Gas Solubilities, Vapor–Liquid Equilibria, and Partial Molal Volumes in Some Hydrogen–Hydrocarbon Systems

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Gas solubilities were measured for hydrogen in *n*-pentane, 2,3-dimethylbutane, cyclohexane, *n*-decane, *m*-xylene, 1,4-diethylbenzene, and 1-methylnaphthalene. Vapor–liquid equilibrium ratios (*K*'s) were measured for the second, third, fifth, and sixth of these systems. Partial molal volumes of hydrogen dissolved in the liquid hydrocarbons were measured for all systems except methylnaphthalene. Temperatures and pressures fell in the ranges 35–320 °C and 200–2400 psi.

Introduction

Because hydrogen is used in petroleum processing, physical properties of hydrogen–hydrocarbon systems are often necessary for the design of refinery units. This paper adds to the previous data (*1*, *2*) which we have reported on such systems. Gas solubilities for seven systems, vapor–liquid equilibrium ratios for four systems, and partial molal volumes for six systems are reported here.

Experimental Section

The hydrocarbons used were American Petroleum Institute standard samples with stated purities of 99.9+ mol %. The experimental method has been described in detail (*1*). Briefly, a small sample of known mass and composition was confined above mercury in a glass capillary. Then, as the liquid mixture was expanded at constant temperature, the pressures at which the first trace of gas appeared (bubble-point pressure) and the last trace of liquid disappeared (dew-point pressure) were measured. The bubble-point pressures yield gas solubilities, and in a two-component system the combination of bubble- and dew-point pressures yields the vapor–liquid equilibrium ratios (*K*'s) for the system.

Partial molal volumes were derived by measuring the expansion which occurs when hydrogen is mixed with liquid hydrocarbon in a glass capillary (*3*).

The temperature can be set from 35 to 370 °C, but it was usually kept below 300 °C to avoid thermal decomposition. Pressure can be set from 100 to 3000 psi, but it was usually kept below 2500 psi to avoid frequent capillary replacement.

Gas Solubilities

Because gas solubilities are fairly linear with "partial pressure", the bubble points can be represented by equations of the form

$$S = a + b(p - p_1^0) + c(p - p_1^0)^2 \qquad (1)$$

where a, b, and c are constants at each temperature and are given in Table I; S is a "solubility" defined by $S = (x_2/x_1)/(p - p_1^0)$; x is a mole fraction in the liquid; p is a bubble pressure, p_1^0 is a vapor pressure, and subscripts 1 and 2 denote hydrocarbon and hydrogen, respectively.

These definitions of "solubility" and "partial pressure" are, of course, only arbitrary devices to simplify the representation of bubble pressure. As a definition of partial pressure, $p - x_1p_1^0$ works somewhat better than $p - p_1^0$, but not enough better to warrant the added complexity in solving eq 1 for x_2 (given p). p_1^0 is an approximate vapor pressure which is calculated from Table II. Of course, this particular p_1^0 must always be used in conjunction with the constants in Table I.

The experimental bubble pressures, along with the deviations from eq 1, are listed in Table III.

Vapor–Liquid Equilibrium Ratios

Vapor–liquid equilibrium ratios, or K's, are defined by

$$K_1 = y_1/x_1 \qquad K_2 = y_2/x_2 \qquad (2)$$

where y and x are mole fractions in the vapor and liquid, and subscripts 1 and 2 refer to hydrocarbon and hydrogen. For a binary system, K is a function of temperature and pressure only.

At each experimental dew point (listed under psi in Table IV) the vapor composition was known, and the corresponding liquid composition was calculated from eq 1. These compositions were then used to calculate the vapor–liquid equilibrium ratios listed in Table IV.

The function pK, where p is the pressure of the system, varies more slowly with pressure than does K. Therefore, interpolation to convenient values of pressure was accomplished by plotting pK as a function or pressure at constant temperature on large-scale graph paper. Reduced versions of these plots are shown in Figures 1–8.

Smoothed K's, listed in Table V, were read from the pK plots. Those values in parentheses are dependent on short extensions of eq 1 (linear form only) to pressures higher than observed bubble pressures. Values of K for two other hydrogen–hydrocarbon systems have been reported (*2*).

Partial Molal Volumes

Partial molal volumes of gases in liquid solutions are necessary in the calculation of thermodynamic properties of solutions from liquid–vapor-equilibrium and gas-compressibility data at high pressures (*1*). Because the literature usually reports only room-temperature partial molal volumes for gas–hydrocarbon systems, and because our apparatus easily combines these measurements with bubble points, we have made numerous high-temperature partial-molal-volume measurements. The volume-expansion method used has been described (*3*).

At gas concentration below 10 or 15 mol %, the volume expansion of liquid per mol of gas dissolved varies linearly with composition at constant temperature and pressure; i.e.

$$\Delta V/n_2 = \bar{V}_2^* + c'x_2 \qquad (3)$$

where ΔV is the measured volume expansion of the liquid when n_2 moles of gas are dissolved in pure hydrocarbon to give a mole fraction x_2, and $\bar{V}_2^*$ is the gas partial molal volume at infinite dilution. $\bar{V}_2^*$ and c' are functions of temperature and pressure only. That the intercept is $\bar{V}_2^*$ follows from the definition

$$\bar{V}_2^* = \lim_{n_2 \to 0} (\Delta V/n_2)_{T,p,n_1}$$

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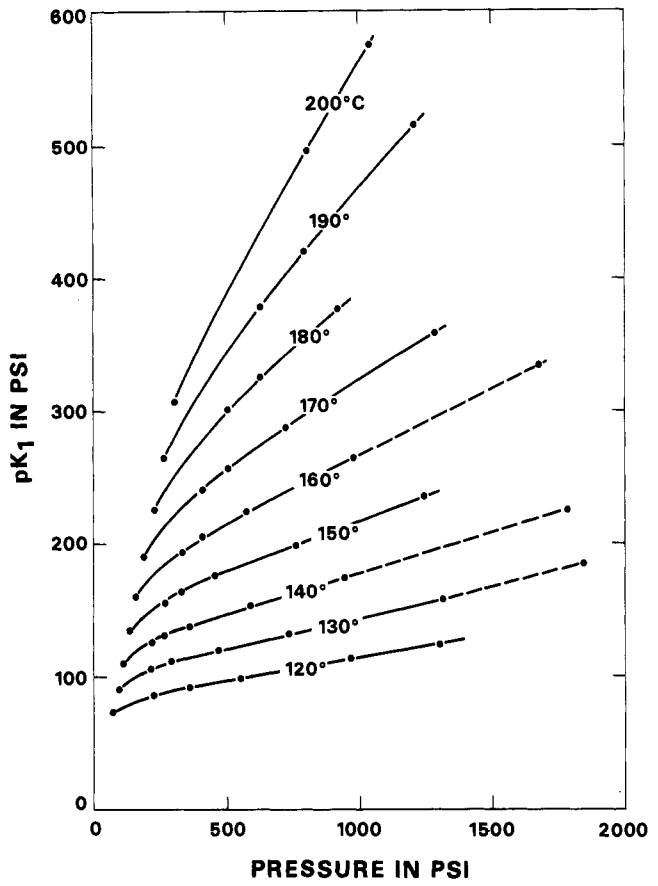

Figure 1. pK_1 for 2,3-dimethylbutane.

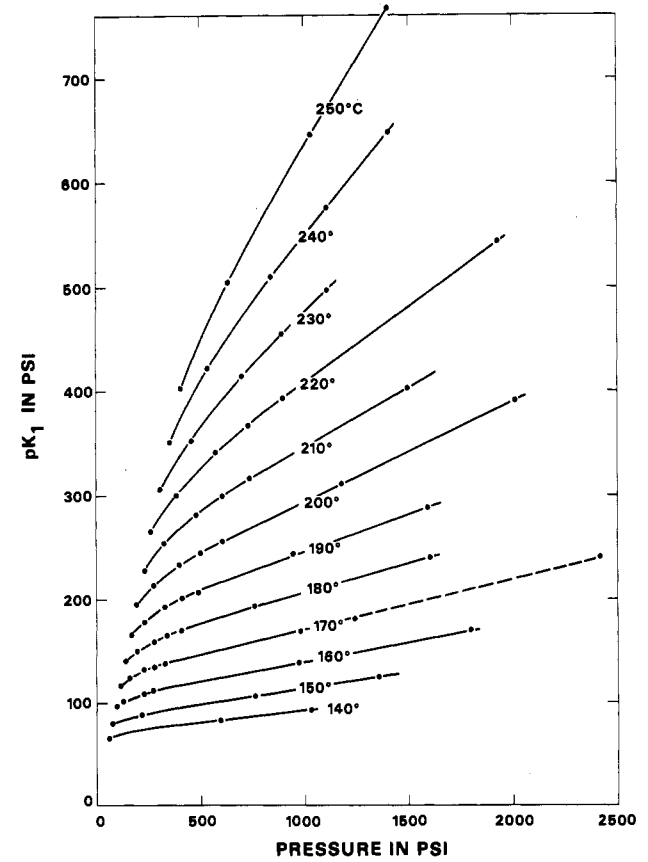

Figure 2. pK_1 for cyclohexane.

Values of c' obtained from eq 3 are approximately related to the composition variation of partial molal volumes $\bar{V}_1$ and $\bar{V}_2$;

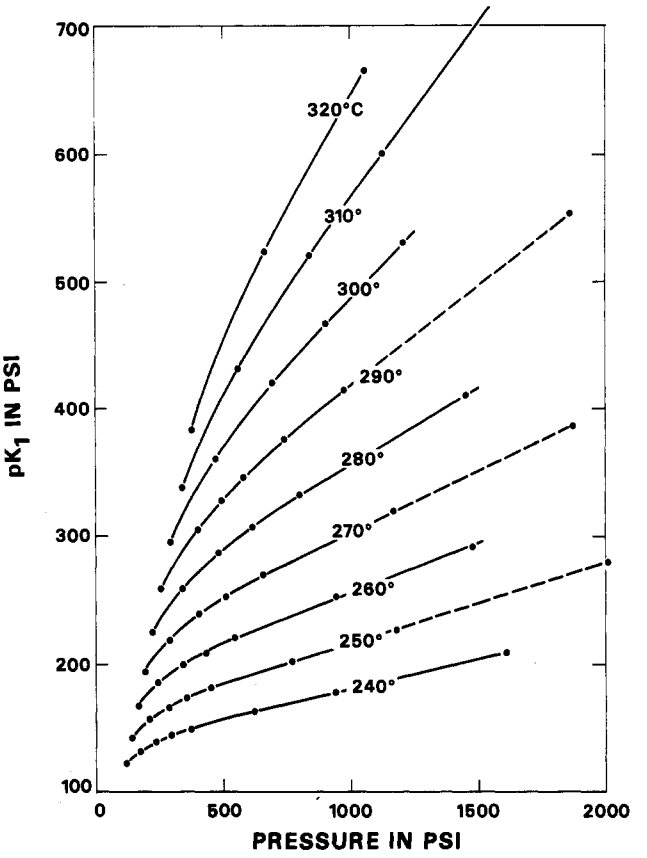

Figure 3. pK_1 for *m*-xylene.

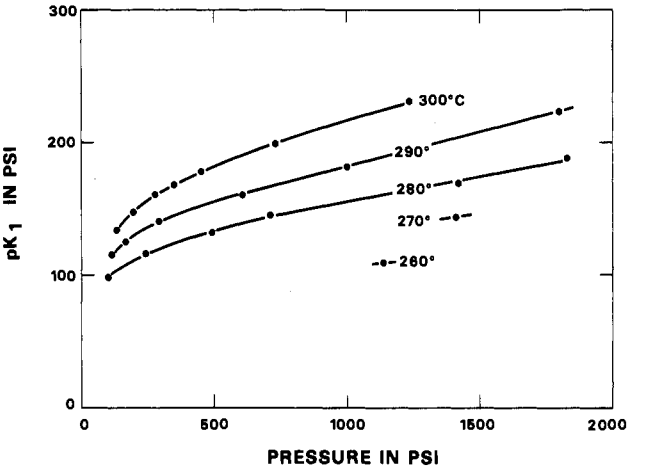

Figure 4. pK_1 for 1,4-diethylbenzene.

i.e., assume that the molal volume of the solution, V, can be represented as a Taylor series in the mole fraction of hydrogen, x_2, for small x_2. Then

$$V = V_1 + b'x_2 + c'x_2^2 + \ldots \quad (4)$$

where V_1 is the molal volume of the pure hydrocarbon, b' and c' are functions of temperature and pressure, and we neglect cubic and higher terms. By definition we have

$$\bar{V}_i = (\partial nV/\partial n_i)_{Tpn} \quad (5)$$

where $n = n_1 + n_2$ is the total number of moles in solution and V, the solution molal volume, is given by $V = x_1\bar{V}_1 + x_2\bar{V}_2$. Applying eq 5 to eq 4 we obtain

$$\bar{V}_1 - V_1 = -c'x_2^2 \quad (6)$$

$$\bar{V}_2 - \bar{V}_2^* = 2c'x_2 \quad (7)$$

Table I. Solubilities of Hydrogen in Hydrocarbons[a]

	n-pentane					2,3-dimethylbutane				n-decane					cyclohexane					m-xylene					1,4-diethylbenzene				1-methylnaphthalene			
t°C	$ax10^3$	$bx10^5$	$cx10^6$	S.D.%	DP,MP	$ax10^3$	$bx10^5$	S.D.%	DP,MP	$ax10^3$	$bx10^5$	$cx10^6$	S.D.%	DP,MP	$ax10^3$	$bx10^3$	$cx10^6$	S.D.%	DP,MP	$ax10^3$	$bx10^5$	$cx10^6$	S.D.%	DP,MP	$ax10^3$	$bx10^5$	S.D.%	DP,MP	$ax10^3$	$bx10^5$	S.D.%	DP,MP
35	.7897	.0036		.14	4,20	.7751	.0004	.05	4,22	.7408	-.0110		.08	4,23																		
40	.8142	.0053		.13	4,19	.7979	.0014	.09	4,21																							
50	.8656	.0084		.17	4,17	.8440	.0043	.06	4,20																							
60	.9196	.0129		.20	4,17	.8931	.0067	.08	5,23																							
70	.9783	.0155		.15	5,20	.9435	.0110	.20	5,23	.8904	-.0073		.09	5,24	.5414	-.0014		.04	3,23													
80	1.0389	.0235		.15	5,19	.9974	.0140	.09	5,21																.5710	-.0060	.22	3,20				
90	1.1057	.0300		.15	5,18	1.0533	.0196	.09	5,20						.6122	.0006		.06	3,20						.6024	-.0064	.23	3,20				
100	1.1774	.0399		.15	5,17	1.1131	.0251	.08	5,19						.6497	.0017		.08	3,19						.6329	-.0057	.30	3,19				
110	1.2573	.0506		.17	5,16	1.1772	.0323	.10	5,18	1.0799	-.0031		.11	6,23	.6885	.0034		.04	4,23	.5757	-.0045		.01	3,22	.6653	-.0053	.28	3,18				
120	1.3452	.0600		.18	5,15	1.2456	.0398	.30	5,17						.7284	.0056		.08	4,23						.6992	-.0054	.27	3,17				
130	1.4481	.0779		.20	5,15	1.3223	.0469	.14	5,16						.7734	.0076		.07	4,21						.7330	-.0029	.32	3,16				
140	1.5614	.1120		.21	5,14	1.4059	.0624	.11	5,15	1.2375	.0021		.11	6,20	.8153	.0105		.09	4,20	.6712	-.0020		.04	3,19	.7670	-.0047	.27	3,22				
150	1.7011	.1466		.24	5,13	1.4987	.0788	.12	5,14						.8621	.0146		.04	4,19						.8042	-.0049	.28	4,20				
160	1.8721	.2035		.31	5,12	1.6042	.1001	.13	5,14	1.3524	.0082		.12	6,18	.9125	.0187		.05	4,18	.7416	.0005		.03	4,23	.8398	-.0027	.21	5,20	.4489	-.0067	.02	3,23
170	2.0911	.3114		.39	5,12	1.7254	.1304	.14	5,13						.9661	.0242		.03	5,23						.8816	-.0045	.30	4,18	.4690	-.0060	.08	3,22
180	2.4108	.4620	.0184	.42	5,11	1.8702	.1727	.19	5,13	1.4775	.0176		.17	6,17	1.0261	.0297		.09	5,22	.8183	.0050		.08	4,20	.9188	-.0003	.31	5,17	.4893	-.0055	.12	3,21
190	2.9667	.9951	.2000	.43	5,9	2.0471	.2409	.22	5,12						1.0905	.0370		.07	5,20						.9638	-.0021	.33	4,17	.5108	-.0045	.08	3,20
200						2.2762	.3639	.18	5,11	1.6207	.0238		.15	6,15	1.1627	.0461		.13	5,20	.9048	.0096		.03	5,24	1.0054	.0018	.32	6,21	.5315	-.0048	.08	3,20
210						2.5938	.6568	.44	5,11						1.2431	.0575		.13	6,19						1.0494	.0055	.21	5,20	.5525	-.0032	.05	3,18
220										1.7832	.0362		.14	6,14											1.0984	.0068	.25	5,20	.5767	-.0039	.09	3,17
230															1.4471	.0937		.22	5,17						1.1499	.0095	.24	5,18	.6008	-.0035	.07	3,17
240										1.9728	.0529		.14	6,13	1.5789	.1273		.29	5,16	1.1208	.0249		.05	5,20	1.2050	.0117	.38	5,17	.6249	-.0022	.04	5,23
250										2.0820	.0636		.16	6,12	1.7573	.1266	.0065	.25	6,15	1.1887	.0304		.08	5,19	1.2620	.0173	.26	6,21	.6511	-.0021	.05	4,22
260										2.2043	.0747		.15	6,11						1.2614	.0389		.07	5,18	1.3244	.0217	.24	6,20	.6782	-.0020	.06	4,21
270										2.3442	.0864		.30	6,11						1.3477	.0464		.15	5,17	1.3943	.0247	.29	6,20	.7053	-.0009	.05	4,20
280										2.5159	.0228	.0106	.25	6,11						1.4443	.0586		.18	5,17	1.4672	.0324	.37	6,19	.7342	.0001	.07	4,20
290										2.7128	-.0112	.0182	.23	6,10						1.5580	.0751		.20	5,16	1.5478	.0412	.31	6,18	.7639	.0012	.10	4,19
300										2.9169	.1295	.0078	.20	6,10						1.6945	.0998		.31	5,15	1.6400	.0495	.42	6,17	.7969	.0016	.13	5,18
310																				1.8844	.0469		.08	5,14								
320																				2.1172	.0449		.49	5,13								

[a] Solubility = $S = (x_2/x_1)/(p - p_1^0)$. $S = a + b\,(p - p_1^0) + c(p - p_1^0)^2$. DP,MP = number of data points, maximum pressure of measurements in hundreds of psi. p is pressure in (lb/in.^{2})/14.696, p_1^0 is a vapor pressure (Table II).

Table II. Vapor Pressure Constants[a] (4)

	A	B	C	T_c, K
n-pentane	6.852 21	1064.630	232.000	470
2,3-dimethylbutane	6.809 83	1127.187	228.900	500
cyclohexane	6.844 98	1203.526	222.863	554
n-decane	6.953 67	1501.268	194.480	619
m-xylene	7.009 08	1462.266	215.105	619
1,4-diethylbenzene	7.000 54	1589.273	202.019	662
1-methylnaphthalene	7.068 99	1852.674	192.716	787

[a] $\log (760\ p_1^0) = A - B/(T + C) + 0.50(T/T_c - 0.75)^2$. Omit last term when $T/T_c < 0.75$. p_1^0 is vapor pressure in (lb/in.^{2})/14.696.

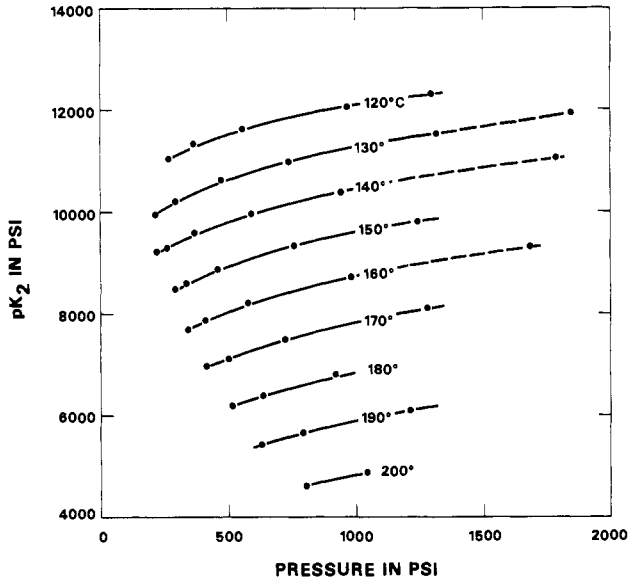

Figure 5. pK_2 for 2,3-dimethylbutane.

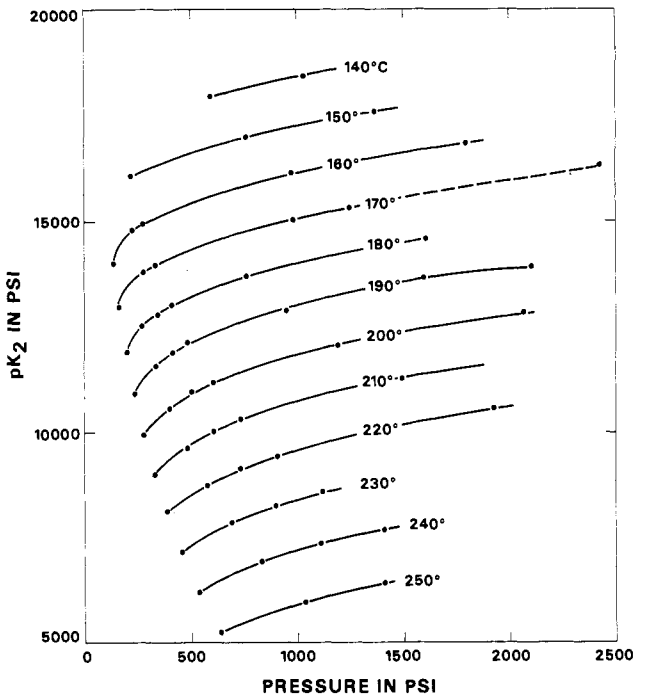

Figure 6. pK_2 for cyclohexane.

and if we use $\Delta V = nV - n_1V_1$, the c' in eq 6 and 7 can be identified with c' of eq 3. It turns out that $c' > 0$ so that $\bar{V}_1$ decreases slowly as H_2 is added and $\bar{V}_2$ increases fairly rapidly. The liquid-phase activity coefficients show this same asymmetry in behavior (*1*).

Experimental values for the solution dilation $\Delta V/n_2$, are available as supplementary material. Because there are several thousand of these values, and because we wish to derive partial molal volumes, an analytical representation is desirable. Previous work (*1*) has shown that the reciprocals of the dilute solution partial molal volumes, $\bar{V}_2^*$, are linear with pressure up to about 1600 psi. A small quadratic term is sufficient to take care of any curvature between 1600 and 2500 psi. The

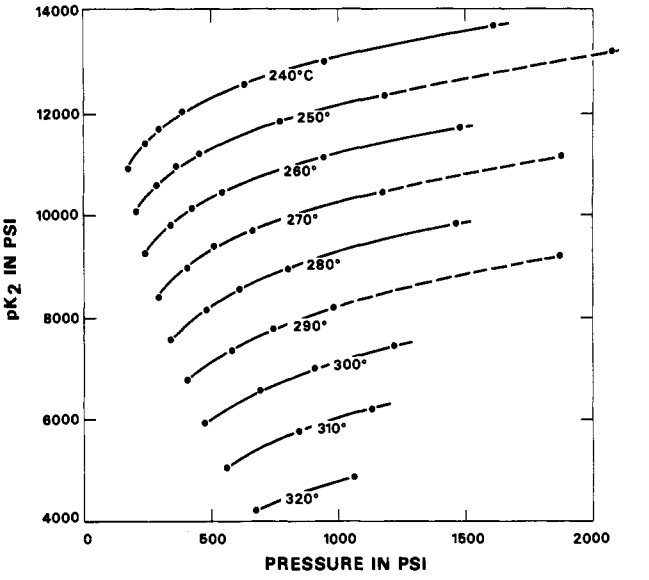

Figure 7. pK_2 for *m*-xylene.

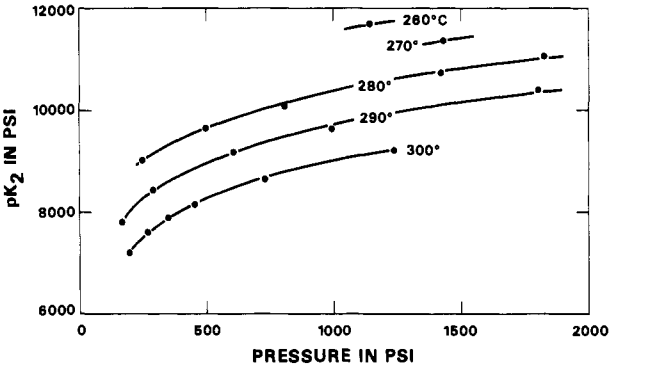

Figure 8. pK_2 for 1,4-diethylbenzene.

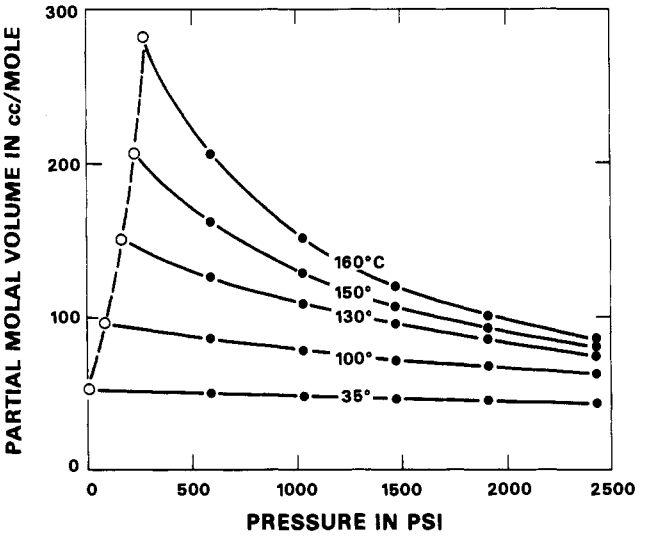

Figure 9. Partial molal volumes of hydrogen, at infinite dilution, in liquid *n*-pentane.

Table III. Measured Solubilities of Hydrogen in Hydrocarbons

n-PENTANE

°C	psi	x_2	Δ%
35.00	508.8	0.02592	-0.01
35.00	1037.2	0.05231	0.10
35.00	1528.4	0.07542	-0.21
35.00	1975.8	0.09596	0.10
40.00	496.1	0.02592	0.01
40.00	1008.3	0.05231	0.05
40.00	1482.7	0.07542	-0.20
40.00	1915.0	0.09596	0.10
50.00	473.6	0.02592	0.02
50.00	953.8	0.05231	0.08
50.00	1398.8	0.07542	-0.23
50.00	1802.1	0.09596	0.13
60.00	454.7	0.02592	-0.00
60.00	904.9	0.05231	0.12
60.00	1322.0	0.07542	-0.24
60.00	1698.7	0.09596	0.13
70.00	439.3	0.02592	-0.06
70.00	862.1	0.05231	0.11
70.00	1252.5	0.07542	-0.15
70.00	1606.4	0.09596	0.17
70.00	2043.2	0.11975	-0.08
80.00	427.6	0.02592	-0.01
80.00	824.2	0.05231	0.10
80.00	1189.7	0.07542	-0.21
80.00	1520.3	0.09596	0.09
80.00	1923.8	0.11975	0.00
90.00	419.5	0.02592	-0.02
90.00	791.2	0.05231	0.10
90.00	1133.2	0.07542	-0.18
90.00	1442.5	0.09596	0.10
90.00	1819.9	0.11975	-0.02
100.00	415.4	0.02592	-0.03
100.00	763.2	0.05231	0.13
100.00	1082.6	0.07542	-0.17
100.00	1371.5	0.09596	0.07
100.00	1722.0	0.11975	-0.00
110.00	415.1	0.02592	-0.01
110.00	740.2	0.05231	0.09
110.00	1038.0	0.07542	-0.18
110.00	1306.4	0.09596	0.12
110.00	1633.2	0.11975	-0.02
120.00	419.1	0.02592	0.08
120.00	721.8	0.05231	0.30
120.00	998.8	0.07542	0.09
120.00	1248.5	0.09596	0.38
120.00	1549.7	0.11975	0.44
130.00	427.0	0.02592	0.06
130.00	708.7	0.05231	0.04
130.00	965.5	0.07542	-0.21
130.00	1197.2	0.09596	0.04
130.00	1476.0	0.11975	0.07
140.00	440.2	0.02592	-0.01
140.00	699.3	0.05231	0.09
140.00	935.1	0.07542	-0.19
140.00	1146.5	0.09596	0.09
140.00	1401.3	0.11975	0.00
150.00	457.4	0.02592	0.05
150.00	694.6	0.05231	0.06
150.00	909.8	0.07542	-0.21
150.00	1102.6	0.09596	0.05
150.00	1333.9	0.11975	0.06
160.00	479.3	0.02592	0.11
160.00	694.1	0.05231	-0.01
160.00	887.7	0.07542	-0.23
160.00	1060.7	0.09596	0.06
160.00	1267.8	0.11975	0.08
170.00	506.2	0.02592	0.07
170.00	696.2	0.05231	0.08
170.00	867.5	0.07542	-0.27
170.00	1019.4	0.09596	0.02
170.00	1199.9	0.11975	0.10
180.00	536.8	0.02592	-0.05
180.00	699.3	0.05231	0.15
180.00	844.1	0.07542	-0.16
180.00	971.4	0.09596	0.06
180.00	1120.8	0.11975	0.00
190.00	567.6	0.02592	-0.04
190.00	693.4	0.05231	0.13
190.00	800.4	0.07542	-0.13
190.00	890.8	0.09596	0.03
190.00	991.9	0.11975	0.00

2,3-DIMETHYLBUTANE

°C	psi	x_2	Δ%
35.00	528.5	0.02679	0.03
35.00	984.3	0.04901	-0.07
35.00	1400.1	0.07759	0.04
35.00	2227.0	0.10488	-0.02
40.00	514.8	0.02679	0.01
40.00	957.2	0.04901	-0.09
40.00	1353.0	0.07759	0.11
40.00	2161.9	0.10488	-0.06
50.00	489.9	0.02679	0.02
50.00	906.6	0.04901	-0.06
50.00	1467.8	0.07759	0.07
50.00	2037.8	0.10488	-0.02
60.00	467.3	0.02679	0.09
60.00	861.0	0.04901	-0.10
60.00	1389.9	0.07759	0.02
60.00	1925.3	0.10488	-0.01
60.00	2385.8	0.12728	0.05
70.00	448.7	0.02679	-0.04
70.00	819.8	0.04901	-0.11
70.00	1313.9	0.07759	0.33
70.00	1822.5	0.10488	-0.11
70.00	2254.1	0.12728	-0.03
80.00	431.8	0.02679	0.07
80.00	782.9	0.04901	-0.12
80.00	1252.5	0.07759	0.05
80.00	1727.2	0.10488	-0.02
80.00	2134.2	0.12728	0.02
90.00	418.5	0.02679	0.05
90.00	749.8	0.04901	-0.11
90.00	1192.3	0.07759	0.08
90.00	1639.3	0.10488	-0.04
90.00	2021.4	0.12728	-0.00
100.00	403.0	0.02679	0.04
100.00	720.7	0.04901	-0.08
100.00	1138.2	0.07759	0.07
100.00	1558.4	0.10488	0.01
100.00	1918.6	0.12728	-0.01
110.00	400.2	0.02679	0.05
110.00	695.4	0.04901	-0.11
110.00	1088.5	0.07759	0.07
110.00	1484.0	0.10488	-0.02
110.00	1821.7	0.12728	-0.00
120.00	395.5	0.02679	0.15
120.00	673.6	0.04901	0.02
120.00	1048.9	0.07759	-0.16
120.00	1415.5	0.10488	0.09
120.00	1732.7	0.12728	0.10
130.00	394.0	0.02679	0.09
130.00	656.5	0.04901	-0.15
130.00	1004.8	0.07759	0.05
130.00	1354.1	0.10488	0.01
130.00	1652.6	0.12728	-0.00
140.00	395.8	0.02679	0.03
140.00	641.3	0.04901	-0.10
140.00	967.0	0.07759	0.08
140.00	1293.2	0.10488	-0.01
140.00	1571.0	0.12728	-0.02
150.00	401.0	0.02679	0.07
150.00	630.6	0.04901	-0.08
150.00	934.8	0.07759	0.09
150.00	1239.3	0.10488	-0.04
150.00	1497.2	0.12728	0.00
160.00	409.6	0.02679	0.05
160.00	623.6	0.04901	-0.10
160.00	906.6	0.07759	0.07
160.00	1188.7	0.10488	-0.01
160.00	1428.0	0.12728	-0.00
170.00	422.1	0.02679	0.04
170.00	620.3	0.04901	-0.10
170.00	881.7	0.07759	0.09
170.00	1142.0	0.10488	-0.02
170.00	1362.1	0.12728	-0.00
180.00	438.1	0.02679	0.06
180.00	620.4	0.04901	-0.12
180.00	859.8	0.07759	0.10
180.00	1098.0	0.10488	-0.04
180.00	1298.3	0.12728	0.01
190.00	458.0	0.02679	0.08
190.00	623.7	0.04901	-0.14
190.00	840.4	0.07759	0.07
190.00	1054.8	0.10488	-0.02
190.00	1234.9	0.12728	0.01
200.00	481.5	0.02679	0.04
200.00	628.9	0.04901	-0.08
200.00	821.2	0.07759	0.07
200.00	1010.3	0.10488	-0.05
200.00	1168.0	0.12728	0.02
210.00	507.8	0.02679	0.11
210.00	635.1	0.04901	-0.20
210.00	798.2	0.07759	0.13
210.00	958.0	0.10488	-0.09
210.00	1089.3	0.12728	0.04

CYCLOHEXANE

°C	psi	x_2	Δ%
35.00	699.1	0.01982	
35.00	1579.0	0.04349	
40.00	675.2	0.01982	
40.00	1523.1	0.04349	
50.00	632.6	0.01982	
50.00	1429.0	0.04349	
60.00	592.7	0.01982	
60.00	1328.6	0.04349	
70.00	560.3	0.01982	-0.03
70.00	1246.8	0.04349	0.06
70.00	2322.4	0.07817	-0.02
80.00	529.7	0.01982	0.04
80.00	1174.8	0.04349	-0.04
80.00	2179.6	0.07817	0.04
90.00	504.5	0.01982	0.05
90.00	1111.0	0.04349	-0.08
90.00	2051.9	0.07817	0.02
100.00	482.2	0.01982	0.06
100.00	1053.1	0.04349	-0.10
100.00	1936.2	0.07817	0.05
110.00	463.7	0.01982	0.05
110.00	1030.7	0.04349	-0.05
110.00	1832.2	0.07817	-0.01
110.00	2390.4	0.10019	0.02
120.00	448.6	0.01982	0.09
120.00	955.7	0.04349	-0.09
120.00	1738.5	0.07817	-0.05
120.00	2261.0	0.10019	0.07
130.00	436.0	0.01982	-0.05
130.00	910.8	0.04349	0.09
130.00	1648.0	0.07817	-0.07
130.00	2138.6	0.10019	0.03
140.00	428.3	0.01982	0.08
140.00	879.8	0.04349	-0.10
140.00	1574.3	0.07817	-0.03
140.00	2037.1	0.10019	0.06
150.00	423.3	0.01982	0.03
150.00	848.6	0.04349	-0.03
150.00	1502.8	0.07817	-0.03
150.00	1937.7	0.10019	0.04
160.00	421.4	0.01982	0.04
160.00	822.5	0.04349	-0.03
160.00	1438.3	0.07817	-0.03
160.00	1847.2	0.10019	0.04
170.00	423.3	0.01982	-0.03
170.00	800.8	0.04349	0.02
170.00	1380.3	0.07817	-0.02
170.00	1764.3	0.10019	0.03
170.00	2308.2	0.12996	-0.02
180.00	428.0	0.01982	0.01
180.00	783.4	0.04349	-0.06
180.00	1326.7	0.07817	0.01
180.00	1686.1	0.10019	0.10
180.00	2197.5	0.12996	-0.07
190.00	436.5	0.01982	0.07
190.00	770.6	0.04349	-0.06
190.00	1280.7	0.07817	-0.05
190.00	1617.5	0.10019	0.02
190.00	2092.7	0.12996	0.03
200.00	449.0	0.01982	0.04
200.00	761.7	0.04349	-0.08
200.00	1238.2	0.07817	-0.05
200.00	1550.9	0.10019	0.15
200.00	1996.7	0.12996	-0.05
210.00	459.2	0.01931	0.09
210.00	465.5	0.01982	0.01
210.00	757.4	0.04349	-0.08
210.00	1202.3	0.07817	-0.14
210.00	1493.4	0.10019	0.06
210.00	1905.2	0.12996	0.03
220.00	485.8	0.01982	0.11
220.00	757.1	0.04349	-0.12
220.00	1167.9	0.07817	-0.06
220.00	1437.9	0.10019	0.01
220.00	1816.3	0.12996	0.03
230.00	509.6	0.01982	0.16
230.00	759.6	0.04349	-0.12
230.00	1138.3	0.07817	-0.14
230.00	1385.9	0.10019	-0.00
230.00	1732.4	0.12996	0.09
240.00	538.1	0.01982	0.16
240.00	766.5	0.04349	-0.14
240.00	1111.2	0.07817	-0.18
240.00	1334.9	0.10019	0.06
240.00	1649.2	0.12996	0.07
250.00	565.9	0.01931	0.10
250.00	570.5	0.01982	-0.08
250.00	775.8	0.04349	-0.13
250.00	1084.0	0.07817	-0.03
250.00	1282.9	0.10019	0.15
250.00	1560.3	0.12996	-0.05

n-DECANE

°C	psi	x_2	Δ%
35.00	530.3	0.02590	0.02
35.00	1087.0	0.05144	0.07
35.00	1609.5	0.07382	-0.13
35.00	2346.0	0.10356	0.06
50.00	488.4	0.02590	
50.00	2150.4	0.10365	
70.00	440.5	0.02590	-0.04
70.00	898.8	0.05144	0.13
70.00	1327.2	0.07382	-0.11
70.00	1927.8	0.10356	0.00
70.00	2429.1	0.12677	0.01
110.00	363.8	0.02590	0.10
110.00	741.1	0.05144	0.00
110.00	1090.9	0.07382	-0.17
110.00	1578.9	0.10356	0.01
110.00	1984.8	0.12677	0.03
110.00	2369.5	0.14764	0.03
140.00	321.3	0.02590	0.02
140.00	648.6	0.05144	0.09
140.00	952.6	0.07382	-0.15
140.00	1375.0	0.10356	0.03
140.00	1725.9	0.12677	0.03
140.00	2057.6	0.14764	0.01
160.00	298.6	0.02590	0.05
160.00	597.9	0.05144	0.02
160.00	874.5	0.07382	-0.15
160.00	1258.3	0.10356	0.06
160.00	1577.4	0.12677	0.01
160.00	1877.9	0.14764	0.01
180.00	281.2	0.02590	-0.10
180.00	553.2	0.05144	0.17
180.00	805.5	0.07382	-0.10
180.00	1155.0	0.10356	0.05
180.00	1444.5	0.12677	-0.00
180.00	1716.9	0.14764	-0.03
200.00	267.8	0.02590	-0.02
200.00	515.9	0.05144	0.13
200.00	745.5	0.07382	-0.11
200.00	1064.3	0.10356	-0.03
200.00	1326.9	0.12677	-0.01
200.00	1573.2	0.14764	0.05
220.00	260.0	0.02590	0.07
220.00	485.5	0.05144	0.07
220.00	693.4	0.07382	-0.12
220.00	981.5	0.10356	-0.00
220.00	1218.9	0.12677	-0.00
220.00	1441.5	0.14764	0.04

TABLE III. CONTINUED

°C	psi	x_2	ΔZ
n-DECANE (CONTINUED)			
240.00	258.7	0.02590	0.01
240.00	462.1	0.05144	0.08
240.00	649.5	0.07382	-0.11
240.00	908.7	0.10356	0.02
240.00	1122.3	0.12677	-0.01
240.00	1322.3	0.14764	0.02
250.00	260.5	0.02590	0.03
250.00	453.2	0.05144	0.06
250.00	630.5	0.07382	-0.12
250.00	875.7	0.10356	-0.00
250.00	1077.6	0.12677	-0.02
250.00	1266.1	0.14764	0.05
260.00	264.2	0.02590	0.03
260.00	446.1	0.05144	0.04
260.00	613.4	0.07382	-0.12
260.00	844.6	0.10356	0.01
260.00	1034.8	0.12677	0.01
260.00	1213.1	0.14764	0.02
270.00	269.5	0.02590	0.14
270.00	440.8	0.05144	0.03
270.00	598.3	0.07382	-0.21
270.00	815.5	0.10356	-0.03
270.00	993.7	0.12677	0.03
270.00	1160.9	0.14764	0.07
280.00	277.0	0.02590	0.04
280.00	437.6	0.05144	-0.02
280.00	584.8	0.07382	-0.11
280.00	*787.7*	*0.10356*	*0.10*
280.00	954.1	0.12677	0.05
280.00	1109.4	0.14764	-0.04
290.00	286.5	0.02590	0.05
290.00	436.0	0.05144	-0.07
290.00	572.6	0.07382	-0.04
290.00	761.8	0.10356	0.04
290.00	915.8	0.12677	0.08
290.00	1059.8	0.14764	-0.05
300.00	299.2	0.02590	-0.00
300.00	436.3	0.05144	0.09
300.00	562.1	0.07382	-0.06
300.00	735.6	0.10356	0.01
300.00	877.4	0.12677	-0.00
300.00	1009.4	0.14764	0.01
m-XYLENE			
35.00	1029.8	0.02521	
35.00	2182.8	0.05130	
50.00	935.3	0.02521	
70.00	829.4	0.02521	
70.00	1744.3	0.05130	
110.00	669.0	0.02521	-0.01
110.00	1397.1	0.05130	-0.00
110.00	2224.3	0.07906	-0.01
140.00	582.2	0.02521	-0.02
140.00	1201.4	0.05130	0.05
140.00	1902.3	0.07906	-0.02
160.00	537.3	0.02521	0.01
160.00	1096.1	0.05130	-0.01
160.00	1725.6	0.07906	-0.04
160.00	2275.6	0.10211	0.03
180.00	502.8	0.02521	0.03
180.00	1006.5	0.05130	0.00
180.00	1573.0	0.07906	-0.11
180.00	2063.4	0.10211	0.06
200.00	478.0	0.02521	0.02
200.00	932.1	0.05130	-0.01
200.00	1440.4	0.07906	-0.04
200.00	1882.7	0.10211	-0.02
200.00	2425.5	0.12907	0.07
210.00	899.5	0.05130	
220.00	463.1	0.02521	0.03
220.00	870.8	0.05130	0.01
220.00	1326.5	0.07906	-0.05
220.00	1721.8	0.10211	-0.03
220.00	2205.1	0.12907	0.04
240.00	459.1	0.02521	0.03
240.00	823.4	0.05130	-0.01
240.00	1229.4	0.07906	-0.05
240.00	1580.9	0.10211	-0.02
240.00	2010.4	0.12907	0.03
250.00	461.3	0.02521	-0.02
250.00	804.9	0.05130	-0.12
250.00	1187.3	0.07906	-0.16
250.00	1517.2	0.10211	-0.06
250.00	1921.3	0.12907	-0.05
260.00	466.7	0.02521	0.05
260.00	789.4	0.05130	-0.01
260.00	1148.0	0.07906	-0.06
260.00	1457.7	0.10211	-0.02
260.00	*1835.0*	*0.12907*	*0.04*
270.00	474.6	0.02521	0.07
270.00	776.3	0.05130	0.01
270.00	1112.3	0.07906	-0.13
270.00	1401.2	0.10211	-0.04
270.00	1752.4	0.12907	0.09
280.00	486.1	0.02521	0.10
280.00	767.2	0.05130	-0.01
280.00	1079.5	0.07906	-0.12
280.00	1348.2	0.10211	-0.07
280.00	1673.3	0.12907	0.12
290.00	500.8	0.02521	0.09
290.00	760.8	0.05130	-0.01
290.00	1049.4	0.07906	-0.15
290.00	1296.9	0.10211	-0.05
290.00	1596.7	0.12907	0.10
300.00	518.6	0.02521	0.16
300.00	757.3	0.05130	-0.06
300.00	1021.5	0.07906	-0.19
300.00	1247.4	0.10211	-0.07
300.00	1519.9	0.12907	0.16
310.00	539.0	0.02521	0.01
310.00	755.2	0.05130	-0.02
310.00	993.1	0.07906	-0.00
310.00	1195.8	0.10211	0.04
310.00	1438.5	0.12907	-0.01
320.00	562.7	0.02521	0.10
320.00	755.5	0.05130	-0.20
320.00	964.9	0.07906	-0.03
320.00	1140.8	0.10211	0.20
320.00	1352.3	0.12907	-0.10
1,4-DIMETHYBENZENE			
35.00	973.6	0.02808	
35.00	1811.8	0.05078	
40.00	943.2	0.02808	
40.00	1754.5	0.05078	
50.00	887.4	0.02808	
50.00	1648.4	0.05078	
60.00	835.5	0.02808	
60.00	1550.8	0.05078	
70.00	790.5	0.02808	
70.00	1464.6	0.05078	
80.00	749.3	0.02808	-0.17
80.00	1386.5	0.05078	0.33
80.00	2143.0	0.07567	-0.13
90.00	710.4	0.02808	-0.16
90.00	1314.3	0.05078	0.31
90.00	2030.6	0.07567	-0.15
100.00	676.1	0.02808	-0.20
100.00	1247.7	0.05078	0.41
100.00	1927.8	0.07567	-0.16
110.00	643.2	0.02808	-0.18
110.00	1186.8	0.05078	0.35
110.00	1830.9	0.07567	-0.16
120.00	612.6	0.02808	-0.18
120.00	1129.9	0.05078	0.31
120.00	1741.6	0.07567	-0.16
130.00	584.6	0.02808	-0.20
130.00	1075.1	0.05078	0.35
130.00	1654.8	0.07567	-0.18
140.00	559.7	0.02808	-0.07
140.00	609.8	0.03046	-0.31
140.00	1029.3	0.05078	0.45
140.00	1581.2	0.07567	0.14
140.00	2157.4	0.10000	-0.21
150.00	536.6	0.02808	-0.29
150.00	984.3	0.05078	0.34
150.00	1509.3	0.07567	0.14
150.00	2057.8	0.10000	-0.19
160.00	514.1	0.02808	0.01
160.00	559.9	0.03046	-0.26
160.00	943.8	0.05078	0.24
160.00	1442.5	0.07567	0.18
160.00	1964.6	0.10000	-0.20
170.00	494.2	0.02808	-0.28
170.00	501.9	0.05078	0.34
170.00	1380.4	0.07567	0.09
170.00	1877.7	0.10000	-0.16
180.00	476.1	0.02808	-0.12
180.00	517.3	0.03046	-0.25
180.00	865.5	0.05078	0.44
180.00	1321.3	0.07567	0.15
180.00	1795.2	0.10000	-0.21
190.00	459.2	0.02808	-0.28
190.00	830.9	0.05078	0.36
190.00	1266.7	0.07567	0.08
190.00	1718.2	0.10000	-0.15
200.00	444.1	0.02808	-0.10
200.00	481.3	0.03046	-0.16
200.00	798.9	0.05078	0.50
200.00	1218.4	0.07567	-0.16
200.00	1646.3	0.10000	-0.23
200.00	2137.6	0.12688	0.13
210.00	431.4	0.02808	-0.11
210.00	772.7	0.05078	0.18
210.00	1168.0	0.07567	0.06
210.00	1578.1	0.10000	-0.24
210.00	2045.6	0.12688	0.09
220.00	419.3	0.02808	-0.05
220.00	745.7	0.05078	0.16
220.00	1123.1	0.07567	0.04
220.00	1515.1	0.10000	-0.30
220.00	1958.6	0.12688	0.17
230.00	409.2	0.02808	-0.04
230.00	720.9	0.05078	0.11
230.00	1080.3	0.07567	0.05
230.00	1453.6	0.10000	-0.30
230.00	1875.9	0.12688	0.16
240.00	401.0	0.02808	-0.07
240.00	697.8	0.05078	0.16
240.00	1040.4	0.07567	0.07
240.00	1396.4	0.10000	-0.30
240.00	1798.4	0.12688	0.16
250.00	394.6	0.02808	-0.04
250.00	677.5	0.05078	0.16
250.00	1003.7	0.07567	0.04
250.00	1342.2	0.10000	-0.35
250.00	1723.5	0.12688	0.12
250.00	2152.2	0.15494	0.05
260.00	390.2	0.02808	-0.07
260.00	659.2	0.05078	0.20
260.00	969.8	0.07567	0.02
260.00	1290.2	0.10000	-0.27
260.00	1653.9	0.12688	0.07
260.00	2059.9	0.15494	0.05
270.00	387.1	0.02808	-0.03
270.00	642.8	0.05078	0.17
270.00	937.4	0.07567	0.04
270.00	1242.5	0.10000	-0.34
270.00	1586.1	0.12688	0.13
270.00	1972.1	0.15494	0.05
280.00	386.6	0.02808	0.03
280.00	629.2	0.05078	0.17
280.00	908.8	0.07567	-0.02
280.00	1198.1	0.10000	-0.44
280.00	1521.6	0.12688	0.14
280.00	1885.0	0.15494	0.11
290.00	388.5	0.02808	-0.07
290.00	617.5	0.05078	0.23
290.00	882.1	0.07567	-0.02
290.00	1153.8	0.10000	-0.29
290.00	1461.1	0.12688	0.09
290.00	1803.4	0.15494	0.06
300.00	392.0	0.02808	-0.09
300.00	607.6	0.05078	0.30
300.00	857.4	0.07567	-0.04
300.00	1114.0	0.10000	-0.38
300.00	1402.3	0.12688	0.09
300.00	1723.9	0.15495	0.09
1-METHYLNAPHTHALENE			
120.00	908.5	0.02222	
120.00	1660.2	0.03940	
130.00	866.0	0.02222	
130.00	1571.0	0.03940	
140.00	823.7	0.02222	
140.00	1499.1	0.03940	
150.00	785.9	0.02222	
150.00	1429.6	0.03940	
160.00	751.0	0.02222	0.03
160.00	1363.6	0.03940	-0.03
160.00	2342.0	0.06525	0.02
170.00	718.0	0.02222	0.09
170.00	1303.8	0.03940	-0.13
170.00	2231.5	0.06525	0.06
180.00	688.1	0.02222	0.14
180.00	1249.2	0.03940	-0.20
180.00	2132.1	0.06525	0.10
190.00	659.8	0.02222	0.07
190.00	1194.0	0.03940	-0.13
190.00	2036.0	0.06525	0.05
200.00	641.1	0.02222	-0.82
200.00	1148.5	0.03940	-0.12
200.00	1957.8	0.06525	0.05
210.00	612.3	0.02222	0.04
210.00	1103.2	0.03940	-0.08
210.00	1876.5	0.06525	0.03
220.00	588.7	0.02222	0.08
220.00	1060.9	0.03940	-0.12
220.00	1801.1	0.06525	0.05
230.00	567.5	0.02222	0.05
230.00	1019.0	0.03940	-0.09
230.00	1729.4	0.06525	0.03
240.00	548.3	0.02222	0.05
240.00	981.1	0.03940	-0.09
240.00	1372.1	0.05445	0.00
240.00	1661.2	0.06525	0.02
240.00	2299.7	0.08816	-0.00
250.00	530.0	0.02222	0.02
250.00	944.8	0.03940	-0.05
250.00	1596.5	0.06525	0.08
250.00	2210.0	0.08816	-0.02
260.00	513.0	0.02222	0.06
260.00	911.8	0.03940	-0.11
260.00	1537.4	0.06525	0.01
260.00	2124.1	0.08816	0.01
270.00	498.6	0.02222	-0.01
270.00	880.5	0.03940	-0.04
270.00	1480.1	0.06525	0.07
270.00	2043.7	0.08816	-0.03
280.00	485.1	0.02222	-0.04
280.00	850.9	0.03940	0.01
280.00	1425.6	0.06525	0.11
280.00	1966.4	0.08816	-0.07
290.00	473.4	0.02222	-0.07
290.00	824.2	0.03940	0.04
290.00	1375.2	0.06525	0.14
290.00	1894.2	0.08816	-0.09
300.00	462.3	0.02222	-0.12
300.00	798.7	0.03940	-0.01
300.00	1101.2	0.05445	0.21
300.00	1327.3	0.06525	0.05
300.00	1823.9	0.08816	-0.13

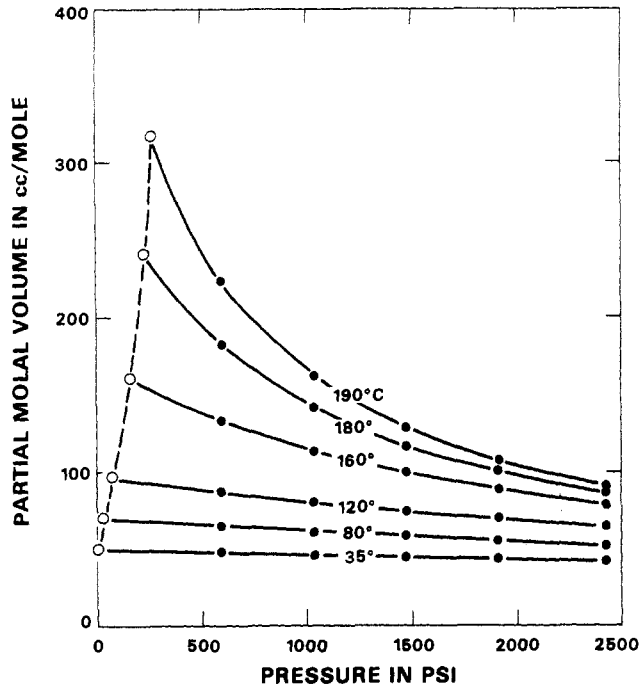

Figure 10. Partial molal volumes of hydrogen, at infinite dilution, in liquid 2,3-dimethylbutane.

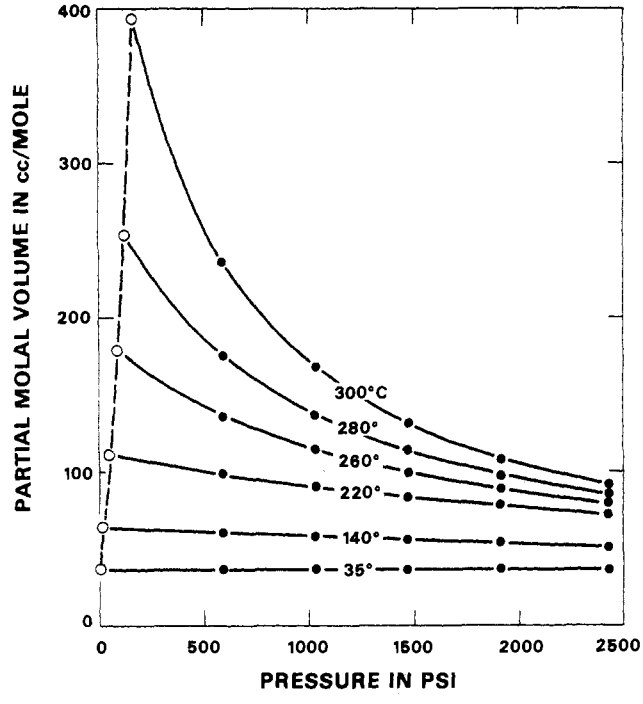

Figure 11. Partial molal volumes of hydrogen, at infinite dilution, in liquid *n*-decane.

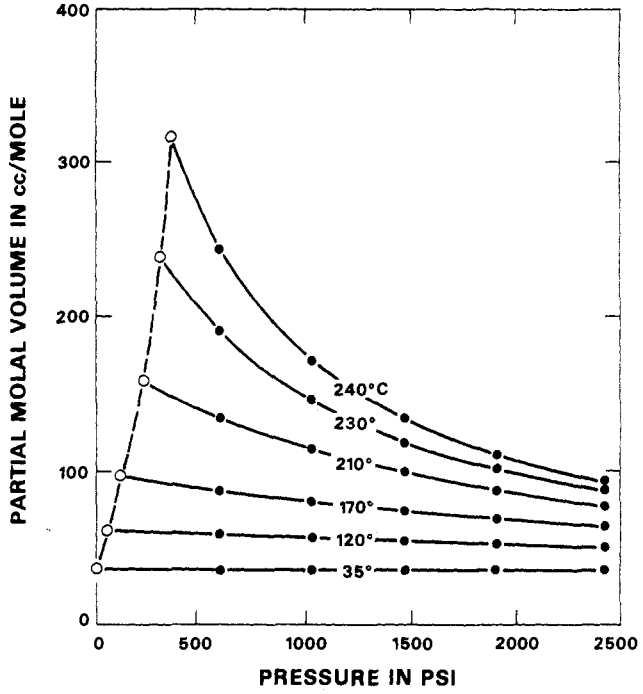

Figure 12. Partial molal volumes of hydrogen, at infinite dilution, in liquid cyclohexane.

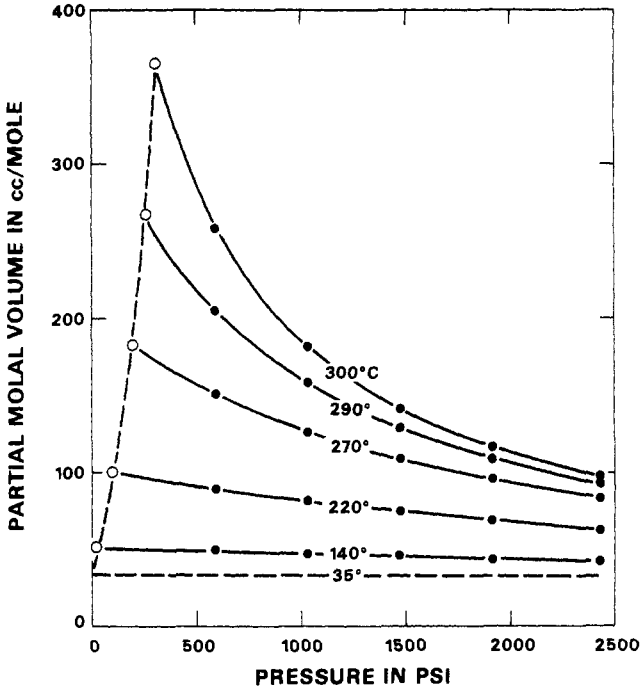

Figure 13. Partial molal volumes of hydrogen, at infinite dilution, in liquid *m*-xylene.

pressure variation of c' is taken care of, between p_1^0 and 2500 psi, by a single term in reciprocal pressure. Thus, eq 3 may be rewritten as

$$\Delta V/n_2 = 100/(a + bu - cu^2) + 100dx_2/u \qquad (8)$$

where u = atmospheres/100 = psi/1469.6, and a, b, c, and d are functions of temperature only.

A nonlinear regression program was used to fit eq 8 to each experimental set of $\Delta V/n_2$ in the supplementary material tables which corresponded to a system at a particular temperature (usually about 30 points). To obtain best values for $\bar{V}_2^*$ a two-step procedure was used. With $c = 0$, eq 8 was fitted by using only values of $\Delta V/n_2$ in the linear region (below 1600 psi). Then a second fit was made by using the complete eq 8 with a, b, and d fixed at the values derived in the first fit, and with no restriction on pressure. a, b, and d, as derived in the first fit, and c, as derived in the second fit, are listed in Table VI. Deviations listed in Table VI and in the supplementary material refer to the second fit.

Partial molal volumes of hydrogen at infinite dilution in hydrocarbons, $\bar{V}_2^*$, were calculated from constants of Table VI and plotted in Figures 9–14. The nearly vertical dashed lines represent vapor pressures of the pure hydrocarbons. Some lower pressure points are shown as open circles to indicate that they are the result of a double linear extrapolation, i.e., into regions of both composition and pressure which are below

Table IV. Measured Vapor-Liquid Equilibrium Ratios

2,3-DIMETHYLBUTANE				CYCLOHEXANE				m-XYLENE				1,4-DIETHYLBENZENE			
°C	psi	y_1/x_1	y_2/x_2	°C	psi	y_1/x_1	y_2/x_2	°C	psi	y_1/x_1	y_2/x_2	°C	psi	y_1/x_1	y_2/x_2
120.00	226.8	0.3788	48.66	140.00	592.8	0.1395	30.27	240.00	175.0	0.7509	62.28	260.00	1138.1	0.0959	10.29
120.00	362.3	0.2527	31.34	140.00	1031.2	0.0898	17.84	240.00	237.9	0.5835	47.93	270.00	1432.3	0.0988	7.93
120.00	556.2	0.1768	20.91	150.00	214.7	0.4169	74.74	240.00	294.5	0.4877	39.79	280.00	241.7	0.4801	37.28
120.00	967.3	0.1164	12.44	150.00	758.6	0.1409	22.42	240.00	371.8	0.4004	32.32	280.00	495.1	0.2643	19.47
120.00	1299.3	0.0956	9.48	150.00	1358.9	0.0917	12.93	240.00	627.7	0.2604	20.02	280.00	809.7	0.1778	12.46
130.00	212.1	0.4981	46.79	160.00	132.0	0.7738	106.23	240.00	948.3	0.1895	13.70	280.00	1420.8	0.1191	7.54
130.00	290.5	0.3807	35.26	160.00	225.3	0.4852	65.69	240.00	1608.9	0.1296	8.51	280.00	1826.4	0.1029	6.07
130.00	469.8	0.2551	22.83	160.00	267.6	0.4180	55.93	250.00	207.9	0.7518	48.36	290.00	164.9	0.7580	47.30
130.00	733.0	0.1798	14.97	160.00	970.8	0.1429	16.61	250.00	284.7	0.5850	37.19	290.00	289.8	0.4820	29.10
130.00	1316.9	0.1204	8.74	160.00	1798.5	0.0944	9.37	250.00	353.9	0.4895	30.85	290.00	600.9	0.2673	15.20
140.00	216.8	0.5761	42.59	170.00	160.0	0.7744	81.17	250.00	449.7	0.4027	24.97	290.00	998.4	0.1816	9.66
140.00	261.7	0.4999	35.43	170.00	228.2	0.5831	58.04	250.00	768.5	0.2635	15.41	290.00	1797.3	0.1242	5.80
140.00	361.2	0.3829	26.54	170.00	276.6	0.4865	49.90	250.00	1177.1	0.1933	10.48	300.00	194.0	0.7591	37.08
140.00	592.4	0.2581	16.86	170.00	329.2	0.4194	42.52	260.00	246.0	0.7530	37.58	300.00	276.3	0.5791	27.48
140.00	941.7	0.1836	11.02	170.00	976.8	0.1730	15.42	260.00	340.1	0.5870	28.78	300.00	346.4	0.4846	22.68
150.00	268.8	0.5782	31.46	170.00	1240.6	0.1457	12.35	260.00	424.6	0.4920	23.90	300.00	449.1	0.3958	18.08
150.00	326.1	0.5024	26.18	180.00	193.1	0.7750	61.67	260.00	543.8	0.4057	19.26	300.00	731.6	0.2714	11.80
150.00	454.5	0.3863	19.54	180.00	272.5	0.5843	45.85	260.00	944.4	0.2677	11.81	300.00	1235.9	0.1868	7.47
150.00	759.0	0.2627	12.31	180.00	337.9	0.4881	37.92	260.00	1474.7	0.1986	7.95				
150.00	1239.8	0.1897	7.91	180.00	403.4	0.4212	32.31	270.00	290.4	0.7545	28.90				
160.00	332.9	0.5811	23.06	180.00	758.9	0.2538	18.06	270.00	406.2	0.5897	22.05				
160.00	404.6	0.5060	19.33	180.00	1242.3	0.1765	11.47	270.00	510.5	0.4953	18.29				
160.00	571.8	0.3910	14.32	180.00	1600.0	0.1497	9.11	270.00	658.5	0.4098	14.73				
160.00	978.9	0.2694	8.90	190.00	231.2	0.7758	47.26	270.00	1168.2	0.2736	8.96				
170.00	410.3	0.5852	16.89	190.00	329.2	0.5859	35.06	280.00	341.7	0.7575	22.09				
170.00	502.6	0.5110	14.13	190.00	410.5	0.4902	28.94	280.00	484.4	0.5932	16.85				
170.00	721.7	0.3979	10.40	190.00	488.9	0.4236	24.87	280.00	614.1	0.4999	13.94				
170.00	1282.1	0.2800	6.32	190.00	946.3	0.2575	13.60	280.00	799.6	0.4154	11.19				
180.00	507.5	0.5912	12.17	190.00	1588.0	0.1814	8.51	280.00	1455.9	0.2821	6.74				
180.00	627.7	0.5186	10.16	190.00	2105.9	0.1559	6.61	290.00	402.1	0.7593	16.79				
180.00	921.1	0.4085	7.40	200.00	274.8	0.7770	36.37	290.00	578.6	0.5982	12.74				
190.00	631.9	0.6004	8.56	200.00	396.6	0.5882	26.71	290.00	742.0	0.5063	10.49				
190.00	793.7	0.5306	7.10	200.00	497.6	0.4930	22.02	290.00	979.2	0.4236	8.37				
190.00	1208.5	0.4268	5.05	200.00	601.8	0.4270	18.62	300.00	473.5	0.7633	12.52				
200.00	803.9	0.6165	5.73	200.00	1183.3	0.2627	10.19	300.00	695.1	0.6054	9.45				
200.00	1039.0	0.5530	4.65	200.00	2069.9	0.1891	6.20	300.00	904.5	0.5159	7.74				
210.00	1085.7	0.6530	3.39	210.00	326.4	0.7785	27.60	300.00	1218.6	0.4362	5.11				
				210.00	477.3	0.5912	20.25	310.00	561.1	0.7694	9.03				
				210.00	603.4	0.4969	16.67	310.00	845.0	0.6166	6.81				
				210.00	734.1	0.4316	14.08	310.00	1128.4	0.5315	5.49				
				210.00	1492.5	0.2702	7.56	320.00	672.9	0.7793	6.26				
				220.00	385.0	0.7805	21.08	320.00	1060.2	0.6366	4.61				
				220.00	573.6	0.5953	15.28								
				220.00	731.3	0.5021	12.55								
				220.00	899.1	0.4380	10.53								
				220.00	1927.4	0.2823	5.47								
				230.00	454.4	0.7834	15.77								
				230.00	691.2	0.6012	11.35								
				230.00	893.8	0.5100	9.26								
				230.00	1112.3	0.4476	7.72								
				240.00	536.7	0.7876	11.61								
				240.00	838.7	0.6100	8.27								
				240.00	1106.0	0.5220	6.67								
				240.00	1402.4	0.4630	5.50								
				250.00	637.5	0.7940	8.25								
				250.00	1035.8	0.6244	5.78								
				250.00	1412.3	0.5434	4.55								

Table V. Smoothed Vapor-Liquid Equilibrium Ratios

2,3-dimethylbutane (1) - hydrogen (2)

psi	120°C K_1	120°C K_2	130°C K_1	130°C K_2	140°C K_1	140°C K_2	150°C K_1	150°C K_2	160°C K_1	160°C K_2	170°C K_1	170°C K_2	180°C K_1	180°C K_2	190°C K_1	190°C K_2	200°C K_1	200°C K_2	psi
300	.298	37.1	.373	34.0	.447	31.3	.533	28.3											300
400	.234	28.4	.291	26.1	.351	24.0	.427	21.8	.506	19.6									400
500	.194	23.1	.242	21.3	.293	19.6	.358	17.8	.430	16.1	.514	14.2							500
600	.167	19.5	.210	18.0	.255	16.6	.311	15.1	.377	13.7	.450	12.2	.532	10.6					600
800	.135	14.9	.169	13.8	.206	12.8	.252	11.7	.309	10.6	.371	9.46	.445	8.27	.526	7.07	.620	5.75	800
1000	.115	12.1	.144	11.3	(.178)	(10.4)	.217	9.59	(.266)	(8.8)	.323	7.82			.468	5.85	.562	4.84	1000
1200	.101	10.2	.128	9.53	(.158)	(8.8)	.193	8.15	(.239)	(7.5)	.290	6.68			.428	5.07			1200
1400	(.092)	(8.9)	(.116)	(8.3)	(.144)	(7.7)			(.219)	(6.5)	(.258)	(5.9)							1400
1600			(.107)	(7.3)	(.134)	(6.8)			(.204)	(5.8)									1600
1800			(.100)	(6.6)															1800

cyclohexane (1) - hydrogen (2)

psi	140°C K_1	140°C K_2	150°C K_1	150°C K_2	160°C K_1	160°C K_2	170°C K_1	170°C K_2	180°C K_1	180°C K_2	190°C K_1	190°C K_2	200°C K_1	200°C K_2	210°C K_1	210°C K_2	220°C K_1	220°C K_2	230°C K_1	230°C K_2	240°C K_1	240°C K_2	250°C K_1	250°C K_2	psi
200					.536	73.2	.645	67.2	.750	59.6															200
300			.307	54.2	.377	50.0	.455	46.2	.537	42.2	.630	38.1	.727	33.7											300
400			.240	41.1	.294	38.1	.354	35.3	.424	32.4	.505	29.6	.582	26.5	.671	23.5	.762	20.4							400
500			.198	33.2	.242	30.8	.293	28.6	.354	26.3	.420	24.3	.490	21.9	.569	19.5	.652	17.1	.732	14.7					500
600	.139	30.0	.170	28.0	.208	26.0	.253	24.2	.305	22.3	.365	20.6	.425	18.6	.498	16.7	.577	14.7	.652	12.7	.738	10.7			600
800	.110	22.8	.135	21.3	.165	19.8	.201	18.5	.244	17.2	.291	15.9	.344	14.5	.405	13.0	.475	11.6	.546	10.2	.624	8.59	.710	6.97	800
1000	.092	18.4	.116	17.3	.140	16.2	.171	15.0	.207	14.0	.246	13.0	.294	11.9	.347	10.8	.410	9.60	.477	8.43	.550	7.22	.636	5.91	1000
1200			.100	14.5	.123	13.6	.150	12.7	.182	11.9	.217	11.0	.262	10.1	.309	9.17	.366	8.22	(.429)	(7.2)	.499	6.23	.583	5.15	1200
1400			(.090)	(12.6)	.110	11.8	(.136)	(11.0)	.163	10.3	.196	9.61	.238	8.81	.281	.801	.334	7.20			.462	5.48	.546	4.58	1400
1600					.100	10.4	(.125)	(9.8)	.150	9.10	.181	8.53	.220	7.82			.310	6.42							1600
1800					.094	9.36	(.116)	(8.8)				7.65	.207	7.03			.292	5.79							1800
2000							(.109)	(8.0)				6.93	.195	6.38											2000
2200							(.104)	(7.3)																	2200
2400							(.099)	(6.8)																	2400

m-xylene (1) - hydrogen (2)

psi	240°C K_1	240°C K_2	250°C K_1	250°C K_2	260°C K_1	260°C K_2	270°C K_1	270°C K_2	280°C K_1	280°C K_2	290°C K_1	290°C K_2	300°C K_1	300°C K_2	310°C K_1	310°C K_2	320°C K_1	320°C K_2	psi
200																			200
300	.482	39.0	.560	35.5	.648	32.1	.743	28.3											300
400	.379	30.1	.442	27.6	.517	25.1	.597	22.4	.680	19.6									400
500	.314	24.6	.370	22.7	.433	20.7	.504	18.6	.578	16.5	.659	14.3	.739	12.0					500
600	.270	20.9	.320	19.2	.376	17.6	.438	16.0	.506	14.2	.583	12.4	.660	10.6	.742	8.67			600
800	.215	16.1	.255	14.9	.301	13.7	.355	12.4	.415	11.2	.482	9.85	.555	8.50	.636	7.12	.720	5.60	800
1000	.180	13.1	.217	12.2	.256	11.2	.303	10.2	.357	9.30	(.417)	(8.2)	.485	7.15	.565	6.03	.645	4.80	1000
1200	.158	11.1	(.191)	(10.3)	.227	9.54	(.268)	(8.8)	.317	7.97	(.374)	(7.1)	.440	6.21					1200
1400	.143	9.64	(.173)	(9.0)	.205	8.32	(.244)	(7.7)	.288	7.00	(.343)	(6.2)							1400
1600	.131	8.54	(.159)	(8.0)			(.225)	(6.8)			(.320)	(5.6)							1600
1800			(.148)	(7.2)			(.211)	(6.2)			(.302)	(5.1)							1800
2000			(.139)	(6.6)															2000

1,4-dietylbenzene (1) - hydrogen (2)

psi	280°C K_1	280°C K_2	290°C K_1	290°C K_2	300°C K_1	300°C K_2	psi
200			.645	40.1	.742	36.4	200
300	.400	30.5	.467	28.1	.543	25.7	300
400	.317	23.4	.370	21.8	.432	20.0	400
500	.267	19.2	.310	17.8	.364	16.5	500
600	.232	16.3	.267	15.2	.316	14.0	600
800	.184	12.6	.214	11.8	.255	10.9	800
1000	.155	10.4	.182	9.70	.216	9.02	1000
1200	.136	8.82	.160	8.27	.190	7.70	1200
1400	.121	7.68	.145	7.21			1400
1600	.111	6.81	.133	6.41			1600
1800	.103	6.11	.124	5.75			1800
2000							2000

Table VI. Liquid Volume Dilations on Mixing Hydrogen and Hydrocarbons[a]

	n-pentane					2,3 dimethyl butane					cyclohexane					n-decane					m-xylene					1,4-diethylbenzene			
°C	a	b	c	d	SD,MD cc/mole	a	b	c	d	SD,MD cc/mole	a	b	c	d	SD,MD cc/mole	a	b	c	d	SD,MD cc/mole	a	b	c	d	SD,MD cc/mole	a	b	d	SD,MD cc/mole
35	1.88	.27			1,4	2.02	.22			1,2	2.74				2,4	2.73										2.91			2,3
40	1.58	.39			3,5	2.12	.14			1,3																2.86			1,3
50	1.61	.32			3,6	1.88	.20			1,3	2.54				2,5											2.69			1,2
60	1.41	.37			3,5	1.79	.19			2,3	2.31	.29			3,5											2.86			1,4
70	1.35	.32			2,4	1.54	.30			1,3	2.25	.18			2,5											2.71			2,3
80	1.20	.34			3,6	1.42	.31			2,4	1.84	.26			2,5											2.63			2,4
90	1.14	.31			3,6	1.36	.25			2,3	1.93	.20			2,4											2.51			2,3
100	1.02	.35			2,4	1.29	.27			2,4	1.76	.31			3,6														
110	.88	.37			2,4	1.17	.30			3,5	1.63	.25			2,5	1.95	.18			2,4									
120	.75	.39			2,7	1.02	.31			2,5	1.61	.21			2,4														
130	.62	.42			3,5	.90	.32			2,5	1.56	.13			1,3														
140	.57	.47		1.3	2,6	.78	.38		.5	3,7	1.35	.21			2,6	1.56	.23			2,5	1.95	.24			3,6				
150	.40	.56	.03	1.6	2,5	.67	.42		.8	3,6	1.25	.23			2,4											1.97	.11		2,6
160	.24	.64	.04	2.0	3,6	.58	.44		1.0	3,6	1.12	.30			3,6	1.29	.24			2,3	1.56	.27			2,4				
170						.45	.43		1.0	3,6	1.01	.33		.8	1,3														
180						.33	.56	.04	1.9	3,6	.93	.32		.9	2,5	1.27	.25		.6	2,4	1.44	.23			3,6	1.61	.16		2,4
190						.20	.62	.05	2.4	3,7	.77	.37		.9	2,6											1.49	.20		2,4
200											.69	.36		1.1	3,8	1.10	.32		1.0	2,6	1.27	.26		1.1	1,3	1.29	.24		2,4
210											.56	.44		2.1	2,4														
220											.42	.54	.04	2.4	2,6	.89	.30		.7	2,4	.98	.36		1.3	1,3	1.13	.25		2,3
230											.30	.58	.04	3.0	2,6											1.11	.30	1.0	2,5
240											.17	.63	.05	3.6	3,9	.82	.33		1.5	2,6	.82	.30		.9	2,6	1.16	.28	1.6	3,5
250																.63	.37		1.2	2,7	.72	.32		1.3	1,5	.97	.29	1.2	2,4
260																.53	.53	.05	2.0	2,6	.60	.39		1.8	2,4	.84	.29	.9	2,5
270																.42	.53	.06	1.7	2,8	.49	.43		2.2	2,8	.81	.31	1.4	2,5
280																.35	.58	.05	2.5	3,7	.36	.49	.04	2.2	3,7	.70	.35	1.6	2,5
290																.26	.61	.06	2.8	4,10	.28	.52	.03	3.1	2,5	.60	.35	1.5	2,5
300																.18	.61	.03	3.2	3,9	.15	.60	.04	3.9	3,5	.51	.41	2.2	2,6

[a] a, b, c, and d are parameters in eq 8. SD and MD are standard and maximum deviations.

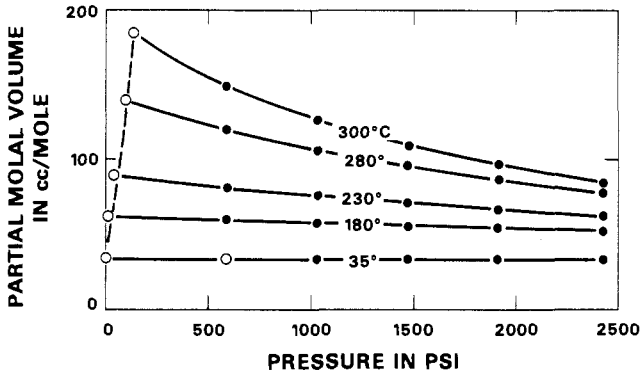

Figure 14. Partial molal volumes of hydrogen, at infinite dilution, in liquid 1,4-diethylbenzene.

those covered by experimental data. The filled-in circles involve only linear extrapolations to $x_2 = 0$, at a constant pressure, within the pressure range of the measurements. Surprisingly, at the lower pressures and higher temperatures, the partial molal volumes of hydrogen are often larger than those of hydrocarbons.

Registry No. Hydrogen, 1333-74-0; *n*-pentane, 109-66-0; 2,3-dimethylbutane, 79-29-8; cyclohexane, 110-82-7; *n*-decane, 124-18-5; *m*-xylene, 108-38-3; 1,4-diethylbenzene, 105-05-5; 1-methylnaphthylene, 90-12-0.

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Supplementary Material Available: Experimental values for solution dilation (13 pages). Ordering information is given on any current masthead page.

Solidification Behavior of the Cinnamic Acid–*p*-Nitrophenol Eutectic System

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The solid–liquid equilibrium of the cinnamic acid–*p*-nitrophenol (CA–pNP) eutectic system has been investigated. Heat of fusion, microstructure, and strength measurements have been made. Infrared spectral studies indicate molecular association in the formation of the eutectic. Thermodynamic functions such as h^E, g^E, and S^E have been calculated and were found to be negative except g^E. Statistical mechanical treatment shows that the surface nucleation theory holds good in the solidification of the present eutectic.

Introduction

Solid materials are of considerable interest both from the fundamental and from the technological point of view. Eutectic materials also come in this category. In order to control the properties of such materials, studies of phase diagram, linear velocity of crystallization, microstructure, compressive strength, and thermodynamic properties are essential (*1*). The present paper describes the chemistry of the cinnamic acid–*p*-nitrophenol (CA–pNP) eutectic system with reference to the above properties.

Experimental Section

Materials and Purification. *p*-Nitrophenol (BDH) and cinnamic acid (BDH) were purified by repeated distillation under reduced pressure. The purity was checked by determining the melting points with the help of a mercury thermometer correct to ±0.1 °C. The melting points are 112.0 and 133.0 °C, respectively. Cinnamic acid is represented as CA and *p*-nitrophenol is represented as pNP.

Phase Diagram and Undercooling Study. The phase diagram of the CA–pNP system has been studied by the thaw melt method (*2*). Mixtures of various compositions were prepared in glass test tubes by repeated heating, chilling, and grinding in a glass mortar. The melting points and thaw points were determined with a mercury thermometer correct to ±0.1 °C. The undercooling study was made in a manner described by Rastogi and Bassi (*3*).

Study of Microstructures. A microscopic method was used for the study of microstructures of components and eutectic. A glass slide was kept in an oven at a temperature higher than the melting points of the eutectic, and a very small amount of the sample was placed on it. As the sample melted completely, the coverslip was glided on it. The slide was allowed to cool and nucleations were started from one side and this was then photographed with a camera under a microscope of desired magnification. The effect of 0.1% 8-hydroxyquinoline and 4-chloroaniline on the microstructure of the eutectic has also been investigated.

Heat of Fusion Measurements. The heats of fusion of the pure components and the eutectic were determined by differential thermal analyzer (Paulik-Paulik-Erdey MOM derivatograph, Hungary) using the method of Vold (*4*). The heating rate was maintained at 2 °C/min, and the temperature was measured by a Pt–Rh thermocouple. From this method only the relative value of the heat of fusion could be determined.

Compressive Strength Measurements. Compressive strengths of components and eutectic in the form of pellets were determined by an universal testing machine. The pellets were prepared by solidifying the molten materials in glass test tubes of uniform diameter and the surfaces were smoothened by rubbing on emery paper. True stress was obtained by dividing the maximum load applied on the pellet (which was capable of breaking the pellet) by the area of the pellet. For calculating true strain, the total number of divisions on the graph (which indicates the maximum compression) was divided by the magnification (magnification was obtained by dividing chart speed by cross head speed) and the value thus obtained was finally divided by the original length of the pellet.

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