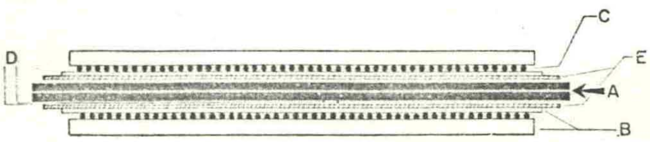

Figure 2. The pyrolysis unit: A, stainless steel tube, 0.006 in. i.d.; B, Fiberglas insulation; C, heating wire; D, thermocouple; E, outer tubing.

recorder. The voltage to the detector was supplied by a 300-V battery. All experiments were carried out at 40 ± 1°.

Solutes. The stearic acid was obtained from Merck and Co., Inc., and the 1-octadecanol from Eastman Kodak. These compounds were recrystallized three times from hot water; only the first portion of solute to crystallize was used. The solutes were then dried, melted, and cooled under vacuum.

The two Carbowaxes (1000 and 4000) were supplied by Applied Science Laboratory.

Experimental Procedure. Prior to each experiment, sample chambers A and B and the tubing between valves 1 and 2 (see Figure 1) were washed with organic solvents, ethanol, and finally distilled water. After drying, the sample chambers were installed and pressurized to 1900 atm. By using valves 1, 2, and 3, the gas was directed through the sample loop and finally into the detector. When the recorder signal dropped to the limit of detectability, it was assumed that organic impurities were adequately purged. The sample chambers were then removed from the system for charging with solute. The sample chambers were filled to capacity, this requiring about 1 cm^3 of solute. They were then returned to the system and pressurized to 1900 atm. Extreme care was taken to avoid contamination during filling.

A plug of solute vapor can be obtained by momentarily routing the gas flow through the sample loop. Plug sampling, however, introduced too much uncertainty into the data. Even with considerable care the peak size varied ±6%.

A superior way for determining solute concentration in the dense gas is by the constant plateau method. Here the carrier gas is flowed steadily through the sample loop for 15–20 min. The recorder trace showed a steep rise followed by a constant plateau. The height of the plateau is proportional to the solute concentration in the carrier gas and to the flow rate, and thus can be used to measure equilibrium concentrations.

The plateau method can be used to check on and correct for the presence of impurities and the possible lack of solubility equilibrium.

Impurities (light hydrocarbons, etc.) were apparent on several occasions, particularly with octadecanol. They were observed and allowed for as follows. Following 30 min of static equilibration, flow causes a steep signal rise, a short plateau, and a slow signal decay to a new plateau. With repetition of this process the initial rise becomes progressively smaller until a true and reproducible plateau trace is obtained. Apparently at this point the volatile impurities have been extracted. This repetition test was made for all systems.

Lack of solubility equilibrium is indicated by a sharp rise, a short plateau, and a decay. Repetition does not lead to a steady plateau. Saturation could be improved by reducing the flow, but this reduces the detector signal. One could also increase the size or length of the sample chamber and sample, thus giving a longer contact time with the carrier gas. It is for this reason that two sample chambers were joined in series in the present study. Sample chamber A can be thought of as a presaturator. Satisfactory saturation was thus achievable with all compounds attempted except Carbowax 6000; the latter was thus not studied further.

Calibration Procedure. To estimate the absolute values of solubilities in compressed gases, the signal size requires calibration. Since the detector responses for the compounds used in this work are unknown, approximate calibration is achieved using the principle that the signal from a flame ionization detector is roughly proportional to the flux of carbon atoms into the flame. A relative response factor, or equivalently, an effective carbon atom number, which accounts for the bonding of carbon atoms to noncarbon atoms, must be employed.

Propane was used as the reference compound. Ten 60-μl peaks were passed through the detector. Assuming the ideal gas law, each peak contained 2.10×10^{-6} mol of propane or 6.29×10^{-6} g-atoms of carbon. From this and the mean area per peak, it was determined that the number of effective gram-atoms of carbon in unit time was equal to

$$\frac{m}{t} = 0.90 \times 10^{-2} R \times E \tag{4}$$

where R is the recorder response in tenths of an inch and E the electrometer setting in millivolts. The outlet gas flow rate was held constant at 39 cc/min. Assuming the CO_2 to be ideal under outlet (atmospheric) conditions, this corresponds to a CO_2 flux of 2.3×10^{-5} mol/sec. Thus the mole fraction of solute in the dense gas is simply

$$X_2 = 3.0 \times 10^{-8} R \times E/\theta \tag{5}$$

where θ is the number of effective carbon atoms in the molecule in relationship to detector response.

Pyrolysis Products. The products of the high pressure pyrolysis of Carbowax 4000 were examined by sampling the column effluent into a low-pressure Porapak Q-S column. Pyrolysis constituents were identified by relative retention times.

Results and Discussion

Density Dependence of Solubility. The accurate mea-