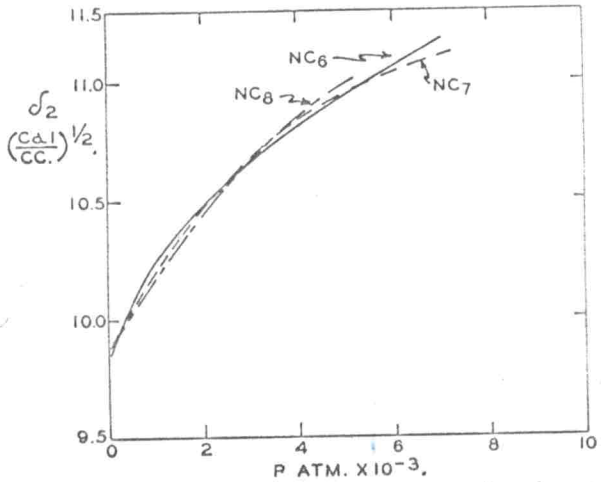

Fig. 2.—Solubility parameter *vs.* pressure for phenanthrene.

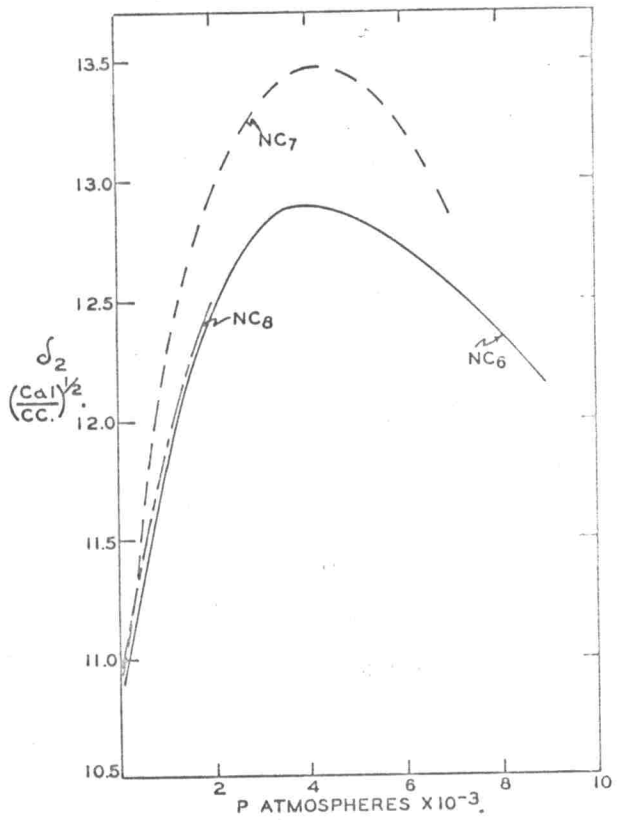

Fig. 3.—Solubility parameters *vs.* pressure for SnI_4.

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.

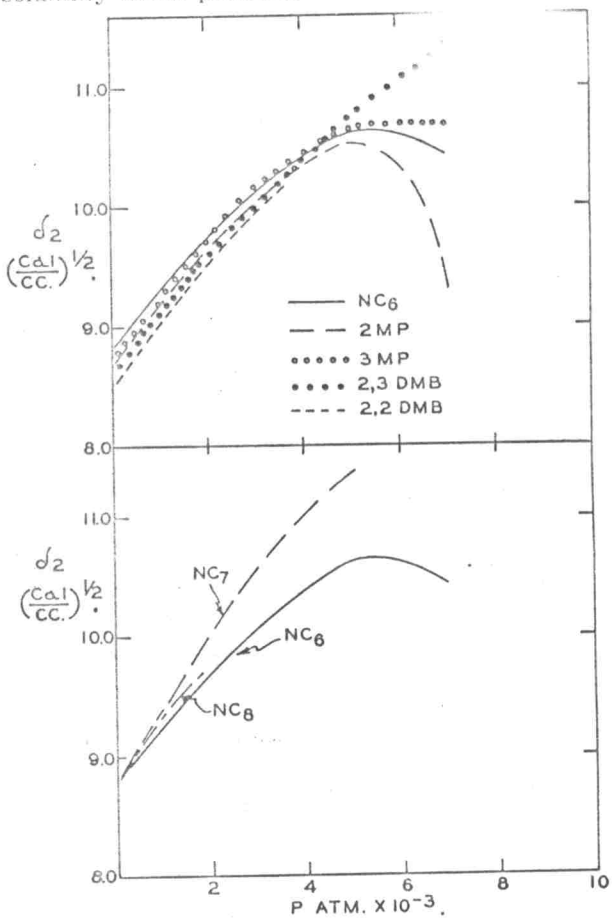

Fig. 4.—Solubility parameter *vs.* pressure for C_2Cl_6.

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.