

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Solubility of Fluorocarbons<sup>1</sup>BY ROBERT L. SCOTT<sup>2</sup>

The intensive study of fluorine and fluorine compounds in the last few years has led to the synthesis of a large number of compounds in which the hydrogen atoms are partially or completely replaced by fluorine atoms. The completely substituted hydrocarbons, commonly known as fluorocarbons, show lower solubility and poorer solvent power than that normally associated with non-polar organic liquids. We propose to see whether the fluorocarbons can be fitted into the framework of the existing "internal pressure" theory of the solubility of non-electrolytes, or whether they are in fact anomalous.

## Theory

The thermodynamic theory of non-electrolyte solutions, as developed by van Laar,<sup>3</sup> Hildebrand<sup>4,5</sup> and Scatchard,<sup>6</sup> may be expressed in its simplest form as follows:

In a mixture of two non-polar liquids, the partial molal free energy of a component is the sum of a term from the entropy of mixing which is assumed to be ideal, and one from the heat of mixing which is derived from the London theory of dispersion forces. We have for  $\overline{\Delta F}_1$  and  $\overline{\Delta F}_2$

$$\overline{\Delta F}_1 = RT \ln x_1 + v_1 (\delta_1 - \delta_2)^2 \phi_2^2 \quad (1a)$$

$$\overline{\Delta F}_2 = RT \ln x_2 + v_2 (\delta_1 - \delta_2)^2 \phi_1^2 \quad (1b)$$

where  $x_1$  and  $x_2$  are the respective mole fractions,  $v_1$  and  $v_2$  are the molal volumes of the pure components,  $\phi_1$  and  $\phi_2$  the volume fractions, and  $\delta_1$  and  $\delta_2$  are solubility parameters, defined as

$$\delta = (\Delta E^V/v)^{1/2} \quad (2)$$

where  $\Delta E^V$  is the energy of vaporization of the pure component and  $v$  its molal volume, all at the temperature  $T$ .  $\Delta E^V/v$  is of course the "internal pressure" or "cohesive energy density."

Where  $\delta_1 = \delta_2$ , there is no heat of mixing and the two components are miscible in all proportions forming an ideal solution. When the difference between  $\delta_1$  and  $\delta_2$  becomes sufficiently great, complete miscibility is no longer possible and two phases may coexist; in such a case we may speak of the solubility of 1 in 2, and for the conjugate phase, the solubility of 2 in 1. As the

absolute value of  $\delta_1 - \delta_2$  increases, these solubilities decrease, until for large differences they have become almost infinitesimal and we speak loosely of "complete insolubility."

While the solubility depends primarily upon the difference of the  $\delta$ 's, it is, of course, in addition, a function of the  $v$ 's and the temperature. For example, when the molal volumes of the two components are equal ( $v_1 = v_2 = v$ ), the condition for complete miscibility is that

$$v(\delta_1 - \delta_2)^2 < 2RT \quad (3)$$

Calculation of the composition of the two conjugate phases is more complex, especially so when the molal volumes are unequal. The details of such a treatment have been given elsewhere,<sup>7</sup> and shall not concern us here.

Further complications are introduced if we consider the effects of volume changes on mixing,<sup>8</sup> non-randomness<sup>9,10</sup> and differences in molecular size.<sup>9,11,12,13</sup> The corrections to be applied in the first two cases are fairly small, but the sizable effect of radical differences in molecular size upon the entropy of mixing is well-known from studies of solutions of linear high polymers.<sup>14,15,16,17</sup>

The effect of moderate differences in size such as we shall be considering here is very imperfectly understood, and for the lack of any more adequate expression, it has been customary to set the entropy of mixing of ordinary liquids equal to the ideal entropy ( $-R \ln x$ ). Since the corrections are presumably small except for extreme differences in size, this neglect is probably not serious.<sup>18</sup> None of these refinements alter the primary dependence of the solubility upon the difference in the solubility parameters  $\delta$ , and since the following discussion will be largely qualitative, we shall not consider them further.

## Solubility Parameters for the Fluorocarbons.

—Calculation of the solubility parameter  $\delta_T$  requires knowledge of the molal volume  $v_T$  and the heat of vaporization  $\Delta H_T^V$  at the desired tempera-

(7) Cf. ref. 5, pp. 51-54, 144-152.

(8) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(9) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge, 1939, pp. 351-370.

(10) J. G. Kirkwood, *J. Phys. Chem.*, **43**, 97 (1939).

(11) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(12) J. H. Hildebrand, *ibid.*, **15**, 225 (1947).

(13) M. L. Huggins, *J. Phys. & Colloid Chem.*, **52**, 248 (1948).

(14) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(15) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(16) A. R. Miller, *Proc. Cambridge Phil. Soc.*, **38**, 109 (1942); **39**, 54 (1943).

(17) E. A. Guggenheim, *Proc. Roy. Soc.*, **A183**, 203 (1944).

(18) A detailed consideration of these various refinements of the original theory will be found in the soon-to-be-published American Chemical Society Monograph: J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," 3d ed., Reinhold Publishing Corp., New York, N. Y., 1948.

(1) First presented before the Division of Physical and Inorganic Chemistry, 113th Meeting of the American Chemical Society, Chicago, Illinois, April, 1948.

(2) Frank B. Jewett Post-Doctoral Fellow, 1946-1948, University of California, Berkeley, California. Present address: Department of Chemistry, University of California, Los Angeles 24, California.

(3) J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1910).

(4) J. H. Hildebrand, *This Journal*, **38**, 1452 (1916); **41**, 1067 (1919); **42**, 2180 (1920); **51**, 66 (1929).

(5) J. H. Hildebrand, "Solubility of Non-electrolytes," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1936.

(6) G. Scatchard, *Chem. Revs.*, **3**, 321 (1931); *Kemisk Maanedstid (Copenhagen)*, **13**, 77 (1932); *Trans. Faraday Soc.*, **33**, 160 (1937).

TABLE I  
 THERMODYNAMIC PROPERTIES OF FLUOROCARBONS<sup>22</sup>

Formula	Name	M. p., °C.	B. p., °C.	$V_{298}^V$ (cm. <sup>3</sup> /mole)	$\Delta H_{298}^V$ (kcal./mole) estimated	$\delta_{298}$ (cal./cm. <sup>3</sup> ) <sup>1/2</sup>
C <sub>4</sub> F <sub>10</sub>	<i>f</i> - <i>n</i> -Butane		-2	163	5.0	5.2
C <sub>5</sub> H <sub>12</sub>	<i>f</i> - <i>n</i> -Pentane		29.5	183 <sup>a</sup>	6.0	5.5
C <sub>6</sub> F <sub>14</sub>	<i>f</i> - <i>n</i> -Hexane		58 <sup>a</sup>	205 <sup>a</sup>	7.1	5.6
C <sub>7</sub> F <sub>16</sub>	<i>f</i> - <i>n</i> -Heptane	-52.8	82.4	227	8.1 <sup>c</sup>	5.7
C <sub>8</sub> F <sub>18</sub>	<i>f</i> - <i>n</i> -Octane		104	253	8.9 <sup>d</sup>	5.7
C <sub>9</sub> F <sub>20</sub>	<i>f</i> - <i>n</i> Nonane		123	279 <sup>a</sup>	9.7	5.7
C <sub>4</sub> F <sub>8</sub>	<i>f</i> -Cyclobutane	-40	-5	133	4.9	5.7
C <sub>5</sub> H <sub>10</sub>	<i>f</i> -Cyclopentane		23.7	152	5.9 <sup>e</sup>	5.9
C <sub>6</sub> F <sub>12</sub>	<i>f</i> -Cyclohexane	>58.2	sublimes 51	170 <sup>a</sup>	6.8 <sup>f</sup>	6.0
C <sub>7</sub> F <sub>14</sub>	<i>f</i> -Methylcyclohexane		77.5	195	7.7 <sup>g</sup>	6.0
C <sub>7</sub> F <sub>14</sub>	<i>f</i> -Dimethylcyclopentane <sup>b</sup>		71.7	199	7.6	5.9
C <sub>7</sub> F <sub>14</sub>	<i>f</i> -Ethylcyclopentane		75.1	198	7.7	6.0
C <sub>8</sub> F <sub>16</sub>	<i>f</i> -1,2-Dimethylcyclohexane <sup>b</sup>		102.6	214	8.6 <sup>h</sup>	6.1
C <sub>8</sub> F <sub>16</sub>	<i>f</i> -1,3-Dimethylcyclohexane <sup>b</sup>		102.1	215		
C <sub>8</sub> F <sub>16</sub>	<i>f</i> -1,4-Dimethylcyclohexane <sup>b</sup>		101.0	216		
C <sub>9</sub> F <sub>18</sub>	<i>f</i> -1,3,5-Trimethylcyclohexane <sup>b</sup>		125.2	235	9.7	6.2
C <sub>6</sub> F <sub>6</sub>	<i>f</i> -Benzene	-11	~83	115	8.1	8.1
C <sub>7</sub> F <sub>8</sub>	<i>f</i> -Toluene	<-70	~105	142	8.9	7.7

<sup>a</sup> Estimated by interpolation. <sup>b</sup> Identity of isomer unknown. <sup>c</sup>  $\Delta H^V$  uncorrected at b. p. 8240 cal. <sup>d</sup>  $\Delta H^V$  uncorrected at b. p. 9100 cal. <sup>e</sup>  $\Delta H^V$  uncorrected at b. p. 6200 cal. <sup>f</sup>  $\Delta H^V$  uncorrected at b. p. 6900 cal. <sup>g</sup>  $\Delta H^V$  uncorrected at b. p. 7830 cal. <sup>h</sup>  $\Delta H^V$  uncorrected at b. p. 8580 cal.

ture. Since we wish to consider solubilities around room temperature, we shall need values of  $\Delta H_{298}^V$  and  $V_{298}^V$ . For most of the fluorocarbons which are liquid at room temperatures, densities in the range 20–30° are known, so calculation or accurate estimation of  $V_{298}^V$  is possible. On the other hand, few heats of vaporization have been reported, and those, without exception, were determined by vapor pressure measurements in the region of the normal boiling point. To convert one of these to  $\Delta H_{298}^V$ , we must multiply it by the compressibility factor  $Pv/RT$  to obtain the true heat of vaporization at the boiling point, and then extrapolate to 25°. If data on vapor densities and heat capacities of liquid and vapor were available, such a calculation would be possible, but no such data have been reported.

Fortunately, another method of estimation may be used. One may deduce<sup>19</sup> from the familiar Hildebrand rule ("Equal entropies of vaporization at equal vapor-volumes") that  $\Delta H_{298}^V$  (or at any other temperature) should be a function of the normal boiling point  $T_b$ . While this relation holds only approximately, remarkably good agreement is shown between the most recent compilation of data<sup>20</sup> for the hydrocarbons and the empirical relation<sup>21</sup>

$$\Delta H_{298}^V = -2950 + 23.7 T_b + 0.02 T_b^2 \quad (4)$$

where  $\Delta H_{298}^V$  is in units of calories/mole and  $T_b$  in degrees Kelvin. Equation (4) holds for the hydrocarbons boiling between -50° and 150° with an

(19) Cf. ref. 5, pp. 101–103.

(20) Selected Values of Properties of Hydrocarbons, Bur. Stand. Circular C461, Govt. Printing Office, Washington, D. C., 1947.

(21) This should replace the cruder Equation (V-24) of ref. 3. The author expects to discuss this more fully in a later paper.

average error of 0.1 kcal. and a maximum error of 0.4 kcal.

Crude estimates of  $\Delta H_{298}^V$  from the sparse vapor pressure measurements on fluorocarbons indicate that they, too, fall on the same curve. We have therefore used values for the normal boiling point to estimate  $\Delta H_{298}^V$  for the fluorocarbons, applying in each case a correction for the deviation of the corresponding hydrocarbon from eqn. (4). In such a way, we obtain the estimated values of  $\delta_{298}$  given in Table I.

In naming the fluorocarbons, we follow the usual "perfluoro" scheme, except that for compactness in the table we symbolize perfluoro by *f*.

**Comparison with Experiment.**—Let us now consider the solubility of the fluorocarbons in the light of the solubility parameters in Table I. In Table II, we tabulate the corresponding values of  $\delta$  for a representative number of substances, ranging from 14.6 for supercooled liquid phosphorus to 5.7 for perfluoro-heptane. Two substances close together in the table (*i. e.*, benzene and hexane) will be miscible in all proportions; those far apart (*i. e.*, hexane and liquid phosphorus) will show only limited solubility in each other.

We will expect the aliphatic fluorocarbons which lie at the lower end of the  $\delta$ -spectrum to be miscible with the aliphatic hydrocarbons and ether. If we take eqn. (3) as a rough guide and use for  $v$  the arithmetic mean of  $v_1$  and  $v_2$ , we obtain for an average  $v$  of 150 at room temperature a maximum  $\delta_1 - \delta_2$  of about 2.8. This would put the dividing line between complete miscibility and partial mis-

(22) Sources of data: *Ind. Eng. Chem.*, **39**, 310–384 (1947), various authors; H. J. Christoffers, E. C. Lingafelter and G. H. Cady, *This Journal*, **69**, 2502 (1947).

cibility of the commoner aliphatic fluorocarbons ( $C_5-C_8$ ) in the region of solvents of  $\delta$ -values from 8.5 to 8.8 (*i. e.*, around carbon tetrachloride). Above this point the solubility will decline with increasing  $\delta$ -values.

TABLE II  
SOLUBILITY PARAMETERS FOR SELECTED SUBSTANCES

	$V_{298}$	$\delta_{298}$
Phosphorus	70	14.6
Iodine	59	14.1
Sulfur	136	11.7
Pyridine <sup>a</sup>	81	10.7
Carbon disulfide	61	10.1
Chlorobenzene <sup>a</sup>	102	9.5
Chloroform <sup>a</sup>	81	9.3
Benzene	89	9.2
Ethyl acetate <sup>a</sup>	99	9.1
Toluene	107	8.9
<i>p</i> -Xylene	124	8.8
Carbon tetrachloride	97	8.6
Cyclohexane	109	8.2
<i>f</i> -Benzene	115	8.1
Methylcyclohexane	128	7.8
<i>n</i> -Octane	164	7.6
Ethyl ether <sup>a</sup>	105	7.5
<i>n</i> -Heptane	147	7.5
<i>n</i> -Hexane	132	7.3
<i>n</i> -Pentane	116	7.0
2,2,4-Trimethylpentane ("isooctane")	166	6.9
<i>f</i> -Dimethylcyclohexane	215	6.1
<i>f</i> -Methylcyclohexane	195	6.0
<i>f</i> -Cyclohexane	170	6.0
<i>f</i> -Cyclobutane	133	5.7
<i>f-n</i> -Heptane	227	5.7

<sup>a</sup> Indicates polar substances.

These conclusions are confirmed by some experimental data on four fluorocarbons<sup>23</sup> shown in Table III. The trend is as predicted and for  $C_7F_{14}$  and  $C_8F_{16}$ , the break is around carbon tetrachloride. The incomplete solubility of the higher

TABLE III  
SOLUBILITY OF FLUOROCARBONS AT 27° (Wt. %)

Fluorocarbon	Solvent	$V_2$	$\delta_1 \rightarrow$	$\delta_2$	$C_7F_{14}^a$	$C_8F_{16}^b$	<i>ca.</i> $C_{12}F_{28}^c$	<i>ca.</i> $C_{20}F_{42}^d$
					195	215	~320	~500
Methanol	41	14.3	Insol.	2.5	Insol.	Insol.	Insol.	Insol.
<i>o</i> -Dichlorobenzene	113	10.0	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.
Acetone	74	9.9	10	9	Insol.	Insol.	Insol.	Insol.
Chloroform	81	9.3	6.9	10	1.3	Insol.	Insol.	Insol.
Benzene	89	9.2	3	4.6	Insol.	Insol.	Insol.	Insol.
Ethyl acetate	99	9.1	15	13	Insol.	Insol.	Insol.	Insol.
Carbon tetrachloride	97	8.6	Misc.	43	3.4	Insol.	Insol.	Insol.
Ethyl ether	105	7.5	Misc.	Misc.	19	Insol.	Insol.	Insol.
"Petroleum ether"	120	7.1	Misc.	Misc.	67	Insol.	Insol.	Insol.

<sup>a</sup> Perfluoromethylcyclohexane. <sup>b</sup> Perfluorodimethylcyclohexane. <sup>c</sup> "Perfluoro kerosene." <sup>d</sup> "Perfluoro lube oil."

(23) E. I. du Pont de Nemours and Co., Organic Chemicals Department New Products Bulletin.

fluorocarbons in ether and petroleum ether is to be ascribed to the greater molal volumes which has the effect of narrowing the solubility limits. The inclusion of polar solvents in the tables is perhaps not entirely justified but substances with "buried" dipoles, such as the halogen compounds and ether, have been shown to follow the simple theory fairly well.<sup>3</sup>

For strongly polar solvents, especially those with hydrogen bonds, this simple internal pressure treatment is demonstrably inadequate, but where the other component is non-polar (*e. g.*, a fluorocarbon) the solubility is invariably less than that predicted from solubility parameters. The solubility of the fluorocarbons in methanol and acetone (Table III) is in accord with such a treatment.

Preliminary reports<sup>24</sup> on the solubility of perfluoro-cyclobutane indicate that it is "soluble" in octane, methyl cyclohexane, octene, carbon tetrachloride, chloroform, ether, acetone and trimethylamine, but "insoluble" in decane and dodecane, aromatic hydrocarbons, chlorobenzene, ethyl bromide and alcohols. In the absence of more quantitative studies, not much can be said about these data, but except for acetone, which is frequently anomalous, and the higher paraffins, they are not unreasonable.

No data are available on the solubility of the aromatic fluorocarbons, perfluoro-benzene and perfluoro-toluene, but by virtue of their higher solubility parameters and lower molal volumes, they should be completely miscible in a wide range of solvents, up to  $\delta$ -values of 11 or 12.

One may note in passing the solution properties of the polymer "Teflon" (polytetra-fluoroethylene)-(CF<sub>2</sub>)<sub>n</sub>. From the now-familiar studies on the solubility of polymers<sup>25,26,27</sup> we might conclude that such a polymer (for which we estimate  $\delta = 6.0$ ), would show complete miscibility in solvents over a range of  $\delta$  from 5-7, and virtually no solubility (although a limited swelling) in others. This would limit the solvents to fluorocarbons in any case. Actually, of course, polytetra-fluoroethylene like polyethylene is partially crystalline, melting<sup>28</sup> about 327°, and like any solid, shows no appreciable solubility at temperatures far below the melting point. Richards<sup>29</sup> has studied the analogous case of the solubility of polyethylene which melts at 115°.

**Acknowledgments.**—The author wishes to thank Dr. H. W. Elley and the du Pont Company for furnishing the solubility data quoted in the article, and Professor Joel H. Hildebrand for many helpful suggestions and discussions.

(24) Dr. H. W. Elley, E. I. du Pont de Nemours and Co., private communication.

(25) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); **44**, 431 (1943).

(26) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

(27) R. L. Scott, *ibid.*, **13**, 178 (1945).

(28) W. E. Hanford and R. M. Joyce, *THIS JOURNAL*, **68**, 2082 (1946).

(29) R. B. Richards, *Trans. Faraday Soc.*, **42**, 10, 20 (1946).

### Summary

Solubility parameters (square roots of the internal pressure) have been calculated for fluorocarbons, and are lower than any other substances liquid at room temperature. From the Hildebrand solubility theory we deduce that the aliphatic fluorocarbons are completely miscible with

aliphatic hydrocarbons and ether, but show only limited solubility in benzene, acetone, etc. Experimental data confirm these predictions, leading to the conclusion that the solubilities of the fluorocarbons are not at all anomalous but are only the thermodynamic consequences of their low solubility parameters.

LOS ANGELES, CALIFORNIA

RECEIVED JULY 20, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## Microwave Absorption and Molecular Structure in Liquids. I. Measurement in Organic Halides at 1.27 Cm. Wave Length<sup>1</sup>

BY WILLIAM M. HESTON, JR., EDWARD J. HENNELLY AND CHARLES P. SMYTH

Dielectric constant and loss factor measurements at a wave length of 9.72 cm. carried out in this Laboratory on water<sup>2</sup> and preliminary measurements upon some twenty organic liquids,<sup>2,3</sup> as well as many measurements scattered through the literature, made evident the desirability of employing newly developed apparatus and techniques in a systematic study of dielectric loss and its dependence upon molecular structure. Such measurements have been made upon the alkyl bromides, the molecules of which vary from the short, compact structures of ethyl bromide and the branched-chain propyl and butyl bromides to the long, flexible and possibly coiled structures of *n*-tetradecyl and *n*-hexadecyl bromides. Rigid molecules, such as those of bromobenzene, chlorobenzene,  $\alpha$ -bromonaphthalene, and  $\alpha$ -chloronaphthalene have also been measured for comparison.

The present paper describes the method and apparatus devised for the measurement at a wave length of 1.27 cm. and reports the values of the dielectric constants and loss factors obtained for 27 pure liquids at temperatures of 1, 25, 40 and 55°. The purification of the liquids, the values of other physical constants necessary for the interpretation of the results and the application of dielectric theory to the results will be given in subsequent papers, which will include other measurements in the 1 to 30 cm. wave length region.

### Experimental Method and Apparatus

This method,<sup>4</sup> which was developed in collaboration with Mr. W. H. Surber, Jr.,<sup>5</sup> is especially suited to the measurement of liquids which have high dielectric loss at the frequency employed. It is based upon the variation in the reflection coefficient of a uniform dielectric layer as the depth of the layer is varied. The termination of the

dielectric layer may be either a short-circuit, or a high impedance circuit. The results contained in this report were obtained with apparatus using a highly conducting termination (short-circuit). Since a directional coupler is used to measure directly the reflected power, the calculations involve only the ratio of the amplitudes of the reflected wave for two different lengths of the dielectric-filled guide. In addition, the wave lengths in the dielectric-filled guide and the air-filled guide are required. Thus, measurement of the shift in the minimum point, such as is required in impedance methods, is eliminated. Since the liquids measured exhibit high loss at this frequency, the waveguide equations are carried through without approximation.

A functional diagram of the apparatus used to measure dielectric constant and absorption is shown in Fig. 1. The 2K33 Raytheon klystron oscillator is square-wave modulated at 1000 c.p.s., since sine wave modulation produces some disturbing frequency modulation. A calibrated resonant cavity wavemeter is used to measure the output wave length,  $\lambda_0$ , of the oscillator, while the wave length in the air-filled guide,  $\lambda_g$ , is measured with the slotted line. The cut-off wave length of the air-filled guide can be easily calculated from these values. An

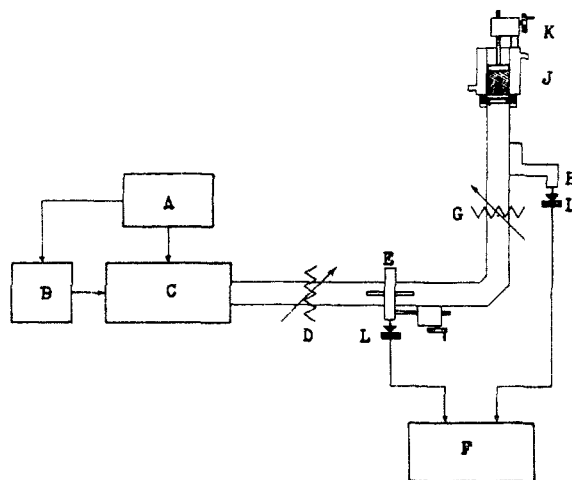


Fig. 1.—Apparatus for measurement at 1.27 cm.: (A) regulated power supply, (B) modulator, (C) 2K33 oscillator, (D) decoupling attenuator, (E) traveling detector, (F) audio amplifier, (G) matching attenuator, (H) directional coupler, (J) thermostated cell, (K) micrometer drive mechanism, (L) 1N26 crystal detectors.

(1) This research was carried out with the support of the Office of Naval Research.

(2) Conner and Smyth, *THIS JOURNAL*, **65**, 382 (1943).

(3) Magat, Schneider and Smyth, unpublished measurements.

(4) Heston, Hennelly and Smyth, Report No. 10, ONR Contract N6ori-105, Task Order IV.

(5) Surber, Technical Report No. 1, ONR Contract N6ori-105, Task Order IV; *J. Applied Phys.*, **19**, 514 (1948); Crouch, *J. Chem. Phys.*, **16**, 364 (1948).