

# SOME THEORETICAL AND PRACTICAL PROBLEMS ON THE VAPOUR—LIQUID EQUILIBRIUM OF 3 NON-IDEAL QUATERNARY SYSTEMS

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## Signs employed

$A, B,$ and $A_{ij}$	Margules or Van Laar constants of the binary system consisting of the components "i" and "j"
$C_{ijk}$	Margules constant of the ternary system consisting of the components "i", "j", and "k"
$P$	Total pressure of the system
$P_i$	Equilibrium vapour pressure of the component "i"
$a_i$	Activity of the component "i"
$p_i$	Partial pressure of the component "i"
$t$	Temperature (°C)
$x_i$	Molar fraction of the component "i" in the liquid phase
$y_i$	Molar fraction of the component "i" in the vapour phase
$\gamma_i$	Activity coefficient of the component "i"
$\varrho_{ij}$	Quotient of the activity coefficients of components "i" and "j"

This theoretical and experimental work relates to the vapour—liquid equilibrium of three non-ideal quaternary systems.

The knowledge of the vapour—liquid equilibrium of these three quaternary systems—systems ethanol-benzene-heptane-water, acetone-ethanol-water-butanol, and ethanol-heptane-toluene-aniline — is necessary from point of view of designing and dimensioning certain industrial distillation. While performing the experimental work and the theoretical calculations, however, numerous problems of fundamental importance have arisen, the solution of which could be connected to statements of general validity.

## 1. Apparatus for measuring vapour—liquid equilibria, suitable for the examination of heterogeneous systems too

The measurement of systems of more components by the aid of the usual devices generally meets difficulties, because samples of higher quantity are required both for the vapour and the liquid phases. In the case of heterogeneous liquid mixtures the above-mentioned problems are rendered more difficult by the necessity of a suitable dispergation of the phases. To solve these problems, the apparatus for measuring equilibria, visible in Fig. 1 was designed by the author and his collaborators. The apparatus functions

on the basis of the principles of recirculation, and is a modification of Othmer's apparatus.

According to the control measurements, the constructed apparatus has proved to be suitable to support and promote, respectively, the theoretical calculations of appropriate correctness by the aid of experimental data.

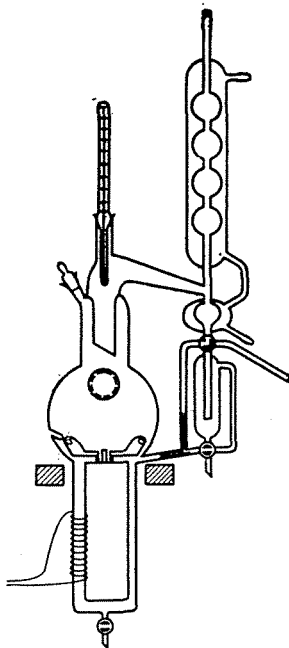


Fig. 1

## 2. Analytical methods

While developing the analytical methods, it had to be taken into consideration that the quantity of the available sample is relatively small, but at the same time the required reliability is comparatively high. Besides, the fact had to be considered that, in order to avoid the accumulation in the working, the time requirement for the analytical work may exceed the period of an equilibrium measurement only in a slight degree.

The analysis of the system ethanol-benzene-heptane-water was performed as follows :

The sample withdrawn during the equilibrium measurement was divided into three parts. In the first part the ethanol was determined by oxidation with potassium bichromate, followed by titrating with ferrous sulphate [1]. In the second part the quantity of the water was measured by Karl Fischer's

titration system of electrical dead-stop [2, 3, 4]. By a multiple-stage extraction carried out with saturated calcium chloride solution, the ethanol and the water were removed from the third part, and the quantity of the benzene and heptane related to each other was determined by measuring the refraction.

A sample of about 3 g weight is necessary to carry out the total quaternary analysis; the relative error of the analysis does not exceed 2 per cent.

In the case of system acetone-ethanol-water-butanol the following method was employed:

From one part of the sample the quantity of the acetone was determined by adding a solution of hydroxyl amine chlorine hydrate, and by titrating the solution with sodium hydroxide, in the presence of bromphenol blue indi-

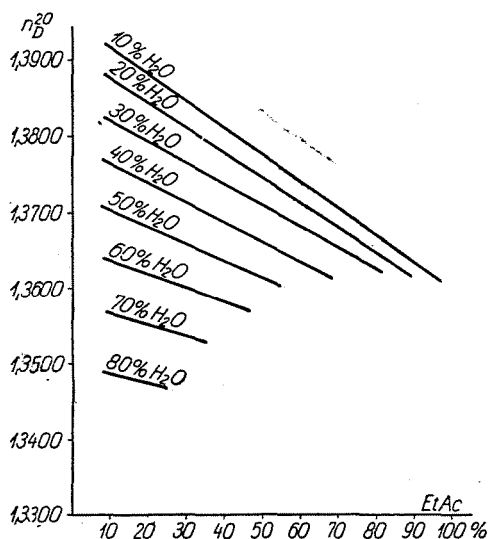


Fig. 2. Refractive index against composition in the system acetone-ethanol-water-butanol.

cator [5, 6]. In the second part of the sample the quantity of the water was determined by Fischer's titration method mentioned in the foregoing [7, 8].

Knowing the absolute quantity of the water and acetone, after measuring the refractive index of the quaternary system, the distribution expressed in percentage of the two other components can be directly read from the reference diagrams constructed by the author. One of the reference diagrams is shown in Fig. 2.

The values of the refractive indices of the acetone and ethanol are nearly equal; therefore the refractive index of the system was plotted as a function of the common concentration of the ethanol and acetone; the isohydrate lines have been marked on the diagram. During these investigations, this method

proved to be very useful. As regards the quaternary composition, the relative analytical error is lower than 3%. The quantity of the necessary sample amounts to 0,5—1 g.

The system *ethanol-heptane-toluene-aniline* was analysed by similar methods. Also here the available sample had to be divided into several parts; by Kjeldahl's method, the quantity of aniline from one part of the sample was determined. From the other part of the sample the ethanol was shaken out with an alkaline calcium chloride solution. In the aqueous phase the ethanol was determined by the above-mentioned bichromate method, while in the hydro-carbon phase the distribution of the heptane and toluene was determined by measuring the refractive index. The relative error of the analysis was always lower than 2%. The quantity of the sample amounted to 0,5—2 g, depending on the aniline content.

### 3. The plotting of quaternary systems

A new method had to be elaborated for plotting the quaternary equilibrium correlations, because none of the references to be found in the literature made the plotting of synoptical and easily designable diagrams possible [9, 10, 11, 12, 13, 14, 15].

A regular tetrahedron was chosen as a starting basis for the plotting method. It can be demonstrated that the composition of a quaternary mixture may be expressed by the distance measured from the lateral faces opposite to the edges representing the pure components, or rather by their values relating to each other.

Composing two orthogonal projections of the tetrahedron set to one of its edges, a square and an isosceles triangle was obtained, respectively.

It can be proved that the composition of a quaternary point in question is determined by the distances of the projection point from the sides of the rectangle, namely the distance of the point being on the projection from the rectangle side opposite to the vertex representing the pure component in question determines the percentile value of the said component.

Further details of this new method of representation was published in a previous article [16].

### 4. Calculations of equilibrium

To calculate the vapour—liquid equilibria of the three quaternary systems, besides the appropriate quaternary systems, the knowledge of the equilibrium of 16 binary systems was necessary, and it was advisable to carry out measurements even in connection with the 12 ternary systems derivable

from these binary systems. The measurements caused no special difficulties, although the accomplishment of the numerous experiments necessitated a great deal of work.

In the case of quaternary equilibrium calculations the quaternary Margules equations of 3 indices were employed, the solving of which necessitated the knowledge of the Margules constants of the binary systems.

The calculation methods which are special, or employed first by the author, are reviewed in case of the systems where they were employed.

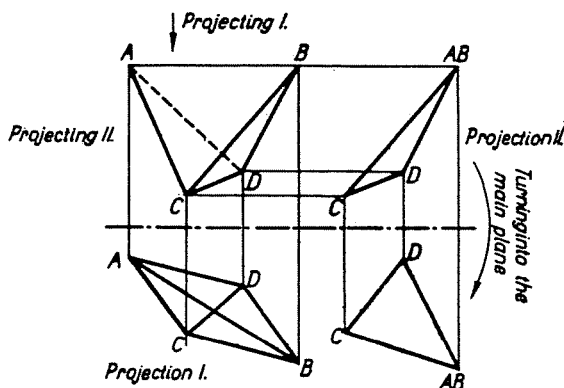


Fig. 3. Representation of a quaternary system by orthogonal projection of a phase diagram of three dimensions

In connection with the calculations of the ternary systems it should be mentioned that the performance of tedious calculations proved to be unnecessary, when employing the new method worked out by the author.

#### 4.1 Calculations of binary systems

The 16 existing binary systems can be divided into the following three groups :

a) Zeotropes : acetone-ethanol, acetone-water, acetone-butanol, ethanol-butanol, benzene-heptane, heptane-toluene, ethanol-aniline, heptane-aniline, toluene-aniline ;

b) Homoazeotropes : ethanol-benzene, ethanol-heptane, ethanol-water, ethanol-toluene ;

c) Hetero-azeotropes : water-butanol (partially heterogeneous), benzene-water, heptane-water (quasi fully heterogeneous).



### 4.11 Zeotropes and homoazeotropes

As the calculation of the equilibrium relations of the binary zeotropes and homoazeotropes based on the experimental work performed by the author, as a rule, encountered no difficulties, only the final results — the constants of the corresponding binary three-suffix Margules equations — are shown.

Table I

System	$A_{ij}$	$A_{ji}$
Acetone-ethanol . . . . .	0,26	0,26
Acetone-water . . . . .	0,97	0,70
Acetone-butanol . . . . .	0,20	0,70
Ethanol-butanol . . . . .	0,00	0,04
Benzene-heptane . . . . .	0,11	0,15
Heptane-toluene . . . . .	0,17	0,12
Ethanol-aniline . . . . .	2,19	-0,95
Heptane-aniline . . . . .	1,29	0,81
Toluene-aniline . . . . .	-0,45	1,50
Ethanol-benzene . . . . .	0,80	0,60
Ethanol-heptane . . . . .	0,83	0,83
Ethanol-toluene . . . . .	0,37	0,96
Ethanol-water . . . . .	0,74	0,40

### 4.12 Hetero-azeotropes

#### 4.12.1 Water—*n* butanol

In order to determine the binary constants of the mixture water—*n* butanol, on basis of known equilibrium data [17, 18, 19] calculations were performed by extrapolation of the logarithms of the corresponding activity coefficients.

The values so obtained ( $A_{ij} = 0,60$  and  $A_{ji} = -1,40$ ) satisfactorily described the equilibrium curve, with the exception of the heterogeneous range.

#### 4.12.2 Benzene-water and heptane-water

In the case of partially heterogeneous system water-butanol it could be seen that the known methods of calculation could not be used to describe the equilibrium curve parallel to the axis  $x$  on the equilibrium diagram.

By the known methods, an appropriate pair of constants could not at all be found for describing the equilibrium curve of these two systems being

practically fully heterogeneous, because the calculated constants had considerably changed in function of the composition of the heterogeneous liquid phase (see Fig. 4).

The change of the constants along the equilibrium curve parallel to the abscissa was continuous in function of the molar fraction  $x$ , that is the scattering did not appear around one certain pair of values; namely, in the latter case, when using this pair of value as constants, the equilibrium curve nearly in its total length could have been calculable with a correctness satisfactory

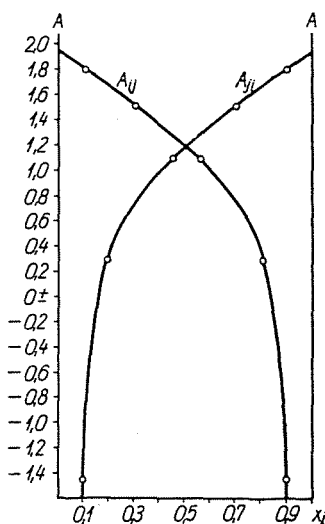


Fig. 4. The dependence on the composition of the Margules constants of the systems benzene—water and heptane—water

to the technical practice. Because of the continuous change of the constants, the choice of one single pair of values had not been tried but, plotting the change of the constants in function of the composition, according to the requirements of the calculation a correct set of equations has been established to determine the constants. Along the total equilibrium curve the equation giving the two constants is as follows:

$$A_{ij} = -\log [10^{-26,3 \cdot (1-x_i)^4} + 10^{-1,75 \cdot (1-x_i)^{-0,29}}]$$

$$A_{ji} = -\log [10^{-26,3x_i^4} + 10^{-1,75x_i^{-0,29}}]$$

The component  $x_i$  of the equation is the liquid-phase molar fraction of the more volatile component of the binary system.

This method which, with the aid of the above-mentioned equations, expresses the Margules constants of the binary system as a function of the

liquid-phase composition of the system, can be properly employed, in the case of practically fully heterogeneous systems, to determine the Margules constants, valid at any point of the equilibrium curve. Moreover, by appropriate modification, the equations can be used, in case of the partially heterogeneous binary systems having a wide heterogeneous range, also to determine the Margules constants valid at the equilibrium points being in the concentration interval of separating the mixture into two phases. These equations are of general validity and, in case of the above-mentioned heterogeneous binary systems, they are, independently of the material quality of the components, suitable to calculate the constants.

The reason for the general validity of the equations in the case of heterogeneous systems is that when determining the Margules constants with the aid of these equations — in each case separately — and when forming the products  $x_i \gamma_i$ , starting from the logarithms of the activity coefficients calculated with the Margules equations, then this multiplication always gives 1 as a result. This means that when substituting, Raoult's law extended to the real mixtures, the vapour composition is given, at any liquid composition, by the ratio of the tension of the component in question and of the total pressure that is the generally common calculation method in case of heterogeneous systems is followed.

As a matter of course, the calculation of the constants has an importance in calculation of such ternary and quaternary vapour—liquid equilibria which contain one or more heterogeneous binary pair of constants, but it is not important in determining the equilibrium curve of heterogeneous binary systems, because this curve could be much more simply calculated when knowing the vapour tension. Then, in the ternary and quaternary equations, the former equations should be substituted for the binary constants of the heterogeneous system. As a matter of course, if the determination of a vapour composition in equilibrium with a ternary or quaternary liquid mixture of a certain definite composition is intended, then the values of the equations calculated to the composition in question should be used, taking into consideration that the component  $x_i$  means the liquid-phase molar fraction of the more volatile component of the heterogeneous binary pair of components.

#### 4.2 Calculations of ternary systems

In connection with the ternary systems extensive investigation were not needed, because the calculation of the ternary constants occurring in the quaternary system, as it will be discussed in detail in Chapter 4.3, was not performed by measurements of the ternary systems, but from quaternary ones.



It may be mentioned that the calculation of the ternary constants by the binary constant in question, using the equations recommended by the literature and having the following type :

$$C_{ijk} = 0,5 (A_{ji} + A_{ik} + A_{ki}) - (A_{ij} + A_{ki} + A_{jk})$$

was generally omitted as this method only seldom gives reliable values.

#### 4.3 Quaternary calculations

It should be taken into consideration that the influence of the ternary constants of the quaternary equations exerted on the values of the composition data obtained by calculation substantially depends on the concentration relations of the components of the mixture of four components used as a basis for calculations. Consequently, e. g. in the quaternary Margules equation of three indices, the effect of the appropriate ternary constant upon  $\log \gamma_i$  ceases to exist at a composition of  $x_i = 0,5$ , because the value of the coefficient  $(1 - 2x_i)$  of the equation becomes zero. In contradiction to this fact, the degree of influence of  $C_{ijk}$  on  $\log \gamma_i$  becomes maximum if  $x_j = x_k$  and, simultaneously, the values of  $x_i$  and  $x_l$  are low.

Among the methods suitable for determining quaternary vapour—liquid relations, the method of back-calculation of the ternary constants with the aid of the composition data of a quaternary equilibrium measurement was chosen. With the intention of determining the average ternary constants from a quaternary measurement, calculations were made with a quaternary equation containing the logarithms of both the activity coefficients and their quotients.

By the logarithms of the activity coefficients calculated from the quaternary equilibrium measurement and of the adequate quaternary Margules equation, the difference of the values obtained, without taking notice of the expressions containing the ternary constants has been written as a function of the ternary constants into equations, and in this way, corresponding to the four components, the set of equations of the first degree consisting of four equations and having four unknown variables has been solved using the data of a quaternary equilibrium measurement.

On the analogy of the above procedure, using the Margules equations evolved to the logarithm of the quotients of the activity coefficient, by the aid of the cyclic permutation employed to the indices, not four but six equations are obtained from the four unknown variables. Even in this case the set of equations is not over-defined, and by the six equations that can be established there is a possibility to choose the three most suitable and most simple equations, independent of each other. The relation concerning the

vapour-phase molar fraction of the components quite obviously gives the fourth equation, according to which

$$\sum_{n=1}^{n=4} \frac{a_n P_n}{P} = \sum_{n=1}^{n=4} \frac{x_n \gamma_n P_n}{P} = 1.$$

The starting step of the solution of both types of equations will be described when reviewing the use of the equations. Although these calculation methods are covertly equivalent to a calculation method accomplished by equations containing a quaternary constant each and so necessitate a quaternary measurement, they render the carrying out of the ternary equilibrium measurements unnecessary which are often difficult and altogether much too labourous, as well as of the very lengthy calculations necessary to evaluate the measurements.

#### 4.31 Calculation of the system ethanol-benzene-heptane-water

When investigating the system forming, while dehydrating the ethanol with azeotropic distillation carried out with a mixture of benzene and gasoline, *n*-heptane was employed as model material in place of the usual gasoline fraction of an average boiling point of 100° C. While investigating the equilibrium of the quaternary system elaborated in this way, the method of calculation starting from the data of the single quaternary equilibrium measurement was employed.

The equilibrium measurements were performed by the quaternary Margules equation of three indices evolved to the logarithm of the quotients of the activity coefficients. The quaternary azeotropic composition data measured by SWIETOSŁAWSKY with differential ebulliometer and with the method of serial distillations served as starting basis [20, 21, 22].

The activity coefficients calculated from the azeotropic composition data have been substituted into the quaternary Margules equations arranged in relation to the ternary constants; one of these quaternary Margules equations is described as follows:

$$\begin{aligned} \Delta Q_{eij} = & (x_j - x_i) (x_k C_{ijk} + x_l C_{ijl}) + x_k x_l (C_{ikl} - C_{jkl}) = \\ & = \{ A_{ji} (x_j - x_i) + x_j (A_{ij} - A_{ji}) (x_j - 2x_i) + \\ & + x_k [A_{ik} - A_{kj} + 2x_i (A_{ki} - A_{ik}) - x_k (A_{jk} - A_{ki})] + \\ & + x_l [A_{il} - A_{lj} + 2x_i (A_{li} - A_{il}) - x_l (A_{jl} - A_{lj})] - \\ & - x_k x_l [A_{ik} - A_{ki} - (A_{lj} - A_{jl})] \} - \log_{eij} \end{aligned}$$

$$\text{where } \log_{eij} = \log \frac{\gamma_i}{\gamma_j}$$

After substituting the binary constants determined as above-mentioned, the set of equations containing four unknown values according to the four

components have been solved to the ternary constants. Using the liquid compositions of the quaternary equilibria measured by the author, the equilibrium vapour compositions were calculated by the so obtained ternary constants values.

As shown in Table II and Fig. 5, the calculated and the measured vapour compositions are in good agreement. The values of the ternary constants used for the calculations are shown together with the values calculated directly from the binary constants in Table III.

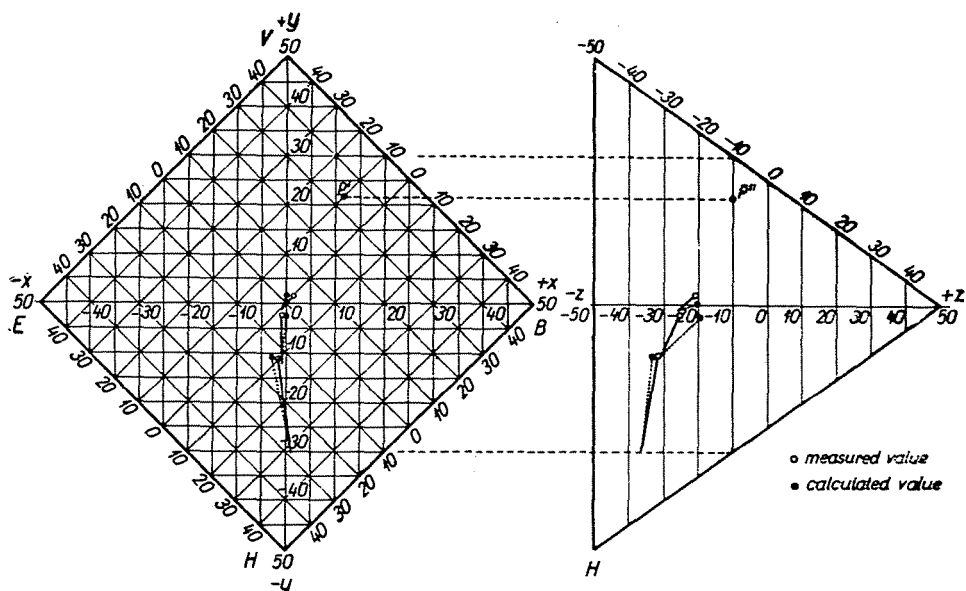


Fig. 5. Vapour—liquid equilibrium diagram of the system ethanol-benzene-heptane-water

It can be stated that, although the values of the binary constants are reliable and, as proved by the results shown in Table II, they were usable in the quaternary calculations too, the ternary constants directly calculated with the binary constants considerably deviate from the values calculated from the quaternary equilibrium.

#### 4.32 Calculation of the system acetone-ethanol-water-*n*-butanol

In the system of acetone-ethanol-water-*n*-butanol, in contrast to the quaternary system arising when dehydrating the ethanol, the elaborated calculation method did not secured suitable results.

The reason for this may be explained by the unsuitability of the ternary constants appertaining to the ternary “sub-systems” of the acetone-ethanol-water-butanol system.

Table II

	$y_l$		$y_j$		$y_k$		$y_l$		t°C.
	measured	calculated	measured	calculated	measured	calculated	measured	calculated	
$x_l = 0,399$ $x_k = 0,129$ $x_j = 0,358$ $x_l = 0,144$	0,335	0,345	0,375	0,364	0,120	0,141	0,170	0,150	66
$x_i = 0,529$ $x_k = 0,111$ $x_j = 0,278$ $x_l = 0,082$	0,399	0,366	0,357	0,331	0,129	0,154	0,115	0,149	67
$x_i = 0,747$ $x_k = 0,039$ $x_j = 0,129$ $x_l = 0,085$	0,528	0,523	0,278	0,291	0,122	0,128	0,072	0,058	69

Table III

	Calculated from quaternary azeotropic composition	Calculated from binary constants
$C_{ijk}$ .....	-4,73	-0,08
$C_{ijl}$ .....	+1,37	+0,38
$C_{ikl}$ .....	+1,42	-0,31
$C_{jkl}$ .....	+0,53	-0,61

Table IV

	Averaged ternary constants calculated from ternary measurements	Ternary constants calculated from binary constants	Ternary constants calculated from quaternary measurement No. I
$C_{ijk}$ .....	+1	-0,32	-2,26
$C_{ijl}$ .....	-2	+1,33	-0,05
$C_{ikl}$ .....	+3	+2,84	+2,22
$C_{jkl}$ .....	-2	+1,19	+1,20

In certain systems having several components it does not suffice to take the formation of the balance of forces into consideration solely on the molecules entering into direct reciprocal action [23, 24].

In such cases the Margules equations of three indices cannot give adequate results. It can be assumed, and it is very probable, that in the case of this system containing polar and functional groups (first considering the two alcohols), in the development of the equilibrium relations considerably from the ideal ones, apart from the hetero-molecular forces the secondary homomolecular actions arising from associations partake as well [25, 26].

The irregularities produced by the association can be taken into correction by introducing an associating factor. The determination of this association

factor is quite difficult and therefore its extension to the quaternary systems was not deemed to be practical.

In quaternary systems it would be very tedious to work with equations having an index number higher than three ; therefore it seems advisable to draw the conclusion that in case of the system in question it appears unnecessary to insist on determining the equilibrium by calculations.

#### 4.33 Calculation of the system ethanol-heptane-toluene-aniline

This system develops during a particular industrial distillation, and it gives rise to numerous very interesting problems [27].

In spite of the asymmetry caused by the high boiling point of aniline, the vapour—liquid calculations proved to be satisfactorily usable.

The ternary constants to be used in the quaternary calculations have been determined by the above-mentioned method, from the data of the quaternary equilibrium measurement No. I. The values of these ternary constants, together with the ternary constants obtained by calculations from the binary constants, as well as from the ternary equilibrium measurements are shown in Table IV.

It can be seen from the Table that the calculation performed with ternary constants, obtained directly from otherwise acceptable binary constants, would not have been successful even in the case of this system. The constants calculated from the ternary measurements are unfounded.

In some cases there is a great difference between the average ternary constants obtained from ternary equilibrium measurements and the ternary constants calculated from quaternary equilibrium measurements. This fact justifies the use of these values calculated with the method discussed by the author to the equilibrium calculations of the systems of four components.

In the quaternary vapour—liquid equilibrium calculations the calculation method employed in developing the quaternary system when dehydrating ethanol was followed and the ternary constants obtained from the first quaternary measurement was used. In this quaternary system the calculations have been carried out with the equations obtained by rearranging the relations evolved to the logarithm of the activity coefficient. The first member of these equations is as follows :

$$\begin{aligned} \Delta Q_{\gamma i} &= (1 - 2x_i) (x_j x_k C_{ijk} + x_j x_l C_{ijl} + x_k x_l C_{ikl}) - 2x_j x_k x_l C_{jkl} = \\ &= \{x_j^2 [A_{ij} + 2x_i (A_{ji} - A_{ij})] + x_k^2 [A_{ik} + 2x_i (A_{ki} - A_{ik})] + \\ &\quad + x_l^2 [A_{il} + 2x_i (A_{li} - A_{il})] + x_j x_k [A_{ji} + A_{ik} - A_{kj} + \\ &\quad + 2x_i (A_{ki} - A_{ik}) + 2x_k (A_{kj} - A_{jk})] + x_j x_l [A_{ji} + A_{il} - \\ &\quad - A_{lj} + 2x_i (A_{li} - A_{il}) + 2x_l (A_{lj} - A_{jl})] + x_k x_l [A_{ki} + \\ &\quad + A_{il} - A_{lk} + 2x_i (A_{li} - A_{il}) + 2x_l (A_{lk} - A_{kl})] + \\ &\quad + 2x_j x_k x_l (A_{ij} - A_{jl})\} - \log \gamma_i \end{aligned}$$

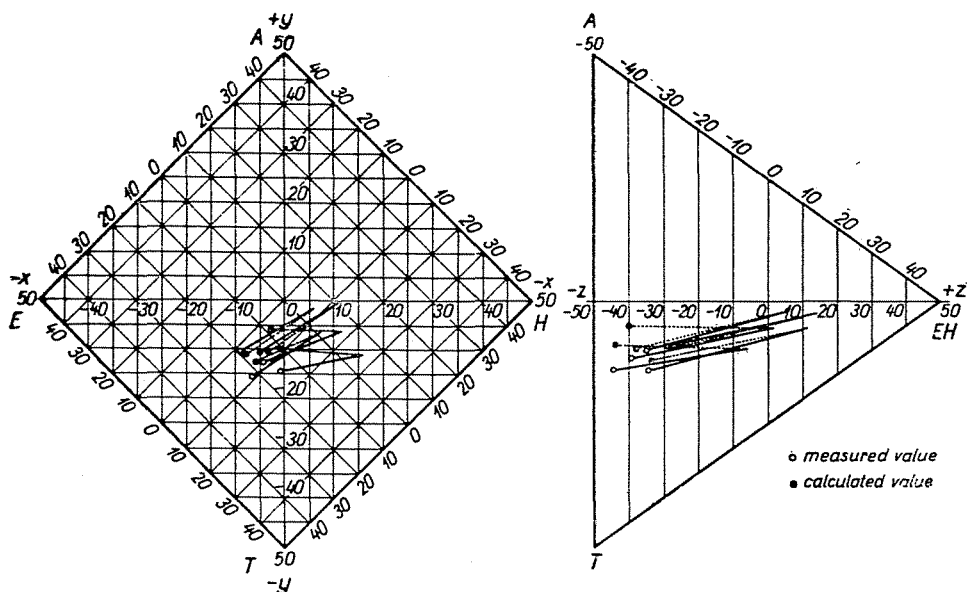


Fig. 6. Vapour-liquid equilibrium diagram of the system ethanol-heptane-toluene-aniline

Table V

Number	Boiling point	$z_i$	$z_j$	$z_k$	$z_l$
I .....	86	0,161	0,125	0,289	0,425
II .....	82,5	0,181	0,181	0,181	0,457
III .....	81	0,259	0,133	0,227	0,381
IV .....	79	0,310	0,175	0,125	0,390
V .....	75	0,391	0,168	0,055	0,386

Table V (continued)

Number	$y_i$			$y_j$			$y_k$			$y_l$		
	calculated with $\gamma$	calculated with $\varrho$	measured	calculated with $\gamma$	calculated with $\varrho$	measured	calculated with $\gamma$	calculated with $\varrho$	measured	calculated with $\gamma$	calculated with $\varrho$	measured
I	0,500	—	0,500	0,283	—	0,283	0,196	—	0,196	0,021	—	0,021
II	0,544	—	0,541	0,345	—	0,316	0,096	—	0,121	0,015	—	0,022
III	0,558	0,564	0,578	0,286	0,270	0,267	0,139	0,146	0,144	0,017	0,020	0,011
IV	0,515	0,530	0,580	0,385	0,362	0,309	0,081	0,090	0,100	0,019	0,018	0,011
V	0,565	—	0,620	0,370	—	0,330	0,042	—	0,035	0,023	—	0,015

As shown in Table V, the measured and the calculated values are in good agreement (see Table V and Fig. 6).

In two cases with the object of checking the determination of the equilibrium composition has been carried out by the equations evolved to the logarithms of the quotients of the activity coefficients as well, and the values being in good agreement with those described above were obtained. This circumstance proves that within such a narrow temperature interval there exist no essential deviation between the calculations performed with two kinds of equations.

Summarizing, it may be stated that in the system ethanol-heptane-toluene-aniline the established new calculation method proves as a result to be very advantageous in its simplicity and satisfactory reliability.

### Summary

A new apparatus for experimental determination of vapour-liquid equilibria has been elaborated. The apparatus functions on basis of the principle of recirculation and it is equally useful to investigate homogeneous and heterogeneous systems.

By critically reviewing the methods published in the literature, a new method for representing quaternary vapour-liquid equilibria was elaborated. This method reflects the space curve characteristic of the equilibrium relations with double orthogonal projection. For establishing empirical equations, a calculation method was elaborated which, at any composition, rendered it possible the use of the constants of heterogeneous binary systems without transformation, in equations deduced to homogeneous ternary and quaternary systems.

A new calculation method for determining, in a theoretical way the vapour-liquid equilibrium of quaternary systems was elaborated by which the calculation of the ternary constants of the quaternary Margules equations of three indices can be carried out without performing any ternary equilibrium measurement.

The new calculation method considerably shortens the experimental work, and at the same time, by considering the ternary constants in a concentration range being the most suitable, with a view to the quaternary equilibrium, it makes the satisfactorily correct calculation of the equilibrium possible in the quaternary system. This method is usable in every quaternary system in which the Margules equations of three indices yield a satisfactory result.

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