EG3029 Chemical Thermodynamics

Vapour/Liquid Equilibrium of Mixtures

General Remarks
Introduction

- In most technical processes there are no pure substances but mixtures of various species
  - Chemical reactors
  - Separation units (distillation, absorption, extraction)
- Phase equilibrium necessary for quantitative treatment
- Here: only non-reacting systems will be considered

General Remarks
Introduction

- Equilibrium is a static condition: balance of all potentials
- Measures of composition
  - Mass or mole fraction $x_i = \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}}$ $x_i = \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$
  - Molar concentration $C_i = \frac{x_i}{V}$
  - Molar concentration in flow processes $C_i = \frac{\dot{n}_i}{q}$
  - Molar mass of mixtures $M = \sum_i x_i M_i$

General Remarks
Phase Rule and Duhem's Theorem

- Phase Rule for multi-phase systems at equilibrium

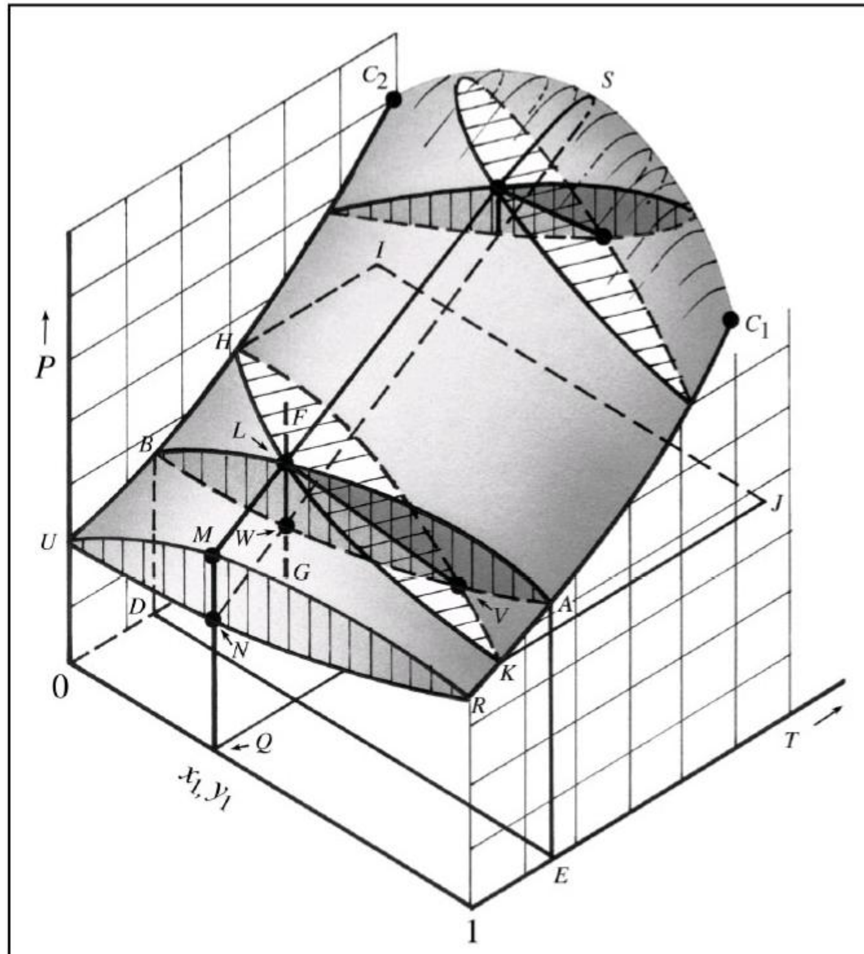
$$\boxed{F = 2 - \pi + N}$$

F degrees of freedom
π number of phases
N number of chem. species

- Duhem's Theorem:
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.

VLE
Qualitative Behaviour

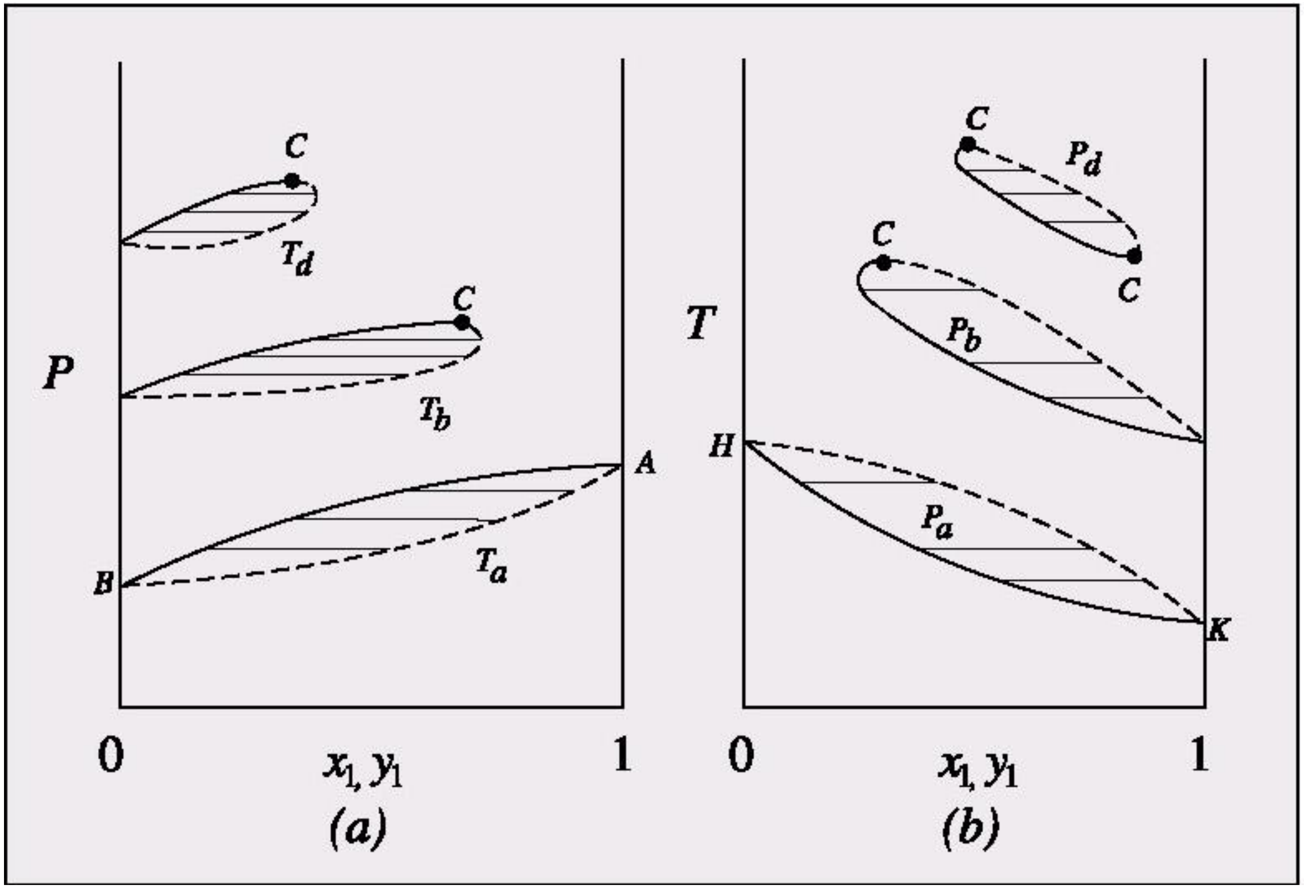
- Systems comprised of 2 chemical species



P T xy diagram for VLE

VLE
Qualitative Behaviour

- *P xy* and *T xy* diagrams

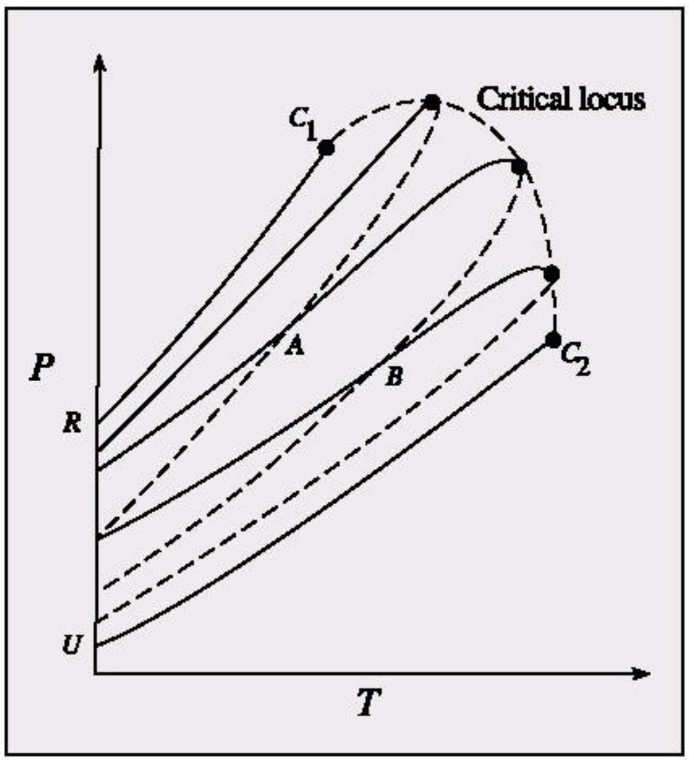


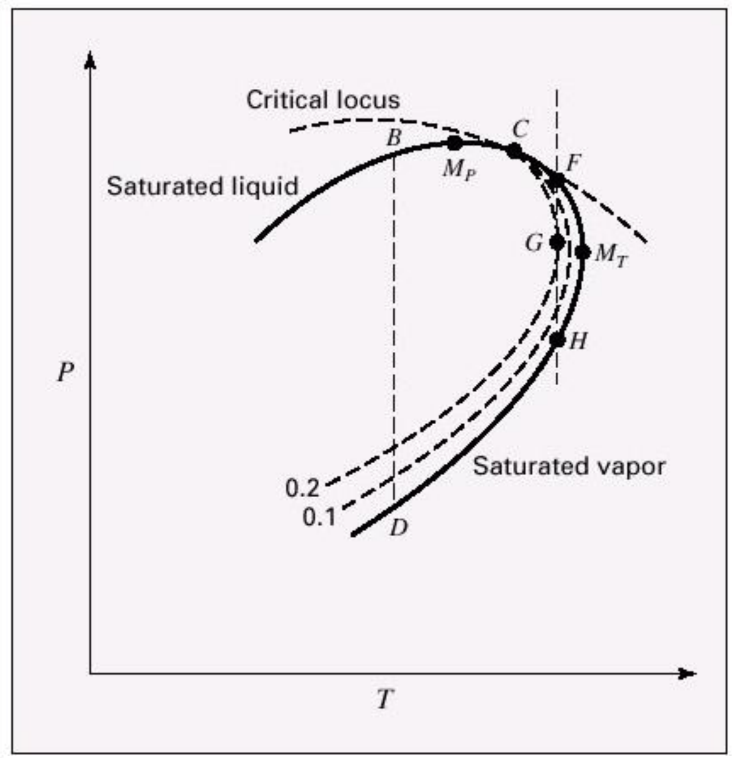
(a) *P xy* diagram for three temperatures.
(b) *T xy* diagram for three pressures.

Solid line: saturated liquid (bubble line); dashed line: saturated vapour (dew line)

VLE
Qualitative Behaviour

- *P T* diagrams at fixed composition

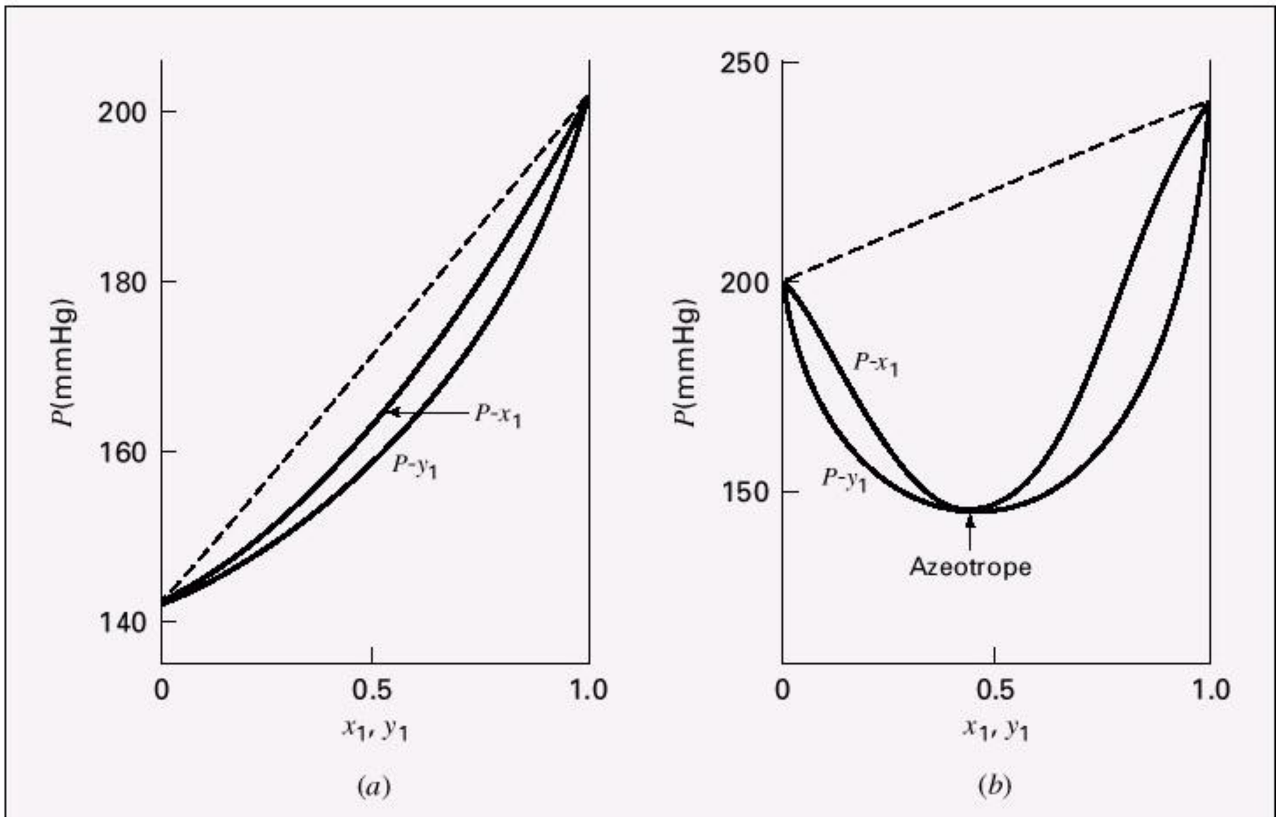




Solid line: saturated liquid (bubble line); dashed line: saturated vapour (dew line)

VLE
Qualitative Behaviour

- *P xy* diagrams at constant *T*

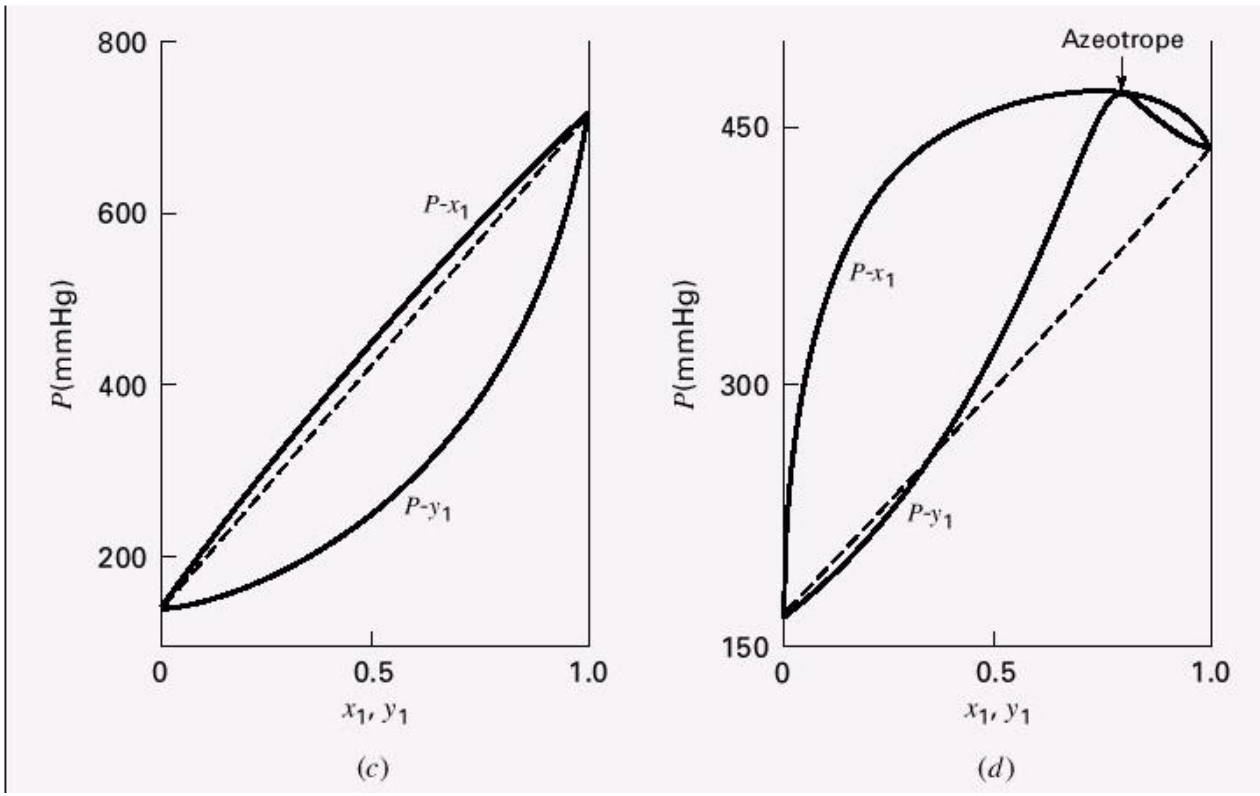


(a) Tetrahydrofuran (1) and carbon tetrachloride (2) at 30°C
(b) Chloroform (1) and tetrahydrofuran (2) at 30°C

Dashed line: *P x* relation for Raoult's law

VLE
Qualitative Behaviour

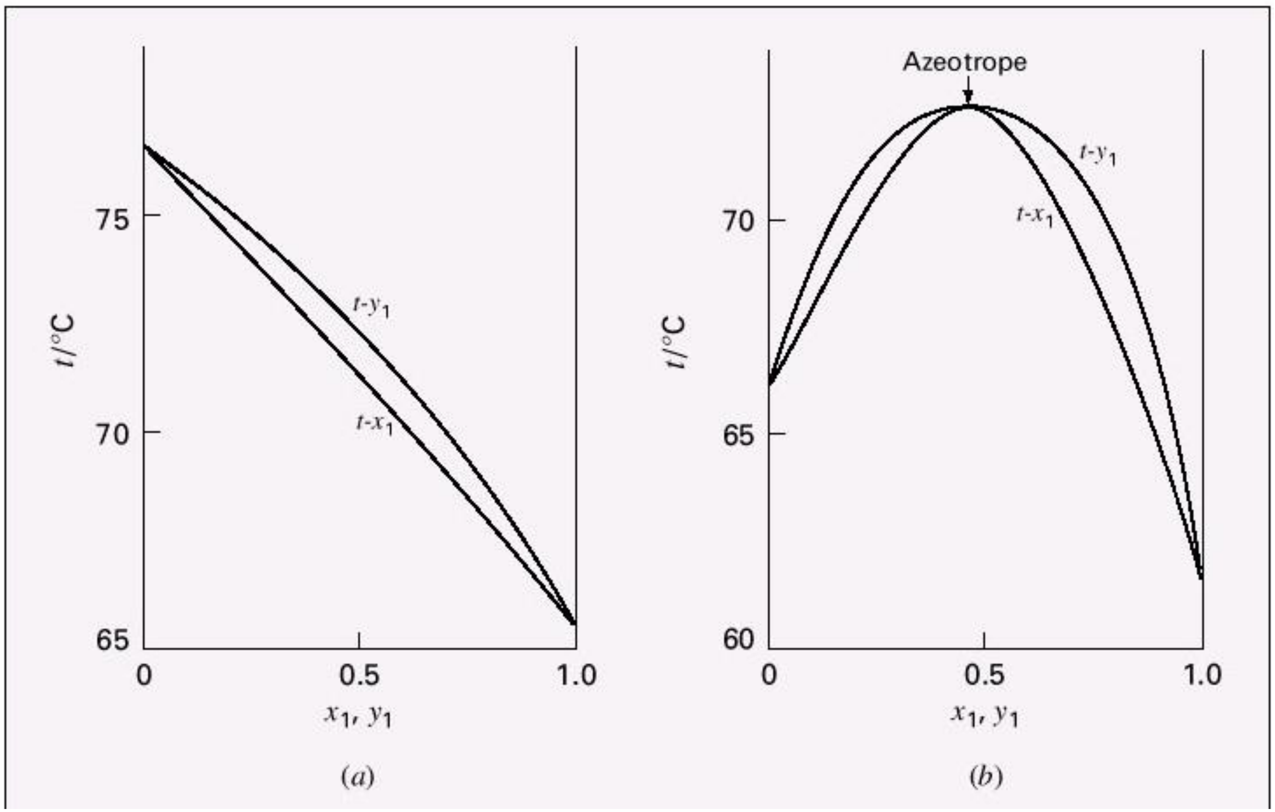
- *P xy* diagrams at constant *T*



(c) Furan (1) and carbon tetrachloride (2) at 30°C
(d) Ethanol (1) and toluene (2) at 65°C
Dashed line: *P x* relation for Raoult's law

VLE
Qualitative Behaviour

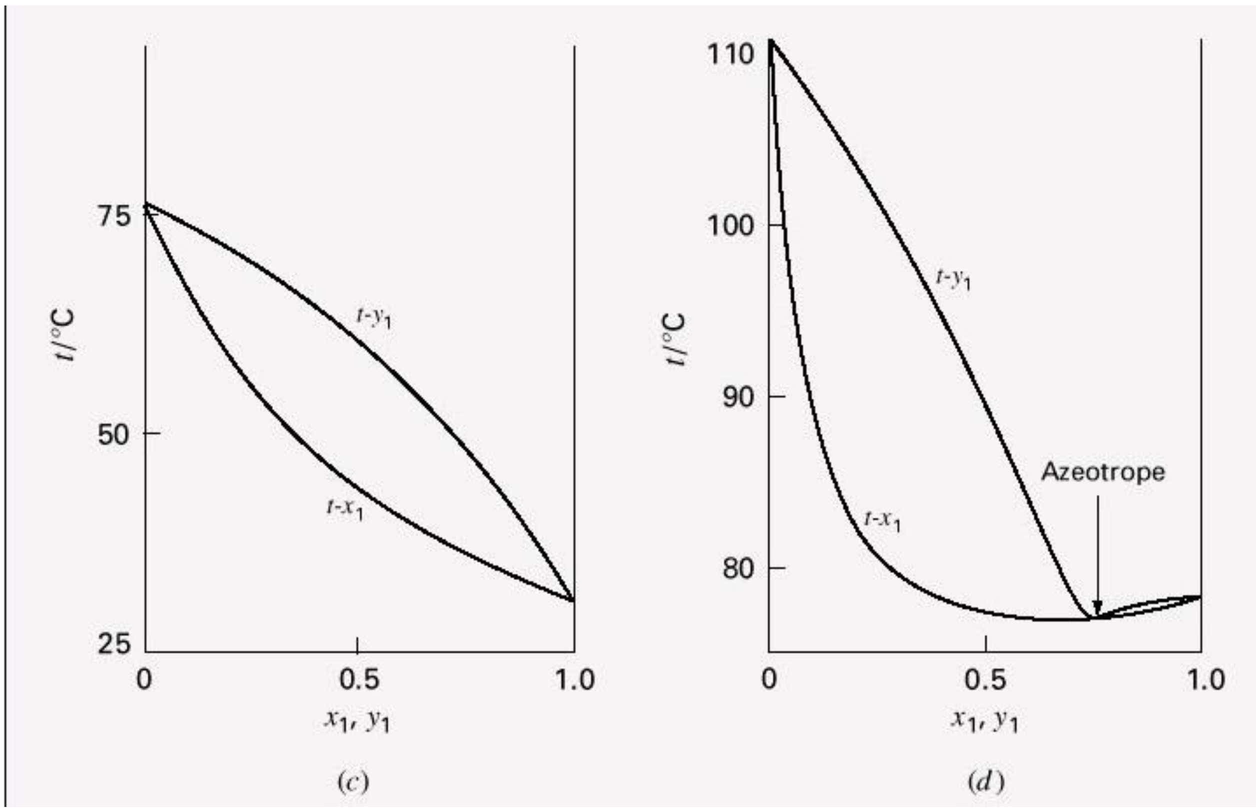
- *T xy* diagrams at constant *P*



(a) Tetrahydrofuran (1) and carbon tetrachloride (2) at 1 atm
(b) Chloroform (1) and tetrahydrofuran (2) at 1 atm

VLE
Qualitative Behaviour

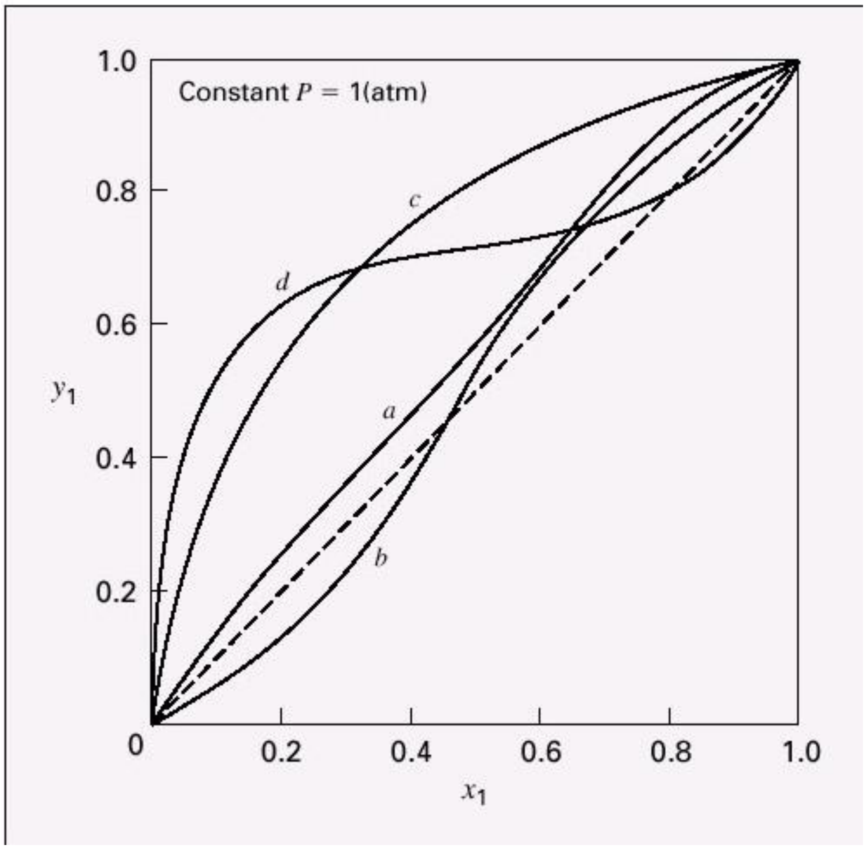
- *T xy* diagrams at constant *P*



(c) Furan (1) and carbon tetrachloride (2) at 1 atm
(d) Ethanol (1) and toluene (2) at 1 atm

VLE
Qualitative Behaviour

- *yx* diagrams at constant *P*



yx diagrams at 1 atm

(a) Tetrahydrofuran and carbon tetrachloride
(b) Chloroform and tetrahydrofuran
(c) Furan and carbon tetrachloride
(d) Ethanol and toluene

VLE
Simple Models: General

- Important goal: mathematical description of VLE
  - Prediction of vapour and liquid compositions at given temperature and pressure
  - Basis for process modelling
- Two simple models for VLE:
  - Raoult's law
  - Henry's law

VLE
Simple Models: Raoult's Law

- Two major assumptions:
  - Vapour phase is an ideal gas
  - Liquid phase is an ideal solution
- Mathematical expression:

$$\boxed{y_i P = x_i P_i^{sat} \qquad (i = 1, 2, \ldots, N)}$$

x_i liquid phase mole fraction
y_i gas phase mole fraction
P_i^{sat} vapour pressure
N number of chem. species

- Only valid for limited number of systems
- Valid for any species present at $x \rightarrow 1$

VLE
Simple Models: Raoult's Law

- Ideal gas mixture properties:
  - Dalton's law: $$P = \sum_i P_i = \sum_i y_i P$$
  - Amagat's law: $$V^t = \sum_i V_i^t = \sum_i y_i V^t$$
  - Kay's rule: $$T_c' = \sum_i y_i T_{c,i}$$ $$P_c' = \sum_i y_i P_{c,i}$$

VLE
Simple Models: Raoult's Law

- Dew point and bubble point calculations:
  - BUBL P: calculate y_i and P for given x_i and T
  - DEW P: calculate x_i and P for given y_i and T
  - BUBL T: calculate y_i and T for given x_i and P
  - DEW T: calculate x_i and T for given y_i and P
- Worked example:
  Prepare a graph showing P vs x_1 and P vs y_1 for T = 75 degC using Raoult's law for the binary system acetonitrile(1)/nitromethane(2)

VLE
Simple Models: Modified Raoult's Law

- To account for deviations from ideal solution behaviour in liquid phase:

$$\boxed{y_i P = x_i \gamma_i P_i^{sat} \qquad (i = 1,2,\ldots,N)}$$

x_i liquid phase mole fraction
y_i gas phase mole fraction
P_i^{sat} vapour pressure
N number of chem. Species
γ_i activity coefficient

- Activity coefficients are typically a function of temperature and chemical composition, e.g.

$$\boxed{\ln \gamma_i = A(T) \cdot x_j^2 \qquad (i, j = 1,2,\ldots,N)}$$

VLE
Simple Models: Henry's Law

- Raoult's law requires vapour pressure data
  - Not applicable if temperature is above the critical temperature of one species
  - No gas dissolution in liquid
- Henry's law:

$$\boxed{y_i P = x_i \mathcal{H}_i \quad (i = 1,2,\ldots,N)}$$

$\mathcal{H}_i$ Henry's constant

Gas	$\mathcal{H}$/bar	Gas	$\mathcal{H}$/bar
Acetylene	1,350	Helium	126,600
Air	72,950	Hydrogen	71,600
Carbon dioxide	1,670	Hydrogen sulfide	550
Carbon monoxide	54,600	Methane	41,850
Ethane	30,600	Nitrogen	87,650
Ethylene	11,550	Oxygen	44,380

Henry's constants for gases dissolved in water at 25°C

VLE
K-Value Correlations

- Equilibrium ratio K_i

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

- With Raoult's law

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

- Worked example:

  Determine dew point and bubble point pressures for a mixture of 10% methane, 20% ethane, and 70% propane at 50 degF.

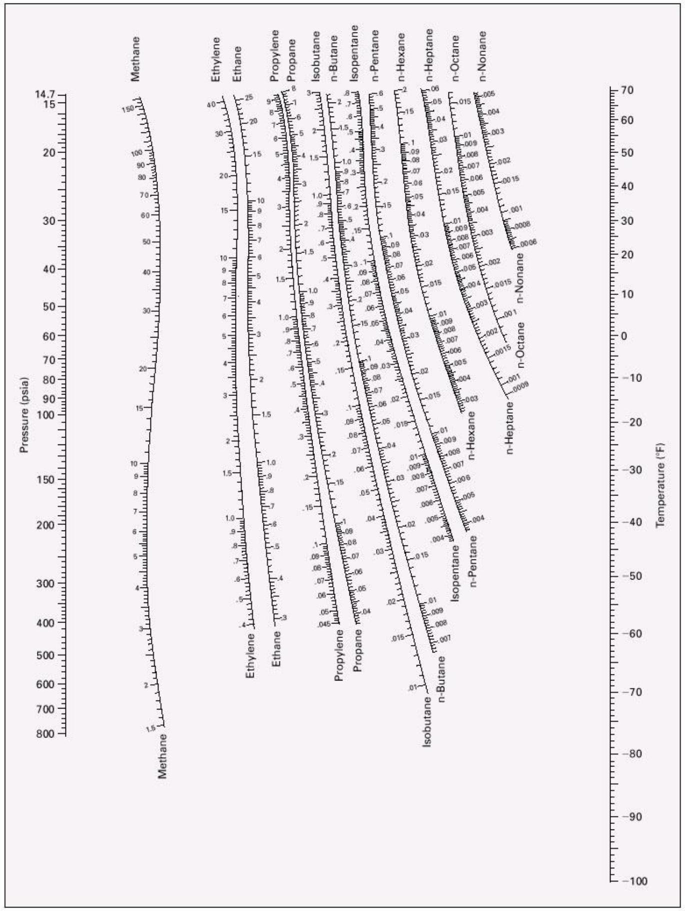


Figure 10.13: *K*-values for systems of light hydrocarbons. Low-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 41, 1953.)

VLE
Flash Calculations

- Flash: liquid at $P \geq P_{\text{bubblepoint}} \rightarrow P$ reduction
  $\rightarrow$ liquid flashes/partially evaporates to produce a 2-phase system in equilibrium
- Introduction of useful quantities:
  - Moles of liquid: $\mathcal{L}$ with mole fractions $\{x_i\}$
  - Moles of vapour: $\mathcal{V}$ with mole fractions $\{y_i\}$
  - Overall mole fraction: $\{z_i\}$