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Artificial neural networks for the solution of the phase stability problem

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Abstract

The prediction of the thermodynamic properties of multiphase systems is complex, because, besides equilibrium calculations, it involves determination of the number and nature of the phases present in the system (phase stability tests). For a system exhibiting a heterogeneous azeotrope, for example, the problem is to develop methods that can tell whether, for a given overall composition, the system lies inside or outside the binodal surface (two liquid phases in equilibrium or a single stable liquid phase). In this work, the application of artificial neural networks (ANNs) for the solution of the phase stability problem, a classification problem, is proposed. The input–output patterns, required for training the networks, were obtained computationally for the range of temperatures that covers liquid–liquid equilibrium, vapor–liquid–liquid equilibrium, vapor–liquid equilibrium and homogenous liquid and vapor. Hence, the ANN must be able to decide between these five possible regions. Two types of ANNs were tested: feedforward neural networks (FNNs) and probabilistic neural networks (PNNs). The results indicate that each kind of ANN is better for different conditions, the developed ANNs were able to predict correctly the type of equilibrium in more than 99.9% of the cases.

Keywords: Thermodynamic properties; Phase stability analysis; Artificial neural networks

1. Introduction

The knowledge of the thermodynamic behavior of a system is very important in the design, simulation and operation of separation processes. Consider, for example, the dehydration of ethanol, produced by the fermentation of sugar cane. The system water–ethanol has a homogeneous azeotropic point at about 90 mol% of ethanol, and thus cannot be separated by simple distillation. To produce anhydrous alcohol for use as a fuel, an entrainer is added to the mixture; the entrainer builds a binary heterogeneous azeotrope with water and a ternary heterogeneous azeotrope with ethanol–water, leading to a heterogeneous azeotropic distillation process.

A heterogeneous stream is thus produced in this process at the top of the column that is then split in a decanter into an entrainer-lean distillate and an entrainer-rich reflux stream. One of the main problems met in analyzing a multiphase distillation process is to determine if and at which of the upper plates of the column the formation of two ternary liquid phases occur. This is a *phase stability problem*. Basically, this kind of problem can be solved by two different approaches [1]. In the first approach, methods are based on the conservation of mass and the equal-fugacity criterion [2]. To obtain the correct solution using these methods one needs to have access to good initial guesses for the composition of those phases. Such methods, however, do not guarantee the attainment of the minimum Gibbs energy of the system, leading frequently to the prediction of trivial solutions or of an incorrect phase distribution. The techniques following the second approach are based in the minimization of the Gibbs energy subjected to the mass conservation and the equal-fugacity criteria [1,3]. These methods can be considered superior, but they are much more computationally demanding. The precision of both the types of methods can be limited by the accuracy of the liquid phase thermodynamic model (EOS, NRTL, etc.).

Although thermodynamically well defined, the phase stability problem still builds a considerable challenge for the design engineer, when trying to use interactive numerical procedures to solve it. So, according to Mohanty [4], the use of this type of procedures for VLE calculations makes it unsuitable for use in real time control. The aim of this work is to develop and evaluate a simple yet accurate method for the solution of the *phase stability* problem for the particular case of a ternary system with

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a heterogeneous azeotropic point, using the properties of the artificial neural networks.

2. Pham and Doherty's method

One of the first solutions of the phase stability problem is the well known tangent-plane criterion [5], which establishes that for a system at a specified pressure and temperature a phase with the overall composition x is stable if the Gibbs free energy surface of the system always lies above the plane tangent to the surface at x. According to this criterion, the necessary and sufficient mathematical condition for the stability of a phase with overall composition x is [6]:

$$F(y) = \sum_{i=1}^{\mathrm{nc}} y_i[\mu_i(y) - \mu_i(x)] \geq 0. \quad (1)$$

μ is the chemical potential of the component i, nc is the number of components in the mixture, and $F(y)$ is the vertical distance from the plane tangent to the Gibbs energy surface at composition x to the Gibbs energy surface at composition y. Furthermore, the points of tangency $F(y) = 0$ are *good estimates for the composition of the phases present in equilibrium*. The difficulty in finding all the solutions of the equation $F(y) = 0$ with complete certainty led to the development of different techniques for its solution [7–9] as well as for the solution of the stability problem.

Pham and Doherty [10] proposed a simple method for the stability analysis of heterogeneous azeotropic ternary systems that have an upper critical solution temperature (UCST), by far the most common in azeotropic distillation. Suppose a ternary system exhibiting a liquid immiscibility, at constant pressure, with overall composition (x_1, x_2) and temperature T_0, as represented by point P in Fig. 1. To answer the question if at these conditions the equilibrium state will have *one* or *two* liquid phases (LLE), Pham and Doherty proposed the use of a maximum temperature criterion. As shown in Fig. 1, if the point P falls in the binodal plane of the system at temperature T_0, then the line drawn vertically upward from P into the T–x will always intersect the binodal envelope at a point P_1, corresponding to the same overall composition and to a temperature $T_{\max}$.

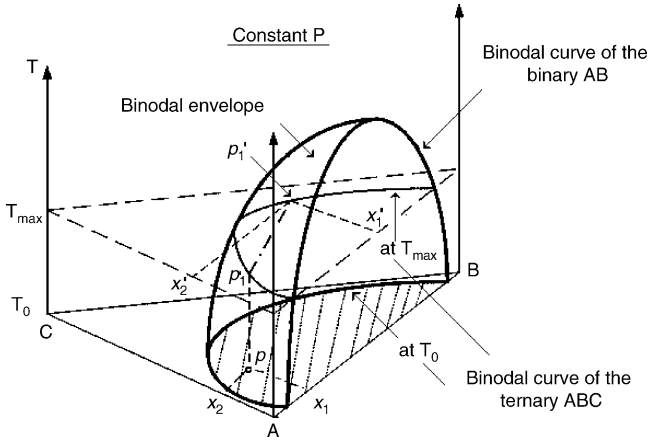

Fig. 1. Schematic ternary phase diagram with liquid immiscibility.

This temperature $T_{\max}$ is thus the maximum temperature for which at the given pressure and overall composition (x_1, x_2) two liquid phases coexist. At temperature $T_{\max}$ there is a second liquid phase, represented by point P_1', which is connected to P_1 by a tie-line, and the two liquid phases at P_1 and P_1' must satisfy the equilibrium condition,

$$x_i\gamma_i(T_{\max}, x) - x_i'\gamma_i(T_{\max}, x') = 0 \quad (i = 1, 2, 3), \quad (2)$$

subject to the conditions,

$$\sum_{i=1}^{3} x_i - 1 = 0, \qquad \sum_{i=1}^{3} x_i' - 1 = 0. \quad (3)$$

γ is the activity coeficient, x and x' are the mole fractions of the liquid phases in equilibrium at the given pressure. Eqs. (2) and (3) build a system of five equations in seven variables; thus, given two values of the x_i (for example, x_1, x_2), the values of $T_{\max}$, x_3, x_1', x_2', x_3' can be calculated. If at the specified pressure and composition (x_1, x_2) the point P lies outside the binodal surface, no solution for $T_{\max}$ will be found; in this case, the search for $T_{\max}$ is made in a restricted range of temperature [TL, TH]. When one of these limit temperatures is reached in the calculations, the phase splitting is not possible and the original mixture is considered homogeneous. When, for a given pressure, the composition (x_1, x_2) lies in the region in which VLLE occurs, the value of $T_{\max}$ found will be a *virtual* one, as the actual equilibrium conditions require that the two liquid phases P_1 and P_1' (Fig. 1) must be in equilibrium with a vapor phase, a condition that is incompatible with the binodal surface.

The determination of $T_{\max}$ was integrated in a computer program used to solve the phase split problem at given temperature, pressure and composition, for a ternary system with a heterogeneous azeotrope. As shown in Fig. 2, this program allows the distinction between the various possible regions of the phase space (liquid homogeneous, vapor homogeneous, VLE, LLE and VLLE).

The calculations of T_{BUB} and T_{DEW} were made based in the procedures presented by Smith et al. [11], through the implementation of a robust algorithm to generate the initial guesses. The calculation of T_{AZEO} was made using the method presented by Pham and Doherty [10]. If LLE is detected, the following calculations are made using the procedure proposed by Walas [12]. This program was used to build the database necessary for the construction of the artificial neural networks.

3. Artificial neural networks (ANNs)

Artificial neural networks were developed in an attempt to imitate, mathematically, the characteristics of the biological neurons. They are composed by interconnected artificial neurons responsible for the processing of input–output relationships. These relationships are learned by training the ANN with a set of input–output patterns. The ANNs can be used for different purposes; approximation of functions and classification are examples of such applications. The most common types of ANNs used for classification are the feedforward