A SIMULATED EXPERIMENT FOR EXAMINING THE EFFECT OF ERRORS IN THE COMPOSITION OF THE EQUILIBRIUM LIQUID–VAPOUR PHASES ON THE CALCULATED NUMBER OF THEORETICAL STAGES OF A RECTIFICATION COLUMN

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Five model binary systems differing in the relative volatilities and their changes were used to simulate the effect of random errors and bias in the L–G equilibrium phase composition on the calculation of the number of theoretical stages of a continuously working rectification column in various operating conditions.

The mole fractions of the components in the liquid and gas phases along with the temperature and pressure (*x*, *y*, *T*, *P*) constitute a complete set of equilibrium data. By their processing one can obtain parameters of the dependences of activity coefficients on composition, which find use in various applications of the equilibrium dependences such as the numerical calculation of rectification separation. It is desirable that the set cover the entire concentration region because this contributes to the precision of the correlation of the equilibrium concentrations. The major factors affecting the accuracy of the data, however, are the purity of the substances, quality of the equilibrium instrument, and errors in the measurement of the complete equilibrium data set.

Previously[1] we examined how the isobaric set of binary equilibrium data is affected by errors in the equilibrium temperature. The effect of random errors and bias in temperatures on the equilibrium phase composition was also assessed with respect to the application of the equilibrium data to the calculation of the number of theoretical stages of a rectification column. As a continuation, in the present work we outline and discuss the problem of how the data are affected by errors in the mole fractions in the phases (*x*, *y*). The equilibrium temperatures will be represented by data from a set of standard equilibrium temperatures.

The analysis of errors in the equilibrium data set via the individual quantities was chosen deliberately in order to demonstrate the demands that must be placed on the precision and accuracy of their determination; the analysis can also indicate which of the prediction methods of equilibrium determination will meet one's demands, regarded in this work through deviations in the calculated number of theoretical stages of the equipment designed. We chose five model systems, shown in Fig. 1, differing in their relative volatility, in their positive or negative deviation from the ideal solution behaviour (Raoult's law), and in the occurrence of a positive azeotropic point. In efforts to gain a complex insight into the effect of errors of the equilibrium phase composition, the design calculation of a rectification column was performed for various operating conditions.

THEORETICAL

Simulated Experiment and Correlation of Equilibrium Data

The equilibrium state was described by the relation

$$P y_i \varphi_i^G = P_i^0 x_i \gamma_i \varphi_{is}^0 \exp[v_i^{0L} (P - P_i^0)/R T] \tag{1}$$

for components $i = 1, 2$.

The secondary virial coefficients of the pure components and the cross virial coefficients required for determining the fugacity coefficients were calculated following Hayden and O'Connell[2] and Nothnagel and coworkers[3]; the saturated vapour pressures of the pure components were derived from Antoine's equation using coefficients according to Wichterle and Linek[4]; and the molar volumes of the liquid components were obtained from the modified Rackett's equation[5].

The dependence of the activity coefficients of the liquid phase components on composition was expressed by Wilson's equations[6]

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

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

the parameters Λ_{12} and Λ_{21} being calculated as

$$\Lambda_{12} = \frac{v_2^{0L}}{v_1^{0L}} \exp\left[\frac{-(\lambda_{12} - \lambda_{11})}{R T} \right] \tag{3a}$$

$$\Lambda_{21} = \frac{v_1^{0L}}{v_2^{0L}} \exp\left[\frac{-(\lambda_{21} - \lambda_{22})}{R T} \right] . \tag{3b}$$

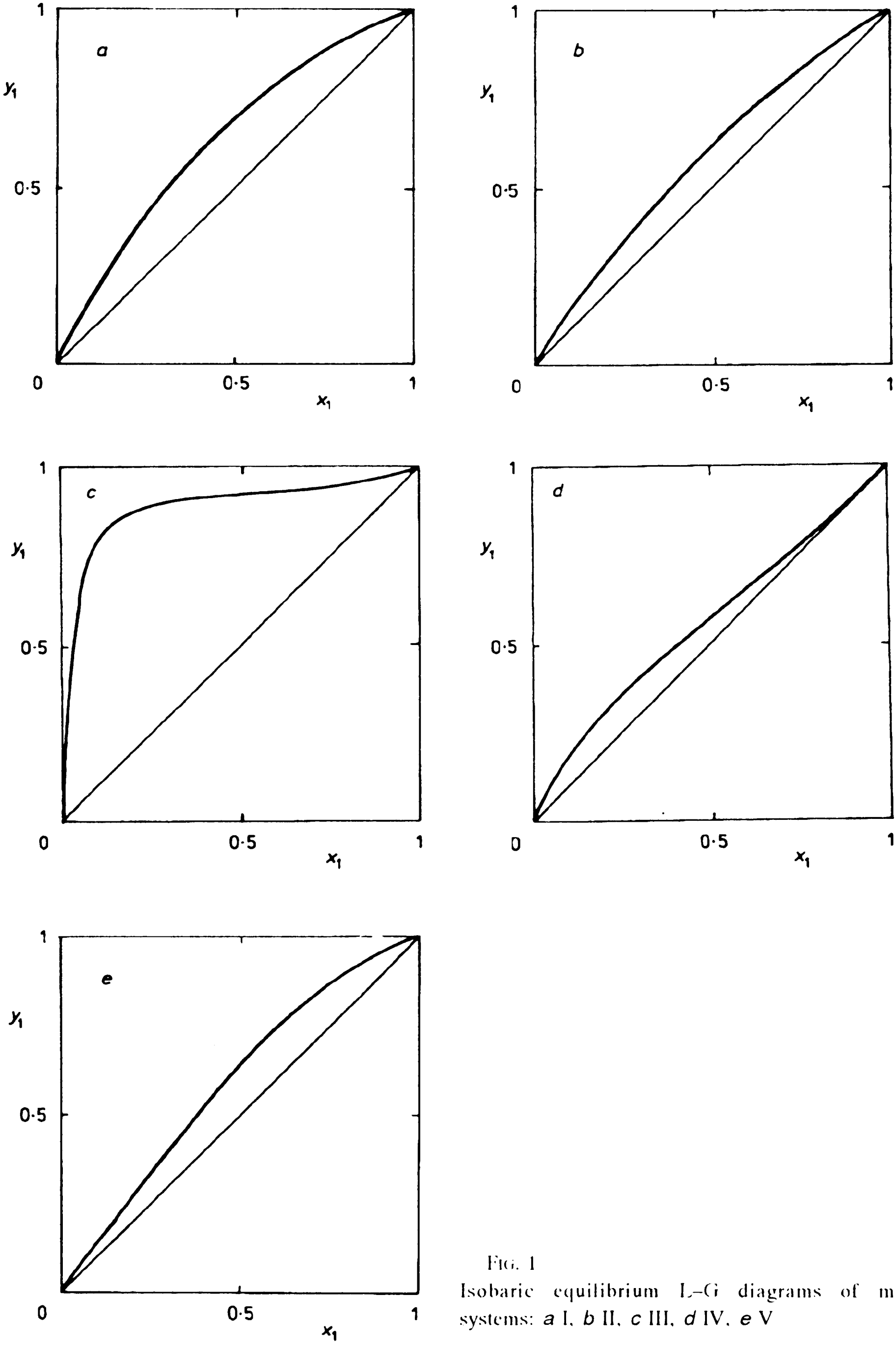

Fig. 1
Isobaric equilibrium L–G diagrams of model systems: *a* I, *b* II, *c* III, *d* IV, *e* V

Based on Eqs (*1*) – (*3*), sets of standard equilibrium data of the selected systems were prepared. The preparation has been described and the values of the energy parameters ($\lambda_{ij} - \lambda_{ii}$) of Wilson's equations have been reported in ref.[1].

In the simulated experiment aimed at preparing the "experimental" equilibrium mole fractions involving random errors it is assumed that the errors are random ones and follow the normal (Gaussian) probability distribution with the variance constant across the entire concentration region. The "experimental" mole fractions can be written as

$$x_{je} = x_j + \sigma_x N_k \tag{4a}$$

$$y_{je} = y_j + \sigma_y N_k \tag{4b}$$

for $j = 1, \ldots, l$ and $k = 1, \ldots, m$; here x_{je} and y_{je} are the experimental equilibrium mole fractions of the lower boiling component in the j-th simulated measurement and x_j, y_j are the corresponding accurate (standard) values. N_k is a number from a sequence of random numbers having the normal distribution with the centre $\mu = 0$ and variance $\sigma^2 = 1$. The products $\sigma_x N_k$ and $\sigma_y N_k$ represent the random errors of a particular measurement. The subscripts j and k refer to the serial number of the experiment and of the random number N, respectively. The way of preparing the numbers N_k has been reported[1].

In evaluating the effect of bias, the "experimental" equilibrium mole fractions will be simulated by the relations

$$x_{je} = x_j \pm \delta_x \tag{5a}$$

$$y_{je} = y_j \pm \delta_y\,, \tag{5b}$$

where δ_x, δ_y are positive or negative bias values. In the simulated experiment, the complete description of the equilibrium state involves four quantities, viz. x_e, y_e, $T_e = T$ and $P_e = P$.

The energy parameters of Wilson's equation are determined by correlation of the prepared set of experimental equilibrium data. The optimum values are found by the method of maximum likelihood in the minimum of the objective function

$$F(\lambda_{12} - \lambda_{11}, \lambda_{21} - \lambda_{22}) = \sum_j \left(\frac{P - P_{je}}{P}\right)^2, \tag{6}$$

where P is the accurate value of the total pressure and P_{je} is the calculated value for the j-th measurement. The calculation of the latter is based on Eq. (*1*) in the form

$$P_{jc} = \sum_{i} (f_i^L/\varphi_i^G)\,, \tag{7}$$

where f_i^L is the fugacity of the component given by the right-hand expression in Eq. (*1*).

The calculation also involves correlation of the mole fractions in the vapour and liquid phases.

The equation for the calculation of y_{1jc} is also obtained by a simple rearrangement as

$$y_{1jc} = \frac{f_{1j}^L/\varphi_{1j}^G}{\sum_{i} (f_{ij}^L/\varphi_{ij}^G)}\,. \tag{8}$$

In a general case, the fugacity coefficients φ_{ij}^G in Eq. (*8*) depend, in addition to the temperature and pressure, also on the vapour phase composition, although this effect is usually low. The effect of errors in the determination of y_{1jc} on the calculated energy parameters of Wilson's equation is also low but not negligible.

The correlation of the mole fractions in the liquid phase was made by applying the procedure[7] based on the equation

$$x_{1jc} = x_{1jc}^{(0)} + \delta(x_{1jc})\,, \tag{9}$$

where $x_{1jc}^{(0)}$ is the value of the mole fraction from the preceding iteration (the starting estimate is the experimental value x_{1je}) and $\delta(x_{1jc})$ is the increment whose optimum value is sought by iteration[7] (see also ref.[1]).

Calculation of the Number of Theoretical Stages

The design calculation of the number of theoretical stages of a rectification column working in the continuous mode was chosen as an example of application of the equilibrium L–G data. The numerical method after Lewis and Matheson[8] was used. The method is based on the assumption of constant molar fluxes of the liquid and vapour. The conditions and requirements associated with the design of the rectification separation for the various systems are as used previously[1]; this makes for a comparison and evaluation of the results from a broader angle.

APPLICATION

Operating Rectification Parameters

Among the adjustable parameters in the designing of the continuous rectification is the reflux ratio. This quantity governs the number of stages necessary to achieve the desired sharpness of separation. The sharpness of separation is given in terms of the mole fractions of the lower-boiling component in the distillate (x_D) and in the tail (x_W). To make it possible to assess whether and how the errors in the equilibrium composition of the phases affect the calculated number of theoretical stages in different operating conditions of the process, three reflux ratio values were used for each system. The reflux data, as well as the values of other parameters specifying the process, are given in Table I. The last column of the table gives the number of theoretical stages obtained for the standard equilibrium data.

Conditions of the Experimental Determination of the Equilibrium Phase Composition

In preparing the equilibrium concentrations by the simulated experiment according to Eq. (*4*), each data set was to include 19 equilibrium points distributed uniformly across the entire concentration region. The calculation was implemented using constant standard deviations of the mole fractions of the lower-boiling components, $\sigma(x_1) = \sigma(y_1)$, which lay within the region of 0 to 0.020.

The random errors $\sigma(x_1)N_k$ and $\sigma(y_1)N_k$ for a chosen $\sigma(x_1) = \sigma(y_1)$ take various positive and negative values. Prior to their assignment to the accurate mole fractions, the serial numbers k ($k = 1, . . ., m$, with $m = 38$) of the errors can be arbitrarily varied while preserving regular sign alternation; in this manner it is possible to prepare an

TABLE I
Specification of continuous rectification parameters and numbers of theoretical stages calculated for the equilibrium data standard

System	x_D	x_F	x_W	R_{min}	N for R/R_{min}		
					1.2	2	∞
I	0.990	0.500	0.010	1.40	23.68	16.60	10.98
II	0.990	0.500	0.010	3.00	37.69	25.66	17.84
III	0.990	0.200	0.005	0.250	13.87	8.03	4.30
IV	0.850	0.500	0.020	3.80	47.78	26.14	17.09
V	0.990	0.500	0.030	2.90	75.97	38.66	21.61

enormously large number of sets of experimental equilibrium data which possess the same $\sigma(x_1)$ and $\sigma(y_1)$ values but differ in the order of errors. Our recent investigation of a similar problem in the field of the liquid–liquid phase equilibrium[9], with a subsequent application of the equilibrium data to the calculation of the number of equilibrium stages of a countercurrent extractor, revealed that such rearrangement of the serial numbers of the random errors can bring about appreciable changes in the total number of stages. This finding led us then to work out a procedure making it possible to determine an acceptable order of the random errors, which we also applied to the present work.

When forming the set of experimental equilibrium concentrations (x_1, y_1) for each system, we first chose at random a constant value of $\sigma(x_1) = \sigma(y_1) = 0.01$, and then we sought a final distribution of random errors such that the formed set of equilibrium data and the calculated relative difference in the number of theoretical stages of the rectification column was closest to the average value of differences in the number of stages. Thirty-eight formed sets of equilibrium data were usually involved in the determination of the average difference in the number of stages. Furthermore it was assumed that the order of errors determined in experiments with $\sigma(x_1) = \sigma(y_1) = 0.01$ will remain the same when using different values of the standard deviations $\sigma(x_1)$ and $\sigma(y_1)$, and that it also will be unaffected by the reflux ratio. The values of the above error distribution characteristics are given in Table II.

TABLE II

Values of the arithmetic mean $\bar{N}_e = \sum N_e/n$, sample standard deviation $s = [\sum(N_e - \bar{N}_e)^2/n]^{1/2}$ average percentage relative difference $\bar{d} = (100/n) \sum (|N_e - N|/N)$, maximum relative difference in the number of theoretical stages of a rectification column d_{max} and the number of sets of equilibrium data n used in seeking the final order of random errors of equilibrium concentrations for a constant value of $\sigma(x_1) = \sigma(y_1) = 0.01$ and for the reflux ratio $R = 1.5 R_{min}$

Parameter	System				
	I	II	III	IV	V
R	2.10	4.50	0.375	5.70	4.35
N	19.41	30.09	9.99	32.88	51.10
$\bar{N}_e$	19.45	30.11	9.96	32.81	51.35
s	0.039	0.093	0.066	0.16	0.65
$\bar{d}$	0.24	0.26	0.53	0.37	1.14
d_{max}	0.67	0.63	1.60	1.34	2.58
n	34	38	38	38	38

The simulated experiment with the systematic errors according to Eq. (5) was performed with constant positive or negative errors $\delta(x_1)$ and $\delta(y_1)$ from the region of 0 to 0.014.

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

Prior to the application, each of the prepared sets of equilibrium mole fractions (x_1, y_1), complemented with the corresponding temperature and the equilibrium data standard, along with the constant total pressure (P = 101 300 Pa) was correlated by Eq. (*6*) to obtain the optimum energy parameters of Wilson's equations.

The number of theoretical stages was calculated for three different reflux ratios, viz. 1.2 $R_{\min}$, 2 $R_{\min}$ and R_∞. The equilibrium sets can be discriminated by the standard deviation $\sigma(x_1) = \sigma(y_1)$ (when assessing the effect of random errors) or by the increment $\delta(x_1) = \delta(y_1)$ (when assessing the effect of bias). The number of theoretical stages calculated with the correlated set of experimental data N_c was finally compared with the value of N obtained with the equilibrium data standard in the form of the relative (percentage) deviation

$$d = 100\,(N_c - N)/N \qquad (10)$$

which provided a basis for assessing the effect of errors in measurement of the equilibrium phase composition on the results of the design calculation. The results so obtained are shown in Figs 2 and 3 as plots of d vs $\sigma(x_1) = \sigma(y_1)$ and d vs $\delta(x_1) = \delta(y_1)$, respectively.

DISCUSSION

In the simulated experiments of the L–G equilibrium it was assumed that the method of composition determination is the same for the liquid and vapour phases, so that it is reasonable to assume that the precision of determination is the same ($\sigma(x_1) = \sigma(y_1)$) or that the bias for the two phases has the same magnitude and sign.

The impact of errors in the determination of the equilibrium composition on the calculated number of theoretical stages is different for the different systems. For systems I and II, which approach systems with ideal behaviour of the phases, it holds that even if the equilibrium mole fractions contain appreciable errors, their correlation makes the equilibrium dependence approach the standard values so closely that the calculated number of theoretical stages is little affected (Figs 2*a*, 2*b* and 3*a*, 3*b*).

For system III, exhibiting an appreciably convex distribution curve, errors in the equilibrium concentrations have a slight effect of the calculated number of stages. The differences d increase with increasing random error and bias in the phase composition, the increase being also dependent on the reflux ratio (Figs 2*c* and 3*c*).

The highly uneven shape of the equilibrium curves of systems IV and V is most sensitive to errors in the phase composition. This is due to the fact that in the side concentration ranges, where the equilibrium curves approach closely the diagonal of the diagram (Fig. 1*d*, 1*e*) and where changes in the phase composition from stage to stage are small, the impact of errors in the equilibrium composition on the calculated number of stages is significant. The differences d are higher if the working reflux ratio is closer to the minimum (Figs 2*d*, 2*e* and 3*d*, 3*e*). It is characteristic of the two systems that with the occurrence of random errors, the differences in the numbers of stages are only negative, which indicates that errors of this kind lower the calculated number of stages. The effect of bias appears in a different manner. While system IV, with a positive deviation from Raoult's law and exhibiting an azeotropic point, responds to positive values of $\delta(x_1) = \delta(y_1)$ by a decrease in the number of theoretical stages ($d < 0$), system V, with a negative deviation from Raoult's law, responds to

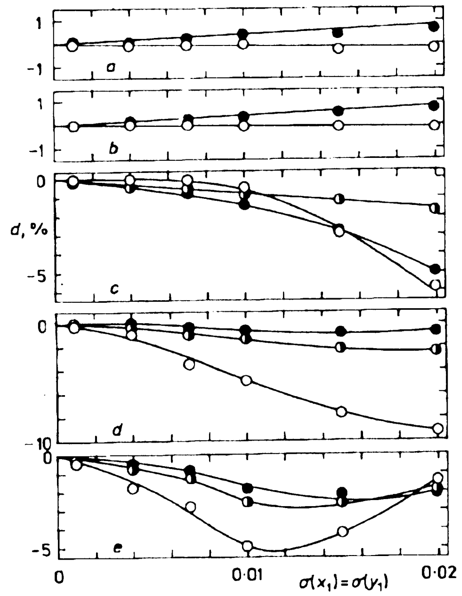

FIG. 2

Dependence of the difference d on the random error of equilibrium mole fractions $\sigma(x_1) = \sigma(y_1)$ for reflux ratios: ○ $1.2\,R_{\min}$, ◑ $2\,R_{\min}$, ● R_{∞}. System: *a* I, *b* II, *c* III, *d* IV, *e* V

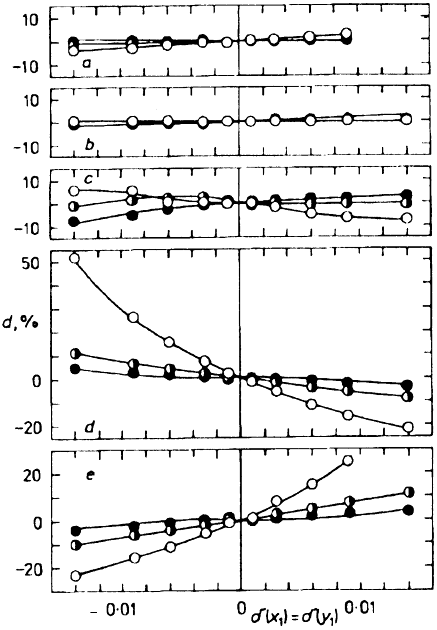

FIG. 3

Dependence of the difference d on the bias of equilibrium mole fractions $\delta(x_1) = \delta(y_1)$ for reflux ratios: ○ $1.2\,R_{\min}$, ◑ $2\,R_{\min}$, ● R_{∞}. System: *a* I, *b* II, *c* III, *d* IV, *e* V positive and negative bias values in the opposite way. Here, also, the overall effect of errors on the d value is reduced by increasing the reflux ratio. The working reflux ratio usually approaches $1.2\,R_{min}$; then, if the bias exceeds the limit of $\delta(x_1) \cong 0.005$, the inaccuracy in the calculated number of theoretical stages may be 10% and more.

SYMBOLS

d	percentage relative deviation in the number of theoretical stages
$\bar{d}$	average value
f	fugacity
F	objective function
n	number of sets of equilibrium data
N_k	number from a sequence of random numbers with normal distribution
N, N_e	number of theoretical stages calculated from the equilibrium data standard and from experimental data, respectively
$\bar{N}_e$	arithmetic mean
P	system pressure
P_i^0	saturated vapour pressure of pure component i
R	gas constant
R, R_{min}, R_∞	working, minimum and maximum reflux ratios, respectively
s	sample standard deviation in the number of theoretical stages
T	thermodynamic temperature
v_i^{0L}	molar volume of pure liquid component i
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
γ	activity coefficient
δ	bias
$\lambda_{12} - \lambda_{11}$, $\lambda_{21} - \lambda_{22}$	energy parameters of Wilson's equation
Λ_{12}, Λ_{21}	parameters of Wilson's equation
σ	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
D	in distillate
e	experimental
F	in raw material
i	any component
j	serial number of equilibrium point

k	serial number of random number
s	saturation
W	in tail
x, y	related with mole fraction in liquid and vapour phases, respectively
1, 2	component with lower and higher boiling temperatures, respectively

REFERENCES

1. Dojčanský J., Bafrncová S., Surový J.: Collect. Czech. Chem. Commun. *57*, 1867 (1992).
2. Hayden J. G., O'Connell J. P.: Ind. Eng. Chem., Process Des. Dev. *14*, 209 (1975).
3. Nothnagel K. M., Abrams D. S., Prausnitz J. M.: Ind. Eng. Chem., Process Des. Dev. *12*, 25 (1973).
4. Wichterle I., Linek J.: *Antoine Vapor Pressure Constants of Pure Compounds*. Academia, Praha 1971.
5. Yamada T., Gunn R. D.: J. Chem. Eng. Data *18*, 234 (1973).
6. Wilson G. M.: J. Am. Chem. Soc. *86*, 127 (1964).
7. Graczová E.: *Thesis*. Slovak Technical University, Bratislava 1989.
8. Lewis W. K., Matheson G. L.: Ind. Eng. Chem. *24*, 494 (1932).
9. Dojčanský J., Bafrncová S., Surový J.: Collect. Czech. Chem. Commun. *53*, 34 (1988).

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