Solubilities of Hydrogen and Oxygen in Polydimethylsiloxanes

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THE SOLUBILITY of hydrogen in octamethylcyclo tetrasiloxane and oxygen in a dimethylsilicone oil have been measured for the first time, using an automatic balance at high pressures. The values, 7×10^{-5} gram hydrogen per gram D_4 per atm. pressure for hydrogen in cyclic tetramer, and 1.9×10^{-4} gram oxygen per gram oil per atm. pressure for oxygen in the oil, are in good agreement with previous data for the solubility of simple gases above their critical temperatures in alkanes. The rate of attainment of solution equilibrium is however much higher for polysiloxanes than for hydrocarbons.

There is a surprising lack of published information concerning the solubility of gases in silicone oils and gums. In view of recent reports on the powerful effects of certain gases—e.g. oxygen—on radiation-induced reactions (*7*), and the use of the presence of molecular hydrogen, for example, in some irradiated systems to indicate particular ion-molecule type mechanisms (*5*), it becomes important to determine solubility data, parallel to that known for alkanes (*3*), for typical silicones used in radiation-induced reaction studies.

EXPERIMENTAL

The silicones used were octamethyl cyclotetrasiloxane (D_4) and 26,000-centistoke polydimethysiloxane oil. The D_4 was purified by distillation. The oil, whose weight average molecular weight was calculated to be 77,000 (*1*), was devolatilized prior to use.

An automatic gravimetric sorption balance capable of operation at pressures up to 20 atm. (*2*), was used to determine solubilities. A simple borosilicate glass bucket was used to hold the D_4, but a sintered alumina bucket was used for the 26,000-centistroke oil, to permit all the exterior surface of the sample to be available to the dissolving gas. The sample weights were about 10 grams. The weights and volumes of these buckets were known accurately, the latter being measured by a liquid displacement technique in a vertical tube of precision bore tubing. Differences in height of the liquid column were measured with a sensitive cathetometer.

The sample was placed in the balance chamber, which was then evaluated carefully. Because D_4 is a fairly volatile species at the experimental temperature, the weight of the sample was measured throughout this process. Tank grade gas was then admitted to the chamber, and its pressure measured on a pair of calibrated Bourdon gages (the master calibration was against a high pressure mercury manometer). The apparent weight of the sample was recorded as a function of time; thus, equilibrium was attained in about an hour. More gas was admitted and the procedures repeated, up to final pressures around 20 atm. The results showed an apparent decrease in weight, due to the buoyancy of the compressed gas. The solubility data were found by subtracting these decreases in weight from the calculated buoyancy weight decrease corrections, which were based on the accurately known "out-of-balance volume" of the balance system and the known gas densities. The final solubility data are shown in Table I.

Table I. Solubilities at 30° C.

H_2 in Octamethylcyclo Tetrasiloxane		O_2 in Dimethylsilicone Oil	
Solubility, g. gas/g. $D_4 \times 10^4$	Gas pressure, atm.	Gas pressure, atm.	Solubility, g. gas/g. oil, $\times 10^4$
4.2	7.6	4.40	7.7
8.8	15.3	7.80	12.8
13.0	21.1	12.02	20.5
		16.31	27.7
		21.41	38.5

DISCUSSION

The observed data conform well with the Henry law in the pressure range studied. The values are of the same order of magnitude as earlier data for the solubility of hydrogen in hexane (*3*). The values are large, corresponding with amounts of the order 1 standard cc. per gram, thus accentuating the need for very careful vacuum manipulation of the oils before reaction studies are commenced. From the known geometry of the alumina bucket and the time taken for the sample to equilibrate after a change in oxygen pressures, the diffusion coefficient of oxygen in the dimethyl silicone oil may be estimated as

$$D = 5 \times 10^{-6} \text{ sq. cm. per sec.,}$$

using the equation for the relationship between the amount of gas diffused in after time *t*, and infinity, seconds cited by Crank (*4*).

This value appears to be moderately high, about 10^3 as great as the corresponding value for polyethylene of similar molecular weight but is reasonable when one considers the ease of segmental motion in polysiloxane chains compared with hydrocarbon chains of similar dimensions. Huggins has estimated from nuclear magnetic resonance measurements (*6*) that short range segmental motions in polysiloxanes occur 100 times as frequently as in polyethylenes under the same conditions. However, assuming such motions are important to the diffusion of small molecules like oxygen, this still leaves a 10-fold difference in the diffusion coefficients in favor of the polysiloxane.

The equilibrium solubilities of super critical gases in polysiloxanes are of the same order of magnitude as those in hydrocarbons, but the rate of attainment of equilibrium is much higher in the former.

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LITERATURE CITED

(1) Barry, A. J., *J. Appl. Phys.* **17**, 1020 (1946).
(2) Cannon, Peter, *Rev. Sci. Instr.* **29**, 1115 (1958).
(3) Cook, M. W., Hanson, D. N., *Ibid.*, **28**, 371 (1957).
(4) Crank, J., "The Mathematics of Diffusion," p. 66, Oxford Univ. Press, N. Y., 1956.
(5) Dorfman, L., *J. Phys. Chem.* **60**, 826 (1956).
(6) Huggins, C. M., General Electric, Schenectady, N. Y., unpublished results.
(7) St. Pierre, L. E., Dewhurst, H. A., *J. Chem. Phys.* **29**, 241 (1958).

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