RESTRICTIONS ON PATTERNS OF RESIDUE CURVES AROUND HETEROGENEOUS AZEOTROPES

HISAYOSHI MATSUYAMA

Department of Chemical Engineering, Kyushu University,
Fukuoka 812

The definition of the residue curve is extended to heterogeneous systems by use of the mean liquid composition to analyze characteristics of heterogeneous azeotropes. The analysis of patterns of residue curves around heterogeneous azeotropes shows that the number of possible types for n -component heterogeneous azeotropes is given by $(n-m+1)$, where m is the number of coexisting liquid phases, and that when $n=m$, in particular, the only possible type is a minimum azeotrope.

Introduction

Heterogeneous azeotropes often play important roles in azeotropic distillation. The first aim in the selection of the entrainer is to find a material which forms heterogeneous azeotropes with one or more of the key components in the given mixture. The selection can be systematized to a certain degree by the classification of vapor-liquid equilibrium relationships of heterogeneous systems.

Homogeneous ternary systems have been classified by use of the following conditions¹⁾:

Cond (1) $2S_1 + 4S_2 + 8S_3 = 2$

Cond (2) *The residue curve has to extend to the point at higher boiling temperature*

where S_1 is the sum of indices of pure materials and S_2 and S_3 , respectively, denote the sums of indices of binary and ternary azeotropes. The extension of Cond (1) to n -component systems is given as follows²⁾:

Cond (1*) $\sum_{r=1}^n 2^r S_r = 1 + (-1)^{n-1}$

where S_r ($r \geq 2$) denotes the sum of indices of r -component azeotropes. Indices of pure materials and azeotropes are determined by the patterns of residue curves around them.

These conditions, however, cannot be directly applied to heterogeneous systems because of the existence of multiple liquid phases. This paper will show that the conditions can be extended to heterogeneous systems by defining the residue curve as the trajectory of the mean liquid composition in differential distillation. By use of the extended concept of the residue curve, restrictions for types of heterogeneous azeotropes will be discussed and the relation $\nu = n - m + 1$ will be obtained where n , m and ν , respec-

tively, denote the number of components, that of coexisting liquid phases and that of possible types of heterogeneous azeotropes.

1. Extension of the Definition of the Residue Curve to Heterogeneous Systems

Consider the differential distillation of m -phase liquid with n -components. Assume that there are $L^{(k)}$ ($k=1, 2, \dots, m$) moles of the k -th phase liquid in the still of composition $x_i^{(k)}$ ($i=1, 2, \dots, n$) and that an amount dL moles of composition y_i ($i=1, 2, \dots, n$) is vaporized in equilibrium with the liquid phases. The residual k -th phase liquid, $L^{(k)} - dL^{(k)}$ moles, will have the composition $x_i^{(k)} + dx_i^{(k)}$. A material balance for the i -th component is given as

$$\sum_{k=1}^m L^{(k)} x_i^{(k)} = y_i dL + \sum_{k=1}^m (L^{(k)} - dL^{(k)}) (x_i^{(k)} + dx_i^{(k)}) \quad (1)$$

where

$$\sum_{k=1}^m L^{(k)} = L \text{ and } \sum_{k=1}^m dL^{(k)} = dL.$$

Ignoring the second-order differential, we obtain

$$\sum_{k=1}^m (L^{(k)} dx_i^{(k)} - x_i^{(k)} dL^{(k)}) + y_i dL = 0 \quad (2)$$

where y_i is given as

$$y_i = p_i^\circ \gamma_i^{(k)} x_i^{(k)} / P, \quad (k=1, 2, \dots, m) \quad (3)$$

in the case of low pressure and ideal gas vapor phase.

Define the mean liquid composition x_i ($i=1, 2, \dots, n$) as follows:

$$x_i = \sum_{k=1}^m L^{(k)} x_i^{(k)} / L \quad (4)$$

The mean liquid composition can be uniquely determined by $L^{(k)}$ and $x_i^{(k)}$. Conversely, $L^{(k)}$ and $x_i^{(k)}$ can be uniquely determined by L and x_i because the liquid phases are in equilibrium with each other.

The differential of x_i can be obtained as

$$dx_i = \sum_{k=1}^m (L^{(k)} dx_i^{(k)} - x_i^{(k)} dL^{(k)}) / L + x_i dL / L \quad (5)$$

Therefore we obtain

$$\sum_{k=1}^m (L^{(k)} dx_i^{(k)} - x_i^{(k)} dL^{(k)}) = L dx_i - x_i dL \quad (6)$$

Substitution of Eq. (6) into Eq. (2) gives

$$L(dx_i/dL) = x_i - y_i \quad (7)$$

Equation (7) can be rearranged by setting $dt = dL/L$ as follows:

$$dx_i/dt = x_i - y_i \quad (8)$$

Since the liquid phases are in equilibrium with each other, the following relations can be obtained.

$$\gamma_i^{(1)} x_i^{(1)} = \gamma_i^{(2)} x_i^{(2)} = \dots = \gamma_i^{(m)} x_i^{(m)} \quad (i=1, 2, \dots, n) \quad (9)$$

Hence, the mean activity coefficient of liquid phase, γ_i , can be defined as

$$\gamma_i = \gamma_i^{(k)} x_i^{(k)} / x_i \quad (i=1, 2, \dots, n; k=1, 2, \dots, m) \quad (10)$$

By use of γ_i , the vapor composition y_i can be rewritten as

$$y_i = p_i^\circ \gamma_i x_i / P \quad (i=1, 2, \dots, n) \quad (11)$$

Thus Eq. (8) can be obtained as

$$dx_i/dt = x_i(1 - p_i^\circ \gamma_i / P) \quad (i=1, 2, \dots, n) \quad (12)$$

The concept of the residue curve can be extended to heterogeneous systems by defining the residue curve as an integral curve of Eq. (12).

Pure compositions are singular points of Eq. (12) because the right-hand sides of Eq. (12) vanish simultaneously at pure compositions. That azeotropic compositions are also singular points of Eq. (12) can be proved as follows:

During the azeotropic transformation, the vapor and liquid compositions are held constant, that is, $dx_i^{(k)} = 0$ and $dL^{(k)} / dL = L^{(k)} / L$. Hence the mean liquid composition, x_i , is also held constant and coincides with the vapor composition y_i . Thus the right-hand sides of Eq. (12) vanish simultaneously at azeotropic compositions.

Equation (12) for the n -component system is a set of n ordinary differential equations. However, one of them is not independent because $\sum_{i=1}^n x_i = 1$. Hence residue curves are drawn on the $(n-1)$ -dimensional simplex. From now on, we call this simplex the "composition simplex".

From the definition of the mean liquid composition, *Cond* (2) obviously holds for heterogeneous systems. It can be concluded that *Cond* (I^*) also holds for heterogeneous systems because the extended definition of the residue curve makes it possible to obtain indices of heterogeneous azeotropes by use of the same procedure used for homogeneous azeotropes²⁾.

2. Analysis of Patterns of Residue Curves around Azeotropes

Let c_i ($i=1, 2, \dots, n$) be the mean liquid composition of an n -component azeotrope in the n -component system and δx_i ($i=1, 2, \dots, n$) be the small deviation from the azeotropic composition. Using Taylor expansion and ignoring the second-order differential, we can obtain a set of linear ordinary differential equations for δx_i

$$\frac{d(\delta x_i)}{dt} = \sum_{j=1}^n G_{ij} \delta x_j \quad (i=1, 2, \dots, n) \quad (13)$$

where G_{ij} is represented as

$$G_{ij} = -c_i \frac{\partial \ln \gamma_i}{\partial x_j} \quad (i=1, 2, \dots, n; j=1, 2, \dots, n) \quad (14)$$

by use of the condition of azeotropy:

$$p_1^\circ \gamma_1 = p_2^\circ \gamma_2 = \dots = p_n^\circ \gamma_n = P \quad (15)$$

(See Appendix 1)

The pattern of residue curves around the azeotrope is determined by the characteristics of roots of

$$|\lambda I - G| = 0 \quad (16)$$

where I is the n -dimensional identity matrix and

$$G = \begin{pmatrix} G_{11} & G_{12} & \dots & G_{1n} \\ G_{21} & G_{22} & & \vdots \\ \vdots & & \ddots & \vdots \\ G_{n1} & \dots & \dots & G_{nn} \end{pmatrix} \quad (17)$$

The following theorem can be obtained from thermodynamic characteristics of the matrix G .

$$\text{Theorem: All roots of } |\lambda I - G| = 0 \quad (16)$$

are real and one of them is necessarily $\lambda=0$ without respect to whether the azeotrope is heterogeneous or homogeneous.

The proof will be given in Appendix 2.

Then the type of azeotrope is determined by the signs of nonzero roots of Eq. (16). If all of nonzero roots are positive, the azeotrope is minimum-boiling, and if all of them are negative the azeotrope is maximum-boiling. Between these two extremes, there are $(n-2)$ types of saddle-point azeotropes. For instance, there is only one type of saddle-point azeotropes in ternary systems and there are two types of saddle-point azeotropes (positive saddle-point and negative saddle-point) in quaternary systems.

Heterogeneous azeotropes, however, cannot take all of these types because of the restriction caused by the immiscibility. The degree of restriction is related to the difference between the number of components and the number of coexisting liquid phases. If an n -component azeotrope exists in the region of m liquid phases, $(n-m+1)$ types are possible for the azeotrope.

A detailed discussion will be given in the next section.

3. Restrictions on Types of Heterogeneous Azeotropes

Let c_i ($i=1, 2, \dots, n$) be the mean liquid composition of an n -component azeotrope in the region of m liquid phases and $c_i^{(k)}$ ($i=1, 2, \dots, n$; $k=1, 2, \dots, m$) be the composition of the k -th liquid phase corresponding to c_i . Then c_i lies on an $(m-1)$ -dimensional simplex composed of the apices $c_i^{(k)}$ ($i=1, 2, \dots, n$; $k=1, 2, \dots, m$). The mean liquid composition on the simplex is given by

$$x_i = \sum_{k=1}^{m-1} \theta^{(k)} c_i^{(k)} + (1 - \sum_{k=1}^{m-1} \theta^{(k)}) c_i^{(m)} \quad (i=1, 2, \dots, n) \quad (18)$$

where $\theta^{(k)} \geq 0$ for all k and $\sum_{k=1}^{m-1} \theta^{(k)} \leq 1$. Since $p_i^\circ \gamma_i x_i / P$ ($i=1, 2, \dots, n$) is constant on the simplex, the following relation can be obtained:

$$\frac{\partial}{\partial \theta^{(k)}} \left(\frac{p_i^\circ \gamma_i x_i}{P} \right) = \sum_{j=1}^n (c_j^{(k)} - c_j^{(m)}) \frac{\partial}{\partial x_j} \left(\frac{p_i^\circ \gamma_i x_i}{P} \right) = 0 \quad (i=1, 2, \dots, n; k=1, 2, \dots, m-1) \quad (19)$$

From this relation and Eq. (14), we have

$$G\mathbf{v}^{(k)} = \mathbf{v}^{(k)} \quad (k=1, 2, \dots, m-1) \quad (20)$$

where

$$\mathbf{v}^{(k)} = \begin{pmatrix} c_1^{(k)} - c_1^{(m)} \\ c_2^{(k)} - c_2^{(m)} \\ \vdots \\ c_n^{(k)} - c_n^{(m)} \end{pmatrix} \quad (k=1, 2, \dots, m-1) \quad (21)$$

Because $\mathbf{v}^{(1)}, \mathbf{v}^{(2)}, \dots, \mathbf{v}^{(m-1)}$ are independent nonzero vectors, Eq. (20) indicates that Eq. (16) has a root $\lambda=1$ of multiplicity $(m-1)$. Hence the number of remaining nonzero roots is equal to $(n-m)$. If $n=m$, the n -component azeotrope is necessarily minimum-boiling and if $n \neq m$, the azeotrope has $(n-m)$ possible types of saddle-point azeotropes, in addition to the minimum azeotrope, according to the number of negative roots among the remaining $(n-m)$ nonzero ones.

4. Illustrative Examples

4.1 Heterogeneous binary azeotropes

It is well known that all heterogeneous binary azeotropes are minimum-boiling because the immiscibility is the result of positive deviation from Raoult's law. This fact can also be derived from the analysis of the pattern of residue curves.

Because $n=m=2$, Eq. (16) for heterogeneous binary azeotropes is quadratic and has only one root $\lambda=1$, except for $\lambda=0$. Hence we can conclude that the azeotropes are minimum-boiling.

4.2 Heterogeneous ternary azeotropes

Heterogeneous ternary azeotropes can be divided

Fig. 1 Ternary azeotrope in the 2-phase region

into two groups, those in the regions of two liquid phases and those in the regions of three liquid phases.

Since Eq. (16) for ternary azeotropes is cubic, it has two roots other than $\lambda=0$. If all nonzero roots are positive, the azeotropes are minimum-boiling and if one of them is negative, they are saddle-point azeotropes.

1) Ternary azeotropes in 2-phase regions Let c_i ($i=1, 2, 3$) be the mean liquid composition of a ternary azeotrope in the region of two liquid phases and $c_i^{(1)}$ and $c_i^{(2)}$ ($i=1, 2, 3$), respectively, be the composition of the 1st and 2nd liquid phases corresponding to c_i . Then c_i has to lie on the tie-line connecting $c_i^{(1)}$ and $c_i^{(2)}$ (See Fig. 1). The mean liquid composition on the line is given by

$$x_i = \theta c_i^{(1)} + (1 - \theta) c_i^{(2)}, \quad (i=1, 2, 3) \quad (22)$$

Since $p_i^\circ \gamma_i x_i / P$ ($i=1, 2, 3$) is constant on the line, we obtain

$$\frac{d}{d\theta} \left(\frac{p_i^\circ \gamma_i x_i}{P} \right) = \sum_{j=1}^3 (c_j^{(1)} - c_j^{(2)}) \frac{\partial}{\partial x_j} \left(\frac{p_i^\circ \gamma_i x_i}{P} \right) = 0 \quad (i=1, 2, 3) \quad (23)$$

From Eqs. (14) and (23), the following relations are derived:

$$(I - G)\mathbf{v} = 0 \quad (24)$$

where I is the three-dimensional identity matrix and

$$\mathbf{v} = \begin{pmatrix} c_1^{(1)} - c_1^{(2)} \\ c_2^{(1)} - c_2^{(2)} \\ c_3^{(1)} - c_3^{(2)} \end{pmatrix} \quad (25)$$

Since $\mathbf{v}$ is a nonzero vector, Eq. (24) is equivalent to

$$|I - G| = 0 \quad (26)$$

This relation indicates that Eq. (16) has a root $\lambda=1$ and that the ternary azeotrope in the 2-phase region can be a minimum azeotrope or a saddle-point azeotrope according to the sign of the remaining one nonzero root. Possible patterns around the azeotrope are shown in Fig. 2.

2) Ternary azeotropes in 3-phase regions Let c_i ($i=1, 2, 3$) be the mean liquid composition of a ternary azeotrope in the three-phase region, and $c_i^{(1)}$, $c_i^{(2)}$ and $c_i^{(3)}$ ($i=1, 2, 3$), respectively, be the composi-

(a) minimum azeotrope (b) saddle-point azeotrope

Fig. 2 Possible patterns around the ternary azeotrope in the 2-phase region

Fig. 3 Ternary azeotrope in the 3-phase region

tion of the 1st, 2nd and 3rd liquid phases corresponding to c_i . Then c_i has to lie on the triangle composed of the three points $c_i^{(1)}$, $c_i^{(2)}$ and $c_i^{(3)}$ (See Fig. 3). The mean liquid composition on the triangle can be given as

$$x_i = \theta^{(1)} c_i^{(1)} + \theta^{(2)} c_i^{(2)} + (1 - \theta^{(1)} - \theta^{(2)}) c_i^{(3)}, \quad (i=1, 2, 3) \quad (27)$$

where $\theta^{(1)} \geq 0$, $\theta^{(2)} \geq 0$ and $\theta^{(1)} + \theta^{(2)} \leq 1$.

By use of Eq. (14) and the condition that $p_i^\circ \gamma_i x_i / P$ is constant on the triangle, we have

$$G \mathbf{v}^{(k)} = \mathbf{v}^{(k)} \quad (k=1, 2) \quad (28)$$

where $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(2)}$ are independent nonzero vectors defined by Eq. (21).

Equation (28) shows that $\lambda=1$ is a double eigenvalue of the matrix G and that it is a double root of Eq. (16). Therefore all nonzero roots of Eq. (16) become positive and this proves that the ternary azeotrope in the 3-phase region is minimum-boiling.

Conclusions

The definition of the residue curve has been extended to describe topological and thermodynamic characteristics of vapor-liquid equilibrium relationships in heterogeneous systems. The extended residue curve makes it possible to classify heterogeneous systems by use of $Cond(I^*)$ and $Cond(2)$. This classification of heterogeneous systems will be helpful in the selection of entrainers for azeotropic distillation processes.

The analysis of the pattern of residue curves has

shown that the possible types of heterogeneous azeotropes are strongly restricted because of immiscibility. An n -component azeotrope in a region of m liquid phases has only $(n-m+1)$ possible types while n -component homogeneous azeotropes have n possible types. When $n=m$, in particular, the azeotrope has only one possible type, a minimum azeotrope.

Appendix 1. Derivation of Eq. (14)

From Eq. (12), G_{ij} is given as

$$G_{ij} = \left[\frac{\partial}{\partial x_j} \{ x_i (1 - p_i^\circ \gamma_i / P) \} \right]_{x_1=c_1, \dots, x_n=c_n} \quad (A-1)$$

Under isothermal conditions, Eq. (A-1) becomes

$$G_{ii} = 1 - p_i^\circ \gamma_i / P - c_i p_i^\circ \gamma_i \left\{ \frac{\partial \ln \gamma_i}{\partial x_i} / P + \left(\frac{\partial \ln \gamma_i}{\partial P} - 1 \right) \frac{\partial P}{\partial x_i} / P^2 \right\} \quad (A-2)$$

$$G_{ij} = -c_i p_i^\circ \gamma_i \left\{ \frac{\partial \ln \gamma_i}{\partial x_j} / P + \left(\frac{\partial \ln \gamma_i}{\partial P} - 1 \right) \frac{\partial P}{\partial x_j} / P^2 \right\} \quad (i \neq j) \quad (A-3)$$

By use of Eq. (15) and $\partial P / \partial x_i = 0$ ($i=1, 2, \dots, n$), we obtain

$$G_{ij} = -c_i \partial \ln \gamma_i / \partial x_j \quad (i, j=1, 2, \dots, n) \quad (14)$$

Under isobaric conditions, Eq. (A-1) can be rewritten

$$G_{ii} = 1 - p_i^\circ \gamma_i / P - c_i p_i^\circ \gamma_i \left\{ \frac{\partial \ln \gamma_i}{\partial x_i} + \left(\frac{d \ln p_i^\circ}{dT} + \frac{\partial \ln \gamma_i}{\partial T} \right) \frac{\partial T}{\partial x_i} \right\} / P \quad (A-4)$$

$$G_{ij} = -c_i p_i^\circ \gamma_i \left\{ \frac{\partial \ln \gamma_i}{\partial x_j} + \left(\frac{d \ln p_i^\circ}{dT} + \frac{\partial \ln \gamma_i}{\partial T} \right) \frac{\partial T}{\partial x_j} \right\} / P \quad (i \neq j) \quad (A-5)$$

Substitution of Eq. (15) and $\partial T / \partial x_i = 0$ ($i=1, 2, \dots, n$) into Eqs. (A-4) and (A-5) gives

$$G_{ij} = -c_i \ln \gamma_i / \partial x_j \quad (i, j=1, 2, \dots, n) \quad (14)$$

Appendix 2. The Proof of Theorem

From the Gibbs-Duhem equation it can be proved that any one of the rows of G can be represented by the linear combination of the other $(n-1)$ rows. This is equivalent to $|G|=0$ and indicates that Eq. (16) has a root $\lambda=0$.

The fact that all of the roots of Eq. (16) are real can be proved as follows:

Let C , D and Γ be matrices defined by

$$C = \begin{pmatrix} c_1 & & 0 \\ & c_2 & \\ & & \ddots \\ 0 & & & c_n \end{pmatrix}, \quad D = \begin{pmatrix} \sqrt{c_1} & & 0 \\ & \sqrt{c_2} & \\ & & \ddots \\ 0 & & & \sqrt{c_n} \end{pmatrix}$$

$$\Gamma = \begin{pmatrix} -\partial \ln \gamma_1 / \partial x_1 & -\partial \ln \gamma_1 / \partial x_2 & \dots & -\partial \ln \gamma_1 / \partial x_n \\ -\partial \ln \gamma_2 / \partial x_1 & -\partial \ln \gamma_2 / \partial x_2 & & \vdots \\ \vdots & & & \vdots \\ -\partial \ln \gamma_n / \partial x_1 & \dots & \dots & -\partial \ln \gamma_n / \partial x_n \end{pmatrix}$$

then G can be written as

$$G = C \Gamma \quad (A-6)$$

Because $c_i \neq 0$ for all $i=1, 2, \dots, n$, the matrices C and D are non-singular and their inverse matrices can be given by

$$C^{-1} = \begin{pmatrix} 1/c_1 & & 0 \\ & 1/c_2 & \\ & & \ddots \\ 0 & & & 1/c_n \end{pmatrix}, \quad D^{-1} = \begin{pmatrix} 1/\sqrt{c_1} & & 0 \\ & 1/\sqrt{c_2} & \\ & & \ddots \\ 0 & & & 1/\sqrt{c_n} \end{pmatrix}$$

Then the matrix $\lambda I - G$ can be written as follows:

$$\lambda I - G = C[\lambda C^{-1} - I] = CD^{-1}[\lambda I - D\Gamma D]D^{-1} \quad (\text{A-7})$$

Hence the determinant $|\lambda I - G|$ can be given as

$$\begin{aligned} |\lambda I - G| &= |CD^{-1}[\lambda I - D\Gamma D]D^{-1}| \\ &= |C||D^{-1}|^2|\lambda I - D\Gamma D| \\ &= |\lambda I - D\Gamma D| \end{aligned} \quad (\text{A-8})$$

Therefore all the roots of Eq. (16) coincide with those of

$$|\lambda I - D\Gamma D| = 0 \quad (\text{A-9})$$

The matrix $D\Gamma D$ is symmetric because $\partial \ln \gamma_i / \partial x_j = \partial \ln \gamma_j / \partial x_i$ and D is symmetric. Then all of the roots of Eq. (A-9) are real since all of the eigenvalues of the real symmetric matrix are real.

Nomenclature

c_i	= mean liquid composition of a heterogeneous azeotrope	[—]
$c_i^{(k)}$	= liquid composition of the k -th phase corresponding to the heterogeneous azeotrope	[—]
G	= matrix defined by Eq. (17)	[—]
L	= total amount of liquid phases	[moles]
$L^{(k)}$	= amount of the k -th liquid phase	[moles]
m	= number of coexisting liquid phases	
n	= number of components	

P	= total pressure	[atm]
p_i°	= vapor pressure of the i -th component	[atm]
S_1	= sum of indices of pure materials	
S_r	= sum of indices of r -component azeotropes ($r \geq 2$)	
$\mathbf{v}$	= vector defined by Eq. (25)	
$\mathbf{v}^{(k)}$	= vector defined by Eq. (21)	
x_i	= mean liquid composition of the i -th component	[—]
$x_i^{(k)}$	= composition of the i -th component in the k -th liquid phase	[—]
y_i	= vapor composition of the i -th component	[—]
γ_i	= mean activity coefficient of the i -th component	[—]
$\gamma_i^{(k)}$	= activity coefficient of the i -th component in the k -th liquid phase	[—]
ν	= number of possible types of heterogeneous azeotropes	

Literature Cited

- 1) Matsuyama, H. and H. Nishimura: *J. Chem. Eng. Japan*, **10**, 181 (1977).
- 2) Matsuyama, H.: *ibid.*, **11**, 66 (1978).