
DATA AND METHODS FOR EQUILIBRIUM STAGE CALCULATIONS

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Prediction methods for phase distribution ratios and enthalpies of coexisting equilibrium vapor and liquid phases are discussed with emphasis on recent developments. Equilibrium stage calculation procedures for multicomponent systems are reviewed, covering: single stage flash vaporization, minimum stages, minimum reflux, empirical correlations of reflux and stages, absorption-stripping factor method, direct and indirect plate-to-plate calculations, computer methods and internal heat balances. In this discussion, several little-known techniques are described.

Equilibrium stage processes, such as absorbers and distillation columns, represent a large portion of the equipment used in the chemical process industry. Absorbers and fractionators are simulated by theoretical columns of equilibrium stages for purposes of calculating component distributions, number of stages and internal flows. These equilibrium stage calculations require thermodynamic data for predicting the distribution of components between vapor and liquid and for making heat and material balances. For multicomponent and multistage systems these equilibrium stage calculations are made by iterative procedures which start with assumed products and/or stage conditions and converge to steady state conditions with vapor-liquid equilibrium and with heat and material balances existing on each stage.

Predicting the component distribution ratios and the enthalpies of coexisting equilibrium vapor and liquid for mixtures has long been a challenging problem for the practitioner of chemical engineering thermodynamics. Also, the development of procedures for making multicomponent, multistage separation calculations has long been an important problem for the chemical engineer engaged in process design work.

Improvements have been made in the data and methods for equilibrium stage calculations during each decade of the 1929 to 1969 period, but the advan-

ces have been much greater since the digital computer entered the picture about 20 years ago. High speed computing hardware plus algorithms or computing software permit making rigorous multicomponent, multistage, multiproduct and multifeed calculations in very short times. The objective of this paper is to review briefly the background and to describe the current status of several different data correlations and calculation methods.

THERMODYNAMIC DATA

Equilibrium stage calculations require two types of thermodynamic properties for the mixtures to be processed in the calculations, *i.e.* the equilibrium vapor-liquid distribution ration, $K = y/x$, and the enthalpy of the mixture. An important distinction between the K and H data needs should be kept in mind. For component distribution calculations, it is necessary to have the K -values for each and every component of the mixtures. Partial enthalpies for the individual components of a mixture are not necessary.

Making available these thermodynamic property tools for the design calculations is not a new problem for the process engineer. Technical data books containing K and H charts have provided the necessary information for making equilibrium stage calculations manually for about four decades. Experimental data and theoretical methods were used in preparing these charts and improving them. Flexibility was added by fitting empirical equations to the K and H versus T and P curves so that these data charts could be used to make equilibrium stage calculations on the digital computer also. As will be brought out in the discussions that follow, the K and H values of co-existing equilibrium vapor and liquid mixtures are thermodynamically interrelated. These interrelationships make it possible to predict H values that are consistent with the K values, which may be from experimental measurements, from charts, or from equations that are solved by the digital computer in a preliminary subroutine before starting the equilibrium stage calculations.

VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION RATIOS

Vapor-liquid equilibrium distribution ratios ($K_i = y_i/x_i$) have been measured experimentally, correlated graphically and predicted analytically. In this paper we are interested in correlation and prediction methods that are used in making equilibrium stage calculations. Most K -value correlation and prediction methods are a combination of theoretical and empirical relationships, *i.e.* are based on some experimental data and some fugacity calculations.

For real gas and non-ideal solutions, the K -value may be formulated by either of the following expressions:

$$K_i = [(p_i^0/P)/\Theta_i] [\gamma_i^L/\gamma_i^V] = (p_i^0/P) (\gamma_i^L/\Theta_i). \quad (1)$$

For ideal vapor mixtures, the vapor activity coefficient $\gamma_i^V = 1.0$, and for ideal liquid solutions, the liquid activity coefficient $\gamma_i^L = 1.0$. The imperfection pressure correction term Θ_i is a pure component fugacity function, modified by the Poynting effect. The ratio of the Raoult's law

K -ratio to imperfection pressure correction, i.e. $[(p_i^0/P)/\theta_i]$ is called the ideal K -value, K_1 . A generalized correlation has been developed giving K_1 as a function of reduced pressure and reduced vapor pressure, the latter variable combining the effects of temperature and component. This correlation is in graphical and equation form, Fig. 1 being the chart, which covers the hypothetical liquid states where $p_r^0 > 1.0$. This is necessary for this correlation method.

Having two activity coefficients, one for each phase as in Eq. (1), would make a K -value prediction very flexible, providing correlations can be developed for both γ_i^V and γ_i^L from experimental data on the compositions of the coexisting equilibrium vapor and liquid phases. Such a correlation has not been proposed for the vapor phase. The Scatchard-Hildebrand regular-solution theory¹⁻³ relationship has been used rather widely for the prediction of γ_i^L , however.

The second form of Eq. (1) contains only one activity coefficient that can be evaluated from experimental data and correlated, using values p_i^0 from vapor pressure equation and θ_i , from an equation of state.

Another K -value prediction relationship is the Chao-Seader⁴ method, which is

$$K_i = (v_i^L \gamma_i^L) / \theta_i. \quad (2)$$

In this correlation the fugacity coefficient, θ_i , was calculated by the Redlich-Kwong equation of state, the activity coefficient, γ_i^L , was found by the Scatchard-Hildebrand equation and the fugacity coefficient, v_i^L , was calculated by a generalized empirical equation from the reduced

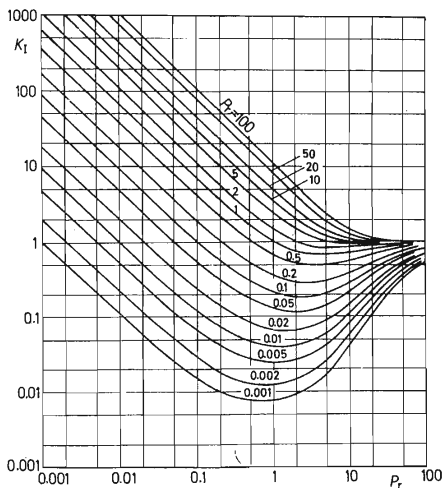


FIG. 1

Ideal K -Ratio as Function of Reduced Pressure and Reduced Vapor Pressure

temperature and acentric factor. A computer algorithm has been prepared for the prediction of vapor-liquid K -values from Eq. (2) and the related expressions for the three right-hand members. This computer form is widely used but has limitations at the higher pressures and for higher boiling components.

In addition to analytical correlations, vapor-liquid K -values can be correlated graphically as plots of K -values against pressure for lines of constant temperature or against temperature for lines of constant pressure. Both K -value and pressure scales are logarithmic, while reciprocal of absolute temperature is usually the best scale for temperature. Nomographic charts have also been used rather widely and successfully in correlating and predicting vapor-liquid K -values. In either of these graphical forms the K -values are independent of composition, except for the effect of the critical convergence pressure, which does vary somewhat with composition but is not an adequate composition parameter.

ENTHALPIES OF MIXTURES

There are two approaches to predicting enthalpies of saturated or dew point vapor and saturated or bubble point mixtures; 1. evaluating and combining enthalpies of the individual components of a mixture, or 2. evaluating the enthalpy for a hypothetical component that is equivalent to the mixture. In one version of the individual component method, enthalpy vs. temperature charts were prepared for each pure hydrocarbon of interest and these were applied to mixtures by assuming that the

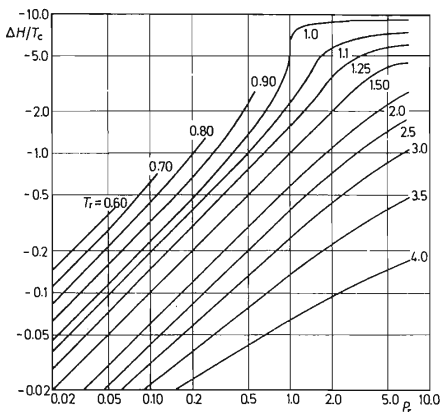


FIG. 2

Two-Parameter Generalized Isothermal Pressure Correction to Enthalpy $\Delta H/T_0$, BTU/mol, °R, of Pure Hydrocarbon Vapors

extrapolated vapor pressure curve was a "vapor-in-liquid-solution" state and that the pure component saturated vapor curve was a "liquid-in-vapor-solution" state. These are of historical interest as several versions of this type of enthalpy charts were in use during the 1940's.

These pure component hydrocarbon enthalpy-temperature charts were prepared by combining the changes in enthalpy at atmospheric pressure calculated from heat capacities with isothermal effects of pressure obtained from the generalized two-parameter correlation shown in Fig. 2. In addition to the effects of temperature and pressure, vapor pressures and heats of vaporization were found and/or calculated and included in the chart preparation.

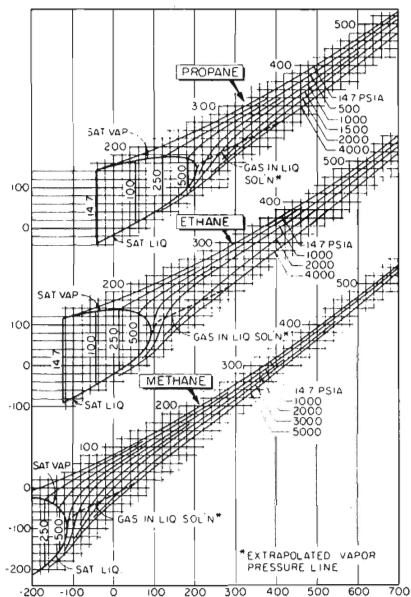


FIG. 3

Typical Hydrocarbon Enthalpy (H , BTU/Lb above liquid at 32°F) Plots with Hypothetical Gas in Liquid Solution Lines

Typical enthalpy-temperature diagrams are shown in Fig. 3 for three light hydrocarbons. On these $H - T$ plots, the dashed lines are drawn through the pressure *vs.* temperature points obtained by extrapolating the vapor pressures above the critical point. These were used as "gas-in-liquid-solution" curves in reading enthalpy values for the light super-critical components of the mixture. Enthalpy values for the higher-boiling components vapor mixtures were read from the pure component saturated-vapor curves at the vapor mixture temperature, even though the system pressure was greater than the pure component vapor pressure at this temperature.

An improvement on this individual component technique of applying this type of enthalpy-temperature chart to mixtures was proposed by Peters⁵ who added to each $H - T$ plot a family of "partial enthalpy" curves for the "gas-in-liquid-solution" region and extended the vapor region isobars across the saturated vapor curve and into the two phase region. The liquid phase partial enthalpy curves were drawn for several constant values of the average molecular weight or molal average boiling point of the liquid phase. These "partial enthalpy" lines for the liquid and vapor components were located by means of ideal solution heats of vaporization that were found *via* the temperature derivative of the ideal solution vapor-liquid K -values at constant pressure, *i.e.* $H^V - H^L = RT^2(\partial \ln K_i/\partial T)_p$. The method used by Peters is illustrated in Fig. 4.

In still another version of the individual component approach, partial enthalpy compilations (tables and/or charts) are made for each component of the mixtures as a function of temperature, pressure and composition, a separate compilation being made for each phase. Partial enthalpy differences for hydrocarbon mixture components have been computed in two ways; 1. by direct solution of the $\Delta \bar{H}_i$ expression derived from the Benedict-Webb-Rubin equation; and 2. by obtaining the temperature derivative of the fugacity coefficients previously found *via* the B-W-R equation.

The first mentioned calculations were made by Papadopoulos and coworkers⁶ for methane, ethane, and propane in solution with other hydrocarbons in both liquid and vapor phases over a range of temperatures and pressures. In the second work mentioned above, Canjar and Edmister⁷ calculated partial enthalpy differences for six hydrocarbons (methane, ethane, ethylene, propylene, propane, and n-butane) in solution with other hydrocarbons and over ranges of pressure and

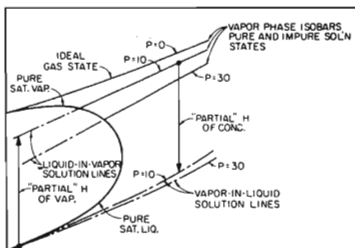


FIG. 4

Enthalpy-Temperature Plot for Pure Component, Illustrating Ideal Solution Partial Enthalpies

temperature. Smoothed values of partial enthalpy were plotted against temperature for lines of constant molal average boiling points of liquid and vapor for each several pressures of each component. The obvious disadvantage to such an enthalpy compilation is the large number of charts and the tedious work of reading them.

Fig. 5 illustrates these partial enthalpy difference plots. The parameter M.A.B.P. is the molal average, boiling point of the vapor or liquid mixture normal or atmospheric boiling points are used. Similar plots to the one given here for ethylene at 400 PSIA were made for the other hydrocarbons and pressures. In addition to these specific plots, a generalized correlation was developed giving the dimensionless quantity $(\bar{H} - H^0)_i / RT_c$ as a function of reduced pressure, reduced temperature and the boiling point ratio. The latter parameter is the ratio of the component boiling point to the molal average boiling point of the mixture. Separate correlations were made for the liquid and vapor phases.

Generalized correlations for the isothermal enthalpy difference appeared in the technical literature over three decades ago. These early ΔH correlations, which were in tabular and graphical forms, served as the basis for the derivation of other charts that were convenient for use in making manual heat balance calculations. The two most recent correlations are those of Lydersen and coworkers⁸ and Curl and Pitzer⁹, both being three parameter correlations.

In the Lydersen and coworkers⁸ correlation, the third parameter, in addition to reduced temperature and pressure, was the critical compressibility factor Z_c . Values of $(H^0 - H)/T_c$ were tabulated as functions of P_r and T_r for Z_c values of 0.23, 0.25, 0.27, and 0.29. In addition to the monophase, tables of properties for saturated vapor and liquid were included. Specifying T_r and P_r for saturated vapor and liquid, as these authors did, fixes the vapor pressure relationships for each Z_c value. This is theoretically possible for pure component systems, but not for mixtures for which the bubble and dew point pressures at a given temperature differ.

In the Curl-Pitzer⁹ correlation the third parameter was the acentric factor, ω . The isothermal enthalpy difference ratio is given as a generalized correlation of this acentric factor, and of reduced

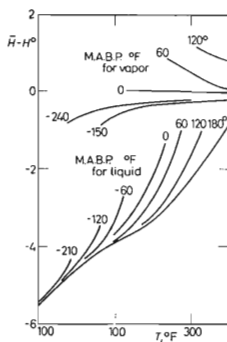


FIG. 5

Partial Enthalpies of Ethylene ($H - H^0$, 1000 BTU/Lb mol) in Vapor and Liquid Hydrocarbon Mixtures at 400 PSIA

temperature and pressure in tabular form. Plots of these generalized functions were prepared by this author¹⁰ and similar charts have been included in a trade publication¹¹.

Figs 6 and 7 are plots of the two parts of this three-parameter correlation for the isothermal effect of pressure on the enthalpy, where

$$(H^0 - H)/RT_c = [(H^0 - H)/RT_c]^0 + \omega[(H^0 - H)/RT_c]^1, \quad (3)$$

where, $[(H^0 - H)/RT_c]^0$ is from Fig. 6, $[(H^0 - H)/RT_c]^1$ is from Fig. 7, ω = acentric factor = $-\log P_r^0 + 1$, $T_r = 0.7$.

This generalized correlation for the isothermal pressure effect on the enthalpy was made for pure components but can be applied to mixtures *via* pseudo critical conditions, *i.e.* molal average of the T_{c1} , P_{c1} and ω_1 values.

The isothermal enthalpy difference for the individual or equivalent component, *i.e.* $\Delta H = H - H^0$; can also be found *via* an equation of state. Two pressure explicit equations of state have been used in making these derivations, *i.e.* the two-constant Redlich-Kwong¹² and the eight-constant Benedict-Webb-Rubin¹³ equations. In terms of pressure-volume-temperature, the isothermal enthalpy difference is given by

$$\frac{\Delta H}{RT} = \left[\frac{H - H^0}{RT} \right] = \frac{1}{RT} \int_{V_\infty}^V \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV + Z - 1. \quad (4)$$

Pressure and the temperature derivative of pressure are found from the equation of state, from

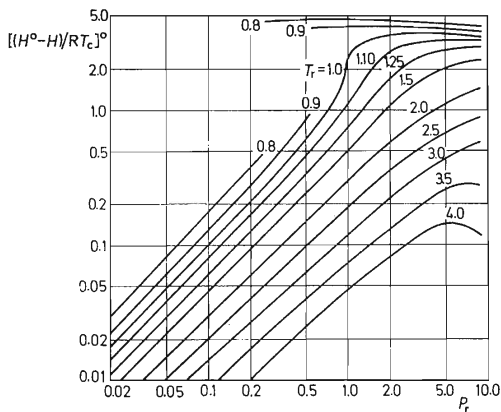


FIG. 6

Simple Fluid Part of Three Parameter Generalized Isothermal Enthalpy Difference $((H - H^0)/RT_c, \text{BTU/mol}, ^\circ\text{R})$ Correlation

which the temperature derivative of pressure is obtained and Eq. (4) integrated to give an expression for ΔH . Generalized expressions for estimating the values of the eight B-W-R constants from critical temperature pressure and acentric factor have been derived¹⁴ and can be used in calculating ΔH .

Digital computers, instead of charts, are obviously the way to calculate mixture enthalpies. An enthalpy prediction method, in which the enthalpy of the saturated vapor mixture was computed by the Redlich-Kwong equation and that of the saturated liquid mixture was found *via* empirical partial enthalpy equations was developed^{15,16} and has been distributed by the Natural Gas Processors Association. This method might be classified as "hybrid" because of the different approaches used for vapor and liquid. The liquid partial enthalpies were found *via* the temperature derivative of the empirical correlation for the liquid fugacity at constant pressure and composition. The liquid fugacity correlation used is part of the Chao-Seader⁴ K -value prediction method, which is also part of the K and H program of NGPA. The liquid phase enthalpy prediction procedure, which includes summing derivative values for all components of the liquid mixture, is the weakest part of this method. In addition, this program does not possess flexibility, *i.e.* experimental x , y values, or separate K -values, cannot be used in the calculation of enthalpy. Also, the vapor enthalpy is not as accurate as the B-W-R value would be.

The Clapeyron equation $\Delta H = T(dP/dT) \Delta V$, gives the heat of vaporization (or condensation) in terms of the slope of the vapor pressure curve and the volume change. A binary form of the Clapeyron equation, which has been known and used for sometime, is illustrated in Fig. 8

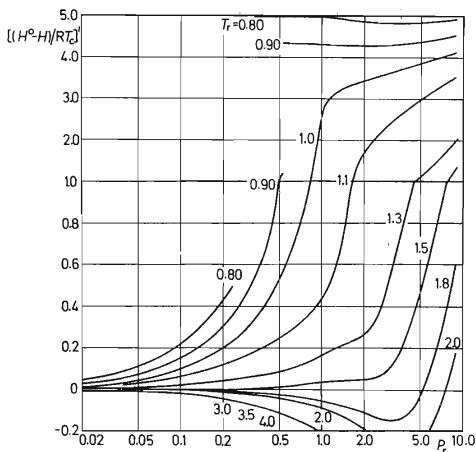


FIG. 7

Correction for Departure from Simple Fluid Part of Three Parameter Generalized Isothermal Enthalpy Difference Correlation

$$\Delta V_c = \sum_1^n x_i (\bar{V}_i^L - \bar{V}_i^V) = [V^L - \sum_1^n x_i \bar{V}_i^V] \quad (8)$$

= change in volume of mixture during differential condensation at P and T ,

$$\Delta H_c = \sum_1^n x_i (\bar{H}_i^L - \bar{H}_i^V) = [H^L - \sum_1^n x_i \bar{H}_i^V] \quad (9)$$

= differential heat of condensation of mixture at P and T .

$$\Delta H_c = T(\partial P / \partial T)_y \Delta V_c. \quad (10)$$

Eq. (10) is the Clapeyron equation for a mixture. Eq. (7) gives the enthalpy of a saturated liquid mixture as a function of the slope of the dew point (*i.e.* coexisting equilibrium vapor) condition and the liquid mol fractions. The partial quantities were found by equation of state relationships in a previous work¹⁷.

EQUILIBRIUM FLASH VAPORIZATION

Component distribution calculations for a single equilibrium stage are basically the same whether the process is a vaporization or a condensation process, or whether the process is adiabatic or with heat addition or removal. A necessary and sufficient condition defining an equilibrium stage process is that the effluent vapor and liquid mixtures coexist in equilibrium. From this phenomena the relationships for making the component distribution calculations follow. These EFV calculations, as they are frequently called, are straightforward in principle and simple in execution. The conventional relationships for distribution of components to vapor and liquid are obtained by combining component material balances with the definition of the vapor-liquid K -value, which gives: $v_i = f_i / (1 + A_i)$ and $l_i = f_i / (1 + S_i)$.

These two expressions may be applied *via* successive approximation calculations to find the L/V ratio or the temperature or pressure condition, the latter affecting the separation *via* the K -values. Although rigorous, these expressions are not as convenient as other forms, especially near the dew and bubble points where the L/V ratio approaches zero or infinity. A general expression for bubble point, dew point and equilibrium flash vaporization is obtained by rearranging these two expressions, subtracting and obtaining

$$\sum \frac{f_i(1 - K_i)}{(L/F)(1 - K_i) + K_i} = 0 \quad (11)$$

Eq. (11) contains an L/F ratio rather than an L/V ratio. This is an advantage because L/F will always be between 0 at the dew point and 1.0 at the bubble point extremes, and can be used for calculations when $0 < L/F < 1.0$. This is a great convenience

as it permits developing one computer program, instead of three, to handle all single stage vapor-liquid equilibrium problems between bubble point and dew point.

After obtaining a converged solution by Eq. (11), the composition of the equilibrium may be found by

$$l_i = \frac{L}{F} \left[\frac{f_i}{(L/F)(1 - K_i) + K_i} \right] \quad (12)$$

and the composition of the equilibrium vapor by

$$v_i = \frac{L}{F} \left[\frac{f_i K_i}{(L/F)(1 - K_i) + K_i} \right] \quad (13)$$

If both l_i and v_i are required, one can be found by one of the above equations and the other by the component balance relationship $f_i = l_i + v_i$, the component form of the overall material balance.

When heat is added or removed during an equilibrium flash vaporization, a heat balance is necessary to find the L/F ratio for the solution of Eq. (8). Writing such a heat balance in terms of the partial enthalpies of the components in the equilibrium vapor and liquid, and rearranging

$$\frac{L}{F} = \frac{Q/F + H^F - \sum z_i \bar{H}_i^V}{\sum x_i (\bar{H}_i^L - \bar{H}_i^V)} \quad (14)$$

The denominator of the right hand side of Eq. (14) has been shown to be the differential heat of condensation (see Eq. (9) which is substituted into Eq. (11) to give

$$\frac{L}{F} = \frac{Q/F + H^F - \sum z_i \bar{H}_i^V}{T(dP/dT)_y \sum x_i (\bar{V}_i^L - \bar{V}_i^V)} \quad (15)$$

The summation term in the right hand side numeration involves the feed mol fractions and the vapor partial enthalpies, while the denominator includes the slope of the dew point curve and the change in volume during differential condensation and the liquid mol fractions.

MINIMUM EQUILIBRIUM STAGES

The minimum number of equilibrium stages possible for making a desired separation, which occurs at total reflux, *i.e.* infinite reflux ratio, with no production of distillate or bottom products, can be easily simulated by calculations. Experimental opera-

tion at total reflux is an effective laboratory procedure for measuring relative volatilities for close boiling mixtures, such as propylene-propane. Minimum equilibrium stages for a given separation is a design limit and, as such, is both interesting and important.

Minimum stages can be calculated easily for any given separation by using the condition that passing vapor and liquid streams have the same composition, *i.e.* the vapor leaving any tray has the same composition as the liquid leaving the tray above. When average relative volatilities can be assumed for the total reflux operation, a convenient algebraic solution is obtained, known as the Fenske¹⁹ equation, $(d/b) (b'/d') = \alpha^{S_m}$ is obtained. This equation is usually applied first to the key components, (d/b) being for the light key and (b'/d') being for the heavy key with $\alpha = K/K'$, to obtain S_m , the total equilibrium stages, including the reboiler and partial condenser. Then this expression is applied to other components, using this value of S_m , to find the distribution of these non-keys to distillate and bottoms.

A similar expression that takes variable relative volatilities into consideration has been proposed by Winn²⁰, who noted that straight lines are usually obtained when K values of mixture components are plotted against the reference component K value, both taken at the same T and P , on log-log coordinates, *i.e.* $K = \beta(K')^\theta$. When $\theta = 1$, $\beta = \alpha$, the relative volatility. Proceeding in the same way used to derive the Fenske equation gives the Winn equation

$$(d/b) (b'/d')^\theta (B/D)^{1-\theta} = \beta^{S_m}, \quad (16)$$

Eq. (16) includes the B/D ratio, which is assumed at the start of the calculations and checked after all the values of d and b are found. The values of S_m that are obtained from the Fenske or Winn equations may be a fractional number of equilibrium stages, which cannot be obtained directly via plate-to-plate calculations at total reflux.

MINIMUM REFLUX

The minimum reflux ratio possible for making a given separation occurs with an infinite number of equilibrium stages, *i.e.* when there are "pinch" or zones of constant composition both above and below the feed plate. This imaginary operation, that cannot be duplicated in practice, is of interest as a limiting case for design. An infinite number of equilibrium stages can be simulated on a digital computer by having the computer run for a large number of equilibrium stages, such as 200, for example. This and other techniques of finding the minimum reflux ratio *via* digital computer calculations are described in the technical literature²¹⁻²³.

In this paper the best short method for predicting the minimum reflux ratio for use with short-cut design procedures is of particular interest. This is widely recognized to be the Underwood²⁴ equation. A simpler derivation than the original follows from the pinch zone relationships, which are: $v_{EP} = d/(1 - A_{EP})$ for the enriching section and $v_{XP} = -b/(1 - A_{XP})$ for the exhausting section. These pinch zone relationships apply to each component of the mixture. Multiplying numerator and denominator of their right hand members by an average relative volatility α , assuming that $A_{EP} = A_{XP} = \Phi$ for the key and other distributed components, if any, and noting that

$d + b = f$ for each component, and then summing and noting that $V_F = V_{EP} - V_{XP}$, gives the Underwood equation

$$\sum(\alpha_i f_i)/(\alpha_i - \Phi) = V_F. \quad (17)$$

The term Φ represents the roots of the equation, and determined by the relative volatilities and the vapor fraction of the feed, V_F . Values of Φ , which are evaluated via Eq. (17) and are one less in number than the number of components, are in between the α values for the components of the mixture.

A similar expression is obtained for the top tray vapor, assuming that $V_{EP} = V_T$, from the enriching pinch condition. This, plus the relationship $V_T = (R_m + 1) D$, leads to the other Underwood expression:

$$\sum(\alpha_i d_i)/(\alpha_i - \Phi) = V_T = (R_m + 1) D. \quad (18)$$

Eq. (18) is solved with values of the roots previously obtained from Eq. (17).

The procedure used in solving Eq. (18) is to specify two values of d_i , and then write Eq. (18) for each value of Φ . These equations, plus the requirement that $D = \sum d_i$, permit solving for the unknown d_i values, and for D and R_m . These distillate values are for minimum reflux only. Other than key distillate compositions for finite reflux and total reflux will be the same but the distillate composition at minimum reflux will be different.

The best α values for applying the Underwood minimum reflux equation are those obtained at the feed temperature or the average of the tower top and bottom temperatures, whichever is higher. This is according to recommendations of Erbar-Maddox²³. The minimum reflux ratio for complex fractionators, *i.e.* fractionators having more than one feed and/or more than two products, has been studied by Short and Erbar²⁵.

EMPIRICAL CORRELATIONS AND SHORT-CUTS

Empirical correlations of the minimum and operating reflux ratios and equilibrium stages have been proposed as a short-cut design procedure for fractionators by: Brown-Martin²⁶, Gilliland²⁷, Erbar-Maddox²⁸, and Gray²⁹. The Gray correlation was an improvement on the earlier Erbar-Maddox correlation. All correlations use the minimum and actual number of equilibrium stages. The Gray²⁹ correlation, which is recommended in preference to the others, is presented in Fig. 9, in which the coordinates are $(L/V)_{OP}$ and (S_m/S) and the parameter is lines of constant $(L/V)_M$. It will be noted that all $(L/V)_M$ curves intersect at $(L/V)_{OP} = 1.0$ and $(S_m/S) = 1.0$ and converge to $(L/V)_{OP} = (L/V)_M$ at $(S/S) = 0$, *i.e.* the minimum reflux ratio. Note also that $L/V = R/(R + 1)$.

These curves are normal for bubble point feed and the (L/V) ratios are those at the top plate, *i.e.* internal reflux divided by top tray vapor. For partially vaporized feed the (L/V) ratio is

calculated from the vapor quantity found by the following empirical relationship developed by Erbar-Maddox²⁸:

$$(V_u - V_k)(Q_c/L_c)_k = [1 - (D/F)](H_u - H_k)_f, \quad (19)$$

where V_u = vapor at unknown condition, V_k = vapor at known condition, Q_c/L_c = heat removed from the condenser per mol of liquid formed in the condenser, D/F = ratio of mol of distillate per mol of feed, H_{uf} = feed enthalpy for unknown case, H_{kf} = feed enthalpy for known case.

The above equation is used to find the top plate vapor quantity for a partially vaporized feed condition, knowing the amount of top tray vapor for the bubble point feed case from previous application of Fig. 9 in a design calculation. Another application of Fig. 9 and Eq. (19) is in calculating the overall plate efficiency for a fractionator from test data. In this case, the same chart readings and calculations are made but in reverse order, *i.e.* the known condition is the partially vaporized feed while the unknown condition is the bubble point feed. This empirical correlation is recommended for application with the Underwood minimum reflux and either Fenske or Winn minimum plates.

Short-cut methods, such as the above are being used widely in process simulation work, as well as doing preliminary design calculations. Thus these short-cut methods are used on digital computers. The reason for using a short-cut method in a computer simulation program is to conserve space and time in the computer for analysis of the process. Plate-to-plate calculations for each fractionator in a process would use excessive computer time. A shortcut design of complex fractionators (more than one feed and/or more than two products) was made by Joyner and coworkers³⁰.

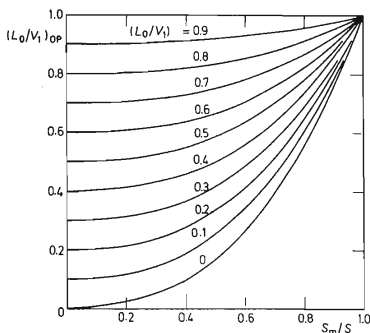


Fig. 9

Gray Modification of Erbar-Maddox Empirical Correlation of Reflux Ratios and Equilibrium Stages for Fractionators

ABSORPTION AND STRIPPING FACTOR METHODS

Functions of the absorption ($A = L/KV$) and the stripping ($S = KV/L$) factors have been used in making equilibrium stage calculations since this approach was first proposed in 1930 for absorbers by Kremser³¹ and applied to fractionators in 1932 by Sounders and Brown³². In 1957, this writer³³ presented new and more convenient relationships of these factors for application to different equilibrium stage processes, such as: fractionators, reboiled absorbers, *etc.* These equations were presented in terms of effective factors for each section of the column and also in terms of the factors on each plate. Two recovery fractions were defined and used in this work. These are Φ_A and Φ_S , which are fraction not absorbed and fraction not stripped, respectively.

$$\Phi_A = [A_1 A_2 A_3 \dots A_n + A_2 A_3 \dots A_n + \dots + A_n + 1]^{-1} = (A_e - 1)/(A_e^{n+1} - 1), \quad (20)$$

$$\Phi_S = [S_1 S_2 S_3 \dots S_m + S_2 S_3 \dots S_m + \dots + S_m + 1]^{-1} = (S_e - 1)/(S_e^{m+1} - 1). \quad (21)$$

These recovery fractions may be evaluated from the A or S factors on each plate or they may be evaluated from effective A and S factors, as indicated by the above relationships.

Fig. 10 is a graphical representation of the above function of effective absorption and stripping factors. As can be seen, the abscissa scale is A_e or S_e while there are two ordinate scales, one on the left and one on the right. As indicated, these ordinates are functions of the effective factor and the number of equilibrium stages, and one ordinate is the complement of the other. In other words, the left hand ordinate of Fig. 10 is f_a or f_s , while the right ordinate is $(1 - f_a)$ or $(1 - f_s)$, as can be seen by the numerical values of the ordinates and the algebraic expressions for the two ordinate scales.

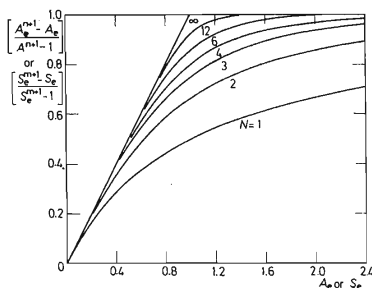


FIG. 10

Kremser-Brown Absorption (Stripping) Factor plot with Proposed Coordinates
 N number of equilibrium stages. A_e Effective absorption factor.

Fig. 10 is the same graph given by Souders and Brown³² except for the definition or label on the ordinate scale. In this early work, the ordinate of Fig. 10 was written in terms of vapor mole fraction difference ratio and called the absorption efficiency. A similar stripping efficiency was expressed in terms of liquid mol fractions. These so-called absorption and stripping efficiencies were not convenient, especially in fractionation calculations. The functions of Φ_A and Φ_S that follow are much more convenient.

A component material balance for an absorber, in terms of Φ_A and Φ_S , is

$$v_1 = \Phi_A v_{n+1} + (1 - \Phi_S) l_0, \quad (22)$$

where v_1 = mol of any component in absorber off-gas, v_{n+1} = mol of same component in wet gas to absorber, l_0 = mol of same component in lean oil. Eq. (22) says that the mol of any component leaving an absorber in the off-gas is the sum of the mol of that component that is not absorbed from the entering wet gas plus the mol of the same component that is stripped from the entering lean oil. The recovery fractions Φ_A and Φ_S are evaluated for the same column of equilibrium stages for the solution of Eq. 22, numbering from top to bottom when calculating Φ_A and numbering from bottom to top in calculating Φ_S .

A component material balance for a stripper, in terms of Φ_S and Φ_A , is

$$l_1 = \Phi_S l_{m+1} + (1 - \Phi_A) v_0, \quad (23)$$

where l_1 = mol of any component in the stripped or denuded oil leaving the stripper, l_{m+1} = mol of the same component in the rich oil charge into the top of the stripper, v_0 = mol of same component in the stripping gas entering the bottom of the stripper. Eq. (23) says that the mol of any component leaving a stripper in the denuded oil is equal to the amount of that same component that is not stripped from the rich oil charge plus the amount of the same component that is absorbed from the stripping gas. The recovery fractions, Φ_S and Φ_A , are evaluated for the same column of equilibrium stages for the solution of Eq. (23), numbering from the bottom to the top in calculating Φ_S and numbering from the top to bottom in calculating Φ_A .

The above equations have had rather wide application for over a decade in absorber design calculations. Recently, Owens and Maddox³⁴ devised an empirical method for making more correct estimates of the effective factors and for estimating the exit gas temperature of an absorber. The temperature is calculated from top tray absorption.

By combining Eq. (22) and (23) with the appropriate expressions for the condenser, reboiler, and feed mesh stages, component distribution expressions can be obtained for different types of columns. For example, the separation in a fractionator with a partial condenser and an equilibrium flash feed stages is represented by

$$\frac{b}{d} = A_F \frac{(A_0 \Phi_{SE} + 1) / \Phi_{AE}}{(S_0 \Phi_{AX} + 1) / \Phi_{SX}} \quad (24)$$

The double subscripts on the recovery fractions designate a function of A or S , firstly, and the column section, secondly. The solution of Eq. (19) is an iterative procedure in which the number of stages in each section, the temperature gradient and the liquid and vapor traffics must be known or assumed before the products are computed. With these first values of the product compositions, it is possible to go back and revise the initial assumptions.

Similar expressions to Eq. (24) have been derived for reboiled absorbers, top-feed fractionators and side-stream fractionators. These component distribution expressions are short-cut design methods and also useful as mathematical models of different equilibrium stage separation processes for use in process simulation.

EQUILIBRIUM STAGE-TO-STAGE CALCULATIONS

Rigorous designs of equilibrium stage separation processes for multicomponent mixtures include making so-called "plate-to-plate" calculations of one form or another, with an objective of finding one of the following, given the other two: 1. number of equilibrium stages, or theoretical plates; 2. reflux and boilup rates; and 3. product compositions and amounts. Mass and heat transfer plus phase equilibrium on each stage are the bases for these stage-to-stage calculations. Heat transfer equilibrium is usually assumed to exist also when the vapor and liquid phases leaving a stage are in equilibrium, *i.e.* the vapor and liquid leaving an equilibrium stage are at the same temperature.

In 1932, Lewis and Matheson³⁵ suggested a "direct" equilibrium stage calculation procedure, in which the objective was to find the number of equilibrium stages for a given separation, as specified by the key-component split, and reflux ratio. Calculations are made from the top toward the feed plate and from the bottom toward the feed plate, starting with assumed distillate, and bottoms products made up of the specified key-component split and estimated amounts of the other components. As the top-down and bottom-up calculations proceed, it is necessary to introduce small amounts of the non-distributed components so that all components will be present in the liquid and vapor streams meshed at the feed plate. This introduction of non-distributed components at different stages in the calculation is a successive approximation and arbitrary operation that is possible in the manual but not in the computer application of this plate-to-plate procedure.

In 1933, Thiele and Geddes³⁶ suggested an "indirect" equilibrium stage calculation procedure, in which the objective is to find the products from a fractionator of a given number of equilibrium stages and reflux ratio. In addition to the number of stages and the internal liquid and vapor traffics it is necessary to assume the temperature gradient before making the component distribution calculations. With this starting information, the Thiele-Geddes procedure permits calculating the products, with which the temperature gradient and the starting material balance can be checked. Bubble and dew point calculations and heat balances are used in revising the temperatures and L/V ratios.

In the original publications, the Lewis–Matheson and the Thiele–Geddes methods were in mol fraction forms, which meant normalizing to $\sum x = 1$ and $\sum y = 1$ at each stage.

Both methods have been simplified by this author by using mol quantities for all components as well as total liquid and vapor streams.

Preliminary calculations required in preparing the distillation problem for the direct and indirect plate-to-plate calculations are essentially the same, as follows:

Step 1: Find the phase condition of the feed by an equilibrium flash vaporization calculation at the given temperature and pressure.

Step 2: Make an overall component material balance to obtain a first approximation of the component distribution between distillate and bottoms products.

Step 3: Using the assumed distillate from Step 2 and an assumed of given reflux ratio, make equilibrium stage calculations for the reflux condenser and top plate. For a vapor product, the equilibrium conditions of temperature and pressure are those that satisfy $\sum (d/K)_i = \sum d_i$. Reflux composition is then found from the $(d/K)_i$ values and the value of L_0 , as follows:

$$l_0 = [L_0 / \sum (d/K)_i] (d/K)_i. \quad (25)$$

Top tray vapor components are found as $v_1 = l_0 + d$ and the top tray temperature, assuming that pressure has already been fixed by the distillate dew point calculation, is the dew point of the top tray vapor at which $\sum (v/K)_1 = \sum v_1$.

Step 4: Using the assumed bottoms product from Step 2, and the boilup rate that corresponds to the reflux rate of Step 3, make equilibrium stage calculations for the reboiler and the bottom plate. The reboiler temperature is the bubble point of the bottoms product, *i.e.* the temperature that satisfies $\sum (bK)_1 = \sum b_1$. The composition of the boilup vapor is then found from the $(bK)_i$ values and the value of V_0 , as follows:

$$v_0 = [V_0 / \sum (bK)_i] (bK)_i. \quad (26)$$

Bottom tray liquid compositions are found as $l_1 = v_0 + b$ and the bottom tray temperature in the bubble point of this bottom tray liquid at which $\sum (lK)_1 = \sum l_1$. At this point, it should be pointed out that the equilibrium stages are numbered from the terminals toward the feed, *i.e.* top-down for the enriching section and bottom-up for the exhausting section.

DIRECT PLATE-TO-PLATE CALCULATIONS

Direct plate-to-plate calculations are made from the above top plate conditions and composition down toward the feed plate. Similar calculations are made from the

bottom plate conditions and compositions up toward the feed plate. In the enriching section these equilibrium stage calculations involve the following related steps:

Step 1: finding stage temperature by a vapor dew point calculation,

Step 2: calculating the composition of the equilibrium liquid, using an assumed total vapor quantity,

Step 3: find the liquid from the next stage by a component material balance, i.e. $l_{j+1} = v_j + b$. Also the following calculations are made at intervals:

Step 4: heat balance to find the boil-up vapor,

Step 5: introduction of small amounts of the non-distributed light components into the vapor. These bottom-up equilibrium stage calculations are continued until the ratio of the keys in the vapor correspond to that in the vapor portion of the feed. The bottom-up calculations give values of v_m and l_{m+1} . These quantities should relate to the components in the feed flash as follows:

$$v_{n+1} - v_m = v_f, \quad (27)$$

$$l_{m+1} - l_n = l_f. \quad (28)$$

If these feed mesh relationships are not satisfied, then it is necessary to revise the values of d and b for the non-meshing components, or revise the intermediate additions of the non-distributed heavies in the top-down and of the non-distributed lights in the bottom-up calculations.

INDIRECT PLATE-TO-PLATE CALCULATIONS

This modification of the Thiele-Geddes³⁶ multicomponent plate-to-plate calculation method uses mole quantity ratios, rather than mole fraction ratios, thus making the mathematical relationships and the numerical calculations simpler. The same preliminary calculations used in the direct plate-to-plate calculations are made with these indirect calculations to establish the terminal conditions of the column, from which the temperature gradient can be constructed more realistically.

The indirect equilibrium stage calculations could be started without making the above-mentioned preliminary calculations. All that is required is to fix the number of equilibrium stages and the liquid and vapor rates in the enriching and exhausting sections and then assume the temperatures on each stage. The number of stages and reflux rate are primary assumptions, while the temperature gradient is a secondary assumption. The temperature gradient can be established more closely if the end points are known from the preliminary calculations.

From the temperatures, the K_i values are found for each component on each stage. With these and the L and V values, the L/KV factors are calculated for the enriching stages and the KV/L factors are found for the exhausting stages. These A and S factors are next used in a straightforward calculation to find the terminal products of the fractionator, starting with $(l/d)_{\text{cond}} = (L/KV)_{\text{cond}}$ enriching and exhausting sections are made by using the following combination of the equilibrium and component material balances

$$(l/d)_{i+1} = [(l/d)_i + 1] (L/KV)_{i+1} \quad (29)$$

and

$$(v/b)_{j+1} = [(v/b)_j + 1] (KV/L)_{j+1} \quad (30)$$

Eq. (29) and (30) give the component ratio on any plate in terms of the ratio for the same component on the previous plate. The calculation procedure is the same in both enriching and exhausting sections, *i.e.* add unity to the previous component ratio and multiply the sum by the absorption or stripping factor for the next plate. These calculations are continued for the specified number of stages, giving values of l_n/d for each component in the enriching section and values of v_m/b for each component in the exhausting section.

The next step in the indirect equilibrium stage calculations is to mesh these l_n/d and v_m/b values with the feed and calculate the values of b and d for each component. This meshing is done by relationships that are obtained by making component material balances around the top and the bottom of the column including the values of (v_t/f) and (l_t/f) from flashing the feed, and then rearranging to give

$$\frac{b}{f} = \frac{(l_n/d) + (l_t/f)}{(l_n/d) + (v_m/b) + 1}, \quad (31)$$

$$\frac{d}{f} = \frac{(v_m/b) + (v_t/f)}{(l_n/d) + (v_m/b) + 1}, \quad (32)$$

The ratio of Eq. (31) to Eq. (32) gives values of (d/b) . Any one of these equations may be solved and then combined with $d + b = f$ to find the b and d values for all components. After meshing and finding the d and b values, the next step is to calculate the liquids and vapors from the various stages and then check the temperatures and make revisions. In the enriching section these calculations are by the following: Step 1: $l_i = (l/d)_i d$; and Step 2: $\sum l_i = \sum l_i K_i$. In the exhausting section the steps are: Step 1: $v_j = (v/b)_j b$; and Step 2: $\sum v_j = \sum (v_j/K_i)$. From these calculations new temperatures can be found for the equilibrium stage calculations can be made.

COMPUTER CALCULATIONS

Early computer methods of making multicomponent distribution calculations for multi-equilibrium stage processes were modified direct (Lewis-Matheson) or indirect (Thiele-Geddes) procedures. The methods of Bonner³⁷, Erbar-Maddox³⁸, and Greenstadt and coworkers³⁹ were of the direct plate-to-plate calculation type. The methods of Lyster and coworkers⁴⁰ and Holland⁴¹ were of the indirect type. All of these early procedures have the disadvantage that all components of the mixture must appear in all streams.

This disadvantage is overcome in the modern stage-by-stage algorithms, in which simultaneous solutions are obtained of the equilibrium relationships and the material balances, the latter being written in such a way that it is possible to reach stage to have liquid or vapor feeds or products. This generality and the large computer permit making calculations for various column configurations.

One such method has been developed by Burman and coworkers⁴², who started with the developments of Rose and coworkers^{43,44} and Ball⁴⁵, and obtained a set of equations for each component in a fractionator in which the plates are numbered from the bottom toward the top. A typical equation for component i on plate j , with external feed, is obtained by making a component material balance, introducing the equilibrium relationship $y_{j,i} = K_{j,i}x_{j,i}$, adding $x_{j,i}$ to both sides and introducing an arbitrary multiplier β for controlling the rate of convergence gives

$$-\beta(V_{j-1}K_{j-1,i})x_{j-1,i} + [\beta(L_j + K_{j,i}V_j) + 1]x_{j,i} - \beta L_{j+1,i} = x_{j,i} + f_{j,i}, \quad (33)$$

β is equal to the time/holdup ratio from the integrated unsteady state balance. When β is small, convergence is slow. When β is large, the calculations move rapidly to convergence.

Writing Eq. (33) for component i over the entire column yields a tridiagonal matrix which can be solved without round off or truncation error. Component distribution and bubble point temperature calculations are made first for the entire column, using assumed liquid and vapor rates, and then heat balances are made to revise the internal reflux ratio.

Sujata⁴⁶ developed a procedure for absorbers using a similar component material balance relationship

$$-S_{j-1,i}l_{j-1,i} + (1 + S_{j,i})l_{j,i} - l_{j+1,i} = f_{j,i}. \quad (34)$$

The right hand term of Eq. (34) contains a feed addition term. Heat balances are used in this method for determining temperatures. In this procedure, Eq. (34) is written for component i over the entire column, giving a tridiagonal matrix which can also be solved without truncation error. Spear and coworkers⁴⁷ evaluated this procedure for a number of absorbers.

The major advantage of the above methods, *i.e.* using Eqs (33) and (34), is that any component can go to zero on any tray without requiring elegant programming to avoid computer problems.

Taylor and Edmister⁴⁸ have proposed a method that also gives rigorous solutions for any type of distillation process by means of a single set of equations employed in a single computer program. Distillation columns with multiple feeds and side streams, absorbers, and reboiled absorbers have been solved successfully by this procedure. Generality is achieved by expressing the material balance and heat balance equations in such a way that it is possible for each stage to have vapor and liquid feeds and products. Various column configurations are obtained by making the appropriate specifications for these quantities. One of the most important aspects of this technique is that it gives the capability of solving a wide variety of design problems directly. Convergence for all types of problems solved by this method is rapid and reliable.

This technique takes advantage of the linearity of the component-material balance equations with respect to component flow rates. A simplified component-material balance for component "i" on equilibrium stage "j" (numbered from top down), which does not have a feed or a product, is combined with equilibrium relationship $l_{j,i} = A_{j,i}v_{j,i}$ to give the following expression

$$-A_{j-1,i}v_{j-1,i} + (1 + A_{j,i})v_{j,i} - v_{j+1,i} = 0. \quad (35)$$

The similarity between Eq. (34) and (35) is interesting. Eq. (34) is a balance of liquid quantities while Eq. (35) is a balance of vapor quantities. Appropriate terms must be added to Eq. (35) for stages having feed and product streams, but these terms do not affect the characteristic linearity of the equation. There is an equation of this type for each stage in the process. It is therefore possible to solve directly for the flow rates $v_{j,i}$ and $l_{j,i}$ in terms of the absorption factors $A_{j,i}$. It is important that these solutions be obtained in a manner that accounts for the large range of compositions that occur within the column, particularly for the light and heavy components.

From the definition of the absorption factor it follows that the component flow rates depend only on the stage temperatures and the total vapor and liquid rates within the column. The total liquid rates can, in turn, be eliminated by use of total material balances. The bubble point equation is used to describe equilibrium requirement of a stage, *i.e.* $\sum K_{j,i}l_{j,i} = L_j$. A simplified heat balance equation for stage number "j", made in terms of individual component (*i.e.* partial) enthalpies, is

$$\sum h_{j-1,i}l_{j-1,i} + \sum H_{j+1,i}v_{j+1,i} = \sum h_{j,i}l_{j,i} + \sum H_{j,i}v_{j,i}. \quad (36)$$

Total stream quantities and enthalpies could also be used in making these heat balances.

The solutions for $l_{j,i}$ and $v_{j,i}$ obtained from the component-material balances can be substituted into these expressions. After the equilibrium constants and the enthalpies have been expressed in terms of the stage temperatures, the final equations contain only the stage temperatures and the internal total liquid rates. The number of equations and unknowns is small enough that simultaneous solutions can be obtained. The equations are non-linear but are readily solved by Newton's method of successive approximations for a set of equations relating more than one unknown.

It is the simultaneous nature of Newton's method that gives the outstanding convergence characteristics of the method. Traditional calculational procedures perform the calculations for each stage separately. In addition, the equilibrium material balance, and heat balance calculations are performed sequentially. The result is that each calculation is only indirectly affected by conditions on the other stages. The method proposed by Taylor and Edmister combines all the unknowns into a single simultaneous solution so new values calculated for each unknown in suc-

cessive trials reflect conditions existing throughout the system. Convergence is obtained in three or four trials for all types of problems. The initial assumptions have no significant effect on the ease with which solutions are obtained.

Changes in temperatures and liquid flows are found by solving a set of non-linear differential equations, such as the following, for ΔT_j and ΔL_j

$$\Delta G_j = \frac{\partial G_j}{\partial T_1} \Delta T_1 + \dots + \frac{\partial G_j}{\partial T_n} \Delta T_n + \frac{\partial G_j}{\partial L_2} \Delta L_2 + \dots + \frac{\partial G_j}{\partial L_{n-1}} \Delta L_{n-1}. \quad (37)$$

The symbol G designates an equilibrium bubble point relationship for each stage and also a heat balance relationship for each stage except the condenser and reboiler. These $2n - 2$ values of G are zero when each stage is at equilibrium and in heat balance.

In the process of solution of Eq. (37) by Newton's method, derivatives of the equilibrium and heat balance equations must be obtained. The complexity of these equations prohibits analytical evaluation of these derivatives. They must therefore be approximated numerically.

This method has been employed to determine the optimum feed location. The reflux and reboil rates required to perform a given separation can be found for a particular feed location. The optimum feed stage is the one for which the required reflux and reboil rates are a minimum. This concept can be extended to find the optimum location for multiple feeds and side streams.

INTERNAL HEAT BALANCES

Two alternate ways of making the heat balances for checking vapor liquid traffics are presented below. A heat balance around the top and any stage of the enriching section gives the liquid quantity in terms of the condenser duty and the enthalpies of the distillate and of the vapor from the plate below, as follows

$$L_j = (Q_c + FH^F + V_{j+1}H_{j+1,i}^Y - DH_D)/H_j^L. \quad (38)$$

Eq. (38) is the heat balance relationship that is used with total (or mixture) enthalpies. For use with partial quantities, another form is derived by rearranging Eq. (38).

$$L_j = \frac{Q_c + FH^F + \sum d(\bar{H}_{j+1,i}^Y - \bar{H}_{D,i})}{\sum x_{j,i}(H_{j,i}^L - \bar{H}_{j+1,i}^Y)}. \quad (39)$$

Q_c is heat added so the sign will be negative, H_D and \bar{H}_D may be for vapor on liquid distillate. The FH^F term is zero for plates above the feed.

The right hand side denominator of Eq. (39) is almost identical to the differential heat of condensation, which was given previously, except for the subscript of the last term. Assume that the right hand side denominator of Eq. (39) can be replaced by

$$\sum x_{j,i}(\bar{H}_{j,i}^L - \bar{H}_{j+1,i}^V) = T \left(\frac{dP}{dT} \right)_y \sum x_{j,i}(\bar{V}_{j,i}^L - \bar{V}_{j+1,i}^V). \quad (40)$$

Combining Eq. (39) and (40) gives the following

$$L_j = \frac{Q_c + FH^F + \sum d_i(\bar{H}_{j+1,i}^V - \bar{H}_{D,i})}{T(dP/dT)_y \sum x_{j,i}(\bar{V}_{j,i}^L - \bar{V}_{j+1,i}^V)}. \quad (41)$$

The partial quantities for the solution of Eq. (41) should be calculated *via* an equation of state. The slope of the vapor dew point curve, *i.e.* $(dP/dT)_y$, is found from vapor-liquid equilibria calculations.

Eqs (38) and (41) include the feed enthalpy in the right hand side numerator thus giving forms of these heat balance equations that can be applied from the top to the bottom of the column, *i.e.* going through the feed plate and down through the exhausting section to the bottom product. The subscripts in the above equations indicate that the stages are numbered from top-down through both sections.

A heat balance around the bottom and any equilibrium stage of the exhausting section give the vapor boilup quantity in terms of the heat added to the reboiler and the enthalpies of the bottoms product and the liquid entering that stage from above, as follows:

$$V_j = (Q_B + FH^F + L_{j+1}H_{j+1}^L - BH_B)/H_j^V. \quad (42)$$

Eq. (42) is the heat balance relationship that is used with mixture enthalpies, similar to Eq. (38). The partial quantity form is obtained by the same procedure followed for the enriching section, starting with the rearranged form of Eq. (42) as follows:

$$V_j = \frac{Q_R + FH^F + \sum b(\bar{H}_{j+1,i}^L - \bar{H}_{B,i})}{\sum y_{j,i}(\bar{H}_{j,i}^V - \bar{H}_{j+1,i}^L)}. \quad (43)$$

Q_R is the heat added at the reboiler, H_B and \bar{H}_B are for the bottoms product, which is always liquid.

The right hand side denominator of Eq. (43) is almost identical to the differential heat of vaporization, except for the subscript of the last term. From this, it seems reasonable to assume the following equality

$$\sum y_{j,i}(\bar{H}_{j,i}^V - \bar{H}_{j+1,i}^L) = T(dP/dT)_x \sum y_{j,i}(\bar{V}_{j,i}^V - \bar{V}_{j+1,i}^L). \quad (44)$$

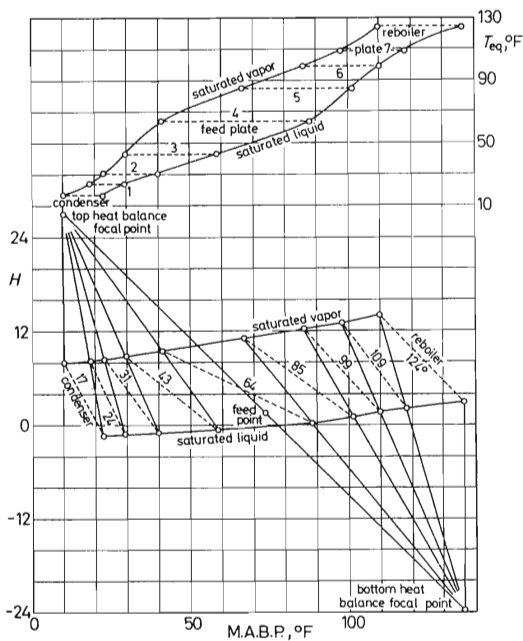


FIG. 11

Enthalpy-Composition Diagram for Atmospheric Pressure Debutanizer

Condenser Duty = 951 400 BTU, Reboiler Duty = 1 340 200 BTU.

Material Balance, mol

Component	Feed	Distillate	Bottoms
Propane	10.0	10.0	0
i-Butane	15.0	15.0	0
n-Butane	25.0	24.7	0.3
Pentane	25.0	0.2	24.8
Hexane	15.0	0	15.0
Heptane	10.0	0	10.0
<i>Total</i>	<i>100.0</i>	<i>49.9</i>	<i>50.1</i>

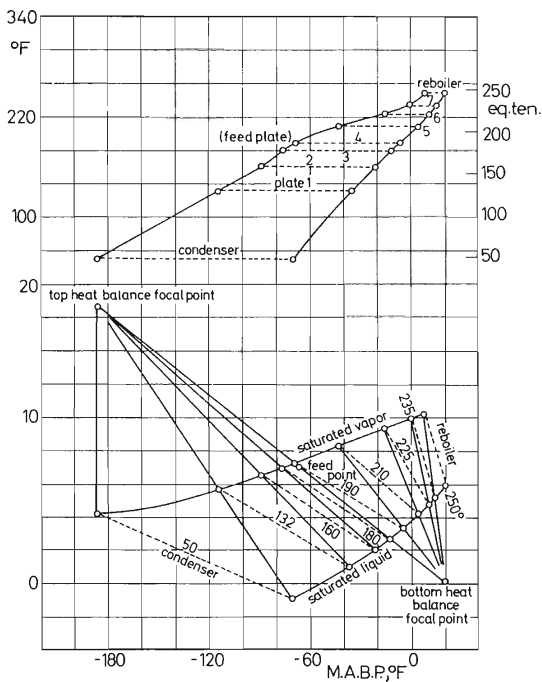


FIG. 12
Enthalpy-Composition Diagram for 400 PSIA Deethanizer

Condenser Duty = 509 000 BTU, Reboiler Duty = 341 000 BTU.

Material Balance, mol

Component	Feed	Distillate	Bottoms
Methane	25	24.62	0.32
Ethane	10	9.32	0.72
Propane	15	7.13	7.87
Butane	50	0.66	49.34
<i>Total</i>	<i>100</i>	<i>41.69</i>	<i>58.41</i>

Combining Eqs (40) and (41) gives the following

$$V_j = \frac{Q_R + FH^F + \sum b_i(\bar{H}_{j+1,i} - \bar{H}_{B,i})}{T(dP/dT)_x \sum y_{j,i}(\bar{V}_{j,i}^V - \bar{V}_{j+1,i}^L)} \quad (45)$$

The partial quantities for the solution of Eq. (45) should be calculated *via* an equation of state. The slope of the bubble point curve, *i.e.* $(dP/dT)_x$, is found from vapor-liquid equilibria calculations. The FH^F terms in Eqs (43) and (45) are zero for the plates below the feed.

Heat balances *via* Eqs (41) and (45) are limited to applications on a digital computer where it is possible to evaluate the partial volumes and enthalpies. In some cases it might be easier to find $(dP/dT)_x$, the slope of the bubble point curve. This will dictate a choice between the equation for L or the equation for V .

ENTHALPY-COMPOSITION DIAGRAM

Figs 11 and 12 illustrate a method for checking plate-to-plate calculations for multi-component, multi-stage hydrocarbon fractionators. For these hydrocarbon mixtures the molal average boiling point was used as the composition parameter. The plots in Figs 11 and 12 were prepared from the results of plate-to-plate calculations which included heat balances as well as material balances and equilibria calculations. The phase boundary diagrams at the top give the temperature-composition gradients for the separations.

The feed to the debutanizer (Fig. 11) is a six component mixture. A 50–50 split of feed to distillate and bottoms was the desired separation for this column. Seven equilibrium plates plus reboiler and condenser with a reflux-to-distillate ratio of 2.0 defined the column for the theoretical distillation calculations.

Final results of these calculations, shown on Fig. 11, were obtained by three sets of trial calculations. Successive approximations were necessary to establish the composition gradients through the column. Calculations were started at top and bottom with assumed products and carried plate-to-plate toward the feed. Nondistributed heavy or light components were introduced in amounts and at points found by trial so as to make the enriching and exhausting calculations converge at the feed plate.

In plotting the results of the plate-to-plate calculations, the molar average boiling point is not a unique characterization of composition. With a large number of components it is possible to vary amounts of individual components and not change the molar average boiling point. The liquid leaving stage 1 and the vapor leaving stage 3 have essentially the same molar average boiling point but not exactly the same component composition.

Similar plate-to-plate calculations for a high pressure deethanizer were used in plotting the diagrams on Fig. 12. The composition of the four component feed

to this column was quite different from the previous example. Seven plates plus reboiler and condenser with a reflux to distillate ratio of 1.7 defined the column for theoretical calculations.

Nonideal conditions prevail in the latter example, so that partial enthalpies and pressure-temperature-composition K values were used in making the calculations. Successive approximations were also necessary to establish composition gradients that converged at the feed plate. All components appeared in both distillate and bottoms, making the calculations more complex than they would have been for a sharp split.

These enthalpy-composition diagrams are useful in two ways: *a*) plotting results of distillation calculations in this way helps check plate-to-plate calculations and locate errors, and *b*) a plot of this kind can be used to find the effect of small changes in reflux ratios. However, a diagram prepared from data obtained by calculations at one reflux ratio cannot be used at a widely different reflux ratio.

LIST OF SYMBOLS

p_i^0	vapor pressure of component i
P	system pressure
$\Theta = (v_i^V/v_i^0) [\exp V_i^L(p_i^0 - P)/RT]$	imperfection-pressure correction for pure component
$\gamma_i^L = f_i^L/f_i^L y_i$	activity coefficient of i in liquid phase
$\gamma_i^V = f_i^V/f_i^V x_i$	activity coefficient of i in vapor phase
$\bar{\Theta}_i = (\Theta_i \gamma_i^V) = (\Phi_i^V/v_i^0) [\exp V_i^L(p_i^0 - P)/RT]$	combined imperfection-pressure and non-ideal vapor correction
$v_i^V = (f/P)_P$	fugacity coefficient of pure component vapor at system temperature and system pressure
$v_i^0 = (f/P)_{p_i^0}$	fugacity coefficient of pure component vapor at system temperature and vapor pressure
$\Phi_i = (\bar{f}_i^V/P y_i)$	fugacity coefficient of component i in vapor mixture at system temperature and vapor pressure
v_i^L	fugacity coefficient of a pure component in the liquid phase at the temperature and pressure of the system
$v_i = y_i V$	mol of i in equilibrium vapor
$\sum v_i = V$	total vapor
$l_i = x_i L$	mol of i in equilibrium liquid
$\sum l_i = L$	total liquid
$f_i = z_i F$	mol of i in feed
N	number of equilibrium stages
x_i	mol fraction in liquid
z_i	mol fraction in feed
$A_i = L/K_i V$	absorption factor
$A_o = [A_B(A_T + 1) + 0.25]^{1/2} - 0.5$	effective absorption factor for n plates
$S_i = K_i V/L$	stripping factor
$S_o = [S_T(S_B + 1) + 0.25]^{1/2} - 0.5$	effective stripping factor for m plates
$\Phi_A = 1 - f_a$	absorption factor function
f_a	fraction absorbed

$\Phi_s = 1 - f_s$ stripping factor function
 f_s fraction stripped

Subscripts

EP enriching pinch
 XP exhausting pinch
i component or stage designation
j stage designation
 cond condenser
 reb reboiler
x constant liquid composition
y constant vapor composition

Superscripts

L liquid phase
V vapor phase
F feed

REFERENCES

- Hildebrand J. H., Scott R. B.: *Solubility of Non-Electrolytes*. Reinhold, New York 1950.
- Scatchard G.: Chem. Rev. 8, 321 (1934).
- Scatchard G.: J. Am. Chem. Soc. 56, 995 (1934).
- Chao K. C., Seader J. D.: A.I.Ch.E.J. 7, 598 (1961).
- Peters H. F.: Pet. Ref. 28, 109 (1949).
- Papadopoulos A., Pigford R. L., Friend L.: Chem. Eng. Progr., Symp. Series 49, 119 (1953).
- Canjar L. N., Edmister W. C.: Chem. Eng. Progr., Symp. Series 49, 73 (1953).
- Lydersen A. L., Greenkorn R. A., Hougren O. A.: Univ. Wisconsin Eng. Expt. Sta. Rep. No 4. Madison, Wisconsin 1955.
- Curl R. F., Pitzer K. S.: Ind. Eng. Chem. 50, 265 (1958).
- Edmister W. C.: Hydrocarbon Processing 46, 165 (1967).
- NGPSA: Engineering Data Book 8th Ed., p. 204. Natural Gas Processors Suppliers Association, Tulsa, Oklahoma 1966.
- Redlich O., Kwong J. N. S.: Chem. Rev. 44, 233 (1949).
- Benedict M., Webb G. B., Rubin L. C., Friend L.: Chem. Eng., Prog. 47, 571, 609 (1951).
- Edmister W. C., Vairogs W. C., Klekers A. J.: A.I.Ch.E.J. 14, 479 (1968).
- Edmister W. C., Persyn C. L., Erbar J. H.: Proceedings of 2nd Annual Convention of Natural Gas Processors Association, Houston, Texas, March 1963.
- Erbar J. H., Persyn C. L., Edmister W. C.: Proceedings of 43rd Annual Convention of Natural Gas Processors Association, New Orleans, Louisiana, March 1964.
- Edmister W. C., Lee B. I.: Presented at International Symposium on Distillation, Brighton, September 1969.
- Lee B. I., Edmister W. C.: Unpublished results.
- Fenske M. R.: Ind. Eng. Chem. 24, 482 (1932).
- Win F. W.: Ref. 37, No 5 (1958).
- Bachelor J. B.: Ref. 36, No 6 (1957).
- Erbar R. C., Joyner R. S., Maddox R. N.: Petro/Chem. Eng. 1961 No 3.

23. Erbar R. C., Maddox R. N.: *J. Chem. Eng.* **40**, 25 (1962).
24. Underwood A. J. V.: *Chem. Eng. Progr.* **44**, 603 (1948).
25. Short T. E., Erbar J. H.: *Petro/Chem. Eng.* **1963**, No 11.
26. Brown G. G., Martin H. Z.: *Trans.A.I.Ch.E.J.* **35**, 679 (1939).
27. Gilliland E. R.: *Ind. Eng. Chem.* **32**, 1101 (1940).
28. Erbar J. H., Maddox R. N.: *Ref.* **40**, No 5 (1961).
29. Gray J. R.: *Thesis*. Oklahoma State University, 1968.
30. Joyner R. S., Erbar J. H., Maddox R. N.: *Petro/Chem. Eng.*, **1962**, No 2.
31. Kremser A.: *Natl. Petrol. News* **22**, 42 (1930).
32. Sounders M., Brown G. G.: *Ind. Eng. Chem.* **24**, 519 (1932).
33. Edmister W. C.: *A.I.Ch.E.J.* **3**, 165 (1957).
34. Owens W. R., Maddox R. N.: *Ind. Eng. Chem.* **60**, 14 (1968).
35. Lewis W. K., Matheson G. L.: *Ind. Eng. Chem.* **24**, 494 (1932).
36. Thiele E. W., Geddes R. L.: *Ind. Eng. Chem.* **25**, 284 (1933).
37. Bonner J. S.: *Proc. Am. Petrol. Inst.* **36**, Sec. III, 238 (1956).
38. Erbar J. H., Maddox R. N.: *Proceedings of 38th Annual Convention of Natural Gasoline Association of America*, Dallas, Texas, April 1959.
39. Greenstadt J., Bard Y., Morse B.: *Ind. Eng. Chem.* **50**, 1644 (1958).
40. Lyster W. N., Sullivan S. L., Billingsley D. W., Holland C. D.: *Ref.* **38**, 221 (1959).
41. Holland C. D.: *Multicomponent Distillation*, p. 190. Prentice-Hall, New York 1963.
42. Burman L. K., Maddox R. N., Erbar J. H.: *Evaluation of a Relaxation Procedure for Multicomponent Distillation Columns*. A.I.Ch.E. Meeting, Dallas, Texas 1966.
43. Rose A., Johnson C. L., Williams T. J.: *Ind. Eng. Chem.* **48**, 1173 (1956).
44. Rose A., Sweeny R. E., Schrodtt V. N.: *Ind. Eng. Chem.* **50**, 737 (1958).
45. Ball W. E.: Presented at A.I.Ch.E. Meeting, New Orleans, Louisiana 1961.
46. Sujata A. D.: *Hydrocarbon Processing* **40**, 137 (1961).
47. Spear R. R., Maddox R. N., Erbar J. H.: *An Evaluation of the Sujata Method for Predicting Absorbed Performance*. A.I.Ch.E. Meeting, Dallas, Texas 1966.
48. Taylor D. S., Edmister W. C.: Presented at International Symposium on Distillation, Brighton, September 1969.