HANDBOOK OF

POLYMER SOLUTION THERMODYNAMICS

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PREFACE

In 1988 the Design Institute for Physical Property Data of the American Institute of Chemical Engineers established Project 881 to develop a **Handbook of Polymer Solution Thermodynamics**. In the area of polymer solutions, the stated purposes were: (1) provide an evaluated depository of data, (2) evaluate and extend current models for polymers in both organic and aqueous solvents, (3) develop improved models, and (4) provide a standard source of these results in a computer data bank and a how-to handbook with accompanying computer software. During the four years of this project most of these objectives have been met and the results are presented in this **Handbook**.

There are a number of individuals who deserve special recognition for their contributions to this project. Dave Geveke wrote the liquid-liquid equilibria portions of the text and created the LLE data bases. Vipul Parekh wrote the sections on the PVT behavior of pure polymers and developed the pure component polymer data base. Manoj Nagvekar, Vitaly Brandt, and Dave Geveke developed the computer programs. Gary Barone almost single handedly generated the extensive VLE data bases. The help of our undergraduate scholars, John T. Auerbach, Brian Lingafelt, Keith D. Mayer, and Kyle G. Smith, was extremely valuable. Technical advice and the basic Chen et al. equation of state program were generously provided by Professor Aage Fredenslund of the Technical University of Denmark. Finally, we wish to acknowledge the dedicated service of our secretary, Cheryl L. Sharpe.

Throughout the project the Penn State staff was assisted and guided by members of the Project Steering Committee. These individuals provided technical advice, critical analysis of the model evaluations and computer programs, additional data references, moral support, and, of course, financial support. Without their generous contributions of time and resources this **Handbook** would not have become a reality.

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Chapter 1

INTRODUCTION

A. OBJECTIVES OF THE HANDBOOK OF POLYMER SOLUTION THERMODYNAMICS

Design and research engineers working with polymers need up-to-date, easy-to-use methods to obtain specific volumes of pure polymers and phase equilibrium data for polymer-solvent solutions. Calculations involving phase equilibria behavior are required in the design and operation of many polymer processes such as polymerization, devolatilization, drying, extrusion, and heat exchange. In addition, there are many product applications requiring this type of information: e.g., miscibility predictions in polymer alloys, solvent evaporation from coatings and packaging materials, substrate compatibility with adhesives, and use of polymers in electronics and prostheses. This **Handbook of Polymer Solution Thermodynamics** contains data bases, prediction methods, and correlation methods to aid the engineer in accurately describing these processes and applications. This **Handbook** provides the necessary background information, the most accurate prediction and correlation techniques, comprehensive data bases, and a software package for DOS based personal computers to implement the recommended models and access the data bases.

Generally the preferred data source is experimental measurement. Only in rare cases are prediction methods able to give more accurate estimates than a carefully executed experiment. Therefore, one of the major objectives of this **Handbook** is to provide comprehensive data bases for the phase equilibria of polymer-solvent systems and pressure-volume-temperature behavior of pure polymers. Thus, data have been compiled from extensive literature searches. These data cover a wide range of polymers, solvents, temperatures, and pressures. The data have been converted into consistent units and tabulated in a common format. Methods of evaluating and formatting these data banks have been established by the DIPPR Steering Committee for Project 881 and the Project Investigators.

No matter how broad the scope of the experimental data is, there will always be a need for data that have not yet been measured or that are too expensive to measure. Another objective of this **Handbook** is to provide accurate, predictive techniques. Predictive techniques not only furnish a source of missing experimental data, they also aid in the understanding of the physical nature of the systems of interest. The most useful predictive methods require as input data only the structure of the molecules or other data that are easily calculated or have been measured. Many of the methods present in this **Handbook** are based on the concept of group contributions which use as input only the structure of the molecules in terms of their functional groups or which use group contributions and readily

available pure component data. In some cases the users of the **Handbook** will need to correlate existing data with the hope of extending the correlation to conditions not available in the original existing data. Several correlative methods of this type are included.

The current state-of-the-art is such that there are no reliable methods of predicting liquid-liquid equilibria of polymer-solvent systems. Thus, the recommended procedures and computer programs included in this **Handbook** treat only vapor-liquid equilibrium. A discussion of the correlation of LLE data is included in Chapter 2.

Chapter 2 is an in depth discussion of the various theories important to phase equilibria in general and polymer thermodynamics specifically. First a review of phase equilibria is provided followed by more specific discussions of the thermodynamic models that are important to polymer solution thermodynamics. The chapter concludes with an analysis of the behavior of liquid-liquid systems and how their phase equilibrium can be correlated.

Chapter 3 contains the recommended predictive and correlative procedures for the specific volume of pure polymer liquids and the calculation of the vapor liquid equilibria of polymer solutions. These methods have been tested and evaluated with the data bases included in this **Handbook**.

Chapter 4 describes the polymer data bases. This chapter is organized into sections discussing the experimental methods available for measuring the thermodynamic data of polymer solutions with an overview of the advantages and disadvantages of each method. The next section, Data Reduction Methods, describes how the experimental measurements from these experiments can be used to calculate the activity coefficients that are necessary for phase equilibria calculations. Finally, a summary of all the systems that are available on the data diskettes is provided. A user can scan this section or use the computer program POLYDATA to find if data are available for a particular system.

The **Computer Programs** section, Chapter 5, describes the two primary computer programs on the diskettes accompanying this **Handbook**. POLYPROG is a program which implements the recommended procedures of Chapter 3. POLYDATA provides an easy method of accessing the data contained in the many data bases. Chapter 6, contains the Appendices. The sections included are Glossary of Terms, Standard Polymer Abbreviations, Nomenclature, Units and Conversion Factors, and References.

Chapter 2

FUNDAMENTALS OF POLYMER SOLUTION THERMODYNAMICS

A. PURE POLYMER PVT BEHAVIOR

Density (or specific volume) is an essential physical property required either directly in the design of polymer processing operations or as an input parameter to obtain various other design variables. In injection molding and extrusion processes, the design is based on theoretical shrinkage calculations. Since these operations are carried out at high pressures, compressibility and thermal expansion coefficients are required over wide regions of pressure, volume, and temperature. The PVT behavior can also be coupled with calorimetric data to calculate the enthalpy and entropy of the polymers in high pressure operations. Since these operations are accompanied by high power requirements, accurate estimates of enthalpies are critical for an energy-efficient design (Isacescu et al., 1971).

Figure 2A-1 shows the dilatometric behavior typically observed in polymers. The melt region corresponds to temperatures above the melting temperature, T_m, for a semi-crystalline polymer and to temperatures above the glass transition temperature, T_g, for an amorphous polymer. The correlation presented in this **Handbook** is only for the equilibrium melt region. Correlations of the PVT behavior of some polymers in the glassy region are given by Zoller (1989). If one wishes to estimate a specific volume of a polymer *in a solution* below T_g or T_m, however, it may be better to extrapolate the liquid behavior. Extensive testing of this hypothesis has not been done.

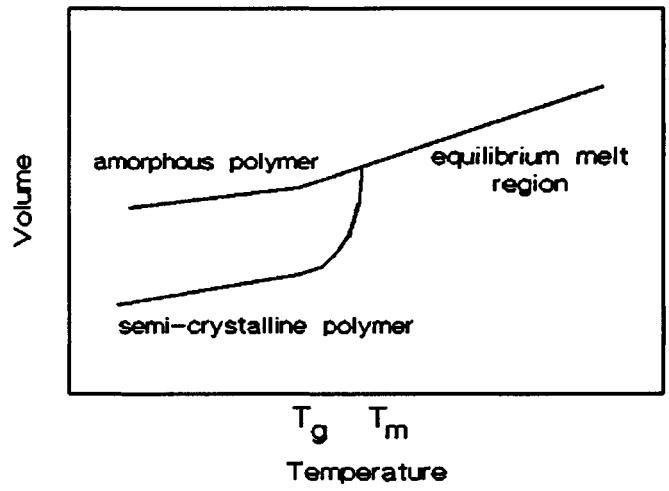

Figure 2A-1. Dilatometric Behavior of Polymers.

The experimental technique used to measure the PVT data is based on the Bridgemann bellows method (Bridgemann, 1964). The polymer sample is sealed with a confining liquid, usually mercury, in a cylindrical metal bellows flexible at one end. The volume change of the sample and the confining liquid with changes in the applied pressure and temperature is obtained from the measurement of the change in length of the bellows. The actual volume of the sample is then calculated using the known PVT properties of the confining liquid. The

accuracy of the apparatus is estimated to be around 0.001 cm^3/g which corresponds to approximately 0.1% for polymer specific volumes. A detailed description of this technique is given by Zoller et al. (1976).

Often empirical models or correlative equations of state are used to describe the PVT behavior of polymers (Zoller, 1989). Such correlations are useful in the interpolation and extrapolation of data to the conditions of interest. When an equation of state based on statistical mechanical theory is used to correlate the data, the resulting equation parameters can also be used in mixing rules to determine the properties of polymer solutions.

A number of models have been developed and applied for the correlation of polymer PVT behavior. One of the first was the purely empirical Tait equation (1888). This equation, originally developed to describe the compressibility of ordinary liquids, has been shown to work well for a wide variety of liquids ranging from water to long-chain hydrocarbon compounds (Nanda and Simha, 1964). This approach has also been successfully applied to polymers (Zoller, 1989). In developing the recommended PVT correlation for this **Handbook** several variations of the Tait correlation, the Flory equation of state (Flory et al., 1964), the Simha-Somcynsky equation of state (Simha and Somcynsky, 1969), and the Sanchez-Lacombe equation of state (Sanchez and Lacombe, 1976) were evaluated. The Tait form given in Section 3B yielded errors which were generally an order of magnitude lower than that found with the other models. In almost all cases, the average error with the Tait model was found to be within the reported experimental error - approximately 0.1% (Zoller et al., 1976).

The High-Danner equation of state given in Section 3E can be used to predict the specific volume of polymers. Parekh (1991) has modified some of the reference volumes in the model to improve the model's accuracy for pure polymer volumes. The deviations in these predictions are generally less than 2%. Additional work needs to be done to establish the reliability and to extend the applicability of the method.

B. PHASE EQUILIBRIA THERMODYNAMICS

The design engineer dealing with polymer solutions must determine if a multicomponent mixture will separate into two or more phases and what the equilibrium compositions of these phases will be. Prausnitz et al. (1986) provides an excellent introduction to the field of phase equilibrium thermodynamics.

The primary criterion for equilibrium between two multicomponent phases is that the chemical potential of each component, μ_i, must be equal in both phases I and II.

$$\mu_i^I = \mu_i^{II} \tag{2B-1}$$

The phases in the system must be in thermal and mechanical equilibrium as well.

$$T_i^I = T_i^{II} \tag{2B-2}$$

$$P_i^I = P_i^{II} \tag{2B-3}$$

In some cases, the chemical potential is not a convenient quantity to calculate for engineering purposes. The fugacity of component i , f_i, is defined in terms of the chemical potential, μ_i, by the expression

$$f_i = RT \ln \mu_i \tag{2B-4}$$

Thus, for Equation (2B-1) to be satisfied, the fugacities of component i must be equal in both phases.

$$f_i^I = f_i^{II} \tag{2B-5}$$

Two methods can be used to calculate the fugacities of a component in equilibrium. The first method requires an equation of state, which can be used with the following expression to calculate the fugacity coefficient.

$$\ln \phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln Z \tag{2B-6}$$

The fugacity is related to the fugacity coefficient by

$$f_i = \phi_i P y_i \tag{2B-7}$$

Here ϕ_i is the fugacity coefficient of component i, P is the pressure, and y_i is the mole fraction of component i. Fugacity coefficients are usually used only for the vapor phase, so y_i is usually meant to represent the mole fraction of component i in the vapor phase and x_i is usually reserved to represent the mole fraction in the liquid phase. Equation (2B-6) can be used with any equation of state to calculate the fugacity of the components in the mixture in any phase as long as the equation of state is accurate for the conditions and phases of interest. An equation of state that is explicit in pressure is required to use Equation (2B-6).

If the equation of state is valid for both phases, then Equation (2B-6) can be applied to calculate the fugacity in both phases. The isochemical potential expression, Equation (2B-1), reduces to

$$\phi_i^I x_i^I = \phi_i^{II} x_i^{II} \tag{2B-8}$$

where x_i^I is the mole fraction of component i in phase I and x_i^{II} is the mole fraction in phase II. In this terminology x_i represents a mole fraction in any phase which could be liquid or vapor. The major difficulty in using Equation (2B-8) is finding an equation of state that is accurate for both the liquid phase and the vapor phase.

The second approach to phase equilibria is to relate the fugacity of a component in the liquid phase to some standard state fugacity and then calculate the deviation from this

standard state. The fugacity in the liquid phase, f_i^L, is calculated from the activity coefficient of component i, γ_i, and the standard state fugacity, f_i°, using the expression

$$f_i^L = \gamma_i x_i f_i^\circ \tag{2B-9}$$

The fugacity of component i in the vapor phase is calculated with an equation of state as in the first case using Equation (2B-7). In this case the isochemical potential expression becomes

$$\phi_i^V y_i P = \gamma_i x_i f_i^\circ \tag{2B-10}$$

Many times the virial equation truncated after the second virial coefficient is used in place of a more complicated equation of state to calculate the fugacity of the components in the vapor phase.

In the case of liquid-liquid equilibria the activity coefficient expression is usually used to calculate the fugacity in both of the liquid phases

$$\gamma_i^I x_i^I f_i^{\circ I} = \gamma_i^{II} x_i^{II} f_i^{\circ II} \tag{2B-11}$$

If the standard state in both phases is the same, then Equation (2B-11) becomes

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \tag{2B-12}$$

All of the expressions described above are exact and can be applied to small non-polar molecules, small polar molecules, non-polar polymers, cross-linked polymers, polyelectrolytes, etc. The difficulty is finding correct and accurate equations of state and activity coefficient models. Many accurate activity coefficient models have been developed to correlate existing activity coefficient data of small molecules or to predict activity coefficients given only the structure of the molecules of interest or other easily accessible data (Danner and Daubert, 1989).

During the past ten years, the chemical process industry has seen an increase in the accuracy and range of applicability of equations of state. Equations of state are becoming a more popular choice for computing and predicting phase equilibria. Most of the research on activity coefficients and equations of state, however, has focused on low molecular weight systems. Relative to small molecules, polymers and polymer solutions are essentially unexplored.

C. MODELING APPROACHES TO POLYMER SOLUTION THERMODYNAMICS

All of the models developed for predicting and correlating the properties of polymer solutions can be classified into two categories: lattice models or van der Waals models. These two approaches can be used to derive activity coefficient models or equations of state. Activity coefficient models are not functions of volume and therefore are not dependent on

the pressure of the fluid. On the other hand, equations of state are functions of volume, and pressure does influence the results.

In both the lattice models and the van der Waals models, the behavior of the molecules is described as the sum of two contributions. The first contribution assumes that there are no energetic interactions between the molecules; only the size and shape of the molecules need to be considered for this part. This is the contribution that would be predominant at very high temperatures where the kinetic energy of the molecules would be large compared to any interaction energies between the molecules. This interaction-free contribution is generally called the combinatorial or the athermal term. In the case of the van der Waals model, it is frequently referred to as the free volume term.

In lattice models each molecule (or segment of a molecule in the case of polymers) is assumed to occupy a cell in the lattice. The arrangement of the molecules or segments is assumed to depend upon only the composition and the size and shape of the molecules. In this case, the combinatorial (athermal) contribution is calculated from the number of arrangements statistically possible in the lattice. This contribution is also referred to as the entropic term.

In the van der Waals model the volume in which the molecules can translate is determined by the total volume of the system less the volume occupied by the molecules. Thus, the term "free volume." In this part of the treatment of the system intermolecular attractions are not taken into account, so this free volume term is the combinatorial (athermal) contribution.

The second contribution in either the lattice or the van der Waals model is that originating from intermolecular attractions. This contribution is commonly referred to as the attractive energy term, the residual term, or the potential energy term. It is also known as the enthalpic contribution since the differences in interaction energies are directly responsible for the heats of mixing. This contribution is calculated by a product of a characteristic energy of interaction per contact and the number of contacts in the system. Van der Waals models use a similar expression for the interaction energy.

In some of the more sophisticated models, the concept of local compositions is used to improve the results. Since the combinatorial contribution is calculated without regard to the interactions between molecules, it leads to a random arrangement of the molecules. In reality, the arrangement of molecules in a pure component or a mixture is affected by the interactions. The concept of local compositions is used to correct the combinatorial contribution for the nonrandomness that results from these interactions. Local composition expressions are a function of the interaction energies between molecules and result in a correction to the combinatorial called the nonrandom combinatorial. There are several theories available to calculate the local composition and the nonrandom combinatorial, but the most widely used theory is Guggenheim's (1952) quasichemical theory. This terminology is used because of the similarity between the equations in Guggenheim's theory and the relationship between the chemical equilibrium constant and the Gibbs energy in chemical reaction equilibria. The major difficulty with using local compositions in activity coefficient models and equations of state is that the resulting models and calculations are usually quite complex. The increased accuracy and more general applicability of the equations, however, is usually worth the increased computational cost.

D. LATTICE MODELS

1. Flory-Huggins Model

Flory (1941) and Huggins (1941, 1942a,b,c) independently developed a theory of polymer solutions that has been the foundation of most of the subsequent developments over the past fifty years. In their work, the polymer-solvent system was modeled as a lattice structure. The combinatorial contributions to the thermodynamic mixing functions were calculated from the number of ways the polymer and solvent molecules were arranged on the lattice sites. These combinatorial contributions correspond to the entropy of mixing. Implicit in the Flory-Huggins treatment of the combinatorial contributions is the assumption that the volume of mixing and the enthalpy of mixing are zero. The number of ways these molecules can be arranged leads to the well-known Flory-Huggins expression for the entropy of mixing in a polymer solution.

$$\frac{\Delta S}{k} = -N_1 \ln \phi_1 - N_2 \ln \phi_2 \tag{2D-1}$$

Here N_1 and N_2 are the number of solvent and polymer molecules, respectively, and the volume fractions ϕ_1 and ϕ_2 are defined by the expressions

$$\phi_1 = \frac{N_1}{N_1 + rN_2} \tag{2D-2}$$

$$\phi_2 = \frac{rN_2}{N_1 + rN_2} \tag{2D-3}$$

where r is the number of segments in the polymer chain. The activity of the solvent, a_1 is given by

$$\ln(a_1) = \ln(1-\phi_2) + \left[1 - \frac{1}{r}\right]\phi_2 \tag{2D-4}$$

Several improvements to Equation (2D-4) have been suggested. Primarily these modifications involve a more exact treatment of the polymer chain in the lattice such as including the probability of overlapping chains. These improvements are not generally applied in view of the approximations inherent in the lattice model of the fluid and the marginal increase in accuracy resulting from these improvements.

Flory (1942) noted that the combinatorial term is not sufficient to describe the thermodynamic properties of polymer-solvent systems. To correct for energetic effects, he suggested adding a residual term, a^{res}, to account for interactions between lattice sites.

$$\ln a_1 = \ln a_1^{comb} + \ln a_1^{res} \tag{2D-5}$$

The residual term suggested by Flory is

$$\ln a_1^{res} = \chi \phi_2^2 \tag{2D-6}$$

where χ has become known as the interaction parameter or the Flory-chi parameter. The critical value of χ for miscibility of a polymer in a solvent is approximately 0.5. For values of χ greater than 0.5 the polymer will not be soluble in the solvent, and for values of χ less than 0.5 the polymer will be soluble in the solvent.

The Flory-Huggins combinatorial term with the Flory χ residual term has been the cornerstone of polymer solution thermodynamics. It established that the major contribution to the excess Gibbs energy and, hence, the activity in polymer solutions, is entropic unlike the enthalpic effects that dominate small molecular systems. As pointed out by many authors, however, there are deficiencies with the Flory-Huggins model. The most serious of these is that the lattice model precludes volume changes when the polymer molecules are mixed with the solvent molecules. Since the total volume that can be occupied in the lattice is a fixed quantity and vacancies are not permitted, volume changes cannot affect the thermodynamic potential functions such as Gibbs energy, and the model exhibits no pressure dependency. Thus, the model is strictly applicable only to liquids which exhibit no volume change of mixing. Furthermore, as originally proposed, χ was independent of composition and temperature. In fact, χ often shows complex behavior as a function of both of these independent variables.

2. Solubility Parameters and the Flory-Huggins Model

Ideal solutions are defined as mixtures that have no volume or enthalpy changes upon mixing, but have an ideal entropy of mixing given by

$$\Delta S_m = R \sum x_i \ln x_i \tag{2D-7}$$

stated in another way, in an ideal solution the excess entropy, S^E, excess volume, V^E, and excess enthalpy, H^E, are all equal to zero.

Regular solutions are defined as those solutions that have zero excess volume and excess entropy changes, but a non-zero excess enthalpy. Polymer solutions are not regular solutions since mixing a polymer with a solvent leads to a non-zero excess entropy change. Therefore, the excess volume, entropy, and enthalpy are all non-zero for a polymer solution. Nevertheless, the concept of regular solutions and the related solubility parameter have been used to predict the thermodynamic properties of polymer solutions. The regular solution and solubility parameter concepts developed by Hildebrand and Scott (1949, 1962) provide a measure of the interaction energies between molecules. These interaction energies, quantified by the solubility parameter, can then be used to estimate the χ parameter for a polymer-solvent system. The solution properties of the solution are easily calculated once the χ parameter is known.

The solubility parameter, δ_i, is defined as the square root of the cohesive energy density. The cohesive energy density is the amount of energy per unit volume that keeps the fluid in the liquid state. An excellent approximation for the cohesive energy of a solvent, c_{ii}, is the heat of vaporization, which is the amount of energy that must be supplied to vaporize the fluid. The solubility parameter is calculated from

$$\delta_i = c_{ii}^{1/2} = \left(\frac{\Delta E_i^{vap}}{v_i} \right)^{1/2} \tag{2D-8}$$

The solubility parameter can be used to estimate the Flory interaction parameter, χ, via:

$$\chi = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \tag{2D-9}$$

where v_1 is the liquid molar volume of the solvent, and δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively.

As mentioned in the previous section a value of χ less than 0.5 indicates that the polymer will be soluble in the solvent. The smaller the value of χ the more soluble the polymer should be. Thus, from Equation (2D-9) it is clear that the closer in value the two solubility parameters are, the more compatible the components will be. When

$$\delta_1 = \delta_2 \tag{2D-10}$$

χ is zero and the optimum condition is obtained. Unfortunately, because of the assumptions in the models, the above criterium should be regarded only as a qualitative measure of miscibility.

Since the Flory interaction parameter, χ, was derived by considering only interaction energies between the molecules, it should not contain any entropic contributions and Equation (2D-9) should yield the correct value for the Flory-χ parameter. Unfortunately, χ contains not only enthalpic contributions from interaction energies, but also entropic contributions. The solubility parameter includes only interaction energies and by the definition of regular solutions does not include any excess entropy contributions. Blanks and Prausnitz (1964) point out that the Flory χ parameter is best calculated from

$$\chi = \chi_s + \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \tag{2D-11}$$

where the entropic contribution to the χ parameter, χ_s, is given by

$$\chi_s = \frac{1}{z} \tag{2D-12}$$

Here z is the coordination number of the lattice; i.e., the number of sites that are nearest neighbors to a central site in the lattice. Blanks and Prausnitz suggest a value of χ_s between 0.3 and 0.4 for best results.

There are many sources of data for the solubility parameters of solvents and polymers. Daubert and Danner (1990) have compiled accurate solubility parameters for over 1250 industrially important low molecular weight compounds. Barton (1983, 1990) has tabulated solubility parameters for most of the industrially important polymers.

Experimental methods for solubility parameters of polymers commonly involve observing the swelling of the polymer as solvent is added. After performing this experiment with a number of solvents with different solubility parameters, the solvent which leads to the greatest degree of swelling for the polymer is the best solvent for that polymer. Since a χ value of zero in Equation (2D-9) indicates the degree of solubility of a polymer in a solvent,

the solubility parameter of the polymer is approximately equal to the solubility parameter of the best solvent.

The problem remains of how to predict the solubility parameter of the polymer given only readily available information such as pure component properties or structure. Barton (1983, 1990) and van Krevelen (1990) have proposed group contribution methods that may be used, but these methods are extremely empirical and give qualitative results at best.

One of the major deficiencies with the solubility parameter concept is that only interaction energies arising from dispersive forces are involved in the definition of the cohesive energy density. Molecules that are polar or that hydrogen bond cannot be modeled with the Hildebrand-Scott solubility parameter. In order to improve the predictive results using the solubility parameter, Hansen (1969) proposed that the cohesive energy be divided into contributions due to dispersion forces, permanent dipole-permanent dipole forces, and hydrogen bonding forces. The overall solubility parameter is calculated from the contributions from these three types of interactions.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \text{(2D-13)}$$

Here δ_d, δ_p, and δ_h are the contributions to the solubility parameter from dispersive forces, dipole-dipole forces, and hydrogen bonding forces, respectively. Since the three forces can occur to varying degrees in different components and can be represented on a three dimensional diagram, this theory is termed the three-dimensional solubility parameter. Barton (1983, 1990) tabulates the contributions to the three dimensional solubility parameter for a variety of solvents and polymers.

Regular solution theory, the solubility parameter, and the three-dimensional solubility parameters are commonly used in the paints and coatings industry to predict the miscibility of pigments and solvents in polymers. In some applications quantitative predictions have been obtained. Generally, however, the results are only qualitative since entropic effects are not considered, and it is clear that entropic effects are extremely important in polymer solutions. Because of their limited usefulness, a method using solubility parameters is not given in this **Handbook**. Nevertheless, this approach is still of some use since solubility parameters are reported for a number of groups that are not treated by the more sophisticated models.

3. Modifications of the Flory-Huggins Model

The major simplifications involved in Equation (2D-4) are that it does not account for the probability of overlapping chains and the volume change upon mixing of the polymer and solvent. The volume change cannot be accounted for in a lattice model when all of the lattice sites are assumed to be filled. The probability that a lattice site is filled, however, can be calculated. Huggins (1941, 1942a,b,c) included in his calculations probabilities that a polymer molecule would encounter a filled lattice site. This led to a slightly different form for Equation (2D-4), but Flory (1970) states that the refinement probably is beyond the limits of reliability of the lattice model.

Wilson (1964) modified the Flory-Huggins theory to account for the local composition affects caused by the differences in intermolecular forces. From these considerations the following expressions for the activity coefficients are derived.

$$\ln(a_1) = \ln(x_1) - \ln(x_1+\Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \quad (2D\text{-}14)$$

$$\ln(a_2) = \ln(x_2) - \ln(x_2+\Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \quad (2D\text{-}15)$$

Although the Wilson activity coefficient model has proven to be useful for solutions of small molecules, it has seen very limited use for polymer solutions most likely because of its increased complexity relative to the Flory-Huggins equation.

The application of the Flory-Huggins model to liquid-liquid equilibria is discussed in Section 2F.

4. Sanchez-Lacombe Equation of State

Sanchez and Lacombe (1976) developed an equation of state for pure fluids that was later extended to mixtures (Lacombe and Sanchez, 1976). The Sanchez-Lacombe equation of state is based on hole theory and uses a random mixing expression for the attractive energy term. Random mixing means that the composition everywhere in the solution is equal to the overall composition, i.e., there are no local composition effects. Hole theory differs from the lattice model used in the Flory-Huggins theory because here the density of the mixture is allowed to vary by increasing the fraction of holes in the lattice. In the Flory-Huggins treatment every site is occupied by a solvent molecule or polymer segment. The Sanchez-Lacombe equation of state takes the form

$$\frac{\tilde{P}}{\tilde{T}} = \ln\frac{\tilde{v}}{\tilde{v}-1} - \frac{\left[1-\frac{1}{r}\right]}{\tilde{v}} - \frac{1}{\tilde{v}^2\tilde{T}} \quad (2D\text{-}16)$$

The reduced density, temperature, and pressure along with the characteristic temperature, pressure, and volume are calculated from the following relationships.

$$\tilde{T} = T/T^* \quad (2D\text{-}17)$$

$$T^* = \epsilon^*/k \quad (2C\text{-}18)$$

$$\tilde{P} = P/P^* \quad (2D\text{-}19)$$

$$P^* = \epsilon^*/v^* \quad (2D\text{-}20)$$

$$\tilde{v} = V/V^* = \frac{1}{\tilde{\rho}} \quad (2D\text{-}21)$$

$$V^* = Nrv^* \quad (2D\text{-}22)$$

where v^* is the close packed volume of a segment that comprises the molecule, and ϵ^* is the interaction energy of the lattice per site.

Costas et al. (1981) and Costas and Sanctuary (1981) reformulated the Sanchez-Lacombe equation of state so that the parameter r is not a regression parameter, but is actually the number of segments in the polymer molecule. In the original Sanchez-Lacombe treatment, r was regressed for several n-alkanes, and it was found that the r did not correspond to the carbon number of the alkanes. In addition, the Sanchez-Lacombe equation of state assumes an infinite coordination number. Costas et al. (1981) replaced the segment length r as an adjustable parameter with z. This modification involves the same number of adjustable parameters, but allows r to be physically significant. Thus, the model is more physically realistic, but there have been no definitive tests to determine whether this improves the correlative results from the model.

5. Panayiotou-Vera Equation of State

Panayiotou and Vera (1982) developed an equation of state based on lattice-hole theory which was similar to the Sanchez and Lacombe equation of state discussed above. The first major difference between the two theories is that in the Panayiotou-Vera theory the volume of a lattice site is arbitrarily fixed to be equal to 9.75×10^{-3} m^3 $kmol^{-1}$, while in the Sanchez-Lacombe theory the volume of a lattice site is a variable quantity regressed from experimental data. Fixing the volume of a lattice site eliminates the need for a mixing rule for lattice sites for mixtures. In addition, a fixed lattice volume eliminates the problem of having different lattice volumes for the mixture and for the pure components. Reasonable values of the volume of the lattice site do not significantly alter the accuracy of the resulting equation of state. The volume should be such that the smallest group of interest has roughly the same volume as the lattice site. Panayiotou and Vera (1982) chose the value 9.75×10^{-3} $m^3/kmol$, which accurately reproduced pressure-volume-temperature data for polyethylene.

The second major difference between the Panayiotou-Vera and the Sanchez-Lacombe theories is that Sanchez and Lacombe assumed that a random mixing combinatorial was sufficient to describe the fluid. Panayiotou and Vera developed equations for both pure components and mixtures that correct for nonrandom mixing arising from the interaction energies between molecules. The Panayiotou-Vera equation of state in reduced variables is

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{z}{2} \ln \frac{\tilde{v}_1 + (q_1/r_1) - 1}{\tilde{v}_1} - \frac{\theta_1^2}{\tilde{T}_1} \qquad \text{(2D-23)}$$

6. Kumar Equation of State

The Kumar equation of state (Kumar, 1986; Kumar et al., 1987) is a modification of the Panayiotou-Vera model that was developed to simplify the calculations for multicomponent mixtures. Since the Panayiotou-Vera equation is based on the lattice model with the quasichemical approach for the nonrandomness of the molecules in the mixture, the quasichemical expressions must be solved. For a binary system the quasichemical expressions reduce to one quadratic expression with one unknown, but the number of coupled

quadratic equations and unknowns increases dramatically as the number of components in the mixture increases. The Kumar modification to the Panayiotou and Vera equation of state involves computing a Taylor series expansion of the quasichemical expressions around the point where the interaction energies are zero; that is, the case of complete randomness. This operation produces an explicit result for the nonrandomness factors which can then be incorporated into the derivation of the equation of state and chemical potential expression. The resulting thermodynamic expressions are cumbersome, but rely only on easily programmed summations.

The advantages of the Kumar equation of state are purely computational. The resulting expressions are approximations to the Panayiotou-Vera equation of state that will reduce to the proper forms for random conditions. Kumar et al. (1987) state that the expressions in Panayiotou and Vera (1982) differ because of errors in the Panayiotou and Vera work. The Vera and Panayiotou expressions have been shown to be correct with the methods described by High (Chapter 5, 1990). Thus, the discrepancies between the Kumar equation of state and the Panayiotou and Vera equation of state must occur in the approximations due to the Taylor series expansion.

7. High-Danner Equation of State

High and Danner (1989, 1990) modified the Panayiotou-Vera equation of state by developing a group contribution approach for the determination of the molecular parameters. The basic equation of state from the Panayiotou-Vera model remains the same:

$$\frac{\tilde{P}_i}{\tilde{T}_i} = \ln \frac{\tilde{v}_i}{\tilde{v}_i - 1} + \frac{z}{2} \ln \frac{\tilde{v}_i + (q_i/r_i) - 1}{\tilde{v}_i} - \frac{\theta_i^2}{\tilde{T}_i} \qquad \text{(2D-24)}$$

As in the Panayiotou-Vera equation of state, the molecules are not assumed to randomly mix; the same nonrandom mixing expressions are used. In addition, as in the Panayiotou-Vera model, the volume of a lattice site is fixed and assumed to be 9.75×10^{-3} $m^3/kmol$.

The major difference between the High-Danner and the Panayiotou-Vera models is that the molecular parameters, ε_{ii} and v^*, are calculated from group contributions in the High-Danner approach. The Panayiotou-Vera formulation provide a correlation method: the molecular parameters must be determined from experimental data. The High-Danner model, however, is capable of predicting polymer-solvent equilibria given only the structure of the polymer and solvent molecules. The molecular interaction energy parameter, ε_{ij}, is calculated from group interaction energies, $e_{kk,T}$ and $e_{mm,T}$, using the expression:

$$\epsilon_{ij,T} = \sum_k \sum_m \theta_k^{(i)} \theta_m^{(j)} (e_{kk,T} e_{mm,T})^{1/2} \qquad \text{(2D-25)}$$

The surface area fractions of group k in component i, $\theta_k^{(i)}$, is calculated from the number of groups of type k in component i, $v_k^{(i)}$, and the surface area of group k, Q_k:

$$\theta_k^{(i)} = \frac{v_k^{(i)} Q_k}{\sum_m v_m^{(i)} Q_m} \tag{2D-26}$$

The molecular hard-core volume or reference volume, v^*, is calculated from the group references volumes, R_k, using the expression:

$$v_{i,T}^* = a_T + \sum_k v_k^{(i)} R_k \tag{2D-27}$$

The molecular interaction energy and reference volume are a function of temperature. Group contribution values are available for these parameters at 300 and 400 K and a simple linear interpolation is performed to find the molecular parameters at the temperature of interest.

Group contributions for the interaction energy, $e_{kk,T}$, the surface area, Q_k, and the reference volume, R_k, for the High-Danner model have been calculated for the alkanes, alkenes, cycloalkanes, aromatics, esters, alcohols, ethers, water, ketones, aromatic ketones, amines, siloxanes, and monochloroalkanes. If solvents and polymers of interest contain these building blocks, the thermodynamic properties can be calculated. More detailed information concerning the High-Danner equation of state is given in Procedure 3E.

8. Oishi-Prausnitz Activity Coefficient Model

Oishi and Prausnitz (1978) modified the highly successful UNIFAC (UNIversal Functional group ACtivity) model (Fredenslund et al., 1975) to include a contribution for free volume differences between the polymer and solvent molecules. The UNIFAC model uses a combinatorial expression developed by Stavermann (1950) and a residual term determined from Guggenheim's quasichemical theory. Oishi and Prausnitz recognized that the UNIFAC combinatorial contribution does not account for the free volume differences between the polymer and solvent molecules. While this difference is usually not significant for small molecules, it is important for polymer-solvent systems. They, therefore, added the free volume contribution derived from the Flory equation of state, which is discussed later, to the original UNIFAC model to arrive at the following expression for the weight fraction activity coefficient of a solvent in a polymer.

$$\ln \Omega_1 = \ln \frac{a_1}{w_1} = \ln \Omega_1^C + \ln \Omega_1^R + \ln \Omega_1^{FV} \tag{2D-28}$$

The free volume contribution is given by

$$\ln \Omega_1^{FV} = 3C_1 \ln \left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_m^{1/3} - 1} \right] - C_1 \left(\frac{\tilde{v}_1}{\tilde{v}_m} - 1 \right) \left[\frac{\tilde{v}_1^{1/3}}{\tilde{v}_1^{1/3} - 1} \right] \tag{2D-29}$$

Here C_1 is an external degree of freedom parameter for the solvent.

The combinatorial and residual contributions Ω^C and Ω^R are identical to the original UNIFAC contributions.

The Oishi-Prausnitz modification, UNIFAC-FV, is currently the most accurate method available to predict solvent activities in polymers. Required for the Oishi-Prausnitz method are the densities of the pure solvent and pure polymer at the temperature of the mixture and the structure of the solvent and polymer. Molecules that can be constructed from the groups available in the UNIFAC method can be treated. At the present, groups are available to construct alkanes, alkenes, alkynes, aromatics, water, alcohols, ketones, aldehydes, esters, ethers, amines, carboxylic acids, chlorinated compounds, brominated compounds, and a few other groups for specific molecules. However, the Oishi-Prausnitz method has been tested only for the simplest of these structures, and these groups should be used with care. The procedure is described in more detail in Procedure 3C of this **Handbook**.

The Oishi-Prausnitz model cannot be defined strictly as a lattice model. The combinatorial and residual terms in the original UNIFAC and UNIQUAC models can be derived from lattice statistics arguments similar to those used in deriving the other models discussed in this section. On the other hand, the free volume contribution to the Oishi-Prausnitz model is derived from the Flory equation of state discussed in the next section. Thus, the Oishi-Prausnitz model is a hybrid of the lattice-fluid and free volume approaches.

E. VAN DER WAALS MODELS

The equations of state that are described in the following sections are all derived from what is called the generalized van der Waals (GvdW) partition function. The GvdW model is based in statistical thermodynamics. It is difficult to discuss this model without recourse to the complexities and terminology used in statistical thermodynamics. The following, however, is an attempt to give a simplistic description of the fundamentals of this approach. For a thorough discussion of the GvdW theory, the presentations of Sandler (1985) and Abbott and Prausnitz (1987) are recommended.

The GvdW model relies on the concept of the partition function. The partition function relates the most probable distribution of energy states in a system of molecules to the macroscopic thermodynamic properties of that system. The energy modes can be divided into translational, rotational, vibrational, electronic, and attractive. The translational energy state depends directly upon the volume (or density) of the fluid - more specifically on the *free volume*. For small molecules the rotational, vibrational, and electronic modes depend only on temperature. For large molecules, however, the rotational and vibrational modes also depend upon the density. The attractive energy of the system depends upon the intermolecular forces between the molecules which in turn depends upon the density and temperature. The density is related to the average distance of separation of the molecules; i.e., their location. Whereas the lattice model describes the location of the molecules or polymer segments in terms of sites on the lattice, the GvdW theory uses the radial distribution function. The radial distribution function is a mathematical expression which gives the probability of finding the center of another molecule as a function of the distance from the center of the first molecule. It is dependent upon the density and temperature of the system. The exact form of the radial

distribution function is unknown; approximations based on assumed potential functions are used. Thus, we arrive at a partition function, Q, which is a complex function of temperature, pressure, and density. The key connection between this complex partition function and the equation of state is a relatively simple relation:

$$P = RT \left[\frac{\partial \ln Q}{\partial V} \right]_T \tag{2E-1}$$

It was with the above approach that the following equations of state were developed.

1. Flory Equation of State

Flory et al. (1964) developed an equation of state based on a van der Waals model given in reduced variables by:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{v}\tilde{T}} \tag{2E-2}$$

where the reduced volume is given by the ratio of the volume to the reference volume

$$\tilde{v} = \frac{v}{v^*} \tag{2E-3}$$

The reduced temperature is given by the ratio of the temperature to the reference temperature:

$$\tilde{T} = \frac{T}{T^*} = \frac{2v^* cRT}{s\eta} \tag{2E-4}$$

where the parameter c is a measure of the amount of flexibility and rotation that is present in a molecule per segment, i.e., the vibrational and rotational energy states. The value of c will be much larger for a polymer molecule than a low molecular weight molecule. The product $s\eta$ is the interaction energy of the molecule per segment. The reduced pressure is calculated by:

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv^{*2}}{s\eta} \tag{2E-5}$$

The Flory equation of state does not reduce to the ideal gas equation of state at zero pressure and infinite volume. Flory and his coworkers derived the equation of state specifically for liquid polymer solutions and were not concerned with the performance of the equation in the vapor phase. Poor vapor phase performance of an equation of state causes considerable difficulty, however, when one tries to apply the equation to higher pressure, higher temperature situations. The Chen et al. equation of state was developed in order to remedy this deficiency of the Flory equation of state.

2. Chen, Fredenslund, and Rasmussen Equation of State

Holten-Andersen et al. (1987) modified the Flory equation of state in order to develop an equation that is applicable to the vapor phase, to make it more applicable to associating fluids, and to introduce a group contribution approach. Chen et al. (1990) revised and improved the equation of state. The final model takes the following form.

$$P = \frac{NRT}{V}\left[\frac{\tilde{v}^{1/3} + \sum x_i C_i}{\tilde{v}^{1/3} - 1}\right] + \frac{E}{V} \qquad (2E\text{-}6)$$

The energy of the system, E, is calculated from:

$$E = \sum_i \frac{1}{2} z q_i N_i \left[\epsilon_{ii} + \frac{\sum_j \theta_j \exp\left(-(\Delta\epsilon_{ji} - T\Delta S_{ji}^{HB})/RT\right)\Delta\epsilon_{ji}}{\sum_k \theta_k \exp\left(-(\Delta\epsilon_{ki} - T\Delta S_{ki}^{HB})/RT\right)}\right]$$

$$-3R \ln\left[\frac{\tilde{v}^{1/3}-1}{\tilde{v}^{1/3}}\right]\left[\sum_i N_i \sum_k v_k^{(i)} C_{T,k}\right] \qquad (2E\text{-}7)$$

which includes local composition contributions from group-group interaction energies, $\Delta\epsilon_{ij}$, and additional contributions due to hydrogen bonding, $\Delta S_{j\,i}^{HB}$. The Chen et al. equation of state combines the free volume expression from the Flory equation of state with a local composition expression for the energy of the system derived from arguments similar to the UNIFAC-FV model of Oishi and Prausnitz (1978).

The Chen et al. equation of state is not as accurate as the Oishi-Prausnitz method described previously, but the Chen et al. equation of state has the advantage of not requiring the pure component densities. The densities of the pure components and the mixtures are calculated through a group contribution approach. The types of groups available include the alkanes, aromatics, ketones, esters, ethers, alcohols, alkenes, and chloroalkenes. There are fewer groups available in the Chen et al. equation of state than the Oishi-Prausnitz model. More details of the Chen et al. equation of state are provided in Procedure 3D of this **Handbook**.

F. LIQUID-LIQUID EQUILIBRIA OF POLYMER SOLUTIONS

1. Thermodynamics of Liquid-Liquid Equilibria

An excellent discussion of the thermodynamics of LLE systems has been given by Sørensen and Arlt (1979, 1980) and Sørensen et al. (1979). The following section is adapted from these references. Consider a binary liquid mixture of $n_1 + n_2$ moles at fixed temperature and pressure. The necessary and sufficient condition for equilibrium is that the total Gibbs free energy of mixing, ΔG, for the mixture is a minimum with respect to all possible changes

at the fixed temperature and pressure. If the mixture Gibbs energy is reduced by splitting into liquid phases I and II, then the Gibbs energy is given by

$$\Delta G = n^{I}\Delta\bar{G}^{I}(n_1^{I}, n_2^{I}) + n^{II}\Delta\bar{G}^{II}(n_1^{II}, n_2^{II}) \qquad (2F\text{-}1)$$

where n_i^{I} and n_i^{II} are the number of moles of component i in phases I and II, respectively, and $\Delta\bar{G}^{I}$ and $\Delta\bar{G}^{II}$ are the molar Gibbs energy of mixing corresponding to n^{I} moles of phase I and n^{II} moles of phase II, respectively.

Figure 2F-1 shows the Gibbs energy of mixing, ΔG, as a function of volume fraction for a binary system with two liquid phases I and II in equilibrium. According to Equation (2F-1), a liquid mixture with a total volume fraction ϕ_2 between ϕ_2^{I} and ϕ_2^{II} will split into two liquid phases with binodal compositions ϕ_2^{I} and ϕ_2^{II}. The Gibbs energy for the mixture will thus lie on the solid line between ϕ_2^{I} and ϕ_2^{II} instead of lying on the hypothetical dashed curve predicted by the model. The solid line is a tangent touching the predicted curve at the binodal compositions.

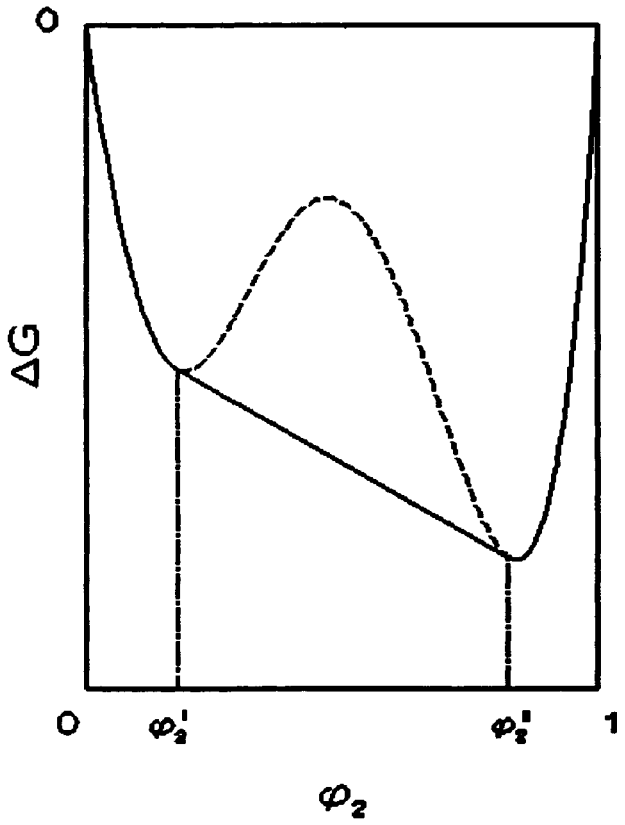

Figure 2F-1. Gibbs Energy of Mixing as a Function of Volume Fraction.
----Hypothetical Predicted ΔG-Curve in Two-Phase Region;
——Real ΔG-Curve

Since the Gibbs energy of mixing, ΔG, is a minimum, a differential change of composition occurring at equilibrium at fixed pressure and temperature will not produce any change in ΔG.

$$d\,(\Delta G)_{P,T} = 0 \qquad (2F\text{-}2)$$

This criterion is a necessary, but not sufficient condition of equilibrium between phases I and II. Equation (2F-2) does not distinguish between a maximum or a minimum. It may result in false solutions as illustrated in Figure 2F-2. The dashed tangent and the solid tangent correspond to liquid-liquid equilibrium compositions representing minima in ΔG. The dashed tangent, however, corresponds to a false solution yielding an erroneous liquid phase with composition ϕ_2^{0}. The correct solution is given by the solid tangent yielding liquid phases with compositions ϕ_2^{I} and ϕ_2^{II}.

For binary equilibria, potential false solutions may be detected by checking the sign of $\partial^2(\Delta G)/\partial\phi_2^{2}$ in the whole composition range between zero and one (Sørensen and Arlt, 1979).

The Gibbs energy surface corresponding to Figure 2F-1 has exactly two inflection points, whereas, more complicated curves such as Figure 2F-2 have three or more inflection points. If more than two inflection points are found, care must be taken that the phase compositions truly correspond to the global minimum.

In Figure 2F-1 the composition where $\partial^2(\Delta G)/\partial\phi_2{}^2$ is equal to zero, or at the inflection point on the Gibbs energy surface, is defined as the spinodal composition. This corresponds to the boundary between an unstable solution and a metastable solution. If the necessary amount of free energy is supplied to the metastable system, the solution will phase separate into two phases with binodal compositions $\phi_2{}^{I}$ and $\phi_2{}^{II}$. The unstable system will always phase separate into the two phases. The temperature where the two points of inflection on the energy surface merge into a single point is defined as the critical solution temperature.

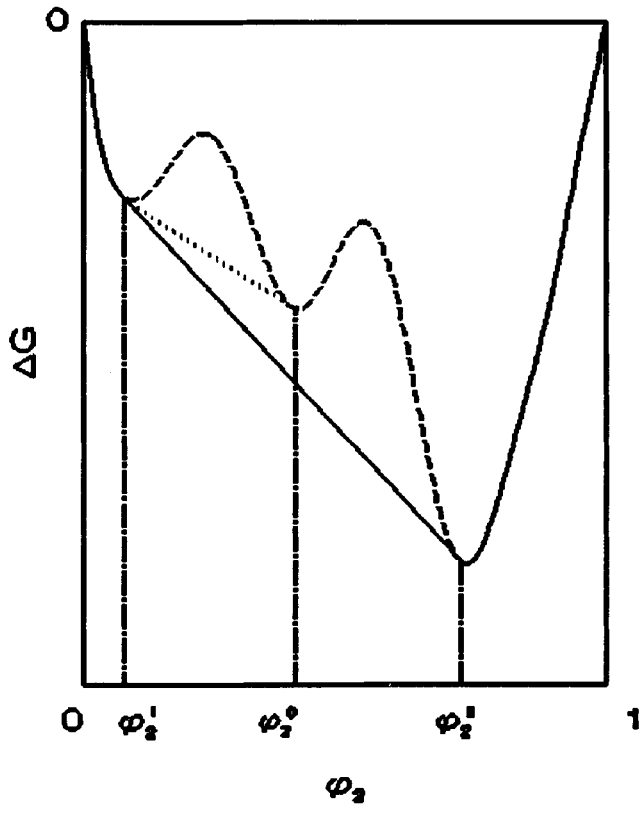

Figure 2F-2. Gibbs Energy of Mixing as a Function of Volume Fraction.
- - Hypothetical Predicted ΔG-Curve in Two-Phase Region;
——Real ΔG-Curve;
• • Tangent Corresponding to False Solution.

2. Types of Liquid-Liquid Equilibria

Binary liquid-liquid equilibria are usually represented as temperature-volume fraction diagrams. These diagrams give the mutual solubilities in the two coexisting liquid phases, as functions of temperature. Figure 2F-3 illustrates six types of phase behavior that have been observed in binary LLE. A horizontal line intersects the phase boundary curve at two points which give the compositions of the two phases in equilibrium at the corresponding temperature.

The six different types of diagrams given in Figure 2F-3 correspond to the different types of critical solution temperatures. Type A systems exhibit only an upper critical solution temperature (UCST). Above the UCST, there exists one liquid phase; below the UCST, there exist two liquid phases. As the heterogeneous mixture (in the two phase region), approaches the UCST, the two phases merge together. Type B systems are a mirror image of type A systems - only a lower critical solution temperature (LCST) is exhibited.

Type C systems exhibit both a LCST and an UCST. This closed-loop phase behavior occurs in some highly polar systems (Siow et al., 1972). Type D systems exhibit neither a LCST nor a UCST. This is either because the LCST is below the freezing point of the mixture,

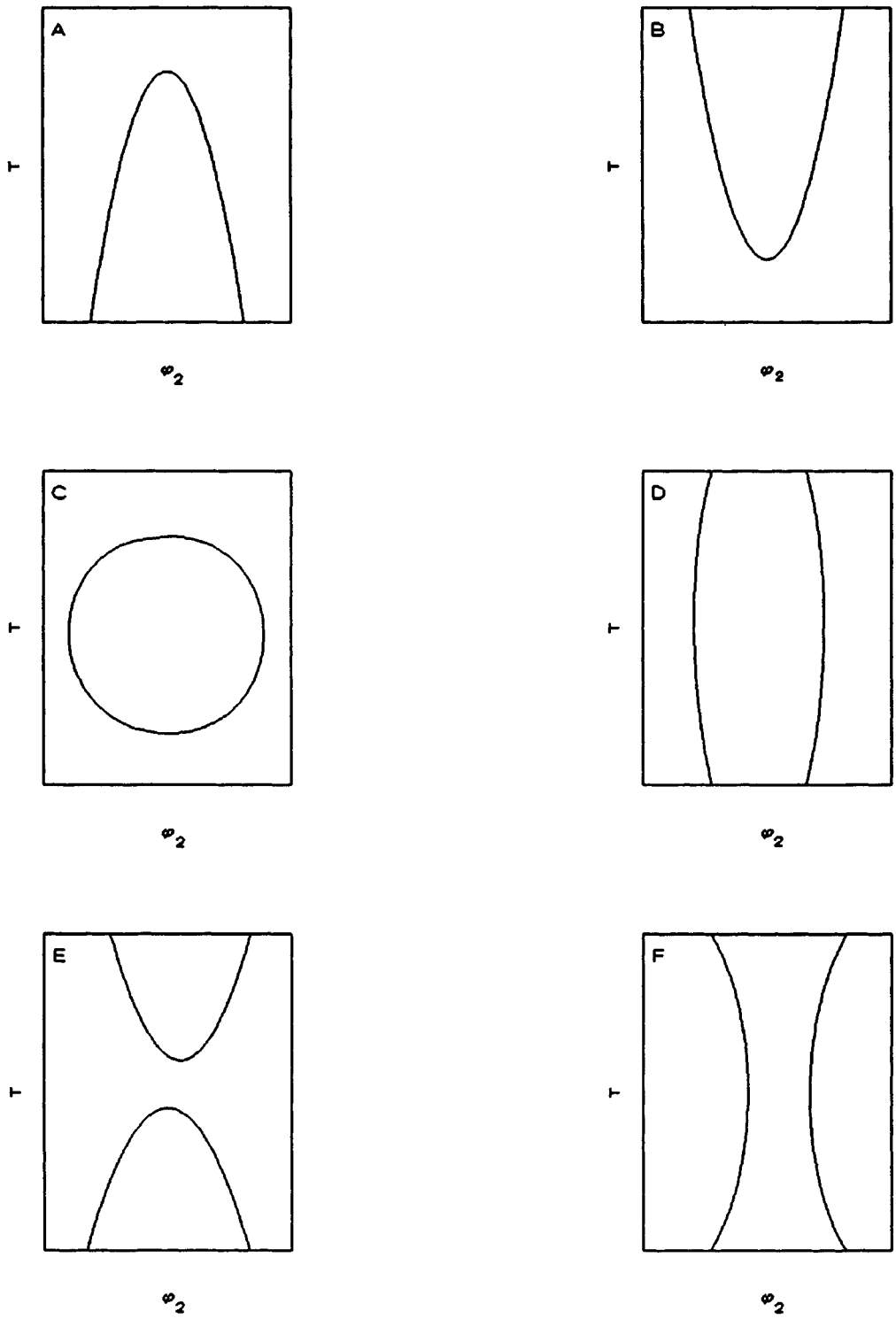

Figure 2F-3. Types of Binary Liquid-Liquid Equilibria

the UCST is above the boiling point of the mixture, or one or both of the critical solution temperatures lie outside the temperature range in which data were recorded.

In type E systems, the LCST is actually greater than the UCST. This phase behavior occurs in systems containing a poor solvent. Increasing the molecular weight of the polymer raises the UCST and lowers the LCST, thus shrinking the region of complete miscibility. For type F systems, the LCST and UCST merge to give an hourglass shape.

Ternary liquid-liquid equilibrium data are usually recorded at constant temperature. Ternary data may be represented by an equilateral-triangular diagram as shown in Figure 2F-4. Each vertex of the triangle represents a pure component. The distance from a point within the triangle to the side opposite the vertex represents the volume fraction of the component in the mixture. The solid line in the triangular diagram is the binodal or two-phase curve. The binodal curve separates the one-phase region from the two-phase region. A tie line, which is shown by the dotted line in Figure 2F-4 connects two points corresponding to the compositions of the two liquid phases in equilibrium. As the plait point is approached, the tie lines become shorter and shorter. Finally, at the plait point only one liquid phase exists.

The various types of ternary systems encountered in practice are shown in Figure 2F-5. Type 1 and type 2 systems are the most common and these consist of one and two immiscible binaries, respectively. Type 3 systems may have three coexisting liquid phases (points a, b, and c). Type O systems consist of three miscible binaries.

Equilateral-triangular diagrams have some practical disadvantages. They require special plotting programs and the scales of their axes cannot be independently enlarged when one wishes to follow changes in a narrow concentration range of one of the componenets. For these reasons, various other kinds of diagrams are used (McCabe and Smith, 1976). For type 1 systems, one method is to use rectangular coordinates and to define the ordinate as the concentration of component 1 and the abscissa as the concentration of a second component on a component 1 free basis. Another method is to use a right-angle triangle in place of the equilateral triangle. Concentrations of two of the components are plotted along the rectangular axes and that of the third component calculated by difference.

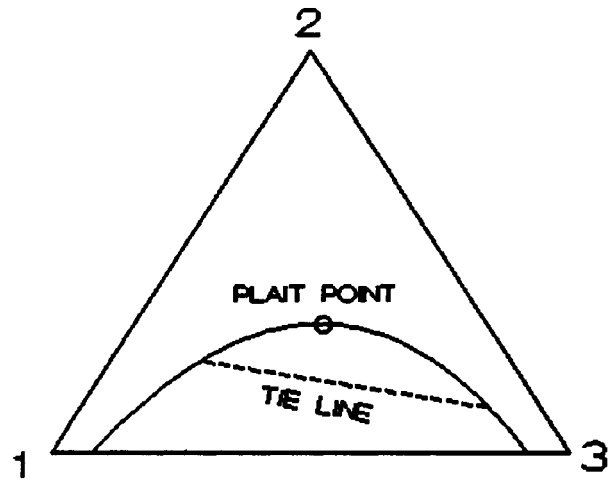

Figure 2F-4. Typical Ternary Liquid-Liquid Equilibria System.

LLE data are usually measured at low pressures (not exceeding 2000 kPa). At these low pressures, pressure has very little influence on the phase compositions. Consequently, pressure is not an important variable in LLE data and is usually not measured or reported.

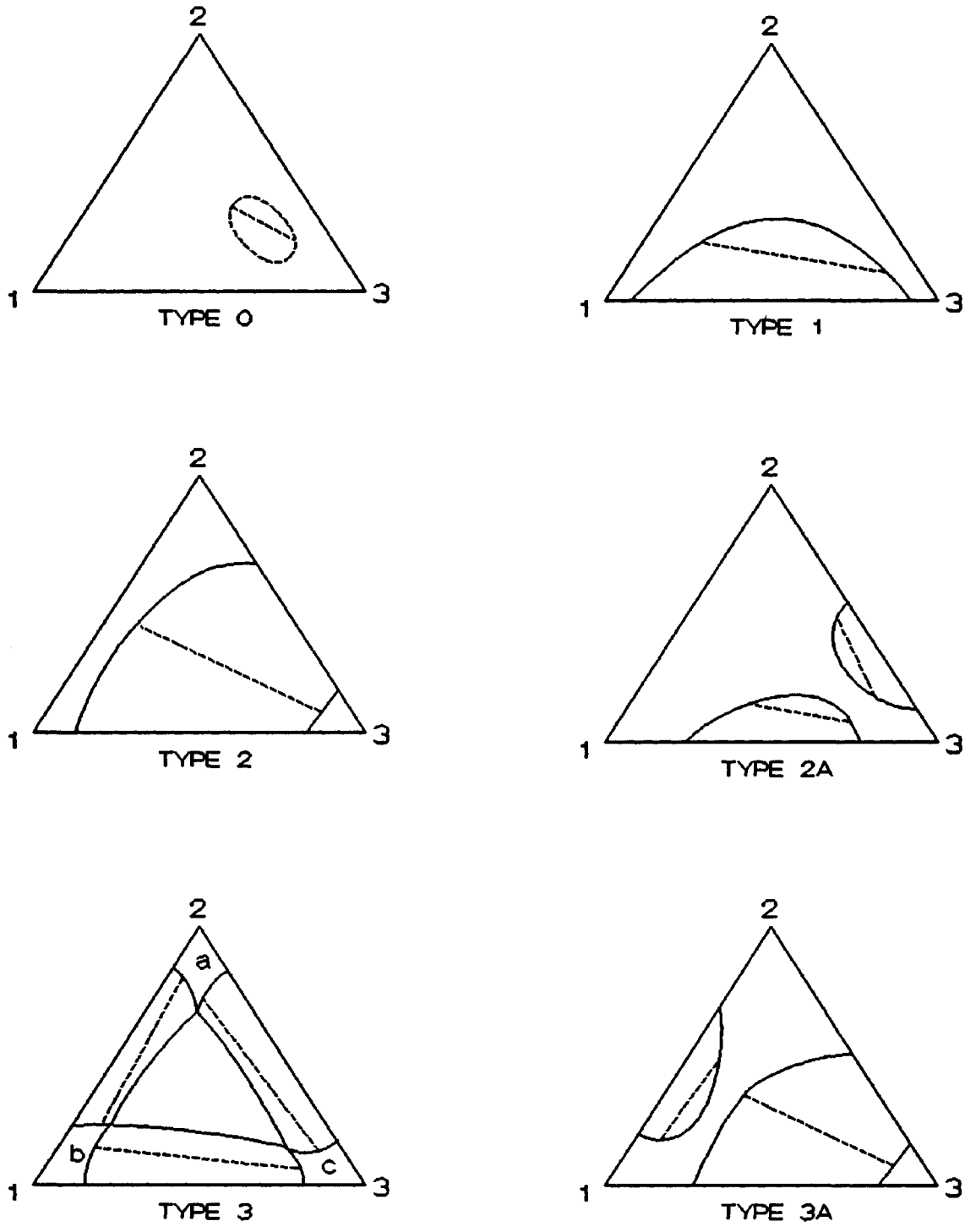

Figure 2F-5. Types of Ternary Liquid-Liquid Equilibria

LLE data cannot be checked for thermodynamic consistency as can be done for vapor-liquid equilibria data (Sørensen and Arlt, 1979). In VLE systems, one of the set of equilibrium values (T, P, x_i, y_i) is calculated from the other and checked against experimental data. For LLE systems, pressure has a small influence on the other quantities. Therefore, pressure cannot be included in such a consistency test.

3. Models for Liquid-Liquid Equilibria

The usual LLE problem consists of determining if phase separation occurs; and if so, what are the compositions of the phases. If a configuration of two liquid phases will have a lower Gibbs free energy than one liquid phase, separation will occur. Thus, the computational problem is to determine where the overall minimum in Gibbs free energy occurs. For this purpose, a thermodynamic model for the excess free energy (or an equation of state) is needed. In addition, mixture parameters for the given thermodynamic model are required. Currently, there are no methods available that can predict LLE of polymer solutions. However, various activity coefficient models have been used to correlate LLE of polymer solutions (Kang and Sandler, 1987; Qian et al., 1991). These include the Flory- Huggins and UNIQUAC models (Abrams and Prausnitz, 1975). These models may potentially be used to extrapolate to other conditions such as temperature, composition, and molecular weight. In addition, it may be possible to compute interaction parameters from binary data to predict ternary data.

A series of papers concerning LLE of polymer solutions have been published by Koningsveld and coworkers, the most recent of which is Koningsveld and Kleintjens (1985). Several of these papers are discussed below.

The Flory-Huggins model will be used for illustrative purposes in the following sections. The advantages of using a Flory-Huggins model are its simplicity, its wide acceptance and familiarity, and that only a knowledge of the components' molar volumes is required. The original model suffered from several weaknesses including the concentration dependency of the parameters and an inability to account for concurrent lower and upper critical solution temperatures. These problems have been eliminated by adding empirical parameters (Koningsveld and Kleintjens, 1971; Koningsveld, 1975, Geveke and Danner, 1991). Although this dilutes the theoretical basis of the model, the results justify this practical approach.

According to the Flory-Huggins theory, the reduced total Gibbs free energy of mixing for a binary mixture is given by

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + g_{12}(\phi_2, T)\, n_1 \phi_2 \qquad (2F\text{-}3)$$

where n_i and ϕ_i are the number of moles and the volume fractions of the binary components, respectively, R is the gas constant, T is the temperature in kelvins, and the interaction parameter, g_{12}, is defined on a per segment basis.

For computational purposes, Qian et al. (1991) regarded the interaction parameter, g_{12}, to be comprised of the product of a concentration-dependent term, $B(\phi_2)$, and a temperature dependent term, C(T).

$$g_{12}(\phi_2, T) = B(\phi_2)\, C(T) \qquad (2F\text{-}4)$$

The form of the concentration-dependent term is taken as

$$B(\phi_2) = (g_{12a} + g_{12b}\phi_2) \tag{2F-5}$$

In general, the Flory-Huggins interaction parameters for binary systems continually increase, remain constant, or continually decrease with concentration and do not go through either a minimum or maximum. A linear relation is capable of adequately describing all of these cases. Third and higher order polynomials have been suggested (Gundert and Wolf, 1989; Qian et al., 1991); however, these may give erroneous results when extrapolating beyond the range of the data. A less empirical expression has been proposed by Koningsveld and Kleintjens (1971).

$$B(\phi_2) = a + \frac{b}{(1 - c\ \phi_2)} \tag{2F-6}$$

This equation is based on theoretical arguments and is a closed expression for an infinite polynomial series. It contains three parameters; a, b, and c; however.

Although the concentration dependence is probably more complex than the linear relation of Equation (2F-5) implies, it is recommended that one initially try this simplified form to limit the number of regression parameters. The ultimate test of the form is the ability of the model to satisfactorily correlate the data. If unsatisfactory results are obtained, the Koningsveld-Kleintjens expression might then be tried.

Due to the complexity of the temperature dependency of the interaction parameters, a three parameter expression is generally necessary to adequately correlate LLE data. The form of the temperature-dependent term proposed by Koningsveld (1975) is

$$C(T) = (1 + \frac{\beta}{T} + \gamma T + \delta \ln T) \tag{2F-7}$$

Therefore, for binary systems, the Gibbs energy is a function of temperature, composition, and the following parameters: g_{12a}, g_{12b}, β, γ, and δ.

For isothermal ternary systems, Geveke and Danner (1991) have modified the Flory-Huggins theory to account for the concentration dependency of the parameters. The reduced total Gibbs free energy of mixing is given by

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_{12})m_1 n_1 \phi_2 + g_{13}(u_{13})m_1 n_1 \phi_3 + g_{23}(u_{23})m_2 n_2 \phi_3 \tag{2F-8}$$

where m_i is the ratio of the molar volume of component i to a reference component's volume, here taken to be that of the solvent, component 1; thus $m_1 = 1$. Variable u_{ij} is defined as the ratio of the volume of the jth component to the combined volume of the ith and jth components, or

$$u_{ij} = \frac{\phi_j}{(\phi_i + \phi_j)} \tag{2F-9}$$

As before, the interaction parameters are assumed to vary linearly with concentration.

$$g_{ij}(u_{ij}) = g_{ija} + g_{ijb}\, u_{ij} \qquad \text{(2F-10)}$$

The modified Flory-Huggins model contains two parameters per binary for a total of six parameters. Therefore, for isothermal ternary systems, the Gibbs energy is a function of composition and the following parameters: g_{12a}, g_{12b}, g_{13a}, g_{13b}, g_{23a}, and g_{23b}.

4. Computation of Liquid-Liquid Equilibria Compositions

The necessary, but not sufficient, condition of equilibrium is the chemical potential of each component, μ_i, must be equal in both phases.

$$\mu_i^{I} = \mu_i^{II} \qquad i = 1,2,...N \quad \text{(components)} \qquad \text{(2F-11)}$$

In addition, the following material balances must be satisfied.

$$\sum_i \phi_i^{I} = \sum_i \phi_i^{II} = 1 \qquad \text{(2F-12)}$$

Thus, for binary systems there are four equations and four unknowns. According to the phase rule, this problem has exactly one solution. For ternary systems, there are five equations and six unknowns. Therefore, one composition must be specified, for example, ϕ_3^{II}, enabling the remaining five to be computed. The chemical potential of the ith component may be obtained by differentiating the total Gibbs free energy of mixing, given by Equations (2F-3) or (2F-8), with respect to n_i.

5. Parameter Estimation from Liquid-Liquid Equilibria Data

The reverse problem of the one in Section 4 consists of obtaining mixture parameters for a given thermodynamic model using a known liquid-liquid equilibrium data set. The parameters may then be used to correlate the original data or to predict unmeasured data. The parameter estimation is carried out by minimizing an objective function.

There are two main strategies for obtaining parameters, p (p_1, p_2, ...), from LLE data at constant temperature and pressure (Sørensen and Arlt, 1979; Sørensen et al., 1979). The first of these is the minimization of chemical potential differences according to Equation (2F-11). Expressed in terms of the least-squares principle, the objective function used is

$$F(p) = \sum_k \sum_i W_i^2 \left[\Delta\mu_{ik}^{I}(\phi_{ik}^{I}, p) - \Delta\mu_{ik}^{II}(\phi_{ik}^{II}, p) \right]^2 \qquad \text{(2F-13)}$$

Where

$i = 1, 2, ..., N$ (components)

$k = 1, 2, ..., M$ (tie lines)

Here W_i is the weighing factor associated with component i. Altena and Smolders (1982) propose W_i be set equal to the reciprocal of m_i to account for the large differences in molar volumes between solvents and polymers. ϕ_{ik}^{I} is the experimental volume fraction of

component i in phase I at tie line k. The calculated chemical potentials depend on the experimental volume fractions and the parameters.

The second strategy for obtaining parameters is the minimization of the experimental volume fractions, ϕ_{ijk}, and the calculated volume fractions, ϕ^c_{ijk}, differences.

$$F(p) = \sum_k \sum_j \sum_i W_i^2 \left[\phi_{ijk} - \phi^c_{ijk}(p) \right]^2 \qquad (2F\text{-}14)$$

Where

j = I, II (phases)

Here ϕ_{ijk} is the volume fraction of component i in phase j at tie line k. The calculated volume fractions depend on the parameters, p.

The objective function based on the isochemical potential criterion does not guarantee that the differences between the experimental and calculated volume fractions will be minimized. This is what is most often wanted. The objective function stated in terms of compositions directly expresses the goal of accurately representing the experimental data. It is computationally more complicated, however, because it contains the computed volume fractions, ϕ^c_{ijk}, which for a given parameter set, must be predicted for each tie line using the method outlined in Section 4.

For ternary systems, in using the composition form of the objective function, one must, for each current parameter estimate, choose a predicted tie line to compare with an experimental one. Renon et al. (1971) accomplished this by setting one composition in one phase of the predicted tie line equal to the corresponding experimental value: $\phi_{32k} = \phi^c_{32k}$.

The parameter estimation first uses the objective function based on the isochemical potential criterion because this does not require qualified initial guesses of the parameters and converges quickly. Then, using these approximate values as the initial guesses, the objective function stated in terms of compositions is used.

For binary data at fixed temperature and pressure, there are two independent measurements, ϕ_2^I and ϕ_2^{II}. This enables a maximum of two parameters to be determined from one tie line. Therefore, it is impossible to determine, from mutual solubility data alone, all of the parameters in the Koningsveld-Kleintjens expression [Equation (2F-6)] for the concentration dependency of the interaction parameter, g_{12}.

6. Sample Correlations of Liquid-Liquid Equilibria Data

Binary and ternary polymer-solution LLE data may be correlated using any of the models described in Section 3 and the methods for computing LLE compositions and estimation of parameters presented in Sections 4 and 5.

For example, the binary data of Siow et al. (1972) for the system acetone-polystyrene (M_w = 19,800) were obtained from the binary LLE database using the data retrieval program, POLYDATA. The regression parameters calculated using the modified Flory-Huggins model are given in Table 2F-1, and the correlation is shown graphically in Figure 2F-6. The data are well represented by the model.

As an example of a correlation of ternary LLE data, the system water-dextran (M_n = 23,000)-poly(ethylene glycol) (M_w = 6,750) at 273 K (Albertsson, 1986) was correlated

also using the modified Flory-Huggins model. The data were recalled from the ternary LLE database using the data retrieval program, POLYDATA. The parameters obtained are presented in Table 2F-2 and the result is shown graphically in Figure 2F-7. Again, an excellent correlation was obtained.

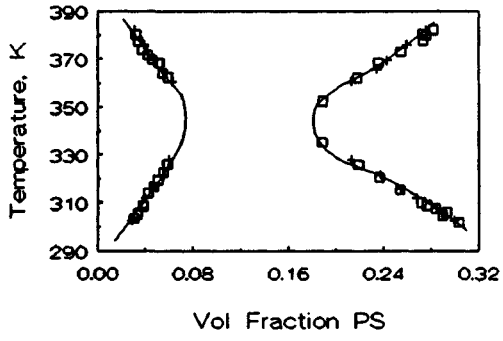

Figure 2F-6. Correlation using a modified Flory-Huggins model (crosses) for the Acetone-Polystyrene ($M_w = 19,800$) system. Experimental data (squares) of Siow et al. (1972).

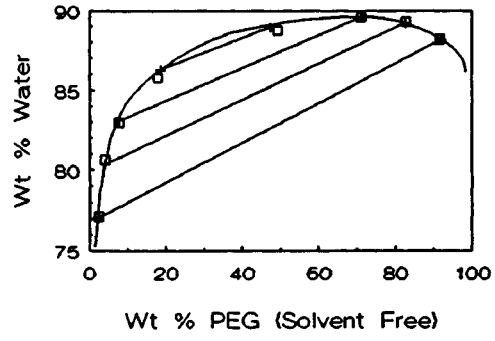

Figure 2F-7. Correlation using a modified Flory-Huggins model (crosses) for Water-Dextran ($M_n = 23,000$) - Poly(ethylene glycol) ($M_w = 6,750$) at 273 K. Experimental data (squares) of Albertsson (1986).

Table 2F-1
Regressed Interaction Parameters for Acetone-Polystyrene ($M_w = 19,800$) Using a Modified Flory-Huggins Model

g_{12a}	g_{12b}	β	γ	δ
26.4	7.05	-20.6	0.000339	-0.176

Table 2F-2
Regressed Interaction Parameters for Water-Dextran ($M_n = 23,000$)-Poly(ethylene glycol) ($M_w = 6,750$) at 273 K Using a Modified Flory-Huggins Model

g_{12a}	g_{12b}	g_{13a}	g_{13b}	g_{23a}	g_{23b}
0.622	0.137	0.0924	-0.440	-0.240	0.0406

G. EFFECT OF POLYDISPERSION

In the Flory and Holten-Anderson equations of state discussed above, the polymer was considered to be monodisperse. Realistically, however, every polymer solution has a distribution of chain lengths. In this case, the same equations hold as for the monodisperse case, but when calculations are performed to arrive at equilibrium conditions all of the chain lengths should be considered. Unfortunately, this complicates the equilibrium calculations considerably. For example, in the case of polymer fractionation, we now have an enormous number of compounds (the solvent and all the polymer molecules with varying chain lengths) in equilibrium between two phases. Fortunately, the different polymer molecules have essentially the same intermolecular forces and will follow the same equation of state. The problem reduces to how to incorporate the distribution of chain lengths into the thermodynamic models if indeed the chain length is an important variable. The calculations of equilibrium conditions involving polydisperse polymer solutions are similar to those for petroleum fractions. In both cases, the solutions contain many components which are thermodynamically similar. Considerable work has been done to increase the accuracy and decrease the cost of equilibrium calculations for petroleum fractions. Pseudocomponents and continuous thermodynamics are the methods used for these phase equilibria calculations and these methods are also applicable to polymer solutions. The pseudocomponent method involves hypothesizing that the mixture is composed of several compounds with well known thermodynamic properties. The pseudocomponents do not necessarily have to be in the real mixture, but the hypothetical mixture of pseudocomponents have to accurately represent the thermodynamic properties of the real mixture. The equilibria of the real mixture is then determined from the equilibria of these pseudocomponents.

Continuous thermodynamics is a relatively new field which is surrounded by controversy. The central idea of continuous thermodynamics is that a mixture containing many similar components can be represented by a distribution function. A polymer solution, therefore, can be represented by a molecular weight or chain length distribution. In the pseudocomponent approach, the method approximates an integral by a series of discrete components, whereas, in the continuous thermodynamic approach a continuous function is used. The continuous thermodynamic approach will approximate the integral more accurately. Cotterman and Prausnitz (1985) state that the pseudocomponent approach is computationally slower than the continuous thermodynamic approach when a large number of pseudocomponents are used. Continuous thermodynamics has its drawbacks, however. Pederson and Fredenslund (1984) point out that when a specific distribution is assumed for the liquid or vapor phase in a flash calculation the overall material balance cannot be satisfied using the same distribution function for all phases. In addition, they state that if the phase equilibrium calculations are done using a quadrature, then the method is equivalent to the pseudocomponent approach. Cotterman and Prausnitz clearly show that the continuous thermodynamic calculations using quadrature are faster than the pseudocomponent approach. Further work needs to be done to resolve the controversy concerning the usefulness of continuous thermodynamics.

Fortunately, the polydispersity of polymers does not significantly affect the vapor-liquid equilibrium of polymer solutions since the polymer remains entirely in the condensed phase. Polydispersity becomes important in the liquid-liquid equilibria of polymer solutions where the

polymer is present in both phases. In any case, the assumption of a monodisperse polymer solution must be examined. McMaster (1973) showed that the critical solution temperature of a solution of two polydisperse polymer species shifts from that of solutions with the two monodisperse species. The more polydisperse one of the polymers becomes the more the critical solution temperature shifts. Koningsveld and Staverman (1968) discussed the effects of polydispersion on polymer fractionation calculations using a continuous thermodynamic method and showed that polydispersion does have a significant effect on the products from the fractionation.

Chapter 3

RECOMMENDED PROCEDURES

A. SELECTION OF MODELS

1. Correlation of Pure Polymer PVT Behavior

In developing the recommended PVT correlation for this **Handbook**, several variations of the Tait correlation, the Flory equation of state (Flory et al., 1964), the Simha-Somcynsky equation of state (Simha and Somcynsky, 1964), and the Sanchez-Lacombe equation of state (Sanchez and Lacombe, 1976) were evaluated. Data covering wide ranges of temperature and pressure for 27 polymers that had varying degrees of branching, tacticity, sizes of the repeat unit, polarity, hydrogen-bonding tendencies, and propensity for crystallization were included. The Tait form given in Section 3B yielded errors which were generally an order of magnitude lower than that found with the other models. In almost all cases, the average error with the Tait model was found to be within the reported experimental error - approximately 0.1% (Zoller, et al. 1976).

The recommended form of the Tait equation is

$$V(P,T) = V(0,T)\left[1 - C \ln\left[1 + \frac{P}{B(T)}\right]\right] \qquad (3A\text{-}1)$$

The parameter C is often considered independent of temperature and it has been shown to take a universal value of 0.0894 for long-chain hydrocarbons (Cutler et al., 1958). Nanda and Simha (1964) obtained excellent correlations for a number of polymers using this value of C. This value was therefore retained in the **Handbook**. The parameter B has the dimensions of pressure, but it is a function only of temperature. Different forms have been used in the literature to describe this temperature dependence, but the exponential form has proven to be a reliable representation. Thus B(T) is given by

$$B(T) = B_0 \exp[-B_1(T - 273.15)] \qquad (3A\text{-}2)$$

The volume at zero (atmospheric) pressure, V(0,T) also needs to be obtained as a function of temperature. Two forms have been proposed for this function.

$$V(0,T) = A_0 + A_1(T - 273.15) + A_2(T - 273.15)^2 \qquad (3A\text{-}3)$$

$$V(0,T) = a \exp[\alpha(T - 273.15)] \qquad (3A\text{-}4)$$

Here α denotes a constant thermal expansivity at zero pressure. The exponential representation, Equation (3A-4) has been shown to yield a good fit of the zero pressure isobar only for a few polymers (Zoller, 1989). Moreover a constant thermal expansivity at zero

pressure could provide the wrong sign of ($d\alpha/dT$) at higher pressures. Thus, the polynomial form, Equation (3A-3) was adopted for use in this **Handbook.**

2. Prediction of Vapor-Liquid Equilibria

During the course of preparing this **Handbook** the available prediction models were evaluated for their ability to accurately predict weight fraction activity coefficients. The methods included were the UNIFAC free volume model (Oishi and Prausnitz, 1978), the Chen et al. (1990) equation of state, and the High-Danner (1990) equation of state.

Over the whole spectrum of polymer-solvent systems there is not one model that is superior. Each model has advantages for different types of systems. If you have data available for a system that is somewhat similar to the system that you wish to predict, it is recommended that you try all three models for the similar system and then use the model that gives the most accurate predictions for the system of interest. This type of selection process can be done relatively easily with the POLYPROG software accompanying this **Handbook.** If no data are available for an analogous system, the choice of a model can be made on the basis of the following evaluations and Table 3A-3.

The prediction of activity coefficients by the three models was examined in two ways. First, which model is the most accurate for a particular type of system? Second, does the best model give reasonably accurate predictions? The polymers and solvents in the experimental data base were categorized according to their organic structure. By pairing the organic structures of the polymer and solvent - i.e., alkane-alkane, ether-aromatic, etc. - 26 different classes were identified within the finite concentration and infinite dilution data bases. In each of these classes, the data were grouped by systems. For the finite data, a system in a class was defined as data from a single literature source with the same polymer molecular weight and temperature. For each system, the percent errors were averaged and then examined to determine the model that gives the smallest percent error, the models that are within 10% of the value of the smallest percent error - i.e. within 2.2% if 2% is the smallest percent error, and the model that gives the worst error. (See Table 3A-1.) The infinite data were examined in exactly the same manner as the finite data except data were assigned to a system based on the number of repeat groups in the polymer (1-5, 6-10, 11-20, 21-100, 101-200, >200) regardless of the temperature or literature source. Based on the actual errors in the predictions and on the most accurate model for a class, denoted by having the greatest sum for the rows 'Best' and 'Within 10%' for a class (See Tables 3A-1 and 3A-2), a specific model is recommended for predicting activity coefficients for each class (Table 3A-3).

Use of the models outside of the classes should be done with caution. In some cases none of the models may be recommended for a particular class. This means that although a particular class was included in the evaluations, the best model still gives unreasonably high errors. Therefore, alternative means should be used if possible to get an activity coefficient for these classes. Finally, for some classes the finite and infinite recommendations disagree. This disagreement only occurred in systems where the data were limited and may change if more data are evaluated.

Overall, UNIFAC-FV is the best model for predicting the weight fraction activity coefficient. It is recommended for 7 of the 16 finite concentration data classes and for 15

of the 22 infinite dilution data classes. The UNIFAC-FV model has, by far, the least number of worst case occurrences. This implies the model rarely predicts unreasonably high results and it has at least a rough quantitative relationship to the experimental data. For the infinite dilute data, when the number of polymer repeat units is greater than 200, UNIFAC-FV is much more accurate than the other models. The major drawback to using the UNIFAC-FV model is finding accurate density data for both the solvent and polymer at the temperature of the system. This information is required to use the UNIFAC-FV model. Thus, coupling the accurate predictions of the UNIFAC-FV model with its large number of subgroups, the UNIFAC-FV model should be selected to predict activity coefficients for any polymer-solvent system that is not covered in Table 3A-3, except aqueous systems. Unfortunately, UNIFAC-FV is not applicable for aqueous mixtures. Calculational problems arise in the free-volume term when treating systems containing water. For these systems, the other prediction methods discussed in the **Handbook** should be considered.

Chen et al. and the High-Danner equations of state are comparable, each having its strengths and weaknesses. The method of Chen et al. performs as well as UNIFAC-FV for the finite data, and almost as well for the infinite data. Also, Chen et al. performs as well as UNIFAC-FV for infinite dilution data where the number of polymer repeat units is under 200. The drawbacks to using Chen et al. are that it has twice as many worst case occurrences as UNIFAC-FV, and it has problems at certain temperatures. The large number of worst point cases implies the model is not as consistent as UNIFAC-FV. At some temperatures the model cannot find a liquid-like root for the solvent and thus cannot predict a value for the activity coefficient. Neither of the other models have this type of temperature problem.

The High-Danner equation of state performs well for predictions of activity coefficients for ether-ether systems and for aromatic polymers at infinite dilution. The drawbacks of High-Danner model are the small number of subgroups and lower accuracy compared to the UNIFAC-FV model. The High-Danner model is the only model that was derived as an equation of state and that has been used as an equation of state for prediction. The other two models are not capable of representing pressure dependence in the vapor or liquid phases.

TABLE 3A-1
SUMMARY OF MODEL EVALUATIONS FOR FINITE DATA

Polymer Solvent	Alkane (27) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		0	21	6
Within 10%		0	0	0
Worst		26	0	1

Polymer Solvent	Alkane (6) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		0	4	2
Within 10%		0	0	0
Worst		6	0	0

Polymer Solvent	Alkane (10) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		0	6	4
Within 10%		0	1	0
Worst		9	1	0

Polymer Solvent	Ether (18) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		4	8	6
Within 10%		0	1	1
Worst		10	8	0

Polymer Solvent	Ether (13) Ether	High-Danner	Chen et al.	UNIFAC-FV
Best		10	1	2
Within 10%		2	0	6
Worst		0	12	1

Polymer Solvent	Ether (1) Chlorinated	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	0	1
Within 10%			0	0
Worst			1	0

Polymer Solvent	Ester (3) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		2	1	0
Within 10%		0	0	0
Worst		0	2	1

Polymer Solvent	Ester (1) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	1	0
Within 10%			0	0
Worst			0	1

Polymer Solvent	Aromatic (12) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		6	1	7
Within 10%		1	1	2
Worst		3	9	0

Polymer Solvent	Aromatic (30) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		13	11	6
Within 10%		1	0	5
Worst		4	14	11

Polymer Solvent	Aromatic (7) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		0	0	7
Within 10%		0	0	0
Worst		3	4	0

Polymer Solvent	Alkene (10) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	2	8
Within 10%			0	0
Worst			8	2

Polymer Solvent	Alkene (6) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	0	6
Within 10%			0	0
Worst			6	0

Polymer Solvent	Alkene (8) Chlorinated	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	3	5
Within 10%			3	0
Worst			1	2

Polymer Solvent	Chlorinated (1) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		0	0	1
Within 10%		0	1	0
Worst		1	0	0

Polymer Solvent	Chlorinated (3) Ether	High-Danner	Chen et al.	UNIFAC-FV
Best		3	0	0
Within 10%		0	1	0
Worst		0	0	3

Value in parenthesis is the number of systems of that particular class. See text for definition of a system.
N/A - method is not applicable

TABLE 3A-2
SUMMARY OF MODEL EVALUATIONS FOR INFINITE DATA

Polymer Solvent	Alkane (2) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		0	2	0
Within 10%		0	0	1
Worst		2	0	0

Polymer Solvent	Alkane (3) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		0	0	3
Within 10%		0	0	0
Worst		1	2	0

Polymer Solvent	Ether (20) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		0	18	2
Within 10%		0	0	0
Worst		20	0	0

Polymer Solvent	Ether (2) Alkene	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	2	0
Within 10%			0	0
Worst			0	2

Polymer Solvent	Ether (20) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		0	13	7
Within 10%		0	1	6
Worst		16	4	0

Polymer Solvent	Ether (4) Chlorinated	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	2	2
Within 10%			0	0
Worst			2	2

Polymer Solvent	Ether (4) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		0	2	2
Within 10%		0	0	0
Worst		2	2	0

Polymer Solvent	Ether (15) Alcohols	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	5	10
Within 10%			0	1
Worst			10	4

Polymer Solvent	Ether (2) Ether	High-Danner	Chen et al.	UNIFAC-FV
Best		0	0	2
Within 10%		0	0	0
Worst		2	0	0

Polymer Solvent	Ether (3) Ester	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	1	2
Within 10%			0	0
Worst			2	1

Polymer Solvent	Ester (4) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		0	1	3
Within 10%		0	0	0
Worst		2	2	0

Polymer Solvent	Ester (4) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		1	0	3
Within 10%		0	0	0
Worst		0	4	0

Polymer Solvent	Ester (1) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		1	0	0
Within 10%		0	0	0
Worst		0	1	0

Polymer Solvent	Ester (1) Alcohols	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	1	0
Within 10%			0	0
Worst			0	1

Polymer Solvent	Ester (8) Chlorinated	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	7	1
Within 10%			0	0
Worst			1	7

Polymer Solvent	Aromatic (6) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		2	1	3
Within 10%		0	2	0
Worst		4	0	2

Polymer Solvent	Aromatic (8) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		7	0	1
Within 10%		0	1	0
Worst		0	4	4

Polymer Solvent	Aromatic (1) Chlorinated	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	0	1
Within 10%			0	0
Worst			1	0

TABLE 3A-2 (continued)

Polymer Solvent	Aromatic (3) Ether	High-Danner	Chen et al.	UNIFAC-FV
Best		1	2	0
Within 10%		0	0	1
Worst		2	1	0

Polymer Solvent	Aromatic (2) Ketone	High-Danner	Chen et al.	UNIFAC-FV
Best		0	0	2
Within 10%		0	0	0
Worst		0	2	0

Polymer Solvent	Alkene (1) Alkane	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	0	1
Within 10%			0	0
Worst			1	0

Polymer Solvent	Alkene (1) Aromatic	High-Danner	Chen et al.	UNIFAC-FV
Best		N/A	0	1
Within 10%			0	0
Worst			1	0

Value in parenthesis is the number of systems that particular class. See text for the definition of a system.
N/A - method is not applicable

Table 3A-3

RECOMMENDED MODELS FOR 26 CLASSES OF VLE POLYMER-SOLVENT SYSTEMS

Finite Concentration		Infinite Dilution	
Polymer-Solvent	Model	Polymer-Solvent	Model
Alkane-Alkane	Chen et al.	Alkane-Alkane	Chen et al./UNIFAC-FV*
Alkane-Ketone	Chen et al.		
Alkane-Aromatic	Chen et al.	Alkane-Aromatic	UNIFAC
		Ether-Alkane	none/Chen et al.**
		Ether-Alkene	Chen et al.*
Ether-Aromatic	Chen et al.	Ether-Aromatic	Chen et al./UNIFAC-FV
Ether-Ether	High-Danner	Ether-Ether	UNIFAC-FV*
Ether-Chlorinated	UNIFAC-FV*	Ether-Chlorinated	Chen at al./UNIFAC-FV
		Ether-Ketone	Chen et al./UNIFAC-FV
		Ether-Alcohol	none
		Ether-Ester	Chen et al./UNIFAC-FV
		Ester-Alkane	UNIFAC-FV
Ester-Aromatic	High-Danner	Ester-Aromatic	UNIFAC-FV
Ester-Ketone	Chen et al.*	Ester-Ketone	High-Danner*
		Ester-Alcohol	Chen et al.*
		Ester-Chlorinated	Chen et al.
Aromatic-Alkane	High-Danner/UNIFAC-FV	Aromatic-Alkane	Chen et al./UNIFAC-FV
Aromatic-Aromatic	High-Danner	Aromatic-Aromatic	High-Danner
Aromatic-Ketone	UNIFAC-FV	Aromatic-Ketone	UNIFAC-FV*
		Aromatic-Chlorinated	UNIFAC-FV
		Aromatic-Ether	any
Alkene-Alkane	UNIFAC-FV	Alkene-Alkane	UNIFAC-FV*
Alkene-Aromatic	UNIFAC-FV	Alkene-Aromatic	UNIFAC-FV*
Alkene-Chlorinated	Chen et al./UNIFAC-FV		
Chlorinated-Aromatic	UNIFAC-FV*		
Chlorinated-Ether	High-Danner		

* Only one or two systems were available for evaluation.

** Chen et al. is recommended only for systems where the molecular weight of the polymer exceeds 200 repeat units.

PROCEDURE B: METHOD FOR ESTIMATING THE SPECIFIC VOLUME OF A PURE POLYMER LIQUID

1. Method

This method is to be used to calculate the specific volume of a pure polymer liquid at a given temperature and pressure. This procedure uses the empirical Tait equation along with a polynomial expression for the zero pressure isobar. The method requires only the equation constants for the polymer.

The specific volume of a polymer at a given pressure P and temperature T is given by

$$V(P,T) = V(0,T)\left[1 - C \ln\left[1 + \frac{P}{B(T)}\right]\right] \qquad (3B\text{-}1)$$

Where:

- $V(P,T)$ = specific volume at pressure P and temperature T, cubic meters per kilogram
- $V(0,T)$ = specific volume at zero pressure and temperature T, cubic meters per kilogram
- $B(T)$ = Tait parameter for the polymer, pascals
- C = 0.0894, a universal constant for polymers
- P = pressure, pascals
- T = temperature, kelvins

The specific volume at zero pressure is given by

$$V(0,T) = A_0 + A_1(T - 273.15) + A_2(T - 273.15)^2 \qquad (3B\text{-}2)$$

Where:

A_0, A_1, A_2 = specific constants for the polymer, given in Table 3B-1.

The Tait parameter, B(T), is a function only of temperature and is given by

$$B(T) = B_0 \exp[-B_1(T - 273.15)] \qquad (3B\text{-}3)$$

Where:

B_0, B_1 = specific constants for the polymer, given in Table 3B-1.

2. Procedure

Step 1: Obtain the constants A_0, A_1, and A_2 for the polymer from Table 3B-1.

Step 2: Determine the specific volume of the polymer at zero pressure, V(0,T), using Equation (3B-2).

Step 3: Obtain the Tait parameter constants B_0 and B_1 for the polymer from Table 3B-1.

Step 4: Calculate the Tait parameter, B(T), using Equation (3B-3).

Step 5: Calculate the specific volume of the polymer at the specified pressure and temperature, V(P,T), using Equation (3B-1).

3. Limitations and Reliability

The method works extremely well for calculations within the temperature and pressure range used to determine the equation constants. The average error in such a case is less than the experimental error of approximately 0.1% reported for volumetric measurements. The accuracy of this method for extrapolations is not known due to the lack of sufficient P-V-T data for polymers.

The application of this procedure is restricted to polymers for which the Tait equation constants have been determined from experimental data. No methods are available to predict these constants. The sensitivity of the equation constants to different molecular weight species of the same polymer is not known.

4. Comments

This method uses the form of the Tait equation which gives the best representation of P-V-T data for most of the polymers. Other forms of the Tait equation which use a different expression for V(0,T) or a different value for the parameter C are available. For a few specific polymers, they might provide a better representation of the P-V-T behavior.

If one needs an estimate of the polymer volume *in a polymer-solvent solution below the glass transition temperature* it may be better to extrapolate using the liquid volume constants. No extensive testing of this hypothesis has been done, however. For the pure polymer in the glassy region, Tait constants for the glassy state should be used. (Zoller, 1989.)

5. Literature Sources

The procedure is based on the method described by P. Zoller, "PVT Relationships and Equations of State of Polymers," Chapter VI, 475, **Polymer Handbook**, 3rd Edition, J. Brandrup, E. H. Immergut (Editors), Wiley-Interscience, New York (1989).

6. Example

Estimate the specific volume of poly(methyl methacrylate) [PMMA] at 2000 bars and 159.0°C.

P = 2000 bars = 2.0×10^8 Pa.

T = 159.0°C = 432.15 K.

Step 1: For PMMA (from Table 3B-1),

$A_0 = 8.2396 \times 10^{-4}$ m^3/kg.

$A_1 = 3.0490 \times 10^{-7}$ $m^3/kg.K$.

$A_2 = 7.0201 \times 10^{-10}$ $m^3/kg.K^2$.

Step 2: Using Equation (3B-2),

$$V(0,T) = 8.2396 \times 10^{-4} + 3.0490 \times 10^{-7}(432.15 - 273.15) + 7.0201 \times 10^{-10}(432.15 - 273.15)^2$$
$$= 8.9019 \times 10^{-4} \text{ m}^3/\text{kg}.$$

Step 3: For PMMA (from Table 3B-1),

$B_0 = 2.9803 \times 10^8$ Pa.

$B_1 = 4.3789 \times 10^{-3}$ 1/K.

Step 4: Using Equation (3B-3),

$$B(T) = 2.9803 \times 10^{8}\{\exp[-4.3789 \times 10^{-3}(432.15 - 273.15)]\}$$
$$= 1.4855 \times 10^{8} \text{ Pa.}$$

Step 5: Using Equation (3B-1),

$$V(P,T) = 8.9019 \times 10^{-4}\{1 - 0.0894 \ln[1 + 2.0 \times 10^{8}/1.4855 \times 10^{8}]\}$$
$$= 8.2232 \times 10^{-4} \text{ m}^3\text{/kg.}$$

An experimental value of 8.222×10^{-4} m^3/kg is available from Olabisi and Simha (1975).

Table 3B-1. Tait Equation Constants for Procedure 3B

Polymer	A_0 (m^3/kg)	A_1 ($m^3/kg.K$)	A_2 ($m^3/kg.K^2$)	B_0 (Pa)	B_1 (1/K)	P Range* (MPa)	T Range* (K)
BR	1.0969E-03	7.6789E-07	-2.2216E-10	1.7596E+08	4.3355E-03	0.1 - 283	277 - 328
HDPE	1.1567E-03	6.2888E-07	1.1268E-09	1.7867E+08	4.7254E-03	0.1 - 200	415 - 472
HMDS	1.2727E-03	1.6849E-06	4.3376E-09	5.8910E+07	1.1203E-02	0 - 900	298 - 343
i-PB	1.1561E-03	6.1015E-07	8.3234E-10	1.8382E+08	4.7833E-03	0 - 196	407 - 514
i-PMMA	7.9770E-04	5.5274E-07	-1.4503E-10	2.9210E+08	4.1960E-03	0.1 - 200	328 - 463
i-PP	1.2033E-03	4.8182E-07	7.7589E-10	1.4236E+08	4.0184E-03	0 - 196	447 - 571
LDPE	1.1004E-03	1.4557E-06	-1.5749E-09	1.7598E+08	4.6677E-03	0.1 - 200	398 - 471
LDPE	1.1615E-03	6.7976E-07	6.9112E-10	1.9325E+08	5.6839E-03	0 - 100	413 - 473
LLDPE	1.1105E-03	1.2489E-06	-4.0642E-10	1.7255E+08	4.4256E-03	0.1 - 200	420 - 473
PA	7.8153E-04	3.6134E-07	2.7519E-10	3.4019E+08	3.8021E-03	0 - 177	455 - 588
PBMA	9.3282E-04	5.7856E-07	5.7343E-10	2.2569E+08	5.3116E-03	0.1 - 200	295 - 473
PC	7.9165E-04	4.4201E-07	2.8583E-10	3.1268E+08	3.9728E-03	0 - 177	430 - 610
PCHMA	8.7410E-04	4.9035E-07	3.2707E-10	3.0545E+08	5.5030E-03	0.1 - 200	383 - 472
PDMS	1.0122E-03	7.7266E-07	1.9944E-09	8.7746E+07	6.2560E-03	0 - 100	298 - 343
PDMS3	1.0736E-03	1.2837E-06	1.4565E-10	7.3947E+07	8.0773E-03	0 - 900	298 - 343
PDMS10	1.0536E-03	1.1041E-06	4.6289E-10	8.1208E+07	7.1257E-03	0 - 900	298 - 343
PDMS20	1.0271E-03	1.1054E-06	-2.7259E-10	8.5511E+07	6.7944E-03	0 - 900	298 - 343
PDMS100	1.0095E-03	1.0662E-06	-3.6476E-10	8.8352E+07	6.3228E-03	0 - 900	298 - 343
PDMS350	1.0056E-03	1.0003E-06	1.2039E-11	9.0488E+07	6.4221E-03	0 - 900	298 - 343
PDMS1000	1.0076E-03	9.1603E-07	8.2159E-10	8.9137E+07	6.3938E-03	0 - 900	298 - 343
PHENOXY	8.3796E-04	3.6449E-07	5.2933E-10	3.5434E+08	4.3649E-03	0 - 177	349 - 574
PIB	1.0890E-03	2.5554E-07	2.2682E-09	1.9410E+08	3.9995E-03	0 - 100	326 - 383
PMMA	8.2396E-04	3.0490E-07	7.0201E-10	2.9803E+08	4.3789E-03	0.1 - 200	387 - 432
PMP	1.2078E-03	5.1461E-07	9.7366E-10	1.4978E+08	4.6302E-03	0 - 196	514 - 592
POM	8.3198E-04	2.7550E-07	2.2000E-09	3.1030E+08	4.4652E-03	0 - 196	462 - 492
PoMS	9.3905E-04	5.1288E-07	5.9157E-11	2.4690E+08	3.6633E-03	0.1 - 180	413 - 471
PS	9.3805E-04	3.3086E-07	6.6910E-10	2.5001E+08	4.1815E-03	0.1 - 200	389 - 469
PTFE	4.6867E-04	1.1542E-07	1.1931E-09	4.0910E+08	9.2556E-03	0 - 392	604 - 646
PVAC	8.2832E-04	4.7205E-07	1.1364E-09	1.8825E+08	3.8774E-03	0 - 100	337 - 393

* Range of experimental data used in the determination of equation constants.

PROCEDURE C: OISHI-PRAUSNITZ METHOD FOR ESTIMATING THE ACTIVITY COEFFICIENTS OF SOLVENTS IN POLYMER SOLUTIONS

1. Method

This method is to be used to predict the activity coefficient of a low molecular weight component in a defined liquid mixture containing one or more solvents in a solution with one or more polymers. The molecules must first be divided into groups as defined by the method. The model parameters for these groups (group areas and volumes and the group interaction parameters for all possible binary pairs of groups) can then be obtained from the specified tables. The procedure also requires the densities of the pure components, both solvents and polymers, and the molecular weights of all components. The number average molecular weights of the polymers are recommended. The method cannot be used to predict the activity coefficients of polymeric species in solution.

The activity coefficient of a solvent in a solution is given by

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^R + \ln \Omega_i^{FV} \qquad (3C\text{-}1)$$

Where:

$\ln \Omega_i$ = the activity coefficient of solvent i at temperature T
$\ln \Omega_i^C$ = the combinatorial contribution to the activity coefficient
$\ln \Omega_i^R$ = the residual contribution to the activity coefficient
$\ln \Omega_i^{FV}$ = the free volume contribution to the activity coefficient
T = temperature of the solution, kelvins

The combinatorial contribution to the activity coefficient, Ω_i^C, is given by the following equation.

$$\ln \Omega_i^C = \ln\frac{\Phi_i}{w_i} + 5q_i \ln \frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i M_i}{w_i} \sum_j \frac{w_j \ell_j}{M_j} \qquad (3C\text{-}2)$$

Where:

i,j = 1,2, ..., m (number of components in the solution)
Φ_i = the molecular volume fraction of component i, given by Equation (3C-3)
w_i = the weight fraction of component i in the polymer solution
q_i = the surface area parameter of component i, given by Equation (3C-7)
θ_i = the molecular area fraction of component i, given by Equation (3C-5)
ℓ_i = a parameter for component i, given by Equation (3C-6)
M_i = molecular weight of component i (number average recommended), kilograms per kilomole

The molecular volume fraction, Φ_i, for each component i is given by

$$\Phi_i = \frac{r_i w_i / M_i}{\sum_j r_j w_j / M_j} \tag{3C-3}$$

Where:

r_i = the volume parameter for component i, given by Equation (3C-4)

$$r_i = \sum_k v_k^{(i)} R_k \tag{3C-4}$$

Where:

$v_k^{(i)}$ = the number of groups of type k in molecule i

R_k = the group volume parameter for group k, given in Table 3C-1

k = 1, 2, ..., n (number of groups in the solution)

The molecular area fraction θ_i for each component i is given by

$$\theta_i = \frac{q_i w_i / M_i}{\sum_j q_j w_j / M_j} \tag{3C-5}$$

The parameter ℓ_i is given by the equation

$$\ell_i = 5(r_i - q_i) - (r_i - 1) \tag{3C-6}$$

The area parameter q_i for each component i is determined by

$$q_i = \sum_k v_k^{(i)} Q_k \tag{3C-7}$$

Where:

Q_k = the group area parameter for group k, given in Table 3C-1

The residual activity contribution to the activity coefficient Ω_i^R for each component is given by

$$\ln \Omega_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{3C-8}$$

Where:

Γ_k = the residual activity coefficient of group k in the defined solution at the given temperature T, given by Equation (3C-9)

$\Gamma_k^{(i)}$ = the residual activity coefficient of group k in a reference solution containing pure component i at the temperature T, given by Equation (3C-9)

The residual activity coefficient of group k in the given solution is given by the following equation

$$\ln \Gamma_k = Q_k \left[1 - \ln\left[\sum_m \theta_m \psi_{mk}\right] - \sum_m \left[\frac{\theta_m \psi_{km}}{\sum_p \theta_p \psi_{pm}} \right] \right] \qquad (3C\text{-}9)$$

Where:

m and p = 1, 2, ..., N (number of groups in the solution)

θ_m = the groups surface area fraction of group m in the given solution, given by Equation (3C-10)

ψ_{mk} = the group interaction parameter for the interaction of group m with group k, given by Equation (3C-12)

The group surface area fraction θ_m for group m is given by

$$\theta_m = \frac{Q_m X_m}{\sum_p Q_p X_p} \qquad (3C\text{-}10)$$

Where:

X_m = mole fraction of group m in the solution, given by Equation (3C-11)

The group mole fraction X_m is calculated from the following equation.

$$X_m = \frac{\sum_j v_m^{(j)} w_j / M_j}{\sum_j w_j / M_j \sum_p v_p^{(j)}} \qquad (3C\text{-}11)$$

Where:

$v_m^{(j)}$ = the number of groups of type m in component j

p = 1, 2, ..., m (number of components in the mixture)

The residual activity coefficient of group k in a reference solution containing only component i, $\Gamma_k^{(i)}$, is similarly determined using Equations (3C-9) through (3C-11) with the exception that the summation indices k, m, and p refer only to the groups present in the pure component and the summations over each component j are calculated only for the single component present in the reference solution.

The group interaction parameter function ψ_{mn} is determined for each possible binary group pair, m and n, by the following equation.

$$\psi_{mn} = \exp(-a_{mn}/T) \qquad (3C\text{-}12)$$

Where:

a_{mn} = the group interaction parameter resulting from the interaction of main groups m and n, given in Table 3C-2, kelvins

The free volume contribution to the activity coefficient Ω_i^{fv} for each component i is given by

$$\ln \Omega_i^{FV} = 3C_i \ln\left[\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}_M^{1/3}-1}\right] - C_i\left[\left(\frac{\tilde{v}_i}{\tilde{v}_M}-1\right)\left(\frac{1}{1-\tilde{v}_i^{1/3}}\right)\right] \qquad (3C\text{-}13)$$

Where:

C_i = an external degree of freedom parameter for solvents = 1.1

$\tilde{v}_i$ = the reduced volume of solvent i, given by Equation (3C-14)

$\tilde{v}_m$ = the reduced volume of the mixture, given by Equation (3C-15)

The reduced volume of solvent i, $\tilde{v}_i$, is given by the following equation.

$$\tilde{v}_i = \frac{v_i M_i}{0.01517 b r_i} \qquad (3C\text{-}14)$$

Where

v_i = specific volume of component i, cubic meters per kilogram

b = proportionality factor = 1.28

The reduced volume of the mixture is calculated from

$$\tilde{v}_m = \frac{\sum_i v_i w_i}{0.01517 b \sum_i \frac{r_i w_i}{M_i}} \qquad (3C\text{-}15)$$

Where

w_i = weight fraction of component i

2. Procedure

Step 1: Determine the specific volume for each pure solvent and polymer in the polymer solution.

Step 2: Determine the molecular weight for each solvent and polymer in the mixture, and calculate the number of repeat groups from the molecular weight of the polymer and the molecular weight of the repeat group.

Step 3: Determine the subgroups, and the main groups to which the subgroups belong, using the molecular structures and the groups given in Table 3C-1.

Step 4: Obtain the group area parameters Q_k, and the group volume parameters R_k, for each group k in the mixture from Table 3C-1.

Step 5: Obtain the interaction parameters, a_{mn}, for every possible binary group pair in the solution from Table 3C-2.

Step 6: Calculate the area and volume parameters, r_i and q_i, for each component using Equations (3C-4) and (3C-7).

Step 7: Calculate ℓ_i for each component i using Equation (3C-6).

Step 8: Calculate the molecular volume fraction, Φ_i, and the molecular surface area fraction, θ_i, for each component i using Equations (3C-3) and (3C-5).

Step 9: Determine the combinatorial contribution to the activity coefficient, Ω_i^c, for each component i using Equation (3C-2).

Step 10: Determine the number of times each group m occurs in each component j, $v_m^{(j)}$, by considering the molecular structure of the components.

Step 11: Calculate the group mole fraction, X_m for each group m in the polymer solution using Equation (3C-11).

Step 12: Calculate the group surface area fraction, θ_m for each group m in the polymer solution using Equation (3C-10).

Step 13: Determine the group interaction parameter function, ψ_{mn}, for every possible binary group pair, corresponding to each group interaction parameter, a_{mn}, obtained in Step 3, using Equation (3C-12).

Step 14: Calculate the residual activity coefficient of each group k in the polymer solution, Γ_k, using Equation (3C-9)

Step 15: Determine the number of occurrences of each type of group m in the reference solution, containing only component i, $v_m^{(i)}$, for each component i.

Step 16: Determine the group mole fraction, X_m, for each group m in the reference solution containing only component i, using Equation (3C-11), for each component i.

Step 17: Calculate the group surface area fraction, θ_m, for each group m in the reference solution containing only component i using Equation (3C-10) for each component.

Step 18: Determine the residual activity coefficient of each group k in the reference solution containing only component i, $\Gamma_k^{(i)}$, using Equation (3C-9), for each component i.

Step 19: Determine the residual contribution to the activity coefficient, Ω_i^R, for each component i using Equation (3C-8).

Step 20: Calculate the reduced volume for each component in the mixture, $\tilde{v}_i$, using Equation (3C-14).

Step 21: Calculate the reduced volume of the mixture, $\tilde{v}_m$, from Equation (3C-15).

Step 22: Calculate the free volume contribution to the activity coefficient, Ω_i^{FV}, from Equation (3C-13).

Step 23: Calculate the activity coefficient, Ω_i, for each component i in the mixture using Equation (3C-1).

3. Limitations and Reliability

The above procedure is used to predict activity coefficients of the solvents in a polymer solution. The method yields fairly accurate predictions. The procedure is less reliable, however, in the dilute regions especially for highly nonideal systems. Such systems are characterized by large infinite dilution activity coefficients. The functional form of the expression for the excess Gibbs energy used in this method is not flexible enough for accurate description of such strongly associating or solvating systems in the dilute regions. Predictions are less accurate for systems containing water and alcohols.

Although Procedure C is a good predictive method, it should not be used as a substitute to reducing good experimental data to obtain activity coefficients. In general, higher accuracy can be obtained from empirical models when these models are used with binary interaction parameters obtained from experimental data.

The combinatorial part of the activity coefficient [Equation (3C-2)] is known as the Staverman-Guggenheim form. This term is intended to account for size and shape effects. The residual contribution accounts for interactions among groups. The Staverman-Guggenheim term has been shown to predict an exaggerated degree of nonideality for systems where the residual contribution is zero (Kikic et al., 1980). Predictions for such systems are expected to be less accurate.

Finally, the method is only applicable in the temperature range of 300-425 K. Extrapolation outside this range is not recommended. The group parameters are not temperature-dependent. Consequently, predicted phase equilibria extrapolate poorly with respect to temperature.

4. Comments

The expression for the combinatorial contribution to the activity coefficient, Ω_i^C, must be modified slightly to calculate activity coefficients at infinite dilution. The ratio of the volume fraction of component i, Φ_i, and the mole fraction x_i can be written as

$$\frac{\Phi_i}{w_i} = \frac{r_i/M_i}{\sum_j r_j w_j/M_j} \qquad (3C\text{-}16)$$

This expression will be finite at infinite dilution of solvent (lim $x_1 \rightarrow 0$). Similarly, the ratio of the molecular surface area fraction, θ_i, and the molecular volume fraction, Φ_i, can be written as

$$\frac{\theta_i}{\phi_i} = \frac{\sum_i r_i w_i/M_i}{\sum_i q_i w_i/M_i} \qquad (3C\text{-}17)$$

This expression will also be finite at infinite dilution.

In some cases mole fraction activity coefficients will be needed. The following expression can be used to calculate mole fraction activity coefficients, γ_i,

$$\ln \gamma_i = \ln \Omega_i + \ln \left[M_i \sum_j \frac{w_j}{M_j} \right] \qquad (3C\text{-}18)$$

5. Literature Sources

The procedure is based on the UNIFAC-Free Volume method developed by T. Oishi and J. M. Prausnitz, "Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method," Ind. Eng. Chem. Process Des. Dev., **17**, 333 (1978). The UNIFAC-FV method is presented by Aa. Fredenslund, J. Gmehling, and P. Rasmussen, **Vapor-Liquid Equilibria Using UNIFAC**, Elsevier Scientific Publishing, New York (1977). The group

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6. Example

Calculate the activity coefficient of (1) cyclohexane in (2) polystyrene (M_n = 49,000) with a weight fraction of cyclohexane of 0.70 (w_1 = 0.70) at 318.15 K.

The specific volume of cyclohexane at 315 K was found to be 1.320×10^{-3} m^3/kg (Daubert and Danner, 1990). The specific volume of polystyrene was reported by Hocker et al. (1971) to be 9.425×10^{-4} m^3/kg.

The molecular weight of the cyclohexane is 84.18 kg/kmol and the number average molecular weight of the polystyrene is given as 49,000 kg/kmol. The molecular weight of the repeat unit (styrene) is 104.2 kg/kmol which gives the number of repeat units to be approximately 470.

Examine the molecular structure of each component and determine the type and number of occurrences of each UNIFAC subgroup:

	Number of Groups Present in Molecule	
	cyclohexane	polystyrene (per repeat unit)
Sub-group	component 1	component 2
CH_2	6	1
ACH	0	5
AC-CH	0	1

Now, the group area parameter, Q_k, and the group volume parameter, R_k, for each group present in the solution are obtained from Table 3C-1

k	Group	R_k	Q_k
1	CH_2	0.6744	0.540
2	ACH	0.5313	0.400
3	ACCH	0.8121	0.348

Determine the UNIFAC interaction parameters, a_{mn}, for each possible binary group pair from Table 3C-2.

a_{11} = 0.0 a_{12} = 61.13 a_{13} = 76.50

a_{21} = -11.12 a_{22} = 0.0 a_{23} = 167.0

$$a_{31} = -69.70 \qquad a_{32} = -146.8 \qquad a_{33} = 0.0$$

Calculate the volume and area parameters, r_i and q_i, for each component i using Equations (3C-4) and (3C-7).

$$r_1 = 6(0.6744) = 4.046$$
$$r_2 = 470(0.6744 + 5(0.5313) + 0.8121) = 1947$$
$$q_1 = 6(0.540) = 3.24$$
$$q_2 = 470(0.540 + 5(0.400) + 0.348) = 1357$$

From Equation (3C-6),

$$\ell_1 = 5(4.046 - 3.24) - (4.046 - 1) = 0.9840$$

$$\ell_2 = 5(1947 - 1357) - (1947 - 1) = 1004$$

Now, the molecular volume fraction, Φ_i, may be calculated for each component i using Equation (3C-3).

$$\Phi_1 = \frac{\frac{(4.046)(0.70)}{84.18}}{\frac{(4.046)(0.70)}{84.18} + \frac{(1947)(0.30)}{49,000}} = 0.738$$

$$\Phi_2 = \frac{\frac{(1947)(0.30)}{49,000}}{\frac{(4.046)(0.70)}{84.18} + \frac{(1947)(0.30)}{49,000}} = 0.262$$

The molecular area fraction, θ_i, is now calculated for each component i using Equation (3C-5).

$$\theta_1 = \frac{\frac{(3.24)(0.70)}{84.18}}{\frac{(3.24)(0.70)}{84.18} + \frac{(1357)(0.30)}{49,000}} = 0.764$$

$$\theta_2 = \frac{\frac{(1357)(0.30)}{49,000}}{\frac{(3.24)(0.70)}{84.18} + \frac{(1357)(0.30)}{49,000}} = 0.236$$

The combinatorial contribution to the activity coefficient Ω_1^C is determined, using Equation (3C-2).

$$\ln \Omega_1^C = \ln \frac{0.738}{0.70} + 5(3.24) \ln \frac{0.764}{0.738} + 0.9840 -$$

$$\frac{0.738\ (84.18)}{0.70} \left[\frac{0.70(0.9840)}{84.18} + \frac{(0.30)(1004)}{49,000} \right] = 0.326$$

Now, considering the number of occurrences of each group m in each component j, $\nu_m^{(j)}$, calculate the group mole fraction, X_m, for each group m in the defined mixture using Equation (3C-11).

$$x_1 = \frac{\frac{0.70}{84.18}(6) + \frac{0.30}{49{,}000}(470)}{\frac{0.70}{84.18}[6+0+0] + \frac{0.30}{49{,}000}[470+5(470)+470]} = 0.7535$$

$$x_2 = \frac{\frac{0.70}{84.18}(0) + \frac{0.30}{49{,}000}5(470)}{\frac{0.70}{84.18}[6+0+0] + \frac{0.30}{49{,}000}[470+5(470)+470]} = 0.2054$$

$$x_3 = \frac{\frac{0.70}{84.18}(0) + \frac{0.30}{49{,}000}(470)}{\frac{0.70}{84.18}[6+0+0] + \frac{0.30}{49{,}000}[470+5(470)+470]} = 0.0411$$

The group surface area fraction, θ_m, is now determined for each group using Equation (3C-10).

$$\theta_1 = \frac{(0.540)(0.7535)}{(0.540)(0.7535) + (0.400)(0.2054) + (0.348)(0.0411)} = \frac{0.4069}{0.5034} = 0.8084$$

$$\theta_2 = \frac{(0.400)(0.2054)}{0.5034} = 0.1632$$

$$\theta_3 = \frac{(0.348)(0.0411)}{0.5034} = 0.0284$$

Now, the group interaction parameter function, ψ_{mn}, for each group pair is obtained using Equation (3C-12).

$$\psi_{12} = \exp\left[-\frac{61.13}{318.15}\right] = 0.825$$

Similarly,

$$\psi_{11} = 1.0 \qquad \psi_{12} = 0.825 \qquad \psi_{13} = 0.786$$
$$\psi_{21} = 1.036 \qquad \psi_{22} = 1.0 \qquad \psi_{23} = 0.592$$
$$\psi_{31} = 1.245 \qquad \psi_{32} = 1.586 \qquad \psi_{33} = 1.0$$

Using Equation (3C-9), the residual activity coefficient of each group k in the defined mixture can be calculated.

$$\ln \Gamma_1 = 540\left[1 - \ln\{(0.8084)(1.0) + (0.1632)(1.036) + (0.0284)(1.245)\}\right.$$

$$- \frac{(0.8084)(1.0)}{(0.8084)(1.0) + (0.1632)(1.036) + (0.0284)(1.245)}$$

$$\left. - \frac{(0.1632)(0.825)}{(0.8084)(0.825) + (0.1632)(1.0) + (0.0284)(1.586)}\right.$$

$$- \frac{(0.0284)(0.786)}{(0.8084)(0.786) + (0.1632)(0.592) + (0.0284)(1.0)}\Bigg]$$

$$\ln \Gamma_1 = 3.183 \times 10^{-3}$$

Similarly,

$$\ln \Gamma_2 = 0.03920$$

$$\ln \Gamma_3 = -0.01849$$

Consider a reference solution containing only component 1

Group	$\nu_m^{(1)}$
1	6
2	0
3	0

Equation (3C-11) is now used to calculate the group mole fraction, X_m, for each group m in the reference solution containing only component 1.

$$X_1^{(1)} = \frac{(6)\frac{1.0}{84.18}}{\frac{1.0}{84.18}(6+0+0)} = 1.0$$

Similarly,

$$X_2^{(1)} = 0.00$$

$$X_3^{(1)} = 0.00$$

Now, the group surface area fraction θ_m for each group m in the reference solution is obtained using Equation (3C-10).

$$\theta_1^{(1)} = \frac{(0.540)(1)}{(0.540)(1) + (0.400)(0) + (0.348)(0)} = 1.0$$

$$\theta_2^{(1)} = 0.00$$

$$\theta_3^{(1)} = 0.00$$

Using Equation (3C-9), the residual activity coefficient of each group k in the reference solution containing only component 1 becomes:

$$\ln \Gamma_1^{(1)} = 0.540 \left[1 - \ln \{(1)(1) + (0)(1.036) + (0)(1.245)\} - \left\{ \frac{(1)(1)}{(1)(1) + (0)(1.036) + (0)(1.245)} + 0 + 0 \right\} \right]$$

$$= 0$$

Similarly,

$$\ln \Gamma_2^{(1)} = 0$$

$$\ln \Gamma_3^{(1)} = 0$$

Now, using Equation (3C-8) the residual contribution to the activity coefficient Ω_1^R becomes:

$$\ln \Omega_1^R = (6)(3.183 \times 10^{-3} - 0) + (0)(0.03920 - 0) + (0)(-0.01849 - 0)$$

$$= 0.0191$$

The free volume contribution is calculated using the reduced volumes of the polymer and the solvent using Equation (3C-14).

$$\tilde{v}_1 = \frac{\left[0.001320 \frac{m^3}{kg}\right]\left[84.18 \frac{kg}{kmol}\right]}{(0.01517)(1.28)(4.0464)} = 1.414$$

$$\tilde{v}_2 = \frac{\left[0.0009425 \frac{m^3}{kg}\right]\left[49{,}000 \frac{kg}{kmol}\right]}{(0.01517)(1.28)(1947)} = 1.2216$$

The reduced volume of the polymer-solvent mixture is calculated using Equation (3C-15).

$$\sum_i \frac{r_i w_i}{M_i} = \frac{(4.046)(0.7)}{84.18} + \frac{(1947)(0.3)}{49000} = 0.04556$$

$$\tilde{v}_m = \frac{(0.001320)(0.7) + (0.0009425)(0.3)}{(0.01517)(1.28)(0.04556)} = 1.3641$$

The free volume contribution to the activity coefficient, Ω_i^{FV}, is found using Equation (3C-13).

$$\ln \Omega_1^{FV} = 3(1.1) \ln \left[\frac{(1.414)^{1/3} - 1}{(1.3641)^{1/3} - 1} \right] - (1.1) \left[\frac{\frac{1.414}{1.3641} - 1}{1 - (1.414)^{-1/3}} \right]$$

$$\ln \Omega_1^{FV} = 0.01247$$

The weight fraction activity coefficient of cyclohexane in polystyrene is found using Equation (3C-1).

$$\ln \Omega_1 = \ln \Omega_1^C + \ln \Omega_1^R + \ln \Omega_1^{FV} = 0.326 + 0.0191 + 0.01247$$

$$\ln \Omega_1 = 0.3576$$

$$\Omega_1 = 1.430$$

An experimental value of 1.425 was reported by Scholte (1970). The UNIFAC-FV computer routine calculates a value of the weight fraction activity coefficient of 1.427.

Table 3C-1. Group Volume and Surface Parameters for Procedure 3C

Main Group	Subgroup	No.	R_k	Q_k	Sample Group Assignment	
1 "CH_2"	CH_3	1	0.9011	0.848		
	CH_2	2	0.6744	0.540	hexane:	2 CH_3, 4 CH_2
	CH	3	0.4469	0.228	2-methylpropane:	3 CH_3, 1 CH
	C	4	0.2195	0.000	2,2-dimethylpropane:	4 CH_3, 1 C
2 "C=C"	CH_2=CH	5	1.3454	1.176	1-hexene:	1 CH_3, 3 CH_2, 1 CH_2=CH
	CH=CH	6	1.1167	0.867	2-hexene:	2 CH_3, 2 CH_2, 1 CH=CH
	CH_2=C	7	1.1173	0.988	2-methyl-1-butene:	2 CH_3, 1 CH_2, 1 CH_2=C
	CH=C	8	0.8886	0.676	2-methyl-2-butene:	3 CH_3, 1 CH=C
	C=C	9	0.6605	0.485	2,3-dimethyl-butene-2:	4 CH_3, 1 C=C
3 "ACH"	ACH	10	0.5313	0.400	benzene:	6 ACH
	AC	11	0.3652	0.120	styrene:	1 CH_2=CH, 5 ACH, 1 AC
4 "$ACCH_2$"	$ACCH_3$	12	1.2663	0.968	toluene:	5 ACH, 1 $ACCH_3$
	$ACCH_2$	13	1.0396	0.660	ethylbenzene:	1 CH_3, 5 ACH, 1 $ACCH_2$
	ACCH	14	0.8121	0.348	cumene:	2 CH_3, 5 ACH, 1 ACCH
5 "OH"	OH	15	1.000	1.200	2-propanol:	2 CH_3, 1 CH, 1 OH
6 "CH_3OH"	CH_3OH	16	1.4311	1.432	methanol:	1 CH_3OH
7 "H_2O"	H_2O	17	0.92	1.40	water:	1 H_2O
8 "ACOH"	ACOH	18	0.8952	0.680	phenol:	5 ACH, 1 ACOH
9 "CH_2CO"	CH_3CO	19	1.6724	1.488	ketone group is 2nd carbon; 2-butanone:	1 CH_3, 1 CH_2, 1 CH_3CO
	CH_2CO	20	1.4457	1.180	ketone group is any other carbon; 3-pentanone:	2 CH_3, 1 CH_2. 1 CH_2CO
10 "CHO"	CHO	21	0.9980	0.948	acetaldehyde:	1 CH_3, 1 CHO
11 "CCOO"	CH_3COO	22	1.9031	1.728	butyl acetate:	1 CH_3, 3 CH_2, 1 CH_3COO
	CH_2COO	23	1.6764	1.420	butyl propanoate:	2 CH_3, 3 CH_2, 1 CH_2COO
12 "HCOO"	HCOO	24	1.2420	1.188	ethyl formate:	1 CH_3, 1 CH_2, 1 HCOO

Table 3C-1 (Continued)

Main Group	Subgroup	No.	R_k	Q_k	Sample Group Assignment	
13 "CH_2O"	CH_3O	25	1.1450	1.088	dimethyl ether:	1 CH_3, 1 CH_3O
	CH_2O	26	0.9183	0.780	diethyl ether:	2 CH_3, 1 CH_2, 1 CH_2O
	CH-O	27	0.6908	0.468	diisopropyl ether:	4 CH_3, 1 CH, 1 CH-O
	FCH_2O	28	0.9183	1.1	tetrahydrofuran:	3 CH_2, 1 FCH_2O
14 "CNH_2"	CH_3NH_2	29	1.5959	1.544	methylamine:	1 CH_3NH_2
	CH_2NH_2	30	1.3692	1.236	propylamine:	1 CH_3, 1 CH_2, 1 CH_2NH_2
	$CHNH_2$	31	1.1417	0.924	isopropylamine:	2 CH_3, 1 $CHNH_2$
15 "CNH"	CH_3NH	32	1.4337	1.244	dimethylamine:	1 CH_3, 1 CH_3NH
	CH_2NH	33	1.2070	0.936	diethylamine:	2 CH_3, 1 CH_2, 1 CH_2NH
	CHNH	34	0.9795	0.624	diisopropylamine:	4 CH_3, 1 CH, 1 CHNH
16 "$(C)_3N$"	CH_3N	35	1.1865	0.940	trimethylamine:	2 CH_3, 1 CH_3N
	CH_2N	36	0.9597	0.632	triethylamine:	3 CH_3, 2 CH_2, 1 CH_2N
17 "$ACNH_2$"	$ACNH_2$	37	1.0600	0.816	aniline:	5 ACH, 1 $ACNH_2$
18 "pyridine"	C_5H_5N	38	2.9993	2.113	pyridine:	1 C_5H_5N
	C_5H_4N	39	2.8332	1.833	3-methylpyridine:	1 CH_3, 1 C_5H_4N
	C_5H_3N	40	2.667	1.553	2,3-dimethylpyridine:	2 CH_3, 1 C_5H_3N
19 "CCN"	CH_3CN	41	1.8701	1.724	acetonitrile:	1 CH_3CN
	CH_2CN	42	1.6434	1.416	propionitrile:	1 CH_3, 1 CH_2CN
20 "COOH"	COOH	43	1.3013	1.224	acetic acid:	1 CH_3, 1 COOH
	HCOOH	44	1.5280	1.532	formic acid:	1 HCOOH
21 "CCl"	CH_2Cl	45	1.4654	1.264	1-chlorobutane:	1 CH_3, 2 CH_2, 1 CH_2Cl
	CHCl	46	1.2380	0.952	2-chloropropane:	2 CH_3, 1 CHCl
	CCl	47	1.0060	0.724	2-chloro-2-methylpropane:	3 CH_3, 1 CCl
22 "CCl_2"	CH_2Cl_2	48	2.2564	1.988	dichloromethane:	1 CH_2Cl_2
	$CHCl_2$	49	2.0606	1.684	1,1-dichloroethane:	1 CH_3, 1 $CHCl_2$
	CCl_2	50	1.8016	1.448	2,2-dichloropropane:	2 CH_3, 1 CCl_2
23 "CCl_3"	$CHCl_3$	51	2.8700	2.410	chloroform:	1 $CHCl_3$
	CCl_3	52	2.6401	2.184	1,1,1-trichloroethane:	1 CH_3, 1 CCl_3
24 "CCl_4"	CCl_4	53	3.3900	2.910	tetrachloromethane:	1 CCl_4
25 "ACCl"	ACCl	54	1.1562	0.844	chlorobenzene:	5 ACH, 1 ACCl

Table 3C-1 (Continued)

Main Group	Subgroup	No.	R_k	Q_k	Sample Group Assignment	
26 "CNO_2"	CH_3NO_2	55	2.0086	1.868	nitromethane:	1 CH_3NO_2
	CH_2NO_2	56	1.7818	1.560	1-nitropropane:	1 CH_3, 1 CH_2, 1 CH_2NO_2
	$CHNO_2$	57	1.5544	1.248	2-nitropropane:	2 CH_3, 1 $CHNO_2$
27 "$ACNO_2$"	$ACNO_2$	58	1.4199	1.104	nitrobenzene:	5 ACH, 1 $ACNO_2$
28 "CS_2"	CS_2	59	2.057	1.65	carbon disulfide:	1 CS_2
29 "CH_3SH"	CH_3SH	60	1.8770	1.676	methanethiol:	1 CH_3SH
	CH_2SH	61	1.6510	1.368	ethanethiol:	1 CH_3, 1 CH_2SH
30 "furfural"	furfural	62	3.1680	2.481	furfural:	1 furfural
31 "DOH"	$(CH_2OH)_2$	63	2.4088	2.248	1,2-ethanediol:	1 $(CH_2OH)_2$
32 "I"	I	64	1.2640	0.992	1-iodoethane:	1 CH_3, 1 CH_2, 1 I
33 "Br"	Br	65	0.9492	0.832	1-bromoethane:	1 CH_3, 1 CH_2, 1 Br
34 "C≡C"	CH≡C	66	1.2920	1.088	1-hexyne:	1 CH_3, 3 CH_2, 1 CH≡C
	C≡C	67	1.0613	0.784	2-hexyne:	2 CH_3, 2 CH_2, 1 C≡C
35 "Me_2SO"	Me_2SO	68	2.8266	2.472	dimethyl sulfoxide:	1 Me_2SO
36 "ACRY"	ACRY	69	2.3144	2.052	acrylonitrile:	1 ACRY
37 "ClCC"	Cl(C=C)	70	0.7910	0.724	trichloroethylene:	1 CH=C, 3 Cl(C=C)
38 "ACF"	ACF	71	0.6948	0.524	hexafluorobenzene:	6 ACF
39 "DMF"	DMF-1	72	3.0856	2.736	dimethylformamide:	1 DMF-1
	DMF-2	73	2.6322	2.120	diethylformamide:	2 CH_3, 1 DMF-2
40 "CF_2"	CF_3	74	1.4060	1.380	perfluorohexane:	2 CF_3, 4 CF_2
	CF_2	75	1.0105	0.920		
	CF	76	0.6150	0.460	perfluoromethyl-cyclohexane:	1 CH_3, 5 CH_2, 1 CF

Table 3C-1 (Continued)

Main Group	Subgroup	No.	R_k	Q_k	Sample Group Assignment	
41* "COO"	COO	77	1.380	1.200	methyl benzoate:	1 CH_3, 1 COO, 1 AC, 5 ACH
42	SiH_3	78	1.6035	1.2632	methylsilane:	1 CH_3, 1 SiH_3
"SiH_2"	SiH_2	79	1.4443	1.0063	diethylsilane:	2 CH_3, 2 CH_2, 1 SiH_2
	SiH	80	1.2853	0.7494	heptamethyl-trisiloxane:	7 CH_3, 2 SiO, 1 SiH
	Si	81	1.0470	0.4099	hexamethyl-disiloxane:	6 CH_3, 1 SiO, 1 Si
43	SiH_2O	82	1.4838	1.0621	1,3-dimethyldisiloxane:	2 CH_3, 1 SiH_2O, 1 SiH_2
"SiO"	SiHO	83	1.3030	0.7639	1,1,3,3-tetramethyl-disiloxane:	4 CH_3, 1 SiHO, 1 SiH
	SiO	84	1.1044	0.4657	octamethylcyclo-tetrasiloxane:	8 CH_3, 4 SiO
44 "NMP"	NMP	85	3.9810	3.2000	N-methylpyrrolidone:	1 NMP

*Use of Group 41 "COO" is recommended only if it is not possible to use Group 11 "CCOO" or Group 12 "HCOO".

Table 3C-2. Group Interaction Parameters for Procedure 3C

	1	2	3	4	5	6	7	8
1 $CH_20.0$	86.02	61.13	76.50	986.5	697.2	1318.0	1333.0	
2 C=C	35.36	0.0	38.81	74.15	524.1	787.6	270.6	526.1
3 ACH	-11.12	3.446	0.0	167.0	636.1	637.3	903.8	1329.0
4 $ACCH_2$	-69.70	-113.6	-146.8	0.0	803.2	603.2	5695.0	884.9
5 OH	156.4	457.0	89.60	25.82	0.0	-137.1	353.5	-259.7
6 CH_3OH	16.51	-12.52	-50.00	-44.50	249.1	0.0	-181.0	-101.7
7 H_2O	300.0	496.1	362.3	377.6	-229.1	289.6	0.0	324.5
8 ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	0.0
9 CH_2CO	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1
10 CHO	505.7	56.30	23.39	106.0	-404.8	-340.2	232.7	-
11 CCOO	114.8	132.1	85.84	-170.0	245.4	249.6	200.8	-36.72
12 HCOO	90.49	-62.55	1967.0	2347.0	191.2	155.7	-	-
13 CH_2O	83.36	26.51	52.13	65.69	237.7	238.4	-314.7	-
14 CNH_2	-30.48	1.163	-44.85	-	-164.0	-481.7	-330.4	-
15 CNH	65.33	-28.70	-22.31	223.0	-150.0	-500.4	-448.2	-
16 $(C)_3N$	-83.98	-25.38	-223.9	109.9	28.60	-406.8	-598.8	-
17 $ACNH_2$	1139.0	2000.0	247.5	762.8	-17.40	-118.1	-367.8	-253.1
18 pyridine	-101.6	-	31.87	49.80	-132.3	-378.2	-332.9	-341.6
19 CCN	24.82	-40.62	-22.97	-138.4	185.4	157.8	242.8	-
20 COOH	315.3	1264.0	62.32	268.2	-151.0	1020.0	-66.17	-
21 CCl	91.46	97.51	4.680	122.9	562.2	529.0	698.2	-
22 CCl_2	34.01	18.25	121.3	140.8	747.7	669.9	708.7	-
23 CCl_3	36.70	51.06	288.5	33.61	742.1	649.1	826.7	-
24 CCl_4	-78.45	160.9	-4.700	134.7	856.3	860.1	1201.0	10000.
25 ACCl	-141.3	-158.8	-237.7	375.5	246.9	661.6	920.4	-
26 CNO_2	-32.69	-1.996	10.38	-97.05	261.6	252.6	417.9	-
27 $ACNO_2$	5541.0	-	1824.0	-127.8	561.6	-	360.7	-
28 CS_2	-52.65	16.62	21.50	40.68	823.5	914.2	1081.0	-
29 CH_3SH	-7.481	-	28.41	-	461.6	382.8	-	-
30 furfural	-25.31	-	157.3	404.3	521.6	-	23.48	-
31 DOH	140.0	-	221.4	150.6	267.6	-	0.0	838.4
32 I	128.0	-	58.68	-	501.3	-	-	-
33 Br	-31.52	-	155.6	291.1	721.9	494.7	-	-
34 C≡C	-72.88	41.38	-	-	-	-	-	-
35 Me_2SO	50.49	422.4	-2.504	-143.2	-25.87	695.0	-240.0	-
36 ACRY	-165.9	-	-	-	-	-	386.6	-
37 ClCC	47.41	124.2	395.8	-	738.9	528.0	-	-
38 ACF	-5.132	-	-237.2	-157.3	649.7	645.9	-	-
39 DMF	-31.95	249.0	-133.9	-240.2	64.16	172.2	-287.1	-
40 CF_2	147.3	-	-	-	-	-	-	-
41 COO	529.0	1397.0	317.6	615.8	88.63	171.0	284.4	-167.3
42 SiH_2	-34.36	-	787.9	-	1913.0	-	-	-
43 SiO	110.2	-	234.4	-	-	-	-	-
44 NMP	13.89	-	-23.88	6.214	796.9	-	832.2	-

Table 3C-2 (Continued)

	9	10	11	12	13	14	15	16
1 CH_2	476.4	677.0	232.1	741.4	251.5	391.5	255.7	206.6
2 C=C	182.6	448.8	37.85	449.1	214.5	240.9	163.9	61.11
3 ACH	25.77	347.3	5.994	-92.55	32.14	161.7	122.8	90.49
4 $ACCH_2$	-52.10	586.6	5688.0	115.2	213.1	-	-49.29	23.50
5 OH	84.00	441.8	101.1	193.1	28.06	83.02	42.70	-323.0
6 CH_3OH	23.39	306.4	-10.72	193.4	-128.6	359.3	266.0	53.90
7 H_2O	-195.4	-257.3	72.87	-	540.5	48.89	168.0	304.0
8 ACOH	-356.1	-	-449.4	-	-	-	-	-
9 CH_2CO	0.0	-37.36	-213.7	-38.47	-103.6	-	-	-169.0
10 CHO	128.0	0.0	-110.3	11.31	304.1	-	-	-
11 CCOO	372.2	185.1	0.0	372.9	-235.7	-	-73.50	-
12 HCOO	70.42	35.35	-261.1	0.0	-	-	-	-
13 CH_2O	191.1	-7.838	461.3	-	0.0	-	141.7	-
14 CNH_2	-	-	-	-	-	0.0	63.72	-41.11
15 CNH	-	-	136.0	-	-49.30	108.8	0.0	-189.2
16 $(C)_3N$	225.3	-	-	-	-	38.89	865.9	0.0
17 $ACNH_2$	-450.3	-	-294.8	-	-	-15.07	-	-
18 pyridine	-51.54	-	-	-	-	-	-	-
19 CCN	-287.5	-	-266.6	-	38.81	-	-	-
20 COOH	-297.8	-	-256.3	312.5	-338.5	-	-	-
21 CCl	286.3	-47.51	35.38	-	225.4	-	-	-
22 CCl_2	423.2	-	-132.9	-	-197.7	-	-	-141.4
23 CCl_3	552.1	242.8	176.5	488.9	-20.93	-	-	-293.7
24 CCl_4	372.0	-	129.5	403.1	113.9	261.1	91.13	-126.0
25 ACCl	128.1	-	-246.3	-	95.50	203.5	-108.4	1088.0
26 CNO_2	-142.6	-	129.3	-	-94.49	-	-	-
27 $ACNO_2$	-	-	-	-	-	-	-	-
28 CS_2	303.7	-	243.8	-	112.4	-	-	-
29 CH_3SH	160.6	-	-	239.8	63.71	106.7	-	-
30 furfural	317.5	-	-146.3	-	-	-	-	-
31 DOH	-	-	152.0	-	9.207	-	-	-
32 I	138.0	-	21.92	-	476.6	-	-	-
33 Br	-142.6	-	24.37	-	736.4	-	-	-
34 C≡C	443.6	-	-	-	-	-	-	-
35 Me_2SO	110.4	-	41.57	-	-122.1	-	-	-
36 ACRY	-	-	175.5	-	-	-	-	-
37 ClCC	-40.90	-	16.99	-	-217.9	-	-	-
38 ACF	-	-	-	-	167.1	-	-	116.5
39 DMF	97.04	-	-	-	-158.2	-	-	-
40 CF_2	-	-	-	-	-	-	-	-
41 COO	-123.4	-	-234.9	65.37	-247.8	-	284.5	-
42 SiH_2	992.4	-	-	-	-	-	-	-
43 SiO	-	-	-	-	-	-	-	-
44 NMP	-	-	-	-	-	-	-	-

Table 3C-2 (Continued)

	17	18	19	20	21	22	23	24
1 CH_2	920.7	287.7	597.0	663.5	35.93	53.76	24.90	104.3
2 C=C	749.3	-	336.9	318.9	204.6	5.892	-13.99	-109.7
3 ACH	648.2	-4.449	212.5	537.4	-18.81	-144.4	-231.9	3.000
4 $ACCH_2$	664.2	52.80	6096.0	603.8	-114.1	-111.0	-12.14	-141.3
5 OH	-52.39	170.0	6.712	199.0	75.62	-112.1	-98.12	143.1
6 CH_3OH	489.7	580.5	36.23	-289.5	-38.32	-102.5	-139.4	-67.80
7 H_2O	-52.29	459.0	112.6	-14.09	325.4	370.4	353.7	497.5
8 ACOH	119.9	-305.5	-	-	-	-	-	1827.0
9 CH_2CO	6201.0	165.1	481.7	669.4	-191.7	-284.0	-354.6	-39.20
10 CHO	-	-	-	-	751.9	-	-483.7	-
11 CCOO	475.5	-	494.6	660.2	-34.74	108.9	-209.7	54.47
12 HCOO	-	-	-	-356.3	-	-	-287.2	36.84
13 CH_2O	-	-	-18.51	664.6	301.1	137.8	-154.3	47.67
14 CNH_2	-200.7	-	-	-	-	-	-	-99.81
15 CNH	-	-	-	-	-	-	-	71.23
16 $(C)_3N$	-	-	-	-	-	-73.85	-352.9	-8.283
17 $ACNH_2$	0.0	-	-281.6	-	287.0	-	-	882.0
18 pyridine	-	0.0	-169.7	-153.7	-	-351.6	-114.7	-165.1
19 CCN	777.4	134.3	0.0	-	88.75	-152.7	-15.62	-54.86
20 COOH	-	-313.5	-	0.0	44.42	-183.4	76.75	212.7
21 CCl	429.7	-	-62.41	326.4	0.0	108.3	249.2	62.42
22 CCl_2	-	587.3	258.6	1821.0	-84.53	0.0	0.0	56.33
23 CCl_3	-	18.98	74.04	1346.0	-157.1	0.0	0.0	-30.10
24 CCl_4	898.2	309.2	492.0	689.0	11.80	17.97	51.90	0.0
25 ACCl	530.5	-	356.9	-	-314.9	-	-	-255.4
26 CNO_2	-	-	0.2827	-	113.0	-	-	-34.68
27 $ACNO_2$	134.9	-	-	-	-	-	-	514.6
28 CS_2	-	-	335.7	-	-73.09	-	-26.06	-60.71
29 CH_3SH	-	-	125.7	-	-27.94	-	-	-
30 furfural	-	-	-	-	-	-	48.48	-133.1
31 DOH	255.4	-	-	-	-	-	-	-
32 I	-	-	-	-	-	-40.82	21.76	48.49
33 Br	-	-	-	5256.0	1169.0	-	-	225.8
34 C≡C	-	-	329.1	-	-	-	-	-
35 Me_2SO	-	-	-	-	-	-215.0	-343.6	-58.43
36 ACRY	-	-	-42.31	-	-	-	-	-85.15
37 ClCC	-	-	304.0	898.2	428.5	-	-149.8	-134.2
38 ACF	-	-	-	-	-	-	-	-124.6
39 DMF	343.7	-	-	-	-	-	-	-186.7
40 CF_2	-	-	-	-	-	-	-	-
41 COO	-22.10	-	-61.60	1179.0	182.2	305.4	-193.0	335.7
42 SiH_2	-	-	-	-	-	-	-	-
43 SiO	-	-	-	-	-	-	-	70.81
44 NMP	-	-	-	-	-	-	-	-

Table 3C-2 (Continued)

	25	26	27	28	29	30	31	32
1 CH_2	321.5	661.5	543.0	153.6	184.4	354.5	3025.0	335.8
2 C=C	393.1	357.5	-	76.30	-	-	-	-
3 ACH	538.2	168.0	194.9	52.07	-10.43	-64.69	210.4	113.3
4 $ACCH_2$	-126.9	3629.0	4448.0	-9.451	-	-20.36	4975.0	-
5 OH	287.8	256.5	157.1	477.0	147.5	-120.5	-318.9	313.5
6 CH_3OH	17.12	75.14	-	-31.09	37.84	-	-	-
7 H_2O	678.2	220.6	399.5	887.1	-	188.0	0.0	-
8 ACOH	-	-	-	-	-	-	-687.1	-
9 CH_2CO	174.5	137.5	-	216.1	-46.28	-163.7	-	53.59
10 CHO	-	-	-	-	-	-	-	-
11 CCOO	629.0	-81.13	-	183.0	-	202.3	-101.7	148.3
12 HCOO	-	-	-	-	4.339	-	-	-
13 CH_2O	66.15	95.18	-	140.9	-8.538	-	-20.11	-149.5
14 CNH_2	68.81	-	-	-	-70.14	-	-	-
15 CNH	4350.0	-	-	-	-	-	-	-
16 $(C)_3N$	-86.36	-	-	-	-	-	-	-
17 $ACNH_2$	287.9	-	-139.3	-	-	-	-136.9	-
18 pyridine	-	-	-	-	-	-	-	-
19 CCN	52.31	-0.5150	-	230.9	21.37	-	-	-
20 COOH	-	-	-	-	-	-	-	-
21 CCl	464.4	32.73	-	450.1	59.02	-	-	-
22 CCl_2	-	-	-	-	-	-	-	177.6
23 CCl_3	-	-	-	116.6	-	-64.38	-	86.40
24 CCl_4	475.8	490.9	534.7	132.2	-	546.7	-	247.8
25 ACCl	0.0	-154.5	-	-	-	-	-	-
26 CNO_2	794.4	0.0	533.2	-	-	-	139.8	304.3
27 $ACNO_2$	-	-85.12	0.0	-	-	-	-	-
28 CS_2	-	-	-	0.0	-	-	-	-
29 CH_3SH	-	-	-	-	0.0	-	-	-
30 furfural	-	-	-	-	-	0.0	-	-
31 DOH	-	481.3	-	-	-	-	0.0	-
32 I	-	64.28	-	-	-	-	-	0.0
33 Br	224.0	125.3	-	-	-	-	-	-
34 C≡C	-	174.4	-	-	-	-	-	-
35 Me_2SO	-	-	-	-	85.70	-	535.8	-
36 ACRY	-	-	-	-	-	-	-	-
37 ClCC	-	379.4	-	167.9	-	-	-	-
38 ACF	-	-	-	-	-	-	-	-
39 DMF	-	-	-	-	-71.00	-	-191.7	-
40 CF_2	-	-	-	-	-	-	-	-
41 COO	1107.0	-124.7	-	885.5	-	-	-	288.1
42 SiH_2	-	-	-	-	-	-	-	-
43 SiO	-	-	-	-	-	-	-	-
44 NMP	-	-	-	-	-	-	-	-

Table 3C-2 (Continued)

	33	34	35	36	37	38	39	40
1 CH_2	479.5	298.9	526.5	689.0	-4.189	125.8	485.3	-2.859
2 C=C	-	31.14	-137.4	-	-66.46	-	-70.45	-
3 ACH	-13.59	-	169.9	-	-259.1	389.3	245.6	-
4 $ACCH_2$	-171.3	-	4284.0	-	-	101.4	5629.0	-
5 OH	133.4	-	-202.1	-	225.8	44.78	-143.9	-
6 CH_3OH	106.3	-	-399.3	-	33.47	-48.25	-172.4	-
7 H_2O	-	-	-139.0	160.8	-	-	319.0	-
8 ACOH	-	-	-	-	-	-	-	-
9 CH_2CO	245.2	-246.6	-44.58	-	-34.57	-	-61.70	-
10 CHO	-	-	-	-	-	-	-	-
11 CCOO	18.88	-	52.08	-28.61	-83.30	-	-	-
12 HCOO	-	-	-	-	-	-	-	-
13 CH_2O	-202.3	-	172.1	-	240.2	-273.9	254.8	-
14 CNH_2	-	-	-	-	-	-	-	-
15 CNH	-	-	-	-	-	-	-	-
16 $(C)_3N$	-	-	-	-	-	-196.3	-	-
17 $ACNH_2$	-	-	-	-	-	-	-334.4	-
18 pyridine	-	-	-	-	-	-	-	-
19 CCN	-	-203.0	-	81.57	3.509	-	-	-
20 COOH	-95.0	-	-	-	-11.16	-	-	-
21 CCl	-125.9	-	-	-	-245.4	-	-	-
22 CCl_2	-	-	215.0	-	-	-	-	-
23 CCl_3	-	-	363.7	-	111.2	-	-	-
24 CCl_4	41.94	-	337.7	369.5	187.1	215.2	498.6	-
25 ACCl	-60.70	-	-	-	-	-	-	-
26 CNO_2	10.17	-27.70	-	-	10.76	-	-	-
27 $ACNO_2$	-	-	-	-	-	-	-	-
28 CS_2	-	-	-	-	-47.37	-	-	-
29 CH_3SH	-	-	31.66	-	-	-	78.92	-
30 furfural	-	-	-	-	-	-	-	-
31 DOH	-	-	-417.2	-	-	-	302.2	-
32 I	-	-	-	-	-	-	-	-
33 Br	0.0	-	-	-	-	-	-	-
34 C≡C	-	0.0	-	-	-	-	-119.8	-
35 Me_2SO	-	-	0.0	-	-	-	-97.71	-
36 ACRY	-	-	-	0.0	-	-	-	-
37 ClCC	-	-	-	-	0.0	-	-	-
38 ACF	-	-	-	-	-	0.0	-	-117.2
39 DMF	-	6.699	136.6	-	-	-	0.0	-
40 CF_2	-	-	-	-	-	185.6	-	0.0
41 COO	-	-	-29.34	-53.91	-198.0	-	-	-
42 SiH_2	-	-	-	-	-	-	-	-
43 SiO	-	-	-	-	-	-	-	-
44 NMP	-	-	-	-	-	-	-	-

Table 3C-2 (Continued)

		41	42	43	44
1	CH_2	387.1	-450.4	252.7	220.3
2	C=C	48.33	-	-	-
3	ACH	103.5	-432.3	238.9	30.04
4	$ACCH_2$	69.26	-	-	46.38
5	OH	190.3	-817.7	-	-504.2
6	CH_3OH	165.7	-	-	-
7	H_2O	-197.5	-	-	-452.2
8	ACOH	-494.2	-	-	-
9	CH_2CO	-18.80	-588.9	-	-
10	CHO	-	-	-	-
11	CCOO	560.2	-	-	-
12	HCOO	-70.24	-	-	-
13	CH_2O	417.0	-	-	-
14	CNH_2	-	-	-	-
15	CNH	-38.77	-	-	-
16	$(C)_3N$	-	-	-	-
17	$ACNH_2$	-89.42	-	-	-
18	pyridine	-	-	-	-
19	CCN	120.3	-	-	-
20	COOH	-337.0	-	-	-
21	CCl	63.67	-	-	-
22	CCl_2	-96.87	-	-	-
23	CCl_3	255.8	-	-	-
24	CCl_4	256.5	-	233.1	-
25	ACCl	-145.1	-	-	-
26	CNO_2	248.4	-	-	-
27	$ACNO_2$	-	-	-	-
28	CS_2	469.8	-	-	-
29	CH_3SH	-	-	-	-
30	furfural	-	-	-	-
31	DOH	-	-	-	-
32	I	68.55	-	-	-
33	Br	-	-	-	-
34	C≡C	-	-	-	-
35	Me_2SO	153.7	-	-	-
36	ACRY	423.4	-	-	-
37	CICC	730.8	-	-	-
38	ACF	-	-	-	-
39	DMF	-	-	-	-
40	CF_2	-	-	-	-
41	COO	0.0	-	-	-
42	SiH_2	-	0.0	-2166.0	-
43	SiO	-	745.3	0.0	-
44	NMP	-	-	-	0.0

Note: "-" indicates parameter not available.

PROCEDURE D: CHEN-FREDENSLUND-RASMUSSEN EQUATION OF STATE FOR ESTIMATING THE ACTIVITY COEFFICIENTS OF SOLVENTS IN POLYMER SOLUTIONS

1. Method

This method is to be used to predict the activity coefficient of a low molecular weight component i in a defined liquid mixture containing one or more solvents in a solution with one or more polymers. This procedure requires the structure of all components in the mixture, group areas and volumes for all groups in the solution, contributions for the degree of freedom parameter, and the group interaction parameters for all possible binary pairs of groups. The number average molecular weights of the polymers are recommended.

The activity coefficient of a solvent in a solution is given by the following equation:

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^{INT} + \ln \Omega_i^{FV} \qquad (3D\text{-}1)$$

Where:

Ω_i = the weight fraction activity coefficient of component i

Ω_i^C = the combinatorial contribution to the weight fraction activity coefficient, given by Equation (3D-2).

Ω_i^{INT} = the interaction or enthalpic contribution to the weight fraction activity coefficient, given by Equation (3D-4).

Ω_i^{FV} = the free volume contribution to the weight fraction activity coefficient, given by Equation (3D-3).

The combinatorial contribution to the activity coefficient, Ω_i^C, is given by the following equation.

$$\ln \Omega_i^C = \ln \frac{\phi_i}{w_i} + 1 - \frac{\phi_i}{x_i} \qquad (3D\text{-}2)$$

Where:

ϕ_i = the molecular volume fraction of component i, given by Equation (3D-16).

x_i = the mole fraction of component i.

w_i = the weight fraction of component i.

The free volume contribution to the weight fraction activity coefficient, Ω_i^{FV}, is given by the following equation.

$$\ln \Omega_i^{FV} = 3(1+C_i) \ln \frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1} - 3C_i \ln \frac{\tilde{v}_i^{1/3}}{\tilde{v}^{1/3}} \qquad (3D\text{-}3)$$

Where:

C_i = the number of external degrees of freedom associated with component i, given by Equation (3D-13)

$\tilde{v}_i$ = the reduced volume of pure component i determined from the equation of state, Equation (3D-5), at the temperature and pressure of the mixture. In this case set $\tilde{v}_i = \tilde{v}$ in Equation (3D-5)

$\tilde{v}$ = the reduced volume of polymer solution mixture determined from the equation of state, Equation (3D-5), at the temperature and pressure of the mixture.

The enthalpic contribution to the activity coefficient, Ω_i^{INT}, is calculated from the following expression.

$$\ln \Omega_i^{INT} = z/2\ q_i \left[\frac{1}{RT}(\epsilon_{ii}(\tilde{v}) - \epsilon_{ii}(\tilde{v}_i)) + 1 - \ln\left[\sum_j \theta_j \exp -\frac{\Delta\epsilon_{ji} - \Delta S_{ji}^{HB}}{RT}\right] - \sum_j \frac{\theta_j \exp\left(-(\Delta\epsilon_{ij} - T\Delta S_{ij}^{HB})/RT\right)}{\sum_k \theta_k \exp\left(-(\Delta\epsilon_{kj} - T\Delta S_{kj}^{HB})/RT\right)}\right] \quad (3D\text{-}4)$$

The volumes of the pure component [$\tilde{v}_i = \tilde{v}$ in Equation (3D-5)] and the mixture, $\tilde{v}$, are determined from the equation of state. The volumes are determined by solving the following equation.

$$P = \frac{NRT}{V}\left[\frac{\tilde{v}^{1/3} + \sum x_i C_i}{\tilde{v}^{1/3} - 1}\right] + \frac{E}{V} \quad (3D\text{-}5)$$

Where:

P = pressure of the system, pascals.

N = total number of moles in the system, kilomoles.

R = gas constant, 8314 J $kmol^{-1}$ K^{-1}

E = energy parameter, given by Equation (3D-6), joules.

Equation (3D-5) can be applied to all pressures and temperatures, but for determining the activity coefficients of solvents in the liquid phase of a polymer solution Equation (3D-5) can be simplified by solving for the volume roots at zero pressure instead of the pressure of the system.

The energy parameter, E, is given by:

$$E = \sum_i \frac{1}{2} z q_i N_i \left[\epsilon_{ii} + \frac{\sum_j \theta_j \exp(-(\Delta\epsilon_{ji} - T\Delta S_{ji}^{HB})/RT)\Delta\epsilon_{ji}}{\sum_k \theta_k \exp(-(\Delta\epsilon_{ki} - T\Delta S_{ki}^{HB}/RT)}\right] - 3R \ln\left[\frac{\tilde{v}^{1/3} - 1}{\tilde{V}^{1/3}}\right]\left[\sum_i N_i \sum_k v_k^{(i)} C_{T,k}\right] \quad (3D\text{-}6)$$

Where:

z = 10 (coordination number).

q_i = surface area of component i, given by Equation (3D-15)

N_i = number of moles of component i, kilomoles.
θ_j = surface area fraction of component j, given by Equation (3D-14)
$\Delta\epsilon_{ji}$ = interaction energy parameter, given by Equation (3D-9), joules per kilomole of contact sites.
ΔS^{HB}_{ji} = hydrogen bonding interaction parameter, given by Equation (3D-7), joules per kilomole-kelvin of contact sites.
$v_m(i)$ = the number of groups of type m in component i
$C_{T,k}$ = degree of freedom parameter, given in Table 3D-1.

The hydrogen bonding contribution to the interaction parameter, ΔS_{ji}^{HB}, is given by the equation

$$\Delta S_{ji}^{HB} = \sum_m \theta_m^{(i)} \sum_n \left(\theta_n^{(j)} - \theta_n^{(i)}\right) \Delta S_{nm}^{HB} \qquad (3D\text{-}7)$$

Where

$$\theta_n^{(i)} = \frac{v_n^{(i)} Q_n}{\sum_m v_m^{(i)} Q_m} \qquad (3D\text{-}8)$$

ΔS_{hm}^{HB} is a parameter that takes into account additional interaction associated with hydrogen bonding between groups. These group contributions are given as the bottom entries along the right hand side and bottom of Table 3D-2. The matrix of ΔS_{hm}^{HB} is not symmetric; i.e., $\Delta S_{hm}^{HB} \neq \Delta S_{mn}^{HB}$. The group contribution values must be selected carefully.

The interaction energy parameter $\Delta\epsilon_{ji}$ is given by

$$\Delta\epsilon_{ji} = \epsilon_{ji} - \epsilon_{ii} \qquad (3D\text{-}9)$$

The contribution to the interaction energy from random configurations, ϵ_{ji}, is calculated from

$$\epsilon_{ji} = \sum_m \sum_n \frac{\theta_m^{(i)} \theta_n^{(j)} \epsilon_{mn}}{\tilde{v}} \qquad (3D\text{-}10)$$

Where:

$$\epsilon_{mn} = -\left[\epsilon_{mm}\ \epsilon_{nn}\right]^{1/2} + \Delta\epsilon_{mn} \qquad (3D\text{-}11)$$

ϵ_{mm} = interaction energies between like groups m, given as the diagonal elements in Table 3D-2, joules per kilomole of interaction sites.
$\Delta\epsilon_{km}$ = interaction energies between unlike groups k and m, given as the off diagonal elements in Table 3D-2, joules per kilomole of interaction sites.

The reduced volume of the mixture is calculated from

$$\tilde{v} = \frac{V}{\sum_i x_i V_i^*} \qquad (3D\text{-}12)$$

Where:

V_i^* = the hard core volume of component i, given by Equation (3D-17), cubic meters per kilomole.

V = the molar volume of the system, cubic meters per kilomole.

The number of external degrees of freedom in component i, C_i, is given by

$$C_i = \sum_k v_k^{(i)} \left[C_{T_o,k} + C_{T,k}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] + \sum_k \frac{R_k}{\sum_m R_m} C_k^o \qquad (3D\text{-}13)$$

Where:

$C_{To,k}$ = degree of freedom parameter, given in Table 3D-1.

$C_{T,k}$ = degree of freedom parameter, given in Table 3D-1.

C_k^o = degree of freedom parameter, given in Table 3D-1.

T = temperature of polymer solution, kelvins.

T_o = 298.15 K (reference temperature)

The surface area fraction of component i, θ_i, is given by the following equation

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad (3D\text{-}14)$$

The surface area of component i, q_i, is given by the following equation.

$$q_i = \sum_m v_m^{(i)} Q_m \qquad (3D\text{-}15)$$

Where:

Q_m = the surface area of group m, given in Table 3D-1.

The molecular volume fraction of component i is given by

$$\phi_i = \frac{x_i V_i^*}{\sum_j x_j V_j^*} \qquad (3D\text{-}16)$$

The hard core volume of component i is given by

$$V_i^* = 21.9662 \sum_m v_m^{(i)} R_m \qquad (3D\text{-}17)$$

Where:

R_m = the hard core volume of group m, given in Table 3D-1.

2. Procedure

Step 1: Determine the subgroups, and the main groups the subgroups belong to, by considering the molecular structure of each compound and the groups given in Table 3D-1.

Step 2: Obtain the group area parameters, Q_k, and the group volume parameters, R_k, for each group k in the polymer solution from Table 3D-1.

Step 3: Determine the number of occurrences of each type of group m in each component i, $v_m^{(i)}$, by considering the molecular structure of the components.

Step 4: Calculate the hard core volume, V_i^*, of each component i from Equation (3D-17).

Step 5: Calculate the molecular volume fraction of each component i, ϕ_i, from Equation (3D-16).

Step 6: Calculate the molecular surface area, q_i, for each component i using Equation (3D-15).

Step 7: Calculate the molecular surface area fraction, θ_i, for each component i using Equation (3D-14).

Step 8: Obtain the external degree of freedom parameters, $C_{To,k}$, $C_{T,k}$, and C_k^o, for each group k from Table 3D-1.

Step 9: Calculate the external degree of freedom parameter for each component, C_i, using Equation (3D-13).

Step 10: Guess a value for the molar volume of the system, V.

Step 11: Calculate the reduced volume of the system using Equation (3D-12).

Step 12: Obtain the like group interaction energy parameters, ϵ_{mm}, and the unlike group interaction energy correction, $\Delta\epsilon_{mn}$, from Table 3D-2.

Step 13: Calculate the group-group interaction energies, ϵ_{mn}, for like and unlike pairs using Equation (3D-11).

Step 14: Calculate the molecular interaction energies, ϵ_{ji}, using Equation (3D-10).

Step 15: Calculate the interaction energy parameter, $\Delta\epsilon_{ji}$, using Equation (3D-9).

Step 16: Calculate the surface area fraction of group n in molecule i, $\theta_n^{(i)}$, from Equation (3D-8).

Step 17: Obtain the unlike group hydrogen bonding interaction energy parameters, ΔS_{nm}^{HB} from Table 3D-2.

Step 18: Calculate the hydrogen bonding interaction energy parameter, ΔS_{ji}^{HB}, using Equation (3D-7).

Step 19: Calculate the energy parameter, E, from Equation (3D-6).

Step 20: Solve the equation of state, Equation (3D-5), for the volume of the system. The equation of state will yield three roots with the lowest being the liquid root of the system.

Step 21: If the value of the molar volume of the system does not equal the value assumed in Step 10 within approximately 0.1%, guess a new molar volume and return to Step 11. If the value of V is equal to the value assumed in Step 10 continue to the next step.

Step 22: Calculate the volume root for pure component i as outlined above (Step 10 through Step 20) assuming that component i is the only species present.

Step 23: Calculate the value of the interaction energy contribution to the activity coefficient, Ω_i^{INT}, from Equation (3D-4).

Step 24: Calculate the value of the free volume contribution to the activity coefficient, Ω_i^{FV}, from Equation (3D-3).

Step 25: Calculate the value of the combinatorial contribution to the activity coefficient, Ω_i^{C}, from Equation (3D-2).

Step 26: Calculate the weight fraction activity coefficient, Ω_i, from Equation (3D-1).

3. Limitations and Reliability

The above procedure is used to predict activity coefficients of the solvents in a defined polymer solution mixture. The method yields fairly accurate predictions. Although Procedure D is a good predictive method, there is no substitute to reducing good experimental data to obtain activity coefficients. In general, higher accuracy can be obtained from empirical models when these models are used with binary interaction parameters obtained from experimental data.

4. Literature Source

The procedure is based on the group contribution equation of state by F. Chen, Aa. Fredenslund, and P. Rasmussen, "A Group-Contribution Flory Equation of State for Vapor-Liquid Equilibria" Ind. Engr. Chem. Res., **29**, 875 (1990).

5. Example

Calculate the activity coefficient of (1) ethylbenzene in a solution with (2) polystyrene (M_n = 97,200) with a weight fraction of ethylbenzene of 0.7850 at 333.15 K.

Examine the molecular structure of each component and determine the type and number of occurrences of each subgroup:

	Number of Groups Present in Molecule	
	ethylbenzene	polystyrene (per repeat unit)
Sub-group	component 1	component 2
CH_3	1	0
CH_2	1	1
CH	0	1
ACH	5	5
AC	1	1

The molecular weight of the repeat unit of the polymer, styrene, is 104.2 kg/kmol. This leads to the number of repeat units being approximately 933. Using the above group

definitions and the number of repeat units, the computer program calculated a weight fraction activity coefficient of 1.28. Hocker and Flory (1971) reported an experimental weight fraction activity coefficient of 1.27.

TABLE 3D-1

Volume, Area, and External Degree of Freedom Group Contributions for the Chen et al. Equation of State

Main Group	Sub Group	R_k	Q_k	$C_{To,k}$	$C_{T,k}$	C_k^o
CH_2	CH_3	0.9011	0.848	-0.07382	-3.570	0.0
	CH_2	0.6744	0.540	0.1080	-3.570	0.0
	CH	0.4469	0.228	0.3442	-3.570	0.0
	C	0.2195	0.000	0.4779	-3.570	0.0
	cy-CH_2	0.6744	0.540	0.007814	-3.570	0.0
ACH	ACH	0.5313	0.400	0.007046	-2.020	0.2
	AC	0.3652	0.120	0.2874	-2.002	0.2
C=O	C=O	0.7713	0.640	0.3562	-6.647	0.0
COO	COO	1.0020	0.880	0.3682	6.139	0.0
CH_2O	CH_2O	0.9183	0.780	0.3180	3.383	0.0
	CHO	0.6908	0.468	0.3180	3.383	0.0
CH_2OCH_2	CH_2OCH_2	1.5927	1.320	0.09449	-6.719	0.0
C=C	CH_2=CH	1.3454	1.176	0.1503	35.95	0.0
	CH=CH	1.1167	0.867	0.1762	35.95	0.0
	CH_2=C	1.1173	0.988	0.4961	35.95	0.0
	CH=C	0.8886	0.676	0.3210	35.95	0.0
CCl	CH_2Cl	1.4654	1.264	-0.2334	-7.668	0.0
	CHCl	1.2380	0.952	0.7095	-7.668	0.0
CCl_2	CH_2CL_2	2.2564	1.988	-0.3587	-7.668	0.0
	$CHCl_2$	2.0606	1.684	-0.07292	-7.668	0.0
CCl_3	$CHCl_3$	2.8700	2.410	-0.004503	6.199	0.0
	CCl_3	2.6410	2.184	0.1945	6.199	0.0
CCl_4	CCl_4	3.3900	2.910	-0.06453	-15.07	0.0
OH	OH	0.7000	1.200	0.03641	6.901	-0.00266
	CH_3OH	1.0000	1.000	0.03172	6.901	-0.00266
H_2O	H_2O	0.9200	1.400	0.008746	-66.09	0.0

TABLE 3D-2

Interaction Energy Group Contributions for the Chen et al. Equation of State

m \ n	CH_2	ACH	CH_2CO		COO	CH_2O CH_2	CH_2O	C=C	CCl	CCl_2	CCl_3	CCl_4	OHH_2O
CH_2	-544	2.73	420	126	110	29	1.57	21.3	21.3	7.71	5.10	413 -2.13	613 1.59
ACH		-840	360	83	52	4.42	-1.86	-19.6	-19.6	-9.92	-4.80	453 -2.34	448 0.70
C=O			-2320	-87	171	n.a.	371	82.5	82.5	145	317	-17.3 1.41	378 -3.22
COO				-1660	-10.7	-31	180	-16.6	-16.6	12.8	123	476 -0.79	-629 0.88
CH_2O					-840	0	70	89.6	-72.6	-130	79.4	-457 1.41	-560 -1.47
CH_2OCH_2						-838	-6.17	n.a.	n.a.	-24.9	n.a.	482 -1.47	-16.39 0.53
C=C							-714	42.4	-5.08	-2.54	-14	1340 -1.62	n.a. n.a.
CCl								-633	n.a.	n.a.	n.a.	275 1.33	n.a. n.a.
CCl_2									-633	n.a.	n.a.	275 1.33	n.a. n.a.
CCl_3										-788	n.a.	330 -2.63	n.a. n.a.
CCl_4											-622	504 -2.10	n.a. n.a.
OH	1.70	2.12	-1.60	1.84	-2.47	1.96	4.65	-1.61	-1.61	2.07	2.03	-1950 0.0	76.8 0.63
H_2O	-0.16	0.049	3.97	-2.69	-0.43	-0.89	n.a.	n.a.	n.a.	n.a.	n.a.	-0.77	-1570 0

The values on the diagonals are ϵ_{mm}, the off-diagonal values are $\Delta\epsilon_{mn}$, and the off diagonal bottom values are ΔS^{HB}_{mn}.

PROCEDURE E: HIGH-DANNER EQUATION OF STATE FOR ESTIMATING THE ACTIVITY COEFFICIENT OF A SOLVENT IN A POLYMER SOLUTION

1. Method

This method is to be used to predict the activity coefficient of a low molecular weight solvent in a solution with a polymer. This procedure requires the structure of all components in the mixture, group reference volumes for all groups in the solution as well as the group interaction parameters for all groups. Use of the number average molecular weight of the polymer is recommended.

The weight fraction activity coefficient of a solvent in a solution is given by the following equation:

$$\ln \Omega_1 = \ln \phi_1 - \ln w_1 + \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left[\frac{\tilde{v}_m}{\tilde{v}-1} \frac{\tilde{v}_1-1}{\tilde{v}_1} \right] + q_1 \left[\frac{2\theta_{1,p}-\theta_1}{\tilde{T}_1} - \frac{\theta}{\tilde{T}_m} \right] + \frac{zq_1}{2} \ln \dot{\Gamma}_{11} \qquad (3E\text{-}1)$$

Where:

- Ω_1 = the weight fraction activity coefficient of solvent 1.
- ϕ_1 = the molecular volume fraction of solvent 1, given by Equation (3E-2).
- w_1 = the weight fraction of solvent 1.
- $\tilde{v}_1$ = the reduced volume of pure solvent 1, calculated from the equation of state, Equation (3E-3) at the temperature and pressure of the mixture.
- $\tilde{v}_m$ = the reduced volume of the mixture, calculated from the equation of state, Equation (3E-4).
- q_1 = surface area parameter for solvent 1, given by Equation (3E-19).
- $\tilde{T}_m$ = reduced temperature of the mixture, given by Equation (3E-8).
- $\tilde{T}_1$ = reduced temperature of solvent 1, given by Equation (3E-7).
- $\theta_{1,p}$ = surface area fraction of solvent 1 in the pure state at the temperature and pressure of the mixture, given by Equation (3E-15).
- θ_1 = surface area fraction of solvent 1 in the mixture, given by Equation (3E-15).
- θ = surface fraction of the molecules in the mixture, given by Equation (3E-14).
- $\dot{\Gamma}_{11}$ = nonrandomness parameter of a molecule of solvent 1 surrounding a central molecule of solvent 1, given by Equation (3E-10).

The molecular volume fraction of the solvent is given by

$$\phi_1 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \qquad (3E\text{-}2)$$

Where:

- V_i^* = the hard core volume of component i, given by Equation (3E-27).

x_i = mole fraction of component i.

The volumes of the pure components, $\tilde{v}_i$, and the mixture, $\tilde{v}$, are determined from the equation of state. The reduced volume of the pure solvent, $\tilde{v}_1$, is calculated by solving the equation of state.

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln\left[\frac{\tilde{v}_1}{\tilde{v}_1 - 1}\right] + \frac{z}{2}\ln\left[\frac{\tilde{v}_1 + (q_1/r_1) - 1}{\tilde{v}_1}\right] - \frac{\theta_1^2}{\tilde{T}_1} \qquad \text{(3E-3)}$$

where:

$\tilde{P}_1$ = reduced pressure of the pure solvent given by Equation (3E-5).

The mixture volume is determined by solving the following equation.

$$\frac{\tilde{P}_m}{\tilde{T}} = \ln\left[\frac{\tilde{v}_m}{\tilde{v}_m - 1}\right] + \frac{z}{2}\ln\left[\frac{\tilde{v}_m + (q/r) - 1}{\tilde{v}}\right] - \frac{\theta^2}{\tilde{T}} \qquad \text{(3E-4)}$$

Where:

$\tilde{P}_m$ = reduced pressure of the mixture, given by Equation (3E-6).

z = 10 (coordination number).

q = surface area parameter for the pure component given by Equation (3E-19) or for the mixture, given by Equation (3E-18).

r = number of occupied lattice sites in the lattice for the pure component or the mixture, given by Equation (3E-20).

The reduced pressure of the pure solvent, $\tilde{P}_1$, is given by

$$\tilde{P}_1 = \frac{P}{P_1^*} = \frac{P}{\frac{z\epsilon_{11}}{2v_h}} \qquad \text{(3E-5)}$$

Where:

P = pressure of the system, pascals.

ϵ_{11} = interactive energy of pure solvent, given by Equation (3E-24).

v_h = 9.75×10^{-3} m^3/kmol (molar volume of lattice sites)

The reduced pressure of the mixture is given by

$$\tilde{P}_m = \frac{P}{P^*} = \frac{P}{\frac{z\epsilon^*}{2v_h}} \qquad \text{(3E-6)}$$

Where:

ϵ^* = energy parameter, given by Equation (3E-9), joules/kilomole.

The reduced temperature of solvent 1, $\tilde{T}_i$, is given by

$$\tilde{T}_1 = \frac{T}{T^*} = \frac{T}{\left[\frac{z\epsilon_{11}}{2R}\right]} \qquad \text{(3E-7)}$$

Where:

ϵ_{ij} = interaction energy between molecules i and j, given by Equation (3E-23), joules per kilomole.

The reduced temperature of the mixture, $\tilde{T}_m$, is given by

$$\tilde{T}_m = \frac{T}{T^*} = \frac{T}{\left[\frac{z\epsilon^*}{2R}\right]} \tag{3E-8}$$

The energy parameter, ϵ^*, is given by

$$\epsilon^* = \bar{\theta}_1\epsilon_{11} + \bar{\theta}_2\epsilon_{22} - \bar{\theta}_1\bar{\theta}_2\dot{\Gamma}_{12}\Delta\epsilon_{12} \tag{3E-9}$$

Where:

$\bar{\theta}_i$ = surface area fraction of component i on a hole free basis, given by Equation (3E-13).

$\Delta\epsilon_{ij}$ = interaction energy difference between molecules i and j, given by Equation (3E-22), joules per kilomole.

The nonrandomness parameter for molecules of type 1 around other molecules of type 1, $\dot{\Gamma}_{11}$, is given by

$$\dot{\Gamma}_{11} = \frac{1 - \bar{\theta}_2\dot{\Gamma}_{12}}{\theta_1} \tag{3E-10}$$

Where:

$\dot{\Gamma}_{12}$ = the nonrandomness parameter for molecules of type 1 around molecules of type 2, given by Equation (3E-11)

$$\dot{\Gamma}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1-\dot{G})}} \tag{3E-11}$$

Where:

$$\dot{G} = \exp\left[\frac{\theta(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})}{RT}\right] \tag{3E-12}$$

The surface area fraction of component i on a hole free basis, $\bar{\theta}_i$, is defined by

$$\bar{\theta}_i = \frac{zq_ix_i}{zq} \tag{3E-13}$$

The surface fraction of molecules in the mixture, θ, is given by

$$\theta = \theta_1 + \theta_2 \tag{3E-14}$$

The surface area fraction of component i, θ_i, is given by the following equation.

$$\theta_i = \frac{x_iq_i}{N_q} \tag{3E-15}$$

The surface area fraction of component i in pure component i, $\theta_{i,p}$, is given in a similar manner

using Equation (3E-15), but using pure component properties only.
Where:

N_q = surface area parameter for the lattice, given by Equation (3E-16).

$$N_q = N_h + q \tag{3E-16}$$

Where:

N_h = the number of holes in the lattice, given by Equation (3E-17).

$$N_h = r(\tilde{v} - 1) \tag{3E-17}$$

The surface area parameter for the mixture, q, is given by

$$q = x_1 q_1 + x_2 q_2 \tag{3E-18}$$

Where the surface area parameter for component i, q_i, is given by

$$q_i = \frac{(z-2)r_i + 2}{z} \tag{3E-19}$$

The number of sites occupied by the molecules in the mixture, r, is given by

$$r = x_1 r_1 + x_2 r_2 \tag{3E-20}$$

The number of sites occupied by a molecule of component i, r_i, is given by

$$r_i = \frac{V_i^*}{V_h} \tag{3E-21}$$

The interaction energy difference between molecules i and j, $\Delta\epsilon_{ij}$, is given by

$$\Delta\epsilon_{ij} = \epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij} \tag{3E-22}$$

The cross interaction energy between molecules i and j is calculated from

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{3E-23}$$

The interaction energy between like molecules i at a given temperature is found from a linear interpolation between values calculated at 300 K and 400 K.

$$\epsilon_{ii} = \epsilon_{ii,300} + \frac{(\epsilon_{ii,400\ K} - \epsilon_{ii,300\ K})}{100}(T-300) \tag{3E-24}$$

The interaction energy between like molecules, ϵ_{ii}, is calculated from group contributions.

$$\epsilon_{ii,300} = \sum_k \sum_m \theta_k^{(i)} \theta_m^{(i)} \sqrt{e_{kk,300} e_{mm,300}} \tag{3E-25}$$

$$\epsilon_{ii,400} = \sum_k \sum_m \theta_k^{(i)} \theta_m^{(i)} \sqrt{e_{kk,400} e_{mm,400}} \tag{3E-26}$$

Where:

$\theta_k^{(i)}$ = is the surface area fraction of group k in component i, given by

Equation (3E-30).

$e_{k,300}, e_{k,400}$ = the interaction energy between groups k at 300 K and 400 K, given in Table 3E-1.

The hard core volume of component i is interpolated between values calculated at 300 K and 400 K to give the hard core volume at the temperature of interest.

$$V_i^* = V_{i,300}^* + \frac{(V_{i,400\ K}^* - V_{i,300\ K}^*)}{100} (T-300) \qquad (3E\text{-}27)$$

Where:

T = temperature of polymer solution, kelvins.

$V^*_{i,300}$ = hard core volume of component i at 300 K, given by Equation (3E-28), cubic meters per kilomole.

$V^*_{i,400}$ = hard core volume of component i at 400 K, given by Equation (3E-29), cubic meters per kilomole.

$$V_{i,300\ K}^* = 0.021231 + \sum_k v_k^{(i)} R_{k,300} \qquad (3E\text{-}28)$$

$$V_{i,400\ K}^* = 0.022373 + \sum_k v_k^{(i)} R_{k,400} \qquad (3E\text{-}29)$$

Where:

$R_{k,300}$ = the hard core volume of group k at 300 K, given in Table 3E-1.

$R_{k,400}$ = the hard core volume of group k at 400 K, given in Table 3E-1.

$v_k^{(i)}$ = the number of groups of type k in component i.

The surface area fraction of group k in component i is given by

$$\theta_k^{(i)} = \frac{v_k^{(i)} Q_k}{\sum_m v_m^{(i)} Q_m} \qquad (3E\text{-}30)$$

Where:

Q_k = the dimensionless surface area of group k given in Table 3E-1.

2. Procedure

Step 1: Determine the groups in the polymer solution. This is to be carried out by considering the molecular structure of each compound and the groups given in Table 3E-1.

Step 2: Obtain the group area parameters, Q_k, the group interaction energy parameters, $e_{kk,300}$ and $e_{kk,400}$, and the group volume parameters, $R_{k,300}$ and $R_{k,400}$, for each group k in the polymer solution from Table 3E-1.

Step 3: Determine the number of occurrences of each type of group k in each

component i, $v_k^{(i)}$, by considering the molecular structure of the components.

Step 4: Calculate the surface area fraction of each group k in molecule i, $\theta_k^{(i)}$, using Equation (3E-30).

Step 5: Calculate the hard core volume, V_i^*, of each component i at 300 and 400 K from Equation (3E-28) and Equation (3E-29).

Step 6: Calculate the hard core volume of each component i at the temperature of interest from Equation (3E-27)

Step 7: Calculate the interaction energy between like molecules at 300 and 400 K from Equations (3E-25) and (3E-26).

Step 8: Calculate the interaction energy between like molecules at the temperature of interest, ϵ_{ii}, from Equation (3E-24).

Step 9: Calculate the interaction energy between unlike molecules, ϵ_{ij}, from Equation (3E-23).

Step 10: Calculate the interaction energy difference, $\Delta\epsilon_{ij}$, from Equation (3E-22).

Step 11: Calculate the number of lattice sites occupied by each component i, r_i, from Equation (3E-21).

Step 12: Calculate the number of lattice sites occupied by the mixture, r, from Equation (3E-20).

Step 13: Calculate the molecular surface area for each component, q_i, from Equation (3E-19).

Step 14: Calculate the effective surface area for the mixture, q, from Equation (3E-18).

Step 15: Guess a value for the reduced volume of the mixture, $\tilde{v}$.

Step 16: Calculate the number of holes in the lattice, N_h, from Equation (3E-17).

Step 17: Calculate the surface area parameter for the mixture, N_q, from Equation (3E-16).

Step 18: Calculate the surface area fraction in the mixture θ_i, and in the pure component i, $\theta_{i,p}$, using Equation (3E-15).

Step 19: Calculate the surface fraction of the molecules in the mixture, θ, using Equation (3E-14).

Step 20: Calculate the surface area for each component on a hole-free basis, $\bar{\theta}_i$, from Equation (3E-13).

Step 21: Determine the parameter $\dot{G}$ from Equation (3E-12).

Step 22: Calculate the nonrandomness parameter between molecules 1 and 2, $\dot{\Gamma}_{12}$, using Equation (3E-11).

Step 23: Calculate the nonrandomness parameter between like molecules 1, $\dot{\Gamma}_{11}$, using Equation (3E-10).

Step 24: Calculate the energy parameter, ϵ^*, from Equation (3E-9).

Step 25: Calculate the reduced temperature for the mixture, $\tilde{T}_m$, from Equation (3E-8).

Step 26: Calculate the reduced temperature of the solvent, $\tilde{T}_1$, from Equation (3E-7).

Step 27: Calculate the reduced pressure of the mixture, $P_{m,}$ from Equation (3E-6)

Step 28: Calculate the reduced pressure of the pure solvent, P_1, from Equation (3E-5).

Step 29: Solve the equation of state, Equation (3E-4), for the volume of the mixture. The equation of state will yield three roots, the lowest being the liquid root.

Step 30: If the value of the reduced volume of the mixture does not equal the value

assumed in Step 15 within approximately 0.1%, guess a new reduced volume root and return to Step 16. If the value of $\tilde{v}$ is equal to the value assumed in Step 15 continue to the next step.

Step 31: Calculate the volume root for the pure solvent, $\tilde{v}_1$, in a similar manner as the mixture reduced volume using Equation (3E-3).

Step 32: Calculate the molecular volume fraction for solvent 1, ϕ_1, from Equation (3E-2).

Step 33: Calculate the weight fraction activity coefficient of the solvent, Ω_1, from Equation (3E-1).

3. Limitations and Reliability

The above procedure is used to predict activity coefficients of a solvent in a polymer solution. If more than two species are present in the mixture a coupled set of quadratic equations results. Then the nonrandomness factors must either be solved numerically as was suggested in a method developed by Abusleme and Vera (1985) or approximated, as in the method discussed by Kumar (1986) and Kumar et al. (1987). The resulting equations are more complicated than the binary case presented in this procedure. The method yields fairly accurate predictions. Although Procedure E is a good predictive method, there is no substitute to reducing good experimental data to obtain activity coefficients. In general, higher accuracy can be obtained from empirical models when these models are used with binary interaction parameters obtained from experimental data.

4. Literature Sources

The procedure is based on the group contribution equation of state by M. S. High and R. P. Danner, "A Group Contribution Equation of State for Polymer Solutions," Fluid Phase Equilibria, **53**, 323 (1989) and M. S. High **Prediction of Polymer-Solvent Equilibria with a Group Contribution Lattice-Fluid Equation of State**, Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 1990. Additional and modified group values are from V. S. Parekh **Correlation and Prediction of the PVT Behavior of Pure Polymer Liquids**, M.S. Thesis, The Pennsylvania State University, University Park, PA, 1991.

5. Example

Calculate the activity coefficient of (1) ethylbenzene in a solution with (2) polystyrene (M_n = 97,200) with a weight fraction of ethylbenzene of 0.7850 at 333.15 K.

Examine the molecular structure of each component and determine the type and number of occurrences of each group:

Sub-group	Number of Groups Present in Molecule: ethylbenzene component 1	polystyrene (per repeat unit) component 2
CH_3	1	0
CH_2	0	1
ACH	5	5
AC-CH_2	1	0
AC-CH	0	1

The molecular weight of the repeat unit of the polymer, styrene, is 104.2 kg/kmol. This leads to the number of repeat units being approximately 933. Using the above group definitions and the number of repeat units, the High-Danner computer program calculated a weight fraction activity coefficient of 1.26. Hocker and Flory (1971) reported an experimental weight fraction activity coefficient of 1.27.

Table 3E-1

Group Contributions for the Group Contribution Lattice Fluid Equation of State

Group	$e_{kk,300}$ (kJ/kmol)	$e_{kk,400}$ (kJ/kmol)	$R_{k,300}$ (m^3/kmol)	$R_{k,400}$ (m^3/kmol)	Q_k
CH_3	640.87	640.79	0.01596	0.01628	0.848
CH_2	943.33	987.68	0.01522	0.01518	0.540
CH	2209.38	2708.76	0.01302	0.01302	0.228
C	5378.38	7731.24	0.00854	0.00762	0.150
-CH=CH-	1054.48	1110.63	0.02412	0.02390	0.867
cy-CH_2	895.44	911.40	0.01260	0.01256	0.540
cy-CH	1727.56	2043.28	0.01255	0.01199	0.228
cy-C	4069.49	5993.67	0.01242	0.01126	0.150
AC-	5452.73	6771.48	0.00623	0.00680	0.120
AC-H	975.38	971.62	0.01054	0.01035	0.400
AC-CH	2780.93	3281.53	0.02733	0.02643	0.348
AC-CH_2	1471.59	1581.80	0.02351	0.02302	0.660
AC-CH_3	994.41	1022.68	0.02465	0.02456	0.968
AC-CO-	2181.98	2275.41	0.02105	0.02263	0.760
-O-	868.47	679.56	0.00670	0.00606	0.240
-OH	1867.92	1466.87	0.00685	0.00752	1.200
H_2O	949.12	1154.31	0.07611	0.07544	1.400
-CH_2C=O-	1542.00	1509.50	0.02968	0.03039	1.180
CH_3C=O-	1237.10	1171.50	0.03117	0.03254	1.488
-COO-	1341.67	1308.80	0.02236	0.02327	1.200
-CHCl-	1364.40	1387.30	0.02902	0.02637	0.952
-CH_2NH-	1280.83	1215.76	0.02490	0.02443	0.936
>SiO<	1064.43	1343.84	0.03376	0.03285	0.466

PROCEDURE F: FLORY-HUGGINS CORRELATION FOR VAPOR-LIQUID EQUILIBRIA OF POLYMER-SOLVENT SYSTEMS

1. Method

This method is to be used to estimate the activity coefficient of a low molecular weight solvent in a solution with a polymer. This procedure, unlike the other procedures in this chapter, is a correlation method because it requires the Flory-Huggins interaction parameter for the polymer-solvent pair which must be obtained from an independent tabulation or regressed from experimental data. In addition, the specific volumes and the molecular weights of the pure solvent and the pure polymer are needed. The number average molecular weight of the polymer is recommended. The method cannot be used to estimate the activity of the polymer in the solution.

The activity coefficient of the solvent in a binary solution is given by

$$\ln\Omega_1 = \ln\left[\frac{\phi_1}{w_1}\right] + \left[1 - \frac{1}{r}\right]\phi_2 + \chi_{12}\phi_2^2 \qquad (3F\text{-}1)$$

Where:

Ω_1 = the weight fraction activity coefficient of the solvent in the solution at temperature T.

ϕ_1 = the volume fraction of the solvent, given by Equation (3F-3).

ϕ_2 = the volume fraction of the polymer, given by Equation (3F-4).

r = the number of segments in the polymer molecule, each segment having the same size as that of the solvent molecule, given by Equation (3F-2).

χ_{12} = Flory-Huggins interaction parameter for the system at temperature T. This parameter must be obtained from a separate source or regressed from experimental data.

w_1 = weight fraction of the solvent.

The number of segments in the polymer molecule is given by

$$r = \frac{v_2 M_2}{v_1 M_1} \qquad (3F\text{-}2)$$

Where:

v_1 = the specific volume of the pure solvent at temperature T, cubic meters per kilogram.

v_2 = the specific volume of the pure polymer at temperature T, cubic meters per kilogram.

M_1 = the molecular weight of the solvent, kilograms per kilomole.

M_2 = the molecular weight of the polymer, kilograms per kilomole.

The volume fraction of the solvent is given by

$$\phi_1 = \frac{v_1 w_1}{(v_1 w_1 + v_2 w_2)} \qquad (3F\text{-}3)$$

Where:

w_2 = the weight fraction of the polymer, given by $(1 - w_1)$.

The volume fraction of the polymer is given by

$$\phi_2 = 1 - \phi_1 \qquad (3F\text{-}4)$$

2. Procedure

Step 1: Obtain the specific volumes of both the pure solvent and the pure polymer at temperature T.

Step 2: Obtain the molecular weights of both the solvent and the polymer.

Step 3: Calculate the volume fraction of the solvent using Equation (3F-3) and the volume fraction of the polymer using Equation (3F-4).

Step 4: Obtain the Flory-Huggins interaction parameter, χ_{12} for the system at temperature T and at the solvent weight or volume fraction.

Step 5: Calculate the number of segments in the polymer molecule using Equation (3F-2).

Step 6: Calculate the weight fraction activity coefficient of the solvent, Ω_1 using Equation (3F-1).

3. Limitations and Reliability

The above procedure gives good results if the interaction parameter is known accurately at the particular physical states of the system i.e., the temperature, weight composition, and the polymer molecular weight. According to the theory, χ_{12} should be independent of polymer concentration and of polymer molecular weight, but it is known to vary significantly with both. The model works well if the interaction parameter at a low solvent concentration is used to estimate the activity coefficient at a higher solvent concentration. Extrapolations to low solvent concentrations using the interaction parameter based on a higher solvent concentration, however, can give very high errors. Finally, the model is not very accurate for polar systems.

4. Literature Source

The procedure is based on the theory described by P. J. Flory, "Statistical Thermodynamics of Polymer Solutions," Chapter XII, **Principles of Polymer Chemistry**, Cornell University Press, Ithaca, NY, (1953).

5. Example

Calculate the activity coefficient of (1) cyclohexane in (2) polystyrene [PS] (M_n = 25,900) at a cyclohexane weight fraction of 0.55 (w_1 = 0.55) and at 317.15 K.

Step 1: The specific volume of cyclohexane at 315 K is 1.32×10^{-3} m^3/kg (Daubert and Danner, 1990). The specific volume of polystyrene was determined using the Tait equation method (Procedure 3B) as 9.54×10^{-4} m^3/kg at 317.15 K and atmospheric pressure.

Step 2: The molecular weight of cyclohexane is 84.18 kg/kmol and the number average molecular weight of the polymer is given as 25,900 kg/kmol.

Step 3: Using Equations (3F-3) and (3F-4),

$$\phi_1 = \frac{(1.32\text{x}10^{-3})(0.55)}{(1.32\text{x}10^{-3})(0.55) + (9.54\text{x}10^{-4})(0.45)} = 0.628$$

$$\phi_2 = 1 - 0.628 = 0.372$$

Step 4: The Flory-Huggins interaction parameter for PS-cyclohexane system at 317.15 K is reported to be 0.72 at a cyclohexane volume fraction of 0.60 in the **Polymer Handbook,** (Brandrup and Immergut, 1989).

Step 5: Using Equation (3F-2),

$$r = \frac{(9.54\text{x}10^{-4})(25900)}{(1.32\text{x}10^{-3})(84.18)} = 222.4$$

Step 6: Using Equation (3F-1),

$$\ln \Omega_1 = \ln \left[\frac{0.628}{0.55}\right] + \left[1 - \frac{1}{222.4}\right] 0.372 + 0.72(0.372)^2 = 0.603$$

$$\Omega_1 = 1.83$$

An experimental value of 1.802 was reported by Krigbaum and Geymer (1959).

Chapter 4

POLYMER DATA BASE

A. INTRODUCTION

In conjunction with the preparation of this **Handbook** a compilation of data for pure polymers and polymer-solvent systems was prepared. This chapter documents these data bases. The actual data are contained on the accompanying disks.

The experimental methods which are most widely used to collect polymer-solvent phase equilibrium data are described in Section 4B. This information should be useful in judging the relative reliability of the methods.

An extensive data search was conducted in an attempt to gather all the useful VLE and LLE data for polymer-solvent phase equilibria. Similar data gathering was being conducted by workers at the Technical University of Denmark and Trieste University in Italy. Data bases were exchanged with these groups. Computer bibliographic searches were used. In addition, Polymer Contents was consulted on a regular basis. Most of the useful literature data in the area of interest were collected up through the beginning of 1992.

The data are reported in many different ways by the different authors. The VLE data base has been developed in terms of weight fraction activity coefficients. Section 4C describes the necessary massaging of the different types of data in order to obtain weight fraction activity coefficients. An example calculation is given for each case.

There are no thermodynamic consistency tests that can be applied to the data. For each system in the infinite dilution VLE data base, the weight fraction activity coefficients were plotted as a function of temperature. In many cases considerable scatter was observed. Some data were found that were significantly outside the anticipated range or which showed contradictory behavior with temperature from that expected. These points were kept in the data base but are indicated by an "R", for Rejected, if they were judged to be clearly erroneous or by an "N", for Not recommended, if they appeared questionable but not obviously incorrect. Similarly, in the finite concentration VLE data base some points were judged to be significant outliers and are indicated accordingly.

Section 4D lists the systems for which data are included on the diskettes. A computer program is provided to retrieve the data from the data files. This program, called POLYDATA, is described in Section 5B.

B. EXPERIMENTAL METHODS

The following experimental methods are referred to in the data bases.

1. Inverse gas chromatography (IGC)

2. Piezoelectric sorption (PZS)
3. Differential vapor pressure (DVP)
4. Gravimetric sorption (GS)
5. Light scattering (LS)
6. Ultracentrifuge (UC)
7. Turbidimetry (TB) and light scattering turbidimetry (LST)
8. Microanalytical (MA)
9. Ultraviolet spectrometry (UVS) and infrared spectrometry (IRS)
10. Size exclusion chromatography (SEC)

In the following sections, brief descriptions of these methods are given. In Section 4C details as to how the experimental data are reduced to weight fraction activity coefficients are given.

1. Inverse Gas Chromatography (IGC)

Inverse gas chromatography (IGC) refers to the characterization of the chromatographic stationary phase (polymer) using a known amount of mobile phase (solvent). The stationary phase is prepared by coating an inert support with polymer and packing the coated particles into a conventional gas chromatography column. The activity coefficient of a given solvent can be related to its retention time on the column. The equipment itself is commercially available, easily automated, and extremely versatile.

IGC is most commonly used for measurements at infinite solvent dilution, i.e., at conditions such that the polymer weight fraction is essentially unity. This is achieved by injecting a very small volume ($< 1\ \mu l$) of solvent into a stream of an inert gas such as helium which is flowing over the polymer-coated stationary phase. Alternatively, the inert gas stream can be "doped" with a constant concentration of the solvent. In this case, the injected volume of solvent is a perturbation to the equilibrium that is maintained between the flowing gas stream and the polymer in the stationary phase. The time it takes for this perturbation to propagate through the column can be related to the activity coefficient in a manner analogous to the infinite dilution case. This variation of IGC (alternatively called finite concentration GC or perturbation GC) allows one to record data up to about 10 weight percent solvent for most systems, and up to 15 or 20 weight percent for some systems.

2. Piezoelectric Sorption (PZS)

In the piezoelectric sorption method the amount of vapor sorbed by a polymer-coated quartz crystal is determined by the change in the crystal's frequency which occurs as a result of this sorption. The relationship between the amount of vapor sorbed and the frequency decrease is fairly linear (Sauerbrey, 1959). In essence, the piezoelectric crystal detector acts as a very sensitive microbalance. With reasonable assumptions for the stability of the crystal's base frequency and the precision of the frequency counter employed, the piezoelectric method allows the detection of as little as 10 nanograms of solvent using a 10 MHz crystal. The limit can be reduced further through the use of higher frequency crystals (King, 1964). The piezoelectric method has been used extensively by Saeki et al. (1981) in the concentration range between 0.6 and 1.0 weight fraction polymer and at temperatures from 296 to 370 K. In contrast to the static sorption methods which employ discrete polymer

chunks as the sample, the polymer sample in this case is coated directly on the piezoelectric crystal as a thin film. This greatly reduces both the time necessary to attain equilibrium and the amount of polymer required.

There is presently no commercially available piezoelectric sorption instrument. The polymer to be characterized must be coated onto the crystal from solution. This step is also very important as the coating must be fairly uniform. Fortunately, the crystals are not only inexpensive, but are also fully reusable after dissolving any old coating. The coating procedure is simple: the crystal is first coated with the polymer of interest by placing a drop of polymer solution on the crystal and evaporating the solvent. The change in crystal frequency at this stage gives the amount of polymer actually coated on the crystal. After equilibration with vapor of the solvent to be tested, the amount of solvent sorbed is calculated from the incremental frequency change caused by the sorption. The activity coefficient of the solvent can then be directly calculated.

3. Differential Vapor Pressure (DVP)

In this procedure the difference in the vapor pressure of a pure solvent and the solvent in equilibrium with a polymer is measured at constant temperature. The weight fraction of solvent is usually determined by determining the volume of solvent which is transferred (distilled over) to a known weight of polymer.

Bawn et al. (1950) and Malcolm et al. (1969) have used variations of this method. The apparatus consists of a U-tube manometer connected at the bend to a mercury reservoir. One arm of the manometer is attached to a vessel containing pure solvent and the other to a vessel containing the polymer and solvent. Both vessels are immersed in a constant temperature bath maintained at a temperature below ambient. Vapor pressures of the pure solvent are measured by evacuating the solution side of the system.

The amount of degassed polymer is determined by weighing it into the solution vessel before this vessel is attached to the system. The amount of solvent is measured by observing with a cathetometer the change in liquid level when thoroughly degassed solvent is distilled into the solution vessel from a vertically mounted, volumetrically calibrated tube. The amount of solvent transferred to the solution is corrected for the amount which exists in the vapor phase above the solution during the vapor pressure measurements. The solutions are usually stirred during the equilibrium process.

4. Gravimetric Sorption (GS)

In this method a sample of polymer is placed in a pan attached to an electronic microbalance or the end of a quartz spring. The extension of the spring is calibrated against the weight it supports. The entire apparatus is contained in a constant temperature bath. Solvent, heated to a lower constant temperature in a separate bath, is admitted to the chamber holding the spring and polymer. Thus the equilibrium pressure in the adsorption chamber is set. As the polymer absorbs solvent the weight increase is noted. For the quartz spring this extension is measured using a cathetometer.

This method tends to be very slow because substantial amounts of polymer are generally used. Due to the low diffusivities of most solvents in the solid polymer, the solvent

vapor requires days or weeks to permeate the polymer and attain equilibrium. If one is interested in measuring the diffusion rather than the equilibrium, however, the long time required to achieve equilibrium is a desirable feature rather than a drawback.

The method can be used for weight fractions of solvent up to 0.75, but the data become very unreliable in this range and small temperature fluctuations cause large swings in the data. A more reasonable upper limit is 0.5 weight fraction solvent.

5. Light Scattering (LS)

Light is scattered when there are fluctuations in the dielectric constant of materials (Kerker, 1969). For a pure component, the irregularities in dielectric constant are caused by density fluctuations which are proportional to the isothermal compressibility. In a solution, however, the composition fluctuations generally lead to much larger oscillations in the dielectric constant than do density variations. The amount of light scattered by a solution that is greater than that of the pure components is called the excess scatter. This excess intensity is the quantity of interest in studying solutions because it is a direct probe of the free energy of the system. For the binary case, the excess scatter monitors the partial derivative of the chemical potential of one species with respect to the other. The entire phase diagram has been mapped out for binary solutions of small miscible molecules by light scattering.

Conventionally, the excess light scattered per unit volume at angle θ from the transmitted beam, i_θ, is reported as a Rayleigh factor (or ratio).

$$R_\theta = \frac{d^2 i_\theta}{I_o(1 + \cos^2\theta)} \tag{4B-1}$$

Where

I_o = the incident intensity of unpolarized light.
d = the distance between the sample and the detector.

The excess light scattered is related to the concentration dependence of the chemical potential by

$$R_\theta = \frac{K\phi_2\bar{V}_1}{(\partial\mu_1/\partial\phi_2)} \tag{4B-2}$$

where $\bar{V}_1$ is the solvent molar volume, and the optical constant

$$K = \frac{2\pi^2\tilde{n}_o^2(d\tilde{n}/dc_2)^2}{N_A\lambda^4} \tag{4B-3}$$

is a function of the solvent refractive index, $\tilde{n}_o$; the change of refractive index with polymer weight per solution volume concentration, $d\tilde{n}/dc_2$; wavelength of light in vacuum, λ; and Avogadro's number, N_A. Light scattering formalisms can be generated to describe multicomponent systems.

For dilute polymer solutions, the partial composition derivative in Equation (4B-2) is a weak function of composition so the scattering intensity increases roughly in proportion to

the solute fraction, ϕ_2. Light scattering is routinely used as a probe of dilute solutions to characterize polymer molecular weight, size, and solvent-solute interactions. On the other hand, once the solution becomes sufficiently concentrated that most molecules overlap, the scattered intensity decreases as the polymer fraction increases. At high polymer concentration, the system configuration is analogous to a block of glass where random positioning of atoms leads to a total destructive interference of the scattered light. The overlap concentration that separates dilute from semi-dilute solutions can be as low as 0.1% for high molecular weight polymers. Not only is the amount of light scattered reduced with increasing concentration, but it is also harder to make the solutions optically clear. For these two reasons, light scattering measurements on moderately concentrated solutions have only been made on polymers that are available in very clean preparations such as polystyrene. The volume fraction of the solute seldom gets much above 0.2.

While Equation (4B-2) permits any light scattering data to be interpreted as partial derivatives of chemical potential or activity, dilute solution measurements are conventionally presented in terms of a virial coefficient expansion of the chemical potential.

$$\frac{Kc}{R_o} = \frac{1}{M_w} + 2D_2c_2 + 3D_3c_2^2 + \ldots + nD_ic_2^{i-1} + \ldots \qquad (4B\text{-}4)$$

Here D_i is the i^{th} virial coefficient of the system. Solutions studied are often sufficiently dilute that terms greater than $2D_2c_2$ can be omitted. Since the expression is in terms of the Rayleigh factor at $\theta = 0$, low angle laser light scattering (LALLS) that make measurements in the $\theta = 2$ to 6 degree range is particularly well suited for this application.

The situation becomes more complex if light scattering measurements are made at larger angles where there is intraparticle interference in the scattered light. The angular variation of intensity is related to the radius of gyration R_G of the polymer.

$$\frac{Kc}{R_\theta|_{c=o}} = \frac{1}{M_w}\left[1 + \left[\frac{16\pi^2}{3\lambda^2}\right] R_G^2 \sin^2\left[\frac{\theta}{2}\right] + \ldots\right] \qquad (4B\text{-}5)$$

Conventionally, such data have been analyzed with a Zimm plot where Kc/R_θ is presented as a function of $[\sin^2(\theta/2) + kc]$ where k is a constant multiplier used to spread the data over a convenient range. Measurements are extrapolated at constant angle to zero concentration values and at constant concentration to zero angle points. Connecting each of these two sets of points give the curves specified by Equations (4B-2) and (4B-5). Either line has a y-axis intercept giving the weight average molecular weight. The slope of the zero angle data yields the second virial coefficient while that of the zero concentration points permits the radius of gyration to be calculated. In many cases, non-linear Zimm plots are encountered. (Kratochvil, 1982) Often this means that the concentration and/or scattering angle is sufficiently large that it is no longer appropriate to drop higher order terms in the Taylor expansion of Equation (4B-2). In other cases, the sample has been contaminated with a small quantity of microaggregates that preferentially scatter a lot of light in the forward direction. In multi-angle laser light scattering (MALLS), the photometer is constructed to simultaneously detect intensity at typically fifteen different angles (Rabek, 1980).

The virial expansion of Equation (4B-4) is inappropriate as the concentration increases since the series no longer converges at sufficiently high solute volume fractions. In this case,

data are conventionally analyzed in terms of a scaling model (Amirzadeh, 1982) or the Flory-Huggins model (Scholte, 1970) for the chemical potential. With a scaling model, the chemical potential on the semidilute regime becomes

$$\mu = K^* \left[\frac{\phi_2}{\phi_2^*} \right]^a \qquad (4B\text{-}6)$$

Where

K^* = a constant.
ϕ_2^* = the overlap volume fraction.
a = a constant equal to 9/4 in an athermal case and 3 in a theta solvent.

For the Flory-Huggins model of the activity, Equations (2C-4)-(2C-6), the data are reported in terms of a concentration dependent chi parameter. Data must be taken or extrapolated to the $\theta=0$ limit in order to remove solution structure effects.

Light scattering or turbidimetric measurements are also used as a quantitative indication of the phase separation. As the system approaches the phase boundary, the scattered light intensity increases very rapidly. Critical opalescence occurs as composition fluctuations in the system become macroscopic in the vicinity of the phase boundary (Stanley, 1985). The solution turns milky. After the system has phase separated, pockets of the dispersed phase cause much more light to be scattered from the suspension than was scattered by the solution. With time, the dispersed emulsion droplets will aggregate giving a sharp phase boundary, but light scattering detects the phase separation much earlier. Most phase maps made for multicomponent systems by light scattering rely on the difference in turbidity between solutions and suspensions. On the other hand, critical opalescence is used to measure the critical solution temperature.

6. Ultracentrifuge (UC)

In a typical ultracentrifuge system the polymer solution is put in a sample tube and rotated at high speeds. An equilibrium is established between the sedimentation and diffusion effects in the tube. Since the centrifugal forces are balanced by the concentration gradient (activity gradient), this technique provides a method for determination of the activities and the chemical potentials in polymer solutions. Schlieren photography techniques are used to measure the refractive index gradient (dn/dh) along the axis of the tube. The concentration gradient (dc/dh) can be determined by,

$$\frac{dc}{dh} = \left[\frac{dn}{dh} \right] \left[\frac{dn}{dw} \right] \qquad (4B\text{-}7)$$

where dn/dw is the correlation of refractive index and concentration, w. To avoid the difficulty of handling volume fractions, Scholte (1970) used weight fraction in the Flory-Huggins equation:

$$\frac{\Delta\mu_1^\circ}{RT} = \ln (1-w_2) + \left[1 - \frac{M_1}{\bar{M}_{n,2}} \right] w_2 + \chi_w w_2^2 \qquad (4B\text{-}8)$$

Where:

$\Delta\mu_1^\circ$ = difference between the chemical potential of the solvent in the solution and the pure solvent.
R = universal gas constant
T = temperature.
w_2 = weight fraction of polymer.
M_1 = molecular weight of solvent.
$\bar{M}_{n,2}$ = number average molecular weight of polymer.
χ_w = Flory chi parameter based on weight fraction.

The final equation which relates the chemical potential to the centrifugal data is:

$$-\left[\frac{w_2}{(1-w_2)}\right] M_1[1-\tilde{v}_2\rho]\omega^2 h = \left[\left(\frac{d\Delta\mu_1^\circ}{dw_2}\right) + RT\left(\frac{M_1}{\bar{M}_{n,2}} - \frac{M_1}{\bar{M}_{w,2}}\right)\right] \frac{\left(\frac{dn}{dh}\right)_\omega}{\left(\frac{dn}{dw_2}\right)} \qquad (4B\text{-}9)$$

Where:

ρ = density of the solution.
$\tilde{v}_2$ = partial specific volume of the polymer.
ω = centrifugal speed.
h = distance to the center of rotation.
$\bar{M}_{w,2}$ = weight average molecular weight of polymer.
$(dn/dh)_\omega$ = refractive index as a function of distance.

This development assumes that for a polydispersed polymer in a single solvent, all polymer components have the same specific volume and the same refractive index and that dn/dw is independent of the molecular weight distribution. Generally the chemical potentials determined from this technique are slightly higher than values determined by other methods. The difference, however, is believed to be within the experimental error. The method is applicable over a concentration range from 0 to 80 weight percent polymer.

7. Turbidimetry (TB) and Light Scattering Turbidimetry (LST)

Liquid-liquid equilibria cloud point curves for binary or ternary systems may be obtained using turbidimetric methods. For binary systems, this method consists of slowly decreasing or increasing the temperature of a turbid polymer-solvent mixture until the agitated mixture becomes clear. The phenomena is reversible because the clear mixture will become turbid again if the temperature change is reversed. The opaqueness of the mixture is determined either visually, which is referred to as turbidimetry, or by measuring the intensity of transmitted light as a function of temperature, which is known as light scattering turbidimetry, as discussed in Section 5. A series of such experiments at various solvent-polymer weight fractions establishes the cloud point curve.

Phase separation in ternary systems may be studied using the cloud point isotherm method. Solvent, here defined as component 1, is added to a turbid mixture containing a mixture of components 2 and 3 until the agitated mixture becomes clear. A series of such experiments at various component 2-component 3 weight ratios establishes the cloud point

isotherm. Although one can obtain data faster with this method than with other LLE methods, it has the disadvantage of providing only the binodal curve; it does not give the tie line compositions.

8. Microanalytical (MA)

For ternary polymer-polymer-solvent systems, the compositions of the equilibrium phases may be determined using a variety of microanalytical methods depending upon the chemical nature of the polymers (Dobry and Boyer-Kawenoki, 1947). Each of the phases is sampled, weighed, and dried to determine the solvent concentration. If the two polymers are sufficiently different chemically, microanalytical determination of carbon and hydrogen may be used. In systems containing polystyrene, the proportion of polystyrene may be determined by precipitating it with acetic acid and weighing the precipitate. Other microanalytical methods have also been used to determine phase compositions.

9. Ultraviolet Spectrometry (UVS) and Infrared Spectrometry (IRS)

Allen et al. (1960) used ultraviolet spectrometry to determine phase compositions in a polymer-polymer-solvent system containing polystyrene and polyisobutylene. At a wavelength of 250-260 nm, polystyrene has a strong adsorption band, which is linearly related to concentration, while polyisobutylene is transparent. Similarly, for a system containing polydimethylsiloxane and polyisobutylene, they used infrared spectrometry because polydimethylsiloxane absorbs at 1261 cm^{-1} and polyisobutylene is transparent at this wavelength. UVS and IRS have been used with other systems which contain only one polymer which has a strong adsorption band.

10. Size Exclusion Chromatography (SEC)

The advent of size exclusion chromatography in the 1960's provided an alternative to drying polymer-polymer-solvent samples to determine the equilibrium phase compositions. Size exclusion chromatography separates solvents from polymers and to a varying extent, polymers from polymers, based on the size of the molecules in solution. Ultraviolet spectrometry and refractive index detectors may be used to determine the concentrations of each of the polymers in each of the phases (Lloyd et al., 1980).

C. DATA REDUCTION PROCEDURES

All experimental data from the literature were entered into a spreadsheet program in the units of the original source. Different sources of data using the same experimental technique were entered into copies of the appropriate spreadsheet to assure that the same data reduction technique was applied.

The pure polymer data base contains pressure-volume-temperature data. The data were first entered into a spreadsheet file in the form given by the author. The data were then converted to standard SI units and written to an ASCII file in the standard format developed for these files.

The standard state used for the finite concentration data was usually the pure solvent at the temperature and pressure of the mixture. In most cases, the Poynting correction (pressure effect on the liquid) could be neglected. The end result of this approximation is that saturation pressure appears in the expression for the activity coefficient, but not the system pressure.

In the sections that follow the techniques used for reducing experimental quantities to weight fractions and weight fraction activity coefficients are described. For the solvents, pure component liquid densities and second virial coefficients were often required and were obtained from Daubert and Danner (1990).

1. Pure Polymer PVT Data

The typical form in which dilatometry data are reported is in terms of a volume difference and a relative volume as a function of temperature and pressure.

$$\Delta V = V_o - V \tag{4C-1}$$

$$V_{rel} = \frac{V}{V_o} \tag{4C-2}$$

Where

V_o = the specific volume at zero pressure (often taken as atmospheric pressure) and the temperature of the system, cubic meters per kilogram.

V = the specific volume, cubic meters per kilogram.

We can solve for V in Equation (4C-1) and substitute into Equation (4C-2). Rearranging we obtain

$$V_o - V_{rel}V_o = \Delta V \tag{4C-3}$$

$$V_o = \frac{\Delta V}{1 - V_{rel}} \tag{4C-4}$$

From this value of V_o, the quantity of interest, V, can be calculated.

$$V = V_{rel}\bar{V}_o \tag{4C-5}$$

In most cases a slightly different value of V_o is obtained for each pair of V_{rel} and ΔV because of rounding errors. Therefore the average value of all the V_o's calculated for each temperature, $\bar{V}_o$, is used.

Example Calculation:

For polyethylene Beret and Prausnitz (1975) give data in the form of ΔV and V_{rel}. At 9×10^7 Pa (900 bars) and 413.2 K (140°C), $\Delta V = 7.94 \times 10^{-5}$ m^3/kg (0.0794 cm^3/g) and $V_{rel} = 0.9375$.

From Equation (4C-4)

$$V_o = \frac{7.94x10^{-5}}{(1 - 0.9375)} = 1.270x10^{-3}\ m^3/kg$$

From Equation (4C-5)

$$V = (0.9375)(1.270x10^{-3}) = 1.191x10^{-3}\ m^3/kg$$

2. Finite Dilution Flory Chi Parameter

The Flory-Huggins equation for the activity of a solvent in a polymer solution is:

$$\ln a_1 = \ln(1-\phi_2) + \left[1-\frac{1}{r}\right]\phi_2 + \chi_{12}\phi_2^2 \qquad (4C\text{-}6)$$

Where

a_1 = activity of the solvent.
χ_{12} = Flory-Huggins interaction parameter.
ϕ_1 = volume fraction of the polymer.

The number of segments in the polymer chain, r, is given by the ratio of the molar volumes of the solvent (1) and the polymer (2).

$$r = \frac{v_2 M_2}{v_1 M_1} = \frac{\rho_1 M_2}{\rho_2 M_1} \qquad (4C\text{-}7)$$

Where

v_i = specific volume of component i, cubic meters per kilogram
M_i = molecular weight of component i, kilogram per kilomole
ρ_i = specific density of component i, kilogram per cubic meter

Volume fractions are calculated as

$$\phi_1 = \frac{w_1 v_1}{w_1 v_1 + w_2 v_2} \qquad (4C\text{-}8)$$

Where

w_i = weight fraction of component i.

Weight fraction is related to the volume fractions as

$$w_1 = \frac{\rho_1 \phi_1}{\rho_1 \phi_1 + \rho_2 \phi_2} \qquad (4C\text{-}9)$$

The weight fraction activity coefficient is related to the activity by

$$\Omega_i = \frac{a_i}{w_i} \qquad (4C\text{-}10)$$

Experimental χ's are usually reported as a function of weight fraction or volume fraction. Both are needed in order to calculate Ω_i. Thus, densities or specific volumes of the solvent and polymer are required.

In some cases, the concentration may be reported as segment fractions or surface area fractions. Segment fractions are usually identical to volume fractions.

Example Calculation:

Ashworth and Price (1986) provide values of χ and volume fraction of the solvent, ϕ_1, for the poly(dimethylsiloxane) (PDMS) - benzene system at 303 K.

Input data: benzene = 1, PDMS = 2.

		Source
χ_{12}	= 0.7317	Given
ϕ_1	= 0.0165	Given
M_2	= 3350	Given
ρ_2	= 0.9523 g/cm^3 = 952.3 kg/m^3	Given
M_1	= 78.11 kg/kmol	Daubert and Danner (1990)
ρ_1	= 11.11 kmol/m^3 = 867.8 kg/m^3	Daubert and Danner (1990)

$$\phi_2 = 1 - \phi_1 = 1 - 0.0165 = 0.9835$$

From Equation (4C-7):

$$r = \frac{(867.8)(3350)}{(952.3)(78.11)} = 39.08$$

From Equation (4C-6):

$$\ln a_1 = \ln (1 - 0.9835) + \left[1 - \frac{1}{39.08}\right](0.9835) + (0.7317)(0.9835)^2 = -2.438$$

$$a_1 = 0.0873$$

From Equation (4C-9)

$$w_1 = \frac{(867.8)(0.0165)}{(867.8)(0.0165) + (952.3)(0.9835)} = 0.0151$$

From Equation (4C-10)

$$\Omega_1 = \frac{0.0873}{0.0151} = 5.78$$

3. Infinite Dilution Flory Chi Parameter

From the expression for activity in Equation (4C-6) the weight fraction activity coefficient of component 1, Ω_1, is calculated as

$$\ln \Omega_1 = \ln \left[\frac{1-\phi_2}{w_1}\right] + \left[1-\frac{1}{r}\right]\phi_2 + \chi_{12}\phi_2^2 \qquad (4C\text{-}11)$$

The infinite dilution activity coefficient of the solvent is calculated from the limit as the weight fraction of component 1 goes to zero. The infinite dilution Flory-Huggins interaction parameter, χ_{12}^{∞}, can be reduced to the infinite dilution activity coefficient, Ω_1^{∞}, by the relation:

$$\Omega_1^{\infty} = \frac{1}{r}\frac{M_2}{M_1}\exp\left[\chi_{12}^{\infty} + 1 - \frac{1}{r}\right] \qquad (4C\text{-}12)$$

Example Calculation:

Ashworth and Price (1986) provide values of χ_{12}^{∞} for the poly(dimethylsiloxane) (PDMS) - benzene system at 303 K.

Input data: benzene = 1, PDMS = 2.

		Source
χ_{12}^{∞}	= 0.7385	Given
M_2	= 3350	Given
ρ_2	= 0.9523 g/cm^3 = 952.3 kg/m^3	Given
M_1	= 78.11 kg/kmol	Daubert and Danner (1990)
ρ_1	= 11.11 kmol/m^3 = 867.8 kg/m^3	Daubert and Danner (1990)

From Equation (4C-7):

$$r = \frac{(867.8)(3350)}{(952.3)(78.11)} = 39.08$$

From Equation (4C-12):

$$\Omega_1^{\infty} = \frac{1}{39.08}\left[\frac{3350}{78.11}\right]\exp\left[0.7385 + 1 - \frac{1}{39.08}\right] = 6.085$$

4. Differential Vapor Pressure, Gravimetric Sorption, and Piezoelectric Sorption Methods

The experimental values reported for the differential vapor pressure, gravimetric sorption, and piezoelectric methods are the weight fraction of solvent in the polymer solution and the pressure of the solvent vapors in equilibrium with the polymer solution. Differential vapor pressure measurements are performed by adding a known amount of solvent to a weighed polymer sample and measuring the vapor pressure of the solvent over the polymer solution (Bawn et al., 1950).

Both the gravimetric sorption and piezoelectric techniques involve enclosing a polymer sample in a chamber with the solvent vapors and measuring the weight of solvent absorbed into the polymer. In the gravimetric sorption technique the polymer sample with the absorbed solvent is weighed using a quartz spring or other form of microbalance. The piezoelectric technique uses the frequency response of a quartz crystal to measure the weight of solvent deposited on the polymer. The weight fraction of solvent in the polymer is calculated directly from the microbalance measurement and the weight of the original polymer sample. The pressure in the sorption chamber is measured with an accurate manometer or pressure transducer. The solvent is supplied to the polymer chamber from a flask of pure solvent operated at saturation pressure at a temperature below that of the polymer sample. The total pressure in the polymer chamber is the vapor pressure of the solvent at the temperature in the solvent flask. Temperature control is obtained by immersing the sorption chamber in a constant temperature air bath, a water bath, or for more accurate temperature control a bath

of a boiling fluid operated at total reflux (Duda et al., 1973). The difference between these methods and the vapor pressure method is that in the differential vapor pressure method the amount of the solvent is determined by measuring a volume of liquid distilled into the polymer. In the other two methods, the amount of solvent on the polymer is measured directly through the microbalance or frequency response of the crystal.

The fugacity of the solvent vapor, f_1, will be equal to

$$f_1 = P \exp\left[\frac{B_{11}P}{RT}\right] \tag{4C-13}$$

Where

P = the equilibrium pressure (saturation pressure of the solvent at the temperature of the solvent flask), pascals.

B_{11} = second virial coefficient for pure component 1, cubic meters per kilomole.

R = gas constant = 8314.0 (Pa)(m^3)/ (kmol) (K).

To calculate the standard state fugacity, we consider the fugacity of a pure component in a condensed phase at pressure P and temperature T which is calculated as

$$f_1^C = P_1^s \phi_1^s \exp\left[\int_{P_1^s}^{P} \frac{v_1^c}{RT}\, dP\right] \tag{4C-14}$$

Where

P_1^s = saturation pressure of component 1 at temperature T, pascals.

v_1^c = molar volume of component 1 in the condensed phase, cubic meters per kilomole.

The first two terms in the product on the right side of Equation (4C-14) give the fugacity at the saturation pressure. The exponential term, the Poynting correction, is a correction to the fugacity for compressing the condensed phase from the saturation pressure to pressure P. Assuming that the condensed phase molar volume does not vary with pressure this relation reduces to

$$f_1^C = P_1^s \phi_1^s \exp\left[\frac{v_1^c}{RT}(P - P_1^s)\right] \tag{4C-15}$$

If we chose our standard state for the activity coefficient to be the pure liquid solvent at pressure P and temperature T, then the above equation becomes the expression for the standard state fugacity. The fugacity coefficient at the saturation pressure can be calculated from the second virial coefficient

$$\phi_1^s = \exp\left[\frac{B_{11}P_1^s}{RT}\right] \tag{4C-16}$$

Thus, the expression for the standard state fugacity of pure liquid at pressure P and temperature T becomes

$$f_1^o = P_1^s \exp\left[\frac{v_1^c(P-P_1^s)+P_1^s B_{11}}{RT}\right] \qquad (4C\text{-}17)$$

The Poynting correction in Equation (4C-17) is usually considered to be negligible so the expression for the standard state fugacity becomes

$$f_1^o = P_1^s \exp\left[\frac{B_{11}P_1^s}{RT}\right] \qquad (4C\text{-}18)$$

Combining Equations (4C-13) and (4C-18) with the definition of the activity coefficient [Equation (4C-10)] gives

$$\Omega_1 = \frac{f_1}{w_1 f_1^o} = \frac{P}{P_1^s w_1} \exp\left[\frac{B_{11}(P-P_1^s)}{RT}\right] \qquad (4C\text{-}19)$$

Example Calculation:

Using a differential vapor pressure method Allen et al. (1965) provided values of the volume fraction of polymer and relative pressure of diethyl ketone with polypropylene at 298.15 K.

Input data: diethyl ketone = 1, polypropylene = 2.

		Source
P_1/P_1^s	= 0.9325	Given
ϕ_2	= 0.8825	Given
ρ_2	= 0.857 g/cm^3	Given
T	= 298.15 K	Given
P_1^s	= 4931 Pa	Daubert and Danner (1990)
B_{11}	= -3.726 m^3/kmol	Daubert and Danner (1990)
ρ_1	= 0.8095 g/cm^3	Daubert and Danner (1990)

$$P_1 = (0.9325)(4931) = 4598\text{Pa}$$

$$\phi_1 = 1 - \phi_2 = 1 - 0.8825 = 0.1175$$

From Equation (4C-9)

$$w_1 = \frac{\rho_1\phi_1}{\rho_1\phi_1+\rho_2\phi_2} = \frac{(0.8095)(0.1175)}{(0.8095)(0.1175) + (0.857)(0.8825)} = 0.1117$$

From Equation (4C-19)

$$\Omega_1 = \frac{4598}{(4931)(0.1117)} \exp\left[\frac{(-3.726)(4598 - 4931)}{(8314)(298.15)}\right] = 8.352$$

5. Gas Chromatograph Data at Infinite Dilution

In gas chromatograph measurements the experimental information obtained from the experiments is usually in terms of retention volume or net retention volume.

$$V_N = V_R - V_G \tag{4C-20}$$

Where

V_N = net retention volume, cubic meters.
V_R = retention volume, cubic meters.
V_G = gas holdup, cubic meters.

The retention volume extrapolated to zero column pressure, V_N^o, is related to the partitioning of the solvent in the gas and liquid phases by (Patterson et al., 1971)

$$k_o = \frac{n_{1,liq}/V_{liq}}{n_{1,gas}/V_{gas}} = \frac{V_N^o}{V_{liq}} \tag{4C-21}$$

Where

V_N^o = net retention volume extrapolated to zero column pressure, cubic meters.
$n_{i,gas}$ = moles of component i in the vapor phase, kilomoles.
$n_{i,liq}$ = moles of component i in the liquid phase, kilomoles.
V_{gas} = volume of vapor phase, cubic meters.
V_{liq} = volume of liquid phase, cubic meters.

At infinite dilution,

$$\left[\frac{P_1}{X_1}\right]^{\infty} = \frac{RT}{V_N^o/n_{2,liq}} \tag{4C-22}$$

The specific retention volume corrected to 0°C is defined as

$$V_g^o = \frac{V_N^o}{m_{2,liq}} \frac{273.15}{T} = \frac{V_N^o}{n_{2,liq}M_2} \frac{273.15}{T} \tag{4C-23}$$

Where

$m_{i,liq}$ = mass of component i in liquid phase, kilograms.
M_i = molecular weight of component i, kilograms per kilomoles.

At infinite dilution

$$\left[\frac{P_1}{X_1}\right]^{\infty} = \frac{273.15\ R}{V_g^o M_2} \tag{4C-24}$$

The mole fraction activity coefficient is defined by

$$\gamma_1 = \frac{a_1}{x_1} = \frac{f_1}{x_1 f_1^o} \tag{4C-25}$$

Nonideal gas behavior is accounted for by introducing the fugacity coefficient of component 1 in the gas mixture.

$$\left[\frac{f_1}{X_1}\right]^\infty = \left[\frac{P_1}{X_1}\right]^\infty \phi_1 \tag{4C-26}$$

The standard state fugacity is calculated from Equation (4C-17). Combining the expressions for the ratio of fugacity to concentration and standard state fugacity

$$\gamma_1^\infty = \left[\frac{f_1}{X_1 f_1^o}\right]^\infty = \left[\frac{P_1}{X_1}\right]^\infty \phi_1 \frac{1}{P_1^s} \exp\left[\frac{v_1^c(P_1^s - P) - B_{11}P_1^s}{RT}\right] \tag{4C-27}$$

Substituting the expression for specific net retention volume we obtain

$$\gamma_1^\infty = \left[\frac{273.15\ R}{V_g^o\ M_2}\right] \phi_1 \frac{1}{P_1^s} \exp\left[\frac{v_1^c(P_1^s - P) - B_{11}P_1^s}{RT}\right] \tag{4C-28}$$

The weight fraction activity coefficient is related to the mole fraction activity coefficient at infinite dilution through the relation

$$\Omega_1^\infty = \gamma_1^\infty \frac{M_2}{M_1} \tag{4C-29}$$

The expression for the weight fraction activity coefficient at infinite dilution is thus obtained.

$$\Omega_1^\infty = \left[\frac{273.15\ R}{V_g^o\ M_1}\right] \phi_1 \frac{1}{P_1^s} \exp\left[\frac{v_1^c(P_1^s - P) - B_{11}P_1^s}{RT}\right] \tag{4C-30}$$

This is the most general form for the weight fraction activity coefficient. The standard state is the liquid at temperature T, but the pressure P must be specified to fully describe the standard state. Many authors define the standard state to be the liquid at temperature T and zero pressure, so the activity coefficient expression becomes

$$\Omega_1^\infty = \left[\frac{273.15\ R}{V_g^o\ M_1}\right] \phi_1 \frac{1}{P_1^s} \exp\left[\frac{P_1^s(v_1^c - B_{11})}{RT}\right] \tag{4C-31}$$

To calculate the fugacity of the solvent in the carrier gas the virial equation truncated after the second virial coefficient is used.

$$\ln \phi_1 = \left[2 \sum_{j=1}^{3} y_j B_{1j} - B_{mix} \right] \frac{P}{RT} \qquad (4C\text{-}32)$$

Where

$$B_{mix} = \sum_i \sum_j y_i y_j B_{ij}$$

y_i = mole fraction of component i in vapor phase.

Since the polymer has an extremely low volatility, which corresponds to $y_2 = 0$, Equation (4C-32) reduces to

$$\ln \phi_1 = \left(2(y_1 B_{11} + y_3 B_{13}) - (y_1^2 B_{11} + y_1 y_3 B_{13} + y_3^2 B_{33}) \right) \frac{P}{RT} \qquad (4C\text{-}33)$$

Here component 3 is the carrier gas which is normally helium in which case the interactions between the solvent and the carrier gas molecules are insignificant; i.e., $B_{13}=0$. Likewise, the interactions between two carrier gas molecules are insignificant and $B_{33}=0$. Therefore, for the infinitely dilute case where $y_1=0$, Equation (4C-33) reduces to

$$\ln \phi_1 = 0 \qquad (4C\text{-}34)$$

or,

$$\phi_1 = 1 \qquad (4C\text{-}35)$$

So, the activity coefficient expression becomes

$$\Omega_1^{\infty} = \left[\frac{273.15\ R}{V_g^o\ M_1\ P_1^s} \right] \exp \left[\frac{P_1^s (v_1^c - B_{11})}{RT} \right] \qquad (4C\text{-}36)$$

Example Calculation:

Chang and Bonner (1975) measured retention volume data for water on poly(ethylene oxide) (PEO) at 343.55 K.

Input data: water = 1, PEO = 2

	Source
$V_g^o = 283.93\ cm^3/g = 0.28393\ m^3/kg$	Given
$T = 343.55\ K$	Given
$M_1 = 18.02\ kg/kmol$	Daubert and Danner (1990)
$V_1^c = 0.01807\ m^3/kmol$	Daubert and Danner (1990)
$P_1^s = 31{,}451\ Pa$	Daubert and Danner (1990)
$B_{11} = -0.9976\ m^3/kmol$	Daubert and Danner (1990)

From Equation (4C-36)

$$\Omega_1^{\infty} = \frac{(273.15)(8314)}{(0.28393)(18.02)(31451)} \exp\left[\frac{(31,451)(0.0187 + 0.79976)}{(8314)(343.55)}\right] = 14.27$$

6. Henry's Law Constant

Some authors report gas chromatographic data in terms of the Henry's Law constant, $H_{1,2}$, which is related to the specific retention volume V_g^o through

$$H_{1,2} = \frac{273.15\ R}{V_g^o M_1} \qquad (4C\text{-}37)$$

Thus Equation (4C-36) reduces to

$$\Omega_1^{\infty} = \frac{H_{1,2}}{P_1^s} \exp\left[\frac{P_1^s(v_1^c - B_{11})}{RT}\right] \qquad (4C\text{-}38)$$

Example Calculation

Lipson and Guillet (1982) provide Henry's Law constants for the chloroform - poly(ethylene-co-vinyl acetate) [P(E&VAC)] system at 338.15 K.

Input data: chloroform = 1, P(E&VAC) = 2

	Source
$H_{1,2}$ = 1.22 atm = 123,590 Pa	Given
T_c = 338.15 K	Given
v_1^s = 0.08489 m^3/kmol	Daubert and Danner (1990)
P_1 = 115,080 Pa	Daubert and Danner (1990)
B_{11} = -0.8693 m^3/kmol	Daubert and Danner (1990)

From Equation (4C-38),

$$\Omega_1^{\infty} = \frac{123,590}{115,080} \exp\left[\frac{(115,080)(0.08489 + 0.8693)}{(8314)(338.15)}\right] = 1.12$$

7. Osmotic Pressure Data

The activity of the solvent can be related to the osmotic pressure using the following equation.

$$a_1 = \exp\left[\frac{-\pi V_1^o}{RT}\right] \qquad (4C\text{-}39)$$

Where

π = osmotic pressure, pascals
V_1^o = molar volume of solvent, cubic meters per kilomole
R = gas constant = 8314.0 (Pa)(m^3) / (kmol) (K)
T = temperature, kelvins

Then the weight fraction activity coefficient of the solvent is given by

$$\Omega_1 = \frac{a_1}{w_1} \qquad (4C\text{-}40)$$

Where

w_1 = weight fraction of the solvent

Example Calculation

Shiomi et al. (1980) provide osmotic pressure data for the methyl ethyl ketone - poly(dimethylsiloxane) (PDMS) system at 293.15 K.

Input data: methyl ethyl ketone = 1, PDMS = 2

		Source
π	= 41.2 x 10^{-4} J/cm^3 = 4120.0 Pa	Given
T	= 293.15 K	Given
w_2	= 0.0956	Given
V_1^o	= 0.089606 m^3/kmol	Daubert and Danner (1990)

$$w_1 = 1 - w_2 = 0.9044$$

From Equation (4C-39),

$$a_1 = \exp\left[\frac{-(4120.0)(0.089606)}{(8314.0)(293.15)}\right] = 0.9998$$

and from Equation (4C-40),

$$\Omega_1 = \frac{0.9998}{0.9044} = 1.1055$$

D. LISTING OF SYSTEMS INCLUDED IN DATA BASES

In the following sections are listings of the pure polymer and polymer-solvent systems that can be retrieved from the data base files included in the **Handbook**. The POLYDATA program is recommended to interactively examine these data bases.

1. Pure Polymer PVT Data

POLYMER	NUMBER AVG. MOLECULAR WT.	WEIGHT AVG. MOLECULAR WT.
BR		
HDPE	5.2E+04	
HMDS	1.624E+02	1.624E+02
i-PB		
i-PMMA		
i-PP		

Pure Polymer PVT Data (Continued)

POLYMER	NUMBER AVG. MOLECULAR WT.	WEIGHT AVG. MOLECULAR WT.
LDPE		
LDPE	2.50E+04	1.90E+05
LLDPE		
P(E&VAC)		
PA-6		
PAR		
PBMA		
PC		
PCHMA		
PDMPO/PS		
PDMS	4.72E+04	1.66E+05
PDMS	5.94E+02	6.65E+02
PDMS	9.58E+02	1.418E+03
PDMS	1.540E+03	1.879E+03
PDMS	4.170E+03	5.921E+03
PDMS	6.560E+03	1.1218E+04
PDMS	7.860E+03	1.7056E+04
PDMS	5.000E+03	
PEEK		
PEG	7.5E+03	
PETP		
PHENOXY		
PIB		
PMMA		
PMP		
POM		
PoMS		
PPFE		
PS	9.07E+04	2.79E+05
PSF		
PT	4.0E+04	
PTFE		
PVAC	8.4E+04	3.3E+05
PVAL		
PVC		

2. Finite Concentration VLE Data

POLYMER	SOLVENT	POLYMER	SOLVENT
BR	Benzene	BR	n-Hexane
BR	Carbon Tetrachloride	BR	n-Nonane
BR	Chloroform	HDPE	Cyclohexane
BR	Cyclohexane	HDPE	n-Decane
BR	Dichloromethane	HDPE	n-Hexane
BR	Ethylbenzene	HDPE	Isooctane

Finite Concentration VLE Data (Continued)

POLYMER	SOLVENT	POLYMER	SOLVENT
HDPE	2,2,4-Trimethylpentane	PIB	Neopentane
IR	Acetone	PIB	n-Octane
IR	Benzene	PIB	n-Pentane
IR	Carbon Tetrachloride	PIB	Propane
IR	Chloroform	PMAA	Water
IR	Cyclohexane	PMMA	Methyl Ethyl Ketone
IR	Dichloromethane	PMMA	Toluene
IR	Ethyl Acetate	PoCS	Benzene
IR	Methyl Ethyl Ketone	PoCS	Methyl Ethyl Ketone
IR	Toluene	POD	Toluene
LDPE	n-Butane	POPG	Methanol
LDPE	1-Butene	i-PP	Dichloromethane
LDPE	n-Heptane	PP	Diethyl Ketone
LDPE	n-Hexane	PP	Diisopropyl Ketone
LDPE	Isobutane	PP	n-Hexane
LDPE	Isobutylene	PpBrS	Toluene
LDPE	n-Pentane	PpClS	Toluene
PAA	Water	PPGDE	Carbon Tetrachloride
PD	Toluene	PPGDE	Chloroform
PDD	Toluene	PpMS	Toluene
PDMS	Benzene	PPOX(PPG)	Benzene
PDMS	Chloroform	PPOX(PPG)	Water
PDMS	Cyclohexane	PS	Acetone
PDMS	Dichloromethane	PS	Benzene
PDMS	Diisobutyl Ketone	PS	n-Butyl Acetate
PDMS	n-Heptane	PS	Carbon Disulfide
PDMS	n-Hexamethyldisiloxane	PS	Carbon Tetrachloride
PDMS	n-Hexane	PS	Chloroform
PDMS	Methyl Ethyl Ketone	PS	Cyclohexane
PDMS	Methyl Isobutyl Ketone	PS	Diethyl Ketone
PDMS	n-Nonane	PS	Dimethyl Methyl Phosphonate
PDMS	n-Octane	PS	1,4-Dioxane
PDMS	n-Pentane	PS	Ethylbenzene
PDMS	Toluene	PS	Methanol
PDMS	2,2,4-Trimethylpentane	PS	Methyl Ethyl Ketone
P(E&VAC)	Cyclohexane	PS	Nitromethane
P(E&VAC)	2,2,4-Trimethylpentane	PS	n-Nonane
PEGDE	Carbon Tetrachloride	PS	n-Octane
PEGDE	Chloroform	PS	n-Propyl Acetate
PEO(PEG)	Benzene	PS	Di-n-Propyl Ether
PEO(PEG)	Chloroform	PS	Toluene
PEO(PEG)	Water	PS	1,2,4-Trimethylbenzene
PH	Toluene	PS	m-Xylene
PIB	Benzene	PT	1,4-Dioxane
PIB	n-Butane	PVAC	Acetone
PIB	Carbon Tetrachloride	PVAC	Benzene
PIB	Cyclohexane	PVAC	3-Chloropropene
PIB	Isobutane	PVAC	2,2,4-Trimethylpentane
PIB	Isopentane	PVAC	Isopropylamine

Finite Concentration VLE Data (Continued)

POLYMER	SOLVENT	POLYMER	SOLVENT
PVAC	n-Propanol	PVC	1,4-Dioxane
PVAC	n-Propyl Chloride	PVC	Di-n-Propyl Ether
PVAC	n-Propylamine	PVC	Tetrahydrofuran
PVAC	Vinyl Acetate	PVC	Toluene
PVAL	Water	PVP	Water
PVAM	Water	SBR	Ethylbenzene
PVC	Dimethyl Methyl Phosphonate		

3. Infinite Dilution VLE Data

POLYMER	SOLVENT	POLYMER	SOLVENT
BR	Acetone	CPE	Methyl Ethyl Ketone
BR	Acetonitrile	CPE	n-Pentane
BR	Aniline	CPE	Tetrahydrofuran
BR	Benzaldehyde	DHPOE	Nitroglycerine
BR	Benzene	DHPOE	Triacetin
BR	Benzyl Alcohol	DHPTM	Triacetin
BR	n-Butanol	DHPTM	Nitroglycerine
BR	n-Butylbenzene	P(GMA&VAC&VC)	Acetone
BR	Carbon Tetrachloride	P(GMA&VAC&VC)	n-Propyl Acetate
BR	Chloroform	P(GMA&VAC&VC)	Vinyl Chloride
BR	Cyclohexane	HDPE	Benzyl Alcohol
BR	Cyclohexanone	HDPE	p-tert-Amyl Phenol
BR	1,2-Dichloroethane	HDPE	Anisole
BR	Dichloromethane	HDPE	Benzyl Acetate
BR	1,4-Dioxane	HDPE	Benzyl Benzoate
BR	N,N-Dimethylformamide	HDPE	Benzyl Phenyl Ether
BR	Ethyl Acetate	HDPE	Benzyl Propionate
BR	Ethyl Formate	HDPE	Biphenyl
BR	Ethylbenzene	HDPE	n-Butane
BR	n-Heptane	HDPE	n-Butyl Acetate
BR	n-Hexane	HDPE	p-tert-Butyl Phenol
BR	Isopropanol	HDPE	Cyclohexanone
BR	Methanol	HDPE	cis-Decahydronaphthalene
BR	Methyl Ethyl	HDPE	trans-Decahydronaphthalene
	Ketone	HDPE	n-Decane
BR	Methyl Isobutyl	HDPE	2,4-Dimethylhexane
	Ketone	HDPE	2,5-Dimethylhexane
BR	Tetrahydrofuran	HDPE	3,4-Dimethylhexane
BR	Toluene	HDPE	n-Dodecane
BR	p-Xylene	HDPE	Ethylbenzene
CPE	Acetone	HDPE	n-Hexane
CPE	Chloroform	HDPE	Mesitylene
CPE	Dichloromethane	HDPE	Methyl Isobutyl Ketone
CPE	Diethyl Ether	HDPE	2-Methylheptane
CPE	Ethyl Acetate	HDPE	3-Methylheptane
CPE	Methanol	HDPE	3-Methylhexane

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
HDPE	2-Nitropropane
HDPE	n-Nonane
HDPE	n-Octane
HDPE	1,2,3,4-Tetrahydro-naphthalene
HDPE	Toluene
HDPE	2,2,4-Trimethylhexane
HDPE	2,2,4-Trimethylpentane
HDPE	m-Xylene
HDPE	p-Xylene
HIPS	Benzene
HIPS	Cyclohexane
HIPS	n-Hexane
P(HPA&VAC&VC)	Acetone
P(HPA&VAC&VC)	n-Propyl Acetate
P(HPA&VAC&VC)	Vinyl Acetate
P(HPA&VAC&VC)	Vinyl Chloride
IR	Acetic Acid
IR	Acetone
IR	Acetonitrile
IR	Aniline
IR	Benzaldehyde
IR	Benzene
IR	Benzyl Alcohol
IR	n-Butanol
IR	Carbon Tetrachloride
IR	Chloroform
IR	Cyclohexane
IR	Cyclohexanone
IR	1,2-Dichloroethane
IR	Dichloromethane
IR	N,N-Dimethylformamide
IR	1,4-Dioxane
IR	Ethyl Acetate
IR	Ethylbenzene
IR	Ethylene Glycol
IR	n-Heptane
IR	n-Hexane
IR	Isopropanol
IR	Methanol
IR	Methyl Ethyl Ketone
IR	Methyl Isobutyl Ketone
IR	2-Methylheptane
IR	2-Methylhexane
IR	2-Methylpentane
IR	n-Octane
IR	n-Pentane
IR	Tetrahydrofuran
IR	Toluene
IR	2,2,4-Trimethylpentane
IR	p-Xylene
LDPE	Acetone
LDPE	Benzene
LDPE	n-Butanol
LDPE	n-Butyl Chloride
LDPE	n-Butylbenzene
LDPE	Carbon Tetrachloride
LDPE	Chloroform
LDPE	Cumene
LDPE	Cyclohexane
LDPE	Cyclohexanol
LDPE	cis-Decahydronaphthalene
LDPE	trans-Decahydronaphthalene
LDPE	n-Decane
LDPE	2,4-Dimethylhexane
LDPE	2,5-Dimethylhexane
LDPE	3,4-Dimethylhexane
LDPE	n-Dodecane
LDPE	Ethylbenzene
LDPE	n-Heptane
LDPE	n-Hexane
LDPE	Isopropanol
LDPE	Mesitylene
LDPE	Methyl Chloride
LDPE	Methyl Ethyl Ketone
LDPE	2-Methylheptane
LDPE	3-Methylheptane
LDPE	3-Methylhexane
LDPE	Monochlorobenzene
LDPE	n-Nonane
LDPE	1-Nonene
LDPE	n-Octane
LDPE	1-Octene
LDPE	3-Pentanone
LDPE	Phenol
LDPE	Sulfur Dioxide
LDPE	Tetrahydrofuran
LDPE	1,2,3,4-Tetra-hydronaphthalene
LDPE	Toluene
LDPE	2,2,4-Trimethylhexane
LDPE	2,2,4-Trimethylpentane
LDPE	Vinyl Acetate
LDPE	m-Xylene
LDPE	p-Xylene
P(AMS&AN)	Benzene
P(AMS&AN)	n-Butanol
P(AMS&AN)	n-Butyl Acetate

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
P(AMS&AN)	n-Butylbenzene
P(AMS&AN)	Chloroform
P(AMS&AN)	Cyclohexanol
P(AMS&AN)	Dichloromethane
P(AMS&AN)	1,4-Dioxane
P(AMS&AN)	n-Dodecane
P(AMS&AN)	Monochlorobenzene
P(AMS&AN)	Methyl Ethyl Ketone
P(AMS&AN)	n-Tetradecane
P(AMS&AN)	Tetrahydrofuran
P(AMS&AN)	Toluene
PAR	o-Dichlorobenzene
PAR	Diethylene Glycol Diethyl Ether
PAR	n-Dodecane
PAR	Ethylbenzene
PAR	Monochlorobenzene
PAR	1,2,3,4-Tetrahydro-naphthalene
PAR	p-Xylene
PBA	Acetone
PBA	Acetonitrile
PBA	Chloroform
PBA	Ethyl Acetate
PBA	n-Hexane
PBA	Methyl Ethyl Ketone
PBA	n-Propanol
PBAD	Acetone
PBAD	Benzene
PBAD	Carbon Tetrachloride
PBAD	Chloroform
PBAD	Dichloromethane
PBAD	Ethyl Acetate
PBAD	n-Heptane
PBAD	n-Hexane
PBAD	Methyl Ethyl Ketone
PBAD	n-Pentane
P(BMA&S)	Benzene
P(BMA&S)	tert-Butylbenzene
P(BMA&S)	Carbon Tetrachloride
P(BMA&S)	1-Chlorobutane
P(BMA&S)	Chloroform
P(BMA&S)	Cyclohexane
P(BMA&S)	n-Decane
P(BMA&S)	Dichloromethane
P(BMA&S)	n-Octane
P(BMA&S)	2,2,4-Trimethylpentane
PBMA	Acetic Acid
PBMA	Acetone
PBMA	Acetonitrile
PBMA	Aniline
PBMA	Benzaldehyde
PBMA	Benzene
PBMA	Benzyl Alcohol
PBMA	n-Butanol
PBMA	n-Butyl Acetate
PBMA	n-Butylbenzene
PBMA	tert-Butylbenzene
PBMA	n-Butylcyclohexane
PBMA	Carbon Tetrachloride
PBMA	1-Chlorobutane
PBMA	Chloroform
PBMA	Cyclohexane
PBMA	Cyclohexanone
PBMA	n-Decane
PBMA	1,2-Dichloroethane
PBMA	Dichloromethane
PBMA	N,N-Dimethylformamide
PBMA	Ethanol
PBMA	Ethyl Acetate
PBMA	Ethylbenzene
PBMA	Ethylene Glycol
PBMA	n-Heptane
PBMA	n-Hexane
PBMA	Isopropanol
PBMA	Methanol
PBMA	Methyl Ethyl Ketone
PBMA	Methyl Isobutyl Ketone
PBMA	2-Methylheptane
PBMA	Monochlorobenzene
PBMA	n-Nonane
PBMA	n-Octane
PBMA	n-Pentane
PBMA	2-Pentanone
PBMA	n-Propanol
PBMA	Tetrahydrofuran
PBMA	2,2,4-Trimethylpentane
PBMA	Toluene
PBMA	Trichloroethylene
PBMA	p-Xylene
P(C&DMS)	n-Decane
P(C&DMS)	o-Dichlorobenzene
P(C&DMS)	Monochlorobenzene
P(C&DMS)	Toluene
PC	n-Decane
PC	o-Dichlorobenzene
PC	Monochlorobenzene
PC	Toluene

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
PCL	Acetone
PCL	Benzene
PCL	Carbon Tetrachloride
PCL	Chloroform
PCL	Dichloromethane
PCL	Ethyl Acetate
PCL	n-Heptane
PCL	n-Hexane
PCL	Methyl Ethyl Ketone
PCL	n-Pentane
PDMPO	Acetophenone
PDMPO	n-Butylbenzene
PDMPO	n-Butylcyclohexane
PDMPO	Cyclohexanol
PDMPO	cis-Decahydronaphthalene
PDMPO	n-Decane
PDMPO	Monochlorobenzene
PDMPO	n-Octane
PDMPO	Toluene
PDMPO	3,4,5-Trimethylheptane
P(DMS&S)	n-Decane
PDMS	Benzene
PDMS	n-Butanol
PDMS	Carbon Tetrachloride
PDMS	Chloroform
PDMS	Cycloheptane
PDMS	Cyclohexane
PDMS	Cyclooctane
PDMS	Cyclopentane
PDMS	n-Decane
PDMS	o-Dichlorobenzene
PDMS	Dichloromethane
PDMS	N,N-Dimethylaniline
PDMS	2,4-Dimethylpentane
PDMS	Dioxane
PDMS	Dodecane
PDMS	Ethyl Acetate
PDMS	Ethylbenzene
PDMS	n-Heptane
PDMS	Hexamethyldisiloxane
PDMS	n-Hexane
PDMS	Mesitylene
PDMS	2-Methylbutane
PDMS	Methylcyclohexane
PDMS	2-Methylheptane
PDMS	2-Methylhexane
PDMS	3-Methylhexane
PDMS	2-Methylpentane
PDMS	3-Methylpentane
PDMS	Monochlorobenzene
PDMS	n-Nonane
PDMS	n-Octane
PDMS	n-Octanol
PDMS	n-Pentane
PDMS	2-Pentanone
PDMS	Pyridine
PDMS	Toluene
PDMS	2,2,4-Trimethylpentane
PDMS	Undecane
PDMS	m-Xylene
PDMS	o-Xylene
PDMS	p-Xylene
P(E&P)	Benzene
P(E&P)	tert-Butylbenzene
P(E&P)	Carbon Tetrachloride
P(E&P)	Chloroform
P(E&P)	Cyclohexane
P(E&P)	n-Decane
P(E&P)	Dichloromethane
P(E&P)	Ethylbenzene
P(E&P)	n-Heptane
P(E&P)	n-Hexane
P(E&P)	n-Octane
P(E&P)	n-Pentane
P(E&P)	Toluene
P(E&P)	2,2,4-Trimethylpentane
P(E&P)	p-Xylene
P(E&VAC)	Acetaldehyde
P(E&VAC)	Acetic Acid
P(E&VAC)	Acetone
P(E&VAC)	Benzene
P(E&VAC)	1-Bromobutane
P(E&VAC)	2-Bromobutane
P(E&VAC)	n-Butanol
P(E&VAC)	sec-Butanol
P(E&VAC)	n-Butyl Chloride
P(E&VAC)	Carbon Tetrachloride
P(E&VAC)	1-Chlorobutane
P(E&VAC)	Chloroform
P(E&VAC)	Cyclohexane
P(E&VAC)	Cyclohexanol
P(E&VAC)	n-Decane
P(E&VAC)	1,2-Dichloroethane
P(E&VAC)	Dichloromethane
P(E&VAC)	Diethyl Ether
P(E&VAC)	1,4-Dioxane
P(E&VAC)	Dipropyl Ether
P(E&VAC)	Ethanenitrile

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
P(E&VAC)	Ethanol
P(E&VAC)	Ethyl Acetate
P(E&VAC)	Formic acid
P(E&VAC)	Furan
P(E&VAC)	n-Heptane
P(E&VAC)	n-Hexane
P(E&VAC)	Isopropanol
P(E&VAC)	Methanol
P(E&VAC)	Methyl Chloride
P(E&VAC)	Methyl Ethyl Ketone
P(E&VAC)	Methyl Propyl Ketone
P(E&VAC)	Methylcyclohexane
P(E&VAC)	Monochlorobenzene
P(E&VAC)	Nitroethane
P(E&VAC)	Nitromethane
P(E&VAC)	1-Nitropropane
P(E&VAC)	2-Nitropropane
P(E&VAC)	n-Octane
P(E&VAC)	1-Octene
P(E&VAC)	n-Pentane
P(E&VAC)	3-Pentanone
P(E&VAC)	Phenol
P(E&VAC)	Propionitrile
P(E&VAC)	Acrylonitrile
P(E&VAC)	n-Propyl Acetate
P(E&VAC)	Sulfur Dioxide
P(E&VAC)	Tetrahydrofuran
P(E&VAC)	2,2,2-Trifluoroethanol
P(E&VAC)	Toluene
P(E&VAC)	Vinyl Acetate
P(E&VAC)	Water
P(E&VAC)	m-Xylene
P(E&VAC)	p-Xylene
PEA	Acetone
PEA	Acetonitrile
PEA	Chloroform
PEA	Ethyl Acetate
PEA	n-Hexane
PEA	Methyl Ethyl Ketone
PEA	n-Propanol
PEAD	Acetone
PEAD	Benzene
PEAD	Carbon Tetrachloride
PEAD	Chloroform
PEAD	Dichloromethane
PEAD	Ethyl Acetate
PEAD	n-Heptane
PEAD	n-Hexane
PEAD	Methyl Ethyl Ketone
PEAD	n-Pentane
PECH	Acetone
PECH	tert-Butanol
PECH	tert-Butyl Acetate
PECH	Carbon Tetrachloride
PECH	Chloroform
PECH	Cyclohexane
PECH	n-Decane
PECH	Dichloromethane
PECH	n-Dodecane
PECH	Ethyl Acetate
PECH	n-Heptane
PECH	n-Hexane
PECH	Isopropanol
PECH	Methanol
PECH	Methyl Ethyl Ketone
PECH	n-Octane
PECH	n-Pentane
PECH	Tetrahydrofuran
PECH	Toluene
PECH	Trichloroethylene
PECH	n-Undecane
PEMA	Acetone
PEMA	Acetonitrile
PEMA	Acrylonitrile
PEMA	Benzene
PEMA	Bromobenzene
PEMA	1-Bromobutane
PEMA	n-Butanol
PEMA	n-Butyl Acetate
PEMA	n-Butylamine
PEMA	n-Butyraldehyde
PEMA	Carbon Tetrachloride
PEMA	Chloroform
PEMA	Cyclohexane
PEMA	n-Decane
PEMA	n-Dodecane
PEMA	Ethanol
PEMA	Ethyl Acetate
PEMA	Ethylbenzene
PEMA	Ethylcyclohexane
PEMA	n-Heptane
PEMA	n-Hexane
PEMA	Isopropanol
PEMA	Methanol
PEMA	Methyl Acetate
PEMA	Methyl Ethyl Ketone
PEMA	Methylcyclohexane
PEMA	Monochlorobenzene

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
PEMA	Nitroethane
PEMA	Nitromethane
PEMA	1-Nitropropane
PEMA	n-Nonane
PEMA	n-Octane
PEMA	1-Octene
PEMA	1-Pentanol
PEMA	2-Pentanol
PEMA	n-Propanol
PEMA	Propionic Acid
PEMA	Propionitrile
PEMA	n-Propyl Acetate
PEMA	Di-n-Propyl Ether
PEMA	Toluene
PEMA	n-Undecane
PEO(PEG)	Acetone
PEO(PEG)	Acetonitrile
PEO(PEG)	Benzene
PEO(PEG)	n-Butanol
PEO(PEG)	n-Butyl Acetate
PEO(PEG)	n-Butyronitrile
PEO(PEG)	Carbon Tetrachloride
PEO(PEG)	1-Chlorobutane
PEO(PEG)	Chloroform
PEO(PEG)	1-Chloropropane
PEO(PEG)	Cyclohexane
PEO(PEG)	n-Decane
PEO(PEG)	1,2-Dichloroethane
PEO(PEG)	1,1-Dichloroethylene
PEO(PEG)	Diethyl Ether
PEO(PEG)	Diethylene Glycol Diethyl Ether
PEO(PEG)	1,2-Dimethoxyethane
PEO(PEG)	1,4-Dioxane
PEO(PEG)	n-Dodecane
PEO(PEG)	Ethanol
PEO(PEG)	Ethyl Acetate
PEO(PEG)	Ethylbenzene
PEO(PEG)	Ethylcyclohexane
PEO(PEG)	n-Heptane
PEO(PEG)	1-Heptene
PEO(PEG)	n-Hexane
PEO(PEG)	1-Hexene
PEO(PEG)	Isopropanol
PEO(PEG)	Methanol
PEO(PEG)	Methyl Acetate
PEO(PEG)	Methyl Ethyl Ketone
PEO(PEG)	Methyl Isobutyl Ketone
PEO(PEG)	Methylcyclohexane
PEO(PEG)	Methylene Chloride
PEO(PEG)	Monochlorobenzene
PEO(PEG)	Nitromethane
PEO(PEG)	n-Nonane
PEO(PEG)	n-Octane
PEO(PEG)	1-Octene
PEO(PEG)	n-Pentane
PEO(PEG)	1-Pentene
PEO(PEG)	n-Propanol
PEO(PEG)	Propionitrile
PEO(PEG)	n-Propyl Acetate
PEO(PEG)	Pyridine
PEO(PEG)	Tetrahydrofuran
PEO(PEG)	Toluene
PEO(PEG)	1,1,1-Trichloroethane
PEO(PEG)	1,1,2-Trichloroethane
PEO(PEG)	n-Undecane
PEO(PEG)	Water
PEO(PEG)	m-Xylene
PEO(PEG)	o-Xylene
PEO(PEG)	p-Xylene
PES	Acetone
PES	Benzene
PES	Carbon Tetrachloride
PES	Chloroform
PES	Dichloromethane
PES	Ethyl Acetate
PES	n-Heptane
PES	n-Hexane
PES	Methyl Ethyl Ketone
PES	n-Pentane
PHA	Acetone
PHA	Acetonitrile
PHA	Chloroform
PHA	Ethyl Acetate
PHA	n-Hexane
PHA	Methyl Ethyl Ketone
PHA	n-Propanol
PHMA	Acetone
PHMA	Acetonitrile
PHMA	Chloroform
PHMA	Ethyl Acetate
PHMA	n-Hexane
PHMA	Methyl Ethyl Ketone
PHMA	n-Propanol
PHMS	Acetone
PHMS	Benzene
PHMS	Carbon Tetrachloride

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT	POLYMER	SOLVENT
PHMS	Chloroform	PL	n-Pentane
PHMS	Dichloromethane	PMA	Acetone
PHMS	Ethyl Acetate	PMA	Acetonitrile
PHMS	n-Heptane	PMA	Benzene
PHMS	n-Hexane	PMA	tert-Butanol
PHMS	Methyl Ethyl Ketone	PMA	tert-Butyl Acetate
PHMS	n-Pentane	PMA	n-Butylbenzene
PIB	Benzene	PMA	tert-Butylbenzene
PIB	Carbon Tetrachloride	PMA	n-Butylcyclohexane
PIB	Chloroform	PMA	Carbon Tetrachloride
PIB	Cyclohexane	PMA	Chloroform
PIB	n-Heptane	PMA	Cyclohexane
PIB	n-Hexane	PMA	cis-Decahydronaphthalene
PIB	n-Octane	PMA	trans-Decahydronaphthalene
PIB	n-Pentane	PMA	n-Decane
PIB	Toluene	PMA	Dichloromethane
P(IBMA&S)	Benzene	PMA	n-Dodecane
P(IBMA&S)	tert-Butylbenzene	PMA	Ethanol
P(IBMA&S)	Carbon Tetrachloride	PMA	Ethyl Acetate
P(IBMA&S)	1-Chlorobutane	PMA	Ethylbenzene
P(IBMA&S)	Chloroform	PMA	n-Heptane
P(IBMA&S)	Cyclohexane	PMA	n-Hexane
P(IBMA&S)	n-Decane	PMA	Isopropanol
P(IBMA&S)	Dichloromethane	PMA	Methanol
P(IBMA&S)	n-Octane	PMA	Methyl Ethyl Ketone
P(IBMA&S)	2,2,4-Trimethylpentane	PMA	Naphthalene
PIBMA	Benzene	PMA	n-Octane
PIBMA	n-Butanol	PMA	n-Pentane
PIBMA	n-Butylbenzene	PMA	n-Propanol
PIBMA	tert-Butylbenzene	PMA	n-Tetradecane
PIBMA	n-Butylcyclohexane	PMA	Tetrahydrofuran
PIBMA	Carbon Tetrachloride	PMA	1,2,3,4-Tetrahydro-
PIBMA	1-Chlorobutane		naphthalene
PIBMA	Chloroform	PMA	3,3,4,4-Tetramethylhexane
PIBMA	Cyclohexane	PMA	Toluene
PIBMA	n-Decane	PMA	Trichloroethylene
PIBMA	Dichloromethane	PMA	2,2,4-Trimethylheptane
PIBMA	Monochlorobenzene	PMA	3,4,5-Trimethylheptane
PIBMA	n-Octane	PMA	2,2,5-Trimethylhexane
PIBMA	2,2,4-Trimethylpentane	PMA	n-Undecane
PL	Acetone	PMCPS	Benzene
PL	Benzene	PMCPS	n-Butanol
PL	Carbon Tetrachloride	PMCPS	n-Decane
PL	Chloroform	PMCPS	n-Dodecane
PL	Dichloromethane	PMCPS	n-Heptane
PL	Ethyl Acetate	PMCPS	n-Hexane
PL	n-Heptane	PMCPS	n-Nonane
PL	n-Hexane	PMCPS	n-Octane
PL	Methyl Ethyl Ketone	PMCPS	2-Pentanone

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
PMCPS	Pyridine
PMCPS	n-Undecane
PMMA	Acetic Acid
PMMA	Acetone
PMMA	Acetonitrile
PMMA	Acetophenone
PMMA	Aniline
PMMA	Benzaldehyde
PMMA	Benzene
PMMA	Benzyl Alcohol
PMMA	n-Butanol
PMMA	n-Butylbenzene
PMMA	1-Chlorodecane
PMMA	Chloroform
PMMA	1-Chlorooctane
PMMA	Cyclohexanol
PMMA	Cyclohexanone
PMMA	o-Dichlorobenzene
PMMA	1,2-Dichloroethane
PMMA	Dichloromethane
PMMA	N,N-Dimethylformamide
PMMA	n-Dodecane
PMMA	Ethyl Acetate
PMMA	Ethylbenzene
PMMA	Ethylene Glycol
PMMA	n-Hexadecane
PMMA	n-Hexane
PMMA	Isopropanol
PMMA	Methanol
PMMA	Methyl Acetate
PMMA	Methyl Ethyl Ketone
PMMA	Methyl Isobutyl Ketone
PMMA	Methyl Methacrylate
PMMA	n-Tetradecane
PMMA	Tetrahydrofuran
PMMA	1,2,3,4-Tetrahydro-naphthalene
PMMA	Toluene
PMMA	m-Xylene
PMMA	p-Xylene
PMTFPS	n-Decane
PMTFPS	n-Heptane
PMTFPS	n-Nonane
PMTFPS	n-Octane
PODMI	n-Decane
PODMI	1-Decanol
PODMI	n-Dodecane
PODMI	1-Heptanol
PODMI	1-Hexanol
PODMI	n-Nonane
PODMI	1-Octanol
PODMI	n-Tridecane
PODMI	n-Undecane
PP	n-Hexane
PPA	Acetone
PPA	Acetonitrile
PPA	Chloroform
PPA	Ethyl Acetate
PPA	n-Hexane
PPA	Methyl Ethyl Ketone
PPA	n-Propanol
PPeMA	Acetone
PPeMA	Acetonitrile
PPeMA	Chloroform
PPeMA	Ethyl Acetate
PPeMA	n-Hexane
PPeMA	Methyl Ethyl Ketone
PPeMA	n-Propanol
PPMA	Acetone
PPMA	Acetonitrile
PPMA	Chloroform
PPMA	Ethyl Acetate
PPMA	n-Hexane
PPMA	Methyl Ethyl Ketone
PPMA	n-Propanol
PS	Acetic Acid
PS	Acetophenone
PS	Acetone
PS	Acetonitrile
PS	Aniline
PS	Anisole
PS	Benzaldehyde
PS	Benzene
PS	Benzyl Alcohol
PS	n-Butanol
PS	n-Butyl Acetate
PS	tert-Butyl Acetate
PS	n-Butylbenzene
PS	tert-Butylbenzene
PS	n-Butylcyclohexane
PS	Carbon Disulfide
PS	Carbon Tetrachloride
PS	Chloroform
PS	Cyclohexane
PS	Cyclohexanol
PS	Cyclohexanone
PS	Cyclopentane
PS	cis-Decahydronaphthalene

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
PS	trans-Decahydronaphthalene
PS	n-Decane
PS	o-Dichlorobenzene
PS	1,2-Dichloroethane
PS	Dichloromethane
PS	Diethyl Ether
PS	Diisopropyl Ether
PS	N,N-Dimethylformamide
PS	1,4-Dioxane
PS	n-Dodecane
PS	Ethanol
PS	Ethyl Acetate
PS	Ethylbenzene
PS	Ethylene Glycol
PS	Fluorobenzene
PS	Formamide
PS	n-Heptane
PS	n-Hexadecane
PS	n-Hexane
PS	n-Hexylbenzene
PS	Isobutanol
PS	Isopropanol
PS	Methanol
PS	Methyl Ethyl Ketone
PS	2-Methylheptane
PS	2-Methylpentane
PS	3-Methylpentane
PS	Monochlorobenzene
PS	Naphthalene
PS	Nitrobenzene
PS	Nitroethane
PS	n-Nonane
PS	n-Octane
PS	1-Octanol
PS	1-Octene
PS	cis-2-Octene
PS	n-Pentane
PS	1-Pentanol
PS	2-Pentanone
PS	n-Pentylbenzene
PS	n-Propanol
PS	n-Propyl Acetate
PS	n-Propylbenzene
PS	Pyridine
PS	Styrene
PS	Tetrachloroethylene
PS	n-Tetradecane
PS	Tetrahydrofuran
PS	3,3,4,4-Tetramethylhexane
PS	1,2,3,4-Tetrahydronaphthalene
PS	Toluene
PS	Trichloroethylene
PS	1,2,4-Trimethylbenzene
PS	3,4,5-Trimethylheptane
PS	2,2,4-Trimethylpentane
PS	Water
PS	m-Xylene
PS	o-Xylene
PS	p-Xylene
PSBMA	Benzene
PSBMA	n-Butylcyclohexane
PSBMA	Carbon Tetrachloride
PSBMA	Chloroform
PSBMA	Cyclohexane
PSBMA	n-Decane
PSBMA	Dichloromethane
PSBMA	n-Octane
PSBMA	2,2,4-Trimethylpentane
PSF	Acetonitrile
PSF	Carbon Tetrachloride
PSF	Chloroform
PSF	Cyclohexanone
PSF	n-Decane
PSF	Dichloromethane
PSF	Diethylene Glycol Dimethyl Ether
PSF	Dimethyl Sulfoxide
PSF	Dimethylacetamide
PSF	Dimethylformamide
PSF	Ethanol
PSF	Fluorobenzene
PSF	n-Heptane
PSF	Methanol
PSF	Methyl Ethyl Ketone
PSF	N-Methylpyrrolidone
PSF	Monochlorobenzene
PSF	n-Octane
PSF	Phenol
PSF	Pyridine
PSF	Sulfolane
PSF	Toluene
PSF	m-Xylene
P(VAC&VAL)	Benzene
P(VAC&VAL)	n-Butanol
P(VAC&VAL)	tert-Butanol
P(VAC&VAL)	Cyclohexanol
P(VAC&VAL)	n-Decane

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT
P(VAC&VAL)	n-Dodecane
P(VAC&VAL)	Ethylbenzene
P(VAC&VAL)	n-Hexadecane
P(VAC&VAL)	Isopropanol
P(VAC&VAL)	n-Nonane
P(VAC&VAL)	2-Pentanol
P(VAC&VAL)	n-Propanol
P(VAC&VAL)	n-Tetradecane
P(VAC&VAL)	Toluene
P(VAC&VAL)	n-Undecane
P(VAC&VC)	Acetaldehyde
P(VAC&VC)	Acetone
P(VAC&VC)	Acetonitrile
P(VAC&VC)	Benzene
P(VAC&VC)	Cyclohexane
P(VAC&VC)	1,2-Dichloroethane
P(VAC&VC)	1,4-Dioxane
P(VAC&VC)	n-Heptane
P(VAC&VC)	Isopropanol
P(VAC&VC)	Methanol
P(VAC&VC)	Methyl Ethyl Ketone
P(VAC&VC)	Nitroethane
P(VAC&VC)	n-Propyl Acetate
P(VAC&VC)	Tetrahydrofuran
P(VAC&VC)	Toluene
P(VAC&VC)	Vinyl Chloride
PVAC	Acetaldehyde
PVAC	Acetone
PVAC	Acetonitrile
PVAC	Benzene
PVAC	n-Butanol
PVAC	tert-Butanol
PVAC	n-Butyl Acetate
PVAC	Butyl Chloride
PVAC	n-Butylbenzene
PVAC	n-Butylcyclohexane
PVAC	Carbon Tetrachloride
PVAC	Chloroform
PVAC	Cyclohexane
PVAC	Cyclohexanol
PVAC	Cyclohexanone
PVAC	cis-Decahydronaphthalene
PVAC	n-Decane
PVAC	1,2-Dichloroethane
PVAC	Diethylene Glycol Diethyl Ether
PVAC	Dioxane
PVAC	n-Dodecane
PVAC	Ethanol
PVAC	2-Ethoxyethanol
PVAC	Ethyl Acetate
PVAC	Ethylbenzene
PVAC	n-Heptane
PVAC	n-Hexadecane
PVAC	n-Hexane
PVAC	Isooctane
PVAC	Isopropanol
PVAC	Methanol
PVAC	2-Methoxyethanol
PVAC	Methyl Ethyl Ketone
PVAC	Methyl Isobutyl Ketone
PVAC	Monochlorobenzene
PVAC	Nitroethane
PVAC	n-Nonane
PVAC	n-Octane
PVAC	1-Octene
PVAC	2-Pentanol
PVAC	3-Pentanone
PVAC	n-Propanol
PVAC	n-Tetradecane
PVAC	Tetrahydrofuran
PVAC	Tetrahydronaphthalene
PVAC	3,3,4,4-Tetramethylhexane
PVAC	Toluene
PVAC	n-Undecane
PVAC	Vinyl Acetate
PVC	Acetaldehyde
PVC	Acetone
PVC	Acetonitrile
PVC	Benzene
PVC	Benzyl Alcohol
PVC	tert-Butanol
PVC	n-Butanol
PVC	n-Butyl Acetate
PVC	Carbon Tetrachloride
PVC	Chloroform
PVC	Cyclohexane
PVC	n-Decane
PVC	1,2-Dichloroethane
PVC	Dichloromethane
PVC	Dioxane
PVC	Ethyl Acetate
PVC	n-Heptane
PVC	Hexane
PVC	Isopropanol
PVC	Methanol
PVC	Methyl Ethyl Ketone
PVC	Methyl Isobutyl Ketone

Infinite Dilution VLE Data (Continued)

POLYMER	SOLVENT	POLYMER	SOLVENT
PVC	Monochlorobenzene	a-PVI	Chloroform
PVC	Nitroethane	a-PVI	Cyclohexane
PVC	2-Nitropropane	a-PVI	n-Decane
PVC	n-Nonane	a-PVI	Dichloromethane
PVC	n-Octane	a-PVI	n-Heptane
PVC	n-Pentane	a-PVI	n-Hexane
PVC	n-Propanol	a-PVI	2,2,4-Trimethylpentane
PVC	Di-n-Propyl Ether	a-PVI	n-Nonane
PVC	Tetrahydrofuran	a-PVI	n-Octane
PVC	Toluene	a-PVI	n-Pentane
PVDF	Acetone	a-PVI	Toluene
PVDF	Acetophenone	a-PVI	Trichloroethylene
PVDF	Benzene	a-PVI	o-Xylene
PVDF	n-Butanol	a-PVI	p-Xylene
PVDF	n-Butyl Acetate	i-PVI	Benzene
PVDF	n-Butylbenzene	i-PVI	Carbon Tetrachloride
PVDF	Carbon Tetrachloride	i-PVI	Chloroform
PVDF	1-Chlorodecane	i-PVI	Cyclohexane
PVDF	1-Chlorooctane	i-PVI	n-Decane
PVDF	Cyclohexanol	i-PVI	Dichloromethane
PVDF	Cyclohexanone	i-PVI	n-Heptane
PVDF	n-Decane	i-PVI	n-Hexane
PVDF	o-Dichlorobenzene	i-PVI	2,2,4-Trimethylpentane
PVDF	Dichloromethane	i-PVI	n-Nonane
PVDF	N,N-Dimethylformamide	i-PVI	n-Octane
PVDF	1,4-Dioxane	i-PVI	n-Pentane
PVDF	n-Dodecane	i-PVI	Toluene
PVDF	Ethanol	i-PVI	Trichloroethylene
PVDF	Ethyl Acetate	i-PVI	o-Xylene
PVDF	n-Heptane	i-PVI	p-Xylene
PVDF	n-Hexane	PVL	Acetone
PVDF	Isopropanol	PVL	Benzene
PVDF	Methanol	PVL	Carbon Tetrachloride
PVDF	Methyl Acetate	PVL	Chloroform
PVDF	Methyl Ethyl Ketone	PVL	Dichloromethane
PVDF	n-Nonane	PVL	Ethyl Acetate
PVDF	n-Octane	PVL	n-Heptane
PVDF	n-Pentane	PVL	n-Hexane
PVDF	2-Pentanol	PVL	Methyl Ethyl Ketone
PVDF	n-Propyl Acetate	PVL	n-Pentane
PVDF	n-Tetradecane	PVME	Acetone
PVDF	Tetrahydrofuran	PVME	Cyclohexane
PVDF	1,2,3,4-Tetrahydro-naphthalene	PVME	Ethyl Acetate
		PVME	Ethylbenzene
PVDF	Toluene	PVME	n-Octane
PVDF	n-Undecane	SBR	Benzene
a-PVI	Benzene	SBR	Cyclohexane
a-PVI	Carbon Tetrachloride	SBR	n-Hexane

4. Binary Liquid-Liquid Equilibria Data

POLYMER	SOLVENT	POLYMER	SOLVENT
a-PS	Decalin	HDPE	Propane
BR	n-Hexane	HDPE	n-Tridecane
BR	2-Methylhexane	HDPE	n-Undecane
BR	n-Octane	LDPE	Diphenyl Ether
BR	2,2,3-Trimethylbutane	PAMS	Methylcyclohexane
BUPVAL	Water	PB	Anisole
CA	Acetone	PB	n-Hexane
CDA	Acetone	P(BMA&a-S)	Methyl Ethyl Ketone
EHEC	Formamide	PBMA	Methyl Ethyl Ketone
EHEC	Water	PDMA	Cyclopentane
HDPE	p-tert-Amyl Phenol	PDMA	n-Heptane
HDPE	Anisole	PDMA	n-Hexane
HDPE	Benzyl Acetate	PDMA	n-Pentane
HDPE	Benzyl Benzoate	PDMA	2,2,4-Trimethylpentane
HDPE	Benzyl Phenyl Ether	PDMPO	Toluene
HDPE	Benzyl Propionate	PDMS	n-Butane
HDPE	Biphenyl	PDMS	Ethane
HDPE	n-Butane	PDMS	Propane
HDPE	n-Butyl Acetate	P(E&P)	n-Hexane
HDPE	p-tert-Butyl Phenol	P(E&P)	3-Methyl Pentane
HDPE	Cyclohexanone	P(E&P)	Methyl Cyclopentane
HDPE	n-Decane	P(E&P)	n-Pentane
HDPE	1-Decanol	PEG	tert-Butyl Acetate
HDPE	Dibenzyl Ether	PEG	Water
HDPE	2,4-Dimethylpentane	P(b-EO&b-POX)	Formamide
HDPE	Diphenyl Ether	P(b-EO&b-POX)	Water
HDPE	Diphenylmethane	PIB	Benzene
HDPE	n-Dodecane	PIB	n-Butane
HDPE	1-Dodecanol	PIB	Diisobutyl Ketone
HDPE	Ethane	PIB	n-Hexane
HDPE	Ethylene	PIB	Isopentane
HDPE	n-Heptane	PIB	n-Octane
HDPE	1-Heptanol	PIB	n-Pentane
HDPE	n-Hexane	PIB	Propane
HDPE	1-Hexanol	PMMA	tert-Butyl Alcohol
HDPE	Isopentyl Acetate	PMMA	1-Chlorobutane
HDPE	beta-Methoxynaphthalene	PMMA	4-Heptanone
HDPE	beta-Naphthol	PMMA	Sulfolane
HDPE	n-Nonane	PMVPD	n-Butyl Acetate
HDPE	1-Nonanol	PMVPD	Methyl Isobutyl Ketone
HDPE	p-Nonylphenol	POEDE	Water
HDPE	n-Octane	PP	Diethyl Ether
HDPE	1-Octanol	PPG	Water
HDPE	p-Octylphenol	PPOX	n-Pentane
HDPE	n-Pentane	PPOX	Propane
HDPE	1-Pentanol	PS	Acetone
HDPE	Phenetole	PS	Benzene
HDPE	o-Phenyl Phenol	PS	n-Butane
HDPE	p-Phenyl Phenol	PS	tert-Butyl Acetate

Binary Liquid-Liquid Equilibria Data (Continued)

POLYMER	SOLVENT	POLYMER	SOLVENT
PS	Cyclohexane	PS	Methylal
PS	Cyclopentane	PS	Methylcyclohexane
PS	Deuterocyclohexane	PS	Methyl Ethyl Ketone
PS	Diethyl Ether	PS	Nitroethane
PS	Diethyl Oxalate	PS	n-Pentane
PS	Dioctyl Phthalate	PS	n-Propyl Acetate
PS	Ethyl Acetate	PS	1,2,4,5-Tetrachlorobenzene
PS	Ethyl Formate	PS	Toluene
PS	Isopropyl Acetate	PVAL	Water
PS	Methyl Acetate		

5. Ternary Liquid-Liquid Equilibria Data

POLYMER 1	COMPONENT 2	SOLVENT
BR	N,N-Dimethylformamide	Cyclohexane
BR	P(ASO-b-BR)	Chloroform
BR	P(ASO-b-BR)	1,1,2-Tetrachloroethane
BR	PMMA	Benzene
BR	PMMA	n-Butyl Acetate
BR	PS	Benzene
BR	PS	Carbon Tetrachloride
BR	PS	Chloroform
BR	PS	Cyclohexane
BR	PS	Styrene
BR	PS	Tetrahydrofuran
BR	PS	1,2,3,4-Tetrahydronaphthalene
BR	PS	Toluene
CDA	Acetone	Water
DEXTRAN	FICOLL	Water
DEXTRAN	HPD	Water
DEXTRAN	HPMC	Water
DEXTRAN	MC	Water
DEXTRAN	NPPEGE	Water
DEXTRAN	PEG	Water
DEXTRAN	P(EG&PG)	Water
DEXTRAN	P(EO&POX)	Water
DEXTRAN	PVAL	Water
DEXTRAN	PVME	Water
DEXTRAN	PVP	Water
EHEC	DEXTRAN	Water
EHEC	PPT	Water
EHEC	Water	Methanol
EHEC	Water	Ethanol
EHEC	Water	n-Propanol
EHEC	Water	n-Butanol
EHEC	Water	1-Pentanol
EHEC	Water	1-Hexanol
EHEC	Water	1-Heptanol

Ternary Liquid-Liquid Equilibria Data (Continued)

POLYMER 1	COMPONENT 2	SOLVENT
FICOLL	PEG	Water
GLUCOSE	PEG	Water
HDPE	n-Nonane	n-Octane
HDPE	PP	Diphenyl Ether
HP	DHPD	Water
HPD	PEG	Water
IR	PS	Benzene
IR	PS	Cyclohexane
IR	PS	Tetrahydrofuran
IR	PS	Toluene
NC	PS	Methyl Ethyl Ketone
a-PAA	1,4-Dioxane	Water
PAA	PACA	Water
P(AA&VAC)	P(ACA&S)	Tetrahydrofuran
P(AA&VAC)	P(S&VPD)	Tetrahydrofuran
P(ACA&S)	P(VAC&VAL)	Tetrahydrofuran
PACA	PEG	Water
PACA	P(VAC&VAL)	Water
PACA	PVAL	Water
PACA	PVME	Water
PAMS	PS	Methylcyclohexane
PBMA	PS	Tetrahydrofuran
P(BSAC)	P(ER&HBA)	Chloroform
PDMS	PIB	Chloroform
PDMS	PS	Ethyl Acetate
PDMS	PS	Methyl Acetate
PDMS	PS	Phenetole
P(E&P)	Ethylene	Hexane
PEA	PVO	Chlorobenzene
PEA	PVO	Toluene
PEG	Cyclohexane	Methanol
PEG	PSA	Water
PEG	PVAC	Water
PEG	P(VAC&VAL)	Water
PEG	PVAL	Water
PEG	PVME	Water
PEG	PVP	Water
PEO	P(MAA&S)	Chloroform
PEO	P(MAA&S)	Tetrahydrofuran
PEO	PS	Benzene
PEO	PS	Chloroform
PEO	PS	Tetrahydrofuran
PESF	Water	Dimethylacetamide
PESF	Water	Dimethylformamide
PESF	Water	Dimethylsulfoxide
PESF	Water	N-Methyl-2-pyrrolidinone
PESF	Water	Tetramethylurea
PIB	PS	Chloroform
PIB	PS	Tetrahydrofuran

Ternary Liquid-Liquid Equilibria Data (Continued)

POLYMER 1	COMPONENT 2	SOLVENT
PIB	PS	Toluene
P(MAA&MMA)	P(S&VPD)	Chloroform
P(MAA&MMA)	P(S&VPD)	1,4-Dioxane
P(MAA&MMA)	P(S&VPD)	Methyl Ethyl Ketone
P(MAA&VAC)	P(S&VP)	Tetrahydrofuran
P(MAA&VAC)	P(S&VPD)	Tetrahydrofuran
PMMA	1-Chlorobutane	4-Heptanone
PMMA	1-Chlorobutane	2-Butanol
PMMA	Cyclohexane	Toluene
PMMA	PS	Chloroform
PMMA	PS	1,4-Dioxane
PMMA	PS	Methyl Ethyl Ketone
PMMA	PS	Tetrahydrofuran
PMMA	PS	Toluene
PmMS	PpMS	Chloroform
PmMS	PS	Chloroform
PoMS	PS	Chloroform
PP	PS	Toluene
PpClS	PpMOS	Benzene
PpClS	PS	Benzene
PpMOS	PS	Benzene
PpMS	PS	Chloroform
PPO	PS	Toluene
PNA	PVAL	Water
PS	n-Butane	n-Pentane
PS	Cyclohexane	N,N-Dimethylformamide
PS	Cyclohexane	Methanol
PS	Cyclohexane	Nitroethane
PS	Methyl Ethyl Ketone	Acetone
PS	PS	Cyclohexane
PS	P(S-b-BR)	Styrene
PS	PT	Tetrahydrofuran
PS	PVAC	Methyl Ethyl Ketone
PS	PVAC	Tetrahydrofuran
PS	PVME	Chloroform
PS	PVME	1,1,2-Trichloroethene
PS	SBR	Tetrahydrofuran
PS	Toluene	Ethane
PSA	PVP	Water
P(S&VPD)	P(VAC&VAL)	Tetrahydrofuran
PSF	Water	Dimethylacetamide
PSF	Water	Dimethylpropyleneurea
PSF	Water	N-methyl-2-pyrrolidinone
PSF	Water	Tetramethylurea
P(S&VP)	P(VAC&VAL)	Tetrahydrofuran
PVME	PVP	Water

Chapter 5

COMPUTER PROGRAMS

A. PHASE EQUILIBRIA CALCULATIONS - POLYPROG

1. Installation

The diskettes that accompany the **Handbook** contain two programs that were designed to facilitate user-friendly, interactive access to the data bases and prediction methods given in the **Handbook**. These programs are distributed as executable files that are compatible with most MS-DOS based computers. A program written in FORTRAN called POLYPROG was developed to implement the procedures given in this **Handbook**, and a second program called POLYDATA was written to extract selected data sets from the data files. The programs have been compiled using Version 5.0 of Microsoft's FORTRAN compiler. The programs run on any MS-DOS compatible computers with or without a math coprocessor. Due to the size of the programs and data bases, a hard disk is required. The input and output menu screens have been created with a software package called Hi-Screen XL licensed from Softway, Inc., San Francisco, CA. The programs and associated files have been compressed using a program called PKSFX that has been licensed from PKWARE, Inc., Glendale, WI.

POLYPROG is an interactive program for the recommended prediction and correlation methods in the **Handbook**. POLYPROG and its associated files are stored in a compressed file called HBPROG on a diskette labeled HBPROG. To install the program POLYPROG, the user should first create a subdirectory (e.g. *md POLYPROG*) on the hard disk to contain all of the files necessary for POLYPROG to run properly. Then, make this subdirectory the current working directory (e.g., *cd POLYPROG*). Insert the diskette labeled HBPROG in the diskette drive, and type *[d]:HBPROG* (where [d] is the drive letter for the diskette drive; for example *A:HBPROG*). This command will extract the compressed files and write them to the currently selected directory for use by POLYPROG. The program can now be started by entering *POLYPROG* followed by a carriage return.

2. Features

The following is a list of the features and capabilities of POLYPROG:

- The user may interactively enter a new solvent-polymer system or access an input file saved during a previous execution of the program.
- The user is given the option to change units for temperature, pressure, mass, and volume during data entry and to save these units as the default set.
- Weight fraction activity coefficients (WFAC), activities, and the partial pressures of the solvent may be calculated over a range of solvent weight fractions and/or

temperatures. A maximum of 101 points is allowed.

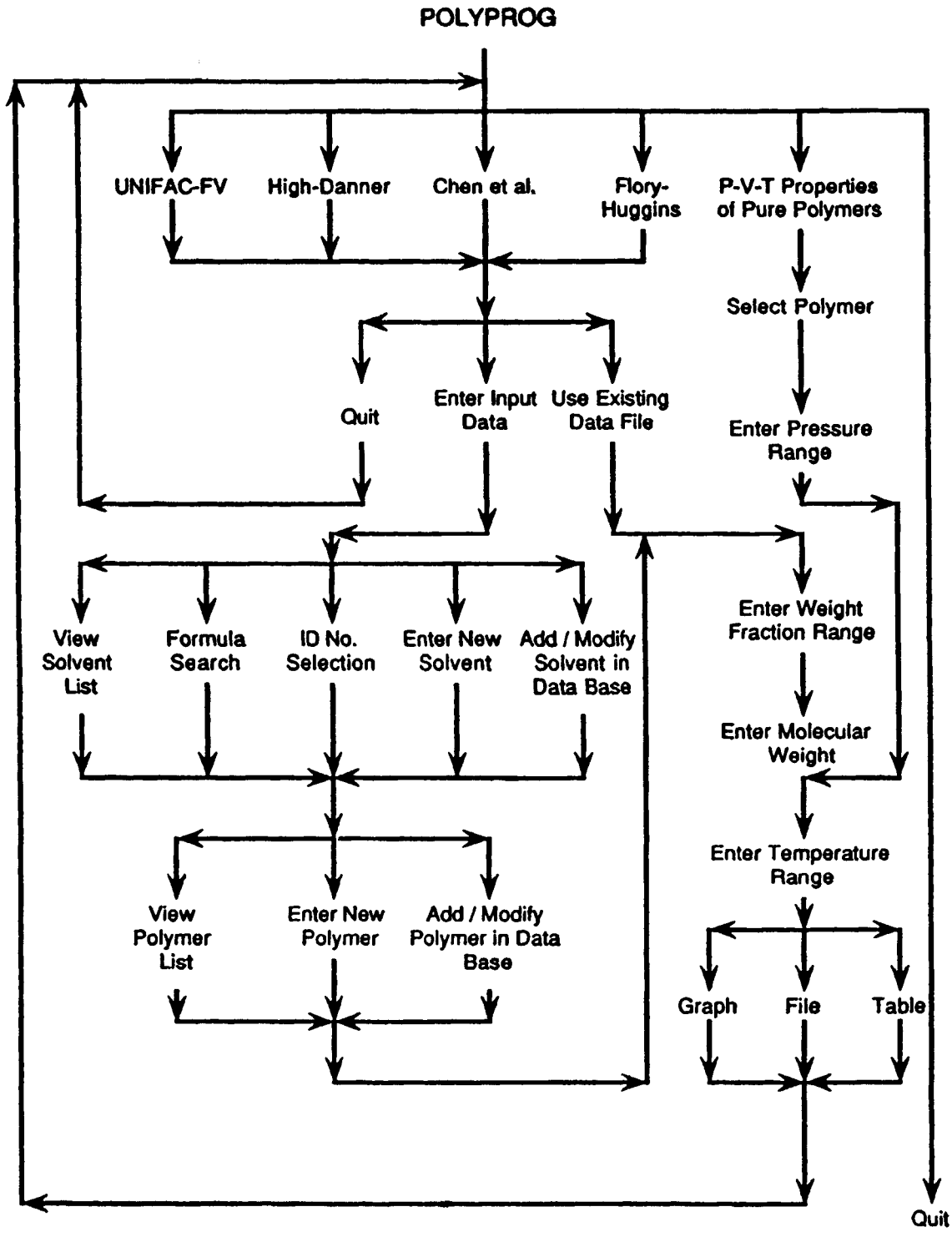
- All data inputs including the subgroups for the solvent and polymer repeat unit are entered in full screen input mode.
- The user has the option to review and/or make changes to the inputs for repetitive calculations.
- The program allows the user to save the inputs in a file for future use. Only one input data set per file is permitted.
- The results can be written to an output file.
- When activity coefficients are calculated over a range of weight fractions and/or temperatures the user is given the option to view the results in tabular and/or graphical format. Tabular output shows the calculated WFAC value, the activity, and the partial pressure of the solvent for each weight fraction at a specified temperature or for each temperature at a specified weight fraction. Plots of any of the three variables versus weight fraction or temperature can be obtained.
- When graphical output is chosen, the user has the option to manually set the scaling for both axes or allow the program to automatically scale the axes.
- The graphical output can be sent to an Epson (or compatible) dot-matrix printer or a Hewlett-Packard (or compatible) laser printer.
- Input data files and output files are standard ASCII files.
- Data can be imported from other sources including the **Handbook** data bases and compared graphically to predicted results from POLYPROG.
- The user can calculate the specific volume of a polymer liquid in the data base over a range of temperatures and pressures.
- The WFAC, activities, and partial pressures can be calculated from the Flory-Huggins model if a value of the interaction parameter is available.
- The required auxiliary data for the calculations are provided in the data bases for the most common solvents and polymers. Provision has been made for editing these data or adding data for new components.
- The user may receive additional information throughout execution of POLYPROG by pressing F1 for HELP.

Programs for all of the methods in Chapter 3 of the **Handbook** are provided in the software package. FORTRAN subroutines for the UNIFAC-FV, High-Danner, Chen et al., and Flory-Huggins models and for the calculation of the P-V-T behavior of pure polymer liquids are also provided.

A user may incorporate these models into custom written software by including the source code in the main program and programming the proper calls to the **Handbook** routines. The subroutines are extensively commented, and detailed documentation for the input arguments, output arguments, and detailed calling procedures are provided in the beginning of each subroutine. The routines are compatible with versions of the 1977 ANSI FORTRAN standard.

Figure 5A-1 is a schematic flow chart of the program. There are several levels of options in the program. A particular option is selected by moving the highlight bar to the corresponding option and pressing ENTER. An option can also be selected by typing the first character of that option. To return to the previous menu or option level you can highlight

Figure 5A-1
Computer Flow Chart for POLYPROG



QUIT and press ENTER, enter a "Q" (for quit current menu), or press the ESC key. Generally, if you try to do something that is not correct, the program will tell you how you should proceed.

The Main Menu is for selection of the prediction or correlation model of interest and offers six self-explanatory choices:

1. UNIFAC-FV Model.
2. High-Danner Model.
3. Chen et al. Model.
4. Flory-Huggins Model.
5. Specific Volume of Pure Polymers.
6. Quit Program.

3. Tutorial Session

The following procedure provides an efficient method of getting acquainted with the POLYPROG program. It was designed to show the quickest way to get results, the graphical capabilities, and the use of input/output files. The first example uses the UNIFAC-FV method to predict equilibria between n-pentane and butadiene rubber (BR) and then compares these results with the predictions of the High-Danner method. The second example uses the Chen et al. model to show how to compare a model's predictions with a set of experimental data. The third example shows how to calculate a weight fraction activity coefficient from the Flory-Huggins method when the chi parameter is known, and the fourth example demonstrates how to calculate a specific volume for a polymer in the data base. In addition to the specifics shown in these examples there are a number of other options available within the POLYPROG program. All options are described on help screens which can be accessed by pressing F1.

Example 1

- Change to the directory containing POLYPROG (e.g., cd POLYPROG).
- Start the program by typing POLYPROG at the DOS prompt. Press ENTER (or RETURN).
- Select <UNIFAC-FV Method>. (To select an item from any menu screen, you can use the cursor keys to highlight the item and press ENTER or simply type the first letter of the item.)
- Select <Enter input data>.
- Select <View solvent list>.
- Highlight <n-Pentane> and press ENTER.
- Select <View polymer list>.
- Highlight
 (Butadiene Rubber) and press ENTER.
- On the menu that appears enter the following data. (Movements from line to line can be made with the TAB key, ENTER key, or cursor keys.)

  Lower weight fraction range (first data block): 0

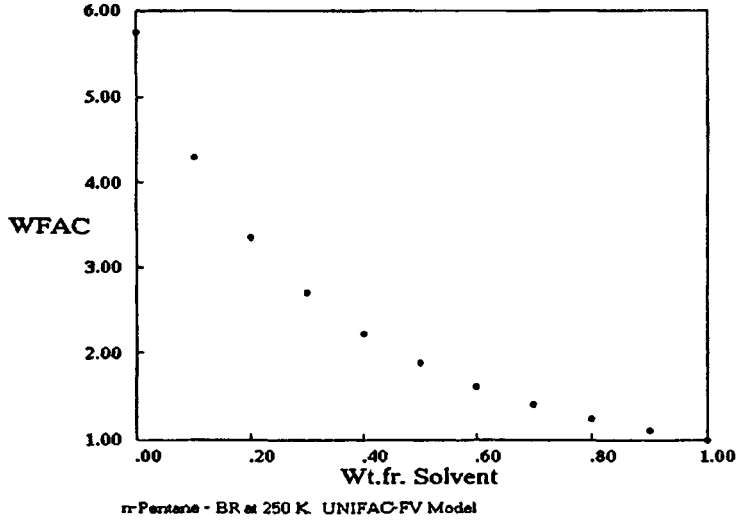
  Upper weight fraction range (second data block): 1

  Molecular weight: 1E+6 (Blank out rest of block with the space bar or with

CTRL END.)

Lower temperature range (K) (first data block): 250.0

- Press F10 to validate all inputs.
- After examining the results obtained, press F2 to enter the graphing option.
- Select <WFAC vs. Wt./Vm. Fr.>. (Weight fraction activity coefficient versus weight fraction or volume fraction.)
- Select <No> to question, "Would you like to bring in data for comparison?"
- Select <Automatic Scaling>.
- Enter "n-Pentane — BR at 250 K. UNIFAC-FV Model" for title.
- Press F10 to validate input.

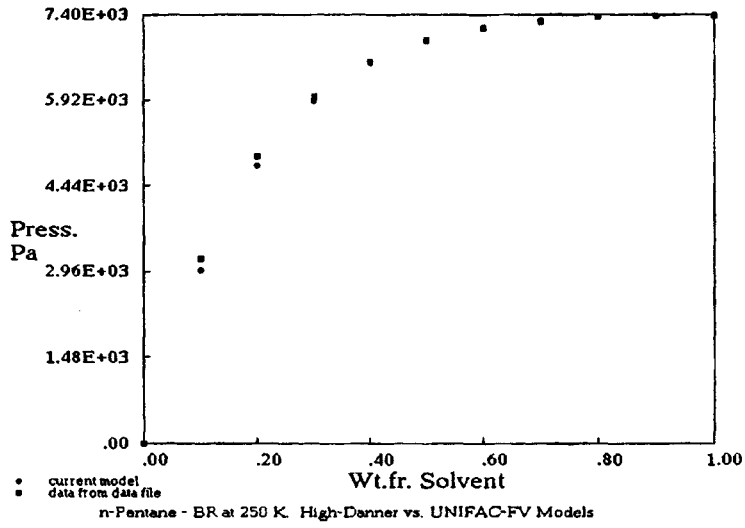


- Press ENTER to exit graph display.
- Press ESC to exit tabular display.
- Select <Write output to a file>.
- Enter "C5BR" for the file name and press ENTER.
- Select <Quit>.
- Select <Quit the UNIFAC-FV Method>.

The UNIFAC-FV results are now to be compared graphically with the predictions of the High-Danner method.

- Select <High-Danner Method>.
- Select <Enter input data>.
- Select <Continue>. This will use the same solvent as used previously, n-pentane in this case.
- Select <Continue>. This will use the same polymer as used previously, BR in this case.
- Press F10 to validate inputs.
- Press F2 to enter the graphing option.

- Select <Pressure vs. Wt./Vm. Fr.>.
- Select <Yes> to question, "Would you like to bring in data for comparison?"
- Press F1 for help on file name extensions.
- Press ESC to exit help screen.
- Enter "C5BR.UNO" for the file name and press ENTER. (This will bring in the data previously calculated for the UNIFAC-FV method.)
- Select <Automatic scaling>.
- Edit title to read, "n-Pentane – BR at 250 K. High-Danner vs. UNIFAC-FV Models"
- Press F10 to validate inputs. (The High-Danner model is the *current model*; the UNIFAC-FV model is the *data from data file*.



- To print the graph be sure printer is turned on and connected as LPT1. For an Epson dot-matrix printer (or compatible) type "E" and press ENTER. For an HP Laserjet printer (or compatible) type "H" and press ENTER. The printing process takes significant time during which the screen remains unchanged. When the printing is finished the bottom line of the screen will reappear.
- Press ENTER to exit graph.
- Press ESC to exit.
- Select <Quit>.
- Select <Quit the High-Danner Method>.

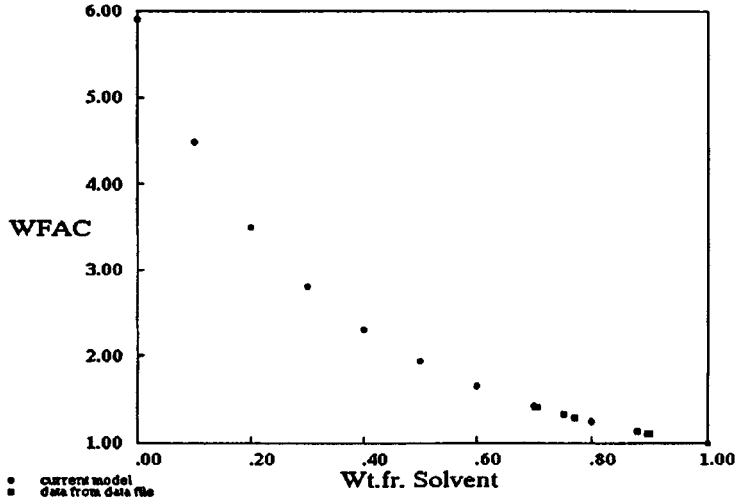
Example 2

This example uses the Chen et al. method to show how experimental results can be compared graphically to model predictions. The file containing experimental data for the polystyrene-ethylbenzene system must first be created using the POLYDATA program. This file contains all the data for this system in the finite concentration VLE data base. The Tutorial for POLYDATA describes how to create this file.

- From the main POLYPROG menu select <Chen et al. Method>.
- Select <Enter input data>.
- Select <Formula search>.
- Enter "C8H10" and press ENTER.
- Highlight <Ethylbenzene> and press ENTER.
- Select <View polymer list>.
- Highlight <PS> (on second screen - Page Down) and press ENTER.
- On the menu enter:
  Upper/Lower weight fraction: 0.0 1.0
  Molecular weight: 9.72E+4
  Lower temperature (K): 283.15
- Press F10 to validate all inputs.
- Press F2 to enter graphing mode.
- Select <WFAC vs. Wt./Vm. Fr.>.
- Select <Yes> to question, "Would you like to bring in data for comparison?"
- Enter "PSETHBEN.DAT" for the file name and press ENTER.

NOTE: The program will import data into the graph only from the first data set in a file created by POLYDATA. The temperature must be within 0.5 kelvins or the weight fraction within 0.01 of the selected value in order for the program to extract the data. Furthermore, if there is a comment in the data file indicated by an "*" any data beyond the "*" will not be imported. To look at other data sets, either edit the data file produced by POLYDATA as desired or create a new data file using the TEMPLATE.DAT file provided.

- Select <Automatic Scaling>.
- Enter "PS-Ethylbenzene at 283.15 K. Chen et al. Model versus Data of Hocker and Flory (1971)" for title.
- Press F10 to validate input.



PS-Ethylbenzene at 283.15 K. Chen et al. Model vs. Data of Hocker and Flory (1971).

- Press ENTER to exit graph.
- Press ESC to quit.
- Select <Quit>.
- Select <Quit the Chen et al. Method>.

Example 3

This example shows how to calculate a weight fraction activity coefficient from the Flory-Huggins method when the chi parameter is known.

- Select <Flory-Huggins Method> from the main menu.
- Select <Enter input data>.
- Select <View solvent list>.
- Highlight <Cyclohexane> and press ENTER.
- Select <View polymer list>.
- Highlight <PS> and press ENTER.
- Select <Volume Fraction>.
- On the menu enter:
  Volume fraction: 0.628
  Molecular weight: 2.6E+4
  INTERACTION PARAMETER: 0.72
  TEMPERATURE (K): 317.15
- Press F10 to validate data. [For this system an experimental weight fraction activity coefficient of 1.802 is given by Krigbaum and Geymer (1959)]
- Press ESC to exit.
- Select <Quit>.
- Select <Quit the Flory-Huggins Method>.

Example 4

This example shows how to use the Tait equation to calculate the specific volume of a polymer included in the data bank.

- Select <Method for Estimation of Specific Volumes> on the main menu.
- Select <View Polymer List>.
- Highlight <PC> (polycarbonate) for the polymer and press ENTER. Note the pressure and temperature limits for the Tait equation. In this case, the pressure limits are 0.0 and 1.77E+08 pascals and the temperature limits are 430 and 610 K.
- Press ENTER
- On menu enter:
  in the pressure (Pa) blocks:

Lower Limit	Upper Limit	Increment
1E+4		
1E+6		
1E+8		

in the temperature (K) blocks:

Lower Limit	Upper Limit	Increment
450	600	25

— Press F10 to validate input.

The screen should now look as follows:

Polymer : POLYCARBONATE Page #1

PRESSURE Pa	TEMPERATURE K	VOLUME m**3/kg
1.00E+04	450.00	8.7875E-04
1.00E+06	450.00	8.7825E-04
1.00E+08	450.00	8.3962E-04
1.00E+04	475.00	8.9251E-04
1.00E+06	475.00	8.9195E-04
1.00E+08	475.00	8.4956E-04
1.00E+04	500.00	9.0662E-04
1.00E+06	500.00	9.0599E-04
1.00E+08	500.00	8.5955E-04
1.00E+04	525.00	9.2109E-04
1.00E+06	525.00	9.2039E-04
1.00E+08	525.00	8.6956E-04
1.00E+04	550.00	9.3592E-04
1.00E+06	550.00	9.3513E-04
1.00E+08	550.00	8.7959E-04

— After reviewing results, press ESC to exit.

— Select <Quit>.

B. DATA RETRIEVAL - POLYDATA

POLYDATA is an interactive program designed to provide easy access to the data bases compiled in conjunction with the **Handbook**. The data bases are lengthy, and searching the files manually with an editor could be done, but would be very inefficient. POLYDATA was designed to make searching for pure polymer and polymer solution data easy.

1. Installation

As with the POLYPROG program, the necessary files for POLYDATA have been compressed using PKSFX. POLYDATA and its files are stored in two self-extracting archive files called HBDATA1 and HBDATA2. To set up the program, it is recommended that the user create a subdirectory on a hard disk (e.g., *md POLYDATA*) and make this subdirectory the current working directory (*cd POLYDATA*). Insert the diskette containing the file HBDATA1 into diskette drive, and type *[d]:HBDATA1* (where *[d]* is the drive letter for the diskette drive). If the same directory created for POLYPROG is to be used to store POLYDATA, the user will be asked if the self-extraction process should overwrite a few files. The user may answer yes or no to the resulting prompt since the files are identical, ancillary files necessary for the

operation of both POLYDATA and POLYPROG. Insert the diskette containing HBDATA2 into the diskette drive, and type *[d]:HBDATA2*.

The CONFIG.SYS file in the root-directory of the computer hard disk should be checked to be sure that it allows the opening of a minimum of 15 files. That is, it should contain the following line:

FILES = X

where X is an integral number of 15 or greater. If this is not true the CONFIG.SYS file must be modified by adding the line

FILES = 15.

If it is necessary to modify the CONFIG.SYS file, the computer must be rebooted before running POLYDATA.

The program can now be started by entering POLYDATA followed by a return.

2. Features

The following is a list of the features and capabilities of POLYDATA:

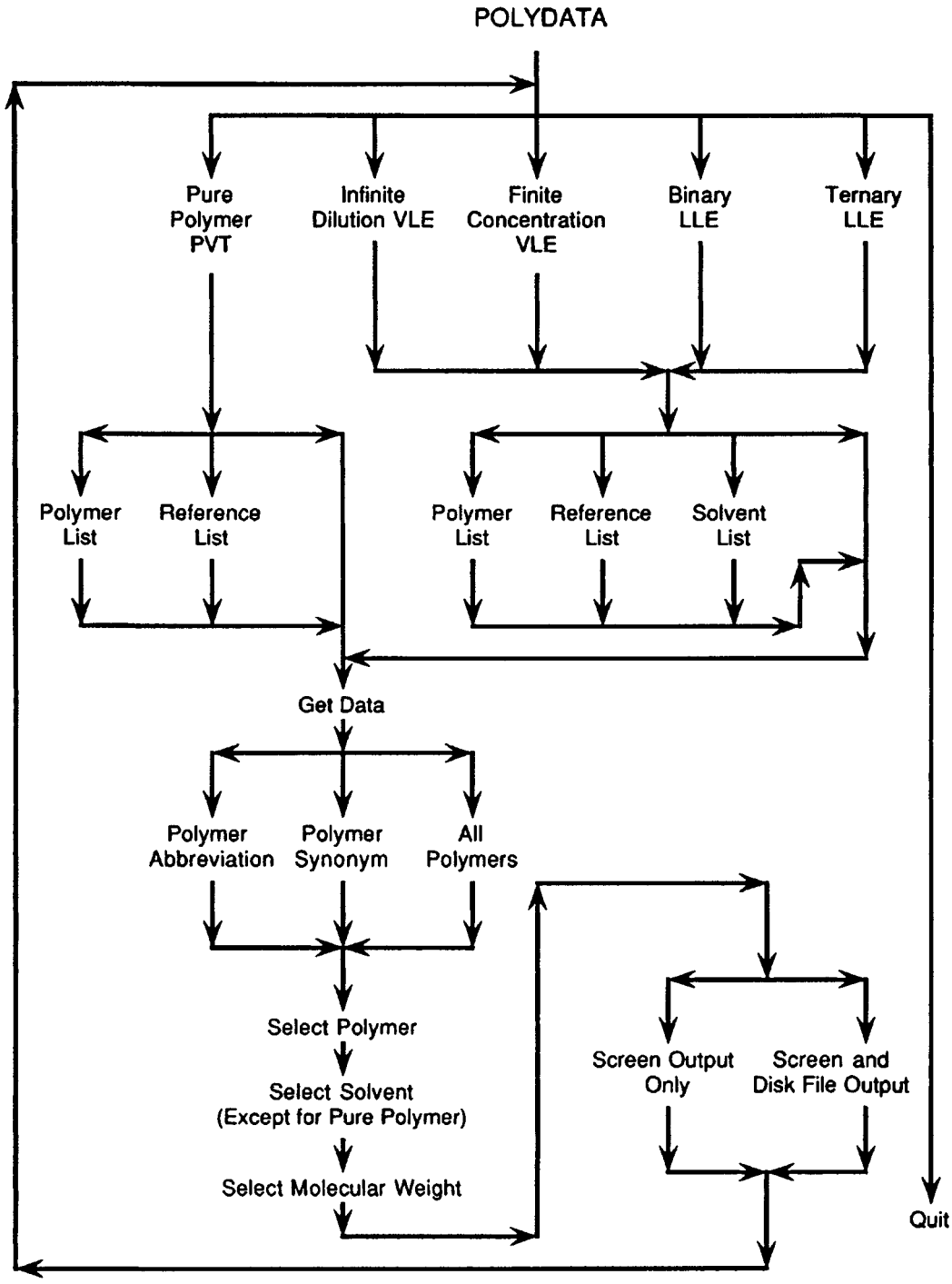
- Data are available for equilibrium pressure-volume-temperature of pure polymer liquids, solvent activity coefficients at infinite dilution, solvent activity coefficients at finite concentrations, and liquid-liquid phase equilibria of binary and ternary polymer solutions.
- The polymer or solvent may be chosen using either the abbreviations listed in the **Handbook** or by entering a synonym for location of the abbreviation (e.g. entering STYRENE to find the abbreviation PS for polystyrene)
- The experimental data found through the search can be written to an output file.
- Output files are standard ASCII files.
- Output files can be imported into POLYPROG for evaluation of model predictions.
- Moving between adjacent screens is accomplished by highlighting the NEXT SCREEN or PREV SCREEN menu options or by pressing the PGUP or PGDN keys.
- The user may receive additional information throughout execution of POLYDATA by issuing F1 for HELP.

Figure 5B-1 is a schematic flow chart of the program. The basic operation of POLYDATA is very similar to that of POLYPROG. There are several levels of options in the program. A particular option is selected by moving the highlight bar to the corresponding option and press ENTER. An option can also be selected by typing the first character of that option. To return to the previous menu or option level you can highlight QUIT and press ENTER, enter a "Q" (for quit current menu), or press the ESC key. Generally if you try to do something that is not correct, the program will tell you how you should proceed.

The Main Menu is for selection of the data base of interest and offers six self-explanatory choices:

1. Pure polymer PVT data bank.
2. Infinite dilution VLE data bank.
3. Finite concentration VLE data bank.
4. Binary LLE data bank.
5. Ternary LLE data bank.
6. Quit program.

Figure 5B-1
Computer Flow Chart for POLYDATA



3. Tutorial Session

In the following example finite concentration VLE data for ethylbenzene in polystyrene are extracted from the data bank and saved in the file (PSETHBEN.DAT) that is used in the Tutorial Session for POLYPROG to demonstrate how to import data into that program.

- Change to the directory containing POLYDATA (e.g., cd POLYDATA).
- Start the program by typing POLYDATA at the DOS prompt and pressing ENTER.
- Select <Finite Concentration VLE Data Bank>.
- Select <Polymer Listing>.
- Select <Screen Only>. This will display all the polymers available in this data base along with the molecular weights if they are known. It also gives the standard abbreviations for these polymers.
- Select <Q=Quit>.
- Select <Solvent Listing>.
- Select <Screen Only>. This will display all the common names of the solvents available in this data bank.
- Select <Q=Quit>.
- Select <Get Data>.
- Select <Abbreviation>.
- Enter "PS" (polystyrene) and press ENTER.
- Select <Select Solvent>.
- Enter "Ethylbenzene" and press ENTER.
- Select the three ethylbenzene systems by pressing ENTER for each one and the down arrow successively.
- Press F6 to get data from the data bank.
- Select <Disk File & Screen>.
- Enter "PSETHBEN.DAT" for the file name and press ENTER.
- Select <Q=Quit to last bank menu>.
- Select <Q=Quit to data bank menu>.
- Select <Quit to Main Menu>.
- Select <Quit Program>.
- Select <Verify>.

The first part of the PSETHBEN.DAT file is as follows:

```
POLYDATA OUTPUT FILE

SYSTEM: PS/Ethylbenzene
* PS obtained from Pressure Chemical Company. (Mw/Mn<1.06)
NUMBER AVERAGE MOLECULAR WEIGHT: 9.72E4
WEIGHT AVERAGE MOLECULAR WEIGHT:
METHOD: Osmotic Pressure
REFERENCE:
Hocker, H.; Flory, P. J. "Thermodyamics of Polystyrene Solutions. Part 2.
Polystyrene and Ethylbenzene", Trans. Faraday Soc. 67, 2270 (1971).
```

TEMP. (K)	WEIGHT FRACTION OF SOLVENT	WEIGHT FRACTION ACTIVITY COEFFICIENT
283.15	0.7014	1.4104
283.15	0.7057	1.4035
283.15	0.7523	1.3206
283.15	0.7705	1.2893
283.15	0.8796	1.1351
283.15	0.8955	1.1154
283.15	0.8993	1.1108
308.15	0.7059	1.4031
308.15	0.7344	1.3516
308.15	0.7839	1.2695
308.15	0.8959	1.1151
333.15	0.7505	1.3237
333.15	0.7850	1.2678
333.15	0.8959	1.1149

SYSTEM: PS/Ethylbenzene
NUMBER AVERAGE MOLECULAR WEIGHT:
WEIGHT AVERAGE MOLECULAR WEIGHT: 2.75E5
METHOD: Gravimetric Sorption
REFERENCE:
Vrentas, J. S.; Duda, J. L.; Hsieh, S. T. "Thermodynamic Properties of Some Amorphous Polymer-Solvent Systems", Ind. Eng. Chem. Prod. Res. Dev. 22, 326 (1983).

TEMP. (K)	WEIGHT FRACTION OF SOLVENT	WEIGHT FRACTION ACTIVITY COEFFICIENT
388.65	0.01642	5.241
388.65	0.0404	4.556
388.65	0.075	4.301
388.65	0.1356	3.775
403.15	0.006115	6.921
403.15	0.02858	5.650
...	...	...

C. FILE FORMATS USED BY POLYDATA

1. Pure Polymers

PURE.DAT: This file contains PVT data for each pure polymer.
Each block is constructed as follows:

First header: Standard polymer abbreviation

Second header:

columns:

1 - 9 : Number average molecular weight
11 - 19 : Weight average molecular weight
51 - 77 : Authors (Must match columns 2-28 in SOURCES.DAT)
78 - 80 : Year of publication (Must match columns 29-31 in SOURCES.DAT)

Comment cards, each beginning with an asterisk.

Data:

columns:

1 - 13 : Pressure, in pascals
14 - 27 : Temperature, in kelvins
28 - 37 : Polymer specific volume, in cubic meters per kilogram

PURE.LST: This file has a list of available polymers in this data base with their associated line number in the PURE.DAT file.

First line - total number of available polymers.

The format of the following lines is:

columns:

1 - 5 : First line number at which data for the polymer can be found in PURE.DAT file
6 - 20 : Standard polymer abbreviation
51 - 60 : Number average molecular weight
61 - 70 : Weight average molecular weight
71 - 102 : Reference header

PURPOL.LIS: This file has a list of polymers in this data base, alphabetically sorted.

First line - number of available polymers.

The format of the following lines is:

columns:

1 - 20 : Standard polymer abbreviation
21 - 30 : Number average molecular weight
36 - 45 : Weight average molecular weight

PURREF.LIS: This file has a list of references used for the pure polymers alphabetically sorted.

First line - number of references.

The format of the following lines is:

columns:

1 - 32 : Reference header

2. Infinitely Dilute Solvent Weight Fraction Activity Coefficients (WFAC)

INFINITE.DAT: This file contains WFAC's for each infinitely dilute solvent system.
Each data block is constructed as follows:
Header: Standard polymer abbreviation/Standard solvent name
Comment cards, each beginning with an asterisk.
Data:
columns:

1	- 10	:	Number average molecular weight of the polymer
11	- 20	:	Weight average molecular weight of the polymer
21	- 30	:	Temperature, in kelvins
31	- 40	:	WFAC
45	- 47	:	Experimental method used
51	- 77	:	Authors (Must match columns 2-28 in SOURCES.DAT)
78	- 80	:	Year of publication (Must match columns 29-31 in SOURCES.DAT)

INFINITE.LST: This file has a list of the infinitely dilute systems in this data base.
First line - total number of systems.
The format of the following lines is:
columns:

1	- 5	:	First line number at which data for the system can be found in INFINITE.DAT file
6	- 20	:	Standard polymer abbreviation
21	- 51	:	Standard solvent name

INFINITE.REF: This file is used to relate the references to the location of the associated data in INFINITE.DAT.
First line - total number of references.
The format of the following lines is:
columns:

1	- 5	:	First line number at which system can be found in INFINITE.DAT file
6	- 37	:	Reference header

INFPOL.LIS: This file has a list of polymers in this data base, alphabetically sorted.
First line - total number of polymers.
The format of the following lines is:
columns:

1	- 30	:	Standard polymer abbreviation

INFSOL.LIS: This file has a list of solvents in this data base, alphabetically sorted.
First line - total number of solvents.
The format of the following lines is:
columns:

1	- 30	:	Standard solvent name

INFREF.LIS: This file has a list of references used in this data base, alphabetically sorted.
First line - total number of references.
The format of the following lines is:
columns:
1 - 32 : Reference header

3. Finite Concentration Solvent Weight Fraction Activity Coefficients (WFAC)

FINITE.DAT: This file contains WFAC's for each finite concentration system.
Each data block is constructed as follows:
First header: Standard polymer abbreviation/Standard solvent name
Second header:
columns:
1 - 10 : Number average molecular weight of the polymer
11 - 20 : Weight average molecular weight of the polymer
45 - 50 : Experimental method used
51 - 77 : Authors (Must match columns 2-28 in SOURCES.DAT)
78 - 80 : Year of publication (Must match columns 29-31 in SOURCES.DAT)
Data:
columns:
1 - 10 : Temperature, in kelvins
11 - 20 : Weight fraction of the solvent
21 - 30 : WFAC

FINITE.LST: This file has a list of finite concentration systems in this data base.
First line - total number of systems.
The format of the following lines is:
columns:
1 - 5 : First line number at which data for the system can be found in FINITE.DAT file
6 - 20 : Standard polymer abbreviation
21 - 50 : Standard solvent name
51 - 60 : Number average molecular weight of the polymer
61 - 70 : Weight average molecular weight of the polymer
71 - 102 : Reference header

FINPOL.LIS: This file has a list of polymers in this data base, alphabetically sorted.
First line - total number of polymers.
The format of the following lines is:
columns:
1 - 30 : Standard polymer abbreviation

FINSOL.LIS: This file has a list of solvents in this data base alphabetically sorted.
First line - total number of solvents.
The format of the following lines is:

columns:

1 - 30 : Standard solvent name

FINREF.LIS: This file has a list of references used in this data base, alphabetically sorted.
First line - total number of references.
The format of the following lines is:
columns:

1 - 32 : Reference header

4. Binary LLE

LLB.DAT: This file contains the data for each binary LLE system.
Each data block is constructed as follows:
First header: Standard polymer abbreviation/Standard solvent name
Second header:
columns:

1 - 10 : Number average molecular weight of the polymer
11 - 20 : Weight average molecular weight of the polymer
45 - 50 : Experimental method used
51 - 77 : Authors (Must match columns 2-28 in SOURCES.DAT)
78 - 80 : Year of publication (Must match columns 29-31 in SOURCES.DAT)

Data:
columns:

1 - 10 : Temperature, in kelvins
11 - 20 : Weight fraction of polymer in phase A
21 - 30 : Weight fraction of polymer in phase B

LLB.LST: This file has a list of binary systems in this data base.
First line - total number of systems.
The format of the following lines is:
columns:

1 - 5 : First line number at which data for the system can be found in LLB.DAT file
6 - 35 : Standard polymer abbreviation
36 - 65 : Standard solvent name
66 - 75 : Number average molecular weight of the polymer
76 - 85 : Weight average molecular weight of the polymer
106 - 137 : Reference header

LLBPOL.LIS: This file has a list of polymers in this data base, alphabetically sorted.
First line - total number of polymers.
The format of the following lines is:
columns:

1 - 30 : Standard polymer abbreviation

LLBSOL.LIS: This file has a list of solvents in this data base, alphabetically sorted.
First line - total number of solvents.
The format of the following lines is:
columns:
1 - 30 : Standard solvent name

LLBREF.LIS: This file has a list of references used in this data base, alphabetically sorted.
First line - total number of references.
The format of the following lines is:
columns:
1 - 32 : Reference header

5. Ternary LLE

LLT.DAT: This file contains the data for each ternary LLE system.
Each data block is constructed as follows:
First header: Standard polymer abbreviation/component 2/standard solvent name
(where component 2 can be either a standard polymer abbreviation or standard solvent name)
Second header:
columns:
1 - 10 : Number average molecular weight of the polymer
11 - 20 : Weight average molecular weight of the polymer
21 - 30 : Number average molecular weight of component 2
31 - 40 : Weight average molecular weight of component 2
45 - 50 : Experimental method used
51 - 77 : Authors (Must match columns 2-28 in SOURCES.DAT)
78 - 80 : Year of publication (Must match columns 29-31 in SOURCES.DAT)
Data:
columns:
1 - 10 : Temperature in kelvins
11 - 20 : Weight fraction of polymer in phase A
21 - 30 : Weight fraction of component 2 in phase A
31 - 40 : Weight fraction of polymer in phase B
41 - 50 : Weight fraction of component 2 in phase B

LLT.LST: This file has list of ternary systems in this data base.
First line - total number of systems.
The format of the following lines is:
columns:
1 - 5 : Line number at which data for the system can be found in LLT.DAT file
6 - 35 : Standard polymer abbreviation/component 2
36 - 65 : Standard solvent name
66 - 75 : Number average molecular weight of the polymer

76 - 85 : Weight average molecular weight of the polymer
86 - 95 : Number average molecular weight of component 2
96 - 105 : Weight average molecular weight of component 2
106 - 137 : Reference header

LLTPOL.LIS: This file has a list of polymers in this data base, alphabetically sorted.
First line - total number of polymers.
The format of the following lines is:
columns:
1 - 30 : Standard polymer abbreviation

LLTSOL.LIS: This file has a list of solvents in this data base, alphabetically sorted.
First line - total number of solvents.
The format of the following lines is:
columns:
1 - 30 : Standard solvent name

LLTREF.LIS: This file has a list of references used in this data base, alphabetically sorted.
First line - total number of references.
The format of the following lines is:
columns:
1 - 32 : Reference header

6. Bibliographic Sources

SOURCES.DAT: This file contains complete references used in the various data bases. The header is the reference header referred to in the data base.
Each block is constructed as follows:
Header:
columns:
1 : *
2 - 28 : Authors
29 - 31 : Year of publication
Data :
complete title of the publication

SOURCES.LST: This file relates the reference headers used in the various data bases to the location of the associated reference in SOURCES.DAT.
First line - total number of references.
The format of the following lines is:
columns:
1 - 5 : Line where reference can be found in the SOURCES.DAT file
6 - 35 : Reference header

7. Polymer Synonyms

SYNONYMS.LIS: This file has the names of polymers and their standard abbreviations.
The format is:
columns:

1	- 80	:	Polymer name
81	- 130	:	Standard polymer abbreviation

SYNONYMS.LST: This file contains a list of polymers and their synonyms.
First line - total number of entries.
Each data block is constructed as follows:
Header:
columns:

1	- 80	:	Standard polymer abbreviation

Subsequent lines:
columns:

6	- 80	:	Synonym

For example:

BR
BR
POLYBUTADIENE
TAKTENE (TN)
ASTYR (TN)
DIENE (TN)
BUDENE (TN)
CIS-4 (TN)

Chapter 6

APPENDICES

A. GLOSSARY OF TERMS

athermal - solutions in which the enthalpy of mixing is zero or the components mix without generating or absorbing heat.

binodal curve - the locus of equilibrium conditions between phases.

canonical ensemble - a hypothetical collection of closed systems which are in thermal equilibrium with each other and with an infinite heat reservoir. Used to determine the thermodynamic properties of a macroscopic system with the same volume and temperature of each system in the ensemble.

cohesive energy density - the difference between the energy of molecules in the ideal gas state and the same molecules in a condensed phase usually the liquid phase.

combinatorial - a contribution to activity coefficient and equation of state models that determines the number of ways that a system can be arranged without varying the total energy of the system. Sometimes referred to as the degeneracy of the system.

configuration - the arrangement fixed by chemical bonds of functional groups along a polymer chain.

conformation - the arrangements due to rotation around chemical bonds of functional groups in molecules in a system of molecules due usually to the properties of the solution.

excluded volume - the volume inaccessible to the center of mass of a molecule due to the non-zero volume of the molecules in a system. See "free volume."

Flory χ - a parameter in the Flory-Huggins equation to account for intermolecular interactions. χ values less than 0.5 are indicative of a solvent which has relatively good solubility with a polymer.

free volume - the volume accessible to the center of mass of a molecule in a system. See "excluded volume".

glass transition temperature - the temperature at which the viscous or rubbery liquid changes to a hard and brittle amorphous material.

hard core volume - the volume of a molecule inaccessible to other molecules.

homogeneous - see "monodisperse"

interaction parameter - The measure of interaction energy between two groups or molecules in a system used in equations of state and activity coefficient models.

lattice theory - a physical model of a pure component or solution assuming that each segment of the molecules in the system occupies a position in a lattice.

monodisperse - a sample of polymers with identical chain lengths

partition function - the mathematical representation of the canonical ensemble used to derive equations of state and activity coefficient models.

polydisperse - a mixture of polymers whose molecules have differing chain lengths but are otherwise identical in chemical structure.

polymer blend - a mixture of two polymers.

reference volume - another term for hard core volume.

regular solutions - solutions that mix with ideal entropy of mixing or mix with zero excess entropy.

spinodal curve - the locus of points that corresponds to the boundary between an unstable solution and a metastable solution. If the necessary amount of free energy is supplied to the metastable system the solution will phase separate into two phases with compositions corresponding to the binodal curve. The unstable system will always phase separate into the two phases.

solubility parameter - the square root of the cohesive energy density that gives a qualitative measure of solubility.

thermoplastic - a qualitative description of a polymer that can be softened with heat and made to take on different shapes and forms.

thermoset - a qualitative description of a polymer that crosslinks during fabrication that cannot be made to deform under high temperatures.

theta point - an ideal state in which the excluded volume effect becomes negligible and the polymer molecule behaves as a random flight chain. At the theta point or theta temperature the effects of intermolecular attractions cancel the excluded volume repulsive forces. The theta temperature is similar to the Boyle temperature of non-ideal gases.

Some of the definitions in this glossary have been adapted from Billmeyer, F. W., **Textbook of Polymer Science**, 3rd ed., Wiley & Sons, New York, NY (1984) and Lapedes, D. N., ed., **McGraw-Hill Dictionary of Scientific and Technical Terms**, 2nd ed., McGraw-Hill, New York, NY (1978).

B. STANDARD POLYMER ABBREVIATIONS

BR	butadiene rubber [polybutadiene]
BUPVAL	butyralized poly(vinyl alcohol)
CA	cellulose acetate
CDA	cellulose diacetate
CPE	chlorinated polyethylene
DEXTRAN	dextran
DHPDOEOA	α,ω-dihydroxy poly(di(oxyethylene)oxyadipyl)
DHPDOEOS	α,ω-dihydroxy poly(di(oxyethylene)oxysuccinyl)
DHPHMC	α,ω-dihydroxy poly(hexamethylenecarbonate)
DHPOE	α,ω-dihydroxy poly(oxyethylene)
DHPOP	α,ω-dihydroxy poly(oxypropylene)

DHPTMC	α,ω-dihydroxy poly(tetramethylene carbonate)
DHPTOEOS	α,ω-dihydroxy poly(tri(oxyethylene)oxysuccinyl)
EHEC	ethyl hydroxyethyl cellulose
FICOLL	ficoll
HDPE	high density polyethylene (linear polyethylene)
HIPS	high impact polystyrene
HMDS	hexamethyldisiloxane
HPD	hydroxypropylenedextran
HPMC	hydroxypropylmethylcellulose
IR	isoprene rubber [polyisoprene]
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MC	methylcellulose
NC	nitrocellulose
NPPEGE	nonyl phenyl poly(ethylene glycol ether)
PA-6	polyamide-6
PAA	poly(acrylic acid)
P(AA&VAC)	poly(acrylic acid-co-vinyl acetate)
PACA	poly(acrylamide)
P(ACA&S)	poly(acrylamide-co-styrene)
PAMS	poly(alpha-methylstyrene)
P(AMS&AN)	poly(alpha-methylstyrene-co-acrylonitrile)
P(AN&BR)	poly(acrylonitrile-co-butadiene)
PAN	polyacrylonitrile
PAR	polyarylate
PASO	poly(arylene sulphonoxide)
P(ASO-b-BR)	arylene sulphonoxide-butadiene rubber block copolymer
PB	poly(1-butylene)
PBA	poly(n-butyl acrylate)
PBAD	poly(butylene adipate)
PBMA	poly(n-butyl methacrylate)
P(BMA&S)	poly(n-butyl methacrylate-co-styrene)
P(BMA&a-S)	poly(n-butyl methacrylate-co-atactic-styrene)
P(BSAC)	poly(bisphenol-a-carbonate)
PC	polycarbonate
P(C&DMS)	poly(carbonate-co-dimethylsiloxane)
PCHMA	poly(cyclohexyl methacrylate)

PCL	poly(epsilon-caprolactone)
PCO	poly(chloromethyl)oxirane
PD	polydecene-1
PDD	polydodecene-1
PDMA	poly(decyl methacrylate)
PDMPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PDMS	poly(dimethylsiloxane)
P(DMS&S)	poly(dimethylsiloxane-co-styrene)
P(E&P)	poly(ethylene-co-propylene)
P(E&VAC)	poly(ethylene-co-vinyl acetate)
PEA	poly(ethyl acrylate)
PEAD	poly(ethylene adipate)
PECH	poly(epichlorohydrin)
PEEK	poly(ether ether ketone)
PEG	poly(ethylene glycol)
P(EG&PG)	poly(ethylene glycol-co-propylene glycol)
PEGDE	poly(ethylene glycol dimethyl ether)
PEMA	poly(ethyl methacrylate)
PEO	poly(ethylene oxide)
P(EO&POX)	poly(ethylene oxide-co-propylene oxide)
P(b-EO&b-POX)	poly(block-ethylene oxide-co-block-propylene oxide)
P(ER&HBA)	poly(ethyleneterephthalate-co-p-hydroxibenzoic acid)
PES	poly(ethylene succinate)
PESF	poly(ethersulfone)
PETP	poly(ethylene terephthalate)
P(GMA&VAC&VC)	poly(glycidyl methacrylate-co-vinyl acetate-co-vinyl chloride)
PH	polyheptene-1
PHA	poly(n-hexyl acrylate)
PHENOXY	phenoxy
PHMA	poly(n-hexyl methacrylate)
PHMS	poly(hexamethylene sebacate)
P(HPA&VAC&VC)	poly(hydroxypropyl acrylate-co-vinyl acetate-co-vinyl chloride)
PI	polyimide
PIB	polyisobutylene
PIBMA	poly(isobutyl methacrylate)

P(IBMA&S)	poly(isobutyl methacrylate-co-styrene)
PL	poly(DL-lactide)
PMA	poly(methyl acrylate)
PMAA	poly(methacrylic acid)
P(MAA&MMA)	poly(methacrylic acid-co-methyl methacrylate)
P(MAA&S)	poly(methacrylic acid-co-styrene)
PMCPS	polymethylcyanopropyl siloxane
PMMA	poly(methyl methacrylate)
P(MAA&VAC)	poly(methylacrylic acid-co-vinyl acetate)
PmMS	poly(m-methylstyrene)
PMP	poly(4-methyl-1-pentene)
PMTFPS	poly(methyl(trifluoropropyl)siloxane)
PMVPD	poly(2-methyl-5-vinylpyridine)
PNA	poly(sodium acrylate)
POD	polyoctadecene-1
PODMI	poly(N-(n-octadecyl)maleimide)
POEDE	poly(oxyethylene)dodecyl ether
POM	poly(oxymethylene)
PoCS	poly(o-chlorostyrene)
PoMS	poly(o-methylstyrene)
POPG	poly(oxypropylene glycol)
PP	polypropylene
PPA	poly(n-propyl acrylate)
PpBrS	poly(p-bromostyrene)
PpCIS	poly(p-chlorostyrene)
PPeMA	poly(n-pentyl methacrylate)
PPFE	poly(perfluoro ethers)
PPG	poly(propylene glycol)
PPGDE	poly(propylene glycol dimethyl ether)
PPMA	poly(n-propyl methacrylate)
PpMOS	poly(p-methoxystyrene)
PpMS	poly(p-methylstyrene)
PPO	poly(phenylene oxide)
PPOX	poly(propylene oxide)
PPT	hydroxypropyl starch
PS	polystyrene
a-PS	atactic-polystyrene

P(S&VP)	poly(styrene-co-vinylpyrrolidone)
P(S&VPD)	poly(styrene-co-4-vinylpyridine)
P(S-b-BR)	styrene-butadiene rubber block copolymer
PSA	poly(sodium acrylate)
PSBMA	poly(sec-butyl methacrylate)
PSF	polysulfone
PT	polytetrahydrofuran
PTFE	poly(tetrafluoroethylene)
PVAC	poly(vinyl acetate)
P(VAC&VAL)	poly(vinyl acetate-co-vinyl alcohol)
P(VAC&VC)	poly(vinyl acetate-co-vinyl chloride)
PVAL	poly(vinyl alcohol)
PVAM	poly(vinyl amine)
PVC	poly(vinyl chloride)
PVDF	poly(vinyldene fluoride)
PVI	poly(vinyl isobutyl ether)
PVL	poly(delta-valerolactone)
PVME	poly(vinyl methyl ether)
PVO	poly(vinyl propionate)
PVP	poly(vinylpyrrolidone)
PVPD	poly(4-vinyl pyridine)
SBR	styrene-butadiene rubber
a-	atactic
-b-	block
c	cis
-g-	graft
i-	isotactic
m-	meta
o-	ortho
p-	para
s-	syndiotactic
t	trans

Copolymers are listed in alphabetical order according to their abbreviations.

C. NOMENCLATURE

a^{comb} = combinatorial contribution to the activity.

a_i = activity of component i.

Δa_{ji} = interaction parameter, kelvins.

a_{mn} = group interaction parameter resulting from the interaction of main groups m and n, kelvins.

a^{res} = residual contribution to the activity.

A_0 = parameter in the Tait equation, cubic meters per kilogram.

A_1 = parameter in the Tait equation, cubic meters per kilogram-kelvin.

A_2 = parameter in the Tait equation, cubic meters per kilogram-kelvin-kelvin.

b = proportionality factor = 1.28.

B_0 = parameter in the Tait equation, pascals.

B_1 = parameter in the Tait equation, per kelvin.

c = degree of freedom parameter.

c_{ii} = cohesive energy density, joules per cubic meter.

c_2 = polymer concentration.

C = parameter in the Tait equation (C = 0.0894); degree of freedom parameter in the Chen equation of state.

C_i = an external degree of freedom parameter for solvents (C_i = 1.1); degree of freedom parameter in the Chen equation of state.

$C_{i,353}$ = number of external degrees of freedom in component i at 353 K.

C_k^o = degree of freedom parameter.

$C_{To,k}$ = degree of freedom parameter.

$C_{T,k}$ = degree of freedom parameter.

D_i = i^{th} virial coefficient in expansion of chemical potential.

E = energy parameter, joules.

ΔE_i^{vap} = energy change of vaporization of component i, joules.

f_i = fugacity of component i, pascals.

f_i^o = standard state fugacity of component i, pascals.

g_{ij} = Flory-Huggins interaction parameter

ΔG = Gibbs energy change, joules.

i_o = excess light scattered per unit volume at angle θ.

I_o = incident light intensity.

k = Boltzmann constant, 1.380662×10^{-23} J/K.

ℓ_i = bulkiness parameter for component i.

M_i = molecular weight of component i, kilograms per kilomole.

M_n = number average molecular weight, kilograms per kilomole.

M_w = weight average molecular weight, kilograms per kilomole.

n_i = number of moles of component i, kilomoles.

$\tilde{n}_o$ = solvent refractive index.

N_A = Avagadro's number, molecules per kilomole.

N_h = number of holes in the lattice.

N_i = number of molecules of component i.

N_q = surface area parameter for the lattice.

P = pressure, pascals.

$\tilde{P}$ = reduced pressure.

P^* = characteristic pressure, pascals.

q_i = surface area parameter of component i.

Q_k = group area parameter for group k.

Q = partition function.

r = number of segments in the polymer molecule for the Flory-Huggins Model.

r_i = volume parameter for component i; number of lattice sites occupied by the segments of a molecule.

R = gas constant = 4184 J/(kmol K).

R_G = Radius of gyration, meters.

R_k = group volume parameter for group k.

R_θ = Rayleigh factor

s = surface area parameter, square meters.

ΔS = entropy change, joules per kelvin.

$\Delta S_{j\,i}^{HB}$ = entropic contribution to the interaction parameter resulting from hydrogen bonding.

T = temperature, kelvins.

T_o = reference temperature, kelvins.

$\tilde{T}$ = reduced temperature.

$\tilde{v}_i$ = reduced volume of solvent i.

$\tilde{v}_M$ = reduced volume of the mixture.

v_h = molar volume of lattice site = 9.75×10^{-3} m^3/kmol.

v_i = molar volume of component i, cubic meters per kilomole.

v^* = characteristic volume, cubic meters.

V_i^* = hard core volume of component i, cubic meters per kilomole.

V = volume, cubic meters.

w_i = weight fraction of component i.

x_i = mole fraction of component i.

X_m = mole fraction of group m in the solution.

y_i = vapor phase mole fraction of component i.

z = coordination number.

Greek Symbols

γ_i = mole fraction activity coefficient of component i.

Γ_k = residual activity coefficient of group k in the defined solution at the given temperature T.

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing pure component i at the temperature T.

δ_i = solubility parameter of component i, square root of (joules per cubic meter).

δ_d = dispersive force contribution to the solubility parameter, square root of (joules per cubic meter).

δ_h = hydrogen bonding force contribution to the solubility parameter, square root of (joules per cubic meter).

δ_p = polar force contribution to the solubility parameter, square root of (joules per cubic meter).

ϵ^* = interaction parameter, joules.

ϵ_{ii} = interaction parameter, joules.

$\Delta\epsilon_{ji}$ = interaction parameter, joules.

$\epsilon_{o,ji}$ = contribution to the interaction energy from random configurations, joules.

η = interaction energy, joules per square meter.

θ_m = group surface area fraction of group or component m in the given solution.

λ = wavelength of light in vacuum, meters.

Λ_{ij} = Wilson's model interaction parameter between components i and j.

μ_i = chemical potential of component i, joules.

$\tilde{\rho}$ = reduced density.

ϕ_i = fugacity coefficient of component i; volume fraction of component i.

χ_{ij} = Flory-Huggins interaction parameter.

χ_s = entropic contribution to the Flory-Huggins interaction parameter.

ψ_{mk} = group interaction parameter for the interaction of group m with group k.

$\nu_k^{(i)}$ = number of groups of type k in molecule i.

Ω_i = weight fraction activity coefficient of solvent i at temperature T.

Ω_i^C = combinatorial contribution to the weight fraction activity coefficient.

Ω_i^R = residual contribution to the weight fraction activity coefficient.

Ω_i^{FV} = free volume contribution to the weight fraction activity coefficient.

Ω_i^{INT} = interaction or enthalpic contribution to the weight fraction activity coefficient.

Subscripts

i = property or variable designated for component i.

Superscripts

I = property or variable for phase I.

II = property or variable for phase II.

L = property or variable for liquid phase.

V = property or variable for vapor phase.

o = standard state property.

D. UNITS AND CONVERSION FACTORS

This section is abstracted from the official AIChE publication, "SI for AIChE," prepared by the AIChE Metrication Committee in 1979. Units and symbols, prefixes, usage format and conversion factors are included. AIChE mandated that SI units be used in all publications and presentations. Such units are used exclusively in this **Handbook**.

1. Units and Symbols

Base and Supplementary Units

SI is a mass-length-time-temperature system built from the seven base units of length, mass, time, temperature, amount of substance, electric current, and luminous intensity. In addition two supplementary units of plane phase angle and solid angle are needed to

adequately describe physical and chemical properties. Table 6D-1 lists the base and supplementary units and their symbols.

Table 6D-1
SI Base and Supplementary Units

Type	Quantity and Symbol	Unit	Unit Symbol
base	length, L	meter	m
base	mass, m	kilogram	kg
base	time, t	second	s
base	temperature, T	kelvin	K
base	amount of substance, n	mole	mol
base	electric current, I	ampere	A
base	luminous intensity, I	candela	cd
supplementary	plane angle, θ	radian	rad
supplementary	solid angle, ω	steradian	sr

*Note on pronunciation: kill'oh gram, can dell'a.

Derived Units

All other units in SI are derived from the nine base and supplementary units. They will often have their own unit name and symbol, but all can be reduced through appropriate definitions to the nine primary units. Table 6D-2 lists the approved derived units with special names and their formulas and symbols. Table 6D-3 is a representative list of derived SI units which are widely used in chemical engineering but which do not have approved names.

Table 6D-2
SI Derived Units with Special Names

Quantity and Symbol	Unit	Unit Symbol	SI-Units Formula
frequency, f	hertz	Hz	s^{-1}
force, F	newton	N	$kg \cdot m/s^2$
pressure, stress, p,τ	pascal	Pa	N/m^2; $kg/m \cdot s^2$
energy, work, quantity of heat, E, W, Q	joule	J	$N \cdot m$; $kg \cdot m^2/s^2$
power, radiant flux, P	watt	W	J/s; $kg \cdot m^2/s^3$
quantity of electricity, electric charge, Q	coulomb	C	$A \cdot s$

Table 6D-2 (Continued)

Quantity and Symbol	Unit	Unit Symbol	SI-Units Formula
electric potential, potential difference, electromotive force, E	volt	V	W/A; $m^2 \cdot kg/A \cdot s^3$
capacitance, C	farad	F	C/V; $A^2 \cdot s^4/kg \cdot m^2$
electrical resistance, R	ohm	Ω	V/A; $m^2 \cdot kg/A^2 \cdot s^3$
conductance, G	siemens	S	A/V; $A^2 \cdot s^3/kg \cdot m^2$
magnetic flux, ϕ	weber	Wb	$V \cdot s$; $m^2 \cdot kg/A \cdot s^2$
magnetic flux density, B	tesla	T	Wb/m^2; $kg/A \cdot s^2$
inductance, L	henry	H	Wb/A; $m^2 \cdot kg/A \cdot s$
luminous flux, F	lumen	lm	$cd \cdot sr$
illuminance, B	lux	lx	$cd \cdot sr/m^2$
radioactivity, λ	becquerel	Bq	s^{-1}
absorbed dose, D	gray	Gy	J/kg

Notes on pronunciation: joule rhymes with tool; pascal rhymes with rascal; siemens as in seamen's.

There is no distinction between the singular and plural of hertz, of siemens, and of lux: 50 hertz, 1 siemens.

Table 6D-3
Some Derived SI Units Used in Chemical Engineering

Property	Common Symbol	SI-Units Formula
thermal conductivity	k	$W/m \cdot K$
heat transfer rate	q	W
heat transfer coefficient	h	$W/m^2 \cdot K$
specific enthalpy	H	J/kg
heat capacity	C_p	$J/kg \cdot K$
Newtonian viscosity	μ	$Pa \cdot s$; $kg/m \cdot s$
kinematic viscosity	v	m^2/s
thermal diffusivity	α	m^2/s
volumetric flowrate	q	m^3/s
power	P	W
entropy	S	J/K
density	ρ	kg/m^3
mass velocity	G	$kg/s \cdot m^2$
concentration	c	kg/m^3
concentration	c	mol/m^3
velocity	u	m/s
acceleration	a, g	m/s^2
mass transfer coefficient	k_c	m/s

Table 6D-3 (Continued)

Property	Common Symbol	SI-Units Formula
mass diffusivity	D	m^2/s
moment	I	$N \cdot m$
thermal flux	q/A	W/m^2
mass flux (molar)	N_a/A	$mol/m^2 \cdot s$
momentum flux	τ_y/A	Pa
mass transfer rate	N_a	mol/s
mass flow rate	w	kg/s
surface tension	γ	N/m
gas constant	R	$Pa \cdot m^3/mol \cdot K$; $J/mol \cdot K$

Symbol Grammar

The first letter of all units when written out is a lower case letter, even though the symbol for the unit may be capitalized (hertz, Hz). (Use of the unit at the beginning of sentences or in titles is excepted.) Written-out plurals are formed regularly by adding *s*, with the exception noted in the footnote to Table 6D-2. Symbols, however, do not add *s* for plural, nor are they followed by a period. A space is left between the last numeral of the number and the first letter of the symbol (but not for °), for example, 22 mm, 500 MW, 35°, 18°C. When the measurement is used as an adjective preceding the noun it modifies, a hyphen replaces the space, as in 150-mm lens.

Two conventions, a center point and a slash (· and /), are used to write the formulas for the derived units in Tables 6D-2 and 6D-3.

a. When two unit symbols are multiplied each symbol is separated by a point (·). (When no confusion exists, the point may be dispensed with, provided that a space is left between the symbols); for example m·mg or mg m is acceptable, but not mmg or mgm.

b. When division is called for, the solidus, or slash (/), is recommended rather than the cumbersome negative exponents. Only one solidus is permitted per symbol complex. (All symbols following the solidus are in the denominator.) For example, m/s^2, Mg/m^3, and $A^2 \cdot s^3/kg \cdot m^2$ are recommended, but not m/s/s, Mg m^{-3}, or $A^2 \cdot s^3$ kg^{-2} m^{-1}.

c. Written-out names for prefixes and symbols are not to be mixed with prefix and unit symbols in the same expression. This convention includes the point and the solidus. Meters per second, m/s, newton meter (or newton-meter), and N·m are correct, but meters/second, m per s, m/second, and newton·meter are not. Symbols are preferred to names.

2. Prefixes

Prefix System

The wide range in magnitude of units used in normal practice requires the use of different-sized units, rather than a powers-of-ten numerical multiplier. Accordingly, SI has

established prefixes for decimal multiples and submultiples of the base, supplementary, and approved derived units. Table 6D-4 lists these prefixes by name, pronunciation, symbol, and magnitude.

Table 6D-4
Magnitude Prefixes for SI Units

Name	Pronunciation	Symbol	Magnitude
atto	a as an*ato*my	a	10^{-18}
femto	fem'toe, *fem* as in *fem*inine	f	10^{-15}
pico	peek'oh	p	10^{-12}
nano	nan'oh	n	10^{-9}
micro	as in *micro*scope	μ	10^{-6}
milli	as in *mili*tary	m	10^{-3}
centi	as in *centi*pede	c	10^{-2}
deci	as in *deci*mal	d	10^{-1}
deka	deck'a	da	10^{1}
hecto	heck'toe	h	10^{2}
kilo	kill'oh	k	10^{3}
mega	as in *mega*phone	M	10^{6}
giga	jig'a	G	10^{9}
tera	as in *terra* firma	T	10^{12}
peta	pet'a	P	10^{15}
exa	ex'a	E	10^{18}

Note: the first syllable of every prefix is accented so as to retain its identity, that is *kill'* oh meter. When written out the prefix is not capitalized even though its symbol may be a capital letter.

Prefix Conventions

a. All prefixes are printed without spacing between the prefix and the unit symbol, for example 10 nm, 1.1 kPa, 7.2 MW. When written out the prefix is not separated from the unit, for example, kilowatt, nanosecond.

b. An exponent attached to a compound prefix-unit implies that the exponent refers to the entire compound not just the base symbol:

1 cm^3 means a volume of a cube 1 cm on aside, that is 10^{-6} m^3, not $10^{-2}m^3$.

c. Compound prefixes are not to be used; for example, nm is acceptable, but not mμm. Except for mm and TT (millimeter and teratesla), all compound forms of prefix and unit symbols will be made up of different symbols.

d. Good practice recommends selection of a prefix which, whenever possible, provides a numerical value between 0.1 and 1000, for example, 10.0 kPa rather than 0.0100 MPa. When a group of values is discussed or tabulated, they should all be expressed in the same unit multiple even though their numerical values lie outside the 0.1-to-1000 range.

e. Values which lie outside the recommended prefix ranges should be expressed in powers of ten times the base unit, that is 7.8×10^{50} m, 1.7×10^{46} kg.

3. Usage Format

Some special usages arise in SI, particularly in respect to well-established nonstandard units. A discussion of some of these follows.

Kilogram

The kilogram is the standard SI base unit for mass, even though it includes a multiplier prefix. However, for the application of other prefix multipliers the base word is the gram; thus 1000 kilograms is 1 Mg, not 1 kkg.

Temperature

Both temperature and temperature interval are expressed in kelvins (K) in standard SI. However, the Celsius scale is also acceptable in use with SI. Thus a temperature difference of 12 K is identically equal to a temperature difference of 12°C, and a temperature of 273.15 K is exactly equal to 0°C by the expression

temperature in °C = temperature in K - 273.15.

Amount of Substance

The amount of substance, the mole (formerly referred to as the gram-mole), symbol mol, is that amount of a substance of a system which contains as many elementary entities as there are in 0.012 kilogram of carbon-12. The elementary entities—atoms, molecules, ions, etc.—must be identified when the mole is used. Thus, the conventional gram-mole of carbon-12 contains Avogadro's number of atoms, which amounts to 0.012 kg or 12 g, obtained by multiplying as follows:

$$(6.023 \times 10^{23} \text{ atoms/mol})(1.661 \times 10^{-27} \text{ kg/u}) \cdot (12 \text{ u/atom}) = 0.012 \text{ kg/mol}$$

where u is the atomic-mass unit. Note that 1000 mol = 1 kmol, not 1 kg-mol.

Liter

For gases and liquids the liter is a much more practical measure of volume, especially in concentration expressions, than the derived unit of cubic meter, m^3. Usage therefore has established the liter (L) as an accepted named unit, even though cubic decimeter (dm^3) is the correct SI designation. The only prefix to be used with liter is milli, that is milliliter (mL). The symbol L is used for liter to prevent confusion with the letter l and the number 1.

Time

Seconds, (s), the SI base unit, is inadequate for long periods of time, and so a minute, (min) of 60 s, an hour (h) of 3600 s, and a day (d) of 86,400 s are accepted. Year and month are problems in that they each have varying magnitude, however AIChE recognizes the 365-day year (yr) as an accepted time unit.

Angles

The measurement of angles in radians is the SI standard, although the degrees-minutes-seconds format is acceptable. It is recommended, however, that *degrees* and *decimal fractions* thereof be used in which 1° is exactly equal to (π/180) rad; thus, 33°45'36" becomes 33.76° in the recommended format.

Commercial Mass Unit

A mass unit frequently used for convenience in the United States and elsewhere is the so-called "metric ton." For commercial use with SI this unit is called the ton (t) and is equal to 1000 kg, or 1 Mg.

Transition Units

Certain units are acceptable in SI for a limited transition period. Of interest to AIChE are the following: ångström (Å), hectare (ha), barn (b), bar (bar), standard atmosphere (atm), curie (Ci), röntgen (R), and rad (rd). Units to be avoided are kg force/m^2, calorie, kilowatt-hr, kilogram force, and poise.

Unacceptable Units

The strictly non-SI units, min, h, d, °, and t are, in general, not to be used in combination with approved SI units to form compound units; that is, use J not kWh, use m/s not m/min, use rad/s not °/s; t/yr is acceptable but not t/s.

4. Conversion

Conversion Problems

In addition to learning the new units and symbols, one must convert the numerical values reported in the cgs or engineering unit systems to the equivalent SI units. The actual conversion is best handled through the use of conversion tables. When the tables are used, ancillary problems of significant figures, accuracy, and rounding become apparent.

Common Conversion Factors

The conversions shown in Table 6D-5 are representative of the properties normally encountered in chemical engineering practice.

a. The properties listed are taken from Tables 6D-1, 6D-2, and 6D-3 and have wide applicability in the profession; others can be calculated from those in the tables.

b. If a conversion from a specified cgs-eng property in the units indicated in the first column is desired, multiplying the number of units by the numerical conversion factor in the second column yields the number of standard or accepted SI units shown at the head of each individual section. For example, (500 hp)·(745.7) = 373,000 W = 373 kW.

c. The units of the conversion factor are the SI units in the individual section heading divided by the units of the first column of the same section. For example for hp under the power heading, the second column property is 745.7 W/hp.

d. Division of a value given in SI units by the appropriate conversion factor will give the cgs-eng units shown in the first column.

Table 6D-5
Conversion Factors
(Four-significant figures)

Multiply the numerical value of units in the first column by the conversion factor in the second column to obtain the standard SI units given at the head of each individual section.

(Engineering units)(conversion factor) = (SI units in heading)

L, Length, m		m, Mass, kg	
Å	1.0×10^{-10}	grain	6.480×10^{-5}
in.	0.02540	oz (av.)	0.02835
ft	0.3048	lb (av.)	0.4536
yd	0.9144	ton (2000 lb)	907.2
mi	1609	ton (metric), t	1000
A, Area, m^2		ton (2240 lb)	1016
barn	1.0×10^{-28}	w, Mass flow rate, kg/s	
in^2	6.452×10^{-4}	lb/yr	1.438×10^{-8}
ft^2	0.09290	t/yr	3.171×10^{-5}
yd^2	0.8361	lb/h	1.260×10^{-4}
acre	4047	lb/min	7.560×10^{-3}
hectare	10,000	ton(2000 lb)/day	0.01050
mi^2	2.590×10^{6}	lb/s	0.4536
V, Volume, m^3		q, Volumetric flow rate, m^3/s	
in^3	1.639×10^{-5}	ft^3/h	7.87×10^{-6}
U.S. fluid ounce	2.957×10^{-5}	BPOD (bbls/24 hr)	1.84×10^{-6}
quart (liq)	9.464×10^{-4}	gpm (gal/min)	6.309×10^{-5}
L, liter	1.0×10^{-3}	ft^3/min	4.72×10^{-4}
U.S. gallon (liq)	3.785×10^{-3}	ft^3/s	0.02832
ft^3	0.02832	n, Amount of substance, mol	
barrel (42 gal)	0.1590	pound-mole	453.6
yd^3	0.7646	gram-mole	1.000
mi^3	4.168×10^{9}	kg-mol	1000

Table 6D-5 (Continued)

T, Temperature, K	
°F	5/9(°F + 459.7)
°C	°C + 273.2
R	5/9
Δ°F, ΔR	5/9
Δ°C, ΔK	1.0
u, Velocity, m/s	
ft/min	0.005080
km/h	0.2778
ft/s	0.3048
mi/h, mph	0.4470
1 mph	= 1.609 km/h
f, Frequency, Hz	
cycles per second	1.0
F, Force, N	
dyne	1.0×10^{-5}
lb_f	4.448
p, Pressure, Pa	
$dyne/cm^2$	0.1000
mm of Hg	133.3
torr	133.3
lb_f/ft^2	47.88
in. of water	248.8
ft of water	2989
in. of Hg	3386
$lb_f/in.^2$, psi	6895
bar	100,000
std atm	101,300
E, Energy; W, work: J	
eV	1.602×10^{-19}
erg	1.0×10^{-7}
dyne • cm	1.0×10^{-7}
W • s	1.0
ft • lb_f	1.356
cal	4.184
Btu	1054
kcal	4184
kW • h	3.6×10^6
P, Power; q, heat transfer rate: W	
ft • lb_f/min	0.02260
Btu/h	0.2929
cal/s	4.184
Btu/m	17.57
hp	745.7
ton of refrig	3517
Light	
footcandle	= 10.76 lux
l lambert	= 3183 cd/m^2
Radioactivity	
1 röntgen	= 2.58×10^{-4} C/kg
1 rd	= 1.0×10^{-2} J/kg
α, ν, D, Diffusivity, m^2/s	
ft^2/h	2.581×10^{-5}
cm^2/s	1.0×10^{-4}
ft^2/s	0.09290
H, ΔH, Enthalpy, enthalpy change, J/kg	
Btu/lb	2324
cal/g	4184
kcal/g	4.184×10^6
C_p, Heat capacity, J/kg • K	
Btu/lb • °F	4184
cal/g • °C	4184
Pcu/lb • °C	4814
Molar enthalpy, molar enthalpy change, J/mol	
Btu/lb-mol	2.324
cal/g-mol	4.184
kcal/g-mol	4184
k, Thermal conductivity, W/m • K	
Btu/h • ft^2 • °F/in.	0.1442
Btu/h • ft^2 • °F/ft	1.730
cal/s • cm • °C	418.4
h, Heat transfer coefficient, $W/m^2 \cdot K$	
Btu/min • ft^2 • °F	0.09457
Btu/h • ft^2 • °F	5.674
cal/s • cm • °C	41,840
μ, Newtonian viscosity, Pa • s	
lb/hr • ft	4.134×10^{-4}
centipoise	0.0010
poise, g/cm • s	0.1000
lb/ft • s	1.488
ρ, Density, mass concentration, kg/m^3	
grain/gal	0.01712
g/L	1.0
lb/ft^3	16.02
lb/gal	119.8
g/cm^3	1000
$lb/in.^3$	27,680
q/A, Thermal flux, W/m^2	
Btu/hr • ft^2	3.152

Table 6D-5 (Continued)

Btu/s • ft^2	11,350
cal/s • cm^2	41,840
a, Acceleration, m/s^2	
cm/s^2	0.010
in./s^2	0.0254
ft/s^2	0.3048
std accel of grav, g,	= 9.807 m/s^2
G, Mass velocity, kg/s • m^2	
lb/hr • ft^2	1.356 x 10^{-3}
lb/s • ft^2	4.882
g/s • cm^2	10.0
c, Molar concentration, mol/m^3	
molarity, g-mol/L	1000
lb-mol/ft^3	16,020
R, Gas constant, J/mol • K (R = 8.314 J/mol • K)	
cm^3 • atm/g-mol • K	0.1013
L • mm Hg/g-mol • K	0.1333
ft^3 • psi/lb-mol • °R	0.7749
ft^3 • atm/lb-mol • °R	11.39
L • atm/g-mol • K	101.3
Btu/lb-mol • °R	4.184
cal/g-mol • K	4.184
σ, Surface tension, N/m	
dyne/cm	0.001
erg/cm^2	0.001
lb$_f$/ft	14.59
lb$_f$/in.	175.1
N/A, Molar flux, mol/s • m^2	
lb-mol/h • ft^2	1.356
lb-mol/s • ft^2	4883
g-mol/s • cm^2	10,000
I, Moment, torque, N • m	
dyne • cm	1.0 x 10^{-7}
in.oz$_f$	7.062 x 10^{-3}
in. • lb$_f$	0.1130
ft • lb$_f$	1.356
S, Entropy, J/K	
cal/K	4.184
Btu/°R	1898
k$_c$, Mass transfer coefficient, m/s	
lb-mol/h • ft^2	
(lb-mol/ft^3)	8.467 x 10^{-5}
g-mol/s • cm^2	
(g-mol/L)	10.0

Note: miles are statute miles. Btu's and calories are from the thermochemical scale.

Significant Figures

a. The conversion factors presented in Table 6D-5 are given to four significant figures, a sufficient degree of accuracy for the vast majority of chemical engineering calculations. The seven-digit conversion factors listed in ASTM Standard E380-76 were used as the basis for the values presented in Table 6D-5.

b. When the conversion factor is applied, the resultant numerical value of the SI unit should have not more and no fewer significant figures than the original numerical value of the converted unit. For example, 62.3 lb converts to 28.26 kg when the four-significant-figure conversion of 0.4536 kg/lb is used, but the original numerical value had no more than three significant figures. The proper answer, therefore, is that 62.3 lb converts to 28.3 kg.

c. To apply the conversion factor properly requires that the precision of the original numerical value be determined before the conversion is performed. The exact conversion factor between feet and meters is 0.3048 m/ft; 1 ft is then 0.3 m, 1.0 ft is 0.30 m, 1.00 ft is 0.305 m, and only 1.000 ft converts to 0.3048 m.

d. When the precision of a number is given or can be reasonably estimated, the converted numerical result follows the same rule for significant figures. For example, 489 ± 2 lb/ft^3 converted to SI units becomes numerically 7833.78 ± 32.04 kg/m^3, but is reported as 7830 ± 30 kg/m^3 since 489 had three significant figures (7830 does also) and ±2 had but one significant figure. Also, 1200 Btu ± 5% implies a three-significant-figure precision (0.05 x 1200 = 60) a change in the tens position), and so the SI conversion results in 1.26 MJ ± 5%.

Rounding

The rounding conventions are as follow:

a. If the highest placed digit of the numerical portion to be dropped is less than 5, then the last digit in the numerical portion that is to be retained is not changed in value; for example, 1.2648 rounded to three significant figures becomes 1.26 since the highest placed digit of the dropped portion is 4, which is less than 5.

b. If the highest placed digit in the portion to be dropped is greater than 5, including digits to the right of the highest placed digit, then increase the last retained digit by 1; for example, 7517 rounded to three significant figures becomes 7.52 x 10^3, 12.51 rounded to two significant figures becomes 13; 0.169531 becomes 0.170 when rounded to three significant figures.

c. If the highest placed digit in the portion to be dropped is exactly 5, including the digits to the right, then the last retained digit is not altered if it is an even digit, but if the last retained digit is an odd number it is increased by one to the next highest even number. For example, 47.5 rounds to 48.0, 0.165 rounds to 0.16, and 505.000 rounds to 500, all for two-significant-figure results.

Unit Equivalences

a. Because SI is built on the base units of length, mass, time, temperature, amount of substance, electric current, luminous intensity, and angle, all other units are derived. In terms of common dimensions SI is an LMtT System. Consequently, force, for instance, becomes a derived unit, and Newton's Second Law of Motion becomes simply F = ma without the need of g_c as in the American Engineering, or LMFtT, System. There exists, however, in SI a large number of unit equivalences that must be utilized. These often must be included in a calculation so that a desired unit is obtained in the result. The unit equivalences most often encountered in chemical engineering are

$$N = kg \cdot m/s^2$$
$$Pa = N/m^2 = kg/m \cdot s^2$$
$$J = N \cdot m = W \cdot s$$
$$Pa \cdot s = kg/m \cdot s$$

Other equivalencies are indicated in the formula column of Tables 6D-2 and 6D-3.

b. The use of multiplier prefixes in multiple-term expressions may lead to errors in magnitude of the final result. It is therefore recommended that prefix multipliers not be used in multiterm expressions. For example in the determination of the Reynolds number, $Du\rho/\mu$, the viscosity (say for water at 288 K) should be 1.1 x 10^{-3} Pa·s rather than 1.1 mPa·s.

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