Faculty of Engineering and Technology
Department of Chemical Engineering
University Of Jordan

Thermodynamics II

Lec 6-Solution Thermodynamics: Applications-part 1

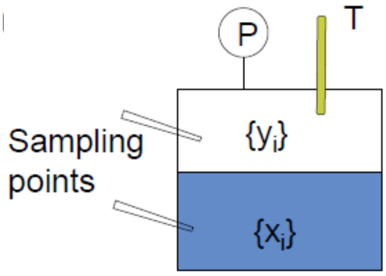
Dr.-Eng. Zayed Al-Hamamre

Content

1. Knows how to collect VLE data from experiment
2. Able to calculate Y_i from the VLE data
3. Able to develop correllation for Y_i from the VLE data
4. Knows how to use the VLE data to determine correlation's parameters
5. Familiar with the commonly available correlations for Y_i

VLE data collection

- The temperature T and P are uniform throughout the vessel, and can be measured with appropriate instruments.
- Vapor and liquid samples may be withdrawn for analysis, and this provides experimental values for mole fractions in the vapor $\{y_i\}$ and mole fractions in the liquid $\{x_i\}$



vapor mixture and a liquid solution coexist in vapor/liquid equilibrium

Liquid phase property from VLE data

- For species *i* in the vapor mixture $\hat{f}_i^v = y_i \hat{\phi}_i^v P$ (Fugacity cannot be measured directly)
- The criterion of vapor/liquid equilibrium, as given by Eq. (11.48), is that $\hat{f}_i^l = \hat{f}_i^v$

$$\Rightarrow \quad \hat{f}_i^l = y_i \hat{\phi}_i^v P$$

- VLE measurements are very often made at pressure low enough ($P \leq 1$ bar) that the vapor phase may be assumed an ideal gas

$$\hat{f}_i^l = \hat{f}_i^v = y_i P$$

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

Liquid phase property from VLE data

- Thus, the fugacity of species i (in both the liquid and vapor phases) is equal to the partial pressure of species i in the vapor phase.
- Its value increases from zero at infinite dilution to P_i^{sat} for pure species i. this is illustrated by the data of Table 12.1 for the methyl ethyl ketone(1)/toluene(2) system at 50°C

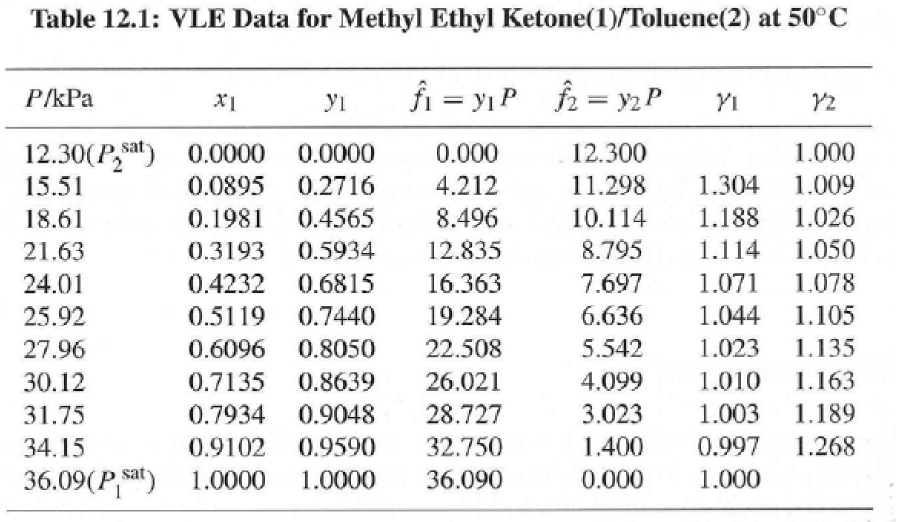


Table 12.1: VLE Data for Methyl Ethyl Ketone(1)/Toluene(2) at 50°C

P/kPa	x_1	y_1	$\hat{f}_1 = y_1 P$	$\hat{f}_2 = y_2 P$	γ_1	γ_2
12.30(P_2^{sat})	0.0000	0.0000	0.000	12.300		1.000
15.51	0.0895	0.2716	4.212	11.298	1.304	1.009
18.61	0.1981	0.4565	8.496	10.114	1.188	1.026
21.63	0.3193	0.5934	12.835	8.795	1.114	1.050
24.01	0.4232	0.6815	16.363	7.697	1.071	1.078
25.92	0.5119	0.7440	19.284	6.636	1.044	1.105
27.96	0.6096	0.8050	22.508	5.542	1.023	1.135
30.12	0.7135	0.8639	26.021	4.099	1.010	1.163
31.75	0.7934	0.9048	28.727	3.023	1.003	1.189
34.15	0.9102	0.9590	32.750	1.400	0.997	1.268
36.09(P_1^{sat})	1.0000	1.0000	36.090	0.000	1.000	

Liquid phase property from VLE data

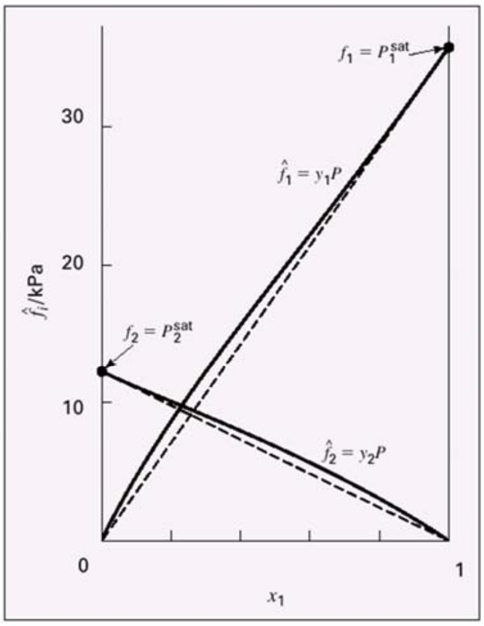


Figure 12.2: Fugacities for methyl ethyl ketone(1)/toluene(2) at 50°C. The dashed lines represent the Lewis/Randall rule.

- The fugacities are plotted as solid lines.
- The straight dashed lines represent the Lewis/Randall rule which expresses the composition dependence of the constituent fugacities in an ideal solution:

$$\hat{f}_i^{id} = x_1 f_i$$

- The Lewis-Randall rule provides the simplest possible model for the composition dependence, to which actual behavior may be compared

Liquid phase property from VLE data

Activity Coefficient

- The activity coefficient as defined by Eq. (11.90) formalizes this comparison:

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} = \frac{\hat{f}_i}{\hat{f}_i^{id}}$$

- Thus the activity coefficient of a species in solution is the ratio of its actual fugacity to the value given by the Lewis/Randall rule at the same *T*, *P*, and composition
- For the calculation of experimental values, both $\hat{f}_i$ and $\hat{f}_i^{id}$ are eliminated in favor of measurable quantities:

$$\gamma_i = \frac{y_i P}{x_i f_i} = \frac{y_i P}{x_i P_i^{sat}} \qquad (i = 1, 2, \ldots, N) \qquad (12.1)$$

- This is a restatement of Eq. (10.5), modified Raoult's law, and is adequate for present purposes, allowing easy calculation of activity coefficients from experimental low pressure VLE data. Values from this equation appears in the last two columns of Table 12.1.

Liquid phase property from VLE data

- Experimental VLE data (measured $P\, x_i\, y_i$) and vapor pressures of pure-species determine activity coefficient γ_i
- The solid lines in both Figs 12.2 and 12.3, representing experimental values of $\hat{f}_i$, become tangent to the Lewis/Randall rule lines at $x_i = 1$.
- This is a consequence of the Gibbs/Duhem equation.
- Thus, the $\hat{f}_i / x_i$ is indeterminate in this limit, and application of L'Hopital's rule yields:

$$\lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = \left(\frac{d\hat{f}_i}{dx_i} \right)_{x_i = 0} \equiv \mathcal{H}_i \qquad (12.2)$$

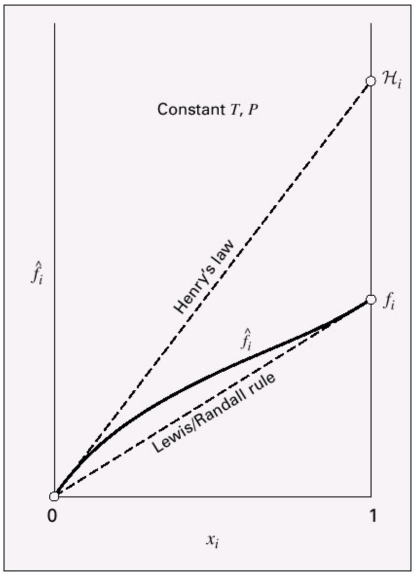


Figure 12.3: Composition dependence of liquid-phase fugacities for species *i* in a binary solution.

Liquid phase property from VLE data

- Equation (12.2) defines Henry's constant H_i as the limiting slope of the $\hat{f}_i - x_i$ curve at $x_i = 0$. as shown by Fig. 12.3, this is the slope of a line drawn tangent to the curve at $x_i = 0$.

$$\Rightarrow \quad \hat{f}_i = x_i H_i$$

- It is of approximate validity for small values of x_i
- Lewis-Randall rule (or Rault's law) is for very rich component while Henry's law is for dilute component

Liquid phase property from VLE data

- Henry's law is related to the Lewis/Randall rule through the Gibbs/Duhem equation.
- Writing Eq. (11.14) for a binary solution and replacing $\hat{M}_i$ by $\hat{G}_i = \mu_i$ gives:

$$x_1\, d\mu_1 + x_2 d\mu_2 = 0 \qquad \text{(const } T, P)$$

- Differentiation of Eq. (11.46) at constant T and P yields: $d\mu_i = RTd\ln \hat{f}_i$

whence

$$\boxed{x_1\, d\ln \hat{f}_1 + x_2 d\ln \hat{f}_2 = 0}$$

Divide by dx_1 and use: $dx_1 = -dx_2$

$$\Rightarrow \quad \boxed{x_1 \frac{d\ln \hat{f}_1}{dx_1} - x_2 \frac{d\ln \hat{f}_2}{dx_2} = 0 \qquad (12.4)} \qquad \text{OR} \qquad \frac{d\hat{f}_1/dx_1}{\hat{f}_1/x_1} = \frac{d\hat{f}_2/dx_2}{\hat{f}_2/x_2}$$

This is a special form of the Gibbs/Duhem equation.

Liquid phase property from VLE data

In the limit as $x_1 \to 1$ and $x_2 \to 0$,

$$\lim_{x_1 \to 1} \frac{d\hat{f}_1/dx_1}{\hat{f}_1/x_1} = \lim_{x_2 \to 0} \frac{d\hat{f}_2/dx_2}{\hat{f}_2/x_2}$$

Because $\hat{f}_1 = f_1$ when $x_1 = 1$, this may be rewritten:

$$\frac{1}{f_1}\left(\frac{d\hat{f}_1}{dx_1}\right)_{x_1=1} = \frac{(d\hat{f}_2/dx_2)_{x_2=0}}{\lim\limits_{x_2 \to 0}(\hat{f}_2/x_2)}$$

$$= 1$$ See Eq. (12.4)

$$\left(\frac{d\hat{f}_1}{dx_1}\right)_{x_1=1} = f_1$$

Liquid phase property from VLE data

This equation is the exact expression of the Lewis/Randall rule as applied to real solutions. It also implies that Eq. (11.83) provides approximately correct values of $\hat{f}_i$ when $x_i \approx 1$:

$$\hat{f}_i \approx \hat{f}_i^{id} = x_i f_i.$$

Henry's law applies to a species as it approaches infinite dilution in a binary solution, and the **Gibbs/Duhem** equation insures validity of the **Lewis/Randall** rule for the other species as it approaches purity.

Excess Gibbs Energy

$\ln\gamma_i$ is a partial property with respect to G^E/RT:

$$\boxed{\frac{G^E}{RT} = \sum_i x_i \ln\gamma_i}$$

- For a binary system

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

$$\lim_{x_i\to 1}\ln\gamma_i = 0$$

$$\lim_{x_i\to 0}\ln\gamma_i = \ln\gamma_i^\infty$$

γ_i^∞ : infinite dilution activity coefficient

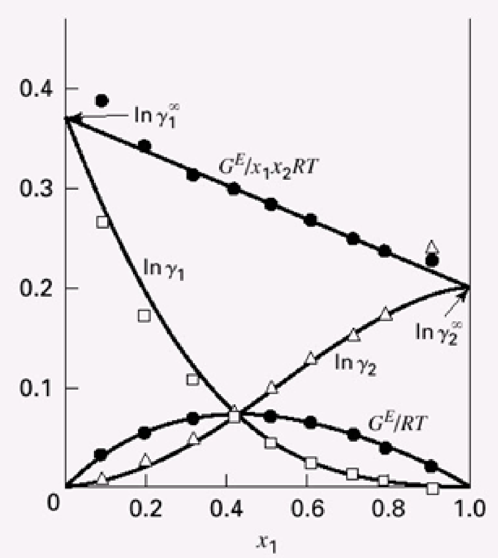
$$\lim_{x_1\to 0}\frac{G^E}{RT} = (0)\ln\gamma_1^\infty + (1)(0) = 0$$

$$\Rightarrow \quad \lim_{x_1\to 1}\frac{G^E}{RT} = 0$$

Excess Gibbs Energy

- The limiting values of $\dfrac{G^E}{x_1x_2RT}$ are equal to the infinite dilution limits of $\ln\gamma_1$ and $\ln\gamma_2$

$$\lim_{x_1\to 0}\frac{G^E}{x_1x_2RT} = \ln\gamma_1^\infty \qquad \lim_{x_1\to 1}\frac{G^E}{x_1x_2RT} = \ln\gamma_2^\infty$$



Proof

$x_1 \to 0$ L'Hopital's rule gives

$$\lim_{x_1\to 0}\frac{G^E}{x_1x_2RT} = \lim_{x_1\to 0}\frac{G^E/RT}{x_1\cdot 1} = \lim_{x_1\to 0}\frac{\dfrac{d\left(G^E/RT\right)}{dx_1}}{1}$$

Differentiating $\dfrac{G^E}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2$ with respect to x_1

Excess Gibbs Energy

$$\frac{d(G^E/RT)}{dx_1} = x_1 \frac{d\ln\gamma_1}{dx_1} + \ln\gamma_1 + x_2 \frac{d\ln\gamma_2}{dx_1} - \ln\gamma_2 \qquad \text{(B)}$$

Recalling that the Gibbs-Duhem equation is

$$x_1\, d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0 \qquad (\text{const } T, P)$$

Dividing by dx_1 **(It is not differentiation !)**

$$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = 0 \qquad (\text{const } T, P)$$

(γ_1 and γ_2 are related to each other)

Substituting into (B) ➡

$$\frac{d(G^E/RT)}{dx_1} = \ln\frac{\gamma_1}{\gamma_2}$$

Excess Gibbs Energy

- The limiting behaviors is to be

$$\lim_{x_1\to 0} \frac{G^E}{x_1 x_2 RT} = \lim_{x_1\to 0} \frac{d\left(G^E/RT\right)}{dx_1} = \lim_{x_1\to 0} \ln\frac{\gamma_1}{\gamma_2} = \ln\gamma_1^\infty$$

Similarly,

$$\lim_{x_2\to 0} \frac{G^E}{x_1 x_2 RT} = \ln\gamma_2^\infty$$

- Because the activity coefficient of a species in solution becomes unity as the species becomes pure, each $\ln\gamma_i \ (i=1,2)$ tends to zero as xi → 1.
- At the other limit, where xi → 0 and species i becomes infinitely dilute, $\ln\gamma_i$ approaches a finite limit, namely, $\ln\gamma_i^\infty$

Liquid phase property from VLE data

First we will use the VLE data for the binary system to,

1. Calculate γ_1 and γ_2 from Modified Raoult's Law
2. Calculate $\ln\gamma_1$ and $\ln\gamma_2$
3. Calculate $\dfrac{G^E}{RT}$ and $\dfrac{G^E}{x_1x_2RT}$:

Eqn 11.99 for binary system,

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

Divide both side by x_1x_2

$$\frac{G^E}{x_1x_2RT} = \frac{1}{x_1x_2}(x_1\ln\gamma_1 + x_2\ln\gamma_2)$$

From the VLE data, we tabulate $\ln\gamma_1$ $\ln\gamma_2$ $\dfrac{G^E}{RT}$ $\dfrac{G^E}{x_1x_2RT}$

Liquid phase property from VLE data

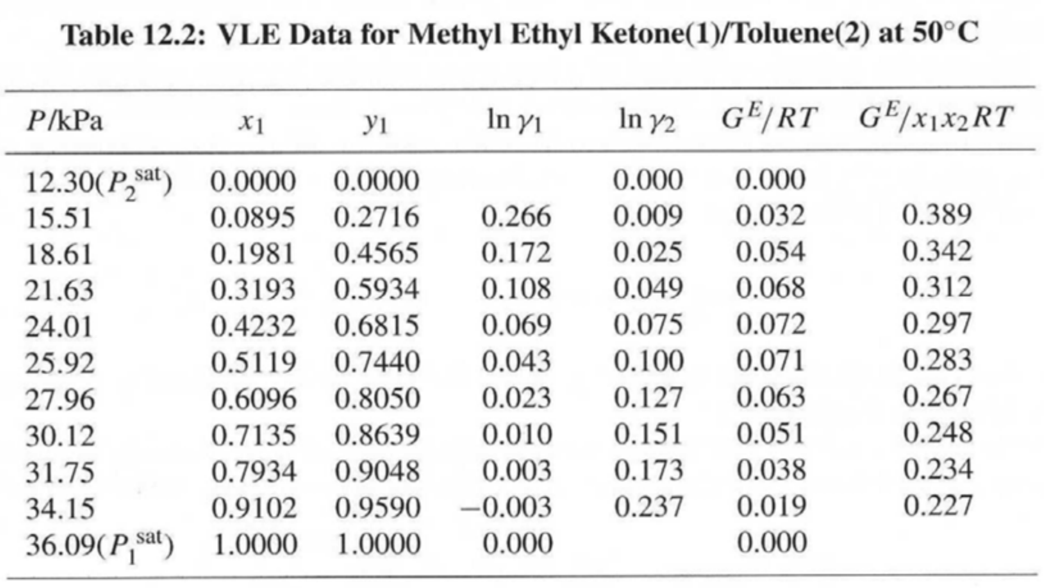


Table 12.2: VLE Data for Methyl Ethyl Ketone(1)/Toluene(2) at 50°C

P/kPa	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	G^E/RT	G^E/x_1x_2RT
12.30(P_2^{sat})	0.0000	0.0000		0.000	0.000	
15.51	0.0895	0.2716	0.266	0.009	0.032	0.389
18.61	0.1981	0.4565	0.172	0.025	0.054	0.342
21.63	0.3193	0.5934	0.108	0.049	0.068	0.312
24.01	0.4232	0.6815	0.069	0.075	0.072	0.297
25.92	0.5119	0.7440	0.043	0.100	0.071	0.283
27.96	0.6096	0.8050	0.023	0.127	0.063	0.267
30.12	0.7135	0.8639	0.010	0.151	0.051	0.248
31.75	0.7934	0.9048	0.003	0.173	0.038	0.234
34.15	0.9102	0.9590	−0.003	0.237	0.019	0.227
36.09(P_1^{sat})	1.0000	1.0000	0.000		0.000	

Data Reduction with Margules Equation

One-parameter Margules equation

$$\frac{G^E}{x_1 x_2 RT} = A \quad = \text{constant}$$

- This symmetric behavior is not sufficient for most nonideal mixtures)

Two-parameter Margules equation

$$\frac{G^E}{x_1 x_2 RT} = A_{21} x_1 + A_{12} x_2 \qquad (12.9a) \qquad \text{a linear composition dependence}$$

or

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

A_{21}, A_{12} fitting constants for experimental VLE data

A reasonable approximation for many types of binary mixtures

A commonly used empirical model of solution behavior

Data Reduction with Margules Equation

- Expressions for $\ln\gamma_1$ and $\ln\gamma_2$ are derived from Eq. (12.9b) by application of Eq. (11.96).

$$\ln\gamma_i = \left[\frac{\partial\left(nG^E / RT\right)}{\partial n_i}\right]_{P,T,n_j}$$

- Converting mole fractions into mole numbers in the two-parameter Margules equation

$$\frac{nG^E}{RT} = \left(A_{21} n_1 + A_{12} n_2\right)\frac{n_1 n_2}{(n_1 + n_2)^2} = \frac{A_{21} n_1{}^2 n_2 + A_{12} n_1 n_2{}^2}{(n_1 + n_2)^2}$$

Differentiating with respect to n_1

$$\ln\gamma_1 = \left[\frac{\partial\left(nG^E / RT\right)}{\partial n_1}\right]_{P,T,n_2} = \frac{2A_{21} n_1 n_2 + A_{12} n_2{}^2}{(n_1 + n_2)^2} - 2\,\frac{A_{21} n_1{}^2 n_2 + A_{12} n_1 n_2{}^2}{(n_1 + n_2)^3}$$

Data Reduction with Margules Equation

Converting to mole fractions

$$= 2A_{21}x_1x_2 + A_{12}x_2^{\,2} - 2\left(A_{21}x_1^{\,2}x_2 + A_{12}x_1x_2^{\,2}\right) = x_2^{\,2}\left[A_{12} - 2A_{12}x_1 + 2A_{21}x_1\right]$$

$$\Rightarrow \quad \ln\gamma_1 = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_1}\right]_{P,T,n_2} = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]$$

Similarly

$$\ln\gamma_2 = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_2}\right]_{P,T,n_1} = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right]$$

- For the limiting conditions at infinite dilution

$$\ln\gamma_1^\infty = A_{12} \qquad \textbf{(as } x_1 \to 0\textbf{)}$$

$$\ln\gamma_2^\infty = A_{21} \qquad \textbf{(as } x_2 \to 0\textbf{)}$$

- Infinite dilution activity coefficient has a significant meaning !

Data Reduction with Margules Equation

For various values of x_1 and the experimental data for vapor pressures (P^{sat}), and using $A_{12} = 0.372 \quad A_{21} = 0.198$

1. Recalculate y_1 and P using BUBL P calculation and Modified Raoult's Law.

2. Recalculate $\ln Y_l$, $\ln Y_2$, G^E/RT , G^E/x_1x_2RT using the Margules correlations.

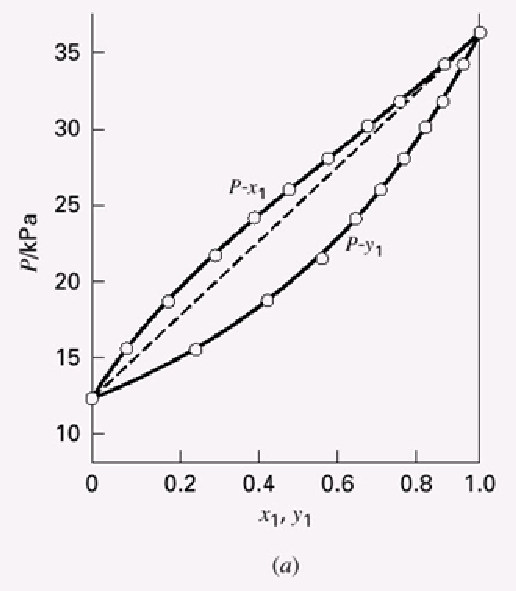
and replot the VLE diagrams for

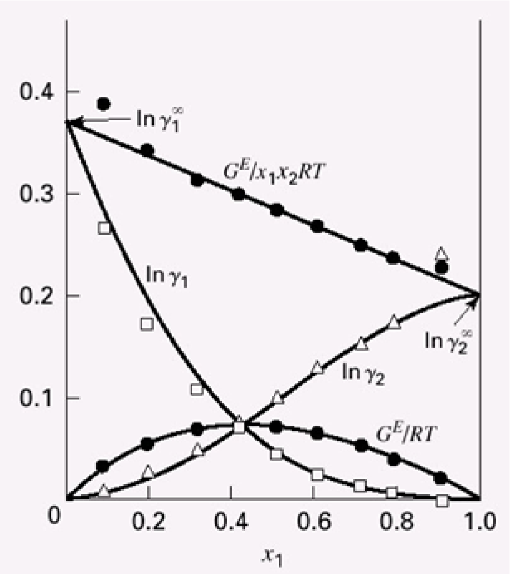
MEK / toluene system

These are represented by solid lines in Fig. 12.6 Observe that the correlations fit the data very well.

Data Reduction with Margules Equation

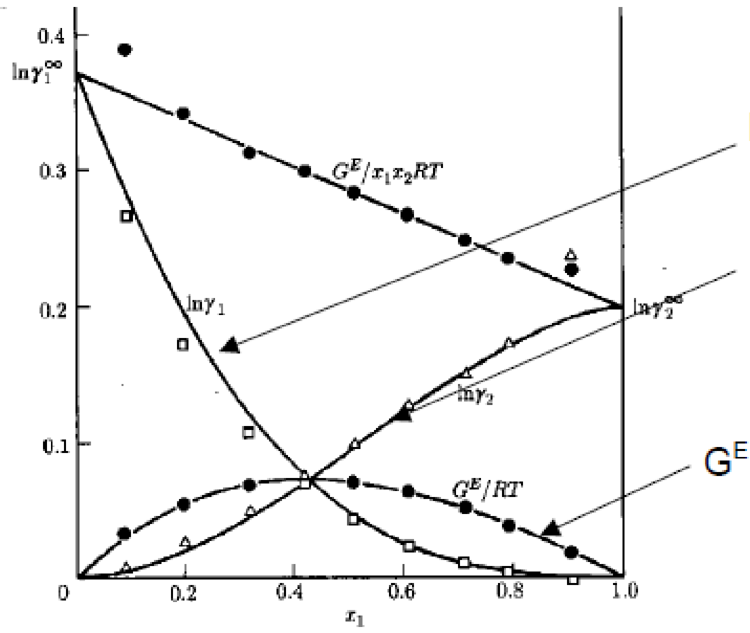
MEK / toluene system $A_{12} = 0.372$ $A_{21} = 0.198$





$$\frac{nG^E}{RT} = \left(0.198x_1 + 0.372x_2\right)x_1x_2$$

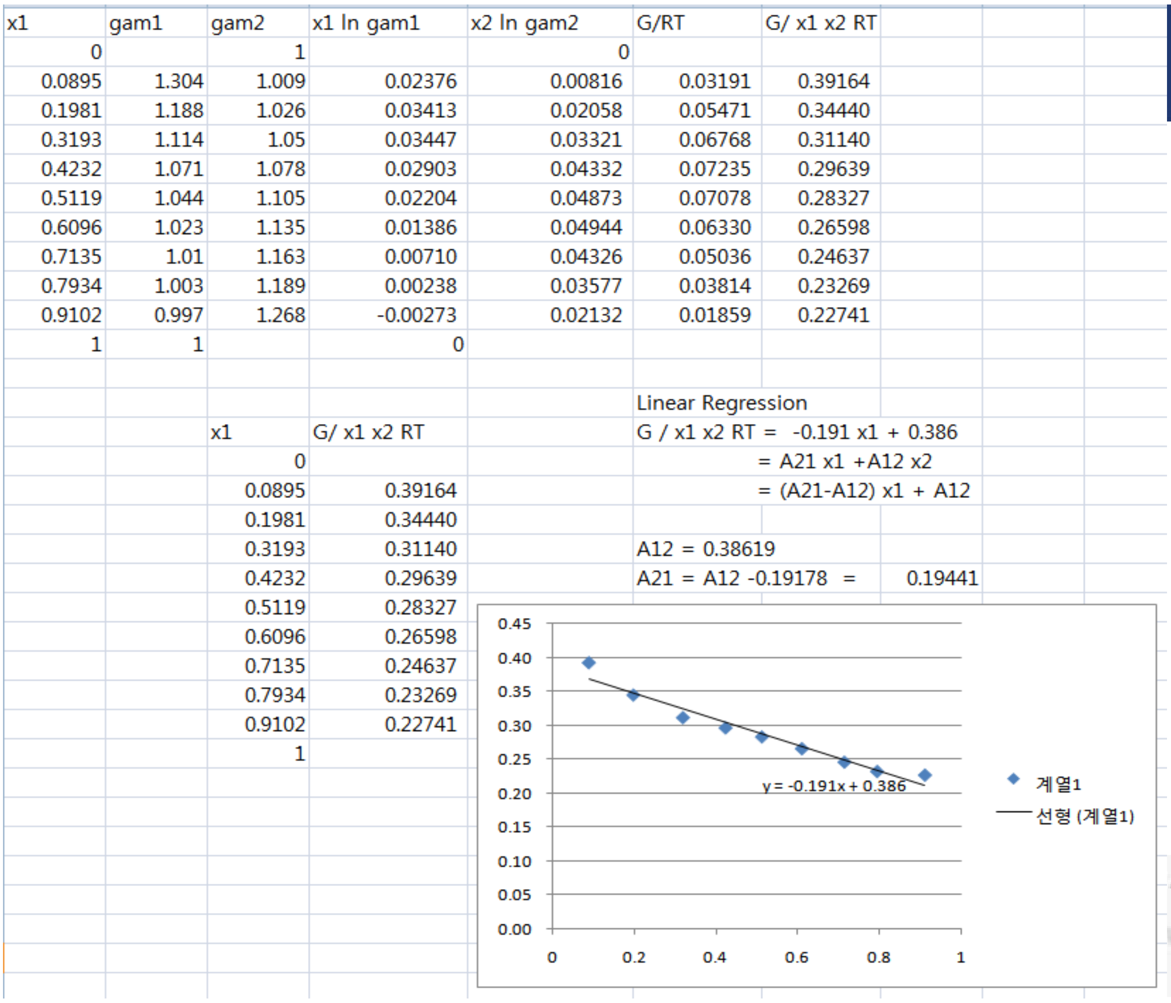
Data Reduction with Margules Equation



$$\ln \gamma_1 = \ln\left(\frac{y_1P}{x_1P_1^{sat}}\right)$$

$$\ln \gamma_2 = \ln\left(\frac{y_2P}{x_2P_2^{sat}}\right)$$

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$



x1	gam1	gam2	x1 ln gam1	x2 ln gam2	G/RT	G/ x1 x2 RT
0		1		0		
0.0895	1.304	1.009	0.02376	0.00816	0.03191	0.39164
0.1981	1.188	1.026	0.03413	0.02058	0.05471	0.34440
0.3193	1.114	1.05	0.03447	0.03321	0.06768	0.31140
0.4232	1.071	1.078	0.02903	0.04332	0.07235	0.29639
0.5119	1.044	1.105	0.02204	0.04873	0.07078	0.28327
0.6096	1.023	1.135	0.01386	0.04944	0.06330	0.26598
0.7135	1.01	1.163	0.00710	0.04326	0.05036	0.24637
0.7934	1.003	1.189	0.00238	0.03577	0.03814	0.23269
0.9102	0.997	1.268	-0.00273	0.02132	0.01859	0.22741
1	1		0			

x1	G/ x1 x2 RT
0	
0.0895	0.39164
0.1981	0.34440
0.3193	0.31140
0.4232	0.29639
0.5119	0.28327
0.6096	0.26598
0.7135	0.24637
0.7934	0.23269
0.9102	0.22741
1	

Linear Regression

G / x1 x2 RT = -0.191 x1 + 0.386

= A21 x1 +A12 x2

= (A21-A12) x1 + A12

A12 = 0.38619

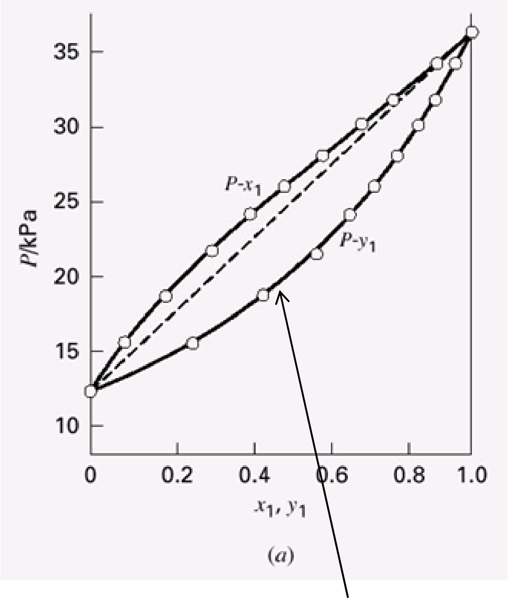
A21 = A12 -0.19178 = 0.19441

Correlation of P-x-y data

Modified Raoult's law

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

$$\Rightarrow \quad y_1 = \frac{x_1\gamma_1 P_1^{sat}}{x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}} \quad \textbf{(at fixed } T\textbf{)}$$



(solid lines obtained from BUBL P calculation)

- Vapor phase is assumed to be an ideal gas mixture
- Liquid phase nonideality is described by two-parameter Margules equation

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

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

- Optimal values of A_{21}, A_{12} reproduce experimental Pxy data

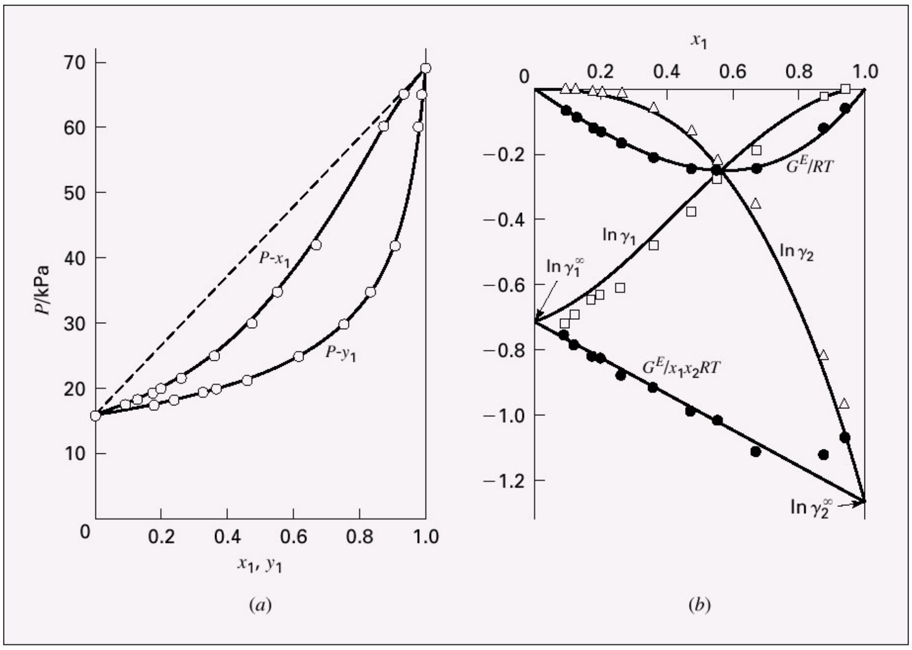
Correlation of P-x-y data

Table 12.3: VLE Data for Chloroform(1)/1,4-Dioxane(2) at 50°C

P/kPa	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	G^E/RT	G^E/x_1x_2RT
15.79(P_2^{sat})	0.0000	0.0000		0.000	0.000	
17.51	0.0932	0.1794	−0.722	0.004	−0.064	−0.758
18.15	0.1248	0.2383	−0.694	−0.000	−0.086	−0.790
19.30	0.1757	0.3302	−0.648	−0.007	−0.120	−0.825
19.89	0.2000	0.3691	−0.636	−0.007	−0.133	−0.828
21.37	0.2626	0.4628	−0.611	−0.014	−0.171	−0.882
24.95	0.3615	0.6184	−0.486	−0.057	−0.212	−0.919
29.82	0.4750	0.7552	−0.380	−0.127	−0.248	−0.992
34.80	0.5555	0.8378	−0.279	−0.218	−0.252	−1.019
42.10	0.6718	0.9137	−0.192	−0.355	−0.245	−1.113
60.38	0.8780	0.9860	−0.023	−0.824	−0.120	−1.124
65.39	0.9398	0.9945	−0.002	−0.972	−0.061	−1.074
69.36(P_1^{sat})	1.0000	1.0000	0.000		0.000	

Margules equation with $A_{21} = -0.72$ $A_{12} = -1.27$

Correlation of P-x-y data



(a) (b)

Figure 12.6: The chloroform(1)/1,4-dioxane(2) system at 50°C. (a) Pxy data and their correlation. (b) Liquid-phase properties and their correlation.

Models for the excess Gibbs energy

- G^E/RT is a function of T, P and composition, but is a very weak function of P (almost independent)

$$\frac{G^E}{RT} = g(x_1, x_2, \cdots, x_N) \qquad \textbf{const } T$$

Redlich/Kister expansion (power series)

$$\frac{G^E}{x_1 x_2 RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots \qquad \textbf{const } T$$

If $B = C = \cdots = 0$

$$\Rightarrow \quad \frac{G^E}{x_1 x_2 RT} = A$$

one-parameter Margules equation

Redlich/Kister expansion

$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2$$

symmetric

Infinite dilution activity coefficient

$$\ln \gamma_1^\infty = A \qquad \ln \gamma_2^\infty = A$$

If $C = \cdots = 0$

$$\Rightarrow \quad \frac{G^E}{x_1 x_2 RT} = A + B(x_1 - x_2)$$

$G^E/x_1 x_2 RT$ is linear in x_1. It is equivalent to

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

two-parameter Margules equation

Van Laar equation

Two-parameter model

- The first theoretical model for activity coefficient

$$\frac{x_1 x_2}{G^E/RT} = A' + B'(x_1 - x_2) = A'(x_1 + x_2) + B'(x_1 - x_2) = (A' + B')x_1 + (A' - B')x_2$$

$$A' + B' = 1/A'_{21} \qquad A' - B' = 1/A'_{12}$$

$$\frac{x_1 x_2}{G^E/RT} = \frac{x_1}{A'_{21}} + \frac{x_2}{A'_{12}} \qquad \text{or} \qquad \frac{G^E}{x_1 x_2 RT} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}$$

From

$$\ln \gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{P,T,n_j}$$

Van Laar equation

$$\Rightarrow \qquad \ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2} \qquad \ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}$$

Infinite dilution activity coefficient

$$\ln \gamma_1^{\infty} = A'_{12} \qquad \ln \gamma_2^{\infty} = A'_{21}$$

Concept of local composition models

- In liquid solutions, local compositions are different from overall mixture composition. Local compositions account for the short-range order, nonrandom orientations of molecules resulting from differences in molecular size and intermolecular forces.

Concept of local composition models

Bulk composition

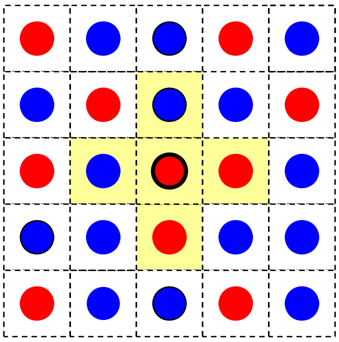
$x_1 = 10/25$

Local composition

$x_{11} = 2/4$

$x_{11} \neq x_1$

Red(1) / Blue(2)



- Nonrandom behavior caused by intermolecular interaction (e.g. red-red pairing is more favored than red-blue pairing)

Wilson equation

$$\frac{G^E}{RT} = -x_1 \ln\left(x_1 + x_2\Lambda_{12}\right) - x_2 \ln\left(x_2 + x_1\Lambda_{21}\right)$$

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

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

Concept of local composition models

- For infinite dilution

$$\ln\gamma_1^{\infty} = -\ln\Lambda_{12} + 1 - \Lambda_{21} \qquad \ln\gamma_2^{\infty} = -\ln\Lambda_{21} + 1 - \Lambda_{12}$$

$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\frac{-a_{ij}}{RT} \quad (i \neq j) \qquad (12.24) \qquad \Lambda_{ij} = 1 \text{ for } i = j.$$

- Local composition models can be generalized to multicomponent systems only with binary parameters.

NRTL equation (Non-Random-Two-Liquid)

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}}$$

$$\ln\gamma_1 = x_2^{\,2}\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{\left(x_2 + x_1 G_{12}\right)^2}\right] \qquad \ln\gamma_2 = x_1^{\,2}\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{\left(x_1 + x_2 G_{21}\right)^2}\right]$$

Concept of local composition models

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

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

α, b_{12}, b_{21} are parameters independent of T and composition

- Infinite dilution activity coefficient

$$\ln\gamma_1^{\infty} = \tau_{21} + \tau_{12}\exp(-\alpha\tau_{12}) \qquad \ln\gamma_2^{\infty} = \tau_{12} + \tau_{21}\exp(-\alpha\tau_{21})$$

Thermodynamic Consistency Tests

- The Gibbs–Duhem equation provides a general relation for the partial molar properties of different species in a mixture that must always be true.
- The activity coefficient of different species can be related to one another.
- Such interrelation can be used to judge the quality of experimental data.
- The development that follows is based on the relation between activity coefficients in a binary mixture of species a and b

the excess Gibbs energy for a binary mixture can be written as:

$$g^E = RT(x_a \ln\gamma_a + x_b \ln\gamma_b)$$

Differentiating with respect to x_a at constant T and P gives:

$$\frac{dg^E}{dx_a} = RT\left[\ln\gamma_a + x_a\frac{d\ln\gamma_a}{dx_a} - \ln\gamma_b + x_b\frac{d\ln\gamma_b}{dx_a}\right] = RT[\ln\gamma_a - \ln\gamma_b]$$

Thermodynamic Consistency Tests

where we have simplified this expression using the Gibbs–Duhem equation:

$$x_a\left(\frac{\partial \ln \gamma_a}{\partial x_a}\right)_{T,P} + x_b\left(\frac{\partial \ln \gamma_b}{\partial x_a}\right)_{T,P} = 0$$

➡

$$dg^E = RT\ln\left(\frac{\gamma_a}{\gamma_b}\right)dx_a$$

integrate over composition from pure b to pure a

$$\int_{\text{pure } b}^{\text{pure } a} dg^E = \int_{x_a=0}^{x_a=1} RT\ln\left(\frac{\gamma_a}{\gamma_b}\right)dx_a$$

Thermodynamic Consistency Tests

Since g^E is a state function, the integral on the left-hand side depends solely on its value at each limit of integration. If we use a Lewis/Randall reference state for both species, the value of g^E is zero for pure a and for pure b. The integral becomes zero,

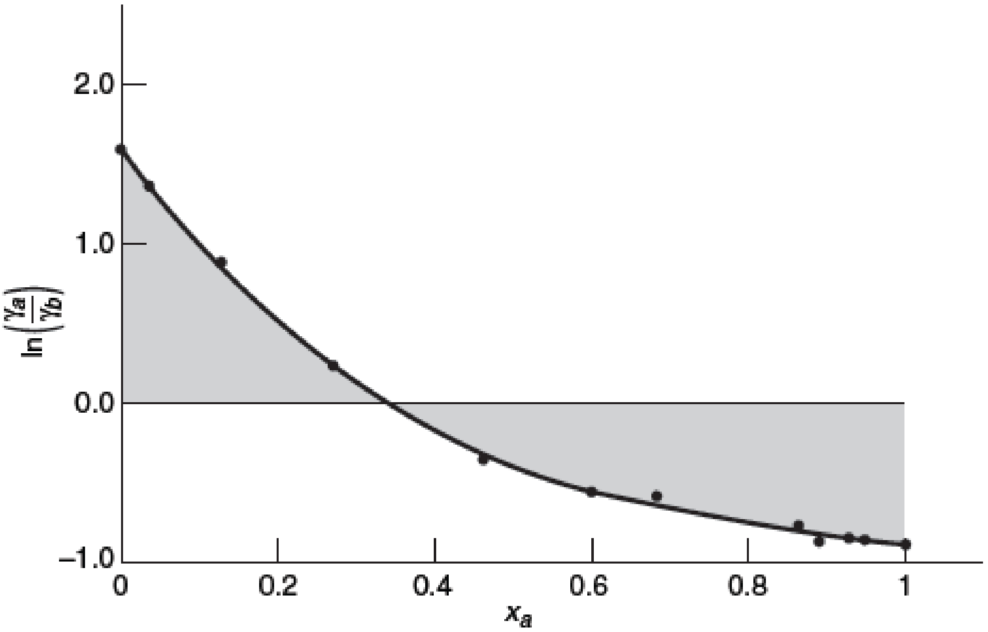
$$\int_0^1 \ln\left(\frac{\gamma_a}{\gamma_b}\right)dx_a = 0$$

- Therefore, to evaluate experimental data for thermodynamic consistency.

plot $\ln(\gamma_a/\gamma_b)$ vs. x_a, the area under the curve should be close to zero.

the *area test*.

Thermodynamic Consistency Tests



Area test for the thermodynamic consistency of a binary mixture of ethanol (a) in water (b) at 60°C.

Excursion

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

For ideal gas mixture, in equilibrium with non-ideal liquid solution $\Phi_i = 1$

$$\gamma_i x_i P_i^{sat} = y_i P \qquad \text{Modified Raoult's Law}$$

For ideal gas mixture in equilibrium with ideal liquid solution $\gamma_i = \Phi_i = 1$

$$x_i P_i^{sat} = y_i P \qquad \text{Raoult's Law}$$

Excursion

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

For VLE calculation, we need

$$\Phi_i = \Phi(T, P, y_1, y_2, \ldots y_{N-1})$$ such eqn 14.6

$$\gamma_i = \gamma(T, x_1, x_2, \ldots x_{N-1})$$ see chap 12 for correlations

$$P_i^{sat} = f(T)$$ such as Antoine Eqn

Excursion

Bubble point calculations

$$\sum_i x_i K_i = \sum x_i \frac{\gamma_i P_i^{sat}}{\Phi_i P} = 1 \qquad y_i = \frac{\gamma_i x_i P_i^{sat}}{\Phi_i P} \qquad (14.8)$$

Bubble pressure calculation,

$$P = \sum_i x_i \frac{\gamma_i P_i^{sat}}{\Phi_i} \qquad (14.10)$$

Bubble temperature calculation,

$$P_j^{sat} = \frac{P}{\sum_i \frac{x_i \gamma_i}{\Phi_i} \frac{P_i^{sat}}{P_j^{sat}}} \qquad (14.13)$$

Since $\{y_i\}$ is not known, we can't evaluate Φ_i . Calculation needs iteration (single loop). For algorithm, see the following Figure 14.1 and 14.3

Excursion

Bubble P calculations

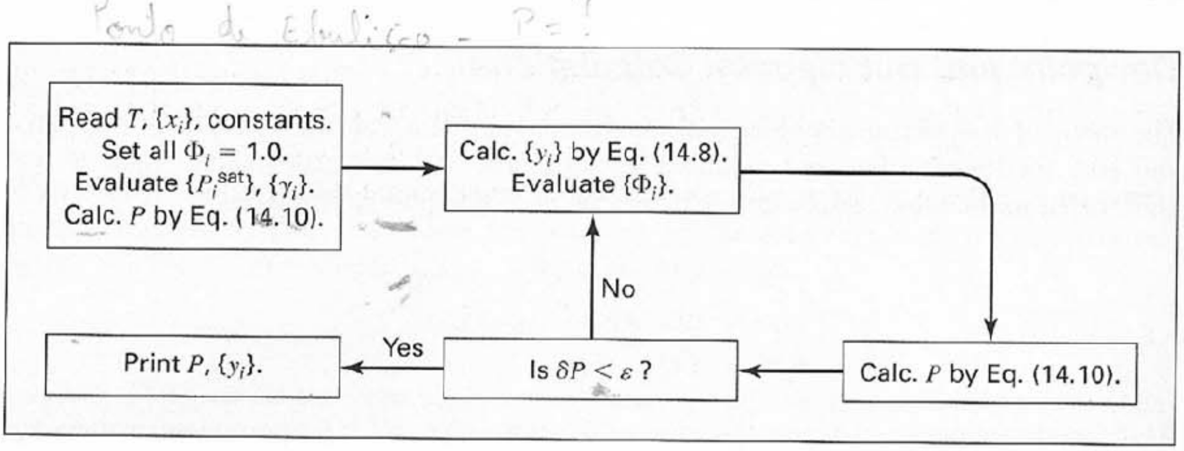


Figure 14.1: Block diagram for the calculation *BUBL P*.

Excursion

Bubble T calculations

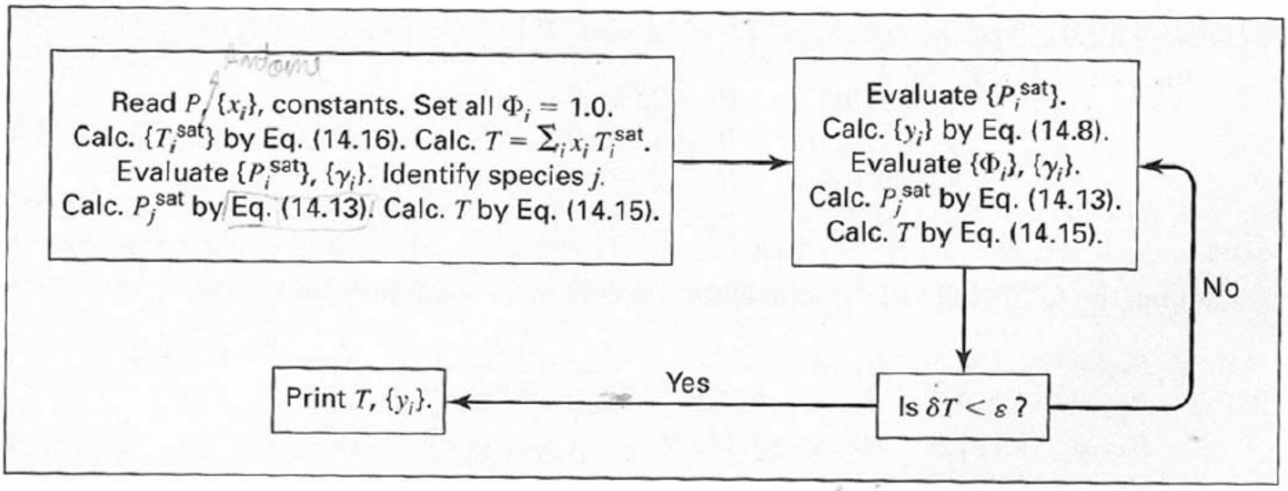


Figure 14.3: Block diagram for the calculation *BUBL T*.

Excursion

Dewpoint caclulations

$$\sum_i \frac{y_i}{K_i} = \sum \frac{y_i}{\dfrac{\gamma_i P_i^{sat}}{\Phi_i P}} = 1$$

$$x_i = \frac{y_i \Phi_i P}{\gamma_i P_i^{sat}} \qquad (14.9)$$

Dew pressure calculation,

$$P = \frac{1}{\sum \dfrac{y_i \Phi_i}{\gamma_i P_i^{sat}}} \qquad (14.11)$$

Since $\{x_i\}$ and P are not known, we can't evaluate Υ_i and ϕ_i . Calculation needs iteration (double loop).
For algorithm, see Figure 14.2

Dew temperature calculation,

$$P_j^{sat} = P \sum \frac{y_i \Phi_i}{\gamma_i} \frac{P_j^{sat}}{P_i^{sat}} \qquad (14.14)$$

Since $\{x_i\}$ and T are not known, we can't evaluate Υ_i and ϕ_i . Calculation needs iteration (double loop).
For algorithm, see Figure 14.4

Excursion

Dew p calculations

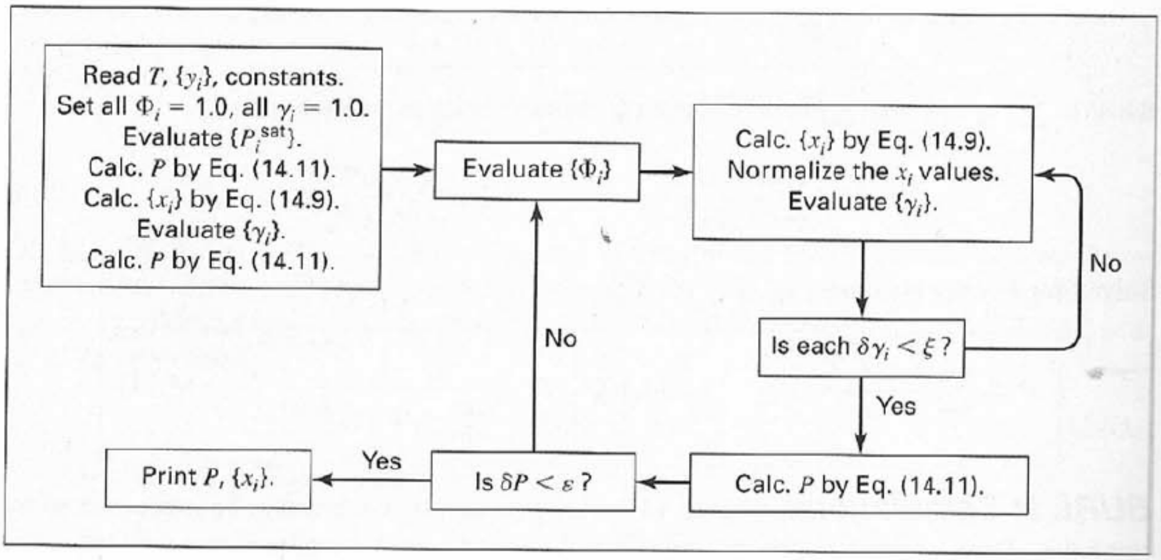


Figure 14.2: Block diagram for the calculation *DEW P*.

Excursion

Dew T calculations

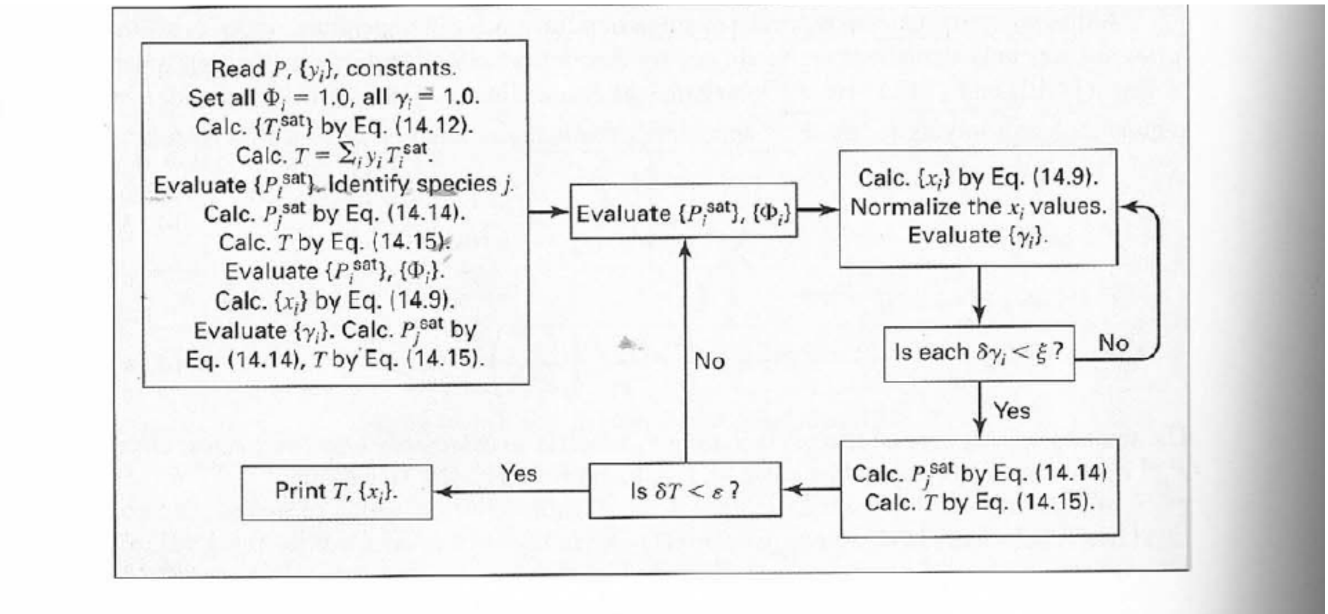


Figure 14.4: Block diagram for the calculation *DEW T*.

Excursion

Flash caclulations

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \qquad (10.16)$$

$$F_y = \sum y_i - 1 = \sum \frac{z_i K_i}{1 + V(K_i - 1)} - 1 = 0 \qquad (10.17) \text{ or } (14.17)$$

$$x_i = \frac{z_i}{1 + V(K_i - 1)} \qquad (14.16)$$

$$F_x = \sum x_i - 1 = \sum \frac{z_i}{1 + V(K_i - 1)} - 1 = 0 \qquad (10.17) \text{ or } (14.17)$$

Excursion

Flash caclulations

$$F = F_x - F_y = 0$$

$$F = \sum \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \qquad (14.19)$$

$$\frac{dF}{dV} = -\sum \frac{z_i(K_i - 1)^2}{\left[1 + V(K_i - 1)\right]^2} \qquad (14.20)$$

So, dF/dV is always negative, hence the F vs. V is monotonic.

This will give rapid convergence for iteration with Newton's method.

$$F + \left(\frac{dF}{dV}\right)\Delta V = F + \left(\frac{dF}{dV}\right)(V_{n+1} - V_n) = 0 \qquad (14.21)$$

Excursion

Flash caclulations

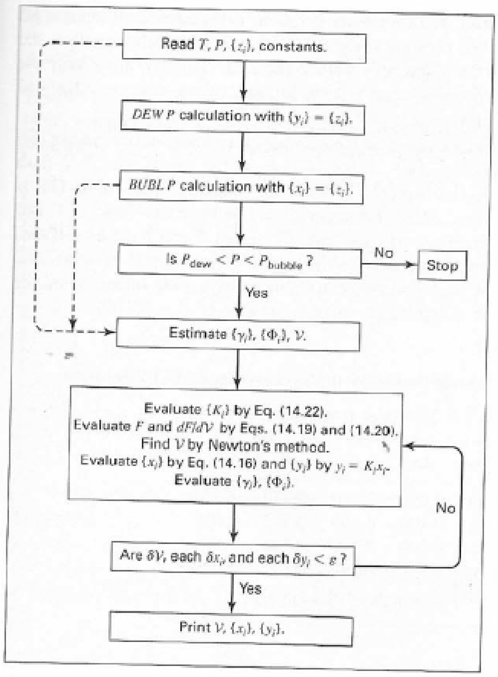


Figure 14.5: Block diagram for a P,T-flash calculation.

Project

The experimental VLE data for 2-propanol (1)/Water (2) at 45 °C are given in the table below.

1- Check the consistency of these data using the area test.

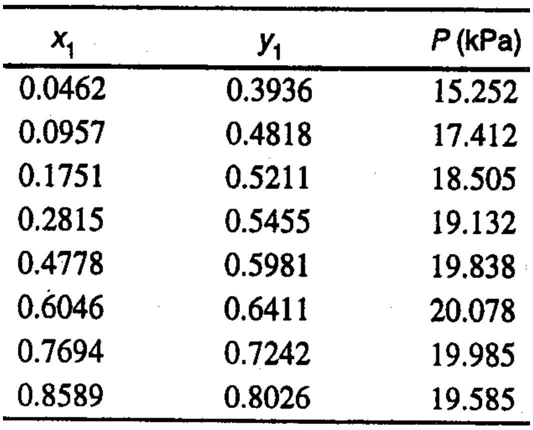
2- Is it possible to use the two-parameters Margules model for such system? Why? If yes, estimate the best parameters: A_{12} and A_{21}.

3- Is it possible to use Van Laar model for such system ? Why? If yes, estimate best parameters: A'_{12} and A'_{21}.

4- Construct the P-x-y diagram from the above two models and using the experimental data .

5- Plot $\ln\gamma_1$, $\ln\gamma_2$, and G^E/RT versus x_1 from the above two models and using the experimental data

- Comment on the results.



x_1	y_1	P (kPa)
0.0462	0.3936	15.252
0.0957	0.4818	17.412
0.1751	0.5211	18.505
0.2815	0.5455	19.132
0.4778	0.5981	19.838
0.6046	0.6411	20.078
0.7694	0.7242	19.985
0.8589	0.8026	19.585