

**Table IX. Comparison of Calculated and Experimental Results from Program BUBL P**

*n*-Pentane(1)-*n*-Butane(2)-Propane(3)-Ethane(4)-Methane(5)<sup>a</sup>

Given		Calculated		Experimental	
<i>T</i> , °F	100	<i>P</i> , psia	289	<i>P</i> , psia	289
<i>x</i> <sub>1</sub>	0.488	<i>y</i> <sub>1</sub>	0.0424	<i>y</i> <sub>1</sub>	0.033
<i>x</i> <sub>2</sub>	0.213	<i>y</i> <sub>2</sub>	0.0526	<i>y</i> <sub>2</sub>	0.044
<i>x</i> <sub>3</sub>	0.120	<i>y</i> <sub>3</sub>	0.0877	<i>y</i> <sub>3</sub>	0.091
<i>x</i> <sub>4</sub>	0.115	<i>y</i> <sub>4</sub>	0.2371	<i>y</i> <sub>4</sub>	0.233
<i>x</i> <sub>5</sub>	0.064	<i>y</i> <sub>5</sub>	0.5802	<i>y</i> <sub>5</sub>	0.599
<i>T</i> , °F	100	<i>P</i> , psia	85	<i>P</i> , psia	96
<i>x</i> <sub>1</sub>	0.802	<i>y</i> <sub>1</sub>	0.1678	<i>y</i> <sub>1</sub>	0.129 <sup>b</sup>
<i>x</i> <sub>2</sub>	0.114	<i>y</i> <sub>2</sub>	0.0733	<i>y</i> <sub>2</sub>	0.068
<i>x</i> <sub>3</sub>	0.045	<i>y</i> <sub>3</sub>	0.0916	<i>y</i> <sub>3</sub>	0.089
<i>x</i> <sub>4</sub>	0.023	<i>y</i> <sub>4</sub>	0.1499	<i>y</i> <sub>4</sub>	0.144
<i>x</i> <sub>5</sub>	0.016	<i>y</i> <sub>5</sub>	0.5175	<i>y</i> <sub>5</sub>	0.570 <sup>b</sup>
<i>T</i> , °F	200	<i>P</i> , psia	771	<i>P</i> , psia	782
<i>x</i> <sub>1</sub>	0.356	<i>y</i> <sub>1</sub>	0.0913	<i>y</i> <sub>1</sub>	0.068
<i>x</i> <sub>2</sub>	0.222	<i>y</i> <sub>2</sub>	0.1076	<i>y</i> <sub>2</sub>	0.097
<i>x</i> <sub>3</sub>	0.160	<i>y</i> <sub>3</sub>	0.1417	<i>y</i> <sub>3</sub>	0.130
<i>x</i> <sub>4</sub>	0.126	<i>y</i> <sub>4</sub>	0.1860	<i>y</i> <sub>4</sub>	0.194
<i>x</i> <sub>5</sub>	0.136	<i>y</i> <sub>5</sub>	0.4734	<i>y</i> <sub>5</sub>	0.511

<sup>a</sup> Reference 10.

<sup>b</sup> See discussion in the text.

The main use of our equations for data reduction follows from their generalization to multicomponent mixtures. With the help of an electronic computer, it is possible to make good estimates of multicomponent phase behavior including the critical region using only the results of binary data reduction. Details of such calculations, including computer programs, are presented in a forthcoming monograph (26).

Since our method requires a considerable amount of binary data, our calculated results for binary systems are almost always more accurate than those obtained by other calculation methods. In a recent review (7) it was shown that common calculation methods can predict *K* factors for binary systems containing paraffins and olefins with root-mean-square deviations

averaging 7 to 20% and sometimes more, depending on the particular method and on the conditions; in the critical region errors are often much larger.

For systems containing nitrogen, carbon dioxide, acetylene, hydrogen sulfide, or hydrogen, common computational methods frequently give large errors of the order of 20% and sometimes errors exceeding 100% (7).

Our method of calculation for binary systems gives *K* factors generally accurate to within a root-mean-square deviation of 3 to 4% provided some good binary experimental data are available for data reduction. This low root-mean-square deviation is only slightly larger for the critical region and for systems containing one or more of the frequently encountered components in petroleum refining outside the paraffin-olefin class.

While it is difficult to generalize, for multicomponent mixtures common calculational methods can predict *K* factors for mixtures containing paraffins or olefins with a root-mean-square deviation of about 15 to 30%, depending on the method and on the conditions (7). For systems containing nitrogen, the errors are only slightly larger; however, for systems containing carbon dioxide, acetylene, hydrogen sulfide, or hydrogen, errors are often much larger (7) especially if the Benedict-Webb-Rubin equation is used or if the Chao-Seader correlation is used at low temperatures.

We estimate that our predicted *K* factors for multicomponent systems have a root-mean-square deviation between 4 and 8%; the lower figure pertains to systems for which there are good binary data and for the region not immediately in the critical. The higher figure pertains to those systems where binary data are sparse and to the region very close to the critical. The general-

**Table X. Comparison of Calculated and Experimental Results from Program BUBL T**

*n*-Pentane(1)-Propane(2)-Methane(3) System

Given				Calculated				Experimental <sup>a</sup>			
P, psia	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	T, ° R	y <sub>1</sub>	y <sub>2</sub>	y <sub>3</sub>	T, ° R	y <sub>1</sub>	y <sub>2</sub>	y <sub>3</sub>
500	0.533	0.355	0.112	619.0	0.092	0.302	0.606	619.7	0.091	0.297	0.612
500	0.362	0.543	0.095	619.9	0.069	0.452	0.479	619.7	0.067	0.461	0.472
500	0.678	0.170	0.152	561.9	0.047	0.087	0.866	559.7	0.049	0.085	0.866
500	0.384	0.577	0.039	679.0	0.152	0.677	0.171	679.7	0.153	0.680	0.167
1000	0.443	0.296	0.261	620.1	0.079	0.178	0.743	619.7	0.080	0.168	0.752
1000	0.298	0.447	0.255	620.3	0.063	0.279	0.658	619.7	0.066	0.277	0.657
1000	0.555	0.139	0.306	564.2	0.043	0.058	0.899	559.7	0.043	0.056	0.901
1000	0.616	0.154	0.230	680.1	0.187	0.129	0.684	679.7	0.181	0.122	0.697
1500	0.482	0.121	0.397	619.9	0.104	0.069	0.828	619.7	0.103	0.068	0.829
1500	0.213	0.320	0.467	558.8	0.037	0.176	0.787	559.7	0.046	0.160	0.794
1500	0.501	0.125	0.374	676.1	0.195	0.095	0.710	679.7	0.206	0.099	0.695

<sup>a</sup> References 4, 11.



ity of our method readily permits application without serious loss of accuracy to systems containing nonpolar (or slightly polar) components outside the paraffin-olefin class.

Our calculated results are generally more accurate than those using common techniques for two reasons: first, our method uses to the fullest possible extent all the thermodynamic tools that have recently become available; of these tools, the new technique for estimating liquid partial molar volumes is especially important. Second, our method avoids arbitrary hypothetical standard states and is based on careful reduction of binary experimental data. The literature is already rich with binary data and more binary experimental results are appearing regularly. The philosophical basis of our method follows from our conviction that whereas it is extremely difficult to predict phase behavior from pure-component data alone, we may expect with few exceptions to predict with confidence multicomponent behavior from at least some binary data in addition to pure-component data, provided we are willing to make an effort to take thermodynamics seriously.

## Nomenclature

$a, b$	= constants in Redlich-Kwong equation of state
$A, B$	= binary parameters given by Equations 34 and 35
$f$	= fugacity
$f^0$	= reference fugacity
$g^E$	= excess Gibbs energy in symmetric convention
$g^{E*}$	= excess Gibbs energy in unsymmetric convention
$g_{(MS)}^{E*}$	= excess Gibbs energy (unsymmetric convention) relative to the mixed solvent
$H_{2(1)}$	= Henry's constant for solute 2 in solvent 1
$k_{ij}$	= characteristic constant for $i$ - $j$ interaction
$n_i$	= number of moles of component $i$
$n_T$	= total number of moles
$N$	= number of components
$NS$	= number of solvent-components
$P$	= total pressure
$P_c$	= critical pressure
$P_{cij}$	= critical pressure characteristic of the $i$ - $j$ interaction
$P^r$	= constant reference pressure
$PO$	= a constant reference pressure of zero
$q$	= effective molar volume
$R$	= gas constant
$T$	= temperature
$T_c$	= critical temperature
$T_{cij}$	= critical temperature characteristic of the $i$ - $j$ interaction
$T^\#$	= characteristic constant of a binary system, used in correlating dilation constants
$v$	= molar volume of the vapor phase or liquid phase
$V$	= total volume of the mixture
$v_c$	= critical volume
$v_{cij}^c$	= critical volume characteristic of the $i$ - $j$ interaction
$\bar{v}_i^L$	= partial molar volume of component $i$ in the liquid mixture
$x$	= mole fraction in the liquid phase
$y$	= mole fraction in the vapor phase
$z$	= compressibility factor
$z_c$	= critical compressibility factor
$z_{cij}$	= critical compressibility factor characteristic of the $i$ - $j$ interaction

## Greek Letter

$\alpha_{22(1)}$	= self-interaction constant of molecules 2 in the environment of molecules 1
$\alpha_{12}$	= interaction constant of molecules 1 and 2
$\gamma$	= activity coefficients for solvent components
$\gamma^*$	= activity coefficients for solute components (in unsymmetric convention)
$\eta_{2(1)}$	= dilation constant of solute 2 in solvent 1

$\eta^\#$	= characteristic constant of a solute, used in correlating dilation constants
$\varphi_i$	= fugacity coefficient of component $i$ in a gas mixture
$\Phi$	= volume fraction as given by Equation 27
$\Psi$	= solute-free solvent volume fraction as given by Equation 69
$\omega$	= acentric factor
$\Omega_a, \Omega_b$	= dimensionless constants in Redlich-Kwong equation

## Superscripts

$E$	= excess quantity
$L$	= liquid phase
$(P^r)$	= at constant reference pressure
$(PO)$	= at constant reference pressure of zero
$s$	= at saturation
$o$	= reference state
$*$	= unsymmetric convention of normalization for activity coefficients

## Subscripts

$c$	= critical
$i$	= component $i$
$ii(j)$	= $i$ - $i$ interaction in the environment of $j$
$ij$	= $i$ - $j$ interaction
$(MS)$	= with reference to mixed solvent
$(SF)$	= solute-free solvent

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