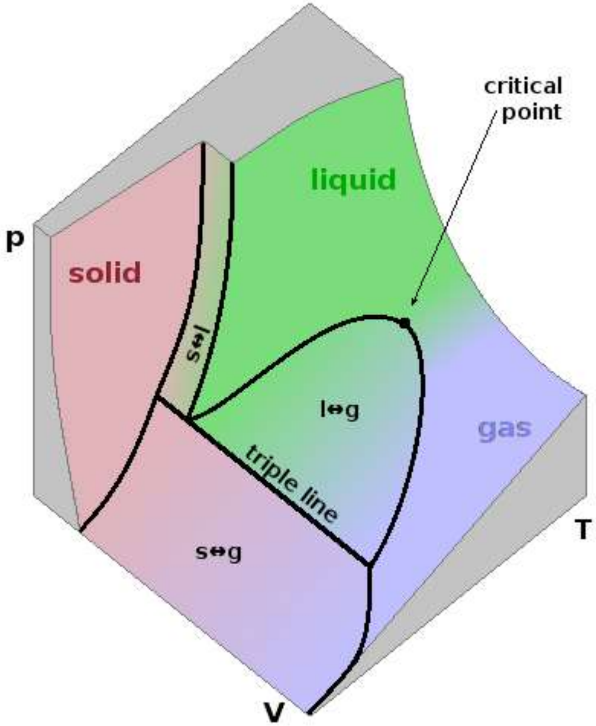
Physical Property, Thermodynamics & Phase Equilibria

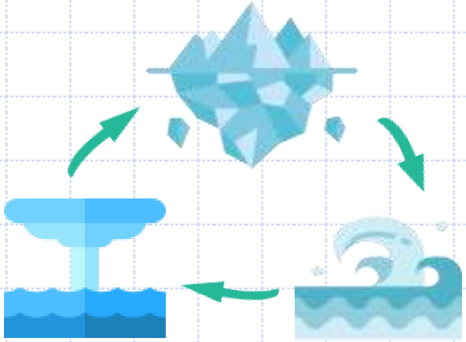
Maurizio Fermeglia
Maurizio.fermeglia@units.it
Department of Engineering & Architecture
University of Trieste



Agenda

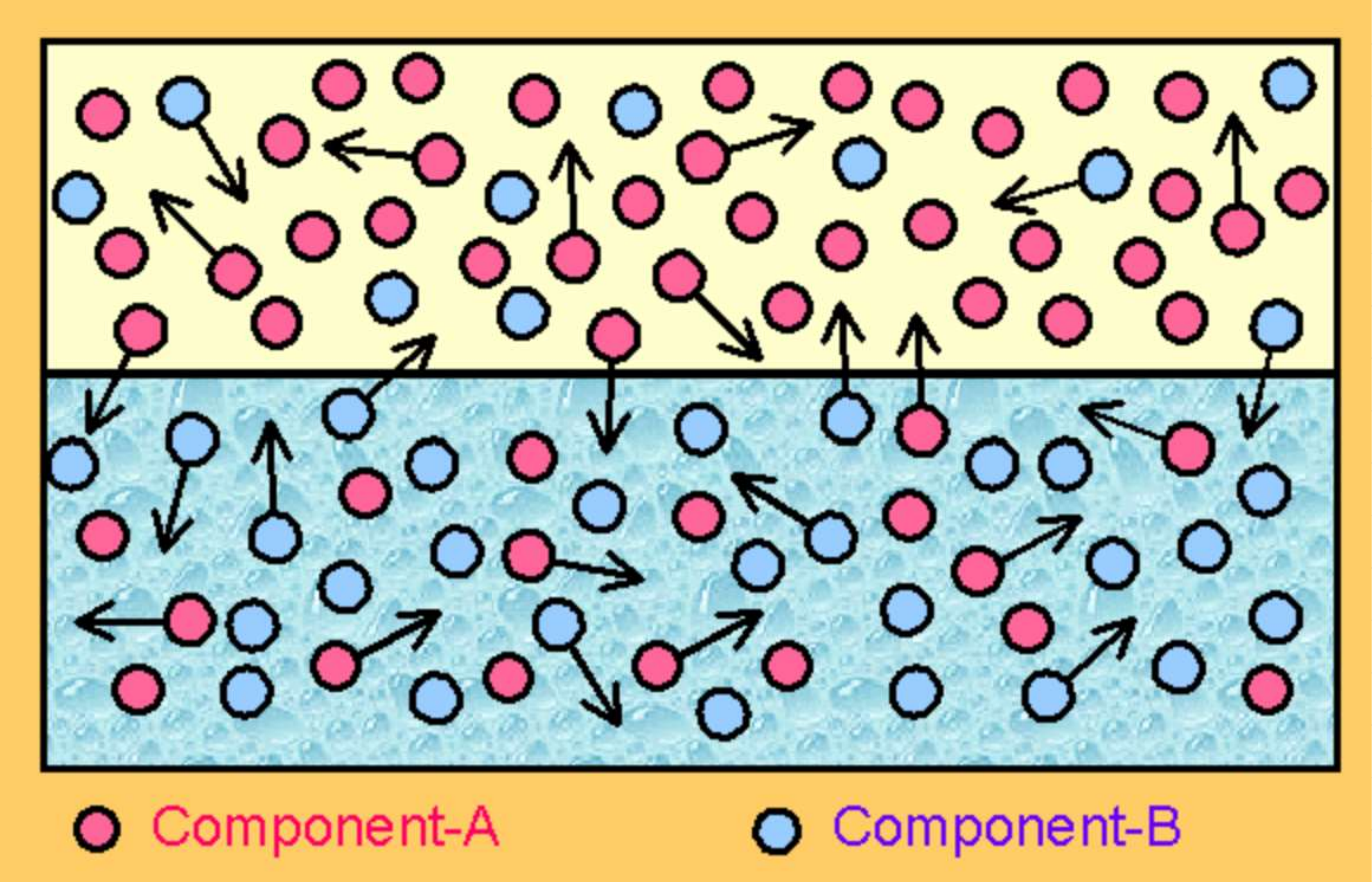
- Thermodynamic properties & phase equilibria
  - Phase equilibrium: pure components
  - Clausius-Clapeyron equation
  - Phase equilibrium: mixtures
  - Fugacity, Fugacity coefficient, Activity coefficient,
  - Calculation of phase equilibria (gamma-phi and phi-phi)
  - Henry’s law
- Phase diagrams
  - Binary T-x and P-x diagrams
  - High pressure diagrams
  - Binary x-y diagrams
  - Azeotropes
  - Other diagrams (activity coefficients, excess enthalpy,…)
- Modeling phase equilibria
  - Activity coefficient models – G^E models
  - Equations of state
  - QM methods: COSMO-RS
- Thermodynamic consistency
  - Barker’s method

Thermodynamic properties & phase equilibria

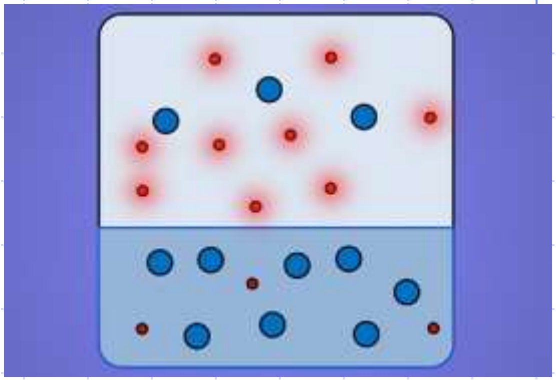


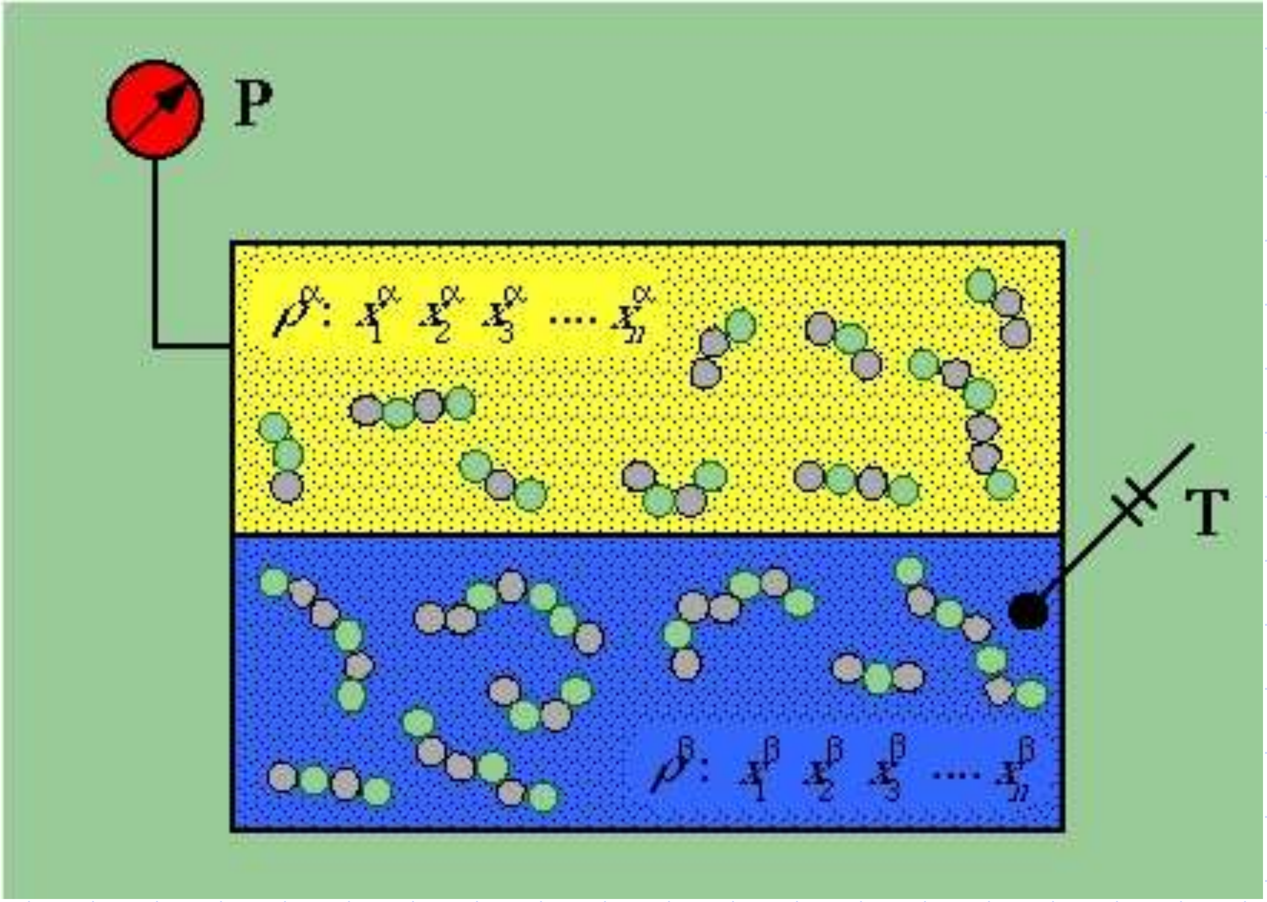
- Phase equilibrium: pure components
- Clausius-Clapeyron equation
- Phase equilibrium: mixtures
- Fugacity, Fugacity coefficient, activity coefficient,
- Calculation of phase equilibria (gamma-phi and phi-phi)
- Henry's law

Vapor liquid contacting system



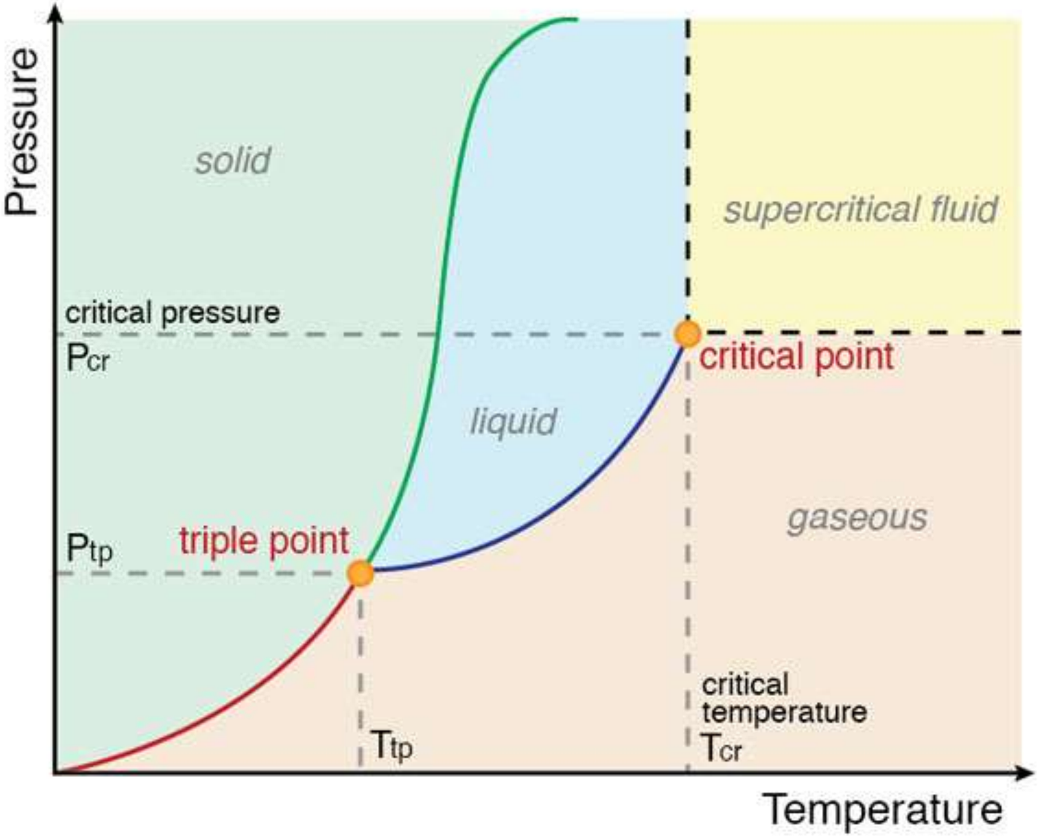
Vapor liquid contacting system

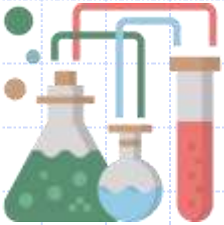




Thermodynamic properties and Phase Equilibrium

- N. of phases
  - Single phase systems
  - Multi phase systems
- N. of components
  - Pure components
  - Mixtures





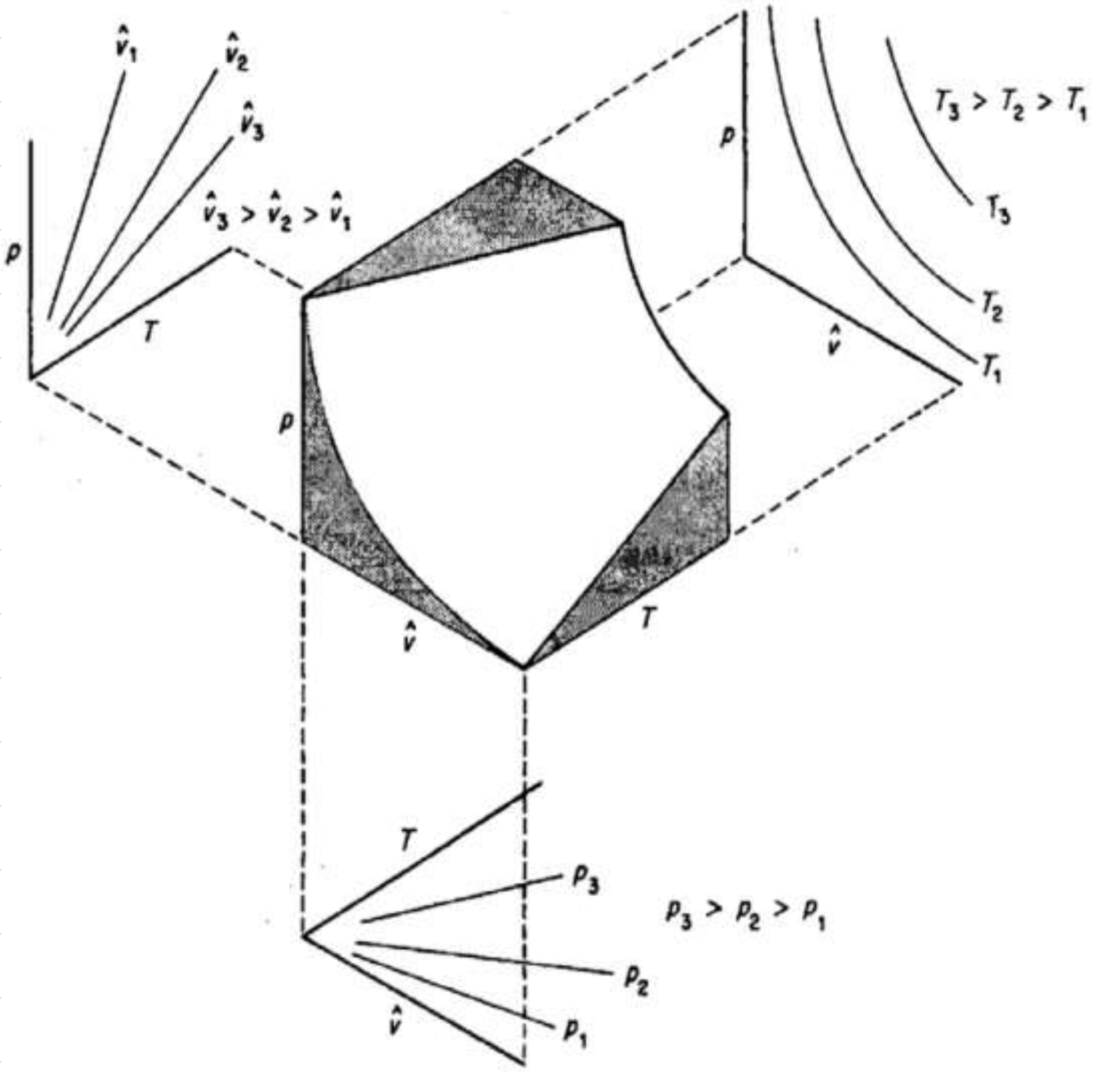
Single Phase systems

- Motivation:
  - most of the material balances in single phase involve liquids and gases and their volumetric properties
- Data is necessary (density, …)
  - Look it up in the data bank → find the right DB and values
  - Estimate it → pay attention to the estimation method
  - Measure it → problems of correlation and extrapolation
- For liquid systems the main problem is mixture density
- For gas system the main problem is the equation of state
  - Ideal gas law
  - Real gases and critical state
  - Van der Waals equation of state and related EOS
  - More complex equations of state
  - Compressibility factor EOS and corresponding states

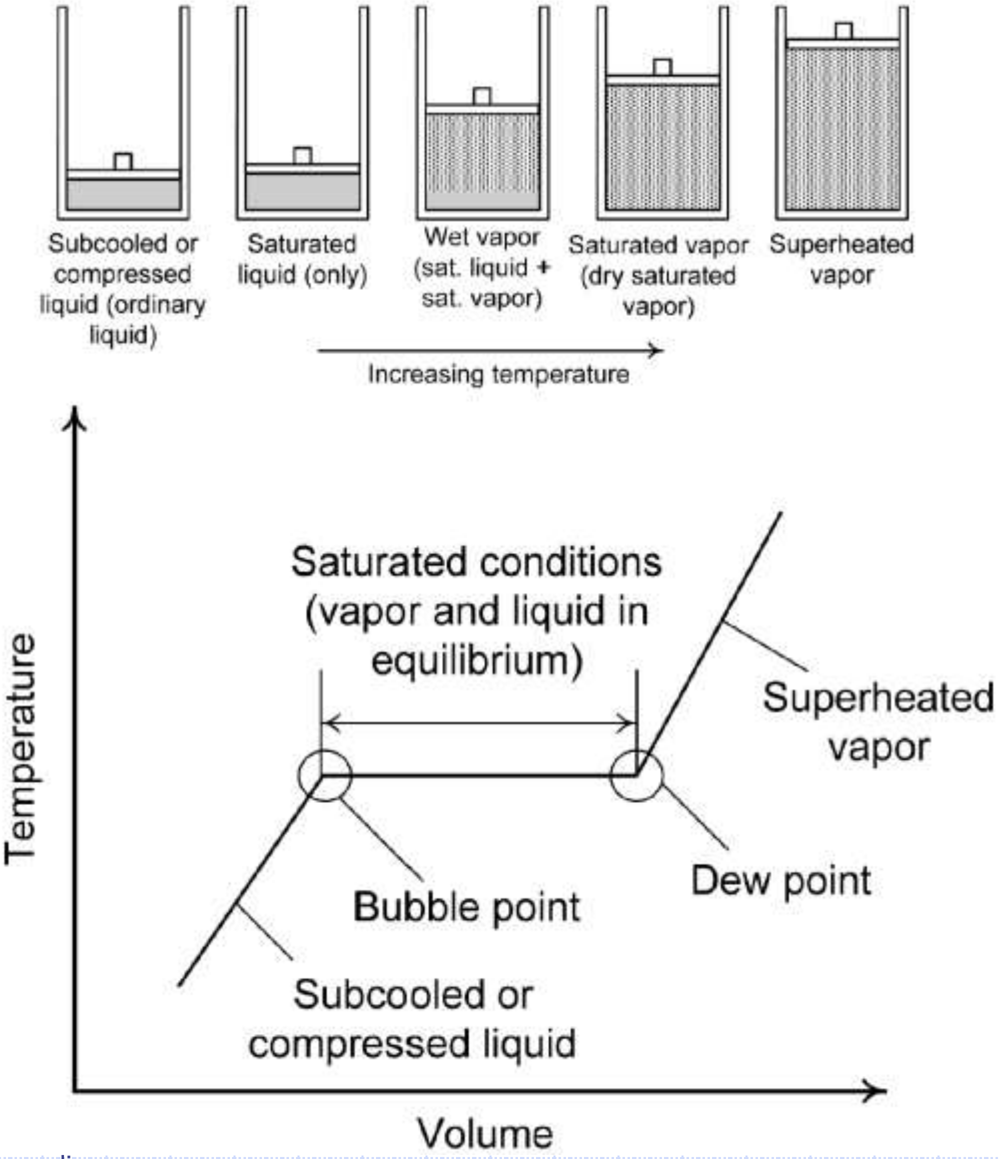
Multi Phase Systems

- One component systems
  - phase diagrams
  - vapor pressure and saturated properties
- Binary Systems
  - Gibbs phase rule
  - General conditions for equilibrium
  - Vapor – liquid equilibrium (all condensable components)
  - Gas – Liquid equilibrium (non condensable component)
  - Other equilibrium: solid – liquid and liquid - liquid
- Multi component systems
- Two phases in equilibrium
- Three or more phases in equilibrium

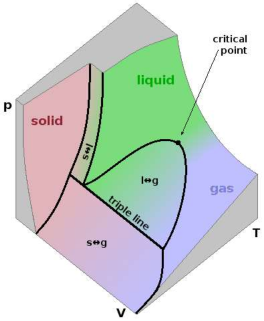
PVT for an ideal gas: pure component

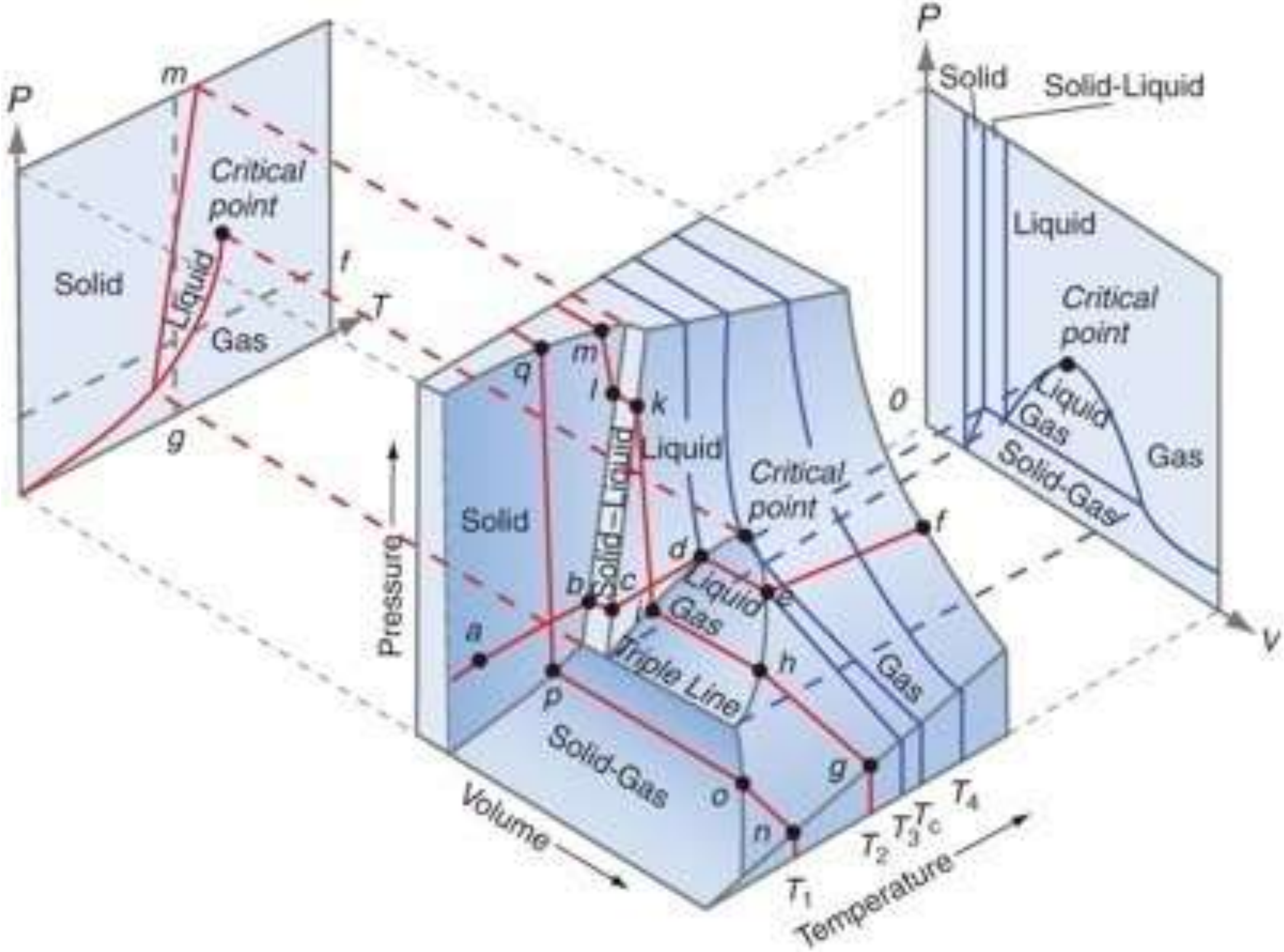


Phase behavior for a pure component

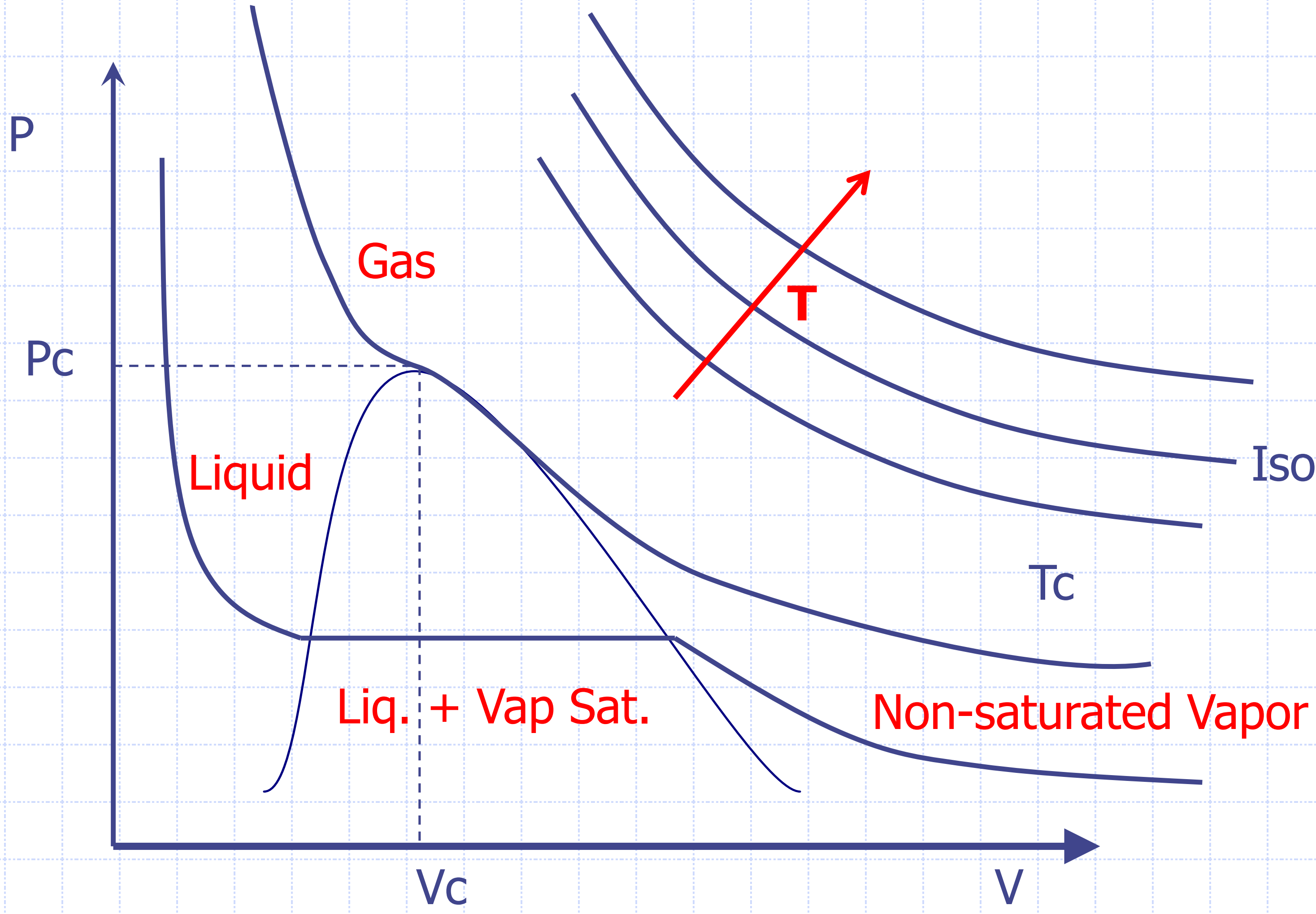


3D Phase diagram: pure component

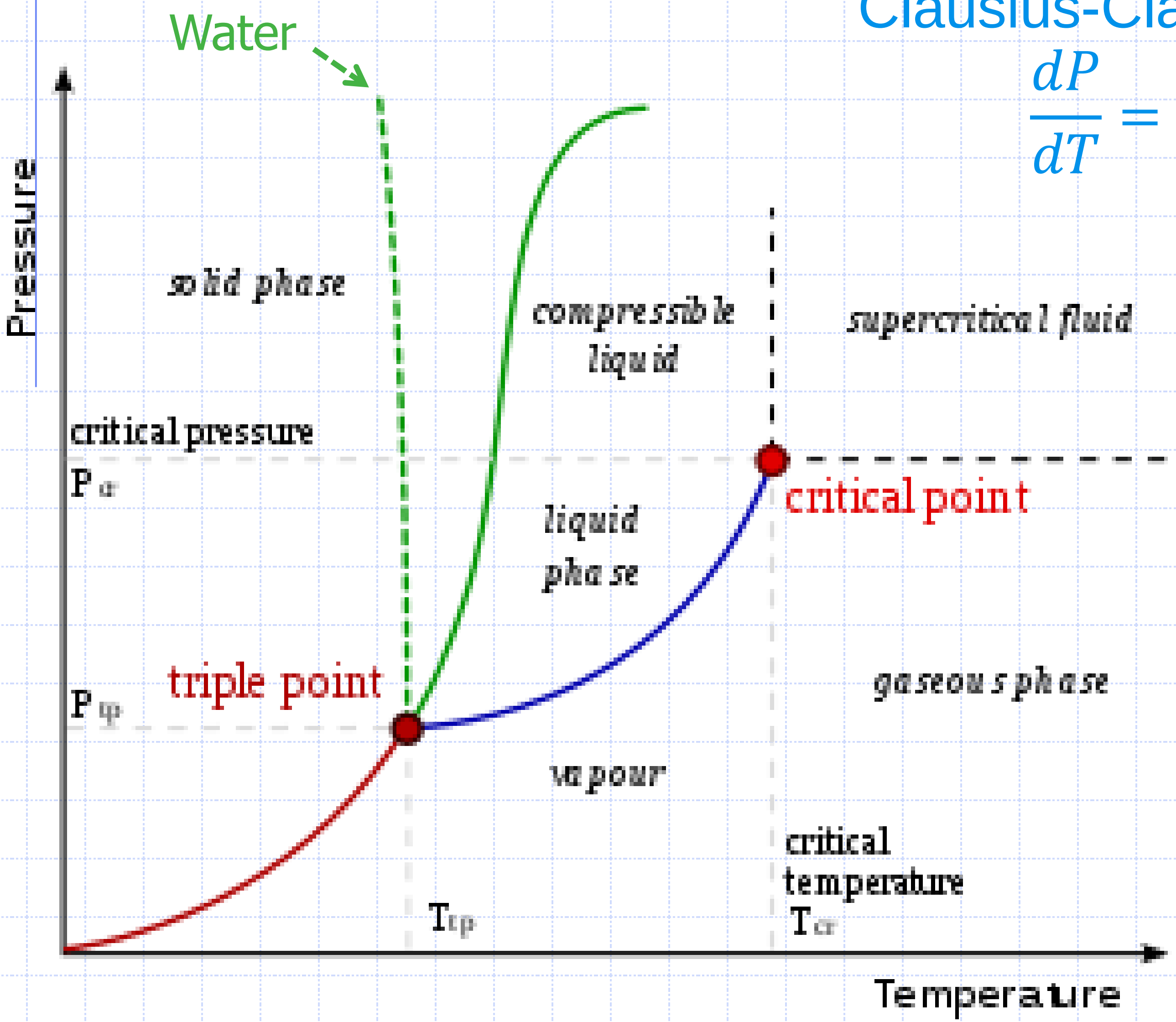




PV diagram for a pure component system



PT diagram for a pure component system



Clausius-Clapeyron Relation

$$\frac{dP}{dT} = \frac{\lambda}{T\Delta v} = \frac{\Delta s}{\Delta v}$$

λ = phase transition latent specific heat

v = specific volume

s = specific entropy

Thermodynamic Potentials

- Four important thermodynamic functions. These are:
  - The total (mean) Internal Energy U (E)
  - The Enthalpy H
  - The Helmholtz Free Energy F
  - The Gibbs Free Energy G
- Any one of these functions can be used to characterize the thermodynamic properties of a macroscopic system. These functions are sometimes called Thermodynamic Potentials (TP) or State functions.
  - Internal Energy U,
  - Enthalpy $H = U + pV$
  - Helmholtz Free Energy $F = U - TS$
  - Gibbs Free Energy $G = U - TS + pV$
- They depend ONLY on the Equilibrium state of the system
- If the integral of df doesn't depend on the path of integration, f is a state function and df is an exact differential.

Internal Energy U

- Macroscopic measure of subatomic and molecular energies
  - It is NOT directly measurable
  - It is a state function – only differences in U are calculated
  - Consequently, it is an exact differential
  - It can be expressed (for a pure component) in terms of two intensive variables (phase rule)
    - Temperature
    - Specific volume
  - U = U(T,V)

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_{T} d\hat{V}$$

  - At constant volume:

$$\hat{U}_2 - \hat{U}_1 = \int_1^2 C_v \, dT$$

Enthalpy H

- Defined as a combination of variables: → H=U +pV
  - It is NOT directly measurable
  - It is a state function – only differences in H are calculated
  - Consequently, it is an exact differential
  - It can be expressed (for a pure component) in terms of two intensive variables (phase rule)
    - Temperature
    - Pressure
  - H = H(T,p)

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp$$

  - At constant pressure:

$$\hat{H}_2 - \hat{H}_1 = \int_1^2 C_p\, dT$$

Thermodynamic Potentials

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

- If we define:
  - N ≡ Number of particles in the system.
  - μ ≡ Chemical potential of the system.
    - chemical potential of a specie is energy that can be absorbed or released due to a change of the particle number of the given specie (chemical reaction or phase transition)
- For each TP, a set of so-called “natural variables” exists.
  - Internal Energy U = U(S,V,N)
  - Enthalpy H = U + pV = H(S,p,N)
  - Helmholtz Free Energy F = U – TS = F(T,V,N)
  - Gibbs Free Energy G = U – TS + pV = G(T,p,N)

Potential	**Variables**
U(S,V,N)	***S,V,N***
H(S,p,N)	***S,p,N***
F(T,V,N)	***V,T,N***
G(T,P,N)	***P,T,N***

Thermodynamic potentials

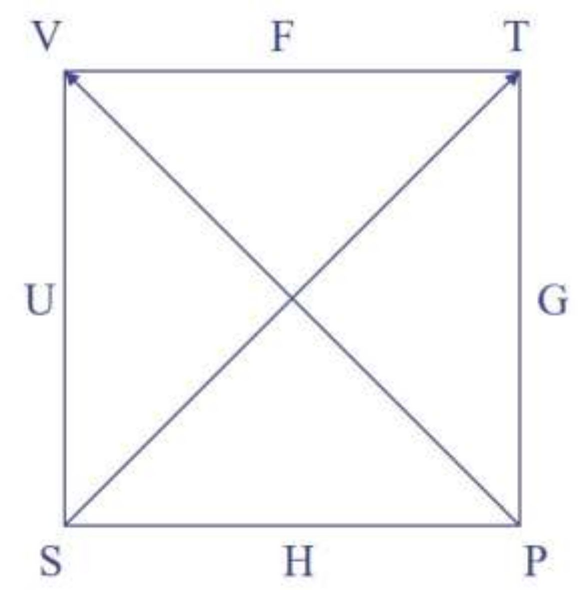
- All thermodynamic properties of a system can be found by taking appropriate partial derivatives of the Thermodynamic Potential.
- The total differentials resulting from the combined 1st & 2nd Laws for each Thermodynamic Potential are:

$$dU(S,V,N) = TdS - PdV + \mu dN$$

$$dH(S,P,N) = T\,dS + VdP + \mu dN$$

$$dF(T,V,N) = -SdT - PdV + \mu dN$$

$$dG(T,P,N) = -SdT + VdP + \mu dN$$



Why Use Maxwell Relations? What Good are They?

- Some variables in thermodynamics are hard to measure experimentally.
  - For example, the entropy
- The Maxwell Relations provide a way to exchange variables.
- They relate theoretical quantities, such as equations of state & entropy to more easily measured quantities
- Internal energy (U), Enthalpy (H), Helmholtz free energy (F) and Gibbs free energy (G) are used to derive the 4 most common Maxwell equations.

Deriving Maxwell Relations: a recipe

- Assume an infinitesimal quasi-static process & express an energy as a function of the other variables. For the internal energy U as a function of T, S, P, V, we have

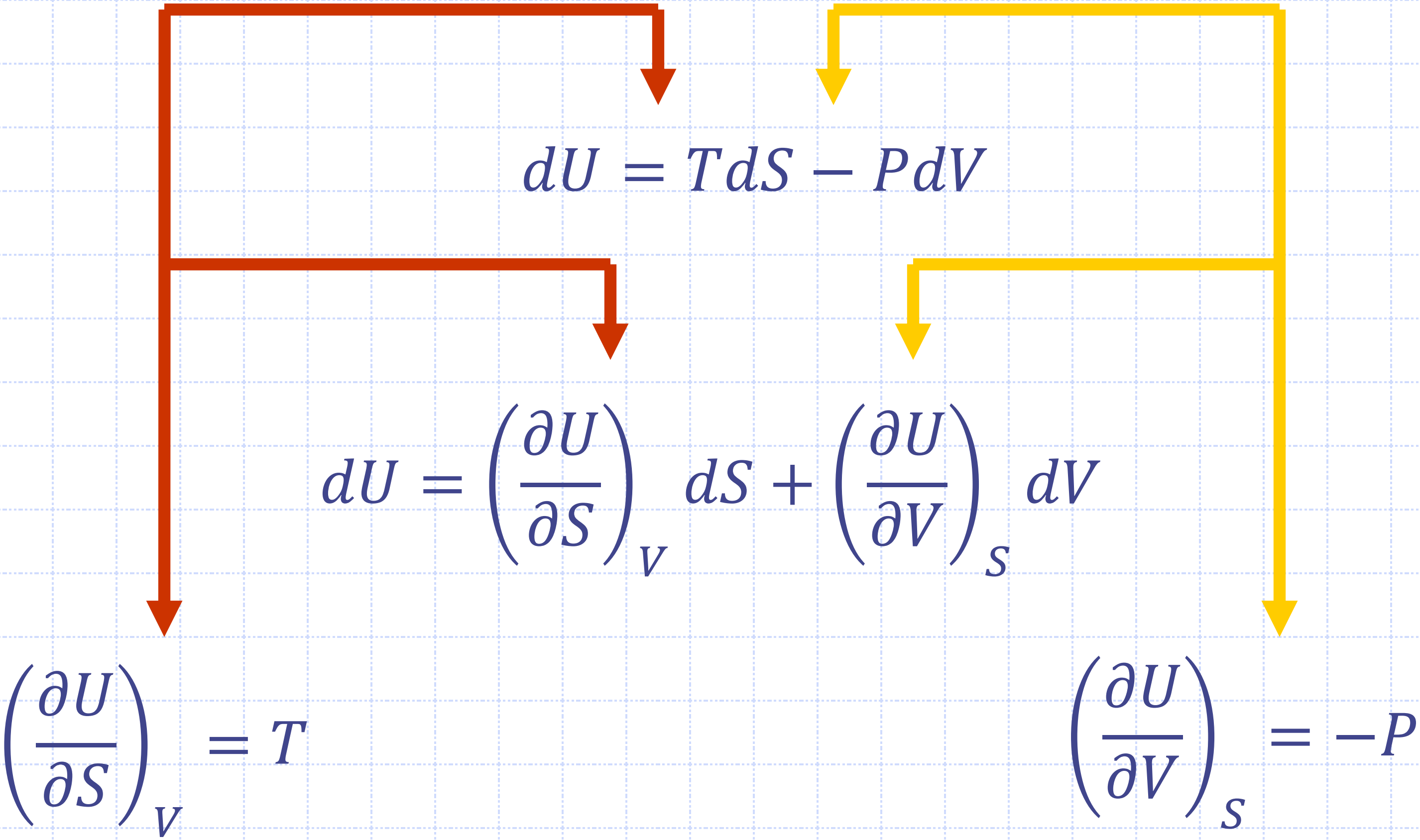
$$dU = TdS - PdV$$

- Next, take the total derivative of the energy with respect to the natural variables.
  - For example, for the internal energy U, natural variables are entropy S & volume, V
  - U is a state function and dU is an exact differential.

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Deriving Maxwell Relations: a recipe

- Now that we have the total derivative with respect to its natural variables, we can refer back to the original equation for the energy U and define, in this example, T and P.



$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Deriving Maxwell Relations: a recipe

- Now if we take into account a rule about partial derivatives for analytic functions (Schwarz theorem):

$$\boxed{\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x},}$$

- Next, when taking the partial derivative of

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

- We obtain the same result, which is equal to $\partial^2 U / \partial S \partial V$ for both derivatives: we have derived a **Maxwell Relation**

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

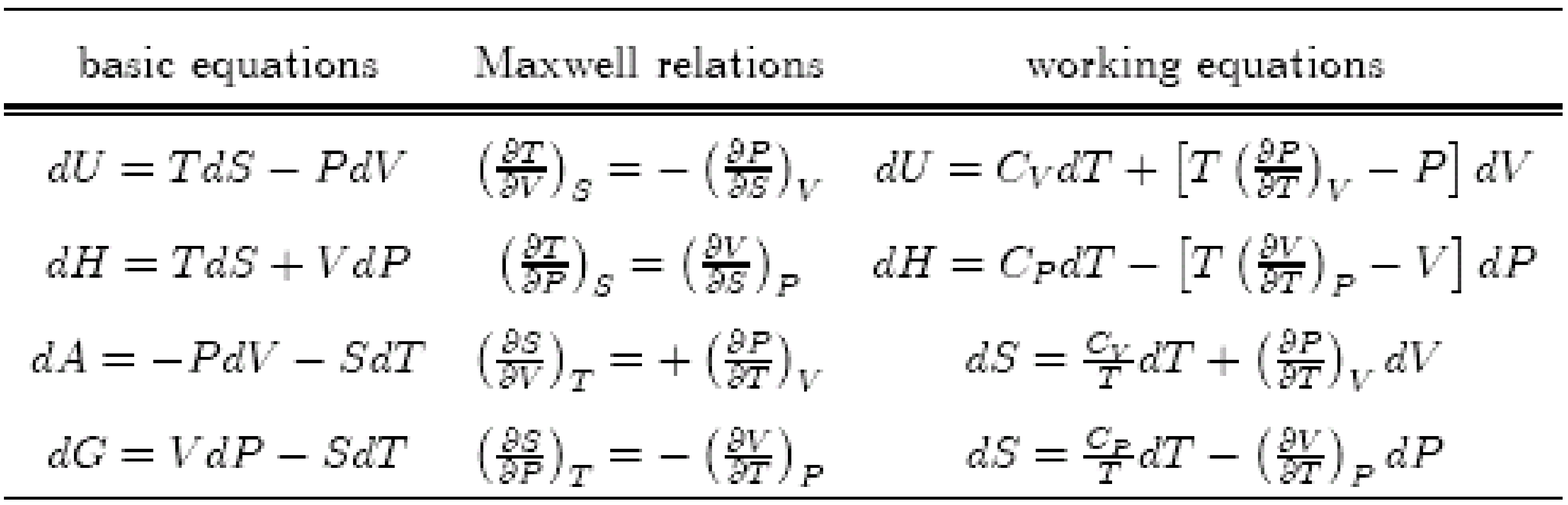
The 4 Most Common Maxwell Relations

- Internal energy (U), Enthalpy (H), Helmholtz free energy (F) and Gibbs free energy (G) are used to derive the 4 most common Maxwell equations.
- These are derived assuming that
  - The external parameter is the volume V
  - The generalized force is the pressure P

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

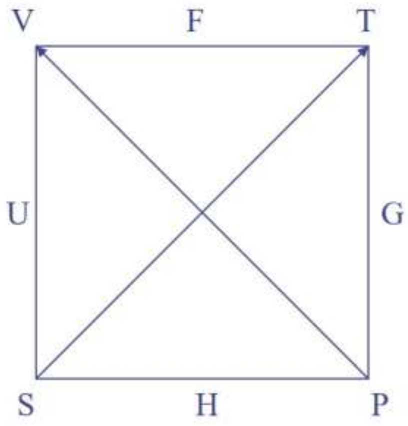
Maxwell Relations



basic equations	Maxwell relations	working equations
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$
$dA = -PdV - SdT$	$\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
$dG = VdP - SdT$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

Clausius-Clapeyron Equation (Maxwell relations)

- Phases (A,B) equilibrium condition:
  - $T_A = T_B; P_A = P_B; G_A = G_B$
  - $dG_A(T,p) = dG_B(T,p)$
  - $\frac{\partial G_A}{\partial T} dT + \frac{\partial G_A}{\partial p} dp = \frac{\partial G_B}{\partial T} dT + \frac{\partial G_B}{\partial p} dp$



- Gibbs-Helmholtz Equation
  - $dG = VdP - SdT \xrightarrow{\qquad\qquad} \frac{\partial G}{\partial T} = -S, \ \frac{\partial G}{\partial p} = \mathrm{V}$
  - $V_A dp - S_A dT = V_B dp - S_B dT \xrightarrow{\qquad\qquad} \frac{dp}{dT} = \frac{S_B - S_A}{V_B - V_A}$
- From II law (ds=dq/T) and phase Transition is isothermal

$$S_B - S_A = \int_A^B \frac{\delta Q}{T} = \frac{1}{T}\int_A^B \delta Q = \frac{\lambda}{T} \Rightarrow \frac{dP^\circ}{dT} = \frac{\lambda_{vap}}{T(V_v - V_l)}$$

- And $V_v >> V_L$:

$$V_v - V_l \cong V_v = {}^{RT}\!/_{P^\circ} \Rightarrow \frac{dP^\circ}{dT} = \frac{\lambda_{vap} P^\circ}{RT^2}$$

Clausius-Clapeyron Equation (Carnot cycle)

- Work from a reversible Carnot cycle

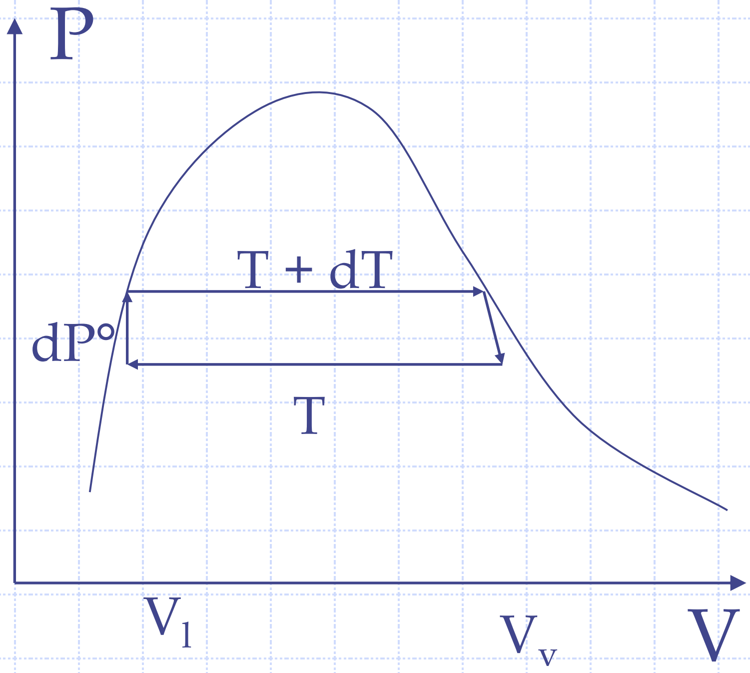
$$dw = (V_v - V_l)[P°(T + dT) - P°(T)] = (V_v - V_l)dP°$$

- Efficiency of a reversible Carnot cycle

$$d\eta = \frac{(V_v - V_l)dP°}{\lambda_{vap}} \quad but \quad d\eta = \frac{dT}{T}$$

$$\frac{dP°}{dT} = \frac{\lambda_{vap}}{T(V_v - V_l)}$$

$$V_v - V_l \cong V_v = {}^{RT}\!/_{P°} \Rightarrow \frac{dP°}{dT} = \frac{\lambda_{vap} P°}{RT^2}$$



Saturation and Vapor Pressure

$$\frac{dP°}{dT} = \frac{\lambda P°}{RT^2}$$

V= volume

v= sp. volume V/m

- Clausius-Clapeyron curve represents the VLE of a pure component = saturation
  - Vapor is saturated when the first drop of liquid is formed (dew point)
  - Liquid is saturated when the first bubble of vapor is formed (bubble point)
- Vapor fraction: mass fraction of the less dense (vapor) phase with respect to the total mass
- Vapor Pressure and Temperature
  - Clausis-Clapeyron expression for moderate pressure when vg>>> vl

$$\ln P = -\frac{\lambda}{R} * \frac{1}{T} + c$$

$$\ln P = A - \frac{B}{(T + C)}$$

  - Semi empirical laws: Antoine
  - where A, B and C are fluid (and units) dependent constants
  - Wagner eq.

$$\ln P_r = \frac{n_1 \cdot \tau + n_2 \cdot \tau^{1,5} + n_3 \cdot \tau^3 + n_4 \cdot \tau^6}{T_r}$$

With $P_r = \frac{P}{P_c}$, the reduced pressure and $T_r = \frac{T}{T_c}$, the reduced temperature, and $\tau = 1 - T_r = 1 - \frac{T}{T_c}$.

Gibbs phase rule

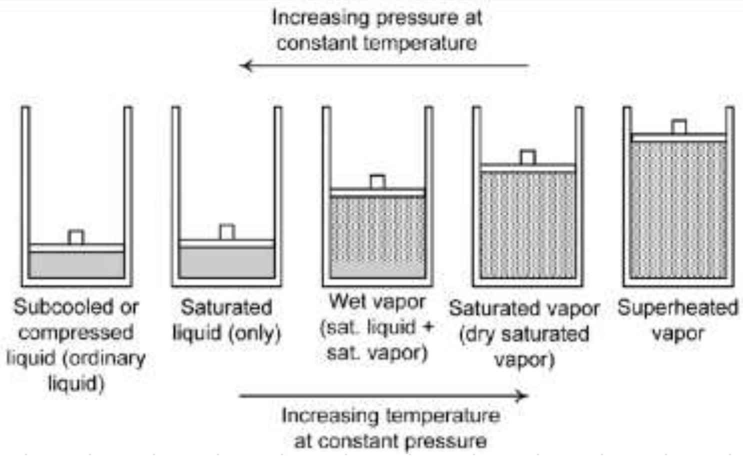
- The variables for describing a process are
  - Extensive (depends on size of system)
  - Intensive (do not)
- The number of intensive variables that can be specified independently is called degree of freedom (DF). If c= # components and P= # phases

$$DoF = \underset{\nwarrow\ \text{T,P}}{2} + c - P$$

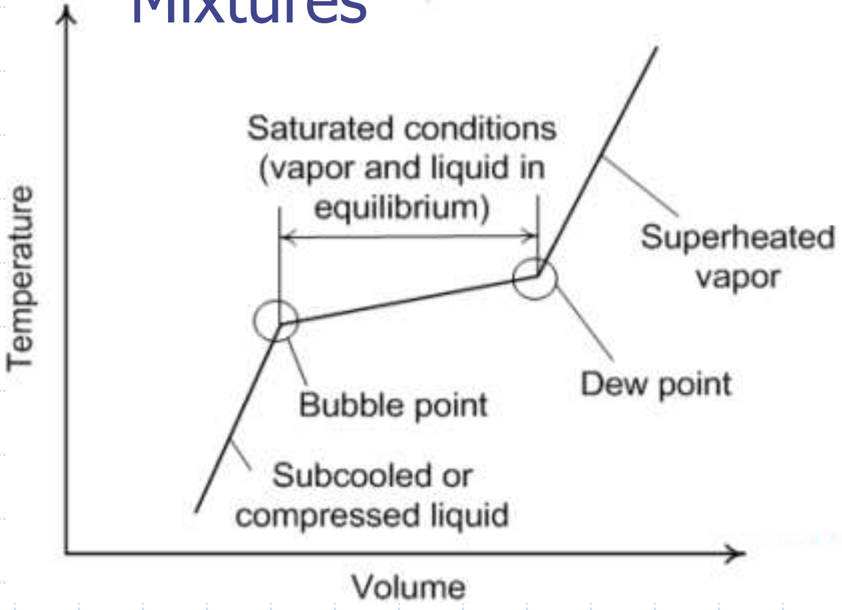
- Valid if no reaction occur
- If r independent reaction occur, the right hand side of the equation should be reduced by r

$$DoF = 2 + c - P - R$$

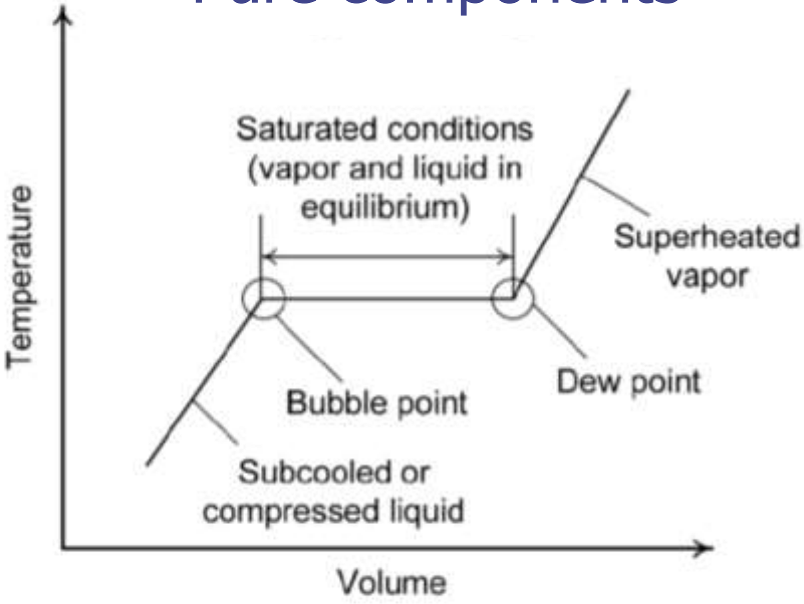
Phase behavior of a mixture of components



Mixtures



Pure components



Mixtures: phase Equilibrium Relationships

$$T^{(1)} = T^{(2)} = T^{(3)} = \cdots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = P^{(3)} = \cdots = P^{(\pi)}$$

$$\bar{G}_1^{(1)} = \bar{G}_1^{(2)} = \bar{G}_1^{(3)} = \cdots = \bar{G}_1^{(\pi)}$$

$$dG(T, p, \boldsymbol{n}) \longrightarrow \frac{\partial G}{\partial n} = \mu(T, p)$$

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} = \cdots = \mu_1^{(\pi)}$$

$$\cdots$$

$$\mu_m^{(1)} = \mu_m^{(2)} = \mu_m^{(3)} = \cdots = \mu_m^{(\pi)}$$

From Chemical Potential μ to Fugacity f

$$d\mu_T = dg_T = vdp = RT\frac{dp}{p} = RTdln(p)$$ **valid for perfect gas**

$$\int_{gp,T,p}^{gr,T,p} d\mu_T = \int_{gp,T,p}^{gr,T,p} RTdln(f)$$

Fugacity represents the pressure of an real gas (gp) whose temperature and molar Gibbs free energy are equal to the ones of a real gas (gr)

$$\mu_i^{(\alpha)} - \mu_i^{0\alpha} = RT\ln\frac{\hat{f}_i^{\alpha}}{f_i^{0\alpha}}$$

$$i = 1,2, \dots, m$$
$$\alpha = 1,2, \dots, \pi$$

$$\mu_i^{01} + RT\ln\frac{\hat{f}_i^{(1)}}{f_i^{01}} = \mu_i^{02} + RT\ln\frac{\hat{f}_i^{(2)}}{f_i^{02}} = \cdots = \mu_i^{0\pi} + RT\ln\frac{\hat{f}_i^{(\pi)}}{f_i^{0\pi}}$$

Phase Equilibrium in terms of Fugacity

$$T^{(1)} = T^{(2)} = T^{(3)} = \cdots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = P^{(3)} = \cdots = P^{(\pi)}$$

$$\hat{f}_1^{(1)} = \hat{f}_1^{(2)} = \hat{f}_1^{(3)} = \cdots = \hat{f}_1^{(\pi)}$$

$$\cdots$$

$$\hat{f}_m^{(1)} = \hat{f}_m^{(2)} = \hat{f}_m^{(3)} = \cdots = \hat{f}_m^{(\pi)}$$

Fugacity coefficient and Equilibrium

$$\hat{\phi}_i = \frac{\hat{f}_i}{Px_i} = \frac{\hat{f}_i}{P_i}$$

- Fugacity is more convenient than chemical potentials...
  - … but equilibrium is best expressed in term of fugacity coefficients
  - ... which is one if the fugacity is equal to the partial pressure
- Fugacity coefficient may be considered as the correction factor to the partial pressure (effective partial pressure)

Phase Equilibrium in terms of Fugacity coefficients ($\varphi\ \varphi$ approach)

$$T^{(1)} = T^{(2)} = T^{(3)} = \cdots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = P^{(3)} = \cdots = P^{(\pi)}$$

$$\hat{\varphi}_1^{(1)} x_1^{(1)} P = \hat{\varphi}_1^{(2)} x_1^{(2)} P = \hat{\varphi}_1^{(3)} x_1^{(3)} P = \cdots = \hat{\varphi}_1^{(\pi)} x_1^{(\pi)} P$$

$$\cdots$$

$$\hat{\varphi}_m^{(1)} x_m^{(1)} P = \hat{\varphi}_m^{(2)} x_m^{(2)} P = \hat{\varphi}_m^{(3)} x_m^{(3)} P = \cdots = \hat{\varphi}_m^{(\pi)} x_m^{(\pi)} P$$

At the Liquid - Vapor Equilibrium

$$\hat{\varphi}_i^L x_i = \hat{\varphi}_i^V y_i \qquad i = 1,2,\dots,m$$

Fugacity from an Equations of State

Equation of State is a function…

$$F(P,V,T,y_1,\dots,y_{n-1})=0$$

Fugacity is obtained by integration

$$d\mu_T=dg_T=vdp=RT\frac{dp}{p}=RTdln(p)$$

$$RTdln(p)=RT\ln\frac{\hat{f}_i^{\alpha}}{p_i^{0\alpha}}=RTln\hat{\varphi}_i=d\mu_T$$

$$RTln\hat{\varphi}_i=\int_0^P\left(v-\frac{RT}{p}\right)dp \quad \rightarrow \quad ln\hat{\varphi}_i=\frac{1}{RT}\int_0^P\left(\frac{pv-RT}{p}\right)dp$$

$$ln\hat{\varphi}_i=\int_0^P(Z-1)\frac{dp}{p} \qquad Z=\frac{pv}{RT}$$

compressibility factor

… may be obtained by differentiation

$$RT\ln\hat{\Phi}_i = \left(\frac{\partial nA^r}{\partial n_i}\right)_{n_j,T,V} - RT\ln Z$$

$$F = \frac{nA^r(V,T,\bar{n})}{RT}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,n} = -\frac{P}{RT} + \frac{n}{V}$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,n} = -\frac{nS^r(T,V,\bar{n})}{RT} - \frac{F}{T}$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V} = \ln\hat{\Phi}_i + \ln Z$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,n} = -\frac{1}{RT}\left(\frac{\partial P}{\partial V}\right)_{T,n} - \frac{n}{V^2}$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,n} = -\frac{nC_V^r}{RT^2} - \frac{2}{T}\left(\frac{\partial F}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial^2 F}{\partial n_i \partial n_j}\right)_{T,V} = \left(\frac{\partial \ln\hat{\Phi}_i}{\partial n_j}\right)_{T,P} + \frac{\bar{V}_i}{RT}\left(\frac{\partial P}{\partial n_j}\right)_{T,V} - \frac{1}{n}$$

$$\left(\frac{\partial^2 F}{\partial T \partial n_i}\right)_{V} = \left(\frac{\partial \ln\hat{\Phi}_i}{\partial T}\right)_{P,n} - \frac{1}{T} + \frac{\bar{V}_i}{RT}\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial^2 F}{\partial T \partial V}\right)_{n} = -\frac{1}{RT}\left(\frac{\partial P}{\partial T}\right)_{V,n} + \frac{P}{RT^2}$$

$$\left(\frac{\partial^2 F}{\partial V \partial n_i}\right)_{T} = -\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V} + \frac{1}{V}$$

Fugacity from Activity Coefficients

Vapor fugacity $\hat{f}_i^V = P y_i \hat{\phi}_i^V$

Liquid fugacity $\hat{f}_i^L = \left(f_i^L\right)_{id} \gamma_i$

Where $\left(f_i^L\right)_{id} = R_i(T,P) x_i$

If pure liquid exists $R_i = \lim_{x_i \to 1} \frac{f_i^L}{x_i} = f_{i,\text{pure}}^L = f_i^L$ at system T and p

Now refer f to p_i^0

At constant v_i and T $$ln \frac{f_i^L(T,p)}{f_i^{L0}(T,p_i^0)} = \frac{v_i}{RT} \int_{p_i^0}^{P} dp = \boxed{\frac{v_i(p - p_i^0)}{RT}}$$

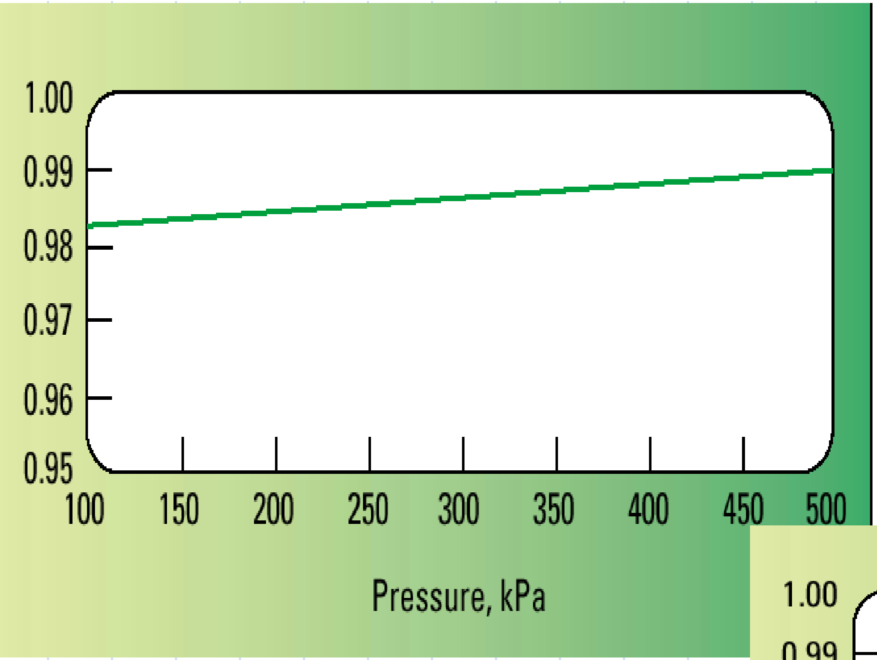
Poynting Factor

Therefore → $$\hat{f}_i^L = f_i^{L0}(T,p_i^0) \exp\left[\frac{v_i^L(P - p_i^o)}{RT}\right] x_i \gamma_i$$

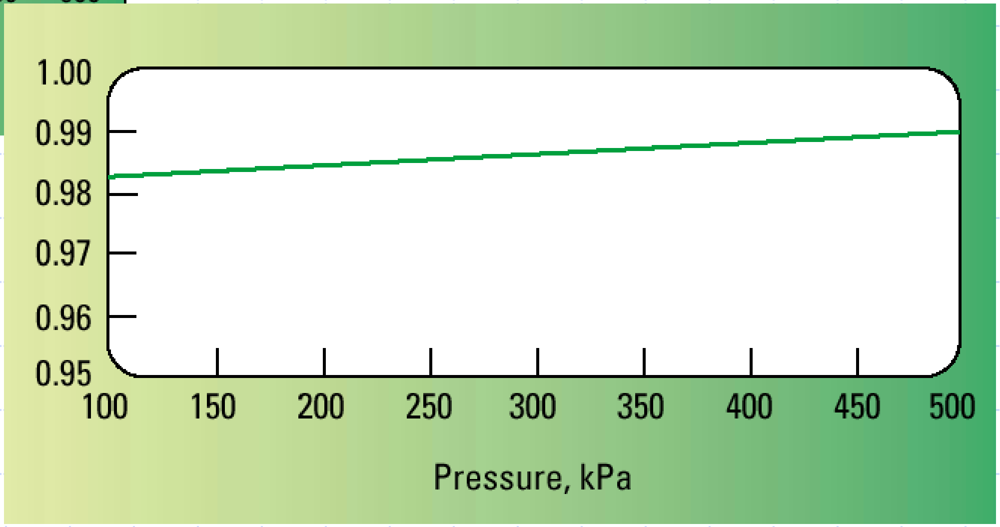
$$\hat{f}_i^V = \hat{f}_i^L \qquad \varphi_i^o = \frac{f_i^{L0}}{p x_i} = \frac{f_i^{L0}}{p_i^0} \to f_i^{L0} = p_i^0 \varphi_i^o$$

VLE $$P y_i \hat{\phi}_i^V = p_i^o \varphi_i^o \exp\left[\frac{v_i^L(P - p_i^o)}{RT}\right] x_i \gamma_i \xrightarrow{\textbf{Low P}} P y_i = p_i^o x_i \gamma_i$$

Order of magnitude of corrections



Fugacity correction ratio for Ethanol @ 150 °C

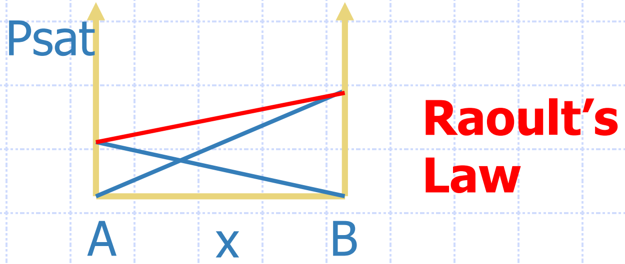


Poynting factor for Ethanol @ 150 °C

Types of VLE Phase behaviour

Ideal systems

- Systems that obey the Raoult's law
- Consist of molecules of the same size and shape and intermolecular forces
- Mixtures at low pressures that may be assumed as ideal mixtures (hydrocarbons, isomers,…)
- Ideal mixtures cannot form azeotropes or multiple liquid phases



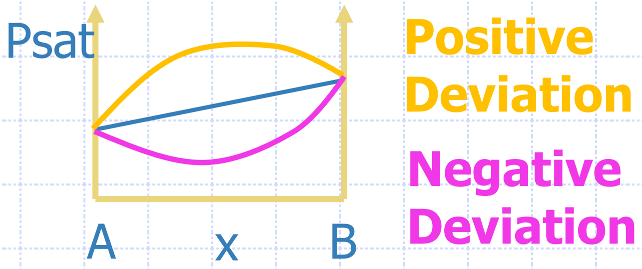
Raoult's Law

Non ideal systems

- Due to interactions between functional groups creatinf non randomness in the mixture
- Due to energy effects created by size and shape differences
- Is accounted for activity coefficients

Types of VLE Phase behavior: effects of non ideality

- $\gamma > 1$ because molecules are dissimilar and tend to aggregate more with molecules of the same species, creating large local concentration. Ge is positive. Positive deviation from ideality
- $\gamma >>>> 1$: liquid may split into two phases
- $\gamma < 1$ when attractive forces between dissimilar molecules are stronger than the forcess between the like molecules. Ge is negative. Negative deviation from ideality
- if $\gamma <$ may have chemical complexes (ammonia water system)



Calculation of phase equilibria

- γ-φ approach:
  - fugacity coefficients in the vapor phase by the Hayden-O'Connell (HOC) model
  - activity coefficients by a suitable GE model
  - NOTE 1: limited pressure range due to HOC and GE models validity
  - NOTE 2: it is essential a correct calculation of the pure component vapor pressure

- φ-φ approach:
  - fugacity coefficients in the vapor phase by an Equation-of-State (EOS) model
  - fugacity coefficients in the liquid phase by same Equation-of-State (EOS) model
  - NOTE 1: simplest EOS's suitable for this application are cubic EOS's
  - NOTE 2: no applicability limits as far as pressure is concerned
  - NOTE 3: computational effort much bigger than for the γ-φ approach

VLE: comparison of two Approaches

γ - φ

- Pros
  - Reliability at low pressure
  - Very good for describing polar mixtures
  - Simplicity
  - Easy programming and low CPU time
- Cons
  - Valid only at low pressure
  - Parameters of the model are highly correlated
  - Consistency at the critical point

φ - φ

- Pros
  - Continuity at the critical point (one model)
  - Parameters are non so strongly correlated
  - Applicable in an high T and P range
  - Describes volumetric properties as well as equilibrium
- Cons
  - Complexity and high CPU time
  - Polar and low pressure mixtures

Calculation of phase equilibria: binary system

$$\begin{cases} y = K_1 x \\ 1 - y = K_2(1 - x) \end{cases}$$

- γ - φ approach: $K_i = \dfrac{\varphi_i^{*V} P_i^{sat} \gamma_i}{\varphi_i^{*} P}$
- φ - φ approach: $K_i = \dfrac{\varphi_i^{L}}{\varphi_i^{V}}$
  - NOTE 1: five possibilities for the calculation: (T, x); (T, y); (P, x); (P, y); (T, P)
  - NOTE 2: the simplest model (at lower pressure)

$$P_b = \gamma_A P_A^{sat} x + \gamma_B P_B^{sat} (1 - x)$$

Fugacity from Henry's law

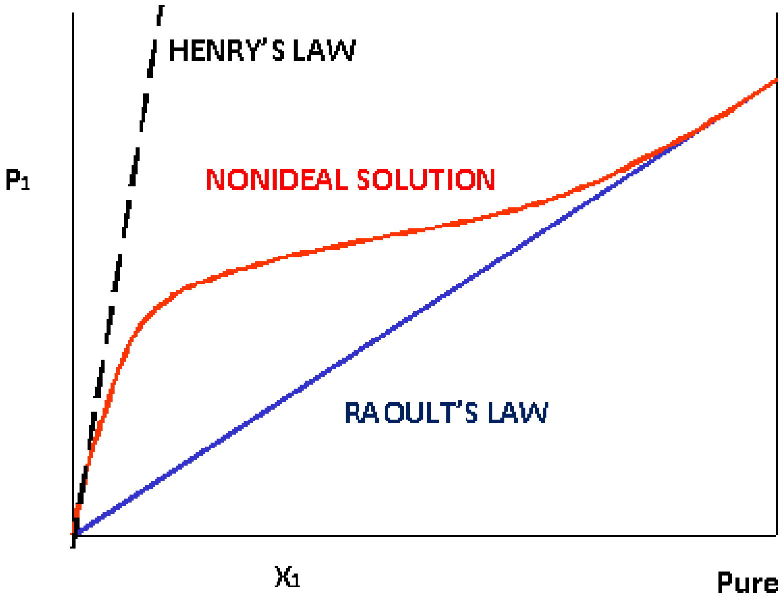
- Vapor phase fugacity $\hat{f}_i^V = Py_i\hat{\phi}_i^V$
- Liquid phase fugacity: $\hat{f}_i^L = \left(f_i^L\right)_{id}\gamma_i$
- Where $\left(f_i^L\right)_{id} = R_i(T,P)x_i$
- Since pure liquid does not exist $R_i = \lim\limits_{x_i \to 0} \dfrac{f_i^L}{x_i} = \dfrac{H_i^{sol}}{\gamma_i^\infty}$

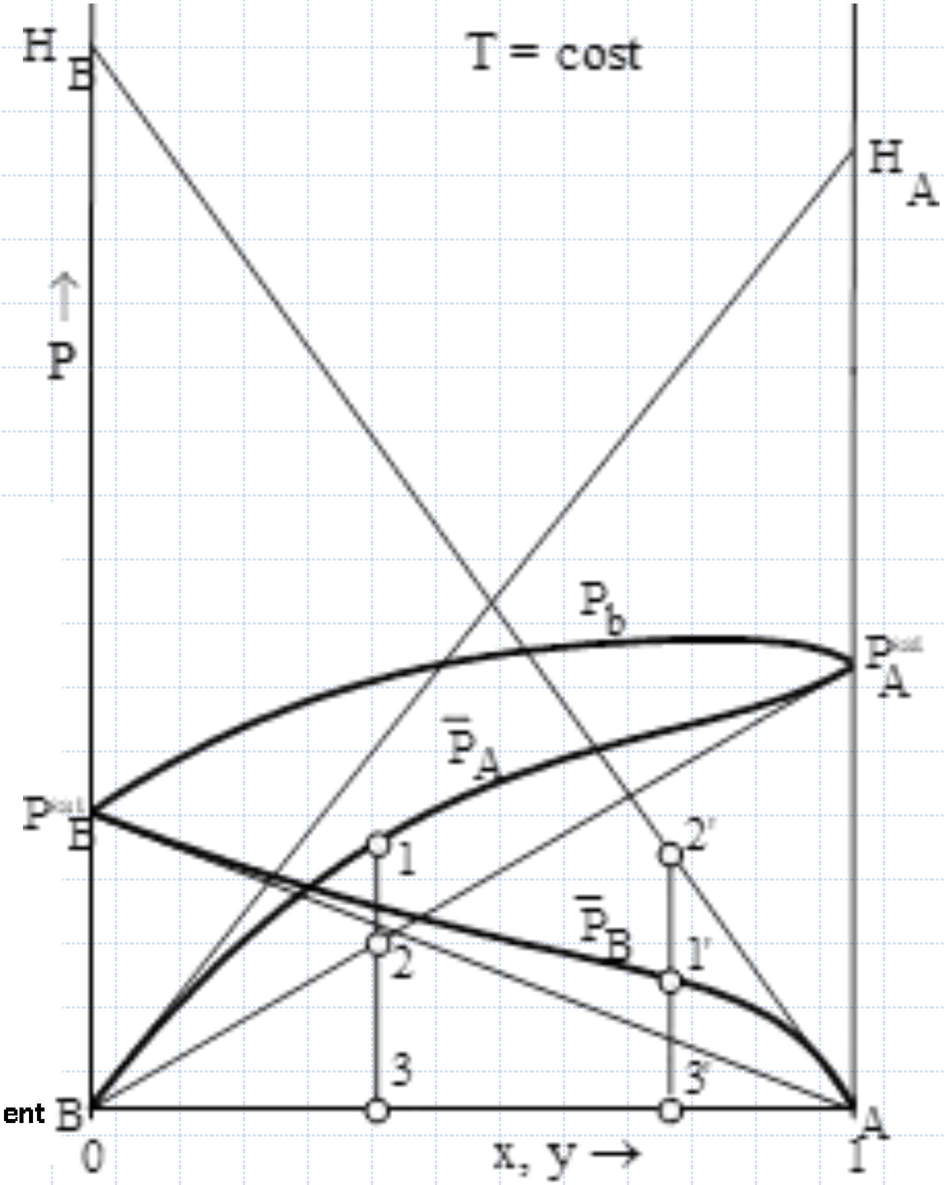
$$\hat{f}_i^L = x_i\gamma_i^* H_i \qquad \gamma_i^* = \gamma_i\ /\gamma_i^\infty \Rightarrow 1\, as\, x_i \Rightarrow 0$$

GLE: $Py_i\hat{\phi}_i^V = x_iH_i\gamma_i^* \xrightarrow{\text{Low P}} Py_i = x_iH_i$

- Henry's law is used to determine the amount of a supercritical component or light gas in the liquid phase
- Only used with Ideal and Activity Coefficient models
- H_i is calculated from temperature-dependent Henry's constants for each solute-solvent pair

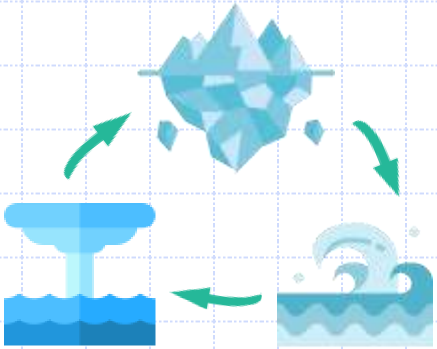
Graphical representation of H



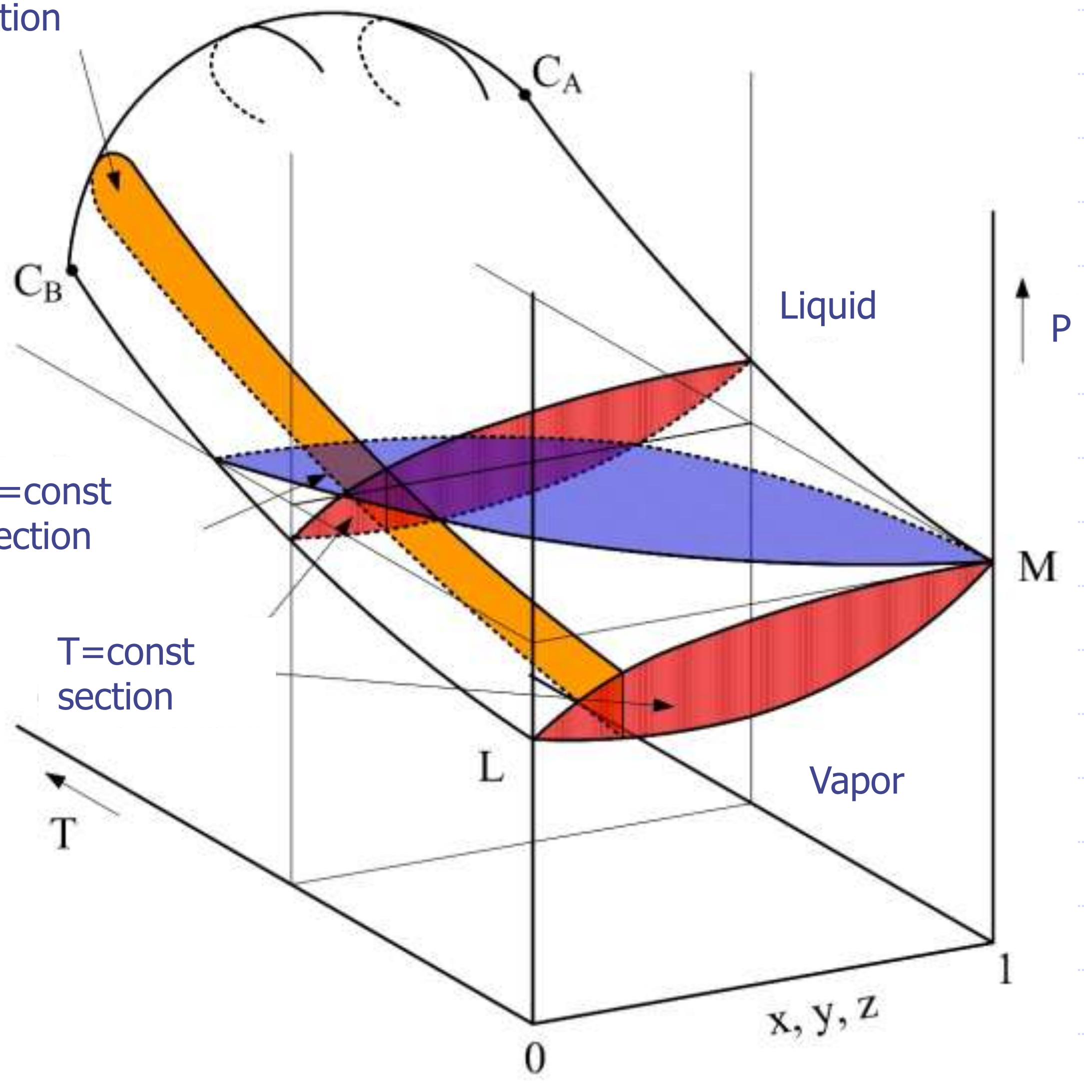


Phase Equilibria diagrams

- Binary T-x and P-x diagrams
- High pressure diagrams
- Binary x-y diagrams
- Azeotropes
- Other diagrams
(activity coefficients, excess enthalpy,…)



VLE diagram for a binary system



Z=const section

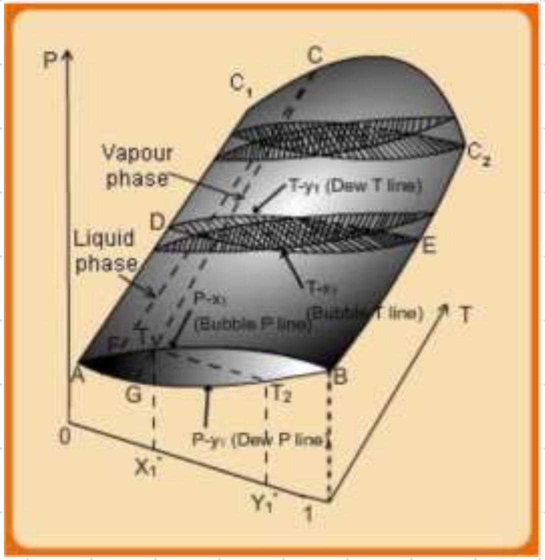
P=const section

T=const section

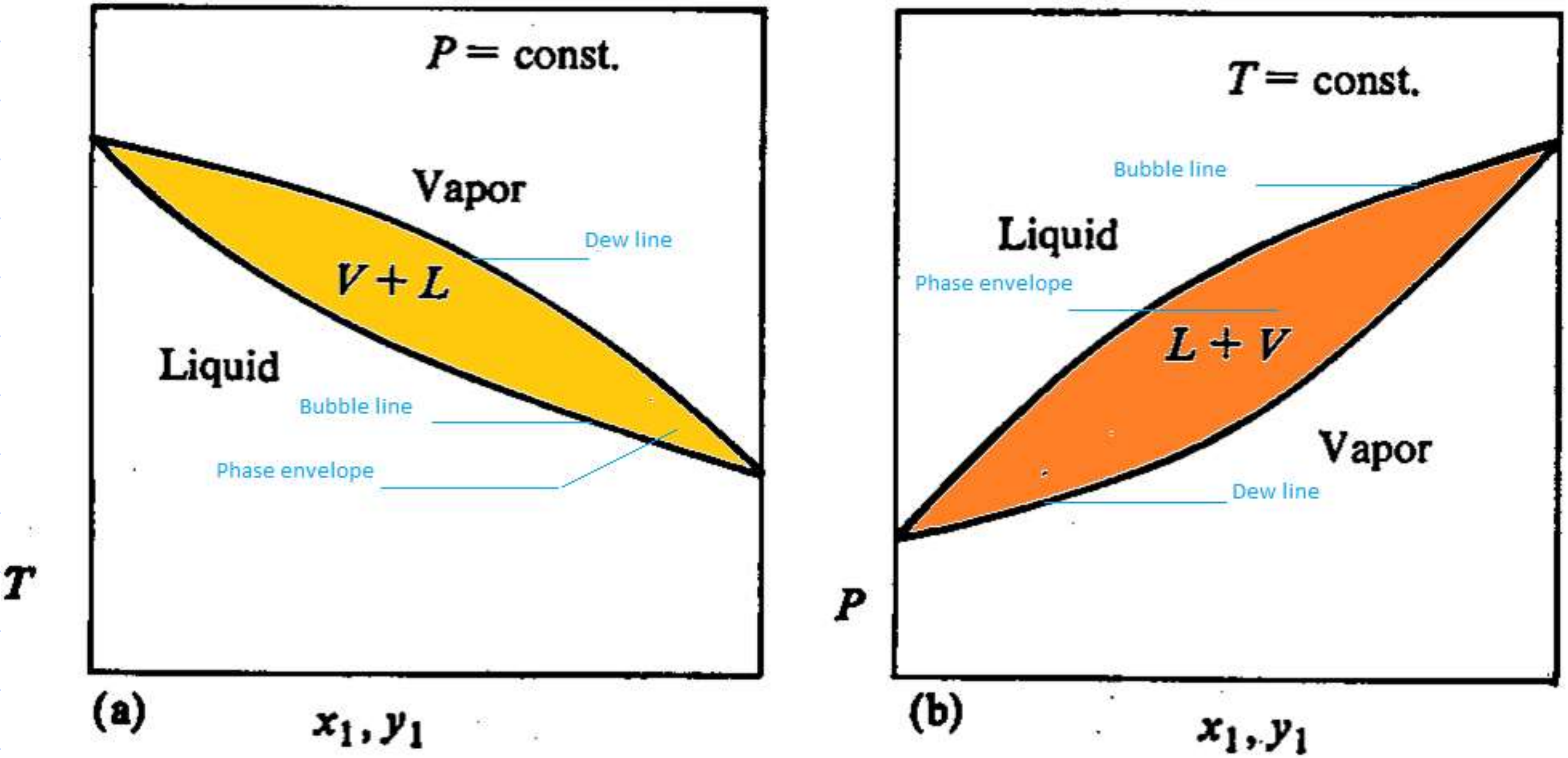
Liquid

Vapor

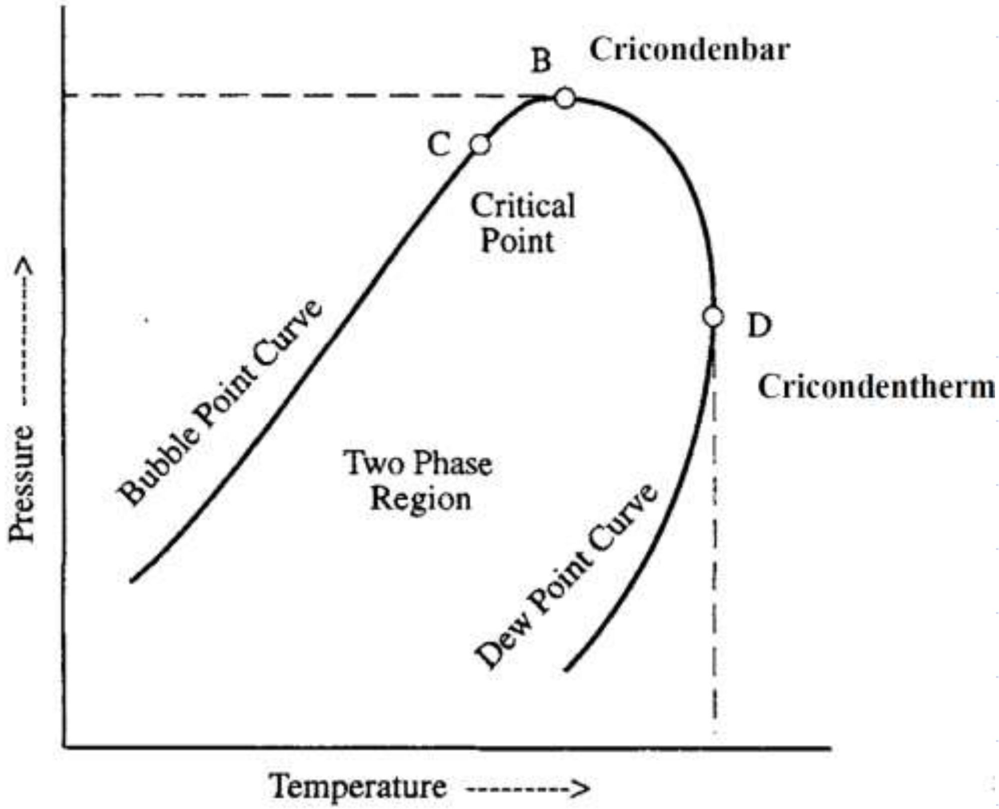
P

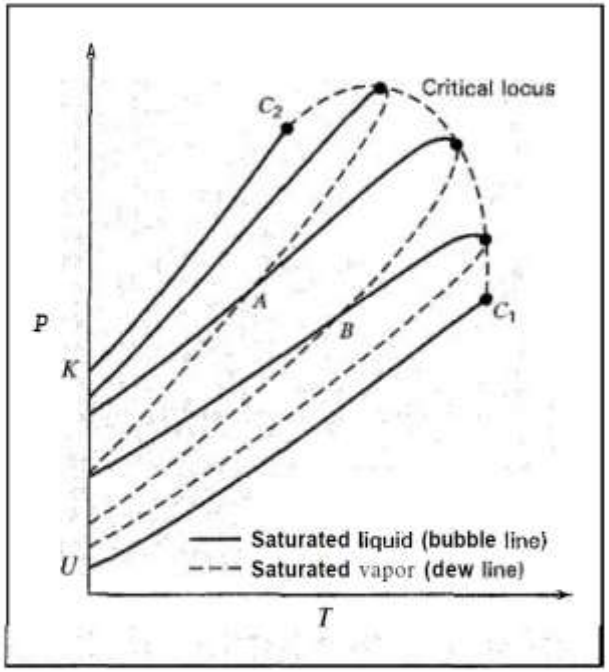


Binary diagrams at constant T / P



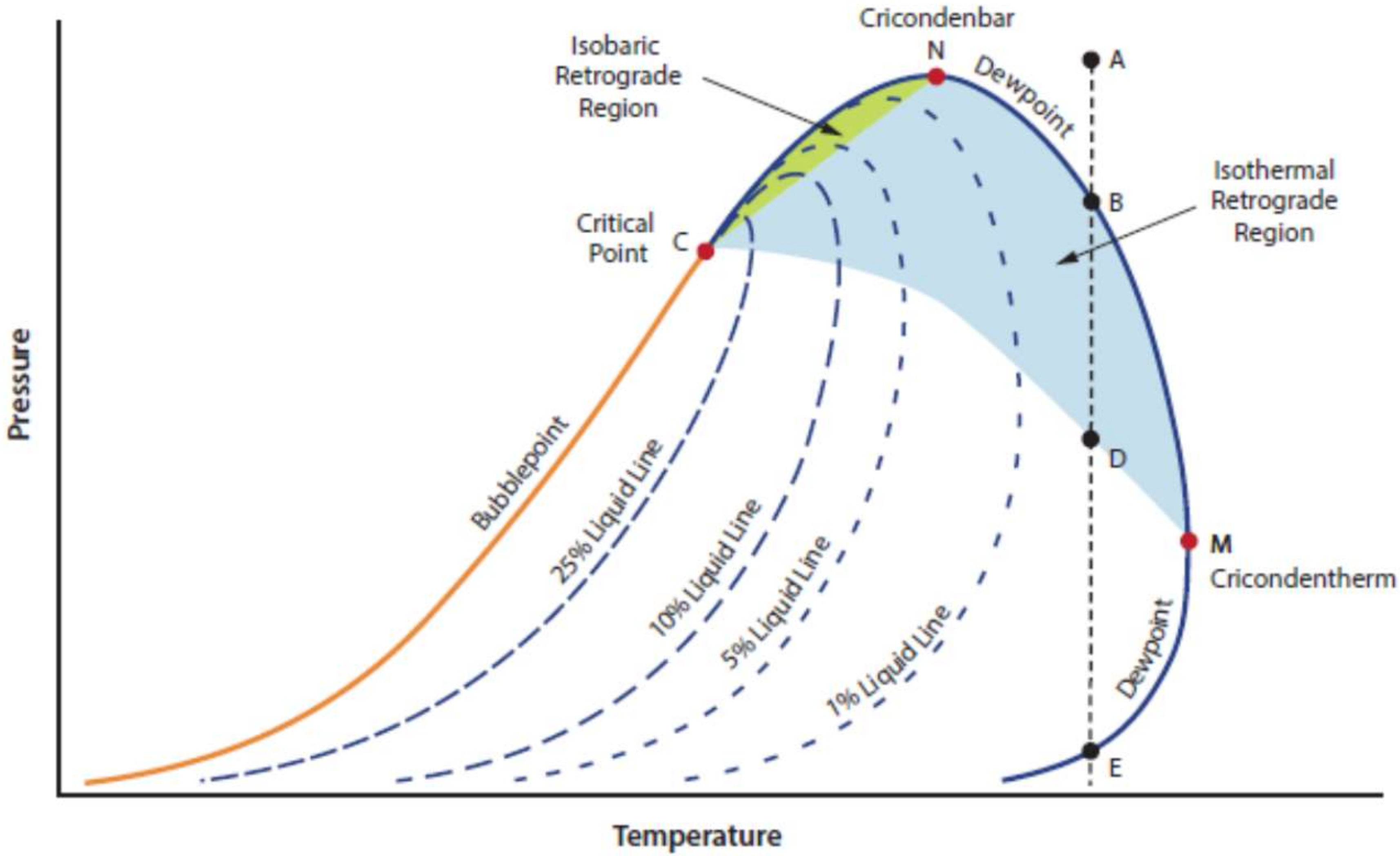
Constant composition diagram





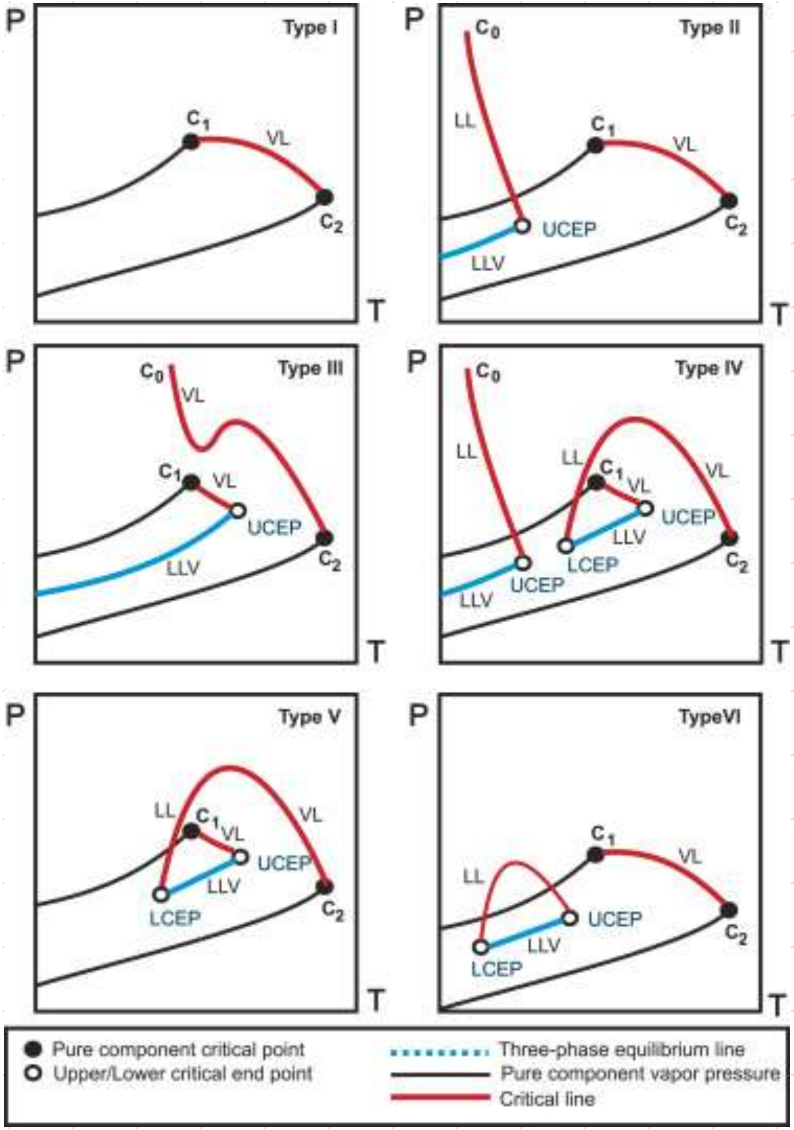
Critical Locus

Retrograde condensation region

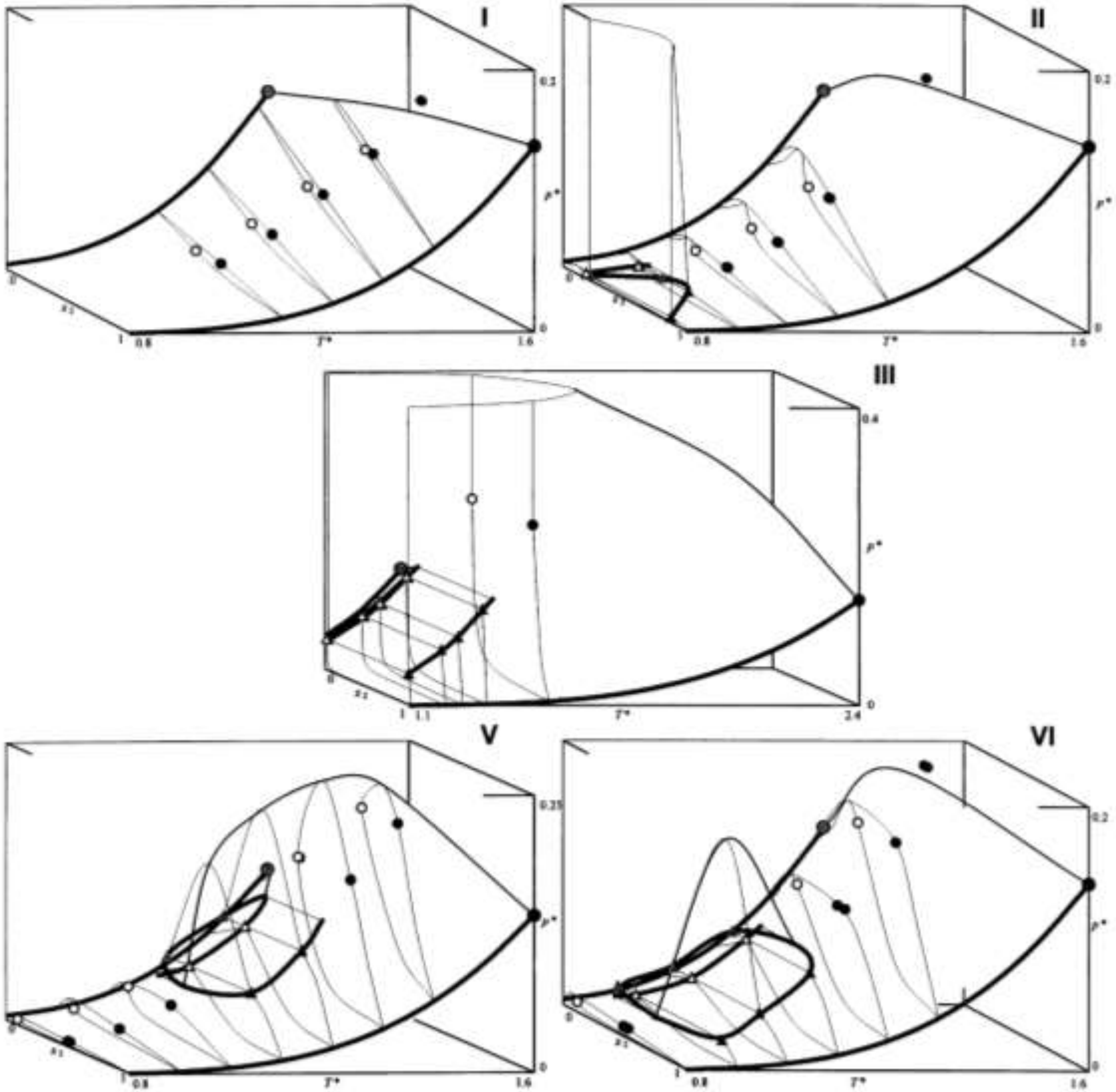


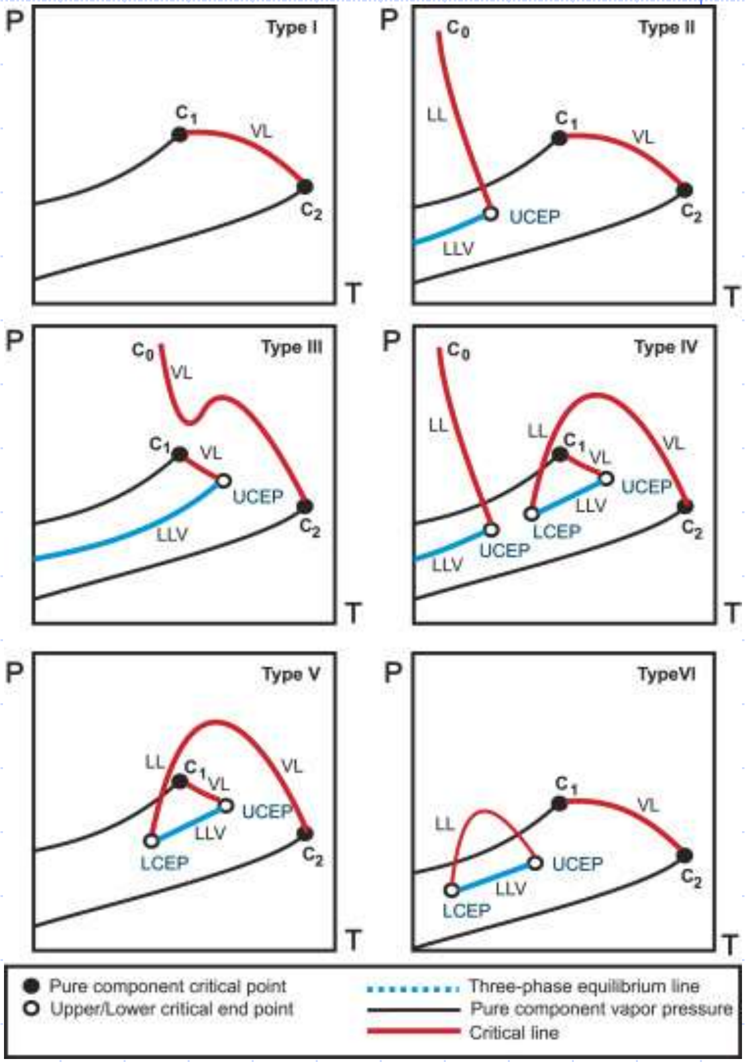
High Pressure

- High pressure phase equilibria
- Type I to type VI mixtures

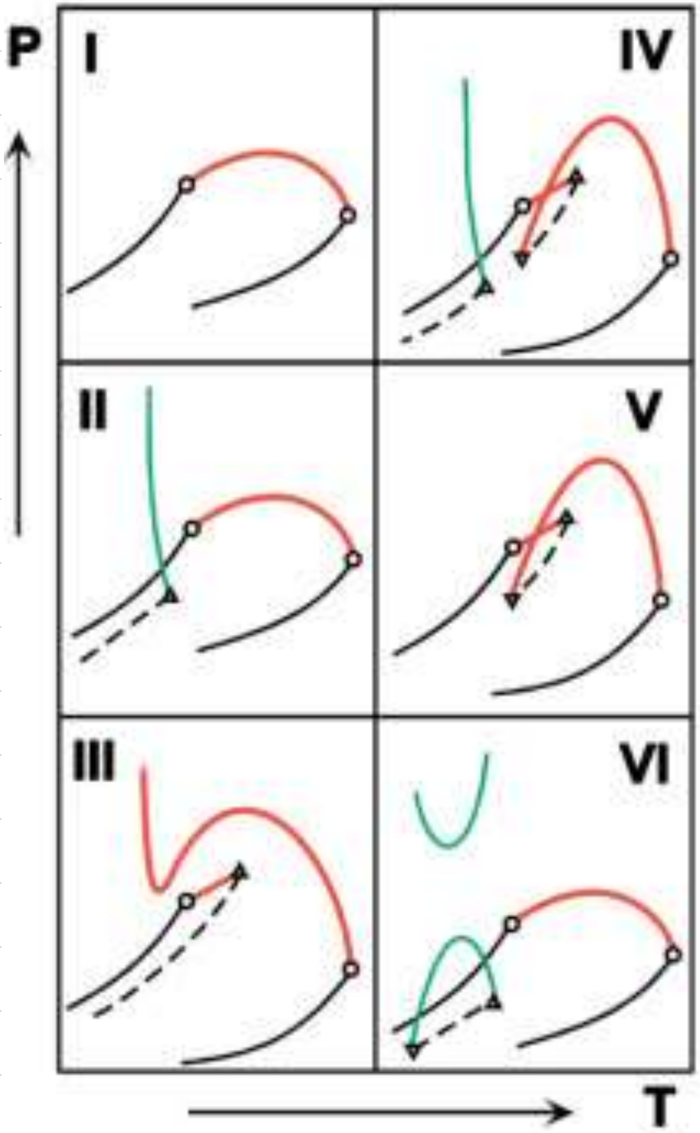


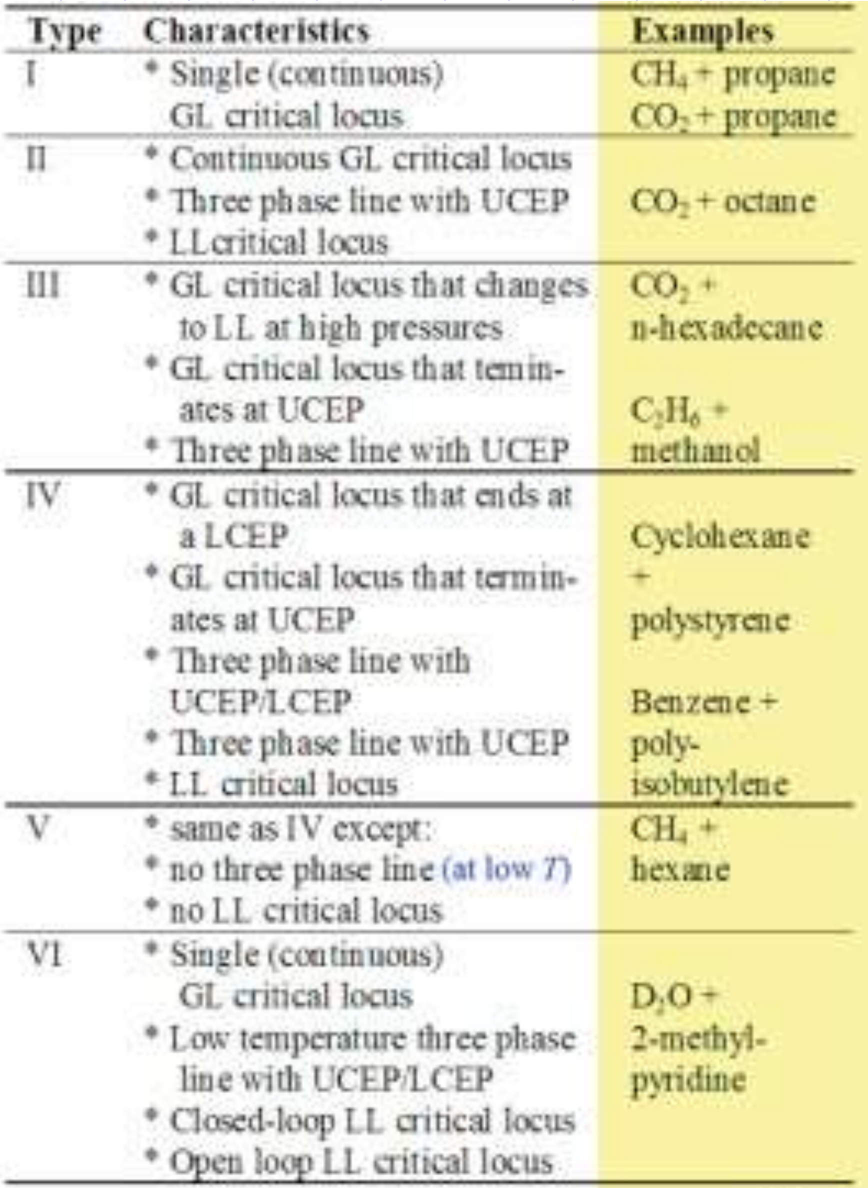
3D P-T-x diagrams for type I, II, III, V, VI





Scott and van Konynenburg classification





Type	Characteristics	Examples
I	* Single (continuous) GL critical locus	CH_4 + propane CO_2 + propane
II	* Continuous GL critical locus * Three phase line with UCEP * LL critical locus	CO_2 + octane
III	* GL critical locus that changes to LL at high pressures * GL critical locus that terminates at UCEP * Three phase line with UCEP	CO_2 + n-hexadecane C_2H_6 + methanol
IV	* GL critical locus that ends at a LCEP * GL critical locus that terminates at UCEP * Three phase line with UCEP/LCEP * Three phase line with UCEP * LL critical locus	Cyclohexane + polystyrene Benzene + poly-isobutylene
V	* same as IV except: * no three phase line (at low T) * no LL critical locus	CH_4 + hexane
VI	* Single (continuous) GL critical locus * Low temperature three phase line with UCEP/LCEP * Closed-loop LL critical locus * Open loop LL critical locus	D_2O + 2-methyl-pyridine

Composition diagram (x-y)

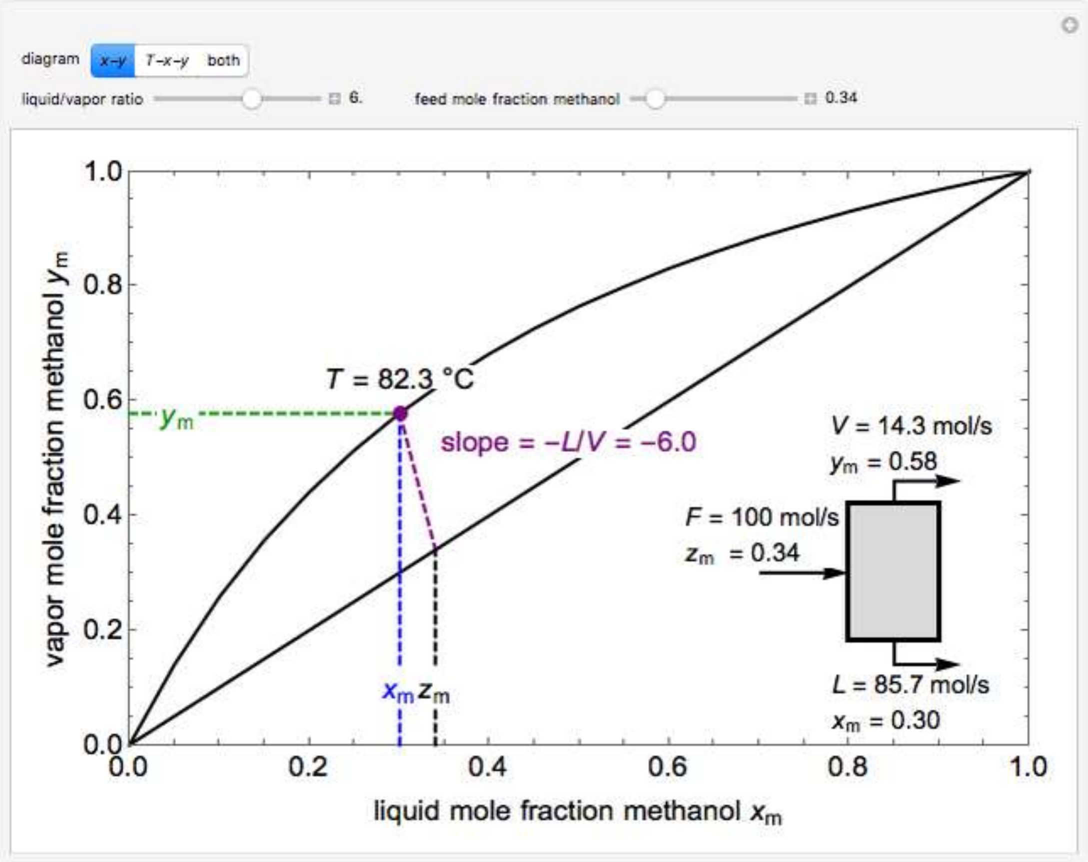
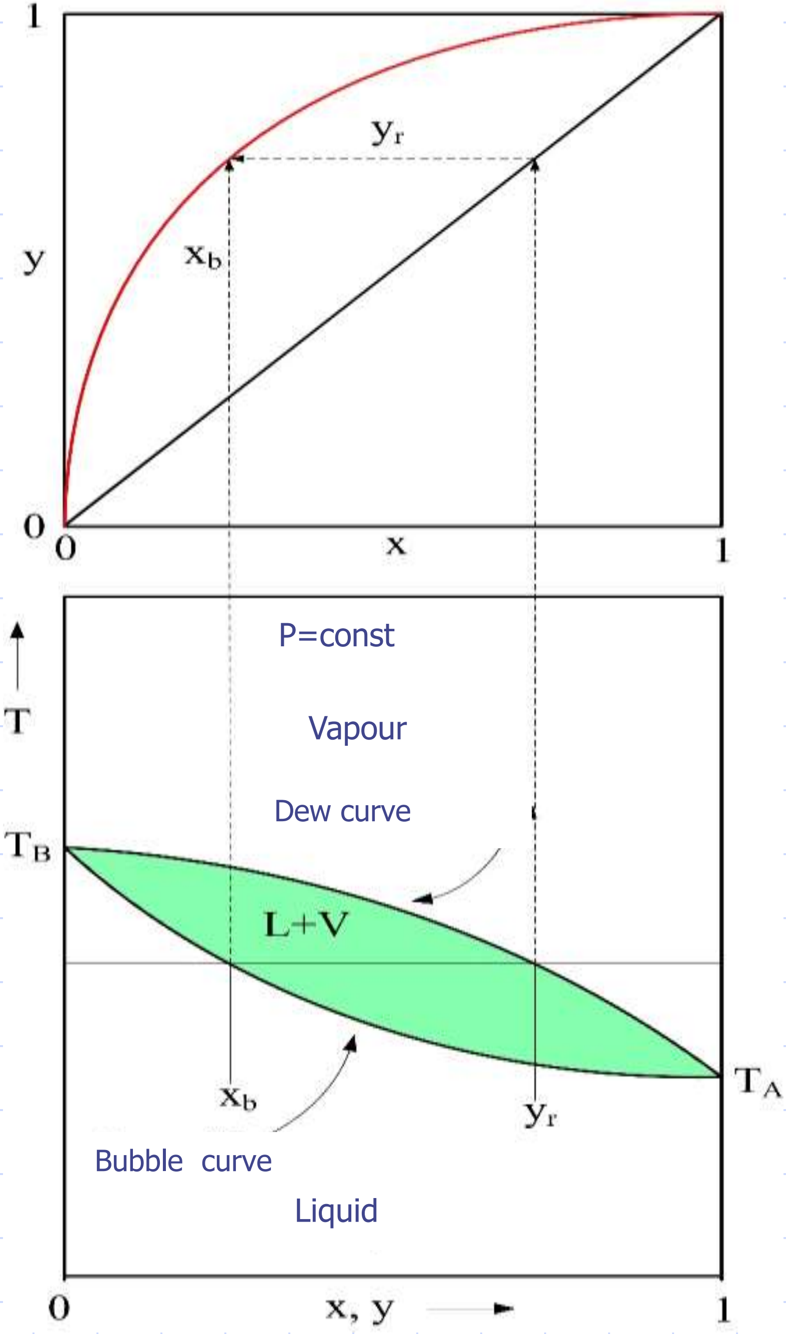


diagram: x–y (selected) | T–x–y | both

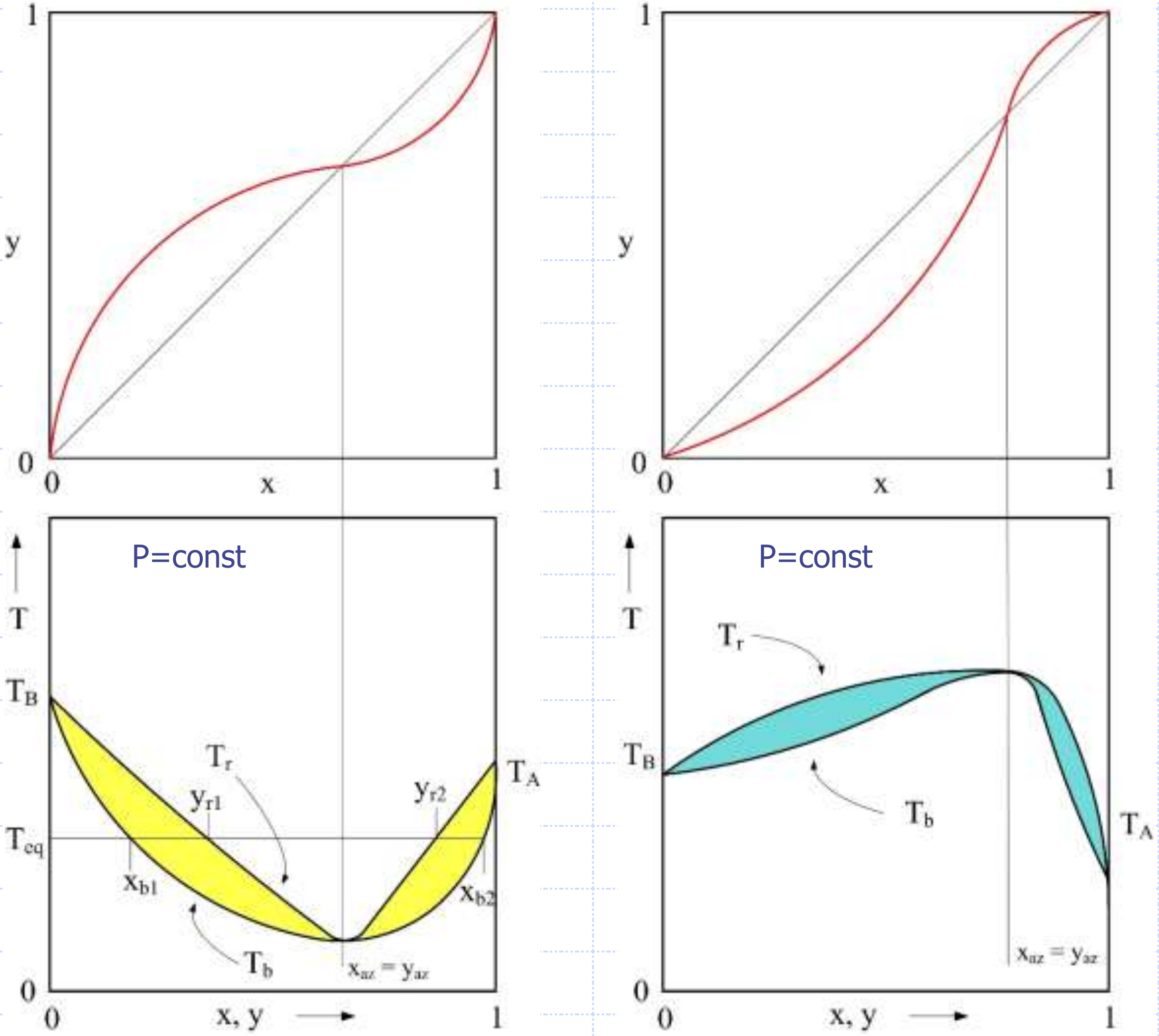
liquid/vapor ratio: 6.

feed mole fraction methanol: 0.34



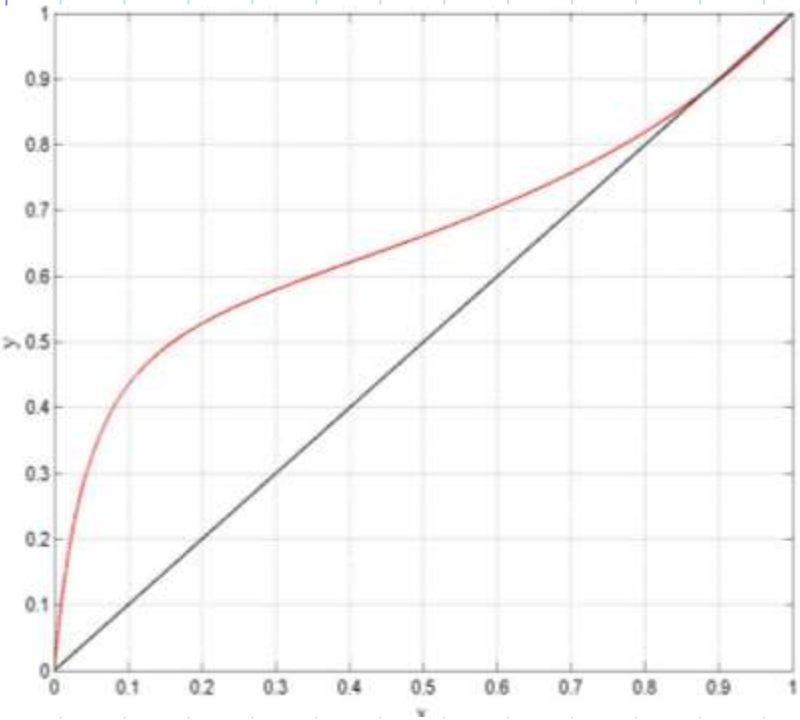
Homogeneous azeotropic systems

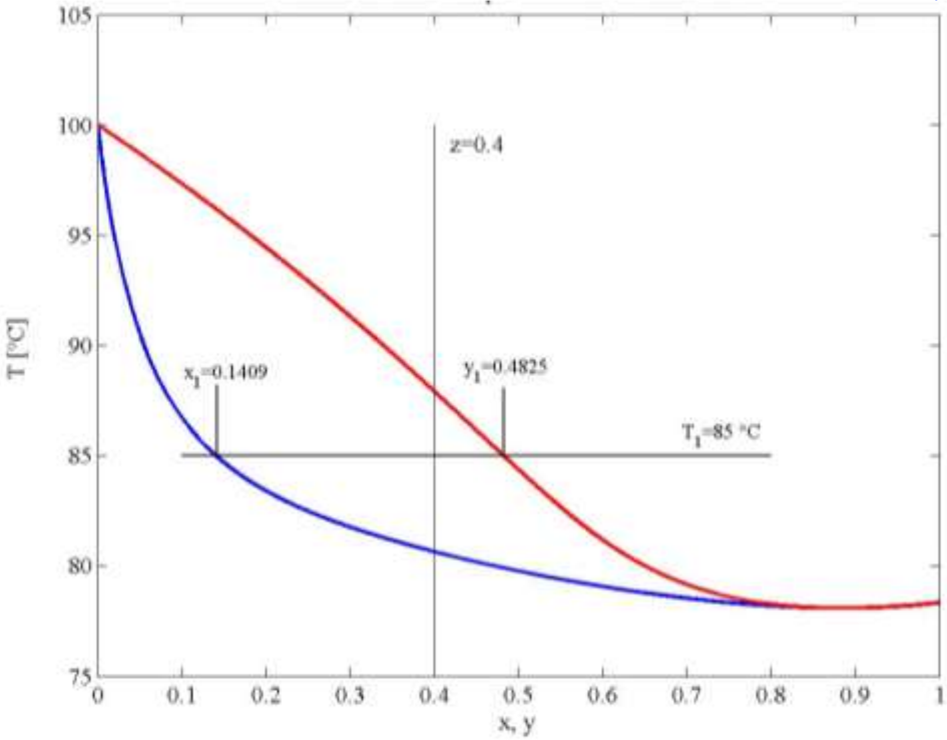
Positive azeotropes are also called *minimum boiling mixtures* or *pressure maximum* azeotropes.



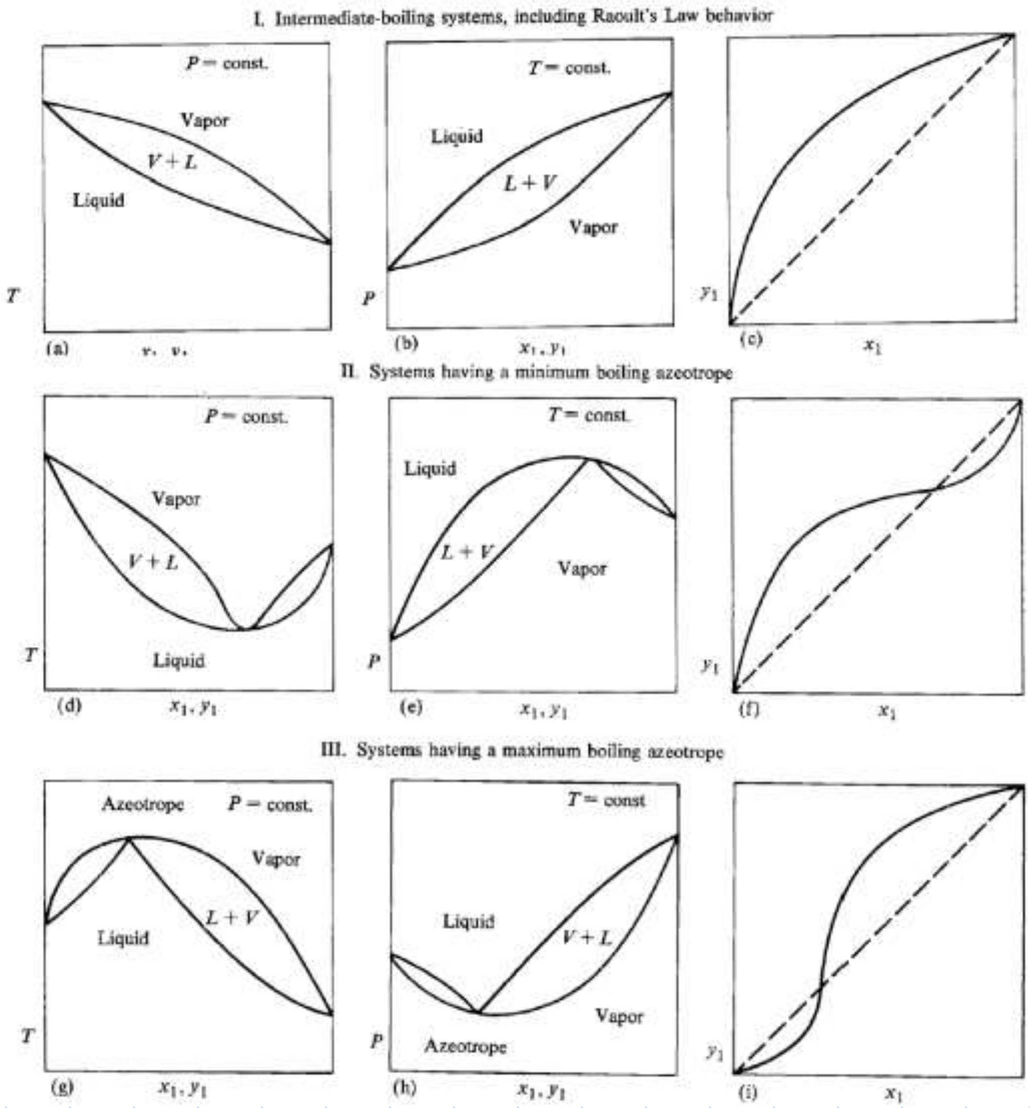
Negative azeotropes are also called *maximum boiling mixtures* or *pressure minimum* azeotropes..

Water - Ethanol @ 1 atm, azeotropic diagram





T-x, p-x, and x-y diagrams of various types



Binary liquid-liquid equilibrium

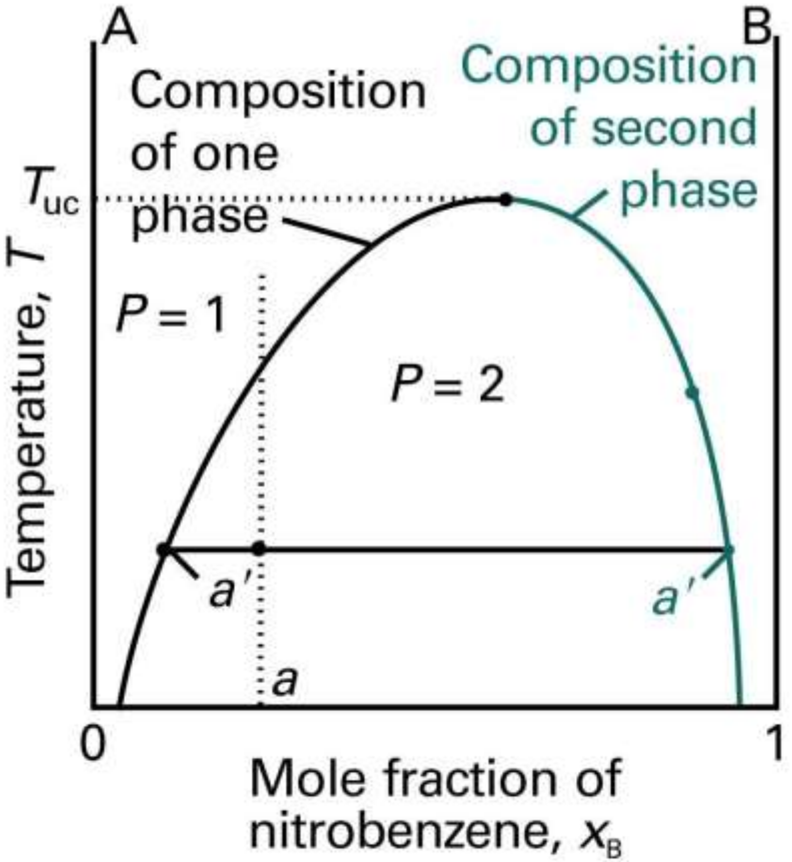


Figure 6-19
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

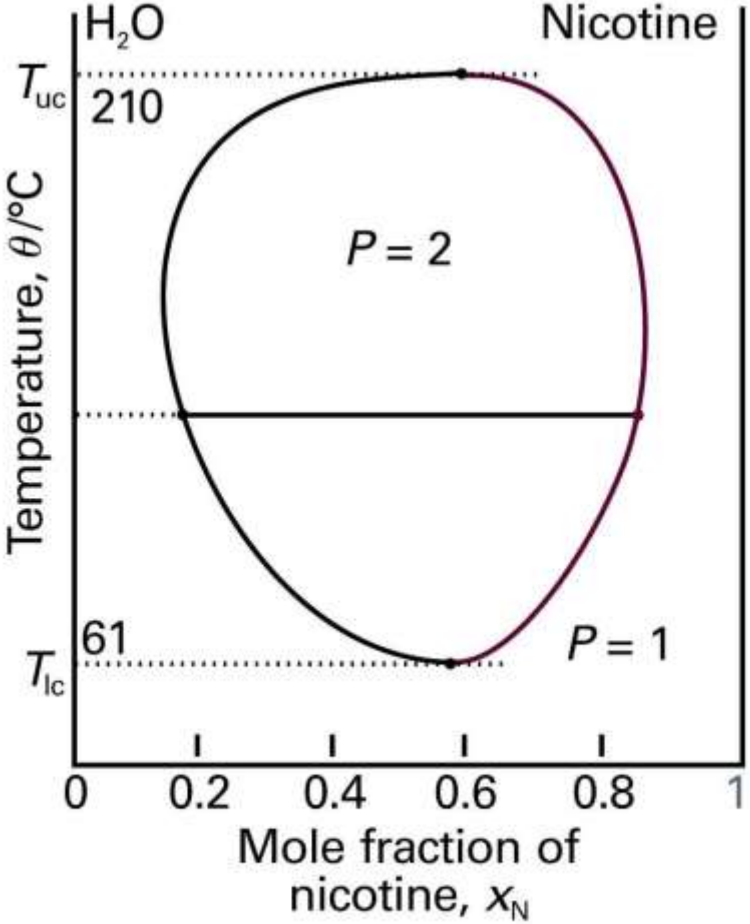


Figure 6-25
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Liquid-liquid equilibrium in presence of an azeotrope

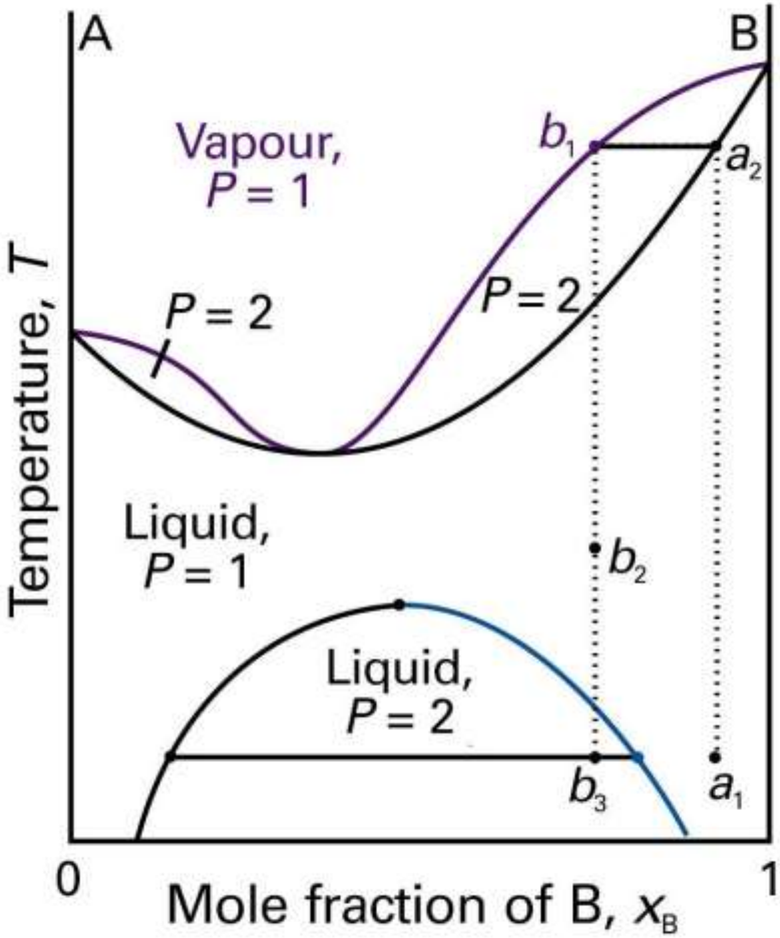


Figure 6-26
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

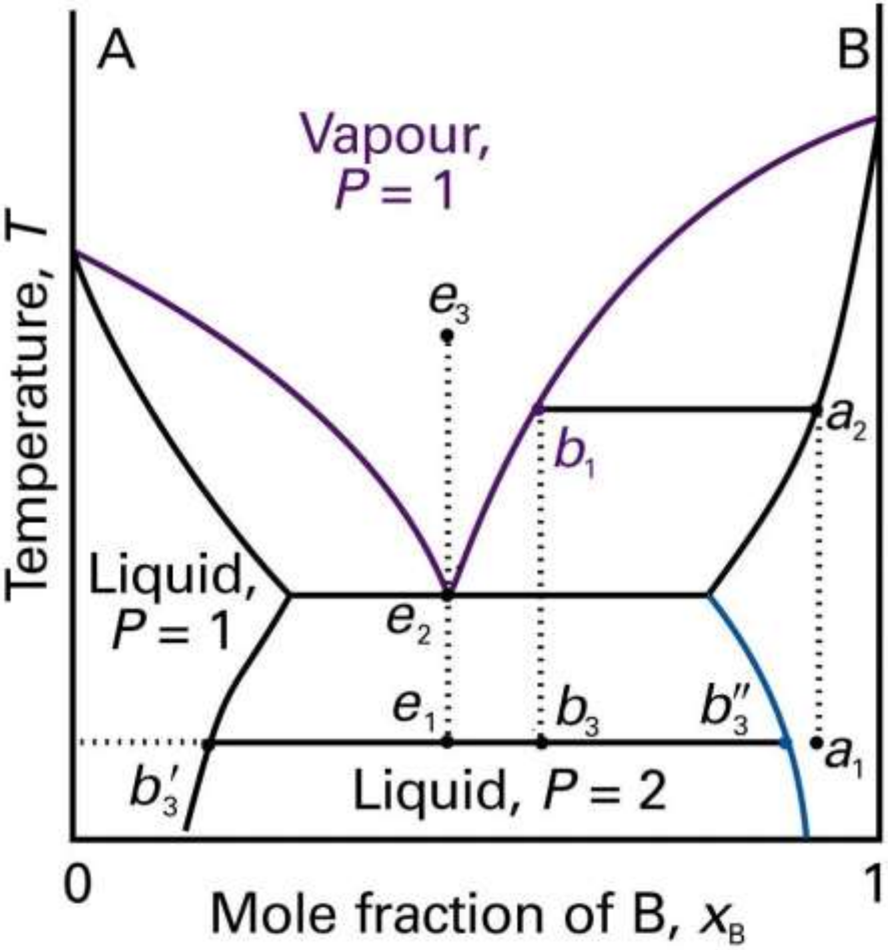
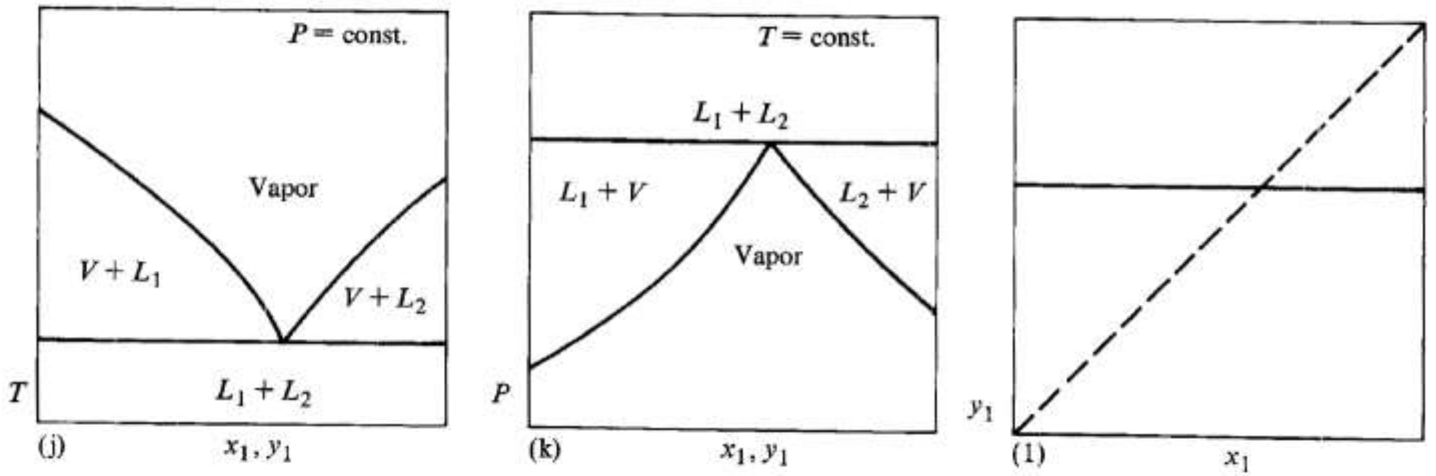


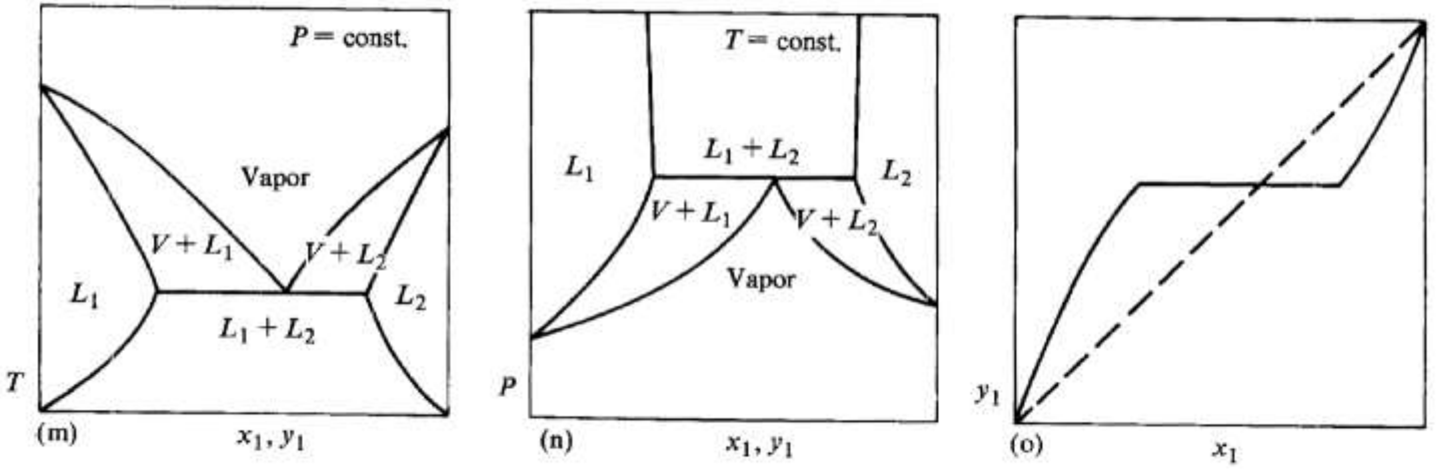
Figure 6-27
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

T-x, p-x, and x-y diagrams of various types

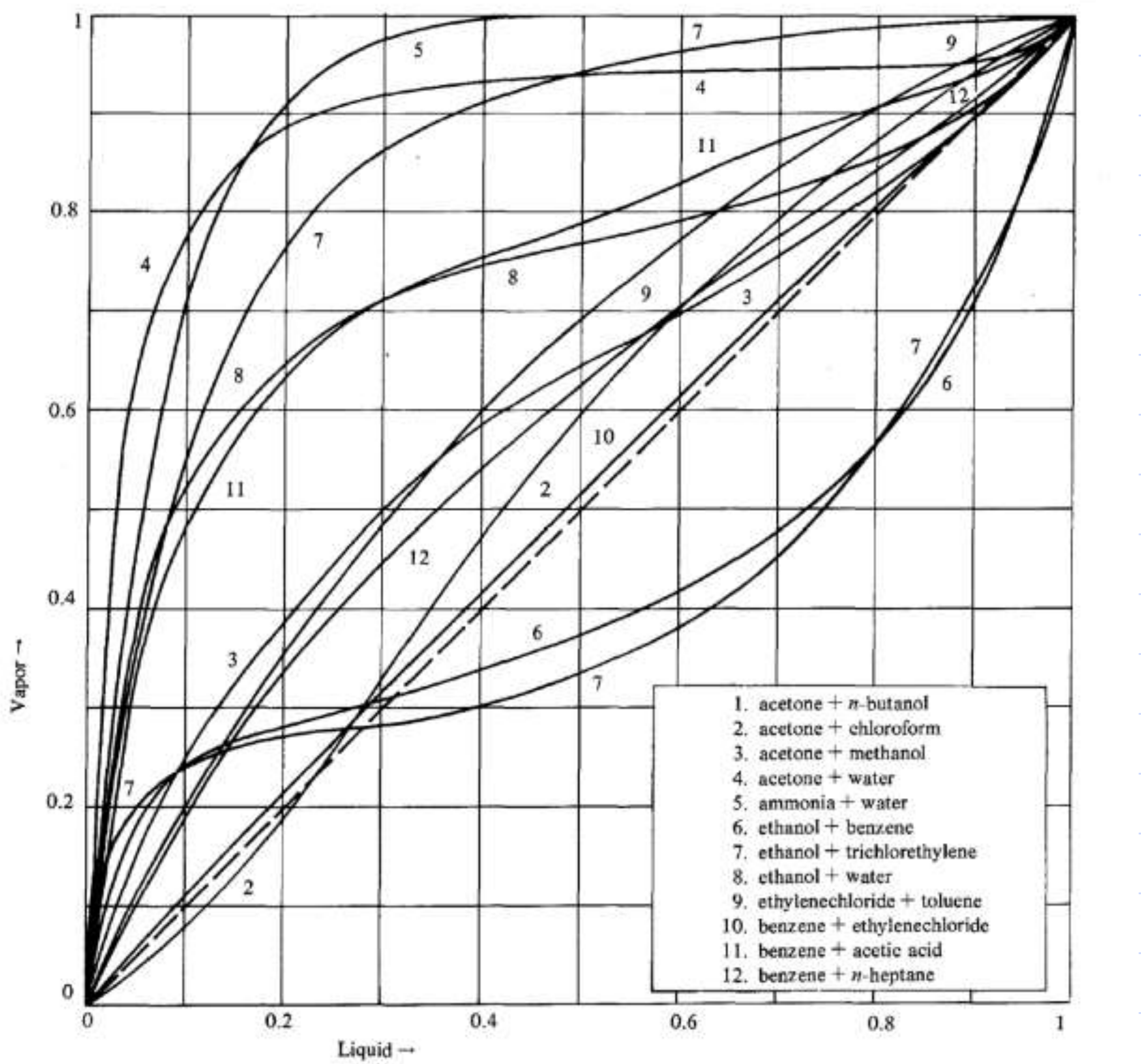
IV. Systems having immiscible liquid phases



V. Systems having partially miscible liquid phases



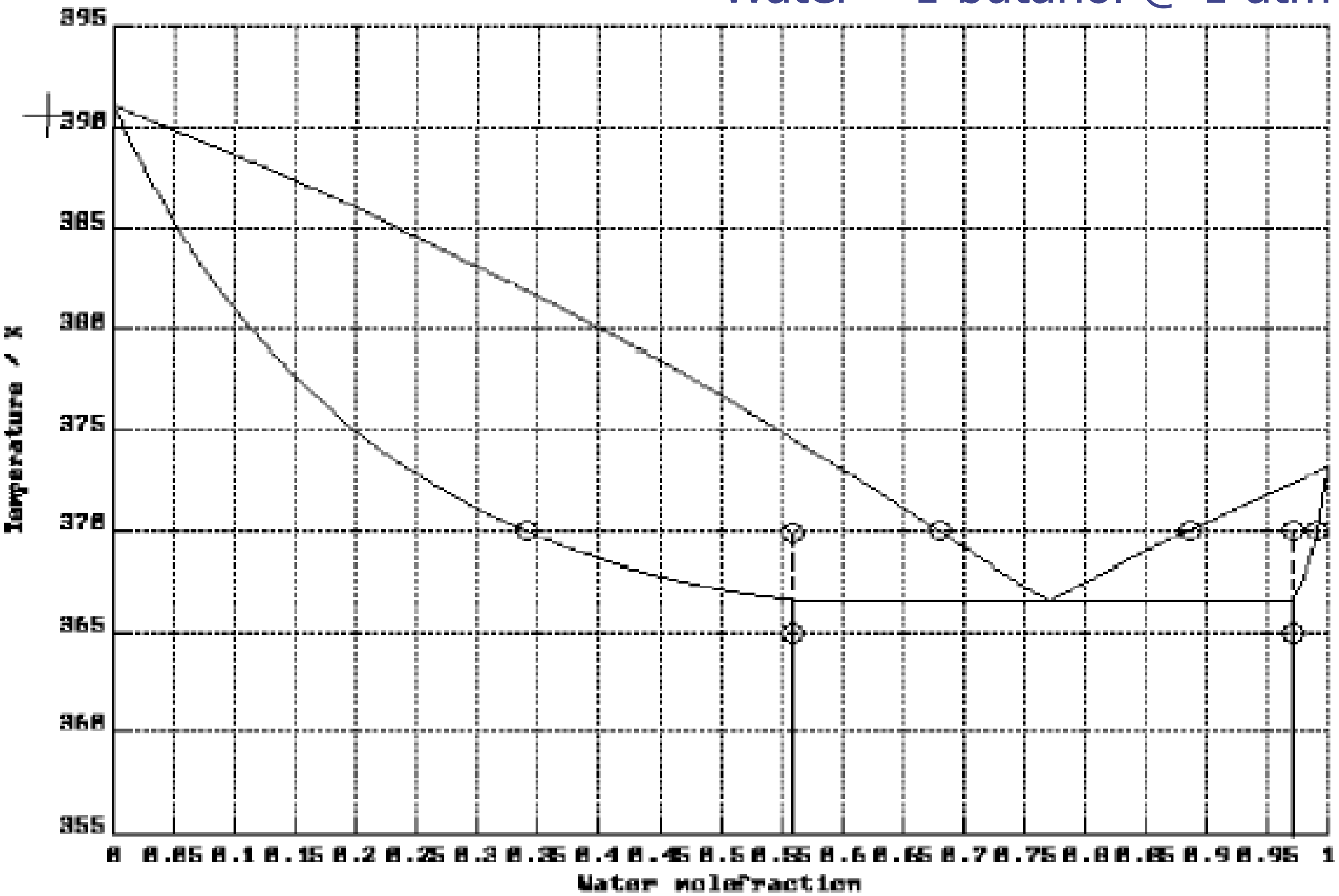
X-y diagrams of various type



Liquid Liquid and VLL equilibrium

- The basic VLLE equation is $Py_i\hat{\varphi}_i^V = f_i^{o1}x_i^1\gamma_i^1 = f_i^{o2}x_i^2\gamma_i^2$

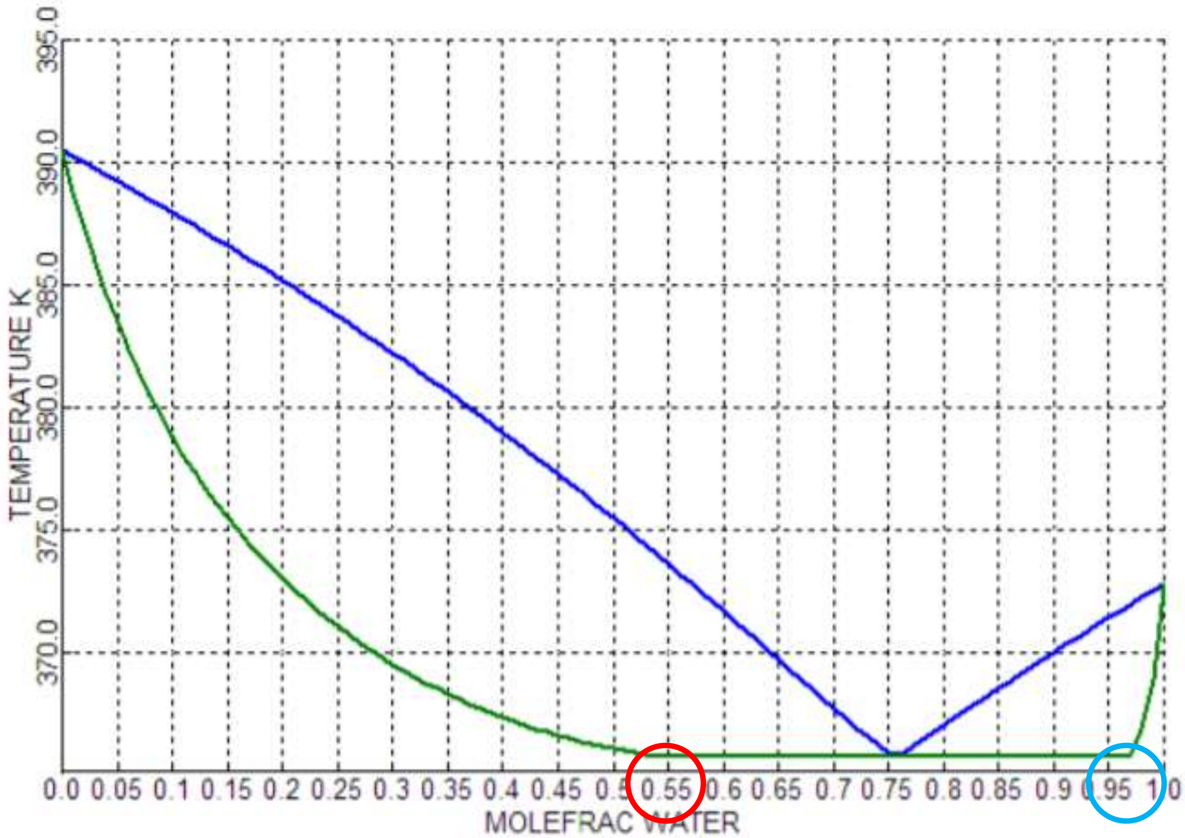
Water – 1 butanol @ 1 atm



LL & VLLE Phase Diagram

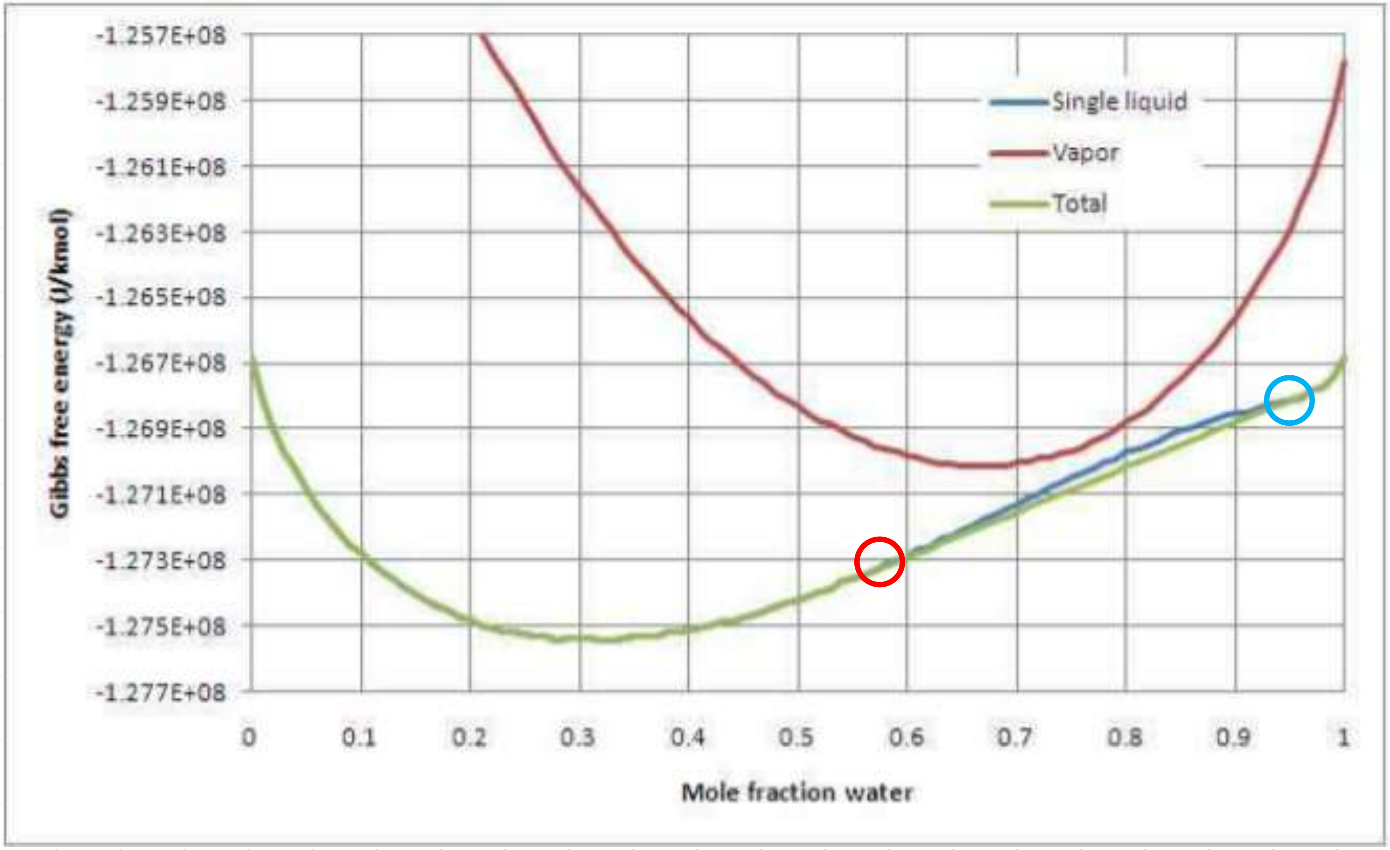
Water - 1-Butanol @ 1 atm - UNIFAC

365 K



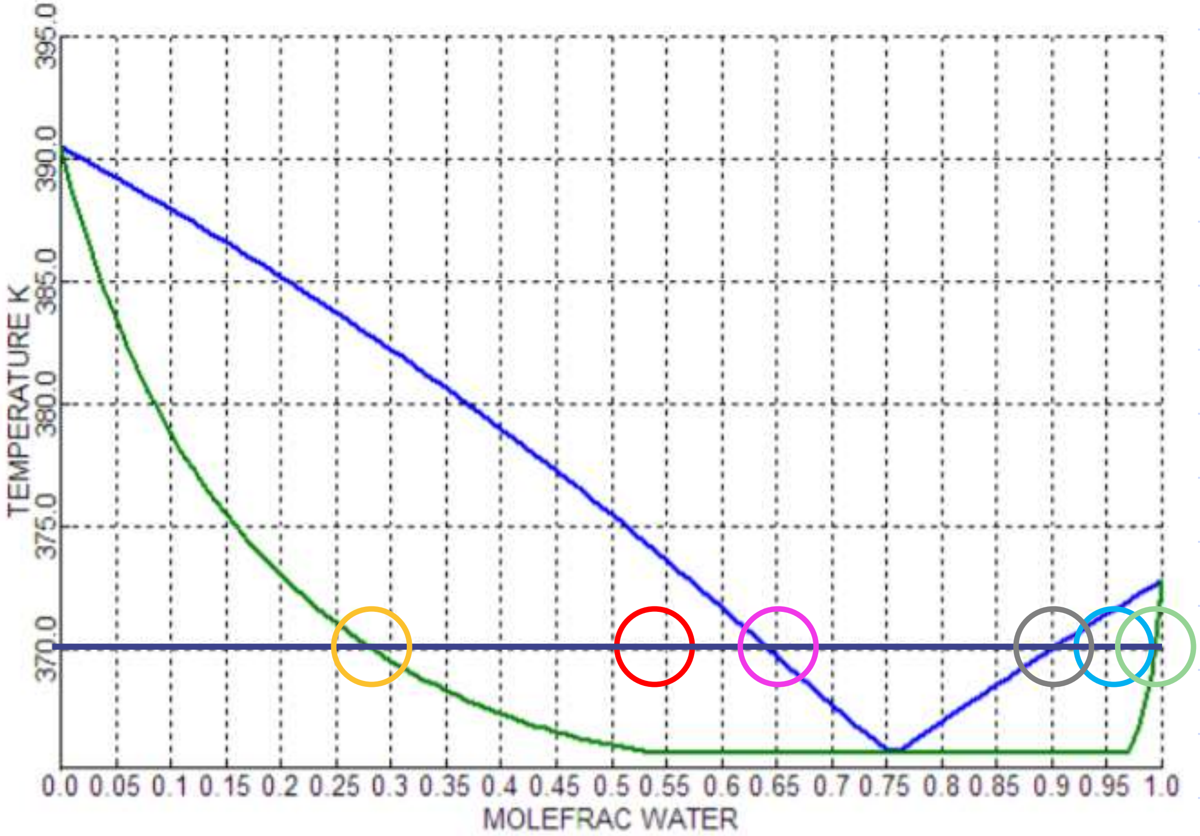
Liquid – Liquid Equilibrium

Water - 1-Butanol @ 1 atm, 365K - UNIFAC



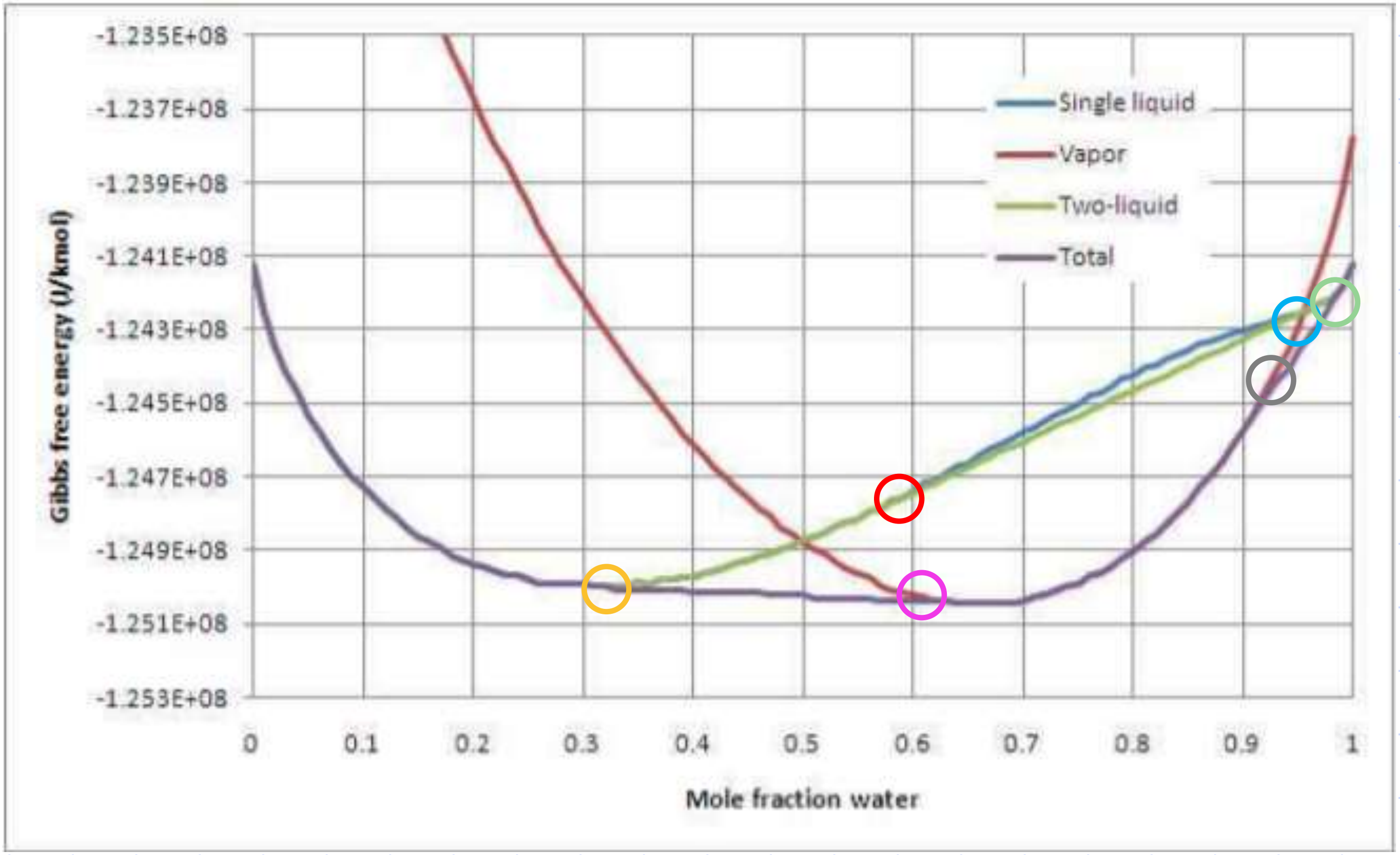
LL & VLLE Phase Diagram

Water - 1-Butanol @ 1 atm - UNIFAC

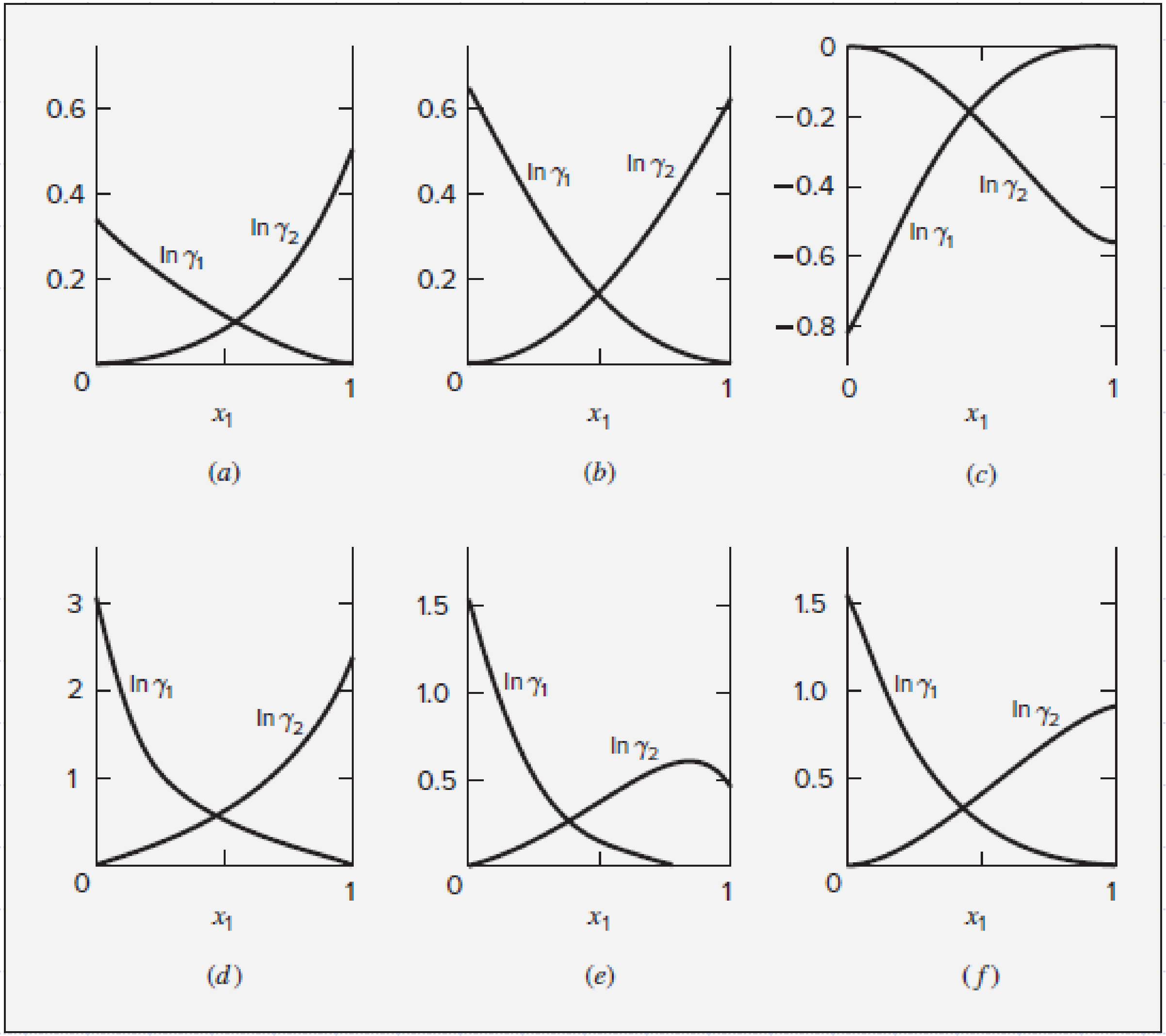


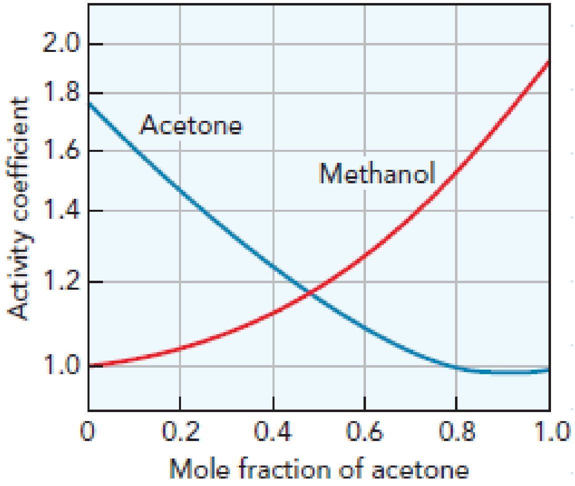
Vapor Liquid Liquid Equilibrium

Water - 1-Butanol @ 1 atm, 370K - UNIFAC

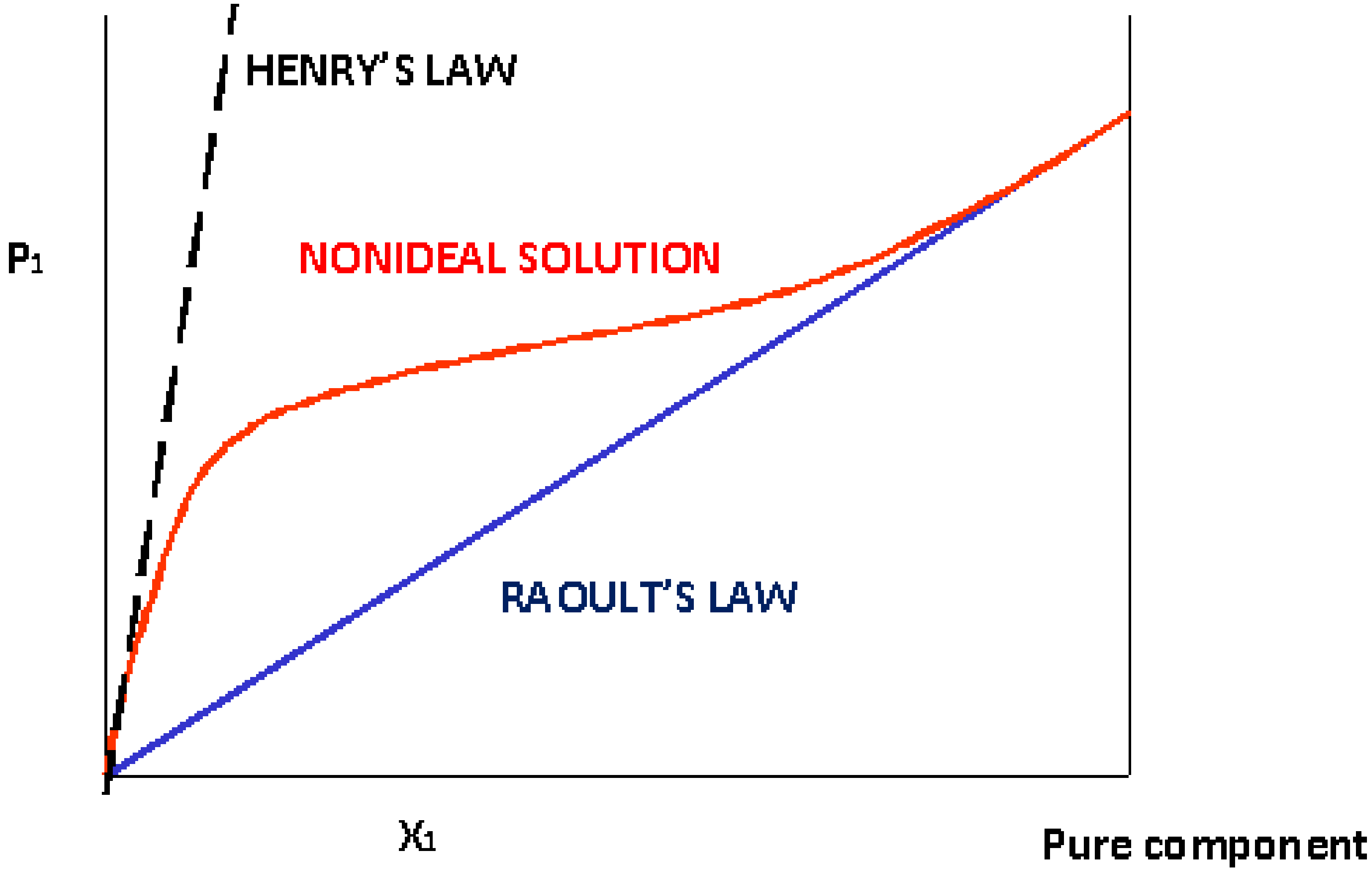


Activity coefficient diagram





Activity coefficients vs. concentration



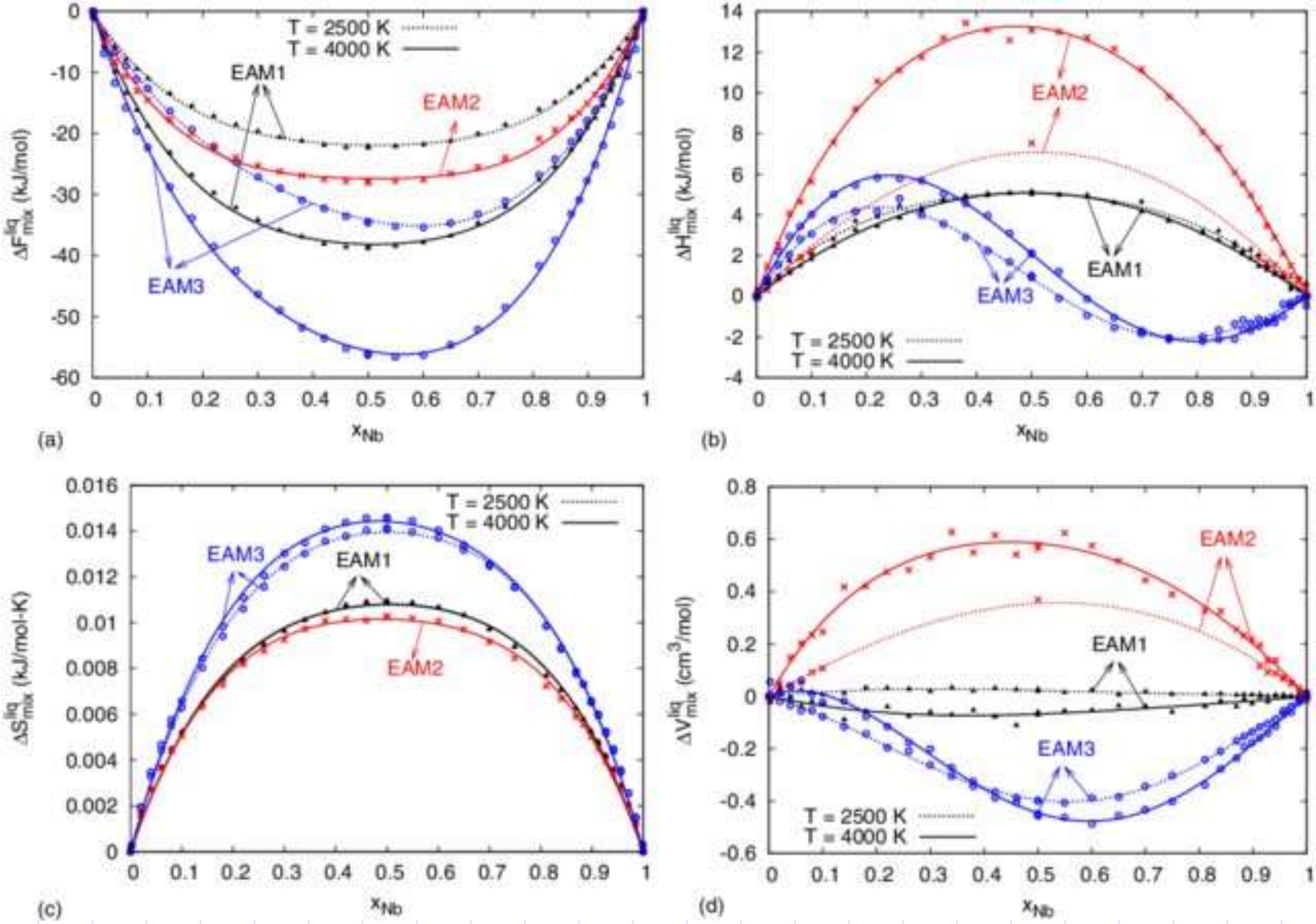
Mixing properties: free energy, enthalpy, entropy and excess volume

Free energy of mixing (a),

enthalpy of mixing (b),

entropy of mixing (c)

excess volume (d)



Enthalpy vs. Composition: Ponchon-Savarit Plot
Bubble point Temperature

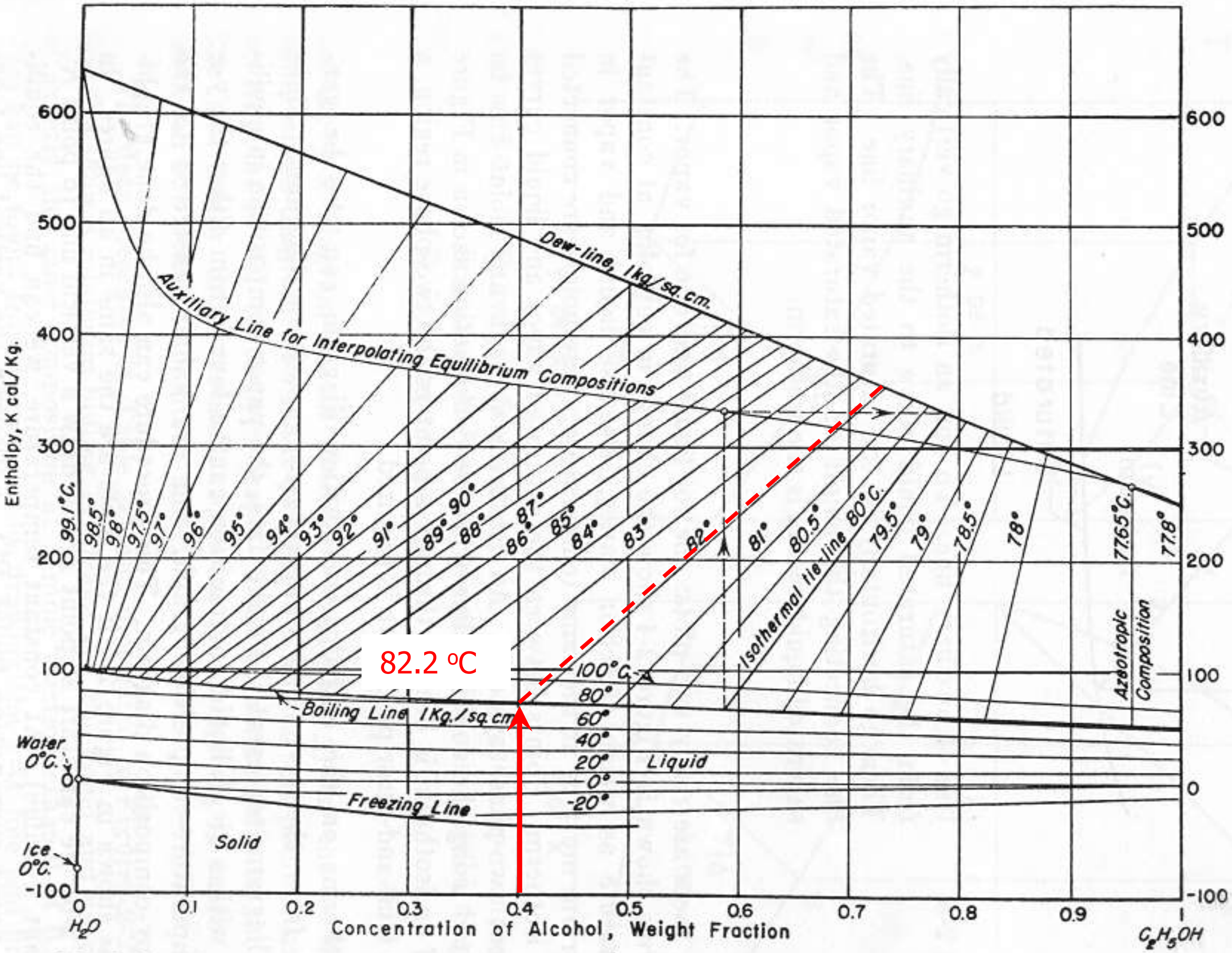
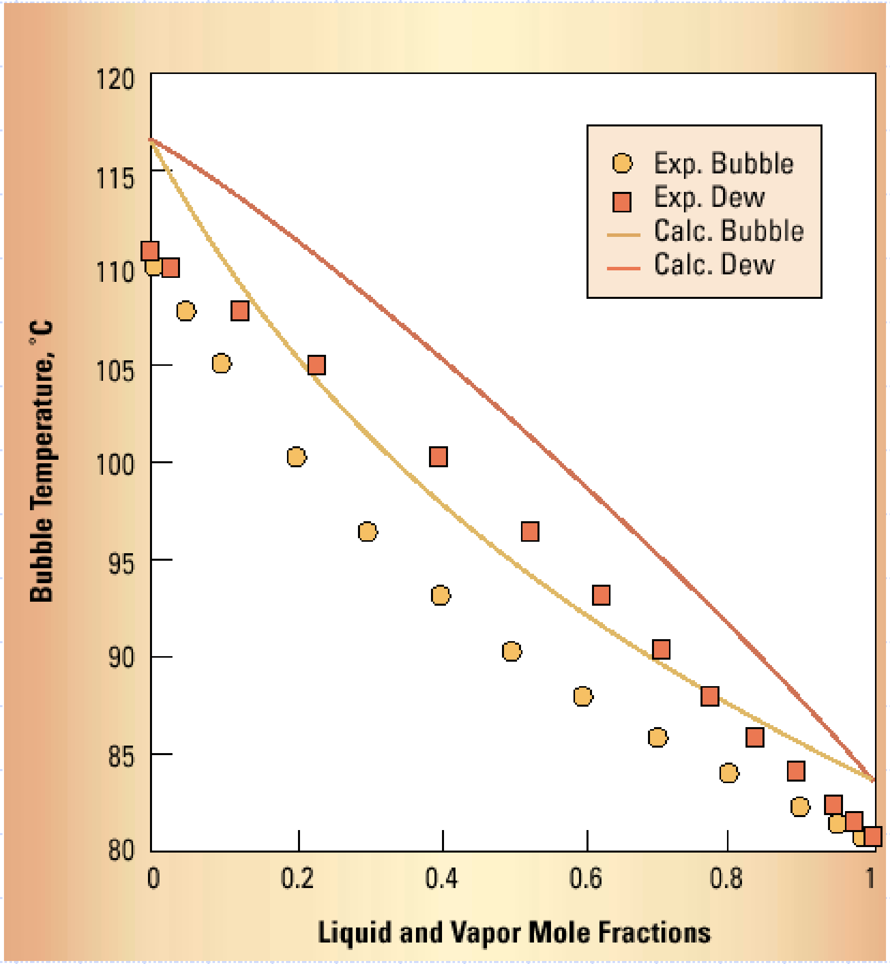


Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

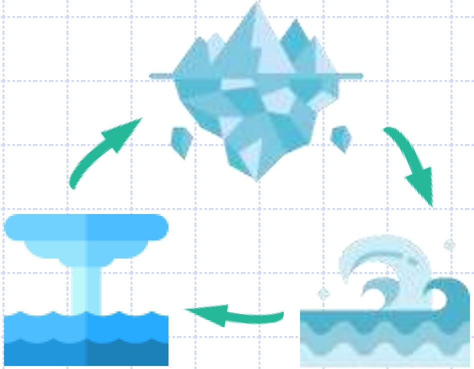
Vapor pressure is crucial in VLE calculation

- The correction given by activity coefficient is insufficient if the vapor pressure is wrong!



Modeling phase equilibria

- Activity coefficient models
- Solubility parameter
- Equations of state
- COSMO-RS



Modeling Phase Equilibrium

- The goals of the modeling are both to correlate existing data and to predict phase equilibrium
- Correlation
  - regressed parameters
  - semi-empirical equations
  - fitting of portions of the phase diagram even with high accuracy
- Prediction
  - physical significance of the parameters
  - theoretically based models need the introduction of additional adjustable parameters
- An ideal model would
  - use easily measured physical properties to predict phase equilibrium at any condition
  - it would be theoretically based.
- No such model exists, and any single model cannot treat all situations
  - → modeling is still case specific
- Many problems still to be solved:
  - critical points - multi-component mixtures - polar systems - association and solvation
- Two big families of models
  - Excess Gibbs energy models (or activity coefficients models)
  - Equations of state models

Excess Gibbs free energy models (G^E models)

- **Polynomial expansions**,
  - according to the Wohl method, which is a polynomial correlation of the system data for both binary and multicomponent systems.
  - number of parameters to be fitted depends on the polynomial expansion used.
  - Equations such as Van Laar and Margules belong to this category.
  - Note that the Margules expansion can be used with different (i.e. increasing) number of adjustable parameters
- Models based on **the local composition concept**
  - introduced by Wilson in 1961.
  - based on a correlation of binary parameters on binary data,
  - multicomponent systems equilibria is done starting from the knowledge of all the binary systems based on component pairs in the mixture of interest.
  - Among others, NRTL and UNIQUAC are the best ones.
  - Wilson defined the local composition concept based on 2 things:
    - interactions among molecules are expressed in terms of binary parameters only;
    - temperature dependency of parameters is made explicit through a Boltzmann-like equation
- **Fully predictive models**
  - group contribution, solubility parameters and quantum chemistry models

Excess Gibbs energy molecular models

- Starting point: Excess Gibbs Energy $$RT\ln\gamma_i = \left(\frac{\partial n_T G^E}{\partial n_i}\right)_{T,P,nj=cost.}$$
- Margules two suffixes: $$\frac{G^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) + \cdots$$
- Redlich Kister:

$$\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots]$$

- Van Laar: $$\frac{G^E}{RT} = x_1 x_2 \frac{A_{12} A_{21}}{A_{21} x_1 + A_{12} x_2}$$
- Wilson: $$\frac{G^E}{RT} = x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$$
- UNIQUAC
- NRTL (electrolyte)

$$\ln\gamma_i = \ln\left(\frac{\varphi_i}{y_i}\right) + \frac{\tilde{z}}{2} q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{y_i}\sum_j y_j l_j -$$

$$-q_i \ln\sum_j \theta_j \tau_{ji} + q_i - q_i \sum_j \frac{\theta_j \quad \tau_{ij}}{\sum_k \theta_k \quad \tau_{kj}}$$

Local composition models

Wilson models

- Wilson model for activity coefficients (binary system) is:

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

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

- Wilson parameter is provided by following equation -

$$\Lambda_{ij} = \frac{V_j}{V_i} exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right]$$

- where, λ12 - λ11 and λ21 - λ22 are binary interaction parameters available from literature for a binary pair.

NRTL model

- Activity coefficient for binary system are defined as -

$$\ln \gamma_1 = x_2^{\,2}\left[\frac{\tau_{21}G_{21}^{\;2}}{(x_1+x_2G_{21})^2}+\frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$$

$$\ln \gamma_2 = x_1^{\,2}\left[\frac{\tau_{12}G_{12}^{\;2}}{(x_2+x_1G_{12})^2}+\frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right]$$

$$\tau_{12}=\frac{g_{12}-g_{22}}{RT} \qquad \tau_{21}=\frac{g_{21}-g_{11}}{RT}$$

$$G_{12}=\exp(-\alpha_{12}\tau_{12}) \qquad G_{21}=\exp(-\alpha_{12}\tau_{21})$$

- Parameter g_{12} - g_{22} and g_{21} - g_{11} are binary parameters available from literature.
- α_{12} is related to non-randomness in mixture and is available from literature for binary pairs.

UNIQUAC model

- Activity coefficient for binary system are defined as -

$$
\begin{aligned}
ln\,\gamma_1 = ln\left(\frac{\varnothing_1}{x_1}\right) + \frac{Z}{2} q_1 ln\left(\frac{\theta_1}{\varnothing_1}\right) + \varnothing_2\left(l_1 - \frac{r_1}{r_2} l_2\right) \\
- q'_1 ln(\theta'_1 + \theta'_2\tau_{21}) \\
+ \theta'_2 q'_1\left(\frac{\tau_{21}}{\theta'_1 + \theta'_2\tau_{21}} - \frac{\tau_{12}}{\theta'_2 + \theta'_1\tau_{12}}\right)
\end{aligned}
$$

$$
\begin{aligned}
ln\,\gamma_2 = ln\left(\frac{\varnothing_2}{x_2}\right) + \frac{Z}{2} q_2 ln\left(\frac{\theta_2}{\varnothing_2}\right) + \varnothing_1\left(l_2 - \frac{r_2}{r_1} l_1\right) \\
- q'_2 ln(\theta'_2 + \theta'_1\tau_{12}) \\
+ \theta'_1 q'_2\left(\frac{\tau_{12}}{\theta'_2 + \theta'_1\tau_{12}} - \frac{\tau_{21}}{\theta'_1 + \theta'_2\tau_{21}}\right)
\end{aligned}
$$

$$
\tau_{12} = exp\left(-\frac{u_{12} - u_{22}}{RT}\right) \qquad \tau_{21} = exp\left(-\frac{u_{21} - u_{11}}{RT}\right)
$$

UNIQUAC model

- Parameter u_{12} - u_{22} and u_{21} - u_{11} are binary parameters available from literature.
- Remaining parameters are calculated as following:

$$\O_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \O_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$

$$\theta'_1 = \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2} \qquad \theta'_2 = \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2}$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1)$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1)$$

- where z is set equal to 10 and r, q & q' are pure component UNIQUAC parameters.

UNIFAC: the UNIversal Functional group Activity Coefficient model

- The activity coefficient is calculated from two components

$$\ln {}^{i}\gamma = \ln {}^{i}\gamma^{C} + \ln {}^{i}\gamma^{R}$$

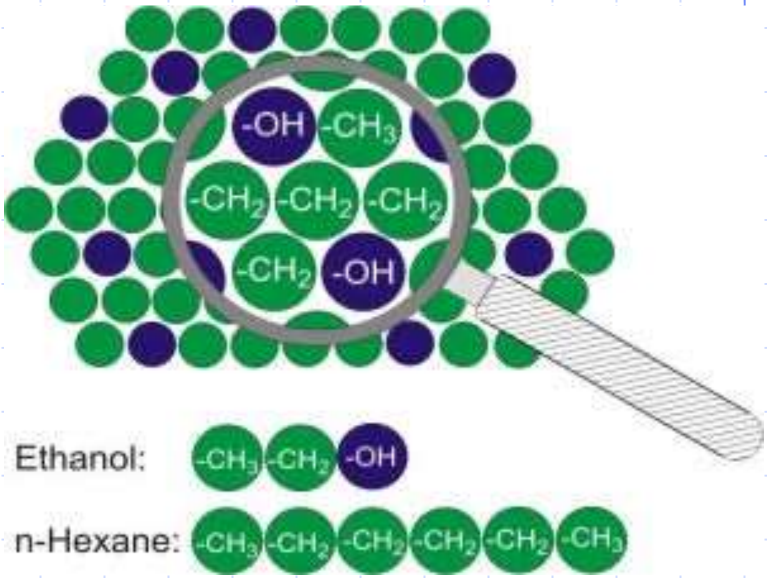
Combinational
(V, SA)

Residual (interactions)
(Experiment Fit)

- The group contribution components consist of
  - volume contributor - R_k
  - surface area contribution - Q_k
  - interaction parameter between functional groups A_{mk}
- To calculate interactions, similar sub-groups are assigned to groups and interactions are between these groups
- Calculate activity coefficients by summing all contributions and interactions

UNIFAC-Simple example

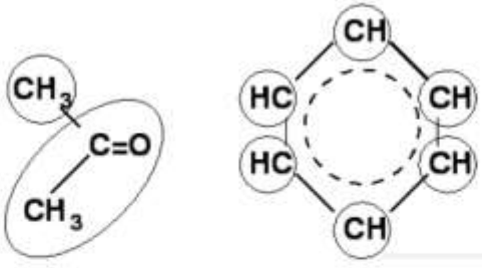
- Ethanol CH_3-CH_2-OH
  - Interaction parameters are fit from experimental data
  - This work is still ongoing and many parameters still not available



	Main Group.	Subgroup	R_k (vol)	Q_k (SA)	A_{mk}
CH_3	"CH_3"	CH_3 (1)	0.9011	0.848	0, 0
CH_2	"CH_2"	CH_2 (2)	0.6744	0.540	0, 0
OH	"OH"	OH (2)	1.000	1.200	986.5, 156.4

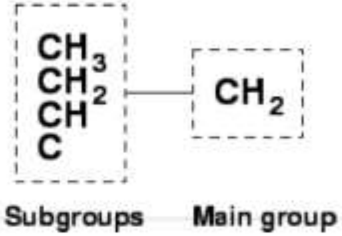
Group contribution model: UNIFAC

UNIFAC



ACETONE

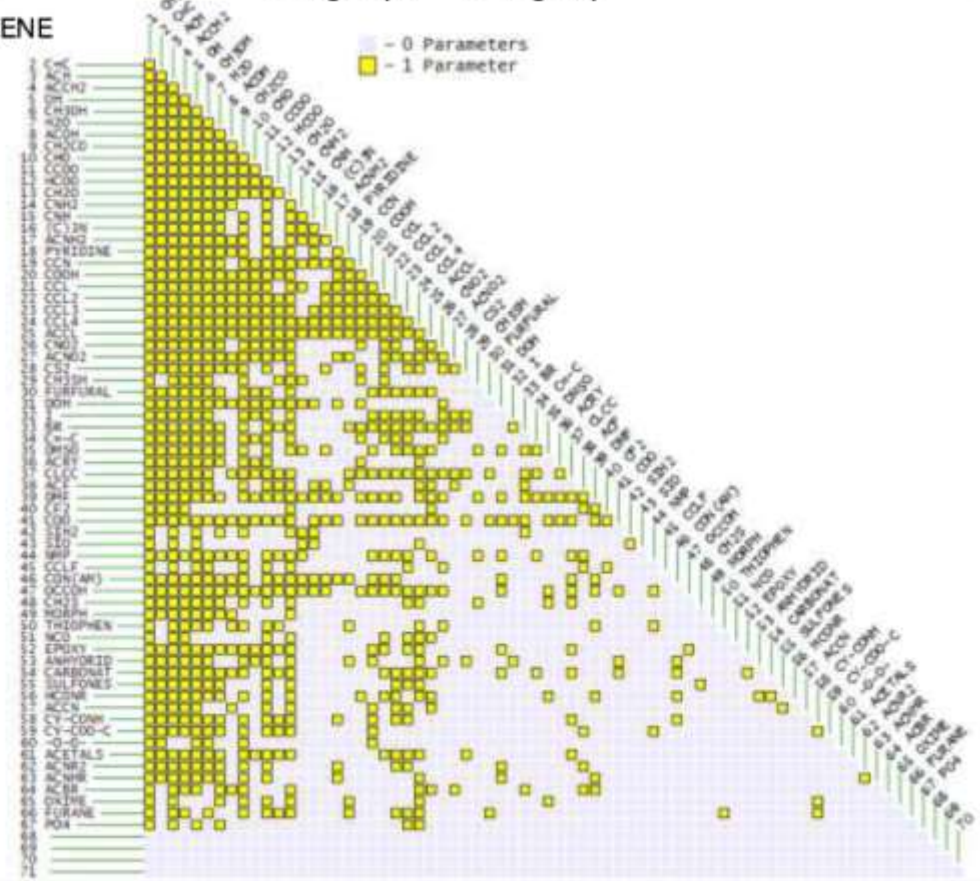
BENZENE



$$\ln\gamma_i = \frac{\sum_j \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_j \frac{G_{ji} w_j}{M_j}} + \sum_j \left[\frac{w_j G_{ji}}{M_j \sum_k \frac{G_{kj} w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_k \frac{\tau_{kj} G_{kj} w_k}{M_k}}{\sum_k \frac{G_{kj} w_k}{M_k}} \right) \right]$$

$$\tau_{ij} = \frac{A_{0ij} + A_{1ij} T}{T}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$



Hildebrand solubility parameter (polymers)

- Gibbs equation: $\Delta G_m = \Delta H_m - T\Delta S_m$
  - Δ, is the value of a variable for a solution minus the values for the pure components considered separately.
- The result obtained by Flory and Huggins is

$$\Delta G_m = RT[\, n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} \,]$$

  - with number of moles n and volume fraction ϕ of solvent (comp.1) and polymer (comp. 2) and the introduction of a parameter χ to take account of the energy of interdispersing polymer and solvent molecules.
- The value of the interaction parameter can be estimated from the Hildebrand solubility parameters δ_a and δ_b

$$\chi_{12} = V_{seg}(\delta_a - \delta_b)^2 / RT$$

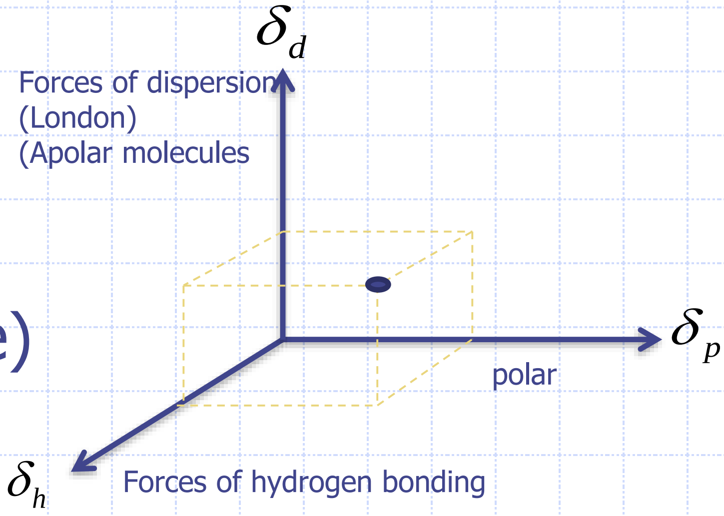
  - where V_{seg} is the actual volume of a polymer segment.
  - δ = square root of the cohesive energy density: $\delta=\sqrt{(\Delta H_{vap} - RT)/V_{molar}}$
  - The cohesive energy density is the amount of energy needed to completely remove unit volume of molecules from their neighbours to infinite separation (an ideal gas).
  - This is equal to the heat of vaporization of the compound divided by its molar volume in the condensed phase.

Hansen Solubility Parameter

- Developed by **Charles Hansen** as a way of predicting if one material will dissolve in another and form a solution
  - They are based on the idea that like dissolves like where one molecule is defined as being 'like' another if it bonds to itself in a similar way.
- Hansen parameters divide the total Hildebrand value into **three parts**: a dispersion force component, a hydrogen bonding component, end a polar component.

$$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$$

- These three parameters can be treated as co-ordinates for a point in three dimensions (Hansen space)
  - The nearer two molecules are in this three dimensional space, the more likely they are to dissolve into each other.



Hansen Solubility Parameter

- To determine if the parameters of two molecules (usually a solvent and a polymer) are within range …
  - an **interaction radius** (R_0) is given to the substance being dissolved.
  - This value determines the radius of the sphere in Hansen space and it's center is the three Hansen parameters.
- To calculate the distance (Ra) between Hansen parameters in Hansen space the formula is used:

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2$$

- Combining this with the interaction radius gives the relative energy difference (RED) of the system:
  - RED = R_a / R_0
  - RED < 1 the molecules are alike and will dissolve
  - RED = 1 the system will partially dissolve
  - RED > 1 the system will not dissolve

Equations of state classification

- An equation of state is a relationship among P, V and T (and composition)
  - Attractive forces
  - Repulsive forces
  - Other forces (electrostatic, hydrogen bonding, …
- Cubic Equations of State: the van der Waals family
  - Van der Waals
  - Soave Redlich Kwong
  - Peng Robinson
  - Volume translation
- Virial equation of state
  - BWR
- Corresponding state
- Perturbation theory
  - The Perturbed Hard Chain Theory
  - The Perturbed Hard Sphere Theory
  - The SAFT Equation

If equations are valid,
EOS are independent
from phases!!

Van der Waals partition function

- Partition function is defined as:

$$Q=\frac{1}{N!}\left(\frac{1}{\Lambda}\right)^{-3N}\left(V_f\right)^N\left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N q_{r,v}{}^N$$

  - L is the De Broglie wave length, function of molecular mass, and T
  - N is the number of molecules
  - Vf is the Free Volume = V-b
  - E_0 is the intermolecular potential
  - $q_{r,v}$ is the degrees of freedom of the molecules

$$V_f = V-\frac{N}{N_A}b = f(\rho) \qquad E_0=-\frac{2aN}{VN_A^2}=f(\rho)$$

$$P=kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,n_i} \Longrightarrow P=\frac{RT}{v-b}-\frac{a}{v^2}$$

Cubic EOS: the van der Waals family

- Cubic EOS's are the simplest model to apply the φ - φ approach for VLE calculation.
  - Cubic in variable v
  - The simplest cubic EOS is the VdW EOS
  - $p = \frac{RT}{v-b} - \frac{a}{v^2} \rightarrow \left(p + \frac{a}{v^2}\right)(v - \mathrm{b}) = \mathrm{RT}$

$$a_C = 0.42175 \frac{R^2 T_C^2}{P_C}$$

$$b_C = 0.125 \frac{R T_C}{P_C}$$

- Easily extended to binary and multi-component systems
  - Mixing rules are crucial
- Only two properties are needed to calculate the VdW parameters
- Pure Component parameters are constrained to:

$$\left(\frac{\partial P}{\partial V}\right)_{Crit} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{Crit} = 0$$

  - But with this the EOS has no more degrees of freedom, namely all parameters are fixed by the critical point conditions
  - Experimental vapor pressure curves is not correctly given

Pure component parameters for the VdW EOS

- Calculating P_{sat} through the VdW EOS: we start from the isofugacity condition:

$$\varphi_i^{*V} = \varphi_i^{*L}$$

$$\varphi_i^{*V} = f\left(P_i^{sat}, T, v^V, a_C, b_C\right)$$

$$\varphi_i^{*L} = f\left(P_i^{sat}, T, v^L, a_C, b_C\right)$$

- At a given T, P_{sat} is the only unknown of the iso-fugacity equation, so it can be obtained in a predictive way.
  - Of course, its calculated value will be different from the experimental one!
- To overcome this problem, a third parameter is needed.
  - A third parameter appropriate to solve the problem of inadequate P_{sat} calculation was first proposed by Soave in 1972. It is known as "parameter alpha".

Pure component parameters for the VdW EOS

- According to Soave's, the VdW EOS is rewritten in the form:

$$P = \frac{RT}{v - b_C} - \frac{\alpha(T) a_C}{v^2}$$

- According to Soave's idea the attractive parameter a is evaluated from a = α(T) a_C, thus substituting a=a_C in both the VdW equation and the expressions of φi^{*V} and φi^{*L}.
  - In this way, the isofugacity condition can be rewritten as:

$$\varphi_i^{*V}(P_i^{sat}, T, \alpha) = \varphi_i^{*L}(P_i^{sat}, T, \alpha)$$

- For a given T, the accurate (experimental) corresponding value of P_{sat} can be used.
  - The value of α is uniquely determined to reproduce this P_{sat} value.

Pure component parameters for the VdW EOS: alpha

- Soave proposed an equation to calculate the function α(T), which holds for non-polar components only:

$$\sqrt{\alpha(T)} = 1 - m\sqrt{1 - T/T_C}$$

$$m = C_1 + C_2\omega + C_3\omega^2$$

- In summary,
  - VdW EOS with the function α(T) is able to accurately calculate P_{sat} in a predictive way for non-polar components.
  - α is obtained without knowing P_{sat}, which is the only unknown of the isofugacity equation.
  - For polar compounds α(T) can be obtained only by fitting P_{sat} experimental values.

Soave Redlich Kwong Equation

- Redlick Kwong Equation

$$p = \frac{RT}{v - b} - \frac{a}{\sqrt{T}v(v + b)}$$

  - Simple, poor for liquids, good when 2Pr<Tr

- Soave Equation

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)}$$

$$a = [1 + m\sqrt{T_r}]^2 * a_c$$

$$m = f(\omega)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

ω = acentric factor

  - Simple, involve acentric factor, best for hydrocarbons

Peng-Robinson Equation

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}$$

$$a = [1 + k\sqrt{T_r}]^2 * a_c$$

$$\mathrm{k} = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$k = f(\omega)$$

ω = acentric factor

- Good for critical conditions properties
- Better than SRK for density of nonpolar liquids
- Wide applications

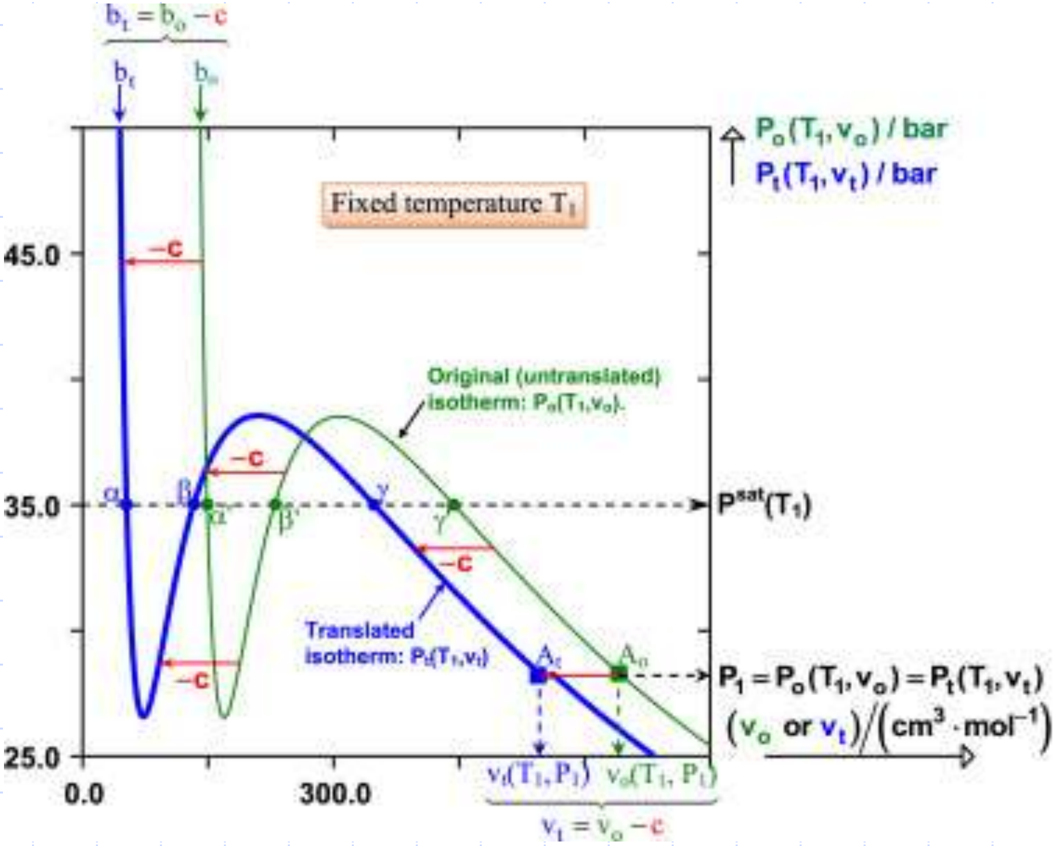
Pure component parameters for the VdW EOS: volume shift

- Peneloux, in 1982, proposed a volume shift (i.e. volume translation) in the EOS, applicable to any cubic EOS:

$$P(T,v)=\frac{RT}{v-b}-\frac{a_c\cdot\alpha(T)}{v^2+ubv+wb^2}\xrightarrow{\theta=v+c}P(T,v)=\frac{RT}{(v+c)-b}-\frac{a_c\cdot\alpha(T)}{(v+c)^2+ub(v+c)+wb^2}$$

  - with $\theta = v + c$
  - c is calculated to exactly reproduce V_{liq} at Tr = 0.8
  - Deviation on V_{liq} is not dependent on ω
  - Attractive parameters of EOS must be universal constants

$$P=\frac{RT}{\theta-b}-\frac{\alpha(T)a_c}{\theta^2}$$



- VTPR
  - Volume Translation Peng Robinson Equation of state

Pure component parameters for the VdW EOS: volume shift

- The c parameter allows better calculation of densities.
  - the value of c can be calculated based of both liquid and vapor density data,
  - obtaining a value which is essentially independent of the temperature,
  - except close to the critical temperature (as a rule of thumb, outside the range $0.9<T_r<1.1$).
- For instance, if the experimental liquid density at ambient condition (20°C and 1 atm) is known, it results:

$$c = (v + c)^{L}_{cal} - v^{L}_{\exp}$$

  - NOTE: the application of the volume shift does not affect calculation of P_{sat} and other properties.
- Do not use temperature dependent volume transition parameter
  - It is thermodynamically inconsistent

The ultimate (generic) cubic EOS's

$$P = \frac{RT}{v + c - b_C} - \frac{\alpha(T) a_C}{(v + c + b_C)(v + c + d)}$$

- A cubic EOS is a third-degree polynomial in v, and as such it may have a maximum of four parameters.
  - Any cubic EOS, including shifted VdW, shifted SRK and shifted PR EOS, can be derived from this equation!
- In summary, the pure component parameters calculation requires the knowledge of:

1. TC/PC, which can also be predicted by a suitable model
2. Psat, or α in the case of non-polar components.
3. an experimental density value

- If any one of the above properties is missing for any of the components involved in the process, it is NOT possible to use a cubic EOS for process simulation.

Applicability of cubic Equations of state

- This issue of missing TC/PC or density is not particularly relevant
  - They can be easily estimated or measured
- It is critical with respect to P_{sat}.
  - If P_{sat} is unpredictable or cannot be measured, cubic EOSs cannot be applied.
  - This happens in the presence of gases and solids (polymers, electrolytes,..).
- In the case of gases, the problem has been solved by a suitable extrapolation of the α function above the critical temperature
  - But only for a limited extrapolation with respect to T .
- With solids there is nothing to do.

- So, it must be concluded that cubic EOS’s cannot be applied to components without a measurable vapor pressure,
- EOSs other than cubic ones have to be used to model systems containing solids.
  - For instance, the PHSC EOS and the SAFT EOS have been developed for polymer solutions, whereas models to represent electrolyte solutions at high pressures are missing .

Mixture parameters for Cubic EOS: classical mixing rules

$$P = \frac{RT}{v_m + c_m - b_m} - \frac{a_m}{(v_m + c_m)^2}$$

$$b_m = \sum_i z_i b_i^*$$

$$a_m = \sum\sum z_i z_j \sqrt{a_i^* a_j^*}\,(1 - k_{ij})$$

$$c_m = \sum_i z_i c_i^*$$

- In summary, to be able to apply a cubic EOS for an accurate calculation of mixture parameters, the following properties must be known:

1. T_C/P_C of all the components
2. P_{sat} (or α in the case of non-polar components) for all the condensable components at the system temperature.
3. a density value of all the components
4. VLE data of all the binary systems formed by all component pairs, to fit k_{ij}'s values

Calculation of VLE (but also LLE) by a cubic EOS

$$\begin{cases} y = K_1 x \\ 1 - y = K_2(1 - x) \end{cases} \qquad K_i = \frac{\varphi_i^L}{\varphi_i^V}$$

for SRK EOS and classical mixing rules:

$$\ln\varphi_i^{L,V} = \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V^{L,V}}\right] dV^{L,V} - \ln\frac{PV^{L,V}}{RT}$$

$$\ln\varphi_i = \frac{b_i^*}{b_m}\left(\frac{Pv_m}{RT} - 1\right) - \ln\left(\frac{Pv_m - Pb_m}{RT}\right) + \ln\left(1 + \frac{b_m}{v_m}\right)\frac{\partial}{\partial n_i}\left[n_T\frac{a_m}{b_m RT}\right]$$

$$\ln\varphi_i^L = \frac{b_i^*}{b_m^L}\left(\frac{Pv_m^L}{RT} - 1\right) - \ln\left(\frac{Pv_m^L - Pb_m^L}{RT}\right) + \Bigg[\frac{a_m^L}{b_m^L}\Bigg(\frac{b_i^*}{b_m^L} - \frac{2b_m^L}{a_m^L}\sum_j\sqrt{\frac{a_i^* a_j^*}{b_i^* b_j^*}}(1 - k_{ij}\Bigg)\Bigg)\Bigg]\ln\left(1 + \frac{b_m^L}{v_m^L}\right)$$

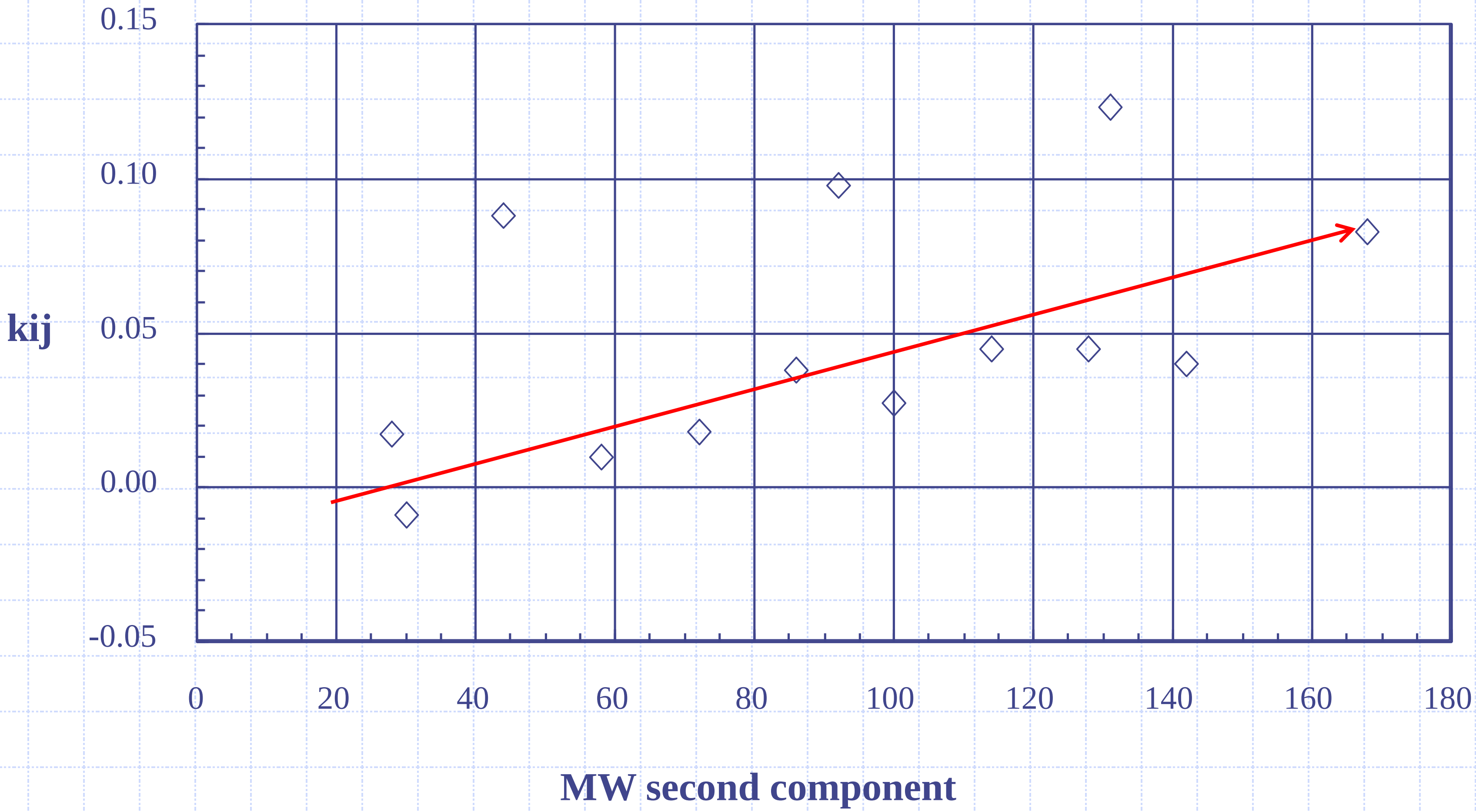
$$\ln\varphi_i^V = \frac{b_i^*}{b_m^V}\left(\frac{Pv_m^V}{RT} - 1\right) - \ln\left(\frac{Pv_m^V - Pb_m^V}{RT}\right) + \Bigg[\frac{a_m^V}{b_m^V}\Bigg(\frac{b_i^*}{b_m^V} - \frac{2b_m^V}{a_m^V}\sum_j\sqrt{\frac{a_i^* a_j^*}{b_i^* b_j^*}}(1 - k_{ij}\Bigg)\Bigg)\Bigg]\ln\left(1 + \frac{b_m^V}{v_m^V}\right)$$

Features of the Cubic Equations of state

- Need three parameters for pure components: Tc, Pc, ω
- The main advantage is the flexibility and the easy of use
- The main disadvantage is its accuracy in the PVT space for both pure components and mixtures
- The applicability is questionable when critical properties are not known (high molecular weight such as polymers)
- Group contribution versions for b and a are available
- Volumetric properties are not accurate in the close vicinity of the critical point
- The physical meaning of the parameters is questionable
- Mixture parameters are difficult to predict

- They are a very powerful and useful correlation tool

Binary interaction parameters for SRK



EOS Models: considerations on k_{ij}'s

- The values of k_{ij}'s have to be fitted to binary data of the mixture property.
  - they have to be known for **all the binary pairs** in the mixture:
  - with NC=3 it means 3 pairs, with NC=4 there are 6 pairs, and so on (the number of pairs largely increases with NC).
- Common features of the k_{ij}'s are:
  - for each pair, either 1 or 2 k_{ij}'s can be used (symmetrical or asymmetrical option). It is often assumed that **$k_{ij} \neq k_{ji}$ to increase the model flexibility**
  - k_{ij} is a **correction factor**. As such, its value must be constant for the given pair of components (and for a specific property). Only a **slight temperature dependency of k_{ij}'s is tolerated**, whereas k_{ij} values must **not depend on composition** (this would cause thermodynamic inconsistency)
  - k_{ij} is a **correction factor**. As a rule of thumb, its absolute value should be less than 0.1, as larger values would indicate that the model is unsuitable for the property calculation
  - since k_{ij} is a binary parameter, **the model can predict the multicomponent** property starting from the knowledge of (all) the binary system values of the same property. In summary, a model with the k_{ij}'s is correlative on the binary and predictive on the multicomponent systems.

Mixture parameters for cubic EOS's

Classical mixing rules:

- In general, the fitting of VLE binary data by a cubic EOS was found to be satisfactory for non-polar systems only.
- In the presence of one (or two) polar components the correlation is often insufficient, indicating that the values of $k_{1,2}$ and $k_{2,1}$ should depend on the composition to ensure better and acceptable performance.
- Unfortunately, this would result into thermodynamic inconsistency problems.

Huron and Vidal mixing rules

- How to extend the EOS to highly non ideal systems?
  - Compromise between EOS and G^E models
  - Huron and Vidal used a simple thermodynamic relationship to derive mixing rules of EOS based on G^E models
  - They equate the G^E energy to fugacity coefficient as computed by EOS
- Basic hypothesis:
  - G^E from a liquid state activity coefficient model is **equal** to G^E from an EOS at **infinite pressure**
  - **Volume** of the mixture at infinite pressures is **equal** to the co-volume
  - **Excess volume** at infinite pressure is zero
- Linear mixing rule for b_m parameter

$$b_m = \sum_i x_i b_i$$

- a_m parameter becomes:

$$a_m = b_m \sum_i \frac{a_i}{b_i} - \frac{G^{E,\infty}}{\Lambda}$$

  - Where L depends on the EOS used (if RK = ln 2)
  - $G^{E,\infty}$ is evaluated at infinite pressure (by NRTL – UNIQUAC).

Huron and Vidal mixing rules

- Limitations of the original HV approach:
  - NRTL parameters must be regressed from experimental data
  - HV mixing rules are not good for non polar mixtures (hydrocarbons)
  - HV mixing rules are not good for low pressure VLE
- Modifications proposed
  - Michelsen (MHV1): zero pressure instead that infinite pressure (q_1=k=.593)

$$\frac{a}{bRT} = \sum_i x_i \frac{a_i}{b_i RT} + \frac{1}{q_1}\left(\frac{G^{E,0}}{RT} - \sum_i x_i ln \frac{b_i}{b}\right) \qquad b = \sum_i x_i b_i$$

  - Dahl and Michelsen (MHV2): second order HV

$$q_1\left(\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right) + q_2\left(\left(\frac{a}{bRT}\right)^2 - \sum_i x_i \left(\frac{a_i}{b_i RT}\right)^2\right) = \left(\frac{G^{E,0}}{RT} - \sum_i x_i ln \frac{b_i}{b}\right)$$

G^E-EOS models

- It took a while before the approach proposed by Huron and Vidal was appreciated by the scientific community
  - but it gave inspiration for a number of similar methods which are referred to as GE-EOS models, all based on the SRK EOS.
- Among others, the MHV2 EOS by Dahl and Fredenslund (1990), the Wong-Sandler (WS) EOS (1992) and the Predictive SRK (PSRK) EOS by Gmehling (1993).
  - MHV2 and PSRK are based on the UNIFAC activity coefficient model and suffer of similar limitations,
  - WS EOS is more theoretically based than HV as regards the second Virial coefficient evaluation.
- GE-EOS approach is not much more than a smart way to address the problem of correlating VLE data of strongly non ideal systems.
  - Therefore, it is suggested to use their simplest formulation, i.e. the one proposed by Huron and Vidal.

Motivation for non cubic EOS

- EOS is a reasonable choice for HP calculations
- Cubic Equations are not suitable for predictions
  - TC e PC are questionable for ‘natural systems’
  - Binary kij are difficult to predict
  - The physical basis of Cubic EOS is poor
- Perturbation theory gives indications
- Perturbed Hard Chain - Perturbed Hard Sphere Chain
  - Theory more complex and gives better model
  - Parameters become ‘predictable’
  - Higher complexity is balanced by good computer codes
- Some examples
  - Carnahan Starling van der Waals
  - PHCT
  - PHSCT
  - SAFT

Van der Waals partition function

- Partition function is defined as:

$$Q = \frac{1}{N!}\left(\frac{1}{\Lambda}\right)^{-3N} \left(V_f\right)^N \left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N q_{r,v}{}^N$$

  - L is the De Broglie wave length, function of molecular mass, and T
  - N is the number of molecules
  - Vf is the Free Volume = V-b
  - E_0 is the intermolecular potential
  - $q_{r,v}$ is the degrees of freedom of the molecules

$$V_f = V - \frac{N}{N_A} b = f(\rho) \qquad E_0 = -\frac{2aN}{VN_A^2} = f(\rho)$$

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,n_i} \quad \Longrightarrow \quad P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Generalized Van der Waals partition function

- Van der Waals partition function is modified (Beret Prausnitz) considering $q_{r,v} = q_{r,v}(est)\, q_{r,v}(int)$
  - External (= influenced by density) contribution from rotation and vibration of the molecules
  - External degrees of freedom = 3 (transl.) * c (transl. equivalent)
  - Internal contributions depend on Temperature only

$$q_{r,v}(ext) \propto \left(\frac{V_f}{V}\right)^{c-1}$$

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,n_i}$$

$$Q = \frac{1}{N!}\left(\frac{V_f}{\Lambda^3}\right)^N \left(\frac{V_f}{V}\right)^{N(c-1)} \left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N [f(T)]^N$$

Carnaham Starling equation

- Perkus Jevick

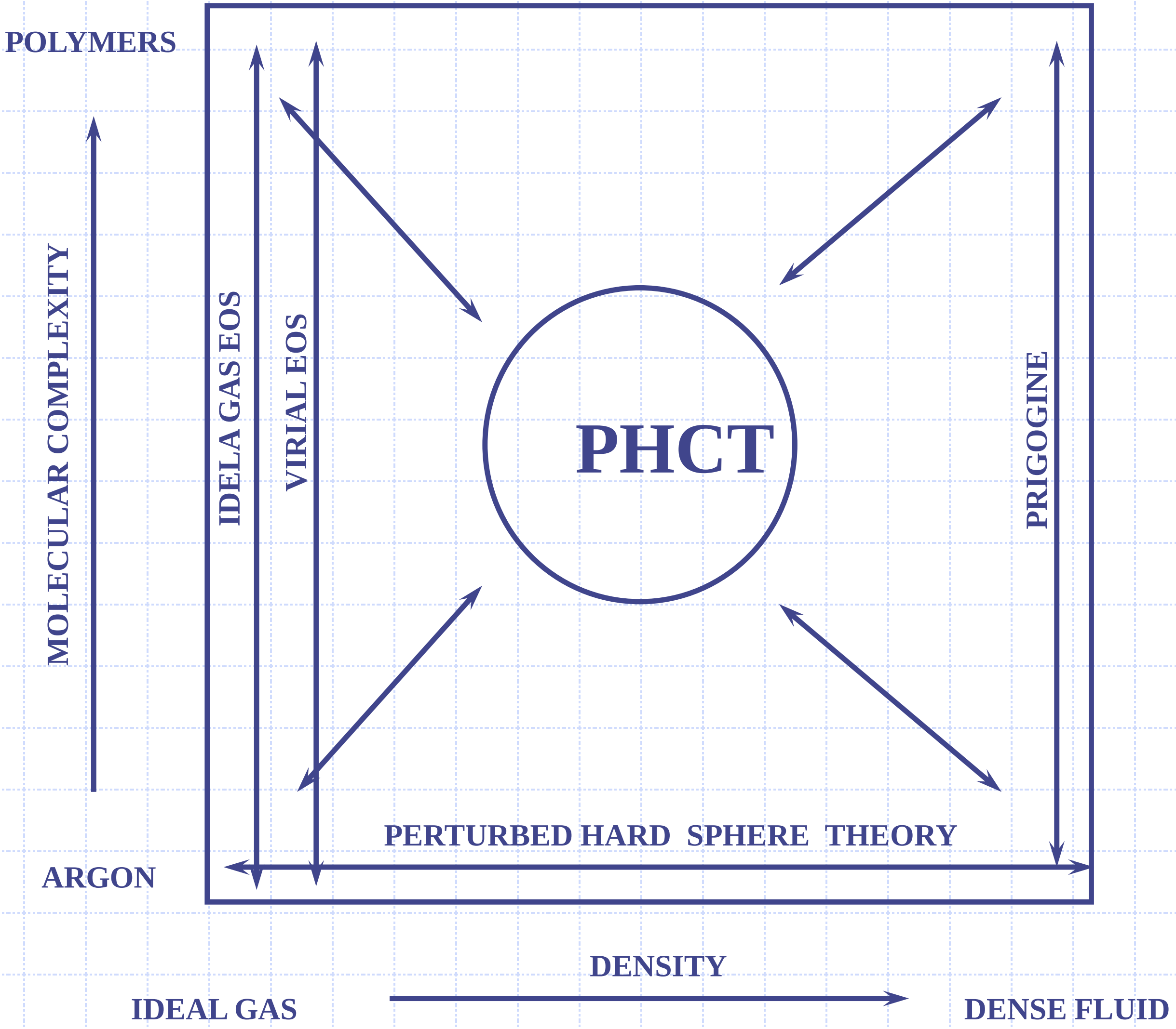
$$\frac{V_f}{V} = \exp\left[\frac{\xi(3\xi-4)}{(1-\xi)^2}\right]$$

$$\xi = 0.74\frac{v_0}{v} \qquad v_0 = \frac{\sigma^3}{\sqrt{2}}N_A$$

- Carnahan – Starling:

$$P = P^{IG} + P^{HS} + P^{ATT} = \frac{RT}{v} + \frac{RT}{v}\left[\frac{\xi(4-2\xi)}{(1-\xi)^3}\right] - \frac{a}{v^2}$$

Perturbed Hard Chain theory



The PHSCT EOS – pure components

$$\left(\frac{P}{\rho kT}\right)_{\mathrm{Ref}} = 1 + r^2 b\rho g(d^+) - (r-1)[g(d^+) - 1]$$

- 3 parameters: *r*, *a* and *b*
- 3 parameters: σ, ε/k and *r*

recasting

$A^* = \pi\, r\, \sigma^2 N_A$

From molecular area *A*

$V^* = (\pi/6)\, r\, \sigma^3 N_A$

From molecular volume V

$E^* = r\, (\varepsilon/k)\, R_g$

From *A**, V* and E_k/E_p –

The PHSCT EOS – binary mixtures

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}({d^+}_{ij}) - \sum_{i}^{m} x_i (r_i - 1)[g_{ii}({d^+}_{ii}) - 1] - \frac{\rho}{kT} \sum_{ij}^{m} x_i x_j r_i r_j a_{ij}$$

$$g_{ij}(\eta, \xi_{ij}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)}$$

$$\eta = \frac{\rho}{4} \sum_{i}^{m} x_i r_i b_i$$

$$\xi_{ij} = \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho}{4} \sum_{k}^{m} x_k r_k b_k \quad {}^{2/3}$$

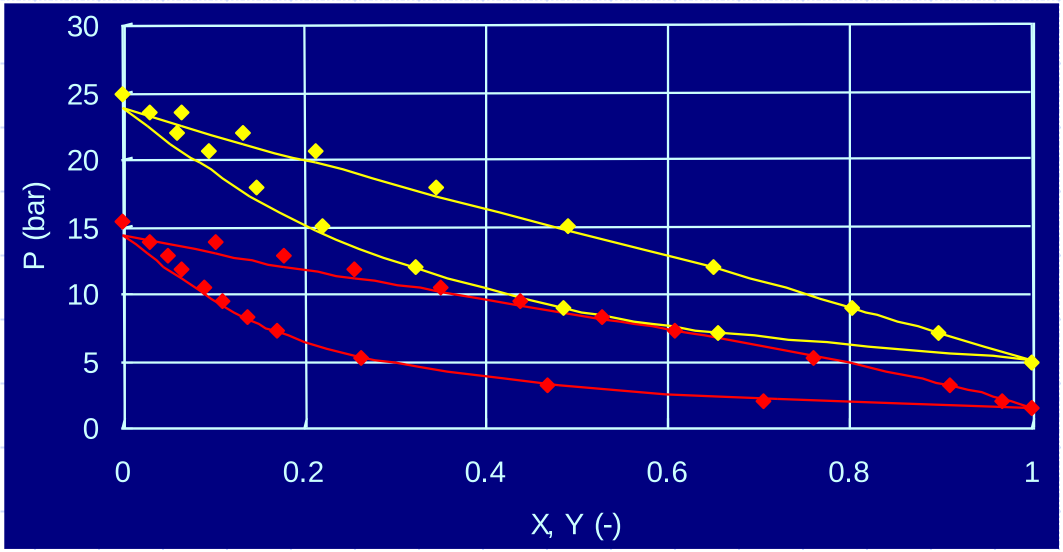
$$a_{ij} = (2\pi/3)\sigma_{ij}^3 \varepsilon_{ij} F_a\left(kT/\varepsilon_{ij}\right)$$

$$b_{ij} = (2\pi/3)\sigma_{ij}^3 F_b\left(kT/\varepsilon_{ij}\right)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right)$$

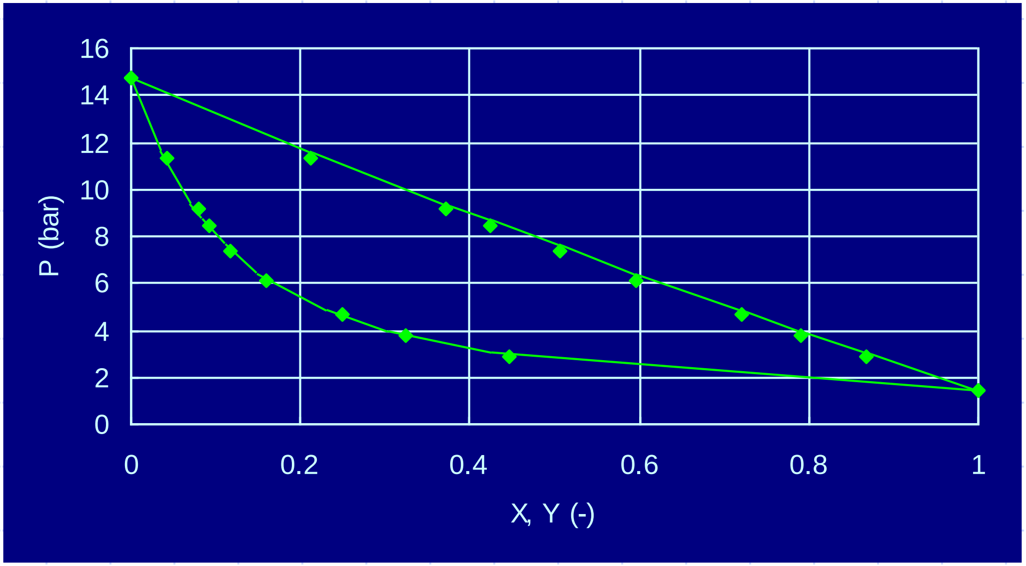
Predictive PHSCT performace: refrigerants



🟥 R13 R14

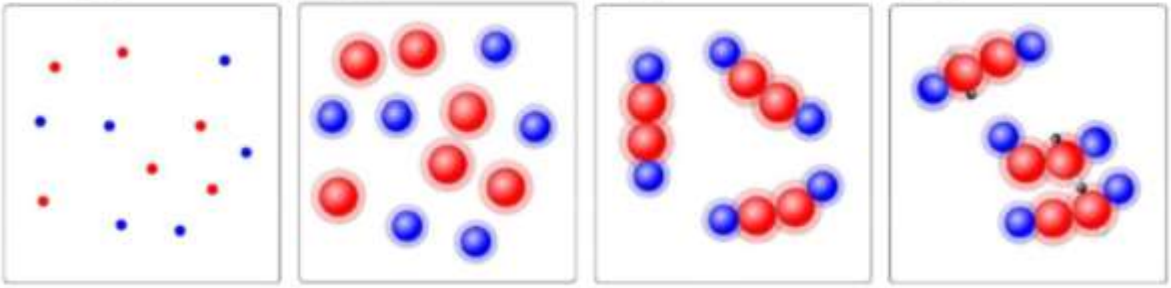
🟨 R22 R23

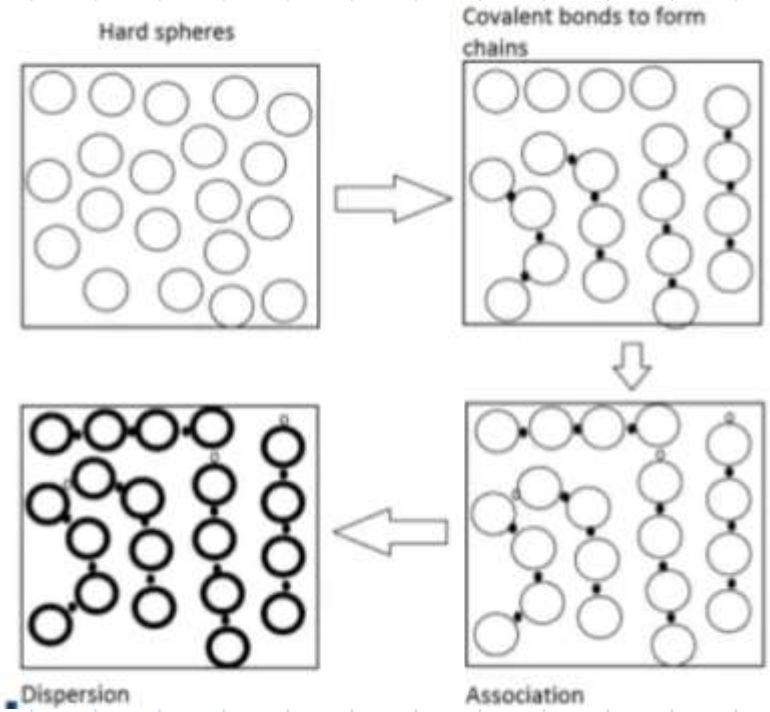
🟩 R23 R134a



Statistical Associating Fluid Theory - SAFT

$$A = A^{Ideal} + A^{Mono.} + A^{Chain} + A^{Assoc.}$$



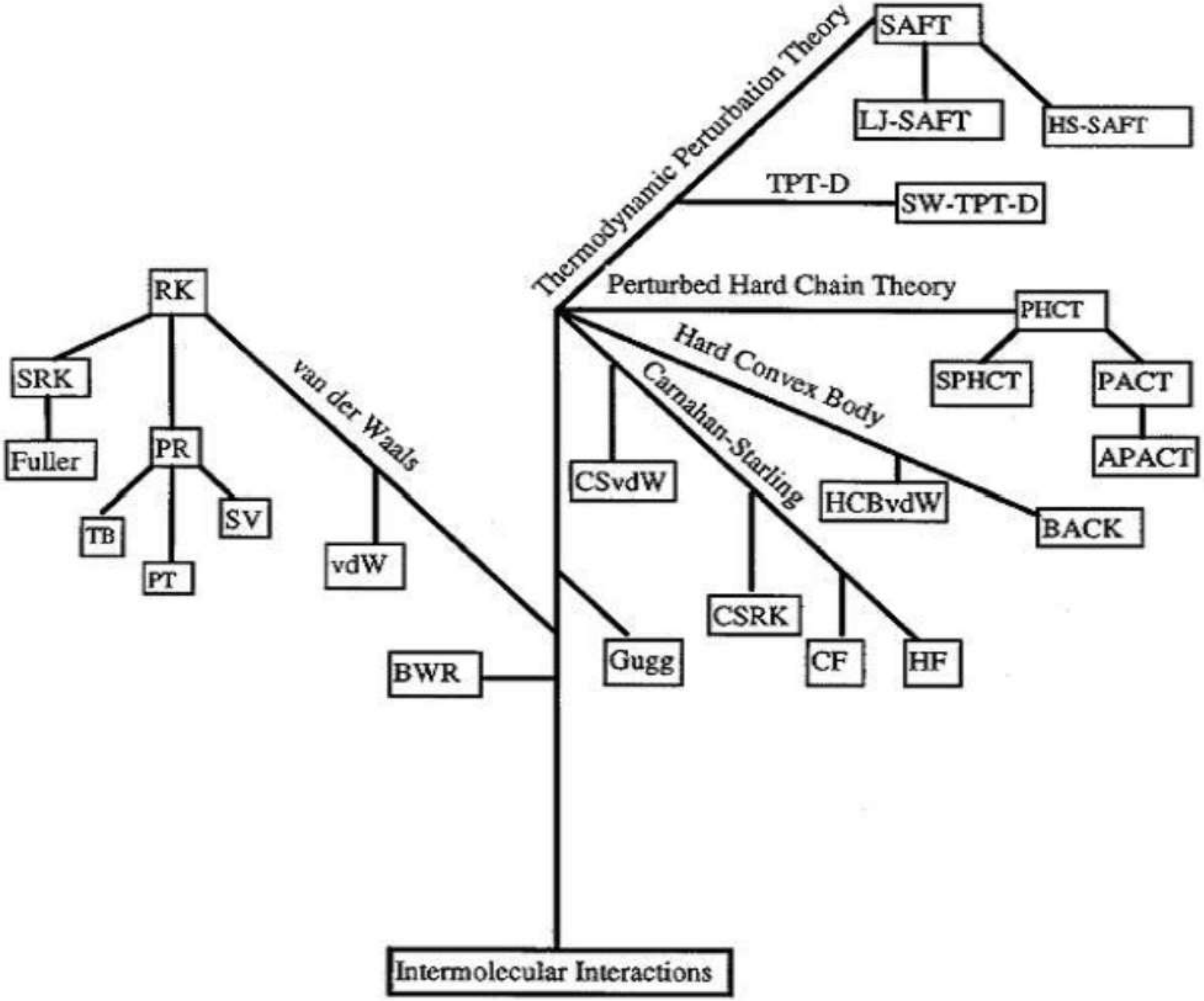


Chapman, Gubbins, Jackson, Radosz, Ind. Eng. Chem. Res. 29*, 1709 (1990)*

Gross, Sadowski, Ind. Eng. Chem. Res. 40*, 1244 (2001)*

Karakatsani, Spyriouni, Economou, AIChE J., 51*, 2328 (2005)*

Relations among EOS (cubic and non cubic)



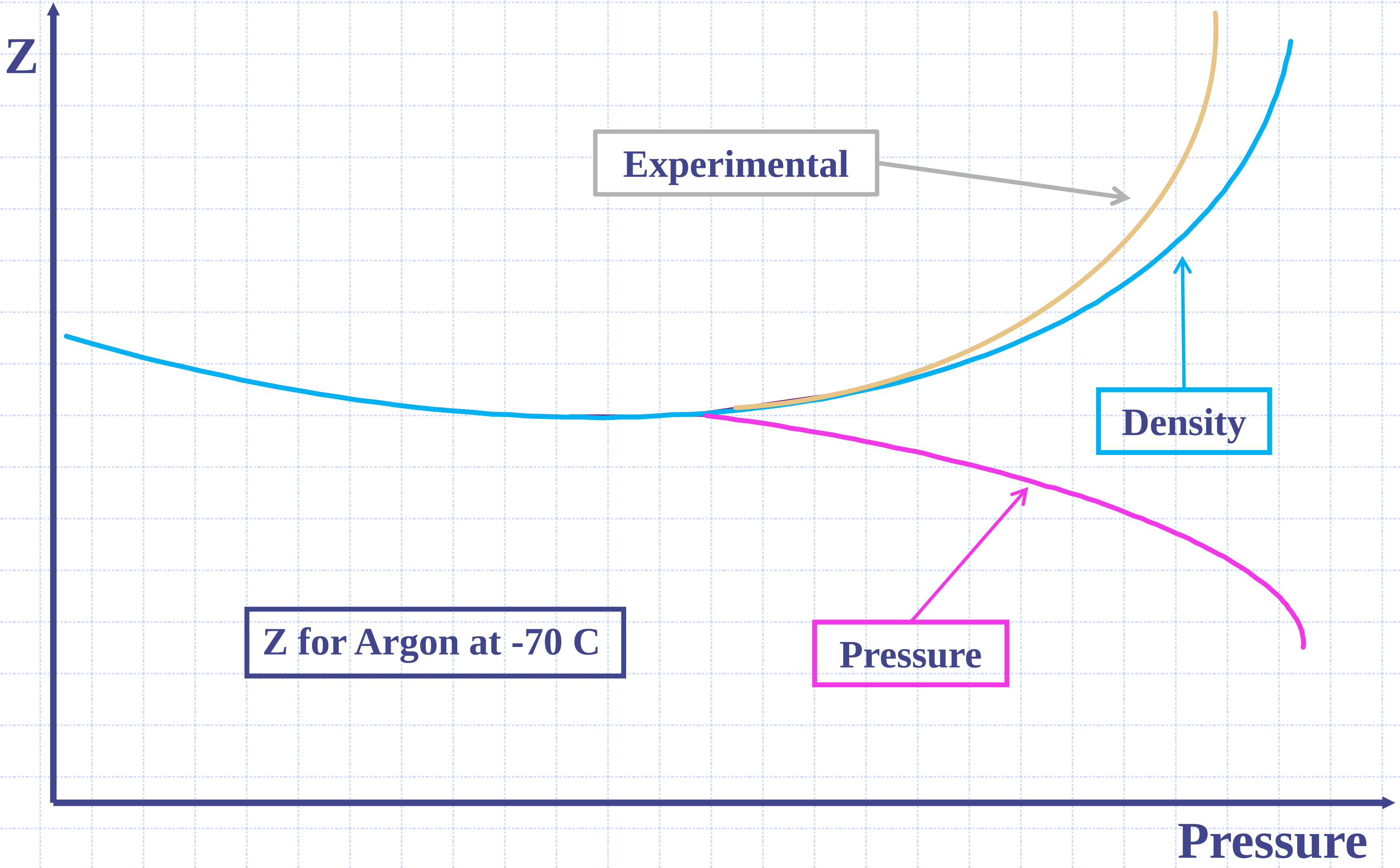
VIRIAL EQUATION OF STATE

- Remarkably general provided the intermolecular potential obeys certain well-defined restrictions
- Takes the interaction into account
  - The second virial coefficient considers interaction between two molecules
  - The higher order coefficients follows in an analogous manner
- The coefficients B, C, .. can be calculated 'a priori' from statistical mechanics

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots$$

$$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots$$

Virial Equation of State



Examples of Virial EOS

- Benedict Webb Rubin Lee Starling

$$P = RT\rho + (B_0RT - A_0 - C_0/T)\rho^2 + (bRT - a)\rho^3 + \\ + \alpha a\rho^6 + \left(c\rho^3/T^2\right)\left(1+\gamma\rho^2\right)\exp\left(-\gamma\rho^2\right)$$

- Hayden O’Connell
  - Complex term for B accounting for associations and chemical effects such as hydrogen bonding
  - No interaction parameters for mixtures
  - Excellent for gamma phi approach
  - Very poor for liquids

CORRESPONDING STATES THEORY

- Derived by van der Waals - most important result
- Based on the critical constraints
  - Variables v, T and P are related by a universal function such that F(Tr,Pr,Vr) = 0
- The EOS for any one fluid is written in reduced coordinates, that equation is also valid for any other fluid.
- The original formulation is a two parameter theory
  - Only for simple molecules
  - In which the force field has a high degree of symmetry
  - Typically small, non polar substances
- For more complex molecules it is necessary to introduce an extra parameter (at least)
  - PlocPlocker extension to mixtures of Lee Kesler equation

Corresponding States Theory: Mixtures

- For mixture the definition is the same

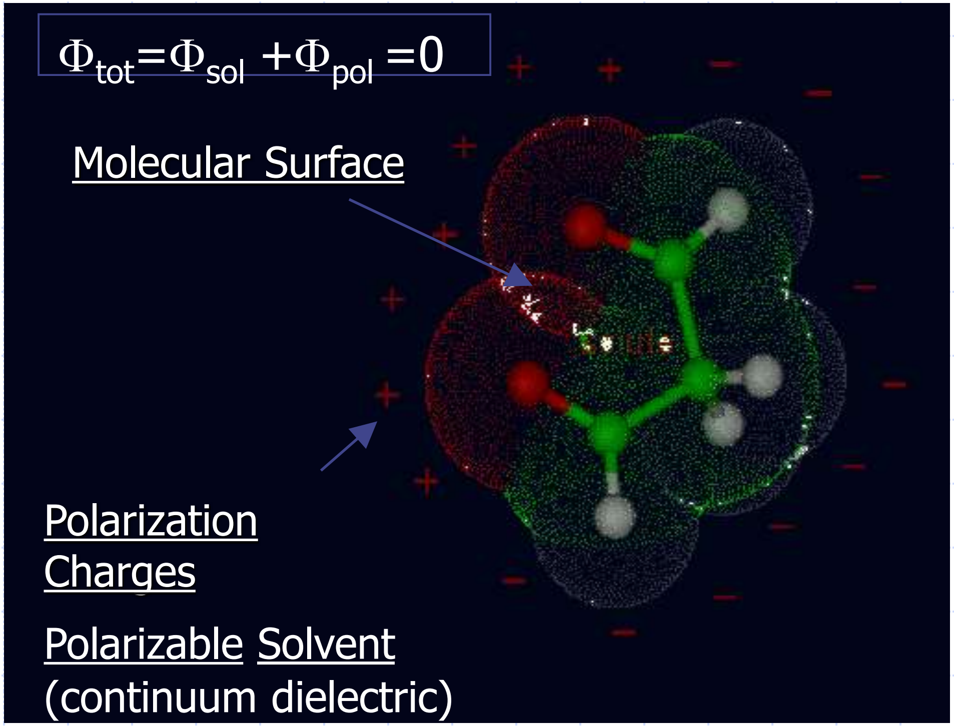
$$F(T_r, V_r, P_r) = \quad z = \Im(T_r, P_r, X)$$

- One has to define the pseudo critical properties

$$T_{cm}\ ,\ v_{cm},\ \omega_m$$

Quantum chemistry models: COSMO-RS

- Extension of the COSMO model beyond the dielectric Continuum solvation Models
  - CSMs, successful but hardly justifiable from a theoretical point of view;
- ideally screened molecules taken as a starting point for the description of molecules in solutions;
- deviations from ideal screening
  - described as pairwise misfit interactions of the ideal screening charges on contacting parts of the molecules in the fluid;
- atom parametrizations based upon DFT calculations

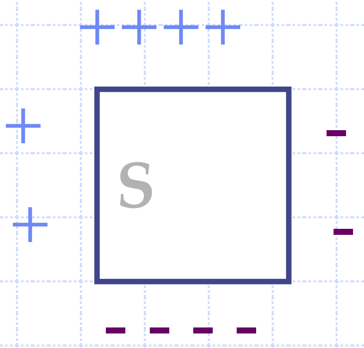


COSMO-RS : Basic Idea (deviation from ideal screening)

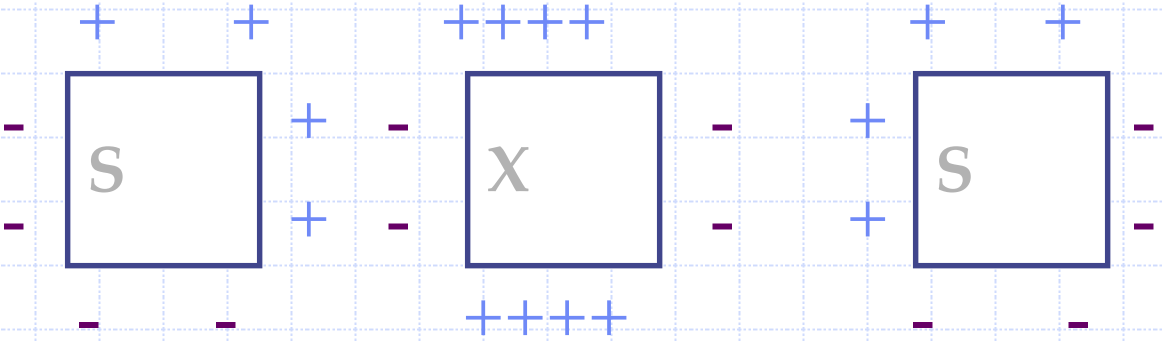
Real situation:

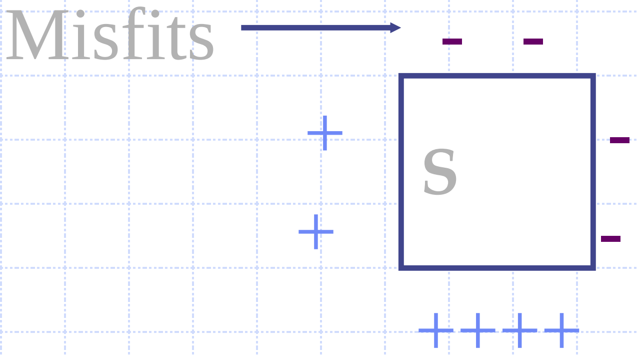
Deviation from

Ideally screen state



$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right)$$





Calculate

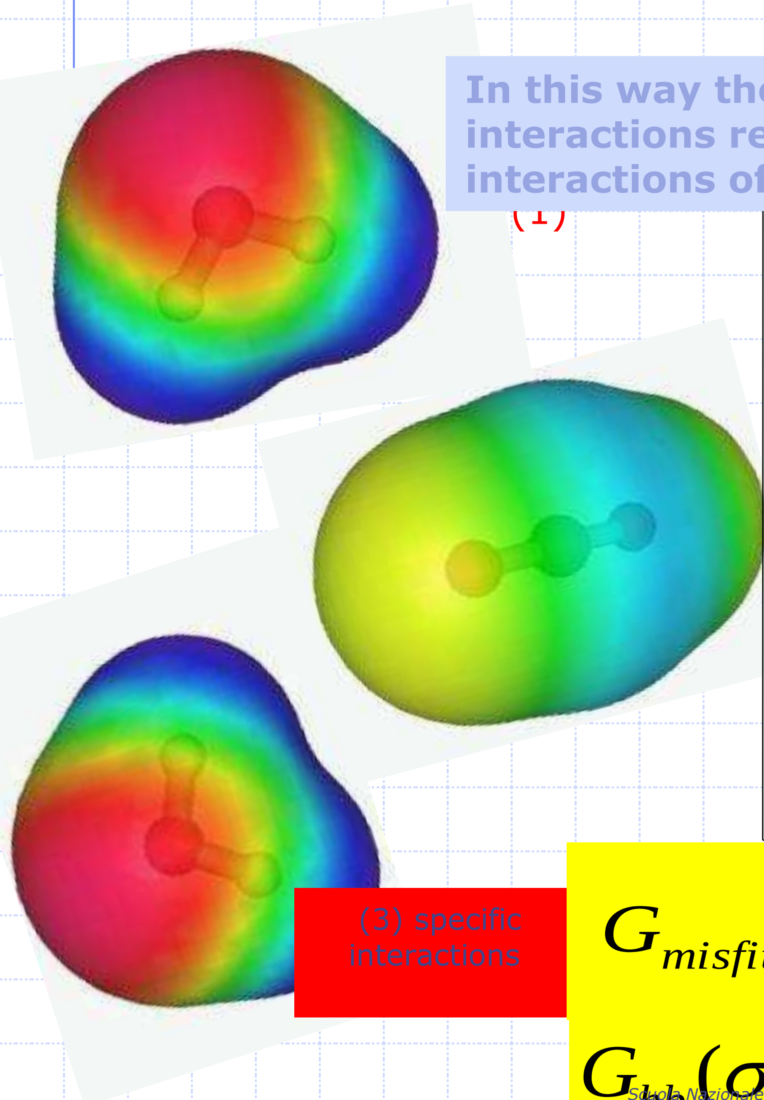
Misfit energy

COSMO-RS:

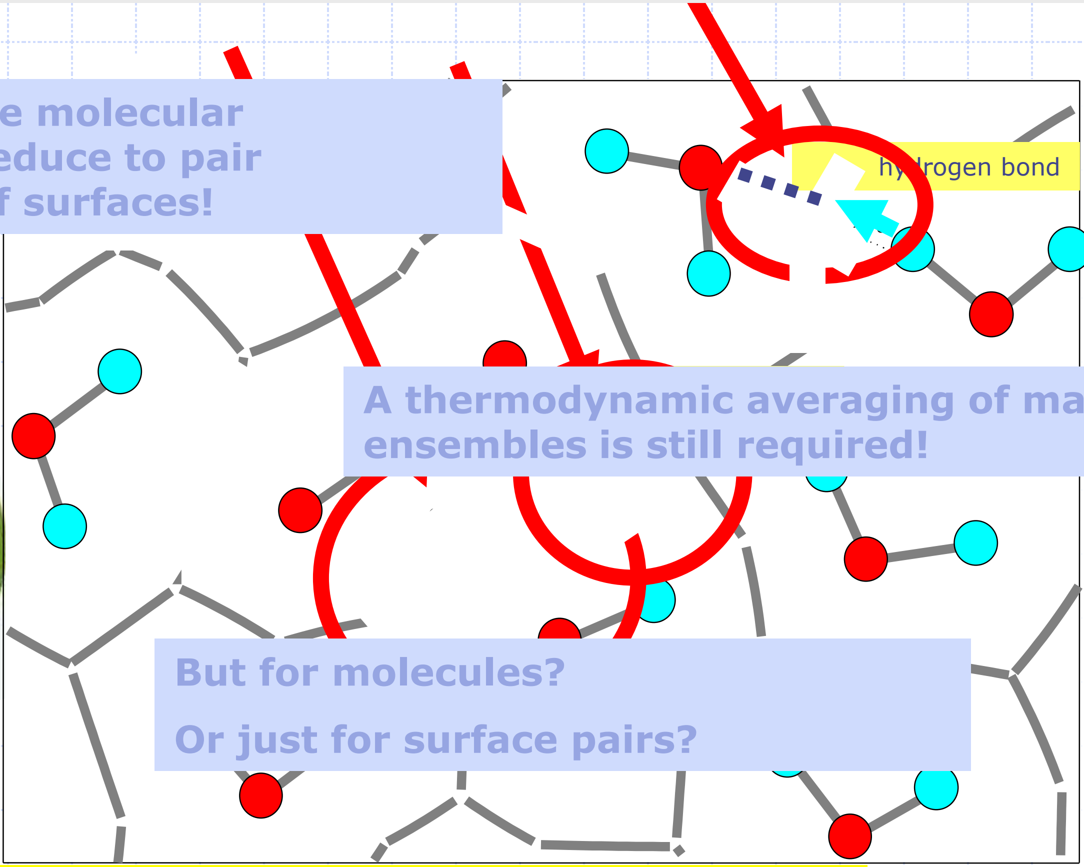
1) Put molecules into ‚virtual‘ conductor (DFT/COSMO)

2) Compress the ensemble to approximately right density

3) Remove the conductor on molecular contact areas (stepwise) and ask for the energetic costs of each step.



In this way the molecular interactions reduce to pair interactions of surfaces!



A thermodynamic averaging of many ensembles is still required!

But for molecules?

Or just for surface pairs?

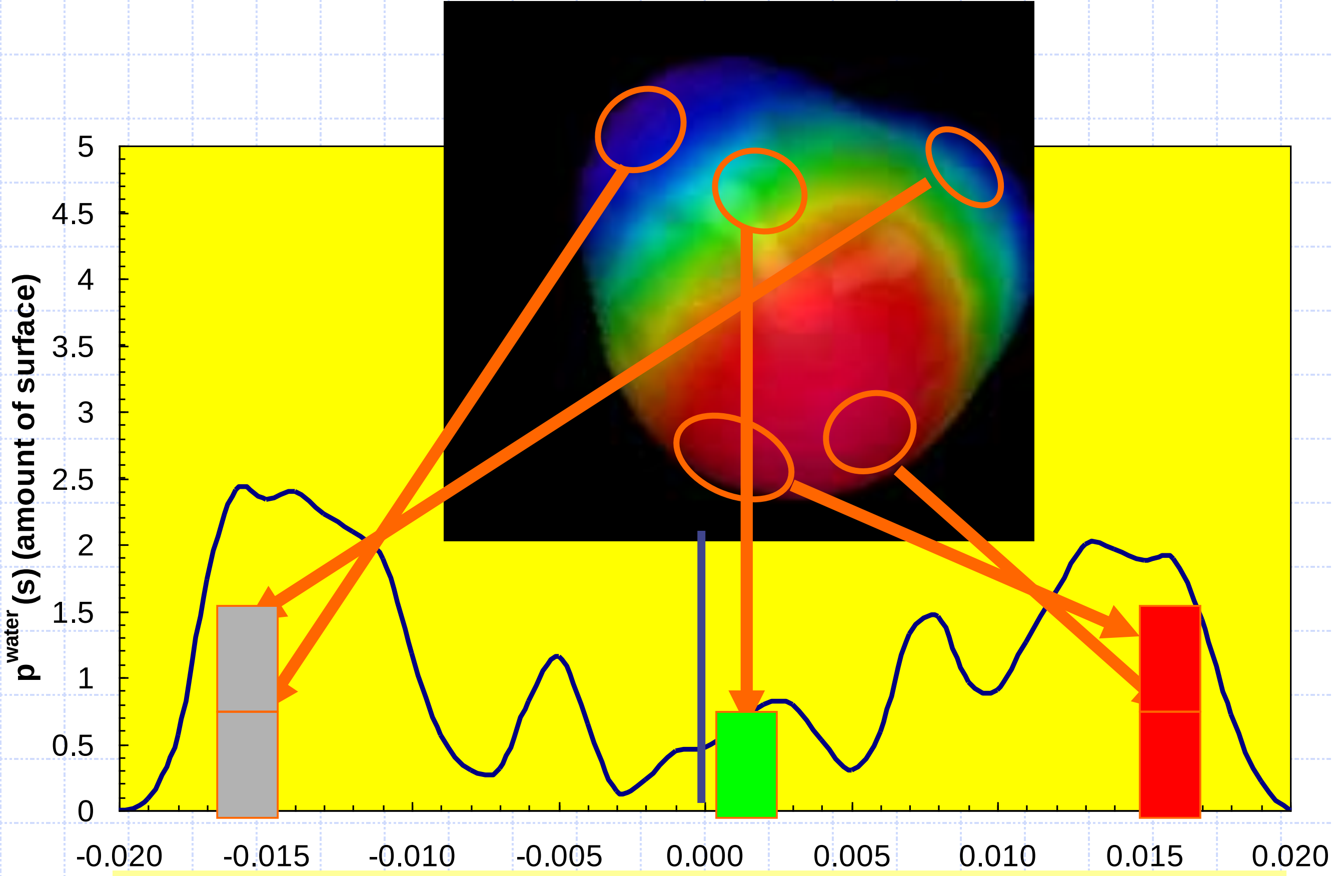
(3) specific interactions

$$G_{misfit}(\sigma,\sigma') = a_{eff}\,\frac{\alpha'}{2}(\sigma+\sigma')^2$$

$$G_{hb}(\sigma,\sigma') = a_{eff}\,c_{hb}(T)\,\min\{0,\sigma\sigma'+\sigma_{hb}{}^2\}$$

For an efficient statistical thermodynamics

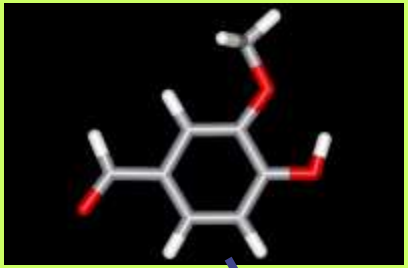
- … reduce the ensemble of molecules to an ensemble of pair-wise interacting surface segments



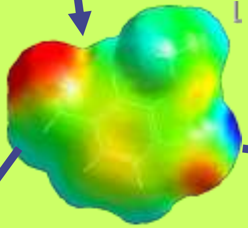
Screening charge distribution on molecular surface reduces to "σ-profile"

Flow Chart of COSMO-*RS*

Chemical Structure



Quantum Chemical Calculation with COSMO (full optimization)



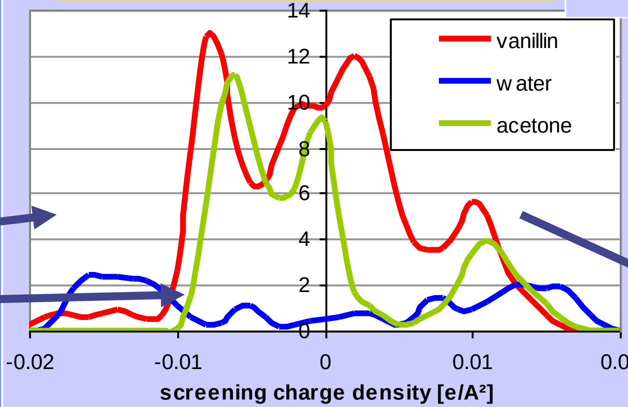
ideally screened molecule energy + screening charge distribution on surface

Database of COSMO-files (incl. all common solvents)

other compounds

DFT/COSMO

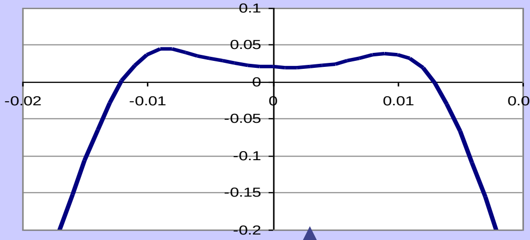
σ-profiles of compounds



σ-profile of mixture

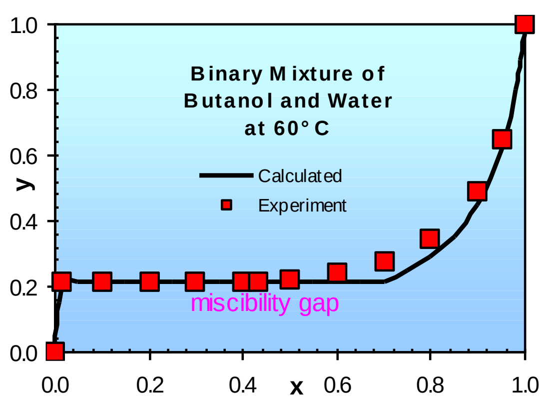
Fast Statistical Thermodynamics

σ-potential of mixture

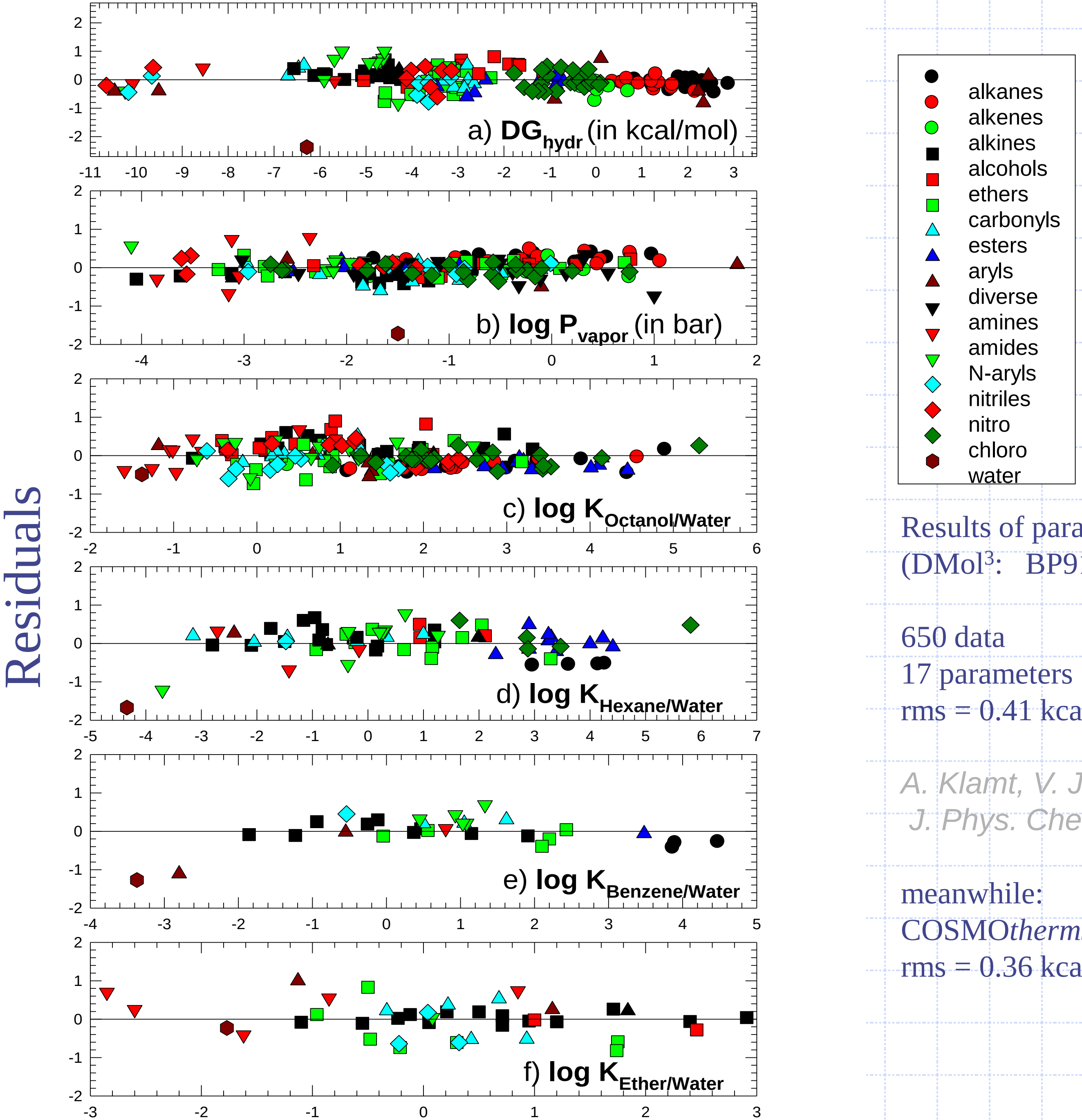


Equilibrium data: activity coefficients vapor pressure, solubility, partition coefficients

Phase Diagrams



COSMO*therm*



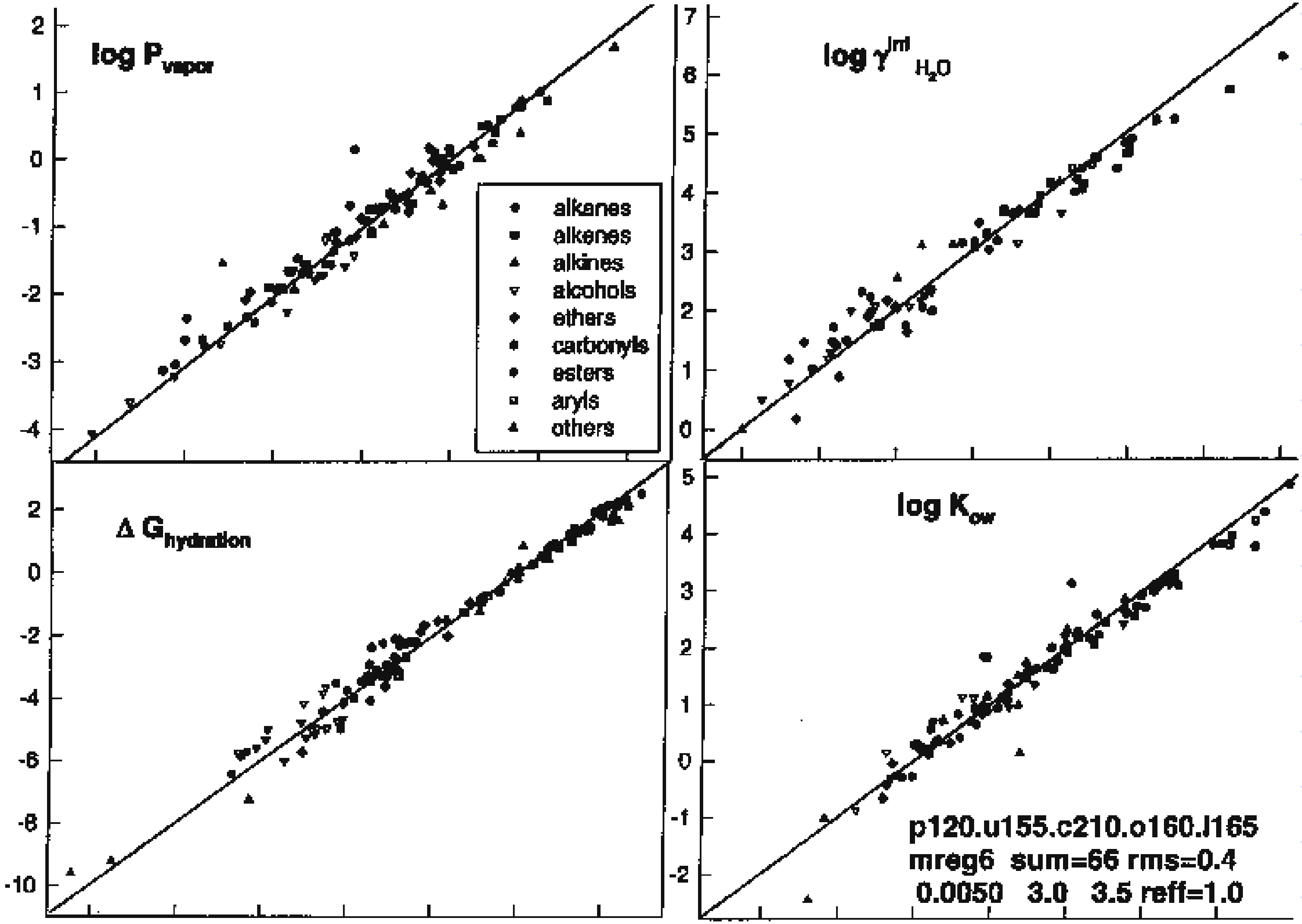
Results of parametrization based on DFT (DMol^3: BP91, DNP-basis

650 data
17 parameters
rms = 0.41 kcal/mol

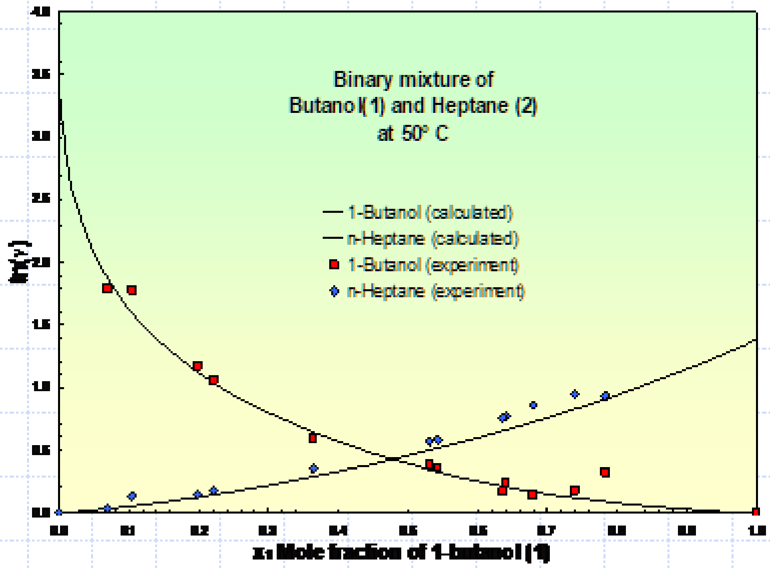
A. Klamt, V. Jonas, J. Lohrenz, T. Bürger, J. Phys. Chem. A, 102, 5074 (1998)

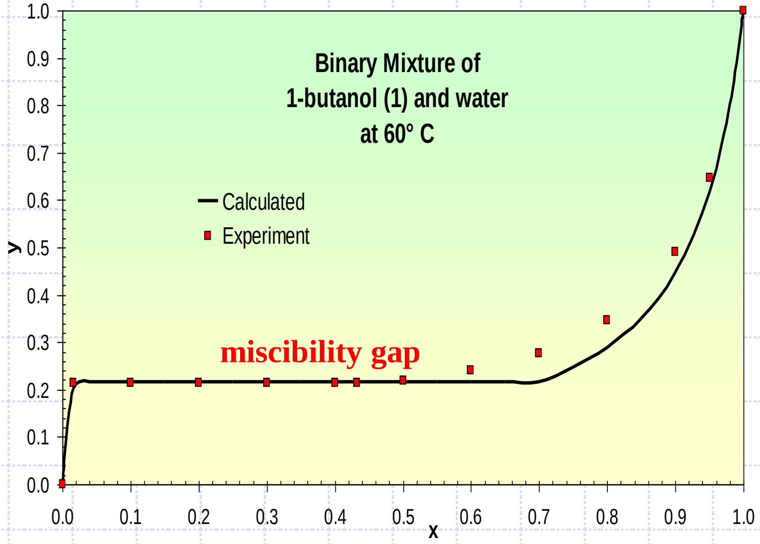
meanwhile:
COSMO*therm5.0* with Turbomole BP91/TZVP
rms = 0.36 kcal/mol

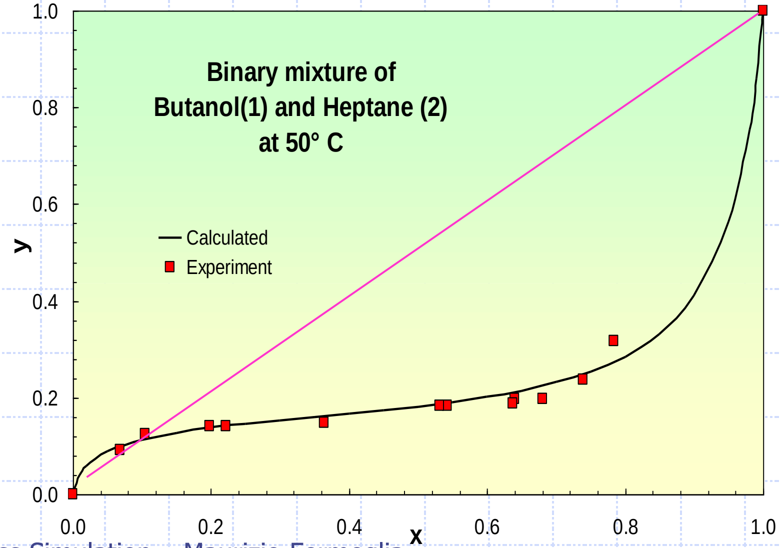
COSMO-RS Results — BAYER

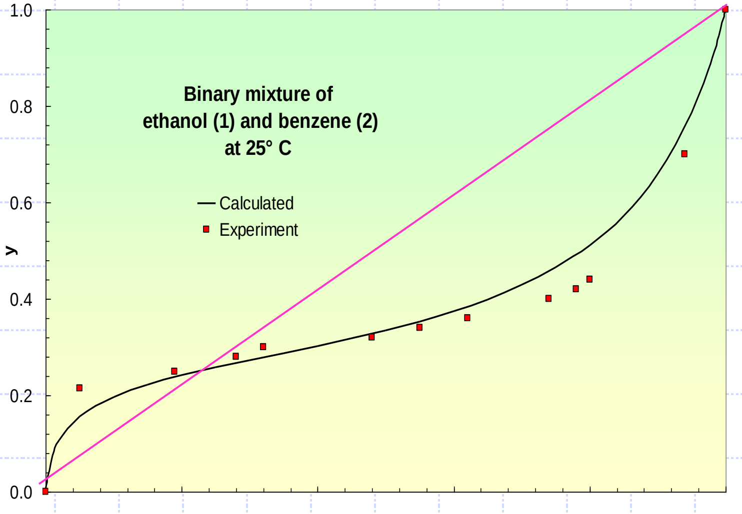


Applications to Phase Diagrams and Azeotropes

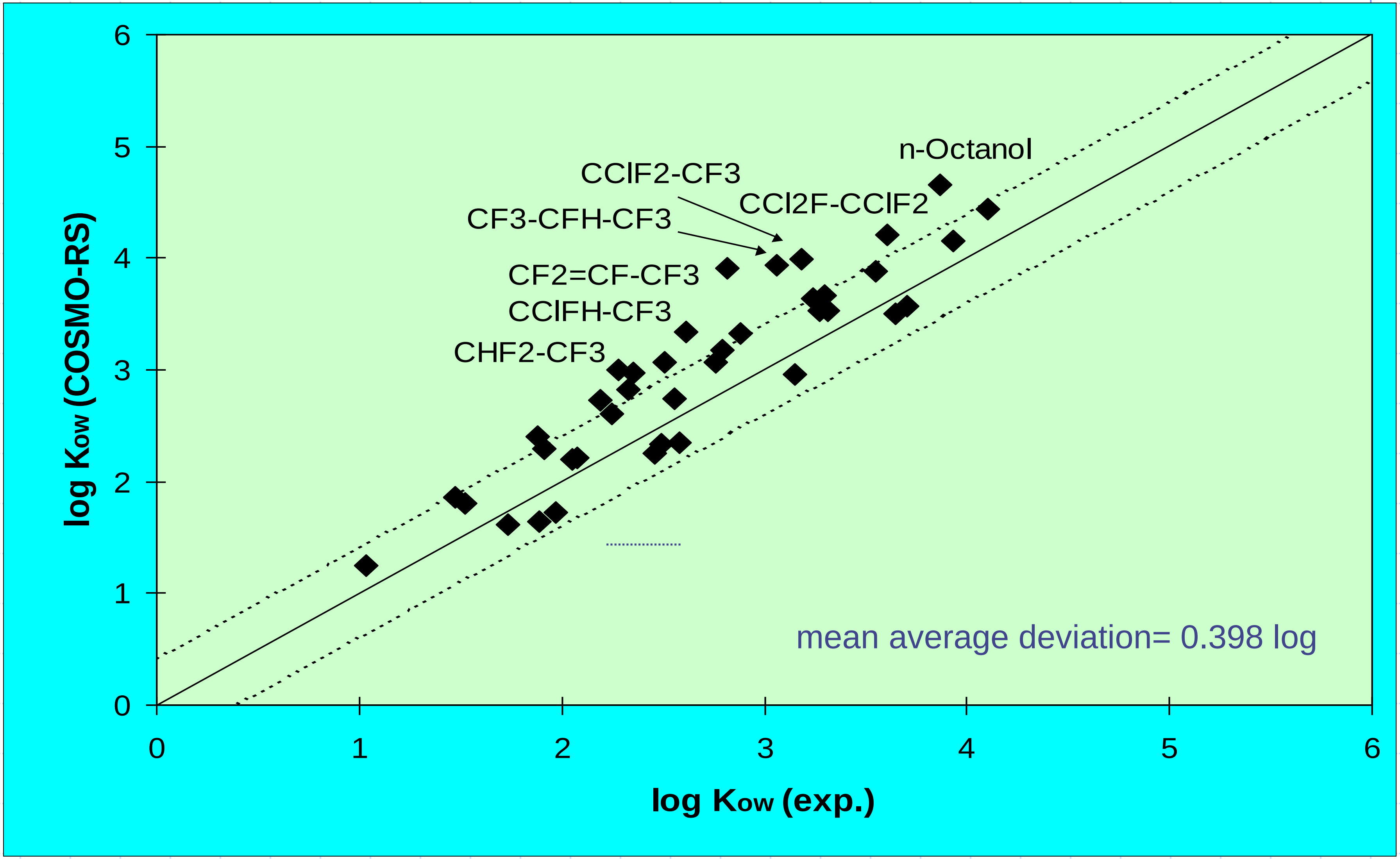




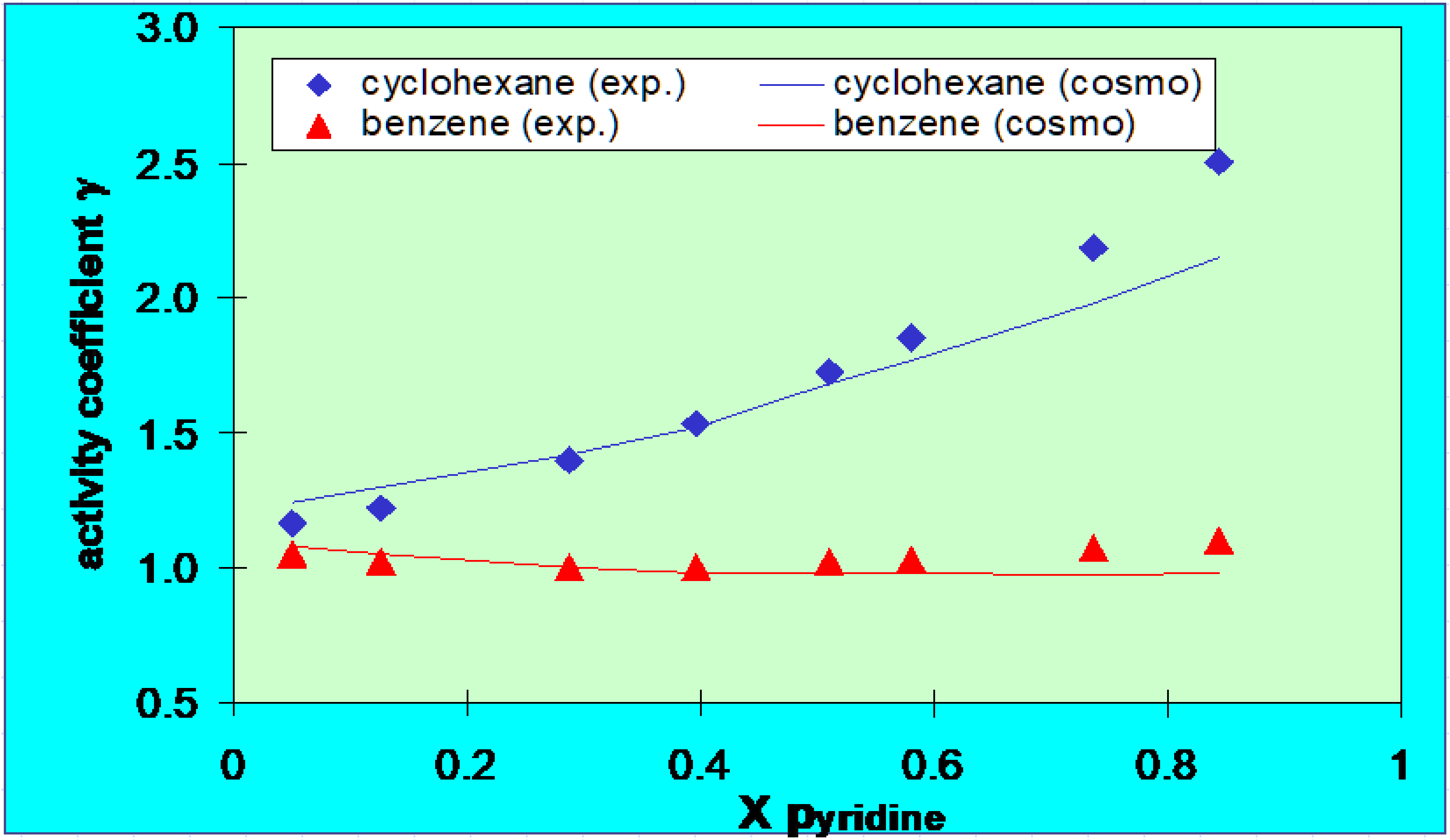




Partition coefficient n-octanol/water

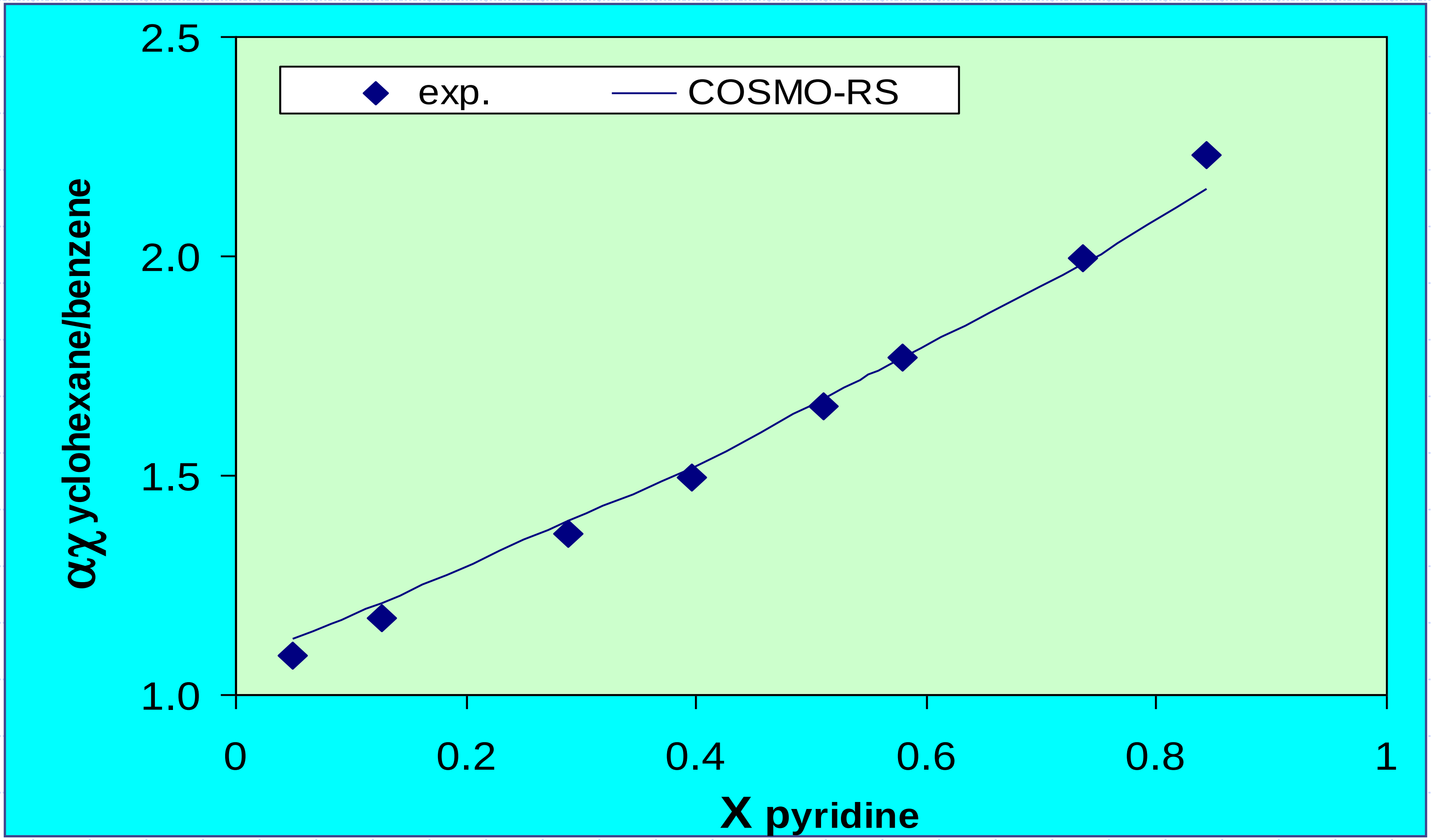


Binary system: Activity coefficient



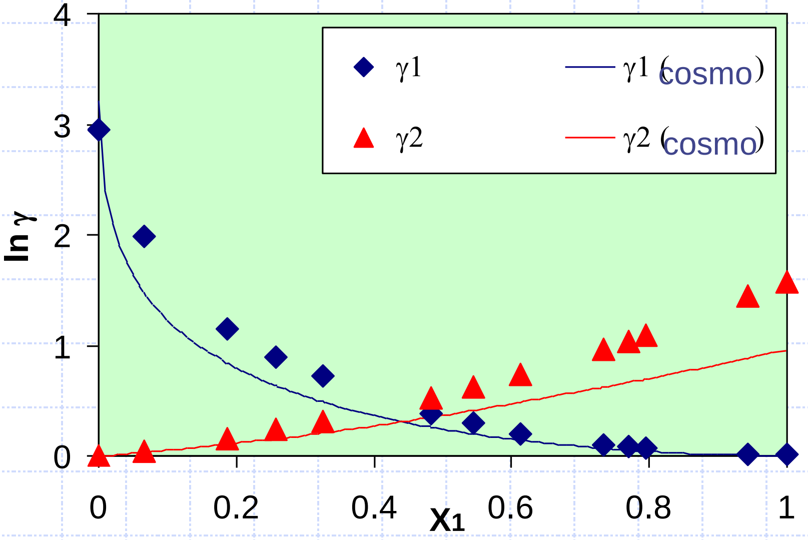
$$\gamma_i = \exp\left(\frac{\mu_{i,S} - \mu_{i,0}}{RT}\right)$$

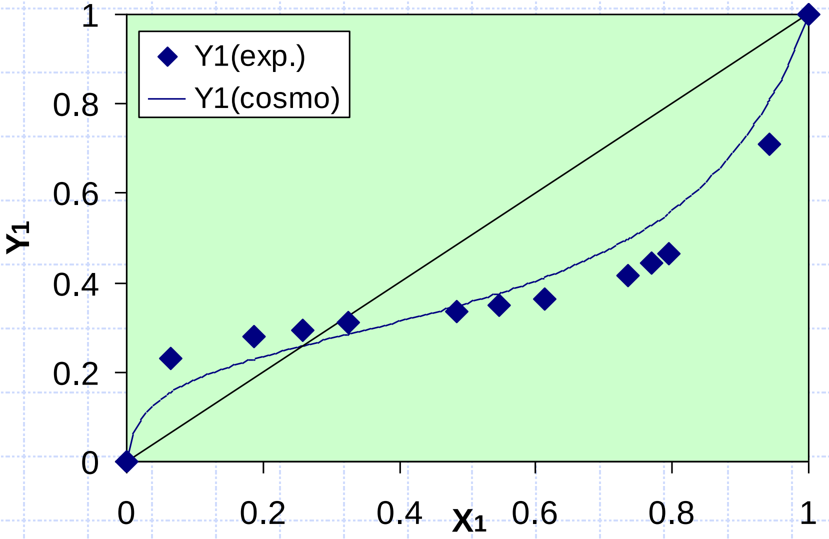
Binary system: Vapor phase concentration (molar)



$$\alpha_{cyclo/benz} = \frac{\gamma_{cyclo} \; P_{0,cyclo}}{\gamma_{benz} \; P_{0,benz}}$$

COSMO-RS - Binary System





Ethanol (1) and Benzene(2)

$$\gamma_i = \exp\left(\frac{\mu_{i,S} - \mu_{i,0}}{RT}\right)$$

$$y_{i,COSMO} = \frac{x_i \, \gamma_i \, P_{0i}^{LV}}{\sum_k x_k \, \gamma_k \, P_{0k}^{LV}}$$

Input: T, x

COSMO-RS: Clausen, I. & Arlt,W.,
“ I. Clausen‘s Ph.D. Thesis“

COSMO-RS

- COSMO-RS - a general theory of molecules in a solvent.
- Predict the chemical potentials of solute molecules in a pure or multi-component solvent.
- Uses a very small number of fitted parameters (8 inherent parameter and an additional 2 for each element).
  - Cavity radius – related to Bondi radius
  - Dispersion coefficient - related to polarizability
- Chemical potentials derived from COSMO-RS can be used to compute properties such as solubility, vapor pressures, partition coefficients, heat of hydration, etc.
- Parameterized by 642 (+230) data points for 217 (+ 100) small molecules containing H, C, N, O, and Cl (+ F, Br, I, S).
- Chemical potential differences reproduced with an RMS accuracy of 0.4 kcal/mol (which corresponds to a factor of 2 in the equilibrium constant).

Summary of COSMO-RS applicability

- Can be calculated for any solvent and solvent mixture at variable temperatures
  - solubility
  - vapor pressure
  - partition coefficients
  - surface tension
  - heat of vaporization
  - heat of mixing
  - liquid-liquid and liquid-gas phase diagrams (azeotropes, miscibility gaps, excess enthalpies and excess free energies.)
- Is able to describe polymer properties like
  - solubility of the polymer in a solvent
  - solubility of a compound in a polymer matrix
  - vapor pressures above polymers
  - partition coefficients for multi phase polymers (e.g. ABS)

Comparison of COSMO-RS with UNIFAC

- PROS
  - COSMO-RS needs very few parameters
  - COSMO-RS is able to handle rare and exotic molecules
  - COSMO-RS is able to handle transition states
  - COSMO-RS is able to resolve isomers
  - COSMO-RS does not make mean field assumptions
  - COSMO-RS does not make additivity assumptions
- CONS
  - COSMO-RS is presently slightly less accurate (in the core region of organic solvents)
  - COSMO-RS needs a time-consuming QM-calculation (but only once per molecule)
  - COSMO-RS is young and full of improvement potential

Analogy of UNIFAC and COSMO-RS

– $x^{(i)}$ = mole fraction of compound i in the mixture

– $\nu_k^{(i)}$ = number of groups of type k in compound i ↔ – $p^i(\sigma)$ = amount of surface of polarity σ in compound i

– Q_k = relative surface area of group k

– Θ_k = surface fraction of group k in the mixture $= \dfrac{\sum_i x^{(i)} \nu_k^{(i)} Q_k}{\sum_i \sum_j x^{(i)} \nu_j^{(i)} Q_j}$ ↔

$$p_S(\sigma) = \frac{\sum_i x^{(i)} p^{(i)}(\sigma)}{\sum_i x^{(i)} \int d\sigma' \, p^{(i)}(\sigma')}$$

= surface fraction with polarity σ in the mixture

– a_{kl} = interaction energy parameter for segments of types k and l (in K)

↔ – $e(\sigma, \sigma')$ = interaction energy of surfaces of polarity σ and σ'

– $\Psi_{kl} = \exp\{-a_{kl}/T\}$ = Boltzmann weight of interaction k,l

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right]$$

(see 1) ↔

$$\mu_s(\sigma) = -T \ln \left[\int d\sigma' \, p_s(\sigma') \exp\left\{ -\frac{e(\sigma,\sigma') + \mu_S(\sigma')}{T} \right\} \right]$$

$$\ln \gamma_{\mathrm{i}}(\text{residual}) = \sum_{\mathrm{k}} \nu_{\mathrm{k}}^{(\mathrm{i})} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] = \sum_{\mathrm{k}} \nu_{\mathrm{k}}^{(\mathrm{i})} \frac{Q_{\mathrm{k}}}{T} [\mu_k - \mu_k^{(i)}]$$

↔

$$\ln \gamma_{\mathrm{i}}(\text{residual}) = \int d\sigma \, p^{(i)}(\sigma) \left[\mu_S(\sigma) - \mu_{S=(i)}(\sigma) \right]$$

$$\mu_k = \frac{T}{Q_k} \ln \Gamma_k$$

1-The statistical thermodynamics of UNIFAC is approximate (mean field arguments) while the statistical thermodynamics of COSMO-RS is exact!

Phase equilibria modelling conclusions

- For low pressure systems use Excess Gibbs energy models
  - Preferably UNIQUAC and NRTL
  - Careful to the values of the parameters
- Use the Henry’s law approach for the incondensable components
- Use EOS for high pressure systems
  - The big question today is still ….. cubic or non cubic
  - Cubic Equations of state are used for ‘classical’ mixtures and for hydrocarbon and also with polar compounds
  - Cubic equations of state are nothing more than a correlation tool for ‘nasty’ systems such as polymers, dense gases,...
  - Non cubic equations of state are superior, provide volumetric properties but are complex
- Use UNIFAC for undefined components, or use the correlations for the pure component parameters of non cubic EOS
- In the intermediate region use the MHV2 Huron and Vidal method for combining EOS and activity coefficients models
- COSMO-RS is a good fully predictive model
  - Useful when group contribution UNIFAC does not work