
10 Determination of Hansen Solubility Parameter Values for Carbon Dioxide

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ABSTRACT

Reference values of the Hansen solubility parameters (HSP) for carbon dioxide (CO₂) have been determined. The methodology adopted for this is based on room temperature solubility of the gas in different liquids of known HSP values. CO₂ gas solubility data, at 25°C and a CO₂ partial pressure of 1 atmosphere, in 101 liquid solvents have been gathered and evaluated, yielding the values: $\delta_d = 15.6 \text{ MPa}^{1/2}$, $\delta_p = 5.2 \text{ MPa}^{1/2}$, and $\delta_h = 5.8 \text{ MPa}^{1/2}$. A methodology for extending this reference set of HSP values to any temperature and pressure has been developed utilizing an equation of state (EOS) of the form $P = f(\rho, T)$.

INTRODUCTION

The HSP concept is widely used for selecting suitable solvents for organic compounds. In addition, HSPs have been applied to biological materials, barrier properties of polymers, as well as the characterization of surfaces, pigments, fillers, and fibers.¹ The basis of the HSP approach is the assumption that the total cohesive energy (E) of a pure compound is made up of the additive contributions from nonpolar (dispersion) interactions (E_d), polar (dipole–dipole and dipole–induced dipole) interactions (E_p), and hydrogen bonding or other specific association interactions including Lewis acid–base interactions (E_h):

$$E = E_d + E_p + E_h \quad (10.1)$$

Dividing each contribution by the molar volume,

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (10.2)$$

gives the square of the total solubility parameter as the sum of the squares of the Hansen dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) solubility parameters, so that

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (10.3)$$

where

$$\delta_d^2 = \frac{E_d}{V}; \quad \delta_p^2 = \frac{E_p}{V}; \quad \text{and} \quad \delta_h^2 = \frac{E_h}{V} \quad (10.4)$$

The determination of HSPs for compounds that are gases at ambient conditions is usually based on room temperature solubility of the gas in a range of different liquids of known δ_d , δ_p , and δ_h . Those liquids that show the highest solubility for the gas are assumed to have HSPs closer to those of the gas than those liquids that have lower solubilities for the gas. 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 are evaluated. From this data, a set of HSP values at a single reference temperature and pressure is determined.

METHODOLOGY

Literature values of CO₂ solubility in various liquid solvents at 25°C have been collected and are summarized in Table 10.1. All the solubility data shown in Table 10.1 was either experimentally determined at a CO₂ partial pressure of 0.1 MPa, or has been corrected to p_{CO_2} MPa using Henry's law,²

$$x_{\text{CO}_2} = \frac{p_{\text{CO}_2}}{K_H} \quad (10.5)$$

where K_H is the Henry's law coefficient, p_{CO_2} is the partial pressure of CO₂, and x_{CO_2} is the mole fraction of dissolved CO₂. In addition to correcting CO₂ partial pressure to 0.1 MPa, it has been necessary to correct the reported values of CO₂ gas solubility to a common set of units. Generally, solubilities have been reported as mole fraction of dissolved CO₂, x_{CO_2} , or as one of the two dimensionless quantities; the Bunsen coefficient or the Ostwald coefficient. The Bunsen coefficient, Ω , is defined as the volume of gas, reduced to 0°C and 0.1 MPa, dissolved per unit volume of solvent at a system temperature, T , under a gas pressure of 1 atmosphere. The Ostwald coefficient, L , is defined as the ratio of the volume of gas absorbed to the volume of the absorbing liquid, all measured at the same temperature.³ If the solubility is small and the gas phase is ideal, the Ostwald coefficient is independent of total pressure and these two coefficients are simply related by⁴:

$$L = \frac{T}{273} \Omega \quad (10.6)$$

The mole fraction of dissolved CO₂ can then be calculated using²

$$x_{\text{CO}_2} = \left[\left(\frac{RT}{Lp_{\text{CO}_2}V_1^0} \right) + 1 \right]^{-1} \quad (10.7)$$

where R is the gas constant, T is the absolute temperature, and V_1^0 the molar volume of the pure solvent. The Hansen dispersion, polar, and hydrogen bonding parameters in Table 10.1 are from Hansen's solubility parameter handbook,⁵ and the total solubility parameter value is calculated from Equation 10.3, noted earlier.

Using the collected values of x_{CO_2} at 25°C and $p_{\text{CO}_2} = .1$ MPa, HSP values were calculated based on a simple weighted average using the data set in Table 10.1, hereafter called *data set #1*. Where multiple CO₂ gas solubility data were available for an individual solvent, an average value for that solvent was used.

TABLE 10.1
CO₂ Solubility in Various Solvents at T = 25°C and a CO₂ Partial Pressure of 1 Atmosphere

Formula	Solvent	Mole Fraction CO ₂	Actual/Ideal	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Ref.
C ₂ H ₄ O ₂	Acetic acid	0.01089	0.4757	14.5	8.0	13.5	21.37	29
C ₂ H ₄ O ₂	Acetic acid	0.01122	0.4899	14.5	8.0	13.5	21.37	30
C ₄ H ₆ O ₃	Acetic anhydride	0.01977	0.8635	16.0	11.7	10.2	22.29	29
C ₃ H ₆ O	Acetone	0.01876	0.8193	15.5	10.4	7.0	19.94	29
C ₃ H ₆ O	Acetone	0.01903	0.8309	15.5	10.4	7.0	19.94	30
C ₃ H ₆ O	Acetone	0.01896	0.8279	15.5	10.4	7.0	19.94	31
C ₃ H ₆ O	Acetone	0.01896	0.8279	15.5	10.4	7.0	19.94	32
C ₃ H ₆ O	Acetone	0.02259	0.9865	15.5	10.4	7.0	19.94	33
C ₃ H ₆ O	Acetone	0.02092	0.9136	15.5	10.4	7.0	19.94	34
C ₇ H ₁₄ O ₂	Amyl acetate	0.02800	1.2227	15.8	3.3	6.1	17.26	35
C ₇ H ₁₄ O ₂	Amyl acetate	0.02452	1.0708	15.8	3.3	6.1	17.26	29
C ₇ H ₁₄ O ₂	Amyl acetate	0.02612	1.1407	15.8	3.3	6.1	17.26	30
C ₅ H ₁₁ Br	Amyl bromide	0.01235	0.5394	20.3	4.8	2.8	21.05	29
C ₅ H ₁₁ Cl	Amyl chloride	0.01424	0.6220	15.5	5.0	1.3	16.34	29
C ₆ H ₇ N	Aniline	0.00493	0.2151	19.4	5.1	10.2	22.50	29
C ₆ H ₇ N	Aniline	0.00486	0.2121	19.4	5.1	10.2	22.50	30
C ₆ H ₇ N	Aniline	0.00487	0.2129	19.4	5.1	10.2	22.50	33
C ₆ H ₇ N	Aniline	0.00487	0.2129	19.4	5.1	10.2	22.50	3
C ₇ H ₆ O	Benzaldehyde	0.01140	0.4979	19.4	7.4	5.3	21.43	30
C ₇ H ₆ O	Benzaldehyde	0.01171	0.5114	19.4	7.4	5.3	21.43	29
C ₆ H ₆	Benzene	0.00962	0.4201	18.4	0.0	2.0	18.51	36
C ₆ H ₆	Benzene	0.00880	0.3843	18.4	0.0	2.0	18.51	29
C ₇ H ₇ Cl	Benzyl chloride	0.00912	0.3983	18.8	7.1	2.6	20.26	29
C ₆ H ₅ Br	Bromobenzene	0.00789	0.3444	20.5	5.5	4.1	21.62	29
C ₄ H ₁₀ O	Butanol	0.00887	0.3872	16.0	5.7	15.8	23.20	32
C ₄ H ₁₀ O	Butanol	0.00734	0.3207	16.0	5.7	15.8	23.20	37
C ₄ H ₁₀ O	Butanol	0.00718	0.3135	16.0	5.7	15.8	23.20	38
C ₄ H ₁₀ O	2-Butanol	0.00660	0.2882	15.8	5.7	14.5	22.19	39
C ₄ H ₁₀ O	t-Butanol	0.00725	0.3166	15.2	5.1	14.7	21.75	40
C ₂₂ H ₄₂ O ₂	Butyl oleate	0.02790	1.2183	14.7	3.4	3.4	15.47	38
C ₄ H ₈ O ₂	Butyric acid	0.01297	0.5665	14.9	4.1	10.6	18.74	29
CS ₂	Carbon disulfide	0.00215	0.0940	20.5	0.0	0.6	20.51	29
CS ₂	Carbon disulfide	0.00328	0.1432	20.5	0.0	0.6	20.51	41
CCl ₄	Carbon tetrachloride	0.01100	0.4803	17.8	0.0	0.6	17.81	35
CCl ₄	Carbon tetrachloride	0.01059	0.4624	17.8	0.0	0.6	17.81	36
CCl ₄	Carbon tetrachloride	0.00904	0.3948	17.8	0.0	0.6	17.81	29
C ₆ H ₅ Cl	Chlorobenzene	0.00938	0.4095	19.0	4.3	2.0	19.58	29
C ₆ H ₅ Cl	Chlorobenzene	0.00981	0.4283	19.0	4.3	2.0	19.58	34
CHCl ₃	Chloroform	0.01121	0.4897	17.8	3.1	5.7	18.95	29
CHCl ₃	Chloroform	0.01277	0.5576	17.8	3.1	5.7	18.95	34
CHCl ₃	Chloroform	0.01126	0.4918	17.8	3.1	5.7	18.95	30
C ₉ H ₁₂	Methyl ethyl benzene	0.01008	0.4401	16.1	7.0	0.0	17.56	29
C ₇ H ₁₄	Cycloheptane	0.00721	0.3148	17.2	0.0	0.0	17.20	42
C ₇ H ₁₂ O	Cycloheptanone	0.01588	0.6934	17.2	10.6	4.8	20.77	43
C ₆ H ₁₂	Cyclohexane	0.00771	0.3367	16.8	0.0	0.2	16.80	44
C ₆ H ₁₂	Cyclohexane	0.00760	0.3319	16.8	0.0	0.2	16.80	2
C ₆ H ₁₂	Cyclohexane	0.00774	0.3380	16.8	0.0	0.2	16.80	42
C ₆ H ₁₂ O	Cyclohexanol	0.00471	0.2057	17.4	4.1	13.5	22.40	45

TABLE 10.1 (CONTINUED)
CO₂ Solubility in Various Solvents at T = 25°C and a CO₂ Partial Pressure of 1 Atmosphere

Formula	Solvent	Mole Fraction CO ₂	Actual/Ideal	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Ref.
C ₆ H ₁₀ O	Cyclohexanone	0.01600	0.6987	17.8	6.3	5.1	19.56	46
C ₈ H ₁₆	Cyclooctane	0.00688	0.3004	17.5	0.0	0.0	17.50	42
C ₈ H ₁₆	Cyclooctane	0.00686	0.2996	17.5	0.0	0.0	17.50	47
C ₅ H ₁₀	Cyclopentane	0.00491	0.2146	16.4	0.0	1.8	16.50	42
C ₅ H ₈ O	Cyclopentanone	0.01641	0.7166	17.9	11.9	5.2	22.11	48
C ₁₀ H ₂₂	Decane	0.01204	0.5256	15.7	0.0	0.0	15.70	32
C ₁₀ H ₂₂	Decane	0.01250	0.5459	15.7	0.0	0.0	15.70	49
C ₁₀ H ₂₂ O	Decanol	0.00973	0.4249	17.5	2.6	10.0	20.32	50
C ₂ H ₄ Br ₂	1,2-Dibromoethane	0.00812	0.3546	17.8	6.4	7.0	20.17	34
C ₂ H ₄ Br ₂	1,2-Dibromoethane	0.00804	0.3509	17.8	6.40	7.0	20.17	29
C ₂ H ₄ Br ₂	1,2-Dibromoethane	0.00797	0.3481	17.8	6.4	7.0	20.17	30
C ₂ H ₄ Br ₂	1,2-Dibromoethane	0.00838	0.3659	17.8	6.4	7.0	20.17	45
C ₃ H ₆ C ₁₂ O	1,3-dichloro-2-propanol	0.00746	0.3258	17.5	9.9	14.6	24.85	29
CH ₂ Cl ₂	Dichloromethane	0.01250	0.5459	18.2	6.3	6.1	20.20	38
C ₈ H ₁₄ O	Dimethyl cyclohexanone	0.01680	0.7336	15.2	8.8	3.3	17.87	51
C ₂ H ₆ OS	Dimethyl sulfoxide	0.00908	0.3965	18.4	16.4	10.2	26.68	44
C ₂ H ₆ OS	Dimethyl sulfoxide	0.00907	0.3962	18.4	16.4	10.2	26.68	52
C ₂ H ₆ OS	Dimethyl sulfoxide	0.00945	0.4125	18.4	16.4	10.2	26.68	33
C ₃ H ₇ NO	Dimethyl formamide	0.01610	0.7031	17.4	13.7	11.3	24.86	32
C ₄ H ₈ O ₂	1,4-Dioxane	0.02272	0.9921	19.0	1.8	7.4	20.47	38
C ₁₂ H ₂₆	Dodecane	0.01428	0.6235	16.0	0.0	0.0	16.00	53
C ₁₂ H ₂₆	Dodecane	0.01290	0.5633	16.0	0.0	0.0	16.00	49
C ₁₂ H ₂₆	Dodecane	0.01191	0.5202	16.0	0.0	0.0	16.00	32
C ₁₂ H ₂₆ O	Dodecanol	0.01811	0.7908	15.5	6.5	10.8	19.98	32
C ₂ H ₆ O	Ethanol	0.00642	0.2804	15.8	8.8	19.4	26.52	30
C ₂ H ₆ O	Ethanol	0.00642	0.2805	15.8	8.8	19.4	26.52	31
C ₂ H ₆ O	Ethanol	0.00725	0.3166	15.8	8.8	19.4	26.52	38
C ₄ H ₈ O ₂	Ethyl acetate	0.02300	1.0044	15.8	5.3	7.2	18.15	38
C ₈ H ₁₀	Ethyl benzene	0.01006	0.4393	17.8	0.6	1.4	17.87	38
C ₂ H ₄ C ₁₂	Ethylene chloride	0.01133	0.4946	19.0	7.4	4.1	20.80	29
C ₂ H ₆ O ₂	Ethylene glycol	0.00220	0.0961	17.0	11.0	26.2	33.11	38
C ₁₀ H ₁₂ O ₂	Eugenol	0.01023	0.4469	15.1	8.8	9.8	20.04	29
C ₅ H ₉ NO ₂	<i>N</i> -formyl morpholine	0.01475	0.6441	16.6	11.7	10.0	22.64	54
C ₃ H ₈ O ₃	Glycerol (glycerin)	0.00009	0.0039	17.4	12.1	29.3	36.16	29
C ₇ H ₁₆	Heptane	0.01328	0.5801	15.3	0.0	0.0	15.30	53
C ₇ H ₁₆	Heptane	0.01190	0.5197	15.3	0.0	0.0	15.30	49
C ₇ H ₁₆	Heptane	0.01194	0.5212	15.3	0.0	0.0	15.30	36
C ₇ H ₁₆	Heptane	0.01202	0.5248	15.3	0.0	0.0	15.30	52
C ₇ H ₁₆ O	Heptanol	0.01258	0.5495	15.1	8.0	13.0	21.47	32
C ₁₆ H ₃₄	Hexadecane	0.01161	0.5069	16.3	0.0	0.0	16.30	32
C ₁₆ H ₃₄	Hexadecane	0.01420	0.6201	16.3	0.0	0.0	16.30	49
C ₆ H ₁₄	Hexane	0.01318	0.5754	14.9	0.0	0.0	14.90	32
C ₆ H ₁₄	Hexane	0.01190	0.5197	14.9	0.0	0.0	14.90	49
C ₆ H ₁₄ O	Hexanol	0.01174	0.5124	14.1	8.6	12.7	20.83	32
C ₅ H ₅ I	Iodobenzene	0.00592	0.2585	19.5	6.0	6.1	21.29	29
C ₅ H ₁₂ O	Isoamyl alcohol	0.00809	0.3530	15.8	5.2	13.3	21.30	30
C ₄ H ₁₀ O	Isobutanol	0.00696	0.3041	15.1	5.7	15.9	22.66	2
C ₄ H ₁₀ O	Isobutanol	0.00690	0.3014	15.1	5.7	15.9	22.66	29

TABLE 10.1 (CONTINUED)
CO₂ Solubility in Various Solvents at T = 25°C and a CO₂ Partial Pressure of 1 Atmosphere

Formula	Solvent	Mole Fraction CO ₂	Actual/Ideal	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Ref.
C ₆ H ₁₂ O ₂	Isobutyl acetate	0.02500	1.0919	15.1	3.7	6.3	16.77	29
C ₄ H ₉ Cl	Isobutyl chloride	0.01410	0.6158	14.7	5.3	0.9	15.65	29
C ₃ H ₈ O	Isopropanol	0.00654	0.2856	15.8	6.1	16.4	23.58	38
CH ₄ O	Methanol	0.00641	0.2797	15.1	12.3	22.3	29.61	32
CH ₄ O	Methanol	0.00564	0.2463	15.1	12.3	22.3	29.61	30
CH ₄ O	Methanol	0.00563	0.2460	15.1	12.3	22.3	29.61	31
CH ₄ O	Methanol	0.00635	0.2774	15.1	12.3	22.3	29.61	29
C ₃ H ₆ O ₂	Methyl acetate	0.02089	0.9123	15.5	7.2	7.6	18.70	29
C ₃ H ₆ O ₂	Methyl acetate	0.02253	0.9837	15.5	7.2	7.6	18.70	34
C ₇ H ₁₄	Methyl cyclo hexane	0.00927	0.4046	16.0	0.0	1.0	16.03	55
C ₇ H ₁₂ O	2-Methylcyclohexanone	0.01660	0.7249	17.6	6.3	4.7	19.28	56
C ₄ H ₈ O	Methyl ethyl ketone	0.02444	1.0672	16.0	9.0	5.1	19.05	33
C ₁₁ H ₁₀	1-Methyl naphthalene	0.00674	0.2943	20.6	0.8	4.7	21.14	38
C ₁₉ H ₃₆ O ₂	Methyl oleate	0.02690	1.1747	14.5	3.9	3.7	15.46	38
C ₆ H ₅ NO ₂	Nitrobenzene	0.01020	0.4455	20.0	8.6	4.1	22.15	29
C ₆ H ₅ NO ₂	Nitrobenzene	0.00997	0.4355	20.0	8.6	4.1	22.15	34
C ₅ H ₉ NO	<i>N</i> -methyl-2-pyrrolidone	0.01590	0.6943	18.0	12.3	7.2	22.96	38
C ₉ H ₂₀	Nonane	0.01231	0.5376	15.7	0.0	0.0	15.70	32
C ₉ H ₂₀ O	Nonanol	0.01481	0.6465	15.3	7.3	12.0	20.77	32
C ₈ H ₁₈	Octane	0.01254	0.5474	15.5	0.0	0.0	15.50	32
C ₈ H ₁₈	Octane	0.01210	0.5284	15.5	0.0	0.0	15.50	49
C ₈ H ₁₈ O	Octanol	0.00930	0.4062	17.0	3.3	11.9	21.01	50
C ₁₈ H ₃₄ O ₂	Oleic acid	0.01570	0.6856	16.2	3.1	5.5	17.39	38
C ₁₅ H ₃₂	Pentadecane	0.01167	0.5094	16.8	0.0	0.0	16.80	32
C ₅ H ₁₂	Pentane	0.01385	0.6048	14.5	0.0	0.0	14.50	32
C ₅ H ₁₂ O	Pentanol	0.00806	0.3519	15.9	4.5	13.9	21.59	29
C ₇ F ₁₆	Perfluoroheptane	0.02088	0.9118	12.0	0.0	0.0	12.00	41
C ₈ H ₇ N	Phenyl acetonitrile	0.00957	0.4180	19.5	12.3	3.8	23.37	34
C ₃ H ₈ O	Propanol	0.00782	0.3414	16.0	6.8	17.4	24.60	57
C ₃ H ₈ O	Propanol	0.00680	0.2969	16.0	6.8	17.4	24.60	58
C ₃ H ₈ O	Propanol	0.00759	0.3316	16.0	6.8	17.4	24.60	29
C ₃ H ₆ O ₂	Propionic acid	0.01234	0.5390	14.7	5.3	12.4	19.95	29
C ₃ H ₅ N	Propionitrile	0.01677	0.7323	15.3	14.3	5.5	21.65	34
C ₅ H ₁₀ O ₂	Propyl acetate	0.02429	1.0607	15.3	4.3	7.6	17.62	34
C ₃ H ₆ Br ₂	Propylene bromide	0.00977	0.4266	17.4	7.5	2.9	19.17	29
C ₄ H ₆ O ₃	Propylene carbonate	0.01074	0.4688	20.0	18.0	4.1	27.22	32
C ₄ H ₆ O ₃	Propylene carbonate	0.01162	0.5073	20.0	18.0	4.1	27.22	33
C ₄ H ₆ O ₃	Propylene carbonate	0.01210	0.5284	20.0	18.0	4.1	27.22	38
C ₅ H ₅ N	Pyridine	0.01193	0.5211	19.0	8.8	5.9	21.75	29
C ₅ H ₅ N	Pyridine	0.01169	0.5104	19.0	8.8	5.9	21.75	30
C ₅ H ₅ N	Pyridine	0.01198	0.5231	19.0	8.8	5.9	21.75	34
C ₉ H ₇ N	Quinoline	0.00912	0.3983	19.4	7.0	7.6	21.98	38
C ₄ H ₈ O ₂ S	Sulfolane	0.00799	0.3489	18.4	16.6	7.4	25.86	32
C ₁₄ H ₃₀	Tetradecane	0.01171	0.5115	16.2	0.0	0.0	16.20	32
C ₁₄ H ₃₀	Tetradecane	0.01360	0.5939	16.2	0.0	0.0	16.20	49
C ₄ H ₈ O	Tetrahydrofuran	0.02700	1.1790	16.8	5.7	8.0	19.46	38
C ₁₀ H ₁₂	Tetrahydronaphthalene	0.00752	0.3285	19.6	2.0	2.9	19.91	38
C ₇ H ₉ N	<i>m</i> -Toluidine	0.00635	0.2771	19.3	3.8	10.1	22.11	29

TABLE 10.1 (CONTINUED)
CO₂ Solubility in Various Solvents at T = 25°C and a CO₂ Partial Pressure of 1 Atmosphere

Formula	Solvent	Mole Fraction CO ₂	Actual/Ideal	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Ref.
C ₇ H ₉ N	<i>o</i> -Toluidine	0.00605	0.2641	19.4	4.2	10.7	22.55	29
C ₇ H ₈	Toluene	0.00994	0.4340	18.0	1.4	2.0	18.16	29
C ₇ H ₈	Toluene	0.01010	0.4411	18.0	1.4	2.0	18.16	55
C ₇ H ₈	Toluene	0.01042	0.4550	18.0	1.4	2.0	18.16	52
C ₇ H ₈	Toluene	0.01039	0.4536	18.0	1.4	2.0	18.16	34
C ₁₂ H ₂₇ O ₄ P	Tributyl phosphate	0.03550	1.5502	16.3	6.3	4.3	18.00	38
C ₂ C ₁₃ F ₃	Trichlorotrifluoroethane	0.01823	0.7961	14.7	1.6	0.0	14.79	59
C ₁₃ H ₂₈	Tridecane	0.01175	0.5132	16.4	0.0	0.0	16.40	32
C ₆ H ₁₅ N	Triethylamine	0.02321	1.0134	17.8	0.4	1.0	17.83	33
C ₈ H ₁₈	2,2,4-Trimethylpentane	0.01387	0.6057	14.1	0.0	0.0	14.10	59
C ₁₁ H ₂₄	Undecane	0.01148	0.5014	16.0	0.0	0.0	16.00	32
C ₁₁ H ₂₄ O	Undecanol	0.01708	0.7457	15.4	6.7	11.2	20.19	32
H ₂ O	Water	0.00070	0.0306	15.5	16.0	42.3	47.81	35
H ₂ O	Water	0.00059	0.0258	15.5	16.0	42.3	47.81	29
H ₂ O	Water	0.00060	0.0261	15.5	16.0	42.3	47.81	30
H ₂ O	Water	0.00061	0.0267	15.5	16.0	42.3	47.81	31
C ₈ H ₁₀	<i>o</i> -Xylene	0.00994	0.4339	17.8	1.0	3.1	18.10	60
C ₈ H ₁₀	<i>m</i> -Xylene	0.01042	0.4552	17.4	1.0	3.1	17.70	29
C ₈ H ₁₀	<i>m</i> -Xylene	0.01063	0.4642	17.4	1.0	3.1	17.70	60
C ₈ H ₁₀	<i>p</i> -Xylene	0.01087	0.4744	17.4	1.0	3.1	17.70	60

Note: $x_{CO_2}^{ideal} = 0.0229$.

$$\delta_d^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{d_i}}{\sum_{i=1}^n x_i}, \quad (10.8)$$

$$\delta_p^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{p_i}}{\sum_{i=1}^n x_i}, \quad (10.9)$$

$$\delta_h^{CO_2} = \frac{\sum_{i=1}^n x_i \delta_{h_i}}{\sum_{i=1}^n x_i}. \quad (10.10)$$

TABLE 10.2
Solvents Showing Greater Than Ideal Solubility for
CO₂ at 25°C

Solvent	$x_{CO_2}^{Exptl}$	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_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

Note: $P_{CO_2} = 1$, $x_{CO_2}^{ideal} = 0.0229$.

A second HSP evaluation was undertaken using a subset of data set # 1. The subset was chosen to consist of solvents where the measured CO₂ solubility was greater than the ideal solubility at 25°C and $p_{CO_2} = .1$ MPa, $x_{CO_2}^{ideal} = 0.0229$. (The calculation of this ideal solubility value is given in the Appendix 10.A.1). This data subset, hereafter called *data set #2*, is comprised of the 10 solvents shown in Table 10.2.

These two evaluations resulted in the following HSP values for CO₂ at 25°C:

Data set #1:

$$\delta_d = 16.4 \text{ MPa}^{1/2}$$

$$\delta_p = 5.5 \text{ MPa}^{1/2}$$

$$\delta_h = 5.8 \text{ MPa}^{1/2}$$

Data set #2:

$$\delta_d = 15.6 \text{ MPa}^{1/2}$$

$$\delta_p = 5.2 \text{ MPa}^{1/2}$$

$$\delta_h = 5.8 \text{ MPa}^{1/2}$$

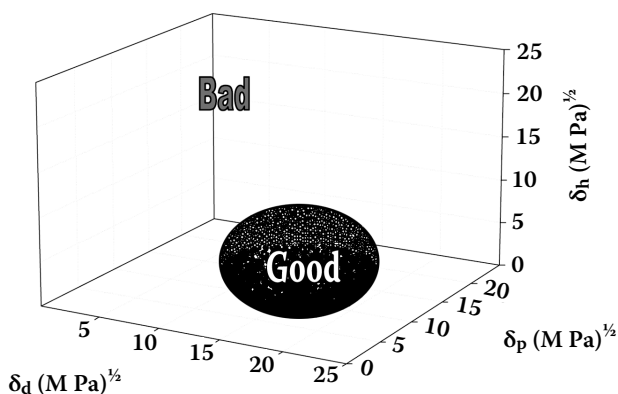


FIGURE 10.1 Interaction radius, where R_o incorporates all good solvents and excludes all bad solvents.

The HSP values derived from the two data sets gave identical results in terms of the hydrogen bonding parameter, δ_h , and similar values for δ_p and δ_d .

To assist in the determination of a final set of HSP values, a second approach, known as the *solubility sphere*,⁵⁻⁷ was also used to evaluate the published solubility data and resulting HSP values for data set #1 and data set #2. The solubility sphere approach is essentially a trial and error method, whereby all the good solvents are included within a sphere in δ_d , δ_p , and δ_h space, whereas simultaneously excluding all the bad solvents. The criterion of good versus bad is arbitrary and is defined based on the particular interaction being evaluated, such as degree of polymer swelling, dissolution, barrier breakthrough time, permeation coefficients higher than a given value, suspension time of a pigment, etc. In this evaluation, we are concerned with optimizing solvents for their CO_2 solubility. Based upon the selected criteria, two-dimensional plots are produced for δ_d vs. δ_p , δ_d vs. δ_h , and δ_p vs. δ_h , and the three circle radii are adjusted until a single optimized radius for all three plots is found. This solubility sphere approach is essentially a trial and error method whereby all the good solvents are included within a sphere in δ_d , δ_p , and δ_h space while simultaneously excluding the bad ones. The resulting radius for the three plots of δ_d vs. δ_p , δ_d vs. δ_h , and δ_p vs. δ_h , is then used to plot a sphere in a three-dimensional plot of δ_d vs. δ_p vs. δ_h . The radius of this sphere is known as the *interaction radius*, R_o , and is considered a fourth parameter in HSP value determinations. Figure 10.1 is a schematic representation of the solubility sphere approach.

The advantage of the solubility sphere approach is that once an interaction radius has been determined, solvents that have not yet been experimentally tested for the desired interaction can be quickly screened and, therefore, should be considered for further study. This solubility sphere evaluation is aided by an equation developed by Skaarup for determining the straight-line distance, R_a , in a plot of δ_d vs. δ_p vs. δ_h between two materials based on their respective HSP values,⁵

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (10.11)$$

where δ_{d2} , δ_{p2} , and δ_{h2} are associated with a given solvent and δ_{d1} , δ_{p1} , and δ_{h1} with the center of the optimized solubility sphere. This equation was developed from plots of experimental data where the leading constant of 4 in the leading right-hand term was found to correctly represent the solubility data as a sphere encompassing the good solvents. An extended discussion of the validity of this coefficient is found in Chapter 2. Further confirmation is found in Chapter 9.

For the present evaluation, a favorable interaction is defined as CO_2 solubility greater than ideal at 25°C and $p_{\text{CO}_2} = 0.1$ MPa, whereas an unfavorable interaction is one where the CO_2 solubility is less than ideal at these same conditions. It is clear that for cases where CO_2 solubility is greater than ideal, and therefore where the (attractive) CO_2 -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) number⁵

$$RED = R_a/R_o \quad (10.12)$$

For an individual solvent, a value of RED < 1 indicates favorable CO₂–solvent interactions, whereas a RED \approx 1 represents a boundary condition between good and bad. Progressively higher values of RED indicate progressively more unfavorable interactions. Computing R_a from Equation 10.11 and the RED from Equation 10.12 allows for easy scanning of large data sets, such as the 101 solvents listed in data set #1. The solubility spheres optimized for data set #1 and data set #2 with the two HSP center points are shown in Figure 10.2a, Figure 10.2b, and Figure 10.2c. As can be seen from these plots, an interaction radius $R_o = 4.0$ for data set #2 incorporates the good solvents, whereas for data set #1, an interaction radius $R_o = 4.7$ is necessary to incorporate the good solvents. In addition, the solubility sphere analysis 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 analysis generated for data set #2 results in the inclusion of only 1 bad solvent (oleic acid). In terms of the solubility sphere technique, occurrences of good solvents falling outside of the sphere radius, and bad solvents falling inside the sphere radius can be viewed as an indication of the goodness of the fit.⁵

CO₂ Solubility in Liquid Solvents, $P_{\text{CO}_2} = 1 \text{ atm.}$, $T = 25^\circ\text{C}$

① Data Set #1

② Data Set #2

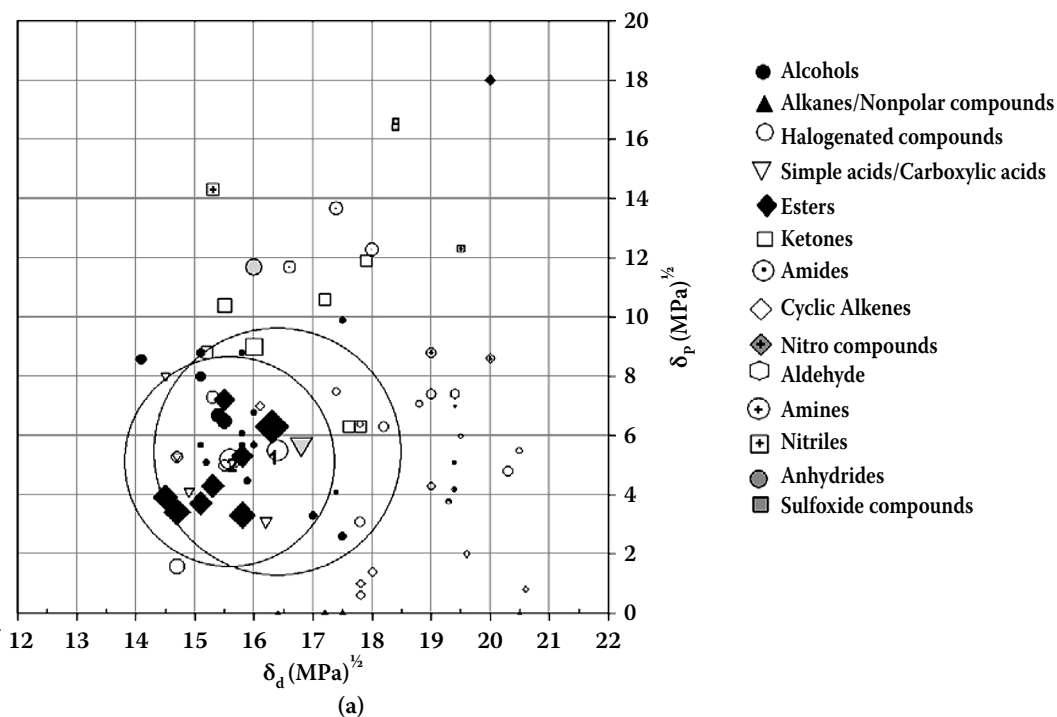


FIGURE 10.2 Two-dimensional plots of CO₂ in organic solvents. (a) δ_p vs. δ_d , (b) δ_h vs. δ_p , and (c) δ_h vs. δ_d .

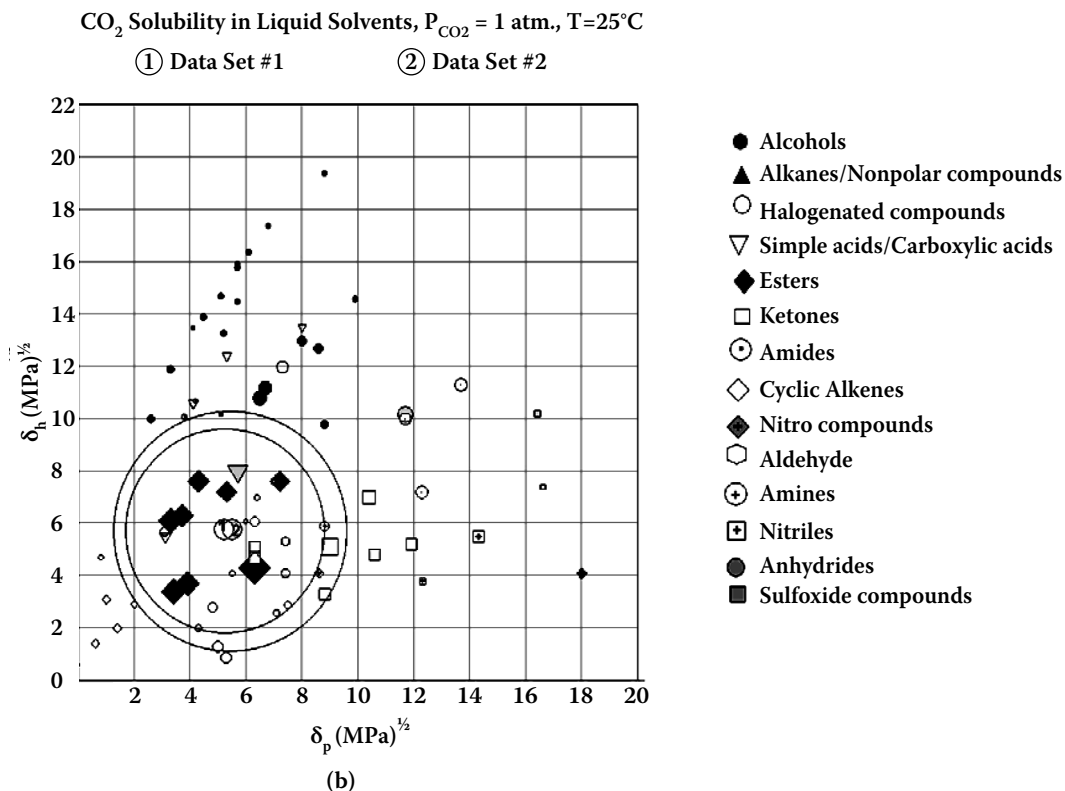


FIGURE 10.2 (Continued)

From the refinement of the two sets of CO₂ HSP values, using the solubility sphere methodology, the HSP values from data set #2 were selected as the optimum reference values for CO₂ at T=25°C;

$$\delta_d = 15.6 \text{ MPa}^{1/2}$$

$$\delta_p = 5.2 \text{ MPa}^{1/2}$$

$$\delta_h = 5.8 \text{ MPa}^{1/2}$$

This determination is further supported based on problems noted by Hansen,⁵ who observed that the approach of using all solvents to establish the center of a solubility sphere can result in this sphere boundary (and center) being determined by the poor solvents or nonsolvents, rather than the best solvents in the middle.

A comparison of these CO₂ values can be made with the large database of HSP values found in *Hansen Solubility Parameters: A User's Handbook*.⁵ Similar values are reported for liquid solvents such as dipropyl ketone: $\delta_d = 15.8 \text{ MPa}^{1/2}$, $\delta_p = 5.7 \text{ MPa}^{1/2}$, and $\delta_h = 4.9 \text{ MPa}^{1/2}$; 1,3-dimethoxybutane: $\delta_d = 15.6 \text{ MPa}^{1/2}$, $\delta_p = 5.5 \text{ MPa}^{1/2}$, and $\delta_h = 5.2 \text{ MPa}^{1/2}$; and ethyl acetate: $\delta_d = 15.8 \text{ MPa}^{1/2}$, $\delta_p = 5.3 \text{ MPa}^{1/2}$, and $\delta_h = 7.2 \text{ MPa}^{1/2}$. It should be noted, however, that the CO₂ optimum HSP reference values correspond to a reference temperature of 25°C and a reference pressure of 90.5 MPa⁸, that is, a higher operating pressure than found in common industrial applications. A methodology for extending this reference set of HSP values to any temperature and pressure has been developed and is discussed in the following sections.

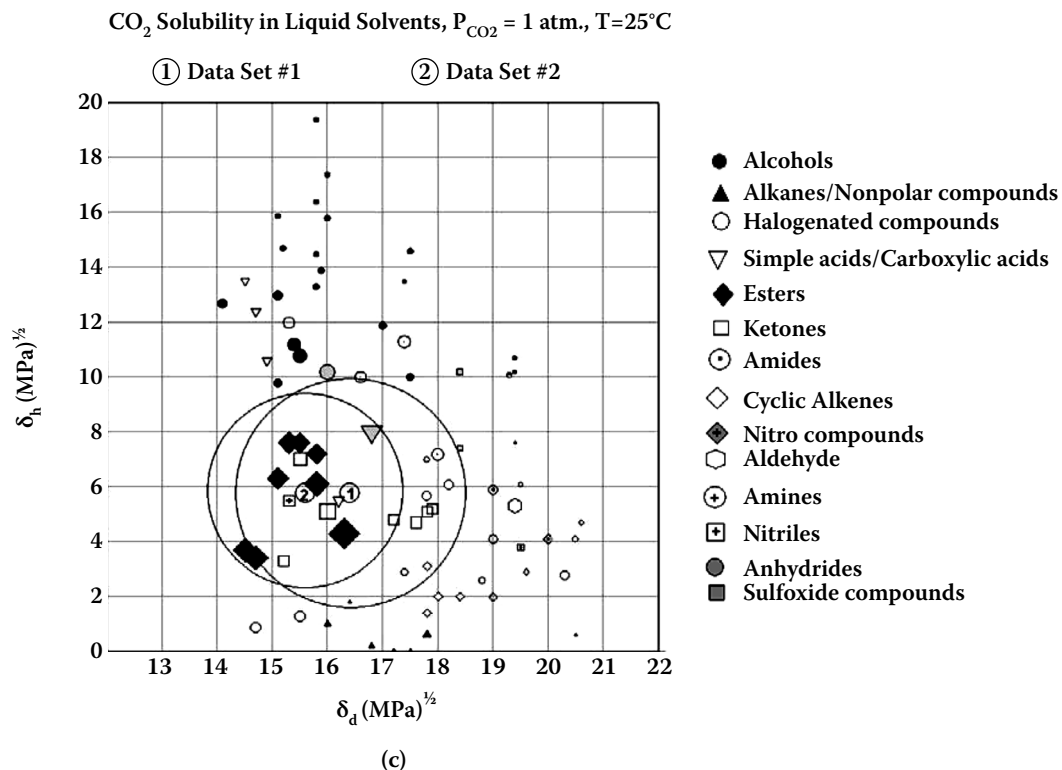


FIGURE 10.2 (Continued)

ONE-COMPONENT HILDEBRAND PARAMETER AS A FUNCTION OF TEMPERATURE AND PRESSURE

Hildebrand's solubility parameter theory was derived from an approximation of the internal pressure of a fluid. This was later termed the cohesive energy density (ced), based on work conducted in 1928,⁹ 1929,¹⁰ 1932,¹¹ and 1950¹² where the two terms, *internal pressure* and *cohesive energy density* were found to be related by the quantity, n , as shown in Equation 10.13:

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{n\Delta E}{V} \quad (10.13)$$

where $(\Delta E/V)$ is defined by Hildebrand as ced, and $(\partial E/\partial V)_T$ is the internal pressure. Hildebrand and coworkers found that for nonpolar/nonassociating liquids, where intermolecular interactions are weak, n is not far from unity⁹⁻¹¹ and the equality of ced and internal pressure is a good approximation. This same work also demonstrates that n is near unity for nonpolar liquids and also for polar liquids where the dipole moment is less than 2 D, and where specific interactions (particularly hydrogen bonding) are largely absent. 1 D is equal to 1.0×10^{-18} (ESO) or 3.336×10^{-30} Cm. Whereas no direct evaluation of the value of n has been found in the literature for carbon dioxide (CO₂), a comparison of the values found by Hildebrand and others¹³⁻¹⁶ strongly suggests that the value of n for CO₂ is expected to be near unity. As a result, the internal pressure and ced are approximately equal.

Accordingly, Hildebrand's solubility parameter, defined as the square root of the ced,¹² can also be approximated by the square root of the internal pressure for nonpolar/nonassociating fluids.

$$\delta = \left(\frac{\Delta E}{V} \right)_T^{1/2} \approx \left(\frac{\partial E}{\partial V} \right)_T^{1/2} \quad (10.14)$$

And the internal pressure can be calculated from the thermodynamic equation of state, Equation 10.15.

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (10.15)$$

so that

$$\delta^2 \approx \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (10.16)$$

Total (one-component) solubility parameters can therefore be calculated using an EOS of the form, $P = f(\rho, T)$. This approach is used in this work to calculate the total solubility parameter for pure CO₂, using the empirical EOS of Huang et al.¹⁷

$$P = \rho R T \left[\begin{array}{l} 1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp(-c_{21} \rho'^2) + b_8 \rho'^4 \exp(-c_{21} \rho'^2) \\ + c_{22} \rho'^2 \exp[-c_{27} (\Delta T)^2] + c_{23} \frac{\Delta \rho}{\rho} \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\ + c_{24} \frac{\Delta \rho}{\rho} \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \end{array} \right] \quad (10.17)$$

where

$$T' = T/T_c; \quad \Delta T = 1 - T'; \quad \rho' = \rho/\rho_c; \quad \Delta \rho = 1 - 1/\rho' \quad (10.18)$$

and,

$$\begin{aligned} b_2 &= \left(c_1 + \frac{c_2}{T'} + \frac{c_3}{T'^2} + \frac{c_4}{T'^3} + \frac{c_5}{T'^4} + \frac{c_6}{T'^5} \right); & b_6 &= \left(\frac{c_{14}}{T'} \right) \\ b_3 &= \left(c_7 + \frac{c_8}{T'} + \frac{c_9}{T'^2} \right); & b_7 &= \left(\frac{c_{15}}{T'^3} + \frac{c_{16}}{T'^4} + \frac{c_{17}}{T'^5} \right) \\ b_4 &= \left(c_{10} + \frac{c_{11}}{T'} \right); & b_8 &= \left(\frac{c_{18}}{T'^3} + \frac{c_{19}}{T'^4} + \frac{c_{20}}{T'^5} \right) \\ b_5 &= \left(c_{12} + \frac{c_{13}}{T'} \right) \end{aligned} \quad (10.19)$$

The state constants (c_i) are as defined in the Huang reference.

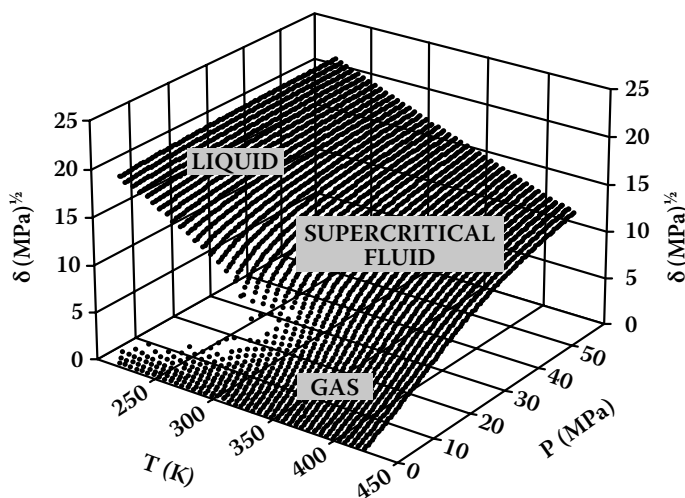


FIGURE 10.3 Total (one-component) solubility parameter of pure CO₂ calculated using Equation 10.16 and Equation 10.17.

It should be noted that there are a wide range of available EOSs for carbon dioxide and a comparison of Huang's and others can be found in a review by Span and Wagner.¹⁸

These equations and the appropriate derivatives are then used to calculate CO₂ solubility parameters over the temperature and pressure range for which the EOS is stated to be valid (220 K ≤ T ≤ 420 K, and 0.1 MPa ≤ P ≤ 60 MPa). Figure 10.3 is a plot of the resulting one-component solubility parameters.

Other notable works include Allada's¹⁹ proposed generalized solubility parameter (that uses analytical equations of state (EOSs), such as Lee-Kelser or modified Redlich-Kwong for evaluation), the modified solubility parameter proposed by Ikushima et al.²⁰ (where the solubility parameter is expressed in terms of reduced parameters), and the EOS model proposed by Panayiotou.²¹ This later work utilizes the lattice fluid theory and a lattice fluid hydrogen bonding model to evaluate solubility parameters and two separate components: physical (or van der Waals) and chemical (or specific, e.g., hydrogen bonding).

THREE-COMPONENT (HANSEN) SOLUBILITY PARAMETERS — PURE CO₂

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. The pressure volume temperature (PVT) EOS that calculates the total (Hildebrand) CO₂ solubility parameter value (Equation 10.16) was used to determine the combination of pressure and molar volume

corresponding to T = 25°C and $\delta_t = \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right)^{1/2} = 17.4 \text{ MPa}^{1/2}$ that gave:

$$P = 91.7 \text{ MPa} \tag{10.20}$$

$$V_{\text{CO}_2} = 39.13 \text{ cm}^3/\text{mole}$$

HSP values at other pressures and temperatures will be based on this set of HSP values, using pressure and temperature integral functions, which will be derived subsequently.

Both temperature and pressure will influence total solubility parameters. However, other than Giddings' extension of the one-component (Hildebrand) solubility parameter model to supercritical fluids,²² 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.^{5,7,23} 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 10.3, where the total CO₂ solubility parameter was calculated using Equation 10.16 and Equation 10.17.

The temperature and pressure dependence of individual HSPs as a function of temperature and pressure has apparently not been evaluated for any liquid, gas, or supercritical fluid. A suggested approach for this calculation is outlined as follows where the temperature derivatives, originally derived by Hansen and Beerbower,²⁴ are verified. Pressure derivatives, not found in any literature search, are derived in a manner parallel to the temperature derivatives. In addition, integral forms are developed.

TEMPERATURE AND PRESSURE EFFECTS ON HSPS: δ_d

Hildebrand¹² in his 1950 work considered the effect of temperature on solubility parameters by recalling the expression for the dependence of E on the volume:

$$E = -\frac{k}{V^n} \quad (10.21)$$

where k is a constant dependent upon the nature of the particular liquid, and n is about 1.5 for normal (nonassociating or van der Waals) liquids. Substituting Equation 10.21 into Hansen's definition for the dispersion solubility parameter,

$$\delta_d = -\frac{k^{1/2}}{V^{(n+1)/2}} \quad (10.22)$$

allows one to calculate the change in δ_d produced by a change in volume by differentiating Equation 10.22.

$$\begin{aligned} \left(\frac{\partial \delta_d}{\partial V}\right)_{T,P} &= k^{1/2} \left(\frac{n+1}{2}\right) \left[V^{-\frac{(n+1)}{2}}\right] \left[V^{-1}\right] \\ &= -\delta_d \left(\frac{n+1}{2}\right) \left(\frac{1}{V}\right) \end{aligned} \quad (10.23)$$

and,

$$\frac{\partial \delta_d}{\delta_d} = -1.25 \frac{\partial V}{V} \quad (10.24)$$

Equation 10.24 can now be differentiated for either a change in temperature or pressure, or integrated. Results of both derivations are shown in Table 10.4 and Table 10.5.

TEMPERATURE AND PRESSURE EFFECTS ON HSPs: δ_p

The first values of δ_p were assigned by Hansen and Skaarup using the Böttcher equation, shown here as Equation 10.25,

$$\delta_p^2 = \frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2 \left[\frac{\text{cal}}{\text{cm}^3} \right] \quad (10.25)$$

A simplified equation was later developed by Hansen and Beerbower,²⁴

$$\delta_p = \frac{37.4\mu}{V^{1/2}} \left[\text{MPa}^{1/2} \right] \quad (10.26)$$

where μ is the dipole moment (in Debyes). This equation is utilized for determining the change in δ_p with respect to either temperature at constant pressure or with respect to pressure at constant temperature.

$$\begin{aligned} \left(\frac{\partial \delta_p}{\partial V} \right)_{T,P} &= - \left(\frac{1}{2} \right) V^{-3/2} (37.4\mu) \\ &= - \frac{1}{2V} \left(\frac{37.4\mu}{V^{1/2}} \right) = - \frac{\delta_p}{2V} \end{aligned} \quad (10.27)$$

and

$$\frac{\partial \delta_p}{\delta_p} = - \frac{\partial V}{2V} \quad (10.28)$$

Equation 10.28 can now be differentiated for either a change in temperature or pressure, or integrated. Results of both derivations are shown in Table 10.4 and Table 10.5.

TEMPERATURE AND PRESSURE EFFECTS ON HSPs: 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,⁵ however, 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 δ_h , which involves experimental heats of vaporization data for hydrogen-bonded substances, which, in turn, are taken from Bondi.²⁵

From Equation 10.4, the hydrogen bonding solubility parameter, δ_h , is defined as:

$$\delta_h^2 = \frac{E_h}{V} \quad (10.29)$$

so that

$$E_h = V\delta_h^2 \quad (10.30)$$

where E_h is the hydrogen bonding contribution to the total cohesive energy. Differentiating Equation 10.30 with respect to temperature at constant pressure,

$$\begin{aligned} \left(\frac{\partial E_h}{\partial T}\right)_P &= V(2\delta_h)\left(\frac{\partial \delta_h}{\partial T}\right)_P + \delta_h^2\left(\frac{\partial V}{\partial T}\right)_P \\ 2V\delta_h\left(\frac{\partial \delta_h}{\partial T}\right)_P &= \left(\frac{\partial E_h}{\partial T}\right)_P - \delta_h^2\left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \quad (10.31)$$

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

Simplifying, rearranging terms, and substituting in the isobaric coefficient of thermal expansion, α ,

$$\left(\frac{\partial \delta_h}{\partial T}\right)_P = \delta_h \left(\frac{\left(\frac{\partial E_h}{\partial T}\right)_P}{2E_h} - \frac{\alpha}{2} \right) \quad (10.32)$$

Bondi,²⁵ 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 (dE_h/dT) were constructed²³ for various functional groups and are shown in [Table 10.3](#) along with experimentally derived values of E_h .²⁵

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 Equation 10.32,

$$\begin{aligned} \left(\frac{\partial \delta_h}{\partial T}\right)_P &= -\delta_h \left(\frac{2.64 \times 10^{-3}}{2} + \frac{\alpha}{2} \right) \\ &= -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2} \right) \end{aligned} \quad (10.33)$$

TABLE 10.3
Experimentally Determined Values of E_h and (dE_h/dT)

Functional Group	Hydrogen-Bond Parameter, E_h (cal/mole)	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

The change in the δ_h with respect to pressure at constant temperature is obtained by utilizing the relationship:

$$\frac{\partial \delta_h}{\partial P} = \frac{\partial \delta_h}{\partial T} \cdot \frac{\partial T}{\partial P} \quad (10.34)$$

where,

$$\frac{\partial T}{\partial P} = -\frac{\beta}{\alpha} \quad (10.35)$$

so that

$$\left(\frac{\partial \delta_h}{\partial P} \right)_T = \delta_h \left(\frac{1.32 \times 10^{-3} \beta}{\alpha} + \frac{\beta}{2} \right) \quad (10.36)$$

Equation 10.36 can be rearranged to a form that can also be easily integrated, [Table 10.5](#).

The derivative forms are summarized in Table 10.4 and the integrated forms in Table 10.5.

The total solubility parameter, incremented for small changes in temperature and pressure, can be calculated from equations (derivative form) in Table 10.4,

TABLE 10.4
Equations (Derivative Form) for the Temperature and Pressure Effects on HSP

	Temperature Increment	Pressure Increment
δ_d	$\left(\frac{\partial \delta_d}{\partial T} \right)_P = -1.25 \delta_d \alpha$	$\left(\frac{\partial \delta_d}{\partial P} \right)_T = 1.25 \delta_d \beta$
δ_p	$\left(\frac{\partial \delta_p}{\partial T} \right)_P = -\delta_p \left(\frac{\alpha}{2} \right)$	$\left(\frac{\partial \delta_p}{\partial P} \right)_T = \delta_p \left(\frac{\beta}{2} \right)$
δ_h	$\left(\frac{\partial \delta_h}{\partial T} \right)_P = -\delta_h \left(1.32 \times 10^{-3} + \frac{\alpha}{2} \right)$	$\left(\frac{\partial \delta_h}{\partial P} \right)_T = \delta_h \left(\frac{1.32 \times 10^{-3} \beta}{\alpha} + \frac{\beta}{2} \right)$

TABLE 10.5
Equations (Integrated Form) for the Temperature
and Pressure Effects on HSP

$$\delta_d \quad \frac{\delta_{dref}}{\delta_d} = \left(\frac{V_{ref}}{V} \right)^{-1.25}$$

$$\delta_p \quad \frac{\delta_{pref}}{\delta_p} = \left(\frac{V_{ref}}{V} \right)^{-0.5}$$

$$\delta_h \quad \frac{\delta_{href}}{\delta_h} = \exp \left[-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right]$$

$$\delta^2 = \left[\delta_d + \left(\frac{\partial \delta_d}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_d}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_p + \left(\frac{\partial \delta_p}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_p}{\partial P} \right)_T \Delta P \right]^2 + \left[\delta_h + \left(\frac{\partial \delta_h}{\partial T} \right)_p \Delta T + \left(\frac{\partial \delta_h}{\partial P} \right)_T \Delta P \right]^2 \quad (10.37)$$

or from the equations (integrated form) in Table 10.5

$$\delta^2 = \left[\frac{\delta_{dref}}{\left(\frac{V_{ref}}{V} \right)^{-1.25}} \right]^2 + \left[\frac{\delta_{pref}}{\left(\frac{V_{ref}}{V} \right)^{-0.5}} \right]^2 + \left[\frac{\delta_{href}}{\exp \left(-1.32 \times 10^{-3} (T_{ref} - T) - \ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right)} \right]^2 \quad (10.38)$$

where the reference values are as determined earlier; $\delta_{dref} = 15.6 \text{ MPa}^{1/2}$, $\delta_{pref} = 5.2 \text{ MPa}^{1/2}$, $\delta_{href} = 5.8 \text{ MPa}^{1/2}$, $V_{ref} = 39.13 \text{ cm}^3/\text{mole}$, and $T_{ref} = 298.15 \text{ K}$.

CO_2 HSP values calculated with the equations in Table 10.4, as a function of temperature and pressure, are shown in the CO_2 HSP surface diagrams illustrated in Figure 10.4.

From this work though, CO_2 HSP values at a temperature of 25°C and a pressure of 200 bar, $\delta_d = 12.2 \text{ MPa}^{1/2}$, $\delta_p = 4.7 \text{ MPa}^{1/2}$, and $\delta_h = 5.2 \text{ MPa}^{1/2}$ can also be compared to liquid solvent HSP values. Comparable liquid solvents include chlorodifluoromethane: $\delta_d = 12.3 \text{ MPa}^{1/2}$, $\delta_p = 6.3 \text{ MPa}^{1/2}$, and $\delta_h = 5.7 \text{ MPa}^{1/2}$; isopropyl ether: $\delta_d = 13.7 \text{ MPa}^{1/2}$, $\delta_p = 3.9 \text{ MPa}^{1/2}$, and $\delta_h = 2.3 \text{ MPa}^{1/2}$; and vinyl trifluoroacetate: $\delta_d = 13.9 \text{ MPa}^{1/2}$, $\delta_p = 4.3 \text{ MPa}^{1/2}$, and $\delta_h = 7.6 \text{ MPa}^{1/2}$. It is also interesting to note that the total solubility parameter value of hexane, a solvent that CO_2 is often closely compared to²⁶⁻²⁸ ($\delta_t = 14.9 \text{ MPa}^{1/2}$) is very near the total solubility parameter of CO_2 (at 25°C and 200 bar), $\delta_t = 14.0 \text{ MPa}^{1/2}$. Yet, when the two are compared in terms of HSP values, little similarity is noted; hexane: $\delta_d = 14.9 \text{ MPa}^{1/2}$, $\delta_p = 0.0 \text{ MPa}^{1/2}$, and $\delta_h = 0.0 \text{ MPa}^{1/2}$.

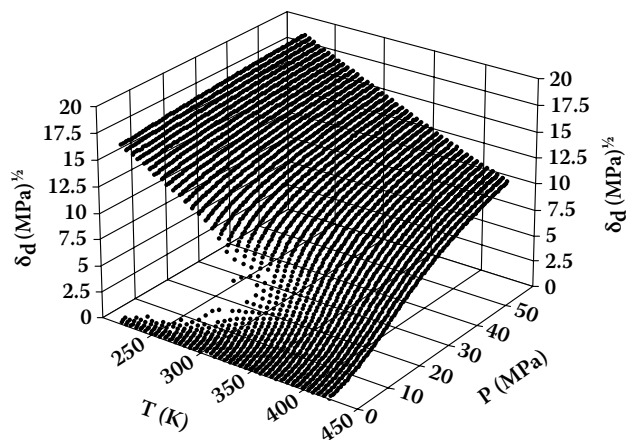
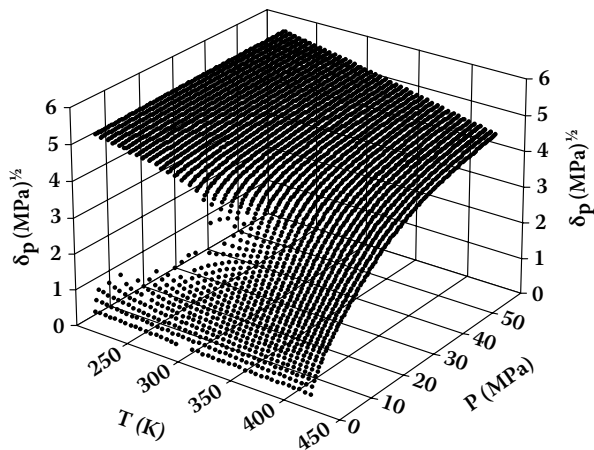
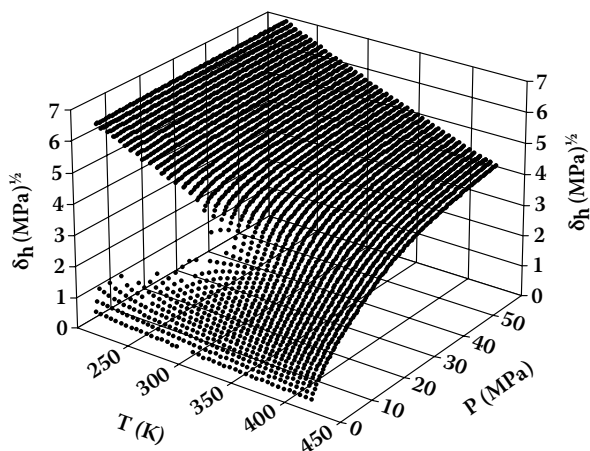
(a) CO₂ dispersion parameter as a function of temperature and pressure.(b) CO₂ polar parameter as a function of temperature and pressure 45K(c) CO₂ hydrogen bonding parameter as a function of temperature and pressure

FIGURE 10.4 HSP values for CO₂ as a function of T and P . (a) CO₂ dispersion parameter as a function of temperature and pressure. (b) CO₂ polar parameter as a function of temperature and pressure. (c) CO₂ hydrogen bonding parameter as a function of temperature and pressure.

CONCLUSION

A set of Hansen solubility parameters at $T = 25^\circ\text{C}$ have been determined for CO_2 , based on the room temperature solubility in different liquid solvents of known HSP values: $\delta_d = 15.6 \text{ MPa}^{1/2}$, $\delta_p = 5.2 \text{ MPa}^{1/2}$, and $\delta_h = 5.8 \text{ MPa}^{1/2}$. Further, this set of HSPs were refined using the RED affinity number and Hansen solubility plots to correlate the solubility of carbon dioxide in the solvents identified in Table 10.1.

It is important to note that the solubility parameter, or rather the difference in solubility parameters, for a given solvent–solute combination has been foremost in determining the mutual solubility of the system.⁵ An analogy to “like dissolves like” is appropriate. Therefore, the accuracy to which the solubility parameters for a binary pair can be known will be valuable in predicting the system's behavior. This work introduces a theoretical methodology for generating solubility parameter values, both one-component Hildebrand and three-component Hansen parameters, for a pure supercritical fluid, using CO_2 as an example. The ability to express molecular interactions, in terms of HSPs, for a pure fluid solvent in a way that unites the liquid, gas, and supercritical phases, represents an advancement in the understanding of the role of solvents in both existing and new applications.

ACKNOWLEDGMENTS

Special thanks to James Rubin of Los Alamos National Laboratory for his excellent assistance and collaboration in the development of this work.

CHAPTER 10 ADDENDUM

Research has been the key to many progressive developments. Significant steps toward improved understanding have been made with limited resources, and these result in still other improvements in the same direction when other resources are applied. The HSP for carbon dioxide reported in the chapter (δ_d , δ_p , and δ_h equal to $15.6 \text{ MPa}^{1/2}$, $5.2 \text{ MPa}^{1/2}$, and $5.8 \text{ MPa}^{1/2}$) were found by a plotting technique with a radius for the solubility sphere of $4.0 \text{ MPa}^{1/2}$. The data used were collected from a wide variety of sources, and the criterion for a good solvent was solubility in excess of the theoretical. A computer analysis of the same data has now shown that it is possible to describe the solubility of carbon dioxide with a slightly different solubility sphere. The δ_d , δ_p , and δ_h values $15.7 \text{ MPa}^{1/2}$, $6.3 \text{ MPa}^{1/2}$, and $5.7 \text{ MPa}^{1/2}$ were found to give a perfect data fit of 1.000 (versus 0.981) with a radius of only $3.3 \text{ MPa}^{1/2}$. Both correlations emphatically show the ability of this procedure, whether by hand or by computer, to correlate gas/liquid solubility data for a wide variety of chemically different solvents. It has not been possible, nor has it been deemed necessary, to revise the contents of this chapter using these slightly different numbers. This note is only to indicate why a slightly different set of HSP is reported elsewhere in this handbook (Table A-1 and Chapter 13, Table 13.4).

SYMBOLS SPECIAL TO THIS CHAPTER

K_H	Henry's law constant (Equation 10.5)
L	Ostwald coefficient in Equation 10.7
P	Pressure
a_i	Activity coefficient of the "i"th component in Appendix 10.A.1, Equation 10.A.1
f_i	Fugacity of the "i"th component in Appendix 10.A.1, Equation 10.A.1
f_i°	Fugacity at standard state in Appendix 10.A.1, Equation 10.A.1
k	Constant in Equation 10.21–Equation 10.23
p_i	Partial pressure of the "i"th component in Equation 10.A.2
p_i^s	Saturation pressure of the "i"th component in Equation 10.A.2
Ω	Bunsen coefficient in Equation 10.6
β	Compressibility
ρ	Density

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APPENDIX 10.A.1: IDEAL SOLUBILITY OF GASES IN LIQUIDS AND PUBLISHED CO₂ SOLUBILITY DATA.

Published CO₂ gas solubility data in 103 liquid solvents were gathered from the available literature and is presented in [Table 10.1](#). Two of these solvents, triethylamine and 1,4-dioxane were subsequently deleted from the data set based on their known tendency to chemically react with CO₂.¹

IDEAL SOLUBILITY OF GASES IN LIQUIDS

Solutions that come close to approximating ideal solutions are those which are very dilute, or those where the molecular species are so nearly alike that a given molecule is subject to the same intermolecular forces (both attractive and repulsive) in the mixture as in its own pure phase. (In very dilute solutions, the intermolecular forces on a solute molecule may be quite different than in the pure solute phase, but the solute molecules are far enough apart that solute–solute interactions do not manifest themselves.) The concept of an ideal solution is often an appropriate approximation

TABLE 10.A.1
Ideal Carbon Dioxide
Solubility Calculated
Using Raoult's Law

T (°C)	$P_{\text{CO}_2}^s$ (atm)	$x_{\text{CO}_2}^{\text{ideal}} = 1/P_{\text{CO}_2}^s$
0	34.40	0.0291
15	50.19	0.0199
20	56.60	0.0177
25	63.50	0.0157
30	71.12	0.0141

Note: $p_{\text{CO}_2} = 1$ atm.

for gases dissolved in liquids, as at modest pressures; most gases are only sparingly soluble in typical liquids.²

Thermodynamically, an ideal solution is defined as one in which the activity, a , equals the mole fraction, x_i , over the entire composition range and over a nonzero range of temperature and pressure.³

$$x_i = a_i = \frac{f_i}{f_i^o} \quad (10.A.1)$$

The activity of a substance gives an indication of how active a substance is relative to its standard state, as it provides a measure of the difference in chemical potential at the state of interest and that at the standard state.⁴ The term *fugacity*, f , was introduced by Lewis⁵ as a measure of thermodynamic escaping tendency and is equal to the effective gas pressure corrected for deviations from ideality. In Equation 10.A.1, f_i is the fugacity of component i at partial pressure p_i , and f_i^o is the fugacity at the saturation pressure of i , P_i^s , at the solution temperature. Equation 10.A.1 is an empirical rule suggested by Lewis and Randall⁵ that assumes imperfect gas mixtures to behave as ideal mixtures.

When deviations from the ideal gas law are small, generally at low pressures, the effect of pressure on the fugacity of component i is negligible, and the fugacity terms in Equation 10.A.1 approach the partial pressure and saturation pressure of i , respectively. In this situation, therefore, the ratio of the partial pressure and saturation pressure can now be used to express the mole fraction, x_i .

$$x_i = \frac{P_i}{P_i^s} \quad (10.A.2)$$

Equation 10.A.2 is known as Raoult's law, and the mole fraction, as calculated from Raoult's law, is referred to as the ideal gas solubility. The ideal solubility calculated from Equation 10.A.2 usually gives correct order of magnitude results provided that P_i^s is not large and the solution temperature is well below the critical temperature of the solvent and not excessively above the critical temperature of the gaseous solute.⁴ Table 10.A.1 evaluates the ideal solubility of CO_2 , calculated using Equation 10.A.2, for the temperature range 0°C to 30°C.

From Table 10.A.1, Raoult's law predicts an ideal CO_2 solubility of $x_{\text{CO}_2}^{\text{ideal}} = 0.0157$ at $T = 25^\circ\text{C}$, and this value has been used in several of the published CO_2 solubility studies.^{2,4,60}

TABLE 10.A.2
Ideal Carbon Dioxide Solubility Calculated Using Raoult's Law and Fugacities

T (°C)	$P_{CO_2}^s$ (atm)	f_{CO_2} $P_{CO_2} = 1 \text{ atm}$	$f_{CO_2}^o$ at $P_{CO_2}^s$	$x_{CO_2}^{ideal}$ $= 1/P_{CO_2}^s$	$x_{CO_2}^{ideal}$ $= f_{CO_2}/f_{CO_2}^o$	% Diff.
0	34.4	.9928	26.51	0.0291	0.0375	28
15	50.19	.9941	36.04	0.0199	0.0276	39
20	56.6	.9944	39.6	0.0177	0.0251	42
25	63.5	.9947	43.3	0.0157	0.0229	46
30	71.12	.9950	47.17	0.0141	0.0211	49

Note: $P_{CO_2} = 1$ atmosphere.

It has been noted by Prausnitz et al.⁴ that the simplest way to reduce Equation 10.A.1 to a more useful form is to rewrite it in the manner suggested by Raoult's law, Equation 10.A.2. In doing so, however, they caution that several assumptions are made, and errors in the use of this estimation technique for the solubility of gases in liquids can be significant, especially, when the saturation pressure of the gas is high. Therefore, in cases where the saturation pressure of the gas is above 1 atmosphere, it is necessary to consider the error in using p_i/p_i^s instead of f_i/f_i^o . Table 10.A.2 gives the saturation pressures of CO₂ for the temperature range 0°C to 30°C, as well as the fugacities and calculated ideal solubilities using both methodologies.

From Table 10.A.2 it appears that the assumption of Raoult's law for the determination of ideal CO₂ solubility in liquids results in significant error. The ideal CO₂ solubility at 25°C and 1 atmosphere partial pressure, as calculated from CO₂ fugacities,⁷ is $x_{CO_2}^{ideal} = 0.0229$ compared with a Raoult's law prediction of $x_{CO_2}^{ideal} = 0.0157$. This value was also used by Gjaldbaek et al.^{8,9} in their work comparing experimental and calculated CO₂ gas solubilities.

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