CHEG325 E1 Cheatsheets

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fundamental relations

pure components

$$dU = TdS - PdV + \underline{G}dN$$

$$dH = TdS + VdP + \underline{G}dN$$

$$dA = -PdV - SdT + \underline{G}dN$$

$$dG = VdP - SdT + \underline{G}dN$$

mixtures

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i$$

partial def of variables

$$\underline{G} = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

$$= \left(\frac{\partial G}{\partial N}\right)_{T,P} = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$\bar{G}_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

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

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial A}{\partial T}\right)_V$$

ideal gas things

$$\underline{U}^{\mathrm{IG}} = C_v^* T$$

$$\underline{H}^{\mathrm{IG}} = C_p^* T$$

$$\Delta S^{\mathrm{IG}} = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

$$\Delta G^{\mathrm{IG}}\Big|_T = RT\ln\frac{P_2}{P_1}$$

legendre (wrt ξ_1)

$$\tilde{\theta} \equiv \theta - \left(\frac{\partial\theta}{\partial\xi_1}\right)_{\xi_{j\neq 1}} \xi_1 = \theta - \tilde{\xi}_1\xi_1$$

$$\left(\frac{\partial\tilde{\theta}}{\partial\tilde{\xi}_1}\right)_{\xi_2,\xi_3\ldots} = -\xi_1$$

volterra

$$\left(\frac{\delta g}{\delta x_i}\right) = \left(\frac{\partial g}{\partial x_i}\right) - \frac{1}{C}\sum_{j=1}^{C}\left(\frac{\partial g}{\partial x_j}\right)$$

$$\bar{g}_i = g + \left(\frac{\partial g}{\partial x_i}\right) - \sum_{j=1}^{C}\left(\frac{\partial g}{\partial x_j}\right) x_j$$

partial molar property

$$\bar{\theta}_i(T,P,\underline{x}) = \left(\frac{\partial(N\underline{\theta})}{\partial N_i}\right)_{T,P,}$$

$$\Delta_{\mathrm{mix}}\theta = \sum_{i=1}^{\mathcal{C}} N_i\left[\bar{V}_i - \underline{V}_i\right] = \theta - \sum_{i=1}^{\mathcal{C}} N_i\underline{\theta}_i$$

gibbs-duhem

$$\sum N_i d\bar{\theta}\,\big|_{T,P} = 0$$

$$\sum x_i d\bar{\theta}\,\big|_{T,P} = 0$$

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right)_{T,P} = 0$$

reactions

$$\alpha A + \beta B \longleftrightarrow \rho R + \ldots$$

- products positive, reactants negative, inerts 0

$$X \equiv \frac{N_i - N_{i,0}}{\nu_i}$$

$$N_i = N_{i,0} + \nu_i X$$

independent reactions

given reactions, use $\underline{\underline{\mathbf{k}}}$

- column for each component, row for each reaction

$$\mathrm{rank}(\mathbf{k}) = \text{number of independent reactions}$$

given components, use $\underline{\underline{\mathbf{a}}}$

- column for each component, row for elements

$$S = \mathrm{rank}(\mathbf{a})$$

$$I = C - S$$

reacting systems

mass balance for reacting system

$$\frac{dN}{dt} = \sum_k^K \dot{N}_k + \sum_i \sum_j \nu_{ij} \dot{X}_j$$

energy balance for reacting system

$$\frac{dU}{dt} = \sum_k^K (\dot{N}\underline{H})_k + \dot{Q} + W_s - P\frac{dV}{dt}$$

for CSTR

$$\frac{dU}{dt} = \sum^C (\dot{N}\underline{H})_{in} + \sum^C (\dot{N}\underline{H})_{out} + \dot{Q}$$

standard state heats of reactions

$$\Delta_{\text{rxn}} H^\circ = \sum_i \nu_i \Delta_{\text{form}} \underline{H}_i^\circ$$

pmp from experiment

$$\Delta_{\text{mix}} \underline{V} - x_1 \left(\frac{\partial \Delta \underline{V}}{\partial x_1} \right)_{T,P} = (\bar{V}_2 - \underline{V}_2)$$

gibbs phase rule

$$\mathcal{F} = C - M - P + 2$$

partial pressure; fugacity

$$P_i = x_i P_{\text{total}}$$

fugacity using ideal gas mixture as reference

$$\bar{f}(T, P, \underline{x}) = P_i \exp \left(\frac{\bar{G}_i(T, P, \underline{x}) - \bar{G}_i^{\text{IGM}}(T, P, \underline{x})}{RT} \right)$$

$$= P_i \exp \left(\frac{1}{RT} \int_0^P (\bar{V}_i - \bar{V}_i^{\text{IG}}) \, dP \right)$$

ideal mixture

$$\bar{f}_i^{\text{IM}} = x_i f_i(T, P)$$

ideal gas mixture

$$\bar{f}_i^{\text{IGM}} = x_i P_{\text{total}}$$

from eos

$$\ln \bar{\phi} = \frac{1}{RT} \int_\infty^{ZRT/P} \left[\frac{RT}{V} - N \left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{j\neq i}} \right] d\underline{V} - \ln Z$$

$$= \ln \frac{\bar{f}_i}{x_i P}$$

fugacity coefficient

$$\bar{\phi}_i = \frac{\bar{f}_i}{x_i P}$$

property	ideal gas mixture	$\Delta_{\text{mix}}\theta$
$\bar{U}^{\text{IGM}}$	$\underline{U}^{\text{IG}}$	0
$\bar{H}^{\text{IGM}}$	$\underline{H}^{\text{IG}}$	0
$\bar{V}^{\text{IGM}}$	$\underline{V}^{\text{IG}}(T, P)$	0
$\bar{S}^{\text{IGM}}$	$\underline{S}^{\text{IG}}(T, P) - R \ln x_i$	$-R \sum x_i \ln x_i$
$\bar{G}^{\text{IGM}}$	$\underline{G}^{\text{IG}}(T, P) + RT \ln x_i$	$RT \sum x_i \ln x_i$
$\bar{A}^{\text{IGM}}$	$\underline{A}^{\text{IG}}(T, P) + RT \ln x_i$	$RT \sum x_i \ln x_i$

property	ideal mixture	$\Delta_{\text{mix}}\theta$
$\underline{U}^{\text{IM}}$	$\sum x_i \underline{U}_i$	0
$\underline{H}^{\text{IM}}$	$\sum x_i \underline{H}_i$	0
$\underline{V}^{\text{IM}}$	$\sum x_i \underline{V}$	0
$\underline{S}^{\text{IM}}$	$\sum x_i \underline{S}_i - R \sum x_i \ln x_i$	$-R \sum x_i \ln x_i$
$\underline{A}^{\text{IM}}$	$\sum x_i \underline{A}_i + RT \sum x_i \ln x_i$	$RT \sum x_i \ln x_i$
$\underline{G}^{\text{IM}}$	$\sum x_i \underline{G}_i + RT \sum x_i \ln x_i$	$RT \sum x_i \ln x_i$
$\bar{S}_i^{\text{IM}}$	$\underline{S}_i(T, P) - R \ln x_i$	$-R \sum x_i \ln x_i$
$\bar{A}_i^{\text{IM}}$	$\underline{A}_i(T, P) + RT \ln x_i$	$RT \sum x_i \ln x_i$
$\bar{G}_i^{\text{IM}}$	$\underline{G}_i(T, P) + RT \ln x_i$	$RT \sum x_i \ln x_i$

excess properties

$$\bar{\theta}_i^{\text{ex}} = \bar{\theta}_i - \bar{\theta}_i^{\text{IM}}$$

$$\Delta_{\text{mix}} \underline{\theta}(T, P, \underline{x}) = \Delta_{\text{mix}} \underline{\theta}^{\text{IM}}(T, P, \underline{x}) + \underline{\theta}^{\text{ex}}$$

excess gibbs

$$\bar{G}_i^{\text{ex}} = \left(\frac{\partial N \underline{G}^{\text{ex}}}{\partial N_i} \right)_{T,P,N_{j\neq i}} = RT \ln \left(\frac{\bar{f}_i}{x_i f_i} \right)$$

$$= RT \ln \left(\frac{\bar{\phi}_i}{\phi_i} \right) = \int_0^P \bar{V}_i - \underline{V}_i \, dP$$

activity coefficient

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{\bar{\phi}_i}{\phi_i}$$

$$RT \ln(\gamma_i) = \bar{G}_i^{ex}$$

g-d for activity coefficients

$$\sum x_i d \ln \gamma_i = 0$$

lewis randall rule (low or high pressure)

$$\bar{f}_i = y_i f_i$$

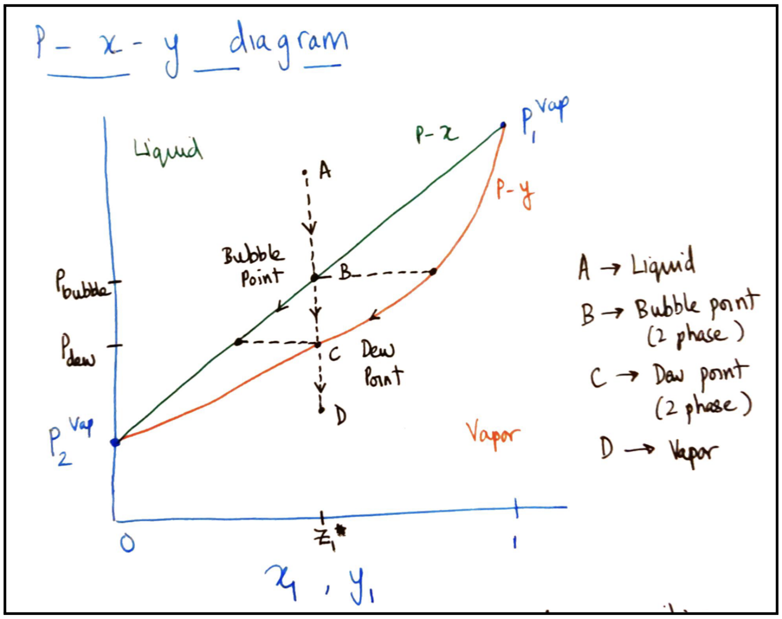
VLE

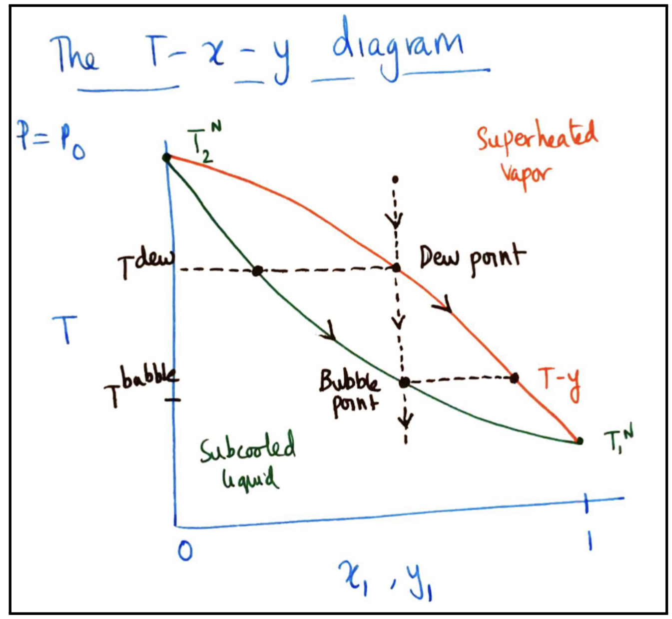
low pressure vle

$$x_i \gamma_i P_i^{\text{vap}} = y_i P_{\text{total}}$$

low pressure; ideal liquid; raoults

$$x_i P_i^{\text{vap}} = y_i P_{\text{total}}$$





useful vle problem solutions

$$\sum x_i P_i^{\text{vap}}(T) = P_{\text{total}}$$

$$P_{\text{total}} = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$$

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

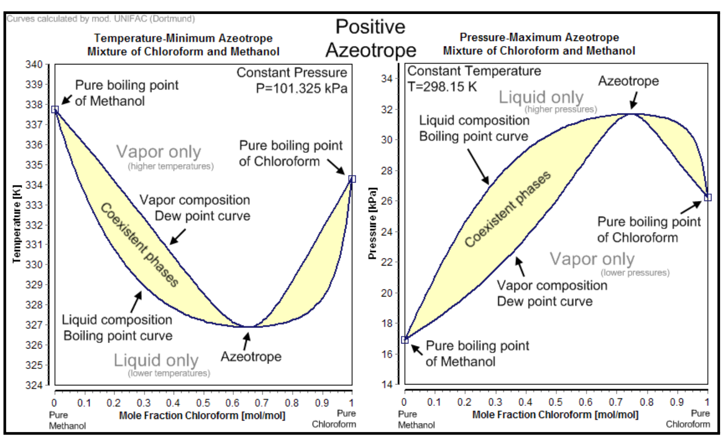
$$y_i = \frac{z_i k_i}{1 + V(k_i - 1)} \qquad x_i = \frac{z_i}{1 + V(k_i - 1)}$$

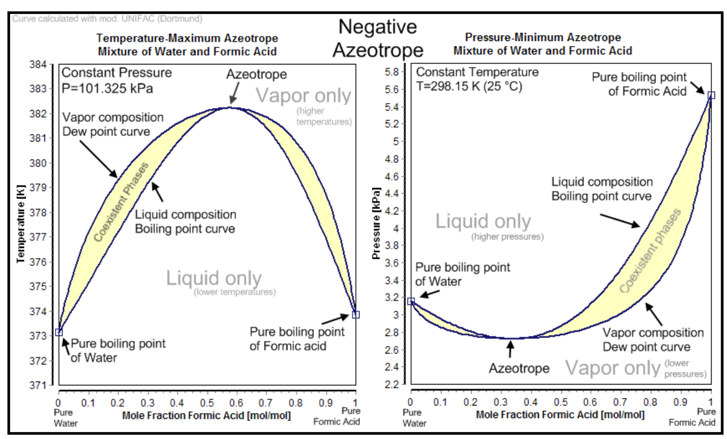
positive azeotrope

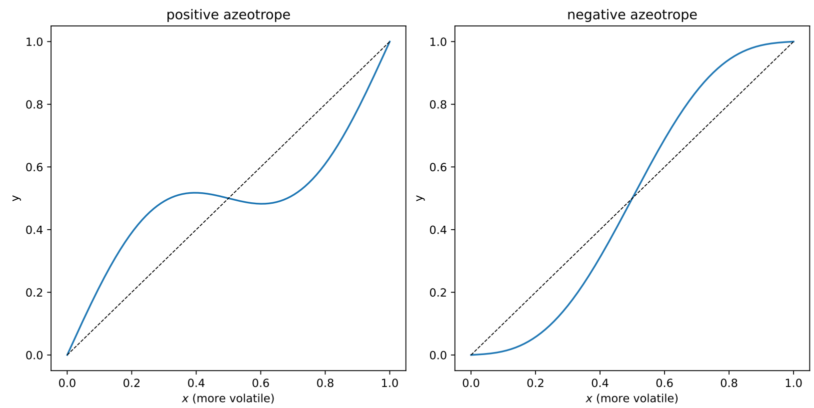
- minimum boiling T; maximum pressure
- $k_i > 1$ before x_{az} (for more volatile)
- positive deviation from raoults

negative azeotrope

- maximum boiling T minimum pressure
- $k_i < 1$ before x_{az} (for more volatile)
- negative deviation from raoults







relative volatility

$$\alpha_{12} = \frac{K_1}{K_2}$$

- relative volatility = 1 at azeotrope
- if pure component limits are on opposite sides of 1, an azeotrope likely exists

reflux ratio, q

$$q = \frac{L}{D}$$

upper operating line

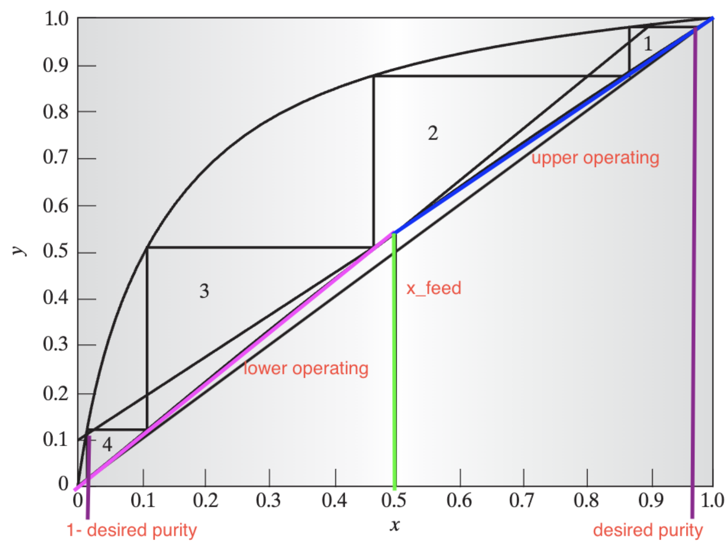
$$y = \frac{x_D}{1+q} + \frac{x_i q}{1+q}$$

slope less than 1

lower operating line

$$y = x\left(\frac{q+\frac{F}{D}}{q+1}\right) - x_b\left(\frac{\frac{F}{D}-1}{q+1}\right)$$

slope greater than 1



activity coeff models

one constant margules

$$\underline{G}^{\text{ex}} = A x_1 x_2 \qquad RT\ln\gamma_1 = A x_2^2$$

- symmetric!

Redlich-Kister

$$\underline{G}^{\text{ex}} = x_1 x_2 \left\{A + B(x_1 - x_2) + C(x_1 - x_2)^2 \ldots\right\}$$

two constant margules (redlich, but only A,B nonzero)

$$RT\ln\gamma_1 = \alpha_1 x_2^2 + \beta_1 x_2^3$$

$$RT\ln\gamma_2 = \alpha_2 x_1^2 + \beta_2 x_1^3$$

$$\alpha_i = A + 3(-1)^{i+1}B$$

$$\beta_i = 4(-1)^i B$$

- no longer necessarily symmetric