Continuous Thermodynamics of Multicomponent Systems

Based on a continuous distribution function instead of the mole fractions of individual components, a consistent building of continuous thermodynamics is presented. It may be favorably used in all cases where there are a large number of very similar chemical species such as in polymers, in heavy petroleum fractions, or in coal-derived liquids.

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SCOPE

Separation processes in the chemical industry such as distillation, extraction, fractionation, crystallization, and others are based on phase equilibria described by chemical thermodynamics. The central quantity is the excess Gibbs energy of the liquid phase. Using empirical or semiempirical expressions for this quantity, it is possible to describe, to correlate, to interpret, or even to predict phase equilibria. Equations developed within the framework of molecular thermodynamics (Wilson equation, NRTL equation, UNIQUAC equation, UNIFAC equation) have proved to be very successful (Wilson, 1964; Renon and Prausnitz, 1968; Abrams and Prausnitz, 1975; Fredenslund et al., 1975).

The description of the composition by mole fractions is no problem if the system contains only two or three components, but a large number of very similar chemical species occurs in many industrial mixtures, for example in polymers, in heavy petroleum fractions, or in coal-derived liquids. In these cases, it is difficult or practically impossible to isolate and to identify the components by ordinary chemical analysis. Thus, the mole fractions of the components are unknown. Even if they were known, it would be a very complicated problem to manage a system of a thousand or more equations for a thousand or more components.

Mixtures of this kind are called complex mixtures. Instead of the mole fractions of individual components, continuous distribution functions are used for describing the composition. In polymer chemistry, the molar mass distribution function is applied for characterization. Petroleum fractions and similar mixtures may be characterized by their true boiling point curves; i.e., boiling point as a function of the amount of distillate using a column with a large number of theoretical plates and high reflux.

Using such continuous distribution functions, there exists an inconsistency with the usual thermodynamics based on mole fractions of individual components. Until now, two possibilities were known for overcoming this inconsistency: the pseudocomponent approach and the key component approach. The pseudocomponent approach consists of approximating the continuous distribution by a discontinuous (bar) distribution where each bar represents a pseudocomponent. In this way, the complex mixture can be treated as a classical multicomponent mixture of these pseudocomponents. Key components are chemical species present in the mixture. Their amounts are fitted in such a way that the multicomponent mixture formed by the key components possesses thermodynamic properties similar to those of the complex mixture. Clearly, both approaches are crude; the number and manner of selection of the pseudo-components or key components are arbitrary.

The content of this paper consists of overcoming this inconsistency in the opposite way; chemical thermodynamics is converted into a form adapted to continuous distribution functions.

Some earlier attempts in this direction are known. To treat internal degrees of freedom, a continuous description was applied within the framework of nonequilibrium thermodynamics by Prigogine and Mazur (1953; compare also de Groot and Mazur, 1969). For petroleum fractions, Hoffman (1964, 1968, 1969a,b) and Roth (1968, 1972) had some early ideas. A treatment using the moments of the distribution function as independent thermodynamic variables has been presented by Gal-Or et al. (1975).

In the usual thermodynamics, the quantities considered are functions depending on the mole fractions of the components. But in continuous thermodynamics, a continuous distribution function occurs instead of these mole fractions and thus the composition dependence becomes a *functional.* While a function f is a mapping that assigns a number y to each number x of a given interval [$y = f(x)$], a functional is a mapping that assigns a number to each function f of a given class of functions.

An example is provided by the definite integral

$$I = \int_a^b f(x)dx$$

where a and b are given numbers. The integral value I depends on the kind of function chosen for f [e.g. exp( ), ln( ), $(\ )^2$, sin( )] but not on its argument x. This argument always passes through the total interval $[a,b]$.

CONCLUSIONS AND SIGNIFICANCE

A consistent building of "continuous thermodynamics" is presented; it is applicable to all mixtures containing a large number of very similar chemical species.

Instead of characterizing the components by a discontinuous index, a continuous characterization variable is used such as the molar mass for polymers or the boiling point temperature for petroleum fractions. This permits one to differentiate, to integrate, or to develop a power series with respect to this variable. These operations are impossible for a discontinuous index. Instead of the well-known sums with respect to discrete components, in continuous thermodynamics integrals occur which often may be calculated analytically, leading to closed formulas. Conventional thermodynamics has to stop at the sums which are to be calculated numerically.

Experimental information on the composition of such complex mixtures is obtained in the form of continuous distribution functions. In usual practice, one is forced to divide these continuous distributions into pseudocomponents or to describe them by key components. These are arbitrary and crude procedures. Continuous thermodynamics permits one to use continuous distribution functions directly for thermodynamic treatment.

In conventional thermodynamics, phase equilibrium is expressed by as many equations for the chemical potentials as there are components present. In continuous thermodynamics, we obtain (in the most simple case) only one equation, valid in the total interval for the occurring values of the characterizing variable. Thus, in continuous thermodynamics the phase equilibrium condition is an equation permitting the calculation of an unknown function such as the distribution function in one of two coexisting phases if the distribution function in the other is known.

The relation between continuous thermodynamics and the pseudocomponent method is similar to that between differential calculus and calculus using quotients of differences. Thus, continuous thermodynamics will facilitate thermodynamic treatment of mixtures containing so many components that the composition is described by continuous distribution functions instead of mole fractions.

INTRODUCTION

We consider an ensemble B of a large number of very similar chemical species. For simplicity, we assume that each species may sufficiently be characterized by the value of one variable, M. This variable may be, for instance, the normal boiling point, the number of carbon atoms, the molar mass, the degree of polymerization, or the number of suitably defined segments. Similarity of the chemical species means that two species distinguished by a small amount of M differ by small amounts of the thermodynamic properties.

DISTRIBUTION FUNCTIONS

Let $n_{B[M',M'']}$ be the amount of substance B with M-values from M' up to M'' ($>M'$). We define the extensive distribution function $w(M)$ by

$$n_{B[M',M'']} = \int_{M'}^{M''} w(M)dM \tag{1}$$

Thus the total amount of substance n_B is given by

$$n_B = \int_M w(M)dM \tag{2}$$

The letter M at the integral means integration for the total domain of definition of M.

In reality, the substance B consists of a finite number of chemical species characterized by $M_1, \ldots M_\omega$; the corresponding amounts of substance shall be $n_1, \ldots n_\omega$. This real discontinuous distribution may be considered as a special case of Eqs. 1 and 2. For this reason, an interval $[M_i^-, M_i^+)$ is demarcated about each value M_i with

$$M_i^- = \begin{cases} M_1 - \dfrac{M_2 - M_1}{2}; & i = 1 \\ M_i - \dfrac{M_i - M_{i-1}}{2}; & i = 2, \ldots \omega \end{cases}$$

$$M_i^+ = \begin{cases} M_i + \dfrac{M_{i+1} - M_i}{2}; & i = 1, \ldots \omega - 1 \\ M_\omega + \dfrac{M_\omega - M_{\omega-1}}{2}; & i = \omega \end{cases} \tag{3}$$

i.e., neighboring intervals touch each other. The symbol [. .,. .) means: lower limit included, upper limit excluded. The length ΔM_i of the interval i is given by

$$\Delta M_i = M_i^+ - M_i^- \tag{4}$$

For homopolymers, we may choose M to be the molar mass. Then we have

$$M_i^- = M_i - M_O/2;$$
$$M_i^+ = M_i + M_O/2;$$
$$\Delta M_i = M_O \tag{5}$$

with M_O as molar mass of the monomer unit.

In the real discontinuous case, we permit the limits of integration in Eq. 1 to be only the interval limits, Eq. 3, or the limits of the domain of definition. Furthermore, the distribution function is assumed to be constant within the intervals. Thus, the real discontinuous distribution is described by the step function

$$w_{\text{dis}}(M) = \begin{cases} n_i/\Delta M_i; & M \in [M_i^-, M_i^+); \quad i = 1, \ldots \omega \\ 0; & \text{otherwise} \end{cases} \tag{6}$$

However, the aim of introducing a distribution function is not to use Eq. 6 but to consider continuous and continuously differen-

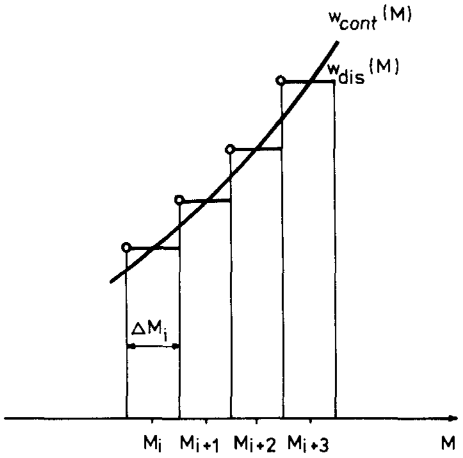

Figure 1. Discontinuous and continuous distribution function.

tiable functions, $w_{cont}(M)$, which are continuous models of the real discontinuous distribution. These functions are smoothed approximations for $w_{dis}(M)$ (Figure 1); i.e., for some neighboring intervals $(j, \dots k)$ we have

$$\sum_{i=j}^{k} n_i \approx \int_{M_j^-}^{M_k^+} w_{cont}(M)dM \tag{7}$$

Of course, by this way, $w_{cont}(M)$ is not defined uniquely, but according to the postulated similarity of the chemical species, small variations of $w(M)$ lead to small variations of the thermodynamic properties too. Thus, details of the applied model function $w_{cont}(M)$ do not appreciably influence measurable quantities. As $w_{dis}(M) = 0$ for $M \geq M_\omega^+$, we may assume $w_{cont}(M)$ goes to zero as fast as we need as $M \rightarrow \infty$.

In practice, these continuous distribution functions are obtained as a result of a characterization experiment such as the determination of the true boiling point curve for petroleum fractions or fractionation for polymers.

Until now, we have only considered the extensive quantities n_i and $w(M)$. Dividing by n_B we obtain the corresponding intensive quantities: the mole fraction X_i and the intensive distribution function $W(M)$.

$$X_i = \frac{n_i}{n_B}; \quad W(M) = \frac{w(M)}{n_B} \tag{8}$$

Accordingly, the relations for these quantities are obtained by dividing Eqs. 1, 2, 6, and 7 by n_B. From Eqs. 2 and 6 we get

$$\sum_{i=1}^{\omega} X_i = 1; \quad \int_M W(M)dM = 1 \tag{9}$$

STATE FUNCTIONALS

In conventional (discontinuous) thermodynamics, a quantity ζ may be considered as a function of temperature T, pressure P and mole numbers $n_1, \dots n_\omega$:

$$\zeta = \zeta_{dis}(T,P,n_1, \dots n_\omega) \tag{10}$$

T and P have been chosen since they are the most important variables in practice. The following considerations may be extended in an analogous manner for other variables.

In the continuous case, instead of $n_1, \dots n_\omega$, the extensive distribution function $w(M)$ is used:

$$\zeta = \zeta(T,P;w) \tag{11}$$

here ζ is a function with respect to T and P, but a *functional* with respect to w (Kehlen and Rätrsch, 1980); a value ζ is associated to each function $w(M)$ at given T and P. This value depends on the total behavior of the function $w(M)$ but not on its argument M. M passes through its total domain of definition. Thus, in Eq. 11 we write w and not $w(M)$, but we use a semicolon to express the difference between T and P on the one hand and w on the other.

As an example, we consider the volume V of an ideal mixture in continuous thermodynamics

$$V = \int_M w(M)\, v_B^*(M,T,P)dM \tag{12}$$

$v_B^*(M,T,P)$ is the molar volume of the pure chemical species characterized by M.

Continuous thermodynamics must be constructed in such a way that the well-known discontinuous theory is reobtained if $w(M) = w_{dis}(M)$:

$$\zeta = \zeta(T,P;w) \Rightarrow \zeta(T,P;w_{dis}) = \zeta_{dis}(T,P,n_1, \dots n_\omega) \tag{13}$$

According to Eq. 6, $w_{dis}(M)$ is a given function of $n_1, \dots n_\omega$. Thus ζ may be considered as a normal function of these variables and Eq. 10 is reobtained. In Eq. 12 the transition to the discontinuous case becomes, according to Eq. 6:

$$\begin{aligned} V &\Rightarrow \int_M w_{dis}(M) v_B^*(M,T,P)dM \\ &= \sum_{i=1}^{\omega} \frac{n_i}{\Delta M_i} \int_{M_i^-}^{M_i^+} v_B^*(M,T,P)dM \\ &= \sum_{i=1}^{\omega} n_i v_{B_i}^*(T,P) \end{aligned} \tag{14}$$

The formula on the righthand side is the well-known discontinuous expression where $v_{B_i}^*(T,P)$ means the molar volume of pure species i. According to Eq. 14, this quantity is to be identified with the mean value of $v_B^*(M,T,P)$ in $[M_i^-, M_i^+)$:

$$v_{B_i}^*(T,P) = \frac{1}{\Delta M_i} \int_{M_i^-}^{M_i^+} v_B^*(M,T,P)dM \tag{15}$$

TOTAL DIFFERENTIAL

In discontinuous thermodynamics of mixtures, the partial derivatives with respect to $n_1, \dots n_\omega$ play the central role. Thus, in continuous thermodynamics, we need the derivative of ζ with respect to the function w. This is a problem in functional analysis. Consideration of the total differential has proved to provide the best approach. As all interesting quantities are thermodynamic variables, we presume in the following considerations that all occurring functions except $w_{dis}(M)$ and $W_{dis}(M)$ be continuous and continuously differentiable if the contrary is not explicitly expressed. In the discontinuous case, Eq. 10, as well as in the continuous case, Eq. 11, we may write

$$\delta\zeta = \frac{\partial\zeta}{\partial T}\delta T + \frac{\partial\zeta}{\partial P}\delta P + D\zeta \tag{16}$$

Here the symbol δ is used instead of d to designate the differentials in order to avoid confusion with differentials belonging to integrations (dM). $D\zeta$ is the differential at constant T and P. In this paper, the specification of variables constant at differentiation is omitted. We always refer to the sets of variables $T,P,n_1, \dots n_\omega$ or $T,P,X_1, \dots X_\omega$ respectively as, $T,P;w$ or $T,P;W$.

In the usual discontinuous theory, we may write

$$D\zeta_{\text{dis}} \equiv \lim_{t\to 0} \frac{\zeta_{\text{dis}}(T,P,n_1 + t\delta n_1, \dots n_\omega + t\delta n_\omega) - \zeta_{\text{dis}}(T,P,n_1, \dots n_\omega)}{t} \tag{17a}$$

$$= \sum_{i=1}^{\omega} \frac{\partial \zeta_{\text{dis}}}{\partial n_i}\delta n_i \tag{17b}$$

where δn_i is an arbitrarily eligible increase of amount of species i. Equation 17a is the definition of the total differential; Eq. 17b follows by splitting the limit (Eq. 17a) into a sum of limits with respect to $n_1, \dots n_\omega$.

In the continuous case, we may write in a completely analogous manner

$$D\zeta \equiv \lim_{t\to 0} \frac{\zeta(T,P;w + t\delta w) - \zeta(T,P;w)}{t} \tag{18a}$$

$$= \int_M \frac{\partial \zeta}{\partial n_M}\delta w(M)dM \tag{18b}$$

Here $\delta w(M)$ is an arbitrarily eligible increase of function $w(M)$, presumed to be a continuous function or at least in pieces a continuous function of M, showing the same behavior as $w(M)$ for $M \to \infty$. Equation 18a is the definition of the total differential of a functional according to Gateaux (see, e.g., Curtain and Pritchard, 1977). This Gateaux derivative is assumed to be linear which corresponds to Eq. 17. Equation 18b may be considered as the definition of the partial derivative of the functional ζ with respect to the function w at the point M; this quantity is designated by $\partial\zeta/\partial n_M$ [not by $\partial\zeta/\partial w(M)$] as we require the symbol for the derivative to be dimensionally correct (compare Eq. 1).

The meaning of the differential $D\zeta$, according to Eq. 18, is completely analogous to the well-known meaning of the differential of a function: If the distribution function $w(M)$ is changed by addition of the function $\delta w(M)$, then the thermodynamic quantity ζ changes at the first approximation by $D\zeta$. The transition from the continuous to the discontinuous case may be performed by analogy to Eqs. 13–15 using Eq. 6 and the corresponding relation for $\delta w_{\text{dis}}(M)$:

$$\delta w_{\text{dis}}(M) = \begin{cases} \delta n_i/\Delta M_i; & M \in [M_i^-, M_i^+); \\ 0; & \text{otherwise} \end{cases} \quad i = 1, \dots \omega \tag{19}$$

leading to

$$\frac{\partial \zeta_{\text{dis}}}{\partial n_i} = \frac{1}{\Delta M_i}\int_{M_i^-}^{M_i^+} \frac{\partial \zeta(T,P;w_{\text{dis}})}{\partial n_M} dM \tag{20}$$

which corresponds to Eq. 15.

PARTIAL DERIVATIVE

While $D\zeta$ results from a global variation of $w(M)$, the partial derivative corresponds to a local variation. Thus, applying ($\Delta\hat{w}$ = const.)

$$\delta w(M') = \begin{cases} \Delta\hat{w}; & M' \in [M, M + \Delta M] \\ 0; & \text{otherwise} \end{cases} \tag{21}$$

an explicit expression for $\partial\zeta/\partial n_M$ may be obtained. The quantity ΔM occurring here is an arbitrary increase of M and must not be confused with ΔM_i defined by Eq. 4. Using Eq. 21, we get from Eq. 18

$$\lim_{t\to 0} \frac{\zeta(T,P;\tilde{w}) - \zeta(T,P;w)}{t} = \int_M^{M+\Delta M} \frac{\partial \zeta}{\partial n_{M''}}\Delta\hat{w}dM'' = \frac{\partial \zeta}{\partial n_{\hat{M}}}\Delta\hat{w}\Delta M \tag{22}$$

with ($\Delta w = t\Delta\hat{w}$)

$$\tilde{w}(M') = \begin{cases} w(M') + \Delta w; & M' \in [M, M + \Delta M] \\ w(M'); & \text{otherwise} \end{cases} \tag{23}$$

The last expression on the righthand side of Eqs. 22 follows by the mean-value theorem of integral calculus where $\hat{M} \in [M, M + \Delta M]$. Division by $\Delta\hat{w}\Delta M$ and limit with respect to ΔM yields

$$\frac{\partial \zeta}{\partial n_M} = \lim_{\substack{\Delta w\to 0\\ \Delta M\to 0}} \frac{\zeta(T,P;\tilde{w}) - \zeta(T,P;w)}{\Delta w\Delta M} \tag{24}$$

While in the usual discontinuous case the partial derivative follows from an increase of amount of species i by Δn_i, in the continuous case, according to Eq. 23, the distribution function $w(M)$ is increased in an interval of the length ΔM at $M' = M$ by the amount Δw (Figure 2). The product $\Delta w\Delta M$ occurring the denominator of Eq. 24 corresponds to an amount of substance finally assigned to the chemical species characterized by M. This again justifies the chosen symbol $\partial\zeta/\partial n_M$.

The use of Eq. 24 will be demonstrated for Eq. 12, where we substitute M by M'. According to Eq. 23, only the interval $[M, M + \Delta M]$ provides a contribution and we obtain

$$\frac{\partial V}{\partial n_M} = \lim_{\substack{\Delta w\to 0\\ \Delta M\to 0}} \frac{\int_M^{M+\Delta M} \Delta w\, v_B^*(M',T,P)dM'}{\Delta w\Delta M}$$

$$= \lim_{\substack{\Delta w\to 0\\ \Delta M\to 0}} v_B^*(\hat{M},T,P) = v_B^*(M,T,P) \tag{25}$$

The mean-value theorem of integral calculus has been used; $\hat{M} \in [M, M + \Delta M]$.

The partial derivative depends on M, the point at which differentiation is performed:

$$\frac{\partial \zeta}{\partial n_M} = \frac{\partial \zeta}{\partial n_M}(M,T,P;w). \tag{26}$$

Generally it is a functional with respect to w at given M,T,P. Thus, the differential of $\partial\zeta/\partial n_M$ and the partial derivative of this quantity with respect to w (i.e., the second partial derivative of ζ) may be formed in complete analogy to Eqs. 18–24. The additional dependence of the functional to be differentiated on M does not disturb the procedure.

Corresponding to the well-known relations of conventional thermodynamics, we assume the second partial derivatives to obey the relations

$$\frac{\partial^2 \zeta}{\partial n_M \partial n_{M'}} = \frac{\partial^2 \zeta}{\partial n_{M'} \partial n_M}; \quad \frac{\partial^2 \zeta}{\partial n_M \partial T} = \frac{\partial^2 \zeta}{\partial T \partial n_M}; \quad \frac{\partial^2 \zeta}{\partial n_M \partial P} = \frac{\partial^2 \zeta}{\partial P \partial n_M} \tag{27}$$

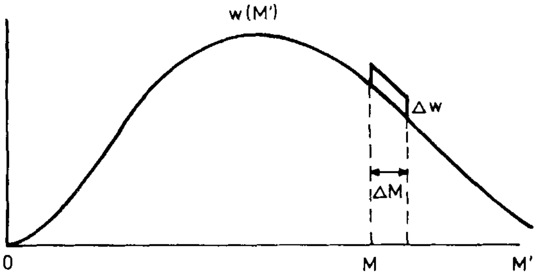

Figure 2. Variation of the extensive distribution function *w*(*M*) for partial differentiation.

Presuming the continuity of the second differential, these relations may be proved.

For the practical realization of the differentiation, it is not necessary to perform the limiting process, Eq. 24, in each case, but one may proceed as follows. The occurring functionals usually are definite integrals with M as the variable of integration within given limits. Thus, derivation means derivation of the integrand, which is a function of $w(M)$. This procedure may be performed as with respect to a normal variable, i.e., using the chain rule with

$$\frac{\partial w(M')}{\partial n_M} = \delta(M' - M) \tag{28}$$

Here $\delta(M' - M)$ is Dirac's function, which equals 0 if $M' - M \neq 0$ and goes to infinity for $M' - M = 0$ in such a way that the integral equals 1:

$$\int_M \delta(M' - M)dM' = 1 \tag{29}$$

This method of practical differentiation could be applied in all considered cases, even if the functional contains two or more integrals. It will be demonstrated for Eq. 12, substituting M by M' again:

$$\begin{aligned}\frac{\partial V}{\partial n_M} &= \int_{M'} \frac{\partial w(M')}{\partial n_M} v_B^*(M',T,P)dM' \\ &= \int_{M'} \delta(M' - M)v_B^*(M',T,P)dM' = v_B^*(M,T,P)\end{aligned} \tag{30}$$

The final result follows since we have a contribution to the integral only from $M' = M$, which equals $v_B^*(M,T,P)$.

Extensive and Intensive Quantities

In thermodynamics it is very important to distinguish between extensive and intensive quantities. If the phase considered is increased to its t-fold size (at constant temperature T and pressure P), then all extensive quantities are also increased to their t-fold sizes whereas all intensive quantities remain constant. Mathematically, this may be expressed using Euler's idea of homogeneous functions: A function $\zeta_{\text{dis}}(T,P,n_1, \ldots n_\omega)$ is called homogeneous (with respect to $n_1, \ldots n_\omega$) of degree k if the relation

$$\zeta_{\text{dis}}(T,P,tn_1, \ldots tn_\omega) = t^k \zeta_{\text{dis}}(T,P,n_1, \ldots n_\omega) \tag{31}$$

is valid for every value of t. Thus, extensive quantities are homogeneous of degree $k = 1$ and intensive quantities are homogeneous of degree $k = 0$. From Eq. 31, in a well-known manner, the relation

$$k\zeta = \sum_i n_i \frac{\partial \zeta}{\partial n_i} \tag{32}$$

may be obtained, which is very important in thermodynamics. The partial derivatives $\partial\zeta/\partial n_i$ are homogeneous functions of degree $k - 1$ (Euler's theorem).

In continuous thermodynamics, these relations are to be generalized to functionals. A functional $\zeta(T,p;w)$ is called homogeneous (with respect to w) of degree k, if the relation

$$\zeta(T,P;tw) = t^k \zeta(T,P;w) \tag{33}$$

is valid for every value of t. Multiplication of the distribution function $w(M)$ at each point M by the same value t corresponds to the increase of the phase to its t-fold size. By the analogous arguments leading from Eq. 31 to Eq. 32, we obtain

$$k\zeta = \int_M w(M) \frac{\partial \zeta}{\partial n_M} dM \tag{34}$$

where $\partial\zeta/\partial n_M$ is a homogeneous functional of degree k-1.

Thus, in continuous thermodynamics *extensive* quantities are homogeneous functionals of degree $k = 1$ (with respect to w). Examples are volume V, enthalpy H, entropy S, and Gibbs energy G. We shall designate these quantities by capital roman letters and use the symbol Z in the general case. Thus, we get from Eq. 34

$$Z = \int_M w(M)z_B(M)dM \tag{35}$$

Here we introduce the partial molar quantity $z_B(M)$ which is defined by

$$z_B(M) = \frac{\partial Z}{\partial n_M} = \lim_{\substack{\Delta w \to 0 \\ \Delta M \to 0}} \frac{Z(T,P;\tilde{w}) - Z(T,P;w)}{\Delta w \Delta M} \tag{36}$$

The differential DZ reads, according to Eq. 18,

$$\begin{aligned}DZ \equiv \lim_{t \to 0} &\frac{Z(T,P;w + t\delta w) - Z(T,P;w)}{t} \\ &= \int_M z_B(M)\delta w(M)dM\end{aligned} \tag{37}$$

Correspondingly, in continuous thermodynamics, *intensive* quantities are homogeneous functionals of degree $k = 0$ (with respect to w). Examples are the molar quantities $z = Z/n_B$ and the partial molar quantities $z_B(M)$. These quantities will be designated by lower case roman letters. Euler's relation, Eq. 34, reads for these quantities, using Eq. 8,

$$\int_M w(M) \frac{\partial z}{\partial n_M} dM = 0; \quad \int_M W(M) \frac{\partial z}{\partial n_M} dM = 0 \tag{38}$$

$$\int_M w(M) \frac{\partial z_B(M')}{\partial n_M} dM = 0; \quad \int_M W(M) \frac{\partial z_B(M')}{\partial n_M} dM = 0 \tag{39}$$

According to Eq. 33 (with $k = 0$, $t = 1/n_B$), intensive quantities may be considered as functionals of $W(M)$ instead of $w(M)$. Thus, we obtain, using Eq. 35,

$$z = \frac{Z}{n_B} = z(T,P;W) = \int_M W(M)z_B(M)dM \tag{40}$$

$$z_B(M) = \frac{\partial Z}{\partial n_M} = z_B(M,T,P;W) \tag{41}$$

MOLAR QUANTITIES IN DEPENDENCE ON *W*(*M*)

To obtain relations on molar quantities $z = Z/n_B$, the convenient starting point is Eq. 37. Introducing the intensive distribution function $W(M)$ instead of $w(M)$, we have to consider Eq. 9. This relation has also to be fulfilled by a varied function $W(M) + \delta W(M)$. Thus, the demand on the variation $\delta W(M)$ is

$$\int_M \delta W(M)dM = 0 \tag{42}$$

which we account for by considering only variations $\delta w(M)$ obeying

$$\int_M \delta w(M)dM = 0. \tag{43}$$

Then, n_B = const. and $\delta W(M) = \delta w(M)/n_B$.

In this way, we obtain from Eq. 37, dividing by n_B and using the homogeneity of z (i.e., $k = 0$),

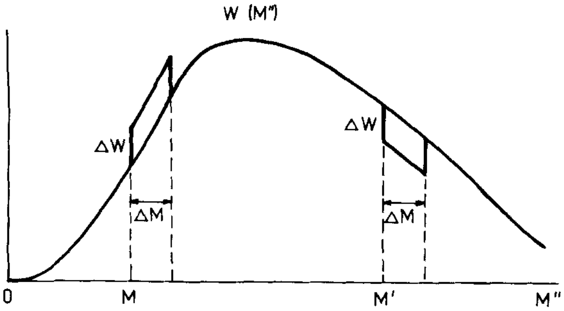

Figure 3. Variation of the intensive distribution function *W(M)* for partial differentiation.

$$Dz = \lim_{t\to 0} \frac{z(T,P;W + t\delta W) - z(T,P;W)}{t} = \int_M z_B(M,T,P;W)\delta W(M)dM \quad (44)$$

The transition from the global variation to the local variation may be performed by analogy to Eqs. 21–24. As Eq. 42 is to be fulfilled, we use ($\Delta\hat{W}$ = const.)

$$\delta W(M'') = \begin{cases} \Delta\hat{W}; & M'' \in [M, M + \Delta M] \\ -\Delta\hat{W}; & M'' \in [M', M' + \Delta M] \\ 0; & \text{otherwise} \end{cases} \quad (45)$$

and obtain from Eq. 44

$$\lim_{t\to 0} \frac{z(T,P;\tilde{W}) - z(T,P;W)}{t} = \int_M^{M+\Delta M} z_B(M'')\Delta\hat{W}dM'' - \int_{M'}^{M'+\Delta M} z_B(M'')\Delta\hat{W}dM'' = z_B(\hat{M}) - z_B(\hat{M}')]\Delta\hat{W}\Delta M \quad (46)$$

with ($\Delta W = t\Delta\hat{W}$)

$$\tilde{W}(M'') = \begin{cases} W(M'') + \Delta W; & M'' \in [M, M + \Delta M] \\ W(M'') - \Delta W; & M'' \in [M', M' + \Delta M] \\ W(M''); & \text{otherwise} \end{cases} \quad (47)$$

The last expression on the right hand side of Eq. 46 follows by the mean value theorem of integral calculus where $\hat{M} \in [M, M + \Delta M]$ and $\hat{M}' \in [M', M' + \Delta M]$. Division by $\Delta\hat{W}\Delta M$ and limit with respect to ΔM yields

$$\left(\frac{\partial z}{\partial X_M}\right)_{[M']} = \lim_{\substack{\Delta W \to 0 \\ \Delta M \to 0}} \frac{z(T,P;\tilde{W}) - z(T,P;W)}{\Delta W \Delta M} = z_B(M) - z_B(M') \quad (48)$$

The reason for choosing the symbol on the lefthand side is the correspondence of the product $\Delta W \Delta M$ to an increase of mole fraction finally assigned to the chemical species characterized by M. The index $[M']$ indicates that this increase takes place on account of the chemical species characterized by M' (Figure 3). If $M' = M$, the derivative equals zero.

The derivative defined by Eq. 48 corresponds to the well-known derivative $\partial z/\partial X_i$ in conventional thermodynamics based on mole fractions. There the auxiliary condition, Eq. 9, usually is accounted for by eliminating one mole fraction by means of Eq. 9 and operating with the independent mole fractions only. In this way, the increase of one independent mole fraction automatically takes place on account of the eliminated dependent mole fraction. The method necessarily applied here in continuous theory has the advantage of not destroying the equivalence of components.

The derivative Eq. 48 depends on M and M', the point of differentiation, and the point of compensation

$$\left(\frac{\partial z}{\partial X_M}\right)_{[M']} = \left(\frac{\partial z}{\partial X_M}\right)_{[M']}(M,M',T,P;W) \quad (49)$$

As the derivative is a functional with respect to W at given M,M',T, and P, the differential of this quantity and the partial derivative with respect of W (i.e., the second partial derivative of z) may be formed by analogy to Eqs. 44 and 48. The additional dependence on M and M' does not disturb the differentiation.

Corresponding to eq. 27, the second partial derivative is assumed to obey the relations

$$\left(\frac{\partial^2 z}{\partial X_M \partial X_{M'}}\right)_{[M'',M''']} = \left(\frac{\partial^2 z}{\partial X_{M'} \partial X_M}\right)_{[M''',M'']};$$
$$\left(\frac{\partial^2 z}{\partial X_M \partial T}\right)_{[M'']} = \left(\frac{\partial^2 z}{\partial T \partial X_M}\right)_{[M'']}; \left(\frac{\partial^2 z}{\partial X_M \partial P}\right)_{[M'']} = \left(\frac{\partial^2 z}{\partial P \partial X_M}\right)_{[M'']} \quad (50)$$

Here M'' and M''' are the points belonging to the compensation of the variations connected with the derivatives at M and M' respectively.

By analogy to Eq. 24, we may formulate a procedure for practical performance of differentiation. Again the functionals usually are definite integrals in which the integrands are functions of $W(M)$. As in the case of $\partial\zeta/\partial n_M$, this differentiation may be performed as with respect to a normal variable using the chain rule with

$$\left(\frac{\partial W(M'')}{\partial X_M}\right)_{[M']} = \delta(M'' - M) - \delta(M'' - M') \quad (51)$$

Finally, two additional relations will be given. As the equation

$$z_B(M) = z - \int_{M'} W(M')[z_B(M') - z_B(M)]dM' \quad (52)$$

is valid identically according to Eqs. 40 and 9, we obtain, using Eq. 48,

$$z_B(M) = z - \int_{M'} W(M')\left(\frac{\partial z}{\partial X_{M'}}\right)_{[M]} dM' \quad (53)$$

This relation permits the calculation of the partial molar quantity $z_B(M)$ starting with the molar quantity z. The corresponding relation in discontinuous theory reads

$$z_{B_i} = z - \sum_{j=1}^{\omega} X_j \left(\frac{\partial z}{\partial X_j}\right)_{[i]} \quad (54)$$

The index $[i]$ indicates that the increase of X_j connected with the derivative takes place on account of X_i, corresponding to the elimination of X_i by means of Eq. 9. Usually, the case $j = i$ is excluded in the sum in Eq. 54, but as we take it, the corresponding derivative equals zero and thus we may include this term as well.

From Eqs. 44, 48, and 42, we see that we may write the differential Dz also in the form

$$Dz = \int_M \left(\frac{\partial z}{\partial X_M}\right)_{[M']} \delta W(M)dM \quad (55)$$

where M' may be chosen arbitrarily. Regarding the corresponding expression in discontinuous theory, the remarks concerning Eq. 54 apply.

Putting $\zeta = z_B(M''')$ we obtain from Eq. 18, in a way analogous to that resulting in Eqs. 44 and 48, the corresponding relations for partial molar quantities:

$$Dz_B(M''') = \lim_{t\to 0} \frac{z_B(M''',T,P;W + t\delta W) - z_B(M''',T,P;W)}{t}$$
$$= \int_M n_B \frac{\partial z_B(M''')}{\partial n_M}\, \delta W(M)dM \qquad (56)$$

$$\left(\frac{\partial z_B(M''')}{\partial X_M}\right)_{[M']} = \lim_{\substack{\Delta W\to 0\\ \Delta M\to 0}} \frac{z_B(M''',T,P;\tilde{W}) - z_B(M''',T,P;W)}{\Delta W \Delta M}$$
$$= n_B\left[\frac{\partial z_B(M''')}{\partial n_M} - \frac{\partial z_B(M''')}{\partial n_{M'}}\right] \qquad (57)$$

The variation $\delta W(M)$ has to fulfill Eq. 42 and $\tilde{W}$ is given by Eq. 47.

The considerations following Eq. 48 may be extended to the case of partial molar quantities. Thus, the relations resulting from Eq. 50 by substituting z by $z_B(M''')$ are assumed to be valid for the second derivatives. The practical realization of the differentiation may be performed by the method specified above using Eq. 51. The relation corresponding to Eq. 55 reads

$$Dz_B(M''') = \int_M \left(\frac{\partial z_B(M''')}{\partial X_M}\right)_{[M']} \delta W(M)dM \qquad (58)$$

The generalized Gibbs-Duhem relation applies also in continuous thermodynamics. Forming the differential DZ on the basis of Eq. 35, comparing with Eq. 37, and substituting M by M''', we obtain

$$\int_{M'''} w(M''')Dz_B(M''')dM''' = 0 \qquad (59)$$

Expressing $Dz_B(M''')$ by Eq. 18b [$\zeta = z_B(M)$] and choosing δw according to Eq. 21, where ΔM may be arbitrarily small, we obtain, using the mean-value theorem of integral calculus,

$$\int_{M'''} w(M''') \frac{\partial z_B(M''')}{\partial n_M} dM''' = 0 \qquad (60)$$

Here M may be chosen arbitrarily. With the help of Eq. 57 the validity of the corresponding relation for intensive distribution functions follows

$$\int_{M'''} W(M''') \left(\frac{\partial z_B(M''')}{\partial X_M}\right)_{[M']} dM''' = 0 \qquad (61)$$

In Eq. 61, M and M' may be chosen arbitrarily.

THERMODYNAMIC POTENTIALS

In continuous thermodynamics, Gibbs' fundamental equation reads

$$T\delta S = \delta U + P\delta V - \int_M \mu_B(M)\delta w(M)dM. \qquad (62)$$

Using Legendre's transformation, the thermodynamic potentials (characteristic functions) may be obtained in the well-known manner. They read

$$\begin{aligned}
U &= U(S,V;w);\\
H &= H(S,P;w) = U + PV;\\
F &= F(T,V;w) = U - TS;\\
G &= G(T,P;w) = U + PV - TS;\\
\tilde{G} &= \tilde{G}(S,V;\mu_B) = U - G = TS - PV;\\
\tilde{F} &= \tilde{F}(S,P;\mu_B) = U - F = TS;\\
\tilde{H} &= \tilde{H}(T,V;\mu_B) = U - H = -PV;
\end{aligned}$$

$$\begin{aligned}
\delta U &= T\delta S - P\delta V + \int_M \mu_B(M)\delta w(M)dM && (63)\\
\delta H &= T\delta S + V\delta P + \int_M \mu_B(M)\delta w(M)dM && (64)\\
\delta F &= -S\delta T - P\delta V + \int_M \mu_B(M)\delta w(M)dM && (65)\\
\delta G &= -S\delta T + V\delta P + \int_M \mu_B(M)\delta w(M)dM && (66)\\
\delta \tilde{G} &= T\delta S - P\delta V - \int_M w(M)\delta\mu_B(M)dM && (67)\\
\delta \tilde{F} &= T\delta S + V\delta P - \int_M w(M)\delta\mu_B(M)dM && (68)\\
\delta \tilde{H} &= -S\delta T - P\delta V - \int_M w(M)\delta\mu_B(M)dM && (69)\\
O &= -S\delta T + V\delta P - \int_M w(M)\delta\mu_B(M)dM && (70)
\end{aligned}$$

Each thermodynamic potential is a function with respect to the first two quantities and a functional with respect to the third one. Thus, for example, the internal energy U is a thermodynamic potential if it is given as a function of entropy S and volume V and as a functional of the distribution function $w(M)$. $\tilde{H}$ is a thermodynamic potential (the "grand potential," used in statistical thermodynamics in the framework of the grand canonical ensemble) if it is given as a function of temperature T and volume V and as a functional of the chemical potential $\mu_B(M)$. Equation 70 is the continuous version of the Gibbs-Duhem relation.

CHEMICAL POTENTIAL

In discontinuous thermodynamics, the well-known expression for the chemical potential of a species i reads

$$\mu_{B_i}(T,P,X) = \mu^*_{B_i}(T,P) + RT\ln X_i + RT\ln f_{B_i}(T,P,X) \qquad (71)$$

Here $\mu^*_{B_i}$ is the chemical potential of the pure species i in the same state of aggregation as the mixture considered; f_{B_i} is the activity coefficient of the species i which equals 1 for the pure species i. X means the totality of all mole fractions. According to Eqs. 6 and 8, we may introduce the discontinuous distribution function $W_{\text{dis}}(M)$ by

$$X_i = W_{\text{dis}}(M_i)\Delta M_i \qquad (72)$$

In the discontinuous theory, the different chemical species are characterized by the discontinuously distributed values M_i (or by the corresponding values of the index i).

Considering Eq. 71, with X_i substituted by Eq. 72, to be valid for all values of M and replacing W_{dis} by W, we obtain the expression for the chemical potential in continuous thermodynamics

$$\mu_B(M,T,P;W) = \mu^*_B(M,T,P) + RT\ln[W(M)\Delta M(M)]$$
$$+ RT\ln f_B(M,T,P;W) \qquad (73)$$

The composition of the mixture now is described by the intensive distribution function W instead of the totality of all mole fractions

X. Thus, μ_B and the activity coefficient f_B become functionals with respect to W; $\mu_B^*(M,T,P)$ is the chemical potential of the pure species characterized by M in the same state of aggregation. $\Delta M(M)$ is the continuous version of ΔM_i and must not be confused with ΔM of Eqs. 21ff. The relation between ΔM_i and $\Delta M(M)$ is simple if $M_1, \ldots M_\omega$ are equidistant with the distance M_O. Then, $\Delta M_i = \Delta M(M) = \text{const}$. If $M_1, \ldots M_\omega$ are not equidistant (e.g., if $M = \tau =$ boiling point), the values ΔM_i assigned to each M_i change irregularly and we may decide whether $\Delta M(M)$ should be more of an interpolating function for these ΔM_i values or more of an approximating function balancing differences between neighboring ΔM_i values and accounting for different densities of M_i values within larger M intervals only. Considering phase equilibria, this question is irrelevant as $\Delta M(M)$ cancels in the corresponding equations.

To absorb $\Delta M(M)$ into the first term, we introduce

$$\mu_{B,O}^*(M,T,P) = \mu_B^*(M,T,P) + RT \ln\Delta M(M) \tag{74}$$

and obtain

$$\mu_B(M,T,P;W) = \mu_{B,O}^*(M,T,P) + RT \ln W(M) + RT \ln f_B(M,T,P;W) \tag{75}$$

In writing expressions like Eqs. 74 and 75, we have to keep in mind that ΔM and W may or may not be dimensionless quantities (depending on the meaning of M) and in the latter case must not occur as arguments of a logarithm. To avoid the cumbersome occurrence of the corresponding units in the formulas, we agree to take these symbols for the numerical values only if they are arguments of a logarithm. Doing so, we always presume use of the same units within one calculation.

The activity coefficient $f_B(M,T,P;W)$ has the same general properties as those in the discontinuous case. It equals 1 for a pure species characterized by M

$$\text{Pure species char. by } M \qquad f_B(M,T,P) = 1 \tag{76}$$

Furthermore, it equals 1 for all species (i.e., for all values of M) and all compositions (i.e., for all functions W) in the case of an ideal mixture

$$\text{Ideal mixture} \qquad f_B(M,T,P;W) = 1 \tag{77}$$

Thus, $\mu_B(M)$ reads for an ideal mixture

$$\mu_B^{id}(M,T,P;W) = \mu_{B,O}^*(M,T,P) + RT \ln W(M) \tag{78}$$

In this simple case, $\mu_B(M)$ depends on the function $W(M')$ at the point M only and not on the total behavior of $W(M')$. According to Eqs. 75 and 78, the chemical excess potential, i.e., the excess of the chemical potential with respect to the ideal mixture, reads

$$\mu_B^E(M,T,P;W) = \mu_B - \mu_B^{id} = RT \ln f_B(M,T,P;W) \tag{79}$$

THERMODYNAMIC FUNCTIONALS

Once the chemical potential is known, all other thermodynamic equilibrium properties may be calculated by means of the well-known thermodynamic relations and of the equations derived above. In the following, we give some of the most important relations.

Molar Gibbs Energy *g*

As the chemical potential is identical with the partial molar Gibbs energy, we obtain, according to Eqs. 75 and 40, [$z = g$; $z_B(M) = \mu_B(M)$]

$$\begin{aligned} g(T,P;W) = \frac{G(T,P;w)}{n_B} &= \int_M W(M)\mu_B(M,T,P;W)dM \\ &= \int_M W(M)\mu_{B,O}^*(M,T,P)dM + RT \int_M W(M) \ln W(M)dM \\ &\quad + RT \int_M W(M) \ln f_B(M,T,P;W)dM \end{aligned} \tag{80}$$

The chemical potential $\mu_B(M)$ may be calculated from G or g according to Eq. 41 or Eq. 53 by

$$\begin{aligned} \mu_B(M,T,P;W) = \frac{\partial G(T,P;w)}{\partial n_M} &= g(T,P;W) \\ &\quad - \int_{M'} W(M') \left(\frac{\partial g(T,P;W)}{\partial X_{M'}}\right)_{[M]} dM' \end{aligned} \tag{81}$$

The Gibbs-Duhem equation reads, according to Eq. 61,

$$\int_{M''} W(M'') \left(\frac{\partial \mu_B(M'',T,P;W)}{\partial X_M}\right)_{[M']} dM'' = 0 \tag{82}$$

where M and M' may be chosen arbitrarily.

Molar Entropy *s*

We obtain from Eq. 80

$$\begin{aligned} s(T,P;W) &= \frac{S(T,P;W)}{n_B} \\ &= -\frac{\partial g(T,P;W)}{\partial T} = \int_M W(M)s_B(M,T,P;W)dM \\ &= \int_M W(M)s_{B,O}^*(M,T,P)dM \\ &\quad - R\int_M W(M) \ln W(M)dM \\ &\quad - R\int_M W(M) \ln f_B(M,T,P;W)dM \\ &\quad - RT\int_M W(M) \frac{\partial \ln f_B(M,T,P;W)}{\partial T} dM \end{aligned} \tag{83}$$

According to Eqs. 41 and 50, the partial molar entropy $s_B(M)$ is given by

$$\begin{aligned} s_B(M,T,P;W) &= \frac{\partial S(T,P;w)}{\partial n_M} = -\frac{\partial \mu_B(M,T,P;W)}{\partial T} \\ &= s_{B,O}^*(M,T,P) - R \ln W(M) - R \ln f_B(M,T,P;W) \\ &\quad - RT \frac{\partial \ln f_B(M,T,P;W)}{\partial T} \end{aligned} \tag{84}$$

For the pure species characterized by M, we have

$$s_B^*(M,T,P) = -\frac{\partial \mu_B^*(M,T,P)}{\partial T} \tag{85}$$

and accordingly we introduced, using Eq. 74,

$$s_{B,O}^*(M,T,P) = -\frac{\partial \mu_{B,O}^*(M,T,P)}{\partial T} = s_B^*(M,T,P) - R \ln\Delta M(M) \tag{86}$$

Let us consider the change of entropy at the isothermal isobaric mixing process. We obtain for an ideal mixture [$f_B(M) = 1$] in the case $\Delta M(M) = M_O = \text{const.}$, according to Eqs. 83, 86, and 9

$$\begin{aligned} \Delta_{\text{mix}}s^{\text{id}}(T,P;W) &= s^{\text{id}}(T,P;W) - \int_M W(M)s_B^*(M,T,P)dM \\ &= -R\int_M W(M) \ln W(M)dM - R \ln M_O \end{aligned} \tag{87}$$

From conventional thermodynamics, it is well known that in the thermodynamic limit of a (countably) infinite number of species $\Delta_{\text{mix}}s \rightarrow \infty$. Therefore, we are interested to see how this result is provided within the framework of continuous thermodynamics. The distribution function $W(M)$ contains no information on the number of actual occuring chemical species. If we reduce the amounts of the present (real) chemical species by half and add corresponding amounts of chemical species with intermediate values of M, then $W(M)$ is not changed according to Eqs. 1–9. Thus, the corresponding increase of $\Delta_{\text{mix}}s$ is described by the decrease of M_O (by half in this case). The thermodynamic limit $\Delta_{\text{mix}}s \rightarrow \infty$, for an infinite number of species, is provided in continuous thermodynamics by $M_O \rightarrow 0$. Thus, a finite value of M_O reflects the real discontinuous structure of matter.

Molar Enthalpy *h*

From Eqs. 80 and 83, we obtain

$$\begin{aligned} h(T,P;W) &= \frac{H(T,P;w)}{n_B} = g(T,P;W) + Ts(T,P;W) \\ &= \int_M W(M) h_B(M,T,P;W) dM \\ &= \int_M W(M) h_B^*(M,T,P) dM \\ &\quad - RT^2 \int_M W(M) \frac{\partial \ln f_B(M,T,P;W)}{\partial T} dM \end{aligned} \tag{88}$$

The partial molar enthalpy $h_B(M)$ is given by

$$\begin{aligned} h_B(M,T,P;W) &= \frac{\partial H(T,P;w)}{\partial n_M} = \mu_B(M,T,P;W) \\ &\quad + Ts_B(M,T,P;W) = \frac{\partial \mu_B(M,T,P;W)/T}{\partial 1/T} \\ &= h_B^*(M,T,P) - RT^2 \frac{\partial \ln f_B(M,T,P;W)}{\partial T} \end{aligned} \tag{89}$$

For the pure species characterized by M, we have

$$\begin{aligned} h_B^*(M,T,P) &= \mu_B^*(M,T,P) + Ts_B^*(M,T,P) \\ &= \mu_{B,O}^*(M,T,P) + Ts_{B,O}^*(M,T,P) \end{aligned} \tag{90}$$

Molar Volume *v*

$$\begin{aligned} v(T,P;W) &= \frac{V(T,P;w)}{n_B} = \frac{\partial g(T,P;W)}{\partial P} \\ &= \int_M W(M) v_B(M,T,P;W) dM \\ &= \int_M W(M) v_B^*(M,T,P) dM \\ &\quad + RT \int_M W(M) \frac{\partial \ln f_B(M,T,P;W)}{\partial P} dM \end{aligned} \tag{91}$$

For the partial molar volume $v_B(M)$, we obtain the relations

$$\begin{aligned} v_B(M,T,P;W) &= \frac{\partial V(T,P;w)}{\partial n_M} = \frac{\partial \mu_B(M,T,P;W)}{\partial P} \\ &= v_B^*(M,T,P) + RT \frac{\partial \ln f_B(M,T,P;W)}{\partial P} \end{aligned} \tag{92}$$

For the pure species characterized by M, we obtain

$$v_B^*(M,T,P) = \frac{\partial \mu_B^*(M,T,P)}{\partial P} = \frac{\mu_{B,O}^*(M,T,P)}{\partial P} \tag{93}$$

Starting with the equations presented, the changes upon mixing, the corresponding excess quantities, and further thermodynamic properties may easily be calculated.

MOLAR EXCESS GIBBS ENERGY AND ACTIVITY COEFFICIENTS

The thermodynamic excess quantities are defined as the excess with respect to the ideal mixture. Thus we obtain in the case of molar Gibbs energy g, from Eqs. 79–82,

$$\begin{aligned} g^E(T,P;W) &= g(T,P;W) - g^{\text{id}}(T,P;W) \\ &= RT \int_M W(M) \ln f_B(M,T,P;W) dM \end{aligned} \tag{94}$$

$$\begin{aligned} RT \ln f_B(M,T,P;W) &= g^E(T,P;W) \\ &\quad - \int_{M'} W(M') \left(\frac{\partial g^E(T,P;W)}{\partial X_{M'}} \right)_{[M]} dM'; \end{aligned} \tag{95}$$

$$\int_{M''} W(M'') \left(\frac{\partial \ln f_B(M'',T,P;W)}{\partial X_M} \right)_{[M']} dM'' = 0 \tag{96}$$

Eq. 94 permits the calculation of g^E from $\ln f_B(M)$ and Eq. 95 the calculation of $\ln f_B(M)$ from g^E. Equation 96 is the Gibbs-Duhem equation, to be obeyed by $\ln f_B(M'')$, where M and M' may be chosen arbitrarily.

According to the equations presented in the last section, the problem of mixtures is reduced to knowledge of $\ln f_B(M)$ or g^E. Empirical relations or relations based on statistical thermodynamics may be used. We give three examples.

(Generalized) Porter's Relation

$$g^E = RT \int_{M'} \int_{M''} A(M',M'') W(M') W(M'') dM' dM'' \tag{97}$$

$A(M',M'')$ is a function which obeys

$$A(M',M'') = A(M'',M'); \qquad A(M',M') = 0 \tag{98}$$

It is chosen to give best fit of the experimental data and may additionally depend on T and P. From Eq. 95, we have

$$\begin{aligned} \ln f_B(M) = \int_{M'} \int_{M''} &[2A(M,M'') \\ &- A(M', M'')] W(M') W(M'') dM' dM'' \end{aligned} \tag{99}$$

Flory-Huggins Relation

$$g^E = RT \int_{M'} W(M') \ln \frac{r(M')}{\bar{r}(W)} dM' \tag{100}$$

Here, a number $r(M)$ of segments is assigned to each chemical species characterized by M. For homopolymers we may choose M to be the number of segments, and then $r = M$. Alternately, we may choose M to be the molar mass and have $r = M/M_S$, where M_S means the molar mass of one segment. $\bar{r}(W)$ is the mean value of $r(M)$

$$\bar{r}(W) = \int_{M'} W(M') r(M') dM' \tag{101}$$

According to Eq. 95, $\ln f_B(M)$ is given by

$$\ln f_B(M) = \ln \frac{r(M)}{\bar{r}(W)} + 1 - \frac{r(M)}{\bar{r}(W)} \tag{102}$$

In this case, g^E does not depend on P and $\ln f_B(M)$ not on T and P

NRTL Equation

The continuous version of the NRTL equation reads

$$g^E = RT \int_{M'} W(M') \times \frac{\int_{M''} W(M'')\tau(M'',M')G(M'',M')dM''}{\int_{M'''} W(M''')G(M''',M')dM'''} dM' \quad (103)$$

Here

$$\tau(M',M'') = [g(M',M'') - g(M'',M'')]/RT$$
$$G(M',M'') = \exp[-\alpha(M',M'')\tau(M',M'')] \quad (104)$$

with

$$g(M',M'') = g(M'',M'); \quad \alpha(M',M'') = \alpha(M'',M') \quad (105)$$

resulting in

$$\tau(M',M') = 0; \quad G(M',M') = 1 \quad (106)$$

Instead of the parameters τ_{12}, τ_{21} and α_{12} for a binary system, the functions $\tau(M',M'')[\neq \tau(M'',M')]$ and $\alpha(M',M'')$ are used. According to Eq. 95, we obtain

$$\ln f_B(M) = \frac{\int_{M'} W(M')\tau(M',M)G(M',M)dM'}{\int_{M''} W(M'')G(M'',M)dM''} + \int_{M'''} W(M''')G(M,M''') \frac{\tau(M,M''') \int_{M''} W(M'')G(M'',M''')dM'' - \int_{M'} W(M')\tau(M',M''')G(M',M''')dM'}{\left(\int_{M''} W(M'')\, G(M'',M''')dM''\right)^2} dM''' \quad (107)$$

Continuous versions of the other relations for g^E and the activity coefficients used in thermodynamics of mixtures may be written in a similar way.

PHASE EQUILIBRIA

For simplicity, we consider an isolated system without chemical reactions containing two phases ′ and ″. The balance equations for internal energy U, volume V and amount of substance read

$$\delta U' + \delta U'' = 0$$
$$\delta V'' + \delta V'' = 0$$
$$\delta w'(M) + \delta w''(M) = 0; \quad M \in [M_a, M_b] \quad (108)$$

The last equation applies to that M interval $[M_a, M_b]$ corresponding to chemical species which are present in the system and for which the exchange between the phases is not impossible in principle; e.g., on account of a membrane. According to Eqs. 62 and 108, the entropy increase δS of the system, which equals the entropy production in this case, is given by

$$\delta S = \delta S' + \delta S'' = \left(\frac{1}{T'} - \frac{1}{T''}\right)\delta U' + \left(\frac{P'}{T'} - \frac{P''}{T''}\right)\delta V' - \int_{M_a}^{M_b} \left(\frac{\mu'_B(M)}{T'} - \frac{\mu''_B(M)}{T''}\right)\delta w'(M)dM \geqq 0 \quad (109)$$

At equilibrium, the equality sign applies and (considering $\delta U', \delta V'$ and $\delta w'(M)$ as virtual changes, arbitrarily chosen) we obtain

$$T' = T''$$
$$P' = P'' \quad (110)$$
$$\mu'_B(M) = \mu''_B(M); \quad M \in [M_a, M_b].$$

Whereas in conventional thermodynamics phase equilibrium is expressed by as many equations for the chemical potentials as there are components, we obtain in continuous thermodynamics only one equation, valid for the total interval of the occurring values of the characterizing variable M.

VAPOR-LIQUID EQUILIBRIUM

The most important application of continuous thermodynamics deals with vapor-liquid equilibrium, especially for petroleum fractions and coal-derived liquids. Such mixtures may be characterized by their true boiling point (TBP) curves in which the mixture is distilled using a column with a large number of theoretical plates and a high reflux ratio. Thus, the assumption is that each component of the mixture distills at the same temperature τ as if it were a pure component. The TBP curve is the plot of the temperature at the top of the column, which is assumed to equal τ, against the amount distilled φ_B^{dist}, Figure 4a. Because of the incomplete resolution of the TBP-distillation and of the very large number of components, we obtain a continuous curve instead of the discontinuous step curve theoretically expected.

For vapor-liquid equilibrium of petroleum fractions or of similar liquids, it is convenient to choose the boiling point temperature τ as a characterizing variable. Thus, we have to substitute τ for M

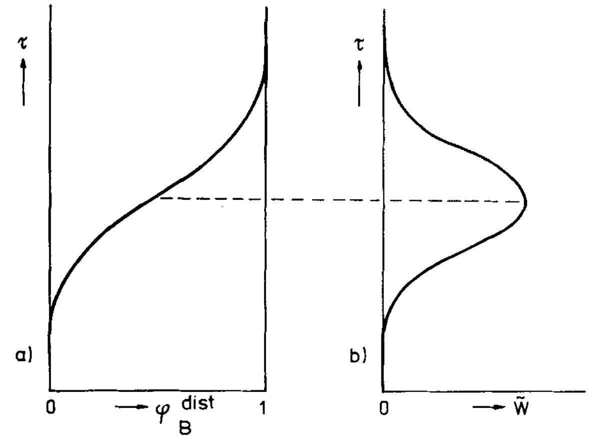

Figure 4. (a) Typical true boiling point curve. (b) Intensive distribution function $W(\tau)$ obtained by differentiation with respect to τ.

in the preceding equations. The true boiling point curve is an integral distribution function related to τ where a point of this curve represents the amount of those species of the ensemble B with boiling point temperatures less than the τ value of the point considered. Thus, the differential distribution function used within the framework of continuous thermodynamics is obtained by differentiation with respect to τ, Figure 4b. The resulting distribution function has been symbolized by $\tilde{W}(\tau)$ instead of $W(\tau)$ as φ_B^{dist} usually is measured by volume or mass instead of amount of substance. Thus, a corresponding transformation must be included to obtain $W(\tau)$.

Starting with Eq. 110, we obtain by analogous arguments as in conventional thermodynamics assuming ideal-gas behavior and neglecting the Poynting correction

$$PW^G(\tau) = W^L(\tau)f_B^L(\tau,T,P;W^L)P^*(\tau,T); \quad \tau \in [\tau_a,\tau_b] \tag{111}$$

Here G indicates the gaseous phase (vapor) and L the liquid phase. $P^*(\tau,T)$ is the vapor pressure of the pure species characterized by τ at the system temperature T.

In the most simple case we may assume the liquid phase to be ideal ($f_B^L = 1$). Then Eq. 111 reduces to the continuous version of Raoult's law:

$$PW^G(\tau) = W^L(\tau)P^*(\tau,T). \tag{112}$$

Integrating with respect to τ, we obtain the relation for the total pressure

$$P = \int_{\tau'} W^L(\tau')P^*(\tau',T)d\tau' \tag{113}$$

Here $W^G(\tau)$ cancels according to the normalization condition, Eq. 9. We use this equation to eliminate P in Eq. 112:

$$W^G(\tau) = \frac{W^L(\tau)P^*(\tau,T)}{\int_{\tau'} W^L(\tau')P^*(\tau',T)d\tau'} \tag{114}$$

Using Eqs. 113 and 114 we may calculate the equilibrium pressure P and the distribution function $W^G(\tau)$ in the gaseous phase if we know the distribution function $W^L(\tau)$ in the liquid phase.

Let us consider the verification of these equations in a special case. The vapor pressure of the pure species will be given by the relation

$$P^*(\tau,T) = P^+ \exp[A(1 - \tau/T)]; \quad P^+ = 101.325 \text{ kPa} \quad A = \Delta_L^G S/R \approx 10.4 \tag{115}$$

which results from the Clausius-Clapeyron equation and from Trouton's rule for the vaporization entropy $\Delta_L^G S$. The distribution function in the liquid phase will be a Gaussian function characterized by the abscissa of the maximum θ^L and the standard deviation σ^L:

$$W^L(\tau) = \frac{1}{\sqrt{2\pi}\sigma^L} \exp\left[-\frac{(\tau - \theta^L)^2}{2\sigma^{L2}}\right] \tag{116}$$

In this case, the integration may be performed exactly using $-\infty$ and ∞ as integration limits, as we may assume the Gaussian function to be roughly equal to zero out of the actual interval $[\tau_a,\tau_b]$. The result reads

$$P = P^+ \exp\left[A(1 - \theta^L/T) + \sigma^{L2}A^2/2T^2\right] \tag{117}$$

$$W^G(\tau) = \frac{1}{\sqrt{2\pi}\sigma^G} \exp\left[-\frac{(\tau - \theta^G)^2}{2\sigma^{G2}}\right] \tag{118}$$

$$\sigma^G = \sigma^L; \quad \theta^G = \theta^L - \frac{\sigma^{L2}A}{T} \tag{119}$$

The total pressure is given by a very simple closed formula and the distribution function in the gaseous phase proves to be a Gaussian function too, with the same standard deviation $\sigma^G = \sigma^L$ and a mean θ^G easily calculated according to Eq. 119.

This example demonstrates an essential advantage of continuous thermodynamics in comparison with the usual discontinuous treatment. The chemical species are characterized by a continuous variable and thus it is possible to differentiate, to integrate, and to expand into a series with respect to this variable. Hence, closed formulas may be obtained in many cases whereas discontinuous theory yields sums which must be calculated numerically.

DISTILLATION

If we wish to treat distillation, the mass balance must be accounted for. For simplicity, let us consider one theoretical plate only (flash distillation). In unit time, the amount of substance n_B [with the intensive distribution function $W(\tau)$] will be flashed and the amounts of substance n_B^L and n_B^G [with the intensive distribution functions $W^L(\tau)$ and $W^G(\tau)$] in the liquid and the gaseous state, respectively, will be removed. The mass balance reads, using the extensive distribution functions,

$$w(\tau) = w^L(\tau) + w^G(\tau) \tag{120}$$

which, according to Eq. 2, results in

$$n_B = n_B^L + n_B^G. \tag{121}$$

Introducing the degree of vaporization,

$$\phi = \frac{n_B^G}{n_B^G + n_B^L} \tag{122}$$

we obtain the balance equation for the intensive distribution functions

$$W(\tau) = (1 - \phi)W^L(\tau) + \phi W^G(\tau) \tag{123}$$

Applying the Gaussian functions, Eqs. 116 and 118, for $W^L(\tau)$ and $W^G(\tau)$, we see that $W(\tau)$ is not also a Gaussian function. But, if σ is not too large, we may approximate the resulting sum by a Gaussian function (with the parameters θ and σ) using equality of extremum coordinates. In this way, we obtain, in the first approximation, from Eqs. 117, 119, and 123

$$\sigma^L = \sigma^G = \sigma \tag{124}$$

$$\theta = (1 - \phi)\theta^L + \phi\theta^G \tag{125}$$

$$\theta^L = \theta + \phi\frac{\sigma^2A}{T} \tag{126}$$

$$\theta^G = \theta - (1 - \phi)\frac{\sigma^2A}{T} \tag{127}$$

$$P = P^+ \exp\left[A\left(1 - \frac{\theta}{T}\right) - \left(\phi - \frac{1}{2}\right)\left(\frac{\sigma A}{T}\right)^2\right] \tag{128}$$

Based upon the previous assumptions, these equations permit the calculation of the distribution function parameters θ^L and σ^L within the liquid phase, and of the distribution function parameters θ^G and σ^G within the gaseous phase, from the corresponding parameters θ and σ within the feed and from the degree of vaporization ϕ. Within the approximation applied, the standard deviations of all three phases are the same. The extremum coordinates θ^L and θ^G increase linearly with increasing degree of vaporization ϕ from the unique existence of the liquid phase ($\phi \to 0$, $\theta^L \to \theta$, $\theta^G \to \theta - \sigma^2A/T$) until the unique existence of the gaseous phase ($\phi \to 1$, $\theta^L \to \theta + \sigma^2A/T$, $\theta^G \to \theta$).

The vapor pressure P decreases exponentially with increasing ϕ at constant T. (With increasing degree of vaporization, the liquid mixture becomes leaner with respect to the more volatile species.) Considering a distillation, the pressure P is constant and we obtain from Eq. 128, by rearranging,

$$\phi = \frac{1}{2} - \frac{\theta}{A\sigma^2} T + \frac{1}{A\sigma^2}\left(1 - \frac{1}{A} \ln \frac{P}{P+}\right) T^2 \qquad (129)$$

Equation 129 is the relation between the degree of vaporization ϕ and the equlibrium temperature T at the specified pressure; i.e., Eq. 129 is the equation describing the equilibrium flash vaporization (EFV) curve for the simplest case. For distillation problems of petroleum and petroleum fractions, this curve is very important. Usually, it is obtained with the help of nomograms based on the special properties of some oils. For mixtures differing in composition, their application is questionable. Continuous thermodynamics permits a calculation without using such nomograms.

The general and more detailed treatment of vapor-liquid equilibria and distillation problems by continuous thermodynamics is the subject of another paper that we are preparing.

FINAL REMARKS

The transition from the usual thermodynamic formulas to the formulas of continuous theory often may be performed simply in the following manner

$$\varphi_i \Rightarrow \varphi(M); \quad \varphi_i \text{ arbitrary} \neq n_i, X_i \qquad (130)$$

$$n_i = w_{\text{dis}}(M_i)\Delta M_i \Rightarrow w(M)\Delta M(M) \qquad (131)$$

$$\sum_{i=1}^{\omega} n_i\varphi_i = \sum_{i=1}^{\omega} w_{\text{dis}}(M_i)\varphi_i\Delta M_i \Rightarrow \int_M w(M)\varphi(M)dM \qquad (132)$$

The intensive versions of Eqs. 131 and 132 read

$$X_i \Rightarrow W(M)\Delta M(M) \qquad (133)$$

$$\sum_{i=1}^{\omega} X_i\varphi_i \Rightarrow \int_M W(M)\varphi(M)dM \qquad (134)$$

This paper shows that the formulas obtained in this way are not simply approximations for the special case but part of the consistent building of continuous thermodynamics.

The treatment presented here may be extended in the following respects:

- There may be an additional component A differing essentially from the chemical species of B. This component has then to be accounted for in the usual discontinuous way. The conditions of phase equilibrium read

$$\mu'_A = \mu''_A$$

$$\mu'_B(M) = \mu''_B(M); \quad M \in [M_a, M_b] \qquad (135)$$

which, in the case of a liquid-liquid equilibrium, result in

$$X'_A f_A(T,P;X'_B W'_B) = X''_A f_A(T,P;X''_B W''_B)$$

$$X'_B W'_B(M) f_B(M,T,P;X'_B W'_B) = X''_B W''_B(M) f_B(M,T,P;X''_B W''_B); \quad M \in [M_a, M_b] \qquad (136)$$

Here X_A and X_B are the mole fractions of component A and the total of all species of B. The phase index has been neglected at f_A and f_B, as we assume f_A and f_B to be the same function or functional of the quantities specifed within both phases. Equation 136 permits, for instance, a concise treatment of the fractionation process of polymers.

- There may be a second ensemble of mutually very similar chemical species differing essentially from the species of the first one. Each ensemble of similar components may then be treated continuously, but the two ensembles have to be treated discontinuously. The aliphatic and the aromatic hydrocarbons within petroleum fractions, for instance, may be managed in this way separately. Another example of application is the problem of polymer compatibility within polymer blends and composites.
- For polymers, we can use distribution functions widely used in polymer chemistry.
- Similar chemical species may be characterized by two or more variables. The molecules of a copolymer for instance may be described by the numbers of the different monomer units. Then, the distribution functions depend on the corresponding number of variables.

NOTATION

A = function in generalized Porter relation
A = Trouton's constant
D = differential at T,P = constant
F = Helmholtz energy
f_A, f_B = activity coefficient
G = Gibbs energy
G = function in NRTL equation
g = molar Gibbs energy
g = function in NRTL equation
H = enthalpy
h = molar enthalpy
h_B = partial molar enthalpy
k = degree of homogeneity
M = variable characterizing the similar chemical species
M_a, M_b = limits of appearing M values
M_O = constant value of ΔM_i or $\Delta M(M)$
M_i^+, M_i^- = limits of interval i
ΔM = increase of M
ΔM_i = length of interval i
$\Delta M(M)$ = continuous version of ΔM_i
n = amount of substance
n_B = total amount of substance of all species belonging to B
P = pressure
P^+ = reference pressure (101.325 kPa)
R = gas constant
r = number of segments
S = entropy
s = molar entropy
s_B = partial molar entropy
$s^*_{B,O}$ = quantity defined by Eq. 86
T = temperature
t = mathematical variable
U = internal energy
V = volume
v = molar volume
v_B = partial molar volume
W = intensive distribution function
$\Delta W, \Delta\hat{W}$ = increase of W
w = extensive distribution function
$\Delta w, \Delta\hat{w}$ = increase of w
X = mole fraction
Z = extensive quantity (general)
z = molar quantity (general)
z_B = partial molar quantity (general)

Greek Letters

α = function in NRTL equation
δ = Dirac's function
δ = differential (instead of d)

ζ = thermodynamic quantity (general)

θ = parameter of Gaussian function

μ_A, μ_B = chemical potential

$\mu^*_{B,O}$ = quantity defined by Eq. 74

σ = parameter of Gaussian function

τ = function in NRTL equation

τ = (normal) boiling point

ϕ = degree of vaporization

φ = general quantity

Superscripts

E = excess

G = gas

id = ideal

L = liquid

$*$ = pure component

$', ''$ = phase $'$ and $''$

Subscripts

A,B = component A, species of B

cont = continuous

dis = discontinuous

$i,j = 1, \ldots \omega$ = species really occurring

$[M']$ = differentiation on account of point M'

mix = change at mixing

Special Terms

continuous = A continuous variable—e.g., M—may assume all values within a given interval:
$M_a \leq M < M_b$.

discontinuous = A discontinuous variable—e.g., i—may assume discrete values only:
$i = 1,2, \ldots \omega$.

excess = An excess quantity is the difference between the (extensive, molar, partial molar) quantity considered within a real mixture and within the same mixture if it were ideal. For a molar quantity:
$z^E(T,P,X) = z(T,P,X) - z^{id}(T,P,X)$.

extensive = Within half of a homogeneous system an extensive quantity has a half-value only (e.g., total amount of substance, amount of substance of a component, volume, internal energy, enthalpy, entropy, Helmholtz energy, Gibbs energy).

intensive = Within half of a homogeneous system an intensive quantity has the same value as that within the total system (e.g., temperature, pressure, chemical potential, mole fraction, molar quantities, partial molar quantities).

molar = A molar quantity z is the quotient of the corresponding extensive quantity Z of the phase and its total amount of substance:

$$z = Z \Big/ \sum_i n_i.$$

partial molar = A partial molar quantity z_{B_i} is the partial derivative of the corresponding extensive quantity Z of the phase with respect to the amount of substance n_i of the species B_i, keeping temperatures, pressure and the amounts of substance of all other species constant:

$$z_{B_i} = \frac{\partial Z}{\partial n_i}.$$

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