Necessary and Sufficient Conditions for Reactive Azeotropes in Multireaction Mixtures

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Necessary and sufficient conditions for azeotropy in reactive mixtures derived show that in the space of transformed compositions, they take the same functional form as the conditions for azeotropy in nonreactive mixtures. In general, reactive azeotropes do not correspond to points of equal mole fraction (or mass fraction) across the coexisting equilibrium phases. The relationship between stationary points in the equilibrium temperature or pressure surface and reactive azeotropes is also considered, as well as their relevance to the Gibbs–Konovalov theorems.

Introduction

Azeotropy is a fascinating subject that has stimulated scientific interest since the 19th century. This phenomenon has an important impact on the field of process engineering, because it can drastically change the feasibility and sequencing of separation systems. Azeotropy in nonreactive mixtures has been studied extensively, and we will show that the concept can be generalized to mixtures undergoing multiple chemical equilibrium reactions giving rise to reactive azeotropes. In the case of nonreactive mixtures, the presence of azeotropes almost always causes the separation to be more difficult, whereas in reactive systems reactive azeotropes may occur and may have the unusual feature of making the separation easier. In such a favorable case, the reactive azeotrope has a composition close to the desired product, and provides a zone of constant composition that allows for the continuous presence of reactants even under evaporation/condensation conditions. In other cases, reactive azeotropes can create distillation boundaries and make a separation difficult or infeasible. In order to assess the different cases and make design decisions, it is important to be able to characterize nonreactive and reactive azeotropes and perform separation feasibility studies.

Experimental studies have been carried out to determine the nature of azeotropes (e.g., see the bibliographies in Lecat, 1949; Horsley, 1973) and to undertake a general classification of their properties. Swietoslawski (1963), Malesinski (1965), and others have thoroughly studied the phenomenon of nonreactive azeotropy, theoretically as well as experimentally, and give an extensive review of investigations on the subject. The theoretical work of Gibbs and Konovalov (see Malesinski, 1965, pp. 54–71) is fundamental to understanding the relationship between azeotropes and the characteristic features of equilibrium phase diagrams. They have shown, for example, that in homogeneous, nonreactive vapor–liquid mixtures azeotropes occur when the composition of coexisting phases is identical, and that this corresponds to a stationary point in the equilibrium temperature or pressure surface. This is one of the Gibbs–Konovalov theorems.

The phenomenon of azeotropy occurs also in reactive mixtures, and Barbosa and Doherty (1987a) have studied the conditions for reactive azeotropy in a multicomponent mixture when a single chemical reaction takes place. Little has been published on the experimental characterization of reactive azeotropes, and in the case of multiple chemical reactions it is difficult to analyze and understand experimental results without a theoretical thermodynamic framework. Experimental vapor–liquid equilibrium (VLE) measurements are available for the reacting systems water–formaldehyde, and water–formaldehyde–methanol, and these data have been studied carefully in the context of reactive azeotropy by Green and Vener (1955), Brandani et al. (1980), Brandani and Di Giacomo (1984), Maurer (1986), and Hasse et al. (1990). In this article we derive general results regarding reactive azeotropy in a multicomponent system undergoing multiple equilibrium reactions. We use the same approach as Barbosa and Doherty (1987a), and the same definition for an azeotropic state given by Rowlinson (1969): "A system is azeotropic when it can be distilled (or condensed) without change of composition" (also see Prigogine and Defay, 1954, Chap. XXVIII).

In the case of multireaction systems at thermodynamic equilibrium, we have derived a new set of variables to describe the composition of the system. In a reacting mixture of c reacting components and I inerts, for a total of C components, undergoing R equilibrium reactions, these transformed compositions are defined (Ung and Doherty, 1995a) as

$$X_i = \left(\frac{x_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1} \mathbf{x}_{\text{Ref}}}{1 - \boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1} \mathbf{x}_{\text{Ref}}} \right) \quad i = 1, \ldots, C - R \qquad (1)$$

$$Y_i = \left(\frac{y_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1} \mathbf{y}_{\text{Ref}}}{1 - \boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1} \mathbf{y}_{\text{Ref}}} \right) \quad i = 1, \ldots, C - R. \qquad (2)$$

The transformed compositions represent the overall compositions of the independent components in each phase (liquid and vapor) and account for the total amount of these chemical species present in any chemical combination, whether it is in the form of a product or of a reactant. This coordinate system captures a special projection of the phase diagram along lines of constant overall composition of the independent components. The transformed compositions have the properties that they sum to unity, and have the same dimensionality as the number of composition degrees of freedom in an isobaric (or isothermal) reactive system, namely, $(C - R - 1)$. Barbosa and Doherty (1987a,b, 1988) have derived similar variables for the case of single-reaction mixtures and applied them to study the influence of chemical reaction on phase equilibrium. We show that in the derivation of the necessary and sufficient conditions for the formation of azeotropes in multiple-reaction mixtures, the transformed compositions can be identified and lead to very simple expressions for the conditions of reactive azeotropy. We also shown how the Gibbs–Konovalov theorems can be extended to the case of reactive mixtures.

Necessary Conditions for Reactive Azeotropy

In this section we derive the necessary conditions for reactive azeotropy. We consider a closed system shown in Figure 1 in which a multicomponent, multireaction liquid mixture is vaporized at constant pressure. There are c reacting components, I inerts, for a total of C components, and R independent reactions. The total mass of the closed system is fixed, but the total number of moles changes due to the reactions.

We show that by applying the criterion for azeotropic states (the compositions do not change during vaporization, $dx_i/dt = dy_i/dt = 0$, $i = 1, \ldots, C$), the following $(C - R - 1)$ necessary conditions for reactive azeotropy for the multiple reaction system are obtained:

$$X_i = Y_i \qquad i = 1, \ldots, C - R - 1. \qquad (3)$$

Let L and V denote the total instantaneous number of moles of liquid and vapor present in the closed system, and ϵ_r the instantaneous extent of reaction r. In addition, x_i is the liquid mole fraction of component i, and y_i the vapor mole fraction of component i.

The material balance on component i is

$$\frac{d(Lx_i)}{dt} + \frac{d(Vy_i)}{dt} = \boldsymbol{\nu}_i^T \dot{\boldsymbol{\epsilon}} \qquad i = 1, \ldots, C, \qquad (4)$$

where $\dot{\boldsymbol{\epsilon}}$ is the column vector of the rate of change in extent of reaction for each reaction.

$$\dot{\boldsymbol{\epsilon}} = \left(\frac{d\epsilon_1}{dt}, \frac{d\epsilon_2}{dt}, \ldots, \frac{d\epsilon_R}{dt} \right) \qquad (5)$$

and

$$\boldsymbol{\nu}_i^T = (\nu_{i1}, \nu_{i2}, \ldots, \nu_{iR}), \qquad (6)$$

where $\boldsymbol{\nu}_i^T$ is the row vector of stoichiometric coefficients of component i for each reaction.

The goal is to eliminate the vector $\dot{\boldsymbol{\epsilon}}$ among the C equations 4 and use the overall mass balance to eliminate L or V. Using the same vector notation as used in the derivation of the transformed composition variables (Ung and Doherty, 1995a), we define R reference components and rewrite R equations using the square matrix $\mathbf{N}$ of stoichometric coefficients for the R reference components in the R reactions. The components are ordered by rows and the reactions by columns:

$$\mathbf{N} = \begin{pmatrix} \boldsymbol{\nu}_{(C-R+1)}^T \\ \vdots \\ \boldsymbol{\nu}_C^T \end{pmatrix} = \begin{pmatrix} \nu_{(C-R+1)1} & \cdots & \nu_{(C-R+1)R} \\ \vdots & \nu_{ir} & \vdots \\ \nu_{C1} & \cdots & \nu_{CR} \end{pmatrix}. \qquad (7)$$

We also replace one of the Eqs. 4 by the overall mass balance. The system of C Eqs. 4 becomes

$$\frac{d(Lx_i)}{dt} + \frac{d(Vy_i)}{dt} = \boldsymbol{\nu}_i^T \dot{\boldsymbol{\epsilon}} \qquad i = 1, \ldots, C - R - 1 \qquad (8)$$

$$\frac{d(L\mathbf{x}_{\text{Ref}})}{dt} + \frac{d(V\mathbf{y}_{\text{Ref}})}{dt} = \mathbf{N}\dot{\boldsymbol{\epsilon}} \qquad (9)$$

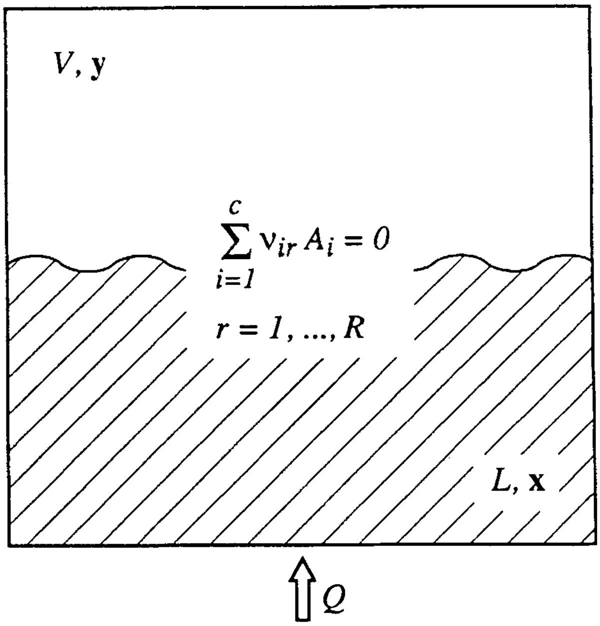

Figure 1. Vaporization of a reactive mixture in a closed system.

$$\frac{dL}{dt}+\frac{dV}{dt}=\boldsymbol{\nu}_{\mathrm{TOT}}^T\dot{\boldsymbol{\epsilon}}, \qquad (10)$$

where

$$\boldsymbol{\nu}_{\mathrm{TOT}}^T=(\nu_{T1},\nu_{T2},\ldots,\nu_{TR}), \qquad (11)$$

where $\boldsymbol{\nu}_{\mathrm{TOT}}^T$ is the row vector of the sum of the stoichiometric coefficients for each reaction.

We expand the derivatives and combine equations to obtain

$$x_i\frac{dL}{dt}+L\frac{dx_i}{dt}+y_i\frac{dV}{dt}+V\frac{dy_i}{dt}=\boldsymbol{\nu}_i^T\dot{\boldsymbol{\epsilon}} \qquad i=1,\ldots,C-R-1 \qquad (12)$$

and

$$\frac{dL}{dt}+\frac{dV}{dt}=\boldsymbol{\nu}_{\mathrm{TOT}}^T\dot{\boldsymbol{\epsilon}} \qquad (13)$$

$$\dot{\boldsymbol{\epsilon}}=\mathbf{N}^{-1}\left[\frac{d(L\boldsymbol{x}_{\mathrm{Ref}})}{dt}+\frac{d(V\boldsymbol{y}_{\mathrm{Ref}})}{dt}\right]. \qquad (14)$$

Therefore,

$$x_i\frac{dL}{dt}+L\frac{dx_i}{dt}+y_i\frac{dV}{dt}+V\frac{dy_i}{dt}=\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\left[\boldsymbol{x}_{\mathrm{Ref}}\frac{dL}{dt}+L\frac{d\boldsymbol{x}_{\mathrm{Ref}}}{dt}+\boldsymbol{y}_{\mathrm{Ref}}\frac{dV}{dt}+V\frac{d\boldsymbol{y}_{\mathrm{Ref}}}{dt}\right] \qquad i=1,\ldots,C-R-1 \qquad (15)$$

and

$$\frac{dL}{dt}+\frac{dV}{dt}=\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\left[\boldsymbol{x}_{\mathrm{Ref}}\frac{dL}{dt}+L\frac{d\boldsymbol{x}_{\mathrm{Ref}}}{dt}+\boldsymbol{y}_{\mathrm{Ref}}\frac{dV}{dt}+V\frac{d\boldsymbol{y}_{\mathrm{Ref}}}{dt}\right]. \qquad (16)$$

Collecting terms in Eqs. 15 and 16 gives

$$\left(\frac{dL}{dt}\right)(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})+\left(\frac{dV}{dt}\right)(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})+L\frac{dx_i}{dt}+V\frac{dy_i}{dt}=\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\left(L\frac{d\boldsymbol{x}_{\mathrm{Ref}}}{dt}+V\frac{d\boldsymbol{y}_{\mathrm{Ref}}}{dt}\right) \qquad i=1,\ldots,C-R-1 \qquad (17)$$

and

$$\left(\frac{dL}{dt}\right)(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})+\left(\frac{dV}{dt}\right)(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})=\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\left(L\frac{d\boldsymbol{x}_{\mathrm{Ref}}}{dt}+V\frac{d\boldsymbol{y}_{\mathrm{Ref}}}{dt}\right). \qquad (18)$$

We now use the fact that by definition, the compositions do not change during an azeotropic process:

$$\frac{dx_i}{dt}=\frac{dy_i}{dt}=0 \qquad i=1,\ldots,C. \qquad (19)$$

By applying the conditions for an azeotropic state to the $(C-R)$ material balance Eqs. 17 and 18, we obtain the following *necessary conditions for reactive azeotropy:*

$$\left(\frac{dL}{dt}\right)(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})+\left(\frac{dV}{dt}\right)(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})=0 \qquad i=1,\ldots,C-R-1 \qquad (20)$$

$$\left(\frac{dL}{dt}\right)(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})+\left(\frac{dV}{dt}\right)(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})=0. \qquad (21)$$

We can use Eq. 21 to further simplify Eqs. 20. Provided that

$$(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})\neq 0 \quad \text{and} \quad (1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})\neq 0, \qquad (22)$$

we can express dV/dt as a function of dL/dt.

Since the lefthand sides of expressions 22 appear in the denominator of the transformed composition variables (Eqs. 1 and 2), expressions 22 must be satisfied in the first place for the transformed composition variables to be defined. This constraint can always be satisfied by picking a suitable choice of R reference components from among the C reacting species. The physical meaning of the constraint (Eq. 22) can be seen from the definition of the transformed mole numbers, from which the transformed compositions are derived. In appendix A of Ung and Doherty (1995b) we derived the transformed mole number of component i as

$$\hat{n}_i=n_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{n}_{\mathrm{Ref}} \qquad i=1,\ldots,C-R. \qquad (23)$$

This physically represents the moles of component i in any chemical combination in the system. Therefore, the transformed number of moles of component i has to be positive. If we take the sum of the transformed mole numbers over all the independent components, we obtain the total transformed number of moles

$$\hat{n}_{\mathrm{TOT}}=n_{\mathrm{TOT}}-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{n}_{\mathrm{Ref}}, \qquad (24)$$

which must also be a positive quantity. Dividing Eq. 24 by the total number of moles n_{TOT} leads to expressions 22.

Since the choice of reference components is simply a choice of the manner in which to visualize the system, it is always possible to choose a set of reference components that will lead to a nonzero value for the transformed total number of moles. If every possible set of reference components led to a zero value for the transformed total number of moles, it would mean that all of the initial number of moles disappeared into nothing. Since this violates conservation of matter, it is always possible to find a set of reference components that satisfy expressions 22.

Between Eqs. 20 and 21 we obtain

$$\left(\frac{dL}{dt}\right)\left[(x_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}}) - (y_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}})\left(\frac{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}})}{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}})}\right)\right] = 0 \qquad i = 1,\ldots,C-R-1, \quad (25)$$

which can be written

$$(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}})\left(\frac{dL}{dt}\right)\left[\left(\frac{x_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}}}{1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}}}\right) - \left(\frac{y_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}}}{1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}}}\right)\right] = 0 \qquad i = 1,\ldots, C-R-1. \quad (26)$$

The $(C-R-1)$ Eqs. 26 give the necessary conditions for reactive azeotropy. The R Eqs. 14 define the vector $\dot{\boldsymbol{\epsilon}}$, and Eq. 21 links dV/dt to dL/dt by the overall mass balance.

Therefore, we have found a set of $(C-R-1)$ necessary conditions for reactive azeotropy: Eqs. 26. During the azeotropic vaporization process, dL/dt is nonzero, and the set of Eqs. 26 becomes

$$\left[\frac{(x_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}})}{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}})}\right] = \left[\frac{(y_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}})}{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}})}\right] \qquad i = 1,\ldots, C-R-1. \quad (27)$$

Writing these necessary conditions in terms of the transformed composition variables defined in Eqs. 1 and 2, we obtain

$$X_i = Y_i \qquad i = 1,\ldots, C-R-1. \quad (28)$$

In the reaction-invariant composition space, these conditions for reactive azeotropy have the same functional form as the conditions for azeotropy for nonreactive mixtures in mole fraction space.

Sufficient Conditions for Reactive Azeotropy

We derive here the sufficient conditions for reactive azeotropy and show that they are the same as the necessary conditions derived above ($X_i = Y_i$ implies $dx_i/dt = dy_i/dt = 0$, $i = 1,\ldots, C$).

At any instant, the liquid and vapor mole fractions are related to the extent of reaction and the initial number of moles n_i^0 (reacting components and inerts included) by the following material balance equation.

$$Lx_i + Vy_i = n_i^0 + \boldsymbol{\nu}_i^T \boldsymbol{\epsilon} \qquad i = 1,\ldots, C. \quad (29)$$

Let us normalize the variables with respect to the initial total number of moles n_{TOT}^0 and define

$$l = \frac{L}{n_{\text{TOT}}^0}; \quad v = \frac{V}{n_{\text{TOT}}^0}; \quad \xi_r = \frac{\epsilon_r}{n_{\text{TOT}}^0} \quad (30)$$

$$n_{\text{TOT}}^0 = \sum_{i=1}^{C} n_i^0 + \sum_{j=1}^{I} n_j^0. \quad (31)$$

Defining the initial overall composition as

$$z_i^0 = \frac{n_i^0}{n_{\text{TOT}}^0} \quad (32)$$

the set of Eqs. 29 becomes

$$lx_i + vy_i = z_i^0 + \boldsymbol{\nu}_i^T \boldsymbol{\xi} \qquad i = 1,\ldots, C. \quad (33)$$

Using the same procedure to eliminate the column vector $\boldsymbol{\xi}$, of dimension R, of the dimensionless extents of reaction, we choose R reference components, and define $\mathbf{N}$ as the square matrix of stoichiometric coefficients of the reference components.

The set of C Eqs. 33 can be divided into three subsets; R equations defining the R reference components, the overall mass balance, and the $(C-R-1)$ equations remaining.

$$lx_i + vy_i = z_i^0 + \boldsymbol{\nu}_i^T \boldsymbol{\xi} \qquad i = 1,\ldots, C-R-1 \quad (34)$$

$$l\boldsymbol{x}_{\text{Ref}} + v\boldsymbol{y}_{\text{Ref}} = \boldsymbol{z}_{\text{Ref}}^0 + \mathbf{N}\boldsymbol{\xi} \quad (35)$$

$$l + v = 1 + \boldsymbol{\nu}_{\text{TOT}}^T \boldsymbol{\xi}. \quad (36)$$

Using Eq. 35 we obtain the following expression for $\boldsymbol{\xi}$

$$\boldsymbol{\xi} = \mathbf{N}^{-1}(l\boldsymbol{x}_{\text{Ref}} + v\boldsymbol{y}_{\text{Ref}} - \boldsymbol{z}_{\text{Ref}}^0), \quad (37)$$

which enables us to eliminate it from Eqs. 34 and 36, thus

$$lx_i + vy_i = z_i^0 + \boldsymbol{\nu}_i^T \mathbf{N}^{-1}(l\boldsymbol{x}_{\text{Ref}} + v\boldsymbol{y}_{\text{Ref}} - \boldsymbol{z}_{\text{Ref}}^0) \qquad i = 1,\ldots, C-R-1 \quad (38)$$

$$l + v = 1 + \boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}(l\boldsymbol{x}_{\text{Ref}} + v\boldsymbol{y}_{\text{Ref}} - \boldsymbol{z}_{\text{Ref}}^0). \quad (39)$$

Collecting terms in Eq. 38 gives

$$l(x_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}}) + v(y_i - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}}) = (z_i^0 - \boldsymbol{\nu}_i^T \mathbf{N}^{-1}\boldsymbol{z}_{\text{Ref}}^0) \qquad i = 1,\ldots, C-R-1, \quad (40)$$

and Eq. 39 may be rearranged to give an explicit expression for v, thus

$$v = \frac{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{z}_{\text{Ref}}^0) - l(1 - v_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{x}_{\text{Ref}})}{(1-\boldsymbol{\nu}_{\text{TOT}}^T \mathbf{N}^{-1}\boldsymbol{y}_{\text{Ref}})} \quad (41)$$

provided that

$$(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \neq 0. \tag{42}$$

We can use Eq. 41 to eliminate v in Eq. 40 to give

$$l(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})+(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \times\left[\frac{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)-l(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}\right] =(z_i^0-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0) \qquad i=1,\ldots,C-R-1. \tag{43}$$

Further manipulation gives

$$\begin{aligned} l\{(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \\ -(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})\} \\ =(z_i^0-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \\ -(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \\ i=1,\ldots,C-R-1 \end{aligned} \tag{44}$$

or

$$\begin{aligned} l(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}}) \\ \times\left[\frac{(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}-\frac{(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}\right] \\ =(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0) \\ \times\left[\frac{(z_i^0-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)}-\frac{(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}\right] \\ i=1,\ldots,C-R-1. \end{aligned} \tag{45}$$

We recognize the appearance of the transformed composition variables, X_i, Y_i, and Z_i^0 in Eq. 45, where

$$X_i=\frac{(x_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})} \qquad i=1,\ldots,C-R-1 \tag{46}$$

$$Y_i=\frac{(y_i-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}})} \qquad i=1,\ldots,C-R-1 \tag{47}$$

and

$$Z_i^0=\frac{(z_i^0-\boldsymbol{\nu}_i^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)} \qquad i=1,\ldots,C-R-1 \tag{48}$$

provided that

$$(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}}) \neq 0 \tag{49}$$

$$(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{y}_{\mathrm{Ref}}) \neq 0 \tag{50}$$

$$(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0) \neq 0 \tag{51}$$

These inequalities are guaranteed by a suitable choice of reference components.

Therefore, Eqs. 45 become

$$l(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})(X_i-Y_i)=(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)(Z_i^0-Y_i) \qquad i=1,\ldots,C-R-1 \tag{52}$$

or

$$\frac{l(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)}(X_i-Y_i)=(Z_i^0-Y_i) \qquad i=1,\ldots,C-R-1. \tag{53}$$

Define

$$\Phi=\frac{l(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{x}_{\mathrm{Ref}})}{(1-\boldsymbol{\nu}_{\mathrm{TOT}}^T\mathbf{N}^{-1}\boldsymbol{z}_{\mathrm{Ref}}^0)}, \tag{54}$$

where Φ is a nonzero constant that represents the transformed liquid fraction in the closed system. Equation 53 then becomes

$$\Phi(X_i-Y_i)=(Z_i^0-Y_i) \qquad i=1,\ldots,C-R-1 \tag{55}$$

or

$$\Phi X_i+(1-\Phi)Y_i=Z_i^0 \qquad i=1,\ldots,C-R-1. \tag{56}$$

This equation is a useful result since it shows that in transformed coordinates the liquid and vapor compositions are related to the overall initial composition by a *lever rule*. Therefore, when

$$X_i=Y_i \qquad i=1,\ldots,C-R-1, \tag{57}$$

Equations 55 become

$$Z_i^0=X_i=Y_i \qquad i=1,\ldots,C-R-1 \tag{58}$$

independently of the value of Φ.

Therefore, a sufficient condition for azeotropy is Eq. 57, since both the righthand side and the lefthand side of Eqs. 55 are equal to zero, regardless of the value of l. This means that for the particular set of equilibrium mole fractions that satisfy Eqs. 57, l (and thus v) are undetermined, which means that at the given pressure the system can be vaporized at constant composition. This is exactly the definition of a reactive azeotropic transformation.

We conclude that conditions 57 are the *necessary and sufficient conditions* for an azeotropic transformation to occur in a two-phase closed system when its components undergo multiple equilibrium chemical reactions. The use of the transformed compositions provides a way of characterizing the phenomenon of reactive azeotropy from experiments and detecting the presence of reactive azeotropes.

Nonreactive Azeotropes that Survive the Reactions

In Ung and Doherty (1995a), we describe how the use of transformed composition variables allows the determination and visualization of the nonreactive azeotropes that are still present in the system after reaction. Independently of the choice of stoichiometric equations used to describe the reactions, the transformed compositions readily provide knowledge of which edge is a *reactive edge* and which is a *nonreactive edge* in the transformed composition solution space. Any azeotrope located on a nonreactive edge will be part of the solution space as a nonreactive azeotrope, and will thus survive reaction. On the other hand, a reactive edge reveals the presence of a dissociation reaction on the edge, and any nonreactive azeotrope that would be located on this edge is not allowed to remain as a nonreactive mixture, but would dissociate and thus not survive the reaction. The same is true for nonreactive azeotropes that are mapped into the reactive solution space in transformed composition variables; they too would not survive the reaction.

It is easy to show that a nonreactive azeotrope surviving the reaction is also a solution of the reactive azeotropy conditions:

$$y = x \Rightarrow X = Y. \tag{59}$$

Therefore, the general conditions for azeotropy in reactive mixtures ($X = Y$) encompass *all* the azeotropes, both reactive and nonreactive, in mixtures with multiple chemical reactions.

Special Conditions Relating Stationary Points in Temperature and Pressure to Reactive Azeotropes

Summary of equations

In a separate article (Ung and Doherty, 1995b), we consider the thermodynamics of reactive mixtures and introduce the transformed molar Gibbs free energy $\hat{g}$ as a more suitable function to describe reactive systems, where $\hat{g}$ is the Gibbs free energy of the system divided by the total transformed number of moles $\hat{n}_{\text{TOT}}$:

$$\hat{g}(T,P,X_1,\ldots,X_{C-R-1}) = \frac{G(T,P,\hat{n}_1,\ldots,\hat{n}_{C-R})}{\hat{n}_{\text{TOT}}}. \tag{60}$$

We have also shown that the Gibbs free energy is a function of pressure, temperature, and $(C-R)$ transformed mole numbers, where the transformed number of moles of species i represents the overall number of moles of that species in any chemical combination throughout the system and thus keeps a constant value as the reactions occur, similarly to the usual mole numbers in nonreactive mixtures. The transformed mole numbers are given in Eq. 23, and the total transformed number of moles is given in Eq. 24.

We also define a matrix of second partial derivatives, $\hat{\mathbf{g}}$, such that

$$\hat{\mathbf{g}} = \begin{pmatrix} \dfrac{\partial^2 \hat{g}}{\partial X_1^2} & \cdots & \dfrac{\partial^2 \hat{g}}{\partial X_1 \partial X_{C-R-1}} \\ \vdots & \left(\dfrac{\partial^2 \hat{g}}{\partial X_i \partial X_j}\right)_{T,P,X_k,k \in \{1,\ldots,C-R-1\},k \neq i,j} & \vdots \\ \dfrac{\partial^2 \hat{g}}{\partial X_{C-R-1} \partial X_1} & \cdots & \dfrac{\partial^2 \hat{g}}{\partial X_{C-R-1}^2} \end{pmatrix} \tag{61}$$

and have shown that for a reactive mixture this matrix must be positive definite for the criterion of material stability (local stability) to be satisfied.

We have also shown that the gradients of temperature and pressure can be written as

$$\nabla T = \left(\frac{-T}{\sum_{j=1}^{C-R} Y_j \Delta \hat{s}_j} \right) \hat{\mathbf{g}}(Y - X) \tag{62}$$

and

$$\nabla P = \left(\frac{1}{\sum_{j=1}^{C-R} Y_j \Delta \hat{v}_j} \right) \hat{\mathbf{g}}(Y - X), \tag{63}$$

where we define ∇T, the gradient of the temperature, which is a column vector of dimension $(C-R-1)$, as

$$\nabla T = \left\{ \left(\frac{\partial T}{\partial X_1} \right)_{P,X_i,i \neq 1,i \in \{1,\ldots,C-R-1\}}, \ldots, \left(\frac{\partial T}{\partial X_{C-R-1}} \right)_{P,X_i,i \neq (C-R-1),i \in \{1,\ldots,C-R-1\}} \right\}^T \tag{64}$$

and ∇P is the gradient of the pressure:

$$\nabla P = \left\{ \left(\frac{\partial P}{\partial X_1} \right)_{I,X_i,i \neq 1,i \in \{1,\ldots,C-R-1\}}, \ldots, \left(\frac{\partial P}{\partial X_{C-R-1}} \right)_{I,X_i,i \neq (C-R-1),i \in \{1,\ldots,C-R-1\}} \right\}^T. \tag{65}$$

Y and X are the column vectors of the $(C-R-1)$ independent transformed composition variables for the vapor phase and the liquid phase, respectively: $Y = (Y_1,\ldots,Y_{C-R-1})^T$ and $X = (X_1,\ldots,X_{C-R-1})^T$.

For a materially stable mixture, the matrix $\hat{\mathbf{g}}$ is positive definite which implies that $\det \hat{\mathbf{g}} \neq 0$. Therefore, $\hat{\mathbf{g}}$ is nonsingular, implying that the vector-matrix products in Eqs. 62 and 63 are not degenerate.

We now use these equations together with the necessary and sufficient conditions for reactive azeotropy to state the generalized Gibbs–Konovalov theorems for reactive mixtures.

Stationary points in temperature

In the previous section, Eq. 62 gives the dependence between temperature and the ith transformed composition, as the pressure and the other transformed compositions are kept at a constant value. This enables us to examine the relationship between extrema of temperature and reactive azeotropes.

In a nonreacting mixture, the denominator of the equation equivalent to Eq. 62 is $\Sigma_{j=1}^{C} y_j \Delta s_j$, and it is always positive (Malesinski, 1965, p. 71). This is not necessarily the case for reactive systems, and we need to pay attention to the denominator of Eq. 62, since we have not been able to rule out the possibility that $\Sigma_{j=1}^{C-R} Y_j \Delta \hat{s}_j$ may be zero.

However, if the condition

$$\sum_{j=1}^{C-R} Y_j \Delta \hat{s}_j \neq 0 \tag{66}$$

is satisfied, then all stationary points in temperature on an isobaric phase diagram are reactive azeotropes:

$$\{\nabla T = 0\} \Rightarrow \{Y = X\} \tag{67}$$

and all reactive azeotropes will generate a stationary point in the temperature surface:

$$\{Y = X\} \Rightarrow \{\nabla T = 0\}. \tag{68}$$

On the other hand, if

$$\sum_{j=1}^{C-R} Y_j \Delta \hat{s}_j = 0, \tag{69}$$

it does not follow that there is a correspondence between reactive azeotropes and stationary points in the temperature surface.

We conclude that with suitable qualifications, that is, $(\Sigma_{j=1}^{C-R} Y_j \Delta \hat{s}_j \neq 0)$, there is an equivalence between stationary points in temperature and reactive azeotropes:

$$\{\nabla T = 0\} \Leftrightarrow \{Y = X\}. \tag{70}$$

Stationary points in pressure

Similar reasoning shows that if

$$\sum_{j=1}^{C-R} Y_j \Delta \hat{v}_j \neq 0, \tag{71}$$

then

$$\{\nabla P = 0\} \Leftrightarrow \{Y = X\}. \tag{72}$$

These conditions are both a simplification and a generalization of the conditions derived by Barbosa and Doherty (1987b) for the case of a single equilibrium chemical reaction.

As pointed out by Barbosa and Doherty (1987b), the conditions of reactive azeotropy and conditions for stationary points in temperature or pressure are similar to the conditions of indifferent states given by Saurel (1901).

Example: Synthesis of MTBE

In the absence of inert component

Methyl *tert*-butyl ether (MTBE) is produced by reacting methanol with isobutene in the presence of inert C_4.

We first consider the ternary system consisting of isobutene (A_1) reacting with methanol (A_2) to produce the desired product MTBE (A_3), where there is no inert:

$$\begin{array}{ccccc} \text{isobutene (1)} & + & \text{methanol (2)} & \rightleftharpoons & \text{MTBE (3)} \\ A_1 & + & A_2 & \rightleftharpoons & A_3 \end{array} \tag{73}$$

The degrees of freedom for the isobaric reactive system are $F = C - R - 1 = 3 - 1 - 1 = 1$. In transformed compositions, the system is one-dimensional, and there are two transformed compositions that sum to unity; thus only one of them is an independent variable.

Using component (A_3) as the reference component, the transformed compositions are

$$X_1 = \left(\frac{x_1 + x_3}{1 + x_3}\right) \tag{74}$$

$$X_2 = \left(\frac{x_2 + x_3}{1 + x_3}\right). \tag{75}$$

We arbitrarily choose X_1 as the independent variable to represent the system. Figure 2 shows the isobaric phase diagram at 1-atm pressure. The model equations and parameters used in this calculation are reported by Ung and Doherty (1995a). The nonreactive mixture has two binary minimum boiling azeotropes (between methanol + MTBE, and methanol + isobutene) and no ternary azeotropes.

Note that there is a constriction in the phase diagram where

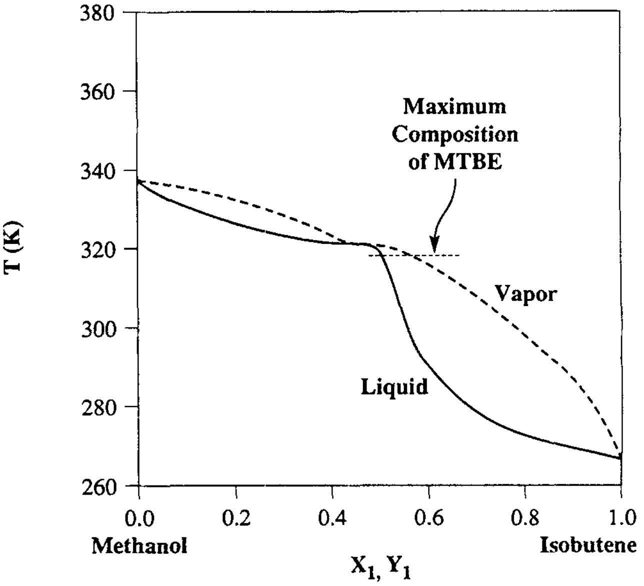

Figure 2. $T - X_1 - Y_1$ **phase diagram in transformed compositions for the reactive mixture isobutene (1)+methanol (2)** $\rightleftharpoons$ **MTBE (3) at 1 atm pressure (50 <** K **< 1,600).**

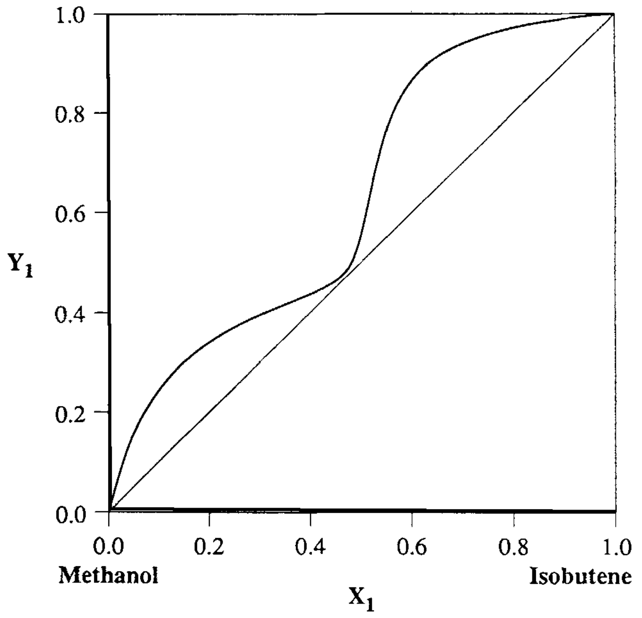

Figure 3. $Y_1 - X_1$ phase diagram in transformed compositions for the reactive mixture isobutene (1)+ methanol (2) $\rightleftharpoons$ MTBE (3) at 1 atm pressure ($50 < K < 1{,}600$).

the vapor and liquid equilibrium curves go through an inflexion point at $X_1 = 0.5$. This indicates the presence of an intermediate-boiling reactive azeotrope between all three components in the mixture, which is not there in the absence of reaction. If we represent the equilibria on a $Y_1 - X_1$ diagram, Figure 3, we see that the curve does not quite touch the 45° line at $X_1 = 0.5$, which means that the point is not exactly an azeotrope, although it is so close that it makes sense to refer to it as a "pseudo" reactive azeotrope. In practice this "pseudo" reactive azeotrope displays all the features of a reactive azeotrope, for example, it would be impossible to distil beyond this point in an equilibrium reactive distillation. To the accuracy of the model, this is a reactive azeotrope, and even though technically the two compositions (liquid and vapor) are not quite equal, we would not have had the ability to discern this without the transformed composition variables.

In the presence of inert

We now study the influence of an inert component on the reactive equilibria, and follow the experimental study of DeGarmo et al. (1992), who used n-butane as a representative inert component in place of the mixed C_4. We label n-butane component A_4. The degrees of freedom for the isobaric reactive system are now $F = C - R - 1 = 4 - 1 - 1 = 2$. The dimension of the solution space increases by one, and we add one more transformed composition given by

$$X_4 = \left(\frac{x_4}{1 + x_3} \right) \tag{76}$$

with the constraint

$$X_1 + X_2 + X_4 = 1. \tag{77}$$

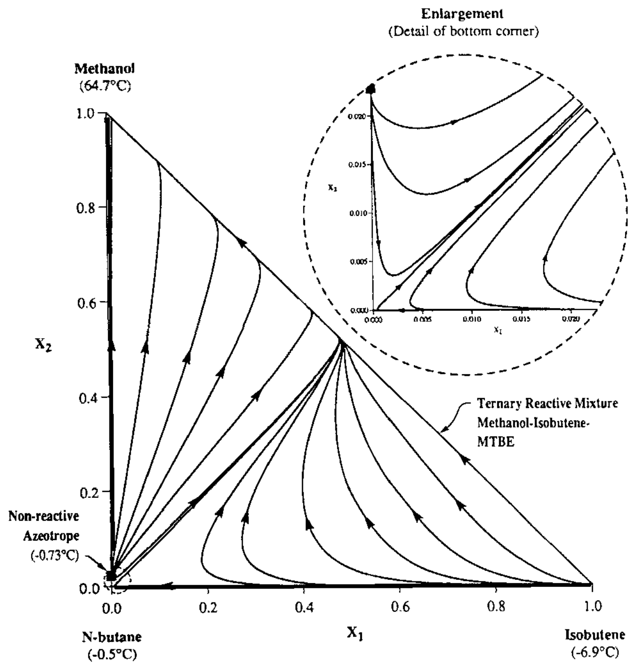

Figure 4. Residue curves in transformed composition variables for the reactive system: isobutene+ methanol $\rightleftharpoons$ MTBE with n-butane as inert (P = 1 atm).

We therefore have two independent variables, and choose to represent the reactive phase equilibria in the $X_1 - X_2$ phase plane. An equivalent way of representing thermodynamic information is to plot residue curve maps instead of phase diagrams (Doherty, 1990). We thus plot the residue curve map of the quaternary reacting system in terms of transformed composition variables. In Figure 4, we plot the reactive system at 1 atm pressure and in Figure 5 at 10-atm pressure. The shape of the solution space depends on the number of components, the number of reactions, and the stoichiometry of the system (Ung and Doherty, 1995a). For this particular reactive system the solution space is a triangle, although other systems are represented by squares, quadrilaterals, and so forth. We see on Figure 4 that the hypotenuse of the triangle is the edge representing the limiting case of no inert, and the curves are constrained to come close to the pseudo reactive azeotrope at $X_1 = X_2 = 0.5$. If we approximately divide the triangle into two regions, from the n-butane vertex to the pseudo azeotrope, we see that the pseudo reactive azeotrope behaves as a stable node from below, whereas it behaves as a saddle from above. This is a characteristic feature of an intermediate boiling azeotrope, which is a nonelementary singular point in the phase plane.

In the enlargement of the left corner of the triangle, we see that the residue curves behave in such a way that it suggests the presence of a saddle reactive azeotrope just inside the triangle. As the pressure is increased, we see in Figure 5 that the curves are not so sharp around the pseudo reactive azeotrope. This is due to the fact that as the pressure increases, the transformed composition in the vapor phase is not so close to the transformed composition in the liquid phase, and the phase diagram "opens up" and the point does not act as a reactive azeotrope anymore. In its place is left a

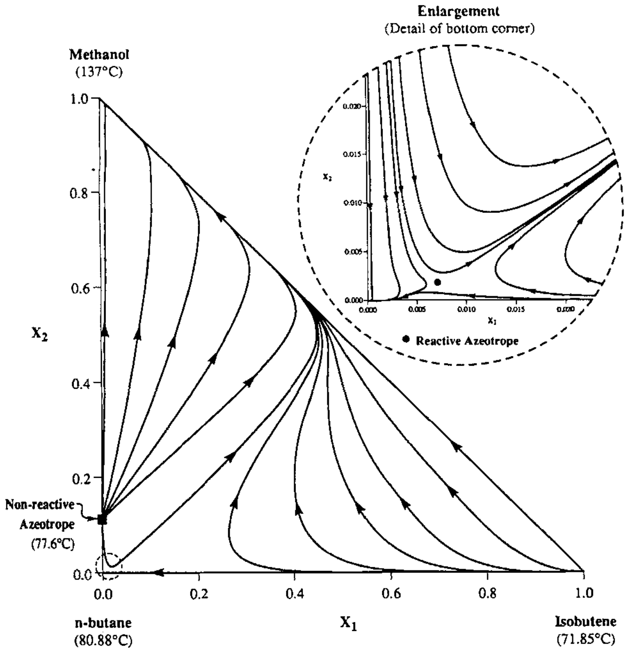

Figure 5. Residue curves in transformed composition variables for the reactive system: isobutene + methanol ⇌ MTBE with *n*-butane as inert (P = 10 atm).

severe tangent pinch. The pressure also has an influence on the other azeotropes, and we see in the enlargement of Figure 5 that the reactive azeotrope in the left corner of the triangle has changed composition with increasing pressure and clearly has the character of a saddle point.

As a final remark we note that the nonreactive mixture exhibits three minimum-boiling binary azeotropes between methanol + MTBE, methanol + isobutene, and methanol + *n*-butane. The first two do not survive the reaction, but the last does, and can be seen in Figures 4 and 5.

Topological Constraint for Reactive Systems Represented by Triangles and Squares

Doherty and Perkins (1979) studied the topological structure of ternary residue curve maps for nonreactive mixtures and showed that the singular points (pure components and azeotropes) of the differential equation describing the simple distillation process obey a global topological constraint. This is useful for determining whether the map is globally consistent.

It can be shown (Ung and Doherty, 1995c) that the equation describing reactive simple distillation when written in terms of transformed compositions has the same form as the equation for simple distillation of nonreactive mixtures in terms of mole fractions. The singular points are again the azeotropes (reactive and surviving nonreactive) and pure components (only a subset of the pure components survive as vertices of the solution space). This implies that we can extend the reasoning and derivation of Doherty and Perkins (1979) and obtain a topological constraint valid for reacting systems.

Define N_1 and S_1 as the number of pure component nodes and saddles, respectively, N_E and S_E as the number of nodes and saddles on an edge (nonreactive or reactive, which could involve 2 or 3 components, respectively), and N_F and S_F as the number of nodes and saddles on the face (could involve 4 components or more), and S_1^* as the number of pure component half-saddles in the triangle. The half-saddle is a nonelementary singular point. The following global topological constraint must hold for reacting mixtures restricted to a triangular solution space in transformed compositions:

$$2N_F - 2S_F + N_E - S_E + N_1 - S_1^* = 2. \qquad (78)$$

The residue curve maps shown in Figures 4 and 5 are both consistent with this equation. In Figure 4, $N_1 = 2$ (methanol and isobutene vertices), $S_1^* = 1$ (*n*-butane vertex), $S_E = 0$, $N_E = 1$ (methanol + *n*-butane azeotrope), and $N_F = S_F = 0$. In this figure there is a nonelementary saddle-node azeotrope on the methanol-isobutene edge that is the intermediate-boiling reactive azeotrope. However, the Poincaré index of such a singular point is zero and it does not enter into the constraint Eq. 78. We have also represented the *n*-butane vertex as a nonelementary half-saddle. This seems geometrically consistent with the inset in Figure 4, and without loss of topological consistency the pure component half-saddle may be substituted for the fine structure that may actually exist in that corner of the solution space (such as a quaternary saddle reactive azeotrope together with a stable node at the *n*-butane vertex). In Figure 4 $N_1 = 3$, $S_1^* = 0$, $S_E = 0$, $N_E = 1$, $S_F = 1$, $N_F = 0$, and again Eq. 78 is satisfied.

This constraint can be rederived for mixtures containing different types of nonelementary singular points. It can also be extended to mixtures represented in square-shaped solution spaces following the logic of Doherty (1990). The idea extends to solution spaces with other shapes, although no attempt has been made to do that here.

Conclusion

We have derived the necessary and sufficient conditions for reactive azeotropy in multicomponent, multireaction mixtures, and shown that they are conveniently written in terms of transformed composition variables. The conditions for reactive azeotropy take the same functional form in terms of transformed compositions as the conditions for azeotropy for nonreactive mixtures in terms of mole fractions. The example system demonstrates that chemical reaction has a significant influence on phase equilibria and azeotropy since it induced the formation of an intermediate-boiling ternary reactive azeotrope and a quaternary reactive azeotrope of the saddle type. In addition, it eliminated two of the nonreactive binary azeotropes (methanol + MTBE, and methanol + isobutene) and left the third nonreactive binary azeotrope between methanol + *n*-butane unaffected.

Our theory provides a thermodynamic framework for understanding azeotropy in reactive systems and should be useful for interpreting experimental data and phase equilibrium calculations.

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Notation

A_i = chemical species
G = total Gibbs free energy
l = normalized liquid molar holdup defined in Eq. 29
$\hat{s}_i$ = transformed molar entropy
v = normalized vapor molar holdup defined in Eq. 29
$\hat{v}_i$ = partial transformed-molar-volume
$\boldsymbol{x}$ = column vector of $(C-1)$ liquid mole fractions
$\boldsymbol{x}_{\mathrm{Ref}}$ = column vector of mole fractions for the R reference components in the liquid phase
$\boldsymbol{X}$ = vector of the $(C-R-1)$ independent liquid transformed composition variables
$\boldsymbol{y}$ = column vector of $(C-1)$ vapor mole fractions
$\boldsymbol{Y}$ = vector of the $(C-R-1)$ independent vapor transformed composition variables
$\boldsymbol{y}_{\mathrm{Ref}}$ = column vector of the mole fractions for the R reference components in the vapor phase
$\boldsymbol{z}^0_{\mathrm{Ref}}$ = column vector of initial overall mole fractions of the R reference components

Greek letters

$\Delta\hat{s}_i$ = difference between the transformed molar entropy in the vapor and in the liquid $\hat{s}_i^v - \hat{s}_i^l = T\Delta\hat{h}_i$
$\Delta\hat{v}_i$ = difference between the transformed molar volume in the vapor and in the liquid $\hat{v}_i^v - \hat{v}_i^l$
ν_{ir} = stoichiometric coefficient of component i in reaction r
ν_{Tr} = sum of all stoichiometric coefficients for reaction r
ξ_r = dimensionless extent of reaction for reaction r

Subscripts and superscripts

k = component
j = inert component
Ref = reference components
0 = initial value
l = liquid phase
T = transpose of matrix or vector
v = vapor phase
-1 = inverse of matrix

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