Vapor-Liquid Equilibrium:

Part II. Correlations from P-x Data for 15 Systems

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Pressure versus composition data for 15 binary systems in vapor-liquid equilibrium at 30°C form the basis for correlation of the excess Gibbs function and the activity coefficients for these systems.

SCOPE

The apparatus described by Gibbs and Van Ness (1972) has been used systematically to measure solution vapor pressures as a function of liquid composition at 30°C for 15 binary systems in vapor-liquid equilibrium (VLE). Data reduction by the method described in the preceding paper for *P-x* data yields correlating equations for the excess Gibbs free energy and the activity coefficients, from which the *P-x-y* relationship at 30°C may be calculated. The systems studied are CCl_4, $CHCl_3$, and CH_2Cl_2, each with tetrahydrofuran and with furan; tetrahydrofuran with furan; CH_2Cl_2 with methyl acetate, with acetone, and with 1,4-dioxane; $CHCl_3$ with 1,4-dioxane; pyridine with acetone, with $CHCl_3$, and with CH_2Cl_2; and *n*-pentanol with *n*-hexane. Heat-of-mixing data, which are available in the literature for most of the systems reported, allow extension of these results to other conditions.

CONCLUSIONS AND SIGNIFICANCE

The rapidity with which *P-x* data may be taken commends the use of such data as the basis for formulation of VLE relationships for binary systems. These are useful in themselves, and they serve also in predictive schemes for multicomponent systems, for which experimental determination is much more tedious.

Routine methods of data reduction are available, as reviewed in the preceding paper, and the reliability of the method depends solely on the reliability of the *P-x* data. Gibbs and Van Ness (1972) demonstrated for the ethanol—*n*-heptane system agreement between results obtained with the present apparatus and data from the literature based on measurements with an equilibrium still. The results presented here are for systems representing a wide range of behavior, from large positive to large negative deviations from ideality.

The experimental apparatus used in this work is fully described by Gibbs and Van Ness (1972). Liquid solutions of known composition are prepared in a thermostated test cell by volumetric metering of degassed liquids from accurate piston-injectors. Direct measurement of pressure in the cell provides for the solution vapor pressure. The raw data* therefore consist of pairs of values for pressure and liquid mole fraction at constant temperature and cover the full composition range from $x_1 = 0$ to $x_1 = 1$.

As indicated by the discussion of *P-x* data in the preceding paper, the raw data are fit by the least-squares spline-fit procedure of Klaus and Van Ness (1967), and this provides the input for the numerical procedure of Mixon et al. (1965) which yields the $g \equiv G^E/RT$ versus x_1 relationship in accord with Equation (9b) of the preceding paper. The resulting numerical values of g/x_1x_2 or of $\ln(\gamma_1/\gamma_2)$ are then fit with respect to x_1 by an appropriate correlating function. For all of the systems considered here except one, a suitable correlation was given by Equations (5) to (7) of the preceding paper. The constants *A*, *B*, and *D* obtained for these 14 systems are listed in Table 1. The equations are given graphical expression in Figure 1, from which one sees that an appreciable range of deviation from ideal-solution behavior is represented. The dichloromethane-furan system showed no significant departure from ideality, and the raw *P* versus *x* data were fit by a straight line. The chloroform-tetrahydrofuran system exhibited large negative deviations and formed a minimum-pressure azeotrope at a mole fraction of chloroform of about 0.46, the only azeotrope observed for the systems studied.

The remaining system, quite different in character from the others, is *n*-Pentanol(1)-*n*-Hexane(2), which shows very large positive deviations from ideality. The calculated values of g/x_1x_2, as shown by Figure 2, are not easily fit by a simple correlation function. The best job is done by the Wilson equation, for which

$$\frac{g}{x_1x_2} = -\frac{\ln(x_1 + G_{21}\,x_2)}{x_2} - \frac{\ln(x_2 + G_{12}\,x_1)}{x_1}$$

However, this equation lacks sufficient flexibility to provide a really adequate representation of the g/x_1x_2 versus x_1 curve over the entire composition range. Thus a least-

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* Tables of raw *P-x* data for the 15 systems considered have been deposited as Document No. 01995 with the National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

Table 1. Correlation of Data at 30°C by the Equation

$$\frac{g}{x_1x_2} = Ax_2 + Bx_1 - Dx_1x_2 \qquad g \equiv G^E/RT$$

	System	A	B	D	σ_1[b]	σ_2[c]
1	Carbontetrachloride (1)—THF[a] (2)	−0.25704	−0.18188	0.04760	0.02	0.11
2	*Chloroform* (1)—THF (2)	−1.39352	−1.58092	0.58606	0.25[d]	0.77[d]
3	Dichloromethane (1)—THF (2)	−0.93341	−0.87287	0.22232	0.48	0.53
4	Carbontetrachloride (1)—furan (2)	0.28639	0.27034	0.01189	0.25	0.34
5	Chloroform (1)—furan (2)	−0.08350	−0.11890	0.02847	0.30	0.37
6	Dichloromethane (1)—furan (2)	0.0	0.0	0.0	—	0.34[e]
7	THF (1)—furan (2)	−0.39970	−0.37125	−0.06410	0.25	0.46
8	Dichloromethane (1)—methyl acetate (2)	−0.42260	−0.63028	0.27851	0.25	0.42
9	Dichloromethane (1)—acetone (2)	−0.58905	−0.76638	−0.11940	0.54	0.71
10	Dichloromethane (1)—1,4-dioxane (2)	−0.63128	−0.95516	−0.06863	0.18	0.51
11	Chloroform (1)—1,4-dioxane (2)	−0.75571	−1.58181	0.12739	0.24	0.26
12	Pyridine (1)—acetone (2)	0.19441	0.20447	0.02998	0.09	0.24
13	Pyridine (1)—chloroform (2)	−1.16104	−0.70714	0.37199	0.38	0.56
14	Pyridine (1)—dichloromethane (2)	−0.57919	−0.44873	0.03523	0.10	0.21

[a] THF = Tetrahydrofuran.

[b] σ_1 = Root mean-square deviation between calculated values of pressure and values given by the spline fit, mm Hg.

[c] σ_2 = Root mean-square deviation between calculated and experimental values of pressure, mm Hg.

[d] Composite for three separate runs, which individually give σ_2 = 0.46, 1.06, 0.66 mm Hg.

[e] Root mean-square deviation of linear fit of P vs. x_1 data.

squares fitting technique provides values for the constants G_{12} and G_{21} which do not lead to a very satisfactory representation of the P versus x data. It is possible however to find a compromise fit which minimizes the average deviation between calculated and measured pressures, and this is accomplished with the constants

$$G_{12} = 0.625$$

$$G_{21} = 0.070$$

The Wilson equation then generates the dashed line of Figure 2.

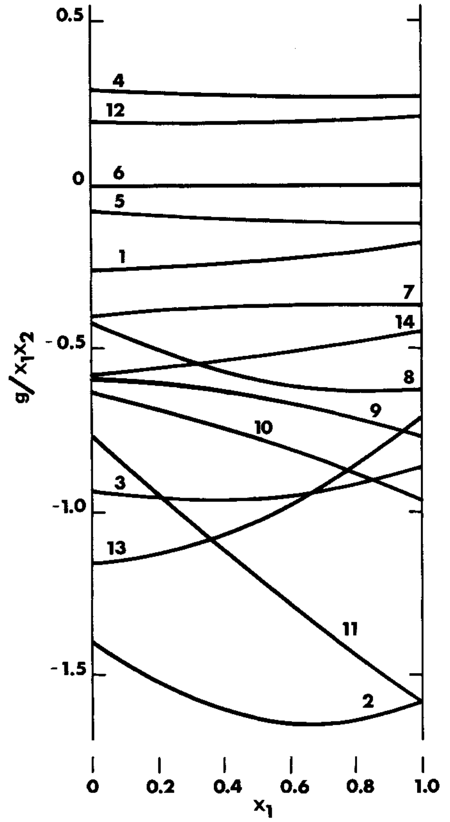

Fig. 1. Graphical representation of the equations of Table 1, showing g/x_1x_2 vs. x_1 at 30°C. The numbers identifying the curves refer to the system numbers of Table 1.

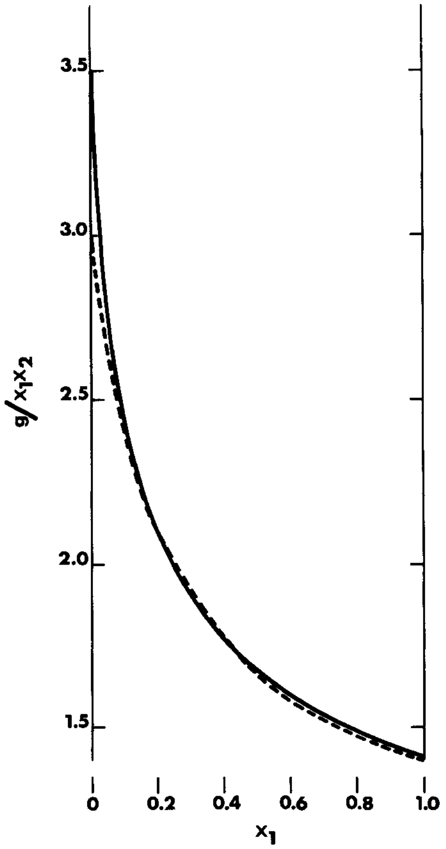

Fig. 2. Plot of g/x_1x_2 vs. x_1 for n-Pentanol(1)—n-Hexane(2) at 30°C. The solid curve represents values from data reduction, and the dashed curve represents a compromise fit by the Wilson equation.

MATERIALS

The n-hexane used in this work was the Pure Grade (99$^+$ mole %) of the Phillips Petroleum Company. All other components were obtained from Matheson Coleman and Bell, and with one exception were Chromatoquality (99$^+$ mole %). The pyridine used was Reagent Grade, meeting A.C.S. Specifications, with a stated assay of 99%. All chemicals were introduced into the apparatus in the as-received condition, and no purification was attempted beyond degassing.

Thorough degassing is of course essential and often requires patience and persistence. Our procedures evolved with experience over a period of some 18 months; however, the apparatus remains the same as that described by Gibbs and Van Ness (1972). It consists of two interconnected flasks separated by a needle valve. The lower flask is readily heated to cause evaporation of liquid, and the upper flask surrounds a cold finger, which permits cooling to effect condensation. The liquid to be degassed is introduced into the lower flask, which contains an amount of activated Linde Type 3A Molecular Sieve to absorb any residual water. After evacuation of the upper flask, the liquid is refluxed between the two flasks for two to three days, with periodic re-evacuation of the upper flask to purge the system of most noncondensables. This is followed by one or more vacuum sublimations of liquid evaporated from the lower flask onto the cold finger, cooled by liquid nitrogen, in the upper flask.

It should be noted that simple freezing and sublimation are not the same thing. Although all materials could be deposited on the cold finger as an ice-like layer resulting from the freezing of condensed liquid, not all could be deposited as snow-like crystals formed directly from the vapor. Thus we were unable to sublime methyl acetate, and we had such difficulty with tetrahydrofuran that we abandoned the effort. Where sublimation is not accomplished, a longer period of refluxing and purging is required. In any event, degassing should continue until successive measurements of vapor pressure show negligible change.

The vapor pressure of a liquid component is sensitive to the completeness of degassing and to purity in general. An indication of the variation of vapor pressures from run to run and a comparison with literature values are provided by Table 2. Where the vapor pressure is reported in one of the two compilations available of critically evaluated data, references c and d of Table 2, it is the only literature value listed. For the other components, reference is made primarily to recent work.

No definitive study seems ever to have been made of the vapor pressures of carbon tetrachloride and chloroform, and a wide range of values is to be found in the literature, a range not fully represented by the values listed. Vapor pressures as given by the spline fit of the raw P-x data are also listed, as these values ultimately become the ones used to determine final correlations. In some cases two different lots of the same material were used during the course of this work, and this is indicated in Table 2. Distinct differences between lots can be noted; however, some of this may result from our increasing proficiency with degassing, as results are listed chronologically. Overall, the comparisons shown in Table 2 suggest that the raw data are of reasonable accuracy.

DISCUSSION

The variety of P-x-y behavior exhibited by the systems studied is illustrated by Figures 3 through 6. All were found amenable to analysis on the basis of just P-x data.

Once the constants in a correlating equation for g/x_1x_2 are found, then one can compute the equilibrium vapor pressures consistent with the correlation, as described in the preceding paper. Such calculated values for the 14 systems listed in Table 1 were compared both with the vapor pressures given by the spline fit of the raw P-x data and with the experimental values themselves. Thus the root mean-square deviation between computed pressures and those of the spline fit is given for the 14 systems in Table

TABLE 2. REPRESENTATIVE VAPOR PRESSURES OF COMPONENTS AT 30°C

Component	P^{sat}, mm Hg Experimental[a]	P^{sat}, mm Hg Spline Fit	P^{sat}, mm Hg Literature
Acetone	286.10	286.22	285.17[c]
	284.28	284.74	
Carbon tetrachloride	142.32	142.28	140.71 (Moelwyn-Hughes & Missen, 1957)
	142.30	142.32	141.3 (Steinbrecher & Bittrich, 1966)
			141.58 (Hlavaty, 1970)
Chloroform	242.86 (I)	242.13[b]	241.63 (Moelwyn-Hughes & Missen, 1957)
	243.29 (I)		242.67 (Kirby & Van Winkle, 1970)
	242.11 (II)		243.9 (Chun et al., 1971)
Dichloromethane	528.26 (I)	527.62	529.87[d]
	528.25 (I)	527.85	
	527.76 (II)	527.09	
	527.90 (II)	527.82	
1,4-Dioxane	47.65 (I)	48.01	47.24 (Cabani et al., 1971)
	46.37 (II)	46.03	47.5 (Steinbrecher & Bittrich, 1966)
Furan	725.24 (I)	724.83	723.20 (Guthrie et al., 1952)
	726.86 (I)	726.44	
	723.99 (II)	724.18	
n-Hexane	188.03	187.93	187.10[c]
Methyl acetate	268.80	269.73	269.06[d]
n-Pentanol	3.72	3.76	3.23[c]
Pyridine	27.51	27.64	27.29 (Osborn & Douslin, 1968)
	27.01	27.81	27.63 (Kind et al., 1968)
	27.61	27.52	
Tetrahydrofuran	201.64	201.64	201.07 (Scott, 1970)
	201.62	200.66[b]	201.29 (Koizumi & Ouchi, 1970)
	201.42		203.18 (Cabani et al., 1971)
	201.04		
	201.09	201.12	

[a] Where more than one lot of material was used, this is indicated by the numerals in parentheses.

[b] These values for the chloroform (1)—tetrahydrofuran (2) system were determined from a combination of three separate sets of P-x data.

[c] API Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compopunds," College Station, Texas.

[d] Manufacturing Chemists Association Research Project, "Selected Values of Properties of Chemical Compounds," College Station, Texas.

1 as σ_1, and similarly the deviation between computed and experimental pressures is given as σ_2. The average value of σ_1 for all 14 systems is 0.26 mm Hg, and the average value of σ_2 is 0.40 mm Hg. Since the spline fit serves to eliminate local scatter in the data, σ_1 should be significantly less than σ_2. Moreover, the P-x relation actually used in the data reduction process is that given by the spline fit, and therefore σ_1 is a better measure of the suitability of the correlating equation than is σ_2.

For the n-Pentanol-n-Hexane system the Wilson equation provides an acceptable but not entirely satisfactory correlation of the data. The root mean-square deviation between calculated and experimental values of P is 1.02 mm Hg, and the maximum deviation is 1.92 mm Hg. These values are significantly larger than those for any of the 14 systems of Table 1. Moreover, the deviations are primarily systematic, resulting from failure of the correlating equation to match the actual behavior of the systems. This is seen from Plot (A) of Figure 7, where the deviation $\Delta P \equiv$ (calculated P) $-$ (experimental P) is shown as a function of x. Had the Wilson parameters been determined from a least-square fit of the g/x_1x_2 values of Figure 2, the representation of g/x_1x_2 would be better, but

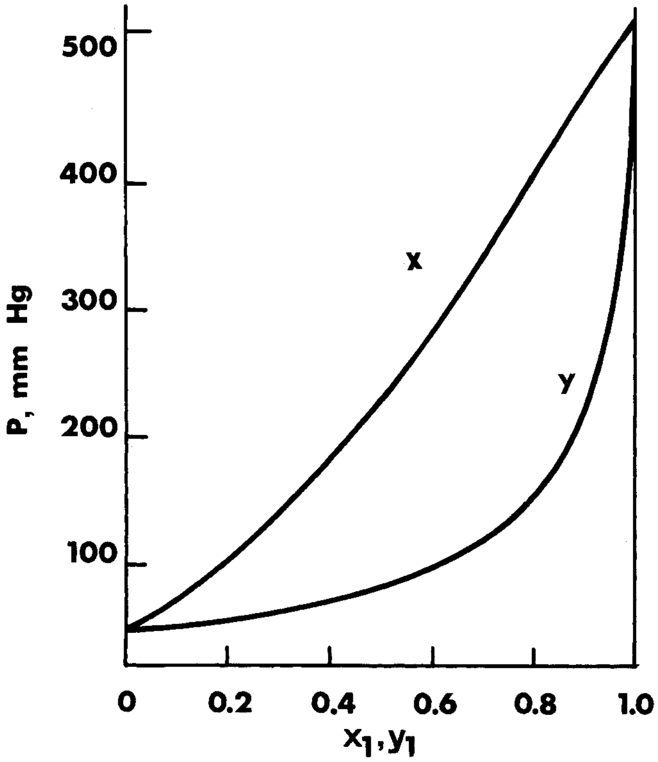

Fig. 3. P-x-y relation for dichloromethane(1)—1,4-Dioxane(2) at 30°C.

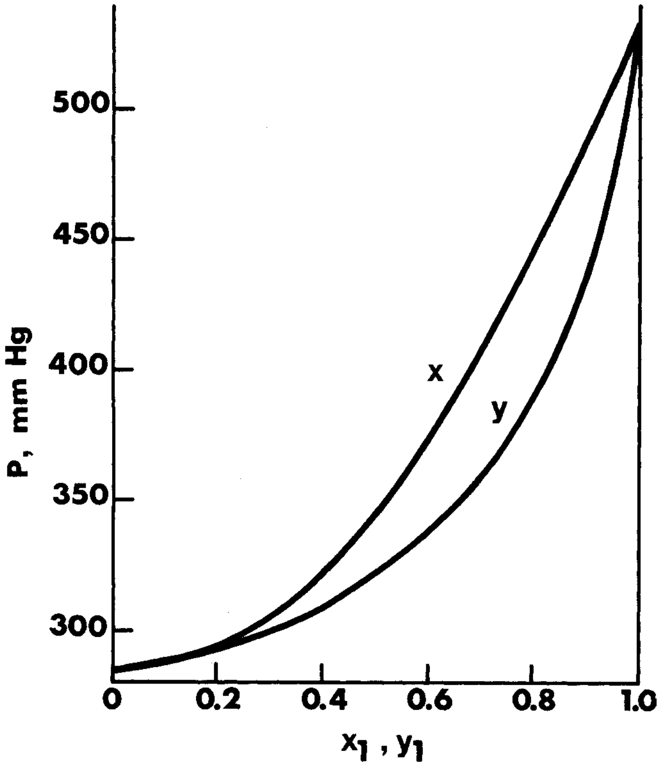

Fig. 4. P-x-y relation for dichloromethane(1)—acetone(2) at 30°C.

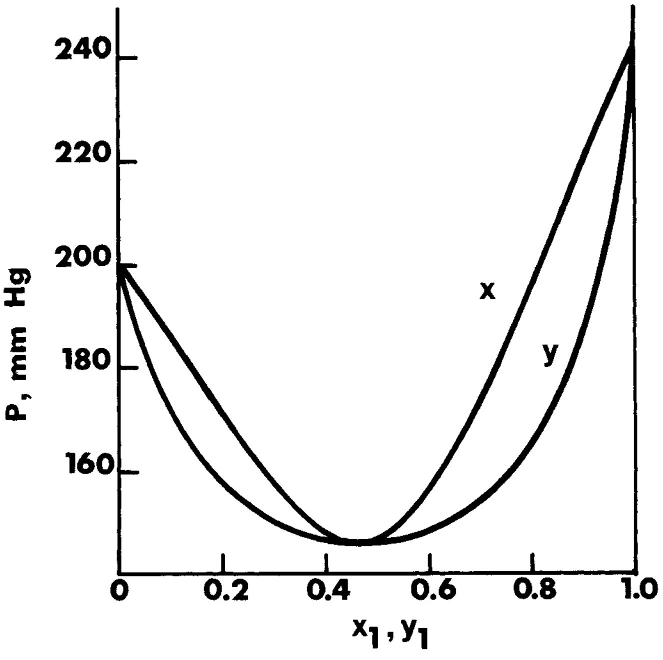

Fig. 5. P-x-y relation for chloroform(1)—tetrahydrofuran(2) at 30°C.

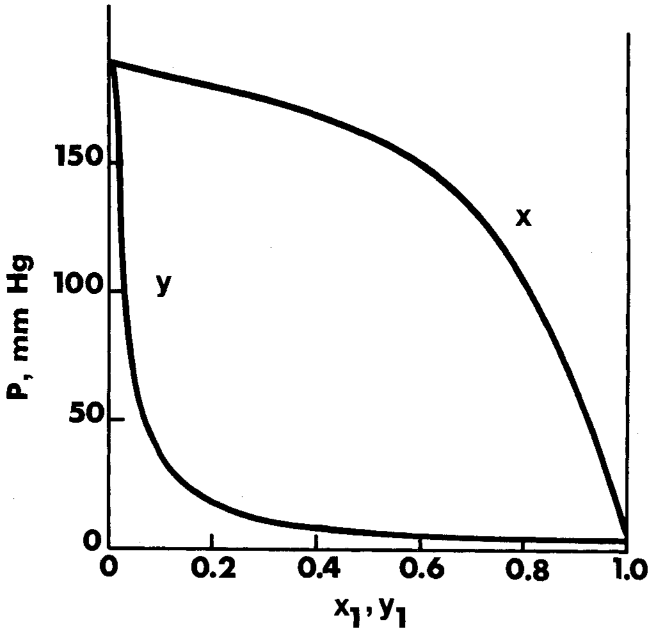

Fig. 6. P-x-y relation for n-pentanol(1)—n-hexane(2) at 30°C.

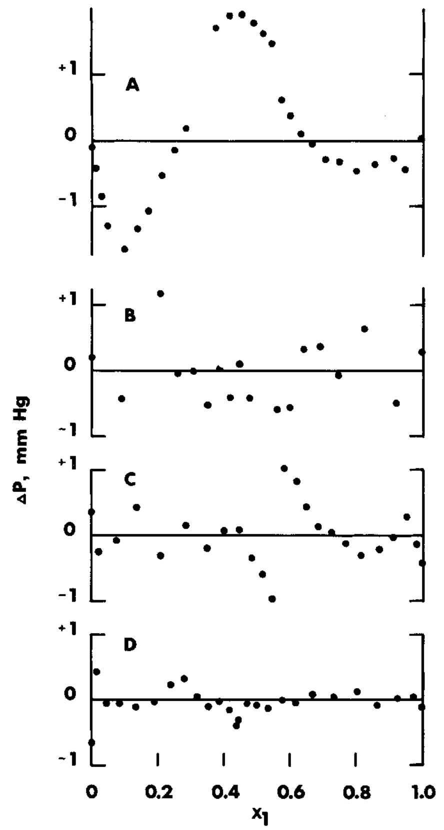

Fig. 7. Deviations between calculated and experimental pressures at 30°C for the systems: (A) *n*-pentanol(1)—*n*-hexane(2), (B) tetrahydrofuran(1)—furan(2), (C) dichloromethane(1)—1,4-dioxane(2), and (D) pyridine(1)—dichloromethane(2).

the pressure deviations ΔP in Figure 7 would be worse, because of the nonlinear relation between P and g/x_1x_2. From the theoretical point of view one wants the best representation of g/x_1x_2, but from the practical viewpoint one wants to be able to calculate a reasonable approximation to the actual P-x curve. In this case, the Wilson equation does not allow both.

The constants shown for the 14 systems of Table 1 were all determined by a least-squares fit of $\ln(\gamma_1/\gamma_2)$ versus x_1 [see Equation (7) of the preceding paper], and the pressure deviations ΔP show little in the way of systematic behavior. This can be seen from Plots (B), (C), and (D) of Figure 7, which are typical results. Plot (B) for tetrahydrofuran–furan shows simple scatter, and a maximum deviation of 1.18 mm Hg. Plot (C) for dichloromethane–1,4-dioxane illustrates the case where the two halves of a run do not exactly meet. The spline fit of the data produces a reasonable compromise. Plot (D) for pyridine–dichloromethane illustrates an exemplary run, at least from a statistical point of view.

The chloroform–tetrahydrofuran system, shown in Figure 5, was more difficult to deal with than the others. Not only is it azeotropic, but the terminal slopes of the P-x curve approach their limiting values at both $x_1 = 0$ and $x_1 = 1$. The problems that this presents are discussed in the preceding paper, and the limiting conditions are illustrated in Figure 7 of that paper. Three separate sets of P-x data were taken for this system and were combined to give one compromise spline fit, as is indicated in both Table 1 and Table 2. Had we selected any one of the three runs as the basis for correlation, the value of σ_2 in Table 1 would have been much smaller than the value reported. However, the availability of three sets of data provides an opportunity for the comparison shown in Figure 8. The runs represented by the open triangles and the solid squares were made consecutively by the same operator and with the same lots of materials, and they are in reasonable agreement. The run indicated by the solid circles was made nearly a year and a half later by a different operator and with a different lot of chloroform. This run clearly deviates from the other two in the chloroform-rich half of the composition range. The deviations near the concentration extremes are somewhat conditioned by the necessity of finding a spline fit that does not violate the slope limitations so closely approached by this system at both ends. Since we have no basis on which to select one run as being superior to the others, all three have been given equal weight in determination of the constants listed in Table 1.

No data for any of the systems reported here have been found in the literature for a temperature of 30°C. However, McGlashan and Rastogi (1958) reported a set of data for the chloroform–1,4-dioxane system at 50°C. Heat of mixing data are available for this system at 30 and 45°C:

$$\Delta H_{30}/x_1x_2 = -4909.1 - 5285.3x_1 + 595.6x_1^2 - 8505.6x_1^3 + 7937.5x_1^4$$

$$\Delta H_{45}/x_1x_2 = -5033.3 - 3614.0x_1 - 3508.6x_1^2 - 1634.2x_1^3 + 4030.5x_1^4$$

where x_1 is molefraction chloroform and ΔH is in Joules/g mole. The equation for 30°C was reported by Van Ness (1967) and that for 45°C is also based on measurements made in our laboratory. Both result from the work of Hughes (1967). Thus the present correlation for g/x_1x_2 at 30°C was extended to 50°C by integration of the Gibbs-Helmholtz equation:

$$\left[\frac{\partial(g/x_1x_2)}{\partial T}\right]_{P,x} = \frac{-\Delta H}{x_1x_2RT^2}$$

Integration was carried out at a series of compositions, and

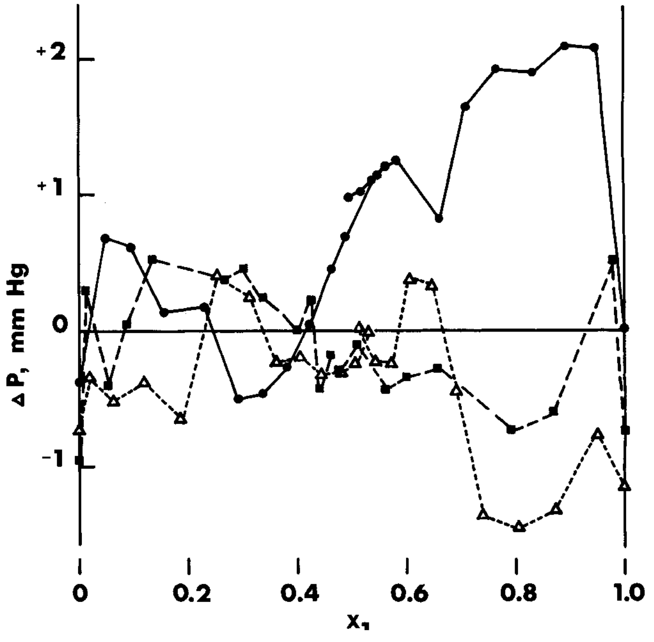

Fig. 8. Deviations between calculated and experimental pressures for three separate runs at 30°C for the system chloroform(1)—tetrahydrofuran(2).

it was assumed that ΔH was linear in T over the temperature interval from 30 to 50°C. The values of g/x_1x_2 so obtained at 50°C were correlated by the equation:

$$\frac{g}{x_1x_2} = -0.6389x_2 - 1.3302x_1 - 0.09727x_1x_2$$

from which one can readily calculate the P-x-y relationship at 50°C [see Equations (6) and (9a) of the preceding paper].The results are shown by Figure 9, where the curves represent the computed values and the points are the raw data of McGlashan and Rastogi (1958). We have used the vapor pressures P_1^{sat} and P_2^{sat} at 50°C reported by McGlashan and Rastogi to establish the curves, which give an entirely reasonable correlation of their raw data. The root mean square deviation in pressure is 2.45 mm Hg and in y is 0.008.

Data are also available in the literature for the pyridine-chloroform system. Findlay and Kenyon (1969) report results for temperatures of 50 and 63.5°C. In addition heat-of-mixing data at 25°C are given by Findlay et al. (1967) and by Becker et al. (1970). Although these two sets of ΔH data are in poor agreement, they are adequate to allow estimates of g/x_1x_2 to be made at 50 and 63.5°C under the assumption that ΔH is independent of T, as reported by Findlay et al. (1967). The results of these calculations give g/x_1x_2 versus x_1 relations at 50 and 63.5°C in very poor agreement with those reported by Findlay and Kenyon (1969). The reason for this is not known.

No corrections were made for vapor-phase nonidealities for the 14 systems of Table 1. Since the second cross virial coefficients are not known, it is not possible to make these corrections in a way that assures that the results would be more nearly correct than they are without correction. Estimates of the virial coefficients were made to check on the influence of neglect of the vapor-phase nonidealities, and calculations show the effect to be within experimental error.

Corrections were made, however, for vapor-phase nonidealities (Van Ness, 1964) for the n-Pentanol(1)-n-Hexane(2) system, because of the strong interaction between alcohol molecules. For n-hexane B_{22} was calculated from the equation given by McGlashan and Potter (1962). For n-pentanol B_{11} was estimated from the Berthelot equation combined with a correction ΔB given by Kunz and Kapner (1971). The cross second virial coefficient was estimated according to the recommendations of Prausnitz (1959). The values so determined are

$$B_{11} = -4300 \text{ cc/g mole}$$
$$B_{22} = -1790 \text{ cc/g mole}$$
$$B_{12} = -2100 \text{ cc/g mole}$$

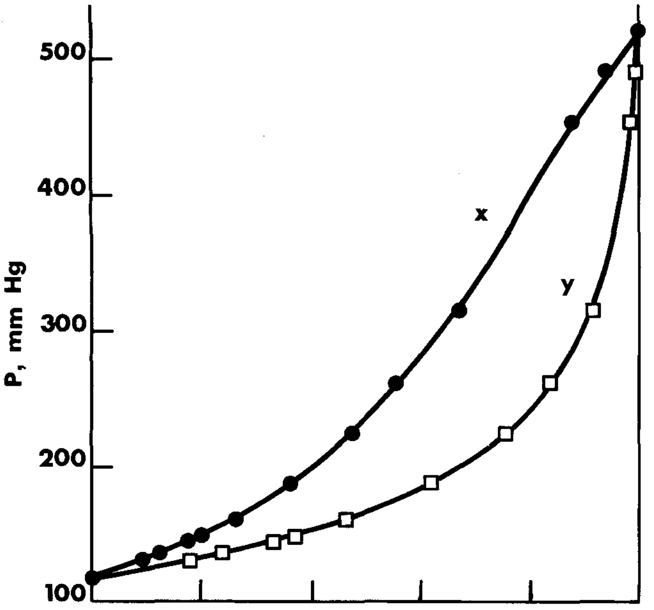

Fig. 9. P-x-y relation for chloroform(1)—1,4-dioxane(2) at 50°C. Lines are calculated from the present correlation. Data points are from McGlashan and Rastogi (1958).

Even for this highly nonideal system the vapor-phase corrections are equivalent to a maximum effect on P of only 0.12 mm Hg.

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NOTATION

A, B, D = empirical constants (see Table 1)
B_{ij} = second virial coefficient
G^E = excess Gibbs function, liquid phase
g = G^E/RT
ΔH = heat of mixing
P = vapor pressure in general
P^{sat} = vapor pressure of a pure component
R = universal gas constant
T = absolute temperature
x = mole fraction, liquid phase
y = mole fraction, vapor phase
γ = activity coefficient, liquid phase
σ_1, σ_2 = root mean-square deviations (see Table 1)
1, 2 = as subscripts, identify the two components of a binary system

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A Feasible-Point Algorithm for Structured Design Systems in Chemical Engineering

Structured design systems are systems in which the equations representing the equality and inequality constraints are sparse and highly precedence orderable. An algorithm has been developed for such systems which is guaranteed, under certain assumptions, to arrive in a finite number of steps at a feasible point (that is, one which satisfies all the constraints) or to identify a subset of the constraints for which no feasible point can be found. The algorithm can be applied to a system with only inequality constraints or to a system with both equality and inequality constraints.

The algorithm uses an indirect approach. It hypothesizes that a subset of constraints has no feasible region and then attempts to verify this conjecture. If successful, the subset is identified as infeasible and obviously no feasible point exists. If unsuccessful, either a new hypothesis can be generated or the algorithm has indirectly found a feasible point.

Limited computational experience with the algorithm indicates that the number of steps required to find a feasible point for a system of constraints has been of the same order of magnitude as the total number of constraints in the system. For linear constraints, the efficiency of the algorithm has been comparable to phase one of the Simplex algorithm of Linear Programming.

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SCOPE

A rather successful and common approach to locating a feasible point for small design problems by hand is to guess at such a point and determine which constraints (if any) are violated. If the violated set contains only a few structurally simple constraints (such as $T \leqq 300°\text{C}$), these are used with the design equation set to guess a new candidate feasible point. The process is repeated until hopefully a feasible point is reached. For a design system with a large number of constraints, the problem of finding a first feasible point may be too formidable to permit a trial-and-error approach. The algorithm presented here provides a practical approach to the feasible-point problem.

The equations representing the constraints for most practical problems in chemical engineering design are highly structured, that is, each equation involves few of the variables and therefore the set of equations is highly precedence orderable. For structured problems, the solution of a set of equations is considered a reasonable task provided the structure is used in developing the solution procedure. Currently systems are under development

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