EFFECT OF ERRORS IN TEMPERATURE MEASUREMENT ON THE ACCURACY OF COMPOSITION OF THE LIQUID–VAPOUR PHASES AND THEIR IMPACT ON THE CALCULATED NUMBER OF THEORETICAL STAGES OF RECTIFICATION COLUMNS

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The effect of random and systematic errors in the determination of the equilibrium temperature on the phase composition in isobaric L–G equilibria was simulated on five binary systems with different size and relative volatility. The impact of the inaccuracies on the calculated number of theoretical stages of a continuously operating rectification column is discussed with respect to the different operating conditions of the separatory process.

Rectification column design calculations require, among other things, accurate phase equilibrium data. From among the several approaches to their obtaining, the experimental approach is considered the most reliable. It is desirable that the experimental isobaric equilibrium data set should be complete and should cover the entire concentration region. Prior to their application, e.g. in the numerical calculation of the rectification separation, the data must be processed to obtain parameters of equations correlating the activity coefficients in dependence on the composition, and also on temperature. Greatest attention should be paid to both the experimental determination of the equilibrium data and their subsequent processing.

As early as 1956, Kiguchi and Ridgway[1] noticed that a 10% error in the relative volatility value brings about a nearly 30% change in the calculated number of stages of a rectification column for the separation of ethane. Hengstebeck[2] considers inaccuracies in the equilibrium data the major cause of some uncertainties in the calculation of distillation equipment, and stresses that this problem has not been receiving appropriate attention. There can be found more such or similar warnings in the literature.

In the present work, the problem of errors in the measurement of temperatures and of their impact on the composition of the equilibrium phases (x, y) is studied by a simulated experiment on several model binary systems; the impact of the errors on the accuracy of the design calculation of theoretical stages of a continuously working rectification column in various operating conditions is also investigated.

THEORETICAL

Simulated Experiment and Correlation of Equilibrium Data

To enable the effect of errors in the temperature measurements on the composition of the equilibrium phases to be examined, a complete reference set of equilibrium data must be available along with experimental, or rather correlated, data obtained from a simulation experiment. The equilibrium state was described in terms of the well-known relation

$$P y_i \varphi_i^{G} = P_i^{0} x_i \gamma_i \varphi_{is}^{0} \exp\left[v_i^{0L}(P - P_i^{0})/RT\right] \qquad (1)$$

for components $i = 1, 2$.

The fugacity coefficients of the vapour phase components were calculated by using the relations

$$\ln \varphi_1^{G} = (B_{11} + \delta_{12} y_2^2)\, P/RT \qquad (2a)$$

and

$$\ln \varphi_2^{G} = (B_{22} + \delta_{12} y_1^2)\, P/RT \qquad (2b)$$

where

$$\delta_{12} = 2 B_{12} - B_{11} - B_{22} \qquad (3)$$

The secondary virial coefficients of the pure components (B_{11}, B_{22}) and the cross coefficient B_{12} were calculated using the formulas by Reid and coworkers[3].

Calculation of the fugacity coefficient of a pure component relied on the equation

$$\ln \varphi_{is}^{0} = B_{ii} P_i^{0}/RT \qquad (4)$$

Antoine's equation with coefficients by Wichterle[4] was used to express the temperature dependence of the saturated vapour pressures of the pure components. The molar volumes of the pure liquid components were obtained by using the modified Rackett's equation[5].

The activity coefficients of the components in the liquid phase were calculated from Wilson's equations[6]

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \qquad (5a)$$

and

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}}\right) \qquad (5b)$$

the parameters Λ_{12} and Λ_{21} being obtained using the formulas

$$\Lambda_{12} = \frac{v_2^{0L}}{v_1^{0L}} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \qquad (6a)$$

and

$$\Lambda_{21} = \frac{v_1^{0L}}{v_2^{0L}} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \qquad (6b)$$

We assume that in the experimental determination of the L–G equilibrium, only the observed temperatures involve random errors. Furthermore, we assume that these errors obey the normal distribution with a constant variance over the entire concentration region. Then the experimental temperature can be expressed as

$$t_{je} = t_j + \sigma_t N_k \qquad (7)$$

where $j = 1, 2, ..., l$; $k = 1, 2, ..., l$; t_{je} and t_j are the experimental and the accurate (reference) temperatures of the j-th measurement, respectively. N_k is a number from a sequence of random numbers with the normal distribution with centre $\mu = 0$ and variance $\sigma^2 = 1$. The root of variance σ_t is the standard deviation of temperature. The product $(\sigma_t N_k)$ represents the random error of measurement. The subscripts j and k relate to the sequence number of the experiment and of number N, respectively.

In setting up the numbers N_k we first generate a set of random numbers RN_k uniformly distributed over the interval (0.1) according to the equation[7]

$$RN_k = (\pi + RN_{k-1})^8 - \text{Int.}(\pi + RN_{k-1})^8 \qquad (8)$$

for $k = 1, 2, ..., l$.

Then the numbers N_k with odd k's ($k = 1, 3, ..., l$) and with even k's ($k = 2, 4, ..., l+1$) are calculated according to the formulas[8]

$$N_k = (-2 \ln RN_k)^{1/2} \cos(2\pi RN_{k+1}) \qquad (9a)$$

and

$$N_k = (-2 \ln RN_k)^{1/2} \sin (2\pi RN_{k+1}) \tag{9b}$$

respectively. The calculation is started using two suitable chosen *RN*.

When assessing the effect of systematic errors, the equilibrium temperature will be simulated with the relation

$$t_{je} = t_j + \delta_t \,, \tag{10}$$

where δ_t is a positive or negative constant systematic error of the quantity in question.

Preparation of the experimental isobaric equilibrium data (x,y) consists in the determination of the optimal values of the energy parameters $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$, which are sought in the minimum of the objective function

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

where P is the accurate value of the total pressure in the isobaric dependence and P_{jc} is the value calculated for the j-th measurement, viz. by using Eq. (*1*) in the form

$$P_{jc} = \sum_i f_i^L / \varphi_i^G \tag{12}$$

for components $i = 1, 2$ (f_i^L is the fugacity of the component given by the right-hand expression in Eq. (*1*)).

Simple rearrangement affords the relation for the calculation of the mole fraction of component (1) in the vapour phase, viz.

$$y_{1jc} = \frac{f_{1j}^L / \varphi_{1j}^G}{\sum_i f_{ij}^L / \varphi_{ij}^G} \tag{13}$$

The mole fraction of the other component y_{2jc} is dependent in agreement with the condition $\sum_i y_{ijc} = 1$. The calculated total pressure P_{jc} is refined iteratively using the y_{1jc} value so calculated.

The errors in the temperature measurements do not affect the y_{1j} values only, they also give rise to some uncertainty in the liquid phase mole fractions. The fractions can be estimated by the procedure[9] based on the equation

$$x_{1jc} = x_{1jc}^{(0)} + \delta (x_{1jc}) \tag{14}$$

where $x_{1jc}^{(0)}$ is the mole fraction value from the previous iteration (the starting value is identified with the reference value) and $\delta(x_{1jc})$ is the increment whose value is determined in the minimum of the function

$$F_2(x_{1j}, y_{1j}) = \left[(y_{1j} - y_{1jc})^2 + (x_{1j} - x_{1jc})^2\right] \tag{15}$$

for each j-th measurement separately. By differentiating Eq. (*15*) with respect to x_{1jc} and putting equal to zero, we obtain by rearrangement

$$\delta(x_{1jc}) = \frac{(y_{1j} - y_{1jc}^{(0)})\,(\partial y_{1jc}/\partial x_{1jc})_{(0)} + (x_{1j} - x_{1jc}^{(0)})}{1 + (\partial y_{1jc}/\partial x_{1jc})_{(0)}^2} \tag{16}$$

In deriving Eq. (*16*) it was assumed[9] that, in addition to Eq. (*14*), Eqs (*17*) and (*18*) hold approximately true:

$$y_{1jc} = y_{1jc}^{(0)} + (\partial y_{1jc}/\partial x_{1jc})_{(0)}\ \delta(x_{1jc}) \tag{17}$$

$$(\partial y_{1jc}/\partial x_{1jc}) = (\partial y_{1jc}/\partial x_{1jc})_{(0)} \tag{18}$$

Using the y_{1jc} and x_{1jc} values calculated by Eqs (*13*) and (*14*), respectively, the total pressure P_{jc} is calculated and the value affects the formed value of function (*11*).

Calculation of the Number of Theoretical Stages

As one of the feasible applications of the liquid–vapour isobaric equilibrium data we chose the design calculation of the number of theoretical stages of a continuously operating rectification column. We used the numerical method by Lewis and Matheson[10], which is based on the iterative calculation of the equilibrium temperature and composition of the liquid leaving a theoretical stage, followed by calculation of the composition of vapour entering the stage. At the beginning one must know, or choose, the composition and status of the material entering the column, composition of the two end products – the distillate and residue, and the reflux ratio, which comprise the operating conditions of the rectification. The method of calculation relied on the assumption of constant ratios of the molar fluxes of the liquid and vapour in the two parts of the column.

APPLICATION

Equilibrium Data Standard

The model systems were chosen to include systems with ideal behaviour as well as systems with positive and negative deviations from Raoult's law. The following five systems were selected: n-hexane–n-heptane (I), cyclohexane–n-heptane (II), methylcyclohexane–aniline (III), n-hexane–benzene (IV), and chloroform–benzene (V). The first two are systems with nearly ideal liquid and vapour phases, with low changes in the relative volatility (from 2.1 to 2.7 for system I and from 1.6 to 1.7 for system II). System III exhibits a positive deviation from the ideal behaviour and the relative volatility attains high values at low concentrations of the more volatile component. System IV, with a positive deviation, forms a low-boiling azeotrope, whereas system V is one with a negative deviation from Raoult's law, with a variable relative volatility.

The original source of equilibrium data taken from ref.[11] was correlated taking into account the real vapour phase according to Eq. (*1*) and Wilson's equation for activity coefficients, and the objective function was used in the form (*11*). For each system (I to V), the back-calculated set of equilibrium data (x, y, T, P) for x_1 changing by an equidistant value of 0.05 at a constant pressure of 101 300 Pa, along with the energy parameters $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$, were regarded as the "accurate" (reference) data. The dependence of the standard distribution data y, x is shown in Figs 1*a* – 1*e*, the energy parameters are given in Table I.

Errors in Temperature Measurements and Their Effect on the Composition of the Equilibrium Phases

Experimental equilibrium temperatures were obtained by simulation using Eq. (*7*), or Eq. (*10*). For each set consisting of 19 points, the standard deviation σ_t as a measure of random errors was chosen within the region of 0.1 to 1.1 °C. When examining the effect of systematic errors, positive or negative constant errors δ_t were chosen within the region of 0.05 to 1 °C. The set of random numbers with normal distribution N_k (for $k = 1, 2, ..., 19$) was set up by the procedure given by Eqs (*8*) and (*9*), and its elements were finally so arranged that positive and negative values alternated regularly.

The experimental and calculated mole fractions x and y of each single measurement were prepared according to Eqs (*13*) and (*14*). The data from the standard set were used as the starting data in the simulation. Using the mole fractions so determined, the total pressure in function (*11*) was calculated. In the minimum of this function were sought the optimum values of the energy parameters of Wilson's equation; the system of equations was solved by the Gauss–Newton method.

The effect of errors of the observed equilibrium temperature on the composition of the equilibrium phases was ultimately expressed as the mean absolute deviation in the

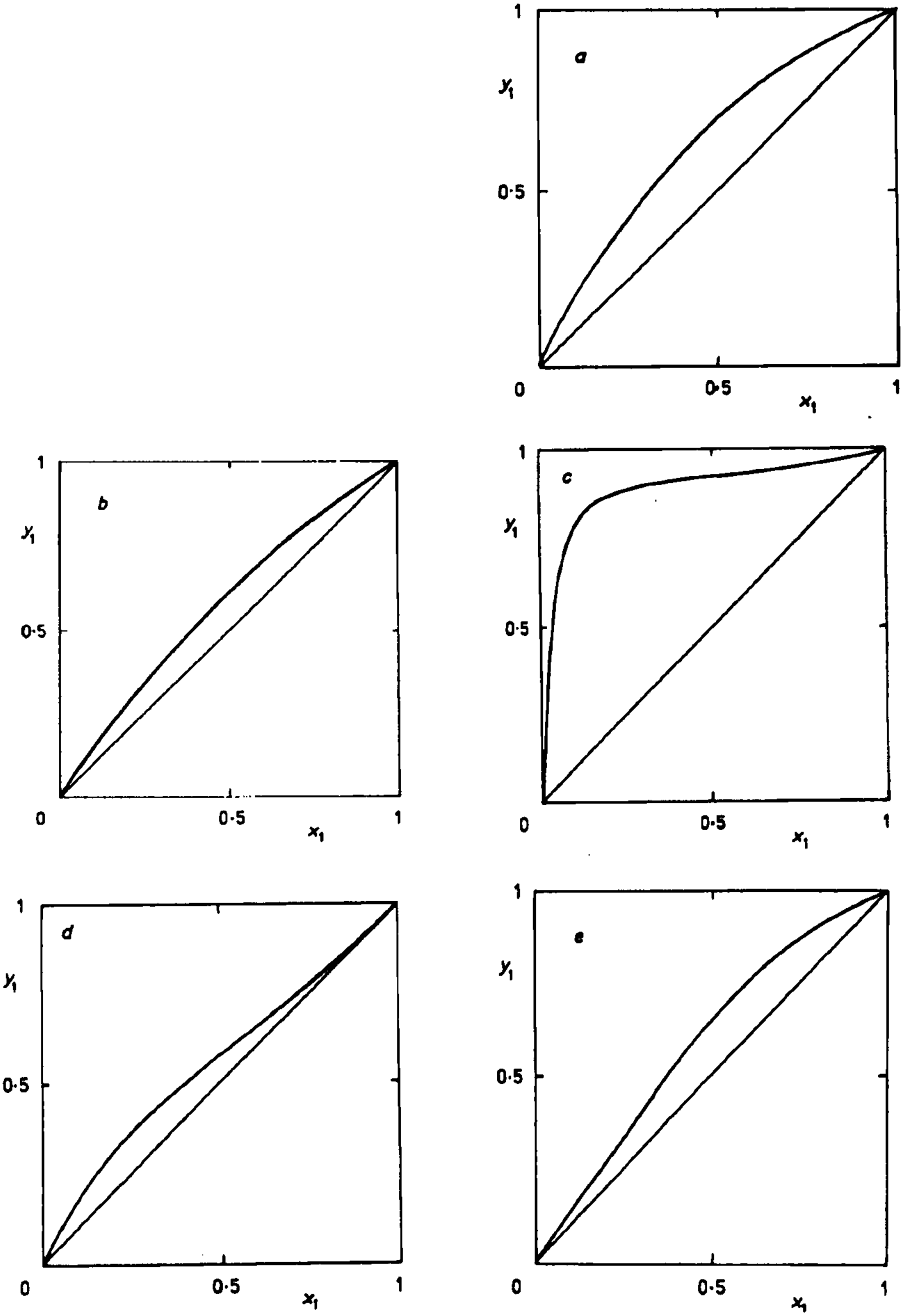

FIG. 1
Isobaric equilibrium diagrams of model binary L–G systems. System: *a* I, *b* II, *c* III, *d* IV, *e* V

mole fractions (S_{MAx1} and S_{MAy1}). For the sake of illustrativeness, only several values of these deviations were included in Table II, corresponding to the values of the random error (σ_t) and systematic error (δ_t) in the equilibrium temperature.

Application of Equilibrium Data to the Calculation of the Number of Theoretical Stages

The calculation of the number of theoretical stages, which is only a part of the complex solution of the designed or evaluated rectification equipment, was chosen as an example of applicability of the equilibrium data. The composition and status of the raw material and compositions of the separation products – distillate and residue – were fixed for each system. The minimum reflux ratio was calculated for these conditions and with respect to the reference source of equilibrium data. Since it was assumed that the errors in the equilibrium data can play a greater or smaller role in dependence on the operating conditions of the process, the calculation of the number of theoretical stages was accomplished at several reflux ratio values (1.2 R_{min}, 2.0 R_{min} and R_{∞}). Thus, the number of theoretical stages was calculated for each entered reflux ratio with a correlated set of equilibrium data, represented by the optimum energy parameters of Wilson's equation. The discriminating parameter of the equilibrium sets was the standard deviation σ_t (assessment of the effect of random errors) or the increment δ_t (assessment of the systematic errors). Finally, the number of theoretical stages calculated

TABLE I
Parameters of Wilson's equation for sets of accurate liquid–vapour equilibrium data at a total pressure of 101 300 Pa

System	Components	$\lambda_{12} - \lambda_{11}$ J mol^{-1}	$\lambda_{21} - \lambda_{22}$ J mol^{-1}
I	n-hexane n-heptane	-1 743.506	2 480.495
II	cyclohexane n-heptane	3 240.875	-2 603.338
III	methylcyclohexane aniline	3 132.749	3 891.918
IV	n-hexane benzene	1 111.038	511.832
V	chloroform benzene	423.779	-1 465.054

with the correlated set of experimental data N_{TSe} was compared with the N_{TS} value obtained with the equilibrium data standard, viz. in the form of the percentage relative deviation

$$d_{NTS} = 100\,(N_{TSe} - N_{TS})/N_{TS} \tag{19}$$

which provided a basis for the assessment of the effect of random or systematic errors in the measurement of the equilibrium temperature on the results of the design calculations. The results are shown in Figs 2 and 3 as the d_{NTS} vs σ_t and d_{NTS} vs δ_t plots.

DISCUSSION

The impact of errors in the determination of temperature during the examination of an L–G equilibrium on the phase composition is nearly the same for the systems at low standard deviations, perhaps with the exception of system III. As anticipated, the uncertainties in the composition of the coexisting equilibrium phases increase with increasing σ_t for all systems studied. System I appeared particularly sensitive in this respect; preparation of the set of experimental equilibrium data by simulation failed at

TABLE II

Mean absolute deviations in the mole fractions of the equilibrium phases due to random errors σ_t and systematic errors δ_t in the equilibrium temperature measurements. Upper rows – $S_{MAx1} \cdot 10^4$, lower rows – $S_{MAy1} \cdot 10^4$

Parameter	System				
	I	II	III	IV	V
σ_t = 0.1 °C	1.3	1.2	0.17	1.7	1.6
	1.3	1.2	1.0	1.9	1.5
σ_t = 0.5 °C	–	3.3	0.86	9.3	7.6
	–	3.4	5.3	9.9	7.4
σ_t = 0.9 °C	–	8.7	1.6	17	14
	–	9.0	9.9	18	14
δ_t = 0.1 °C	4.3	0.85	0.84	5.2	4.1
	4.2	0.85	2.5	5.4	4.1
δ_t = -0.1 °C	4.1	8.8	0.79	5.4	4.0
	4.0	8.9	2.5	5.5	4.0
δ_t = 1 °C	–	41	9.8	53	–
	–	42	25	54	–
δ_t = -1 °C	–	48	9.6	54	42
	–	48	24	55	41

errors $\sigma_t \geq 0.5$ °C. This trend was also observed when examining the effect of systematic errors. If the temperature in the equilibrium measurements is determined with a precision of $\sigma_t = 0.1$ °C, the effect of these errors on the precision of the equilibrium mole fractions in the phases (x, y) will be $1 \,.\, 10^{-4}$ to $2 \,.\, 10^{-4}$. This span of errors approaches the lower limit in a high-precision experimental determination of the equilibrium phase composition. Similarly, a constant systematic errors of $\delta_t = \pm 0.1$ °C gives rise to an uncertainty in (x, y) of $1 \,.\, 10^{-4}$ to $1 \,.\, 10^{-3}$ according to the kind of system.

Figures 1 and 2 demonstrate that errors in the equilibrium data due to inaccuracies in the temperature measurements solely have virtually no effect on the calculated number of theoretical stages for systems I, II and III, or this effect is insignificant. Perhaps, only for system III with a very convex equilibrium y–x curve and at a reflux ratio of 1.2 R_{min} and at $\sigma_t > 0.5$ °C, the relative deviations in the number of theoretical stages take values about 5%.

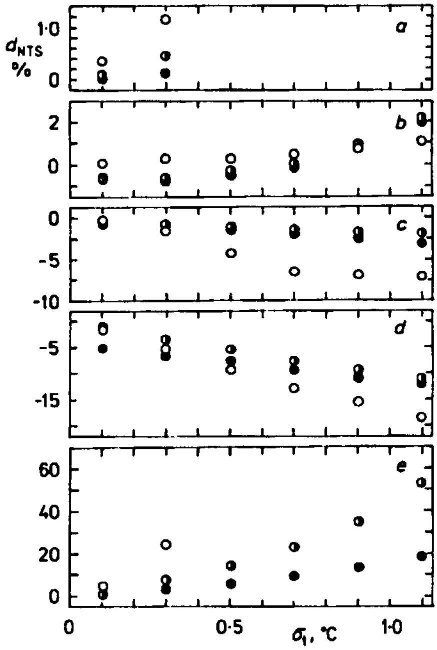

FIG. 2

Dependence of d_{NTS} on the random error of equilibrium temperature σ_t at various reflux ratios. System: *a* I, *b* II, *c* III, *d* IV, *e* V. Reflux ratio: ○ 1.2 R_{min}, ◑ 2 R_{min}, ● R_∞

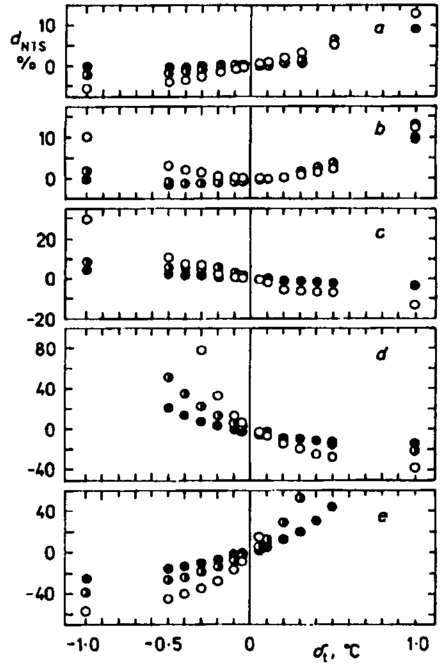

FIG. 3

Dependence of d_{TNS} on equilibrium temperature bias δ_t at various reflux ratios. System: *a* I, *b* II, *c* III, *d* IV, *e* V. Reflux ratio: ○ 1.2 R_{min}, ◑ 2 R_{min}, ● R_∞

The situation is substantially different for systems IV and V. Their equilibrium curves (Figs 1*d*, 1*e*) are unsymmetrical. Taking into account the fact that 1.2 R_{min} is a value approaching quite closely the optimum reflux ratio for the stage type of a rectification column, then from this aspect a 10% deviation in N_{TS} can be reached in system IV with equilibrium data derived from $\sigma_t \geq 0.5$ °C and in system V even from $\sigma_t \geq 0.2$ °C. Systematic error in the temperature data has a similar effect. For instance, if a constant systematic error of $\delta_t = \pm 0.05$ °C is introduced in the equilibrium temperature measurement, the d_{NTS} values can be expected to be 10 to 15%. The enhanced sensitivity of systems IV and V to errors in the equilibrium data and their impact on N_{TS} can be understood so that at lower (V) or higher (IV) concentrations of the lower-boiling component 1, the vapour and liquid compositions vary but little from stage to stage (the working and equilibrium lines lie close to another), and so even very low changes in the inaccuracies of the equilibrium data give rise to relatively high changes in the number of stages N_{TS}.

SYMBOLS

B_{11}, B_{22}	secondary virial coefficients of the components
B_{12}	cross virial coefficient
d_{NTS}	percentage relative deviation
f	fugacity
F_1, F_2	objective function
N	number from a sequence of random numbers with normal distribution
N_{TS}, N_{TSe}	number of theoretical stages
P	system pressure
P_i^0	saturated vapour pressure of pure component *i*
R	gas constant
R, R_{min}	reflux ratio
RN	random number from normal distribution
S_{MAx1}, S_{MAy1}	mean absolute deviation
t	temperature
T	thermodynamic temperature
v_i^{0L}	molar volume of pure liquid component *i*
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_{12}	quantity given by Eq. (3)
δ_t	systematic error
$\delta(x_{1jc})$	mole fraction increment
$\lambda_{12} - \lambda_{11}$, $\lambda_{21} - \lambda_{22}$	energy parameters of Wilson's equation
Λ_{12}, Λ_{21}	parameters of Wilson's equation
π	Ludolf's number
σ_t	standard deviation
φ_i^G	fugacity coefficient of component *i* in the mixture
φ_{is}^0	fugacity coefficient of pure component *i*

Superscripts

L	liquid phase
0	pure component
(0)	previous iteration
G	vapour phase

Subscripts

c	calculated, correlated
e	experimental
i	any component
j	sequence number of equilibrium point
k	sequence number of random number
NTS	number of theoretical stages
s	saturation
t	related to temperature
TS	theoretical stage
(0)	previous iteration
1, 2	component with lower and higher boiling temperatures, respectively

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