

THE FUNDAMENTAL EQUATION OF DISTILLATION

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ABSTRACT

The different methods of multicomponent distillation of ideal mixtures like simple distillation, reversible distillation or distillation in plate- or packed-columns including the effect of mass transfer may be described by a set of the same fundamental equation. The fundamental equation contains the highest boiling, the lowest boiling and one intermediate boiling component and has the same structure but differently defined concentrations and coefficients depending on the method of distillation. Since even real mixtures with azeotropes may be converted to an ideal system, also their performance may be predicted at least qualitatively by the fundamental equation of distillation.

INTRODUCTION

The calculation of the distillation of a real multicomponent mixture is nowadays carried out by numerical computer methods. For complex mixtures this often requires to study a large number of cases before a technically and economically feasible solution is found. For ideal mixtures, however, there is a complete theory which allows to answer any question like

- the possible product compositions
- the minimum reflux ratio
- the concentration profile for any reflux ratio
- the effect on mass transfer on the the concentration profile
- the minimal energy consumption
- the concentration profiles at reversible thermodynamic conditions

and so on for plate- as well as packed-distillation columns in the form of closed mathematical solutions [1,2,3]. The following will show that the theory of the distillation of ideal mixtures may be reduced to one fundamental equation and that the results and insights from the theory also apply at least qualitatively to real mixtures. The understanding of the distillation of a real multicomponent mixture of any complexity is thus strongly simplified.

THE THEORY OF DISTILLATION OF IDEAL MIXTURES

Ideal mixtures are defined as mixtures which thermodynamic vapour-liquid-equilibrium follows the simple relation

$$y_i^* = \frac{\alpha_i \cdot x_i}{E} \quad (1)$$

where

$$E = \sum_1^k \alpha_i \cdot x_i \quad (2)$$

and the relative volatilities

$$\alpha_i = p_i^0 / p_r^0 \quad (3)$$

are the vapour pressure p_i^0 of the component i related to the vapour pressure p_r^0 of a reference component r . In the context of this paper we assume that the relative volatilities may be regarded as constant.

We shall limit our development of the fundamental equation to the case of total reflux as the general case of any reflux may be transformed to this case by a linear transformation as shown e.g. in [1]. In addition, it is assumed that the mass transfer resistance is located completely in the vapour phase.

For constant flowrates of the vapour and the liquid at total reflux the mole fraction of the vapour y_i and the mole fraction of the liquid x_i in any cross section of the distillation column are equal, i.e.

$$y_i = x_i \quad (4)$$

The mass transfer rate between the two phases is taken as

$$n_i = \rho \cdot \beta \cdot (y_i^* - x_i) \quad (5)$$

assuming that the mass transfer coefficient β is constant and the same for all components.

From a mass balance for a differential column section follows

$$G \cdot dx_i = \rho \cdot \beta \cdot (y_i^* - x_i) \cdot dA = \rho \cdot \beta \cdot (y_i^* - x_i) \cdot a \cdot F \cdot dh \quad \text{or} \quad (7)$$

$$dNTU = \frac{dx_i}{y_i^* - x_i} = \frac{\rho \cdot \beta \cdot a \cdot F}{G} \cdot dh \quad (8)$$

where NTU is the "Number of Transfer Units" with the solution

$$\begin{aligned} NTU &= \ln k_{ij} + (\alpha_i \cdot \ln x_j - \alpha_j \cdot \ln x_i) / (\alpha_i - \alpha_j) \\ &= \frac{\rho \cdot \beta \cdot a \cdot F}{G} \cdot H \end{aligned} \quad (9)$$

Since Eq. (9) may also be written with the components i and k , i.e.

$$\begin{aligned} NTU &= \ln k_{ik} + (\alpha_i \cdot \ln x_k - \alpha_k \cdot \ln x_i) / (\alpha_i - \alpha_k) \\ &= \frac{\rho \cdot \beta \cdot a \cdot F}{G} \cdot H \end{aligned} \quad (10)$$

and as the left hand side of the Eqs. (9) and (10) are equal it follows

$$\ln \frac{x_i}{x_j} = \ln k_i + e_i \cdot \ln \frac{x_k}{x_j} \quad (11)$$

where
$$e_i = \frac{\alpha_i - \alpha_j}{\alpha_i - \alpha_k} \quad (12)$$

The constant k_i in Eq. (11) is given by the starting composition of the distillation line as a solution of Eq. (11) is called. It is interesting to note that the variables in Eq. (11) are the mole ratios rather than the mole fractions.

Solutions of Eq. (11) are given in Fig. 1 for a ternary system with $\alpha_1 = 1$, $\alpha_2 = 3$ and $\alpha_3 = 4$ which closely resembles the system Nitrogen (1) - Argon (2) - Oxygen (3).

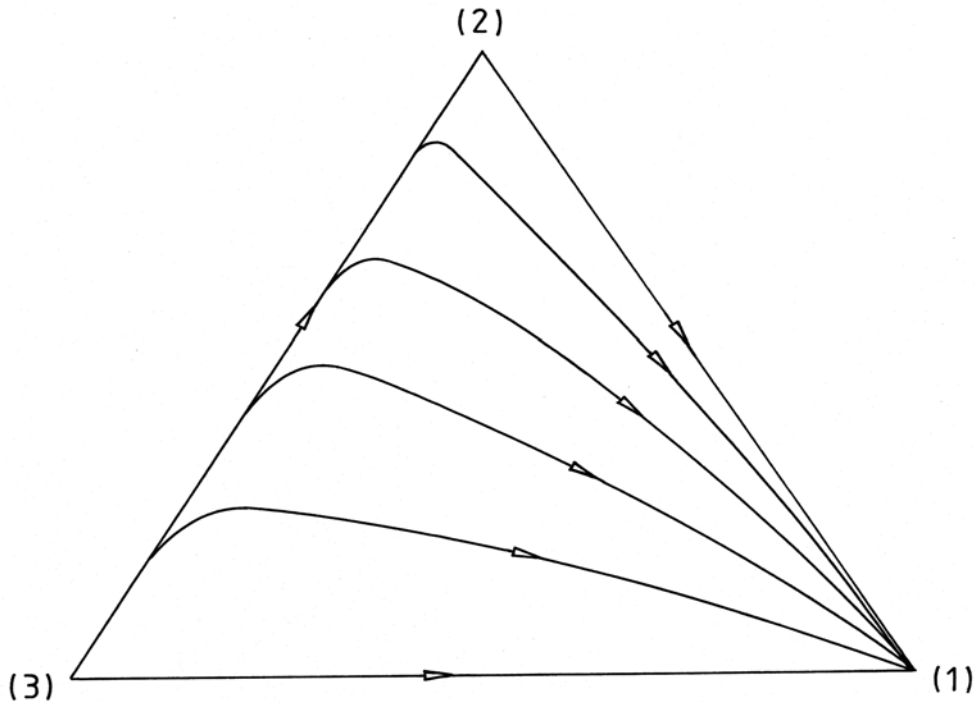


Fig. 1: Distillation lines of an ideal ternary mixture ($\alpha_1 = 1, \alpha_2 = 3, \alpha_3 = 4$)

Eq. (11) can also be written in the form

$$(\varepsilon_i - \varepsilon_j) \cdot \Phi_k + (\varepsilon_j - \varepsilon_k) \cdot \Phi_i + (\varepsilon_k - \varepsilon_i) \cdot \Phi_j = 0 \quad (13)$$

which we call the **Fundamental Equation of Distillation** as the different methods of distillation like reversible distillation, simple distillation, distillation with theoretical trays and so on can be expressed in this form [4,5].

The simple distillation of a ternary mixture e.g. as described by the well known Rayleigh differential equation [6]

$$\frac{dx_i}{dx_j} = \frac{y_i^* - x_i}{y_j^* - x_j} \quad (14)$$

yields by integration Eq. (11) and thus Eq. (13).

The variables Φ_i and the coefficients ε_i of the fundamental equation of distillation (13) depend on the method of distillation and are defined in Table 1. For the case of subtotal reflux an additional linear transformation of the mole fractions is required to obtain a solution in the form of Eq. (13) or Table 1 [1].

Table 1: Variables to be used in Eq. (13)

	ε_i	ε_j	ε_k	Φ_i	Φ_j	Φ_k
Reversible distillation	α_i	α_j	α_k	$x_i/x_{i,0}$	$x_j/x_{j,0}$	$x_k/x_{k,0}$
Simple batch distillation	α_i	α_j	α_k	$\ln(x_i/x_{i,0})$	$\ln(x_j/x_{j,0})$	$\ln(x_k/x_{k,0})$
Distillation with packings						
▪ Resistance on the gas side	α_i	α_j	α_k	$\ln(x_i/x_{i,0})$	$\ln(x_j/x_{j,0})$	$\ln(x_k/x_{k,0})$
▪ Resistance on the liquid side	$1/\alpha_i$	$1/\alpha_j$	$1/\alpha_k$	$\ln(x_i/x_{i,0})$	$\ln(x_j/x_{j,0})$	$\ln(x_k/x_{k,0})$
Distillation with theoretical trays	$\ln\alpha_i$	$\ln\alpha_j$	$\ln\alpha_k$	$\ln(x_i/x_{i,0})$	$\ln(x_j/x_{j,0})$	$\ln(x_k/x_{k,0})$

As the Eqs. (11,12) may be written for any three components of a multicomponent system it follows that for a system of k components there are $k-2$ independent sets of ternary systems. By taking $j = 1$ as the lowest and k as the highest boiling component and i as one of the intermediate boiling components of the multicomponent system, it follows that the multicomponent system may be regarded as a superposition of $k-2$ independent ternary systems. The behaviour of a multicomponent ideal system is thus completely described by the behaviour of the related ternary systems.

The independency of the ternary systems is due to fact that the variables in Eq. (11) are the mole ratios rather than the mole fractions. They are coupled, however, by the mass balance in the form of

$$\frac{1}{x_1} = \sum_1^k \frac{x_i}{x_1} \quad (15)$$

which serves to express the distillation line in form of the mole fractions or the mole fractions as a function of the Number of Transfer Units or the column height in combination with Eq. (9).

For a quaternary mixture e.g there are two independent Eqs. (11)

$$\begin{aligned} \ln \frac{x_2}{x_1} &= \ln k_2 + e_2 \cdot \ln \frac{x_4}{x_1} \quad \text{with } e_2 = \frac{\alpha_1 - \alpha_2}{\alpha_1 - \alpha_4} \quad \text{and} \\ \ln \frac{x_3}{x_1} &= \ln k_3 + e_3 \cdot \ln \frac{x_4}{x_1} \quad \text{with } e_3 = \frac{\alpha_1 - \alpha_3}{\alpha_1 - \alpha_4}. \end{aligned} \quad (16)$$

Inserting related triplets x_2/x_1 , x_3/x_1 and x_4/x_1 from Eq. (16) into Eq. (15) allows to calculate the distillation lines of the quaternary system as given in Fig. 2 in the form of a tetrahedron. For a more detailed analysis see [1,3,4]

DISTILLATION OF REAL MIXTURES

Real systems differ from ideal systems mainly by the more complex equilibrium relation requiring most importantly the introduction of the activity coefficient γ_i into the relative volatilities, i.e. Eq. (3) extends to

$$\alpha_i = p_i^0 \cdot \gamma_i / p_r^0 \cdot \gamma_r. \quad (17)$$

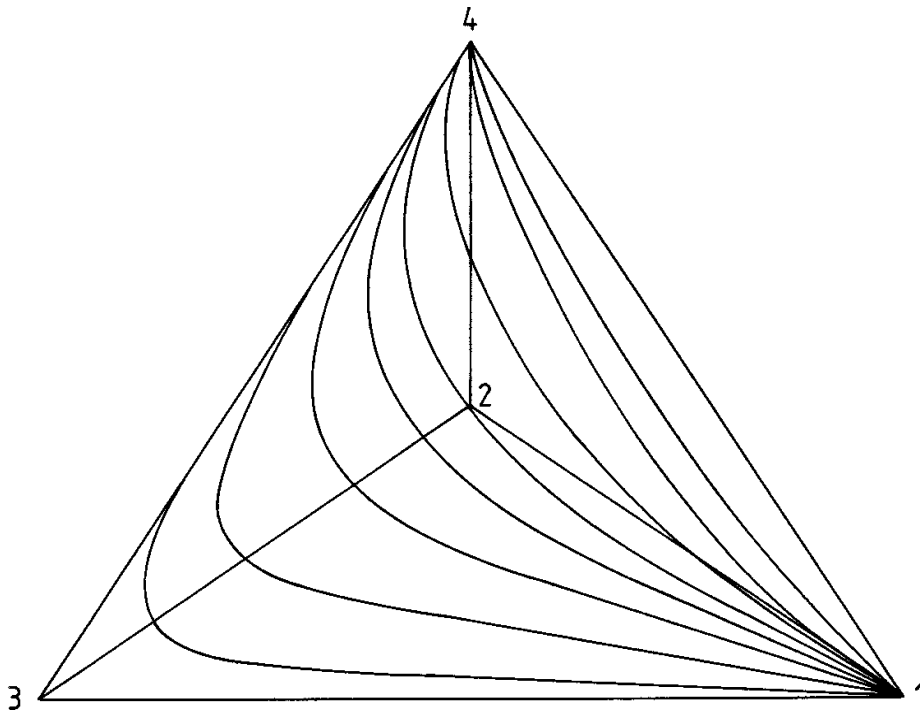


Fig. 2: Distillation lines of an ideal quaternary system ($\alpha_1 = 4, \alpha_2 = 3, \alpha_3 = 2, \alpha_4 = 1$)

As long as the real mixture has no azeotrope, i.e. as long as all relative volatilities α_i of a real mixture as defined by Eq. (17) are different from one within the composition range (except for α_r), Eq. (11) may be used to qualitatively calculate the distillation lines of any real mixture. The agreement will be the better, the less the activity coefficients deviate from one.

If, however, the real system exhibits one or more azeotropes and as azeotropes behave like pure components with respect to distillation [7], a real mixture with k components and a azeotropes may be regarded as a „degenerated“ ideal system with $(k+a)$ pseudo components.

Fig. 3 for example shows distillation lines of the ternary system Acetone-Chloroform-Acetonitrile. Due to the azeotrope of the binary system Acetone-Chloroform, which behaves as an intermediate boiling “pseudo component“ with respect to distillation, this real ternary system may be considered to be a „degenerated“ quaternary system. It is furthermore unique in the sense that the distillation takes place only on two lateral faces of the tetrahedron representing the degenerated quaternary system, i.e. within the face Acetone-binary Azeotrope-Acetonitrile and the face Chloroform-binary Azeotrope-Acetonitrile of Fig. 3 and not inside the tetrahedron Acetone-Chloroform-binary Azeotrope-Acetonitrile.

The fact that the azeotrope splits the ensemble of real distillation lines in two independent fields of distillation lines allows to approximate these two fields of real distillation lines by fields of ideal distillation lines. By fitting the two fields of ideal distillation lines to the Gibbs diagram of Fig. 3 an excellent agreement is obtained

between the real and the approximated distillation lines as shown in Fig. 4. The $\gamma_i \cdot p_i^0$ data used in calculating the ideal distillation lines are summarized in Table 2.

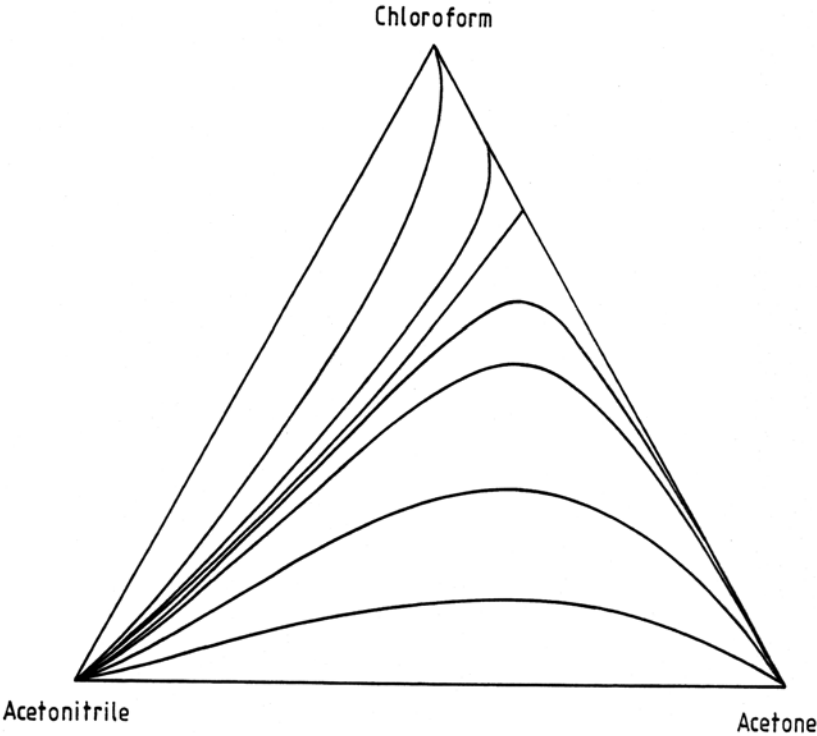


Fig. 3: Distillation lines of the ternary system Acetone-Chloroform-Acetonitrile

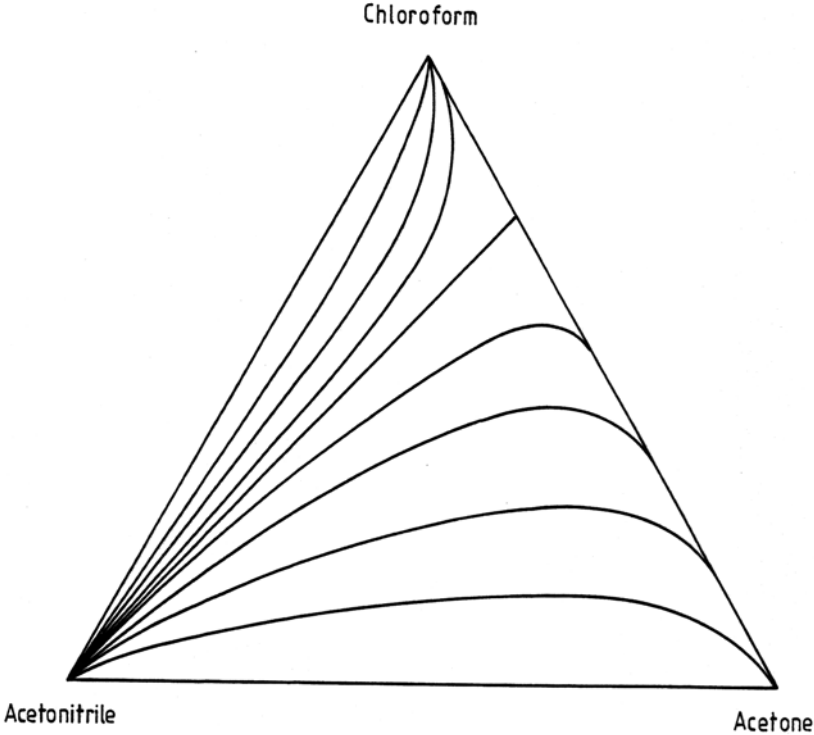


Fig. 4: Ideal Distillation lines of the system Acetone-Chloroform-Acetonitrile

Table 2: Products of activity coefficient times vapour pressure of the ternary mixture: Acetone-Chloroform-Acetonitrile

Component i	Acetone	Chloroform (2)	Azeotrope	Acetonitrile (4)
$\gamma_i \cdot p_i^0$ in bar	1.831	1.536	1.354	0.805

An example of a rather complex system is the ternary system Acetone-Chloroform-Methanol as given in Fig. 5. With three binary azeotropes and one ternary azeotrope this system may be considered as a seven component system with three quaternary systems consisting of:

- the binary Azeotrope (7), the Acetone (1), the ternary Azeotrope (5) and the binary Azeotrope (4),
- the binary Azeotrope (6), the ternary Azeotrope (5), the Chloroform (2) and the binary Azeotrope (4) and
- the binary Azeotrope (7), the binary Azeotrope (6), the ternary Azeotrope (5) and the Methanol (3).

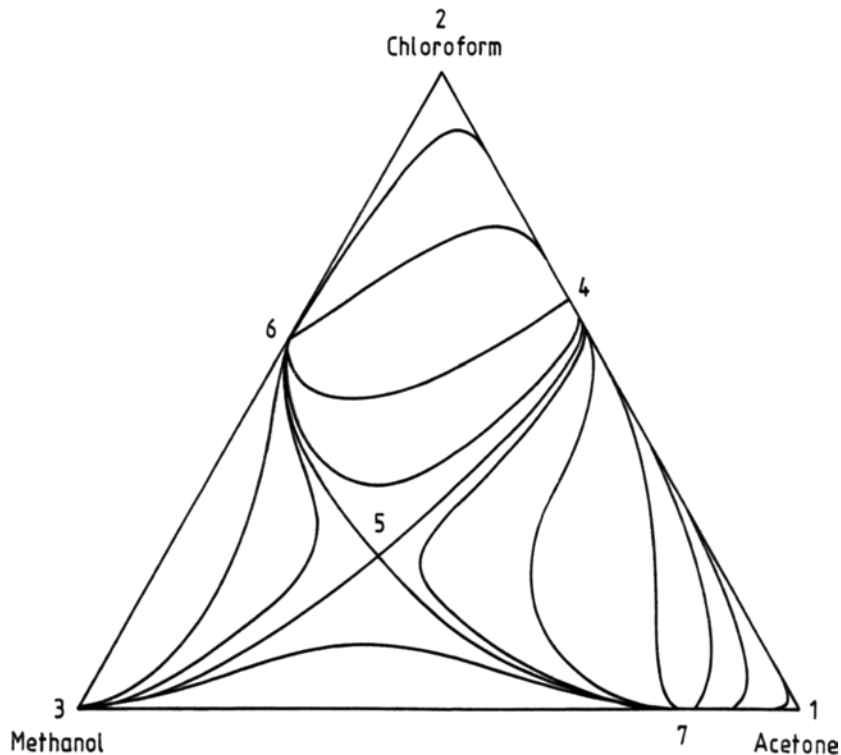


Fig. 5: Distillation lines of the ternary system Acetone-Chloroform-Methanol

Again, taking the product $\gamma_i \cdot p_i^0$ of the pure components and the azeotropes in the respective subsystems as constant (see Table 3), the real distillation lines of these subsystems may be approximated by ideal distillation lines as shown in Fig. 6.

The difference between the real and the ideal distillation lines is larger than in Fig. 5, however, because of the rather complex thermodynamic equilibrium of this system. In this seven-component system, the quaternary subsystem 7-6-5-3 resembles the

Table 3: Products of activity coefficient times vapour pressure of the ternary mixture: Acetone-Chloroform-Methanol

Component i	Azeotrope (7)	Azeotrope (6)	Acetone (1)	Azeotrope (5)
$\gamma_i \cdot p_i^0$ in bar	1.165	1.155	1.140	1.042
Component i	Chloroform (2)	Azeotrope (4)	Methanol (3)	
$\gamma_i \cdot p_i^0$ in bar	0.964	0.839	0.834	

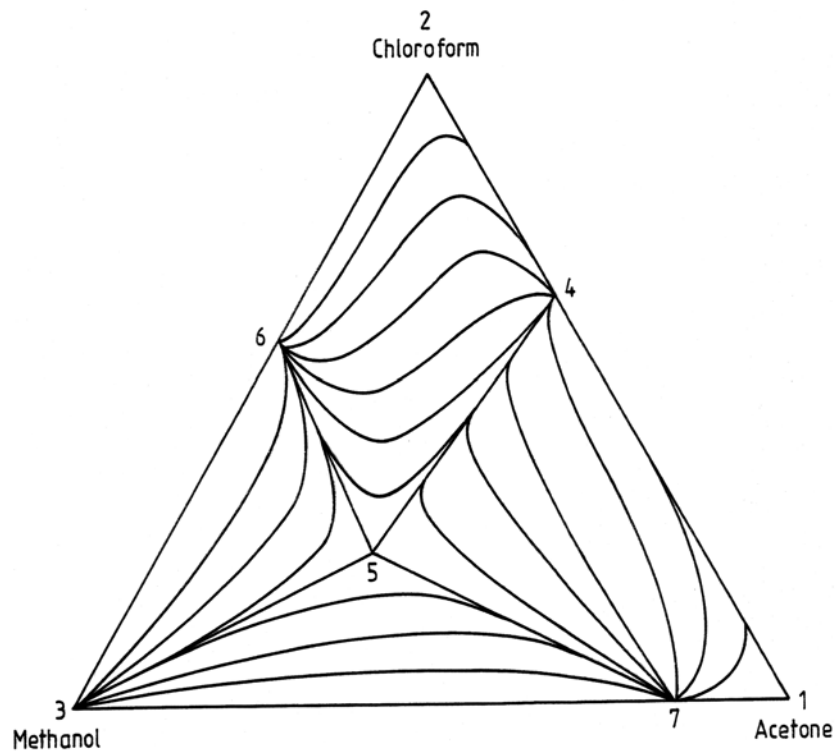


Fig. 6: Ideal Distillation lines of the system Acetone-Chloroform-Methanol

system in Fig. 5, i.e. the distillation takes place within the two outer lateral faces 7-5-3 and 6-5-3 of the related ideal quaternary system. The other two quaternary subsystems are simulated by calculating first the distillation lines of the related ideal quaternary and second by turning the tetrahedron in such a way that the projected corners of the tetrahedron coincide with the composition of the related pure components and azeotropes in the Gibbs triangle of Fig. 5. A more detailed description of this procedure is given elsewhere [4,5].

Following the above described method any real ternary or multicomponent system may be approximated by ideal systems or subsystems. Doherty et al. [8] published a

rather complete list of possible ensembles of distillation lines of real ternary systems and all of these may be approximated by ideal systems.

CONCLUSIONS

It is shown that the distillation of ideal multicomponent mixtures may be reduced to a superposition of the related ternary mixtures and that the different methods of distillation of a ternary mixture may be described by one single fundamental equation.

Taking into account that an azeotrope behaves like a pure component in distillation, the behaviour of any complex real mixture may be approximated by the behaviour of appropriately chosen ideal mixtures.

The large body of knowledge developed from the theory of multicomponent distillation may, therefore, also be applied to better understand the distillation of real multicomponent systems.

ACKNOWLEDGEMENT

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NOMENCLATURE

A	interfacial area
a	volumetric interfacial area
e	defined by Eq. (12)
E	defined by Eq. (2)
F	cross sectional area
G	vapour flowrate
H	total height
h	height
k	constant
L	liquid flowrate
NTU	Number of Transfer Units
n	mass transfer rate
p^0	vapour pressure
x	liquid mole fraction
y	vapour mole fraction

Greek symbols

α	relative volatility
β	mass transfer coefficient
γ	activity coefficient
ε	relative volatility function defined in Table 1
ρ	vapour density
Σ	sum
Φ	concentration function defined in Table 1

Indices

1	lowest boiling component
i	component i or medium boiling component
j	component j
k	component k or highest boiling component
o	initial mole fraction
*	equilibrium state

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