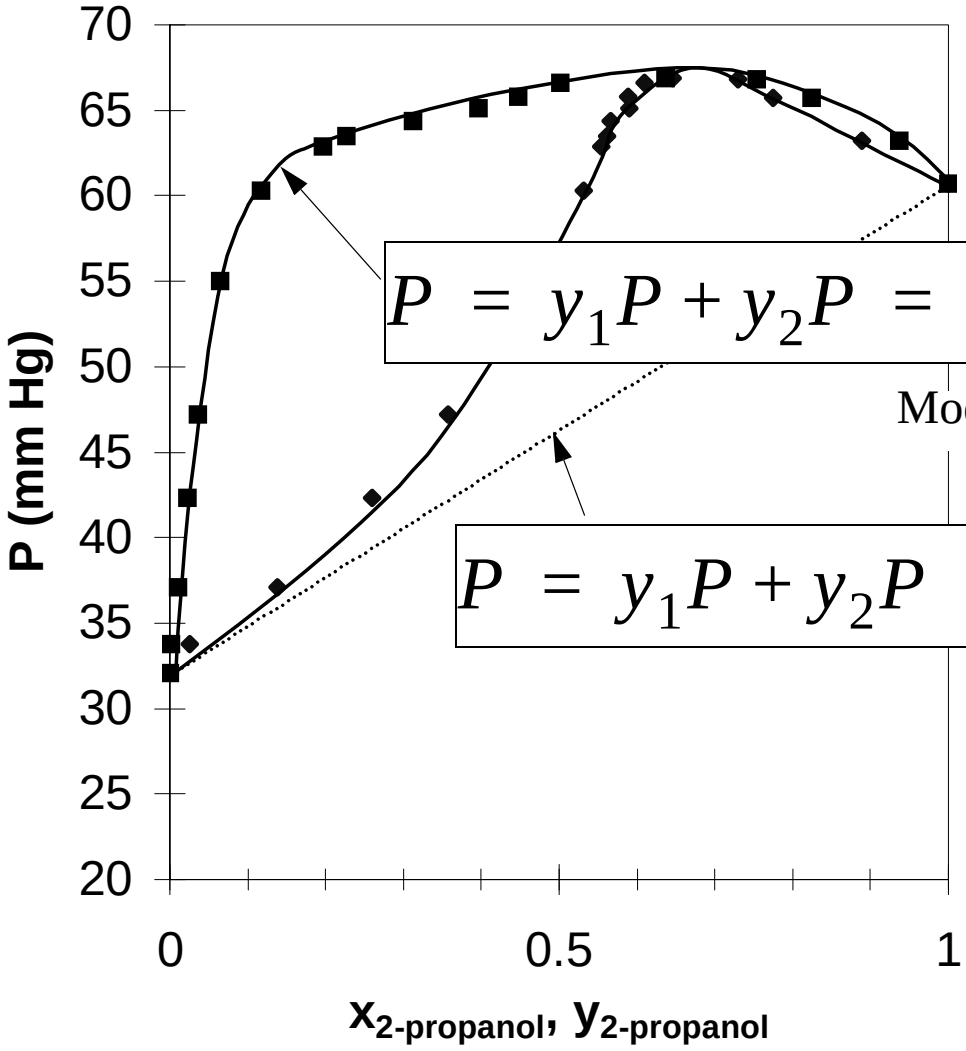


$$P = y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

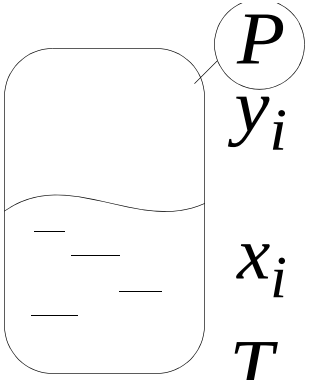
Modified Raoult's Law

$$P = y_1 P + y_2 P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

Raoult's Law

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

2-propanol + water, 30°C



$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Experiment:

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

Stage I

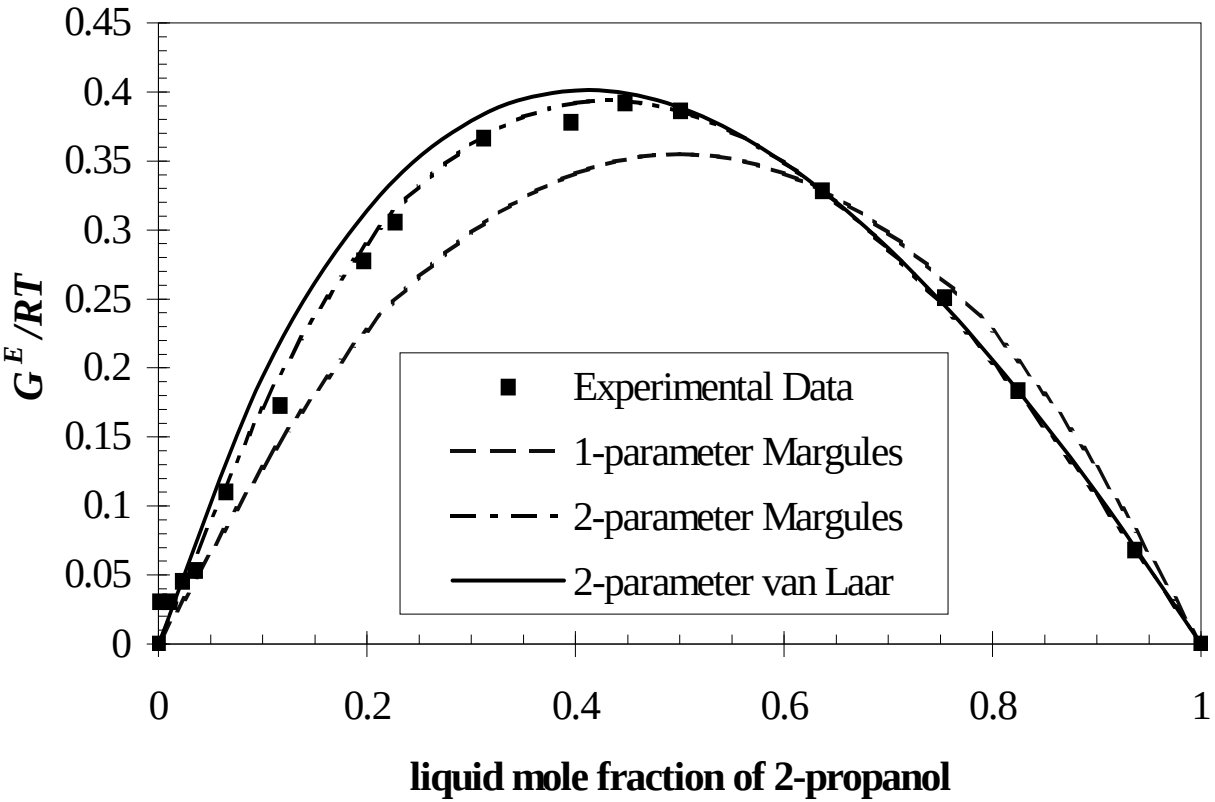
Model for G^E, γ_i.
(Model parameters fitted to experimental γ_i).

Stage II

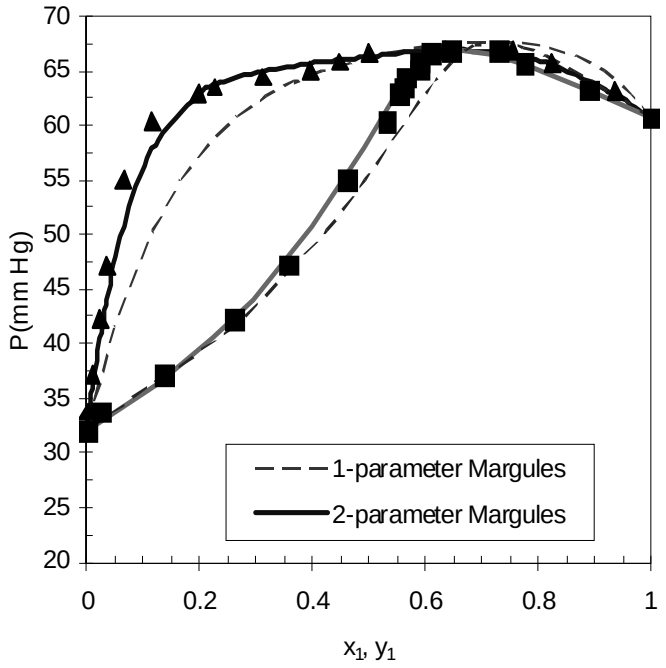
Bubble, Dew, Flash Calculations.
Process Design.
Process Troubleshooting.
e.g.

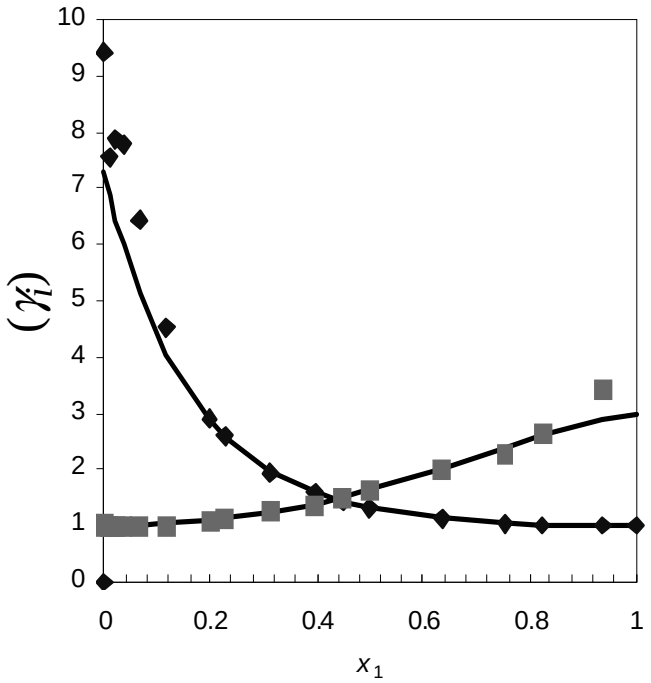
$$x_i \gamma_i P_i^{sat} = y_i P$$

Stage III



$$\frac{G^E}{RT} = A_{12}x_1x_2 \qquad \ln\gamma_i = A_{12}(1-x_i)^2$$





$$\frac{G^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1]$$

$$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$$

Gibbs-Duhem Equation

$$0 = -\underline{S}dT + \underline{V}dP - \sum_i n_i d\mu_i$$

$$\sum_i n_i d\mu_i = 0 \text{ at constant } T, P$$

$$\sum_i n_i d\mu_i^E = 0, \quad \sum_i n_i d\mu_i^E = RT\sum_i n_i d\ln\gamma_i = 0$$

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_i}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_i}\right)_{T,P} = 0 \text{ binary at fixed } T \text{ and } P$$

Relations Between Various Excess Properties

$$H^E = U^E + PV^E,\ G^E = H^E - TS^E,\ A^E = U^E - TS^E$$

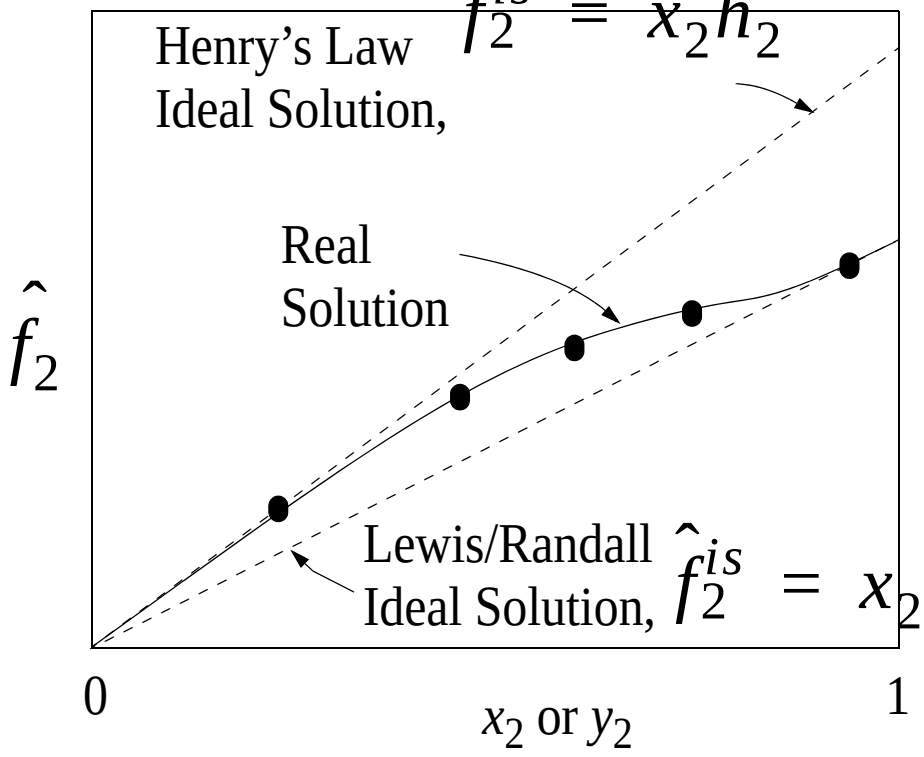
$$\left(\frac{\partial G^E}{\partial T}\right)_{P,\,x} = -S^E;\ \left(\frac{\partial \bar{G}_i^E}{\partial T}\right)_{P,\,x} = -\bar{S}_i^E$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,\,x} = V^E;\ \left(\frac{\partial \bar{G}_i^E}{\partial P}\right)_{T,\,x} = \bar{V}_i^E \text{ for } P^\circ = P_{\text{system}}$$

$$\left(\frac{\partial G^E/T}{\partial T}\right)_{P,\,x} = \frac{-H^E}{T^2};\ \left(\frac{\partial \bar{G}_i^E/T}{\partial T}\right)_{P,\,x} = \frac{-\bar{H}_i^E}{T^2}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\,x} = \frac{-\bar{H}_i^E}{RT^2}$$

Henry's Law



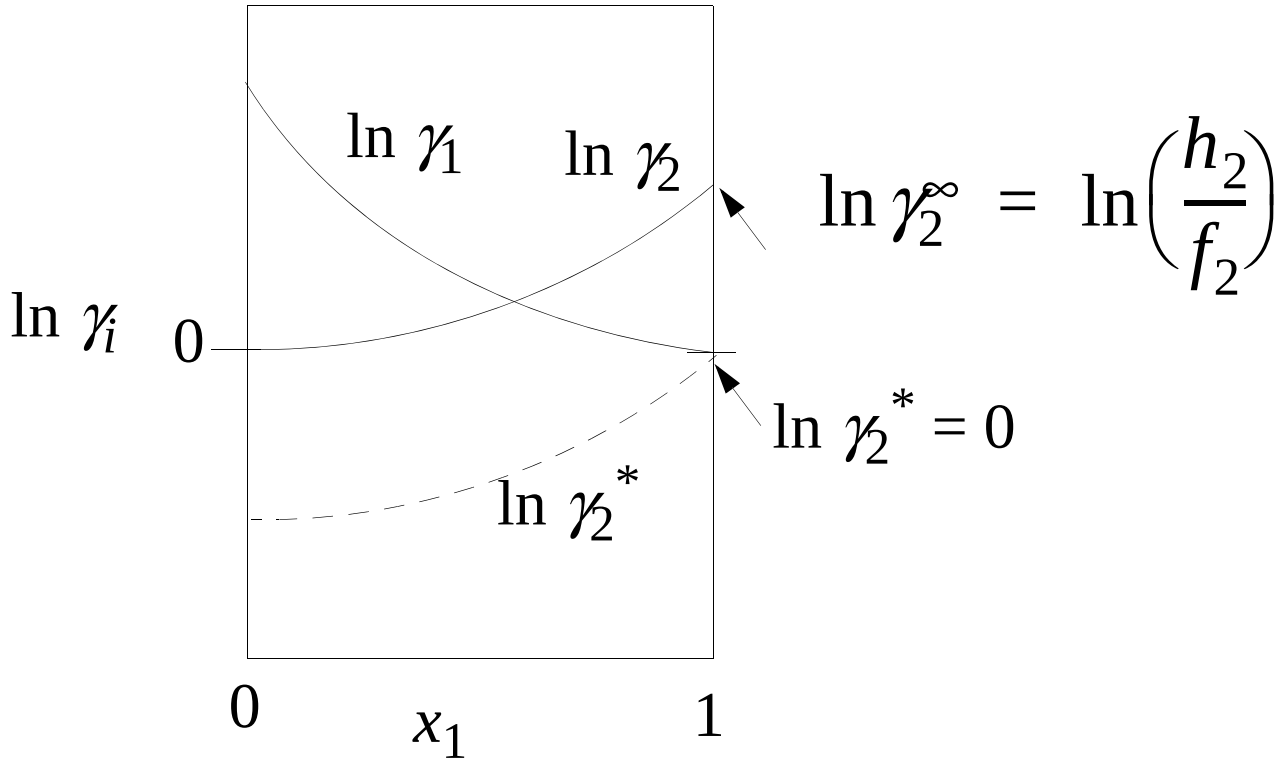
$f_2^\circ = h_2$

$f_2^\circ = f_2$

$f_2 \approx \varphi_2^{sat} P_2^{sat}$
common for liquid

$f_2 \approx \varphi_2 P$
common for vapor

$$\boxed{h_i = \gamma_i^\infty f_i}$$


ln γ_1
ln γ_2
ln γ_2^{∞} = ln$\left(\frac{h_2}{f_2}\right)$
ln γ_i
0
ln γ_2^* = 0
ln γ_2^*
0
x_1
1

$$\ln\gamma_i^* = \ln\gamma_i - \ln\gamma_i^\infty$$

Margules, one parameter

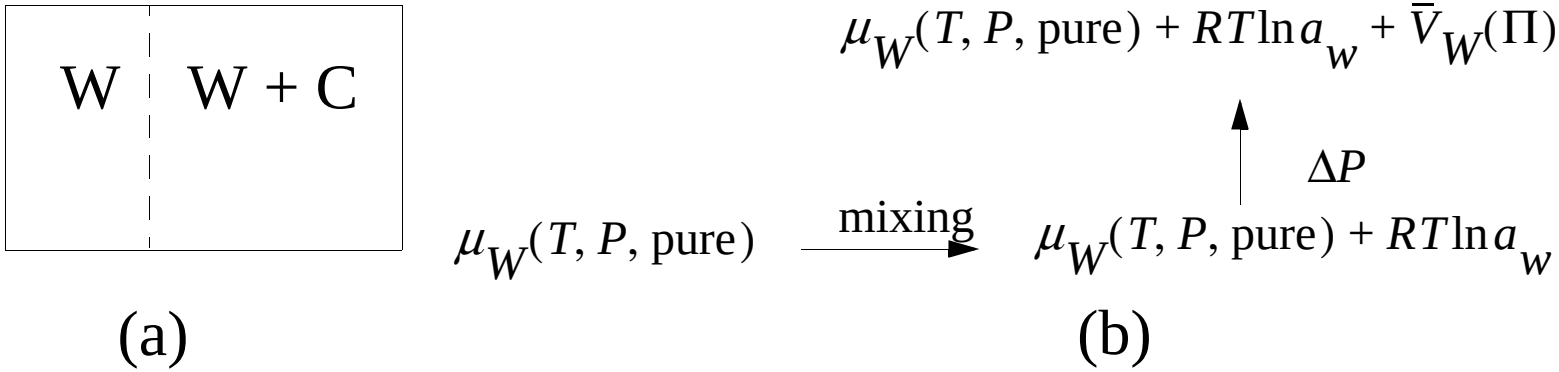
$$\ln\gamma_2^* = \ln\gamma_2 - \ln\gamma_2^\infty = A_{12}x_1^2 - A_{12} = A_{12}(x_1^2 - 1)$$

$$\ln\gamma_1 = A_{12}(x_2^2)$$

Henry's Law on the molal activity scale

$$\hat{f}_i = x_i\gamma_i^* h_i = m_i\gamma_i^{\square}/(K_H) \quad x_i = m_i x_w 0.001 M_{w,w}$$

Osmotic Pressure



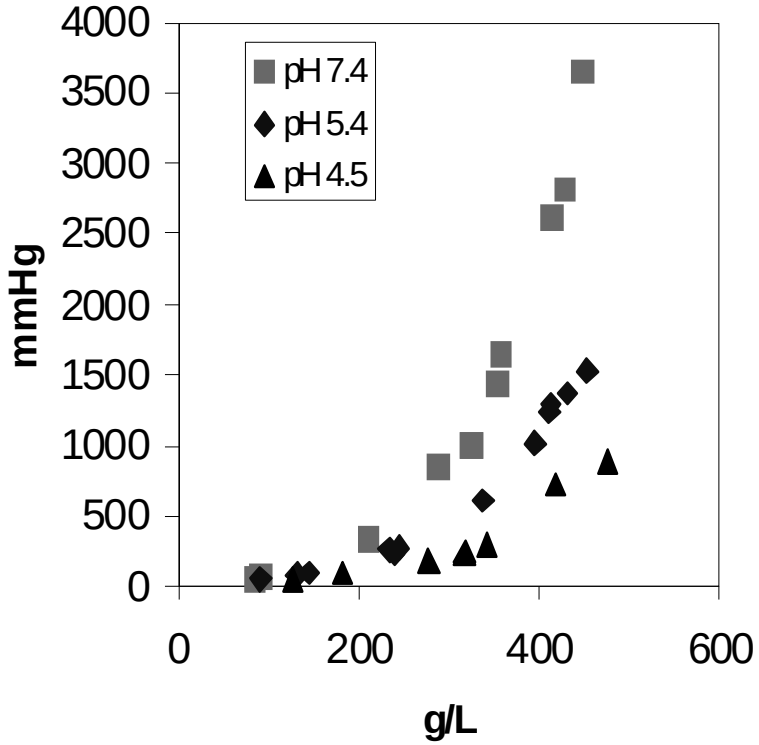
$$\Pi = -\frac{RT}{\bar{V}_W}\ln a_W,$$

McMillan-Mayer framework

$$RT\ln a_W = -RTV_W([C] + B_2(T)[C]^2 + B_3(T)[C]^3 + \ldots)$$

$$\frac{\Pi}{RT} = \frac{C_i}{M_{w,\,i}}(1 + B_2(T)C_i + B_3(T)C_i^2 + \ldots)$$

C_i the solute mass density **(in units of grams/(volume of solution))**



Osmotic pressure in mmHg for solutions of bovine serum albumin (BSA) in water at 25°C at different pH values.

isotonic -