[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Solubility of Chlorine in Normal Perfluoro-heptane and other Liquids

BY J. CHR. GJALDBAEK AND J. H. HILDEBRAND*

In a recent paper[1] dealing with the solubility of nitrogen in a number of liquids, we showed that it is possible to account for a wide range of solubilities, from mole fraction 39.1×10^{-4} in normal perfluoroheptane to 2.23×10^{-4} in carbon disulfide, by now familiar theories based upon a model process of mixing two liquids, provided the parameters relating to nitrogen at 25°, far above its critical point, are semi-empirically adjusted. It has seemed to us very desirable, especially for the better understanding of the solvent power of fluorocarbons, to study the solubility of chlorine in a fluorocarbon in order to have a gas for which the necessary data can be accurately known.

Many years ago Taylor and Hildebrand[2] determined the solubility of chlorine in ethylene bromide, carbon tetrachloride, silicon tetrachloride, and heptane, and they pointed out that the order of decreasing solubility, expressed as mole per cent., is the order of increasing difference in internal pressure, but we felt confident, at the outset of the present investigation, that chlorine would show its maximum solubilities not in the fluorocarbons, as with nitrogen, but in solvents of much higher internal forces or "solubility parameters," which are square roots of their energies of vaporization per cc.

Experimental Procedure.—The chlorine gas was from the Ohio Chemical Co. Normal perfluoroheptane (C_7F_{16}) was distilled and a middle portion (about 500 cc.) was used, with boiling point 82.33–82.42° at 753.8 mm.

Chlorine gas was bubbled slowly through the solvent for about an hour. A large Dewar equipped with motor-driven stirrer was used as a thermostat; the temperature was held constant to 0.1° by hand control. A sample of the saturated solution was forced into a weighing pipet, weighed and emptied into a solution of potassium iodide and sulfuric acid. The liberated iodine was determined by titration with standard sodium thiosulfate using starch solution as indicator at the end of the titration. The calculation of the solubility was carried out as described by Taylor and Hildebrand, using vapor pressure data for perfluoroheptane as determined by Fowler and co-workers.[3] The measurements are given in Table I and plotted in Fig. 1, together with the "ideal solubility," $\log f_2/f_2^0$, taking the figures for the fugacity, f_2, of chlorine from the paper by Taylor and Hildebrand,[2] also for comparison, $\log 1/p_2^0$, which does not allow for the deviations of chlorine from perfect gas laws.

TABLE I

SOLUBILITY OF Cl_2 IN n-C_7F_{16} AT 760 MM. EXPRESSED AS BUNSEN COEFFICIENT, α, AND MOLE FRACTION x_2

t, °C.	α	x_2
0	20.1	0.164[a]
15.6		.1165
15.8		.1174
19.8		.1101
20.0	12.3	.110[b]
22.0		.1051
25.0	10.7	.0977
25.3		.0975

[a] Extrapolated. [b] Interpolated.

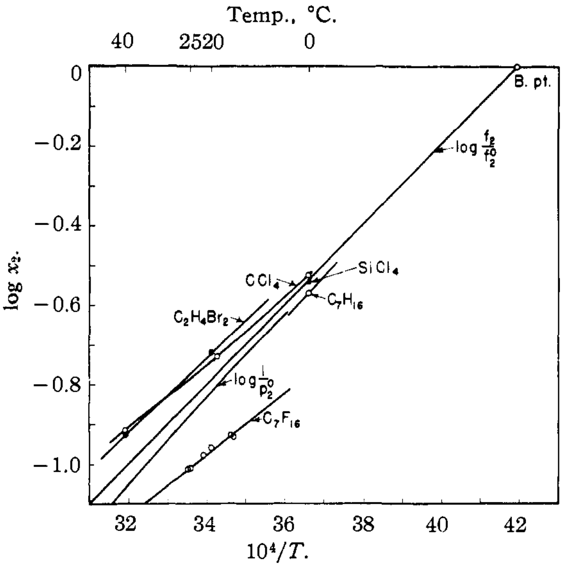

Fig. 1.—Solubility of chlorine.

We wished, also, to learn how closely the partial molal volume of chlorine in solution agrees with its pure liquid volume, so we determined the density of solutions of known chlorine content, with the result shown in Table II. The partial molal volume of chlorine in these solutions, $\bar{v}_2$, was calculated by aid of the equation of definition, $V = N_1\bar{v}_1 + N_2\bar{v}_2$, ($N$ = number of moles) setting $\bar{v}_1 = v_1$, which is a close approxima-

TABLE II

PARTIAL MOLAL VOLUME OF Cl_2 IN n-C_7H_{16}

t, °C.	Wt. % Cl_2	x_2	$\bar{v}_2$	v_2 (pure Cl_2)
0.0	1.986	0.0988	49.6	48.4 (at 3.66 atm.)
0.0	1.915	.0966	49.2	
25.0	1.652	.0841	52.3	50.8 (at 7.52 atm.)
25.0	1.342	.0694	53.1	

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* Editorial Board 1932–1939.

[1] J. Chr. Gjaldbaek and J. H. Hildebrand, THIS JOURNAL, **71**, 3147 (1949).

[2] Nelson W. Taylor and J. H. Hildebrand, *ibid.*, **45**, 682 (1923).

[3] R. D. Fowler, J. M. Hamilton, J. S. Kasper, C. E. Weber, W. B. Burford and H. C. Anderson, *Ind. Eng. Chem.*, **39**, 375 (1947).

TABLE III

SOLUBILITY OF CHLORINE IN MOLE PER CENT.; COMPARISON OF OBSERVED AND CALCULATED VALUES

	0°					25°				
			100 x_2					100 x_2		
	v	δ	Obs.	Eq. 2	Eq. 3	v	δ	Obs.	Eq. 2	Eq. 3
C_7F_{16}	218	6.10				227	5.85	9.8	7.3	14.1
C_7H_{16}	143	7.65	27.0	24.1	32.3					
$SiCl_4$	111	7.80	28.8	25.1	29.8					
CCl_4	94	9.00	29.8	28.6	31.7	97.0	8.60	16.7	14.3	16.4
Cl_2	48.4	9.20		(28.6)		50.8	8.70		(14.3)	
$C_2H_4Br_2$						86.7	10.40	17.2	11.5	12.8

tion when $N_1 \gg N_2$. The small difference between $\bar{v}_2$ thus determined and v_2 for pure liquid chlorine indicates that the expansion that would occur upon mixing the two pure liquids would be very small.

Discussion

Figure 1 shows, first, certain interesting qualitative relations. The solubility of chlorine in all the solvents except perfluoroheptane is not far from the ideal solubility, as given by f_2/f_2^0, in accordance with the comparatively small differences in their internal pressures, or δ-values, whereas perfluoroheptane, whose δ-value is much smaller than that of chlorine, 5.9 *vs.* 9.2, at 25°, is a much poorer solvent.

The plot illustrates, also, the error that would be introduced by using $1/p_2^0$ to define the ideal solubility of chlorine in this region instead of f_2/f_2^0, which corrects for gas imperfections.

According to present theory, solubility is enhanced by disparity in molal volume and diminished by disparity in internal pressure. The former causes deviations from ideal entropy, the latter from ideal (zero) heat of mixing the pure liquid components. Because the molal volume of chlorine is much smaller than the molal volumes of all the solvents here represented, all these solubilities are increased by this factor, and most of all in perfluoroheptane. This effect suffices to raise the solubility of chlorine above the ideal value in carbon tetrachloride and ethylene bromide. But in heptane and particularly in perfluoroheptane the heat term is so large as to offset the entropy term and to keep the solubility less than the ideal. The entropy correction can be expressed quantitatively by the "Flory–Huggins" equation

$$R \ln a_2 = R\left[\ln \phi_2 + \left(1 - \frac{v_2}{v_1}\right)\phi_1\right] \qquad (1)$$

and the heat term by the "van Laar–Scatchard–Hildebrand" equation

$$\ln a_2 = \ln x_2 + \frac{v_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad (2)$$

which, combined, give

$$\ln a_2 = \ln \phi_2 + \left(1 - \frac{v_2}{v_1}\right)\phi_1 + \frac{v_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad (3)$$

where a denotes activity, ϕ volume fraction, δ the solubility parameter. The subscript 1 denotes the solvent, 2 the chlorine.

For the activity of chlorine, we use f_2/f_2^0, the ratio of its fugacity at one atmosphere to its fugacity at its saturation pressure at the same temperature, as calculated by Taylor and Hildebrand. The solubility parameters, δ, are those given by Hildebrand and Scott,[4] except for perfluoro-heptane where we have used vapor pressure data of Fowler, *et al.*,[3] to calculate the heat of vaporization, correcting for gas imperfection with the Berthelot equation of state; the critical temperature was also reported by Fowler, *et al.*, and the critical pressure was estimated assuming the law of corresponding states.

Table III shows that Equation 2 gives values for x_2 which are too small. Equation 3 raises the calculated values, too much in the case of perfluoroheptane, where $v_1/v_2 = 4.47$, a very large disparity.

Figure 1 shows that the temperature coefficient of the solubility is slightly less than ideal for ethylene bromide and carbon tetrachloride and much less for perfluoroheptane. This is a matter of entropy which can be explained on the basis of the ratio v_1/v_2. The values of $\Delta \log x_2$ *vs.* $\Delta\, 1/T$ can be read from the curve and compared with the same slope of the values calculated by aid of Equation 3. Table IV shows the agreement to be, on the whole, within the accuracy expected from the uncertainties in the various experimental quantities involved.

TABLE IV

OBSERVED AND CALCULATED VALUES OF $-(\Delta \log x_2/(\Delta\, 1/T)$

	Obs.	Calcd.
C_7F_{16}	730	750
CCl_4	830	930
From f_2/f_2^0		974

We express our gratitude to the Office of Naval Research for its support of this research.

Summary

1. The solubility of chlorine in normal perfluoroheptane has been determined to be 11.0 mole per cent. at 20° and 9.77 mole per cent. at 25°. The partial molal volume of chlorine in normal perfluoroheptane has been determined as $\bar{v}_2 = 49.4$ cc. at 0° and 52.7 cc. at 25°, values

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(4) J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," third edition, Chapter XV and Appendix 1, Reinhold Publishing Corporation, New York, N. Y., 1950.

which are close to the molar volume of pure liquid chlorine at the respective temperatures.

2. The new solubility measurements have been tabulated together with existing data in four other solvents and it has been shown that the equation $\ln a_2 = \ln \phi_2 + (1 - (v/v_1)\phi_1 + (v_2\,\phi^2/RT)\,(\delta_1 - \delta_2)^2$ accounts fairly well for the observed values of the solubility without empirical adjustment of the parameters.

3. The temperature coefficient of solubility is in reasonable accord with the above equation.

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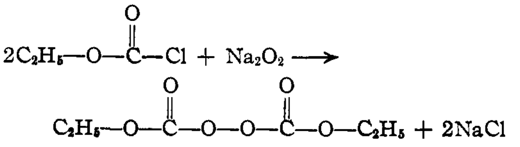
Some Reactions of Diisopropyl Peroxydicarbonate

BY SAUL G. COHEN* AND DONALD B. SPARROW†

Introduction

Dialkyl peroxydicarbonates of the structure $\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}R}$, I, are formally similar to the diacyl peroxides, $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}R}$, (II), the hydrocarbon groups in (II) being replaced by alkoxy groups in (I). The peroxydicarbonates and the free radicals, $\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\cdot}$ which appear to be formed in their decomposition are derivatives of the thermally, unstable monoalkyl carbonic acids, $\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}$, just as the diacyl peroxides and the carboxylate free radicals[1] are related to the more stable carboxylic acids.

Diethyl peroxydicarbonate was apparently prepared both by the decomposition of ethyl triphenylmethyl-azo-carboxylate, $(C_6H_5)_3C{-}N{=}N{-}COOC_2H_5$, in the presence of oxygen, and by the interaction of sodium peroxide and ethyl chlorocarbonate.[2]



$$\mathrm{2C_2H_5{-}O{-}\overset{O}{\overset{\|}{C}}{-}Cl + Na_2O_2 \longrightarrow C_2H_5{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_2H_5 + 2NaCl} \quad (1)$$

The latter reaction was utilized in the Columbia Chemical Division, Pittsburgh Plate Glass Company, in the preparation of many such esters, which were found to be efficient polymerization initiators.[3,4]

We are reporting the results of a study of the reactions of diisopropyl peroxydicarbonate in ethylbenzene and in the polymerization of styrene in ethylbenzene and in both systems in the presence of quinone and hydroquinones.

Rates of Decomposition and Polymerization.—The rates of decomposition of diisopropyl peroxydicarbonate were determined (a) in ethylbenzene, and (b) in 3.46 m./l. of styrene in ethylbenzene at 54.3°, and (c) in 3.46 m./l. of styrene in benzene at 54.0°. The data are plotted in Fig. 1 according to a first order rate expression. The decompositions showed apparent first order kinetics to about 75% of completion, and slowed up at higher conversion. The over-all kinetic order was less than three halves and it may well be that, as in the case of benzoyl peroxide,[5,6] a first order "thermal" decomposition and a radical induced decomposition of higher order occur concomitantly. The first order rate constants, calculated from the curves, are (a) 4.5×10^{-5}, (b) 5.2×10^{-5}, and (c) 5.0×10^{-5} sec.$^{-1}$ (respectively). The rate of decomposition in 3.46 m./l. of styrene in benzene at 54.0° is equal to that of benzoyl peroxide in a similar medium at 82.0° as calcu-

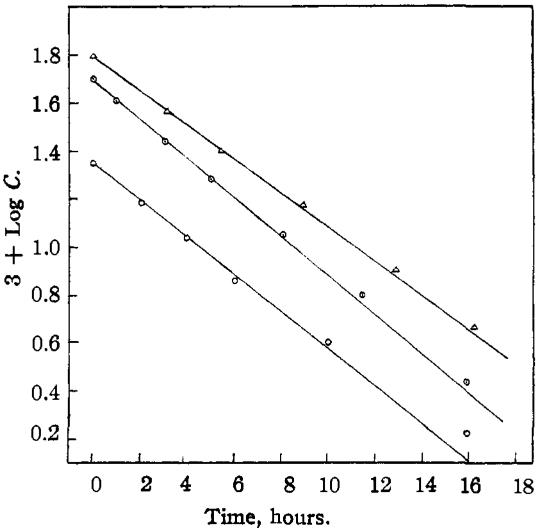


Fig. 1.—Decomposition of diisopropyl peroxydicarbonate: △, in ethylbenzene, 54.3°; ⊙, in 3.46 mil. styrene in ethylbenzene, 54.3°; ○, in 3.46 mil. styrene in benzene, 54.0°.

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* Harvard University Ph.D. 1940.

† Harvard College, A.B. 1943.

(1) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(2) Wieland, vom Hove and Borner, *Ann.*, **446**, 31 (1926).

(3) Strain, U. S. Patent 2,370,588, February 27, 1945; Strain, U. S. Patent 2,464,062; Pechukas, U. S. Patent 2,464,056, March 8, 1949.

(4) Strain, Bissinger, Dial, Rudoff, DeWitt, Stevens and Langston, THIS JOURNAL, **72**, Feb. (1950).

(5) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(6) Cass, *ibid.*, **68**, 1976 (1946).