x_1 H_1 + x_2 P_2^{sat}$$

Assuming $x_1 = 0.01$

$$P = (0.01)(990) + (0.99)(0.01227) = 9.912$$

$$y_1 P = x_1 H_1 \quad \text{assuming } y_1 = 1.0$$

Justified the assumption $x_1 = 0.01$

$$y_2 P = x_2 P_2^{sat}$$

$$y_2 = 0.0012$$

$$y_1 = 0.9988$$

Justified the assumption

VLE modified Raoult's law

- Account is taken of deviation from solution ideality in the liquid phase by a factor inserted into Raoult's law:

$$y_i P = x_i \gamma_i P_i^{sat} \quad (i = 1, 2, 3, \dots, N)$$

The activity coefficient, $f(T, x_i)$

$$P = \sum_i x_i \gamma_i P_i^{sat}$$

$$P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}}$$

For the system methanol (1)/methyl acetate (2), the following equations provide a reasonable correlation for the activity coefficients:

$$\ln \gamma_1 = (2.771 - 0.00523T)x_2^2 \quad \ln \gamma_2 = (2.771 - 0.00523T)x_1^2$$

The Antoine equations provide vapor pressures:

$$\ln P_1^{sat} / kPa = 16.59158 - \frac{3643.31}{T(K) - 33.424} \quad \ln P_2^{sat} / kPa = 14.25326 - \frac{2665.54}{T(K) - 53.424}$$

Calculate

- (a): P and $\{y_i\}$ for T = 318.15 K and $x_1 = 0.25$
 - (b): P and $\{x_i\}$ for T = 318.15 K and $y_1 = 0.60$
 - (c): T and $\{y_i\}$ for P = 101.33 kPa and $x_1 = 0.85$
 - (d): T and $\{x_i\}$ for P = 101.33 kPa and $y_1 = 0.40$
 - (e): the azeotropic pressure and the azeotropic composition for T = 318.15 K
-

(a) for T = 318.15, and $x_1 = 0.25$

$$P_1^{sat} = 44.51 \quad P_2^{sat} = 65.64 \quad \gamma_1 = 1.864 \quad \gamma_2 = 1.072$$

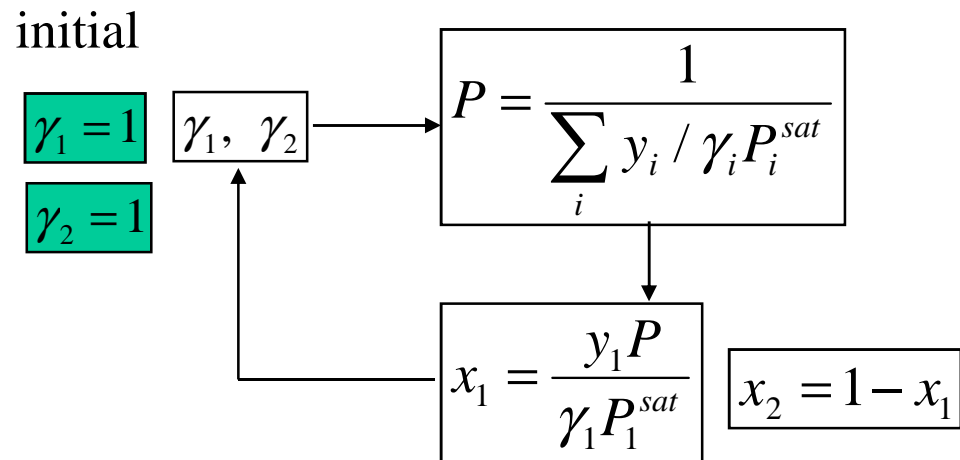
$$P = \sum_i x_i \gamma_i P_i^{sat} = (0.25)(1.864)(44.51) + (0.75)(1.072)(65.64) = 73.50$$

$$y_i P = x_i \gamma_i P_i^{sat} \longrightarrow y_1 = 0.282 \quad y_2 = 0.718$$

(b): for $T = 318.15 \text{ K}$ and $y_1 = 0.60$

$$P_1^{sat} = 44.51 \quad P_2^{sat} = 65.64$$

A iterative process is applied, with



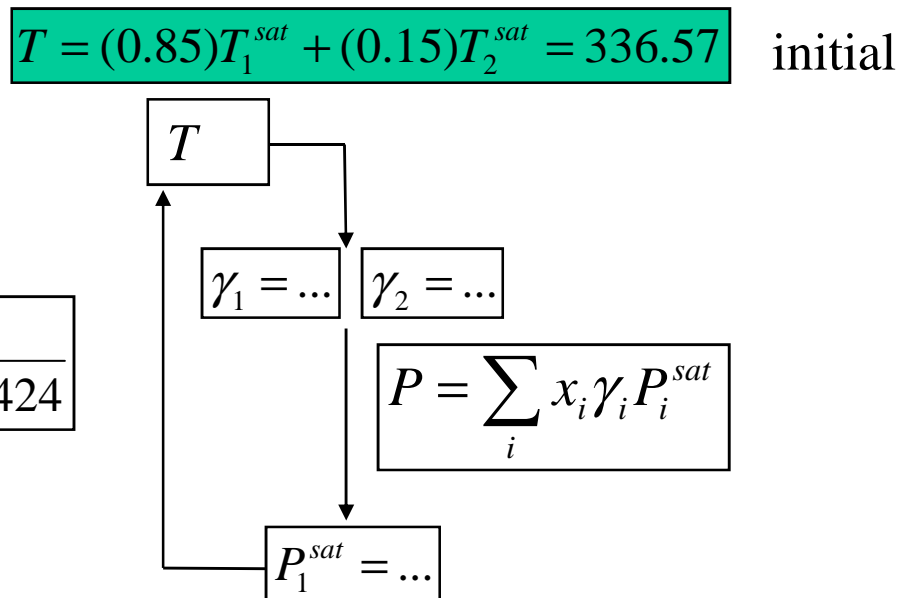
Converges at: $P = 62.89 \text{ kPa}$ $\gamma_1 = 1.0378$ $\gamma_2 = 2.0935$ $x_1 = 0.8169$

(c): for $P = 101.33 \text{ kPa}$ and $x_1 = 0.85$

$$T_1^{sat} = 337.71 \quad T_2^{sat} = 330.08$$

A iterative process is applied, with

$$\ln P_1^{sat} / \text{kPa} = 16.59158 - \frac{3643.31}{T(\text{K}) - 33.424}$$



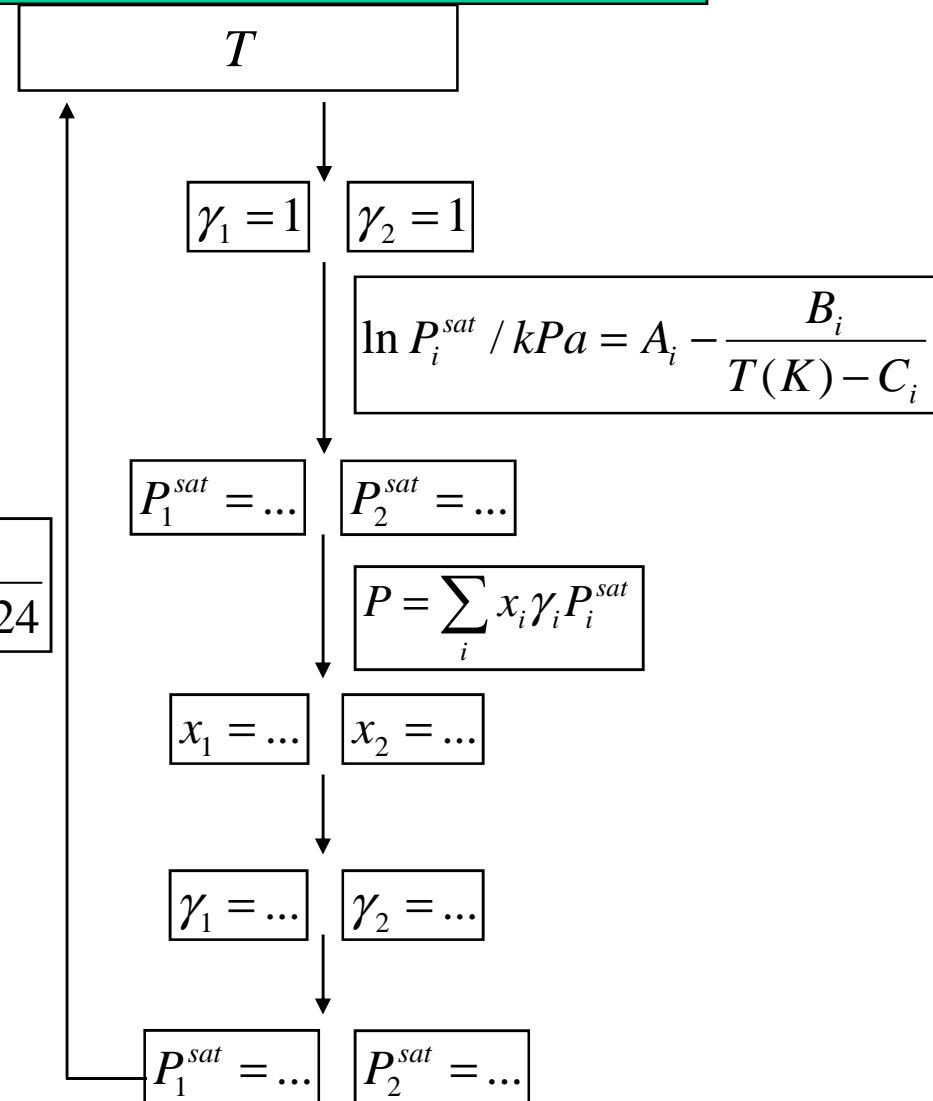
Converges at: $T = 331.20 \text{ K}$ $\gamma_1 = 1.0236$ $\gamma_2 = 2.1182$ $y_1 = 0.670$ $y_2 = 0.330$

(d): for $P = 101.33 \text{ kPa}$ and $y_1 = 0.40$

$$T_1^{sat} = 337.71 \quad T_2^{sat} = 330.08$$

A iterative process is applied, with

$$T = (0.40)T_1^{sat} + (0.60)T_2^{sat} = 333.13 \quad \text{initial}$$



$$\ln P_1^{sat} / kPa = 16.59158 - \frac{3643.31}{T(K) - 33.424}$$

Converges at: $T = 326.70K$ $\gamma_1 = 1.3629$ $\gamma_2 = 1.2523$ $x_1 = 0.4602$ $x_2 = 0.5398$

(e): the azeotropic pressure and the azeotropic composition for $T = 318.15 \text{ K}$

Define the relative volatility: $\alpha_{12} \equiv \frac{y_1/x_1}{y_2/x_2}$ $\xrightarrow{y_i P = x_i \gamma_i P_i^{sat}}$ $\alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}}$

Azeotrope \longrightarrow $y_1 = x_1$ $y_2 = x_2$ \longrightarrow $\alpha_{12} = 1$

$$\alpha_{12} \Big|_{x_1=0} = \frac{P_1^{sat} \exp(2.771 - 0.00523T)}{P_2^{sat}} = 2.052 \quad \Bigg| \quad \alpha_{12} \Big|_{x_1=1} = \frac{P_1^{sat}}{P_2^{sat} \exp(2.771 - 0.00523T)} = 0.224$$

Since α_{12} is a continuous function of x_1 : from 2.052 to 0.224, $\alpha_{12} = 1$ at some point

There exists the azeotrope!

$$\alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}} = 1 \longrightarrow \frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{sat}}{P_1^{sat}} = 1.4747$$

$$\left. \begin{array}{l} \ln \gamma_1 = (2.771 - 0.00523T)x_2^2 \\ \ln \gamma_2 = (2.771 - 0.00523T)x_1^2 \end{array} \right\} \ln \frac{\gamma_1}{\gamma_2} = (2.771 - 0.00523T)(x_2 - x_1) = (2.771 - 0.00523T)(1 - 2x_1)$$

$$x_1^{az} = 0.325 = y_1^{az} \longrightarrow \gamma_1^{az} = 1.657$$

$$P^{az} = \gamma_1^{az} P_1^{sat} = 73.76 \text{ kPa}$$

VLE from K-value correlations

- A convenient measure, the *K-value*:

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

– the “lightness” of a constituent species, i.e., of its tendency to favor the vapor phase.

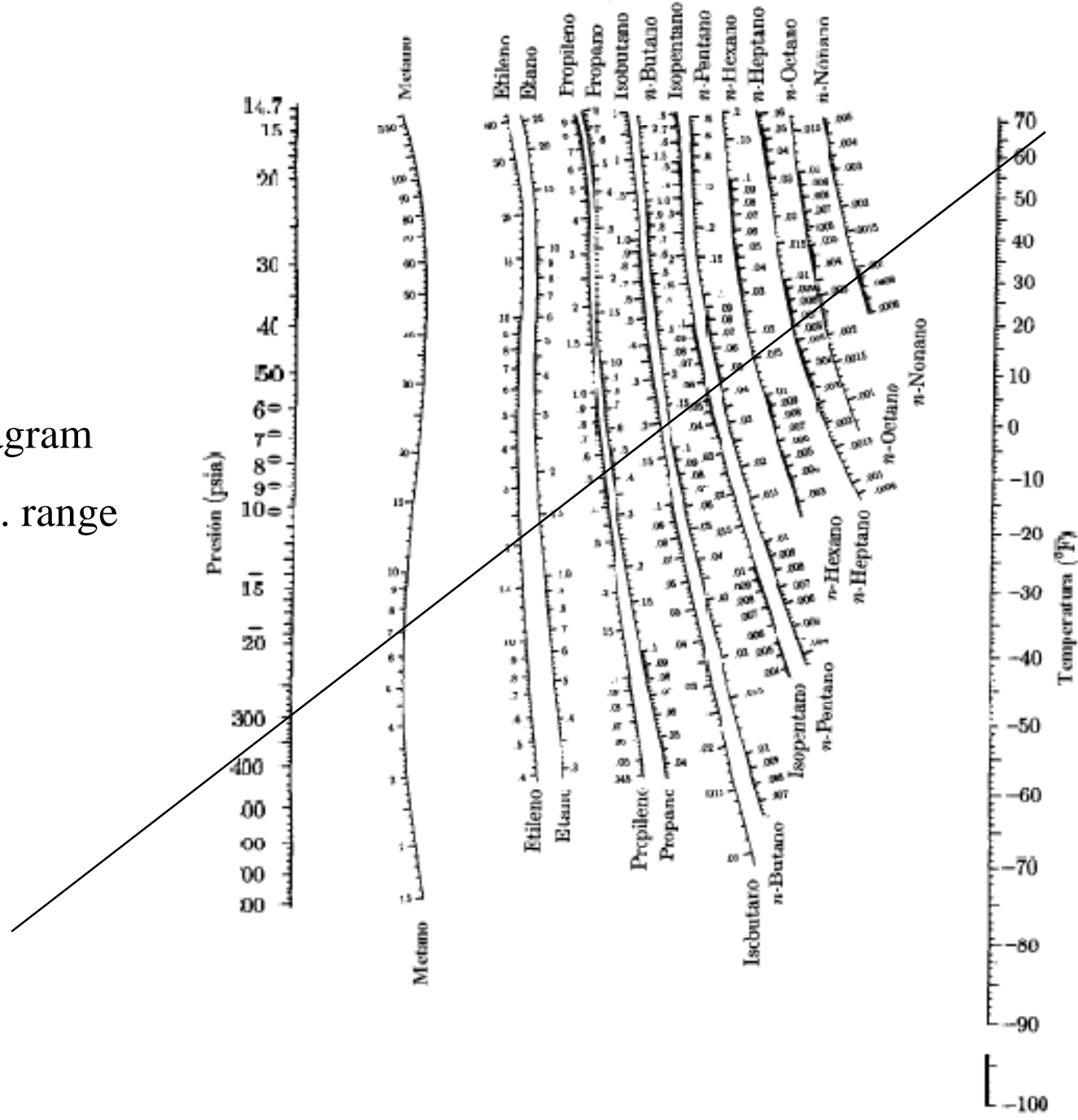
– The Raoult’s law:

$$K_i = \frac{P_i^{sat}}{P}$$

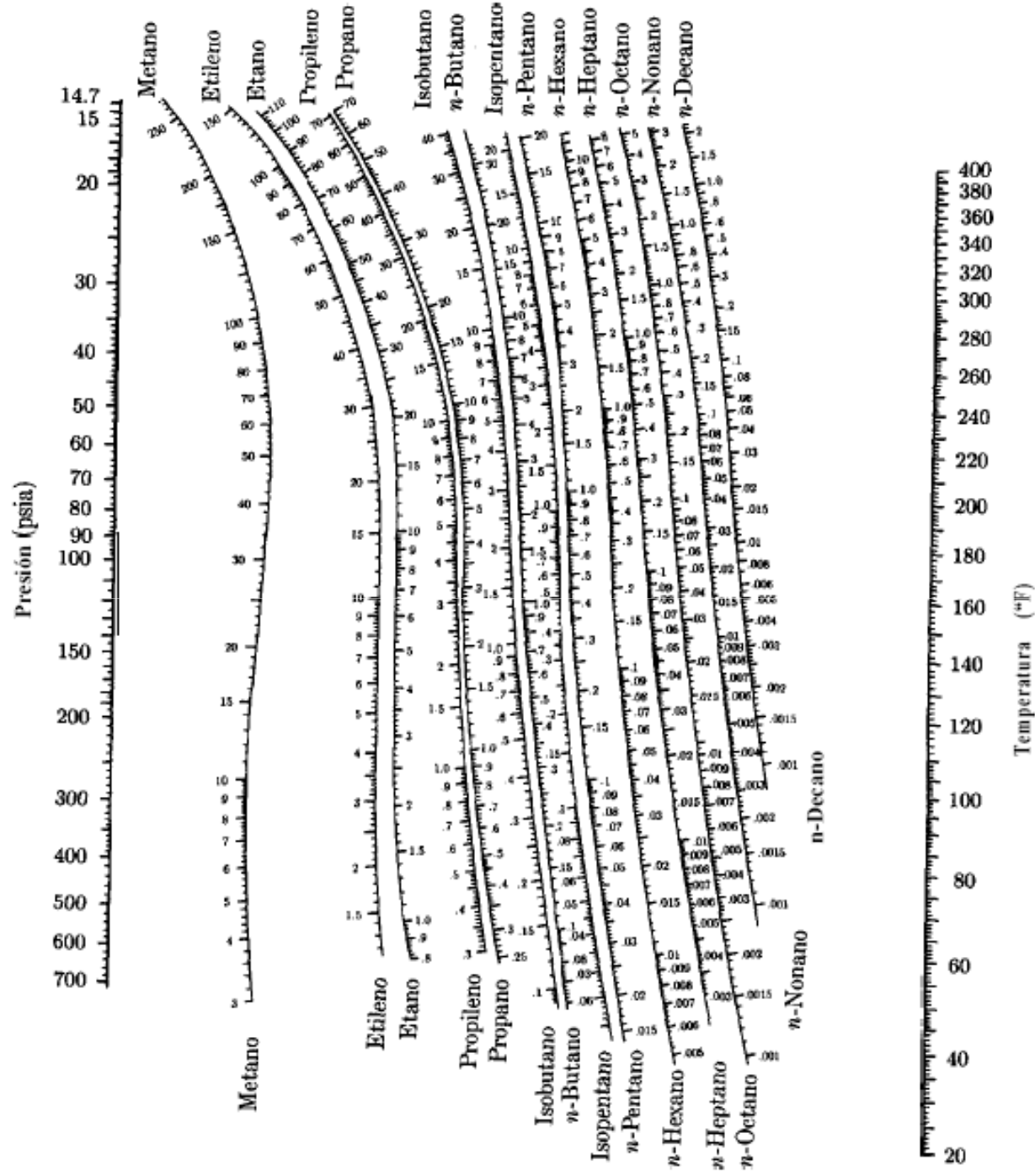
– The modified Raoult’s law:

$$K_i = \frac{\gamma_i P_i^{sat}}{P}$$

De Priester Diagram
For Low-Temp. range




De Priester's Diagram for High-Temp. range



For a mixture of 10 mol-% methane, 20 mol-% ethane, and 70 mol-% propane at 50°F, determine: (a) the dewpoint pressure, (b) the bubblepoint pressure. The K-values are given by Fig. 10.13.


(a) at its dewpoint, only an insignificant amount of liquid is present:

		P = 100 (psia)		P = 150 (psia)		P = 126 (psia)	
Species	y_i	K_i	y_i / K_i	K_i	y_i / K_i	K_i	y_i / K_i
Methane	0.10	20.0	0.005	13.2	0.008	16.0	0.006
Ethane	0.20	3.25	0.062	2.25	0.089	2.65	0.075
Propane	0.70	0.92	0.761	0.65	1.077	0.762	0.919
		$\Sigma (y_i / K_i) = 0.828$		$\Sigma (y_i / K_i) = 1.174$		$\Sigma (y_i / K_i) = 1.000$	



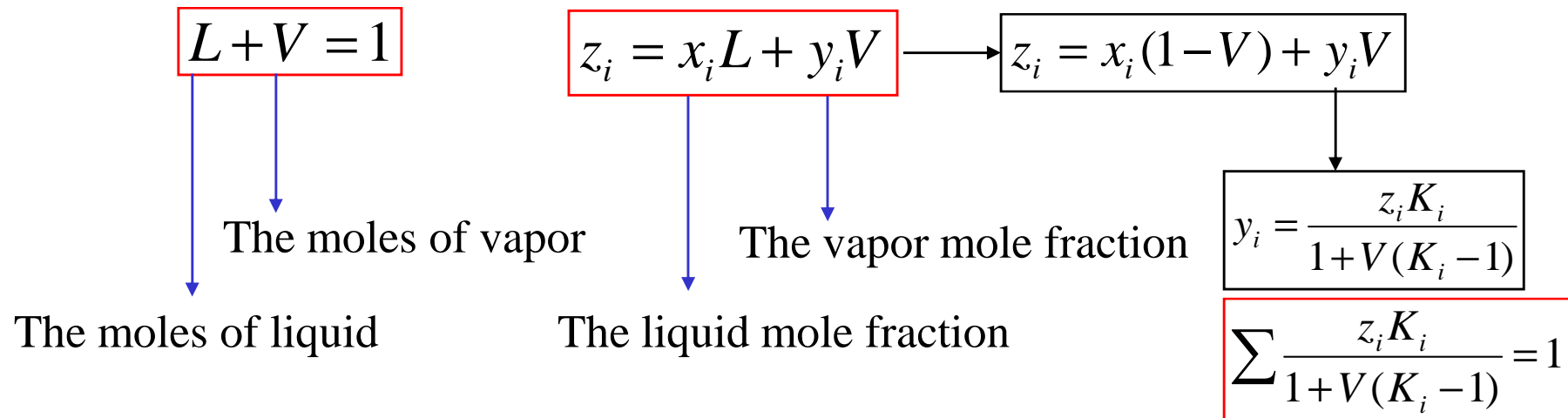
(b) at bubblepoint, the system is almost completely condensed:

		P = 380 (psia)		P = 400 (psia)		P = 385 (psia)	
Species	x_i	K_i	$x_i K_i$	K_i	$x_i K_i$	K_i	$x_i K_i$
Methane	0.10	5.60	0.560	5.25	0.525	5.49	0.549
Ethane	0.20	1.11	0.222	1.07	0.214	1.10	0.220
Propane	0.70	0.335	0.235	0.32	0.224	0.33	0.231
		$\Sigma (x_i K_i) = 1.017$		$\Sigma (x_i K_i) = 0.963$		$\Sigma (x_i K_i) = 1.000$	



Flash calculations

- A liquid at a pressure equal to or greater than its bubblepoint pressure “flashes” or partially evaporates when the pressure is reduced, producing a two-phase system of vapor and liquid in equilibrium.
- Consider a system containing one mole of nonreacting chemical species:



The system acetone (1)/acetonitrile (2)/nitromethane(3) at 80°C and 110 kPa has the overall composition, $z_1 = 0.45$, $z_2 = 0.35$, $z_3 = 0.20$, Assuming that Raoult's law is appropriate to this system, determine L , V , $\{x_i\}$, and $\{y_i\}$. The vapor pressures of the pure species are given.

Do a *BUBL P* calculation, with $\{z_i\} = \{x_i\}$:

$$P_{\text{bubl}} = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}} = (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) = 132.40 \text{ kPa}$$

Do a *DEW P* calculation, with $\{z_i\} = \{y_i\}$:

$$P_{\text{dew}} = \frac{1}{y_1 / P_1^{\text{sat}} + y_2 / P_2^{\text{sat}} + y_3 / P_3^{\text{sat}}} = 101.52 \text{ kPa}$$

Since $P_{\text{dew}} < P = 110 \text{ kPa} < P_{\text{bubl}}$, the system is in the two-phase region,

$$L = 1 - V = 0.2636 \text{ mol}$$

$$K_i = \frac{P_i^{\text{sat}}}{P} \rightarrow K_1 = 1.7795 \quad K_2 = 0.8895 \quad K_3 = 0.4575 \rightarrow \sum \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \rightarrow V = 0.7364 \text{ mol}$$

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)}$$

$$x_1 = 0.2859$$

$$x_2 = 0.3810$$

$$x_3 = 0.3331$$

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

$$y_1 = 0.5087$$

$$y_2 = 0.3389$$

$$y_3 = 0.1524$$