6-30-1954

A study of methods for predicting the change in azeotropic composition with pressure and with temperature

Adolf Joseph Pribush
New Jersey Institute of Technology

Recommended Citation

Pribush, Adolf Joseph, "A study of methods for predicting the change in azeotropic composition with pressure and with temperature" (1954). *Theses*. 2269.
https://digitalcommons.njit.edu/theses/2269

A STUDY OF METHODS
FOR
PREDICTING THE CHANGE IN AZEOTROPIC COMPOSITION
WITH
PRESSURE AND WITH TEMPERATURE

BY

ADOLF PRIBUSH

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1954

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

____

____

NEWARK, NEW JERSEY
JUNE, 1954

ACKNOWLEDGEMENT

This work was carried out under the guidance of Joseph Joffe, Department of Chemical Engineering, Newark College of Engineering.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Tables of Pressure-Temperature-Composition Data for Binary Azeotropes and Physical Properties of Their Components:

INTRODUCTION

Much data can be found in the literature giving the pressure-temperature-composition relationship for azeotropic systems at one pressure, usually atmospheric. Comparatively few data, however, have been published giving compositions over a range of pressures and temperatures for azeotropic systems. Such data may be useful in application to the separation of liquid mixtures by azeotropic distillations, or even simple fractionations, at pressures other than atmospheric. It may be found, for instance, that a particular system that forms an azeotrope at atmospheric pressure (and therefore cannot be separated beyond the azeotropic composition by means of a simple fractionation at atmospheric pressure) becomes non-azeotropic at another pressure, enabling a complete separation by means of a simple fractionation.

In the absence of complete pressure-temperature-composition data for many azeotropic systems, it is desirable to have reliable mathematical relationships available for predicting such data. A number of relationships for predicting the change in azeotropic composition with change in pressure and temperature can be found in literature, but not all of them have been checked sufficiently against experimental data to enable their use with a knowledge of the degree of accuracy that can be expected.

Object

The object of this paper is to present the results of a study of methods for predicting the change in azeotropic composition with pressure and with temperature, and to indicate the usefulness of the methods.

Scope

A study was made of the types and formation of azeotropes, the general effect of pressure and temperature on azeotropes, and published methods for predicting the effect of pressure and temperature on the composition of azeotropes. Each of these phases of study is presented in consecutive order to supply background information.

Limitations. Two methods were tested with experimental data. Each method was tested with experimental data for ten azeotropic systems for which the most complete data could be found in literature. Only binary systems were used. The systems included maximum and minimum-boiling homogeneous azeotropes, and one minimum-boiling heterogeneous azeotrope. One of the methods tested represents a pressure-composition relationship, and the other represents a temperature-composition relationship.

The information presented in this paper is based on a literature search covering the years 1937-1953.

Materials and Equipment

All calculations were made with a calculating machine in conjunction with a five-place logarithm table. The calculations are reported to at least one place beyond that of the data found in the literature. Where vapor pressure data for pure components appeared with azeotropic data, it was used in the calculations made for its respective azeotropic system for the sake of consistency. Where vapor pressure data for pure components did not appear with their respective azeotropic systems, published vapor pressure tables were used.

Procedures

In the case of the equation tested for predicting the azeotropic temperature-composition relationship, the constants were determined by two methods. The method of least squares was used for those systems having ten or fewer points, and the method of averages was used for those systems having more than ten points.

The vapor pressure data for pure components used in the equation tested for predicting azeotropic pressure-composition relationship was obtained from the sources mentioned above, using a log vapor pressure versus $1/(^{\circ}C + 230)$

relationship.

Findings

The findings, and the azeotropic and pure component vapor pressure data obtained from the literature, are presented in table form for easy reference.

Plan of Thesis

The plan of the thesis is to present general information concerning definitions, theory of formation, and relationship of pressure, temperature, and composition, of azeotropes for background information. A short review is then given of published methods for predicting the change in composition of azeotropes with the change in pressure and temperature, indicating the nature of their derivation, references, and expected accuracy. The results of testing two equations for adequacy in predicting the change in composition of azeotropes with the change in pressure and temperature are then presented and evaluated. In the final section of the text, conclusions are given concerning the work covered by this paper.

DEFINITIONS AND THEORY OF AZEOTROPE FORMATION

Definitions

An azeotrope is characterized by a constant boiling point and composition, at a fixed pressure, of a mixture of two or more liquid compounds. It is also called a constant boiling mixture (C.B.M.). An azeotrope cannot be separated into its components by a simple fractionation at a given pressure, since the composition and boiling point will remain constant.

Some azeotropes exist as one liquid phase (homogeneous mixtures) and others exist as two or more liquid phases (heterogeneous mixtures). This serves as a basis for the classification of azeotropes. They are further subclassified as minimum-boiling or positive azeotropes, and maximum-boiling or negative azeotropes. The positive and negative classifications indicate that the mixture shows positive, or negative, deviations from Raoult's law. Homogeneous azeotropes have been found to exist as minimum and maximum-boiling mixtures. All reported heterogeneous azeotropes are minimum-boiling mixtures (16).

Formation of Azeotropes

The partial pressure of a component in equilibrium with a solution in a binary system that adheres to Raoult's law will be directly proportional to its mole fraction in the system. For such a system, the vapor pressure of the mixture could not be greater than that of the component with the highest vapor pressure, or less than that of the component with the lowest vapor pressure, and an azeotrope could not occur. Such a system would be ideal, and the non-ideality activity coefficient would be equal to unity. However, only a few binary mixtures follow Raoult's law at all concentrations. Most systems exhibit either positive or negative deviations from Raoult's law. For those cases where a combination of the magnitude of deviation from Raoult's law, plus the magnitude of the boiling point difference of the two components is such that the vapor pressure of the system will be greater than that of the component with the highest vapor pressure, or less than that of the component with the lowest vapor pressure, an azeotrope will occur. Heterogeneous azeotropes tend to form when the deviations are of such magnitude that immiscible liquid phases are formed.

GENERAL EFFECTS OF PRESSURE AND TEMPERATURE ON AZEOTROPES

Effect of Pressure and Temperature on Composition

In examining the experimental data of binary azeotropic systems, it can be seen that the composition changes with a change in pressure and temperature. The nature of this change in composition is indicated by Wrewski's rule which can be stated as follows:*

> "When the boiling point of a positive azeotrope rises, its composition changes in favor of the component with the higher molecular latent heat of vaporization.----Conversely, in the case of negative azeotropes, when the boiling point rises, there is an increase in the concentration of the component with the lower latent heat of vaporization."

A graphical representation of this rule is given for a positive azeotrope by Swietoslawski (21). It is pointed out by Swietoslawski, that the upper limit in the increase of pressure (temperature) is the critical point of one of the components. Some azeotropes are known to become non-azeotropic before this point is reached, and others are known to be azeotropic up to the critical point of the components. Experimental data for the ethyl alcohol-water azeotrope shows that this system follows Wrewski's rule (see Table No. 22).

---

*Perry, J. H., ed., Chemical Engineers' Handbook, Third Edition, p. 631.

The mole fraction of water (the component having the higher molecular latent heat) increases as the pressure (temperature) increases. The data shows that the system becomes non-azeotropic at low pressures. It should be possible theoretically, therefore, to obtain a complete separation of alcohol from water by means of a simple fractionation using a pressure at which the system is non-azeotropic (16).

Pressure-Temperature Relationship

In a study of the vapor pressure-temperature relationship of azeotropes, Licht and Denzler (8) found that equations analogous to the Clapeyron equation should apply to all types of azeotropes. They found that azeotropes have vapor pressure-temperature curves that are similar to those of pure components, and extend over the pressure range of the azeotrope for a particular system.

Othmer and Ten Eyck (13), using the Clausius-Clapeyron equation as a basis, and the fact that the composition of the liquid phase is the same as that of the vapor phase ($x_1=y_1$) for an azeotropic system in equilibrium, derived a series of equations that show straight line relationships on a logarithmic plot. In one set of equations the variables are partial pressures, compositions (of either vapor or liquid), and activity coefficients, versus the total pressure of the azeotrope. In another set of equations the variables are total pressure, partial pressures, compositions (of either vapor or liquid), and activity coefficients, versus the vapor pressure of a pure component. The slopes of the equations involve latent heat ratios and heats of solutions. However, these equations do not exactly define the azeotropic system because the heat ratios were assumed constant in their derivations in order to allow integration of the basic differential equation.

The Cox chart, which is a plot of the Antoine equation, has been used by Nutting and Horsely (12) to predict the azeotropic vapor pressure-temperature curve from two points of azeotropic data, or from the average slope of the pure component vapor pressure curves and one point of azeotropic data. All three curves are represented as a straight line on the Cox chart.

$$\log P = A - B/(t + 230) \qquad \text{Antoine equation} \quad 1$$

where:

P = pressure.
t = temperature, °C.
A = constant.
B = constant.

It is shown by Pennington (14), however, that one Antoine line on a Cox chart can only represent one azeotropic composition at some temperature, but not all azeotropic compositions at once. He therefore objects to the idea that an azeotrope can be represented by a straight line. He indicates a method, in his paper, for determining the true azeotropic curve by the use of a series of Antoine lines, each one representing one azeotropic composition at some temperature. He states that the slope of such a curve can be used to calculate the true molar latent heat of vaporization when substituted in the Clausius-Clapeyron equation.

PUBLISHED METHODS FOR PREDICTING THE EFFECT OF PRESSURE AND TEMPERATURE ON THE COMPOSITION OF AZEOTROPIC SYSTEMS

A number of methods for predicting the effect of pressure and temperature on the composition of azeotropic systems can be found in literature. Some of the methods are based on theoretical considerations, and others have been derived empirically. Several of these methods are reviewed in this section.

The modified Clausius-Clapeyron equation. As mentioned eariler in this paper, Othmer and Ten Eyck (13) have derived a group of equations that show straight line relationships on logarithmic plots when certain properties of azeotropic systems are plotted against others. They used the Clausius-Clapeyron equation as a basis, and also, the condition that $x_1 = y_1$ for an azeotropic system in equilibrium. The ratio of the heat quantities was assumed constant in the derivation. One of the equations derived is represented by Equation 2, which gives the relationship of an azeotropic system in terms of composition and azeotropic pressure as a straight line on a logarithmic plot.

$$\log y_1 = (L_1/L_z - 1) \log P_z + C \qquad 2$$

where:

y_1 = composition of component 1 in vapor phase (mole or wt. %).
L_1 = molal latent heat of component 1 from solution.
L_z = molal latent heat of azeotropic solution.
P_z = total pressure of azeotrope.
C = constant.

Using the relationship represented by Equation 2, azeotropic points at two pressures, or one azeotropic point and heat data (slope), will completely define an azeotropic system. The disadvantage of this equation is that azeotropic data at more than one pressure, and heat data, are not usually available. Othmer and Ten Eyck point out that the error involved, in the assumption that the heat ratio is constant, would be small, since the change in partial heat of solution of the pure component with concentration change is extremely small compared to the latent heat of vaporization of the pure component.

A number of azeotropic systems are plotted on a logarithmic plot by Othmer and Ten Eyck, and the experimental points are shown to fit very well on a straight line.

<u>Equation based on the two-suffix Margules equation</u>. Another method for predicting the composition of azeotropic systems with a change in pressure is given by Equation 3.

$$1/x_1 = \left(\frac{\log P_z/P_1}{\log P_z/P_2}\right)^{1/2} \neq 1 \qquad 3$$

where:

x_1 = concentration of the more volatile component in the liquid phase (mole fraction).
P_z = total pressure of azeotrope.
P_1 = vapor pressure of pure component 1 at azeotrope boiling point.
P_2 = vapor pressure of pure component 2 at azeotrope boiling point.

Equation 3 was derived from the symmetrical two-suffix Margules equation for calculating activity coefficients. It may be used for estimating the composition of binary azeotropes when only the total pressure of the azeotrope and the vapor pressures of the pure components at the boiling point of the azeotrope are known. An accuracy of better than ± 10% is claimed for this method (16).

Method of Carlson and Colburn. A method for predicting the composition of a homogeneous azeotrope with change in temperature, that is based on Equation 4 and the property of homogeneous azeotropes that $x_1 = y_1$, is given in a paper by Carlson and Colburn (3).

$$P\,y_1 = r_1\,P_1\,x_1 \tag{4}$$

$$P = r_1\,P_1 = r_2\,P_2 \tag{4a}$$

$$r_1/r_2 = P_2/P_1 \tag{4b}$$

where:

P = total pressure of the system.
P_1 = vapor pressure of pure component 1.
P_2 = vapor pressure of pure component 2.
r_1 = non-ideality activity coefficient for component 1.
r_2 = non-ideality activity coefficient for component 2.
x_1 = concentration of component 1 in the liquid phase (mole fraction or mole percent).
y_1 = concentration of component 1 in the vapor phase (mole fraction or mole percent).

The relationship 4b is developed from Equation 4 for the condition that $x_1 = y_1$. If a plot is made of r_1/r_2 versus the mole fraction of the most volitile component, and another is made of P_2/P_1 versus temperature, both on the same scale, then azeotropes can be picked off where the ordinates for the two curves are equal. This method can be used when activity coefficient and vapor pressure data are available for the pure components of a system.

When activity coefficient data are not available, they can be estimated from azeotropic data at one temperature using either the Margules or the Van Laar equations. (Carlson and Colburn have found that better results are obtained with the Van Laar equations than with the Margules equations (3).) The Van Laar constants are determined from the azeotropic composition data at one temperature, and are then substituted back into the Van Laar equations to estimate the activity coefficients at other concentrations. Since the activity coefficient data are obtained from data at one temperature, some error will be involved in extrapolating to other temperatures. This method will be most accurate when applied to systems where the azeotrope is in the middle half of the composition range.

Azeotropic pressures can then be obtained, from data already calculated, by means of Equation 4a.

The reference point equation. It is suggested by Hougen and Watson (7) that the azeotropic composition data over a range of temperatures, obtained by the above method of Carlson and Colburn, be used in conjunction with Equation 5 to calculate azeotropic pressures.

$$P_z = \frac{P'_z\,(x_1P_1 + x_2P_2)}{(x'_1P'_1 + x'_2P'_2)} \qquad 5$$

where:

P_z = vapor pressure of the azeotrope at temperature t.
P_1 = vapor pressure of component 1 at temperature t.
P_2 = vapor pressure of component 2 at temperature t.
P'_z = vapor pressure of the azeotrope at the reference temperature t'.
P'_1 = vapor pressure of component 1 at the reference temperature t'.
P'_2 = vapor pressure of component 2 at the reference temperature t'.
x_1 = mole fraction of component 1 in the azeotrope at temperature t.
x_2 = mole fraction of component 2 in the azeotrope at temperature t.
x'_1 = mole fraction of component 1 in the azeotrope at the reference temperature t'.
x'_2 = mole fraction of component 2 in the azeotrope at the reference temperature t'.

The pressures thus obtained can then be used in Equation 4a to obtain more reliable activity coefficient data, which might be used to obtain a complete equilibrium curve by means of the Margules or Van Laar equations. It is pointed out that insufficient work along this line has been done to allow an evaluation of the possible errors involved.

Equation 5 is an empirical equation for predicting azeotropic pressures from azeotropic composition data at different azeotropic boiling points and component vapor pressure data at corresponding temperatures. It is one of the equations tested in this paper against experimental data. The results are given in the next section.

<u>The curves of Horsely</u>. A series of plots for forty-five systems have been published by Horsely (5) that can be used to estimate boiling point and composition data for azeotropes. These plots were based on equations developed by Lecat for certain related groups of binary systems. Using the plot for the methanol-benzene system, Horsely was able to predict the boiling point of the azeotrope to within ± 1 to ± 3°C, and the composition to an accuracy of ± 1 to ± 4 weight percent, over a range of pressures from 200 to 11,000 Mm. Hg. Boiling point data at different pressures for the pure components are required in order to use the plots. Horsely has found that agreement between predicted and experimental values for most systems is not too good, and suggests that the value of this method lies mainly to serve as a guide in estimating the effect of pressure on azeotropes.

<u>The log x equation</u>. A linear relationship for the azeotropic composition as a function of the azeotropic

boiling point has been introduced in a paper by Skolnik (19). The relationship is expressed by Equation 6.

$$\log x = A - BT \qquad 6$$

where:

x = mole percent of one component in the azeotrope.
T = azeotropic boiling point ($^{\circ}K$).
A = a constant.
B = a constant.

Skolnik shows by a series of plots that this equation represents a number of homogeneous maximum-boiling and hydrocarbon-water heteroazeotropes very well. However, the majority of these systems shown have four or less points. In the homogeneous minimum-boiling classification, the methanol-benzene system is shown to be represented fairly well, but the ethanol-water and ethyl acetate-carbontetrachloride azeotropes are not represented too well.

Some azeotropic systems become non-azeotropic before the critical points of the components are reached. The point of non-azeotropy would be represented by Equation 6 for a condition when x = 100 mole percent. It would also be the point where the vapor pressure curves of the azeotrope and one of the pure components crossed. Skolnik found this point for the methanol-benzene system solving the Antoine equation for methanol and for the azeotrope, and checked the corresponding temperature with that obtained from Equation 6 when x = 100 mole percent for methanol. The temperature obtained from the Antoine equations was 202°C, and that obtained from the log x equation was 219°C. Skolnik felt that this was a good check considering the possibility for error in extrapolating the vapor pressure data.

Pennington (14) considered the log x equation as a possibility for representing the 1,1-difluoroethane-dichlorodifluoromethane system. He rejected it on the grounds that it does not allow x to become zero and therefore cannot truely represent an azeotropic system if Swietoslawski's (21) graphical representation of a maximum-pressure type of azeotrope is correct. Pennington also checked the log x equation against experimental data from four azeotropic systems and found that it did not fit the observed data as well as the T-parabola type of equation which will be considered next.

The T-parabola equation. The T-parabola equation of the type represented by Equation 7 was selected by Pennington (14) to represent the 1,1-difluoroethane-dichlorodifluoromethane system after finding that it gave a better fit than several other equations tested against experimental data for this and three other systems.

$$T = A + Bx + Cx^2 \qquad 7$$

where:

T = boiling point of the azeotrope (°K).
x = composition of one component in the azeotrope (mole %).
A = a constant.
B = a constant.
C = a constant.

The T-parabola equation also allows x to become zero, which allows extrapolation over the entire range of azeotropism for the system using this one equation. However, at least three azeotropic points are required to determine the constants and it is not a linear relationship, therefore, it cannot be applied as readily as the log x equation.

Two of the foregoing equations were selected for testing against experimental azeotropic data, Equations 5 and 6. Equation 5 was selected because no indication of its applicability or adequacy in predicting the pressure-composition relationship for azeotropic systems could be found in the literature. Equation 6 was selected for testing because it appeared to be the most easily applicable, being a linear relationship and requiring only two azeotropic points to define a system. For those systems that become non-azeotropic before the critical points of the components are reached, only one azeotropic point and the point of non-azeotropy, determined from the Antoine equation, are required. Extrapolating over the entire range of the azeotrope is made possible by solving the equation for each component separately, for when one component is 100 mole percent, the other is zero mole percent. In this manner, the points of non-azeotropy can be determined at both ends of the azeotropic system, if such points exist. The work of Skolnik (19) and Pennington (14) indicated that the log x equation represented most azeotropic systems fairly well, and therefore, it was decided to check this equation more extensively.

The results of testing Equations 5 and 6 against published experimental azeotropic data are given in the next section.

EQUATIONS TESTED FOR ADEQUACY IN PREDICTING CHANGE IN AZEOTROPIC COMPOSITION WITH CHANGE IN PRESSURE AND TEMPERATURE

The Reference Point Equation (Pressure vs. Composition)

Method of testing. Published data from ten binary azeotropic systems were used in testing Equation 5. The systems included seven homogeneous minimum-boiling, two homogeneous maximum-boiling, and one heterogeneous minimum-boiling azeotrope. The azeotropic reference point used in making the calculations was that for atmospheric pressure, or as close to atmospheric as was given in the experimental data. It was felt that this point would be the most accurate since it could be most easily checked against the results of other investigators. Also, it represented a mid-point for most systems. Wherever possible, experimental data from only one investigator were used to avoid the possibility of introducing errors in measurement due to different techniques used by different investigators.

In making the calculations, Equation 5 was simplified to Equation 5a.

$$P_z = K' \, (x_1P_1 + x_2P_2) \qquad \text{5a}$$

The vapor pressure data of the pure components were obtained by interpolating and extrapolating from published vapor pressure data using a log P versus $1/(^{\circ}C + 230)$ relationship. The calculations were made with a calculating machine in conjunction with a five-place logarithm table.

For all systems except the two homogeneous minimum-boiling systems, the experimental azeotropic composition data, and the vapor pressure data for the pure components, were substituted into the equation and the corresponding azeotropic pressures were calculated and compared with the observed values of total pressure. In the case of the two homogeneous maximum-boiling systems, hydrogen chloride-water and hydrogen bromide-water, the azeotropic boiling points were above the critical points of hydrogen chloride and hydrogen bromide except for the lowest point. Therefore, no vapor pressure data existed for these two components in the range of the azeotrope, and the equation could not be applied. Instead, the equation was revised to Equation 5b and used as such to calculate pseudo vapor pressure data for these two components.

$$P_1 = (P_z/K' - x_2P_2) \,/\, x_1 \qquad \text{5b}$$

The reference points used for these systems were the lowest given in the experimental data, since they were the only points below the critical points of the components in question. This pseudo vapor pressure data was then plotted on vapor pressure graph paper along with a plot of vapor pressure data extrapolated from below the critical points of the two components, for the purpose of comparison.

<u>Findings</u>. The systems used and a summary of the results are presented in Tables 1 and 1a. Tables 2 through 9 give the results for the individual systems tested with the exception of the two homogeneous maximum-boiling systems, to which the equation (Equation 5) did not apply. Figures 1 and 2 represent the results obtained for these two systems using Equation 5b.

In the homogeneous minimum-boiling group, Equation 5 predicted the azeotropic pressures to an overall accuracy of ± 3% in all systems except the methanol-benzene system. For this system the equation's accuracy was of the order of ± 15% overall.

There was a trend for the equation to become less accurate as the pressure increased, or decreased, from the reference pressure. For those systems where the overall accuracy was ± 3%, the deviations were as high as ± 6% at pressures of one atmosphere distant from the reference pressure. An exception to this was the n-propanol-water system, for which the percent deviation steadily decreased as far as seven atmospheres away from the reference pressure. The methanol-benzene system also showed the general trend of increasing percent deviation with increase, or decrease, in pressure from the reference pressure. The fact that it showed so great a deviation is probably due in part to the fact that this system was tested over a much wider span of pressures than any of the other systems. A contributing factor to this trend is the probable reduced accuracy of vapor pressure data at low and high pressures. A straight line relationship was used to extrapolate the vapor pressure data, and the vapor pressure curves are probably non-linear at very low pressures. At high pressures, a slight error in the data used for extrapolation can be magnified a great deal.

The fact that a clear-cut trend for all systems of this type was not obtained probably indicates that errors are present in the experimental azeotropic data. This appears to be especially the case for the methanol-benzene system, for which other experimental data can be found in the literature which do not agree with the data used in this paper (6).

Generally, the results indicate that for homogeneous minimum-boiling azeotropes, Equation 5 will predict the total azeotropic pressure with an accuracy of from ± 3% to ± 6%, within the range of one atmosphere above or below the reference pressure (atmospheric), with the higher deviation occurring as the pressure increases or decreases from the reference pressure. At pressures greater than one atmosphere from the reference pressure (atmospheric), deviations in the magnitude of ± 20% to ± 30% can be expected.

For the one heterogeneous minimum-boiling system tested, (Table 9, ethyl acetate-water) the results indicate that Equation 5 applies in the same manner as for homogeneous minimum-boiling azeotropes. Although larger deviations were obtained at low pressures (+ 16%) there is no justification for stating that this applies to all systems of this type, since only one such system was tested.

Figures 1 and 2 show that the vapor pressure data for hydrogen chloride and hydrogen bromide, above their respective critical points, obtained by substituting experimental data into Equation 5c, does not coincide with the vapor pressure data for these components extrapolated past their critical points from experimental data below their critical points. Therefore it can be concluded that Equation 5 does not apply to homogeneous maximum-boiling systems above the critical points of the components.

The Log x Equation (Composition vs. Temperature)

Method of testing. Published data from ten azeotropic binary systems were used in testing Equation 6. The systems included seven homogeneous minimum-boiling, two homogeneous maximum-boiling, and one heterogeneous minimum-boiling azeotrope. The method of least squares was used for those systems having ten or fewer points, and the method of averages was used for those systems having more than ten points. The equation was tested for both components of each system.

Findings. The systems used and a summary of the results are presented in Tables 10 and 10a. The results are given for each system separately in Tables 11 through 20. In general it was found that agreement between calculated and observed results was fairly good, less than one mole percent average deviation for a majority of the systems. Equation 6 seemed to represent all types of systems equally well, considering the nature of the experimental data used for each case.

The equation was solved for each component of each system primarily to enable the prediction of non-azeotropic points for the systems. It was found that in most cases better agreement between calculated and observed values was obtained using one component than when the other component was used, when predicting azeotropic compositions. The reason for this is not apparent from the results since no pattern or trend can be detected, and therefore, no conclusions can be drawn as to which component to use in a particular case to obtain the best results (e.g., the most,or least, volatile component, or, the component at the upper, or lower, end of the composition range of the system).

Equations 6 and 7 are compared in Table 21 for their ability to predict non-azeotropic points and to fit experimental data for four systems. The T-parabola type of equation is shown to be superior to the log x type of equation not only when compared to the log x equation as one equation, but also when the other component is represented by x. However, the differences in the results of the two equations are not great. These results agree with Pennington's findings for these two equations (14).

CONCLUSIONS

It has been shown that the reference point equation (Equation 5) can be used to estimate the pressures of binary homogeneous minimum-boiling and heterogeneous minimum-boiling azeotropes, from azeotrope temperature-composition data, with an accuracy of from ± 3% to ± 6% for most systems in the range of one atmosphere pressure above or below the reference pressure (atmospheric). At higher pressures, an accuracy of ± 20% to ± 30% should be expected. The accuracy of this equation is dependent upon the accuracy of the pure component vapor pressure data used.

It has also been shown that Equation 5 does not apply to binary homogeneous maximum-boiling azeotropes in the range above the critical points of the components.

Constants for the log x equation (Equation 6) have been calculated and tabulated for both components of ten binary azeotropic systems. It has been shown that the log x equation represents the composition-temperature relationship for these systems very well. Non-azeotropic points of a system can be estimated, when they exist, by solving the log x equation for x = 100 mole percent for each component separately.

A comparrison was made between the log x equation and the T-parabola equation (Equation 7) for their adequacy in predicting the temperature-composition relationship and non-azeotropic points for four binary azeotropic systems. It was shown that the T-parabola equation gave results that compared more favorably with observed data than did the log x equation, although the differences were not markedly great. However, the T-parabola is not a linear relationship and requires at least three azeotropic points in order to determine the constants. In this respect it is not as easy to apply as the log x equation, which is a linear relationship requiring only two azeotropic points to determine the constants for a system.

In addition, several other methods for predicting the effect of temperature and pressure on the composition of binary azeotropic systems, found in the literature, have been reviewed briefly and evaluated on the basis of evidence presented by other investigators.

Finally, the complete experimental data, found in the literature, for the thirteen azeotropic systems used in testing Equations 5 and 6 have been tabulated and presented in the appendix for easy reference.

TABLE 1. SYSTEMS USED TO TEST EQUATION 5

No.	System	Temp. Range, °C.	Pressure Range, Mm.	Composition Range,[a] Mole %	Reference
	Homogeneous Minimum-Boiling Azeotropes				
1	Ethyl alcohol-water	33.35-95.35	94.9-1451.3	88.69-100	(11,22)
2	Ethyl acetate-ethyl alcohol	-1.37-91.35	25.0-1475.5	78.01-45.13	(10)
3	Methanol-benzene	26-149	200-11,000	55.7-80.7	(5)
4	CCl_4-ethyl acetate	47.36-76.15	285.7-789.2	55.6-58.2	(17,18)
5	n-Butane-SO_2	-35-3	349.6-2014	40.5-35.6	(9)
6	trans-2-Butene-SO_2	-29-3	349.6-1558	27.7-32.5	(9)
7	n-Propanol-water	87-151	740-5930	43.17-45.15	(8)
	Heterogeneous Minimum-Boiling Azeotrope				
8	Ethyl acetate-water	-1.90-89.08	25.0-1441.3	64.95-84.56	(10)
	Homogeneous Maximum-Boiling Azeotropes				
9	HCl-water	48.724-122.98	50-1220	10.624-13.126	(2)
10	HBr-water	74.12-137.34	100-1200	16.505-18.091	(1)

[a] Composition given is for that of the first component listed.

TABLE 1a. SUMMARY OF RESULTS FOR EQUATION 5

No.	System	Average Deviation Mm. Hg	Average Deviation Percent	No. of Points
	Homogeneous Minimum-Boiling Azeotropes			
1	Ethyl alcohol-water	6.25	3.04	8
2	Ethyl acetate-ethyl alcohol	9.58	1.70	10
3	Methanol-benzene	1190	15.73	5
4	CCl_4-ethyl acetate	6.84	1.37	6
5	n-Butane-SO_2	43.40	2.59	5
6	trans-2-Butene-SO_2	27.88	2.04	4
7	n-Propanol-water	82.5	2.7	5
	Heterogeneous Minimum-Boiling Azeotrope			
8	Ethyl acetate-water	15.75	6.27	20
	Homogeneous Maximum-Boiling Azeotropes			
9	HCl-water[a]	----	----	17
10	HBr-water[a]	----	----	12

---

[a] Equation 5 does not apply in the range tested.

TABLE 2. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE ETHYL ALCOHOL-WATER SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	94.9	100.53	-5.63	5.933
2	100.0	104.93	-4.93	4.930
3	129.7	135.73	-6.02	4.641
4	198.4	203.65	-5.25	2.646
5	404.6	412.92	-8.32	2.056
6*	760.0	------	----	-----
7	1075.4	1070.01	5.39	0.501
8	1451.3	1443.12	8.18	0.564
Av. deviation disregarding sign--			6.25	3.039

---

*Reference point.

[a] Reference for azeotropic data: (11,22).

TABLE 3. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE ETHYL ACETATE-ETHYL ALCOHOL SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	25.0	24.43	0.57	2.280
2	77.4	75.95	1.45	1.873
3	117.2	115.16	2.04	1.741
4	219.9	215.15	4.75	2.160
5	423.0	418.19	4.81	1.137
6	578.2	573.57	4.63	0.801
7*	760.0	-------	----	-----
8	948.0	956.27	-8.27	0.872
9	1121.0	1139.07	-18.07	1.612
10	1475.5	1516.79	-41.29	2.798
Av. deviation disregarding sign--			9.58	1.697

---

*Reference point.

[a] Reference for azeotropic data: (10).

TABLE 4. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE METHANOL-BENZENE SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	200	183	17	8.50
2	400	393	7	1.75
3*	760	---	---	----
4	6,000	7,271	-1271	21.18
5	11,000	14,465	-3465	31.50
Av. deviation disregarding sign--			1190	15.73

*Reference point.

[a] Reference for azeotropic data: (5).

TABLE 5. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE CARBON TETRACHLORIDE-ETHYL ACETATE SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	285.7	288.67	-2.97	1.04
2	385.2	381.85	3.35	0.87
3	484.5	474.18	10.32	2.13
4	583.7	573.82	9.88	1.69
5	685.0	677.30	7.70	1.12
6*	789.2	------	----	----
Av. deviation disregarding sign--			6.84	1.37

*Reference point.

[a] Reference for azeotropic data: (17,18).

TABLE 6. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE n-BUTANE-SULFUR DIOXIDE SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	349.6	346.03	3.57	1.02
2*	752.4	------	----	----
3	1436.5	1413.34	23.16	1.61
4	1436.5	1416.02	20.48	1.43
5	2014	2140.39	-126.39	6.28
Av. deviation disregarding sign--			43.40	2.59

*Reference point.

[a] Reference for azeotropic data: (9).

TABLE 7. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE TRANS-2-BUTENE-SULFUR DIOXIDE SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	349.6	351.93	-2.33	0.67
2*	752.4	------	----	----
3	1428.8	1471.73	-42.93	3.00
4	1558	1596.37	-38.37	2.46
Av. deviation disregarding sign--			27.88	2.04

*Reference point.

[a] Reference for azeotropic data: (9).

TABLE 8. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE n-PROPANOL-WATER SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1*	740	----	--	---
2	1790	1727	63	3.5
3	2830	2723	107	3.8
4	3860	3770	90	2.3
5	5930	5860	70	1.2
Av. deviation disregarding sign--			82.5	2.7

*Reference point.

[a] Reference for azeotropic data: (8).

TABLE 9. PREDICTION OF AZEOTROPE PRESSURE FROM EQUATION 5 IN THE ETHYL ACETATE-WATER SYSTEM

No.	Azeotrope Pressure Observed[a], Mm. Hg	Azeotrope Pressure Calculated, Mm. Hg	Deviation, Mm. Hg	Deviation, Percent
1	25.0	29.18	-4.18	16.72
2	50.0	58.10	-8.10	16.20
3	78.5	90.76	-12.26	15.62
4	82.2	95.05	-12.85	15.63
5	150.0	166.09	-16.09	10.73
6	176.0	194.26	-18.26	10.38
7	250.0	268.78	-18.78	7.51
8	329.8	348.13	-18.33	5.56
9	420.0	436.72	-16.72	3.98
10	446.2	442.74	3.46	0.78
11	606.0	613.17	-7.17	1.18
12	613.8	635.99	-22.19	3.62
13	745.0	746.89	-1.89	0.25
14*	760.0	------	----	----
15	875.0	871.79	3.21	0.37
16	903.5	896.37	7.13	0.79
17	984.3	971.96	12.34	1.25
18	1177.9	1152.80	25.10	2.13
19	1415.0	1369.95	45.05	3.18
20	1441.3	1395.15	46.15	3.20
Av. deviation disregarding sign--			15.75	6.27

---

*Reference point.

[a] Reference for azeotropic data: (10).

Original Job 41463

Log P - (2 Cycle) x (t C - 230°)
FOR STRAIGHT-LINE PLOTTING

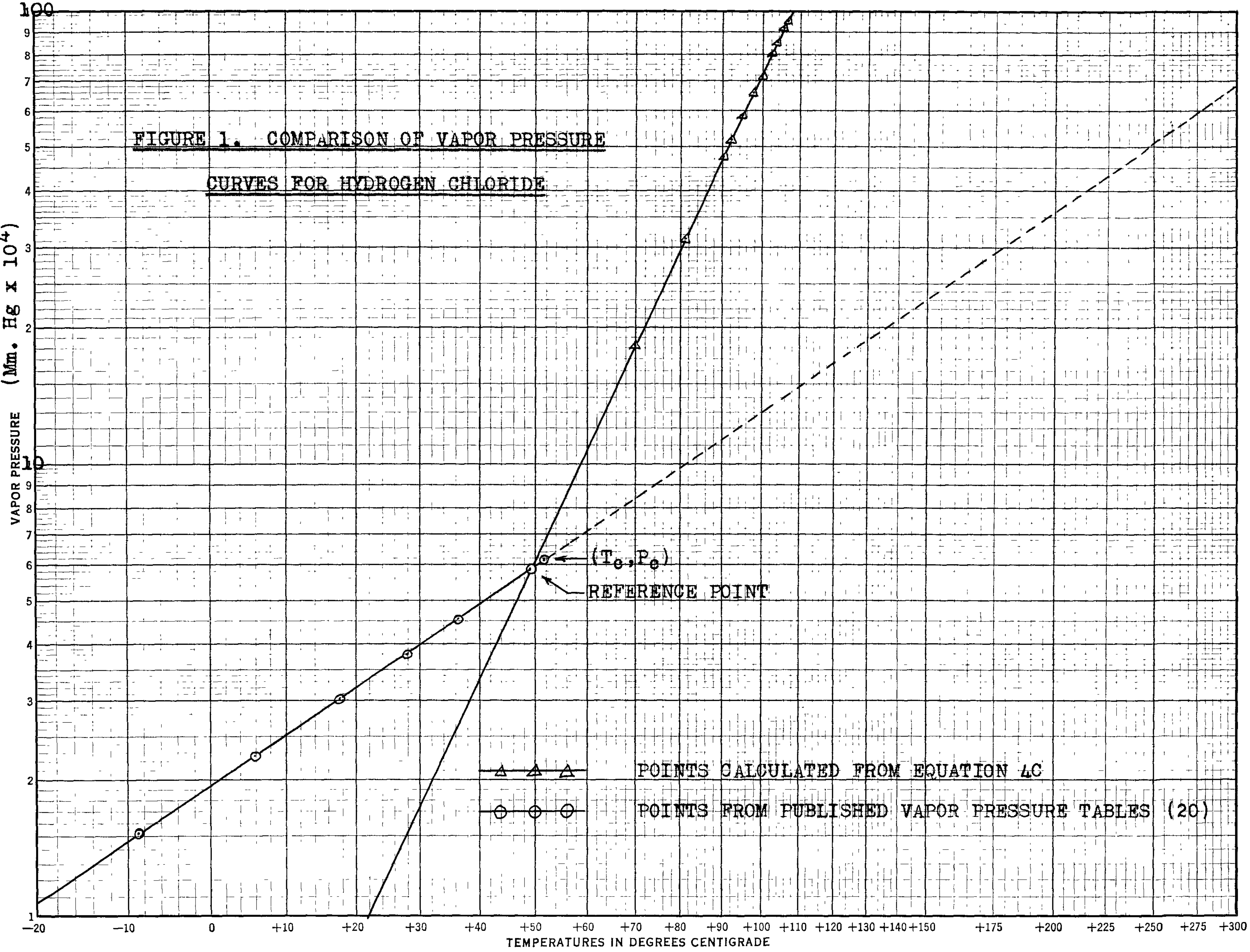

FIGURE 1. COMPARISON OF VAPOR PRESSURE CURVES FOR HYDROGEN CHLORIDE

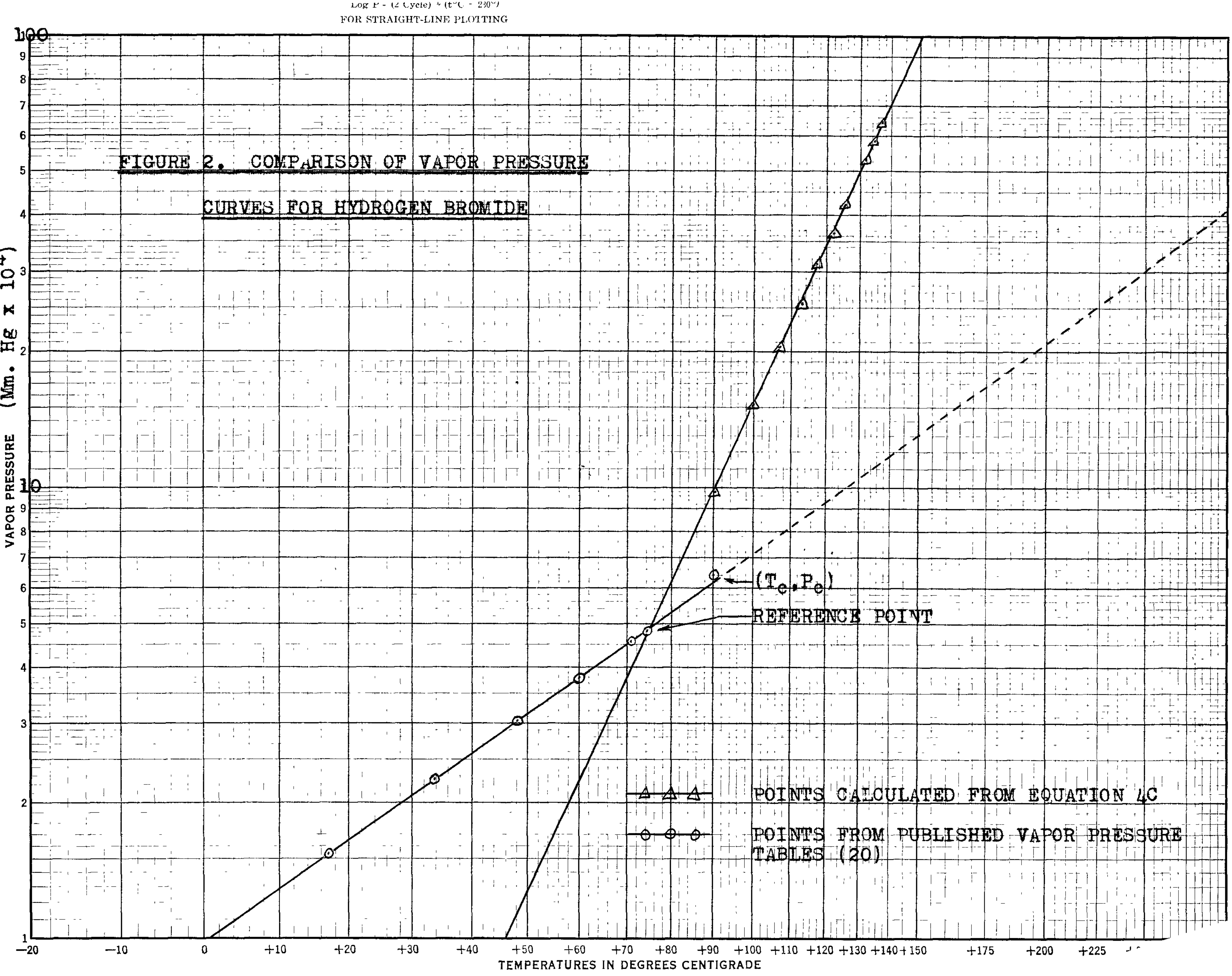

FIGURE 2. COMPARISON OF VAPOR PRESSURE CURVES FOR HYDROGEN BROMIDE

TABLE 10. SYSTEMS USED TO TEST EQUATION 6

No.	System	Temp. Range, °C.	Pressure Range, Mm.	Composition Range[a], Mole %	Reference
	Homogeneous Minimum-Boiling Azeotropes				
1	Ethyl alcohol-water	33.35-95.35	94.9-1451.3	88.69-100	(11,28)
2	Ethyl acetate-ethyl alcohol	-1.37-91.35	25.0-1475.5	78.01-45.13	(10)
3	Methanol-benzene	26-149	200-11,000	55.7-80.7	(5,19)
4	CCl_4-ethyl acetate	47.36-76.15	285.7-789.2	55.6-58.2	(17,18)
5	n-Butane-SO_2	-35-3	349.6-2014	40.5-35.6	(9)
6	Isobutene-SO_2	-35-3	349.6-1824	46.0-37.5	(9)
7	DCDFM[b]-DFE[c]	-30.5-40.08	----	65.36-55.22	(14)
	Heterogeneous Minimum-Boiling Azeotrope				
8	Ethyl acetate-water	-1.9-89.08	25.0-1441.3	84.56-64.95	(10)
	Homogeneous Maximum-Boiling Azeotropes				
9	HCl-water	48.724-122.98	50-1220	13.126-10.624	(2)
10	HBr-water	74.12-137.34	100-1200	18.091-16.505	(1)

---

[a] Composition given is for that of the first component listed.
[b] DCDFM = dichlorodifluoromethane.
[c] DFE = 1,1-difluoroethane.

TABLE 10a. SUMMARY OF RESULTS FOR EQUATION 6

No.	System	Constants[a] A	Constants[a] B	Av. Deviation, Mole %	No. of Points
	Homogeneous Minimum-Boiling Azeotropes				
1	Ethyl alcohol-	2.22630	0.0007713	0.86	8
	water	-4.05609	-0.0143062	2.10	
2	Ethyl acetate-	2.48849	0.0021885	1.76	10
	ethyl alcohol	0.15963	-0.0043640	0.37	
3	Methanol-	1.3508	-0.0013152	0.56	10
	benzene	2.52933	0.0028802	1.40	
4	CCl_4-	3.07827	0.0380721	0.53	6
	ethyl acetate	-0.87244	-0.0072389	0.74	
5	n-Butane-	1.99659	0.0016007	0.42	7
	SO_2	1.55771	-0.0008994	0.4	
6	Isobutene-	2.14299	0.0019337	3.14	6
	SO_2	1.37539	-0.0014295	3.1	
7	DCDFM[b]-	2.06353	0.0010246	0.12	4
	DFE[c]	1.16256	-0.0015656	0.24	
	Heterogeneous Minimum-Boiling Azeotrope				
8	Ethyl acetate-	2.31008	0.0013730	0.265	20
	water	0.12664	-0.0039570	0.68	
	Homogeneous Maximum-Boiling Azeotropes				
9	HCl-	1.57192	0.0013772	0.046	17
	water	1.87979	-0.0001807	0.037	
10	HBr-	1.52875	0.0007596	0.062	12
	water	1.78092	-0.0003631	0.908	

---

[a] The constants for both components of each system are given ($\log x = A - BT$, where: x = mole %, T = °K).

[b] DCDFM = dichlorodifluoromethane.

[c] DFE = 1,1-difluoroethane.

TABLE 11. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE ETHYL ALCOHOL-WATER SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % EthOH	Deviation[b], Mole % x=EthOH	Deviation[b], Mole % $x=H_2O$
1	306.51	98.73	1.00	-0.86
2	307.36	98.63	1.07	-0.82
3	312.36	96.74	0.05	0.67
4	320.79	93.57	-1.89	3.22
5	336.20	91.94	-0.74	3.39
6	351.31	89.47	-0.76	1.20
7	360.28	88.91	0.10	-1.45
8	368.51	88.69	1.18	-5.20
Av. deviation disregarding sign--			0.85	2.10

[a] Reference for azeotropic data: (11,22).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 12. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE ETHYL ACETATE-ETHYL ALCOHOL SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % EthAc	Deviation[b], Mole % x=EthAc	x=EthOH
1	271.79	78.01	-0.27	-0.04
2	291.87	73.37	2.62	-0.31
3	300.18	71.00	2.15	-0.29
4	313.66	66.02	2.63	0.46
5	329.47	60.08	1.63	0.64
6	337.59	56.85	0.66	0.54
7	344.97	53.87	-0.27	0.26
8	351.29	51.12	-1.32	0.00
9	356.21	49.03	-2.13	-0.38
10	364.51	45.13	-3.93	-0.81
Av. deviation disregarding sign--			1.76	0.37

---

[a] Reference for azeotropic data: (10).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 13. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE METHANOL-BENZENE SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % Methanol	Deviation[b], Mole % x=Methanol	Deviation[b], Mole % x=Benzene
1	299.16	55.7	0.20	-2.23
2	298.16	55.6	0.27	-2.40
3	316.16	57.5	-0.75	0.66
4	313.16	58.7	0.80	-1.10
5	329.86	59.9	-1.00	2.14
6	329.86	59.9	-1.00	2.14
7	331.46	61.5	0.30	0.96
8	330.16	61.9	0.94	0.22
9	397.16	74.8	0.13	0.91
10	422.16	80.7	0.16	-1.28
Av. deviation disregarding sign--			0.56	1.40

[a] Reference for azeotropic data: (5,19).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 14. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE CARBON TETRACHLORIDE-ETHYL ACETATE SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % CCl_4	Deviation[b], Mole %	
			$x = CCl_4$	$x = EthAc$
1	320.52	72.60	0.48	-1.64
2	328.38	67.75	1.98	0.29
3	334.48	63.73	-0.07	0.89
4	339.88	60.76	-0.10	0.53
5	344.72	58.2	-0.12	-0.17
6	349.31	55.60	-0.42	-0.91
Av. deviation disregarding sign--			0.53	0.74

---

[a] Reference for azeotropic data: (17,18).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 15. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE n-BUTANE-SULFUR DIOXIDE SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % n-Butane	Deviation[b], Mole % x=n-Butane	Deviation[b], Mole % x=SO_2
1	238	40.5	-0.77	0.4
2	255	39.3	0.54	-0.5
3	255	38.9	0.14	-0.1
4	254	39.7	0.79	-0.8
5	268	36.9	-0.05	0.2
6	268	36.6	-0.35	0.5
7	276	35.6	-0.28	0.4
Av. deviation disregarding sign--			0.42	0.4

[a] Reference for azeotropic data: (9).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 16. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE ISOBUTENE-SULFUR DIOXIDE SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % Isobutene	Deviation[b], Mole % x=Isobutene	x=SO_2
1	243	46.0	-1.11	1.2
2	259	44.2	0.33	0.0
3	273	45.6	4.38	-3.9
4	273	46.4	5.18	-4.7
5	276	36	-4.67	5.0
6	276	37.5	-3.17	3.5
Av. deviation disregarding sign--			3.14	3.1

---

[a] Reference for azeotropic data: (9).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 17. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE DICHLORODIFLUOROMETHANE-1,1-DIFLUOROETHANE SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % DCDFM	Deviation[b], Mole % x=DCDFM	x=DFE
1	242.66	65.36	0.06	-0.23
2	273.16	60.60	-0.17	0.47
3	298.06	57.47	0.17	-0.05
4	313.24	55.22	-0.06	-0.20
Av. deviation disregarding sign--			0.12	0.24

[a] Reference for azeotropic data: (14).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 18. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE ETHYL ACETATE-WATER SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % EthAc	Deviation[b], Mole % x=EthAc	x=H_2O
1	271.26	84.56	-2.06	-0.41
2	283.21	83.22	-0.19	-0.89
3	291.61	81.99	0.76	-1.07
4	292.54	81.63	0.64	-0.87
5	304.51	78.21	0.23	0.33
6	307.98	77.51	0.38	0.34
7	315.71	75.32	0.05	0.92
8	322.22	73.55	-0.19	1.23
9	328.10	72.38	0.00	1.02
10	329.60	72.26	0.22	0.77
11	337.49	70.42	0.16	0.60
12	337.76	70.22	0.02	0.73
13	342.99	69.18	0.13	0.35
14	343.54	68.85	-0.08	0.53
15	347.54	68.05	-0.01	0.19
16	348.39	67.78	-0.10	0.21
17	350.82	67.38	0.02	-0.10
18	356.11	66.18	-0.06	-0.52
19	361.65	65.05	-0.04	-1.17
20	362.24	64.95	-0.02	-1.26
Av. deviation disregarding sign--			0.265	0.68

---

[a] Reference for azeotropic data: (10).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 19. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE HYDROGEN CHLORIDE-WATER SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % HCl	Deviation[b], Mole % x=HCl	Deviation[b], Mole % $x=H_2O$
1	321.884	13.126	-0.321	0.189
2	343.116	12.557[c]	-0.014	-0.010
3	354.365	12.158	0.027	-0.022
4	363.397	11.870[c]	0.082	-0.064
5	365.240	11.754[c]	0.034	-0.017
6	368.189	11.655[c]	0.045	-0.026
7	370.738	11.557	0.040	-0.020
8	372.813	11.471[c]	0.030	-0.011
9	375.369	11.385[c]	0.036	-0.020
10	377.127	11.305	0.019	-0.005
11	378.724	11.247	0.018	-0.005
12	379.584	11.214[c]	0.016	-0.005
13	381.019	11.158	0.010	-0.001
14	381.744	11.130	0.008	0.001
15	383.167	11.089	0.017	-0.011
16	389.345	10.831	-0.026	0.017
17	395.14[c]	10.624	-0.035	0.009
Av. deviation disregarding sign--			0.046	0.037

---

[a] Reference for azeotropic data: (2).

[b] Deviations have a positive sign when the calculated value is smaller.

[c] Interpolated.

TABLE 20. DEVIATIONS FROM OBSERVED VALUES IN PREDICTING AZEOTROPIC COMPOSITIONS FROM EQUATION 6 IN THE HYDROGEN BROMIDE-WATER SYSTEM

No.	Azeotrope Boiling Point[a], °K.	Azeotrope Composition[a], Mole % HBr	Deviation[b], Mole %	
			x=HBr	x=H_2O
1	347.28	18.091	-0.302	1.182
2	363.51	17.785	-0.106	0.385
3	373.07	17.523	-0.071	-0.009
4	380.16	17.316	-0.061	-0.293
5	386.10	17.156	-0.012	-0.546
6	390.98	17.020	-0.032	-0.751
7	395.16	16.901	-0.104	-0.926
8	398.95	16.800	-0.019	-1.-90
9	402.29	16.710	-0.007	-1.236
10	405.28	16.638	0.008	-1.375
11	407.96	16.566	0.012	-1.494
12	410.50	16.505	-0.012	-1.614
Av. deviation disregarding sign--			0.062	0.909

---

[a] Reference for azeotropic data: (1).

[b] Deviations have a positive sign when the calculated value is smaller.

TABLE 21. A COMPARISON OF THE LOG X AND THE T-PARABOLA EQUATIONS FOR ADEQUACY IN PREDICTING THE TEMPERATURE-COMPOSITION RELATIONSHIP AND NON-AZEOTROPIC POINTS OF AZEOTROPIC SYSTEMS

System	Method Used	Component (x)	Av. Deviation, Mole %	Temp. at Non-azeotropy, °K. At Low Pressure	Temp. at Non-azeotropy, °K. At High Pressure	Reference[a]
DCDFM[b]-	log x	DFE	0.24	-----	534.9	
DFE[c]	log x	DCDFM	0.12	63	-----	
	T-parabola	DFE	0.11	112	967	(14)
EthOH[d]-	log x	EthAc	1.76	223.2	-----	
EthAc[e]	log x	EthOH	0.44	-----	423.4	
	T-parabola	EthOH	0.24	184.4	401.1	(14)
EthOH-	log x	EthOH	0.85	-----	423.3	
water	log x	water	2.10	293.4	-----	
	T-parabola	water	----	314.0	565.3	
	Experimental		----	307	-----	(14)
MeOH[f]-	log x	Benzene	1.40	183.8	-----	
Benzene	log x	MeOH	0.56	-----	493.6	(14,19)
	T-parabola	MeOH	0.56	Neg. value	481	(14)
	Antoine	MeOH	----	-----	475	(19)

---

[a] Where no reference is given, the data was calculated by the Author.

[b] DCDFM = dichlorodifluoromethane.

[c] DFE = 1,1-difluoroethane.

[d] EthOH = ethyl alcohol.

[e] EthAc = ethyl acetate.

[f] MeOH = methyl alcohol.

APPENDIX

TABLES

OF

PRESSURE-TEMPERATURE-COMPOSITION DATA

FOR

BINARY AZEOTROPES

AND

PHYSICAL PROPERTIES OF THEIR COMPONENTS

TABLE 22

	Component 1	Component 2
System	Ethyl Alcohol	Water
Formula	C_2H_6O	H_2O
Formula Weight	46.07	18.016
Normal Boiling Point, °C.	78.4	100.0
Melting Point, °C.	-112	0.0
Critical Temperature, °C.	243.5	374.2
Critical Pressure, Mm. Hg	47,956	165,680

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[a]	Component 2[a]
1	-----	70.0	100.00	------	-----
2	33.35	94.9	98.73	94.7	38.0
3	34.2	100.0	98.63	98.9	39.9
4	39.20	129.7	96.74	129.4	52.7
5	47.63	198.4	93.37	198.1	81.7
6	63.04	404.6	91.94	403.0	171.2
7	78.15	760.0	89.47	755.4	329.0
8	87.12	1075.4	88.91	1066.4	470.5
9	95.35	1451.3	88.69	1439.3	642.0

---

[a] Reference: (11,22).

TABLE 23

	Component 1	Component 2
System	Ethyl Acetate	Ethyl Alcohol
Formula	$C_4H_8O_2$	C_2H_6O
Formula Weight	88.10	46.07
Normal Boiling Point, °C.	77.1	78.4
Melting Point, °C.	82.4	-112
Critical Temperature, °C.	250.1	243.5
Critical Pressure, Mm. Hg	28,804	47,956

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[a]	Component 2[b]
1	-1.37	25.0	78.01	22.2	10.7
2	18.71	77.4	73.37	68.7	40.4
3	27.02	117.2	71.00	105.5	66.4
4	40.50	219.9	66.02	191.3	138.2
5	56.31	423.0	60.08	362.4	298.2
6	64.43	578.2	56.85	487.7	427.9
7	71.81	760.0	53.87	635.0	585.2
8	78.13	948.0	51.12	784.7	754.8
9	83.05	1121.0	49.03	920.4	914.3
10	91.35	1475.5	45.13	1190.8	1246.7

---

[a] Reference: (10).

[b] Reference: (11).

TABLE 24

	Component 1	Component 2
System	Methanol	Benzene
Formula	CH_4O	C_6H_6
Formula Weight	32.04	78.11
Normal Boiling Point, °C.	64.7	80.1
Melting Point, °C.	-97.8	5.5
Critical Temperature, °C.	240.0	290.5
Critical Pressure, Mm. Hg	59,812	38,076

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[b]
1	26	200	55.7	126.9	95.03
2	25	223	55.6	120.4	90.7
3	42	400	57.5	279.0	191.9
4	40	---	58.7	254.2	176.6
5	56.7	725.5	59.9	537.2	341.7
6	56.7	737	59.9	537.2	341.7
7	58.3	760	61.5	-----	-----
8	57	760	61.9	544.2	345.5
9	124	6,000	74.8	5118.2	2594.2
10	149	11,000	80.7	9951.8	4589.8

---

[a] References: (5,19).

[b] Reference: (5).

TABLE 25

	Component 1	Component 2
System	Carbon Tetrachloride	Ethyl Acetate
Formula	CCl_4	$C_4H_8O_2$
Formula Weight	153.84	88.10
Normal Boiling Point, °C.	76.75	77.1
Melting Point, °C.	-22.6	-82.4
Critical Temperature, °C.	283.1	250.1
Critical Pressure, Mm. Hg	34,200	28,804

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[b]
1	47.36	285.7	72.60	279.36	250.21
2	55.22	385.2	67.75	366.93	342.26
3	61.32	484.5	63.73	453.55	431.93
4	66.72	583.7	60.75	547.06	527.66
5	71.56	685.0	58.2	643.37	627.46
6	76.15	789.2	55.60	746.78	735.83

---

[a] References: (17,18).

[b] Reference: (20).

TABLE 26

	Component 1	Component 2
System	n-Butane	Sulfur Dioxide
Formula	C_4H_{10}	SO_2
Formula Weight	58.12	64.06
Normal Boiling Point, °C.	-0.6	-10.0
Melting Point, °C.	-135	-73.2
Critical Temperature, °C.	152.8	157.2
Critical Pressure, Mm. Hg	27,360	59,052

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
	Boiling Point,	Pressure,	Composition, Mole %		
No.	°C.	Mm. Hg	Component 1	Component 1[b]	Component 2[b]
1	-35	349.6	40.5	164.89	204.80
2	-18	752.4	39.3	294.73	516.80
3	-18	752.4	38.9	294.73	516.80
4	-19	752.4	39.7	286.68	491.46
5	-5	1436.5	36.9	463.22	950.14
6	-5	1436.5	36.6	463.22	950.14
7	3	2014	35.6	869.12	1231.37

---

[a] Reference: (9).

[b] Reference: (20).

TABLE 27

	Component 1	Component 2
System	trans-2-Butene	Sulfur Dioxide
Formula	C_4H_8	SO_2
Formula Weight	56.10	64.06
Normal Boiling Point, °C.	1.0	-10.0
Melting Point, °C.	-105.4	-73.2
Critical Temperature, °C.	----	157.2
Critical Pressure, Mm. Hg	----	59,052

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[b]
1	-29	349.6	32.5	207.10	289.09
2	-14	752.4	31.6	414.23	628.94
3	1	1428.8	27.8	762.88	1226.37
4	3	1558	27.7	822.72	1331.37

---

[a] Reference: (9).

[b] Reference: (20).

TABLE 28

	Component 1	Component 2
System	Isobutene	Sulfur Dioxide
Formula	C_4H_8	SO_2
Formula Weight	56.10	64.06
Normal Boiling Point, °C.	-6.7	-10.0
Melting Point, °C.	----	-73.2
Critical Temperature, °C.	----	157.2
Critical Pressure, Mm. Hg	----	59,052

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1	Component 2[b]
1	-30	349.6	46.0	----	273.34
2	-14	752.4	44.2	----	628.94
3	0	1428.8	45.6	----	1176.38
4	0	1428.8	46.4	----	1176.38
5	3	1702.4	36	----	1331.37
6	3	1824	37.5	----	1331.37

---

[a] Reference: (9).

[b] Reference: (20).

TABLE 29

	Component 1	Component 2
System	n-Propanol	Water
Formula	C_3H_8O	H_2O
Formula Weight	60.09	18.016
Normal Boiling Point, °C.	97.8	100.0
Melting Point, °C.	-127	0.0
Critical Temperature, °C.	263.7	374.2
Critical Pressure, Mm. Hg	37,924	165,680

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[c]
1	87	740	43.17	493.5	468.7
2	110	1790	43.78	1191.3	1074.56
3	124	2830	44.07	1885.6	1687.81
4	135	3860	44.52	2595.8	2347.26
5	151	5930	45.15	4006.1	3667.00

---

[a] Reference: (8).

[b] Reference: (16).

[c] Reference: (4,15).

TABLE 30

	Component 1	Component 2
System	DCDFM[a]	DFE[b]
Formula	F_2CCl_2	$C_2H_4F_2$
Formula Weight	120.92	66.05
Normal Boiling Point, °C.	-29.2	-24.7
Melting Point, °C.	-155	----
Critical Temperature, °C.	111.5	108
Critical Pressure, Mm. Hg	30,096	----

	Azeotropic Data[c]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1	Component 2
1	-30.50	----	65.36	----	----
2	0.00	----	60.60	----	----
3	24.90	----	57.47	----	----
4	40.08	----	55.22	----	----

---

[a] DCDFM = dichlorodifluoromethane.

[b] DFE = 1,1-difluoroethane.

[c] Reference: (14).

TABLE 31

	Component 1	Component 2
System	Ethyl Acetate	Water
Formula	$C_4H_8O_2$	H_2O
Formula Weight	88.10	18.016
Normal Boiling Point, °C.	77.1	100.0
Melting Point, °C.	-82.4	0.0
Critical Temperature, °C.	250.1	374.2
Critical Pressure, Mm. Hg	28,804	165,680

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[a]	Component 2[b]
1	-1.90	25.0	84.56	21.5	3.986
2	10.05	50.0	83.22	43.1	9.240
3	18.45	78.5	81.99	67.8	15.921
4	19.38	82.2	81.63	71.2	16.873
5	31.35	150.0	78.21	127.2	34.373
6	34.82	176.0	77.51	149.3	41.756
7	42.55	250.0	75.32	209.1	63.295
8	49.06	329.8	73.55	273.1	88.284
9	54.94	420.0	72.38	343.7	117.7
10	56.44	446.2	72.26	364.1	126.4
11	64.33	606.0	70.42	484.4	181.9
12	64.60	613.8	70.22	492.4	184.2
13	69.83	746.0	69.18	592.0	222.0
14	70.38	760.0	68.85	603.5	237.5
15	74.38	875.0	68.05	692.9	218.6
16	75.23	903.5	67.78	713.0	291.9
17	77.66	984.3	67.38	772.8	322.8
18	82.95	1177.9	66.18	917.6	399.8
19	88.49	1415.0	65.05	1089.7	496.4
20	89.08	1441.3	64.95	1109.5	507.7

---

[a] Reference: (10).

[b] References: (4,15).

TABLE 32

	Component 1	Component 2
System	Hydrogen Chloride	Water
Formula	HCl	H_2O
Formula Weight	36.47	18.016
Normal Boiling Point, °C.	-85	100
Melting Point, °C.	-114.3	0.0
Critical Temperature, °C.	51.4	374.2
Critical Pressure, Mm. Hg	62,016	165,680

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[c]
1	48.724	50	13.126	58,891	86.81
2	69.956	150	12.557[d]	------	233.3
3	81.205	250	12.158	------	372.7
4	90.237	370	11.870[d]	------	530.51
5	92.080	400	11.764[d]	------	568.65
6	95.029	450	11.655[d]	------	634.58
7	97.578	500	11.557	------	696.55
8	99.653	540	11.471[d]	------	750.62
9	102.209	600	11.385[d]	------	821.90
10	103.967	640	11.305	------	874.06
11	105.564	680	11.247	------	923.94
12	106.424	700	11.214[d]	------	951.67
13	107.859	740	11.158	------	999.59
14	108.584	760	11.130	------	1024.46
15	110.007	800	11.089	------	1074.81
16	116.185	1000	10.831	------	1317.80
17	122.98[d]	1220	10.624	------	1635.33

---

[a] Reference: (2).

[b] Reference: (20).

[c] Reference: (4,15).

[d] Interpolated.

TABLE 33

	Component 1	Component 2
System	Hydrogen Bromide	Water
Formula	HBr	H_2O
Formula Weight	80.92	18.016
Normal Boiling Point, °C.	-67	100
Melting Point, °C.	-87.0	0.0
Critical Temperature, °C.	90.0	374.2
Critical Pressure, Mm. Hg	64,144	165,680

	Azeotropic Data[a]			Vapor Pressure of Pure Components, Mm. Hg	
No.	Boiling Point, °C.	Pressure, Mm. Hg	Composition, Mole % Component 1	Component 1[b]	Component 2[c]
1	74.12	100	18.091	46,620	278.52
2	90.35	200	17.785	------	532.80
3	99.91	300	17.523	------	757.56
4	107.00	400	17.316	------	970.60
5	112.94	500	17.156	------	1187.81
6	117.82	600	17.020	------	1389.15
7	122.00	700	16.901	------	1586.04
8	125.79	800	16.800	------	1783.63
9	129.13	900	16.710	------	1974.01
10	132.12	1000	16.638	------	2158.06
11	134.80	1100	16.566	------	2333.84
12	137.34	1200	16.505	------	2512.64

[a] Reference: (1).

[b] Reference: (20).

[c] Reference: (4,15).

REFERENCES

1. Bonner, Walter D., Bonner, Lyman G., and Guerney, Francis J., "Azeotropic Hydrobromic Acid Solutions at Pressures of 100 Mm. to 1200 Mm.," The Journal of the American Chemical Society, Vol. 55, April 6, 1933, pp. 1406-1409.

2. Bonner, W. D., and Wallace, R. E., "The Boiling Points of Constant Boiling Hydrochloric Acids," The Journal of the American Chemical Society, Vol. 52, No. 5, May, 1930, pp. 1747-1750.

3. Carlson, Harrison C., and Colburn, Allan P., "Vapor-Liquid Equilibria of Nonideal Solutions," Industrial and Engineering Chemistry, Vol. 34, No. 5, May, 1942, pp. 581-589.

4. Hodgman, Charles D. (ed.), Handbook of Chemistry and Physics, Thirtieth Edition. Cleveland, Ohio: Chemical Rubber Publishing Company, 1947.

5. Horsley, L. H., "Graphical Methods for Predicting Azeotropism and Effeft of Pressure on Azeotropic Constants," Azeotropic Data, (Advances in Chemistry Series 6). Washington, D. C.: American Chemical Society, 1952, pp. 321-328.

6. Horsley, L. H., "Table of Azeotropes and Nonazeotropes," Azeotropic Data, (Advances in Chemistry Series 6). Washington, D. C.: American Chemical Society, 1952, p. 30.

7. Hougen, Olaf A., and Watson, Kenneth M., Chemical Process Principles--Part Two, Thermodynamics. New York: John Wiley and Sons, Inc., 1948, pp. 662-663.

8. Licht, William, Jr., and Denzler, C. G., "Azeotropic Mixtures," Chemical Engineering Progress, Vol. 44, No. 8, August, 1948, pp. 627-638.

9. Matuzak, M. P., and Frey, F. E., "Separating Butenes from Butanes," Industrial and Engineering Chemistry, Analytical Edition, Vol. 9, No. 3, March 15, 1937, pp. 111-115.

10. Merriman, R. W., "The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures Above and Below the Atmospheric Pressure--Part I and Part II," *Journal of the Chemical Society*, Vol. 103, 1913, pp. 1790-1816.

11. Merriman, R. W., "The Vapor Pressure of the Lower Alcohols and Their Azeotropic Mixtures With Water--Part 1," *Journal of the Chemical Society*, Vol. 103, Part II, 1913, pp. 628-636.

12. Nutting, H. S., and Horsley, L. H., "Graphical Method for Predicting Effect of Pressure of Azeotropic Systems," *Azeotropic Data*, (Advances in Chemistry Series 6). Washington, D. C.: American Chemical Society, 1952, pp. 318-320.

13. Othmer, D. F., and Ten Eyck, E. H., Jr., "Correlating Azeotropic Data," *Industrial and Engineering Chemistry*, Vol. 41, No. 12, December, 1949, pp. 2897-2900.

14. Pennington, W. A., "Effect of Temperature on Azeotropy in 1,1-Difluoroethane and Dichlorodifluoromethane," *Industrial and Engineering Chemistry*, Vol. 44, No. 10, October, 1952, pp. 2397-2401.

15. Perry, John H. (ed.), *Chemical Engineers' Handbook*, Second Edition. New York: McGraw-Hill Book Company, Inc., 1941.

16. Perry, John H. (ed.), *Chemical Engineers' Handbook*, Third Edition. New York: McGraw-Hill Book Company, Inc., 1950.

17. Schutz, Philip W., "Binary Liquid Systems. I. Vapor-Liquid Equilibria in the System Carbon Tetrachloride-Ethyl Acetate," *The Journal of the American Chemical Society*, Vol. 61, October, 1939, pp. 2691-2693.

18. Schutz, Philip W., and Mallonee, Robert E., "Binary Liquid Systems. II. The Azeotropic Composition of Carbon Tetrachloride-Ethyl Acetate Mixtures as a Function of the Pressure," *The Journal of the American Chemical Society*, Vol. 62, June, 1940, pp. 1491-1492.

19. Skolnik, Herman, "Effect of Pressure in Azeotropy," Industrial and Engineering Chemistry, Vol. 43, No. 1, January, 1951, pp. 172-176.

20. Stull, Daniel R., "Vapor Pressure of Pure Substances," Industrial and Engineering Chemistry, Vol. 39, April, 1947, pp. 517-148.

21. Swietoslawski, W., Ebulliometric Measurements. New York: Reinhold Publishing Corporation, 1951, pp. 102-122.

22. Wade, John, and Merriman, R. W., "Formation of Azeotrope Mixtures of Ethyl Alcohol and Water Under Pressures From 1450 Mm. to 100 Mm. of Mercury," Journal of the Chemical Society, Vol. 99, Part I, 1911, pp. 998-1004.
