

Continuous thermodynamics

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Abstract - 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 identifying the components by a discontinuous index, a continuous identification variable is used such as the boiling-point temperature. This permits to differentiate, to integrate, or to develop a power series with respect to this variable. These operations are impossible for a discontinuous index. To demonstrate, continuous thermodynamics is applied to flash calculations of petroleum fractions described by a True Boiling Point (TBP) curve, to the liquid-liquid equilibrium and to the fractionation process of polymer solutions described by the well-known molar mass distribution.

INTRODUCTION

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 occur in many industrial mixtures, for example, in petroleum, in petroleum fractions, in coal-derived liquids, in polymers, or in vegetable oils. 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 multicomponent mixtures or poly-disperse mixtures. Instead of the mole fractions of individual components, continuous distribution functions are applied for describing the composition.

Using such continuous distribution functions involves an inconsistency with the usual thermodynamics based on mole fractions of individual components. Until now, two possibilities have been 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 these 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 pseudocomponents or key components are arbitrary.

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

FUNDAMENTALS

An ensemble B of a large number of similar chemical species is considered and the species are assumed to be identified sufficiently by the value of one variable z in such a way that two species distinguished by small differen-

ces of τ also differ in small amounts of the thermodynamic properties. This variable is chosen to be the (normal) boiling-point temperature of the pure species. But other quantities, such as molar mass or segment number, may be used likewise.

The extensive distribution function $w(\tau)$ for the ensemble B is defined by equating the integral

$$\int_{\tau'}^{\tau''} w(\tau) d\tau \quad (1)$$

to the amount of all species with τ -values between τ' and τ'' . Then, the overall amount of substance n_B is given by

$$n_B = \int_{\tau} w(\tau) d\tau ; \quad \int_{\tau} = \int_{\tau_0}^{\tau^0} . \quad (2)$$

The integration has to be performed for the total domain of τ between the limits of the occurring τ -values, τ_0 and τ^0 . Dividing $w(\tau)$ by n_B , the intensive distribution function $W(\tau)$, corresponding to the mole fractions in usual thermodynamics, is obtained:

$$W(\tau) = \frac{w(\tau)}{n_B} ; \quad \int_{\tau} W(\tau) d\tau = 1. \quad (3a, b)$$

Petroleum fractions and similar complex mixtures can be characterized by their True Boiling Point (TBP) curves which may be determined experimentally by distillation using a column with a large number of theoretical plates and by applying a high reflux ratio. Therefore, the temperature at the top of the column is identified with the boiling-point temperature τ of the corresponding pure species. The distribution function $W(\tau)$ is obtained by differentiation with respect to τ .

There is also the possibility to determine the TBP-curves by gaschromatographic simulation. If an indifferent stationary phase is used, the gas chromatographic separation is effected according to the vapor pressures which, for similar substances, are clearly related to the boiling-point temperatures. Thus, the gas chromatogram may be calibrated with respect to the boiling-point temperatures. By applying flame ionisation detection (FID), the area below the gas chromatogram proves to be proportional to mass.

In usual thermodynamics an arbitrary extensive quantity z (e.g. volume, enthalpy, Gibbs free energy) of a phase may be considered as a function of temperature T , pressure P and the amounts of substances n_1, \dots, n_c :

$$z = z_{dis}(T, P, n_1, \dots, n_c) . \quad (4)$$

In the continuous case the extensive distribution function $w(\tau)$ occurs, instead of n_1, \dots, n_c (refs 1-3):

$$z = z(T, P; w) . \quad (5)$$

In continuous thermodynamics, z is a function with respect to T and P , but a functional with respect to w . A functional is a mapping assigning a number to each function of a given class of functions. An example is the definite integral with fixed limits: the integral value is assigned to each function occurring as integrand. Here, a value z is assigned to each function $w(\tau)$ (at given values of T, P). This value z depends on the total course of the function w but not on its argument τ . (The quantity τ always passes through the total definition range.) Hence, in Eq. (5) w is written and not $w(\tau)$. The different kinds of variables, usual variables (such as T, P), being called for distinction variable scalars, and variable functions are separated by a semicolon. As an example, the volume v of an ideal mixture is considered

$$v = \int_{\tau} w(\tau) V_B^*(\tau) d\tau ; \quad v = \sum_{i=1}^c n_i V_{B_i}^* . \quad (6a, b)$$

Here, $V_B^*(\tau)$ is the molar volume of the pure species of the ensemble B identified by the boiling-point temperature τ . The function $V_{B_i}^*(\tau)$ is

obtained by interpolating the V_B^* -values of real discrete species. To compare, Eq. (6b) shows an analogous relation in traditional thermodynamics. The most important differences are:

- In continuous thermodynamics the species are identified by a continuous variable τ instead of a discrete index i .
- The composition is described by a continuous distribution function $w(\tau)$ instead of the amounts of substances n_1, \dots, n_C .
- The thermodynamic quantities (here v) are functionals of the distribution function $w(\tau)$, instead of functions of the amounts of substances n_1, \dots, n_C .

To perform thermodynamic considerations, the starting point is the relation for the chemical potential. In traditional thermodynamics the well-known relation reads

$$\mu_i = \mu_i^*(T, P) + RT \ln X_i + RT \ln \gamma_i ; \quad (7)$$

μ_i^* is the chemical potential of the pure chemical species i . The second term on the right hand side describes an ideal mixture and the last term accounts for deviations from such a mixture. For this reason, the activity coefficient γ_i is introduced where $\gamma_i = 1$ for $X_i = 1$.

The corresponding relation in continuous thermodynamics reads

$$\mu(\tau) = \mu_0^*(\tau, T, P) + RT \ln W(\tau) + RT \ln \gamma(\tau) \quad (8)$$

Once the chemical potential is known, all other thermodynamic equilibrium properties may be calculated by means of the well-known thermodynamic relations. Since the chemical potential equals the partial molar Gibbs free energy, the molar Gibbs free energy G itself reads

$$\begin{aligned} G(T, P; W) &= \int_{\tau} W(\tau) \mu(\tau, T, P; W) d\tau \quad (9) \\ &= \int_{\tau} W(\tau) \mu_0^*(\tau, T, P) d\tau + RT \int_{\tau} W(\tau) \ln W(\tau) d\tau + RT \int_{\tau} W(\tau) \ln \gamma(\tau) d\tau. \end{aligned}$$

The molar excess Gibbs free energy G^E equals the third term on the right hand side of this relation. Other thermodynamic quantities may be obtained in the usual manner. Thus, the molar entropy S , the molar enthalpy H , and the molar volume V may be calculated by

$$S = -\partial G / \partial T; \quad H = G + TS; \quad V = \partial G / \partial P \quad (10)$$

VAPOR-LIQUID EQUILIBRIUM

Regarding the vapor-liquid equilibrium the most important problem is that of flash calculations. A feed phase F splits into a liquid phase L and a gaseous phase G . Temperature, pressure and feed distribution are specified; the distributions and relative amounts of the outlet streams are to be calculated. The feed and outlet streams are related through material balances; the two outlet streams are assumed to be in thermodynamic equilibrium.

The material balances read in continuous thermodynamics (refs. 4,5)

$$w^F(\tau) = w^L(\tau) + w^G(\tau) \quad (11)$$

applying the extensive distribution functions. Whereas in usual thermodynamics the material balances are expressed by as many equations as components that are present or as pseudo-components that are postulated, in continuous thermodynamics only one equation is obtained, valid for the total interval of the occurring values of the identification variable τ . Hence, in continuous thermodynamics the material balance is a function equation, i.e. an equation permitting the determination of an unknown function.

According to Eq. (2) integration results in

$$n_B^F = n_B^L + n_B^G \quad (12)$$

The degree of vaporization ϕ is defined as the quotient of the amount of substance in the gaseous phase n_B^G , divided by the amount of substance n_B^F in

the feed phase

$$\phi = n_B^G / n_B^F \quad (13)$$

On combining these equations and introducing the intensive distribution functions $W(\tau)$, the material balance reads

$$W^F(\tau) = (1 - \phi) W^L(\tau) + \phi W^G(\tau). \quad (14)$$

In continuous thermodynamics the phase equilibrium condition reads

$$\mu^G(\tau) = \mu^L(\tau) \quad (15)$$

The chemical potentials must be equal for all occurring species. Like the mass balance, the phase equilibrium relationship applies to the total range of the occurring τ -values. Hence, it is also a function equation. On applying the expression for the chemical potential shown above and a similar relation for the vapor phase, the phase equilibrium condition results in (refs. 4,5)

$$PW^G(\tau) \varphi(\tau) = W^L(\tau) \gamma(\tau) P^*(\tau, T) \varphi^*(\tau). \quad (16)$$

Here, P is the equilibrium pressure, $W^G(\tau)$ and $W^L(\tau)$ are the intensive distribution functions in the gaseous and the liquid phase, respectively, and $\gamma(\tau)$ is the activity coefficient in the liquid phase. $P^*(\tau, T)$ is the vapor pressure of the pure chemical species identified by τ at the system temperature T . The quantity $\varphi(\tau)$ is the fugacity coefficient of this species in the mixture, and $\varphi^*(\tau)$ designates its fugacity coefficient as pure gaseous phase. In Eq. (16) the Poynting correction is neglected. This relation is the continuous version of the well-known discrete relation for the vapor-liquid equilibrium. It also applies to the total occurring τ -interval, i.e. it is a function equation.

If the phases are assumed to behave ideally, then $\gamma(\tau) = 1$, $\varphi(\tau) = 1$, $\varphi^*(\tau) = 1$ and the relation simplifies to the continuous version of Raoult's law reading

$$PW^G(\tau) = W^L(\tau) P^*(\tau, T). \quad (17)$$

To treat the flash problem the material balance and the phase equilibrium relationship are to be combined. Both equations are valid for all τ -values of the given τ -interval. They permit the calculation of the unknown distribution functions $W^L(\tau)$ and $W^G(\tau)$ from $W^F(\tau)$. On rearranging, they result in

$$W^L(\tau) = \frac{P}{(1 - \phi)P + \gamma(\tau) P^*(\tau, T) \varphi^*(\tau) / \varphi(\tau)} W^F(\tau) \quad (18)$$

$$W^G(\tau) = \frac{\gamma(\tau) P^*(\tau, T) \varphi^*(\tau) / \varphi(\tau)}{(1 - \phi)P + \gamma(\tau) P^*(\tau, T) \varphi^*(\tau) / \varphi(\tau)} W^F(\tau). \quad (19)$$

Since both distribution functions are normalized to one, integration and subtraction results in the so-called flash equation

$$0 = \int_{\tau} \frac{P - \gamma(\tau) P^*(\tau, T) \varphi^*(\tau) / \varphi(\tau)}{(1 - \phi)P + \gamma(\tau) P^*(\tau, T) \varphi^*(\tau) / \varphi(\tau)} W^F(\tau) d\tau. \quad (20)$$

As pointed out above, the distributions of the coexisting phases, $W^L(\tau)$ and $W^G(\tau)$, and the relative amount of the gaseous phase, ϕ , are to be calculated from these three equations. Since $\gamma(\tau)$ depends on $W^L(\tau)$ and $\varphi(\tau)$ depends on $W^G(\tau)$, the unknown distribution functions and ϕ , the unknown scalar, are combined in a complicated way. However, in many cases considered in practice, $\gamma(\tau)$ depends on $W^L(\tau)$ by means of a functional and, analogously, $\varphi(\tau)$ depends on $W^G(\tau)$ by means of a functional. In this case, the problem of the unknown distribution functions may be separated and solved exactly.

To show this, $\gamma(\tau)$ is assumed to be calculated by the Flory-Huggins relation

$$\ln \gamma(\tau) = \ln \frac{r(\tau)}{\bar{r}} + 1 - \frac{r(\tau)}{\bar{r}}; \quad \bar{r} = \int_{\tau} r(\tau) W^L(\tau) d\tau. \quad (21a, b)$$

Here, all molecules are imagined to be divided into segments, and $r(\tau)$ is the number of segments of the species identified by τ . The quantity \bar{r} is the (number) average segment number of the liquid phase. It is this quantity \bar{r} which provides the dependence of $\gamma(\tau)$ on $W^L(\tau)$ and, hence, the coupling of the function equation for $W^L(\tau)$ and the scalar equation for ϕ . However, the quantity \bar{r} is a functional of $W^L(\tau)$. This means that it is a scalar itself, but depends on the total course of the function $W^L(\tau)$. Thus, it is possible to consider \bar{r} as an additional scalar unknown and its defining equation as an additional scalar equation. This equation contains $W^L(\tau)$. But $W^L(\tau)$ may be replaced by Eq. (18), where now on the right hand side $W^L(\tau)$ does not occur but only the two unknown scalars ϕ and \bar{r} .

Hence, in this way, Eq. (18) gives $W^L(\tau)$ in an exact and explicit form. The two scalar unknowns ϕ and \bar{r} are to be calculated from two scalar equations: the flash relation, Eq. (20), and the relation for \bar{r} , Eq. (21b), replacing $W^L(\tau)$ as discussed. Thus, in this case the flash problem needs only the calculation of these two equations by numerical methods. Then $W^L(\tau)$ is given explicitly.

This possibility of separation of the distribution function problem is always met if the dependence of $\gamma(\tau)$ on $W^L(\tau)$ has the form of a functional. Furthermore, if $\varphi(\tau)$ depends on $W^G(\tau)$ also by means of a functional, then again analogous arguments apply.

Hence, in the considered case which is often met, the distribution functions $W^L(\tau)$ and $W^G(\tau)$ are given by simple explicit and exact relations. Only a small number of scalar equations is to be solved by numerical methods: the flash equation and one equation for each occurring functional.

In the simplest version of continuous thermodynamics presented above all chemical species occurring are considered as similar. Thus, they all are described by one distribution function. In a more refined version the presence of several ensembles of very similar species in the mixture may be accounted for describing each ensemble by its own distribution function. In this way, for example, the aromatic, naphthenic and paraffinic hydrocarbons in a petroleum fraction may be treated separately. Furthermore, some individual components may additionally be present. They can also be included into the formalism. Such an individual component can be a solvent for the selective extraction of aromatics or for extractive distillation. In the refined version the UNIFAC-model provides a convenient method to account for the real behavior of the liquid phase.

LIQUID-LIQUID EQUILIBRIUM

Here, the most important problem is that of the liquid-liquid equilibrium in polymer solutions and polymer mixtures. Examples are the high-pressure synthesis of low density polyethylene (during the synthesis the polyethylene is formed as solute in supercritical polyethylene and then the pressure is lowered leading to the equilibrium of a polymer-lean and a polymer-rich phase), the polymer-polymer compatibility and the problem of polymer fractionation.

Considering polymers, the molar mass distribution function is well-known from polymer characterization. In the framework of continuous thermodynamics it is applied directly to calculate phase equilibria. To show the principles, a solution of a solvent A and a polydisperse polymer B is considered. The individual species of the polymer B are identified by their segment numbers r . The segment number r is defined as the ratio of the hard core volume of the species considered and of the hard core volume of an arbitrarily chosen standard segment. The essence of continuous thermodynamics consists of considering r as a continuously variable quantity. The composition of the polymer is described by the distribution function

$W(r)$ defined by the statement that $W(r) dr$ gives the relative segment fraction of all polymer species with segment numbers between r and $r + dr$. If r_0 is the lowest and r^0 the largest occurring segment number of polymer molecules, the normalization relation reads

$$\int W(r) dr = 1; \quad \int = \int_{r_0}^{r^0}. \quad (22)$$

In continuous thermodynamics, the condition for equilibrium between two phases ' and '' as expressed by the chemical potentials writes (refs. 6-8)

$$\mu'_A = \mu''_A, \quad (23)$$

$$\mu'_B(r) = \mu''_B(r). \quad (24)$$

The last relation is valid for all occurring segment numbers from r_0 to r^0 . In comparison to traditional thermodynamics the continuous identification variable r occurs, instead of a discrete identification index.

To treat phase equilibria the starting point is formed by the relations for the chemical potential. In discrete thermodynamics convenient equations for polymer solutions read

$$\mu_A = \mu_A^* + RT \left[\ln(1 - \psi) + 1 - \frac{r_A}{\bar{r}} \right] + r_A RT \ln \bar{\gamma}_A, \quad (25)$$

$$\mu_{B_i} = \mu_{B_i}^* + RT \left[\ln \psi_{B_i} + 1 - \frac{r_{B_i}}{\bar{r}} \right] + r_{B_i} RT \ln \bar{\gamma}_{B_i} \quad (26)$$

Here, the first term is the chemical potential of the pure species. The second term is the well-known Flory-Huggins contribution; ψ_{B_i} signifies

the segment fraction of the species i of the polymer B, and ψ is the overall segment fraction of the polymer B:

$$\psi = \psi_B = \sum_i \psi_{B_i} \quad (27)$$

r_A and r_{B_i} are the segment numbers of the species indicated, and \bar{r} is the number average segment number taken with respect to all species present in the mixture. The third term describes the deviation from a Flory-Huggins mixture. It generalizes the classical χ -term. For this end, the segmentmolar activity coefficients $\bar{\gamma}_A$ and $\bar{\gamma}_{B_i}$ are introduced.

In the continuous treatment the relation for μ_A is not changed. However, the chemical potential for the polymer species now reads

$$\mu_B(r) = \mu_{B,0}^*(r) + RT \left[\ln \psi W(r) + 1 - \frac{r}{\bar{r}} \right] + r RT \ln \bar{\gamma}_B(r) \quad (28)$$

The species are identified by the continuous variable r instead of the discrete index i and the composition is described by the continuous distribution function $W(r)$ instead of the segment fractions of the discrete species.

Application of these relations for the chemical potentials to the phase equilibrium condition for the liquid-liquid equilibrium results in

$$1 - \psi'' = (1 - \psi') \exp r_A \varphi_A \quad (29)$$

$$\psi'' W''(r) = \psi' W'(r) \exp r \varphi_B(r) \quad (30)$$

with

$$\varphi_A = \frac{1}{\bar{r}''} - \frac{1}{\bar{r}'} + \ln \bar{\gamma}_A' - \ln \bar{\gamma}_A'' \quad (31)$$

$$\varphi_B(r) = \frac{1}{\bar{r}''} - \frac{1}{\bar{r}'} + \ln \bar{\gamma}_B'(r) - \ln \bar{\gamma}_B''(r) \quad (32)$$

In phase separation experiments a feed phase F is split into two coexisting phases ' and ''. If ϕ is the total amount of segments (solvent + polymer) in phase '' divided by the total amount of segments (solvent + polymer) in the feed, the mass balance for the polymer species in continuous thermodynamics reads

$$\psi^F W^F(r) = (1 - \phi) \psi' W'(r) + \phi \psi'' W''(r), \quad (33)$$

and, after integration,

$$\psi^F = (1 - \phi) \psi' + \phi \psi''. \quad (34)$$

For the total number average segment number \bar{r} which in continuous thermodynamics is given by

$$\frac{1}{\bar{r}} = \frac{1 - \psi}{\bar{r}_A} + \frac{\psi}{\bar{r}_B}; \quad \frac{1}{\bar{r}_B} = \int \frac{W(r)}{r} dr \quad (35)$$

the mass balance relationships lead to

$$\frac{1}{\bar{r}^F} = \frac{1 - \phi}{\bar{r}'} + \frac{\phi}{\bar{r}''} \quad (36)$$

In phase separation experiments the composition of the feed (i.e. ψ^F and $W^F(r)$) is usually known. The relations between the quantities referring to phase ' and those referring to phase '' are provided by Eqs. (33), (34), and (36). They permit to eliminate in the phase equilibrium relationships the quantities referring to one of the two existing phases, e.g. the quantities referring to phase '. On doing so, the phase equilibrium relationships read

$$1 - \psi'' = \frac{1 - \psi^F}{\phi + (1 - \phi) \exp[-r_A \varphi_A]}, \quad (37)$$

$$\psi'' W''(r) = \frac{\psi^F W^F(r)}{\phi + (1 - \phi) \exp[-r \varphi_B(r)]}. \quad (38)$$

When applying these relations, one has to keep in mind that, in the general case, $\varphi_B(r)$ depends on $W''(r)$ via the segmentmolar activity coefficients $\bar{\gamma}_A$ and $\bar{\gamma}_B(r)$. The equations for these quantities may be obtained from the relation for the excess segmentmolar Gibbs energy \bar{G}^E . In the general case, the excess segmentmolar Gibbs energy depends on T , ψ and on the distribution function $W(r)$ (considering the pressure to be constant). But in many relations used in practice the dependence on $W(r)$ is neglected as an approximation. Then also the segmentmolar activity coefficients do not depend on $W(r)$ and, furthermore, $\bar{\gamma}_B$ does not depend on the identification variable r .

Then φ_B also does not depend on r and depends on $W''(r)$ only by means of \bar{r}'' . But, as shown above, this quantity is a functional of $W''(r)$, i.e. a scalar. Considering this scalar as an additional unknown of the problem, the second equation provides a direct and explicit relation to calculate $W''(r)$ from the feed distribution $W^F(r)$.

Of course, this relation contains the unknowns of the problem, ψ'' , \bar{r}'' and ϕ (or T); but these quantities are simply unknown scalars and not unknown functions. Hence, it proves possible to separate in this way the problem of the unknown distribution functions from the problem of the scalar unknowns and to solve the function problem exactly. A simple example for this possibility is provided by Huggins' χ -parameter concept ($r_A = 1$)

$$\bar{G}^E = \chi \psi (1 - \psi); \quad \chi = \chi(T) \quad (39)$$

$$\ln \bar{\gamma}_A = \chi \psi^2; \quad \ln \bar{\gamma}_B = \chi (1 - \psi)^2 \quad (40a, b)$$

The dependence of the excess segmentmolar Gibbs energy \bar{G}^E on the distribution function is often important, and then this dependence may not be neglected. Therefore, the question is how to proceed in this case. The inspection of the corresponding relations shows that this dependence usually is provided by the occurrence of further functionals (e.g. moments) of the distribution function. This means that also in this case the separation is possible and that the exact solution of the distribution function problem is again provided by Eqs. (37), (38). The only difference is that, in addition to ψ'' , \bar{r}'' and ϕ (or T), the mentioned functionals occur as further unknown scalars of the problem. In the following, for the sake simplicity, such additional unknowns are assumed not to occur. However, the generalization to more general cases is straight forward.

To generalize the treatment for a series of successive phase equilibria, i.e. for polymer fractionation (refs. 9-16), the introduction of the precipitation rate K is convenient. In the continuous case K is a continuous function of r defined as the quotient of the amounts of segments of all polymer species with segment numbers between r and $r + dr$ in phase " and in the feed phase F , respectively:

$$K(r) = \phi \frac{\psi'' w''(r) dr}{\psi^F w^F(r) dr} = \phi \frac{\psi'' w''(r)}{\psi^F w^F(r)}. \quad (41)$$

Combination with Eq. (38) leads to

$$K(r) = \frac{\phi}{\phi + (1 - \phi) \exp[-r \rho_B(r)]}. \quad (42)$$

The introduction of the precipitation rate $K(r)$ permits to write the relations between the distribution functions $w'(r)$ and $w''(r)$ in the coexisting phases and the distribution function $w^F(r)$ of the feed polymer in a simple form

$$\psi' w'(r) = \frac{1 - K(r)}{1 - \phi} \psi^F w^F(r), \quad (43)$$

$$\psi'' w''(r) = \frac{K(r)}{\phi} \psi^F w^F(r). \quad (44)$$

As discussed above, these relations provide directly the unknown distribution functions $w'(r)$ and $w''(r)$. The scalar unknowns of the problem are ψ'' , \bar{r}'' and ϕ (or T). They may be calculated from the relations

$$1 - \psi'' = \frac{1 - \psi^F}{\phi + (1 - \phi) \exp[-r_A \rho_A]}, \quad (45)$$

$$\psi'' = \int \frac{K(r)}{\phi} \psi^F w^F(r) dr, \quad (46)$$

$$\frac{1}{\bar{r}''} = \frac{1 - \psi^F}{r_A} + \int \frac{1}{r} \frac{K(r)}{\phi} \psi^F w^F(r) dr. \quad (47)$$

The first relation results from the phase equilibrium condition for the solvent A. The second equation results from the phase equilibrium condition for the polymer, Eq. (44), by integration. And the last equation results from the definition of \bar{r} , Eq. (35), as applied to phase " .

As examples the two basic fractionation procedures, the successive precipitation fractionation (SPF) and the successive solution fractionation (SSF) will be considered (Fig. 1). In both cases a homogeneous polymer solution called feed phase F splits by lowering the temperature into two coexisting phases, a polymer-lean phase ' and a polymer-rich phase " which are separated. In SPF the polymer is isolated from phase " as fraction 1. Phase ' forms directly the feed phase for the next fractionation step etc.

In the case of SSF the polymer fraction 1 is obtained from phase ' . Phase " is diluted by adding solvent up to the volume of the original feed phase corresponding, to a very good approximation, to the same total amount of segments. This phase is used as feed phase for step 2 etc.

In the last fractionation step the polymer of phase ' in the case of SPF, and of phase " in the case of SSF forms the final fraction. All coexisting

pairs of phases ' and '' are presumed to be in equilibrium. Hence, it is possible to apply the equations discussed above. To indicate the different separation steps 1,2,... the corresponding number, in general i or j, is added as subscript.

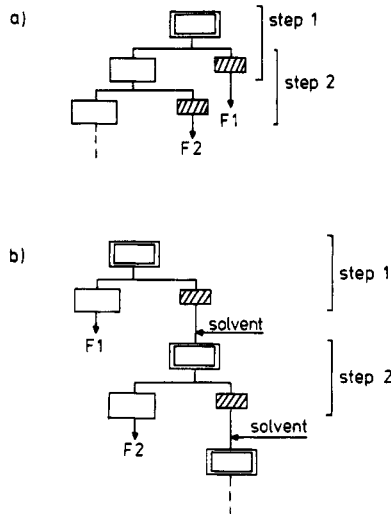


Fig. 1. Fractionation schemes: a) successive precipitation fractionation, b) successive solution fractionation. original feed or phases with equal volume, polymer-lean phase ('), polymer-rich phase ('').

In SPF phase ' from step i is used directly as feed phase for step (i + 1). Hence, the following relations are valid:

$$\psi_{i+1}^F = \psi_i' \tag{48}$$

$$W_{i+1}^F(r) = W_i'(r) \tag{49}$$

$$\bar{r}_{i+1}^F = \bar{r}_i' \tag{50}$$

On adding the subscript i Eqs. (43), (44) read

$$\psi_i' W_i'(r) = \frac{1 - K_i(r)}{1 - \phi_i} \psi_i^F W_i^F(r) \tag{51}$$

$$\psi_i'' W_i''(r) = \frac{K_i(r)}{\phi_i} \psi_i^F W_i^F(r) \tag{52}$$

Hence, successive substitution according to the fractionation scheme results in

$$\psi_i'' W_i''(r) = \frac{K_i(r)}{\phi_i} \prod_{j=1}^{i-1} \frac{1 - K_j(r)}{1 - \phi_j} \psi_1^F W_1^F(r) \tag{53}$$

This equation enables the direct and explicit calculation of the distribution of the polymer fraction i, $W_i''(r)$, to be made from the distribution function $W_1^F(r)$ of the original polymer. The structure of this relation corresponds to the fractionation scheme applied. In steps $j = 1, \dots, i-1$ the polymer-lean phase ' is taken corresponding to the occurrence of the factor $(1 - K_j(r))/(1 - \phi_j)$ for $j = 1, \dots, i-1$. In step i the polymer-rich phase '' is taken corresponding to the factor $K_i(r)/\phi_i$.

To perform the calculation the composition of the original polymer solu-

tion, i.e. ψ_1^F and $W_1^F(r)$, must be given. Furthermore, the equation contains the unknowns ψ_j , \bar{r}_j'' and ϕ_j (or T_j) for all steps $j = 1, \dots, i$. These quantities are to be calculated successively, i.e. at first for $j = 1$, then for $j = 2$ etc., from the set of three relations, Eqs. (45) - (48), where the feed distribution of each step may be expressed by the feed distribution of the first step, $W_1^F(r)$, on the basis of the above equations.

According to the remarks made above, in SSF the total number of segments is the same in all feed phases to a very good approximation. This leads to the relation

$$\psi_{i+1}^F W_{i+1}^F(r) = \phi_i \psi_i'' W_i''(r) \quad (54)$$

On combining this relations with the LLE equations for the distribution functions the distribution function of the i -th polymer fraction $W_i'(r)$ is given in direct and explicit form by the relation

$$\psi_i' W_i'(r) = \frac{1 - K_i(r)}{1 - \phi_i(r)} \prod_{j=1}^{i-1} K_j(r) \psi_1^F W_1^F(r) \quad (55)$$

Again, this relation corresponds to the fractionation scheme. In steps $j = 1, \dots, i-1$ the polymer-rich phase '' is taken corresponding to the occurrence of the factor $K_j(r)$ for $j = 1, \dots, i-1$. The denominator ϕ is absent due to the occurrence of ϕ in the relation resulting from the fractionation scheme. In step i the polymer-lean phase ' is taken corresponding to the factor $(1 - K_i(r))/(1 - \phi_i)$. The unknown quantities are ψ_j'' , \bar{r}_j'' , and ϕ_j (or T_j) for $j = 1, \dots, i$. They can be calculated successively with the help of Eqs. (45) - (47), where again the feed distribution of each step may be expressed by the feed distribution of the first step. Again, these relations are to be solved numerically for each step.

It can be seen from the treatment that a very important advantage of continuous thermodynamics in considering polymer fractionation consists in providing exact and explicit formulas for the distribution functions of all fractions. Only a relatively small number of equations is to be solved numerically. The traditional pseudocomponent method leads only to the segment fractions of the arbitrarily chosen pseudocomponents.

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