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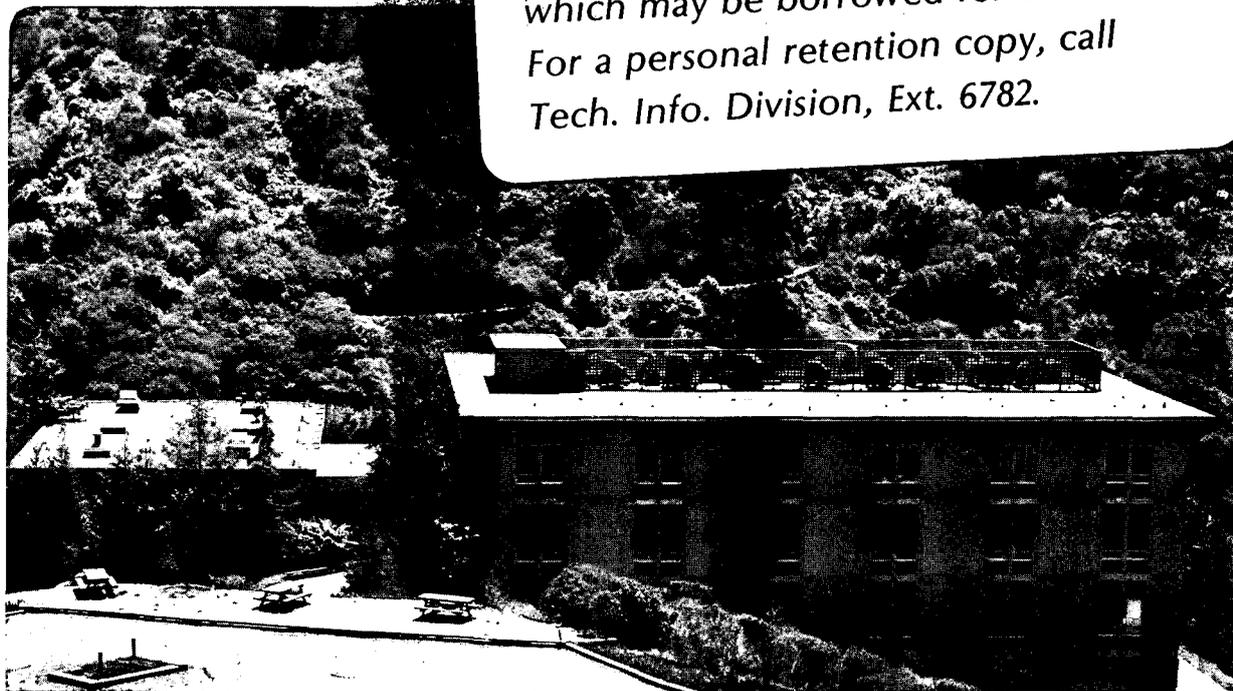
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Phase Equilibria for Mixtures Containing Very Many Components. Development and Application of Continuous Thermodynamics

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ABSTRACT

For some multicomponent mixtures, where detailed chemical analysis is not feasible, the composition of the mixture may be described by a continuous distribution function of some convenient macroscopic property such as normal boiling point or molecular weight. To attain a quantitative description of phase equilibria for such mixtures, this work has developed thermodynamic procedures for continuous systems; that procedure is called continuous thermodynamics. To illustrate, continuous thermodynamics is here used to calculate dew points for natural-gas mixtures, solvent loss in a high-pressure absorber and liquid-liquid phase equilibria in a polymer fractionation process.

Continuous thermodynamics provides a rational method for calculating phase equilibria for those mixtures where complete chemical analysis is not available but where composition can be given by some statistical description. While continuous thermodynamics is only the logical limit of the well-known pseudo-component method, it is more efficient than that method because it is less arbitrary and because required computer time is much lower.

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Introduction

Since the natural world consists of many phases and since the interchange of matter between phases constitutes the basis of many separation operations, much attention has been given toward a quantitative theory for phase equilibria for mixtures. The fundamental basis for such theory is Gibbs' definition and use of the chemical potential μ_i for component i ; therefore, there is an implicit assumption in conventional Gibbsian thermodynamics that component i can be identified and that its concentration in a given phase can be measured. Unfortunately, however, that assumption is not always valid because, in a mixture containing a very large number of components, it is often not practical--indeed it may be impossible--to perform the extensive (perhaps prohibitive) chemical analysis needed to determine the concentrations of all components. Examples of such mixtures are heavy fossil fuels (petroleum, shale oil, coal-derived liquids, tars, etc.), solutions of polydisperse polymers, and mixtures of fatty acids or esters in vegetable oils.

This work is concerned with extension of Gibbsian thermodynamics to those mixtures whose composition is not given by a series of discrete values of concentration (e.g., mole fraction, weight fraction, moles per liter, etc.) but, instead, by some statistical measure of composition as given by a continuous distribution function of one or more macroscopic properties such as normal boiling point, degree of aromaticity, number of carbon atoms per molecule, Lewis basicity or, most convenient for many cases, molecular weight. We call this extension "continuous thermodynamics" which is shorter but equivalent to the possibly more descriptive term "thermodynamics of continuous mixtures".

While various authors have published suggestions for calculating phase equilibria in continuous systems (e.g., Bowman, 1949; Edmister, 1955; Aris and Gavalas, 1966; Hoffman, 1968; Gal-Or et al., 1975), these suggestions have been restricted to specific physico-chemical models (e.g., Raoult's law, relative volatilities independent of

composition, ideal-gas mixtures); these early workers did not concern themselves with the general problem of continuous thermodynamics whose fundamentals are independent of the physico-chemical model chosen to represent chemical potential. Another area where these ideas have been applied is in polymer solutions (e.g., Scott, 1953; Koningsveld and Staverman, 1968; Solc, 1969; Flory and Abe, 1978; Irvine and Kennedy, 1982). Only in the last few years have there been studies along fundamental lines (e.g., Vrij, 1978; Blum and Stell, 1979; Dickinson, 1980; Smith and Rowlinson, 1980; Kehlen and Rätzsch, 1980; Salacuse and Stell, 1982; Gualtieri et.al., 1982; Briano and Glandt, 1983). However, these studies have stressed mathematical relationships, representing the viewpoint of theoretical physicists, with little attention to engineering applications. Our goal here is to develop continuous thermodynamics from the viewpoint of applied science and to illustrate some possible uses for chemical process design.

Thermodynamic Framework

To indicate the difference between a discrete mixture and a continuous mixture, Figure 1 shows on the left how we normally represent composition in a discrete mixture using mole fractions as composition variables. In this case, the mixture has ten identified components; the mole fraction x_i for component i is given by a bar in the upper left part and the summation of all x_i is shown in the lower left part of Figure 1. For a continuous mixture, shown on the right, we do not have discrete identified components but instead, we assume that we can characterize the mixture using a single distribution variable I ; instead of mole fractions, we now have a distribution function $F(I)$ such that the fraction of molecules (in the mixture) characterized by the range I to $I+\Delta I$, is given by $F(I)\Delta I$. Instead of the normalization condition given by a summation shown at the bottom on the left side, we now have a normalization given by an integral shown at the bottom on the right side.

If we have at equilibrium two phases designated by ' and ", then, following Gibbs, we know how to write the equation of equilibrium for the discrete case; for every component i , the chemical potentials must satisfy

$$\mu_i' = \mu_i'' \quad \text{for every } i \quad (1)$$

Therefore, if we have k components, we must simultaneously solve k equations.

However, for the continuous case, again assuming that a single distributed variable I is sufficient, the equation of equilibrium now is

$$\mu'(I) = \mu''(I) \quad \text{for all } I \quad (1a)$$

For the discrete mixture, we have a well-known method for calculating μ_i' from an equation of state which relates pressure P to total volume V and to mole numbers n_i, n_j, \dots :

$$\mu_i' = \int_V \left\{ \left[\frac{\partial P}{\partial n_i} \right]_{T, V, n_j} - \frac{RT}{V} \right\} dV - RT \ln \frac{V}{n_i RT} + \mu(T) \quad (2)$$

A similar relation holds for μ_i'' .

For the continuous mixture, as discussed in Appendix I, we can derive an analogous method for calculating $\mu'(I)$:

$$\mu'(I) = \int_V \left\{ \left[\frac{\delta P}{\delta n_c F(I^+)} \right]_{T, V, I^+ = I} - \frac{RT}{V} \right\} dV - RT \ln \frac{V}{n_c F(I) RT} + \mu(T) \quad (2a)$$

where $F(I)$ is the distribution function in phase ' and n_c is the total number of moles of the continuous mixture. A similar relation holds for $\mu''(I)$.

For simplicity, the discussion above assumes that one distributed variable I is sufficient to describe the composition of the continuous mixture. However, as briefly discussed in Appendix II, this is not a necessary assumption; instead of distribution

function $F(I)$, we may use distribution function $F(I,J)$ where two different distributed variables I and J are used to describe the composition. The general relations of continuous thermodynamics hold for any number of distributed variables but practical calculations become more complex when that number exceeds unity.

While Equations (2) and (2a) are applicable to any fluid phase, they are most useful for vapor-liquid equilibria at advanced pressures, as shown later. For liquid-liquid equilibria (or for vapor-liquid equilibria at low pressures) it is more useful to express the Gibbs energy G' of phase ' as a function of $F(I)$ and then to calculate the chemical potential from

$$\mu'(I) = \left(\frac{\delta G'}{\delta n_e F(I^*)} \right)_{T,P,I^*=I} \quad (3)$$

For example, consider a solution of a polydisperse polymer (2) in a solvent (1) and suppose that the Gibbs energy of this solution is given by the continuous-thermodynamic analogue of the Flory-Huggins equation

$$G = n_1 \ln \Phi_1 + \int_I n_2 F(I) \ln \Phi(I) dI + \chi \Phi_1 \int_I \Phi(I) dI \left(n_1 + \int_I n_2 F(I) m(I) dI \right) + n_1 g_1^o + \int_I n_2 F(I) g_2^o dI \quad (4)$$

where $F(I)$ is the molar probability distribution, n is the number of moles, Φ is the volume fraction, χ is the Flory interaction parameter, $m(I)$ is the molar volume ratio of polymer to solvent at I and g^o is the Gibbs energy of the pure component.

In that case, the chemical potential $\mu'(I)$ for the polymer would be given by Equation (3) with the additional restraint that n_1 is held constant. The chemical potential for the solvent is found from

$$\mu_1 = \left(\frac{\partial G'}{\partial n_1} \right)_{T,P,n_2} \quad (5)$$

An example using Equation (4) is shown later.

Distribution Function

To describe the composition of the continuous mixture, we must choose not only appropriate distributed variables I, J, \dots but also some function F to indicate how these variables are distributed. In general, then, we require a function $F(I, J, \dots)$; only if variables I, J, \dots are truly independent can we replace that function by the product of the marginal distribution functions $F_I(I) \cdot F_J(J) \dots$. We consider here only the simplest case where one distributed variable is sufficient.

In statistics, the function F is referred to as a probability density function and the integral of F is a cumulative density function. To avoid confusion with other interpretations of the term "density function", we here refer to F as a probability distribution function or, more simply, as a distribution function and the integral of F as a cumulative distribution function.

The choice of F is determined primarily by its ability to represent reality to a sufficient degree of approximation. However, another consideration in the choice of F is mathematical convenience; if we want to solve Equation (1a) analytically, some functions F are much more suitable than others. On the other hand, analytical solutions, while desirable, may not be essential; for some complex mixtures, numerical procedures may be unavoidable. For our introductory purposes here, however, we seek mathematical simplicity. A useful distribution function for that purpose is the gamma distribution function (also known as the Schultz (1940) distribution) shown in Figure 2:

$$F(I) = \frac{(I-\gamma)^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)} \exp -\left(\frac{I-\gamma}{\beta}\right) \quad (6)$$

where Γ is the gamma function (Johnson and Kotz, 1970). Whitson (1983) has shown how the gamma distribution may be used to characterize the high molecular-weight

portion of crude oils.

Parameter γ fixes the origin where F is zero. If we want F to be zero when $I=0$, then $\gamma=0$. Regardless of γ , $F(\infty)=0$. The mean Θ and the variance σ^2 are given by

$$\Theta = \alpha\beta + \gamma \quad (7)$$

$$\sigma^2 = \alpha\beta^2 \quad (8)$$

The normalization condition is

$$\int_{\gamma}^{\infty} F(I) dI = 1 \quad (9)$$

In the mixture, discrete components can be included in addition to the continuous part of the mixture; this case is called "semi-continuous". Frequently, discrete components fall in the range 0 to γ . Appendix III discusses first, some details concerning mixtures that contain continuous fractions and discrete components and second, mixtures that contain two or more continuous fractions.

We now illustrate some applications of continuous thermodynamics using the gamma distribution function.

Raoult's Law for a Continuous Liquid Mixture

Following an example presented by Kehlen and Rätzsch (1980), we consider a continuous mixture of normal paraffins. For the discrete case, Raoult's law is

$$y_i P = x_i P_i^{sat}(T) \quad (10)$$

where y_i is the vapor-phase mole fraction, x_i is the liquid-phase mole fraction, P is the total pressure and P_i^{sat} is the vapor pressure of component i , all at system temperature T . For a continuous mixture, Raoult's law is

$$F^V(I)P = F^L(I)P^{sat}(T,I) \quad (10a)$$

where superscripts V and L designate the vapor and liquid phases.

Whereas Kehlen and Rätzsch used a normal (Gaussian) distribution for $F(I)$ with I chosen to be the normal boiling point, we instead use for $F(I)$ the gamma distribution with I =normal boiling point. This choice is determined by physical considerations; we find that our choice gives a more realistic representation of paraffins than that of Kehlen and Rätzsch.

Total pressure P is given by the summation of all of the partial pressures:

$$P = \int_{\gamma}^{\infty} F^L(I)P^{sat}(T,I)dI \quad (11)$$

To express the vapor pressure as a function of temperature and normal boiling point, we use Trouton's rule and the Clausius-Clapeyron equation, yielding

$$P^{sat}(T,I) = P^0 \exp\{A(1-I/T)\} \quad (12)$$

where P^0 and A are constants. If P^{sat} is in bar, $P^0 = 1.013$ bar and, for normal paraffins, $A = 10.6$.

Let the liquid phase be described by a gamma distribution with mean Θ_L and variance σ_L^2 . We then find that the vapor is also described by a gamma distribution with

$$\Theta_V - \gamma = (\Theta_L - \gamma) \left\{ 1 + A\sigma_L^2 / T(\Theta_L - \gamma) \right\}^{-1} \quad (13)$$

$$\sigma_V^2 = \sigma_L^2 \left(\frac{\Theta_V - \gamma}{\Theta_L - \gamma} \right)^2 \quad (14)$$

Figure 3 shows some calculated results at 10 bar using $\gamma = 250$. The liquid phase is characterized by distribution function parameters $\alpha = 2.5$ and $\beta = 50$. The calculated bubble temperature is 422 K and the vapor-phase distribution parameters are $\alpha = 2.5$

and $\beta=22.2$. As expected, the mean normal boiling point of the vapor is appreciably lower than that of the liquid.

Dew-Point Calculation for a Natural Gas Using an Equation of State

We consider a natural gas which contains mostly methane, some ethane, propane and butane and a small amount of "heavies". At fixed pressure, the dew-point temperature is sensitive to the molecular-weight distribution of the "heavies". To describe the thermodynamic properties of this mixture, we use an equation of state similar to Soave's modification of the Redlich-Kwong equation but corrected to give better results for heavy hydrocarbons.

The equation of state is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (15)$$

where $a(T)$ is a function of temperature.

For low-molecular-weight fluids, $a(T)$ and b are given by Soave's formulas (Soave, 1972). For heavier paraffins (C_4 - C_{40}), $a(T)$ and b were determined from vapor pressure data. For these heavier fluids, we find that $a^{1/2}(T)$ and b are linear functions of molecular weight as shown in Figure 4. Using these results in Equation (15), coupled with the gamma distribution function (I =molecular weight), we then calculate chemical potentials as indicated by Equation (2a). Some details are given in Appendix IV.

To illustrate, we calculate dew-point temperatures for a natural gas at 100 bar; the composition of the natural gas is given in Table 1.

In the first calculation, we assume that the vapor-phase distribution of "heavies" is given by the gamma distribution with mean = 86 (molecular weight of hexane) and variance = 245. The calculated dew-point temperature is 363 K and the composition of the first condensate is given in the first horizontal line of Table 2a. Details of the

"heavies" in the condensate are given in Table 2b. The upper left portion of Figure 5 shows the distribution of "heavies" in both phases.

In the second calculation, we raise the mean of the vapor-phase distribution to 114 (molecular weight of octane) but retain the variance at 245. The dew-point temperature is now much higher, 418 K; distributions for both phases are shown in the lower left corner of Figure 5.

In the third calculation, we retain the original mean (86) but raise the variance to 525. The dew-point temperature is now only 20 degrees higher than that in the first calculation. Distributions for both phases are shown in the upper right corner of Figure 5.

In the fourth calculation, we use two gamma distributions to characterize the "heavies" in the vapor: 90 mole percent of the "heavies" are in the first distribution with mean = 86 and variance = 245 while 10 mole percent are in the second distribution with mean = 128 and variance = 245. When the overall distribution for the vapor phase is plotted, there is a slight "bump" near molecular weight 128, barely visible in the lower right plot of Figure 5. However, the bump is clearly visible in the liquid-phase distribution. Because of the vapor-phase "bump", the dew-point temperature is now 17 degrees higher than that in the first calculation.

The dew-point calculations summarized above are illustrative. However, we have also calculated dew-point conditions for a real natural gas at 20.7 bar described by Bergman, Katz and Tek (1975); the composition of that gas is given in Table 3.

Using experimental data for the vapor-phase "heavies", we represent these with a gamma distribution (I =molecular weight) with mean = 70.7 and variance = 96.9. The calculated dew-point temperature is 275.6 K which is close to that measured (272 K). Calculated and observed compositions of the first condensate are shown in Figure 6. Calculated and observed results are in good agreement when we consider that our calculation used no binary parameters; in our calculations $a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij})$ with all

$k_{ij} = 0$. Small values of k_{ij} (especially for CO_2 -hydrocarbons) would improve the calculated results.

Solvent Loss in a High-Pressure Absorber

We consider an absorber operating at 40 bar to recover intermediate hydrocarbons (C_3, C_4, C_5) from a natural gas containing primarily methane and a trace of nitrogen; the solvent is a (continuous) mixture of heavy paraffins. Near the top of the column, we have a semi-continuous liquid whose composition is shown in Figure 7; in this figure, the mean of the continuous fraction is arbitrarily set at 128. The liquid contains 66.8 mole percent solvent (continuously distributed heavy paraffins).

We now want to calculate the loss of solvent in the stripped gas leaving the absorber. To do so, we make a semi-continuous bubble-point calculation using the equation of state described earlier [Equation (15)]. We keep constant the liquid-phase mole fractions of the discrete components but we allow the mean of the continuous part of the liquid to vary from 100 to 156. We keep fixed the variance = 180. We compute the mole percent "heavies" (i.e., lost solvent) in the stripped gas; results are shown in Table 4. As the mean of the solvent's composition rises, the "heavies" content of the effluent falls dramatically as the (gas-free) solvent's mean molecular weight goes from 100 to 156.

Flash Calculation for Fractionation of a Polydisperse Polymer Solution

As a final example, we consider a solution of polydisperse polystyrene in cyclohexane studied by Breitenbach and Wolf (1967); the total concentration of polymer is 0.87 mass percent and the mass distribution of polymer molecular weight is given by a gamma distribution with $\Theta = 2.19 \times 10^5$ and $\sigma^2 = 24.6 \times 10^9$. This solution is chilled to 21.6°C, forming two phases: the polymer-rich phase is called the gel and the solvent-rich phase is called the sol. The thermodynamic properties are given by the

Flory-Huggins equation. Osmotic-pressure data indicate that near room temperature the Flory parameter χ is in the range 0.5-0.55 for dilute polymer concentrations (Höcker et. al., 1971).

We now calculate the molecular-weight distributions of the polymer in these two phases and the distribution ratio $K(I)$ defined by

$$K(I) = \frac{F^{SOL}(I)}{F^{GEL}(I)} \quad (16)$$

We use Equations (3), (4) and (5). Details are given in Appendix V.

We find that the calculations are very sensitive to χ . When we use $\chi=0.528$, we obtain excellent agreement with the data reported by Breitenbach and Wolf, as shown in Figure 8; this figure also shows the sensitivity to χ . Calculated distributions for both phases, shown in Figure 9, are in very good agreement with experiment. We find the amount of polymer in the sol phase is 0.35 mass percent and in the gel phase 9.74 mass percent. The ratio of the mass of the sol phase to the original feed is 0.957.

Conclusions and Future Applications

For some fluid mixtures containing very many components, the composition is more easily described by a continuous distribution function than by mole fractions for every component. For those mixtures where some but not all of the components are readily identified, the composition may be represented by a semi-continuous distribution. When Gibbsian (discrete) thermodynamics is extended to such mixtures, we obtain expressions for the chemical potential that are determined by the assumed distribution function as well as by the molecular-thermodynamic model chosen to represent the thermodynamic properties of the mixture. In this work we use a gamma distribution for one distributed variable but, in principle, any desired distribution function may be used for one or more variables. Any desired molecular-thermodynamic model may be used; in this work, we have performed dew-point and

bubble-point calculations using an equation of state and a fractionation calculation for a polymer solution using the Flory-Huggins model.

One advantage provided by continuous thermodynamics is economy in computer requirements. If we have many components, conventional Gibbsian thermodynamics requires simultaneous solution of many equations; if there are k components, then we must simultaneously solve k equilibrium equations [Equation (1)]. For continuous mixtures, it has previously been common practice to approximate the continuous composition by several pseudo-components and to write Equation (1) for each of these. The choice of pseudo-components is somewhat arbitrary and, unfortunately, this arbitrariness may sometimes produce unreliable results.

When continuous thermodynamics is used, Equation (1), applied to each component, is replaced by a single Equation (1a) for all distributed components; computing effort can thereby be reduced. To illustrate, consider a 20-component system at 5 bar, shown in the top part of Figure 10. We calculate the dew-point temperature using first, the pseudo-component method and second, continuous thermodynamics. Our calculations are based on an equation of state [Equation (15)]. Results are shown in the lower part of Figure 10. Using the pseudo-component method, we approximate the composition in a series of calculations using 1, 3, 5, 10 and 15 discrete pseudo-components. Computing time rises dramatically as the number of discrete pseudo-components rises. However, in continuous thermodynamics, all distributed components are included in a single calculation, giving the horizontal lines shown in the lower half of Figure 10. When all 20 components are used in the conventional (discrete) calculation, computer time requirements are about 30 times larger than those using continuous thermodynamics.

Future work in continuous thermodynamics is likely to follow along several lines:

- (1) Improved methods are needed for flash calculations to avoid the approximations inherent in the method of moments (see Appendix V).
- (2) Present experience is limited to conventional analytical distribution functions; that experience must be extended to other (not necessarily analytical) distribution functions to attain a better representation for real mixtures.
- (3) While those calculational techniques now available use only one distributed variable, it is necessary to use two (possibly more) distributed variables to represent the properties of continuous mixtures that are more complex than a homologous series of paraffins or a solution of a polydisperse polymer. For example, to describe a continuous mixture of coal-derived liquids, molecular weight (or boiling point) is not sufficient; additional distributed variables may be aromaticity and sulfur content. Alternately, a complex continuous mixture could be described as the sum of several homologous series (e.g., series of paraffins, naphthenes and aromatics in a fossil fuel, or series of fatty acids and fatty esters in a vegetable oil) where each homologous series is a function of the same distributed variable but where the details of the molecular-thermodynamic model vary from one series to another. Some preliminary efforts toward that end have been reported by Kehlen and Rätzsch (1983) but much remains to be done.

Continuous thermodynamics provides a potentially useful tool for chemical process design.

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Appendix I

Derivation of an Expression for the Chemical Potential in a Continuous Mixture

To derive Equation (2a), it is necessary to start with an expression for the Gibbs energy for a homogeneous phase in terms of the mole numbers, n_i , of a discrete system (Prausnitz, 1969):

$$G = \int_V \left[P - \frac{\sum_i n_i RT}{V} \right] dV - RT \sum_i n_i \ln \frac{V}{n_i RT} + \sum_i n_i (u_i^\circ - Ts_i^\circ + RT) \quad (I-1)$$

where u_i° and s_i° are the molar internal energy and entropy of pure i as an ideal gas at temperature T and 1 bar.

To replace the discrete mole numbers with continuous extensive distribution functions, a limiting procedure is used. We can imagine slicing an extensive distribution function, $n_c F(I)$ (where n_c is the total number of moles which are continuously distributed) into a series of equal-width divisions of width ΔI where each slice has a height $n_j F(I_j)$; here I_j is the value of I at the midpoint of the j^{th} interval. The continuous function $F(I)$ is now replaced by a series of bars. The area of each bar represents a discrete mole number. The approximation becomes exact when ΔI shrinks to zero:

$$\lim_{\Delta I \rightarrow 0} \Delta I F(I_j) = n_j \quad (I-2)$$

Equation (I-2) may be substituted for the mole numbers in Equation (I-1) and when used with the definition of a Riemann integral (Korn and Korn, 1968)

$$\lim_{\Delta I \rightarrow 0} \sum_{j=1}^k \Psi(I_j) \Delta I = \int_I \Psi(I) dI \quad (I-3)$$

we obtain the Gibbs energy of a continuous mixture:

$$G = \int_V \left[P - \frac{\int_I n_c F(I) RT dI}{V} \right] dV - RT \int_I n_c F(I) \ln \frac{V}{n_c F(I) RT} dI \\ + \int_I n_c F(I) (u^\circ - Ts^\circ + RT) dI + RT \ln(dI) \quad (I-4)$$

The term $R T \ln(dI)$ cancels out whenever differences in Gibbs energy are taken at constant T , as discussed by Salacuse and Stell (1982); these authors define the chemical potential of a continuous mixture by

$$\mu(I) = \left[\frac{\delta G}{\delta n_c F(I^*)} \right]_{T, P, I^* = I} \quad (1-5)$$

The above is a functional derivative in which the functional, G , is differentiated with respect to the function, $n_c F(I)$, at a fixed value of I designated by I^* .

To illustrate functional differentiation, consider Ψ to be an integral of an expression containing the function $n_c F(I)$:

$$\Psi = \int_I f(n_c F(I)) dI \quad (1-6)$$

where the functional Ψ assigns a number to the function $n_c F(I)$ for all I ; the integration extends over the entire range of I for which $F(I)$ is defined; typically, that range may be from zero to infinity. Then, the functional derivative is simply (Hansen and McDonald, 1976)

$$\frac{\delta \Psi}{\delta n_c F(I)} = \frac{df}{dn_c F(I)} \quad (1-7)$$

Using the above result, together with Equation (1-5), an expression for the chemical potential follows directly, as given by Equation (2a).

Equation (2a) is a general result. It may be used to evaluate the chemical potential for various molecular models such as equations of state of the form

$$P = P(T, V, n_i, n_j, \dots, n_c F(I)). \quad (1-8)$$

where n_i, n_j, \dots refer to mole numbers of discrete components while n_c is the number of moles of continuous mixture.

The temperature-dependent term of Equation (2a), $\mu(T)$, cancels out in all phase equilibrium calculations which are performed at constant temperature.

Appendix II

Multivariate Description of Composition

For some mixtures, the composition may not be adequately described by a single distribution variable such as molecular weight. We may, in principle, use continuous thermodynamics with any number of variables but, for simplicity, we consider here the case for two variables such as molecular weight and fraction aromaticity. Then, the composition is described by a joint probability distribution, $F(I,J)$, as a function of two variables I and J . This function defines a probability surface (instead of a curve for the single-variable case) and must be normalized such that

$$\int_I \int_J F(I,J) dI dJ = 1 \quad (\text{II-1})$$

If we have an expression for the function $F(I,J)$, we can evaluate the probability distribution of I , $F_I(I)$, by integrating over J :

$$F_I(I) = \int_J F(I,J) dJ \quad (\text{II-2})$$

where $F_I(I)$ is the marginal probability distribution. If variables I and J are independent of each other

$$F(I,J) = F_I(I) \cdot F_J(J) \quad (\text{II-3})$$

Equation (II-3) is a useful when the two variables are not correlated because it leads to mathematical simplifications. A major difficulty is to determine appropriate independent distribution variables. However, regardless of whether I and J are independent, the criterion for equilibrium between two phases at constant temperature is

$$\mu'(I,J) = \mu''(I,J) \quad (\text{II-4})$$

Equation (II-4) refers to the chemical potential surfaces for all values of I and J .

Useful expressions for μ' and μ'' may be found from a molecular thermodynamic model. For example, if we have an equation of state of the form

$$P = P(T, V, n_c, F(I,J)) \quad (\text{II-5})$$

we calculate the chemical potential in phase ' from

$$\begin{aligned} \mu'(I,J) = & \int_V \left\{ \left[\frac{\delta P}{\delta n_c F(I^+, J^+)} \right]_{T,P,I^+=I,J^+=J} - \frac{RT}{V} \right\} dV \\ & - RT \ln \frac{V}{n_c F(I,J) RT} + \mu(T) \end{aligned} \quad (\text{II-6})$$

A similar expression holds for $\mu''(I,J)$.

Multivariate calculations can also be used for semi-continuous mixtures.

Appendix III

Simultaneous Representation of Discrete and Continuous Composition

Many fluid mixtures which are, in part, continuous, may also contain appreciable amounts of components which are more conveniently described as discrete components (e.g., light hydrocarbons in a gas-condensate system or solvents in polymer solutions). Therefore, to obtain a realistic compositional representation, we must be able to describe mixtures containing both discrete and continuous components (semi-continuous mixtures).

We can derive expressions for thermodynamic properties for a semi-continuous mixture using the procedures of Appendix I. Using the limiting procedure described there, discrete components are represented as weighted Dirac delta functions.

As an example, let $\rho(I)$ be the distribution function for a mixture which contains some discrete components which are represented by Dirac delta functions. The normalization equation is

$$\int_I \rho(I) dI = 1 \quad (\text{III-1})$$

The discrete components are represented by:

$$\rho_i(I^+) = x_i \delta(I - I_i^+) \quad (\text{III-2})$$

where x_i is the weighting factor of the Dirac delta function for each discrete component j . Since the integral of a Dirac delta function is unity, Equation (III-1) becomes (for k discrete components):

$$\sum_i^k x_i + \int_I \eta F(I) dI = 1 \quad (\text{III-3})$$

Equation (III-3) shows that the weighting factors, x_i , are the mole fractions of the discrete components i and η is the mole fraction of the continuous fraction. The continuous fraction is described by a distribution function such that:

$$\int_I F(I) dI = 1 \quad (\text{III-4})$$

By applying the above procedure to molecular models for mixtures (e.g., equations of state or expressions for the Gibbs energy), the models may be generalized to semi-continuous mixtures.

We may further extend the composition representation to allow for multiple continuous fractions, each weighted by an overall mole fraction, η_j , and each described by a distribution function, $F_j(I)$.

This procedure is useful for describing systems with multimodal continuous fraction distributions which are represented by a sum of single-modal distributions. In addition, we can also consider systems where different homologous series are to be treated simultaneously, each one as a function of the same distribution variable.

We can write the normalization equation for systems of k discrete components and l continuous fractions by analogy to Equation (III-3):

$$\sum_i^k x_i + \sum_j^l \int_I \eta_j F_j(I) dI = 1 \quad \text{(III-5)}$$

where, for each continuous fraction,

$$\int_I F_j(I) dI = 1 \quad \text{(III-6)}$$

Equation (III-5) may be incorporated into molecular models to represent the composition dependence in semi-continuous systems.

Appendix IV

Equation-of-State Calculations for Semi-Continuous Systems

To perform dew-point or bubble-point calculations, we use one equation of state to describe both vapor and liquid properties. To apply Equation (15) to semi-continuous mixtures, we use Equations (2) and (3) to evaluate the chemical potential. It is therefore necessary to introduce discrete and continuous compositions into Equation (15) via mixing rules for parameters a and b . For a system with k discrete components and l continuous fractions, we use the procedures of Appendix I and III; we obtain:

$$b_m = \sum_i^k x_i b(i) + \sum_i^l \eta_i \int F_i(I) b(I) dI \quad (\text{IV-1})$$

$$\begin{aligned} a_m = & \sum_i^k \sum_j^k x_i x_j a(i,j) + 2 \sum_i^k \sum_j^l x_i \eta_j \int F_j(I) a(i,I) dI \\ & + \sum_i^l \sum_j^l \eta_i \eta_j \int_I \int_{I^*} F_i(I) F_j(I^*) a(I,I^*) dI dI^* \end{aligned} \quad (\text{IV-2})$$

where x_i and η_i are mole fractions of the discrete and continuous fractions.

For normal alkanes from C_4 to C_{40} , vapor pressure data (Zwolinski and Wilhoit, 1971) were fit over a wide temperature range. The following relations were found to represent the data with an overall root-mean-square error of 3.9%:

$$b(I) = b_0 + b_1 I \quad (\text{IV-3})$$

$$a(I,I)^{\frac{1}{2}} = a_0(T) + a_1(T) I \quad (\text{IV-4})$$

where I is molecular weight. For the range 223 to 723 K, the temperature dependence is given by

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

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

Table IV-1 gives all constants.

For low-molecular weight fluids, the Soave expressions are used (Soave, 1976). The cross terms in the mixing rules are given by a corrected (k_{ij}) geometric mean:

$$\alpha(i,j) = \alpha(i,i)^{k_{ij}} \alpha(j,j)^{k_{ij}} (1-k_{ij}) \quad (\text{IV-7})$$

For continuous fractions, all k_{ij} are assumed to be independent of molecular weight.

Phase-equilibrium criteria may be rewritten in terms of fugacity coefficients, φ_i .
For discrete components:

$$y_i \varphi_i = x_i \varphi_i \quad i=1,k \quad (\text{IV-8})$$

For continuous components:

$$\eta_i F_i(I) \varphi_i(I) = \eta_i'' F_i''(I) \varphi_i''(I) \quad i=1,l \quad (\text{IV-9})$$

The fugacity coefficients are determined in a manner similar to that for the chemical potential. For a discrete component, we calculate the fugacity coefficient for each phase:

$$RT \ln \varphi_i = \int_V \left\{ \left[\frac{\partial P}{\partial n_i} \right]_{T,V,n_j} - \frac{RT}{V} \right\} dV - RT \ln Z \quad (\text{IV-10})$$

where Z is the compressibility factor. Using Equation (15) with all $k_{ij}=0$,

$$RT \ln \varphi_i = RT \ln \frac{\nu}{\nu-b} + RT \frac{b(i)}{\nu-b} + \frac{ab(i)}{b^2} \left\{ \ln \frac{\nu+b}{\nu} - \frac{b}{\nu+b} \right\} - \frac{2 \left\{ \sum_j^k x_j \alpha(i,j) + \sum_j^l \eta_j \int_I F_j(I) \alpha(i,I) dI \right\}}{b} \ln \frac{\nu+b}{\nu} - RT \ln Z \quad (\text{IV-11})$$

where ν is the molar volume. For each continuous fraction:

$$RT \ln \varphi_i(I) = \int_V \left\{ \left[\frac{\delta P}{\delta n_i F_i(I^*)} \right]_{T,V,I^*=I} - \frac{RT}{V} \right\} dV - RT \ln Z \quad (\text{IV-12})$$

Then, with all $k_{ij}=0$:

$$RT \ln \varphi_i(I) = RT \ln \frac{\nu}{\nu-b} + RT \frac{b(I)}{\nu-b} + \frac{ab(I)}{b^2} \left\{ \ln \frac{\nu+b}{\nu} - \frac{b}{\nu+b} \right\} - \frac{2 \left\{ \sum_j^k x_j \alpha(I,j) + \sum_j^l \eta_j \int_{I^*} F_j(I^*) \alpha(I,I^*) dI^* \right\}}{b} \ln \frac{\nu+b}{\nu} - RT \ln Z \quad (\text{IV-13})$$

When we apply Equation (IV-13) to both phases ' and ', the ratio of $\varphi_i(I)$ in the two phases, expressed as an explicit function of molecular weight, I , may be written:

$$\ln \frac{\varphi_i''(I)}{\varphi_i'(I)} = C_1 + C_2 I \quad (\text{IV-14})$$

where C_1 and C_2 are combinations of terms from Equation (IV-13) which are independent of the variable I . The form of Equation (IV-14) is a direct result of the mixing rules and the linear approximations made in Equations (IV-3) and (IV-4).

Equation (IV-14) allows us to relate the distribution functions for each continuous fraction in phases ' and '' by equating the statistical moments of the distribution functions in each phase through Equation (IV-9). This is called "the method of moments." As a result, if we choose gamma distributions to represent the composition of one phase, we find that the other phase in equilibrium is also described by gamma distributions and we can relate the distribution-function parameters through C_1 and C_2 :

$$\gamma_i' = \gamma_i'' \quad (\text{IV-15})$$

$$\alpha_i' = \alpha_i'' \quad (\text{IV-16})$$

$$\beta_i' = \frac{\beta_i''}{1 + C_2 \beta_i''} \quad (\text{IV-17})$$

$$\frac{\eta_i'}{\eta_i''} = \exp(C_1 + C_2 \gamma_i'') \left(\frac{1}{1 - C_2 \beta_i''} \right)^{\alpha_i''} \quad (\text{IV-18})$$

These equations permit a closed-form solution for determination of phase envelopes as needed for dew-point or bubble-point calculations.

Table IV-1
Constants for Equation-of-State Parameters
(for the range 223 to 723 K)

| $b \text{ (cm}^3/\text{mol)}$ | | | |
|-------------------------------------|-------------|-------------|-------------------------|
| | b_0 | b_1 | |
| | -12.4 | 1.60 | |
| $a \text{ (bar-cm}^6/\text{mol}^2)$ | | | |
| i | $a_i^{(0)}$ | $a_i^{(1)}$ | $a_i^{(2)}$ |
| 0 | 194.83 | -1.8659 | 5.5602×10^{-3} |
| 1 | 100.65 | -.11297 | 3.8206×10^{-5} |

Appendix V

Semi-Continuous Polymer Fractionation Calculations

Figure 9 shows a schematic representation of a polymer-fractionation calculation. The sol and gel phases form upon lowering the temperature of the feed phase; they are in equilibrium and obey the criteria of Equations (1) and (1a). Further, the sol and gel phases are related to the feed through material balances.

We assume that the composition of the polydisperse polymer in each phase is represented as a function of molecular weight by the gamma distribution function [Equation (6)]. This enables us to solve analytically the equilibrium equation and to relate distribution-function parameters in the sol and gel phases. The procedure is analogous to the equation-of-state calculation described in Appendix IV. We use the Flory-Huggins expression for the Gibbs energy of each phase [Equation (4)].

It is not possible, however, to solve the material balance exactly, given the restraint that the polymer distribution is described by the same type of distribution function in each phase. Therefore, to avoid numerical solution of the material balance equation, we use an approximate method of solution which is based upon statistical moments of the material balance equation.

To illustrate, we write the material balance for a one-solvent (1), polydisperse polymer (2) system in terms of the volume fraction ϕ and a parameter ξ which is the ratio of the volume of the sol phase to that of the feed. The excess volume is zero in the Flory-Huggins theory, and we can write:

$$\phi_1^F = \xi \phi_1' + (1-\xi) \phi_1'' \quad (\text{V-1})$$

where ' and '' denote the sol and gel phases, respectively. For the polymer, at every value of molecular weight, I , we write:

$$\phi^F(I) = \xi \phi'(I) + (1-\xi) \phi''(I) \quad (\text{V-2})$$

The expression for the volume distribution of the polymer is related to the mass probability distribution, $F(I)$ by:

$$\phi(I) = \frac{n_2 \Theta_N \frac{F(I)}{I} m(I)}{n_1 + n_2 \Theta_N \int_I \frac{F(I)}{I} m(I) dI} \quad (\text{V-3})$$

where n is the number of moles, Θ_N is the number-average molecular weight and $m(I)$ is the molar volume ratio of polymer to solvent; $m(I)$ is assumed to be a linear function of molecular weight,

$$m(I) = \frac{v_2 I}{v_1} \quad (V-4)$$

where v_2 is the polymer specific volume and v_1 is the solvent molar volume.

Using the definition of $\Phi(I)$ and

$$\Phi_2 = \int_I \Phi(I) dI . \quad (V-5)$$

we multiply each term in Equation (V-3) by I and integrate over the range of I to derive the relation between the first statistical moments:

$$\Phi_2^F \alpha^F \beta^F = \xi \Phi_2' \alpha' \beta' + (1-\xi) \Phi_2'' \alpha'' \beta'' \quad (V-6)$$

By multiplying Equation (V-3) by I^2 and integrating (second statistical moment), we derive:

$$\Phi_2^F \alpha^F (\alpha^F + 1) (\beta^F)^2 = \xi \Phi_2' \alpha' (\alpha' + 1) (\beta')^2 + (1-\xi) \Phi_2'' \alpha'' (\alpha'' + 1) (\beta'')^2 \quad (V-7)$$

Since the shift parameters (γ) are the same in all phases, we can relate α and β in the three phases through Equations (V-6) and (V-7). By specifying feed composition, interaction parameter χ and pure-component volumes, we calculate the compositions and relative amounts of the sol and gel phases.

The method of moments is an approximation because it introduces error into the material balances. In some, but not all cases, this error is not of major significance.

Table 1

Composition of a Natural Gas at 100 Bar

| Component | Mole Percent |
|---------------|--------------|
| (1) Methane | 83 |
| (2) Ethane | 6 |
| (3) Propane | 4 |
| (4) Butane | 2 |
| (5) "Heavies" | 5 |

Table 2A

Dew-Point Conditions at 100 Bar

| "Heavies" in Vapor | | Dew-Point Temp, K | Mole Percent of First Condensate | | | | |
|---|----------|----------------------|----------------------------------|-----|-----|-----|---------------------|
| Mean | Variance | | (1) | (2) | (3) | (4) | (5) |
| 86 (Hexane) | 245 | 363 | 35.0 | 5.5 | 6.4 | 5.6 | 47.5 ^(a) |
| 114 (Octane) | 245 | 418 | 32.1 | 4.4 | 4.6 | 3.7 | 55.2 ^(b) |
| 86 (Hexane) | 525 | 383 | 32.0 | 4.9 | 5.7 | 4.9 | 52.5 ^(c) |
| 86 (Hexane) | 245 | 380 | 33.1 | 5.0 | 5.7 | 4.9 | 51.2 ^(d) |
| <i>bump</i> ^(e) 128 (Nonane) | 245 | | | | | | |

(a),(b),(c),(d): For details of condensed "heavies", see Table 2B
 (e): Bump contains 10 mole percent of vapor-phase "heavies".

Table 2B

Details of "Heavies" in First Condensate

| | Mean | Variance |
|-------------|------|----------|
| (a) | 98 | 433 |
| (b) | 122 | 309 |
| (c) | 122 | 2150 |
| (d) | 97 | 418 |
| <i>bump</i> | 139 | 418 |

Bump contains 31 mole percent of condensed "heavies".

Table 3

Composition of a Real Natural Gas at 20.7 Bar
(Bergman, Katz and Tek - Sample 58)

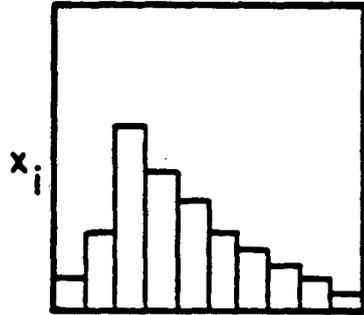
| Component | Mole Percent | | |
|------------------|----------------|-----------------|------------------|
| | Vapor Measured | Liquid Measured | Liquid Predicted |
| 1 Nitrogen | 0.20 | 0.03 | 0.04 |
| 2 Carbon Dioxide | 0.84 | 0.06 | 0.13 |
| 3 Methane | 84.63 | 10.40 | 11.70 |
| 4 Ethane | 7.92 | 6.90 | 6.67 |
| 5 Propane | 3.80 | 10.30 | 12.00 |
| 6 Butane | 2.05 | 21.40 | 21.00 |
| 7 "Heavies" | 0.79 | 50.91 | 48.46 |

Table 4

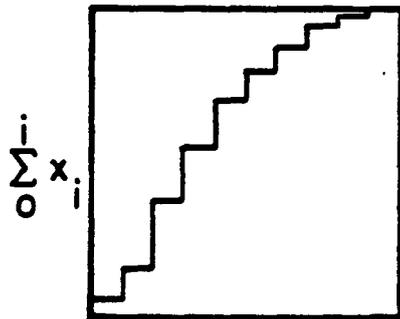
"Heavies" Content of Stripped Gas at Top of Absorber
(variance = 180)

| Mean of "Heavies" in Liquid | Mole Percent "Heavies" in Gas |
|-----------------------------|-------------------------------|
| 100 | 0.213 |
| 114 | 0.058 |
| 128 | 0.018 |
| 142 | 0.005 |
| 156 | 0.002 |

**Finite-Component
(Discrete)
Mixture**



Component No. i



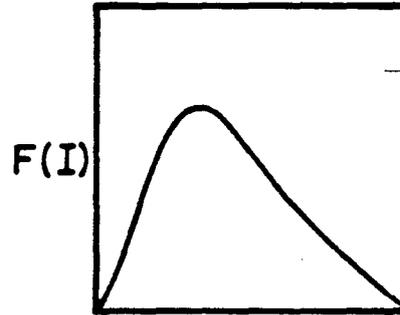
Component No. i

$$\sum_{\text{all } i} x_i = 1.0$$

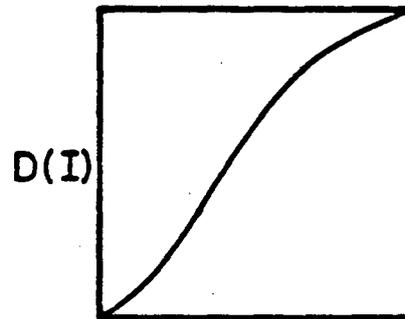
x = Mole Fraction

I is a characterizing quantity, e.g., molecular weight.

**Infinite-Component
(Continuous)
Mixture**



Distribution Variable I



Distribution Variable I

$$D(I=\infty) = \int_0^{\infty} F(I) dI = 1.0$$

F = Distribution Function

FIGURE 1

**DISCRETE AND CONTINUOUS COMPOSITION
FOR A MULTICOMPONENT MIXTURE**

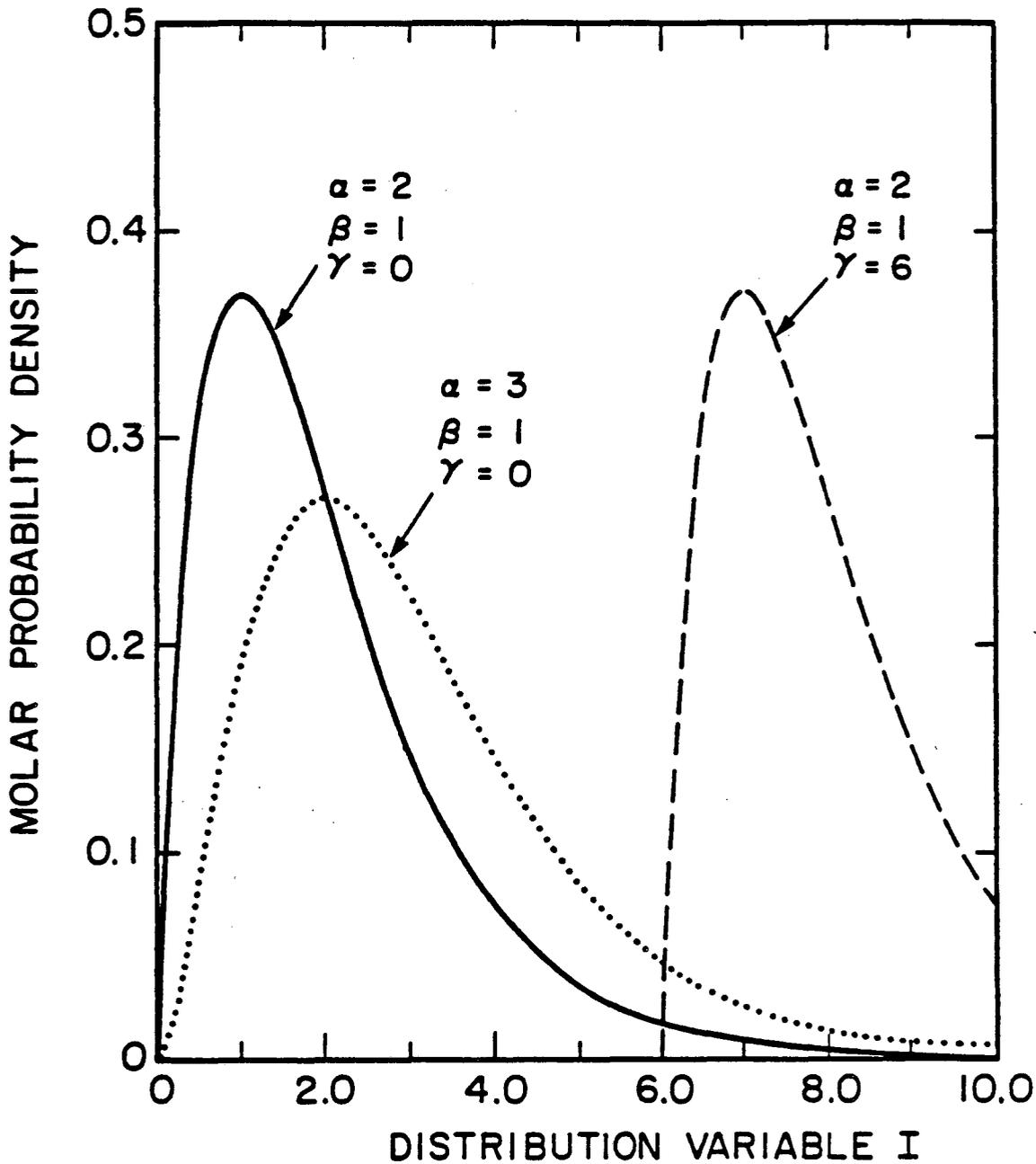


FIGURE 2
GAMMA DENSITY FUNCTION
FOR CONTINUOUS OR SEMI-CONTINUOUS
DISTRIBUTIONS

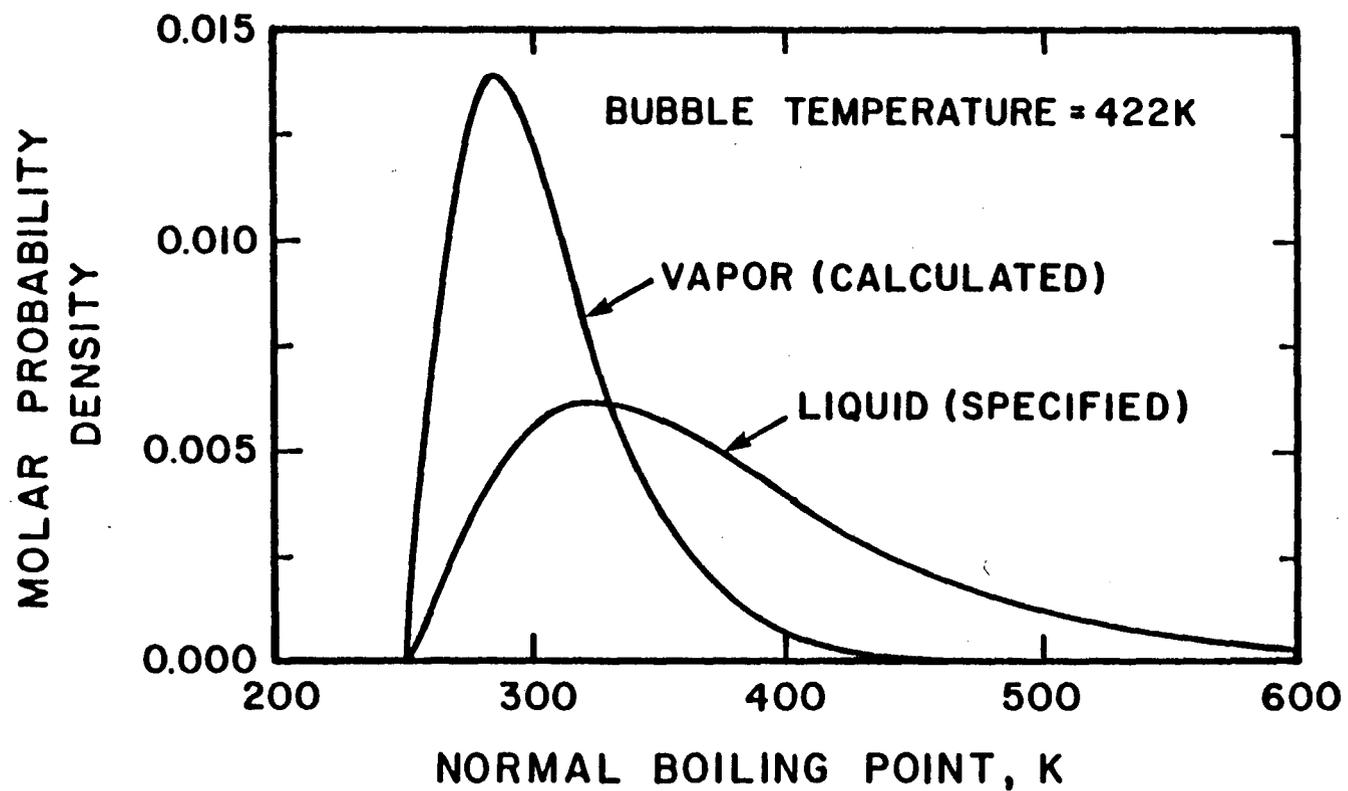


FIGURE 3
BUBBLE-POINT CALCULATION FOR
A CONTINUOUS MIXTURE OF PARAFFINS
USING RAOULT'S LAW

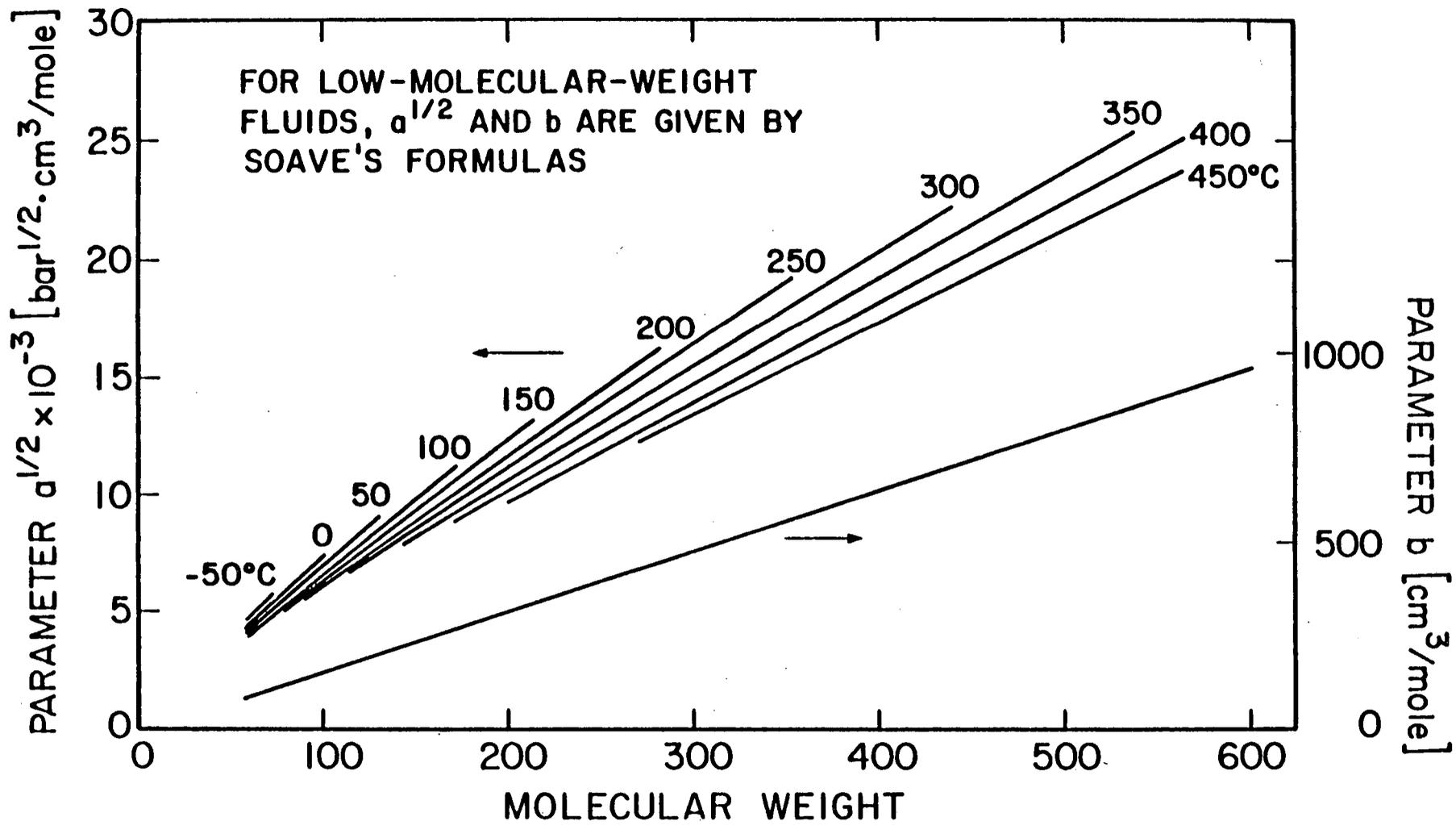


FIGURE 4

CORRELATION OF EQUATION-OF-STATE PARAMETERS

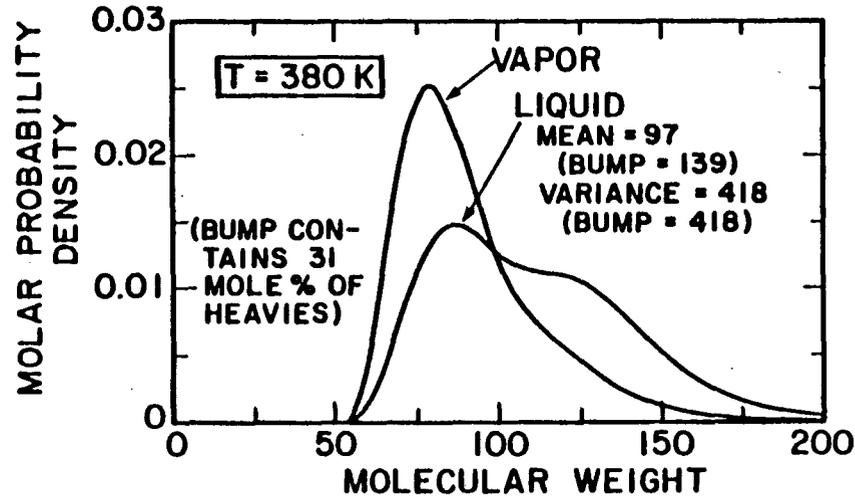
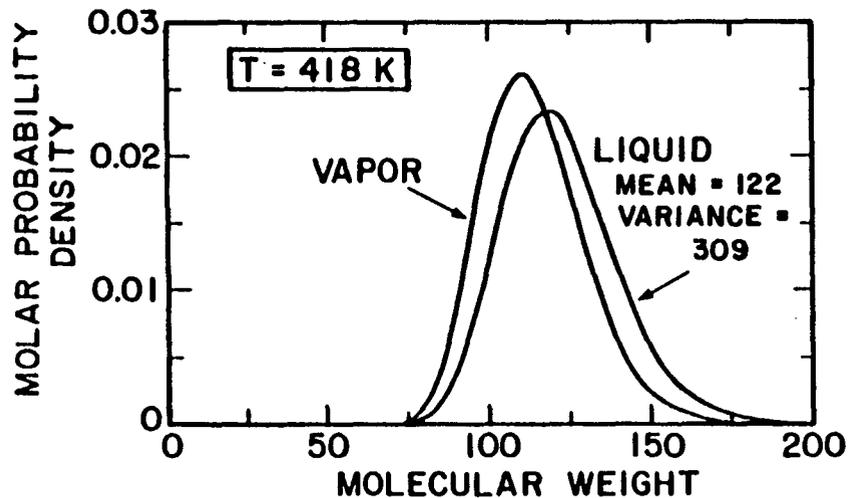
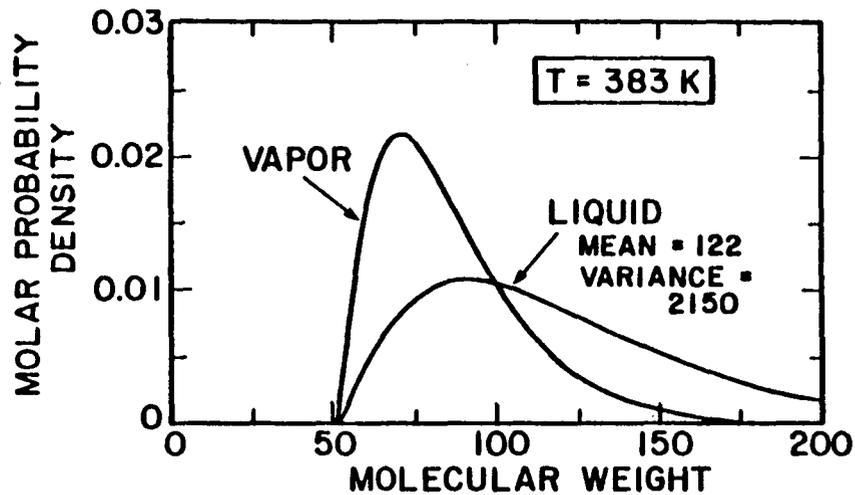
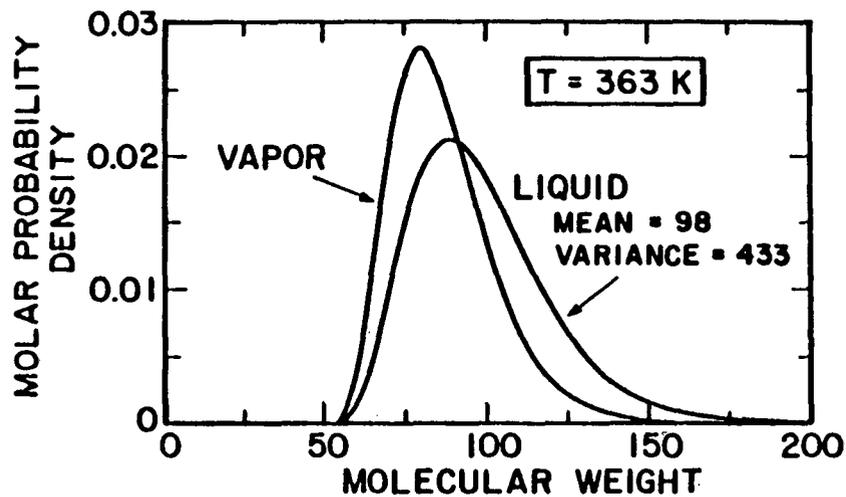


FIGURE 5
DEW-POINT CALCULATIONS FOR A SEMI-CONTINUOUS
MIXTURE AT 100 BAR

LIQUID-PHASE DISTRIBUTION

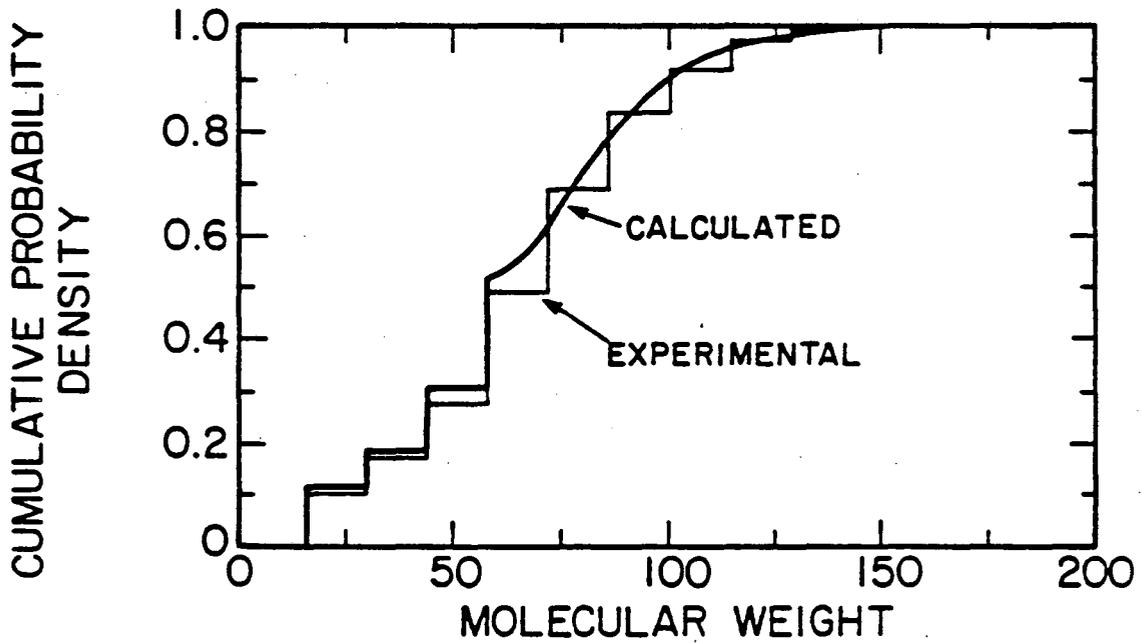
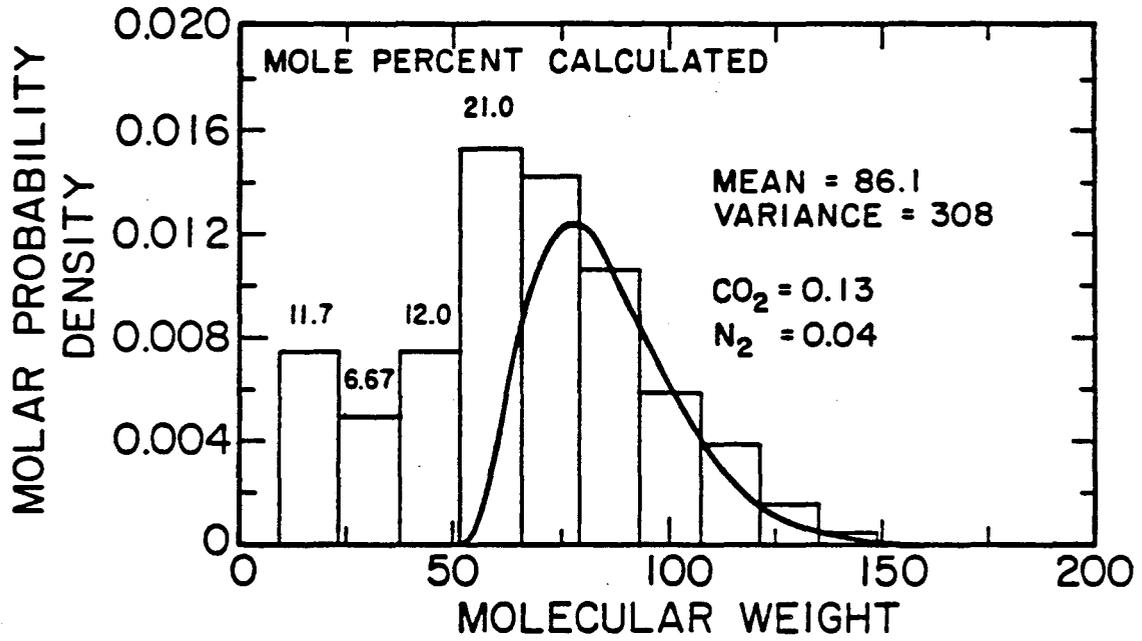


FIGURE 6
CALCULATED AND EXPERIMENTAL DEW-POINT
CONDITIONS

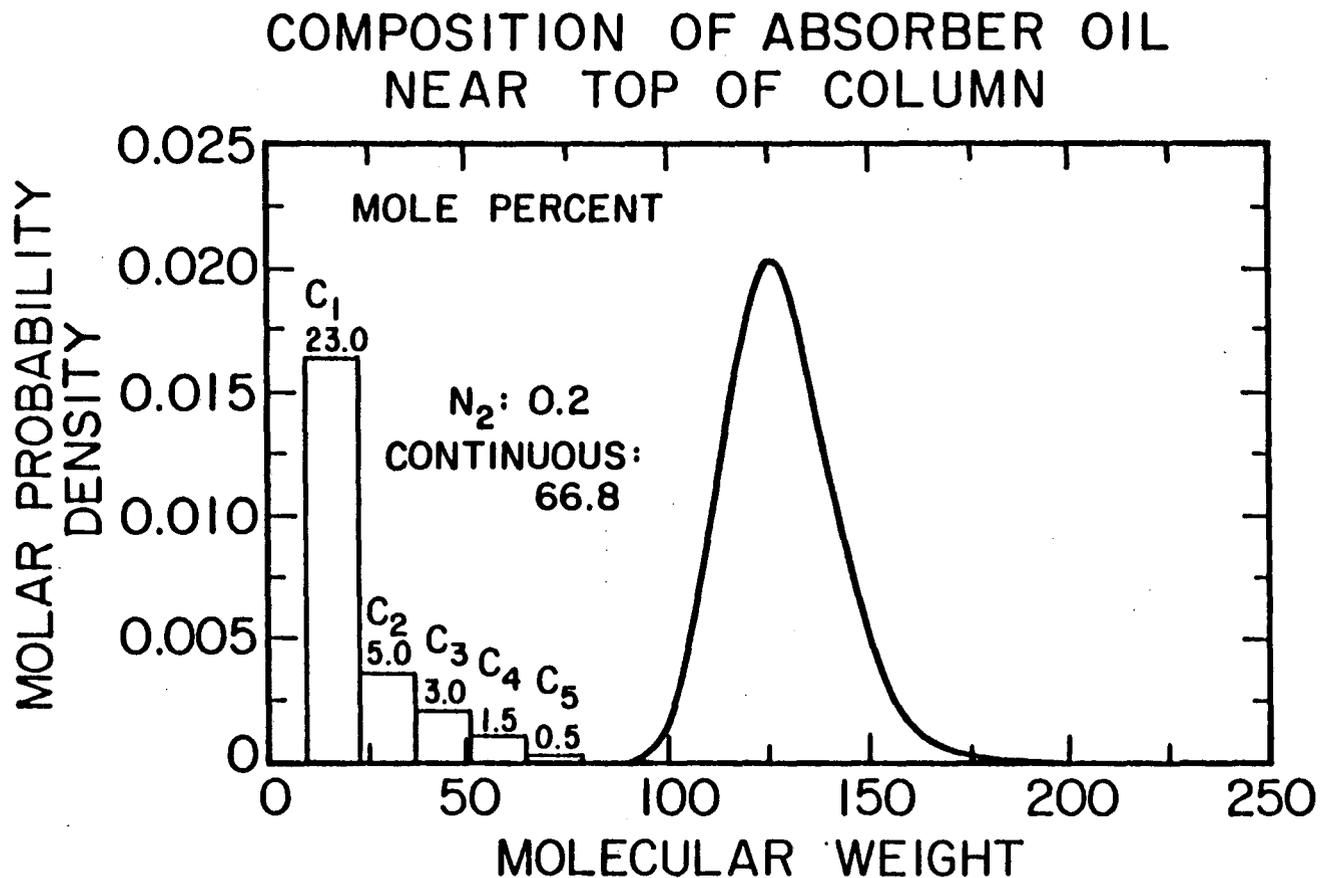


FIGURE 7
BUBBLE-POINT CALCULATIONS FOR A
SEMI-CONTINUOUS ABSORBER OIL AT 40 BAR

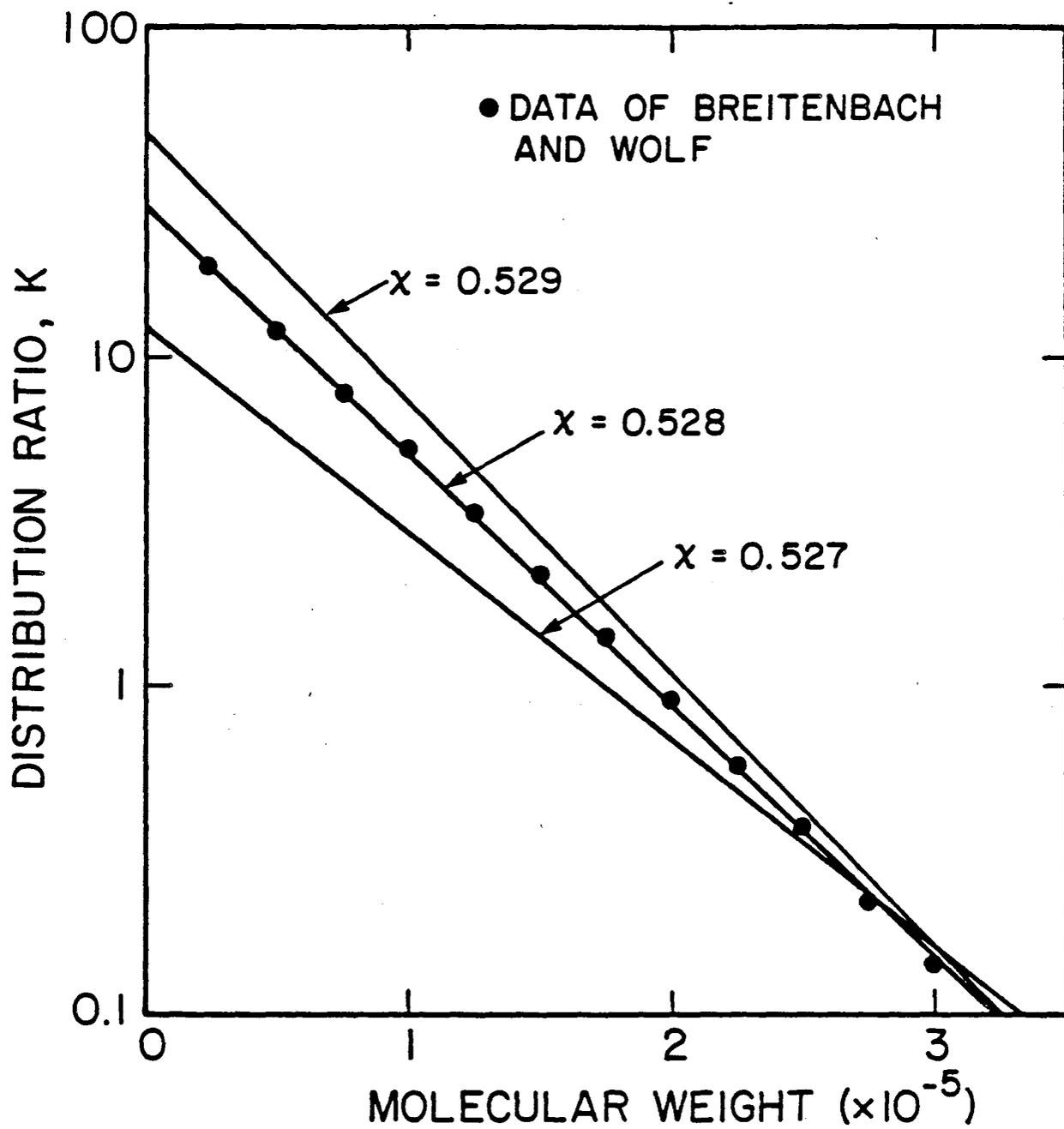


FIGURE 8
DISTRIBUTION RATIO K FOR
POLYSTYRENE IN CYCLOHEXANE

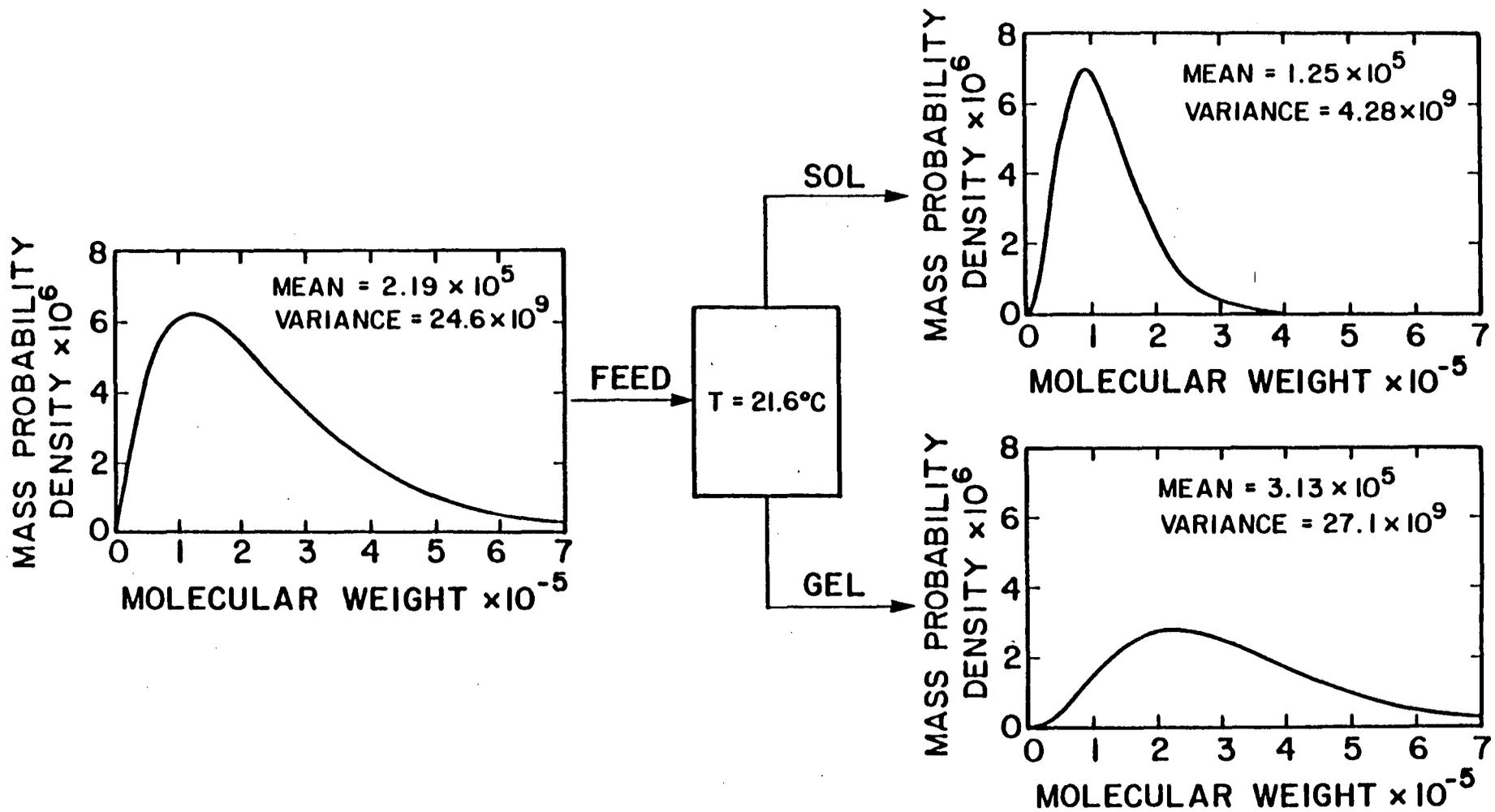
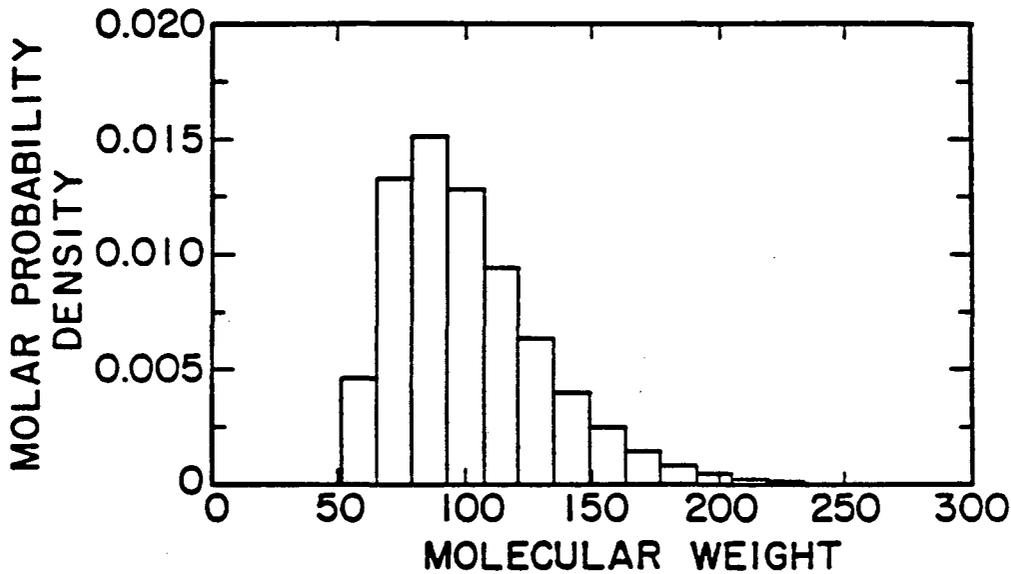


FIGURE 9
PHASE EQUILIBRIA IN THE SYSTEM
(POLYDISPERSE) POLYSTYRENE/CYCLOHEXANE

ASSUMED COMPOSITION OF VAPOR PHASE
FOR A 20-COMPONENT SYSTEM: C₄-C₂₃



CALCULATED RESULTS USING DISCRETE
OR CONTINUOUS COMPOSITION

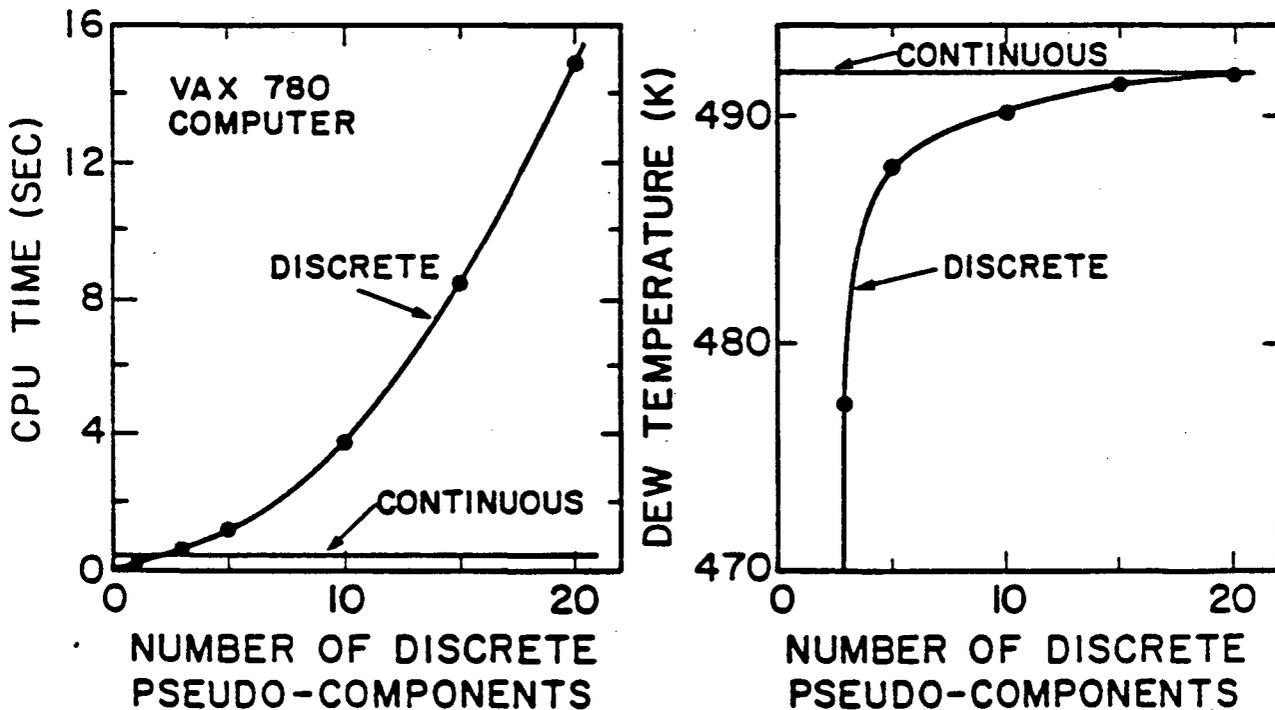


FIGURE 10

COMPUTER-TIME REQUIREMENTS FOR DEW-POINT
CALCULATIONS FOR A MODEL SYSTEM AT 5 BAR

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