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Part. III. *P-V-T-x* Data and Second Virial Coefficients of Propane-Perfluorocyclobutane Mixtures

P-V-T-x **data for the propane-perfluorocyclobutane system are reported in this paper. The data cover a temperature range from 329.4 to 397.7°K and a pressure range from 60 to 6920 kPa. The low pressure compressibility measurements were used to determine second virial coefficients of pure propane and pure perfluorocyclobutane and for seven of their mixtures. The prediction of second virial coefficients using an extended corresponding states principle is also reported. Excellent predictions of the second virial coefficients of both pure components and mixtures have been obtained using, in the case of mixtures, a binary interaction coefficient obtained from a study of the critical states of the system.**

SCOPE

It is often convenient to represent the volumetric and thermodynamic properties of gases and gas mixtures by the virial equation of state. Virial coefficients are also of interest because they provide a link between experimental measurements and intermolecular forces.

An objective of our work was to extend our measurements of the critical states and vapor-liquid equilibria in the propane-perfluorocyclobutane system to the single phase regions of the phase diagram. The gas phase compressibility measurements may then be used to obtain second virial coefficients for the system. More generally, our objective was to obtain comprehensive data for mixtures that exhibit positive azeotropic behavior in their critical region. Critical states and vapor-liquid equilibria in the propane-perfluorocyclobutane system have already been reported by us in Parts I and II of this work.

A second objective of this work was to use our second virial coefficient data to test the predictive capabilities of an extended Corresponding States Principle. It is well known that Corresponding States methods may be used to correlate second virial coefficients. However, our aim was to see if our method was capable of predicting second virial coefficients of both pure components and mixtures using, in the case of mixtures, information obtained from a study of their critical states.

CONCLUSIONS AND SIGNIFICANCE

Volumetric data for the propane-perfluorocyclobutane system covering a temperature range from 329.4 to 397.7°K and a pressure range from 60 to 6920 kPa are reported in this paper. The low pressure measurements have been used to determine second virial coefficients for both the pure components and seven of their mixtures over the temperature range studied. This data set completes our comprehensive measurements of the volumetric and phase behavior of the propane-perfluorocyclobutane system. The data presented in the three papers in this series cover the gas phase, the two phase region, the critical region and the liquid phase region of this highly non-ideal system, which exhibits positive azeotropic behavior up to its citical region.

We have used our data to test the ability of an extended Corresponding States Method to correlate and predict a major part of the phase diagram of the propane-perfluorocyclobutane system. We have already shown how a binary interaction coefficient obtained from a study of the critical states of the system may be used to predict the azeotropic locus and vapor-liquid equilibria in the system. We have extended the Corresponding States method here to second virial coefficients of both pure fluids and mixtures. We show below how second virial coefficients may be predicted using a value of the binary interaction coefficient obtained from our study of the critical states. It therefore seems feasible that the extended Corresponding States Principle may be used to predict the complete phase diagram of mixtures using information obtained from the more readily available second virial coefficients.

INTRODUCTION

An investigation of the P-V-T-x behavior of the propane-perfluorocyclobutane system was undertaken as part of a continuing project on the phase diagrams of mixtures which exhibit azeotropic behavior in their critical region. The critical locus of this system and its correlation using an extended corresponding states principle was reported in Part I of this paper (Barber et al., 1980). In Part II (Kay et al., 1980) dew and bubble point measurements as well as the azeotropic locus and its prediction using the extended corresponding states method were presented.

In this paper, we report the measurements of P-V-T-x data and second virial coefficients of the two pure components as well as seven binary mixtures. The corresponding states method used in our previous work is extended to second virial coefficients.

EXPERIMENTAL

Details of the apparatus used have been given fully in Part I of this work and are not repeated here.

The measurement of the P-V isotherms has also been described in Part I.

The sample mass and composition were determined from the isothermal P-V measurements themselves. The calculations yielded at the same time the second virial coefficients of the material being studied.

The low pressure data, to within their experimental uncertainty, could be represented by a truncated virial equation:

$$\frac{PV}{nRT} = 1 + \frac{Bn}{V} + \frac{Cn^2}{V^2} \tag{1}$$

This equation may be rearranged to give for each data point (along an isotherm):

$$y_k = \left(\frac{P_kV_k}{nRT} - 1\right)\frac{V_k}{n} = B + \frac{Cn}{V_k} \tag{2}$$

When $P \rightarrow 0$, $[(P_kV_k)/(nRT)] \rightarrow 1$ and $n \rightarrow [(P_kV_k/(RT)]$. Values of B, C and n were obtained from a set of isothermal compressibility measurements by minimizing the sum of the squares of the deviations of all experimental points from the regression line given by Eq. 2. The calculations were performed on a digital computer.

The sequence of experimental measurements was as follows. First, propane was loaded in the sample tube which was then fastened in the compressor block. Volumetric measurements of the propane were then made at various temperatures between 329.41 and 397.73°K. At each temperature, a value of n, the number of moles of sample, was obtained as outlined above. In all cases, the agreement in the values of n was one part in 1000 or better. An average of the values was taken as the number of moles of propane (n_1). The sample tube was then removed from the compressor block and perfluorocyclobutane was added to give a mixture of approximately the desired composition. The sample tube was replaced and volumetric measurements of the mixture were made at a series of temperatures. The average of the number of moles of mixture computed for each isotherm was taken as $n_1 + n_2$, the total moles of mixture. The composition was thus obtained with a precision of 0.1 mol %. Additional details of the experimental apparatus and procedure are given elsewhere (Barber, 1968).

EXPERIMENTAL RESULTS

Selected experimental data at four temperatures for the molar volumes of the pure components and of propane-perfluorocyclobutane mixtures are given in Tables 1 through 4. The complete set of data, including those at intermediate temperatures and pressures, are given elsewhere (Barber, 1968). Low pressure data (usually between 60 and 420 kPa) along various isotherms were selected for the calculation of second virial coefficients as described above. The data were selected on the basis of statistical tests which ensured that no higher order virial terms than those appearing in Eq. 1 were required for their representation. Second virial coefficients thus calculated are given in Table 5. The data for propane (Figure 1) agree closely with those of McGlashan and Potter (1962), while data for perfluorocyclobutane (Figure 2) show close agreement with the data of Douslin et al. (1959). No values of the second virial coefficient of propane-perfluorocyclobutane mixtures have been reported in the literature. The precision of our experimental values, as determined from a regression analysis, is ±0.002 m^3kmol^{-1} or less.

THE PREDICTION OF SECOND VIRIAL COEFFICIENTS OF PURE FLUIDS AND FLUID MIXTURES

We have also attempted to predict second virial coefficients of the propane-perfluorocyclobutane system using an extension of the Corresponding States Principle developed by Leland, Rowl-

TABLE 1. SELECTED EXPERIMENTAL VOLUMETRIC DATA OF PROPANE(1)–PERFLUOROCYCLOBUTANE (2) MIXTURES AT 329.4°K

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.0000$		$x_2 = 0.0752$		$x_2 = 0.1405$		$x_2 = 0.2073$		$x_2 = 0.2543$	
114	23.59	2046	0.1043	2063	0.1126	62	44.05	143	18.83
130	20.66	2766	0.1030	3454	0.1095	73	37.01	158	16.95
156	17.15	3499	0.1015	4822	0.1076	83	32.42	172	15.56
288	9.081	4788	0.0994	6176	0.1060	114	23.57	219	12.15
373	6.850	6156	0.0980	6899	0.1055	143	18.52	275	9.589
515	4.873	6801	0.0978			194	13.46	420	6.139
700	3.499					284	8.752	2060	0.1214
1374	1.589					1983	0.1145	2740	0.1196
1967	0.0997					2394	0.1128	3417	0.1182
2368	0.0991					3071	0.1105	4807	0.1155
3771	0.0975					4114	0.1097	6201	0.1137
5149	0.0962					5458	0.1066	6907	0.1130
6895	0.0959					6835	0.1055		

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.3651$		$x_2 = 0.5139$		$x_2 = 0.7517$		$x_2 = 1.0000$	
79	34.85	199	13.22	188	13.98	171	15.36
90	29.94	216	12.09	199	13.12	280	9.147
110	24.33	234	11.11	212	12.27	416	5.920
134	19.85	273	9.418	226	11.47	558	4.210
165	17.88	325	7.750	241	10.67	710	3.129
181	14.55	345	7.260	276	9.220	1004	0.1475
217	12.00	2094	0.1285	317	7.889	1706	0.1450
250	10.26	2769	0.1268	343	7.211	3771	0.1427
1903	0.1223	4115	0.1243	1377	0.1370	5821	0.1403
2401	0.1207	5479	0.1224	2758	0.1340	6848	0.1403
3455	0.1180	6900	0.1209	4118	0.1316		
4800	0.1160			5515	0.1300		
6560	0.1143			6913	0.1290		

TABLE 2. SELECTED EXPERIMENTAL VOLUMETRIC DATA OF PROPANE(1)-PERFLUOROCYCLOBUTANE (2) MIXTURES AT 348.57°K

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.0000$		$x_2 = 0.0752$		$x_2 = 0.1405$		$x_2 = 0.2073$		$x_2 = 0.2543$	
121	23.69	62	46.36	142	20.16	68	42.40	152	19.19
134	21.35	76	37.65	155	18.45	86	33.31	166	17.60
149	19.07	100	28.71	167	17.11	110	25.85	206	14.26
295	9.419	127	22.30	190	15.03	116	17.05	272	11.04
375	7.280	163	17.28	218	13.05	247	11.16	321	9.490
527	5.092	230	12.05	262	10.81	315	8.560	419	7.560
1037	2.445	268	10.25	3099	0.1282	2940	0.1308	3081	0.1384
2059	1.044	2943	0.1190	4134	0.1222	4110	0.1233	4141	0.1315
2822	0.6096	3411	0.1160	5499	0.1177	5496	0.1185	5503	0.1260
2872	0.1125	4126	0.1128	6842	0.1144	6887	0.1153	6580	0.1236
3769	0.1092	4806	0.1102						
5167	0.1053	6821	0.1058						
6896	0.1017								

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.3641$		$x_2 = 0.5139$		$x_2 = 0.7517$		$x_2 = 1.0000$	
83	34.62	214	13.03	201	13.90	173	16.24
89	32.19	234	11.88	207	13.45	292	9.391
100	28.61	251	11.10	232	11.93	433	6.131
122	23.22	272	10.11	264	10.39	553	4.660
154	18.35	290	9.432	304	8.921	991	2.290
196	14.34	357	7.480	357	7.549	1373	0.1591
272	10.12	2535	0.1452	2103	0.1506	2386	0.1569
2743	0.1427	3110	0.1428	2757	0.1479	3418	0.1545
4114	0.1322	4130	0.1379	4132	0.1433	4452	0.1522
5510	0.1268	5510	0.1335	5485	0.1404	5603	0.1512
6822	0.1229	6898	0.1303	6899	0.1373	6907	0.1492

inson and others (Leland and Chappelear, 1968; Teja and Rowlinson, 1973; Teja, 1975). We extend the Corresponding States Method to second virial coefficients below.

Two fluids i and o are said to be in corresponding states if the compressibility Z_i of fluid i at temperature T and volume V may be obtained from a knowledge of its critical properties T_{cii} and V_{cii} and the known compressibility Z_o of reference fluid o.
We may therefore write:

$$Z_{ii}[T,V] = Z_o[T/f_{ii}, V/h_{ii}] \qquad (1)$$

where

$$f_{ii} = T_{cii}/T_{co} \qquad (2)$$

and

$$h_{ii} = V_{cii}/V_{co} \qquad (3)$$

We may rewrite Eq. 1 for the second virial coefficient as follows: (the second virial coefficient being independent of volume):

$$B_{ii}[T] = h_{ii}B_o[T/f_{ii}] \qquad (4)$$

Equations 2–4 hold strictly for sets of spherical conformal sub-

TABLE 3. SELECTED EXPERIMENTAL VOLUMETRIC DATA FOR PROPANE(1)-PERFLUOROCYCLOBUTANE(2) AT 368.19°K

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.0000$		$x_2 = 0.0752$		$x_2 = 0.1405$		$x_2 = 0.2543$		$x_2 = 0.5139$	
127	23.74	70	4370	714	3.937	165	18.31	229	12.90
144	20.98	86	3531	1331	1.990	174	17.29	249	11.81
167	17.97	115	2633	2072	1.159	190	15.83	267	10.96
311	9.451	161	1877	2774	0.7657	229	13.11	324	8.879
376	7.699	197	1532	4122	0.2208	286	10.44	633	4.318
511	5.596	238	1257	5479	0.1380	352	8.41	1426	1.718
1133	2.392	264	1132	6849	0.1282	726	3.901	2794	0.6358
1716	1.478					1438	1.819	4152	0.1691
2744	0.7940					2750	0.7656	5516	0.1521
3995	0.3480					4127	0.2088	6844	0.1446
4452	0.1330					5497	0.1494		
5469	0.1216					6889	0.1385		
6843	0.1146								

P (kPa)	V (m^3kmol^{-1})	P (kPa)	V (m^3kmol^{-1})
$x_2 = 0.7517$		$x_2 = 1.0000$	
214	13.82	188	15.84
225	13.12	309	9.448
253	11.57	418	6.850
274	10.65	714	3.891
317	9.099	1388	1.655
375	7.571	1848	0.9991
2879	0.1815	2055	0.1775
4100	0.1628	2749	0.1727
5484	0.1551	4121	0.1668
6903	0.1499	5510	0.1626
		6922	0.1581

TABLE 4. SELECTED EXPERIMENTAL VOLUMETRIC DATA FOR PROPANE(1)-PERFLUOROCYCLOBUTANE (2) MIXTURES AT 397.73°K

P (kPa)	V (m^{3}kmol^{-1})	P (kPa)	V (m^{3}kmol^{-1})	P (kPa)	V (m^{3}kmol^{-1})	P (kPa)	V (m^{3}kmol^{-1})	P (kPa)	V (m^{3}kmol^{-1})
$x_2 = 0.0000$		$x_2 = 0.1405$		$x_2 = 0.2543$		$x_2 = 0.5139$		$x_2 = 0.7517$	
139	23.46	698	4.446	173	18.82	234	13.72	234	13.73
156	20.89	1425	2.064	199	16.38	253	12.61	246	13.00
174	18.74	2750	0.9543	226	14.41	276	11.54	262	12.17
252	12.81	4117	0.5289	257	12.64	327	9.621	304	10.43
379	8.340	5485	0.3032	340	9.481	383	8.087	355	8.831
702	4.396	6844	0.1922	743	4.192	441	6.992	706	4.184
1379	2.141			1616	1.795	1050	2.766	1362	2.005
2746	0.9512			2781	0.9276	2750	0.8688	2758	0.7885
4119	0.5361			4175	0.5077	4121	0.6183	4114	0.3332
5494	0.2973			5490	0.2952	5504	0.2442	5524	0.2046
6870	0.1735			6918	0.1978	6845	0.1893	6915	0.1816

P (kPa)	V (m^{3}kmol^{-1})
$x_2 = 1.0000$	
213	15.17
345	9.211
455	6.878
718	4.190
1460	1.844
2412	0.8833
3752	0.2332
5501	0.1940
6875	0.1841

TABLE 5. SECOND VIRIAL COEFFICIENTS OF PROPANE (1)–PERFLUOROCYCLOBUTANE (2) MIXTURES

	Second Virial Coefficient B (m^{3}kmol^{-1})								
T(°K)	$x_2 = 0.0752$	$x_2 = 0.1405$	$x_2 = 0.2073$	$x_2 = 0.2543$	$x_2 = 0.3641$	$x_2 = 0.5139$	$x_2 = 0.7517$	$x_2 = 0.0000$	$x_2 = 1.0000$
329.41	—		−0.333	−0.348	−0.370	−0.406	−0.483	−0.310	−0.595
338.42	−0.308	−0.310	−0.313	−0.322	−0.348	−0.382	−0.453	−0.292	−0.553
348.57	−0.279	−0.290	−0.299	−0.304	−0.321	−0.354	−0.426	−0.274	−0.517
358.97	−0.262	−0.263	−0.273	−0.283	−0.299	−0.328	−0.392	−0.256	—
368.19	−0.246	—	—	−0.263	—	−0.310	−0.371	−0.244	−0.450
377.99	—	—	—	−0.246	—	−0.288	−0.340	−0.231	−0.424
387.74	—	—	—	−0.232	—	−0.269	−0.323	−0.219	−0.389
397.73	—	—	—	−0.222	—	−0.251	−0.296	−0.204	−0.363

stances in which the molecules interact with two parameter potentials.

The sets of substances over which Eq. 4 holds may be extended by introducing shape factors (Leland and Chappelear, 1968) in Eqs. 2 and 3. Thus,

$$f_{ii} = \left(\frac{T_{cii}}{T_{co}}\right) \theta_{ii} \tag{5}$$

$$h_{ii} = \left(\frac{V_{cii}}{V_{co}}\right) \Phi_{ii} \tag{6}$$

where the sample factors Φ_{ii} and Φ_{ii} are slowly varying functions of reduced temperatures T_{Ri} and reduced volume V_{Ri}. Analytical expressions for the shape factors of the n-alkanes relative to methane have been reported by Leland and Chappelear (1968) as follows:

$$\theta_{ii} = 1 + (\omega_{ii} - \omega_0)\{0.0892 - 0.8493 \ln T_{Ri} - 0.6759/T_{Ri}(0.3063 - 0.4506/T_{Ri})(V_{Ri} - 0.5)\} \tag{7}$$

$$\phi_{ii} = (Z_{co}/Z_{cii})[1 + (\omega_{ii} - \omega_0)\{0.3903(V_{Ri} - 1.0177) - 0.9426 \times (V_{Ri} - 0.7633) \ln T_{Ri}\}] \tag{8}$$

where the ω's are Pitzer's acentric factors. When $T_{ri} > 2.0$, its value

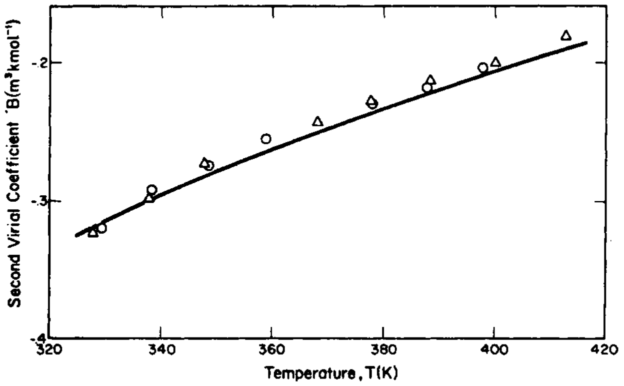

Figure 1. Second virial coefficients of propane: O this work; Δ McGlashan and Potter (1962). The solid line is predicted with the extended corresponding states method.

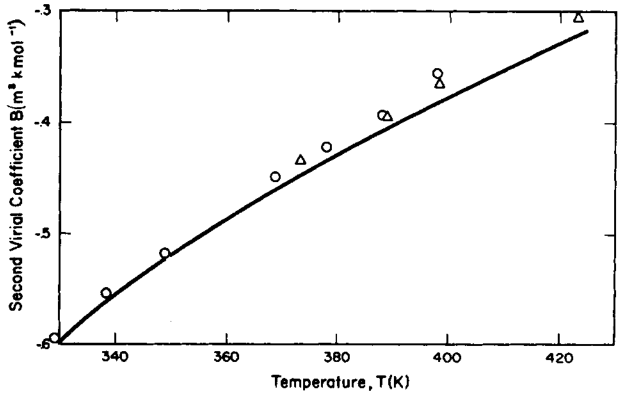

Figure 2. Second virial coefficients of perfluorocyclobutane: O, this work; Δ, Douslin et al. (1959). The solid line is predicted with the extended Corresponding States Method.

in both Eqs. 7 and 8 is set equal to 2.0; when $T_{Ri} < 0.5$, it is set equal to 0.5. Similary, when $V_{Ri} > 2.0$, its value in both equations is set equal to 2.0 and when $V_{Ri} < 0.5$, it is set equal to 0.5. Thus, the shape factors are slowly varying functions of temperature and volume (*In a mixture, there is a slight additional dependence on* composition). The shape factor correlations were derived by comparing the compressibility and fugacity-pressure ratio of the n-alkanes with the compressibility and fugacity-pressure ratio of methane as a function of reduced temperature and volume. The volume dependence of the shape factors is important mainly at reduced volumes less than 2.0 (i.e., at high densities). For the purpose of calculating second virial coefficients, this density dependence may be ignored. We therefore set $V_{Ri} > 2.0$ in Eqs. 7 and 8 which become:

$$\theta_{ii} = 1 + (\omega_{ii} - \omega_0)\{0.54865 - 0.8493 \ln T_{Ri} - 0.6759/T_{Ri}\} \tag{9}$$

$$\phi_{ii} = (Z_{co}/Z_{cii})[1 + (\omega_{ii} - \omega_0)\{0.38339 - 1.16571 \ln T_{Ri}\}] \tag{10}$$

Although Eqs. 7 and 8 are valid strictly for the n-alkanes, they have been used successfully for the prediction of phase equilibria and thermodynamic properties for a variety of fluids (Teja, 1979) and, indeed, have been used in the earlier part of this work (Barber et al., 1981). We may therefore assume the validity of Eqs. 9 and 10 for both propane and perfluorocyclobutane. The calculation of the second virial coefficients of these substances at any temperature therefore requires only a knowledge of their properties T_{cii}, V_{cii}, Z_{cii} and ω_{ii}; together with a knowledge of the variation of the second virial coefficient of the reference substance (methane) with temperature. For the latter, we have used the theoretically based equation of Sengers, Klein and Gallaher (1972). This reproduces methane data with relative deviation of 0.05% and, because of its theoretical basis, may be used for extrapolation. The choice of the reference equation is, nevertheless, arbitrary and other equations could equally have been used.

Equation 4 may be extended to mixtures by assuming that the mixture can be replaced by a hypothetical equivalent substance. This is the so-called one-fluid model for mixtures and leads to:

$$B_m[T] = hB_o[T/f] \tag{11}$$

where the quantities f and h depend on the composition of the mixture. In our previous studies, we have utilized the van der Waals one-fluid prescription to relate f and h to composition. Thus:

$$fh = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \tag{12}$$

$$h = \sum_i \sum_j x_i x_j h_{ij} \tag{13}$$

When using this prescription, the like terms ($i = j$) are obtained from pure-component properties, but the unlike terms ($i \neq j$) require mixture data for their evaluation. The usual procedure is to write (Barber et al., 1981)

$$f_{ij} = \xi_{ij}(f_{ii} f_{ij})^{1/2} \tag{14}$$

and

$$h_{ij} = {}^1\!/_8(h_{ii}^{1/3} + h_{jj}^{1/3})^3 \tag{15}$$

where the binary interaction coefficient ξ_{ij} must be obtained from experimental data.

For the propane-perfluorocyclobutane system, we have used a value of $\xi_{ij} = 0.89$ obtained from our study of the critical states of the system. (Barber et al., 1981). This value has already been used to predict the azeotropic locus and vapor-liquid equilibria of the system with considerable success. We have used the same value to predict second virial coefficients of propane-perfluorocyclobutane mixtures in this work. Although the equation of state used for the reference substance (methane) is different in this study from that used in our study of critical states, and the shape factor relationships (Eqs. 9–10) are different, the extended Corresponding States method is entirely analogous and we expect close agreement between the optimum values of ξ_{ij} obtained. Our predicted values of second virial coefficients with $\xi_{ij} = 0.89$ are shown in Figure 3. As can be seen, excellent agreement is obtained between prediction and experiment. The average absolute deviation between predicted and experimental values for the 54 data points was found to be 1.80% and the maximum deviation was 5.6%. This is well within the experimental accuracy of the data and demonstrates the truly remarkable predictive capabilities of the extended Corresponding States Principle. A binary interaction coefficient obtained from the study of critical states has been used successfully to make quantitative predictions of the azeotropic locus, vapor-liquid equilibria and, now, second virial coefficients of the system. It should therefore be possible to make quantitative predictions of the whole phase diagram using information obtained from second virial coefficients provided, of course, that the phase diagram and volumetric data for the reference substance are available.

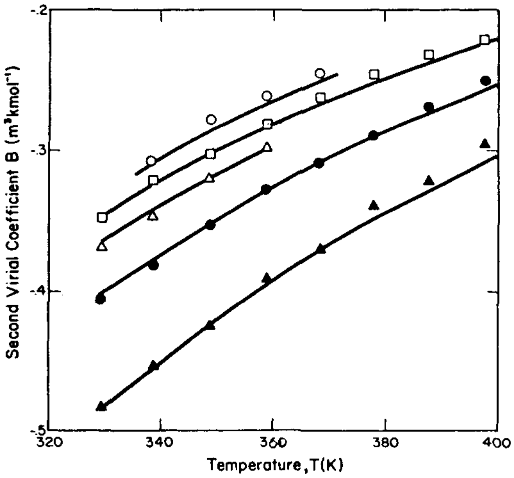

Figure 3. Second Virial Coefficients of propane: (1)—perfluorocyclobutane (2) mixtures. ○, experimental; $x_2 = 0.0752$; □ experimental $x_2 = 0.2543$; △ experimental $x_2 = 0.3641$; ● experimental $x_2 = 0.5139$; ▲ experimental $x_2 = 0.7517$. The solid lines are predicted using the extended Corresponding States Method with $\xi_{ij} = 0.89$.

NOTATION

B = second virial coefficient
C = third virial coefficient
f = energy parameter in Corresponding States method
h = volume parameter in Corresponding States method
n = number of moles
P = pressure
R = gas constant
T = thermodynamic temperature
V = volume
x = mole fraction
Z = compressibility

Greek letters

θ = energy shape factor
Φ = volume shape factor
ξ = binary interaction coefficient
ω = Pitzer's acentric factor

Subscripts

c = critical
i,j = component i,j
k = data point k
m = mixture
o = reference substance
R = reduced quantity

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Thinning of a Liquid Film as a Small Drop or Bubble Approaches a Solid Plane

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When a small drop or bubble approaches a solid surface, a thin liquid film forms between them, drains, until an instability forms and coalescence occurs. A hydrodynamic theory is developed for the first portion of this coalescence process: the drainage of the thin liquid film while it is still sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. This theory describes the time rate of change of the film profile, given only the drop radius and the required physical properties. Predictions are compared with profiles measured by Platikanov (1964) for gas bubbles. It is concluded that, even with only a trace of surfactant present, the liquid-gas interface may be nearly immobile (tangential components of velocity are zero) and the surface viscosities will have little effect upon the drainage rate.

SCOPE

The rate at which drops or bubbles suspended in a liquid coalesce is important to the preparation and stability of emulsions, of foams, and of dispersions; to liquid-liquid extraction; to the formation of an oil bank during the displacement of oil from a reservoir rock. On a smaller scale, when two drops (bubbles) in a liquid phase approach each other or when a drop (bubble) approaches a solid surface, a thin liquid film forms between them, drains, until an instability forms and coalescence occurs. We must understand the factors controlling the rate of coalescence.

In order to simplify the problem, we will consider only the first portion of this coalescence process as a drop approaches a solid wall: the drainage of the thin liquid film while it is still sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. Our objective is to develop a hydrodynamic theory for both pure and surfactant systems that decribes the configuration of the liquid film formed as a function of time and in this way predict the rate at which this film drains. We will not consider the development and growth of instabilities in these thin films that would lead to coalescence.

We will limit our attention to small drops or bubbles and to liquid films so thin that we may apply the Reynolds lubrication theory approximation.

Our analysis may be considered a refinement of that proposed by Hartland (1969).

CONCLUSIONS AND SIGNIFICANCE

Our theory for the drainage of a liquid film between a small drop and a solid surface, while employing the same basic differential equation (Eq. 52), is an improvement on Hartland's (1969) development. We require less a priori information, we have a more reliable initial condition, and our boundary conditions are in better agreement with experimental observations.

We have been able to accurately describe some of the experimental profiles measured by Platikanov (1964) for gas bubbles at short times.

Our theory is not only more complete but also more accurate than the estimates offered by Frankel and Mysels (1962). Their theory includes one free parameter; ours, none.

The comparison between our theory and the data of Platikanov (1964) for bubbles suggests that, even when there is only a trace of surfactant present, the liquid-gas interface may be nearly immobile. By immobile, we mean that the tangential

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