

5 Pure Component Solubility Parameters

5.1 Hildebrand Solubility Parameters – Pure CO₂

In his high pressure gas chromatography work, Giddings²⁵⁹ recognized that gases subjected to high pressures, where densities approach those of liquids, acquire solvent properties much like liquids (see Table 2-1). This similarity with liquid solvents led Giddings to develop a corresponding states approach, based on Hildebrand's (liquid) solubility parameter concept.

5.1.1 Giddings Approximation

Hildebrand and Scott,²⁶⁰ developed a relationship between the solubility parameter and the critical pressure, P_c , from the equality of eqn (4-18), when $n = 1$, eqn. (4-15), and eqn. (4-21).

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E}{V}; \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2}; \quad \text{and } \delta = \left(\frac{\Delta E}{V}\right)^{1/2} \quad (5-1)$$
$$\therefore \delta = \frac{a^{1/2}}{V}$$

where a is known as the van der Waals attraction parameter and the volume, V , is identified with van der Waals parameter b . This determination of V was originally proposed by van Laar,²⁶¹ who assumed that liquids not significantly expanded could be

approximated by the minimum volume according to the van der Waals equation, namely the parameter b ,²⁶²

$$\mathbf{d} = \frac{a^{1/2}}{b} \quad (5-2)$$

Expressing the van der Waals parameters a and b in terms of critical properties,

$$a = \frac{27R^2T_c^2}{64P_c}, \text{ and } b = \frac{RT_c}{8P_c} \quad (5-3)$$

so that

$$\therefore \mathbf{d} = \frac{\left(\frac{27R^2T_c^2}{64P_c}\right)^{1/2}}{\frac{RT_c}{8P_c}} = (27P_c)^{1/2} \quad (5-4)$$

However, Hildebrand found that to obtain satisfactory agreement with directly measured values of $(\partial P/\partial T)_V$, referred to by Hildebrand as the “thermal pressure coefficient”,²⁶³ the numerical constant $\sqrt{27}$ should be replaced with 1.25, so that

$$\mathbf{d} = 1.25P_c^{1/2} \quad (5-5)$$

where P_c is the critical pressure in atmospheres and \mathbf{d} is in $(\text{cal}/\text{cm}^3)^{1/2}$.

Hildebrand²⁶⁴ compared the accuracy of eqn. (5-5) with solubility parameter values calculated from eqn. (5-1) and eqn. (5-77) (reviewed later in this chapter). The result of his comparison is reproduced in Table 5.1.

Table 5-1. Comparison of solubility parameter equations.

Substance	Eqn. (5-77) $d \cong \left(\frac{\Delta H^V - RT}{V_m} \right)^{1/2}$	V (L)	a (liter ² atm)	Eqn. (5-1) $d \cong \frac{a^{1/2}}{V}$	P _c (atm)	Eqn. (5-5) $d = 1.25P_c^{1/2}$
n-Hexane	7.3	132	24.4	5.8	29.5	6.8
Ethyl ether	7.5	105	17.4	6.2	35.5	7.4
Cyclohexane	8.2	109	22.8	6.8	40.4	8.0
Carbon tetrachloride	8.6	97	20.4	7.2	45.0	8.4
Benzene	9.15	89	18.0	7.4	47.7	8.6
Chloroform	9.3	81	25.4	9.7	65.8	10.1
Carbon disulfide	10.0	61	11.6	8.7	76	10.9

All values were determined at 25°C; **d** units in cal^{1/2} cm^{-3/2}.

As can be seen from the table, the approximate ranking of the solvents according to solubility parameter value is retained, but the numerical values for individual substances differ considerably.

Giddings followed the development of Hildebrand and Scott, but instead of using the van Laar assumption, eqn. (5-2), he substituted van der Waals' constants and used reduced variables,

$$a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c} \quad \text{and} \quad b = \frac{V_c}{3} \quad (5-6)$$

$$V_r = \frac{V}{V_c} \Rightarrow V = V_r V_c = 3V_r b$$

and

$$\mathbf{d} = \frac{\left(\frac{27R^2T_c^2}{64P_c}\right)^{1/2}}{3V_r b} = \frac{\left(\frac{27R^2T_c^2}{64P_c}\right)^{1/2}}{3V_r \left(\frac{RT_c}{8P_c}\right)} = \frac{(3P_c)^{1/2}}{V_r} = (3P_c)^{1/2} \mathbf{r}_r \quad (5-7)$$

Giddings then adopted Hildebrand's empirical constant of 1.25 in place of $\sqrt{3}$,

$$\mathbf{d} = 1.25P_c^{1/2} \mathbf{r}_r \quad (5-8)$$

Giddings extended this equation, strictly applicable only to liquids, to supercritical fluids by assuming the equivalence of gases and liquids at a common density. This equivalence says simply that the solubility parameter remains a simple linear function of density in the liquid, gas, and supercritical fluid regions. That is, density changes smoothly and continuously as you trace a path, shown in Figure 5-1, from the liquid region, around the critical point (in the supercritical fluid region), and into the gas region.

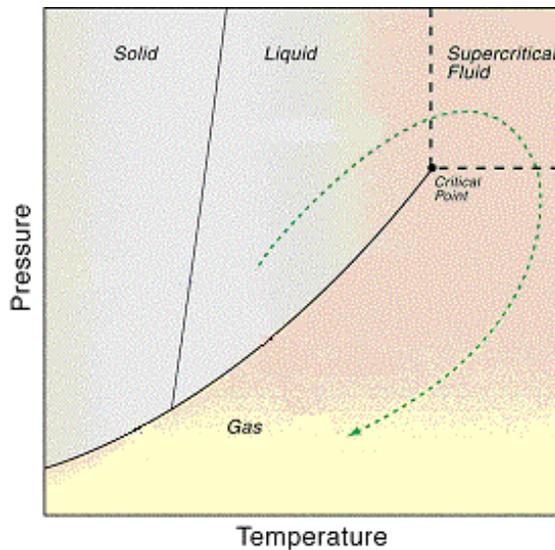


Figure 5-1. Schematic illustration of the continuous change in fluid density on going from a liquid, to a supercritical fluid, to a gas.

This corresponding states assumption leads to the following equation for describing the solubility parameter of a fluid, applicable to the liquid, supercritical, or gas state

$$\mathbf{d} = 1.25 P_c^{1/2} \left(\frac{\mathbf{r}_r}{\mathbf{r}_{r(liq)}} \right) \quad (5-9)$$

where $\mathbf{r}_{r(liq)}$ is reduced density of the liquid phase at its normal boiling point. Giddings made an analysis of some fluids “commonly used as chromatographic stationary phases” and determined an average value of $\mathbf{r}_{r,liq} = 2.66$, so that,

$$\begin{aligned} \mathbf{d} &= 1.25 P_c^{1/2} \mathbf{r}_r^{SCF} / 2.66 \\ &= 0.47 P_c^{1/2} \mathbf{r}_r^{SCF} \end{aligned} \quad (5-10)$$

Equation (5-10) has become the most widely used method to calculate the (1-component) solubility parameter for supercritical fluids.^{265,266,267,268} Unfortunately, little or no experimental verification of relations such as the one presented by Giddings exists, and hence their accuracy cannot be assessed. This type of empirical correlation, however, is expected to be less accurate for fluids that are gases at room temperature and pressure and for polar and/or hydrogen bonding fluids where specific interactions occur.

The liquid solvents evaluated by Giddings to arrive at the value $\mathbf{r}_r^{liquid} = 2.66$ are unknown. In Tables 5-2, 5-3, and 5-4, values of $\mathbf{r}_r^{liquid} = \mathbf{r}_{1 atm BP} / \mathbf{r}_c$ are given for a range of fluids, including those which are gases and liquids at room temperature and pressure

(RTP). CO₂ sublimates from a gas to solid phase at 25°C and 1 atm, and therefore boiling point data are not available, at the stated conditions, for this compound.

Table 5-2. *Reduced density of (gaseous) fluids at the normal boiling point.*

Fluid (Gas at RTP)	r_C (g/cm ³)	$r_{1 \text{ atm BP}}$ (g/cm ³)	$\frac{r_{1 \text{ atm BP}}}{r_c}$
Sulfur Dioxide	0.524	1.462	2.79
Argon	0.536	1.39	2.59
Nitrogen	0.311	0.808	2.60
Helium	0.0696	0.125	1.80
Krypton	0.9085	2.412	2.65
Hydrogen	0.031	0.0708	2.28
Oxygen	0.436	1.141	2.62
Methane	0.1625	0.4241	2.61
Propane	0.225	0.582	2.59
			<i>Average = 2.50</i>

Table 5-3. *Reduced density of (liquid) fluids at the normal boiling point.*

Fluid (Liquid at RTP)	r_C (g/cm ³)	$r_{1 \text{ atm BP}}$ (g/cm ³)	$\frac{r_{1 \text{ atm BP}}}{r_c}$
<i>n</i> -Pentane	0.232	0.609	2.63
Benzene	0.3063	0.818	2.67
Toluene	0.291	0.779	2.68
Acetone	0.2683	0.745	2.78
Acetic acid	0.351	0.911	2.60
Formic acid	0.4322	1.059	2.45
Acetonitrile	0.2373	0.708	2.98
<i>p</i> -Dioxane	0.369	0.936	2.54
Pyrrolidine	0.2856	0.793	2.78
Pyridine	0.3268	0.889	2.72
Aniline	0.340	0.868	2.55
			<i>Average = 2.67</i>

Additional errors will likely arise when empirical relations designed for pure fluids are used to calculate the solubility parameter for fluid mixtures, particularly if one or more of the components is highly polar.

Table 5-4. *Reduced density of (polar liquid) fluids at the normal boiling point.*

Fluid (Polar Liquid at RTP)	r_C (g/cm³)	$r_{1 \text{ atm BP}}$ (g/cm³)	$\frac{r_{1 \text{ atm BP}}}{r_C}$
Methanol	0.2715	0.75	2.76
Phenol	0.4104	1.16	2.83
Isopropyl alcohol	0.2735	0.713	2.61
Ammonia	0.235	0.683	2.91
			<i>Average = 2.78</i>
			<i>Overall Average of All Fluids = 2.63</i>

5.1.2 Thermodynamic Equation of State

As previously discussed, Hildebrand derived an approximation of the internal pressure, calling this approximation the cohesive energy density, by assuming a particular volume dependence of E (see eqn. (4-16)).

$$\delta^2 = \left(\frac{\Delta E}{V} \right)_T \approx \left(\frac{\partial E}{\partial V} \right)_T \quad (5-11)$$

but from the thermodynamic equation of state, eqn. (4-11)

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (5-12)$$

so that

$$\mathbf{d}^2 \approx \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (5-13)$$

Total (1-component) solubility parameters can therefore be calculated using an equation of state (EOS) of the form, $P = f(\mathbf{r}; T)$. This approach has been used in this work to calculate the total solubility parameter for pure CO₂, using the empirical EOS of Huang *et al.*²⁶⁹

$$P = \mathbf{r} R T \left[\begin{aligned} &1 + b_2 \mathbf{r}' + b_3 \mathbf{r}'^2 + b_4 \mathbf{r}'^3 + b_5 \mathbf{r}'^4 + b_6 \mathbf{r}'^5 + b_7 \mathbf{r}'^2 \exp(-c_{21} \mathbf{r}'^2) + b_8 \mathbf{r}'^4 \exp(-c_{21} \mathbf{r}'^2) \\ &+ c_{22} \mathbf{r}'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \mathbf{r}}{\mathbf{r}'} \exp[-c_{25} (\Delta \mathbf{r})^2 - c_{27} (\Delta T)^2] \\ &+ c_{24} \frac{\Delta \mathbf{r}}{\mathbf{r}'} \exp[-c_{26} (\Delta \mathbf{r})^2 - c_{27} (\Delta T)^2] \end{aligned} \right] \quad (5-14)$$

where

$$T' = T/T_c; \quad \Delta T = 1 - T'; \quad \mathbf{r}' = \mathbf{r}/\mathbf{r}_c; \quad \Delta \mathbf{r} = 1 - 1/\mathbf{r}' \quad (5-15)$$

Table 5-5. Huang equation of state constants, C_i .

i	C_i	i	C_i
1	0.376194	15	-2.79498
2	0.118836	16	5.62393
3	-3.04379	17	-2.93831
4	2.27453	18	0.988759
5	-1.23863	19	-3.04711
6	0.250442	20	2.32316
7	-0.115350	21	1.07379
8	0.675104	22	-0.599724×10^{-4}
9	0.198861	23	0.885339×10^{-4}
10	0.216124	24	0.316418×10^{-2}
11	-0.583148	25	10
12	0.119747×10^{-1}	26	50
13	0.537278×10^{-1}	27	80,000
14	0.265216×10^{-1}		

and,

$$\begin{aligned}
 b_2 &= \left(c_1 + \frac{c_2}{T'} + \frac{c_3}{T'^2} + \frac{c_4}{T'^3} + \frac{c_5}{T'^4} + \frac{c_6}{T'^5} \right) & b_6 &= \left(\frac{c_{14}}{T'} \right) \\
 b_3 &= \left(c_7 + \frac{c_8}{T'} + \frac{c_9}{T'^2} \right) & b_7 &= \left(\frac{c_{15}}{T'^3} + \frac{c_{16}}{T'^4} + \frac{c_{17}}{T'^5} \right) \\
 b_4 &= \left(c_{10} + \frac{c_{11}}{T'} \right) & b_8 &= \left(\frac{c_{18}}{T'^3} + \frac{c_{19}}{T'^4} + \frac{c_{20}}{T'^5} \right) \\
 b_5 &= \left(c_{12} + \frac{c_{13}}{T'} \right) & &
 \end{aligned} \tag{5-16}$$

These equations and the appropriate derivatives (presented in the Appendix A) have been written into a computer program and CO₂ solubility parameters have been calculated over the temperature and pressure range for which the EOS is stated to be valid ($220 \text{ K} \leq T \leq 420 \text{ K}$, and $1 \text{ atm} \leq P \leq 600 \text{ atm}$). Figure 5-2 is a plot of the resulting solubility parameters.

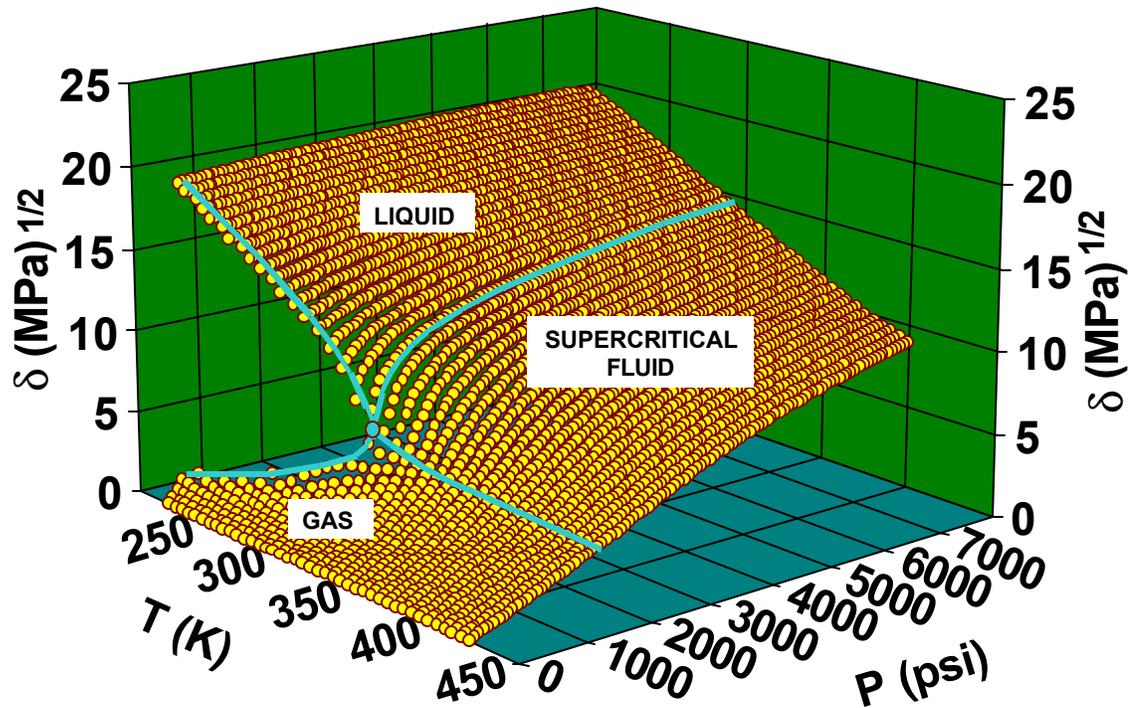


Figure 5-2. Total (1-component) solubility parameter of pure CO₂, calculated using eqns. (5-13) and (5-14).

Figure 5-3 is a contour plot comparison of CO₂ solubility parameter values calculated with Giddings approximation, eqn. (5-10), versus CO₂ solubility parameter values calculated from the CO₂ equation of state eqn. (5-14) and eqn. (5-13). Values on the contour plot lines represent values of $\left(\frac{\mathbf{d} \text{ from Giddings}}{\mathbf{d} \text{ from EOS}} \right)$. In the supercritical fluid region (identified by the dashed lines), the solubility parameters obtained from Giddings' approximation are 10 to 20 % greater than those calculated from the EOS. Similarly, in the low-temperature gas region, Giddings' equation underestimates the true solubility parameter by about 15%.

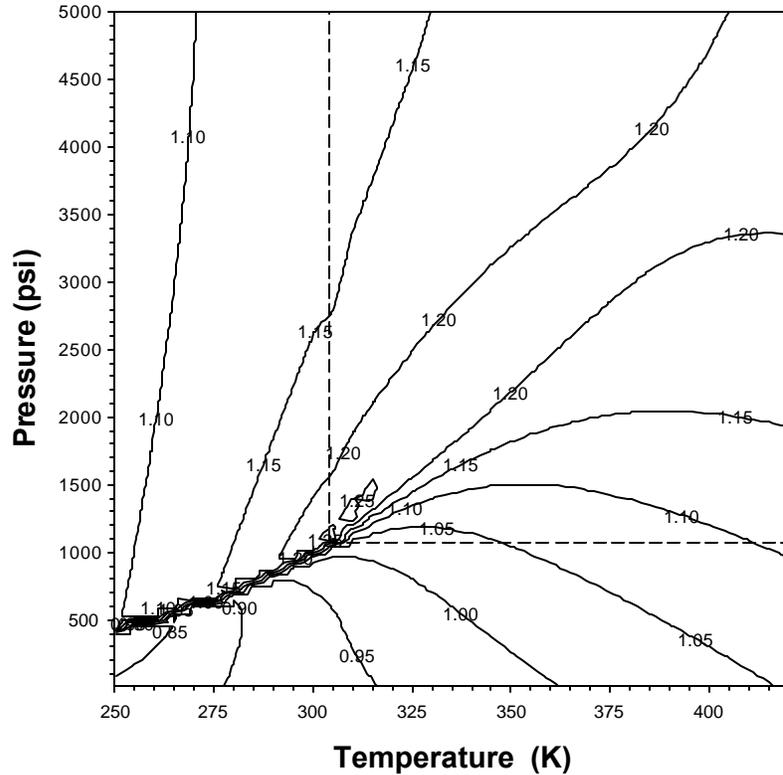


Figure 5-3. Contour plot comparison of Giddings solubility parameter approximation (eqn. 5-10) versus equation of state solubility parameter calculation (eqn. 5-13) for CO₂.

5.2 3-Component (Hansen) Solubility Parameters – Pure CO₂

While the thermodynamic equation of state method gives an accurate representation of the total (1-component) solubility parameter for CO₂ over a range of temperatures and pressures, we have seen that the (Hildebrand) 1-component model does not accurately predict the solubility behavior of a real fluid. We need to be able to express the solubility behavior of CO₂ in terms of 3-component (Hansen) Solubility Parameters (d_d , d_p , d_h). Extending the HSP methodology to supercritical fluids would significantly enhance the understanding of their solvent properties; however, no such studies appear to have been

done. For strictly nonpolar gases (gases with no permanent dipole or higher moments, such as argon), the values of \mathbf{d}_p and \mathbf{d}_h will be zero, and we could equate \mathbf{d}_d with the total solubility parameter, \mathbf{d}_{Total} . However, CO₂, which possesses a large quadrupole moment and can display Lewis acid-base characteristics, has non-zero values for both \mathbf{d}_p and \mathbf{d}_h .²⁷⁰

Determination of HSP's for (ambient condition) gases is usually based on room temperature solubility of the gas in different liquids of known \mathbf{d}_d , \mathbf{d}_p , and \mathbf{d}_h . Those liquids that show the highest solubility for the gas are assumed to have HSP's closer to those of the gas than those liquids which have lower solubilities for CO₂. In the following section, published data of CO₂ gas solubility (at 25 °C and a CO₂ partial pressure of 1 atmosphere) in a large number of liquid solvents is evaluated. From this data, a set of HSP values at a particular temperature and pressure can be determined. HSP values at other pressures and temperatures will be based on this set of HSP values, using pressure and temperature derivative functions, which will be derived subsequently.

5.2.1 Optimized CO₂ HSP Values from Published Solubility Data

Published CO₂ solubility data at 25°C and 1 atmosphere partial pressure of CO₂ in various liquid solvents are collected in Appendix B. CO₂ HSP values were calculated based on a simple weighted average,

$$\mathbf{d}_d^{CO_2} = \frac{\sum_{i=1}^n x_i \mathbf{d}_{d_i}}{\sum x_i}, \quad (5-17)$$

$$\mathbf{d}_p^{\text{CO}_2} = \frac{\sum_{i=1}^n x_i \mathbf{d}_{p_i}}{\sum x_i}, \quad (5-18)$$

$$\mathbf{d}_h^{\text{CO}_2} = \frac{\sum_{i=1}^n x_i \mathbf{d}_{h_i}}{\sum x_i}. \quad (5-19)$$

using the entire data set of 101 solvents, hereafter called data set #1, as well as the subset of data where the measured CO₂ solubility was greater than the ideal solubility at 25 °C and 1 atmosphere, $x_{\text{CO}_2}^{\text{ideal}} = 0.0229$ (CO₂ ideal solubility development is included in the Appendix B). This subset of data, hereafter called data set #2, is comprised of 10 solvents.

These analyses resulted in the following HSP values for CO₂ at 25°C

$$\begin{aligned} \text{Data set \#1:} \quad & \mathbf{d}_d = 16.4 \text{ MPa}^{1/2} \\ & \mathbf{d}_p = 5.5 \text{ MPa}^{1/2} \\ & \mathbf{d}_h = 5.8 \text{ MPa}^{1/2} \end{aligned}$$

$$\begin{aligned} \text{Data set \#2:} \quad & \mathbf{d}_d = 15.6 \text{ MPa}^{1/2}, \\ & \mathbf{d}_p = 5.2 \text{ MPa}^{1/2} \\ & \mathbf{d}_h = 5.8 \text{ MPa}^{1/2} \end{aligned}$$

The experimental CO₂ solubilities and HSP values for the solvents included in data set #2 are shown in Table 5-6, while the values for data set #1 are given in Appendix B.

Table 5-6. CO₂ solubility, and HSP values for the solvents included in Data Set #2.

Solvent	$x_{CO_2}^{Exptl}$	d_d (MPa) ^{1/2}	d_p (MPa) ^{1/2}	d_h (MPa) ^{1/2}
Tributyl phosphate, (C ₁₂ H ₂₇ O ₄ P)	0.03550	16.3	6.3	4.3
Amyl acetate, (C ₇ H ₁₄ O ₂)	0.02800	15.8	3.3	6.1
Butyl oleate, (C ₂₂ H ₄₂ O ₂)	0.02790	14.7	3.4	3.4
Tetrahydrofuran (C ₄ H ₈ O)	0.02700	16.8	5.7	8.0
Methyl oleate (C ₁₉ H ₃₆ O ₂)	0.02690	14.5	3.9	3.7
Isobutyl acetate (C ₆ H ₁₂ O ₂)	0.02500	15.1	3.7	6.3
Methyl ethyl ketone (C ₄ H ₈ O)	0.02444	16.0	9.0	5.1
Propyl acetate (C ₅ H ₁₀ O ₂)	0.02429	15.3	4.3	7.6
Ethyl acetate (C ₄ H ₈ O ₂)	0.02300	15.8	5.3	7.2
Methyl acetate (C ₃ H ₆ O ₂)	0.02253	15.5	7.2	7.6

A second approach, known as the solubility sphere,^{271,272,273} was also used to evaluate the published solubility data. The solubility sphere approach is essentially a trial and error method, whereby all the “good” solvents are included within the sphere and all the “bad” ones are excluded, and the radius of this sphere is known as the interaction radius, or R_o . The criterion of “good” versus “bad” can vary, based on the interaction being studied. This can include percentage polymer swelling, dissolution, breakthrough times, permeation coefficients higher than a given value, long-time suspension of a pigment, etc. Based upon the criteria selected, spheres are then produced for three plots, d_d vs. d_p , d_d vs. d_h , and d_p vs. d_h , and the sphere radius R_o is adjusted until an identical radius for each of the three plots can be found which incorporates the “good” interactions

and excludes the “bad” interactions. Using this approach, other solvents or compounds of interest can be screened to determine if they are within the interaction radius, R_o , and therefore appropriate (“good”), or inappropriate (“bad”) for the application they are being considered. This type of evaluation or predictability is aided by an equation developed by Skaarup for determining the distance, R_a , between two materials based on their respective HSP values,²⁷⁴

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (5-20)$$

where \mathbf{d}_{d2} , \mathbf{d}_{p2} , and \mathbf{d}_{h2} are associated with a given solvent and \mathbf{d}_{d1} , \mathbf{d}_{p1} , and \mathbf{d}_{h1} with the center of the solubility sphere. This equation was developed from plots of experimental data where the constant “4” was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents. Figure 5-4 is a schematic representation of this approach.

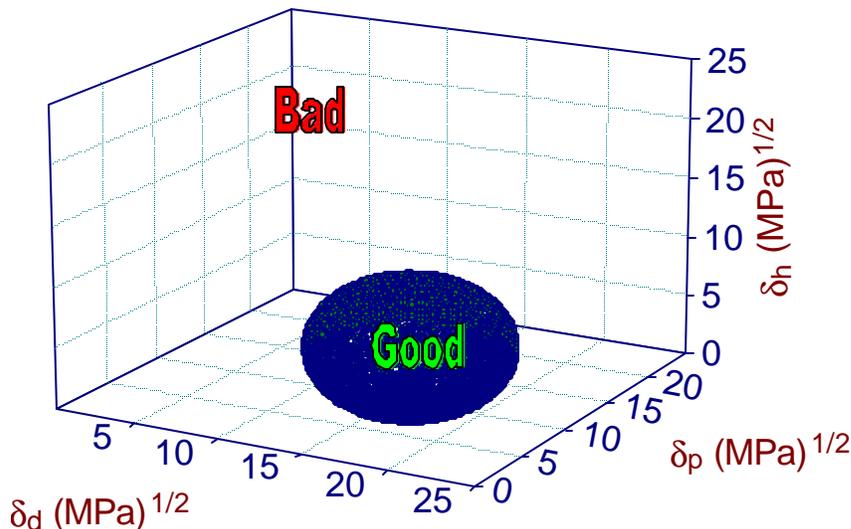


Figure 5-4. Interaction radius, where R_o incorporates all “good” solvents and excludes all “bad” solvents.

For this evaluation, “good” was defined as solvents with the CO₂ solubility greater than ideal and “bad” were those solvents where the CO₂ solubility is less than ideal. It is clear that for cases where CO₂ solubility is greater than ideal (where the (attractive) CO₂/solvent interactions are greater than solvent/solvent interactions) R_a should be less than R_o . A convenient index for relative “goodness” of a solvent is the ratio R_a/R_o , which has been called the relative energy difference (RED) number

$$RED = \frac{R_a}{R_o} \quad (5-21)$$

For an individual solvent, an RED less than 1 indicates high affinity, while an RED value close to 1 is a boundary condition (between “good” and bad”). Progressively higher RED numbers indicate progressively lower affinities.²⁷⁵ Computing R_a from eqn. (5-20) and the RED from eqn. (5-21) allows for easy scanning of large data sets, such as the 101 solvents in data set #1 used for the HSP optimization. The solubility spheres optimized for data set #1 and data set #2 with the two HSP center points are shown in Figures 5-5a, b, and c. As can be seen from these spheres, an interaction radius $R_o = 4.0$ for data set #2 incorporates the “good” solvents as defined, whereas for data set #1, an interaction radius $R_o = 4.7$ is necessary to incorporate the “good” solvents. In addition, the solubility sphere for data set #1 results in the inclusion of 7 “bad” solvents (2-Methylcyclohexanone, cyclohexanone, oleic acid, dichloromethane, trichloromethane, propylene bromide, and 1,2-dibromoethane) whereas the sphere generated for data set #2 results in the inclusion of only 1 “bad” solvent (oleic acid), for which the high CO₂ solubility may be a result of a chemical reaction with CO₂, similar to the type of reaction described in Section 2.2. In terms of the Sphere technique, occurrences of “good”

solvents falling outside of the sphere radius, and “bad” solvents falling inside the sphere radius are known as errors and can be viewed as an indication of the “goodness” of the fit. The Excel[®] spreadsheet of RED calculations is given in Appendix B.

Literature R_o values for the polymers evaluated in Chapter 6 are reportedly based on the dissolution behavior of the respective polymers in a range of liquid solvents. These R_o values will be identified in this work by R_o^{liq} .

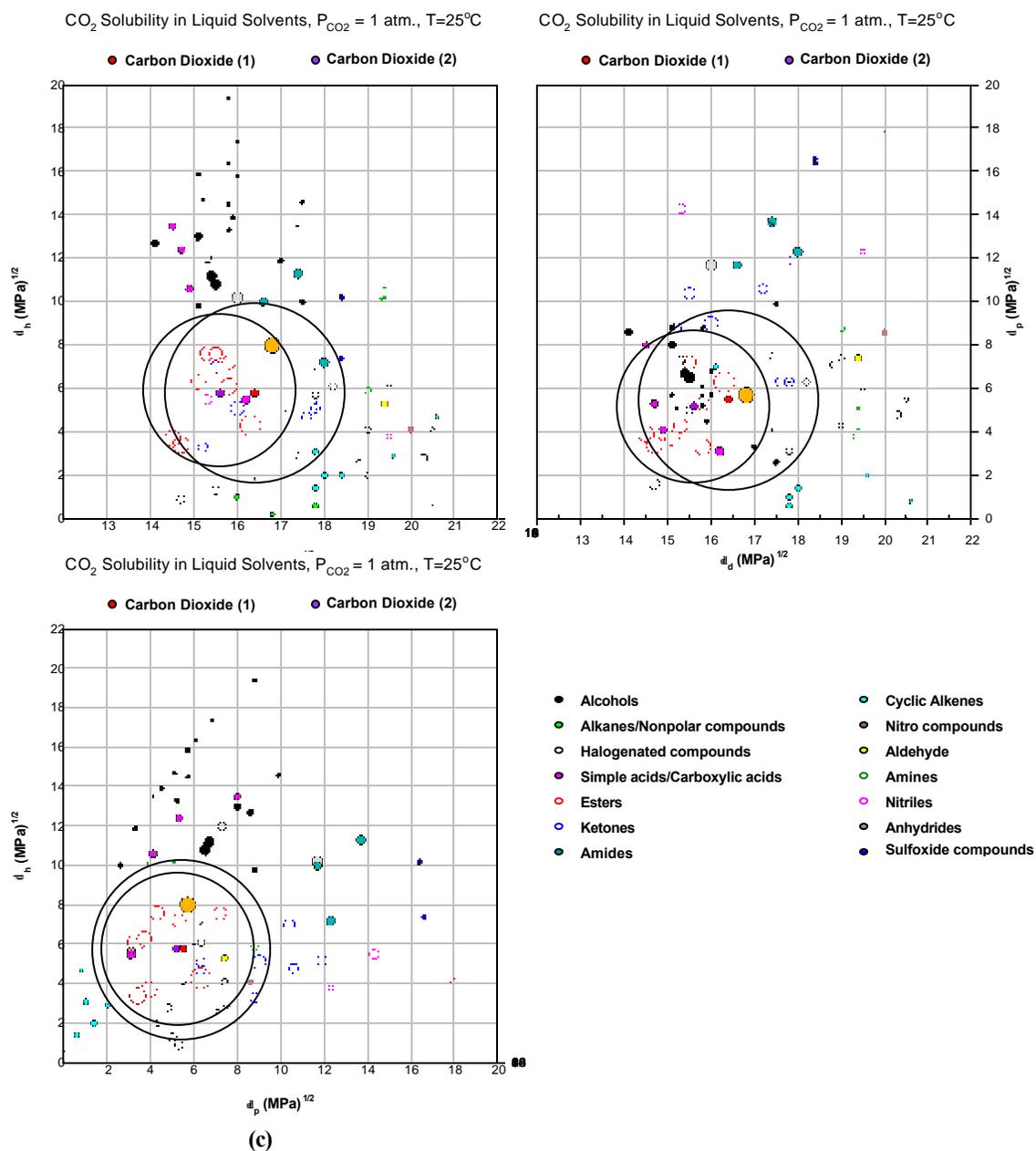


Figure 5-5. Solubility sphere plots of CO₂ in organic solvents. (a) d_h versus d_h , (b) d_p versus d_h , and (c) d_h versus d_p .

Using the optimization routines to identify CO₂ HSP points and then the solubility sphere as a graphical representation of “good” and “bad” solvents, it has been determined that the set of HSP’s optimized from data set #2,

$$\begin{array}{l} \mathbf{d}_d = 15.6 \text{ MPa}^{1/2} \\ \mathbf{d}_p = 5.2 \text{ MPa}^{1/2} \\ \mathbf{d}_h = 5.8 \text{ MPa}^{1/2} \end{array} \quad (5-22)$$

best characterize CO₂ at $T = 25^\circ\text{C}$. The rationale of this choice is further supported by problems noted by Hansen,²⁷⁶ who notes the approach of using all solvents to establish the center of a solubility sphere results in this sphere boundary (and center) being determined by the poor solvents or nonsolvents, rather than the best solvents in the middle.

It is next necessary to establish a pressure corresponding to this $T = 25^\circ\text{C}$ set of HSP values in order to use them to determine HSP’s at arbitrary conditions of T and P. From eqn. (4-27), the determined HSP values for CO₂ result in a total CO₂ solubility parameter of $17.4 \text{ MPa}^{1/2}$,

$$\begin{aligned} \mathbf{d}_T^2 &= \mathbf{d}_d^2 + \mathbf{d}_p^2 + \mathbf{d}_h^2 \\ &= (15.6)^2 + (5.2)^2 + (5.8)^2 = 304.04 \text{ MPa} \\ &= 17.4 \text{ MPa}^{1/2} \end{aligned} \quad (5-23)$$

The PVT equation of state, which calculates total CO₂ solubility parameters (Section 5.1.2) was used to determine the combination of pressure and molar volume

corresponding to $T = 25^\circ\text{C}$ and $\mathbf{d}_T = \left(\frac{\partial P}{\partial T} \right)_V - P = 17.4 \text{ MPa}^{1/2}$, which gave

$$\begin{array}{l}
 P = 13,300 \text{ psi} \quad (905 \text{ atm}) \\
 V^{CO_2} = 39.13 \text{ cm}^3/\text{mole}
 \end{array}
 \tag{5-24}$$

5.3 Temperature and Pressure Effects

Both temperature and pressure will influence total solubility parameters. However, other than Giddings' extension of the 1-component (Hildebrand) solubility parameter model to supercritical fluids (Section 5.1.1), there appears to be no published reports on methods to calculate total solubility parameters as a function of pressure, and only limited reports on the calculation of solubility parameters as a function of temperature.^{277,278,279} Generally, an increase in pressure at constant temperature will increase the total solubility parameter through an increase in the solvent density. Similarly, an increase in temperature at constant pressure will decrease the total solubility parameter. Both of these trends can be seen in Figure 5-2, where the total CO₂ solubility parameter, calculated using eqns. (5-13) and (5-14), is seen to be similar in appearance to the PVT surface, shown in Figure 2-3, illustrating the predominant dependence of solubility parameter on density.

The temperature and pressure dependence of individual HSP's, as a function of temperature and pressure, has apparently not been evaluated for any liquid, gas or supercritical fluid. An approximate approach for this calculation is outlined in the following Sections, where the temperature derivatives, originally derived by Hansen and Beerbower,²⁸⁰ are verified. Pressure derivatives, not found in any literature search, are

derived in a manner parallel to the temperature derivatives. In addition, integrals forms are developed

5.3.1 Temperature and Pressure Effects on HSP's : δ_d

From Section 4.2.3, the dispersion solubility parameter, d_d , was defined as

$$\delta_d^2 = \frac{E_d}{V} \quad (5-25)$$

where E_d is the dispersion, or nonpolar, contribution to the total cohesive energy, E . Hildebrand, in his 1950 work, discusses the effect of temperature on solubility parameters by recalling the expression for the dependence of E on the volume²⁸¹

$$E = -\frac{k}{V^n} \quad (5-26)$$

where k is a constant dependent upon the nature of the particular liquid and n is about 1.5 for normal liquids. Substituting eqn. (5-26) into Hansen's definition for the dispersion solubility parameter, eqn. (5-25),

$$\delta_d^2 = -\frac{k}{V^{n+1}} \quad (5-27)$$

so that

$$\delta_d = -\frac{k^{1/2}}{V^{(n+1)/2}} \quad (5-28)$$

The change in dU produced by a change in volume can be calculated by taking the partial derivative of eqn. (5-28) with respect to volume at constant temperature and pressure,

$$\begin{aligned} \left(\frac{\partial \delta_d}{\partial V} \right)_{T,P} &= k^{1/2} \left(\frac{n+1}{2} \right) \left[V^{-\frac{(n+1)}{2}} \right] [V^{-1}] \\ &= \frac{k^{1/2}}{V^{\frac{(n+1)}{2}}} \left(\frac{n+1}{2} \right) [V^{-1}] \\ &= -\delta_d \left(\frac{n+1}{2} \right) \left(\frac{1}{V} \right) \end{aligned} \quad (5-29)$$

and

$$\frac{\partial \delta_d}{\delta_d} = - \left(\frac{n+1}{2} \right) \frac{\partial V}{V} = - \left(\frac{1.5+1}{2} \right) \frac{\partial V}{V} = -1.25 \frac{\partial V}{V} \quad (5-30)$$

Equation (5-30) can now be differentiated for either a change in temperature or pressure, or integrated. The partial derivatives will be discussed first, followed by the integration of eqn. (5-30).

The partial derivative of dU with respect to temperature at constant pressure is

$$\left(\frac{1}{\delta_d} \right) \left(\frac{\partial \delta_d}{\partial T} \right)_p = -1.25 \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_p \quad (5-31)$$

The isobaric coefficient of thermal expansion, α is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (5-32)$$

so that by combining eqn. (5-31) and eqn. (5-32),

$$\boxed{\left(\frac{\partial \mathbf{d}_d}{\partial T}\right)_P = -1.25 \mathbf{d}_d \mathbf{a}} \quad (5-33)$$

The same type of derivation can be performed to generate an expression for the change in \mathbf{d}_d with respect to pressure at constant temperature:

$$\left(\frac{1}{\delta_d}\right)\left(\frac{\partial \delta_d}{\partial P}\right)_T = -1.25\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \quad (5-34)$$

The isothermal compressibility, \mathbf{b} is defined by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad (5-35)$$

so that by substituting eqn. (5-35) into eqn. (5-34),

$$\boxed{\left(\frac{\partial \mathbf{d}_d}{\partial P}\right)_T = 1.25 \mathbf{d}_d \mathbf{b}} \quad (5-36)$$

The integrated form of eqn. (5-30) is obtained by integrating between the limits of an initial reference state \mathbf{d}_{dref} , V_{ref} (at P_{ref} and T_{ref}), to some new \mathbf{d}_d , V (at P and T),

$$\int_{\mathbf{d}_{dref}}^{\mathbf{d}_d} \frac{\partial \mathbf{d}_d}{\mathbf{d}_d} = -1.25 \int_{V_{ref}}^V \frac{\partial V}{V} \quad (5-37)$$

and

$$\ln \mathbf{d}_{dref} - \ln \mathbf{d}_d = -1.25(\ln V_{ref} - \ln V) \quad (5-38)$$

$$\ln \frac{\mathbf{d}_{dref}}{\mathbf{d}_d} = -1.25 \ln \frac{V_{ref}}{V} \quad (5-39)$$

$$\boxed{\frac{\mathbf{d}_{dref}}{\mathbf{d}_d} = \left(\frac{V_{ref}}{V} \right)^{-1.25}} \quad (5-40)$$

5.3.2 Temperature and Pressure Effects on HSP's: δ_p

From Section 4.2.3, the polar solubility parameter, \mathbf{d}_p , was defined as;

$$\delta_p^2 = \frac{E_p}{V} \quad (5-41)$$

where E_p is the polar contribution to the total cohesive energy. The first values of \mathbf{d}_p were assigned by Hansen and Skaarup using the Böttcher equation, as described in Section 5.4.2.2.1,

$$\delta_p^2 = \frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2 \quad \left[\frac{cal}{cm^3} \right] \quad (5-42)$$

A simplified equation was later developed by Hansen and Beerbower,²⁸²

$$\delta_p = \frac{37.4\mu}{V^{1/2}} \quad [MPa^{1/2}] \quad (5-43)$$

where μ is the dipole moment. This equation is utilized for determining the change in \mathbf{d}_p with respect to either temperature at constant pressure or with respect to pressure at constant

temperature. First, the partial derivative of eqn. (5-43) with respect to volume at constant temperature and pressure is determined,

$$\begin{aligned} \left(\frac{\partial \delta_p}{\partial V} \right)_{T,P} &= - \left(\frac{1}{2} \right) V^{-3/2} (37.4\mu) \\ &= - \frac{1}{2V} \left(\frac{37.4\mu}{V^{1/2}} \right) = - \frac{\delta_p}{2V} \end{aligned} \quad (5-44)$$

and

$$\frac{\partial \delta_p}{\delta_p} = - \frac{\partial V}{2V} \quad (5-45)$$

Equation (5-45) can now be differentiated for either a change in temperature or pressure, or integrated. Differentiating \mathbf{d}_p with respect to temperature at constant pressure,

$$\left(\frac{1}{\delta_p} \right) \left(\frac{\partial \delta_p}{\partial T} \right)_P = - \left(\frac{1}{2} \right) \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (5-46)$$

Substituting in the isobaric coefficient for thermal expansion, \mathbf{a}

$$\boxed{\left(\frac{\partial \mathbf{d}_p}{\partial T} \right)_P = -\mathbf{d}_p \left(\frac{\mathbf{a}}{2} \right)} \quad (5-47)$$

A similar derivation can be performed to calculate the change in \mathbf{d}_p due to pressure at constant temperature,

$$\left(\frac{1}{\delta_p} \right) \left(\frac{\partial \delta_p}{\partial P} \right)_T = - \left(\frac{1}{2} \right) \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (5-48)$$

and substituting for the isothermal compressibility, \mathbf{b}

$$\boxed{\left(\frac{\partial \mathbf{d}_p}{\partial P}\right)_T = \mathbf{d}_p \left(\frac{\mathbf{b}}{2}\right)} \quad (5-49)$$

The integrated form of eqn. (5-45) is

$$\int_{\mathbf{d}_{pref}}^{\mathbf{d}_p} \frac{\partial \mathbf{d}_p}{\mathbf{d}_p} = -0.5 \int_{V_{ref}}^V \frac{\partial V}{V} \quad (5-50)$$

so that by integrating, we have

$$\ln \mathbf{d}_{pref} - \ln \mathbf{d}_p = -0.5(\ln V_{ref} - \ln V) \quad (5-51)$$

$$\ln \frac{\mathbf{d}_{pref}}{\mathbf{d}_p} = -0.5 \ln \frac{V_{ref}}{V} \quad (5-52)$$

$$\boxed{\frac{\mathbf{d}_{pref}}{\mathbf{d}_p} = \left(\frac{V_{ref}}{V}\right)^{-0.5}} \quad (5-53)$$

5.3.3 Temperature and Pressure Effects on HSP's: δ_h

In Hansen's early work, the hydrogen bonding parameter was almost always found by subtracting the polar and dispersion energies of vaporization from the total energy of vaporization. This is still widely used where the required data are available and reliable. Hansen,²⁸³ however, while noting that "there is no rigorous way of arriving at values of the temperature dependence of the hydrogen bonding solubility parameter", developed an empirical approach for the determination of the temperature dependence of \mathbf{d}_h which

involves experimental heats of vaporization data for hydrogen-bonded substances, which, in turn, are taken from Bondi.²⁸⁴

From Section 4.2.3, the hydrogen bonding solubility parameter, \mathbf{d}_h , was defined as

$$\delta_h^2 = \frac{E_h}{V} \quad (5-54)$$

so that

$$E_h = V\delta_h^2 \quad (5-55)$$

where E_h is the hydrogen bonding contribution to the total cohesive energy. Differentiating eqn. (5-55) with respect to temperature at constant pressure,

$$\begin{aligned} \left(\frac{\partial E_h}{\partial T} \right)_P &= V(2\delta_h) \left(\frac{\partial \delta_h}{\partial T} \right)_P + \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P \\ 2V\delta_h \left(\frac{\partial \delta_h}{\partial T} \right)_P &= \left(\frac{\partial E_h}{\partial T} \right)_P - \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P \end{aligned} \quad (5-56)$$

$$\left(\frac{\partial \delta_h}{\partial T} \right)_P = \frac{\left(\frac{\partial E_h}{\partial T} \right)_P - \delta_h^2 \left(\frac{\partial V}{\partial T} \right)_P}{2V\delta_h}$$

Simplifying, rearranging terms and substituting in the isobaric coefficient of thermal expansion, \mathbf{b}

$$\left(\frac{\partial \delta_h}{\partial T}\right)_P = \left(\frac{1}{2V\delta_h}\right)\left(\frac{\partial E_h}{\partial T}\right)_P - \frac{\delta_h}{2}\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial \delta_h}{\partial T}\right)_P = \left(\frac{\delta_h}{2V\delta_h^2}\right)\left(\frac{\partial E_h}{\partial T}\right)_P - \delta_h\left(\frac{\alpha}{2}\right) \quad (5-57)$$

$$\left(\frac{\partial \delta_h}{\partial T}\right)_P = \delta_h \left[\frac{\left(\frac{\partial E_h}{\partial T}\right)_P}{2E_h} - \frac{\alpha}{2} \right]$$

Bondi,²⁸⁵ through exploratory calculations, has shown that the difference between the heat of vaporization of a hydroxylic compound (a compound displaying strong hydrogen bonding) and that of its hydrocarbon (or other nonpolar) homomorph constitutes a good measure of hydrogen bond strength. This work also discusses the decrease in the heat of formation of the hydrogen bond with increasing temperature. Reference curves of $\left(\frac{dE_h}{dT}\right)$ were constructed²⁸⁶ for various functional groups and are shown in Table 5.7, along with experimentally derived values of E_h .²⁸⁷

Table 5-7. Experimentally determined values of E_h and $\left(\frac{dE_h}{dT}\right)$.

Functional Group	Hydrogen-bond parameter, E_h (cal/mole)	$\frac{dE_h}{dT}$ (cal/mole · K)
—OH (aliphatic)	4650 ± 400	-10
—NH ₂ (aliphatic)	1350 ± 200	-4.5
—CN (aliphatic)	500 ± 200	-7.0
—COOH (aliphatic)	2750 ± 250	-2.9

Averaging the rate of change of the hydrogen bond heat of vaporization with temperature (dE_h/dT), and dividing by the average excess heats of vaporization (heat of vaporization of the hydrogen bonding compound minus the heat of vaporization of its nonpolar homomorph) results in the following form of eqn. (5-57):

$$\begin{aligned} \left(\frac{\partial \mathbf{d}_h}{\partial T} \right)_P &= -\mathbf{d}_h \left(\frac{2.64 \times 10^{-3}}{2} + \frac{\mathbf{a}}{2} \right) \\ &= -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{\mathbf{a}}{2} \right) \end{aligned} \quad (5-58)$$

The change in the \mathbf{d}_h with respect to pressure at constant temperature is obtained by utilizing the relationship

$$\frac{\partial \mathbf{d}_h}{\partial P} = \frac{\partial \mathbf{d}_h}{\partial T} \cdot \frac{\partial T}{\partial P} \quad (5-59)$$

and, from eqns. (5-32) and (5-35),

$$\frac{\partial T}{\partial P} = -\frac{\mathbf{b}}{\mathbf{a}} \quad (5-60)$$

so that

$$\left(\frac{\partial \mathbf{d}_h}{\partial P} \right)_T = -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{\mathbf{a}}{2} \right) \cdot \left(-\frac{\mathbf{b}}{\mathbf{a}} \right) \quad (5-61)$$

and

$$\left(\frac{\partial \mathbf{d}_h}{\partial P} \right)_T = \mathbf{d}_h \left(\frac{1.32 \times 10^{-3} \mathbf{b}}{\mathbf{a}} + \frac{\mathbf{b}}{2} \right) \quad (5-62)$$

Equation (5-58) can be rearranged to a form that can be easily integrated,

$$\begin{aligned} \left(\frac{\partial \mathbf{d}_h}{\partial T} \right)_P &= -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{\mathbf{a}}{2} \right) \\ &= -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{dV}{2VdT} \right) \\ \frac{d\mathbf{d}_h}{\mathbf{d}_h} &= - \left(1.32 \times 10^{-3} dT + \frac{dV}{2V} \right) \end{aligned} \quad (5-63)$$

Upon integration of eqn. (5-63) from $(\mathbf{d}_{href}, T_{ref}$ and $V_{ref})$ to $(\mathbf{d}, T$ and $V)$,

$$\int_{\mathbf{d}_{href}}^{\mathbf{d}_h} \frac{d\mathbf{d}_h}{\mathbf{d}_h} = - \left(1.32 \times 10^{-3} \int_{T_{ref}}^T dT + .5 \int_{V_{ref}}^V \frac{dV}{V} \right) \quad (5-64)$$

$$\ln \frac{\mathbf{d}_{href}}{\mathbf{d}_h} = -1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \quad (5-65)$$

$$\boxed{\frac{\mathbf{d}_{href}}{\mathbf{d}_h} = \exp \left[-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right]} \quad (5-66)$$

The total solubility parameter, incremented for small changes in temperature and pressure, can be calculated from eqns. (5-33), (5-36), (5-47), (5-49), (5-58) and (5-62) using

$$\mathbf{d}^2 = \left[\mathbf{d}_d + \left(\frac{\partial \mathbf{d}_d}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_d}{\partial P} \right)_T \Delta P \right]^2 + \left[\mathbf{d}_p + \left(\frac{\partial \mathbf{d}_p}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_p}{\partial P} \right)_T \Delta P \right]^2 + \left[\mathbf{d}_h + \left(\frac{\partial \mathbf{d}_h}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_h}{\partial P} \right)_T \Delta P \right]^2$$

(5-67)

or from eqns. (5-40), (5-53) and (5-66) using

$$\mathbf{d}^2 = \left[\frac{\mathbf{d}_{dref}}{\left(\frac{V_{ref}}{V} \right)^{-1.25}} \right]^2 + \left[\frac{\mathbf{d}_{pref}}{\left(\frac{V_{ref}}{V} \right)^{-0.5}} \right]^2 + \left[\frac{\mathbf{d}_{href}}{\exp \left(-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right)} \right]^2$$

(5-68)

The derivative forms are summarized in Table 5.8 and the integrated forms in Table 5.9.

Table 5-8. Equations (derivative form) for the temperature and pressure effects on HSP's.

	Temperature increment	Pressure increment
\mathbf{d}_d	$\left(\frac{\partial \mathbf{d}_d}{\partial T} \right)_P = -1.25 \mathbf{d}_d \mathbf{a}$	$\left(\frac{\partial \mathbf{d}_d}{\partial P} \right)_T = 1.25 \mathbf{d}_d \mathbf{b}$
\mathbf{d}_p	$\left(\frac{\partial \mathbf{d}_p}{\partial T} \right)_P = -\mathbf{d}_p \left(\frac{\mathbf{a}}{2} \right)$	$\left(\frac{\partial \mathbf{d}_p}{\partial P} \right)_T = \mathbf{d}_p \left(\frac{\mathbf{b}}{2} \right)$
\mathbf{d}_h	$\left(\frac{\partial \mathbf{d}_h}{\partial T} \right)_P = -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{\mathbf{a}}{2} \right)$	$\left(\frac{\partial \mathbf{d}_h}{\partial P} \right)_T = \mathbf{d}_h \left(\frac{1.32 \times 10^{-3} \mathbf{b}}{\mathbf{a}} + \frac{\mathbf{b}}{2} \right)$

Table 5-9. Equations (integrated form) for the temperature and pressure effects on HSP's.

d_d	$\frac{\delta_{dref}}{\delta_d} = \left(\frac{V_{ref}}{V} \right)^{-1.25}$
d_p	$\frac{\delta_{pref}}{\delta_p} = \left(\frac{V_{ref}}{V} \right)^{-0.5}$
d_h	$\frac{d_{href}}{d_h} = \exp \left[-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{.5} \right]$

Appendix C includes results of the equations summarized in Table 5-9 for CO₂.

5.4 Cosolvent Solubility Parameters

5.4.1 1-Parameter Models (Hildebrand)

As established for CO₂, total (Hildebrand) solubility parameters can be determined for nonpolar and weakly polar solvents using an appropriate equation of state and equating the calculated internal pressure to the cohesive energy density (see eqn. (4-17)). However, EOS data are often unavailable for compounds used as cosolvents or is available only over a very limited range of T and/or P. In these cases, the total solubility parameter can be found from the isobaric coefficient of thermal expansion, \mathbf{a} , and the isothermal compressibility, \mathbf{b} , since it can be shown that

$$\boxed{\left(\frac{\partial E}{\partial V} \right)_T = T \cdot \left(\frac{\mathbf{a}}{\mathbf{b}} \right)_V - P.} \quad (5-69)$$

where, as before,

$$\mathbf{a} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \mathbf{b} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (5-70)$$

An alternative method for calculating the total (Hildebrand) solubility parameter is based on equating the cohesive energy density to the heat of vaporization.

The molar cohesive energy, E , can be divided into two parts:²⁸⁸ (1) the molar vaporization energy, required to vaporize a mole of the liquid to its saturated vapor (at constant volume), ${}_l\Delta_g E$, and (2) the energy, required to expand the saturated vapor to infinite volume at constant temperature; that is, the energy necessary to completely separate the molecules, ${}_g\Delta_\infty E$, so that

$$E = {}_l\Delta_g E + {}_g\Delta_\infty E \quad (5-71)$$

The molar vaporization energy is related to the molar vaporization enthalpy, ${}_l\Delta_g H$, by²⁸⁹

$${}_l\Delta_g E = {}_l\Delta_g H - PV \quad (5-72)$$

Assuming ideal behavior for the vapor phase, so that $PV = RT$,

$${}_l\Delta_g E = {}_l\Delta_g H - RT \quad (5-73)$$

The isothermal energy of expansion is related to the isothermal heat of expansion, i.e., the enthalpy change on isothermally expanding 1 mole of saturated vapor to zero pressure, ${}_g\Delta_\infty H$, by

$${}_g\Delta_\infty E = {}_g\Delta_\infty H + p_s V \quad (5-74)$$

where p_s is the saturation vapor pressure at temperature T and V is the molar volume of the liquid. The molar cohesive energy can therefore be written as

$$E = {}_l\Delta_g H + {}_g\Delta_\infty H - RT + p_s V \quad (5-75)$$

At pressures below 1 atmosphere ${}_g\Delta_\infty H$ and $p_s V$ are usually negligible,²⁹⁰ so that

$$E = {}_l\Delta_g H - RT \quad (5-76)$$

and the total solubility parameter, $(E/V)^{1/2}$, can therefore be written as

$$\delta = \left(\frac{\Delta H - RT}{V} \right)^{1/2} \quad (5-77)$$

where ${}_l\Delta_g H$ is identified with the molar heat of vaporization, ΔH .

From eqn. (5-77), it can be seen that total solubility parameter values of liquids can be calculated from the molar volume and molar heat of vaporization, determined at temperature T . It is usually possible to find a reliable value for the molar volume, but discrepancies frequently exist between reported values for ΔH , depending on whether the reported value is obtained experimentally, from calorimetric measurements, or by an estimation method. Some of these estimation methods will now be discussed.

The heat of vaporization is the difference between the enthalpy of the saturated vapor and that of the saturated liquid at the same temperature. Most estimation methods for ΔH are based on the Clausius-Clapeyron equation,²⁹¹ where it can be shown that ΔH is related to the slope of the saturated vapor-pressure curve by

$$\frac{dp_s}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{(RT^2/p_s)\Delta Z} \quad (5-78)$$

Here, p_s is the saturation vapor pressure, and ΔV and ΔZ are the differences in the molar volume and compressibility factor of saturated vapor and saturated liquid, respectively. Other empirical formulas relate ΔH at T to the heat of vaporization at the normal boiling point, T_b . Several variations of this type exist, including those due to Riedel,²⁹²

$$\Delta H_b \left(\frac{J}{mol} \right) = 1.093 RT_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right] \quad (5-79)$$

Chen,²⁹³

$$\Delta H_b \left(\frac{J}{mol} \right) = RT_c T_{br} \frac{3.978 T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}} \quad (5-80)$$

Vetere,²⁹⁴

$$\Delta H_b \left(\frac{J}{mol} \right) = RT_c T_{br} \frac{0.4343 \ln P_c - 0.69431 + 0.89584 T_{br}}{0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} T_{br}^{-2}} \quad (5-81)$$

and Hildebrand,²⁹⁵

$$\Delta H_b \left(\frac{cal}{mol} \right) = 17.0 T_b + 0.009 T_b^2 \quad (5-82)$$

In eqns. (5-79) to (5-82), P_c and T_c refer to the critical pressure and temperature, respectively, and T_{br} is the reduced boiling temperature (T_b/T_c). A number of other methods for estimating ΔH have been proposed, however none appear to offer significant advantages over those given above.

A third correlation for the latent heat of vaporization as a function of temperature makes use of the fact that ΔH decreases continuously with temperature along the boiling line and vanishes at the termination of the boiling line, i.e., the critical point. An early functional relationship proposed to express the variation of ΔH with T is the Watson equation²⁹⁶

$$\frac{\Delta H_{v2}}{\Delta H_{v1}} = \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^n \quad (5-83)$$

where subscripts 1 and 2 refer to temperatures 1 and 2. A common choice of n is 0.375 or 0.38. Other variations of the Watson relation exist in the literature, with different functional forms for the temperature dependence.

Despite the differences between values obtained from the various estimation methods, the molar vaporization enthalpies (ΔH) and the solubility parameters (δ) obtained from them generally do not differ too widely, and each of the variety of methods usually provides values that are acceptable for many purposes. However this methodology will only be applicable below the critical temperature, as ΔH , as noted earlier, vanishes at T_c .

5.4.2 Calculation of HSP's

The total cohesive energy density can also be subdivided into contributions from various types of molecular interactions. In all cases, however, some approximations or assumptions are made, and the expressions resulting from these assumptions and approximations are not exact even for liquids, let alone polymers. Rather, the

expressions are best considered as useful, empirical relations which have some theoretical foundation but which are chosen for their practical usefulness in particular situations. The most important situation where caution is required is where specific interactions *within* a component exist. The most common of these, and the most problematic, is hydrogen bonding within a pure component.²⁹⁷

Methods to calculate individual HSP's depend to a great extent on what data are available. Commonly, a total solubility parameter is first determined from Hildebrand's original 1-component solubility parameter model, using either eqn. (4-21) or eqn. (5-77). The general approach is then to calculate two of the three parameters, \mathbf{d}_d , \mathbf{d}_p , \mathbf{d}_h , from methods to be described below and to then obtain the third parameter by difference from the total solubility parameter. HSP values calculated this way are available in the literature for a large number of liquid solvents and polymers.^{298,299}

5.4.2.1 Dispersion Solubility Parameter, δ_d

5.4.2.1.1 Homomorph Method

The initial approach to dividing the total solubility parameter into components representing dispersion, polar, and hydrogen bonding interactions was based on the homomorph concept and empirically on the basis of many experimental observations.³⁰⁰ The dispersion component, ΔE_d , was calculated directly from the energy of vaporization of the nonpolar homomorph. Following the additional recommendation that the homomorph should have the same molar volume as well as a similar structure to that of the polar compound, Blanks and Prausnitz³⁰¹ published a homomorphic plot of the energy of vaporization for straightchain hydrocarbons against molar volume at various reduced

temperatures. On the same basis, Weimer and Prausnitz³⁰² prepared homomorph plots of the cohesive pressure against molar volume at various temperatures for normal alkanes, cycloalkanes, and aromatic hydrocarbons. Using the appropriate homomorph, ΔE , used to approximate ΔE_d , or the cohesive energy density (\mathbf{d}_d^2) as a function of molar volume and reduced temperature, is obtained. The dispersion solubility parameter is then

$$\delta_d = \sqrt{\frac{\Delta E_d}{V}} \quad (5-84)$$

5.4.2.1.2 Index of refraction (n_D) Correlation

The main idea in this correlation is that the interaction energy between nonpolar molecules, due to van der Waals-London forces, is dependent on the polarizability (see eqn. (3-1)).³⁰³ The polarizability, in turn, is related to the refractive index, n_D , by the Lorentz-Lorenz equation,

$$\frac{4}{3} \frac{\mathbf{p}}{V} N \mathbf{a} = \frac{n_D^2 - 1}{n_D^2 + 2} \quad (5-85)$$

where N is the number of molecules per cubic centimeter (the Loschmidt number) and \mathbf{a} is the average polarizability of the molecule. Subsequently, Koenhen and Smolder³⁰⁴ found a nearly linear relationship between \mathbf{d}_d and n_D for 60 nonpolar and polar liquid organic solvents in the region of n_D values ($1.3 < n_D < 1.6$).

$$\begin{aligned} \mathbf{d}_D &= 9.55n_D - 5.55 \quad (\text{cal/cm}^3)^{1/2} \\ &= 19.5n_D - 11.4 \quad (\text{MPa}^{1/2}) \end{aligned} \quad (5-86)$$

The relation resulted in a correlation coefficient of 0.90 and a standard error of 0.32.

5.4.2.1.3 Group contribution method

This method provides a quick estimate of the dispersion parameter (or polar or hydrogen bonding parameters) based on a summing of the dispersion (or polar or hydrogen bonding) contribution of individual structural units within the molecule,

$$\delta_d = \frac{\sum F_{id}}{V} \quad (5-87)$$

where F_{id} is the molar attraction constant for dispersion forces of a specific functional group i . Molar attraction constants have been derived by Koenhen and Smolders,³⁰⁵ van Krevelen,³⁰⁶ and Hansen and Beerbower.³⁰⁷ A summary of these tables is presented in Barton.³⁰⁸ When using the group contribution method, it is essential to check that the molar attraction constants and cohesion parameter data from different literature sources are based on the same models and assumptions, and are therefore self-consistent.

5.4.2.2 *Polar Solubility Parameter, δ_p*

5.4.2.2.1 Böttcher Equation

Böttcher derived an empirical relation for calculating the contribution of permanent dipoles to the cohesion energy of a liquid or a gas. This energy is given as W in eqn. (5-88).³⁰⁹

$$W = \frac{-4\mathbf{p}}{3} \frac{dN_A^2}{M} \frac{\mathbf{e} - 1}{2\mathbf{e} + n_D^2} \frac{(n_D^2 + 2)}{3} \mathbf{m}^2 \quad (\text{calories}) \quad (5-88)$$

Hansen and Skkaarup³¹⁰ equated (W/V) with δ_p to assign polar HSP values:

$$\delta_p = \sqrt{\frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2} \quad \left(\frac{\text{cal}}{\text{cm}^3}\right)^{1/2} \quad (5-89)$$

The use of this equation requires the molar volume (V), dipole moment (μ), refractive index (n_D), and the dielectric constant (ϵ) of the compound.

5.4.2.2.2 Hansen/Beerbower Equation

This equation is a simplified version of the Böttcher equation, eqn. (5-89), and has been used extensively by Hansen.³¹¹

$$\delta_p = 37.4 \frac{\mu}{V^{1/2}} \quad (\text{MPa})^{1/2} \quad (5-90)$$

An extensive listing of dipole moments can be found in McClellan.³¹² It must be noted that $\mu = 0$ (for nonpolar molecules) is not a sufficient basis to assign $\delta_p = 0$.³¹³

5.4.2.2.3 Group Contribution Method

When the dipole moment of a molecule is unknown, group contributions can be used to estimate δ_p :

$$\delta_p = \frac{\sqrt{\sum F_{ip}^2}}{V} \quad (5-91)$$

Molar attraction constants have been derived by Koenhen and Smolders,³¹⁴ van Krevelen,³¹⁵ and Hansen and Beerbower.³¹⁶ A summary of these tables is presented in Barton.³¹⁷

5.4.2.3 *Hydrogen Bonding Solubility Parameter, δ_h*

5.4.2.3.1 Difference Method

In early tabulations of HSP's, the hydrogen bonding parameter was almost always found by subtracting the sum of the polar and dispersion energies from the total energy of vaporization, so that

$$(\delta_h)^2 = \delta^2 - \delta_d^2 - \delta_p^2 \quad (5-92)$$

This is still widely used where the required data are available and reliable.

5.4.2.3.2 Group Contribution Method

Estimation methods based on group contribution are considered reasonably reliable for most of the required calculations. Hansen and Beerbower,³¹⁸ however, have determined that the group contribution method using molar attraction constants, as in eqn. (5-87) and eqn. (5-91), is not directly applicable to the calculation of δ_h . Instead, they have assumed that hydrogen bonding contributions from structural units within a molecule to the overall molecular hydrogen bonding cohesive energy are additive, leading to

$$\delta_h = \left(\frac{\sum U_h}{V} \right)^{1/2} \quad (5-93)$$

Caution is needed, however, in adding group contributions in the use of a single hydrogen bonding parameter to describe an interaction really requiring both donor and acceptor components. Hydrogen bonding parameter group contributions, based on structural group, have been comprised by Koenhen and Smolders,³¹⁹ van Krevelen,³²⁰ and Hansen and Beerbower.³²¹ A summary of these tables is presented in Barton.³²²

Figure 5-6 gives a summary of the methods for the determination of HSP values.

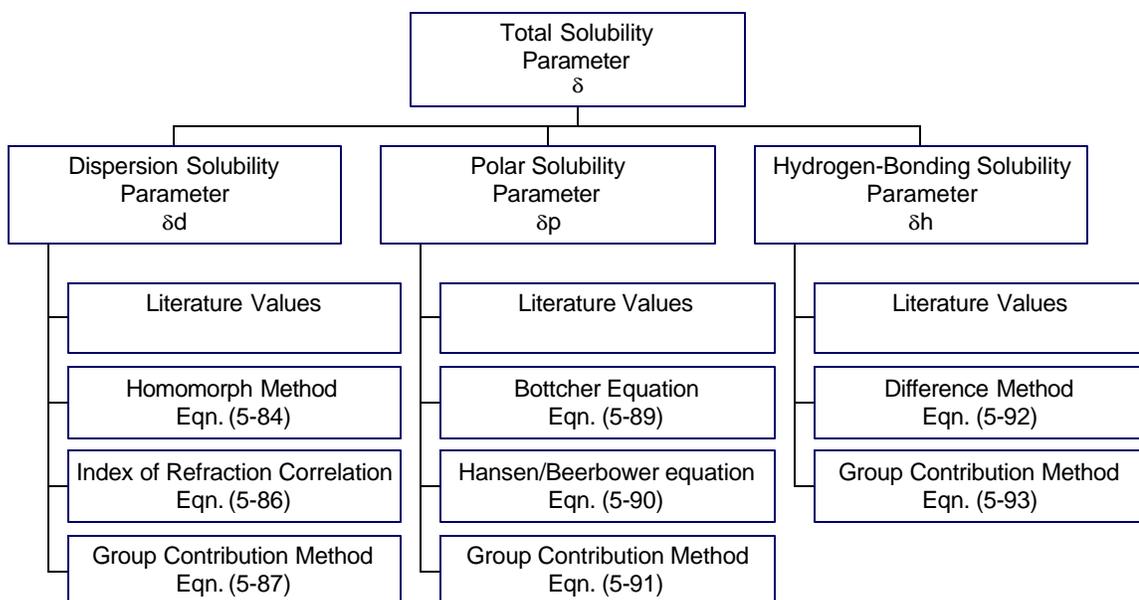


Figure 5-6. Available methods for the calculation of Hansen solubility parameters δ_d , δ_p , δ_h .

5.4.3 Temperature and Pressure Effects

Adjusting cosolvent HSP values for temperature and pressure effects will require obtaining either an EOS for the desired cosolvent, or reliable coefficient of thermal expansion (**a**) and isothermal compressibility (**b**) data. Depending on which of the two methods is used, cosolvent HSP values can be adjusted using the derivative equations summarized in Table 5-8, or the integrated equations summarized in Table 5-9.

5.5 Polymer Solubility Parameters

5.5.1 1-Component Models (Hildebrand)

The solubility parameters of polymers can be evaluated directly from the heat of vaporization and eqn. (5-77) only for those polymers that can be vaporized. However, as with the solvent and cosolvent (section 5.1.2 and 5.4.1), polymer solubility parameters can be approximated from calculation of the internal pressure, eqn. (5-12), along with suitable PVT data or EOS,

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (5-94)$$

It has been observed, however, that the internal pressure of polymers measured above and below the glass transition temperature, T_g , shows unusual behavior.³²³ At temperatures above T_g , where the polymer is in the rubber state, the variation of internal pressure with temperature is qualitatively indistinguishable from the behavior shown by

other organic molecules. However, as the temperature is lowered and T_g is reached, the internal pressure has been observed to drop, falling rapidly with decreasing temperature. Yet in passing through T_g , no sudden change in the magnitude of the internal pressure should be expected.³²⁴ This behavior is illustrated in Figure 5-7, where the internal pressure, P_i , is plotted against T from 20°C to 150°C for polymethylmethacrylate (PMMA).³²⁵

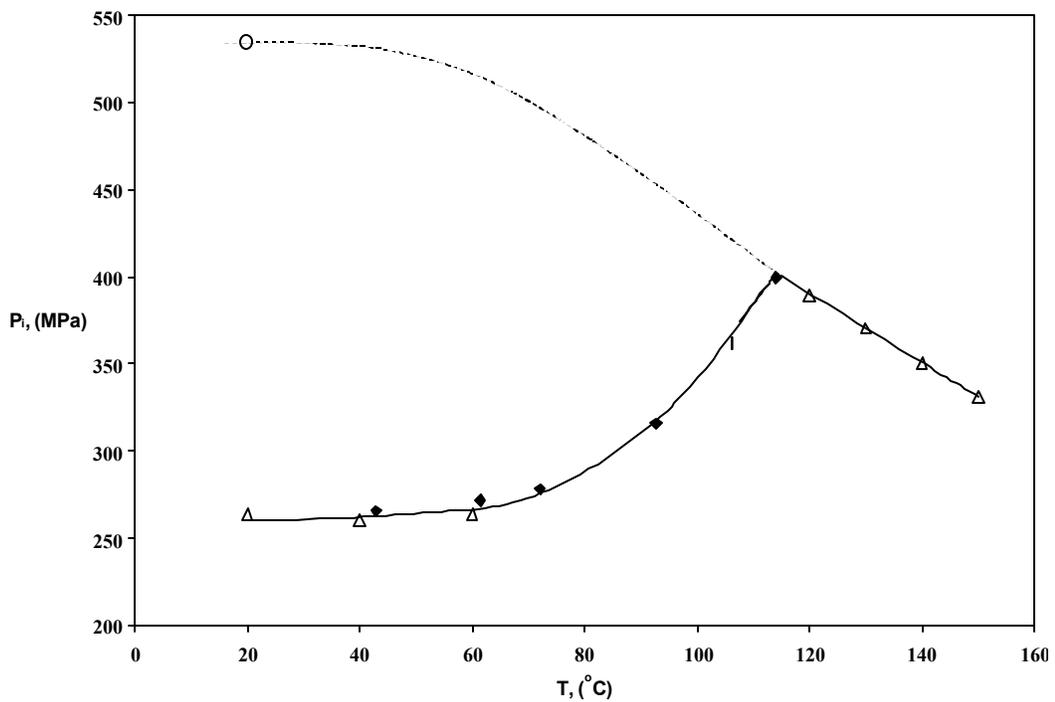


Figure 5-7. The internal pressure of PMMA as a function of temperature. Symbols: \circ data of Allen, Sims and Wilson,³²⁶ \blacktriangle data of Hellwege, Knappe and Lehmann,³²⁷ \triangle calculated from solution data after Hansen³²⁸.

Additionally, internal pressure values have been calculated from eqn. (5-69)

$$\left(\frac{\partial E}{\partial V} \right)_T = T \cdot \left(\frac{\mathbf{a}}{\mathbf{b}} \right)_V - P \quad (5-95)$$

and **a** and **b** are determined from polymer PVT data. Representative PVT data for PMMA, poly(vinyl butyral), and PC are shown in Figures 5-8, 5-9, and 5-10.

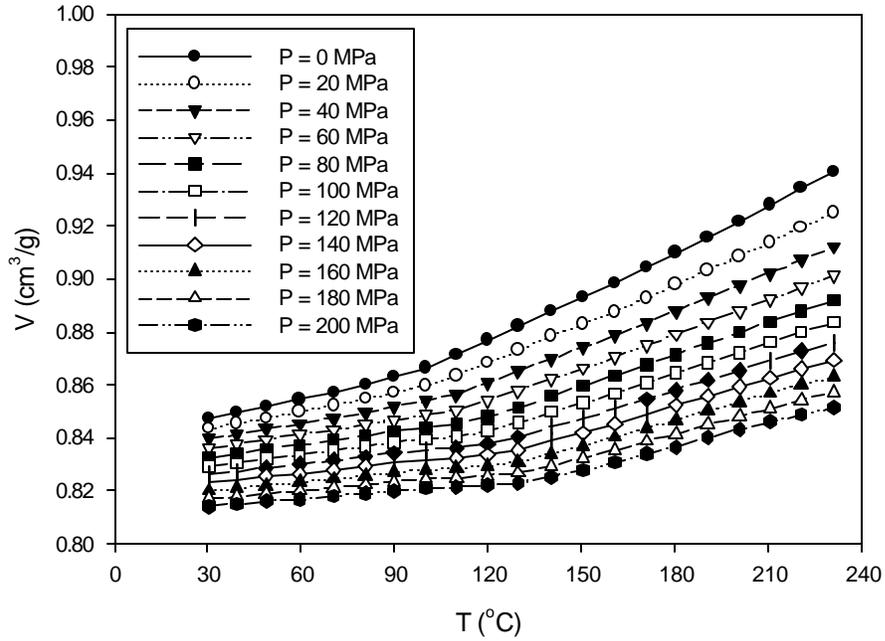


Figure 5-8. Plots of standard PVT for PMMA ($M = 1 \cdot 10^5$).³²⁹

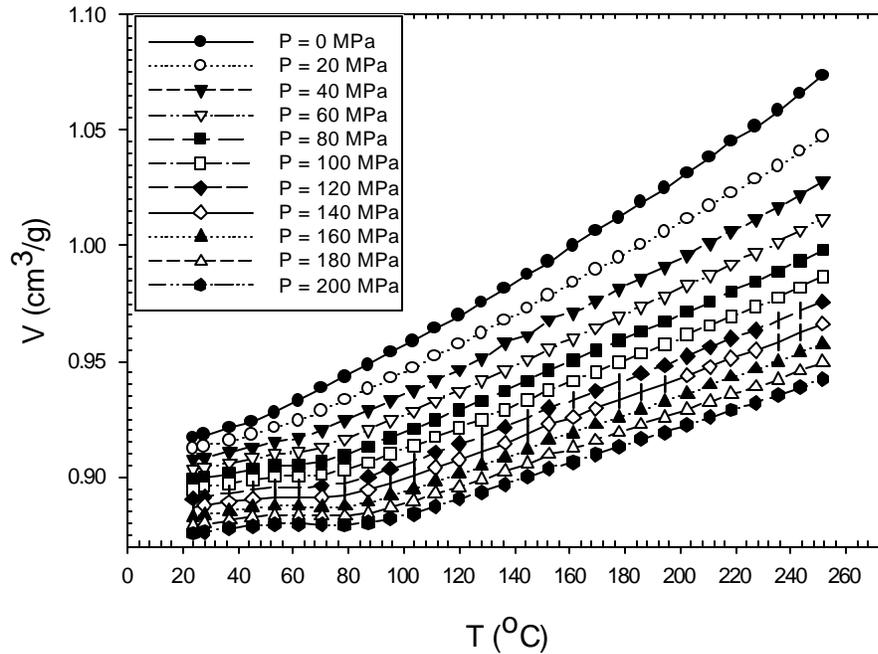


Figure 5-9. Plots of standard PVT Poly(vinyl butyral).³³⁰

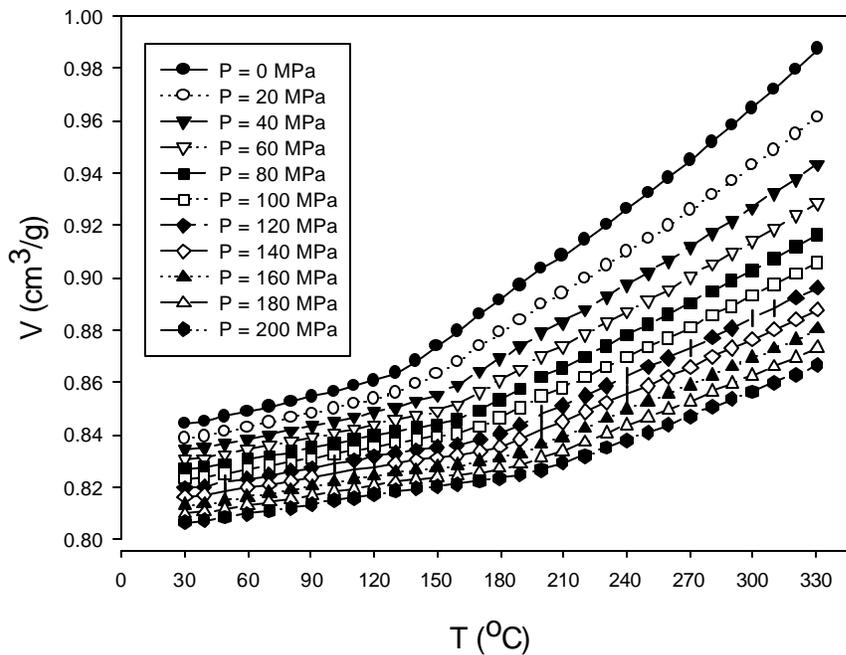


Figure 5-10. Plots of standard PVT for Polycarbonate.³³¹

From an examination of the PVT data plotted in Figure 5-8 through 5-10, noticeable “breaks”, or changes in slope, in the various isobars are observed for each of the polymers. This change in slope represents the polymers glass transition (from rubber to glass on cooling). Therefore, the data well to the left of the break represents PVT data for the polymer’s glass state, while the PVT data to the right of the break, represents data for the polymer’s rubber state. Although not quantified at this time, it is apparent that the isobaric thermal expansion coefficient, \mathbf{a} , decreases significantly, whereas the effect on the isothermal compressibility, \mathbf{b} , is much less marked in the rubber-glass transition.³³² The lower values of \mathbf{a} in the glass versus rubber state will also result in a lower internal pressure, for the glass, as calculated from eqn. (5-95).

In considering the reason for this apparent decrease in internal pressure it is necessary to reconsider the concept of internal pressure, as utilized in this work, as an equilibrium quantity. It is therefore applicable to materials, including polymers, only when local, internal equilibrium can be maintained, i.e., above T_g . Internal pressure, as defined in section 4.1 has no meaning below T_g . It is therefore pointless to talk about the internal pressure (as defined here) of a polymer below T_g , since T_g represents the loss of internal degrees of freedom of the polymer matrix, and, at any temperature below T_g , the polymer is therefore in a nonequilibrium state.

Experimental PVT data, such as shown in Figures 5-8 to 5-10, is available in the literature for some polymers. One excellent source is a compilation by Zoller and Walsh.³³³ In the absence of extended tabulations of measured data, empirical models for the PVT behavior of polymers must be used. The most widely employed equation for representing the PVT data for polymers is the Tait equation.³³⁴ The Tait equation relates the specific volume, $V(P,T)$, in terms of the zero-pressure volume, $V(0,T)$, and the Tait parameter, $B(T)$,

$$V(P,T) = V(0,T) \left(1 - C \ln \left[1 + \frac{P}{B(T)} \right] \right) \quad (5-96)$$

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

$$B(T) = B_o \exp(- B_1 T) \quad (5-97)$$

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

$$V(0,T) = A_0 + A_1T + A_2T^2 \quad (5-98)$$

where B_0 , B_1 , A_0 , A_1 and A_2 are material dependent parameters and T is in degrees Centigrade.

The Tait equation provides a convenient means to compute the of thermal expansion coefficient, \mathbf{a} , and isothermal compressibility, \mathbf{b} ,

$$\mathbf{a}(P,T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \mathbf{a}(0,T) - PB_1 \mathbf{b}(P,T) \quad (5-99)$$

and

$$\mathbf{b}(P,T) = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{C/(P + B(T))}{1 - C \ln(1 + P/B(T))} \quad (5-100)$$

where

$$\mathbf{a}(0,T) = \frac{A_1 + 2A_2T}{A_0 + A_1T + A_2T^2} \quad (5-101)$$

This allows for calculation of the internal pressure, and the solubility parameter, using eqn. (5-95).

Application of the Tait equation, however, is restricted to polymers where the parameters A_i , B_i have been regressed from experimental data, since no methods are currently available to estimate them from chemical structure. Tabulated values are currently available for 56 polymers.³³⁵

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. These equations will be briefly mentioned here, along with a reference containing more detailed discussions.

1. Spencer and Gilmore³³⁶ modified the van der Waals equation of state for polymers, employing a constant value for the internal pressure instead of the van der Waals' attractive term $\left(\frac{a}{V^2}\right)$,

$$(P + \mathbf{p})(V - \mathbf{w}) = RT \quad (5-102)$$

where P is the external pressure, π is the internal pressure, V is the volume, and ω is the polymer volume at absolute zero 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.³³⁷

2. Weir³³⁸ developed an empirical isobaric equation to describe the PVT relationship of polymers. Along an isobar, the volume is expressed as a polynomial equation in temperature

$$V = V_o[(1 + a_1P + a_2P^2) + (1 + b_1P + b_2P^2)T + (1 + c_1P + c_2P^2)T^2] \quad (5-103)$$

where V_o is the specific volume at 21°C, a_i , b_i and c_i are material constants of the polymer. The Weir equation, with its 10 undetermined coefficients, is cumbersome to use. Furthermore, it is also noted to be less accurate than the Tait equation.³³⁹

3. Whitaker and Griskey³⁴⁰ observed that at any given temperature, 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 for this corresponding states curve is

$$V = \left[\frac{0.01205}{\rho_o^{0.9421}} \right] P^{n-1} \left(\frac{T}{T_g} \right)^{m+1} R \quad (5-104)$$

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 polymer 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. Although the Whitaker-Griskey equation has limited predictive capability if ρ_o and T_g of the polymer are known, it does not have the accuracy offered by the other empirical PVT equations.³⁴¹

4. Hartman and Haque³⁴² derived an equation of state by combining the theoretical temperature dependence of thermal pressure from Pastine and Warfield³⁴³ with the zero pressure isobar of the Simha-Somcynsky³⁴⁴ equation of state and an empirical volume dependence of the thermal pressure. The equation, in reduced form, is given by

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln \tilde{V} \quad (5-105)$$

where

$$\tilde{P} = \frac{P}{P_o}; \quad \tilde{V} = \frac{V}{V_o}; \quad \tilde{T} = \frac{T}{T_o} \quad (5-106)$$

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, and T_o is defined implicitly from the relation $V(P_o, T_o) = V(0, 0)$. The Hartman-Haque equation is a relatively new but promising empirical equation of state with only three parameters and has an accuracy comparable to the Tait equation. Both the Tait and Hartman-Haque equations have been evaluated for a variety of polymers.³⁴⁵

Other correlation methods can also be utilized for determining polymer solubility parameter values. As with solvent and cosolvent, a polymer internal pressure can be used as an approximation of the cohesive energy density and \mathbf{d}^2 . Correlations between internal pressure and cohesive energy density have also been evaluated for polymer systems. A theoretical derivation by Voeks³⁴⁶ resulted in

$$\frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\Delta E}{V}\right)} = n \approx 1.3 \quad (5-107)$$

Where the internal pressure and cohesive energy density are again related by the quantity n (see eqn. 4-18).

Values of internal pressure and cohesive energy density for a number of polymers are

Table 5-10. Comparison of internal pressure and cohesive energy density of polymers at 20°C.

Polymer	$\left(\frac{\partial E}{\partial V}\right)_T$ (bar)	$\left(\frac{\Delta E}{V}\right)_T$ (bar)	n
Polyethylene	3200	2500/2900	1.3/1.1
Polyisobutylene	3300	2500/2700	1.3/1.2
Polystyrene	4600	3000/3600	1.5/1.3
Polyvinyl acetate	4300	3600/5100	1.2/0.8
Polyethyl acrylate	4400	3500/3700	1.3/1.2
Polymethyl methacrylate	3800	3400/6900	1.1/0.6
Polypropylene oxide	3700	2300/4200	1.6/0.9
Polydimethyl siloxane	2400	2200/2400	1.1/1.0

compared in Table 5-10,³⁴⁷ which shows eqn. (5-107) to be a valid first approximation.

Another method to estimate total solubility parameters of polymers is based on surface tension. Since surface tension is a direct manifestation of intermolecular forces, it may therefore be expected that a relation exists between surface tension and cohesive energy density. The relationship is³⁴⁸

$$d^2 \approx \frac{g^{3/2}}{0.75} \quad (5-108)$$

where γ is in mJ/m^2 and \mathbf{d}^2 is in J/cm^3 . Values of surface tension for polymer melts have been determined and are available in the literature. According to Macleod's relation, the surface tension varies with density according to³⁴⁹

$$\gamma = \gamma^o \rho^{\kappa} \quad (5-109)$$

where γ^o and κ are constants, independent of temperature. The κ is known as Macleod's exponent, and usually has a value of 3.0-4.5 for polymers³⁵⁰. Alternatively, the interfacial energy of solid polymers may be calculated from an additive function, known as the parachor, by applying the following equation.

$$\mathbf{g} = \left(\frac{P_s}{V} \right)^4 \quad (5-110)$$

where P_s is the parachor parameter and V is the molar volume of the repeat unit. Parachor atomic and structural contribution constants were originally introduced by Sugden³⁵¹ and later modified by Mumford and Phillips,³⁵² and by Quayle.³⁵³ The group contributions to the parachor as presented by different investigators are given in Table 5-11.³⁵⁴

Table 5-11. Atomic and structural contribution to the Parachor.

Unit	Values assigned by $[(\text{cm}^3/\text{mol}) \times (\text{mJ}/\text{m}^2)^{1/4}]$		
	Sugden	Mumford and Phillips	Quayle
CH ₂	39.0	40.0	40.0
C	4.8	9.2	9.0
H	17.1	15.4	15.5
O	20.0	20.0	19.8
O ₂ (in esters)	60.0	60.0	54.8
N	12.5	17.5	17.5
S	48.2	50.0	49.1
F	25.7	25.5	26.1
Cl	54.3	55.0	55.2
Br	68.0	69.0	68.0
I	91.0	90.0	90.3
Double bond	23.2	19.0	16.3-19.1
Triple bond	46.4	38.0	40.6
3-membered ring	16.7	12.5	12.5
4-membered ring	11.6	6.0	6.0
5-membered ring	8.5	3.0	3.0
6-membered ring	6.1	0.8	0.8
7-membered ring		-4.0	4.0

In Table 5-12, polymer solubility parameter values obtained in the literature are compared with values calculated from the polymer surface tension, eqn (5-108) and eqn. (5-110).

Table 5-12. *Polymer surface tension and solubility parameters.*

Polymer	Surface Tension mJ/m ²		Solubility Parameter MPa ^{1/2}		
	Observed	Calculated from P _s	Eqn. (5-108) Lit. γ	Eqn. (5-110) from P _s	Lit.
Polytetrafluoroethylene	18.5	26	10.3	13.3	13.1
Poly(dimethyl siloxane)	24	21.5	12.5	11.5	14.9
Polyisobutylene	27	30.5	13.7	15.0	16.3
Polypropylene	29	32.5	14.4	15.7	16.6
Polyethylene	31	31.5	15.2	15.3	16.5
Poly(vinyl acetate)	37	40	17.3	18.4	19.2
Poly(vinyl alcohol)	37	59	17.3	24.6	25.6
Poly(ethylene terephthalate)	41.5	49	18.9	21.4	21.7
Poly(methyl methacrylate)	39	42	18.0	19.0	22.4
Poly(vinyl chloride)	39	42	18.0	19.0	19.4
Polycarbonate	45	42.5	20.1	19.2	20
Poly(vinyl butyral)	38	-	16.6	-	23

Another polymer property that shows a general correlation with cohesive energy is the glass transition temperature, T_g . It is generally observed that there is an approximately linear dependence of T_g on cohesive energy density, so that polymers with high values of T_g tend to have high (Hildebrand) total solubility parameters.³⁵⁵ Although there is no direct mathematical relationship, Table 5-13 illustrates the general trend (with the exception of poly(vinyl alcohol), and poly(vinyl butyral)) in polymer glass transition values and solubility parameters.

Table 5-13. Polymer glass transition temperatures and solubility parameters.

Polymer	T _g (°C) ^{356,357}	δ, (MPa) ^{1/2} 358
Poly(dimethyl siloxane)	-128	14.9
Polyethylene	-125	16.4
Natural rubber	-72	16.6
Polybutadiene	-25	17.6
Poly(tetrafluoroethylene)	27	13.1
Poly(vinyl acetate)	30	19.3
Poly(vinyl butyral)	51	23.1
Poly(ethyl methacrylate)	66	18.6
Poly(ethylene terephthalate)	69	21.8
Poly(vinyl chloride)	75	19.4
Poly(vinyl alcohol)	85	25.6
Poly(methyl methacrylate)	105	18.8
Polycarbonate	148	20.0

5.5.2 Calculation of Polymer HSP's

Hansen's original solubility parameter work was developed out of studies into film drying and solvent retention, the phenomenon that solvent can be found in many paint and varnish films years after their application. The assumption was that hydrogen bonding between the solvent and polymer molecules was responsible for this retained solvent. Although this assumption was ultimately found to be false, the statement that hydrogen bonding had no significant effect on solvent retention without defining hydrogen bonding was not satisfactory for Hansen. Therefore, in order to better define hydrogen bonding and polar bonding, Hansen initiated a study based on the Hildebrand solubility parameter. This study eventually led to the concept of a three dimensional solubility parameter,³⁵⁹ a concept that has gone on to become an important tool for the study of solubility, swelling, and other physical interactions between polymers and solvents. For this reason, extensive compilations exist of total solubility parameters and

dispersion and polar HSP's for polymers. Also, hydrogen-bonding HSP's have been determined from turbidimetric titrations of solubility in solvents and from swelling of polymers in solvents, where the solvent has been previously characterized for its HSP's.

Because many polymers are amorphous and, therefore, "liquid-like" in some of their properties, their solubility behavior can be treated by many of the methods used for liquids. For this reason, the correlations developed in Section 5.4.2 for cosolvents, are also applicable for polymers.

5.5.2.1 Dispersion Solubility Parameter, δ_d

Two of the relations discussed in Section 5.4.2.1 can be utilized for polymers: the index of refraction correlation and the group contribution method.

5.5.2.1.1 Index of refraction (n_D) Correlation

Koenhen and Smolder³⁶⁰ predicted δ_d for several polymers using the index of refraction, n_D ,

$$\begin{aligned} \delta_D &= 9.55n_D - 5.55 \quad (\text{cal/cm}^3)^{1/2} \\ &= 19.5n_D - 11.4 \quad (\text{MPa}^{1/2}) \end{aligned} \quad (5-111)$$

5.5.2.1.2 Group contribution method

As discussed earlier for cosolvent HSP's, this method provides a quick estimate of the dispersion parameter (a similar approach has been developed for the polar and

hydrogen HSP's) based on a summing of the contributions of individual structural units within the molecule to the total dispersion energy

$$\delta_d = \frac{\sum F_{id}}{V} \quad (5-112)$$

where F_{id} is the molar attraction constant for dispersion forces of a specific group i . Molar attraction constants have been derived by Koenhen and Smolders,³⁶¹ van Krevelen,³⁶² and Hansen and Beerbower.³⁶³ A summary of these tables is presented in Barton.³⁶⁴

5.5.2.2 Polar Solubility Parameter, δ_p

Two of the relations discussed in Section 5.4.2.2 can be utilized for polymers: the Hansen/Beerbower equation and the group contribution method.

5.5.2.2.1 Hansen/Beerbower Equation

If the dipole moment of the polymer is known, eqn. (5-113) can be used to predict δ_p . The measured average dipole moments of polymers are generally 70-90% of the dipole moment of the corresponding monomer unit, therefore for polymer m values not found in the literature, an estimated dipole moment of 80% of the dipole moment of the monomer is recommended,³⁶⁵ so that

$$\delta_p = 37.4 \frac{\mu}{V^{1/2}} \quad (MPa)^{1/2} \quad (5-113)$$

5.5.2.2.2 Group Contribution Method

When the dipole moment of a molecule is unknown, group contributions can be used to estimate the polar solubility parameter.

$$\delta_p = \frac{\sqrt{\sum F_{ip}^2}}{V} \quad (5-114)$$

Molar attraction constants have been derived by Koenhen and Smolders,³⁶⁶ van Krevelen,³⁶⁷ and Hansen and Beerbower.³⁶⁸ A summary of these tables is presented in Barton.³⁶⁹

5.5.2.3 *Hydrogen Bonding Solubility Parameter, δ_h*

5.5.2.3.1 Difference Method

In the earlier tabulations, the hydrogen bonding parameter was almost always found by subtracting the sum of the polar and dispersion energies from the total energy of vaporization, so that

$$(\delta_h)^2 = \delta^2 - \delta_d^2 - \delta_p^2 \quad (5-115)$$

This is still widely used where the required data are available and reliable.

5.5.2.3.2 Group Contribution Method

As with the calculation of \mathbf{d}_h for cosolvents, Hansen and Beerbower have assumed that the contribution of individual molecular subunits to the total hydrogen bonding cohesive energy are additive, leading to

$$\delta_h = \left(\frac{\sum U_h}{V} \right)^{1/2} \quad (5-116)$$

Hydrogen bonding contributions, based on structural group, have been compiled by Koenhen and Smolders,³⁷⁰ van Krevelen,³⁷¹ and Hansen and Beerbower.³⁷² A summary of these tables is presented in Barton.³⁷³

In Figure 5-11 a summary of the methods for determining polymer HSP values is

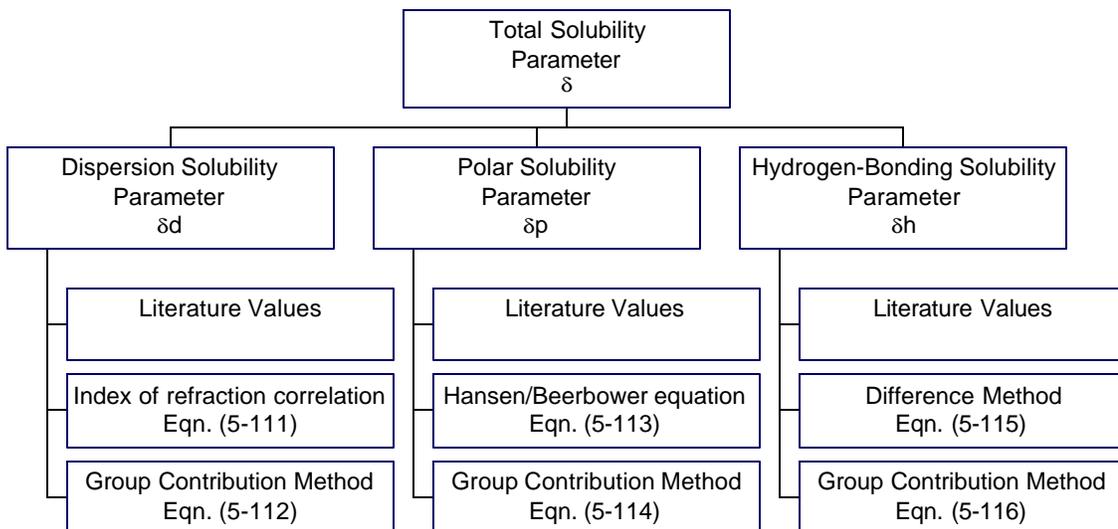


Figure 5-11. Diagram of the components, \mathbf{d}_d , \mathbf{d}_p , \mathbf{d}_h , to the total Hansen solubility parameter, \mathbf{d} and methods for their determination.

shown.

5.5.3 Temperature and Pressure Effects

Adjusting polymer HSP values for temperature and pressure effects can be approached in several ways. One option is the use of published PVT data for the given polymer and using the equations developed in Section 5.3 and summarized in Table 5-9. Alternatively, the coefficient of thermal expansion and the isothermal compressibility in the rubber state, along with the equations developed in Section 5.3 and summarized in Table 5-8 can be used. Lastly, empirical equations of state (such as the Tait equation) can be used to generate the necessary PVT data or ***a*** and ***b*** for use in either the derivative or integrated equations. All of these approaches, however, are applicable only to PVT states in the polymer's rubber phase.