TABLE I

SOLUBILITY OF PHENANTHRENE, 25°

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (3.26), 500 (2.72), 1000 (2.26), 2000 (1.80), 4300 (1.04), 7150 (0.50), 8750 (0.36)

n-Heptane

1 (4.01), 500 (3.21), 900 (2.92), 1000 (2.72), 2000 (1.84), 3430 (1.11), 5000 (0.84), 7000 (0.52)

n-Octane

1 (4.64), 490 (3.81), 1000 (2.84), 1960 (1.97), 3850 (1.20), 5200 (0.88)

CS_2

1 (23.5), 500 (16.2), 1000 (12.5), 2000 (7.3), 4000 (4.5), 6000 (2.9), 7000 (2.2)

TABLE II

SOLUBILITY OF SnI_4

The pressure is given in atmospheres followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (0.470), 10 (0.443), 480 (0.315), 1000 (0.199), 2000 (0.099), 3100 (0.057), 5100 (0.047), 7200 (0.033), 9100 (0.019)

n-Heptane

1 (0.553), 470 (0.383), 980 (0.163), 2000 (0.048), 3000 (0.031), 4600 (0.019), 7200 (0.018)

n-Octane

1 (0.621), 500 (0.429), 1000 (0.245), 1500 (0.148), 2000 (0.115)

CS_2

1 (14.61), 1000 (7.99), 2000 (5.64), 3600 (3.45), 5000 (1.96), 7000 (0.77), 10,000 (0.11)

TABLE III

SOLUBILITY OF C_2Cl_6

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (13.92), 400 (9.84), 1000 (6.36), 2000 (3.40), 3300 (1.72), 5000 (0.64), 5830 (0.29), 6750 (0.26)

n-Heptane

1 (15.18), 410 (10.48), 1000 (6.79), 2000 (2.30), 2970 (1.63), 4000 (0.83), 5000 (0.40)

n-Octane

1 (15.72), 400 (10.35), 1000 (6.33), 2000 (3.44)

CS_2

1 (19.5), 500 (12.0), 1000 (8.0), 1970 (4.1), 3400 (2.3), 5000 (1.3), 7000 (0.31)

2-Methylpentane

1 (13.02), 400 (9.15), 1000 (5.76), 1950 (3.14), 3350 (1.43), 5000 (0.52), 6900 (0.22)

3-Methylpentane

1 (13.52), 400 (9.56), 1000 (6.21), 2000 (3.15), 3500 (1.19), 5000 (0.61), 7000 (0.18)

2,3-Dimethylbutane

1 (13.15), 400 (9.19), 990 (5.74), 1970 (2.83), 3500 (1.15), 4950 (0.51), 6800 (0.14)

2,2-Dimethylbutane

1 (12.02), 400 (8.48), 990 (5.41), 2000 (2.72), 3500 (0.98), 4500 (0.45)

TABLE IV

SOLUBILITY OF ANTHRACENE

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

CS_2

1 (0.84), 240 (0.70), 500 (0.59), 1000 (0.41), 2000 (0.27), 4000 (0.13)

various temperatures by Dorfman and Hildebrand.[1] The density coefficient of solubility varies considerably more rapidly at constant pressure than at constant temperature. A similar result was found for SnI_4 in *n*-heptane.

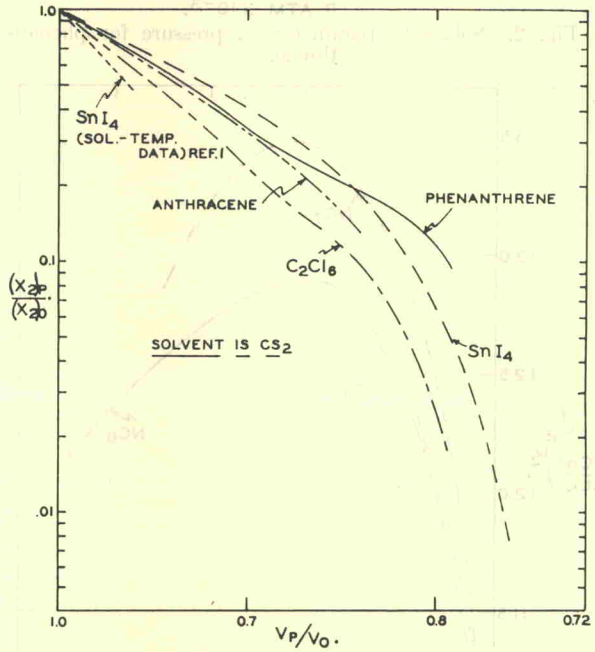

Fig. 1.—Relative solubility *vs.* relative molar volume of solvent.

It is useful to compare our atmospheric pressure data with values in the literature. In Table V

TABLE V

COMPARISON OF SOLUBILITIES OBTAINED IN THIS WORK WITH PUBLISHED SOLUBILITY VALUES OF SnI_4 (MOLE %)

Solvent	Dorfman and Hildebrand[1]	This work
Heptane	0.533	0.552
CS_2	14.64	14.61

Solubility of phenanthrene (mole %)

Solvent	Hildebrand Ellefson and Beebe[3]	This work Eastman	Recrystallized
CS_2	25.5	23.5	21.6
n-Hexane	4.2	3.26	3.09

Solubility of anthracene (mole %)

Solvent	Ref. 2	This work
CS_2	1.09	0.84

we see such a comparison. We find excellent agreement for the solubility of SnI_4 in CS_2 and in heptane, but no agreement for the solubility of

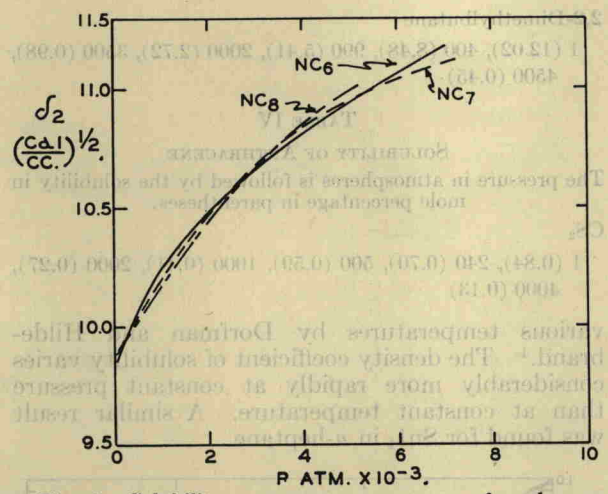

Fig. 2.—Solubility parameter *vs.* pressure for phenanthrene.

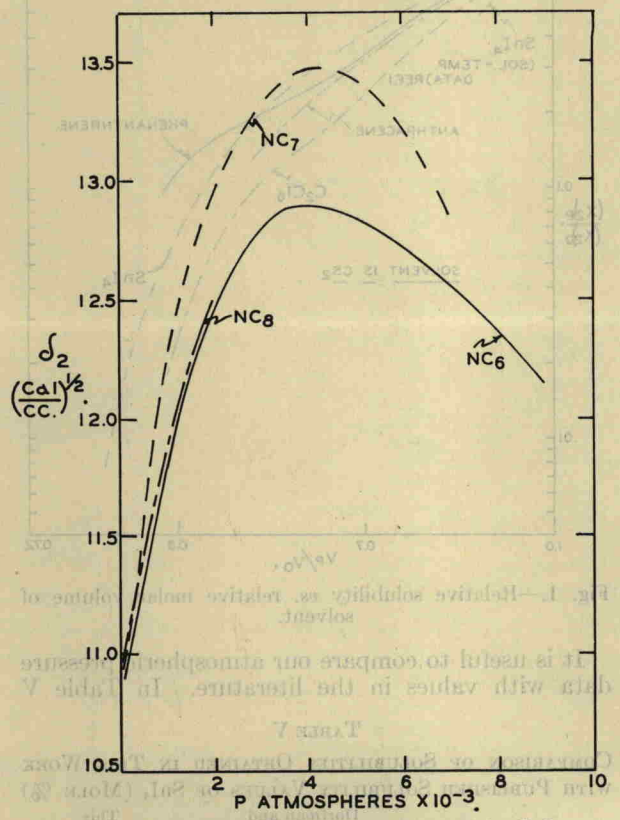

Fig. 3.—Solubility parameters *vs.* pressure for SnI_4.

phenanthrene and anthracene in heptane. We have no good explanation of this. We tried two different batches of Eastman phenanthrene, and recrystallized one batch several times. We never obtained any variation from batch to batch greater than 10%, and the more highly purified batches deviated most widely from Hildebrand's values.

Comparison of Theory and Results.—By far the most widely used theory of solutions is that developed by Scatchard and Hildebrand. Recently theories with a sounder basis in statistical mechanics have been developed by Guggenheim,[5] Kirkwood[6] and Prigogine and co-workers.[7] These, however, are not readily applied to a discussion of solubility under pressure.

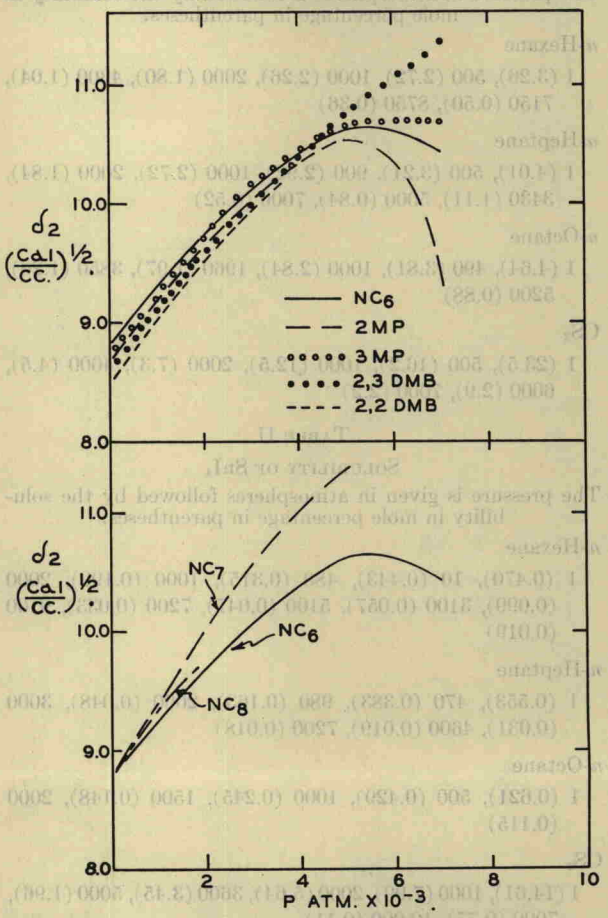

Fig. 4.—Solubility parameter *vs.* pressure for C_2Cl_6.

To discuss our results we shall use the S–H theory. This theory gives[8] for the partial molal free energy of the solute

$$\Delta\bar{F}_2 = V_2\varphi_1^2(\delta_2 - \delta_1)^2 + RT \ln X_2 \qquad (1)$$

if the entropy of mixing is ideal, or

$$\left[\Delta\bar{F}_2 = V_2\varphi_1^2(\delta_2 - \delta_1)^2 + RT \ln \varphi_2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right)\right] \qquad (2)$$

if the Flory–Huggins entropy is used. Here

V_i = molal vol. of i (of the supercooled liquid for the solute)
X_2 = mole fraction of solute (measured)
φ_i = vol. fraction of i
δ_i = solubility parameter of i
$= \left(\frac{-E}{V}\right)^{1/2}$

where $-E$ = cohesive energy, at one atmosphere, the energy of vaporization into a perfect gas.

It is not hard to show[8] that

$$\overline{\Delta F_2} = RT \ln X_2^i \qquad (3)$$

(5) E. A. Guggenheim, "Mixtures," Oxford Univ. Press, New York, N. Y., 1952.

(6) Z. Salzberg and J. H. Kirkwood, *J. Chem. Phys.*, **20**, 1538 (1952); **21**, 2169 (1953).

(7) I. Prigogine and V. Mathot, *ibid.*, **20**, 49 (1952); I. Prigogine and A. Bellemans, *Disc. Faraday Soc.*, No. 15, 80 (1953); I. Prigogine, N. Trappeniers and V. Mathot, *ibid.*, No. 15, 93 (1953). See also other articles referred to in these papers.

(8) J. H. Hildebrand and R. L. Scott, "The Solubility on Nonelectrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.