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Direct Solution Of The Isothermal Gibbs-Duhem Equation For Multicomponent Systems

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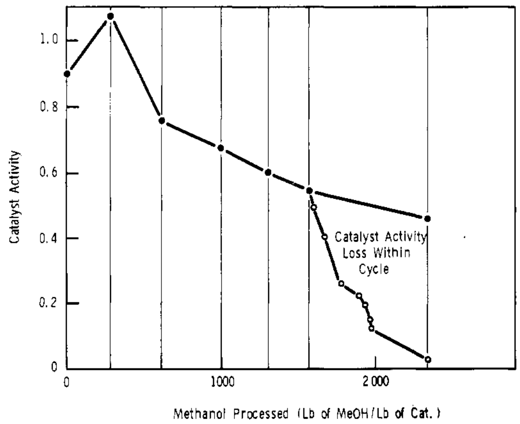

Figure 19. Initial catalyst activity in each cycle of kinetic aging test.

Concluding Remarks

The results of this process variable study have demonstrated the feasibility of converting methanol to high octane gasoline in a fluid bed reactor. In addition, some effects of temperature, pressure, and space velocity on methanol conversion and product selectivities were defined. The concentrations of methanol, dimethyl ether, and water in the reactor effluent were in thermodynamic equilibrium.

A kinetic aging test with a total of 54 days on stream was made. The unreacted methanol in the reactor effluent provided a means of measuring catalyst deactivation in each cycle and from cycle to cycle. Most of the activity loss related to coke formation was restored by regeneration. However, steaming of the catalyst caused some irreversible deactivation.

Certain data described in this paper were used to establish operating conditions for process aging tests (i.e., 2 months duration) with complete methanol conversion in the fluid bed unit. The fluid bed technology for the conversion of methanol to high octane gasoline is being advanced in another study which involves the design, construction, and operation of a 4 BPD pilot plant.

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Direct Solution of the Isothermal Gibbs–Duhem Equation for Multicomponent Systems

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The numerical solution of the relative volatility form of the isothermal Gibbs–Duhem equation for multicomponent systems is carried out by a relaxation technique for two ternary systems at five different temperatures. This direct method of solution eliminates calculating and differentiating the excess Gibbs free energy as required by other indirect methods.

Scope

The viability of theoretically determining vapor compositions from experimental vapor pressures over liquid mixtures under isothermal conditions has been well established by numerous investigators, and the various techniques for accomplishing the calculations are given by Prausnitz et al. (1967), Van Ness (1970), and Mixon et al. (1965). The incentive for using this method is great since the cost associated with making vapor composition measurements is eliminated, and as suggested by Manley (1973) and Van Ness et al. (1973), the results may be more accurate. This paper presents an alternative technique to those already established and provides a set of differential equations linking the experimental P–x data and the relative volatilities. These equations are shown to be soluble by an iterative numerical algorithm similar to that used by Mixon et al. (1965). The resulting technique is similar to those already established and has some of the advantages and disadvantages of each.

Introduction

The classical technique for solution of the isothermal Gibbs–Duhem equation as demonstrated by Prausnitz et al. (1967) yields correlation constants for an analytical equation expressing the excess Gibbs free energy as a function of liquid

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composition. This is a most useful result since the correlation can then be used directly to calculate K values for distillation design. However, if the excess Gibbs free energy function is complex, then some smoothing of the experimental data results from the necessary assumption of an analytical form for the function. Also, at higher pressures it is sometimes necessary to make substantial and arbitrary extrapolations when calculating the liquid phase standard state fugacities.

When distillation design studies are made, computer run time often becomes excessive and expensive, and much of the time is used in calculating K values. Since at higher pressures the use of an excess Gibbs free energy expression for describing the phase equilibrium information requires iterative calculations, it is not always the best method for correlating the data. Typical alternate methods are given by Soave (1972) and Hala et al. (1967). For this reason, and others not discussed, the classical technique for theoretically determining vapor compositions from isothermal vapor pressure data is not always used.

A second technique as demonstrated by Van Ness (1970) eliminates the calculation of the excess Gibbs free energy entirely and provides a differential equation directly relating the experimental vapor pressure data and the vapor compositions to be calculated. This "direct" technique does not require the assumption of any analytical expressions; however, it is necessary to interpolate and numerically differentiate the experimental vapor pressure data. The advantage is that all the numerical smoothing is done directly with the experimental data, and it is relatively easy to assure that a minimum amount of knowledge is lost. Of course, once the vapor compositions have been obtained, the data must still be correlated for use in design. Also, care must be exercised in selecting the appropriate way of handling the vapor pressure data because it is possible to develop thermodynamically unacceptable relationships, and then the differential equation cannot be solved. Another drawback to this technique is that the marching type solution used must always proceed in the direction of increasing pressure. This presents only minor problems for binary systems; however, possibly for this reason, the technique has never been developed for multicomponent systems.

In order to eliminate the analytical expressions required in the classical technique, Mixon et al. (1965) devised a third technique which yields numerical values for the excess Gibbs free energy. Using this technique it is necessary only to interpolate, and not to differentiate, the experimental vapor pressure data; however, the calculated excess Gibbs free energies must be numerically differentiated in order to get vapor compositions. This handling of the abstract excess Gibbs free energy data rather than the experimental vapor pressure data is undesirable because it can more easily lead to loss of knowledge about the system. Also, application of this technique to systems containing supercritical components is difficult since suitable standard states must be defined for each component. Because the excess Gibbs free energy is used, this technique could be described (as could also the classical technique) as "indirect". In this respect, it is basically different from the "direct" technique already described. Nevertheless, it is quite powerful and has been successfully applied to several ternary systems.

In this paper we present variation on the second technique which is direct and which is applied to multicomponent systems. The basic differential equations (10) given below provide a direct relationship between the experimental vapor pressure data and the relative volatilities. Relative volatilities have been chosen to describe the vapor composition because they are closely related to the cost of an appropriately designed distillation column for the separation of the chemicals in question. The validity of the basic equations and the viability of the numerical method are demonstrated by application of the technique to two ternary systems.

Theory

The isothermal Gibbs–Duhem equation is

$$\frac{V\mathrm{d}P}{RT} = \sum_i n_i \,\mathrm{d}\ln f_i \tag{1}$$

Writing eq 1 for both liquid and gas phases and then subtracting gives

$$\frac{1}{RT}\left(\frac{V^{\mathrm{V}}}{N^{\mathrm{V}}} - \frac{V^{\mathrm{L}}}{N^{\mathrm{L}}}\right)\mathrm{d}P = \sum_i \left[y_i \,\mathrm{d}\ln f_i^{\mathrm{V}} - x_i \,\mathrm{d}\ln f_i^{\mathrm{L}}\right] \tag{2}$$

Because $f_i^{\mathrm{L}} = f_i^{\mathrm{V}}$ at equilibrium, eq 2 becomes

$$\Delta Z \,\mathrm{d}\ln P = \sum_i (y_i - x_i)\mathrm{d}\ln f_i \tag{3}$$

in which

$$\Delta Z = Z^{\mathrm{V}} - Z^{\mathrm{L}} = \frac{P}{RT}\left(\frac{V^{\mathrm{V}}}{N^{\mathrm{V}}} - \frac{V^{\mathrm{L}}}{N^{\mathrm{L}}}\right) = \frac{P(v^{\mathrm{V}} - v^{\mathrm{L}})}{RT} \tag{4}$$

The equation for the vapor fugacity of a component "i" is

$$f_i \equiv \Phi_i y_i P \tag{5}$$

Substituting eq 5 into eq 3 yields

$$\Delta Z \,\mathrm{d}\ln P = -\sum_i x_i \,\mathrm{d}\ln y_i + \sum_i (y_i - x_i)\mathrm{d}\ln \Phi_i \tag{6}$$

From the definition of relative volatility

$$y_i \equiv K\alpha_i x_i \tag{7}$$

in which $K \equiv y_l/x_l$. Component l is arbitrarily designated as the reference component. This makes x_i for all $i \neq l$ the independent variables, and α_i for $i \neq l$ the dependent variables, since $\alpha_l = 1$. x_l is not considered an independent variable since it is calculated by $x_l = 1 - \Sigma_i' x_i$, in which

$$\sum_i{}' \equiv \sum_{\substack{i=1\\ i\neq l}}^{n}$$

Substituting eq 7 into eq 6 gives, after appropriate manipulation (see Appendix for detail)

$$\begin{aligned}(1/K)\Delta Z \,\mathrm{d}\ln P = \sum_i{}'(\alpha_i - 1)\mathrm{d}x_i + \sum_i{}'(\alpha_i \\ - 1/K)x_i[\mathrm{d}\ln \alpha_i + \mathrm{d}\ln(\Phi_i/\Phi_l)]\end{aligned} \tag{8}$$

in which $(1/K)$ can be expressed as

$$1/K = 1 + \sum_i{}'(\alpha_i - 1)x_i \tag{9}$$

Substituting eq 9 into eq 8, differentiating the resulting expression with respect to $x_{j\neq l}$ and rearranging, we obtain

$$\sum_i{}'(\alpha_i - 1)S_{ij} - (\alpha_j - 1) = -P_j \tag{10}$$

in which

$$\begin{aligned}S_{ij} \equiv x_i \Bigg\{P_j - \left(\frac{\partial \ln \alpha_i}{\partial x_j}\right)_{x_{m\neq j,l}} - \left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial x_j}\right]_{x_{m\neq j,l}} \\ + \sum_k{}' x_k \left[\left(\frac{\partial \ln \alpha_k}{\partial x_j}\right)_{x_{m\neq j,l}} + \left\{\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial x_j}\right\}_{x_{m\neq j,l}}\right]\Bigg]\end{aligned} \tag{11}$$

and in which

$$P_j \equiv \Delta Z\left(\frac{\partial \ln P}{\partial x_j}\right)_{x_{m\neq j,l}}$$

Equation 10 is the general expression of the relative volatility form of the rigorous coexistence equation for any component j in a multicomponent system of n components, where both vapor and liquid phases are present and temperature is held constant.

At $x_j = 1$, $x_i = 0$ for all $i \neq j$, eq 10 reduces to

$$[\alpha_j]_{x_j=1} = \frac{1}{1 - [P_j]_{x_j=1}} \tag{12}$$

since $[\alpha_j]_{x_j=1} > 0$, then

$$P_{x_j=1} > \left[\Delta Z \left(\frac{\partial P}{\partial x_j}\right)_{x_{m\neq j,l}} \right]_{x_j=1} \tag{13}$$

The total derivative d ln (Φ_i/Φ_l) can be expressed as a function of $y_{i\neq l}$ and P by

$$\mathrm{d}\ln(\Phi_i/\Phi_l) = \sum_k{}' \left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial y_k}\right]_{P,y_{m\neq k,l}} \mathrm{d}y_k + \left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial \ln P}\right]_{y_{m\neq l}} \mathrm{d}\ln P \tag{14}$$

In order to evaluate two of the terms in eq 11 we differentiate eq 14 with respect to $x_{j\neq l}$ obtaining

$$\left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial x_j}\right]_{x_{m\neq j,l}} = \sum_k{}' \left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial y_k}\right]_{P,y_{m\neq k,l}} \left(\frac{\partial y_k}{\partial x_j}\right)_{x_{m\neq j,l}} + \left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial \ln P}\right]_{y_{m\neq l}} \left(\frac{\partial \ln P}{\partial x_j}\right)_{x_{m\neq j,l}} \tag{15}$$

Differentiating eq 7 with respect to $x_{j\neq l}$, we obtain

$$\left(\frac{\partial y_i}{\partial x_j}\right)_{x_{m\neq j,l}} = -K^2\alpha_i x_i \left\{\alpha_j - 1 + \sum_k{}' \alpha_k x_k \left(\frac{\partial \ln \alpha_k}{\partial x_j}\right)_{x_{m\neq j,l}} - \frac{1}{K}\left[\left(\frac{\partial \ln \alpha_i}{\partial x_j}\right)_{x_{m\neq j,l}} + \left(\frac{\partial \ln x_i}{\partial x_u}\right)_{x_{m\neq j,l}}\right]\right\} \tag{16}$$

in which, if $i \neq j$, $(\partial \ln x_i/\partial x_j)_{x_{m\neq j,l}} = 0$ and if $i = j$ then $(\partial \ln x_i/\partial x_j)_{x_{m\neq j,l}} = 1/x_i$.

If we assume that the vapor phase of the multicomponent system follows the virial equation of state truncated after the second virial coefficient, then

$$Z^{\mathrm{V}} = 1 + BP \tag{17}$$

where

$$B = \sum_i \sum_j y_i y_j B_{ij}$$

Let $\delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj}$ and assume that $B_{ij} \equiv B_{ji}$.

With these assumptions the appropriate terms on the right side of eq 15 can be expressed as (we have used the commonly known relationships between the fugacity and an equation of state)

$$\left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial \ln P}\right]_{y_{m\neq l}} = \ln(\Phi_i/\Phi_l) = P\{B_{ii} - B_{ll} + K \sum_j \alpha_j x_j (\delta_{ij} - \delta_{lj}) \tag{18}$$

and

$$\left[\frac{\partial \ln(\Phi_i/\Phi_l)}{\partial y_k}\right]_{P,y_{m\neq k,l}} = P(\delta_{ik} - \delta_{lk} - \delta_{il}) \tag{19}$$

Also, it is assumed that the liquid phase of the mixture obeys

$$v^{\mathrm{L}} = \sum_i x_i v_i^{\mathrm{L}}$$

With these assumptions eq 4 can be expressed as

$$\Delta Z \equiv Z^{\mathrm{V}} - Z^{\mathrm{L}} = 1 + P \sum_i x_i \left\{K\alpha_i(B_{ii} + \frac{K}{2}\sum_j \alpha_j x_j \delta_{ij}) - \frac{v_i^{\mathrm{L}}}{RT}\right\} \tag{20}$$

Computational Procedure

The method of solution for eq 10, the multicomponent isothermal coexistence equation, is based on a point relaxation technique.

Define a vector

$$\mathbf{X} \equiv (x_1, x_2, \ldots, x_{l-1}, \quad x_{l+1}, \ldots, x_n)$$

where $n - 1$ x's are varied independently, and x_l is excluded. The components of vector **X** will satisfy $x_1 + x_x + \ldots + x_{l-1} + x_l + x_{l+1} + \ldots + x_n = 1$, the material balance equation for the liquid phase.

At every point **X** in the $n - 1$ dimensional space a vector of dependent variables will exist

$$\mathbf{A} \equiv (\alpha_1, \alpha_2, \ldots, \alpha_{l-1}, \quad \alpha_{l+1}, \ldots, \alpha_n)$$

containing $n - 1$ components.

A function F is defined in terms of eq 10 as follows

$$F(\mathbf{X}) = P_j - (\alpha_j - 1) + \sum_i{}'(\alpha_i - 1)S_{ij} = 0 \tag{21}$$

which will be evaluated at a point **X** in the $(n - 1)$ dimensional space. There will be $n - 1$ equations like eq 21, one for each independent component j, at each point **X**.

Equation 10 can be solved by an explicit relaxation technique. Expanding eq 10 at any point **X**, and expressing it in matrix form

$$\begin{bmatrix} (S_{1,1} - 1) & S_{1,2} & S_{1,n} \\ S_{2,1} & (S_{2,2} - 1) & S_{2,n} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ S_{n,1} & S_{n,2} & (S_{n,n} - 1) \end{bmatrix} \cdot \begin{bmatrix} (\alpha_1 - 1) \\ (\alpha_2 - 1) \\ \cdot \\ \cdot \\ \cdot \\ (\alpha_n - 1) \end{bmatrix} = \begin{bmatrix} -P_1 \\ -P_2 \\ \cdot \\ \cdot \\ \cdot \\ -P_n \end{bmatrix} \tag{22}$$

or in short matrix notation $S\mathbf{A} = \mathbf{P}$ where matrix S and vector **P** are based on the previous values of vector **A**. The elements subscripted with l are not included in eq 22.

Equation 22 is solved for the new values of vector **A**. A convergence factor (pK) is introduced to speed convergence

$$\mathbf{A}_{\mathrm{new}}' = (1 - pK)^*\mathbf{A}_{\mathrm{old}} + pK \cdot \mathbf{A}_{\mathrm{new}} \tag{23}$$

A new vector **A** is calculated at every point in the lattice and compared with the old vector **A**. Convergence is reached when the new vector **A** is close to the old vector **A** by some small number ϵ, at all points in the lattice. If this condition is not met the procedure is repeated evaluating matrix S and vector **P** of eq 22 with the vector $\mathbf{A}_{\mathrm{new}}'$ calculated by eq 23.

Results

The method was tested with two sets of ternary data. Table I shows the results of the direct solution of the multicomponent isothermal coexistence equation for the ternary data of Martinez-Ortiz (1976). The results appear to be satisfactory. No additional data are reported in the literature for this ternary system under the conditions reported by Martinez-Ortiz (1976). Carmichael et al. (1962) report data for this ternary system, but the data are not under the conditions of the data used for this study so comparison was not possible.

Table II shows the results of the solution of eq 10 for the ternary data of Steele et al. (1976). These vapor compositions are close to the values calculated by Steele (1975), using the classical technique, and agreement is considered satisfactory. The data reported by Steele et al. (1976) show the presence

Table I. Vapor Phase Compositions Calculated by Direct Solution of Eq 10 for the System Isobutane (1)–Isobutylene (2)–*n*-Butane (3). Initial Approximation for the Relative Volatility: Ratio of the Pure Component Vapor Pressures. Component 3 Taken as the Reference Component. $\Delta X = 0.025$, $pK = 0.30$

		40 °F			70 °F		
x_1	x_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2
0.25	0.00	19.93	0.3293	0.0000	34.76	0.3195	0.0000
0.50	0.00	22.15	0.5944	0.0000	38.27	0.5837	0.0000
0.75	0.00	24.37	0.8137	0.0000	41.79	0.8071	0.0000
0.00	0.25	19.16	0.0000	0.3012	33.58	0.0000	0.2967
0.25	0.25	21.38	0.3086	0.2707	37.17	0.3012	0.2693
0.50	0.25	23.62	0.5613	0.2471	40.64	0.5532	0.2480
0.75	0.25	25.87	0.7703	0.2297	44.26	0.7674	0.2326
0.00	0.50	20.40	0.0000	0.5554	35.67	0.0000	0.5514
0.25	0.50	22.66	0.2961	0.5030	39.21	0.2891	0.5040
0.50	0.50	25.02	0.5390	0.4610	42.97	0.5324	0.4676
0.00	0.75	21.49	0.0000	0.7846	37.48	0.0000	0.7815
0.25	0.75	23.87	0.2892	0.7108	41.26	0.2826	0.7174

		100 °F			130 °F			160 °F		
x_1	x_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2
0.25	0.00	56.84	0.3101	0.0000	88.03	0.3032	0.0000	130.47	0.2958	0.0000
0.50	0.00	62.00	0.5732	0.0000	95.46	0.5651	0.0000	140.51	0.5565	0.0000
0.75	0.00	67.30	0.8015	0.0000	102.98	0.7953	0.0000	150.90	0.7903	0.0000
0.00	0.25	55.20	0.0000	0.2916	85.92	0.0000	0.2874	127.78	0.0000	0.2836
0.25	0.25	60.46	0.2946	0.2679	93.40	0.2889	0.2670	137.99	0.2835	0.2659
0.50	0.25	65.73	0.5475	0.2492	100.89	0.5408	0.2506	148.32	0.5355	0.2584
0.75	0.25	71.11	0.7658	0.2342	108.61	0.7623	0.2377	158.98	0.7607	0.2393
0.00	0.50	58.39	0.0000	0.5465	90.63	0.0000	0.5421	134.47	0.0000	0.5382
0.25	0.50	63.68	0.2837	0.5061	98.16	0.2790	0.5067	144.79	0.2746	0.5073
0.50	0.50	69.20	0.5268	0.4732	106.13	0.5225	0.4775	155.61	0.5188	0.4812
0.00	0.75	61.25	0.0000	0.7798	94.89	0.0000	0.7774	140.56	0.0000	0.7748
0.25	0.75	66.88	0.2759	0.7241	102.89	0.2723	0.7277	151.32	0.2680	0.7320

[a] Pressure calculated by the equation given by Martinez-Ortiz (1976).

Table II. Vapor Phase Compositions Calculated by Direct Solution of Eq 10 for the System Isobutane (1)–1-Butene (2)–1,3-Butadiene (3). Initial Approximation for the Relative Volatility: Ratio of the Pure Component Vapor Pressures. Component 3 Taken as the Reference Component. $\Delta X = 0.025$, $pK = 0.25$

		40 °F			70 °F		
x_1	x_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2
0.25	0.00	23.58	0.3308	0.0000	40.62	0.3169	0.0000
0.50	0.00	25.41	0.5614	0.0000	43.48	0.5518	0.0000
0.75	0.00	26.42	0.7669	0.0000	45.03	0.7648	0.0000
0.00	0.25	21.20	0.0000	0.2700	37.21	0.0000	0.2666
0.25	0.25	23.81	0.3124	0.2350	41.01	0.3017	0.2374
0.50	0.25	25.21	0.5452	0.2223	43.17	0.5389	0.2262
0.75	0.25	25.78	0.7753	0.2247	44.03	0.7718	0.2282
0.00	0.50	21.71	0.0000	0.5152	37.91	0.0000	0.5128
0.25	0.50	23.84	0.3001	0.4647	41.01	0.2917	0.4706
0.50	0.50	24.77	0.5425	0.4575	42.49	0.5366	0.4634
0.00	0.75	21.90	0.0000	0.7529	38.16	0.0000	0.7526
0.25	0.75	23.47	0.2945	0.7055	40.57	0.2870	0.7130

		100 °F			130 °F			160 °F		
x_1	x_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2	P,[a] psia	y_1	y_2
0.25	0.00	65.78	0.3058	0.0000	101.08	0.2970	0.0000	148.92	0.2894	0.0000
0.50	0.00	69.84	0.5438	0.0000	106.82	0.5371	0.0000	156.51	0.5311	0.0000
0.75	0.00	72.08	0.7629	0.0000	109.92	0.7610	0.0000	160.55	0.7593	0.0000
0.00	0.25	60.98	0.0000	0.2639	94.65	0.0000	0.2618	140.48	0.0000	0.2599
0.25	0.25	66.24	0.2933	0.2393	101.80	0.2864	0.2410	149.89	0.2806	0.2423
0.50	0.25	69.48	0.5334	0.2296	106.19	0.5285	0.2326	155.69	0.5241	0.2352
0.75	0.25	70.77	0.7688	0.2312	108.05	0.7661	0.2339	158.16	0.7636	0.2364
0.00	0.50	61.93	0.0000	0.5107	95.93	0.0000	0.5090	142.15	0.0000	0.5075
0.25	0.50	66.40	0.2850	0.4753	101.95	0.2795	0.4791	149.93	0.2748	0.4823
0.50	0.50	68.54	0.5316	0.4684	104.94	0.5271	0.4729	153.96	0.5230	0.4770
0.00	0.75	62.37	0.0000	0.7523	96.49	0.0000	0.7519	142.83	0.0000	0.7514
0.25	0.75	65.74	0.2811	0.7189	101.08	0.2763	0.7237	149.02	0.2722	0.7278

[a] Pressure calculated by the equation given by Martinez-Ortiz (1976).

of an azeotrope at the 1-butene rich end, and the method presented here did not present any difficulty in solving the coexistence equation at the azeotrope.

Tables III and IV show the pure component and mixture virial coefficients and liquid specific volumes that were used for the solution of eq 10. The mixture virial coefficient were

Table III. Second Virial Coefficients and Liquid Molar Volumes for the System Isobutane (1)–Isobutylene (2)–*n*-Butane (3)

T, °F	mL/g-mol $-B_{11}$	$-B_{22}$	$-B_{33}$	δ_{12}	δ_{13}	δ_{23}	v_1^L	v_2^L	v_3^L
40	796	705	933	−1	4	3	101	91	97
70	708	690	825	−1	3	3	105	95	101
100	642	614	717	0	3	3	109	98	104
130	572	565	622	0	3	2	114	102	108
160	516	511	554	0	2	2	120	107	113

Table IV. Second Virial Coefficients and Liquid Molar Volumes for the System Isobutane (1)–1-Butene (2)–1,3-Butadiene (3)

T, °F	mL/g-mol $-B_{11}$	$-B_{22}$	$-B_{33}$	δ_{12}	δ_{13}	δ_{23}	v_2^L	v_3^L
40	790	719	699	0	1	2	91	84
70	704	714	692	−1	1	2	94	87
100	636	633	623	−1	1	1	99	90
130	568	560	541	−1	1	1	103	94
160	514	500	484	−1	0	1	108	98

Table V. Analysis of the *P*–*x* Fitting Procedure

System	Type of fit for the P–x data	Root mean square ΔP,[a] psia 40 °F	70 °F	100 °F	130 °F	160 °F
Isobutane (1)–isobutylene (2)–n-butane (3)	Polynomial fit 4th degree on two variables x_1 and x_2; 30 points at each temperature	0.016	0.016	0.015	0.019	0.020
Isobutane (1)–1-butene (2)–1,3-Butadiene (3)	Polynomial fit 4th degree on two variables x_1 and x_2; 32 points at each temperature	0.028	0.039	0.040	0.055	0.083

[a] Root-mean-square $\Delta P = [\Sigma_i (\Delta P_i)^2/(N-1)]^{1/2}$; $\Delta P_i = P$ (experimental) $- P$ (calculated).

calculated by the method of Tsonopoulos (1974) for both systems. For the system in Table IV the pure component virial coefficients and the liquid molar volume are those reported by Steele (1975); the liquid molar volume for isobutane is not reported in Table IV because it is identical with the one reported in Table III. For isobutane and n-butane in Table III the pure component virial coefficients and the liquid specific volume are those reported by Canjar and Manning (1967); for isobutylene the values are based on the data reported by Barron et al. (1962).

Table V shows the quality of the P-x fit used for the solution of eq 10. The root-mean-square ΠP falls within the experimental uncertainty of the original investigators. The quality of the P-x fit is a critical factor of the computational method, and a polynomial fit of the P-x data was used. A spline fit could have been used had the polynomial fit been inadequate.

The application of eq 10 to four hightly nonideal binary systems is described elsewhere by Martinez-Ortiz and Manley (1977), and the calculated vapor compositions agreed closely with experimental values. This, together with the close agreement with Steele (1975) mentioned previously, tends to confirm the validity of the method.

Experience from the application of this method indicates that an adequate P–x correlation obtained from good P–x data is quite important in obtaining convergence. Although we have not yet derived the appropriate criteria, there are P–x equations for which no solution to eq 10 exists. If such a relationship is developed through improper correlation of the experimental data, the method will not converge. The other important factor is the parameter pK in eq 23, which controls the step size increment on the relative volatility toward the correct solution. In the case where $pK = 1$ the new vector $\mathbf{A}$ comes directly from the solution of eq 22 tending to overcorrect the values of the relative volatilities causing divergence. If the value of pK is different from one (we have experimented with values between 0 and 1) an averaging effect between the vector $\mathbf{A}$ used to calculate matrix S, and the new vector $\mathbf{A}$ calculated from eq 22 is produced, and convergence is facilitated.

There are limited ternary P–x–y data of acceptable quality in the literature which can be used to test the present method further. Some apparently acceptable P–x–y data are those of Severns et al. (1955), which were not investigated in this study. The ternary P–x data of Abbott et al. (1975) are available, appear to be of high quality, and could be used. A quick attempt was made to correlate the ternary P–x data of Abbott et al. (1975) and solve eq 10. A polynomial fit was used with a pK value of 1 and convergence was not obtained. Nevertheless, we believe that the correlation of the data could be improved by using a bicubic spline fit, and with a proper pK value, convergence could be obtained.

Conclusions and Significance

A new form of the isothermal Gibbs–Duhem equation directly relating the relative volatilities of a multicomponent system to the vapor pressures over liquid mixtures of varying composition has been derived and solved for two ternary systems. The solution is carried out using a relaxation technique which, unlike previous "direct" methods does not depend on the direction of integration, and consequently is easily applicable to multicomponent systems. In contrast to other "indirect" methods of solution, this new "direct" method eliminates calculating and differentiating the excess Gibbs free energy which can introduce unnecessary errors into the analysis of total pressure data. Also, the problem of specifying suitable standard states for supercritical components is not encountered.

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Appendix

To derive eq 8 from eq 6, note that

$$\sum_i x_i \, \mathrm{d} \ln y_i = \sum_i x_i \, \mathrm{d} \ln K + \sum_i x_i \, \mathrm{d} \ln \alpha_i + \sum_i x_i \, \mathrm{d} \ln x_i$$

since $y_i = K\alpha_i x_i$, $\ln y_i = \ln K + \ln \alpha_i + \ln x_i$, and $\mathrm{d} \ln y_i = \mathrm{d} \ln K + \mathrm{d} \ln \alpha_i + \mathrm{d} \ln x_i$. Then

$$\sum_i x_i \, \mathrm{d} \ln y_i = \mathrm{d} \ln K + \sum_i{}' x_i \, \mathrm{d} \ln \alpha_i$$

because

$$\sum_i x_i = 1; \qquad \mathrm{d} \ln \alpha_l = \mathrm{d} \ln 1 = 0; \qquad \sum_i \mathrm{d}x_i = 0$$

But using eq 9

$$\mathrm{d} \ln K = -\mathrm{d} \ln (1/K) = -K\mathrm{d}(1/K)$$

$$= -K \sum_i{}' [(\alpha_i - 1)\mathrm{d}x_i + x_i \mathrm{d}\alpha_i]$$

So

$$-(1/K)\sum_i \mathrm{x}_i \,\mathrm{d}\ln y_i = \sum_i{}'(\alpha_i - 1)\mathrm{d}x_i + \sum_i{}'\alpha_i x_i \,\mathrm{d}\ln\alpha_i - (1/K)\sum_i{}'x_i\,\mathrm{d}\ln\alpha_i = \sum_i{}'(\alpha_i - 1)\mathrm{d}x_i + \sum_i{}'(\alpha_i - 1/K)x_i\,\mathrm{d}\ln\alpha_i$$

Similarly

$$(1/K)\sum_i (y_i - x_i)\,\mathrm{d}\ln\Phi_i = \sum_i{}'(\alpha_i - 1/K)x_i\,\mathrm{d}\ln(\Phi_i/\Phi_l)$$

Nomenclature

$\mathbf{A}$ = vector of relative volatilites for every component of a system
B = second virial coefficient
f = fugacity
G^{E} = excess Gibbs function, liquid phase
g = G^{E}/RT
K = ratio of mole fraction of component n in the vapor to mole fraction of component n in the liquid
n = total number of components
N = total number of moles
n_i = number of moles of component i
P = vapor pressure in general
P_j = $\Delta Z(\partial \ln P/\partial x_j)_{x_{m\neq j,l}}$
P_i^{SAT} = vapor pressure of pure i
pK = convergence parameter
R = universal gas constant
S = defined by eq 11
T = absolute temperature
V = total volume
v = specific volume
$\mathbf{X}$ = vector of liquid mole fractions of all the components of a system
x_i, = mole fraction of i, liquid phase
y_i, = mole fraction of i, vapor phase

Greek Letters

α_i = relative volatility of i
δ_{ij} = $2B_{ij} - B_{ii} - B_{jj}$
ϵ = small positive number
Δ = difference
Φ_i = fugacity coefficient of i in a gas mixture

Subscripts

i, j, k, l = component i, j, k, l
ij = i–j interaction

Superscripts

E = excess property
L = identify liquid phase
SAT = saturated
V = identify vapor phase

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The Effective Power Dependence of the Heat Transfer Coefficient for Fully Developed Turbulent Convection in a Tube

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The effective power dependence of the heat transfer coefficient on the various independent variables is shown to be a significant function of the Reynolds and Prandtl numbers, particularly as the Prandtl number decreases. Therefore fixed "rules of thumb" regarding this power dependence, for use in preliminary design, may be quite misleading, particularly if liquid metals are considered. The variation of the corresponding effective power dependence of the pressure gradient (or flow rate) is, however, found to be quite small over the complete range of Reynolds numbers. This analysis is based on recent general correlating equations and represents an improvement over prior results based on simple power-law expressions with a limited range of applicability.

Introduction

The power dependence of the coefficient for turbulent forced convection on the physical properties and independent variables is an important consideration in design and operation. Such information provides valuable "rules of thumb" for the preliminary choice of fluids, dimensions, and operating conditions even though the ultimate design and conditions are to be optimized with a computer.

Previous analyses of the power dependence have all been based on simple power-law relationships between Nu, Re, Pr,