Handbook of Diffusion and Thermal Properties of Polymers and Polymer Solutions

0057926

HANDBOOK OF DIFFUSION AND THERMAL PROPERTIES OF POLYMERS AND POLYMER SOLUTIONS

James M. Caruthers
Kwang-Chu Chao
Venkat Venkatasubramanian
Rogelio Sy-Siong-Kiao
Carlos R. Novenario
Anantha Sundaram

School of Chemical Engineering
Purdue University
West Lafayette, IN 47907-1283

Published by
Design Institute for Physical Property Data®
American Institute of Chemical Engineers

© Copyright 1998
Design Institute for Physical Property Data (DIPPR®)
American Institute of Chemical Engineers
3 Park Avenue, New York, N.Y. 10016-5901
U.S.A.

It is sincerely hoped that the information presented in this document will lead to improvements in process technology for the entire industry; however, neither the American Institute of Chemical Engineers, or its directors, officers, employees or members, its consultants, DIPPR Committees or Subcommittees, their members, their employees, nor their employer's officers and directors warrant or represent, expressly or implied , the correctness or accuracy of the content of the information presented in this document, nor its fitness for any use or for any purpose, nor can they or will they accept any liability or responsibility whatsoever for the consequences of its use or misuse by anyone.

Library of Congress Cataloging-in-Publication Data

Handbook of diffusion and thermal properties of polymers and polymer
solutions / James M. Caruthers ...[et al.].
Includes bibliographical references (p. -).
ISBN 0-8169-0762-5
1. Polymers--Permeability. 2. Polymers --Thermal properties.
3. Polymer solutions--Thermal properties. I. Caruthers, James M.
QD381.9.P45H36 1998 98-36293
547'. 70456--dc21 CIP

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the copyright owner.

Preface

In 1992 the Design Institute for Physical Property Data® of the American Institute of Chemical Engineers established Project 922 to develop a *Handbook of Diffusion and Thermal Properties of Polymers and Polymer Solutions*. The objectives were to (i) evaluate existing predictive and correlative models for the PVT behavior, diffusivity, and thermal conductivity of polymers and polymer solutions, (ii) extend the existing models for polymer thermophysical properties, (iii) examine and archive the experimental data for these thermophysical properties, and (iv) provide a PC-based computer program for the retrieval of the experimental data and ready implementation of the predictive/correlative models. During the past four years of this project most of these objectives have been met.

The staff at Purdue University was assisted throughout this project by the members of the Project Steering Committee. The members of the Steering Committee have provided valuable technical advice, critical analysis of the property models, additional references to experimental data, and evaluation of the *Handbook*. In addition, the companies represented on the Project Steering Committee have provided generous financial support towards this project. Special thanks go to Mr. Mark Drake and Dr. José Dionisio who served as Chairmen of the Project Steering Committee. The industrial sponsors of DIPPR® Project 922 are:

Organization	Representative
Air Products & Chemicals, Inc.	Vipul Parekh
Allied Signal, Inc.	William Hammond
ARCO Chemical Co.	Maureen Buzdygon
Aspen Technology	Constantinos Bokis / Marcello Marchetti
B.F. Goodrich Co.	Merrill Galloway
Chiyoda Corp.	Akio Shindo
DIPPR	Theodore B. Selover, Jr.
Dow Chemical Co.	Joe Weller
Dow Corning Corp.	Ora Flaningam
3M Company	Ilyess H. Romdhane
Mitsui Eng. & Ship Building Co.	Yoshikazu Izawa
Phillips Petroleum Co.	José Dionisio
Rexam Graphics Corp.	Mark Drake
Rohm & Haas Co.	Ronald Myers
Shell Development Co.	Ray N. French
Simulation Sciences, Inc.	John Cunningham
Union Carbide Corp.	Clyde Rhodes, II

Table of Contents

Handbook of Diffusion and Thermal Properties of Polymers and Polymer Solutions

Preface iv

Chapter 1: Introduction 1

Chapter 2: Fundamentals of Polymer Thermodynamics 3
- 2.1 Introduction 3
- 2.2 Empirical Models for the PVT Behavior of Polymer Melts 4
  - 2.2.1 Group Methods for the PVT Behavior 4
  - 2.2.2 Tait Equation 5
  - 2.2.3 Other Empirical Equations 6
  - 2.2.4 Group Methods for the Heat Capacity 8
- 2.3 Equation of State Models for Chain Molecules 9
  - 2.3.1 Basic Statistical Mechanics 9
  - 2.3.2 Cell Model 9
  - 2.3.3 Lattice Fluid Model 13
  - 2.3.4 Hole Model 14
  - 2.3.5 Polymer Chain of Rotators 18
  - 2.3.6 Perturbed Hard-Sphere-Chain 21
  - 2.3.7 Discussion 23
- 2.4 Heat Capacity 26
- 2.5 Heat of Polymerization 30

Chapter 3: Fundamentals of Solvent Diffusivity and Thermal Conductivity 37
- 3.1 Introduction 37
- 3.2 Diffusivity of Solvents 38
  - 3.2.1 Self-Diffusion vs. Mutual-Diffusion 38
  - 3.2.2 Free Volume Models for the Self-Diffusion Coefficient 39
  - 3.2.3 Configurational Entropy Model for the Self-Diffusion Coefficient 42
  - 3.2.4 Discussion 45
- 3.3 Thermal Conductivity 47

Chapter 4: Procedures 50
- 4.1 Specific Volume 50
  - 4.1.1 Tait Equation 50
  - 4.1.2 Polymer Chain-of-Rotators Equation of State 56
  - 4.1.3 Prigogine Cell Model Equation of State 68
  - 4.1.4 Flory-Orwoll-Vrij Equation of State 71
  - 4.1.5 Dee-Walsh Equation of State 74
  - 4.1.6 Sanchez-Lacomb Equation of State 77
  - 4.1.7 Simha-Somcynsky Equation of State 80
  - 4.1.8 Hartmann-Haque Equation 84
  - 4.1.9 Perturbed Hard-Sphere-Chain Equation of State 87
- 4.2 Thermal Expansion Coefficient 91
  - 4.2.1 Tait Equation 91
  - 4.2.2 Using an Equation of State 92

此为试读，需要完整PDF请访问：www.ertongbook.com

- 4.3 Heat Capacity 94
  - 4.3.1 Heat Capacity from an Equation of State 94
    - 4.3.1.1 Polymer Chain-of-Rotators Equation of State 94
    - 4.3.1.2 Flory-Orwoll-Vrij Equation of State 97
    - 4.3.1.3 Sanchez-Lacombe Equation of State 99
    - 4.3.1.4 Prigogine Square Well Equation of State 101
    - 4.3.1.5 Dee-Walsh Equation of State 103
  - 4.3.2 Generalized Equation of van Krevelen 105
- 4.4 Heat of Polymerization 107
- 4.5 Diffusion Coefficient 117
  - 4.5.1 Vrentas-Duda Free Volume Model 117
  - 4.5.2 Configurational Entropy Model 134

Chapter 5: Data Base 142
- 5.1 PVT 142
- 5.2 Heat Capacity 142
- 5.3 Heat of Polymerization 143
- 5.4 Self Diffusion Coefficients 144
- 5.5 Mutual Diffusion Coefficients 145
- 5.6 Thermal Conductivity 149

Chapter 6: Computer Programs 150
- 6.1 Introduction 150
  - 6.1.1 Software Organization 150
- 6.2 Main-Menu 151
- 6.3 PVT 152
  - 6.3.1 View PVT Data 152
    - 6.3.1.1 PVT Grapher 154
  - 6.3.2 Edit/Update PVT Database 155
    - 6.3.2.1 Example: Edit Tait Parameters 155
    - 6.3.2.2 Import PVT Data 156
    - 6.3.2.3 Export PVT Data 156
  - 6.3.3 Prediction from Models 157
    - 6.3.3.1 PVT Predictor: Option Screen 157
    - 6.3.3.2 PCOR Parameters from Structure 158
    - 6.3.3.3 Generating PTV Predictions from Model 158
  - 6.3.4 Analysis of Experimental Data 160
    - 6.3.4.1 Fit Parameters to Data 160
- 6.4 Diffusivity 162
  - 6.4.1 View Diffusivity Data 162
    - 6.4.1.1 Example: View Mutual-Diffusivity Data 162
  - 6.4.2 Edit/Update Diffusivity Database 163
    - 6.4.2.1 Example: Edit Vrentas-Duda Model Parameters 163
    - 6.4.2.2 Importing Diffusion Data 164
  - 6.4.3 Prediction of Diffusivity at Different Temperatures and Solvent Concentrations 166
    - 6.4.3.1 Generating Diffusivity Predictions 167
  - 6.4.4 General Comments 168
- 6.5 Heat Capacity 168
  - 6.5.1 View Heat Capacity Data 168
  - 6.5.2 Prediction from Models 169
    - 6.5.2.1 Predict Residual Heat Capacity 169
    - 6.5.2.2 Ideal Gas Heat Capacity Calculations 170
    - 6.5.2.3 Displaying the Calculated Heat Capacity 171

6.6 Heat of Polymerization 171
  6.6.1 View Heat of Polymerization Data 171
  6.6.2 Edit Parameters of Models 171
  6.6.3 Prediction of Heat of Polymerization 172
6.7 Miscellaneous Screens 173
  6.7.1 Edit Parameters 173
  6.7.2 Molecular Weight Input Screen 174
  6.7.3 On-line HELP 174
  6.7.4 Full-Name Lists 174

Chapter 7: References 176

Appendix A: Abbreviations for Polymers and Solvents 193

Chapter 1

Introduction

Engineers and scientists that are involved in the design and operation of polymer manufacturing and processing operations need reliable methods for estimating a variety of physical properties. The dependence of specific volume on pressure and temperature is important in a variety of polymer manufacturing operations like injection molding, where thermal expansion can affect the final shape of a part. In addition, transport properties are important in designing manufacturing operations like devolatilization, injection molding, sheet/film forming, etc. The *Handbook of Diffusion and Thermal Properties of Polymers and Polymer Solutions* contains data bases for the PVT behavior, solvent diffusivity, and thermal conductivity for a wide variety of polymers and polymer-solvent systems, as well as both correlative and predictive methods for estimating these properties. The *Handbook* provides the essential background information, a critical review of the various methods, detailed methodology on how to implement the various estimation methods, comprehensive data bases, and a PC-based software package for easy implementation of the recommended models and access to the available experimental data.

In a design situation it is always desirable to have direct experimental data for the polymer system of interest; therefore, we have attempted to provide a complete data base for the properties addressed in the *Handbook*. However, one of the very attractive features of polymers is the ease which the molecular structure can be modified in order to address a particular application; consequently, experimental data are often not available for the specific polymer of interest. A major objective of the *Handbook* is to provide a critical review of (i) various correlative methods that have been proposed to estimate PVT behavior and solvent diffusivity when there are only limited data and (ii) predictive methods when no experimental data are available.

In Chapter 2 a comprehensive review will be provided of the methods for correlating or predicting the pressure-volume-temperature surfaces for polymer melts. Methods for estimating the specific volume for non-equilibrium situations like the glassy state or the semicrystalline state are not as well developed for polymers; thus, the *Handbook* will only focus on the PVT behavior for polymers in the melt. This chapter will first review various empirical methods that have been proposed for describing the density and coefficient of thermal expansion for polymer melts and will subsequently review the various polymer equation-of-state models that have been proposed. Finally, the chapter will review the various methods for estimating heat capacity and heat of polymerization.

In Chapter 3 methods for describing and/or predicting the self-diffusion of low molecular weight solvents in polymers will be reviewed. Determination of the mutual diffusion coefficient for solvent diffusion requires estimation of the solvent's activity coefficient in addition to the self-diffusion coefficient. Since the determination of activity coefficients for polymer-solvent systems was the focus of the DIPPR® Project 881, the data and methodology for correlating and/or predicting solvent activity will not be discussed in this *Handbook*. The last part of Chapter 3 will include a discussion of the data and currently existing correlation methods for describing the thermal conductivity for polymer melts.

The various recommended correlative and predictive methods for estimating PVT behavior and solvent diffusivity are described in detail in Chapter 4. The objective of Chapter 4 is to provide the practicing engineer a detailed description of how to implement the various methods including worked examples.

Chapter 5 includes a listing of all the polymer and polymer-solvent systems that are included in the data base. The actual experimental data are much too voluminous to be included in this Chapter; however, all the data are contained on the diskettes that are included with the *Handbook* as well as a listing of the original source of various data sets.

The PC-based software package that is included with the *Handbook* will be described in Chapter 6. The appropriate procedures needed in order to navigate the various screens for implementation of the different correlative or predictive methods will be described as well as how to access the experimental data base. Since the software package includes extensive on-line help, Chapter 6 will not attempt to provide an exhaustive description of the software.

Finally, references are given in Chapter 7 and a list of abbreviations for both polymers and solvents is provided in Appendix A.

The various data bases, correlative models, predictive models, and PC-based software have been reviewed by members of the DIPPR 922 Steering Committee. This review ensures that data and recommended methodologies are appropriate and that they have been tested in a variety of industrial design situations.

Chapter 2

Fundamentals of Polymer Thermodynamics

2.1 Introduction

The starting point for a description of the physical properties of polymers or polymer solutions must be the equilibrium thermodynamic behavior. The equilibrium behavior is important in its own right, being the key phenomenon in a variety of applications; for example, vapor-liquid equilibrium is the driving force in devolatilization, and liquid-liquid equilibrium is important in numerous polymerization processes where phase separation occurs during the course of the reaction. There are, of course, numerous other applications where the equilibrium thermodynamic behavior is an important consideration. In addition, the equilibrium behavior is also important as a point of departure in describing the nonequilibrium behavior of polymers; for example, the properties of a polymer glass depend upon the temperature and pressure dependent specific volume in the melt just prior to formation of the glass. Also, the transport behavior may depend upon the thermodynamic properties of the system; specifically, the driving force for mass flux in multicomponent mass transport is usually assumed to be the chemical potential gradient (Bird, et. al., 1960). In this Chapter various methods for describing selected thermodynamic properties of polymer melts and polymer solutions will be presented.

The first thermodynamic property to be considered is the pressure-volume-temperature, i.e. PVT, behavior (or equivalently the density, coefficient of thermal expansion, and bulk modulus or bulk compressibility). The PVT behavior of polymer melts is directly important in a number of engineering applications; for example, during injection molding and other polymer processing operations, the polymer melt may be subjected to very large pressures, and the properties of the resulting solid can depend upon the specific volume in the melt immediately prior to formation of the glassy solid. In addition, a primary requirement of an equation of state is an accurate description of the PVT behavior.

The second set of thermodynamic properties to be considered are the heat capacity and the heat of polymerization. The heat of polymerization is obviously important in designing polymerization reactors, where removal of heat generated during the reaction is an important design consideration. The heat capacity is also important in the design of polymerization reactors; in addition, the heat capacity will also be one of the physical properties needed in order to estimate the temperature rise that will occur in a variety of polymer processing operations

Another thermodynamic property of engineering significance is the vapor liquid equilibrium, i.e. VLE, or equivalently, the activity coefficient of the solvent in a polymer-solvent system. The VLE behavior is important in the design of polymerization processes, where the heat of reaction may cause vaporization of the solvent, as well as in devolatilization unit operations, where removal of the solvent from the polymer is the design objective. In addition, the concentration dependence of the solvent's chemical potential is needed in order to relate the mutual diffusion coefficient, which is the relevant physical property to describe mass transfer in polymer-solvent systems, to the self diffusion coefficient, which is the property that can be most readily estimated, as will be discussed in Chapter 3. Methods for estimating the solvent activity for polymer-solvent systems was the subject of a previous DIPPR project (Danner and High, 1993) and thus will not be addressed in this Chapter.

The remainder of this Chapter will be organized as follows: In Section 2.2, various empirical models for PVT behavior and heat capacity will be presented. In Sections 2.3, 2.4, and 2.5 equation of state models will be discussed respectively for PVT behavior, heat capacity, and heat of polymerization.

2.2 Empirical models for the PVT Behavior and Heat Capacity of Polymer Melts

2.2.1 Group Methods for the PVT Behavior

A variety of group methods have been proposed to calculate the density of organic materials, where the density of the substance of interest is the sum of the contributions from the various molecular groups that comprise the material. Van Krevelen (1976, 1990) has developed an extensive group table for the molar volumes of various structural units for rubbery and glassy polymers at room temperature. The average deviation between the experimentally measured density at room temperature and the predictions from the van Krevelen groups is 1.5% for rubbery polymers and 1.2% for glassy polymers. An alternative group approach involves the van der Waals volume, which is the hard core volume that can not be penetrated by neighboring groups. An extensive table of the group contributions to the van der Waals volume, V_w, has been developed by Bondi (1964, 1968), Slonimskii, et al. (1970), and Askadskii (1987) for nearly 100 structural groups. The polymer's rubbery and glassy volumes, V_r and V_g respectively, at room temperature have been correlated with the van der Waals molar volumes (van Krevelen, 1976, 1990), where $V_r/V_w = 1.60 \pm 0.035$ and $V_g/V_w = 1.60 \pm 0.045$ with an average deviation of approximately 3% between the predictions and the experimentally measured density.

The group methods described in the previous paragraph can be used to estimate the polymer's density at room temperature; however, the coefficient of thermal expansion is needed to estimate the density at other temperatures. Using the Simha-Boyer model of isobaric thermal expansion which assumes that (i) volume in the glass, rubber, and crystalline states are linear functions of temperature and (ii) the molar volume of the supercooled liquid at 0 K equals the molar volume of the crystal at 0 K, van Krevelen (1976) has proposed a method for estimating the molar thermal expansivity $E = (\partial V/\partial T)_p$, where V is the molar volume. Specifically, the molar thermal expansivity has been correlated with the van der Waals volume as follows: for rubbery polymers $E_r = 10.0 \times 10^{-4}\, V_w$ and for glassy polymers $E_g = 4.5 \times 10^{-4}\, V_w$, where V_w can be estimated from the Bondi groups. An average error between the predicted E and the experimentally determined E was 8% for rubbery polymers and 15% for glassy polymers. If it is assumed that the correlation between V_r/V_w and V_g/V_w described in the preceding paragraph is valid, the molar isobaric coefficient of thermal expansion

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{E}{V} \tag{2.1}$$

at room temperature is 6.25×10^{-4} K^{-1} for all rubbers and 2.9×10^{-4} K^{-1} for all glasses (van Krevelen, 1976) independent of the chemical composition.

Group methods have also been developed by van Krevelen (1976) to estimate the bulk modulus, using the longitudinal sound velocity u which is related to the longitudinal modulus $M = 4K/3 + G$ by

$$u^2 = \frac{M}{\rho} = \frac{1}{\rho}\left(\frac{4}{3}K + G\right) \approx \frac{K}{\rho} \tag{2.2}$$

where K is the bulk modulus and G is the shear modulus. For liquids the bulk modulus is typically much greater than the shear modulus, and thus, M being proportional to K is often an acceptable approximation, although for polymer melts just above T_g or T_m this approximation is questionable because the shear and the bulk modulus become the same order of magnitude in the solid state. Rao (1940, 1941) proposed that a quantity U called the Rao function given by

此为试读,需要完整PDF请访问: www.ertongbook.com

$$U = V u^{1/3} \tag{2.3}$$

and that U is a molar additive quantity for organic liquids. Combining Equations 2.2 and 2.3, the following group method for the bulk modulus has been proposed

$$K = V\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{U}{V}\right)^6 \tag{2.4}$$

The Rao function is available for 37 different groups and the predictions of the bulk modulus are generally within 10% of the experimental data (van Krevelen, 1976). Two alternative group methods that employ the Gruneisen relationship or the sublimation energy instead of the Rao function have also been proposed by van Krevelen (1976) for estimating the bulk modulus.

These group methods can provide a useful estimate of the density, coefficient of thermal expansivity, and the bulk modulus at room temperature and atmospheric pressure for those polymers where group values are available. Since experimental PVT surfaces for polymers are slightly curved, the coefficient of thermal expansion and the isothermal bulk modulus will be functions of temperature and pressure; however, in order to use these group methods to estimate the PVT surface, one must assume that the coefficient of thermal expansion and bulk modulus are constants. The error in making this assumption may not be too large for temperatures near room temperature and pressures near one atmosphere; however, care must be exercised in using these methods for estimating the PVT behavior for more extreme conditions.

2.2.2 Tait Equation

The most widely employed equation for representing the PVT data for polymers is the Tait equation (Tait, 1888), which was originally developed for water and has been applied to a wide variety of polymeric liquids (Zoller, 1989; Rodgers, 1993). The Tait equation relates the specific volume, V(P,T), in terms of the zero-pressure volume, V(0,T), and the Tait parameter, B(T), as follows:

$$V(P,T) = V(0,T)\left\{1 - C\ln\left[1 + P/B(T)\right]\right\} \tag{2.5}$$

The parameter C is often taken to be independent of temperature and pressure, and a universal value of 0.0894 is commonly assumed (Cutler *et al.*, 1958). B(T) is parameterized as

$$B(T) = B_0 \exp(-B_1 T) \tag{2.6}$$

and the zero-pressure volume V(0,T) is parameterized by

$$V(0,T) = A_o + A_1 T + A_2 T^2 \tag{2.7}$$

where B_0, B_1, A_0, A_1 and A_2 are material dependent parameters and T is in °C . An alternative expression that may be employed for V(0,T) is

$$V(0,T) = V_0 \exp(\alpha T) \tag{2.8}$$

where α is the zero pressure coefficient of thermal expansion and V_0 is the volume at temperature T_0. Although the Tait equation is simple, it does have a mathematical deficiency (MacDonald, 1966); specifically, at sufficiently high pressures the Tait equation predicts a negative volume, which is physically impossible. This problem illustrates that the Tait equation is empirical and can only be used with confidence over the range of temperatures and pressures that were used to determine the material parameters.

The Tait equation contains five material parameters (when V(0,T) is given by Equation 2.7 that must be determined from experimental PVT data. These parameters have been determined for nearly 60 different polymer melts (Zoller, 1989; Rodgers, 1993). The Tait equation accurately reproduces the PVT data, with typical errors of about 0.1% over a wide range of temperatures and pressure (Zoller, 1989; Danner and High, 1993), which is approximately equal to the experimental error reported by Zoller *et at.* (1976). The Tait equation has also been used to describe the PVT behavior of polymer glasses (Zoller, 1989), where the parameters are obviously different from those of polymer melts.

The Tait equation provides a convenient means to compute the volumetric coefficient of thermal expansion, α, and isothermal compressibility, β, as follows

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P = \alpha(0,T) - PB_1\beta \tag{2.9}$$

$$\beta = -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_T = \frac{C/(P+B)}{1-C\ln(1+P/B)} \tag{2.10}$$

where

$$\alpha(0,t) = \frac{A_1 + 2A_2T}{A_o + A_1T + A_1T^2} \tag{2.11}$$

2.2.3 Other Empirical PVT Equations

A variety of other empirical equations have been proposed to describe the PVT behavior of polymers, although none of these equations have been used as extensively as the Tait equation.

Spencer and Gilmore (1949, 1950) modified the van der Waals equation of state for polymers, employing a constant value for the internal pressure instead of the van der Waals' term, a/V^2. The Spencer-Gilmore empirical equation of state for polymers is

$$(P + \pi)(V - \omega) = RT \tag{2.12}$$

where P is the external pressure, π is the internal pressure, V is the volume, ω is the volume at absolute zero temperature, R is the gas constant and T is the absolute temperature. The Spencer-Gilmore equation is a very simple two-parameter equation. However, it has only been applied with moderate success to a limited number of polymers, with errors as high as 0.01 cm^3/g (Zoller, 1989).

Wier (1953, 1954) developed an empirical isobaric equation to describe the PVT relationship of polymers. In each isobar, the volume is expressed as a polynomial equation in terms of temperature,

$$V = V_o\left(a + bT + cT^2\right) \tag{2.13}$$

where V_0 is the specific volume at 21 °C, a, b and c are the polynomial coefficients and T is the temperature in degree Celsius. The three polynomial coefficients are then expressed in polynomial form in terms of pressure as

$$a = 1 + a_1P + a_2P^2 + a_3P^3 \tag{2.14a}$$

$$b = b_o + b_1P + b_2P^2 \tag{2.14b}$$

$$c = c_o + c_1P + c_2P^2 \tag{2.14c}$$

where a_i, b_i and c_i are material constants of the polymers. Equation 2.13 is able to represent experimental specific volume data to within a few tenths of a percent over the ranges of temperatures and pressures studied; however, considerable experimental data are required to obtain the ten material parameters.

Whitaker and Griskey (1967) developed an empirical PVT relationship for polymers. They observed that at any given pressure, the correlation between the compressibility factor, i.e. PV/RT, and a reduced temperature, T/T_g, resulted in a family of curves that can be collapsed into a single master curve. Their equation is

$$V = \left[\frac{0.01205}{\rho_o^{\,0.9421}}\right] P^{n-1} \left(\frac{T}{Tg}\right)^{m+1} R \tag{2.15}$$

where n and m are universal parameters for all polymers that depend on pressure and are given graphically in the original article. Consequently, only the density at 25 °C and 1 atm, ρ_o, and the glass transition temperature, T_g, are needed to estimate the temperature and pressure dependent specific volume. However, this equation does not have the accuracy offered by the other empirical PVT equations, exhibiting an average percent deviation of 2.2 %.

Hartman and Haque (1985) derived an equation of state by combining the theoretical temperature dependence of thermal pressure from Pastine and Warfield (1981) with the zero-pressure isobar of the Simha-Somcynsky (1969) equation of state and an empirical volume dependence of the thermal pressure. The equation in reduced form is given by

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln \tilde{V} \tag{2.16}$$

where

$$\tilde{P} = \frac{P}{P_o}; \qquad \tilde{V} = \frac{V}{V_o}; \qquad \tilde{T} = \frac{T}{T_o} \tag{2.17}$$

and P_o, V_o and T_o are the reducing parameters. P_o is the isothermal bulk modulus extrapolated to zero temperature and pressure. V_o is the polymer liquid volume extrapolated to zero temperature and pressure. T_o is defined implicitly from the relation $V(P_o,T_o) = V(0,0)$. The Hartman-Haque equation is a simple three-parameter equation of state with a degree of accuracy within 0.001 cm^3/g.

Table 2.1 summarizes the various empirical equations of state discussed. The two-parameter Spencer-Gilmore and Whitaker-Grisky equations must be used with care because of the large correlation error. However, the Whitaker-Grisky equation may have limited predictive capability, if the density at 25 °C and 1 atm and the glass transition temperature of the polymer are known. The Wier equation which contains 10 parameters is cumbersome to use; furthermore, it is less accurate than the Tait and Hartman-Haque equations. Of all the empirical equations of state, the Tait equation is the most commonly used. Hartman-

Haque equation is a relatively new but promising empirical equation of state with only three parameters, and yet, it is as accurate as the Tait equation. Both the Tait and Hartman-Haque equations have been evaluated for a wide variety of polymers (Rodgers, 1993a).

2.2.4 Group Methods for Heat Capacity

Group methods for estimating the specific heat at constant pressure, c_p, have been developed by Shaw (1969) for liquids, and Satoh (1948) for solids, and Wunderlich and Jones (1969) for polymer solids. These group methods for estimating c_p have been analyzed by Van Krevelen (1983), where it was concluded that the molar heat capacity at 298 K can be estimated with a mean deviation of 3.5% for polymer liquids and within 2% for polymer solids. By averaging the available experimental data, the relative increase in the heat capacity with temperature was estimated to be $1.2 \times 10^{-3}\ K^{-1}$ for polymer liquids with an average error of 30% and $3.0 \times 10^{-3}\ K^{-1}$ for polymer solids with an average error of just 5%. Warfield, et al. (1969) has proposed a method for estimating the constant volume heat capacity, where the c_p/c_v ratio is a universal function of T/T_g for amorphous polymers and another universal function of T/T_m for semicrystalline polymers.

Table 2.1 Empirical Equations of State

Spencer-Gilmore

$$(P + \pi)(V - \omega) = RT$$

Wier

$$V = V_o\left[(1 + a_1P + a_2P^2) + (1 + b_1P + b_2P^2)T + (1 + c_1P + c_2P^2)T^2\right]$$

Whitaker-Griskey

$$V = \left[\frac{0.01205}{(\rho_o)^{0.9421}}\right]P^{n-1}\left(\frac{T}{T_g}\right)^{m+1} R$$

Tait

$$V(T,P) = \left(A_o + A_1T + A_2T^2\right)\left\{1 - C\ln\left[1 + \frac{P}{B_o\exp(-B_1T)}\right]\right\}$$

Hartman-Haque

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln\tilde{V}$$

2.3 Equation of State Models for Chain Molecules

2.3.1 Basic Statistical Mechanics

In contrast to the group methods and the empirical PVT equations described in the previous two sections, an equation of state is built upon a particular molecular picture of the polymer and/or solvent system. First, a molecular model is constructed to idealize the various states that may occur in the polymer and/or solvent system of interest and the energy associated with each of these states. Next, the partition function Q, which is the summation of the Boltzmann's distribution of energies over all possible states of the system, is computed; specifically,

$$Q = \sum_i \exp\left(-\frac{E_i}{kT}\right) \tag{2.18}$$

where E_i is the energy of state i, T is the absolute temperature, and k is the Boltzmann constant. And finally, the equation of state (EOS) is determined from the partition function from the standard statistical mechanical relationship (McQuarrie, 1973)

$$P = kT\frac{\partial \ln Q}{\partial V} \tag{2.19}$$

The difference between the various equation of state models is the choice of how to idealize the molecular structure of the polymer or polymer-solvent system in order to obtain a mathematically tractable expression for the partition function.

2.3.2 Cell Model

In order to simplify Equation 2.18, it is traditionally assumed that the total energy can be factored into the sum of (i) the kinetic energy, which only depends upon the individual momenta of all the molecules in the system and (ii) the potential energy, which only depends upon the configuration of all molecules in the system (McQuarrie, 1973). The partition function then given by

$$Q = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \int \cdots \int \exp\left(-\frac{U(R)}{kT}\right) dR \tag{2.20}$$

where $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N\}$ defines the configuration of the system which depends upon the spatial location $\mathbf{r}_i$ of all N particles, m is the mass of the particles, and h is Planck's constant. In addition, the potential energy $U(\mathbf{R})$ of the system is usually assumed to be the sum of the potential $u(r_{ij})$ between all pairs of particles

$$U(\mathbf{R}) = \sum_{ij} u(r_{ij}) \tag{2.21}$$

where r_{ij} is the distance between particles i and j. A specific molecular model can now be introduced in order to evaluate the multidimensional configuration integrals in Equation 2.20.

In the cell model developed by Lennard-Jones and Devonshire (1937) the total volume of the system is divided into a regular lattice of identical cells, with one particle in each and every cell. The particle moves within its cell in a potential field determined by the surrounding particles, where changes in cell volume account for the compressibility of the system. These assumptions allow the multidimensional integral in the configurational partition function to be evaluated using only the integral of a single cell. The cell model developed by Lennard-Jones and Devonshire forms the basis for the various cell models, which differ only in the form of the intermolecular potential and the local geometry of the cell.

Prigogine *et al.* (1953, 1975) applied the Lennard-Jones and Devonshire cell model to describe both simple and polymeric liquids, where the configurational partition function is given by

$$Q = g\,\Psi^{N} \exp\left[\frac{E_o}{kT}\right] \tag{2.22}$$

g is a combinatorial factor, E_o is the lattice energy, and Ψ is the partition function for an individual cell given by

$$\Psi = 4\pi \int_{cell} \exp\left[-\frac{\omega(r)-\omega(0)}{kT}\right] r^2 dr \tag{2.23}$$

The potential energy $\omega(r)$ depends upon the location r of the particle inside the cell. Prigogine assumed that the 3n degrees of freedom of the n-mers can be separated into two groups: the internal degrees of freedom which depend only on the valency forces and the external degrees of freedom which depend only on the intermolecular forces. Only the external degrees of freedom contribute to the PVT equation of state. 3c degrees of freedom are assigned to the external degrees of freedom. Prigogine showed that the cell partition function, Ψ, can be expressed as

$$\Psi = \left[\psi(T,V)\right]^{3c} \tag{2.24}$$

so that the configurational partition function can be written as

$$Q = g\left[\psi(T,V)\right]^{3cN} \exp\left[-\frac{E_o}{kT}\right] \tag{2.25}$$

The function $\psi(T,V)$ is often referred to as the free volume $v_f(T,V)$.

In order to explicitly evaluate the cell partition function, Prigogine *et al.* (1953) employed two alternative assumptions for the cell potential, resulting in two different equations of state. Both forms assumed hexagonal close packing for the cell geometry. First it was assumed that the cell potential is harmonic, given by

$$\omega(r) - \omega(0) = k(V)r^2 \tag{2.26}$$

where k(V) is a spring constant depending on the cell volume, V, and r is the distance from the center of the cell. The second assumption is that the cell potential is a square-well potential, given by

$$\omega(r) - \omega(0) = 0 \qquad 0 < r < a - s \tag{2.27}$$

$$\omega(r) - \omega(0) = +\infty \qquad r > a - s \tag{2.28}$$

此为试读，需要完整PDF请访问：www.ertongbook.com