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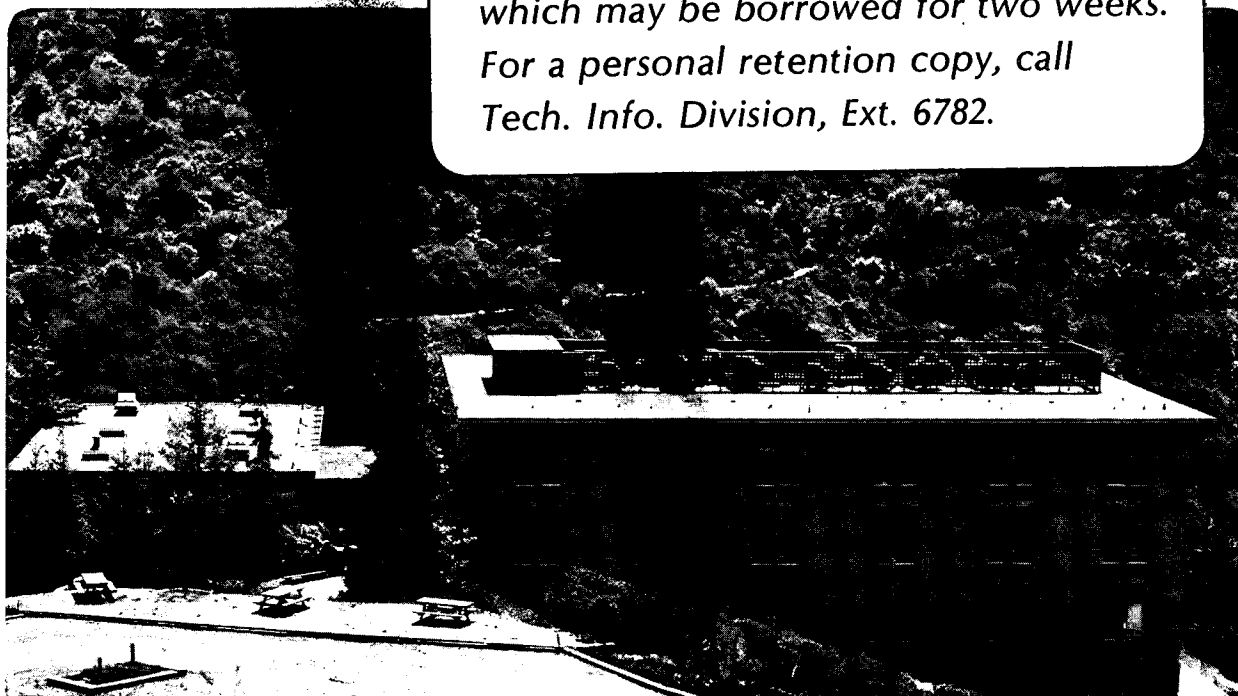
FLASH CALCULATIONS FOR CONTINUOUS OR SEMI-CONTINUOUS  
MIXTURES USING AN EQUATION OF STATE

R.L. Cotterman and J.M. Prausnitz

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**Flash Calculations for Continuous or Semi-Continuous  
Mixtures Using an Equation of State**

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### Abstract

For a fluid mixture containing very many components, the usual discrete composition variables (e.g. mole fractions) can be replaced by a continuous distribution function. When that distribution function is introduced into an equation of state, an expression for the chemical potential is obtained. Phase-equilibrium calculations are often straightforward when a simple algebraic form is used for the distribution function. However, when phase-equilibrium calculations are combined with material balances, as in flash calculations, it is not always possible to obtain a completely self-consistent result because if a simple algebraic form is used for the feed-stream distribution function, it does not follow that this form also holds for the two effluent-stream distribution functions.

This work describes two procedures for performing flash calculations using continuous thermodynamics. The first procedure, called the method of moments, provides only an approximation because it does not strictly satisfy all material balances; however, in some cases this approximation can be very good. A second procedure, called the quadrature method, uses efficient Gaussian integration; it does not use an algebraic form for the distribution function but provides exact solutions to the flash problem at selected values of the distribution variable. Both procedures are illustrated with realistic examples, including fluid mixtures where a selected component (e.g.  $CO_2$ ) is considered as a discrete component while all others are considered as continuous components; this is the semi-continuous case. Calculations are also given for fluid mixtures containing several homologous series (or ensembles) as found, for example, in petroleum mixtures where the ensembles may be paraffinic, naphthenic and aromatic hydrocarbons.

Compared to conventional pseudo-component methods, flash calculations using continuous thermodynamics have an important advantage because they require no arbitrary identification of pseudo-components.

Calculated results using the quadrature method are compared to experimental data for phase equilibria in a natural-gas mixture. Agreement is very good for compositions of coexisting phases and for liquid yield during retrograde condensation.

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## Introduction

Many of the fluid mixtures found in nature and in the chemical industry are ill-defined in the sense that the mixture contains far too many components for standard chemical analysis toward identifying the components and their concentrations; common examples are petroleum, coal-derived liquids and vegetable oils. Such mixtures can, however, be characterized upon separation of fractions (e.g. by fractional distillation, extraction or crystallization) and subsequent physical measurements for each fraction (e.g. molecular weight, boiling point and density). Phase equilibria for such mixtures are usually computed using standard thermodynamic procedures wherein each fraction is considered to be some equivalent pure component; such computations are said to use the pseudo-component method.

An alternate procedure for calculating phase equilibria in ill-defined mixtures is based on the view that the mixture contains not a finite number of pseudo-components but instead, an infinite number of true components. The composition of such a mixture is not described through conventional discrete concentrations (such as mole fractions) for each component but instead, through a continuous distribution function whose independent variable is some appropriate characterizing quantity such as boiling point or molecular weight. The equilibrium properties of a continuous mixture are described upon extension of well-known thermodynamic methods for discrete mixtures. That extension is often called continuous thermodynamics.

Based on earlier work by Rätzsch and Kehlen(1980), Salacuse and Stell(1982) and Gualtieri, Kincaid and Morrison(1982), Cotterman, Bender and Prausnitz(1984) presented a general procedure for calculating phase equilibria using continuous thermodynamics. In particular, it was shown how an equation of state of the van der Waals form can be used to perform such calculations for continuous or semi-continuous mixtures; the latter are those where the concentrations of some components (usually those present in excess) are given by discrete values while those of other components

are given by a distribution function.

To apply phase-equilibrium thermodynamics to engineering design, it is necessary to establish procedures for performing flash calculations. This work presents two such procedures within the framework of continuous thermodynamics and then discusses their advantages relative to one another and relative to the pseudo-component method. Comparisons between calculated and experimental results are presented for a gas-condensate mixture.

### **Flash-Calculation Procedures**

For mixtures with a finite number of components, many numerical procedures have been suggested to solve the set of isothermal flash equations (see e.g., King, 1980; Michelsen, 1982; Nghiem, Aziz and Li, 1983). However, for a mixture with a continuous distribution of components, these procedures require extensive modifications, as discussed below.

Flash-calculation procedures for continuous mixtures have been reported for petroleum distillations (e.g., Bowman, 1949; Hoffman, 1968; Taylor and Edmister, 1971). However, these procedures are restricted to simple models, such as Raoult's Law, coupled with numerical integration methods or approximation functions to solve the material-balance equations. Fractionation calculations for polymer systems use similar methods for liquid-liquid separations (e.g., Scott, 1945; Koningsveld and Staverman, 1968; Huggins and Okamoto, 1967) based on dividing a polymer distribution into a large number of discrete fractions, suitable for numerical integration. An analytical procedure has been presented by Gualtieri, Kincaid and Morrison (1982) for approximate flash calculations in dilute semi-continuous mixtures. Recent work by Rätzsch and Kehlen (1983) gives a formal mathematical analysis of phase equilibrium in continuous systems with approximations for flash calculations based on Raoult's Law with compositions described by Gaussian (normal) distributions.

We present first a general formulation of the governing equations for isothermal flash calculations in continuous or semi-continuous systems. We then discuss two techniques for solving these equations.

To fix ideas, Figure 1 shows schematically an isothermal vapor-liquid flash for a continuous system. Temperature, pressure and feed composition are specified; the compositions and relative amounts of the outlet streams are to be calculated. The feed and outlet streams are related through material balances; the two outlet streams are assumed to be in thermodynamic equilibrium.

For a mixture with a continuous distribution of components, the composition is described by a molar distribution function  $F$  whose independent variable  $I$  is some characterizing property such as molecular weight. This function,  $F(I)$ , is normalized such that

$$\int_I F(I) dI = 1 \quad (1)$$

over the pertinent range of  $I$ .

Semi-continuous mixtures are those where the concentrations of some components are assigned discrete values while the concentrations of others are described by a distribution function. The continuous fraction is weighted with a mole fraction,  $\eta$ , and each discrete component  $i$  is weighted with mole fractions, designated by, say,  $x_i$ . For  $n$  discrete components, the normalization is

$$\sum_i^n x_i + \eta \int_I F(I) dI = 1 \quad (1a)$$

The feed stream is related to the outlet streams through a set of material balances. We define the fraction vaporized,  $\xi$ , as the ratio of moles of vapor to moles of feed. For every discrete component,  $i$ , the material balance is



$$z_i = \xi y_i + (1-\xi)x_i \quad (2)$$

where  $z_i$ ,  $y_i$  and  $x_i$  are feed, vapor and liquid mole fractions for component  $i$ , respectively.

For the continuous fraction, we introduce a distribution function,  $F(I)$ , and a mole fraction,  $\eta$ , for each phase. For all  $I$ ,

$$\eta^F F^F(I) = \xi \eta^V F^V(I) + (1-\xi) \eta^L F^L(I) \quad (3)$$

where superscripts  $F$ ,  $V$ , and  $L$  designate feed, vapor and liquid, respectively.

Since the two effluent streams are at equilibrium, we require first, for every component  $i$

$$\mu_i^V = \mu_i^L \quad (4)$$

and second, for all  $I$

$$\mu^V(I) = \mu^L(I) \quad (5)$$

where  $\mu$  is the chemical potential.

The essence of the flash problem is to solve simultaneously material balances [Equations (2) and (3)] and phase equilibria [Equations (4) and (5)].

### Phase Equilibria from an Equation of State

As discussed previously (Cotterman, et.al., 1984), chemical potentials in continuous (or semi-continuous) fluid mixtures can be found from an equation of state. For the vapor phase,

$$\mu^V(I) = \int_{V^0}^V \left\{ \frac{\delta P}{\delta n_c F(I^+)} \right\}_{T,V,I^+=I} dV - \frac{RT}{V} dV - RT \ln \frac{P^0 V^V}{n_c^V F^V(I) RT} + RT + \mu^0(T,I) \quad (6)$$

where  $F(I)$  is the molar distribution function,  $n_c$  is the number of moles of continuous

components,  $V$  is the total volume,  $P$  is the system pressure,  $P^o$  is the ideal-gas reference pressure (taken to be 1 bar) and  $\mu^o$  is the chemical potential of a species at  $I$  in a continuous mixture that is an ideal gas at temperature  $T$  and 1 bar. A similar relation holds for  $\mu^L(I)$ .

To illustrate, we use an equation of state similar to Soave's (1972) modification of the Redlich-Kwong equation of state. For a pure component,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (7)$$

where  $b$  is a molecular size parameter and energy parameter  $a(T)$  is a function of temperature.

Parameters  $a(T)$  and  $b$  were fit to pure-component vapor-pressure data. For a homologous series of hydrocarbon components,  $a(T)$  and  $b$  are linear functions of molecular weight. To extend this equation of state to mixtures, we use standard mixing rules as discussed previously. Appendix I gives details of the equation of state.

It was shown earlier (Cotterman, et.al., 1984) that, when Equation (7) is used, the distribution functions for two equilibrated phases can be related to one another. For example, if a gamma distribution describes the composition in one phase, that of the other phase is also described by a gamma distribution. The gamma distribution is

$$F(I) = \frac{(I-\gamma)^{\alpha-1} \exp(-\frac{I-\gamma}{\beta})}{\Gamma(\alpha)\beta^\alpha} \quad (8)$$

where  $\Gamma$  is the gamma function and where  $\alpha$  and  $\beta$  are adjustable parameters. The mean is given by  $\alpha\beta + \gamma$  and the variance by  $\alpha\beta^2$ . Shift parameter  $\gamma$  indicates the origin of  $F(I)$ ; that parameter is the same for both phases.

Relations can then be developed between parameters  $\alpha$  and  $\beta$  for the vapor phase and those for the liquid phase, so as to give a set of non-linear equations; solution of these equations gives the dew point or bubble point in a continuous or semi-

continuous mixture. If the composition of one phase is specified, the composition of the other can be found without approximations.

When extended to flash calculations, however, the material balances must also be satisfied. Unfortunately, the material balances introduce a third distribution function, viz. that of the feed. For the general case, there is no universal distribution function, applied to all three streams, for which phase equilibria and material balances can be satisfied for all values of index  $I$ . Therefore, the flash calculation for a continuous or semi-continuous mixture can only be solved approximately. We now present two approximate procedures which give good results while maintaining low computer-time requirements.

### The Method of Moments

The method of moments is a direct extension of our previous work on dew-point and bubble-point calculations. We assume that, to within a well-defined approximation, for all three streams, the composition of the continuous fraction of each stream of the flash calculation is described by a gamma distribution function. Using Equations (3) and (5), we can relate approximately the parameters which characterize each of all three gamma distributions.

Since it is not possible to relate the distribution-function parameters exactly, we use Equation (3) to guide us in developing an approximate solution. By multiplying each term of Equation (3) by index  $I$ , and integrating over the pertinent range of  $I$ , we generate a relation between the first moments (or means) of the distribution functions,  $F(I)$ . We can repeat this procedure with other integral powers of  $I$  to generate a set of moment equations of the form:

$$\eta^F M_r^F = \xi \eta^V M_r^V + (1-\xi) \eta^L M_r^L \quad (9)$$

where  $M_r$  is the  $r^{\text{th}}$  statistical moment about the origin of the distribution  $F(I)$ .  $M_r$  is

defined by

$$M_r \equiv \int_I I^r F(I) dI \quad (10)$$

where, more generally,  $I$  must be replaced by  $(I - \gamma)$ .

To satisfy the material balance exactly, all moment equations ( $r=1,2,\dots,\infty$ ) for the continuous fraction must be satisfied. The gamma distribution function contains only two parameters,  $\alpha$  and  $\beta$ ; therefore, only two moment equations can be considered. The zeroth moment is necessarily satisfied through the overall material balance. Therefore, we choose the first and second moment equations to relate our distribution-function parameters; we neglect higher moments. Some error is thereby introduced into the material balance. By choosing to satisfy only the lower moment relations, we fail to satisfy higher moment relations. For many cases, however, this error is not significant. Details of the method of moments are given in Appendix II.

Figure 2 shows results of a flash calculation for a semi-continuous mixture using the method of moments; the molar distributions of the continuous fractions in each stream are shown as a function of molecular weight. The area under each curve represents the number of moles based on a total feed stream of one mole.

The feed contains 40 mol % carbon dioxide while the remainder is a continuous distribution of paraffins with a mean molecular weight of 100 and a variance of 800. We use binary interaction parameter  $k_{12}=0.12$  for carbon dioxide(1)-paraffin(2) interactions [see Appendix I]. Calculations are shown at two pressures, 10 and 50 bar, at temperatures where the moles of the continuous fraction are evenly split between the vapor and the liquid; this is where the error in the material balance is largest. Table 1 presents additional results for this flash calculation.

In the example shown at the top of Figure 2 at 50 bar, the feed is flashed to form a vapor and a liquid whose continuous distributions are similar. The specified feed is shown as a solid line; the sum of the vapor and liquid curves is shown as a dotted line.

The difference between these two curves represents the error in the material balance. At 50 bar, the material balance is satisfied very well over the molecular weight range. The relative error in the maximum of the feed distribution functions is 1.5%.

At 10 bar, the shapes of the vapor and liquid distributions are much different and the material balance error is larger--the relative error in the maximum of the feed distribution is 3.5%.

These comparisons represent worst-case results; they suggest that the error in the material balance is negligible in many cases.

### The Quadrature Method

The second procedure for solving flash-calculation equations in continuous or semi-continuous systems introduces numerical integration by Gaussian quadrature into integral-algebraic Equations (3) and (5).

Gaussian quadrature provides an efficient method of integrating a function by summing a finite number of weighted function evaluations at specified values of the integration variable called quadrature points. For each of these points, phase equilibria and material balances are satisfied exactly. For  $s$  quadrature points,

$$\int_I f(I) dI = \sum_{p=1}^s w(I_p) f(I_p) \quad (11)$$

where  $w(I_p)$  is the weighting function and  $f(I_p)$  is the function to be integrated at the quadrature point,  $I_p$ . Details describing quadrature integration may be found in texts on numerical methods (e.g., Lapidus, 1962 or Hamming, 1973).

The quadrature points and weighting factors are not arbitrary. They are roots of a class of orthogonal polynomials which effectively approximate an integral by a polynomial of degree  $(2p - 1)$ . For tabulated values, see Abramowitz and Stegun (1972).

Appendix III describes the implementation of quadrature integration into the flash-calculation equations. In this procedure, the composition distribution of the continuous fraction of each stream is described by a collection of quadrature points, rather than by a continuous distribution function. Equations (3) and (5) are replaced by  $s$  sets of the following equations:

$$\eta^F F^F(I_p) = \xi \eta^V F^V(I_p) + (1-\xi) \eta^L F^L(I_p) \quad (12)$$

$$\mu^V(I_p) = \mu^L(I_p) \quad (13)$$

The continuous functional relations [Equations (3) and (5)] are replaced by a finite set of algebraic equations (12) and (13).

The quadrature method is analogous to the well-known pseudo-component procedure. However, in the quadrature procedure, the definition of the quadrature points is not arbitrary. Usually, six to ten points are sufficient to characterize a distribution for phase-equilibrium calculations.

Unlike the method of moments, the quadrature method may be used with an arbitrary feed distribution function,  $F^F(I)$ , analytical or not. Similarly, there are no restrictions on the molecular-thermodynamic model.

Flash calculations using the quadrature method give values for the outlet streams' distribution functions,  $F^V(I)$  and  $F^L(I)$ , at each feed quadrature point. Thus, while the method of moments gives an approximate but complete representation of composition for the outlet streams, the quadrature method gives these functions only at discrete points, but it does so exactly.

Figure 3 shows results for a flash calculation for a semi-continuous mixture using the quadrature method. The feed contains 40 mol %  $CO_2$  while the remainder is a continuous distribution of paraffins. At 510 K and 50 bar, the fraction vaporized is 0.640. The calculated vapor stream is rich in  $CO_2$  (52.1 mol %) while the liquid contains only

18.6 mol %  $CO_2$ . For the  $CO_2(1)$ -paraffin(2) interaction, we again use  $k_{12}=0.12$ .

Calculated results for the liquid and vapor distributions are shown as solid points. The dashed curves are interpolations using cubic spline fits. Figure 4 shows additional results for the same mixture.

On the left side of Figure 4, we compare computer-time requirements for flash calculations. The method of moments requires 1.50 CPU seconds while the quadrature method requirement varies between 1.13 and 2.53 CPU seconds depending on the number of quadrature points chosen.

The diagram on the right in Figure 4 shows the sensitivity of the calculated fraction vaporized to the number of quadrature points. For more than 4 points, the fraction vaporized does not change significantly. From the results shown in Figure 4, we conclude that, for this simple system, six quadrature points are sufficient to maintain both high accuracy and low computer-time requirements.

### **Extension to More Complex Mixtures**

In the discussion above, we have considered simple, unimodal distribution functions for mixtures composed primarily of paraffins. We can extend our procedures to more complicated distributions as required for more complex mixtures.

Cotterman, et.al.(1984) showed that dew-point and bubble-point calculations could be performed for mixtures described not by one distribution function but by a sum of gamma distributions. For such mixtures, flash calculations can also be performed using the method of moments; details are given in Appendix II.

The quadrature method accepts an arbitrary distribution for describing composition. Therefore, there are no restrictions on the shape or modality of the feed distribution. However, the more complex the distribution, the more quadrature points are required to represent integral properties accurately.

We are not restricted to systems containing only one homologous series. An elegant method to characterize more complicated systems (avoiding multivariate distribution functions) is to consider the mixture composed of various ensembles, as also proposed by Kehlen and Rätzsch (1983). An ensemble is a collection of chemically-similar components. For example, a hydrocarbon mixture may contain three homologous series: paraffins, aromatics and naphthenes; each of these forms an ensemble described by a particular distribution function.

Figure 5 illustrates the ensemble concept. Within each phase of a semi-continuous mixture, there is a distribution function for each continuous ensemble, weighted by a mole fraction,  $\eta$ . Each ensemble is considered as a separate component. Since the mole fractions in each phase must be normalized, for  $m$  ensembles and  $n$  discrete components, we write for the liquid phase,

$$\sum_1^n x_i + \sum_k^m \eta_k^L \int_I F_k^L(I) dI = 1 \quad (14)$$

We have similar normalization conditions for the vapor phase and for the feed.

We write a phase-equilibrium criterion for each ensemble  $k$ :

$$\mu_k^V(I) = \mu_k^L(I) \quad (15)$$

The material balance for the flash is, for each ensemble  $k$ ,

$$\eta_k^F F_k^F(I) = \xi \eta_k^V F_k^V(I) + (1-\xi) \eta_k^L F_k^L(I) \quad (16)$$

The chemical potential for each ensemble is calculated using the same equation of state; however, we use a different set of parameters for each ensemble. Multiple ensembles may be incorporated into both the method of moments and the quadrature method. The discussions in Appendices II and III include multiple ensembles.



Figure 6 presents results for a flash calculation using the quadrature method for a semi-continuous mixture containing distributions of aromatics and paraffins at 570 K and 50 bar. Table 2 gives mole fractions of components in each phase (all  $k_{ij}=0$ ). Ten quadrature points are used to describe the composition of each continuous ensemble; these points need not be the same for all ensembles. Calculated results for the liquid and for the vapor are shown as points. The dashed curves represent interpolations. The heavy, solid curve shows the sum of the individual ensembles.

### Comparison of the Quadrature Method to the Pseudo-Component Method

In the next examples, phase-equilibrium calculations using the quadrature method are compared to those using the pseudo-component method first, for a mixture of paraffins at 5 bar and second, for a mixture of  $CO_2(1)$  and paraffins(2) at 20 bar where the interaction parameter,  $k_{12}$ , is a function of molecular weight.

For the first example, Figure 7 shows the composition of a 24-component feed mixture of normal paraffins. Using all 24 components, Table 3 shows the bubble-point and dew-point temperatures as well as a flash result at 480K. All  $k_{ij}$  are set to zero. These calculations were repeated using first, a six-point quadrature method and then, using the pseudo-component method with three different lumping criteria for defining pseudocomponents. Calculated bubble points agree within 10 K for all methods but calculated dew points, where the characterization of the high-molecular-weight tail is important, show a large range. Results from the quadrature method are very close to those from the exact 24-component result. By contrast, results using the pseudo-component method depend on how the pseudocomponents are chosen. The quadrature method eliminates the arbitrariness required in defining pseudocomponents.

For the flash calculation, all methods give a similar fraction vaporized because that fraction is not sensitive to details in the composition distributions. Using similar programming schemes, computer-time requirements are reported. The exact

calculation, using all 24 components, requires 1.2 CPU seconds while the six-point quadrature method and the six pseudo-component methods require 0.45 CPU seconds.

For the second example, the paraffin distribution shown in Figure 7 is mixed with  $CO_2$  to produce a feed with 40 mol %  $CO_2$ . Binary interaction parameters between  $CO_2(1)$  and paraffins(2) were fit to binary vapor-liquid equilibrium data to obtain a  $k_{12}$  as a function of molecular weight,  $I$ :

$$k_{12} = 0.100 + 0.109 \exp(-0.007874 I) \quad (17)$$

Equation (17) gives an adequate representation of binary  $CO_2$ -paraffin equilibria for normal paraffins between butane and eicosane. Table 4 gives results of bubble-point, dew-point and flash calculations at 20 bar. As in the previous example, bubble-point temperature and fraction vaporized are not sensitive to the calculation method. However, dew-point temperatures depend strongly on how the "heavies" are characterized.

In both of the previous examples, flash-calculation computer-time requirements for the quadrature method and for the grouping schemes are a factor of 3 less than those for the 24-component calculation. A 6-component quadrature method calculation requires approximately the same computer time as a lumped 6-pseudocomponent method. By introducing interaction parameters for all binary pairs containing  $CO_2$ , computer times double for all schemes.

These simple examples illustrate the advantages of the quadrature method over conventional lumped-pseudocomponent methods for flash calculations. For engineering applications, the quadrature method may be incorporated without significant modification into existing numerical algorithms for flash calculations and for design of staged separation operations.

## Comparison of Calculated and Experimental Results for Natural-Gas Condensation

To illustrate the application of the quadrature method to real mixtures, flash-calculation results are compared with experiment for a gas-condensate system. Hoffmann, Crump and Hocott(1953) report dew-point and flash results in the retrograde region for a reservoir-gas sample at 367 K. These authors give quantitative analyses for light hydrocarbons to  $C_6$  and for distillation cuts such that each cut corresponds to a normal paraffin in the range  $C_7$  to  $C_{22}$ . In addition, liquid densities and liquid-vapor ratios are tabulated.

In our calculations, the reservoir-gas mixture is considered to be a semi-continuous mixture of discrete light hydrocarbons ( $C_1-C_4$ ) and a continuous "heavies" fraction. Using the quadrature method, nine quadrature points are chosen to represent the heavies distribution. The composition data of Hoffmann et.al. are converted to molar distributions by dividing the mole fraction of each distillation cut by the width of the molecular-weight range covered (in this case, 14). Table 5 gives compositions and the top portion of Figure 8 shows the heavies distribution in the feed with the specified quadrature points. The molar distribution at each quadrature point is obtained by interpolating between the midpoints of the cuts.

We use once again the equation of state discussed earlier. To describe the heavies, we use equation-of-state constants fit to vapor pressures of normal alkanes. Binary interaction parameters,  $k_{ij}$ , are set equal to zero for all pairs except the methane-heavies pair where we use 0.085, obtained by matching the calculated dew-point pressure at 367 K to the experimental value, 264.66 bar. Table 5 shows calculated and experimental liquid compositions at the dew point.

Hoffmann et.al. report flash results at six pressures between 35.5 and 200.9 bar in the retrograde region. Upon specifying the feed composition, the compositions and relative amounts of the vapor and liquid streams are calculated at each pressure. Calculated and experimental results are in good agreement; Table 6 gives typical results

at an intermediate pressure.

Figure 8 shows the distributions of heavies in the equilibrium phases. The bars represent experimental distributions; the smooth curve is an interpolation between calculated values of the molar distribution at quadrature points. The lower portion of Figure 8 shows a predicted bimodal distribution in the liquid phase, barely evident in the feed distribution. Calculations at other pressures give similar results.

Figure 9 presents calculated and experimental equilibrium ratios [ $K_i = y_i / x_i$ ] for each component as a function of pressure at 367 K.

As a final example, Figure 10 shows the liquid yield, or liquid-vapor ratio, as a function of pressure at 367 K. Since experimental results are presented as volume ratios, our calculated molar ratios are converted to volumetric units. Vapor volumes are corrected to standard conditions of 15.5 °C (60 °F) and 1.013 bar using the ideal-gas law. Experimental liquid densities are tabulated at system  $T$  and  $P$ . Table 7 compares calculated and experimental results.

At constant temperature, a reduction of pressure through the retrograde region produces two dew points. Figure 10 shows the measured dew point at 264.66 bar. Assuming that no solid phases are formed, a second dew point is encountered at 0.015 bar. In between these two dew points, there is an observed maximum in the liquid-vapor ratio, correctly predicted by the flash calculations.

Similar comparisons between calculated and experimental results have been reported using pseudo-component calculations (Starling, 1966; Katz and Firoozabadi, 1978).

Using our modified Redlich-Kwong-Soave equation of state, the quadrature method works well for natural-gas mixtures where the average molecular weight of the heavies is below (about) 400. For prediction of phase equilibria in higher-molecular-weight systems, typical of crude oils, a better molecular model is needed. Toward that end, current work is in progress to apply the perturbed-hard-chain theory (Donohue

and Prausnitz, 1978) to semi-continuous mixtures for phase-equilibrium calculations.

## Conclusions

Continuous thermodynamics provides a convenient procedure for calculating phase equilibria for ill-defined mixtures where concentrations are not given by standard discrete variables but instead, by a continuous distribution function of some characterizing continuous variable. Toward application of continuous thermodynamics in process design, two procedures are here described for performing flash calculations. The first procedure, using the method of moments, is mathematically attractive but may introduce intolerable errors in the material balance. The second procedure, using the quadrature method, is less elegant but probably more useful for engineering work. Both methods appear to have possibly important advantages over the traditional pseudo-component method because continuous thermodynamics avoids arbitrariness in the definition of pseudocomponents without an increase in computational requirements. Continuous thermodynamics may be particularly useful for calculating those thermodynamic properties (for example, isobaric dew-point temperature) that are often sensitive to the arbitrary definition of pseudocomponents.

For retrograde condensation in a gas-condensate system, there is good agreement between calculated and experimental phase compositions and liquid yields. While the computational procedures discussed here are general, application to higher-molecular-weight systems will require a molecular-thermodynamic model which is better than that used in this work. Efforts toward that end are in progress.

The procedures discussed here may be useful for computer-aided design of separation operations and for simulation of reservoir behavior for enhanced oil recovery. Computer programs for performing flash calculations using continuous thermodynamics will be made available upon request.

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## Nomenclature

### Symbols

$a$	Equation-of-state attractive-energy parameter
$b$	Equation-of-state molecular-size parameter
$C^{(1)}, C^{(2)}$	Functions derived from equation of state
$F(I)$	Molar distribution function
$I$	Distributed variable (taken here as molecular weight)
$K$	Equilibrium Ratio
$k$	Binary interaction parameter
$M$	Statistical moment of distribution function
$m$	Number of continuous components
$n$	Number of discrete components
$P$	Absolute pressure
$R$	Gas constant
$s$	Number of Quadrature Points
$T$	Absolute temperature
$V$	Total volume
$v$	Molar volume
$w$	Quadrature-point weighting factor
$x$	Discrete-component mole fraction in liquid
$y$	Discrete-component mole fraction in vapor
$z$	Discrete-component mole fraction in feed
$Z$	Compressibility factor

### Subscripts

$i, j$	Discrete components
$k, l$	Continuous components
$p, q$	Quadrature points
$r$	Statistical moments

### Superscripts

$F$	Feed stream
$L$	Liquid stream
$V$	Vapor stream

Greek Symbols

$\alpha, \beta, \gamma$	Gamma-distribution-function parameters
$\Gamma$	Gamma function
$\mu$	Chemical potential
$\eta$	Continuous-component mole fraction
$\varphi$	Fugacity coefficient
$\xi$	Fraction of feed vaporized



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Table 1

Flash-Calculation Results Using the Method of Moments

P (bar)	T (K)	$\xi$	Vapor			Liquid		
			$y_{CO_2}$	Mean	Variance	$x_{CO_2}$	Mean	Variance
10	422	0.688	56.5	88.1	363	3.6	111.8	954
50	512	0.635	52.2	94.4	596	18.7	105.8	943

Table 2

Flash-Calculation Results for a Semi-Continuous, Multi-Ensemble  
Mixture Using the Quadrature Method

Component	Mole %		
	Feed	Vapor	Liquid
$C_1$	38.5	50.0	12.0
$C_2$	4.5	5.8	1.9
$C_3$	3.0	3.6	1.6
$C_4$	2.0	2.2	1.7
paraffins	36.0	29.4	50.9
aromatics	16.0	9.3	31.9

Table 3

Comparison of the Quadrature Method to the Pseudo-Component Method  
for a Paraffin Mixture at 5 bar

"Heavies" Characterization	Bubble Point (K)	Dew Point (K)	Flash Calculation T=480 K	
			$\xi$	CPU(sec)
All 24 components	436.3	539.2	0.559	1.25
6-Point Quadrature Method	437.0	540.3	0.557	0.45
6 Pseudocomponents (equal number)	445.2	535.9	0.566	0.45
6 Pseudocomponents (equal molar)	440.2	513.4	0.565	0.45
6 Pseudocomponents (equal mass)	444.9	524.8	0.524	0.45

Table 4

Comparison of the Quadrature Method to the Pseudo-Component Method  
for a  $CO_2$ -Paraffin Mixture at 20 bar

"Heavies" Characterization	Bubble Point (K)	Dew Point (K)	Flash Calculation T=450 K	
			$\xi$	CPU(sec)
All 24 components	267.7	569.8	0.498	2.30
6-Point Quadrature Method	267.7	570.0	0.500	0.75
6 Pseudocomponents (equal number)	267.7	566.7	0.491	0.75
6 Pseudocomponents (equal moles)	267.7	551.2	0.495	0.75
6 Pseudocomponents (equal mass)	267.7	561.2	0.487	0.75

**Table 5**

**Dew-Point Results for a Natural-Gas Mixture at 367 K**

(Calculated Dew Pressure = 264.66 bar)

Component	Mole %		
	Vapor specified	Liquid	
		calculated	experimental
$C_1$	91.35	51.99	52.00
$C_2$	4.03	4.53	3.81
$C_3$	1.53	2.47	2.37
$C_4$	0.82	1.90	1.72
Heavies	2.27	39.12	40.10

**Table 6**

**Flash-Calculation Results at 367 K and 138.87 bar**

Component	Mole %				
	Feed specified	Vapor		Liquid	
		calculated	experimental	calculated	experimental
$C_1$	91.35	92.17	92.18	35.72	34.19
$C_2$	4.03	4.03	4.03	4.08	3.62
$C_3$	1.53	1.51	1.57	2.72	2.87
$C_4$	0.82	0.80	0.78	2.52	2.57
Heavies	2.27	1.48	1.44	54.96	56.75

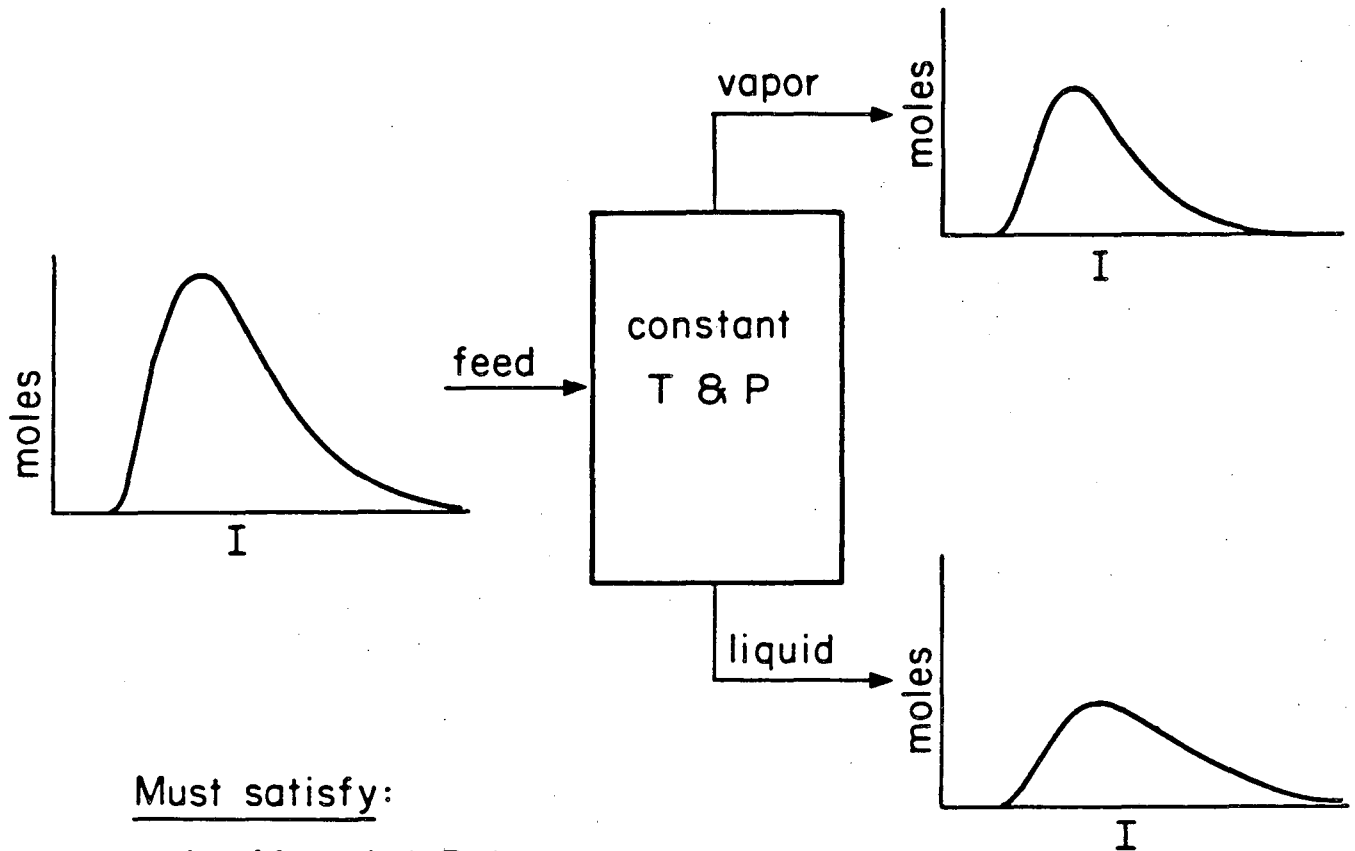
Table 7

**Liquid-Vapor Ratio for Retrograde Condensation  
in a Natural-Gas Mixture at 367 K**

Pressure (bar)	Liquid-Vapor Ratio		
	calculated		experimental
	(mol/mol) × 10 <sup>3</sup>	(m <sup>3</sup> /m <sup>3</sup> ) × 10 <sup>6</sup>	(m <sup>3</sup> /m <sup>3</sup> ) × 10 <sup>6</sup>
0.015 <sup>†</sup>	0.		
35.48	11.04	88.61	84.69
69.94	13.65	94.98	95.14
104.41	14.50	96.02	95.32
138.87	13.78	86.80	87.35
173.33	11.47	67.98	69.83
200.90	8.48	48.39	50.92
264.66 <sup>†</sup>	0.	0.	0.

<sup>†</sup> Dew point of gas mixture

Vapor volumes corrected to standard conditions [15.5 °C (60 °F) and 1.013 bar] using ideal-gas law. For the liquid, conversion from molar to volumetric units is based on experimental density data.



Must satisfy:

1. Material Balance

$$\eta^F F^F(I) = \xi \eta^V F^V(I) + (1 - \xi) \eta^L F^L(I)$$

$F(I)$  = distribution function

$I$  = distributed variable  
(e.g., molecular weight)

$\eta$  = mole fraction

$\xi$  = fraction vaporized

2. Phase Equilibria

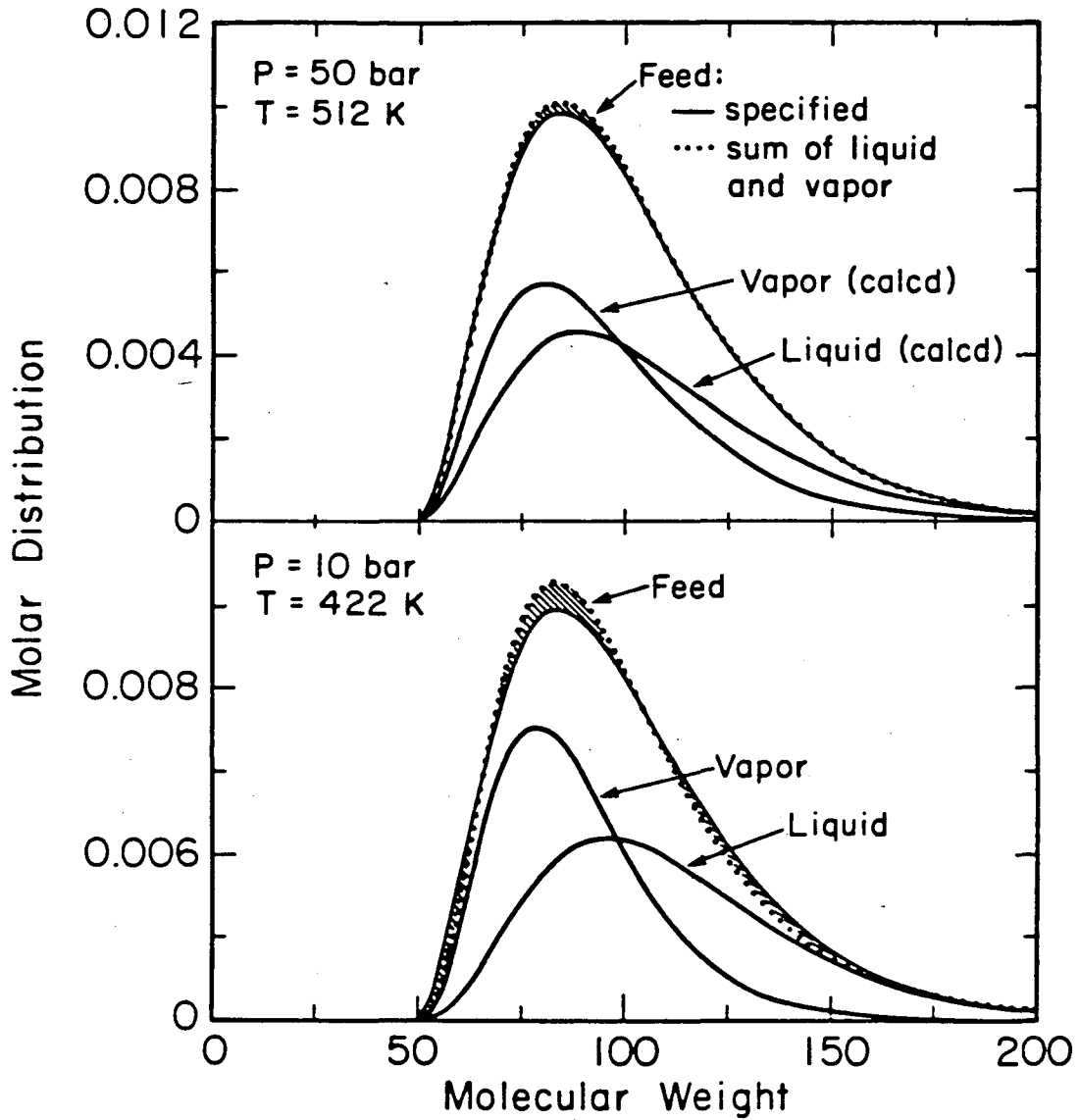
$$\mu^V(I) = \mu^L(I) \quad \text{for all } I$$

$\mu(I)$  = chemical potential

FIGURE 1

FLASH CALCULATION FOR A CONTINUOUS MIXTURE

Feed: 40% CO<sub>2</sub>, 60% paraffins (continuous).



Error in material balance indicated by shaded area.

FIGURE 2

FLASH CALCULATION RESULTS FOR A  
SEMI-CONTINUOUS MIXTURE USING  
METHOD OF MOMENTS



Feed: 40% CO<sub>2</sub>, 60% paraffins (continuous)

T = 510 K    P = 50 bar     $\xi = 0.639$

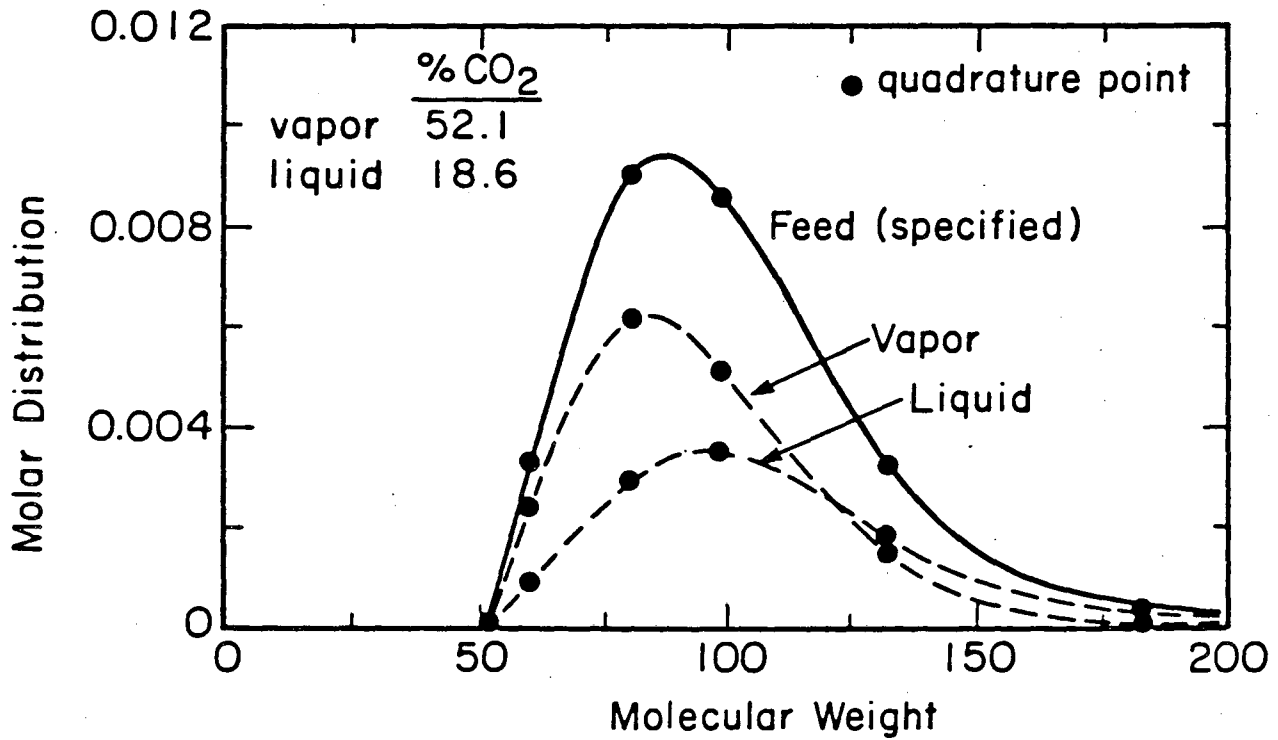


FIGURE 3

FLASH CALCULATION RESULTS FOR A SEMI-CONTINUOUS MIXTURE USING THE QUADRATURE METHOD

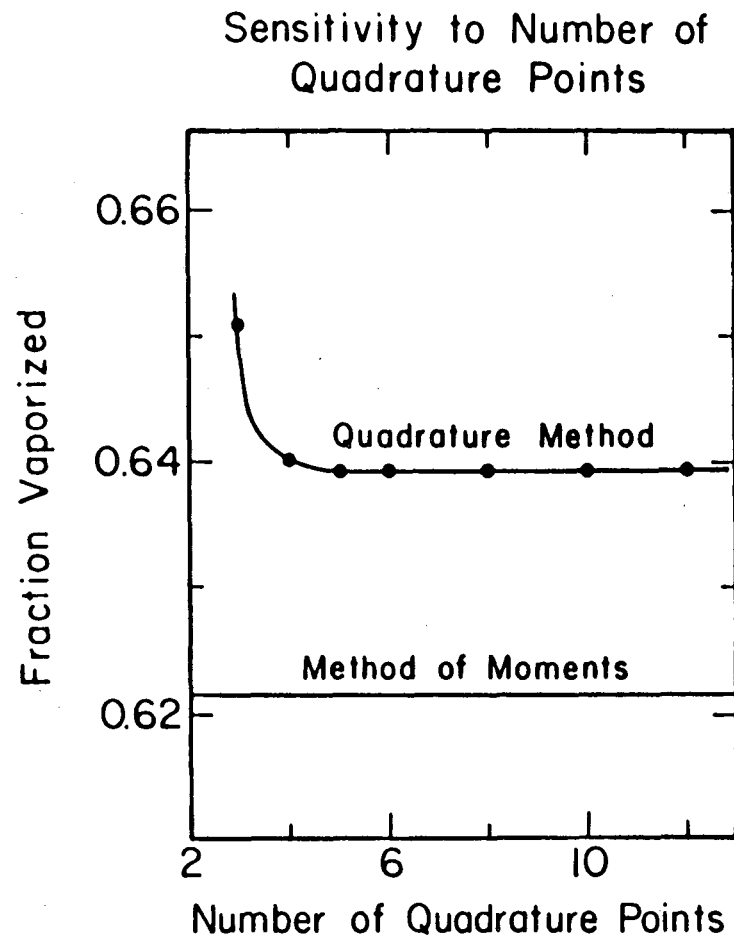
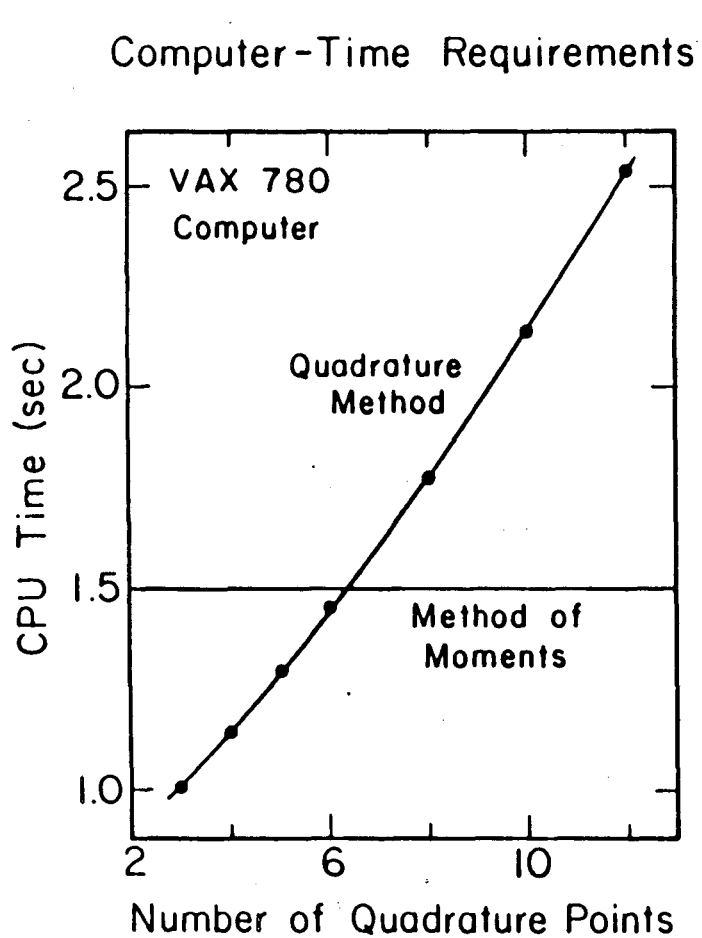


FIGURE 4

FLASH-CALCULATION RESULTS USING THE  
QUADRATURE METHOD

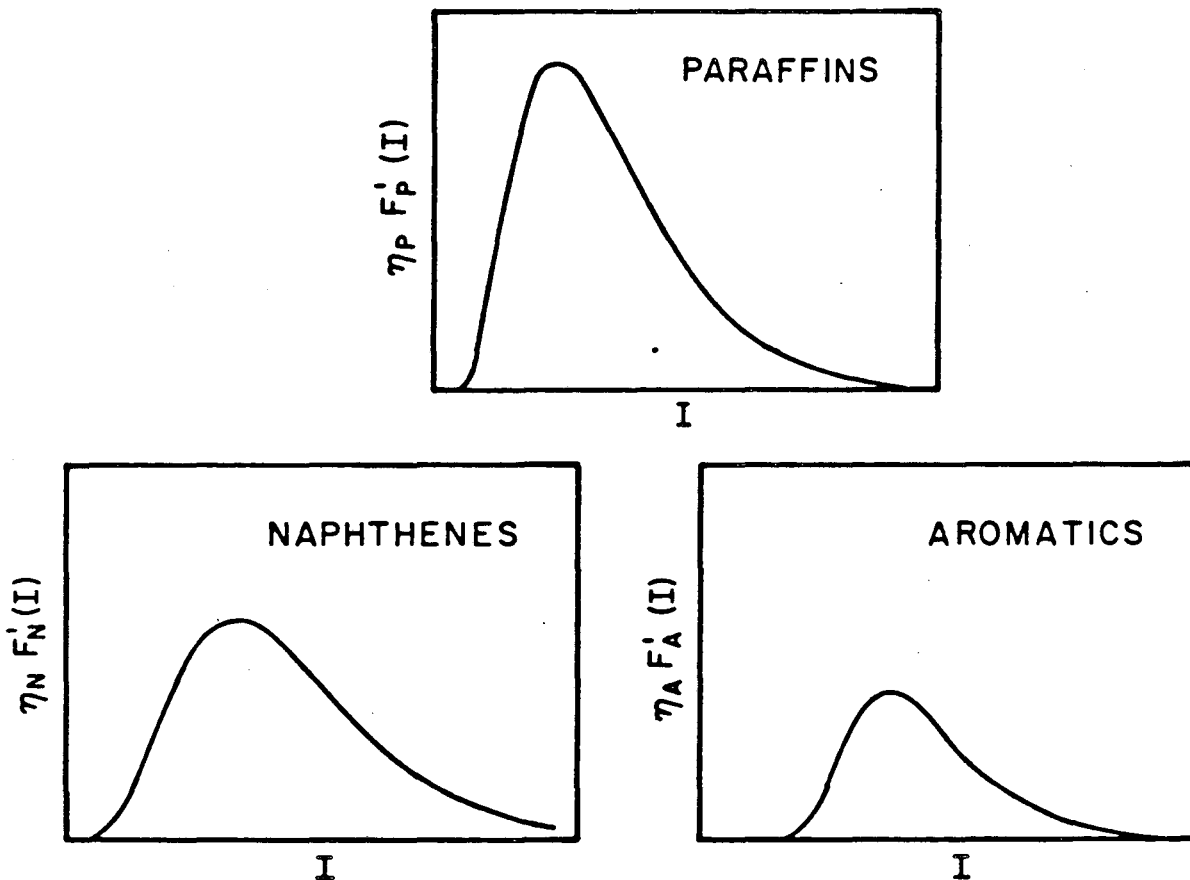
For a mixture of paraffins, naphthenes and aromatics

$$\mu_P^I(I) = \mu_P^{II}(I)$$

$$\mu_N^I(I) = \mu_N^{II}(I)$$

$$\mu_A^I(I) = \mu_A^{II}(I)$$

Three distributions for phase 'I',



We can then find the corresponding distributions for phase "II".

Material Balance for each phase

$$\eta_P + \eta_N + \eta_A = 1$$

FIGURE 5

FLUID-PHASE EQUILIBRIA FOR A SYSTEM  
CONTAINING THREE ENSEMBLES

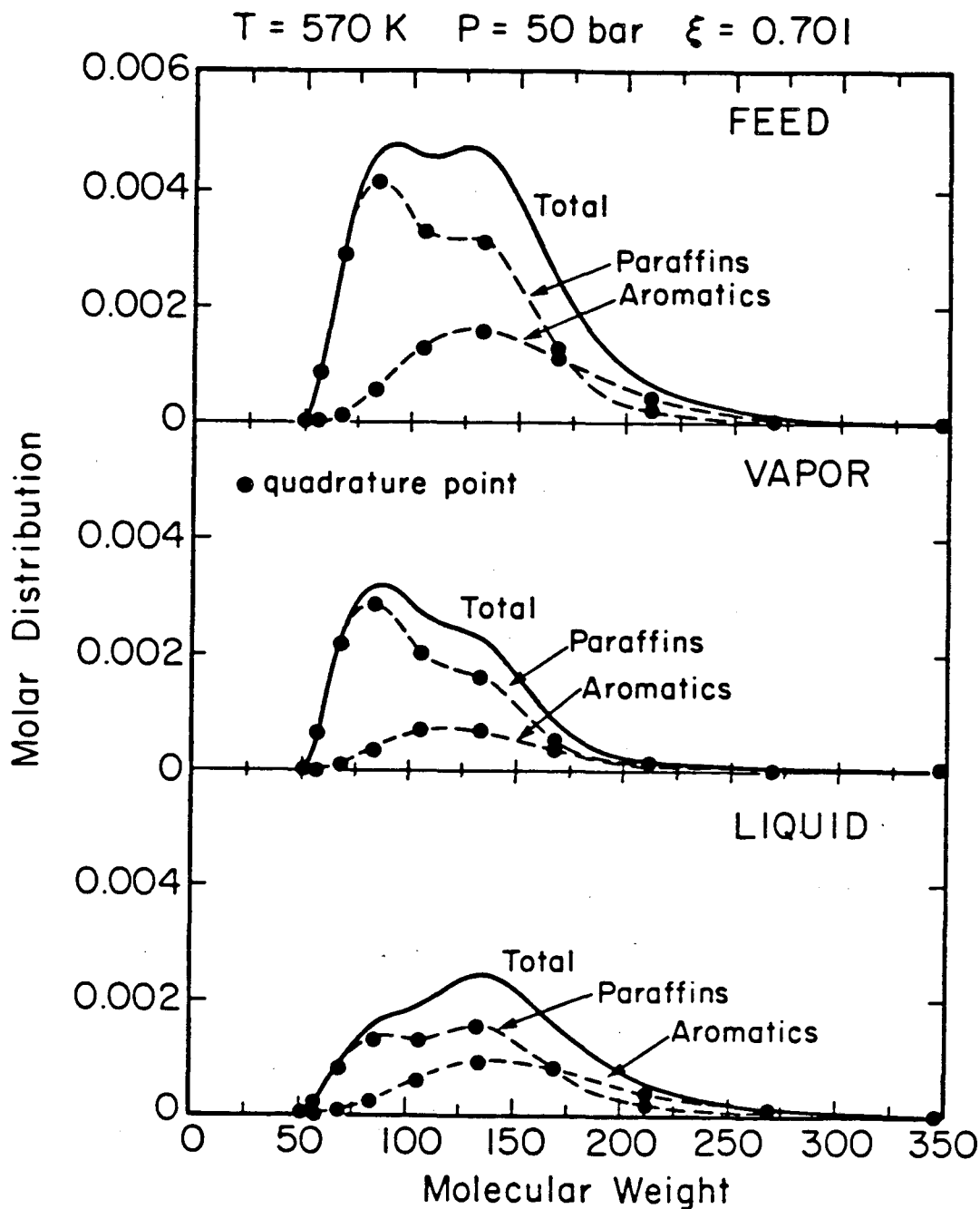


FIGURE 6

QUADRATURE METHOD FOR MIXTURE  
CONTAINING CONTINUOUS DISTRIBUTIONS  
OF PARAFFINS AND AROMATICS

Assumed feed composition for a 24-component system:  $C_4-C_{27}$

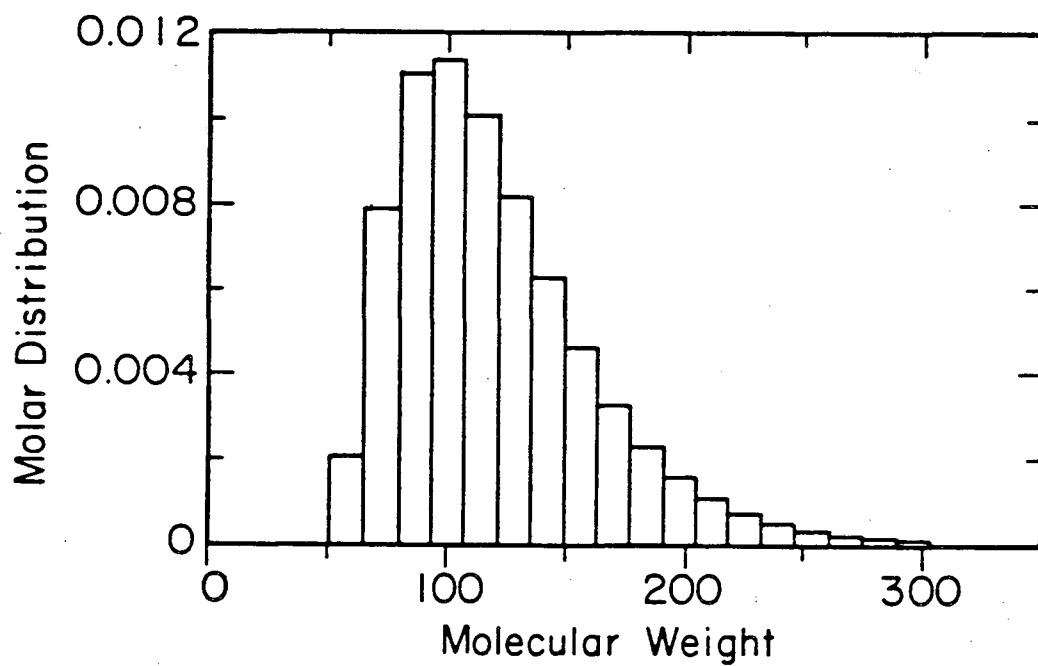


FIGURE 7

COMPARISON OF THE QUADRATURE METHOD  
TO PSEUDO-COMPONENT METHOD FOR  
PHASE-EQUILIBRIUM CALCULATIONS AT 5 BAR

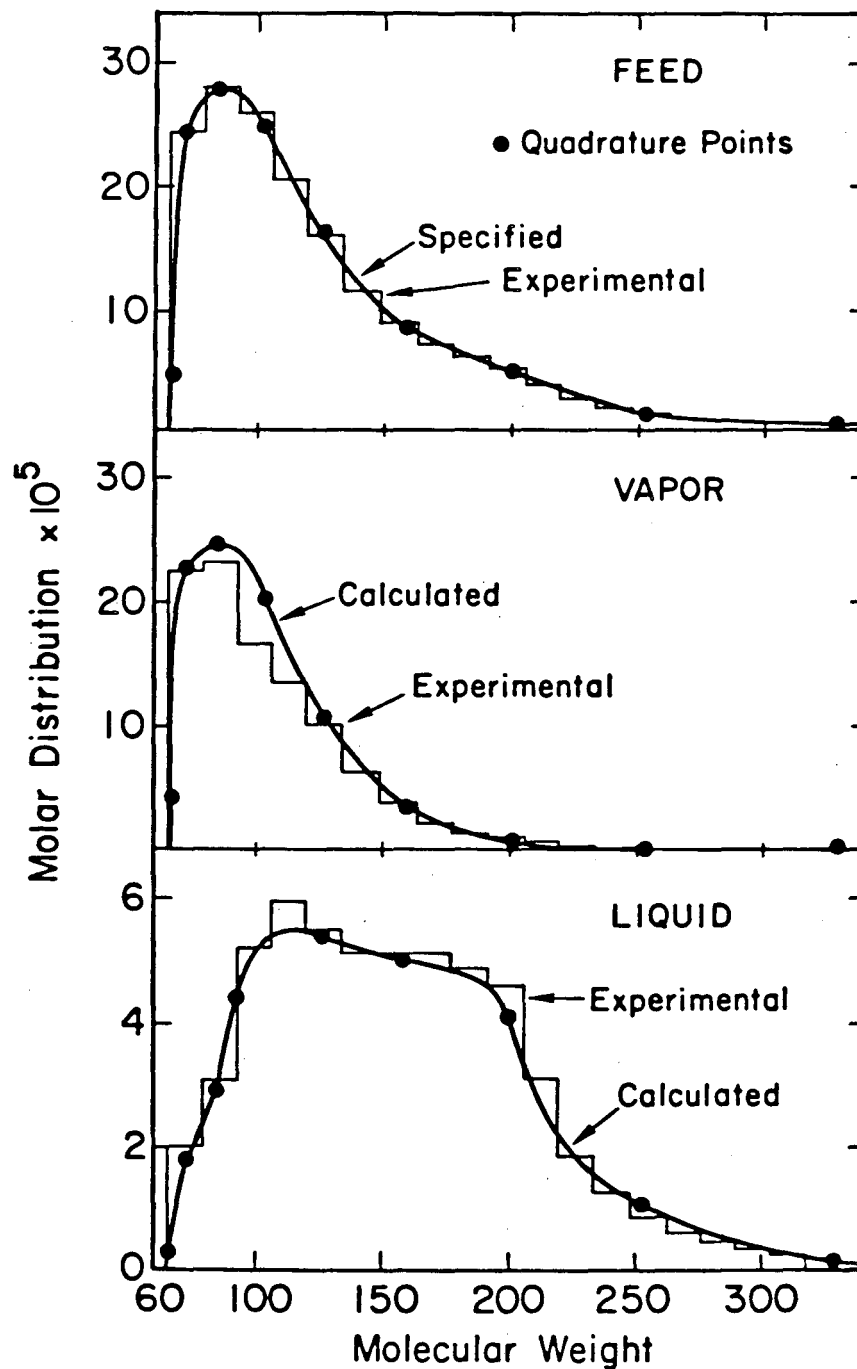


FIGURE 8

CALCULATED AND EXPERIMENTAL DISTRIBUTION  
OF HEAVIES FOR RETROGRADE CONDENSATION  
IN A NATURAL-GAS MIXTURE AT 367 K AND  
139 BAR

(Data of Hoffmann, Crump, and Hocott)

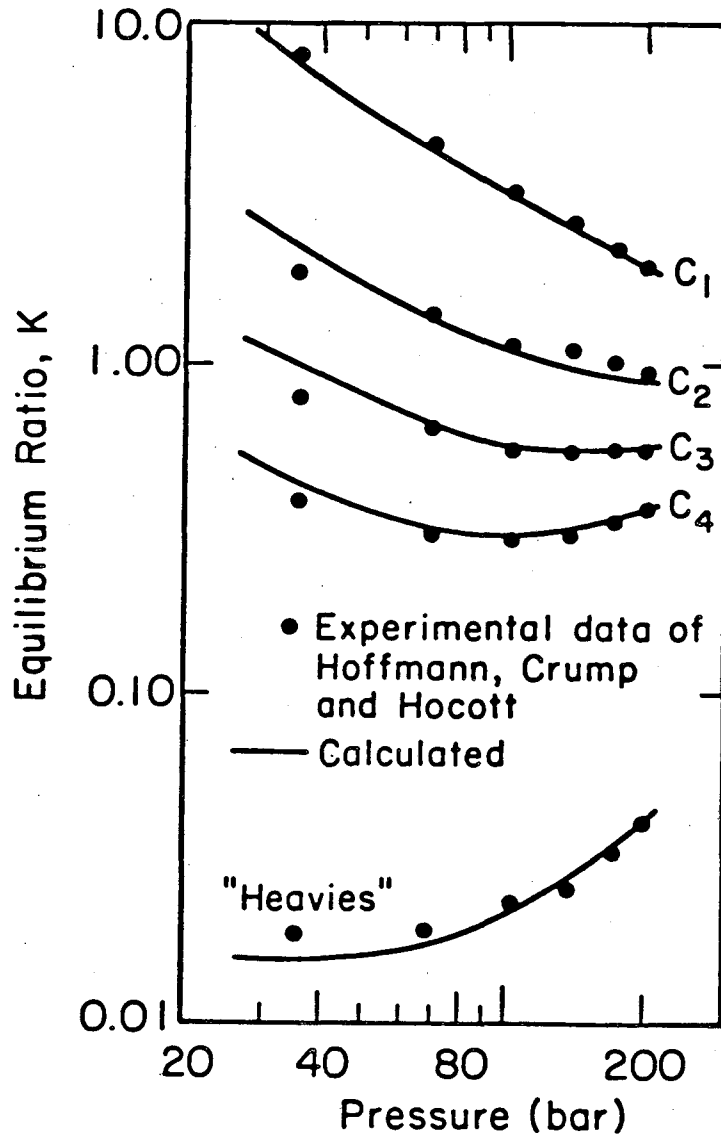
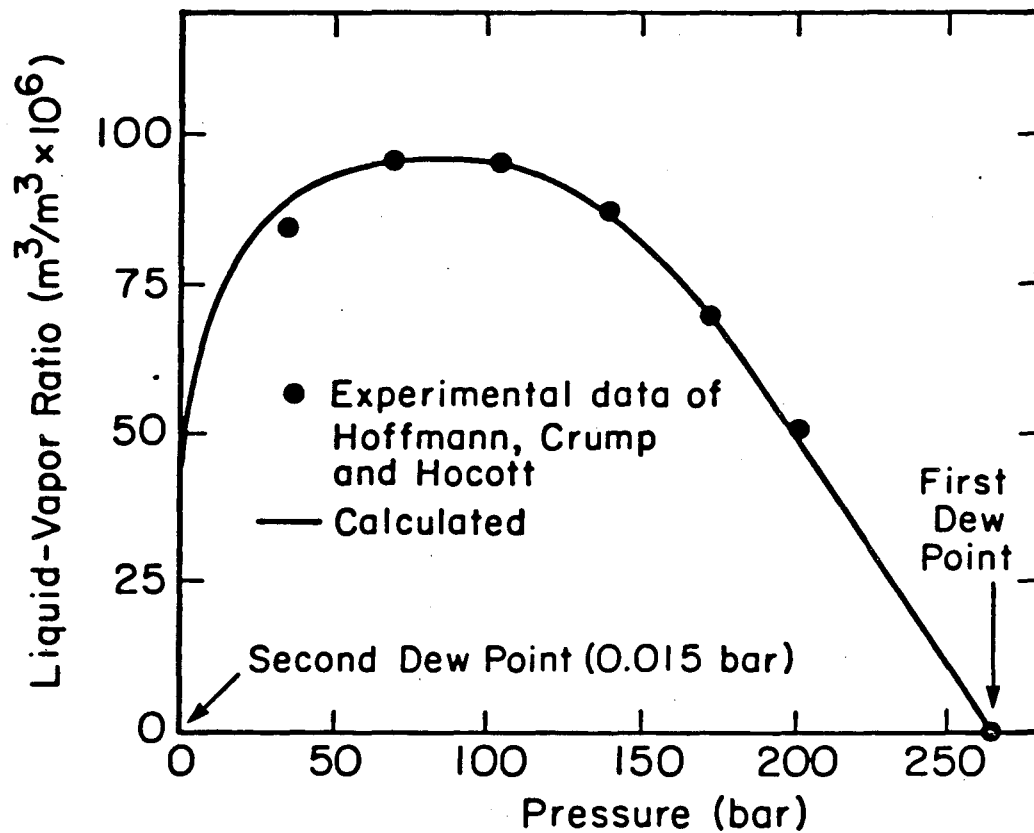


FIGURE 9

CALCULATED AND EXPERIMENTAL EQUILIBRIUM RATIOS IN THE RETROGRADE REGION FOR A NATURAL-GAS MIXTURE AT 367 K



Vapor volume corrected to standard conditions:  
15.5°C (60 F) and 1.013 bar.

FIGURE 10

CALCULATED AND EXPERIMENTAL LIQUID-VAPOR  
RATIO IN THE RETROGRADE REGION FOR A  
NATURAL-GAS MIXTURE AT 367 K



## Appendix I

### Equation of State for Semi-continuous Mixtures

To perform phase-equilibrium calculations, we use one equation of state to describe both vapor and liquid properties. Equation (7) is applied to semi-continuous mixtures via mixing rules for parameters  $a$  and  $b$ . For a system with  $n$  discrete components and  $m$  continuous components (or ensembles), we obtain for the liquid phase:

$$b = \sum_i^n x_i b(i) + \sum_k^m \eta_k^L \int F_k^L(I) b(I) dI \quad (I-1)$$

$$a = \sum_i^n \sum_j^n x_i x_j a(i,j) + 2 \sum_i^n \sum_k^m x_i \eta_k^L \int F_k^L(I) a(i,I) dI \\ + \sum_k^m \sum_l^m \eta_k^L \eta_l^L \int \int F_k^L(I) F_l^L(I^+) a(I,I^+) dI dI^+ \quad (I-2)$$

where  $x_i$  and  $\eta_k^L$  are liquid-phase mole fractions for the discrete and continuous fractions. Similar relations hold for the vapor phase.

Expressions for  $a$  and  $b$  for pure components were fit to vapor-pressure data (Zwolinski and Wilhoit, 1971) for several homologous series (or ensembles) of hydrocarbons. Table I-1 lists the homologous series considered. For our purposes here, these series represent average properties of the paraffinic, aromatic and naphthenic constituents of petroleum mixtures. For each ensemble, the following relations represent the data:

$$b(I) = b_0 + b_1 \cdot I \quad (I-3)$$

$$a^{\mathcal{H}}(I,I) = a_0(T) + a_1(T) \cdot I \quad (I-4)$$

where  $I$  is molecular weight. The temperature dependence of  $a_0(T)$  and  $a_1(T)$  is given by:

$$a_0(T) = a_0^{(0)} + a_0^{(1)} \cdot T + a_0^{(2)} \cdot T^2 \quad (I-5)$$

$$a_1(T) = a_1^{(0)} + a_1^{(1)} \cdot T + a_1^{(2)} \cdot T^2 \quad (I-6)$$

where  $T$  is in kelvins. Table I-2 gives all constants for specified ranges of temperature and molecular weight. For low-molecular-weight fluids, the Soave(1972) expressions are used to find parameters  $a$  and  $b$ .

The cross terms in the mixing rules are given by a geometric mean corrected with a binary interaction parameter,  $k$

$$a(i,j) = a^{1/2}(i,i)a^{1/2}(j,j)(1-k_{ij}) \quad (I-7a)$$

$$a(i,I) = a^{1/2}(i,i)a^{1/2}(I,I)(1-k_{iI}) \quad (I-7b)$$

$$a(I,I^+) = a^{1/2}(I,I)a^{1/2}(I^+,I^+)(1-k_{II^+}) \quad (I-7c)$$

For discrete-discrete cross terms, interaction parameter  $k_{ij}$  is set to a constant value. For discrete-continuous interactions,  $k_{iI}$  is constant for the method of moments (Appendix II) but, for the quadrature method (Appendix III),  $k_{iI}$  may be expressed as a function of molecular weight by fitting binary vapor-liquid equilibrium data. Interactions between continuous components usually are adequately described by the geometric mean approximation; in that event,  $k_{II^+}$  is set equal to zero.

Table I-1

Ensembles for Vapor-Pressure Correlation

Ensemble	Molecular-Weight Range	Temperature Range (K)	Average RMS % Deviation in Vapor Pressure
Paraffin (n-alkanes)	58-563	223-723	3.91
Aromatic (alkyl-benzenes)	78-303	298-673	1.99
Naphthene (alkyl-cyclohexanes)	84-309	298-673	4.48

Table I-2

Constants for Equation-of-State Parameters<sup>†</sup>

(Equations I-3,4,5 and 6)

Ensemble	$b$ ( $cm^3/mol$ )		
	$b_0$	$b_1$	
Paraffins	-12.400	1.6000	
Aromatics	-30.848	1.4547	
Naphthenes	-37.145	1.6013	
Ensemble	$a_0$ ( $bar - cm^6/mol^2$ )		
	$a_0^{(0)}$	$a_0^{(1)}$	$a_0^{(2)}$
Paraffins	194.83	-1.8659	$5.5602 \times 10^{-3}$
Aromatics	933.28	-4.9650	$9.0332 \times 10^{-3}$
Naphthenes	434.99	-4.9395	$10.0650 \times 10^{-3}$
Ensemble	$a_1$ ( $bar - cm^6/mol^2$ )		
	$a_1^{(0)}$	$a_1^{(1)}$	$a_1^{(2)}$
Paraffins	100.650	-.112970	$3.8206 \times 10^{-5}$
Aromatics	85.466	-.067780	$6.9715 \times 10^{-7}$
Naphthenes	91.903	-.078747	$5.7932 \times 10^{-6}$

<sup>†</sup> Ranges of molecular weight and temperature are given in Table I-1.

## Appendix II

### Flash Calculations Using the Method of Moments

Phase-equilibrium criteria for semi-continuous mixtures may be rewritten in terms of fugacity coefficients,  $\varphi_i$ . For each discrete component:

$$y_i \varphi_i^V = x_i \varphi_i^L \quad (\text{II-1})$$

For each continuous component (or ensemble):

$$\eta_k^V F_k^V(I) \varphi_k^V(I) = \eta_k^L F_k^L(I) \varphi_k^L(I) \quad (\text{II-2})$$

where superscripts V and L refer to vapor and liquid phases.

Fugacity coefficients are determined in a manner similar to that for chemical potential. For each discrete component, the fugacity coefficient in each phase, for a mixture containing  $n$  discrete components and  $m$  continuous components, is

$$\begin{aligned} RT \ln \varphi_i = & RT \ln \frac{v}{v-b} + RT \frac{b(i)}{v-b} + \frac{ab(i)}{b^2} \left[ \ln \frac{v+b}{v} - \frac{b}{v+b} \right] \\ & - \frac{2}{b} \left[ \sum_j^n x_j a(i,j) + \sum_k^m \eta_k \int_I F_k(I) a(i,I) dI \right] \ln \frac{v+b}{v} - RT \ln Z \end{aligned} \quad (\text{II-3})$$

where  $v$  is the molar volume and  $Z$  is the compressibility factor. For each continuous component,

$$\begin{aligned} RT \ln \varphi_k(I) = & RT \ln \frac{v}{v-b} + RT \frac{b(I)}{v-b} + \frac{ab(I)}{b^2} \left[ \ln \frac{v+b}{v} - \frac{b}{v+b} \right] \\ & - \frac{2}{b} \left[ \sum_i^n x_i a(I,i) + \sum_l^m \eta_l \int_{I^*} F_l(I^*) a(I,I^*) dI^* \right] \ln \frac{v+b}{v} - RT \ln Z \end{aligned} \quad (\text{II-4})$$

Applying Equation (II-4) to both phases V and L, the ratio of  $\varphi_k(I)$  in the two phases may be expressed as an explicit function of molecular weight,  $I$ :

$$\ln \frac{\varphi_k^L(I)}{\varphi_k^V(I)} = C_k^{(1)} + C_k^{(2)} \cdot I \quad (\text{II-5})$$

where  $C_k^{(1)}$  and  $C_k^{(2)}$  are combinations of terms from Equation (II-4) for each ensemble  $k$  which are independent of the variable  $I$

This result allows us to relate the distribution-function parameters in the vapor and liquid phases to each other. If each ensemble in the liquid phase is described by a

gamma distribution function (with parameters  $\gamma_k^L$ ,  $\alpha_k^L$  and  $\beta_k^L$ ), the vapor composition is also described by gamma distribution functions with

$$\gamma_k^V = \gamma_k^L \quad (II-6)$$

$$\alpha_k^V = \alpha_k^L \quad (II-7)$$

$$\beta_k^V = \frac{\beta_k^L}{1 - C_k^{(2)}\beta_k^L} \quad (II-8)$$

$$\frac{\eta_k^V}{\eta_k^L} = \exp(C_k^{(1)} + C_k^{(2)}\gamma_k^L) \left[ \frac{1}{1 - C_k^{(2)}\beta_k^L} \right]^{\alpha_k^L} \quad (II-9)$$

Equations (II-6 to 9) permit an exact solution to the phase-equilibrium criterion [Equation (II-2)] for each continuous fraction.

The material balance for each discrete component is given by Equation (2) and for each continuous component by Equation (16). We use Equation (16) to develop relations between distribution-function parameters for the feed, vapor and liquid streams using the first and second statistical moments of each distribution function (here chosen to be gamma distribution functions).

The first moment, the mean, is written

$$M_1 = \int_{\gamma}^{\infty} IF(I)dI = \alpha\beta + \gamma$$

The second moment is

$$M_2 = \int_{\gamma}^{\infty} I^2 F(I)dI = \alpha\beta^2 + (\alpha\beta + \gamma)^2$$

These relations are substituted into the material balance, Equation (9), to obtain two equations for each continuous fraction. After some simplification, we write

$$\eta_k^F \alpha_k^F \beta_k^F = \xi \eta_k^V \alpha_k^V \beta_k^V + (1-\xi) \eta_k^L \alpha_k^L \beta_k^L \quad (II-10)$$

$$\eta_k^F \alpha_k^F (\alpha_k^F + 1) \beta_k^{F2} = \xi \eta_k^V \alpha_k^V (\alpha_k^V + 1) \beta_k^{V2} + (1-\xi) \eta_k^L \alpha_k^L (\alpha_k^L + 1) \beta_k^{L2} \quad (II-11)$$

The zeroth moment gives the overall balance

$$\eta_k^F = \xi \eta_k^V + (1-\xi) \eta_k^L \quad (II-12)$$

Shift parameter  $\gamma$  is the same in all streams

$$\gamma_k^F = \gamma_k^V = \gamma_k^L \quad (II-13)$$

Selection of the first and second moments is arbitrary; other moments could have been chosen. In addition, this formulation assumes that the composition distribution in each stream is described by a two-parameter gamma distribution function or a sum of gamma distributions.

While other distribution functions may be used to improve the material balance through additional parameters, they will not allow an exact solution to the phase equilibrium criteria as given by Equations (II-6 to 9). However, approximate relations between distribution-function parameters in equilibrium phases can be derived by equating moments of equilibrium Equation (II-2), analogous to the procedure used for the material balance equation.

### Appendix III

#### Flash Calculations Using the Quadrature Method

The quadrature method is based upon approximating a continuous distribution function by a sum over  $s$  quadrature points. For a semi-continuous mixture with  $n$  discrete components and  $m$  continuous components (or ensembles), the normalization condition for the liquid stream is written

$$\sum_i^n x_i + \sum_k^m \eta_k^L \sum_p^s w_k(I_p) F_k^L(I_p) = 1 \quad (\text{III-1})$$

Similar equations apply to the feed and vapor streams. The quadrature points,  $I_p$ , and the weighting factors,  $w_k(I_p)$ , are the same in all streams; their selection is discussed later.

The phase-equilibria criterion, Equation (15), must be satisfied at each quadrature point  $p$  for each continuous component  $k$ :

$$\mu_k^V(I_p) = \mu_k^L(I_p) \quad (\text{III-2})$$

In terms of fugacity coefficients,  $\varphi_k$ ,

$$\eta_k^V F_k^V(I_p) \varphi_k^V(I_p) = \eta_k^L F_k^L(I_p) \varphi_k^L(I_p) \quad (\text{III-3})$$

An expression for the fugacity coefficient, derived using Equation (7), is given by

$$\begin{aligned} RT \ln \varphi_k(I_p) = & RT \ln \frac{v}{v-b} + RT \frac{b(I_p)}{v-b} + \frac{ab(I_p)}{b^2} \left[ \ln \frac{v+b}{v} - \frac{b}{v+b} \right] \\ & - \frac{2}{b} \left\{ \sum_i^n x_i a(I_p, i) + \sum_l^m \eta_l \sum_q^s w_l(I_q) F_l(I_q) a(I_l, I_l) \right\} \ln \frac{v+b}{v} - RT \ln Z \end{aligned} \quad (\text{III-4})$$

where

$$b = \sum_i^n x_i b(i) + \sum_k^m \eta_k \sum_p^s w_k(I_p) F_k(I_p) b(I_p) \quad (\text{III-5})$$

and

$$\begin{aligned} a = & \sum_i^n \sum_j^n x_i x_j a(i, j) + 2 \sum_i^n \sum_k^m x_i \eta_k \sum_p^s w_k(I_p) F_k(I_p) a(i, I_p) \\ & + \sum_k^m \sum_l^m \eta_k \eta_l \sum_p^s \sum_q^s w_k(I_p) F_k(I_p) w_l(I_q) F_l(I_q) a(I_p, I_q) \end{aligned} \quad (\text{III-6})$$



Parameters  $b(I_p)$  and  $a(I_p, I_p)$  are evaluated at the quadrature points using constants for the appropriate ensemble. Cross coefficients for equation-of-state constant  $a$  are given by a geometric mean corrected with binary interaction parameters,  $k_{ij}$  [see Equations (7)].

Equations (III-4)-(III-6) are written for each equilibrium phase to relate  $F_k^V(I_p)$  to  $F_k^L(I_p)$ . Fugacity coefficient expressions for discrete components are derived by analogy to Equation (II-3).

Finally, we write a material balance at each quadrature point for each ensemble

$$\eta_k^F F_k^F(I_p) = \xi \eta_k^V F_k^V(I_p) + (1-\xi) \eta_k^L F_k^L(I_p) \quad (\text{III-7})$$

To specify quadrature points and weighting factors, we select the type of Gaussian quadrature (determined by the range of the variable  $I$ ) and the number of quadrature points. Using molecular weight as the distributed variable, we choose a semi-infinite integration method, Laguerre-Gauss quadrature, for which  $\gamma \leq I < \infty$ . This integration method works well when the "tail" of the function to be integrated decreases exponentially or faster. For smooth distribution functions with only one or two modes, we find that six to ten quadrature points is usually sufficient for flash calculations.

Laguerre-Gauss quadrature requires that the quadrature points be scaled to match the distributed variable. This is easily done by scaling the tabulated quadrature points by a constant value. We choose this scale factor by plotting the logarithm of  $F^F(I)$  as a function of  $I$ . For many distribution functions, the tail of the distribution produces a linear region on semi-log coordinates. The negative inverse slope of this linear region is the quadrature-point scale factor.

As an example, for a gamma distribution [Equation (8)] with mean 100, variance 800 and shift 50, the negative inverse slope of  $\ln F(I)$  plotted versus  $I$  is approximately 19. To represent adequately the maximum of this distribution function, we use a lower value of 10 to scale quadrature points to the range of  $(I-\gamma)$ .

Results are not very sensitive to the value of the scale factor provided that factor is of the correct order of magnitude. For multimodal distributions, the scale factor should be chosen to produce quadrature points in the molecular-weight range where the distribution function has the most curvature.

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