

**Tsonopoulos Correlation * for Second Virial Coefficients
(nonpolar compounds)**

$$\frac{BP_c}{RT_c} = f^{(0)} + \omega f^{(1)}$$

where:

$$f^{(0)} = .1445 - \frac{.330}{T_R} - \frac{.1385}{T_R^2} - \frac{.0121}{T_R^3} - \frac{.000607}{T_R^8}$$

$$f^{(1)} = .0637 + \frac{.331}{T_R^2} - \frac{.423}{T_R^3} - \frac{.008}{T_R^8}$$

and where $T_R = T/T_c$

Second virial cross coefficients B_{ij} are calculated using the above equations along with the following combining rules for T_c , P_c and ω :

$$T_{c_{ij}} = (1 - k_{ij}) \sqrt{T_{c_i} T_{c_j}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$P_{c_{ij}} = \frac{4 T_{c_{ij}} \left(\frac{P_{c_i} V_{c_i}}{T_{c_i}} + \frac{P_{c_j} V_{c_j}}{T_{c_j}} \right)}{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^3}$$

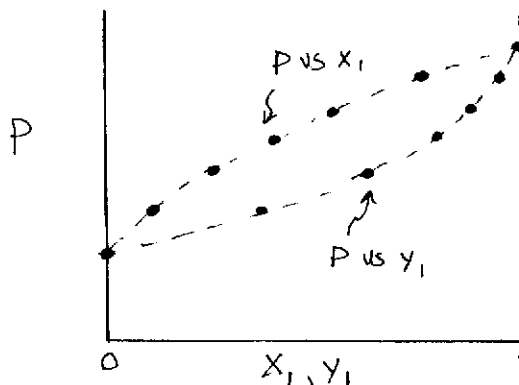
* Tsonopoulos, C. AIChE J. 20, 263, 1974.

Plotting more than one variable on the x-axis with TK

It seems like TK will not allow you to plot more than one variable on the x-axis, but it can be done. The following example will show how to do this. Suppose we have a set of vapor-liquid equilibrium data and we wish to plot it on a P-x-y graph. In this example, the data are:

x_1	y_1	P(bar)
.000	.000	4.46
.150	.486	8.62
.339	.716	13.79
.463	.802	17.24
.685	.906	24.13
.876	.968	31.03
1.000	1.000	36.33

We wish to plot P vs x_1 and P vs y_1 on the same graph like so:



The problem is that TK will only allow you to place one variable on the x-axis. We can get around this problem by defining new lists X and Y in the following way:

	X	Y	
x_1 Values	.000	4.46	P values
	.150	8.62	
	.339	13.79	
	.463	17.24	
	.685	24.13	
	.876	31.03	
	1.000	36.33	
y_1 Values	.000	4.46	P values
	.486	8.62	
	.716	13.79	
	.802	17.24	
	.906	24.13	
	.968	31.03	
	1.000	36.33	

Note that the first 7 values in X are the 7 x_1 values and the next 7 entries in X are the 7 values of y_1 . The first 7 values in Y are the 7 pressures and the next 7 entries in Y are a repeat of the same 7 pressures.

These new lists can be prepared using the listcopy function like so (placed on the rule sheet):

```
call listcopy ('x1, 'X, 1, 7, 1)
call listcopy ('y1, 'X, 1, 7, 8)
call listcopy ('p, 'Y, 1, 7, 1)
call listcopy ('p, 'Y, 1, 7, 8)
```

The first statement says take entries 1 through 7 of list x1 and copy them to the list X starting at position 1. The second line says take entries 1 through 7 of list y1 and copy them to X starting at position 8. Hence, at the end, list X will have 14 entries. The first 7 will be the x_1 values and the last 7 will be the y_1 values.

The last two lines do the analogous thing for list Y. It will consist of 7 values of p followed by the same 7 values of p.

Note: When you are doing the equilibrium calculations to generate the p-x-y results, comment out these listcopy lines. Then once the p-x-y lists have been generated, comment out all lines except the listcopy lines (and uncomment those) and hit f9 (not fl0) to generate the X and Y lists.

Now, on the plot sheet, indicate that X is to be plotted on the x-axis. On the y-axis, indicate that entries 1 through 7 of list Y are to be plotted and then, on the next line, indicate that entries 8 through 14 of list Y are to be plotted. For example:

<u>Y Axis</u>	<u>Style</u>	<u>Character</u>	<u>Symbol Count</u>	<u>First</u>	<u>Last</u>
Y	symbol	*		1	7
Y	symbol	o		8	14

In this example, this will result in a P-x curve indicated by symbols * and a P-y curve indicated by symbol o.

This idea can be extended to plot four curves: an experimental P-x, an experimental P-y, a calculated P-x and a calculated P-y. With this technique, it is easy to represent the calculated results by curves and the experimental results by symbols.

Important Relations for G^E and γ_i

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (1)$$

Use: Allows values of G^E to be calculated from experimental values of the activity coefficients.

$$-\frac{H^E}{RT^2} dT + \frac{V^E}{RT} dP - \sum x_i d \ln \gamma_i = 0 \quad (2)$$

Gibbs-Duhem equation. Use: Allows experimentally determined values for activity coefficients to be tested for thermodynamic consistency. Generally applied at constant T with V^E neglected.

$$\left(\frac{\partial n G^E / RT}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \ln \gamma_i \quad (3)$$

Use: Allows algebraic expressions for the activity coefficients to be obtained from an algebraic expression for G^E .

$$\left(\frac{\partial G^E / RT}{\partial P} \right)_{T, n} = \frac{V^E}{RT} \quad (4)$$

$$\left(\frac{\partial G^E / RT}{\partial T} \right)_{P, n} = -\frac{H^E}{RT^2} \quad (5)$$

Use: These give the pressure and temperature dependence of G^E . The first (eqn 4) is not generally used since we neglect the pressure dependence of G^E . This corresponds to assuming $V^E = 0$. The second equation (eqn 5) provides a relationship between vapor-liquid equilibrium data and heat of mixing data.

$$\hat{f}_i = \gamma_i x_i f_i \quad (6)$$

Use: relates activity coefficient γ_i of species i in mixture to the fugacity \hat{f}_i of species i in mixture

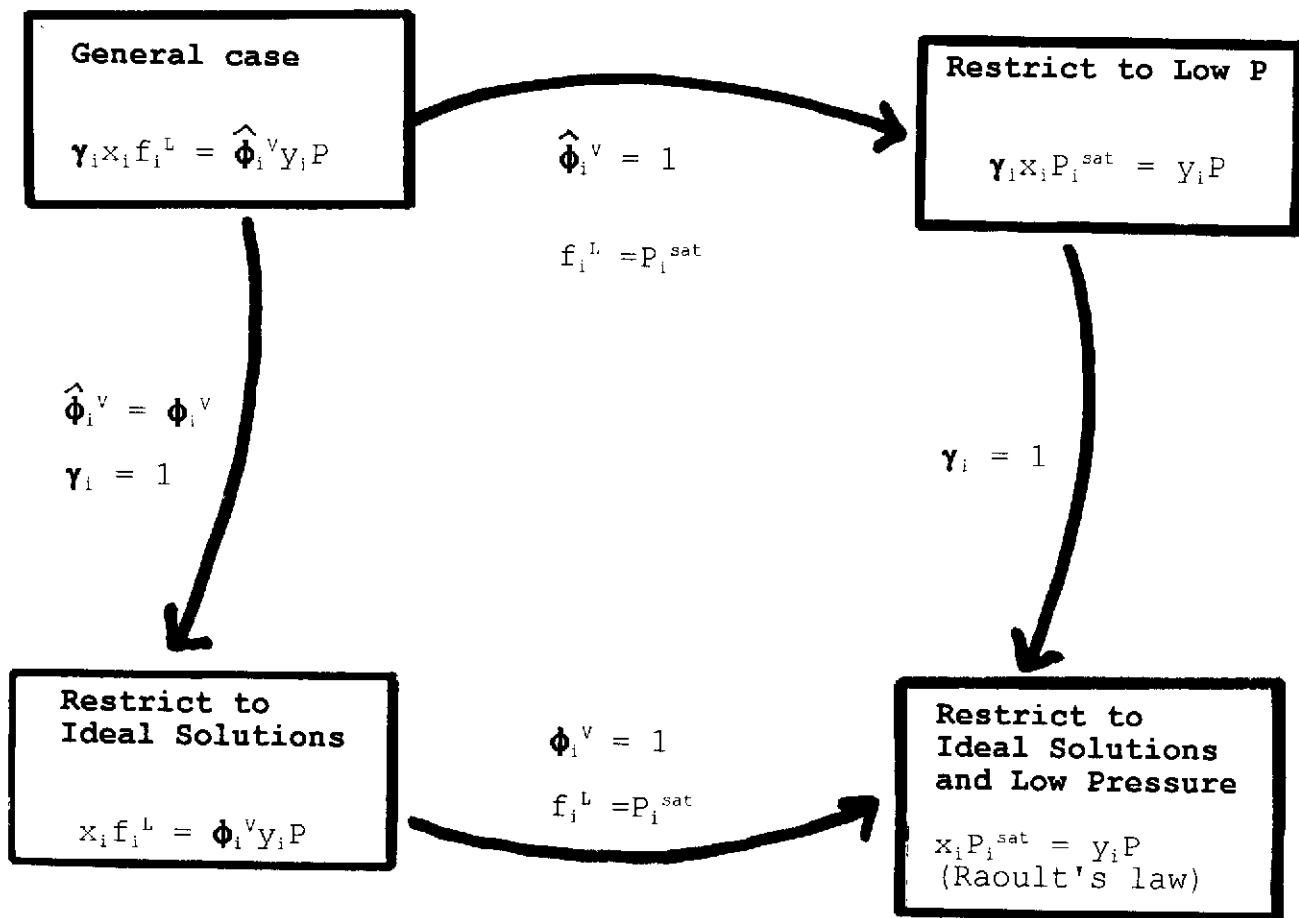
Various Approximations in the Gamma-Phi Method

$$f_i^L = \phi_i^{sat} P_i^{sat} \exp(V_i^L [P - P_i^{sat}] / RT)$$

$$\ln \hat{\phi}_i^V = \int_0^P (\bar{Z}_i - 1) / P \, dP$$

$$\ln \phi_i^V = \int_0^P (Z_i - 1) / P \, dP$$

$$\ln \phi_i^{sat} = \int_0^{P_i^{sat}} (Z_i - 1) / P \, dP$$



G^E , $\ln \gamma_1$ and $\ln \gamma_2$
for binary systems

Activity Coefficient
Models

Equation	G^E/RT	Parameters	$\ln \gamma_1$ and γ_2
2-Suffix Margules	$A_{12}x_1x_2$	A	Ax_2^2 Ax_1^2
Margules (3 Suffix)	$x_1x_2(A_{21}x_1 + A_{12}x_2)$	A_{12} A_{21}	$[A_{12} + 2(A_{21} - A_{12})x_1]x_2^2$ $[A_{21} + 2(A_{12} - A_{21})x_2]x_1^2$
van Laar	$1/(1/A_{12}x_1 + 1/A_{21}x_2)$	A_{12} A_{21}	$A_{12} \left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2} \right)^2$ $A_{21} \left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2} \right)^2$
Wilson	$-x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2)$	Λ_{12} Λ_{21}	$-\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$ $-\ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$
NRTL	$x_1x_2 \left[\frac{\tau_{21}G_{21}}{x_1 + G_{21}x_2} + \frac{\tau_{12}G_{12}}{G_{12}x_1 + x_2} \right]$	τ_{12} τ_{21} α_{12}	$x_2^2 \left[\frac{G_{21}}{x_1 + x_2G_{21}} \right]^2 + \left(\frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2} \right)$ $x_1^2 \left[\frac{G_{12}}{x_2 + x_1G_{12}} \right]^2 + \left(\frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2} \right)$ $G_{12} = \exp(-\alpha_{12}\tau_{12})$ $G_{21} = \exp(-\alpha_{21}\tau_{21})$

Note: $\alpha_{12} = \alpha_{21}$ but $\tau_{12} \neq \tau_{21}$

G^E , $\ln \gamma_1$ and $\ln \gamma_2$
for Binary Systems

Equation	G^E/RT	Parameters	$\ln \gamma_1$ and γ_2
UNIQUAC	$x_1 \left[\ln \frac{\phi_1}{x_1} + \frac{q_1 z}{2} \ln \frac{\theta_1}{\phi_1} - q_1 \ln(\theta_1 + \theta_2 \tau_{21}) \right]$ $+ x_2 \left[\ln \frac{\phi_2}{x_2} + \frac{q_2 z}{2} \ln \frac{\theta_2}{\phi_2} - q_2 \ln(\theta_1 \tau_{12} + \theta_2) \right]$	τ_{12} τ_{21}	$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R$ $\ln \gamma_1^C = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + \varphi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right)$ $\ln \gamma_1^R = -q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \vartheta_2 q_2 \left(\frac{\tau_{21}}{\theta_1 + \vartheta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_1 \tau_{12} + \vartheta_2} \right)$ $\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R$ $\ln \gamma_2^C = \ln \frac{\phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2} + \varphi_1 \left(l_2 - \frac{r_2}{r_1} l_1 \right)$ $\ln \gamma_2^R = -q_2 \ln(\theta_1 \tau_{12} + \vartheta_2) + \vartheta_1 q_2 \left(\frac{\tau_{12}}{\theta_1 \tau_{12} + \vartheta_2} - \frac{\tau_{21}}{\vartheta_1 + \vartheta_2 \tau_{21}} \right)$
			$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad z = 10$
			q_i area parameter of component i
			r_i volume parameter of component i
			u_{ij} parameter of interaction between components i and j ; $u_{ij} = u_{ji}$
			z coordination number
			γ_1^C combinatorial part of activity coefficient of component i
			γ_1^R residual part of activity coefficient of component i
			$\delta_i = \frac{q_i x_i}{\sum_j q_j x_j}$ area fraction of component i
			$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$ volume fraction of component i

Binary Activity-Coefficient Correlations at Infinite Dilution

Two Suffix Margules (Porter)

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

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

van Laar & Margules (3 Suffix)

$$A_{12} = \ln \gamma_1^\infty$$

$$A_{21} = \ln \gamma_2^\infty$$

Wilson

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

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

NRTL

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

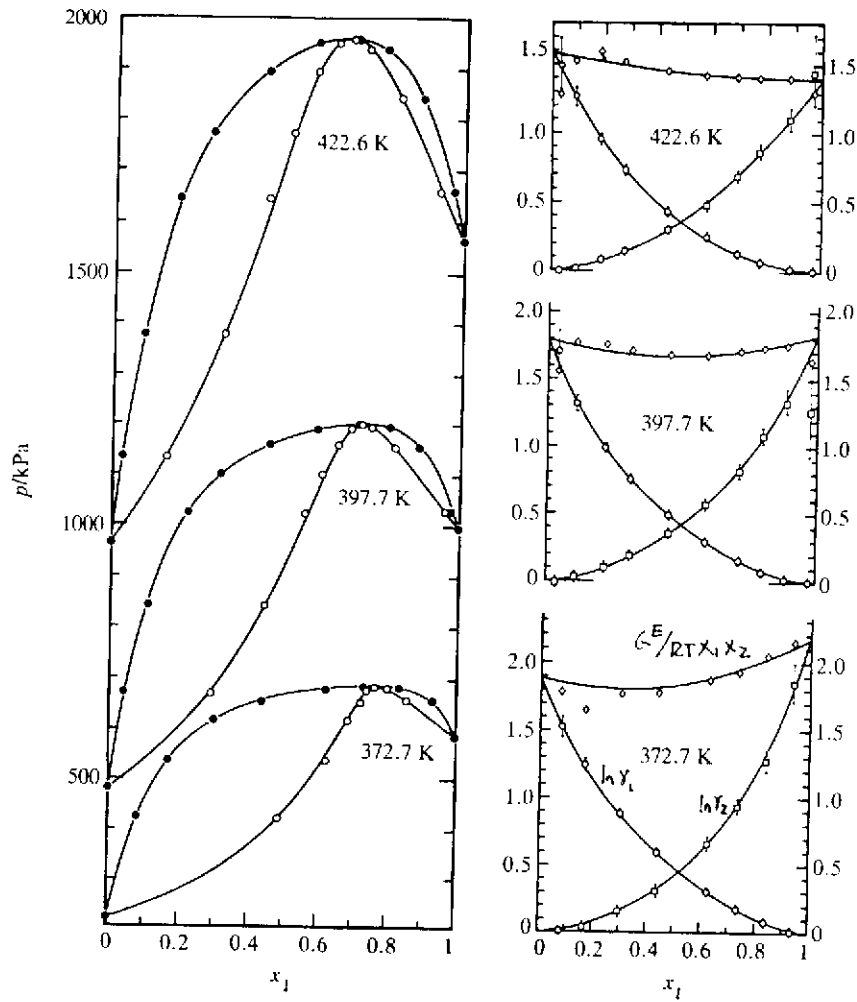
$$\tau_{12} + \tau_{21} \exp(-\alpha_{12} \tau_{21}) = \ln \gamma_2^\infty$$

UNIQUAC

$$\ln \gamma_1^\infty = \ln \left(\frac{r_1}{r_2} \right) + \frac{z}{2} q_1 \ln \left(\frac{q_1 r_2}{q_2 r_1} \right) + l_1 - \frac{r_1}{r_2} l_2 - q_1 \ln \tau_{21} + q_1 (1 - \tau_{12})$$

$$\ln \gamma_2^\infty = \ln \left(\frac{r_2}{r_1} \right) + \frac{z}{2} q_2 \ln \left(\frac{q_2 r_1}{q_1 r_2} \right) + l_2 - \frac{r_2}{r_1} l_1 - q_2 \ln \tau_{12} + q_2 (1 - \tau_{21})$$

A System with Positive Deviations from Ideality



n-pentane (1) - Ethanol (2)

$\ln \gamma = 2$ corresponds to $\gamma = 7.4$

A System with Negative Deviations from Ideality

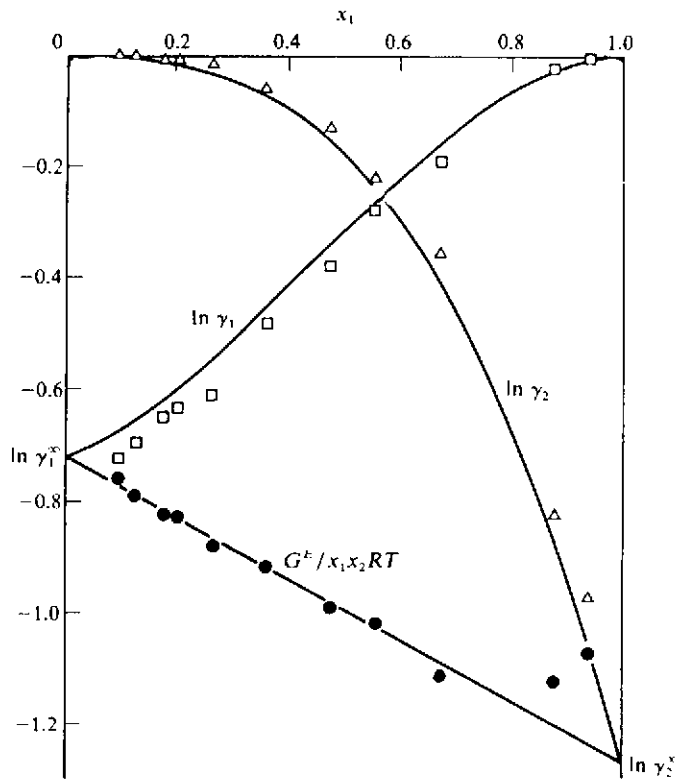
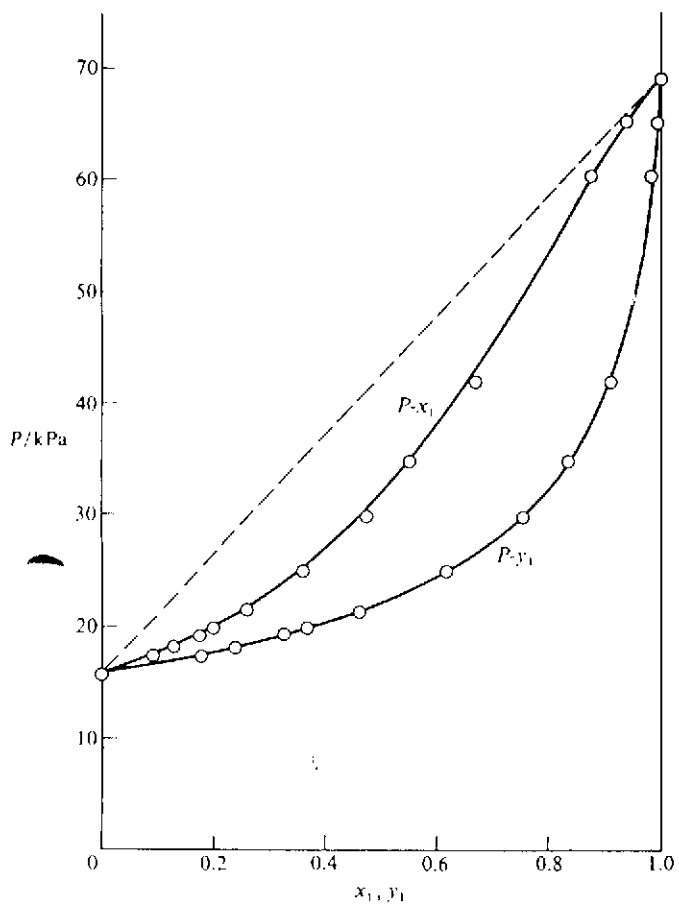


Figure 11.9 Pxy data at 50°C for chloroform(1)/1,4-dioxane(2).

A Nearly Ideal System

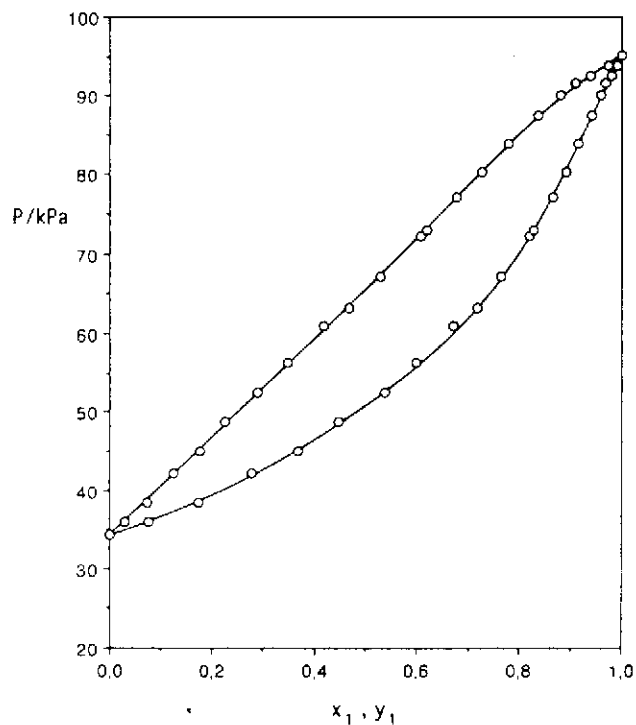
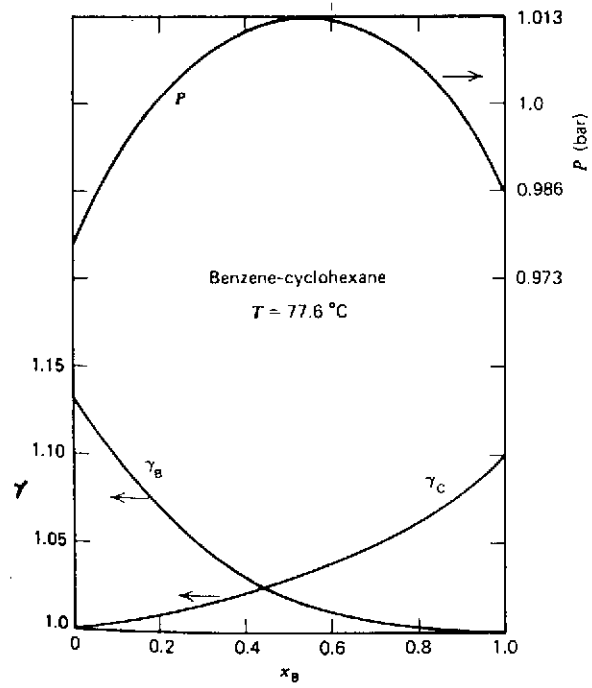


Figure 1. Vapor-liquid equilibrium data for 2-methyl-2-butanol (1) + 2-methyl-1-butanol (2) at 373.15 K.

Table 1. Vapor-Liquid Equilibrium Data for the 2-Methyl-2-butanol (1) + 2-Methyl-1-butanol (2) at 373.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	34.35		
0.030	0.075	35.93	0.931	0.979
0.074	0.173	38.36	0.929	0.978
0.126	0.279	42.10	0.951	0.976
0.177	0.369	45.00	0.969	0.981
0.226	0.447	48.77	0.995	0.989
0.291	0.538	52.54	1.000	0.970
0.349	0.599	56.26	0.993	0.980
0.418	0.670	60.87	1.001	0.974
0.467	0.717	63.10	0.993	0.944
0.530	0.765	67.09	0.991	0.943
0.606	0.820	72.15	0.997	0.925
0.618	0.827	72.97	0.997	0.927
0.676	0.865	77.00	1.005	0.898
0.727	0.893	80.35	1.005	0.880
0.778	0.915	83.80	1.002	0.895
0.838	0.942	87.50	0.999	0.872
0.881	0.959	90.00	0.994	0.862
0.911	0.969	91.50	0.987	0.885
0.940	0.980	92.50	0.977	0.856
0.973	0.991	93.85	0.998	0.867
1.000	1.000	95.18		

A Nearly Ideal System with an Azeotrope



Gibbs Energies and P-x-y Diagrams for Several Systems

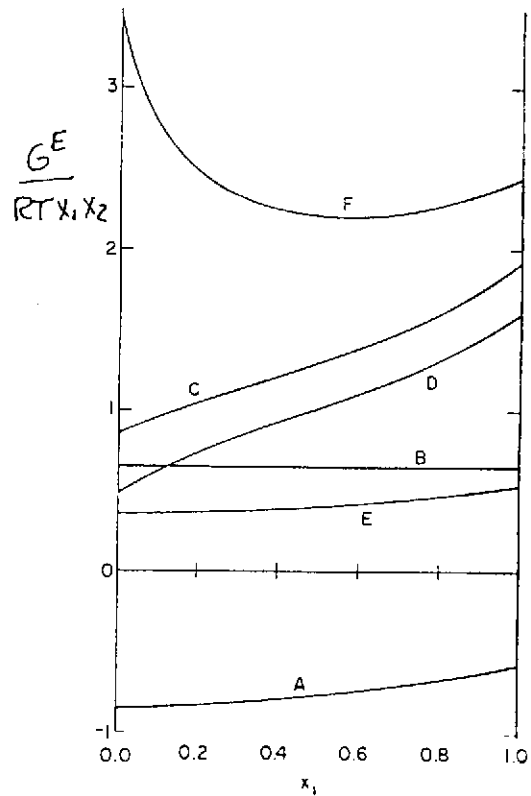


Fig. 10. g/x_1x_2 vs. x_1 at 50°C representing correlations for (A) acetone-chloroform, (B) acetone-methanol, (C) chloroform-methanol, (D) chloroform-ethanol, (E) chloroform-n-heptane, and (F) ethanol-n-heptane. First named compound is component 1

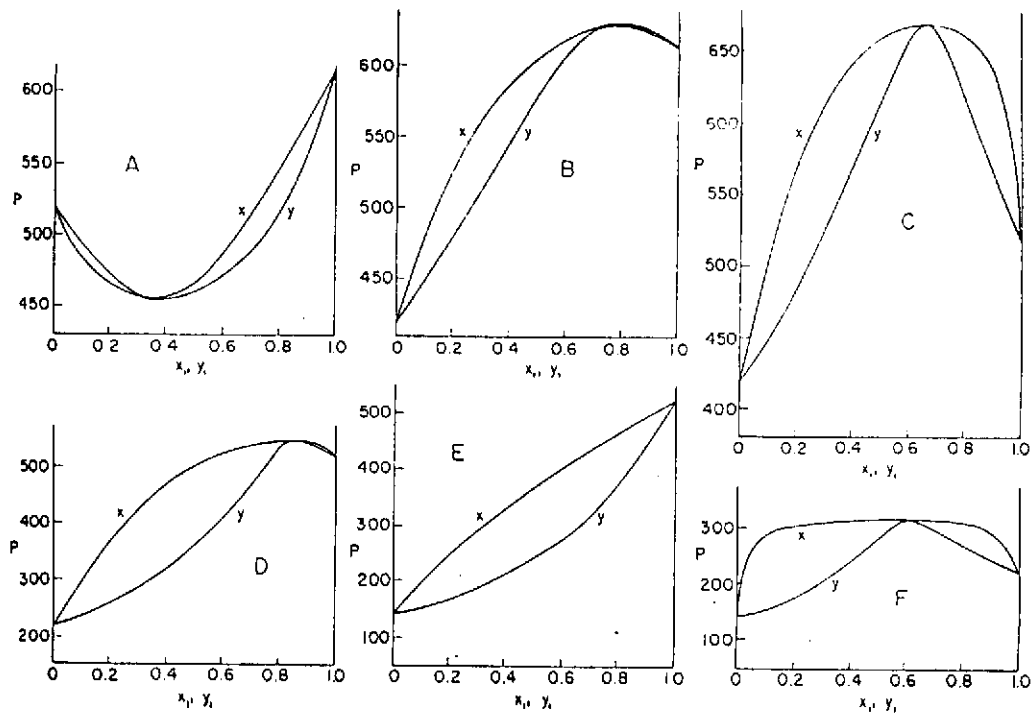
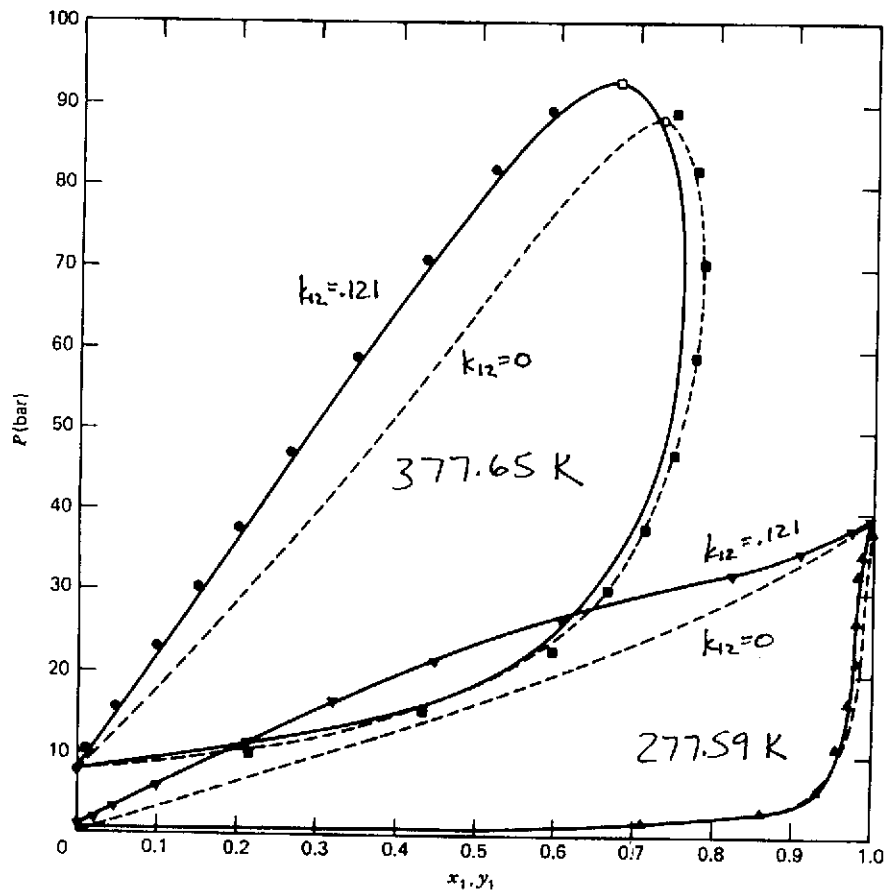


Fig. 11. P-x-y diagrams at 50°C for (A) acetone-chloroform, (B) acetone-methanol, (C) chloroform-methanol, (D) chloroform-ethanol, (E) chloroform-n-heptane, and (F) ethanol-n-heptane. First named compound is component 1. P is in mm Hg.

Illustration of the Importance of Binary Interaction Coefficients for VLE from Cubic Equations of State



Vapor-liquid equilibrium of the carbon dioxide (1)-isopentane system. The experimental data of G. J. Besserer and D. B. Robinson [*J. Chem. Eng. Data* **20**, 93 (1976)] are shown at 277.59 K (∇ = liquid and \blacktriangle = vapor) and 377.65 K (\bullet = liquid and \blacksquare = vapor). The dashed curves are the predictions using the Peng-Robinson equation of state with $k_{12} = 0$, and the solid lines are the correlation using the same equation of state with $k_{12} = 0.121$. The points \circ and \square are the estimated mixture critical points at 377.65 K using the same equation of state with $k_{12} = 0$ and 0.121, respectively.

Temperature Dependence of the Equilibrium Constant

$$\ln\left(\frac{K(T)}{K(298)}\right) = \frac{\Delta H_{298}^{\circ}}{RT^{*}}\left(1 - \frac{1}{x}\right) + \Delta A\left(\frac{1}{x} - 1 + \ln x\right) + \frac{T^{*}\Delta B}{2}\left(x + \frac{1}{x} - 2\right) \\ + \frac{T^{*2}\Delta C}{3}\left(\frac{x^2}{2} + \frac{1}{x} - \frac{3}{2}\right) + \frac{\Delta D}{2T^{*2}}\left(\frac{1}{x^2} - \frac{2}{x} + 1\right)$$

where

$$x = T/T^{*} \quad \text{where } T^{*} = 298.15 \text{ K} \quad \text{and } T \text{ is in K}$$

$$\Delta H_{298}^{\circ} = \sum \nu_i \Delta H_{f,i,298}^{\circ}$$

$$K(298) = \exp[-\Delta G_{298}^{\circ}/(298.15 \text{ R})] \quad \text{where } \Delta G_{298}^{\circ} = \sum \nu_i \Delta G_{f,i,298}^{\circ}$$

and where

$$\Delta F = \sum \nu_i F_i \quad \text{where } F = A, B, C \text{ and } D$$

and where A_i , B_i , C_i , and D_i are the coefficients in the heat capacity expressions for pure i in its standard state:

$$C_{p,i}/R = A_i + B_i T + C_i T^2 + D_i/T^2$$