EFFECT OF RANDOM ERRORS AND BIAS OF ISOBARIC EQUILIBRIUM *x, y* AND *t* DATA OF LIQUID–VAPOUR BINARY SYSTEMS ON THE CALCULATED NUMBER OF THEORETICAL PLATES OF A RECTIFICATION COLUMN

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The effect of random errors and bias of temperature and phase composition data in the isobaric L–G equilibrium on the calculated number of theoretical plates of a continuously working rectification column at various reflux ratios was investigated. Five model binary systems exhibiting different behaviour and relative volatility were used.

The isobaric liquid–vapour equilibrium data are prerequisite in design and simulation calculations of rectification columns. The basic set of equilibrium x, y, t data at P = const, which is usually experimentally prepared, is first processed prior to their application in the numerical procedures to obtain parameters of equations correlating the activity coefficients of the components in the liquid phase in dependence on composition, and on temperature.

The precision of the equilibrium data employed is, of course, closely related with the error of the temperature and phase composition measurements, and this will in turn affect the precision of calculation of the rectification column. This was the subject of the two preceding papers[1,2]. The one was concerned with the effect of errors in the measurement of the equilibrium temperature on the isobaric equilibrium dependence, whereas the other dealt with the effect of errors in the measurement of the equilibrium phase composition. The effect of error in the total pressure measurement can be neglected in this case. Gaining insight into the effect of the various kinds of error is useful, if for no other reason, because one can assess which of them is decisive and whether the effects of errors of the various quantities lower or increase one another.

The problems were examined by a simulated experiment using the following five model systems: n-hexane–n-heptane (I), cyclohexane–n-heptane (II), methylcyclohexane–aniline (III), n-hexane–benzene (IV), and chloroform–benzene (V). The total pressure was invariably 101 300 Pa. The systems differ in their relative volatility, in the sense of their deviation from the ideal solution behaviour, and in the existence of a positive azeotropic point. By way of illustration, the distribution equilibrium diagrams are shown in Fig. 1.

THEORETICAL

Simulated Experiment and Correlation of Equilibrium Data

The equilibrium state of the systems was described quantitatively using the well-known equation

$$P\, y_i\, \varphi_i^{\mathrm{G}} \;=\; P_i^{\mathrm{o}}\, x_i\, \gamma_i\, \varphi_{i\mathrm{s}}^{\mathrm{o}} \exp[v_i^{\mathrm{oL}}\,(P - P_i^{\mathrm{o}})/\boldsymbol{R}T\,] \qquad (1)$$

for components $i = 1, 2$.

The secondary virial coefficients of the pure components and the virial cross coefficients required to derive the fugacity coefficients were calculated following Hayden and O'Connel[3] and Nothnagel and coworkers[4]. The saturated vapour pressures of the pure components were obtained from Antoine's equation using coefficients by Wichterle and Linek[5], and the molar volumes of the liquid components were calculated by the modified Rackett equation[6].

The dependence of the activity coefficients of the components in the liquid phase on composition was expressed through the Wilson equations[7]

$$\ln \gamma_1 \;=\; -\ln(x_1 + x_2\,\Lambda_{12}) \;+\; x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2\,\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\,\Lambda_{21}} \right) \qquad (2a)$$

$$\ln \gamma_2 \;=\; -\ln(x_2 + x_1\,\Lambda_{21}) \;-\; x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2\,\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\,\Lambda_{21}} \right), \qquad (2b)$$

where the Λ parameters are calculated as

$$\Lambda_{12} \;=\; \frac{v_2^{\mathrm{oL}}}{v_1^{\mathrm{oL}}} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{\boldsymbol{R}T} \right) \qquad (3a)$$

$$\Lambda_{21} \;=\; \frac{v_1^{\mathrm{oL}}}{v_2^{\mathrm{oL}}} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{\boldsymbol{R}T} \right). \qquad (3b)$$

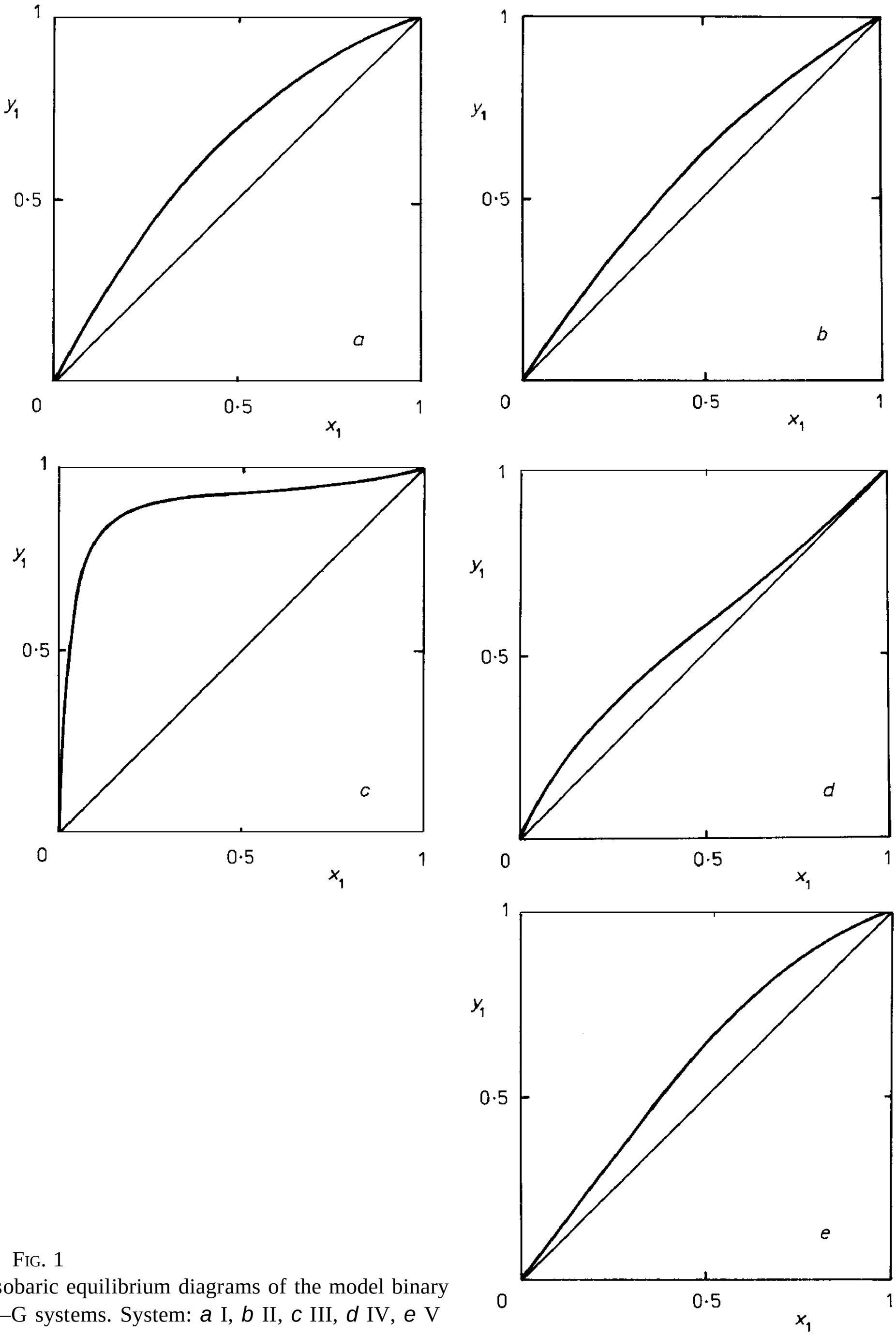

FIG. 1
Isobaric equilibrium diagrams of the model binary L–G systems. System: *a* I, *b* II, *c* III, *d* IV, *e* V

Sets of standard equilibrium data of the five systems treated were prepared based on Eqs (*1*) – (*3*). The preparation has been described in detail in ref.[1], where the values of the energy parameters ($\lambda_{ij} - \lambda_{ii}$) of the Wilson equations are also given.

When preparing the "experimental" equilibrium mole fractions and temperatures involving random errors we postulated that the errors are random quantities with a normal probability distribution, with a constant dispersion variance across the entire concentration region. Then the "experimental" mole fractions and temperature can be written as

$$x_{j\mathrm{e}} = x_j + \sigma_x N_k \tag{4a}$$

$$y_{j\mathrm{e}} = y_j + \sigma_y N_k \tag{4b}$$

$$t_{j\mathrm{e}} = t_j + \sigma_t N_k \tag{4c}$$

for $j = 1, . . ., l$; $k = 1, . . ., m$; $x_{j\mathrm{e}}$, $y_{j\mathrm{e}}$, $t_{j\mathrm{e}}$ and x_j, y_j, t_j are the experimental and accurate (standard) values, respectively, of the equilibrium mole fractions of the lower-boiling-temperature component and of the equilibrium temperature in the j-th simulated measurement. N_k is a number from a sequence of random numbers with normal distribution and with the centre $\mu = 0$ and variance $\sigma^2 = 1$. The products $\sigma_x N_k$, $\sigma_y N_k$ and $\sigma_t N_k$ represent random errors of the equilibrium quantities in a measurement. The subscripts j and k refer to the serial numbers of the experiment and random number, respectively. The procedure for preparation of the numbers N_k has been described[1]. Their order in the preparation of experimental values of x, y and t remained the same as in the papers[1,2].

When assessing the effect of bias, the "experimental" equilibrium mole fractions and temperature were simulated by the relations

$$x_{j\mathrm{e}} = x_j \pm \delta_x \tag{5a}$$

$$y_{j\mathrm{e}} = y_j \pm \delta_y \tag{5b}$$

$$t_{j\mathrm{e}} = t_j \pm \delta_t , \tag{5c}$$

where δ is a positive or negative constant bias of the quantity in question. The equilibrium state is then described completely by the four quantities x_e, y_e, t_e and P_e, where P_e is identical with the standard pressure P = 101 300 Pa.

The equilibrium data sets, involving random errors or bias, are processed separately in three subsequent iteration cycles.

In the first cycle the Wilson equation parameters are optimized for all experimental equilibrium data of the set simultaneously, using constant values of the independent parameters x_{1jc} and t_{jc} (approximated at the beginning by the experimental values), by using the target function

$$F_1(\lambda_{12} - \lambda_{11}, \lambda_{21} - \lambda_{22}) = \sum_j \left(\frac{P_{je} - P_{jc}}{P_{je}} \right)^2 \qquad (6)$$

in which $P_{je} = P$ is the experimental (accurate) total pressure value and P_{jc} is the calculated value in the j-th measurement. The Gauss–Newton method was applied to the optimization of the energy parameters of the Wilson equations.

The P_{jc} values in Eq. (*6*) are calculated according to Eq. (*1*) in the form

$$P_{jc} = \sum_i (f_{ic}^{L} / \varphi_{ic}^{G}) , \qquad (7)$$

where f_{ic}^{L} is the fugacity of the component given by the right-hand side of Eq. (*1*).

The calculation of P_{jc} also includes that of y_{1jc}. The relation for the latter quantity is obtained by a simple rearrangement of Eq. (*1*), viz.

$$y_{1jc} = \frac{f_{1j}^{L} / \varphi_{1j}^{G}}{\sum_i (f_{ij}^{L} / \varphi_{ij}^{G})} \qquad (8)$$

for $i = 1, 2$. The fugacity coefficients φ_{ij}^{G} in Eq. (*8*) depend, as well as on temperature and pressure, on the vapour phase composition. The effect of the latter is usually low, and the effect of error in the determination of y_{1je} on the energy parameters of the Wilson equation can also be regarded as low if not negligible.

In the second cycle of the iteration treatment, the minimum of the target function

$$F_2(x_{1jc}) = \sum_j [(y_{1je} - y_{1jc})^2 + (x_{1je} - x_{1jc})^2] \qquad (9)$$

is sought with respect to the independent parameters x_{1jc}, for each measurement separately. The procedure[8] based on the condition

$$\partial F_2(x_{1jc})/\partial x_{1jc} = 0 \qquad (10)$$

was used.

The following equations are approximately valid:

$$x_{1jc} = x_{1jc}^{(0)} + \Delta x_{1jc} \qquad (11)$$

$$y_{1jc} = y_{1jc}^{(0)} + (\partial y_{1jc}/\partial x_{1jc})^{(0)}\, \Delta x_{1jc} \qquad (12)$$

and

$$\partial y_{1jc}/\partial x_{1jc} = (\partial y_{1jc}/\partial x_{1jc})^{(0)}\,. \qquad (13)$$

The Δx_{1jc} value in Eq. (*11*) refines the mole fraction $x_{1jc}^{(0)}$ from the preceding iteration, whereas y_{1j} in Eq. (*12*), as a part of the equilibrium dependence $y_{1c} = f(x_{1c})$, can be expanded in a Taylor series in the neighbourhood of the starting value $y_{1jc}^{(0)}$ corresponding to the starting value of $x_{1jc}^{(0)}$.

If the condition (*10*) is applied to Eq. (*9*) and relations (*11*) through (*13*) are employed in the rearrangement, the following equation is obtained:

$$\Delta x_{1jc} = \frac{(x_{1je} - x_{1jc}^{(0)}) + (y_{1je} - y_{1jc}^{(0)})\,(\partial y_{1jc}/\partial x_{1jc})^{(0)}}{1 + [(\partial y_{1jc}/\partial x_{1jc})^{(0)}]^2}\,. \qquad (14)$$

A refined x_{1jc} value is obtained on determining Δx_{1jc} and substituting in Eq. (*11*).

The third cycle of the iteration treatment consists in seeking the minimum of the target function

$$F_3(t_{jc}) = \sum_j [w_P^2(P_{je} - P_{jc})^2 + w_t^2(t_{je} - t_{jc})^2] \qquad (15)$$

with respect to the independent parameters t_{jc}, separately for each measurement. The statistical weights were applied in the form

$$w_P = \sigma_t/\sigma_P \qquad (16a)$$

$$w_t = \sigma_t/\sigma_t = 1 \qquad (16b)$$

As in the preceding cycle, the condition

$$\partial F_3(t_{j\mathrm{c}})/\partial t_{j\mathrm{c}} = 0 \qquad (17)$$

and the relations

$$t_{j\mathrm{c}} = t_{j\mathrm{c}}^{(0)} + \Delta t_{j\mathrm{c}} \qquad (18)$$

$$P_{j\mathrm{c}} = P_{j\mathrm{c}}^{(0)} + (\partial P_{j\mathrm{c}}/\partial t_{j\mathrm{c}})^{(0)}\,\Delta t_{j\mathrm{c}} \qquad (19)$$

and

$$\partial P_{j\mathrm{c}}/\partial t_{j\mathrm{c}} = (\partial P_{j\mathrm{c}}/\partial t_{j\mathrm{c}})^{(0)} \qquad (20)$$

were applied.

Rearrangement of Eq. (*17*) gives the equation

$$\Delta t_{j\mathrm{c}} = \frac{w_t^2(t_{j\mathrm{e}} - t_{j\mathrm{c}}^{(0)}) + w_p^2(P_{j\mathrm{e}} - P_{j\mathrm{c}}^{(0)})\,(\partial P_{j\mathrm{c}}/\partial t_{j\mathrm{c}})^{(0)}}{w_t^2 + w_p^2[(\partial P_{j\mathrm{c}}/\partial t_{j\mathrm{c}})^{(0)}]^2}\,. \qquad (21)$$

By determining $\Delta t_{j\mathrm{e}}$, the modified $t_{j\mathrm{c}}$ value is also obtained from Eq. (*18*). The weights w_t and w_p are introduced to balance the substantially higher $(P_{j\mathrm{c}} - P_{j\mathrm{e}})^2$ values as compared to the $(t_{j\mathrm{e}} - t_{j\mathrm{c}})^2$ values, so as to prevent the effect of deviations of total pressure from predominating. While the σ_t values are given by the chosen conditions of the simulated experiment and vary gradually from 0.1 °C to 0.9 °C, σ_p was put equal to 30 Pa for all experiments. The use of statistical weights in Eq. (*15*) appeared a necessary provision improving markedly the correlated equilibrium values and energy parameters in the Wilson equations.

Using the $x_{1j\mathrm{c}}$ and $t_{j\mathrm{c}}$ values determined in the second and third cycles of the iteration treatment, the pressure $P_{j\mathrm{c}}$ and the energy parameters are calculated within the first cycle. This alternation of cycles is terminated if the values of function (*6*) in two successive cycles differ less than by a preselected tolerance.

Calculation of the Number of Theoretical Plates

A design calculation of the number of theoretical plates of a continuously working rectification column was performed as an application of the equilibrium L–G data. The numerical method after Lewis and Matheson[9] was employed, based on the assumption of constant molar flows of the liquid and vapour. The conditions and requirements associated with the rectification partition of the systems were as in the previous work[1,2].

APPLICATION

Rectification Parameters

The reflux ratio (R) is a parameter which can be chosen when solving a continuous rectification problem, and its value determines the number of plates necessary to achieve a required sharpness of separation. Three reflux ratio values, viz. $R = 1.2\,R_{min}$, $R = 2.0\,R_{min}$, and R_∞, were applied consecutively to each of the systems treated. The sharpness of separation entered in terms of the mole fraction of the lower-boiling-temperature component in the distillate (x_D) and waste (x_W) and of the feed (boiling liquid) composition (x_F) and state were as in the previous work[1,2]. A substantial part of the concentration range (95 to 98%) of the equilibrium dependences is thus utilized. The numerical values of the quantities mentioned are given in Table I. The last three columns of the table give the numbers of theoretical plates calculated with the equilibrium data standard set.

TABLE I
Continuous rectification parameters and number of theoretical plates calculated for the standard equilibrium data set

System	x_D	x_W	x_F	R_{min}	N for R/R_{min}		
					1.2	2	∞
I	0.990	0.010	0.500	1.40	23.68	16.60	10.98
II	0.990	0.010	0.500	3.00	37.69	25.66	17.84
III	0.990	0.005	0.200	0.25	13.87	8.03	4.30
IV	0.850	0.020	0.500	3.80	47.78	26.14	17.09
V	0.990	0.030	0.500	2.90	75.97	38.66	21.61

Parameters of the Simulated L–G Equilibrium Experiment

The complete sets of equilibrium x, y and t values at a constant pressure P in the simulated experiment according to Eq. (*4*) were prepared so that each set contained 19 binary equilibrium points which were uniformly distributed along the concentration region. A constant standard deviation of temperature, σ_t, was chosen from among the values of 0.1, 0.3, 0.5 and 0.9 °C, a constant standard deviation of the mole fraction of the lower-boiling-temperature component, $\sigma_x = \sigma_y$, was selected from among the values of 0.001, 0.004, 0.007, 0.010 and 0.015. All combinations of the σ_t and $\sigma_x = \sigma_y$ were consecutively applied.

The random errors $\sigma_t N_k$, $\sigma_x N_k$, and $\sigma_y N_k$ take various positive or negative values for the standard deviations chosen. Their serial numbers k ($k = 1, . . ., m$, where $m = 19$ when creating errors in t and $m = 38$ when creating errors in x and y) were kept in the order in which they were determined based on the evaluation of about 40 equilibrium sets at the given imprecision level. The evaluation was, naturally, made for each system separately; the results are given in ref.[2].

The simulated experiment with systematic errors according to Eq. (*5*) was performed using constant positive or negative values of δ_t (0.05 and 0.4 °C) and $\delta_x = \delta_y$ (0.001, 0.004, 0.007, 0.010 and 0.014) and their possible combinations.

Application of Equilibrium Data in the Calculation of the Number of Theoretical Plates

Each of the equilibrium data sets, prepared with respect to a preselected precision represented by the σ_t and $\sigma_x = \sigma_y$ (random errors) or δ_t and $\delta_x = \delta_y$ (bias) standard deviations, was correlated prior to application so as to determine the optimum parameters in the Wilson equations. It should be noted that in the simulated experiments of the L–G equilibria the composition of the liquid and vapour phases was determined by the same method and so the same precision (as well as bias) of their determination can be expected ($\sigma_x = \sigma_y$, $\delta_x = \delta_y$).

Using the source of isobaric equilibrium data so prepared, the number of theoretical plates was calculated always for three reflux ratio values, viz. $R = 1.2\,R_{\mathrm{min}}$, $R = 2\,R_{\mathrm{min}}$, and R_∞. The number of theoretical plates calculated for the correlated set of experimental equilibrium data, N_e, was finally compared with the value of N obtained with the equilibrium data standard set, viz. in the form of the percent relative deviation

$$d = 100\,(N_e - N)/N. \qquad (22)$$

The *d* values can be used to evaluate the results, e.g. assess the effect of error in the measurement of temperature and phase composition on the design calculation of a rectification column. The results are given in Tables II and III.

DISCUSSION

The impact of errors in the determination of the equilibrium temperature and equilibrium phase composition on the calculated number of theoretical plates is different for the different systems.

In the case of systems I and II, which approach closely the ideal phase behaviour, the influence of random errors in *t*, *x* and *y* (within the range examined) on the calculated number of theoretical plates is insignificant (Table II). Even if the mole fractions and

TABLE II

Effect of random errors in equilibrium temperature (σ_t) and equilibrium phase composition ($\sigma_x = \sigma_y$) on the deviation in the calculated number of theoretical plates (d) for two different reflux ratio values (R); values of $\sigma_x = \sigma_y$ lay within the range of 0.001 to 0.015

System	σ_t, °C	d, %	
		$R = 1.2\,R_{\min}$	R_∞
I	0.1	0.2 to −0.1	0.1 to 0.6
	0.3	1.1 to 0.7	0.1 to 0.7
II	0.1	0.1 to 0.0	−0.7 to −0.1
	0.3	0.2 to 0.0	−0.5 to −0.1
	0.5	0.2 to 0.1	−0.4 to 0.3
	0.9	0.6 to 0.7	0.9 to 2.3
III	0.1	−0.1 to −4.0	−0.2 to −3.0
	0.3	−1.4 to −4.7	−0.7 to −1.7
	0.5	−0.8 to −0.4	−0.6 to −0.8
	0.9	−6.7 to −7.3	−2.3 to −5.4
IV	0.1	0.4 to −1.5	−0.3 to −0.4
	0.3	−6.0 to −11.6	−2.1 to −2.4
	0.5	−6.6 to −13.0	−2.9 to −3.5
	0.9	−15.8 to −20.5	−6.6 to −6.9
V	0.1	4.3 to −4.4	0.3 to −2.6
	0.3	21.2 to 7.2	2.9 to 0.5
	0.5	13.7[a] to 7.8[a]	5.6 to 2.3
	0.9	34.1[a] to 23.8[a]	12.9 to 8.6

[a] $R = 2\,R_{\min}$.

TABLE III
Effect of bias in equilibrium temperature (δ_t) and equilibrium phase composition ($\delta_x = \delta_y$) on the deviation in the calculated number of theoretical plates (*d*) for two different reflux ratio values (*R*)

System	δ_t, °C	$\delta_x = \delta_y$	*d*, %	
			$R = 1.2\ R_{min}$	R_∞
I, II	0.05	[a]	0.1 to 2.7	–0.5 to 0.7
		[b]	0.2 to –3.2	–0.6 to –1.1
	–0.05	[a]	–0.1 to 3.0	–0.8 to 0.8
		[b]	–0.6 to –3.8	–0.9 to –1.1
	0.4	[a]	6.6 to 9.7	6.0 to 6.5
		[b]	2.9 to –0.1	1.7 to 0.1
	–0.4	[a]	–3.3 to 0.3	–1.4 to –1.1
		[b]	–3.6 to –5.1	–1.4 to –1.6
III	0.05	[a]	–1.1 to –8.2	–0.1 to 3.0
		[b]	–0.1 to 5.3	–0.2 to –7.1
	–0.05	[a]	0.1 to –8.2	0.5 to 3.0
		[b]	0.3 to 6.4	0.3 to –5.9
	0.4	[a]	–7.0 to –13.5	–2.4 to –1.8
		[b]	–6.9 to –6.0	–2.5 to –4.5
	–0.4	[a]	7.6 to 6.7	2.8 to 3.4
		[b]	8.1 to 27.0	2.8 to 1.9
IV	0.05	[a]	–6.0 to –24.2	–1.4 to –4.9
		[b]	–2.3 to 38.1	–1.0 to 2.8
	–0.05	[a]	2.8 to –19.3	1.4 to –2.6
		[b]	7.4 to 67.8	2.1 to 5.8
	0.4	[a]	–25.7 to –35.3	–8.1 to –10.2
		[b]	–23.8 to –8.0	–7.8 to –6.0
	–0.4	[a]	95.5 to 22.7	17.9 to 11.0
		[b]	35.8[e] to 60.6[e]	–12.8 to 11.8
V	0.05	[c]	17.7 to 29.5	2.6 to 3.7
		[d]	11.0[e] to 17.8[e]	4.5 to 6.2
		[b]	11.3 to –15.0	2.0 to –1.6
	–0.05	[a]	–8.2 to 22.4	–2.0 to 1.4
		[b]	–12.0 to –28.6	–2.6 to –6.4
	0.4	[a]	99.4[e] to 140[e]	29.3 to 32.9
		[b]	94.1[e] to 71.9[e]	28.7 to 26.3
	–0.4	[a]	–40.0 to –31.1	–13.7 to –10.8
		[b]	–41.8 to –48.1	–14.1 to –16.9

[a] 0.001 to 0.014; [b] –0.001 to –0.014; [c] 0.001 to 0.004; [d] 0.007 to 0.014; [e] $R = 2\ R_{min}$.

equilibrium temperatures include considerable errors, the equilibrium dependence will approach the standard values owing to the correlation performed. The effect of bias, particularly in temperature, is somewhat more pronounced (Table III).

System III, having a markedly convex distribution equilibrium curve, is slightly more sensitive to random errors in the equilibrium composition and temperature than systems I and II. The deviation in the calculated number of plates, for the highest temperature and phase composition errors considered, is lower than 10%. Bias induces a similar response. Positive temperature and phase composition bias leads to underestimation of the number of theoretical plates (the *d* values are negative), whereas negative temperature or phase composition bias brings about overestimation of the number of theoretical plates (*d* is positive). Appreciable deviations in the calculated number of plates ($d >$ 20%) can be expected if marked negative temperature bias (δ_t = –0.4 °C) combines with marked composition bias ($\delta_{x,y} \geq 0.01$). This unfavourable effect, however, decreases as the reflux ratio is increased.

System IV, whose equilibrium distribution curve has an unsymmetrical shape (Fig. 1*d*), is a system exhibiting a positive deviation from Raoult's law, giving rise to a low-boiling azeotrope. The effect of random errors in the equilibrium data on the precision of the calculated number of theoretical plates is considerably higher than for systems I through III. Random errors in temperature as well as in the phase composition cause the calculated number of theoretical plates to be lower than that for the equilibrium data standard set (*d* is negative). Within the region of errors used, the *d* values are mostly below 20% (Table II). Positive δ_t and $\delta_{x,y}$ bias lowers the number of calculated plates whereas negative bias increases it (Table III), the effect of negative bias being higher than that of positive bias. Even for the values of δ_t = –0.4 °C and $\delta_{x,y}$ = –0.001 the equilibrium dependence is distorted to such an extent that the reflux ratio 1.2 $R_{\min}$ (the minimum reflux ratio was invariably determined from the equilibrium data standard set) was even lower than the $R_{\min}$ as would correspond to the altered values of the equilibrium dependence. It is well known that a required sharpness of rectification separation can only be achieved if the working reflux ratio is higher than $R_{\min}$.

The last system treated, system V (Fig. 1*e*), involves a liquid phase which exhibits a negative deviation from an ideal solution. We know from our previous study[1,2] that random temperature errors in system V cause overestimation of the number of theoretical plates whereas random errors in equilibrium composition have an opposite effect. If errors of the two kinds combine, the effect of the error in temperature predominates, so that the calculated number of theoretical plates is higher than that obtained for the standard equilibrium data set. The *d* values (which are positive), are appreciable (about 20%) even for σ_t = 0.3 °C, $\sigma_{x,y}$ = 0.001 and for $R = 1.2\ R_{\min}$. If the error in temperature is higher (σ_t > 0.3 °C), a reflux larger than 1.2 $R_{\min}$ must be applied. Positive (negative) bias both in temperature and in phase composition increases (decreases) the calculated number of plates. If bias in temperature and in phase composition occur simultaneously, the overall deviation in the calculated number of plates will be primarily governed by the temperature bias. For instance, a relatively low temperature bias, $\delta_t = 0.05$ °C, will bring about a deviation of the calculated number of theoretical plates of about 15%.

Calculations of rectification columns are usually based on original experimental equilibrium data. If these do not exist, they are often derived by alternative ways, such as the group contributions method. Regardless of their origin, details concerning their measurement and precision are mostly available. Such set of information, along with a quantitative analysis of the effect of errors on the calculated number of theoretical plates of a rectification column such as that made in the present paper, gives an idea of the precision of the calculation performed. The importance of a proper choice of the equilibrium data is illustrated by the effect of inaccuracy as was observed in this work in the case of systems IV and V.

SYMBOLS

d	percent relative deviation of the number of theoretical plates
f_i	fugacity of component *i*
F	target function
N_k	number from a sequence of random numbers possessing the normal distribution
N, N_e	number of theoretical plates calculated for the standard equilibrium data set and for experimental data, respectively
P	system pressure
P_i^o	saturated pressure of pure component *i*
$\mathbf{R}$	gas constant
R, R_min, R_∞	working, minimum and maximum reflux ratio, respectively
t	temperature in degrees Centigrade
T	thermodynamic temperature
v_i^o	molar volume of pure component *i*
w	statistical weight
x_i	mole fraction of component *i* in the liquid phase
y_i	mole fraction of component *i* in the vapour phase
γ_i	activity coefficient of component *i*
δ	bias
$\lambda_{12} - \lambda_{11}$, $\lambda_{21} - \lambda_{22}$	Wilson equation energy parameters
Λ_{12}, Λ_{21}	Wilson equation parameters
σ	standard deviation
φ_i	fugacity coefficient of component *i* in the mixture
φ_i^o	fugacity coefficient of pure component *i*

Superscripts

G	gas phase
L	liquid phase
o	pure component
(0)	preceding iteration

Subscripts

c	calculated, correlated
D	in distillate
e	experimental
F	in feed
i	i-th component
j	j-th equilibrium point
k	k-th random number
P	related to pressure
s	saturated state
t	related to temperature
W	in waste
x, y	related to mole fraction in the L and G phase, respectively
1, 2	component with lower and higher boiling temperature, respectively.

REFERENCES

1. Dojcansky J., Bafrncova S., Surovy J.: Collect. Czech. Chem. Commun. *57*, 1867 (1992).
2. Dojcansky J., Bafrncova S., Surovy J.: Collect. Czech. Chem. Commun. *58*, 506 (1993).
3. Hayden J. G., O'Connell J. P.: Ind. Eng. Chem., Process. Des. Dev. *14*, 209 (1975).
4. Nothnagel K. M., Abrams D. S., Prausnitz J. M.: Ind. Eng. Chem., Process. Des. Dev. *12*, 25 (1973).
5. Wichterle I., Linek J.: *Antoine Vapor Pressure Constants of Pure Compounds*. Academia, Prague 1971.
6. Yamada T., Gunn R. D.: J. Chem. Eng. Data *18*, 234 (1973).
7. Wilson G. M.: J. Am. Chem. Soc. *86*, 127 (1964).
8. Graczova E.: *Thesis*. Slovak Technical University, Bratislava 1989.
9. Lewis W. K., Matheson G. L.: Ind. Eng. Chem. *24*, 494 (1932).

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