

Reactive Distillation and Kinetic Azeotropy

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The general pattern of trajectories of equilibrium distillation with nonequilibrium reversible reaction in the liquid phase is discussed. In some cases there is a continuous line of singular points belonging to different ratios of the evaporation rate and the reaction rate. These points are the kinetic azeotropes. When this line has a common intersection point with the hypersurface of chemical equilibrium, then the evaporation ratio approaches zero at the intersection point and the equilibrium reactive azeotrope, described by Barbosa and Doherty, exists there. The continuation of the kinetic azeotropy line after crossing the equilibrium surface is not a set of singular points. The stationary point of reactive distillation can be controlled, along the line of kinetic azeotropy, by the evaporation ratio.

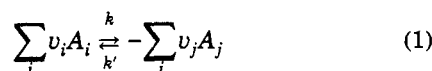
Introduction

The topological characterization of simple distillation processes accompanied by equilibrium reaction(s) has already been discussed by Barbosa and Doherty (1987, 1988ab). In the case of equilibrium reactions the chemical equilibrium is supposed to be reached instantaneously, and consequently the dimension of the state space is reduced by one. Barbosa and Doherty introduced the term *reactive azeotrope* to denote liquid compositions which remain unchanged in the course of reactive distillation with instantaneously reached chemical equilibrium.

If chemical equilibrium is not reached instantaneously, then the trajectories of liquid composition are not restricted to remain on a hypersurface, and therefore this case is more complex. In this study we are interested in the general shape of the composition trajectories, in whether stationary (singular) points exist in these systems, where these points are generally and particularly situated, and if there are reactive distillation regions separated by some separatrices. The practical merit of this information is the highlight on the spontaneous running of these processes, on their appropriate design procedures, and on the possible operation and control procedures applicable to them. We speak about azeotropy when a composition trajectory of a generalized (e.g., reactive) distillation process is a nonmoving point. In other words, any singular point in the composition domain is called an azeotrope, excluding the pure component vertices. In contrast to the *equilibrium* reactive azeotrope, the stationary points of simple distillation with nonequilibrium reaction kinetics will here be called *kinetic azeotropes*.

Kinetic Azeotropy

Consider a system of c chemical compounds, as components, characterized by some vapor-liquid equilibrium (VLE) behavior, and consider the following reversible chemical reaction in which they participate:



where the stoichiometric coefficients ν_i of components A_i are positive, while those with indices j are negative. Which side components are called reactants and which are called products is irrelevant in our discussion.

The reaction rate can generally be expressed as:

$$r = k \prod_i C_i^{\alpha_i} - k' \prod_j C_j^{\alpha_j} \quad (2)$$

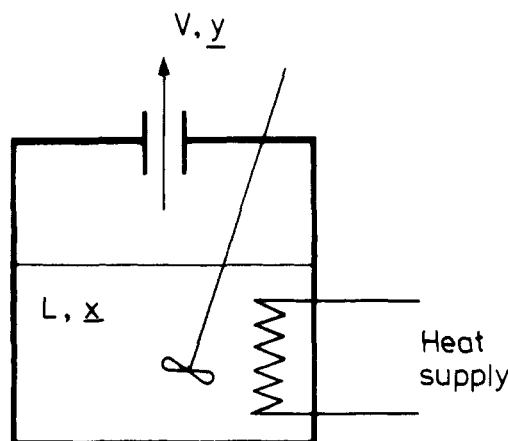


Figure 1. Simple reactive distillation.

where the C molar concentrations can be expressed as a function of the mole fractions and the molar density as

$$C_i = \rho x_i \quad (i = 1, 2, \dots, c) \quad (3)$$

Therefore

$$r = k \rho^p \epsilon \quad (4)$$

where

$$\epsilon = \prod_i x_i^{\alpha_i} - \frac{\rho^q}{K} \prod_j x_j^{\alpha_j} \quad (5)$$

$$p = \sum_i \alpha_i \quad (6)$$

$$q = -p + \sum_j \alpha_j \quad (7)$$

$$K = k/k' \quad (8)$$

The differential component balances around a perfectly mixed vessel shown in Figure 1 can be formulated as

$$d(Lx_i) = -Vy_i dt - v_i \frac{r}{\rho} L dt \quad (i = 1, 2, \dots, c) \quad (9)$$

or, in a more detailed form:

$$L dx_i + x_i dL = -Vy_i dt - v_i k L \rho^{p-1} \epsilon dt \quad (i = 1, 2, \dots, c) \quad (10)$$

Perfect mixing is plausible assumption in a boiling system.

Due to the following sum of rate constraints,

$$\sum_i x_i = 1 \quad (11)$$

$$\sum_i y_i = 1 \quad (12)$$

$$\sum_i dx_i = 0 \quad (13)$$

the summation over index i produces

$$dL = -V dt - v_T k L \rho^{p-1} \epsilon \quad (14)$$

where

$$v_T = \sum_i v_i + \sum_j v_j \quad (15)$$

This can be substituted to eq 10, yielding the differential equation of the reactive distillation:

$$\frac{dx_i}{dt} = \frac{V}{L}(x_i - y_i) - (v_i - x_i v_T) k \rho^{p-1} \epsilon \quad (i = 1, 2, \dots, c) \quad (16)$$

By introducing dimensionless time

$$d\xi = \frac{V}{L} dt \quad (17)$$

the final form is

$$\frac{dx_i}{d\xi} = (x_i - y_i) - (v_i - x_i v_T) \kappa \epsilon \quad (i = 1, 2, \dots, c) \quad (18)$$

where

$$\kappa \equiv \frac{kL}{V} \rho^{p-1} \quad (19)$$

(The number of independent equations is just $c - 1$ because of the sum of rate equations.) This differential equation is an autonomous one if the ratio simplex κ is fixed. κ is inversely proportional to the ratio of the vaporization rate and the reaction rate, and is characteristic to whether the process tends to behave as simple distillation or reaction or as a mixed process.

The singular points are defined by the derivatives in eq 18 being equal to zero:

$$(x_i - y_i) - (v_i - x_i v_T) \kappa \epsilon = 0 \quad (i = 1, 2, \dots, c) \quad (20)$$

Assuming $\epsilon \neq 0$ (i.e., the chemical equilibrium is not reached), the common $\kappa \epsilon$ term can be eliminated producing the following system of equations:

$$\frac{y_i - x_i}{v_i - x_i v_T} = \frac{y_j - x_j}{v_j - x_j v_T} \quad (i, j = 1, 2, \dots, c) \quad (21)$$

This is a system of $c - 2$ independent equations and assigns a continuous line in the $(c - 1)$ dimension Euclidean space of independent mole fractions. This line is called the *extended line of kinetic azeotropy*. This is a necessary condition for the singularity (all the singular points should lie in this line) but is not always sufficient. Another criterion is that κ be a physically interpretable value. The line section where this sufficient condition is satisfied is called the *line of kinetic azeotropy*.

At infinite evaporation rate, or at zero reaction rate, or at zero ratio of the evaporation/reaction rates, κ

approaches zero:

$$\lim_{V \rightarrow \infty} \kappa = 0 \quad (22)$$

and thus the equations expressing the reactionless case is yielded. On the other hand, when the evaporation rate or ratio is zero,

$$\lim_{V \rightarrow 0} \kappa = \infty \quad (23)$$

Naturally, in this case the coefficient of κ should be zero:

$$\epsilon = 0 \quad (24)$$

This is a single equation constraint, and therefore the points satisfying it form a $(c - 2)$ -dimension hypersurface in the $(c - 1)$ -dimension space of independent mole fractions. This hypersurface is called the *equilibrium surface*. This is the case of instantaneous chemical equilibrium, discussed by Barbosa and Doherty (1988b). If there is intersection between the equilibrium surface and the line of kinetic azeotropy, then the common point is, plainly, the *point of reactive azeotropy*. The existence of a reactive azeotrope is equivalent to the existence of such an intersection.

At other points of the extended line of kinetic azeotropy κ cannot be infinite, and ϵ is not zero. Therefore κ can be expressed as

$$\kappa = \frac{y_i - x_i}{(v_i - x_i v_T) \epsilon} \quad (25)$$

At the reactive azeotrope ϵ changes sign; therefore κ as a function along the extended line of kinetic azeotropy has an essential singularity in that point. At one side of the equilibrium surface κ is positive and therefore physically interpretable; at the other side it is negative. The line section falling to the positive side is the line of kinetic azeotropy. All its points are singular points belonging to continuously changing κ . The points of the line at the other side are *not* singular points.

In the particular cases we have studied all the points of kinetic azeotropy were stable nodes. However, a general rule for the sign of the eigenvalues of the Jacobians at these points has not yet been formulated.

If the kinetic azeotropes are stable nodes, then the stable endpoint of the reactive distillation depends on κ , which itself depends on V/L and k . Since k is determined by the boiling temperature, the endpoint and the course of the process can only be controlled by varying V/L .

We have not found reactive distillation regions or separatrices in systems where pure distillation azeotropes do not exist. Even in systems with simple distillation regions all the trajectories ran to the corresponding point of the line of kinetic azeotropy, independently of the starting point. This does not mean that separatrices do not exist; this is only a preliminary empirical result.

The trajectories in the systems of more than three components can only be imagined with great effort. However, the line of kinetic azeotropy can easily be constructed by tracking the given criteria started from one of the pure component vertices. All the mole fractions and the κ values together with the eigenvalues of the Jacobian can be plotted over a single variable.

In the remaining parts of this article illustrative examples will be shown.

Example 1: The Simplest Case

Consider a system of three components A, B, and C, whose VLE is described by constant relative volatilities

α_A of A and α_B of B related to C. Suppose, for the sake of simplicity, the volatility sequence

$$\alpha_A > \alpha_B > 1 \quad (26)$$

A reversible chemical reaction takes place in the liquid phase as follows:



The reaction rate equations, again for the sake of simplicity, correspond to the stoichiometry

$$r = k\rho^2 x_A x_B - k'\rho x_C \quad (28)$$

Let the two independent mole fractions belong to components A and B; then the differential equations governing the process are

$$\frac{dx_A}{d\xi} = x_A - y_A - \kappa(1-x_A)\epsilon \quad (29)$$

$$\frac{dx_B}{d\xi} = x_B - y_B - \kappa(1-x_B)\epsilon \quad (30)$$

where

$$\kappa = k\rho(L/V) \quad (31)$$

and

$$\epsilon = x_A x_B - \frac{1 - x_A - x_B}{\rho K} \quad (32)$$

Pure Component Vertices.

$\mathbf{x} = (1,0)$ [pure A] is a singular point.

$\mathbf{x} = (0,1)$ [pure B] is a singular point.

$\mathbf{x} = (0,0)$ [pure C] is *not* a singular point, because the right-hand sides of the differential equations are not zero there.

Edges.

The A-B edge is an invariant subdomain.

The A-C edge and the B-C edge are *not* invariant subdomains. The trajectories are departing from these edges.

Interior of the Domain. Applying the equilibrium equation

$$y_i = \frac{\alpha_i x_i}{\sum_j \alpha_j x_j} \quad (33)$$

where the relative volatility of C is just 1, we get, after eliminating $\kappa\epsilon$

$$(\alpha_A - 1)x_A(1 - x_A) = (\alpha_B - 1)x_B(1 - x_B) \quad (34)$$

This *extended line of kinetic azeotropy* is a hyperbola with the following center

$$(x_A)_{\text{center}} = 1/2 \quad (35)$$

$$(x_B)_{\text{center}} = 1/2 \quad (36)$$

The axes of the hyperbola are parallel with the axes of the coordinate system. The length of the radius along the x_A

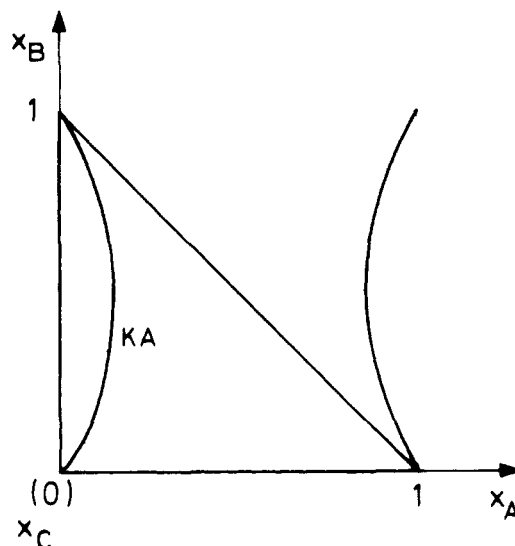


Figure 2. Hyperbola line for example 1. KA, extended line of kinetic azeotropy.

axis and along the x_B axis are, respectively:

$$a = \frac{1}{2}(1 - \omega)^{1/2} < \frac{1}{2} \quad (37)$$

$$b = \frac{1}{2}(\Omega - 1)^{1/2} \quad (38)$$

where

$$\Omega = \frac{1}{\omega} = \frac{\alpha_A - 1}{\alpha_B - 1} \quad (39)$$

The pure component vertices B and C lie on the left-hand-side branch of the hyperbola, while the pure component vertex A lies on the right-hand-side branch. The slope of the hyperbola can be expressed at the vertices as

$$\lim_{x_A \rightarrow 0} \left| \frac{dx_B}{dx_A} \right| = \lim_{x_A \rightarrow 1} \left| \frac{dx_B}{dx_A} \right| = \Omega > 1 \quad (40)$$

It follows that only the left-hand-side branch runs inside the composition domain; see Figure 2.

The chemical equilibrium ($\epsilon = 0$) can be expressed as

$$x_A = \frac{1 - x_B}{1 + K\rho x_B} \quad (41)$$

This is another second-order curve, and it connects the pure component vertices A and B. Whether the two curves cross can be determined according to the slopes in the pure component vertex B.

$$\lim_{x_A \rightarrow 0} \left(\frac{dx_B}{dx_A} \right)_{\epsilon=0} = -(1 + \rho K) \quad (42)$$

It follows that intersection exists, if

$$1 + \rho K > \Omega \quad (43)$$

After some algebraic manipulation, the intersection point

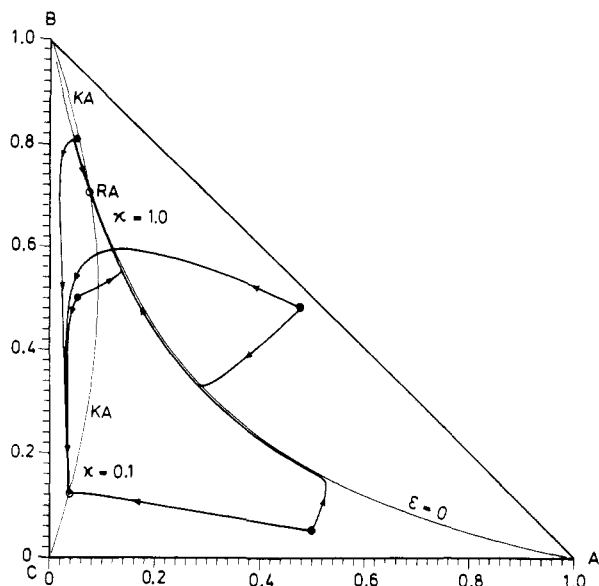


Figure 3. Residue curves, line of kinetic azeotropy, and chemical equilibria line for example 1. KA, extended line of kinetic azeotropy; $\epsilon = 0$, line of chemical equilibria; RA: point of (equilibrium) reactive azeotrope.

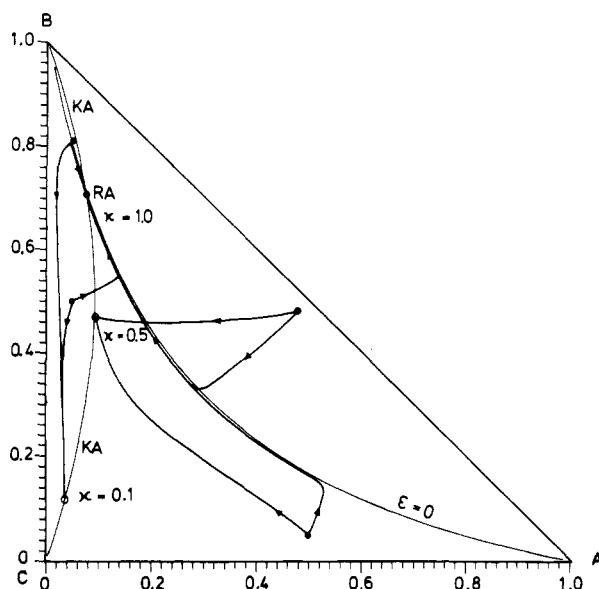


Figure 4. Residue curves, line of kinetic azeotropy and chemical equilibria line for example 1. KA, extended line of kinetic azeotropy; $\epsilon = 0$, line of chemical equilibria; RA, point of (equilibrium) reactive azeotrope.

can be expressed as

$$x_A = \frac{1}{\rho K}(-1 + [\omega(1 + \rho K)]^{1/2}) \quad (44)$$

$$x_B = \frac{1}{\rho K}(-1 + [\Omega(1 + \rho K)]^{1/2}) \quad (45)$$

This is the point of *equilibrium reactive azeotropy* (RA).

Numeric calculations were performed with the values $\alpha_A = 4$, $\alpha_B = 2$, and $\rho K = 4$. The two lines together with some of the kinetic reactive residue curves are shown in Figures 3 and 4. The curves are shown in two figures just to avoid a too great line density. (At the same time, there is some duplication between the two figures.) The hyperbola connecting C with B is the extended line of kinetic azeotropy, and the hyperbola connecting A with B is the line of chemical equilibrium. Their common point, very near the point denoted by $\kappa = 1.0$, is a reactive

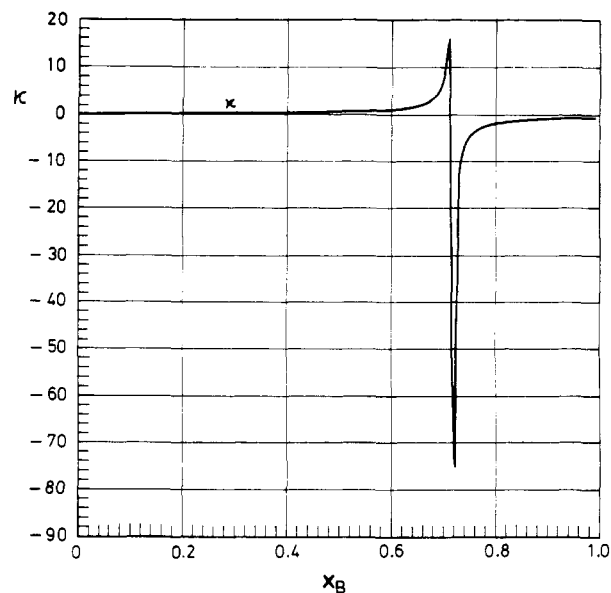


Figure 5. κ plotted against x_B for example 1.

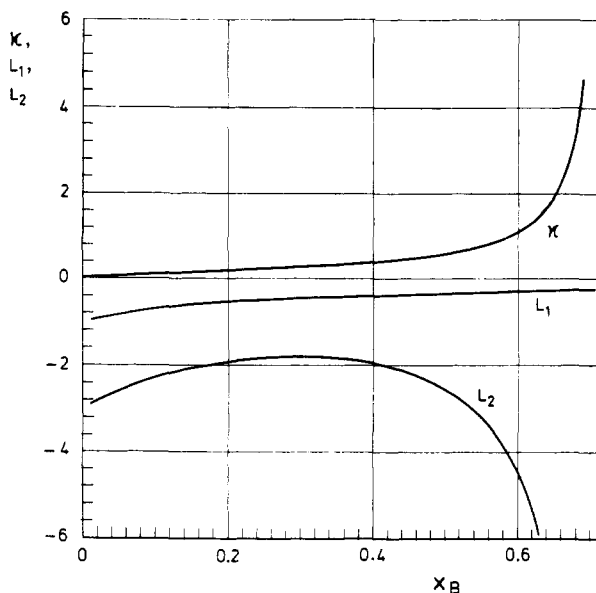


Figure 6. Eigenvalues (L_1 and L_2) plotted against x_B where k is positive.

azeotrope. Kinetic residue curves were started from points (0.5,0.1), (0.1,0.5), (0.06,0.81), and (0.48,0.48); the starting compositions are denoted by filled circles in the figures. The trajectories were calculated with different κ values, namely $\kappa = 0.1, 0.5$, and 1.0 . It can be seen that the trajectories started from different compositions arrive at the same common point on the line of kinetic azeotropy, if the same κ is used. Continuously changing κ values lead the trajectories to any point of the continuous KA line. Any given positive κ assigns a stable node in the line of kinetic azeotropy, from point (0,0) to the reactive azeotrope. The reactive azeotrope is at the intersection of the KA line and the $\epsilon = 0$ line, and belongs to infinite κ . This can be even better illustrated by plotting κ along x_B , shown in Figure 5. In this figure κ monotonically increases, approaches positive infinity below the mole fraction of the reactive azeotrope, drops down to negative infinity at that point, and monotonically increases after, but never reaches zero again in the composition domain. The eigenvalues of the Jacobian along the line of kinetic azeotropy, together with κ itself, are plotted in Figure 6. Both the eigenvalues are continuously real and negative

Table 1. Antoine Coefficients and Molar Volumes

	A	B	C	v
isopentene	6.861 62	1047.811	232.061	105.90
formic acid	6.944 59	1295.260	218.000	37.91
isopentyl formate	8.053 00	2060.140	275.079	83.11

Table 2. Wilson Interaction Coefficients

1	2	$A_{1,2}$	$A_{2,1}$
A	B	-57.3060	1860.9282
A	C	55.0482	432.7491
B	C	415.4465	621.9025

where κ is positive. It follows that all these compositions are stable nodes. If there is enough liquid in the still, then the remaining still composition in the distillation still will be arbitrarily near the kinetic azeotrope. Where the trajectories will arrive on the line of kinetic azeotropy can be controlled by the V/L ratio, through the κ value, according to eq 31.

Example 2: A Realistic Three Component Case

Although there are a lot of real examples where liquid-phase nonequilibrium reversible reaction is accompanied by vapor-liquid separation, e.g., transesterifications, it is rather difficult to find a real *three-component* case at normal circumstances with well-studied chemical kinetics and VLE. In the following *atmospheric* example the components are A, 2-methyl-1-butene; B, formic acid; and C, *tert*-pentyl formate. The ester is formed from the acid and the isopentene in a reversible quasihomogeneous reaction.

Neither the real kinetics nor the VLE can be completely found in the literature. Instead, the VLE model and kinetics were compiled on the basis of non complete data, and data of similar processes. For example, the data of the system 2-methyl-2-butene + acetic acid was used to substitute Wilson interaction coefficients in the 2-methyl-2-pentene + formic acid system. The following model cannot be considered as a good scientific or industrial tool for modeling this system, but only as a qualitative model charged with large uncertainty:

Antoine coefficients (Torr and Celsius) and molar volume (liters per kilomole) are listed in Table 1. Liquid-phase activity coefficients were calculated using the Wilson model with the interaction coefficients (calories per mole) given in Table 2. Both the Wilson model together with the Antoine vapor pressure equation, and the vapor-phase association are taken into account according to the formulas given in the data collection of Gmehling et al. (1982). The association coefficients of formic acid were $A_D = -10.743$ and $B_D = 3083.0$.

The kinetic model is based on the article of Gehlawat and Hsarma (1971). The reaction rate is expressed as

$$r = k\rho^2\left(x_Ax_B - \frac{1}{\rho K}x_C\right) \quad (46)$$

where

$$k\rho^2 = 1.23687 \times 10^{-4} \exp(0.045196T) \text{ (s}^{-1}\text{)} \quad (47)$$

$$\frac{1}{\rho K} = 1.87352 \times 10^{-8} \exp(0.059807T) \quad (48)$$

and the T temperature is expressed in Kelvin. Equation 47 is not used in the calculations, but κ is used, instead. Both eq 47 and eq 48 are numeric approximations in the range of the boiling temperatures under atmospheric pressure.

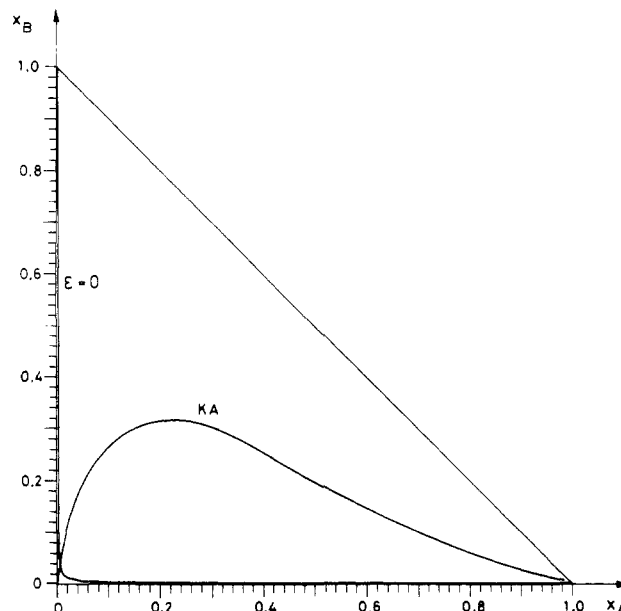


Figure 7. Extended line of kinetic azeotropy (KA) in example 2. A section of the equilibrium line is also shown near the vertical axis.

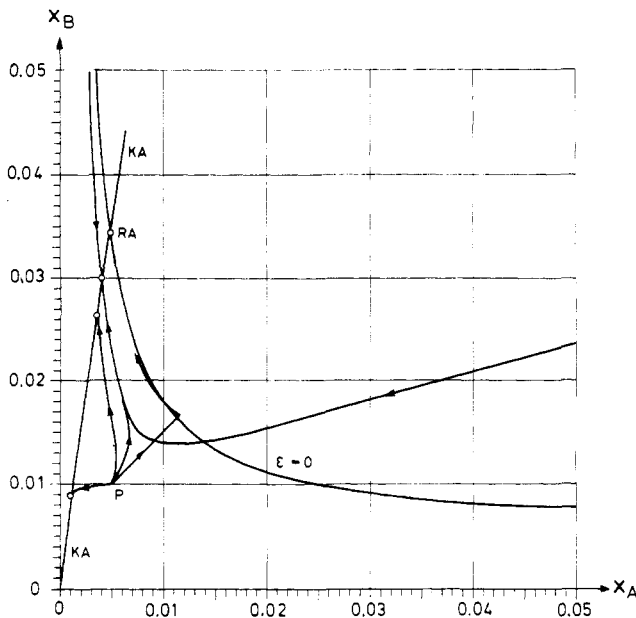


Figure 8. Enlarged area of the composition domain in example 2. KA, extended line of kinetic azeotropy; $\epsilon = 0$, line of chemical equilibria; RA, point of (equilibrium) reactive azeotrope.

The extended line of kinetic azeotropy is shown labeled by KA in Figure 7. The line of chemical equilibrium runs very near the origin, and hence the behavior of this system is demonstrated in Figure 8, which shows an enlarged area of the triangle near the origin, i.e., the point of pure component C. The line starting from the origin with high slope is the KA line. Its intersection with the equilibrium line is situated at about (0.005, 0.00345). This point is the equilibrium reaction azeotrope, and is labeled by RA. The line of kinetic azeotropy is the section from the origin to RA. From point P four residue curves are traced with different κ values; these lines arrive at different points on the (0, RA) section of the KA line. One of them (with the greatest κ) runs directly to the equilibrium line, turns sharply, and traces that line to arrive at a point very near RA. Two other residue curves, starting from outside the displayed area, were traced with κ identical to the second largest κ applied from point P. These curves arrive at a common point on line KA.

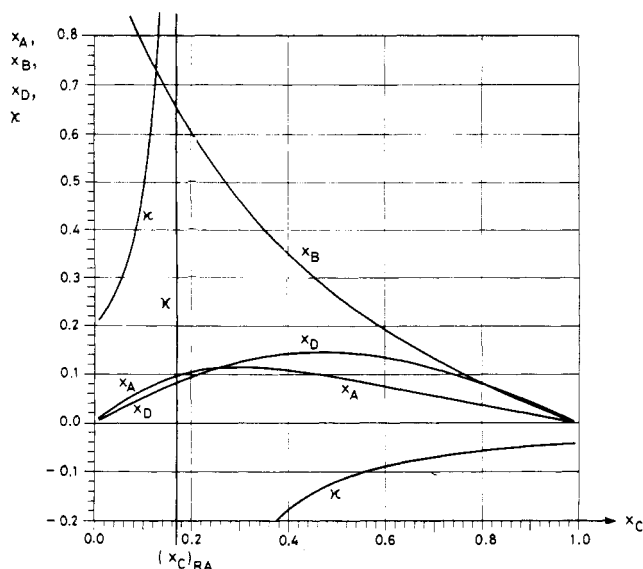


Figure 9. Plot for example 3.

Example 3: A Simple Four-Component Case

Consider a system of four components A, B, C, and D, whose VLE is described by constant relative volatilities 1.728, 1.44, 1.2, and 1.0, respectively. A reversible chemical reaction takes place in the liquid phase as follows:



The reaction rate equations, again for the sake of simplicity, correspond to the stoichiometry; i.e., the exponents in the rate equation are all equal to the absolute values of the stoichiometric coefficients:

$$\epsilon = x_A x_B - (1/K) x_C x_D \quad (50)$$

Due to the particular symmetry in this case, ρ plays only a role in κ .

Stereoscopic illustration would be necessary to show the chemical equilibrium surface, the KA line, and the residue curves at different κ values. The determination of the RA point (if it exists) involves solving a system of nonlinear algebraic equations. Instead, we may calculate the KA line as a function of a mole fraction, here either x_C or x_D . Plotting the values of κ , the location of the reactive azeotrope can also be easily determined, together with the characterization of the points in the KA line. This is shown in Figure 9, where x_C is the independent variable. The reactive azeotrope can be found at the mole fractions where κ has infinite discontinuity; this is situated at about $x_C = 0.017$, $x_D = 0.065$, $x_A = 0.08$. The mole fractions plotted in this diagram between $x_C = 0.0$ and the location of the reactive azeotrope belong to the points of the line of kinetic azeotropy. The corresponding κ values can also be read from the diagram.

Summary

If a simple vapor-liquid equilibrium process is accompanied by a nonequilibrium reversible chemical reaction, then the residue curves are different from those where the chemical reaction instantaneously reaches equilibrium. In the case of nonequilibrium reaction the residue curves are not restricted to run in the $(c - 2)$ -dimension hypersurface in the $(c - 1)$ -dimension space of independent mole fractions of a c -component mixture, but they fill in the whole composition domain. The general pattern of trajectories of equilibrium distillation with nonequilibrium reversible reaction in the liquid phase is discussed here.

There can be a continuous line of singular points belonging to different ratios of the evaporation rate and the reaction rate. The points of this line are called kinetic azeotropes. When this line has a common intersection point with the hypersurface of chemical equilibrium, then the evaporation ratio approaches zero at the intersection point, and the equilibrium reactive azeotrope, described by Barbosa and Doherty, exists there. This point can be easily found by tracing the line of kinetic azeotropy. This line usually starts from a pure component vertex (or perhaps from a VLE azeotrope). The continuation of the kinetic azeotropy line after crossing the equilibrium surface is not a set of singular points. The stationary point of reactive distillation can be controlled, along the line of kinetic azeotropy, by the evaporation ratio. This is illustrated in three simple examples.

Nomenclature

- a = exponent in the chemical rate equations
- A = general symbol of chemical compounds
- A, B, C, D = symbols of particular compounds in order of decreasing volatilities
- C = molar concentration
- K = chemical reaction equilibrium ratio
- k = reaction rate coefficient
- L = liquid holdup
- p = defined in eq 6
- q = defined in eq 7
- r = reaction rate
- t = time
- t = temperature, °C
- T = temperature, K
- V = vapor flow rate
- x = mole fraction in liquid phase
- y = mole fraction in vapor phase

Greek Letters

- α = relative volatility related to the least volatile component
- ϵ = deviation from chemical equilibrium
- κ = ratio simplex
- ν = stoichiometric coefficient
- ξ = dimensionless time
- ρ = molar density
- ω, Ω = defined in eq 39

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