2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 16

Room 3-442
Friday, April 5, 11:00am - 1:00pm

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Room 3-351d

Liquid-vapor equilibria in ideal mixtures

Raoult’s law
principle of distillation
boiling point elevation
freezing point depression
Henry’s law

Raoult's law

Assume an ideal mixture and/or solution behavior of component 1 in both phases a and b

$$\mu_{1a}(T,p,y_{1a}) = \mu_{11a}(T,p) + RT\ln y_{1a} = \mu_{11a}(T,p^{ab}_{\text{sat},11}(T)) + \int_{p^{ab}_{\text{sat},11}(T)}^{p} v_{11a}(T,\tilde p)\,\mathrm{d}\tilde p + RT\ln y_{1a}$$

$$\mu_{1b}(T,p,y_{1b}) = \mu_{11b}(T,p) + RT\ln y_{1b} = \mu_{11b}(T,p^{ab}_{\text{sat},11}(T)) + \int_{p^{ab}_{\text{sat},11}(T)}^{p} v_{11b}(T,\tilde p)\,\mathrm{d}\tilde p + RT\ln y_{1b}$$

Recall that $\mu_{11a}(T,p^{ab}_{\text{sat},11}(T)) = \mu_{11b}(T,p^{ab}_{\text{sat},11}(T))$ by definition of $p^{ab}_{\text{sat},11}(T)$, so at MSE, $\mu_{1a} = \mu_{1b}$:

$$RT\ln(y_{1a}/y_{1b}) = \int_{p^{ab}_{\text{sat},11}(T)}^{p} \big[v_{11b}(T,\tilde p) - v_{11a}(T,\tilde p)\big]\,\mathrm{d}\tilde p \tag{1}$$

Liquid-vapor equilibrium, $a = \text{g}$, $b = \text{f}$, with

2 non-volatile solute, 3 non-condensable gas

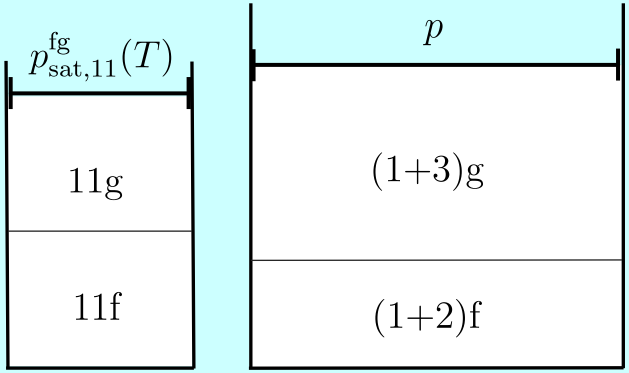
$v_{11\text{g}}(T,\tilde p) = RT/\tilde p$, $v_{11\text{f}} = \text{const}$:

$$RT\ln(y_{1\text{g}}/y_{1\text{f}}) = [p - p^{\text{fg}}_{\text{sat},11}(T)]v_{11\text{f}} - RT\ln[p/p^{\text{fg}}_{\text{sat},11}(T)]$$

and noting that $[p - p^{\text{fg}}_{\text{sat},11}(T)]v_{11\text{f}}/RT \ll 1$

$y_{1\text{g}}/y_{1\text{f}} \approx p/p^{\text{fg}}_{\text{sat},11}(T)$ or, equivalently,

$p_{11\text{g}} = y_{1\text{g}}\,p = y_{1\text{f}}\,p^{\text{fg}}_{\text{sat},11}(T)$ **Raoult's law**, 1887



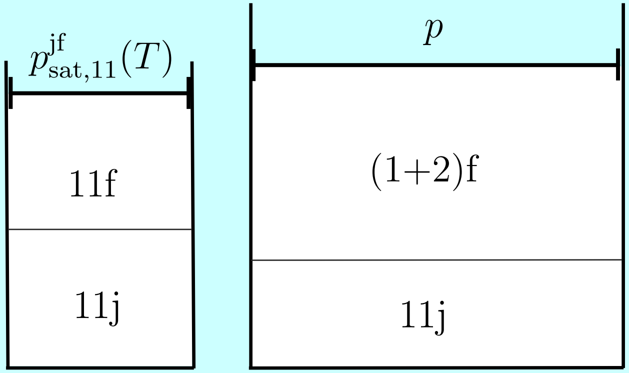
Liquid-solid equilibrium, $a = \text{f}$, $b = \text{j}$, with

2 non-freezing solute so that $y_{1\text{j}} = 1$

$v_{11\text{f}} = \text{const}$, $v_{11\text{j}} = \text{const}$, $v^{\text{jf}}_{11} = v_{11\text{f}} - v_{11\text{j}}$:

$RT\ln(y_{1\text{f}}/y_{1\text{j}}) = [p - p^{\text{jf}}_{\text{sat},11}(T)](v_{11\text{j}} - v_{11\text{f}})$ or

$$y_{1\text{f}} = \exp\big(-[p - p^{\text{jf}}_{\text{sat},11}(T)]v^{\text{jf}}_{11}/RT\big)$$



Raoult's law

Liquid-vapor equilibrium, $a = \mathrm{g}$, $b = \mathrm{f}$, with **1 and 2 both volatile and condensable**

$$p_{11\mathrm{g}} = y_{1\mathrm{g}}\, p = y_{1\mathrm{f}}\, p^{\mathrm{fg}}_{\mathrm{sat},11}(T) \qquad p_{22\mathrm{g}} = y_{2\mathrm{g}}\, p = y_{2\mathrm{f}}\, p^{\mathrm{fg}}_{\mathrm{sat},22}(T) \qquad y_{1\mathrm{g}} + y_{2\mathrm{g}} = 1 \qquad y_{1\mathrm{f}} + y_{2\mathrm{f}} = 1$$

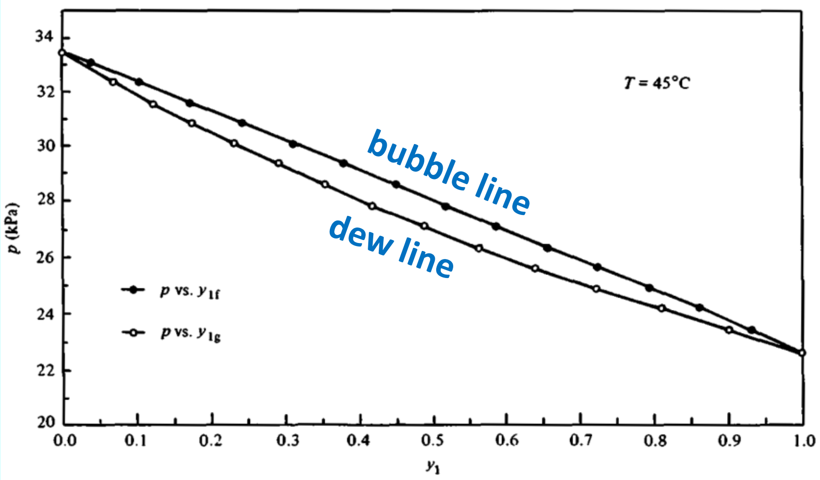
$$p = y_{1\mathrm{f}}\, p^{\mathrm{fg}}_{\mathrm{sat},11}(T) + (1 - y_{1\mathrm{f}})\, p^{\mathrm{fg}}_{\mathrm{sat},22}(T)$$ **bubble line**

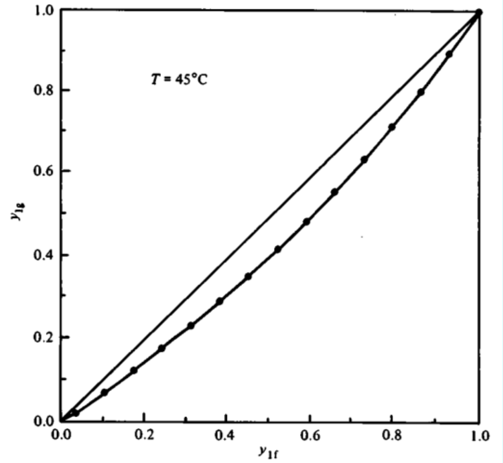
$$\frac{1}{p} = \frac{y_{1\mathrm{g}}}{p^{\mathrm{fg}}_{\mathrm{sat},11}(T)} + \frac{1 - y_{1\mathrm{g}}}{p^{\mathrm{fg}}_{\mathrm{sat},22}(T)}$$ **dew line**

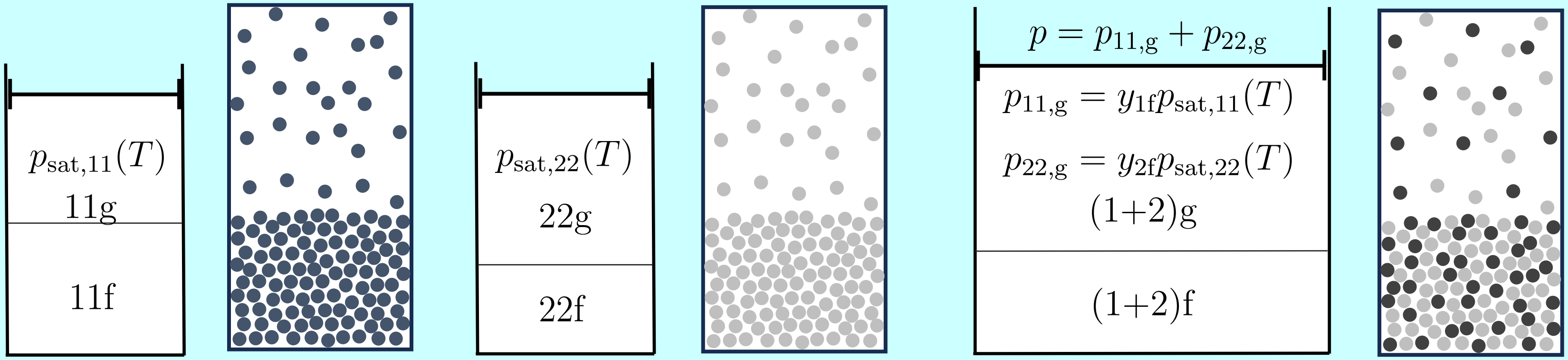
$$y_{1\mathrm{g}} = \frac{y_{1\mathrm{f}}}{(\alpha_{12} - 1)\, y_{1\mathrm{f}} - \alpha_{12}}$$

where $\alpha_{12} = p^{\mathrm{fg}}_{\mathrm{sat},22}(T)/p^{\mathrm{fg}}_{\mathrm{sat},11}(T)$

is the relative volatility





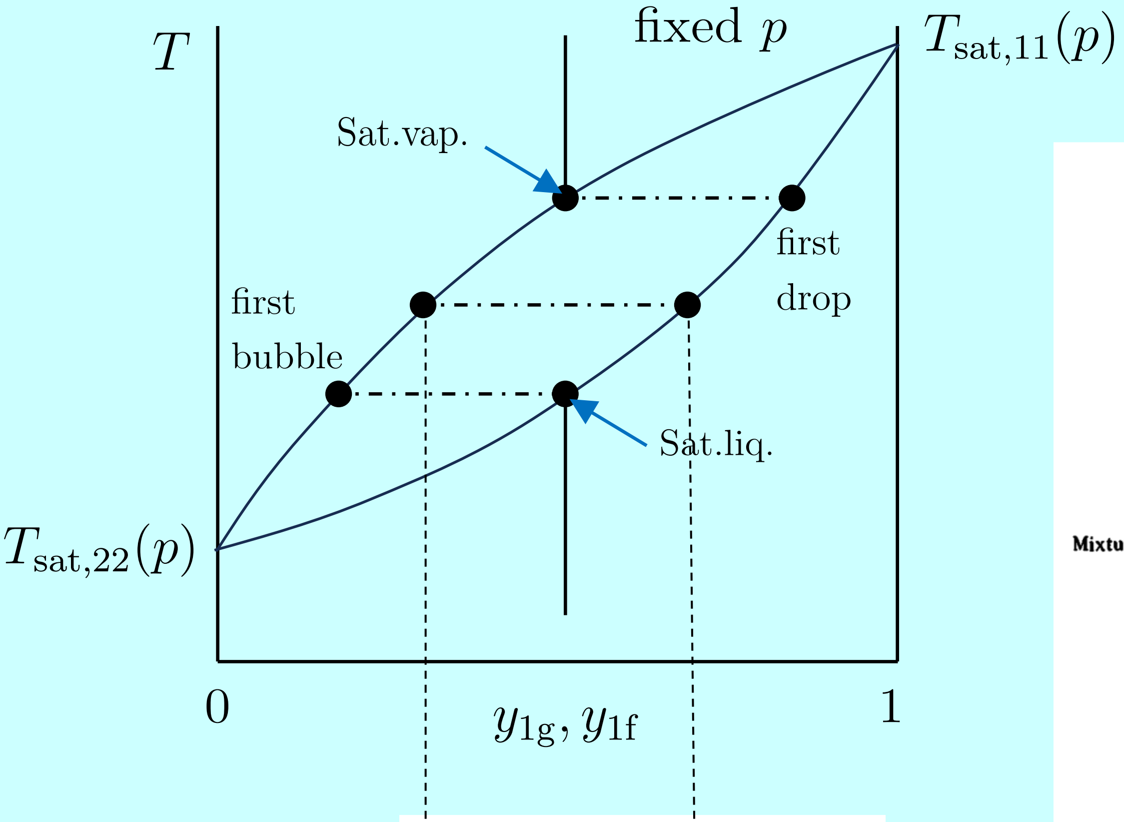


$$p = p_{11,\mathrm{g}} + p_{22,\mathrm{g}}$$

$$p_{11,\mathrm{g}} = y_{1\mathrm{f}} p_{\mathrm{sat},11}(T)$$

$$p_{22,\mathrm{g}} = y_{2\mathrm{f}} p_{\mathrm{sat},22}(T)$$

Principle of distillation



$$y_{1\text{g}} = \frac{y_{1\text{f}}}{(\alpha_{12} - 1)\, y_{1\text{f}} - \alpha_{12}}$$

where $\alpha_{12} = p^{\text{fg}}_{\text{sat},22}(T)/p^{\text{fg}}_{\text{sat},11}(T)$

is the relative volatility

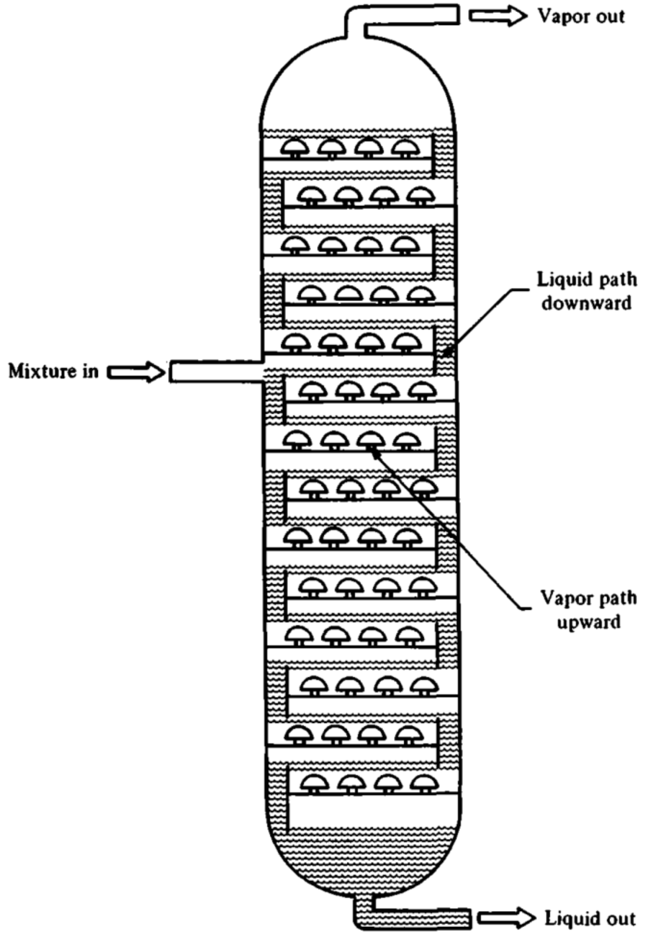
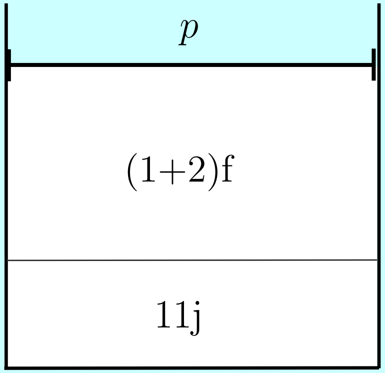


Figure 27.8 Schematic of a distillation column.

Freezing point depression and boiling point elevation



Differentiate Raoult's law

$$RT\ln y_{1\mathrm{f}} = -[p - p^{\mathrm{jf}}_{\mathrm{sat},11}(T)]\, v^{\mathrm{jf}}_{11}(T)$$

assuming $v^{\mathrm{jf}}_{11}(T) = v_{\mathrm{f}11} - v_{\mathrm{j}11} = \mathrm{const}$

$$R\ln y_{1\mathrm{f}}\,\mathrm{d}T + RT\frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}} = -v^{\mathrm{jf}}_{11}\,\mathrm{d}p + v^{\mathrm{jf}}_{11}\,\mathrm{d}p^{\mathrm{jf}}_{\mathrm{sat},11}(T)$$

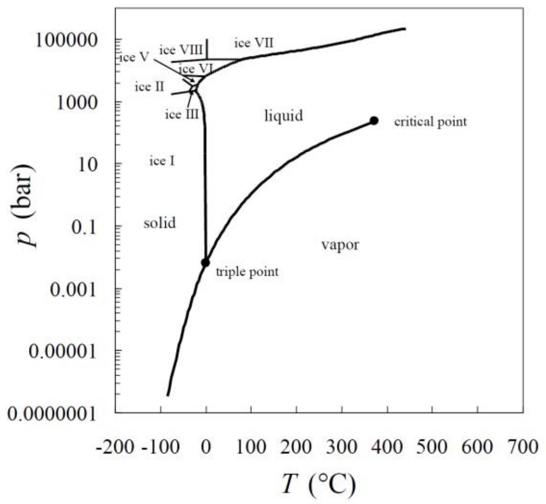
$$R\ln y_{1\mathrm{f}}\,\mathrm{d}T + RT\frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}} = -v^{\mathrm{jf}}_{11}\,\mathrm{d}p + \frac{h_{\mathrm{jf},11}(T)}{T}\mathrm{d}T$$

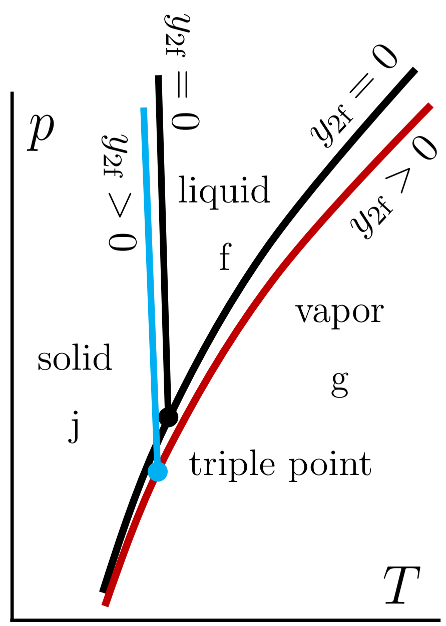
where we used Clausius-Clapeyron

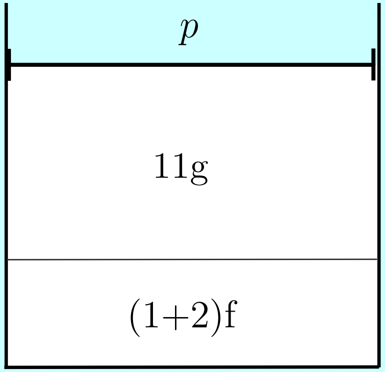
$$\frac{\mathrm{d}p^{\mathrm{jf}}_{\mathrm{sat},11}(T)}{\mathrm{d}T} = \frac{h_{\mathrm{jf},11}(T)}{T v_{\mathrm{jf},11}(T)}$$

Finally, using $\mathrm{d}y_{1\mathrm{f}} = -\mathrm{d}y_{2\mathrm{f}}$ and noting that for a dilute solution $R\ln y_{1\mathrm{f}} \ll h_{\mathrm{jf},11}/T$ we get

$$\left(\frac{\partial T}{\partial y_{2\mathrm{f}}}\right)_p = -\frac{RT^2}{y_{1\mathrm{f}}\, h_{\mathrm{jf},11}(T)}$$







Differentiate Raoult's law

$$p = y_{1\mathrm{f}}\, p^{\mathrm{fg}}_{\mathrm{sat},11}(T)$$

$$\ln p = \ln y_{1\mathrm{f}} + \ln p^{\mathrm{fg}}_{\mathrm{sat},11}(T)$$

$$\frac{\mathrm{d}p}{p} = \frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}} + \mathrm{d}\ln p^{\mathrm{fg}}_{\mathrm{sat},11}(T)$$

$$\frac{\mathrm{d}p}{p} = \frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}} + \frac{h_{\mathrm{fg},11}(T)}{RT^2}\mathrm{d}T$$

where we used Clausius-Clapeyron

$$\frac{\mathrm{d}p^{\mathrm{fg}}_{\mathrm{sat},11}(T)}{\mathrm{d}T} = \frac{h_{\mathrm{fg},11}(T)}{T v_{\mathrm{fg},11}(T)}$$

$$\frac{\mathrm{d}\ln p^{\mathrm{fg}}_{\mathrm{sat},11}(T)}{\mathrm{d}T} \approx \frac{h_{\mathrm{fg},11}(T)}{RT^2}$$

Finally, using $\mathrm{d}y_{1\mathrm{f}} = -\mathrm{d}y_{2\mathrm{f}}$ we get

$$\left(\frac{\partial T}{\partial y_{2\mathrm{f}}}\right)_p = \frac{RT^2}{y_{1\mathrm{f}}\, h_{\mathrm{fg},11}(T)}$$

Non-ideal mixtures

Duhem-Margules relations
excess mixing properties

Margules, van Laar, Redlich-Kister, Wilson, and Prausnitz models

Henry's law

Lennard-Jones binary mixture model

Experimental measurement of SES properties of mixtures:

Mixture properties from the partial properties

So, in general (i.e., for small and large systems) we proved

$$S = \sum_{i=1}^{r} n_i\, s_i - \left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \xrightarrow{n \text{ large}} \boxed{S = \sum_{i=1}^{r} n_i\, s_i}$$

$$V = \sum_{i=1}^{r} n_i\, v_i + \left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \xrightarrow{n \text{ large}} \boxed{V = \sum_{i=1}^{r} n_i\, v_i}$$

$$\sum_{i=1}^{r} n_i\, \mu_{i,j} = -\left(\frac{\partial Eu}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} \xrightarrow{n \text{ large}} \boxed{\sum_{i=1}^{r} n_i\, \mu_{i,j} = 0} \quad \textbf{Duhem-Margules relation}$$

Moreover, recalling the definitions of Eu and partial properties

$$Eu = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = F + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = G - \boldsymbol{\mu}\cdot\boldsymbol{n} = H - TS - \boldsymbol{\mu}\cdot\boldsymbol{n}$$

$$\mu_i = e_i - Ts_i + pv_i = f_i + pv_i = g_i = h_i - Ts_i$$

we also find the following relations, which justify calling partial properties that way:

$$E = \sum_{i=1}^{r} n_i\, e_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \xrightarrow{n \text{ large}} \boxed{E = \sum_{i=1}^{r} n_i\, e_i}$$

$$F = \sum_{i=1}^{r} n_i\, f_i + Eu - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \xrightarrow{n \text{ large}} \boxed{F = \sum_{i=1}^{r} n_i\, f_i}$$

$$G = \sum_{i=1}^{r} n_i\, g_i + Eu = \sum_{i=1}^{r} n_i\, \mu_i + Eu \xrightarrow{n \text{ large}} \boxed{G = \sum_{i=1}^{r} n_i\, g_i = \sum_{i=1}^{r} n_i\, \mu_i}$$

$$H = \sum_{i=1}^{r} n_i\, h_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \xrightarrow{n \text{ large}} \boxed{H = \sum_{i=1}^{r} n_i\, h_i}$$

Modeling non-ideal SES behavior of mixtures:

Duhem-Margules relation, excess mixing properties

Recall, we defined $\mu_{i,j}(T,p,n\boldsymbol{y}) = \left(\dfrac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} = \left(\dfrac{\partial^2 G}{\partial n_j \partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \left(\dfrac{\partial \mu_j}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \mu_{j,i}(T,p,n\boldsymbol{y})$

and proved that $Eu = 0$ (i.e., the Euler relation) implies the Duhem-Margules relations (which are valid, therefore, within the simple-system model, i.e., for large n)

$$\sum_{i=1}^{r} n_i\, \mu_{i,j} = 0 \quad \forall j \qquad \Rightarrow \qquad \frac{\partial(\mu_1,\dots,\mu_r)}{\partial(n_1,\dots,n_r)} = \det \mathrm{Hess}(G)\big|_{T,p} = 0$$

Indeed, the Duhem-Margules relations can be viewed as a homogeneous system of linear equations in the n_i's, which has nontrivial solutions only if the determinant of the matrix of coefficients is zero.

Define $\mu_i^{\mathrm{id}} = \mu_{ii}(T,p) + RT\ln y_i$ and $\mu_i^{\mathrm{ex}} = \Delta h_i^{\mathrm{mix}} - T\Delta s_i^{\mathrm{ex}}$ so that $\mu_i(T,p,\boldsymbol{y}) = \mu_i^{\mathrm{id}}(T,p,y_i) + \mu_i^{\mathrm{ex}}(T,p,\boldsymbol{y})$

where $\Delta s_i^{\mathrm{ex}} = \Delta s_i^{\mathrm{mix}} - \Delta s_i^{\mathrm{id}}$ is the **excess mixing entropy** of component i and $\Delta s_i^{\mathrm{id}} = -R\ln y_i$.

Since $\dfrac{\partial \ln y_i}{\partial n_j} = \dfrac{\delta_{ij}}{n_i} - \dfrac{1}{n}$ so that $\displaystyle\sum_{i=1}^{r} n_i \frac{\partial \ln y_i}{\partial n_j} = \sum_{i=1}^{r} \delta_{ij} - \sum_{i=1}^{r} \frac{n_i}{n} = 1 - 1 = 0$ we have $\displaystyle\sum_{i=1}^{r} n_i\, \mu_{i,j}^{\mathrm{id}} = 0.$

So, modeling non-ideal behavior requires that $\displaystyle\sum_{i=1}^{r} n_i\, \mu_{i,j}^{\mathrm{ex}}(T,p,\boldsymbol{y}) = \sum_{i=1}^{r} n_i \frac{\partial\left(\Delta h_i^{\mathrm{mix}} - T\Delta s_i^{\mathrm{ex}}\right)}{\partial n_j} = 0 \quad \forall j$

Defining $\displaystyle G^{\mathrm{id}} = \sum_{i=1}^{r} n_i \mu_i^{\mathrm{id}} = \sum_{i=1}^{r} n_i\left(\mu_{ii}(T,p) + RT\ln y_i\right)$ and $\displaystyle G^{\mathrm{ex}} = \sum_{i=1}^{r} n_i \mu_i^{\mathrm{ex}} = \sum_{i=1}^{r} n_i\left(\Delta h_i^{\mathrm{mix}} - T\Delta s_i^{\mathrm{ex}}\right)$

we can write $\mu_i^{\mathrm{id}} = \left(\dfrac{\partial G^{\mathrm{id}}}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} \qquad \mu_i^{\mathrm{ex}} = \left(\dfrac{\partial G^{\mathrm{ex}}}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} \qquad \dfrac{\partial(\mu_1^{\mathrm{ex}},\dots,\mu_r^{\mathrm{ex}})}{\partial(n_1,\dots,n_r)} = \det \mathrm{Hess}(G^{\mathrm{ex}})\big|_{T,p} = 0$

Modeling non-ideal SES behavior of mixtures:

simple and complex model relations for binary mixtures

$g^{\rm id} = y_1\, g_{11}(T,p) + y_2\, g_{22}(T,p) + RT\,(y_1 \ln y_1 + y_2 \ln y_2)$ **ideal mixture**

$\mu_1^{\rm id} = g_{11}(T,p) + RT \ln y_1 \qquad \mu_2^{\rm id} = g_{22}(T,p) + RT \ln y_2 \qquad$ recall $\mu_{ii}(T,p) = g_{ii}(T,p)$

$g^{\rm ex}_{\rm M1} = A(T,p)\, y_1 y_2$ **Margules, one parameter** (1895)

$\mu^{\rm ex}_{1,\rm M1} = A\, y_2^2 \qquad \mu^{\rm ex}_{2,\rm M1} = A\, y_1^2$

$g^{\rm ex}_{\rm M2} = [A(T,p)\, y_2 + B(T,p)\, y_1]\, y_1 y_2$ **Margules, two parameters** (1895)

$\mu^{\rm ex}_{1,\rm M2} = y_2^2\,[(2B-A) + 2(A-B)y_2] \qquad \mu^{\rm ex}_{2,\rm M2} = y_1^2\,[(2A-B) + 2(B-A)y_1]$

$g^{\rm ex}_{\rm vL} = \left(y_1/B(T,p) + y_2/A(T,p)\right)^{-1} y_1 y_2$ **van Laar** (1913)

$\mu^{\rm ex}_{1,\rm vL} = A\left(1 + Ay_1/By_2\right)^{-2} \qquad \mu^{\rm ex}_{2,\rm vL} = B\left(1 + By_2/Ay_1\right)^{-2}$

$g^{\rm ex}_{\rm RK} = y_1 y_2 \sum_{k=0}^{K} A_k(T,p)(y_1 - y_2)^k$ (Guggenheim (1937), **Redlich-Kister** (1948), Scatchard (1949)

$g^{\rm ex}_{\rm W} = -C(T,p)\left\{y_1 \ln\left[y_1 + y_2\,\frac{v_{22}}{v_{11}}\exp\left(\frac{\epsilon_{11}-\epsilon_{12}}{RT}\right)\right] + y_2 \ln\left[y_2 + y_1\,\frac{v_{11}}{v_{22}}\exp\left(\frac{\epsilon_{22}-\epsilon_{12}}{RT}\right)\right]\right\}$ **Wilson** (1964)

$g^{\rm ex}_{\bf NRTL} =$ Non-Random Two-Liquid model, Renon-**Prausnitz** (1968)

$g^{\rm ex}_{\bf UNIQUAC} =$ UNIversal QUAsi-Chemical model, Abrams-**Prausnitz** (1975)

$g^{\rm ex}_{\bf UNIFAC} =$ UNIquac Functional-group Activity Coefficient model, Fredenslund-Jones-**Prausnitz** (1975)

Recall $\Delta h_i^{\rm mix} = \left(\dfrac{\partial(\mu_i^{\rm ex}/T)}{\partial(1/T)}\right)_{p,\boldsymbol{y}} = \mu_i^{\rm ex}\left[1 + \left(\dfrac{\partial \ln \mu_i^{\rm ex}}{\partial \ln T}\right)_{p,\boldsymbol{y}}\right] \qquad \Delta s_i^{\rm mix,ex} = \left(\dfrac{\partial(\mu_i^{\rm ex})}{\partial T}\right)_{p,\boldsymbol{y}}$

For example, assuming A and B constant in M1, M2, and vL yields $\Delta h_i^{\rm mix} = \mu_i^{\rm ex}$ and $\Delta s_i^{\rm mix,ex} = 0$ so that

For M1: $A = \Delta h^{\rm mix}_{1,\rm M1}\big|_{y_2=1} = \Delta h^{\rm mix}_{2,\rm M1}\big|_{y_1=1}$

For M2 and vL: $A = \Delta h^{\rm mix}_{1,\rm M2,vL}\big|_{y_2=1} \qquad B = \Delta h^{\rm mix}_{2,\rm M2,vL}\big|_{y_1=1}$

Modeling non-ideal SES behavior of mixtures:

simple and complex model relations for binary mixtures

$$g^{\rm id} = y_1\, g_{11}(T,p) + y_2\, g_{22}(T,p) + RT\,(y_1 \ln y_1 + y_2 \ln y_2)$$

$$\mu_1^{\rm id} = g_{11}(T,p) + RT\ln y_1 \qquad \mu_2^{\rm id} = g_{22}(T,p) + RT\ln y_2$$

$$g^{\rm ex}_{\rm M1} = A(T,p)\, y_1 y_2$$ **Margules, on**

$$\mu^{\rm ex}_{1,\rm M1} = A\, y_2^2 \qquad \mu^{\rm ex}_{2,\rm M1} = A\, y_1^2$$

$$g^{\rm ex}_{\rm M2} = [A(T,p)\, y_2 + B(T,p)\, y_1]\, y_1 y_2$$ **Margules, tw**

$$\mu^{\rm ex}_{1,\rm M2} = y_2^2\,[(2B - A) + 2(A - B) y_2] \qquad \mu^{\rm ex}_{2,\rm M2} = y_1^2\,[(2A -$$

$$g^{\rm ex}_{\rm vL} = \left(y_1/B(T,p) + y_2/A(T,p)\right)^{-1} y_1 y_2$$ **van Laar**

$$\mu^{\rm ex}_{1,\rm vL} = A\left(1 + A y_1/B y_2\right)^{-2} \qquad \mu^{\rm ex}_{2,\rm vL} = B\left(1 + B y_2/A y_1\right)$$

$$g^{\rm ex}_{\rm RK} = y_1 y_2 \sum_{k=0}^{K} A_k(T,p)(y_1 - y_2)^k$$ (Guggenheim (19

$$g^{\rm ex}_{\rm W} = -C(T,p)\left\{y_1 \ln\left[y_1 + y_2 \frac{v_{22}}{v_{11}} \exp\left(\frac{\epsilon_{11} - \epsilon_{12}}{RT}\right)\right] + y_2 \ln\right.$$

$g^{\rm ex}_{\bf NRTL} =$ Non-Random Two-Liquid model, Renon-**P**

$g^{\rm ex}_{\bf UNIQUAC} =$ UNIversal QUAsi-Chemical model, Abram

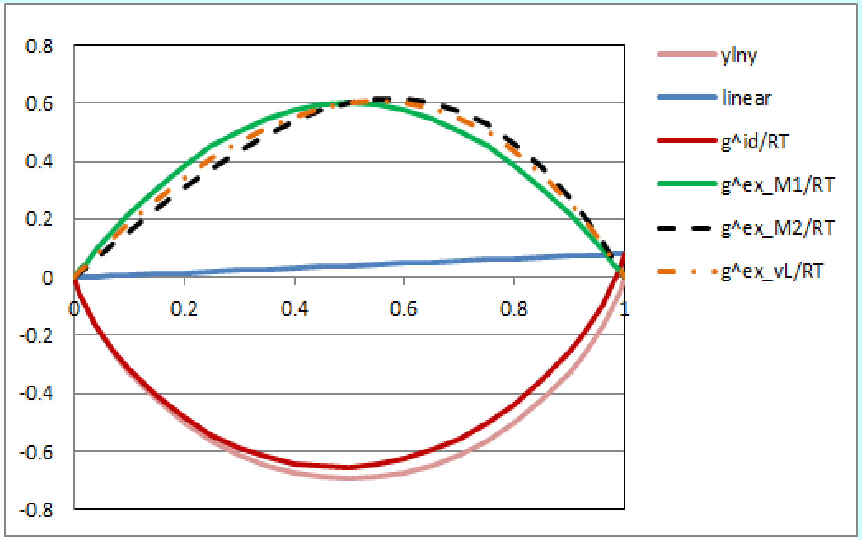
$g^{\rm ex}_{\bf UNIFAC} =$ UNIquac Functional-group Activity Coeffi

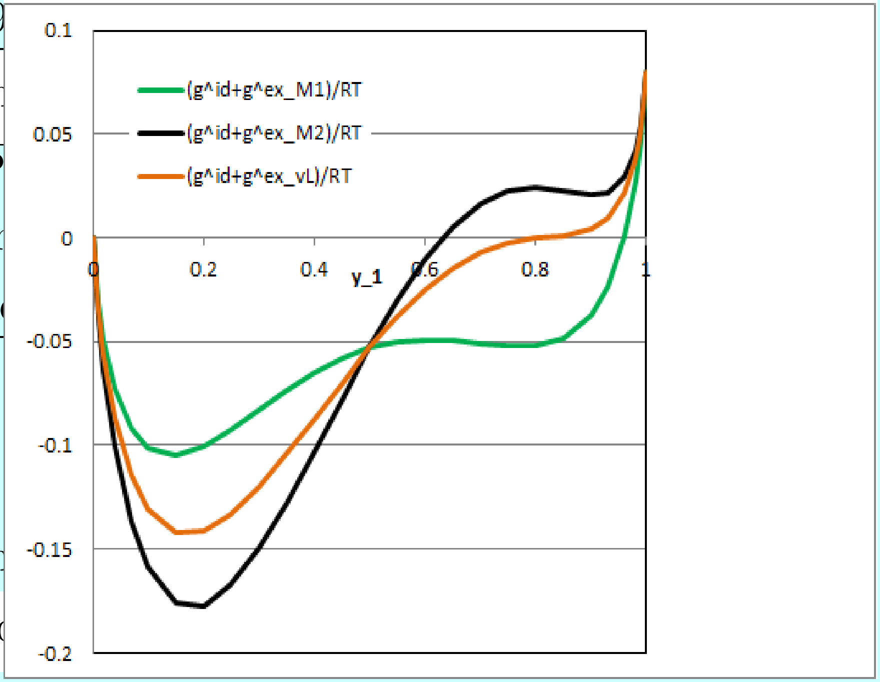
Recall $\Delta h_i^{\rm mix} = \left(\dfrac{\partial(\mu_i^{\rm ex}/T)}{\partial(1/T)}\right)_{p,\boldsymbol{y}} = \mu_i^{\rm ex}\left[1 + \left(\dfrac{\partial \ln \mu_i^{\rm ex}}{\partial \ln T}\right)_{p,\boldsymbol{y}}\right]$

For example, assuming A and B constant in M1, M2, an

For M1: $A = \Delta h^{\rm mix}_{1,\rm M1}\Big|_{y_2=1} = \Delta h^{\rm mix}_{2,\rm M1}\Big|_{y_1=1}$

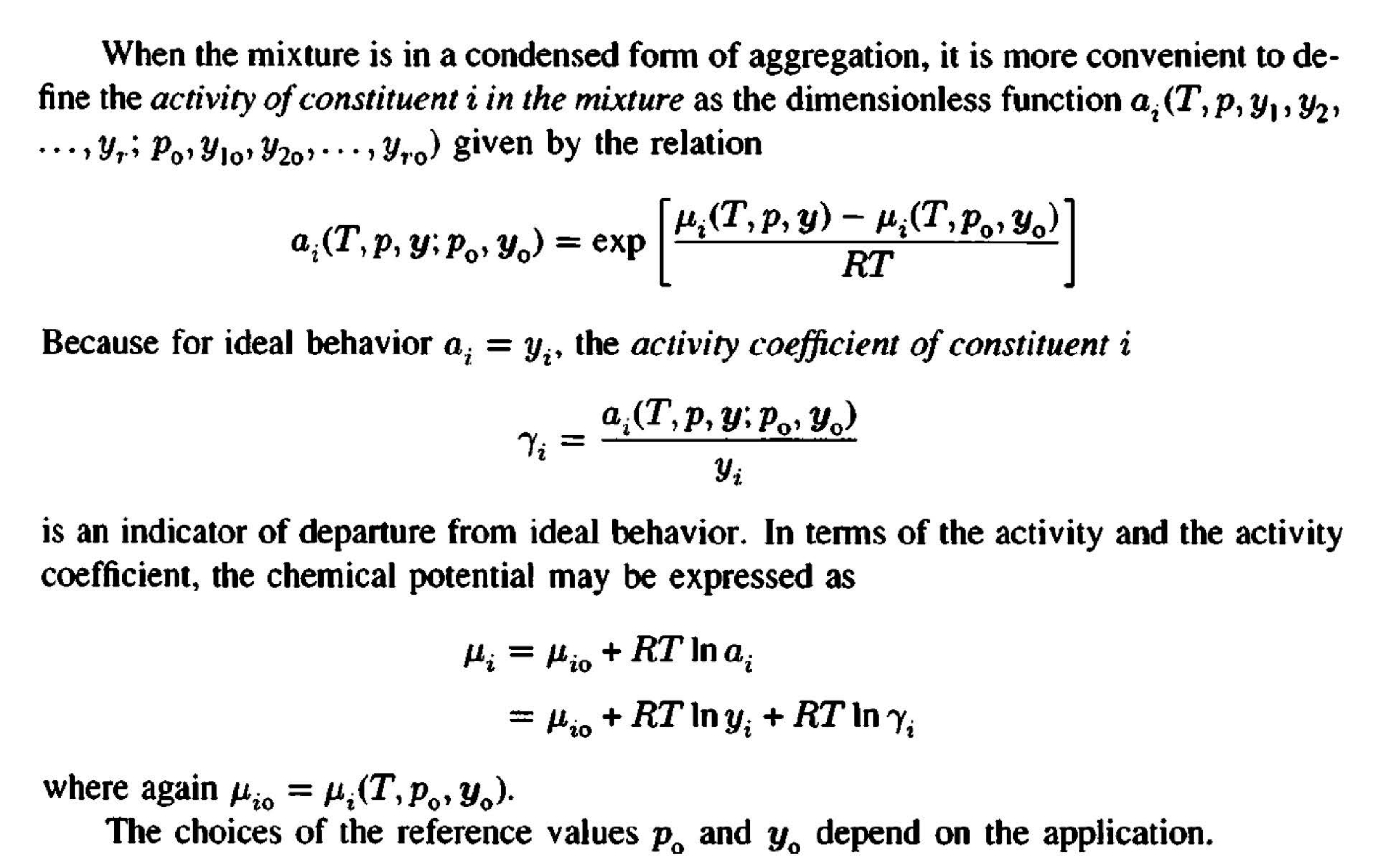
For M2 and





Alternative traditional ways to represent chemical potentials:

Activities and activity coefficients



When the mixture is in a condensed form of aggregation, it is more convenient to define the *activity of constituent i in the mixture* as the dimensionless function $a_i(T, p, y_1, y_2, \ldots, y_r; p_o, y_{1o}, y_{2o}, \ldots, y_{ro})$ given by the relation

$$a_i(T, p, y; p_o, y_o) = \exp\left[\frac{\mu_i(T, p, y) - \mu_i(T, p_o, y_o)}{RT}\right]$$

Because for ideal behavior $a_i = y_i$, the *activity coefficient of constituent i*

$$\gamma_i = \frac{a_i(T, p, y; p_o, y_o)}{y_i}$$

is an indicator of departure from ideal behavior. In terms of the activity and the activity coefficient, the chemical potential may be expressed as

$$\begin{aligned}\mu_i &= \mu_{io} + RT \ln a_i \\ &= \mu_{io} + RT \ln y_i + RT \ln \gamma_i\end{aligned}$$

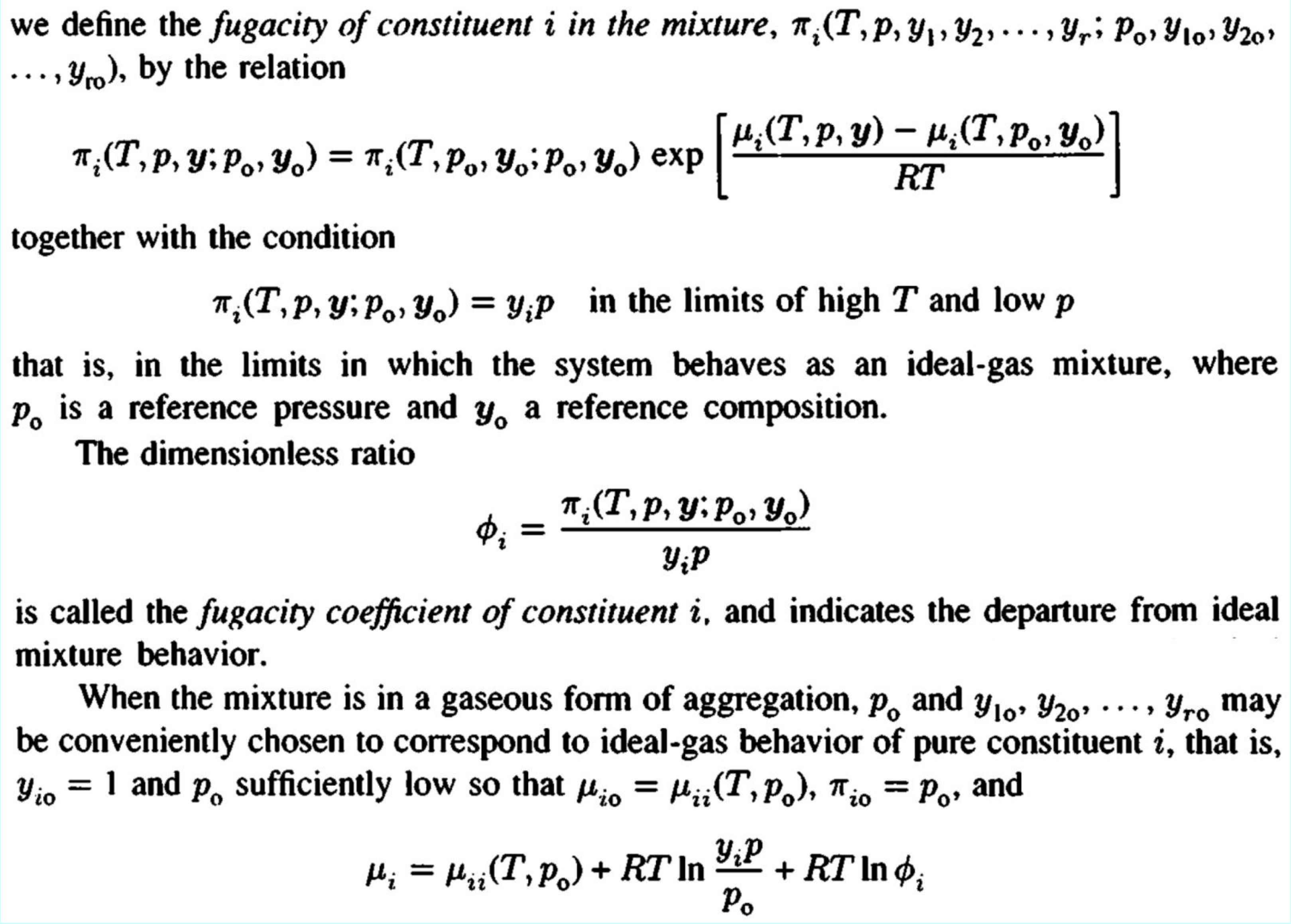
where again $\mu_{io} = \mu_i(T, p_o, y_o)$.

The choices of the reference values p_o and y_o depend on the application.

Equations and figures adapted from pp.515-516 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Alternative traditional ways to represent chemical potentials:

Fugacities and fugacity coefficients



we define the *fugacity of constituent i in the mixture*, $\pi_i(T, p, y_1, y_2, \ldots, y_r; p_o, y_{1o}, y_{2o}, \ldots, y_{ro})$, by the relation

$$\pi_i(T, p, y; p_o, y_o) = \pi_i(T, p_o, y_o; p_o, y_o) \exp\left[\frac{\mu_i(T, p, y) - \mu_i(T, p_o, y_o)}{RT}\right]$$

together with the condition

$$\pi_i(T, p, y; p_o, y_o) = y_i p \quad \text{in the limits of high } T \text{ and low } p$$

that is, in the limits in which the system behaves as an ideal-gas mixture, where p_o is a reference pressure and y_o a reference composition.

The dimensionless ratio

$$\phi_i = \frac{\pi_i(T, p, y; p_o, y_o)}{y_i p}$$

is called the *fugacity coefficient of constituent i*, and indicates the departure from ideal mixture behavior.

When the mixture is in a gaseous form of aggregation, p_o and $y_{1o}, y_{2o}, \ldots, y_{ro}$ may be conveniently chosen to correspond to ideal-gas behavior of pure constituent i, that is, $y_{io} = 1$ and p_o sufficiently low so that $\mu_{io} = \mu_{ii}(T, p_o)$, $\pi_{io} = p_o$, and

$$\mu_i = \mu_{ii}(T, p_o) + RT \ln \frac{y_i p}{p_o} + RT \ln \phi_i$$

Equations and figures adapted from pp.515-516 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Alternative traditional ways to represent chemical potentials:

activities for the Margules and van Laar models

Margules, 1 parameter

$$\ln a_1' = \ln y_1 + \frac{A}{RT}(1-y_1)^2$$

$$\ln a_2' = \ln(1-y_1) + \frac{A}{RT}(y_1)^2$$

van Laar

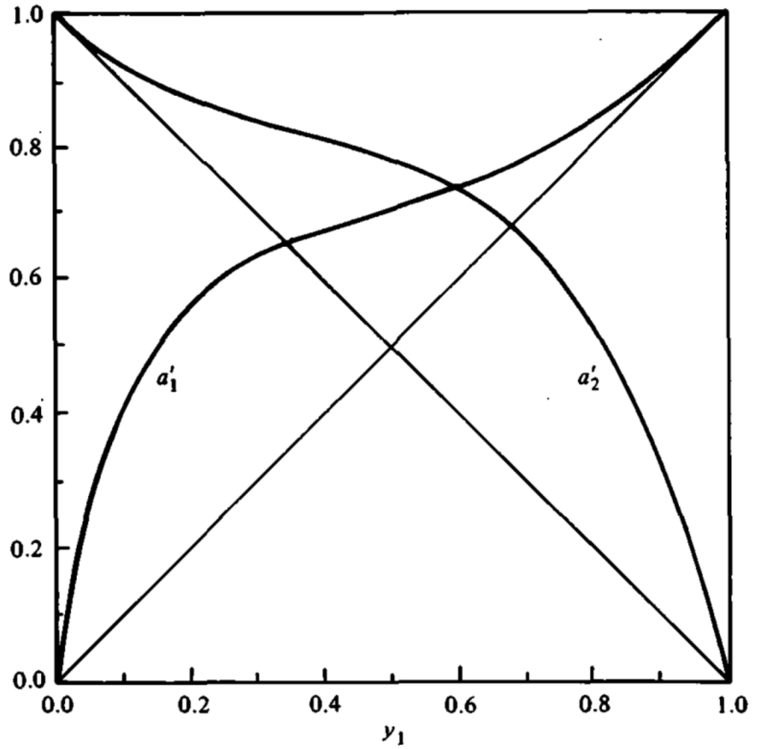
$$\ln a_1' = \ln y_1 + \frac{A/RT}{\left[1 + Ay_1/B(1-y_1)\right]^2}$$

$$\ln a_2' = \ln(1-y_1) + \frac{B/RT}{\left[1 + B(1-y_1)/Ay_1\right]^2}$$

Margules, 2 parameters

$$\ln a_1' = \ln y_1 + \frac{2B-A}{RT}(1-y_1)^2 + \frac{2(A-B)}{RT}(1-y_1)^3$$

$$\ln a_2' = \ln(1-y_1) + \frac{2A-B}{RT}(y_1)^2 + \frac{2(B-A)}{RT}(y_1)^3$$



Equations and figures adapted from pp.522-524 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Simple model of non-ideal liquid-vapor equilibrium:

liquid-vapor equilibrium modeled with the van Laar models

The conditions of mutual stable equilibrium of the two coexisting phases

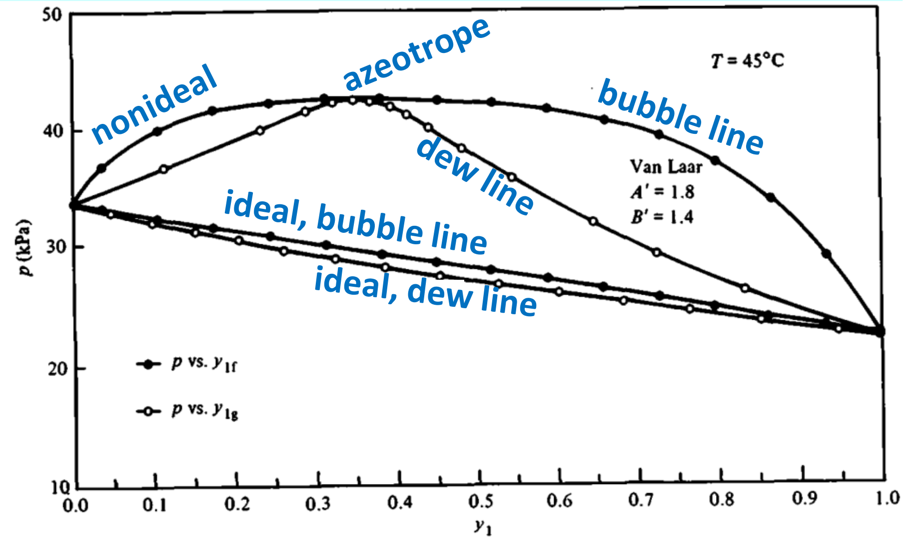
$$y_{1g}p = a_{1f}\,p_{\mathrm{sat},11}(T)$$

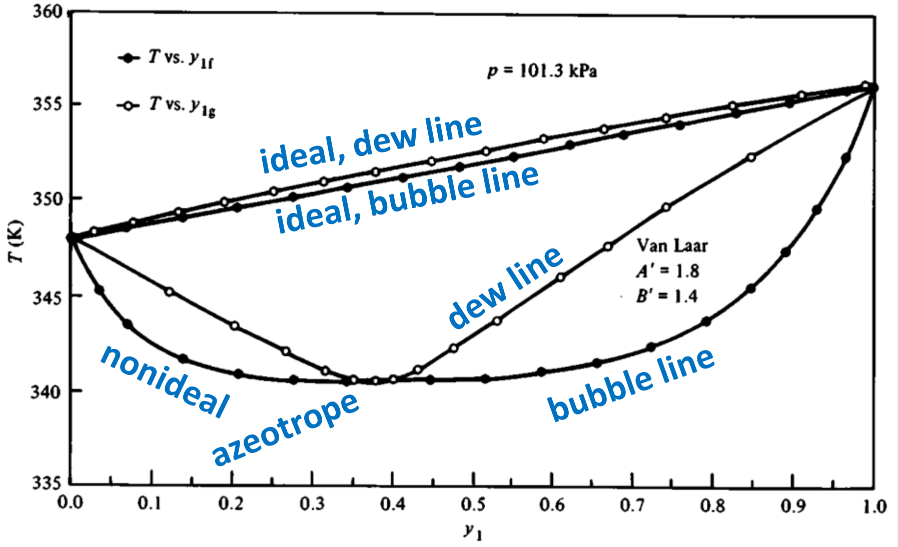
$$y_{2g}p = a_{2f}\,p_{\mathrm{sat},22}(T)$$

approximated by the van Laar equations

$$p = y_{1f}\exp\left\{\frac{A/RT}{\left[1 + Ay_{1f}/B(1-y_{1f})\right]^2}\right\}p_{\mathrm{sat},11}(T) + (1-y_{1f})\exp\left\{\frac{B/RT}{\left[1 + B(1-y_{1f})/Ay_{1f}\right]^2}\right\}p_{\mathrm{sat},22}(T)$$

$$\frac{1}{p} = \frac{y_{1g}}{p_{\mathrm{sat},11}(T)}\exp\left\{-\frac{A/RT}{\left[1 + Ay_{1f}/B(1-y_{1f})\right]^2}\right\} + \frac{1-y_{1g}}{p_{\mathrm{sat},22}(T)}\exp\left\{-\frac{B/RT}{\left[1 + B(1-y_{1f})/Ay_{1f}\right]^2}\right\}$$





Equations and figures adapted from pp.522-525 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Simple model of non-ideal liquid-vapor equilibrium:

liquid-vapor equilibrium modeled with the van Laar models

The conditions of mutual stable equilibrium of the two coexisting phases

$$y_{1g}p = a_{1f}\,p_{\mathrm{sat},11}(T)$$
$$y_{2g}p = a_{2f}\,p_{\mathrm{sat},22}(T)$$

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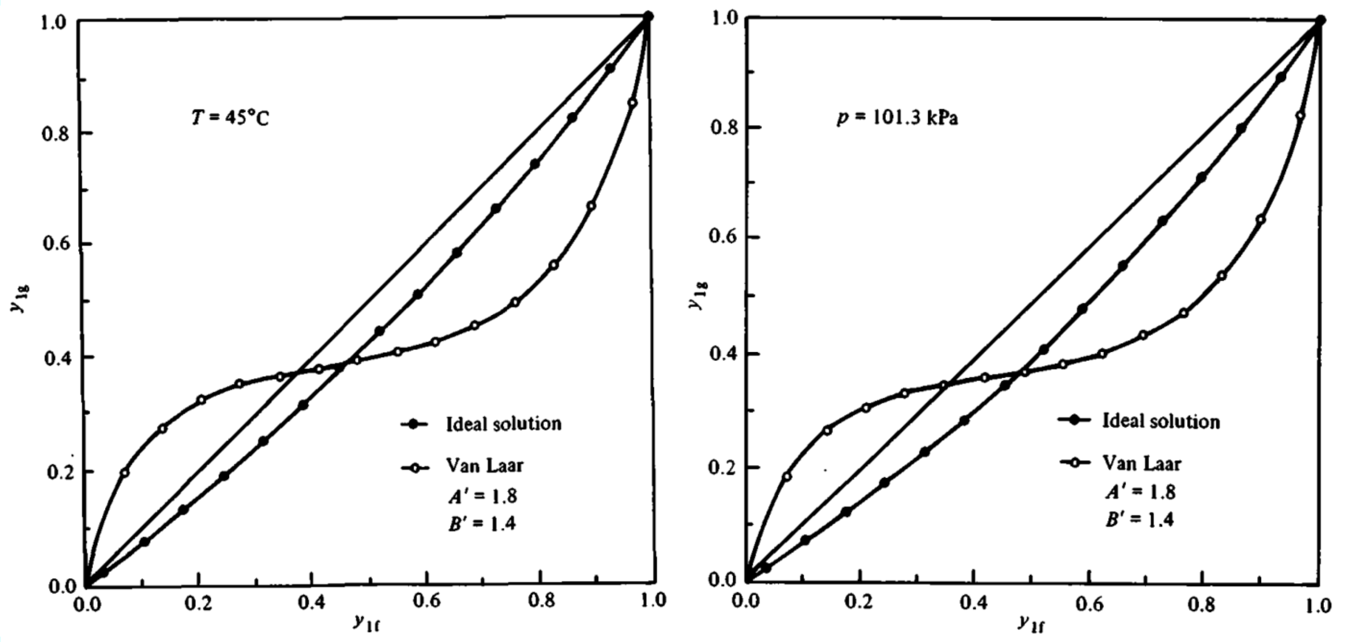
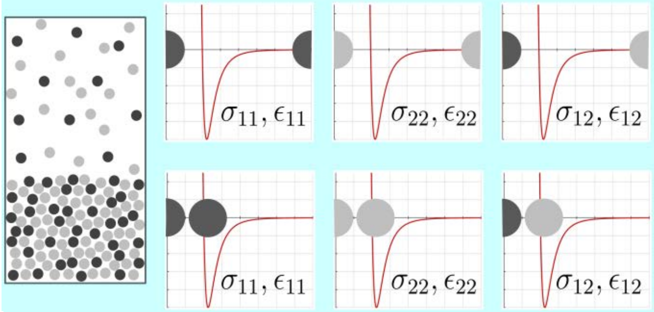
$$\frac{1}{p} = \frac{y_{1g}}{p_{\mathrm{sat},11}(T)}\exp\left\{-\frac{A/RT}{\left[1 + Ay_{1f}/B(1-y_{1f})\right]^2}\right\} + \frac{1-y_{1g}}{p_{\mathrm{sat},22}(T)}\exp\left\{-\frac{B/RT}{\left[1 + B(1-y_{1f})/Ay_{1f}\right]^2}\right\}$$



Equations and figures adapted from pp.522-525 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

MD and MC modeling of non-ideal SES mixture behavior:

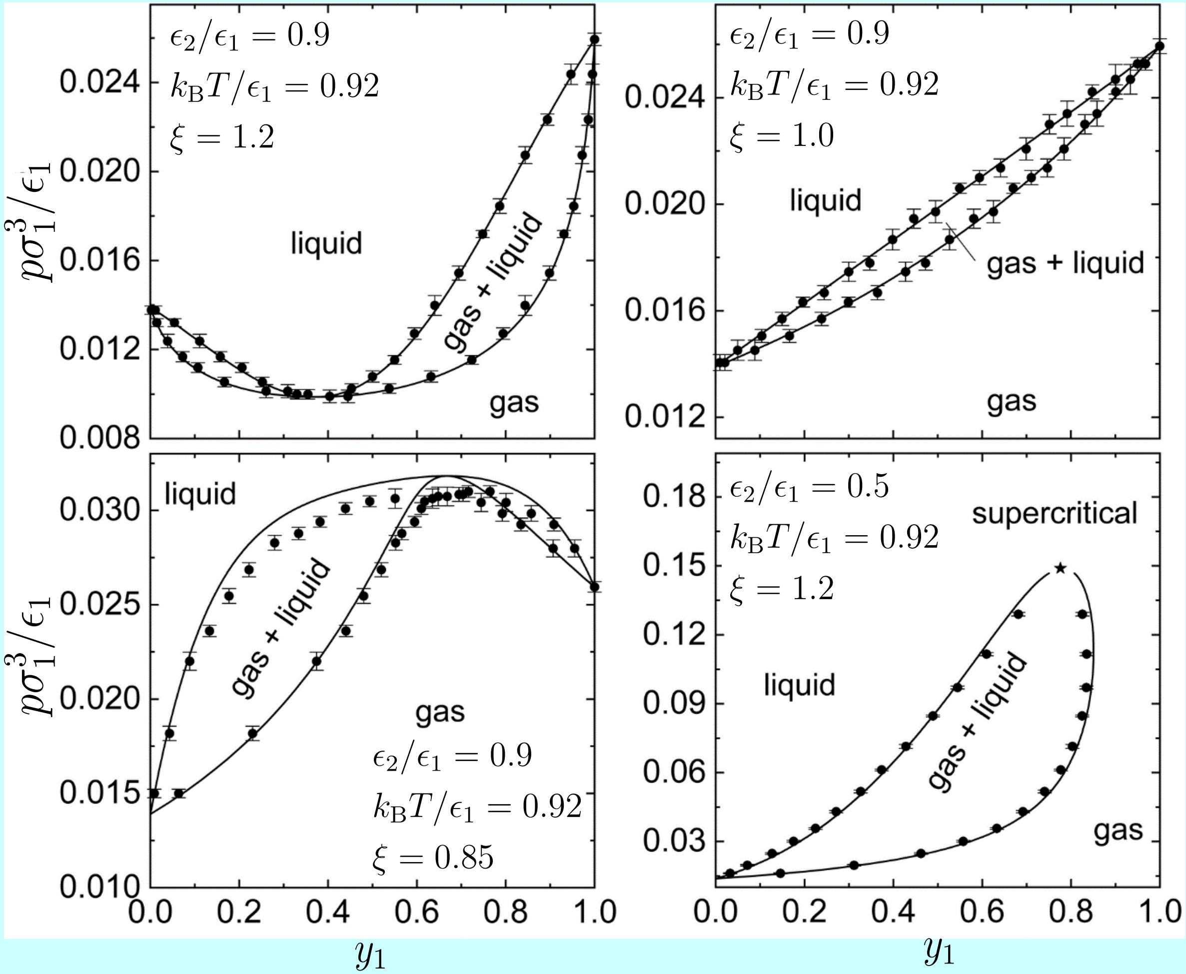
Lennard-Jones binary mixture



$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2} \qquad \epsilon_{12} = \xi\sqrt{\epsilon_{11}\epsilon_{22}}$$

with $\xi = 1$ these are the Lorentz(1881)-Berthelot(1898) mixing rules

For $\xi = 1$ mixture behavior is close to ideal (Raoult's law). For $\xi > 1$ ($\xi < 1$) attraction (repulsion) between unlike particles is stronger than between like particles, and the mixture tends to form a high-boiling (low-boiling) azeotrope, i.e., higher (lower) pressures than for ideal behavior are required to stabilize the vapor–liquid equilibrium. Very low values of ξ result in liquid–liquid miscibility gap.



Figures adapted from Wikipedia, by TimeStep89, CC BY 4.0.

Liquid-vapor equilibria in non-ideal mixtures

stability and miscibility gap
liquid-liquid spinodal decomposition

Liquid-vapor equilibria for non-ideal binary mixtures

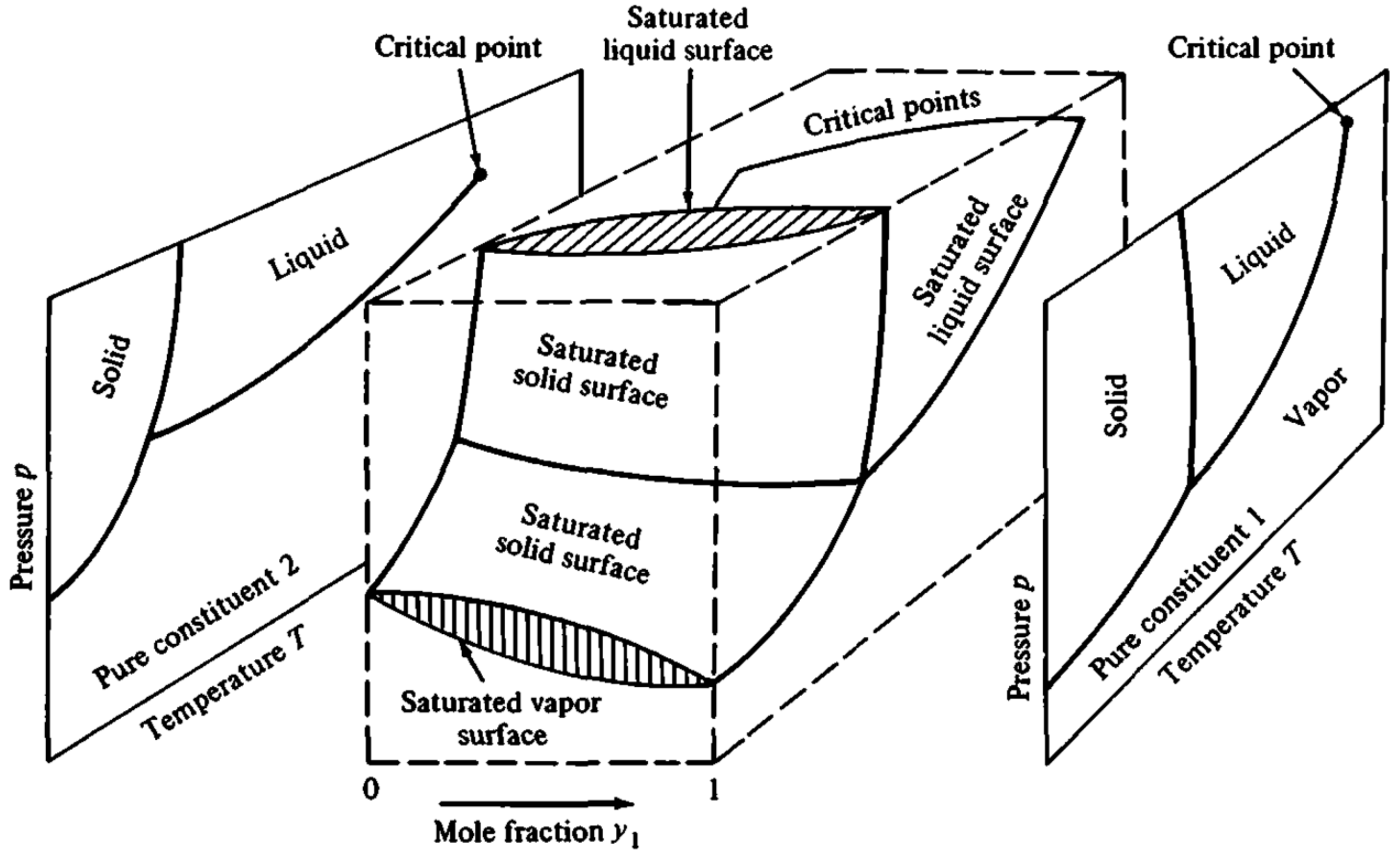


Figure 26.1 On a $T - p - y_1$ diagram, two-phase states are represented by points in a region delimited by two saturation surfaces. The diagrams in Figures 26.1 to 26.5 are based on C. E. Wales, *Chem. Eng.*, May 27, p. 120, June 24, p. 111, July 22, p. 141, Aug. 19, p. 167, Sept. 16, p. 187 (1983).

Figure from p.470 of Gyftopoulos, Beretta, Thermodynamics. Foundations and Applications, Dover, 2005

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Slides 12–16:

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Slide 17:

Four p-x phase diagrams of binary Lennard-Jones mixtures courtesy of TimeStep89 on Wikipedia. License CC BY.

Slide 19:

Figure 26.1 from the book *Thermodynamics: Foundations and Applications* courtesy of Elias P. Gyftopoulos and Gian Paolo Beretta.

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Spring 2024