

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

Ethane(1)-Methane(2)-Hydrogen(3) System^a

T, °R	Given			Calculated				Experimental ^a			
	x ₁	x ₂	x ₃	P, psia	y ₁	y ₂	y ₃	P, psia	y ₁	y ₂	y ₃
209.3	0.720	0.275	0.0046	199.4	0.0002	0.0570	0.9428	195.7	0.00020	0.0431	0.957
209.3	0.353	0.628	0.0192	520.7	0.0001	0.0490	0.9509	502.0	0.00006	0.0461	0.954
209.3	0.328	0.597	0.0754	2436	0.0002	0.0419	0.9579	1990	0.00016	0.0357	0.964
209.3	0.753	0.211	0.0362	2037	0.0002	0.0186	0.9812	1985	0.00035	0.0137	0.986
209.3	0.904	0.0788	0.0168	986.8	0.0001	0.0078	0.9921	981.9	0.00022	0.0054	0.995
209.3	0.905	0.0637	0.0312	2133	0.0002	0.0063	0.9935	1965	0.00026	0.0044	0.996
259.4	0.451	0.518	0.0313	712.8	0.0016	0.1495	0.8489	749.6	0.0017	0.136	0.862
259.4	0.505	0.438	0.0573	1420	0.0016	0.0975	0.9009	1490	0.00161	0.0910	0.907
259.4	0.503	0.440	0.0574	1418	0.0016	0.0979	0.9005	1990 ^b	0.00206	0.0535 ^b	0.944
259.4	0.673	0.280	0.0473	1476	0.0018	0.0669	0.9313	1500	0.00210	0.0540	0.944
259.4	0.699	0.267	0.0340	1061	0.0018	0.0725	0.9258	1013	0.00196	0.0633	0.935
309.7	0.768	0.203	0.0291	740.7	0.0143	0.1457	0.8400	748.7	0.0137	0.130	0.856
309.7	0.780	0.162	0.0584	1500	0.0108	0.0768	0.9124	1500	0.0114	0.0695	0.919
309.7	0.829	0.100	0.0712	1986	0.0102	0.0422	0.9475	1980	0.0109	0.0356	0.953
309.7	0.901	0.0725	0.0266	745.5	0.0146	0.0534	0.9320	749.0	0.0140	0.0450	0.941
309.7	0.354	0.624	0.0222	489.5	0.0137	0.5348	0.4515	517.4	0.0141	0.492	0.494
309.7	0.517	0.417	0.0660	1234	0.0106	0.2108	0.7786	1485	0.0122	0.188	0.800
359.5	0.544	0.444	0.0122	528.1	0.0683	0.6543	0.2775	521.1	0.0816	0.696	0.222
359.5	0.514	0.411	0.0745	1557	0.0410	0.3038	0.6552	1410	0.047	0.318	0.635
359.5	0.549	0.368	0.0827	1728	0.0398	0.2580	0.7022	1790	0.0469	0.264	0.689
359.5	0.738	0.238	0.0241	643.3	0.0644	0.3180	0.6176	699.2	0.0656	0.318	0.616
433.0	0.590	0.395	0.0148	813.1	0.2359	0.6427	0.1214	837.7	0.240	0.645	0.115
433.0	0.731	0.210	0.0590	1162	0.1975	0.2992	0.5033	1200	0.204	0.300	0.496
433.0	0.704	0.228	0.0676	1283	0.1880	0.3027	0.5093	1400	0.187	0.288	0.525
433.0	0.665	0.245	0.0901	1578	0.1727	0.2850	0.5423	1605	0.187	0.297	0.516
459.7	0.798	0.117	0.0845	1383	0.2698	0.1668	0.5634	1520	0.308	0.169	0.523
459.7	0.640	0.300	0.0595	1287	0.2929	0.4015	0.3057	1217	0.346	0.406	0.248
459.7	0.632	0.266	0.102	1773	0.2721	0.3072	0.4207	1610	0.319	0.339	0.342

^a Reference 9. ^b Experimental data seem to be in error; compare with the line immediately above. See discussion in the text.

in the pressure. While it is not possible to explain such disagreement with certainty, close scrutiny of the experimental data suggests that for some of the reported points there may be appreciable experimental error. For example, in the system ethane-methane-hydrogen at -200° F, the measured pressure is 1490 psia when the liquid composition is 50.5 mole per cent ethane, 43.8 mole per cent methane, 5.73 mole per cent hydrogen. However, at the same temperature and for a very similar liquid composition (50.3 mole per cent ethane, 44.0 mole per cent methane, 5.74 mole per cent hydrogen) the measured pressure is 1990 psia. It is most unlikely that such a small change in liquid composition could produce such a large change in the total pressure. The reported vapor composition in the first case is 0.161 mole per cent ethane and 9.10 mole per cent methane; in the second case, it is 0.206 mole per cent ethane and 5.35 mole per cent methane. It is not likely that such a

small change in liquid composition could account for a factor of nearly 2 in the K value of methane. Our calculations suggest that the experimental results for the first case are more reliable than those for the second case.

In the binary system hydrogen sulfide-carbon dioxide at 100° F, the measured pressure is 600 psia when the liquid composition is 84 mole per cent hydrogen sulfide and 16 mole per cent carbon dioxide. However, in the ternary system hydrogen sulfide-carbon dioxide-methane at 100° F, the measured pressure is again 600 psia even though the liquid now contains 2 mole per cent methane with 81 mole per cent hydrogen sulfide and 17 mole per cent carbon dioxide. Our calculated pressure for this ternary mixture is 744 psia. Since methane is a highly supercritical component at 100° F, we would expect that introduction of 2 mole per cent methane raises the total pressure beyond that for the methane-free binary system. Uncertainties in experi-

mental results are unfortunately, not rare, especially in ternary (and higher) systems, because of severe experimental problems.

Experimental and observed results for the five-component system (Table IX) are generally in good agreement. When the liquid phase is predominantly *n*-pentane, the predicted *K* factor for methane is a little lower than that reported by De Priester (10). Our model parameters for methane-*n*-pentane were obtained from the very good data of Sage and Lacey (38) which reproduce extremely well the methane-*n*-pentane, and methane-propane-*n*-pentane systems. It appears that De Priester's extrapolated data for the *n*-pentane-methane system disagree somewhat with those of Sage and coworkers.

BUBL T program. The main program, BUBL T, performs a bubble-temperature calculation. The pressure and the liquid-phase compositions are the known variables. The program calculates the equilibrium temperature and vapor compositions. Since the temperature is unknown, all the temperature-dependent thermodynamic quantities enter into the iterative loop.

After the data have been read in by INPUT, the first guess of temperature is made by utilizing the known liquid-phase compositions and total pressure, using approximately seven tenths of the pseudocritical temperature of the mixture. The temperature-dependent quantities are then calculated in subroutines RSTATE, ACTCO, and VOLPAR. The liquid-phase fugacities are then calculated by Equation 78, and vapor-phase compositions are calculated for the first time, using $\varphi_i = 1$. These vapor-phase compositions (after normaliza-

tion) are then immediately used to recalculate φ_i (subroutine PHIMIX) and new y_i 's are calculated. These calculations are repeated until $\sum y_i$ attains a constant value. The stoichiometric criterion $\sum y_i = 1$ is then tested and, if not satisfied, the deviation from unity is used to readjust the temperature. The loop is then entered at RSTATE and the iteration repeated until SUMY is constant and equals unity. When these conditions are satisfied, the problem is solved and the equilibrium results are printed out. Table X shows results of predicted ternary bubble temperatures and compositions calculated from binary data only.

Conclusion

In this work, we have described a method for reducing binary vapor-liquid equilibrium data to thermodynamically significant functions. For describing the vapor phase we use a well-known, two-parameter equation of state modified for mixtures to take into account deviations from the geometric mean approximation. For the liquid phase, we define the excess Gibbs energy with reference to a mixture which follows Henry's law; thereby we avoid the use of any arbitrary hypothetical standard states. The composition dependence of the activity coefficients is given by an equation similar to that of van Laar, modified to take into account the tendency of liquid mixtures to dilate in the critical region. Most important, we calculate the pressure dependence of the activity coefficient with realistic estimates of the liquid-phase partial volumes; these quantities, more than any others, provide the key to progress in high-pressure thermodynamics.

Table VIII. Comparison of Calculated and Experimental Results from Program BUBL P
Hydrogen Sulfide(1)-Carbon Dioxide(2)-Methane(3) System at 100° F

Given			Calculated				Experimental ^a			
x_1	x_2	x_3	<i>P</i> , psia	y_1	y_2	y_3	<i>P</i> , psia	y_1	y_2	y_3
0.840	0.160	0.000	624	0.6259	0.3741	0.000	600	0.608	0.392	0.000
0.810	0.170	0.020	744	0.5551	0.3329	0.1120	600 ^b	0.660	0.222	0.118
0.937	0.044	0.0190	605	0.6996	0.1190	0.1814	600	0.684	0.115	0.201
0.891	0.101	0.008	601	0.6726	0.2593	0.0681	600	0.644	0.259	0.097
0.870	0.122	0.008	627	0.6430	0.2950	0.0620	600 ^c	0.630	0.317	0.053
0.967	0.000	0.033	657	0.6839	0.000	0.3161	600 ^c	0.710	0.000	0.290
0.955	0.029	0.016	564	0.7439	0.0850	0.1712	600	0.690	0.066	0.244
0.891	0.000	0.109	1162	0.502	0.000	0.498	1200 ^c	0.049	0.000	0.510
0.843	0.042	0.115	1177	0.4856	0.0613	0.4531	1200	0.470	0.095	0.435
0.747	0.137	0.116	1121	0.4614	0.1801	0.3585	1200	0.445	0.201	0.354
0.683	0.213	0.104	1050	0.4494	0.2675	0.2831	1200	0.418	0.278	0.304

^a Reference 35.

^b Experimental data seem to be in error; compare with line immediately above. See discussion in the text.

^c These binary data are somewhat in disagreement with those of Sage's which, in turn, are given correctly by the calculations.