

where  $X_{2i}$  is the "ideal solubility" of the solid.

To evaluate solubility parameters under pressure the relationship

$$\left(\frac{\partial E}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - P \left(\frac{\partial V}{\partial p}\right)_T \quad (4)$$

is used. Then

$$E_P = E^\circ + \int_1^P \left(\frac{\partial E}{\partial p}\right)_T \partial P \quad (5)$$

The  $p$ - $v$ - $t$  data of Bridgman<sup>9</sup> were used. The volumes of the supercooled liquids were estimated from Bridgman's data on compressibility of organic solids and volume changes on melting under pressure. It can be shown that no reasonable change in these values would change our calculations materially.

In these equations  $X_{2i}$  and  $\delta_2$  are not known under pressure. The solutions were considered in pairs; one solvent in each pair was  $\text{CS}_2$ . It was then possible to solve for  $\delta_2$ , the solubility parameter of the solute, using either the Flory-Huggins entropy (eq. 2) or the ideal entropy (eq. 7). Both calculations were made. In Figs. 2-4 are shown the calculated values of  $\delta_2$  using the Flory-Huggins entropy. There were no significant differences in the trends obtained using eq. 1 or 2.

(9) P. W. Bridgman, *Proc. Amer. Acad.*, **49**, 1 (1913); **66**, 1 (1931); **76**, 9 (1945).

The measure of the applicability of the S-H theory is the consistency of the solubility parameter of the solute  $\delta_2$  calculated from different solvent pairs. From Fig. 2, it can be seen that the theory describes phenanthrene solutions quite well. From Fig. 3 and 4 we note that the theory gives consistent results for  $\text{SnI}_4$  and  $\text{C}_2\text{Cl}_6$  in hexane and octane, but that solubility parameters for these almost spherical solutes in heptane are high, particularly at the higher pressures. It is known that the odd-numbered normal paraffin chains pack differently than those with an even number of links. Their freezing points are displaced to a lower temperature indicating there are fewer ways of packing them in a lattice. It would seem that the deviation of heptane is due to an entropy effect not accounted for in eq. 2.

In Fig. 4 are shown the solubility parameters for  $\text{C}_2\text{Cl}_6$  calculated for solutions in the isomers of hexane. The agreement is good to 5000 atmospheres, but beyond this point there is a spread in solubility parameters far outside experimental error. Apparently there are different packing effects for different isomers, and these become important at high densities.

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