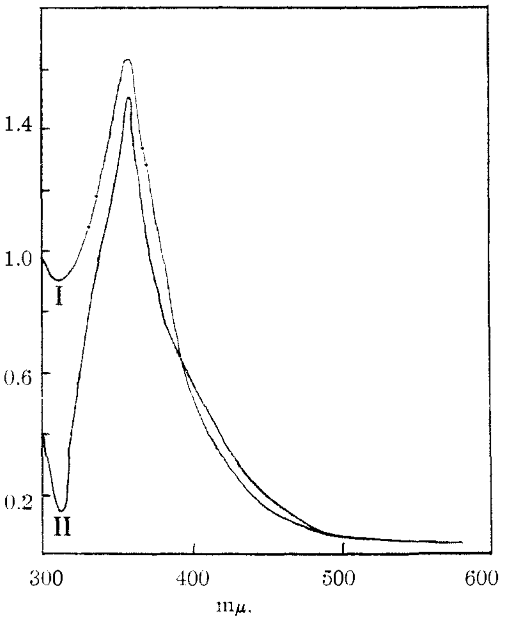

Fig. 5.—Yellow complex of orthophenanthroline and Fe(III): I, formed directly; II, formed by aging of blue complex; pH 3, Fe 4 × 10^{-4} M, orthophenanthroline 12 × 10^{-4} M.

cells due to the intense absorption of the complex. For graphical purposes, the extinction values are calculated on the basis of 1-cm. cells.

Further observations on the blue complex of iron(III) and orthophenanthroline have shown that on standing the color changes from a blue to a yellowish color. This change is first observed in about three days and is complete in a week. In order to test this further, a solution of the red complex was prepared from 0.5 ml. of iron(II) and 1.5 ml. of orthophenanthroline. This was oxidized to the blue form with dilute cerium(IV) ion solution, the solution was adjusted to pH 3.0 with dilute ammonium hydroxide, and diluted to 25 ml.

An absorption curve was obtained in the range 300 to 600 mμ. The color at the time of measurement was yellow. Results are shown in Fig. 5, curve II. Points plotted are the extinction of the complex minus the extinction of the same amount of orthophenanthroline that was used in complex formation for previously stated reasons. The two curves in Fig. 5 show the same characteristics. This suggests the possibility that the blue complex, FeR_3, may be a stable intermediate slowly rearranging to the yellow form on standing.

Since the yellow color is apparently produced from a separate and distinct complex, it was of interest to make further studies of its empirical formula.

Slope Ratio Method.—Two series of solutions were prepared; in one series orthophenanthroline was the constant component in excess with variable concentrations of iron(III). In the other series, iron was held constant and the concentration of the orthophenanthroline was varied. The pH of the solution was adjusted to 3.0 with a pH meter, using dilute H_2SO_4 and NaOH. Color formation is immediate and extinction measurements made even after 20 hours showed no appreciable fading, indicating a highly stable complex.

Extinction measurements were made at 400 mμ. This wave length was chosen since the absorption of the orthophenanthroline at 400 mμ is negligible. The slope ratio obtained from Fig. 1 (curves V and VI) is 1.62:1 indicating an empirical formula of Fe_2R_3 for the yellow complex.

Method of Continuous Variations.—Curve II in Fig. 3, resulting from the application of this method, indicates a formula of Fe_2R_3 in agreement with the previous finding.

Fayetteville, Ark.

[Contribution from the Pennsylvania State College and the University of Florida]

Conductivities of Five Substances in Trifluoroacetic Acid

By J. H. Simons[1] and Keith E. Lorentzen

Received March 31, 1952

An apparatus was constructed for producing and measuring conductances of substances in liquid trifluoroacetic acid. The conductivities over a range of dilutions at 25° in this apparatus were determined for H_2O, CF_3CO_2K, $(C_4F_9)_3N$, $(C_4H_9)_2O$ and $(C_4H_9)_3N$. Low conductivities were found for H_2O, $(C_4H_9)_2O$ and $(C_4F_9)_3N$ and moderate ones for CF_3CO_2K and $(C_4H_9)_3N$.

Trifluoroacetic acid has been shown to have a high dielectric constant with a value of about 40 at 25°[2] and to increase rapidly with a rise of temperature. It is also known to be a strongly acidic substance. The combination of high dielectric constant and high acidity gives rise to interest in its properties as a solvent for ionizable substances. It would be interesting, for example, to compare conductivities in it with similar measurements in hydrogen fluoride.[3]

A number of technical difficulties needed to be overcome before conductance measurements of value could be obtained. A sample of high purity was required from a relatively small sample of crude acid. Its purity needed to be maintained through several series of measurements. Due to the hygroscopic and corrosive nature of the material, exclusion of laboratory air was necessary as well as freedom from contact with base metals or stopcock grease. Because of a great range of conductivities to be measured, cells of different cell constants were required. Four cells were arranged so that any one of the four could be used. The apparatus was constructed so that dilutions could be made without exposing the materials to the air or cause them to come into contact with contaminating substances. It was uncertain that electrode surfaces prepared in the usual manner in aqueous solutions would function satisfactorily, but no great difficulty was experienced.

Preparation of Materials.—Trifluoroacetic acid was produced electro-chemically from acetic acid.[4] The barium salt was prepared, dried and then treated with sulfuric acid to obtain the acid relatively free from water. After a further treatment with sulfuric acid, it was transferred to a recrystallization flask similar to one previously used for acetic acid.[5] The acid was recrystallized to constant freez-

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(1) College of Engineering, University of Florida, Gainesville, Florida.

(2) J. H. Simons and K. E. Lorentzen, This Journal, **72**, 1426 (1950).

(3) J. H. Simons, *Chem. Revs.*, **8**, 213 (1931).

(4) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

(5) H. L. Ritter and J. H. Simons, This Journal, **67**, 757 (1945).

ing point. The final product had b.p. 71.0°, reported 71.1°,[6] and f.p. −15.25 ±0.05°, reported −15.25 to −15.28°.[7]

Potassium trifluoroacetate was prepared from the pure acid and potassium hydroxide. The salt was dried *in vacuo* at 100°. Tri-*n*-butylamine obtained commercially was fractionally distilled and dried over potassium hydroxide pellets; b.p. 82.0 to 85.0° at 7.5 to 8.0 mm., n^{23}D 1.428. Tributforyl nitride produced from $(C_4H_9)_3N$ electrochemically[3] was fractionally distilled and dried over potassium hydroxide pellets; b.p. 175.0 to 175.7°, n^{23}D 1.398.

Di-*n*-butyl ether was fractionally distilled and dried over freshly cut sodium; b.p. 140.5°, n^{23}D 1.400, reported b.p. 142.4°,[8] n^{20}D 1.399.[9]

The potassium chloride used in calibration of conductance cells was purified in the conventional manner, and the conductivity water had a specific conductance of 10^{-6} ohm^{-1} cm.$^{-1}$.

Apparatus.—The apparatus was constructed of glass parts sealed together. The solutions were made, dilutions accomplished, measurements over the entire range of dilutions determined, and the cells and other parts rinsed in the same apparatus and with the solutions coming in contact only with glass, platinum and mercury. Air was excluded, and contact of the solution with a stopcock and its attendant grease did not occur until after the measurements were made and the solutions discarded.

Although the apparatus was all one piece of glass, it can best be described by dividing it into two parts: (a) the dilution system and (b) the cell assembly.

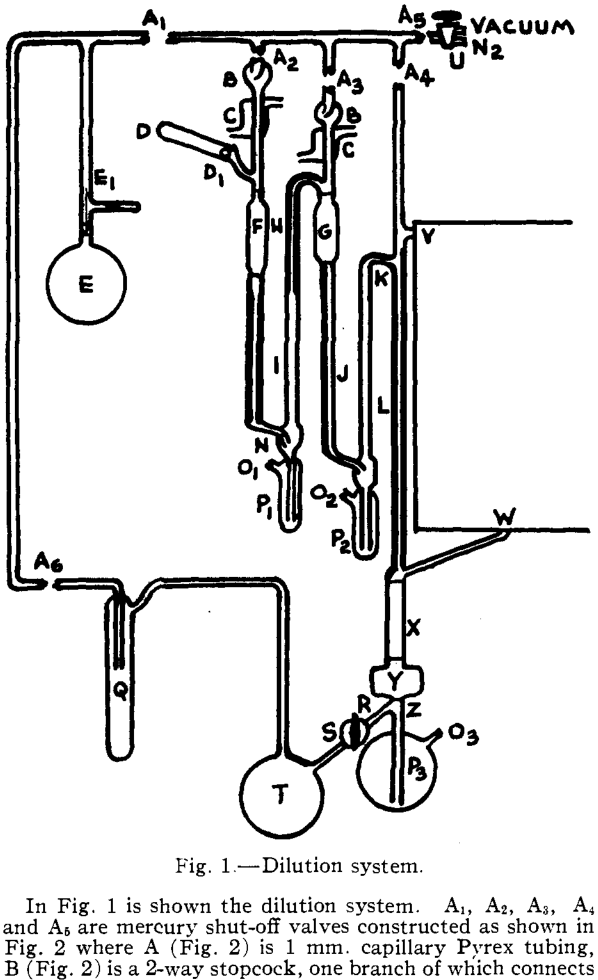

Fig. 1.—Dilution system.

In Fig. 1 is shown the dilution system. A_1, A_2, A_3, A_4 and A_5 are mercury shut-off valves constructed as shown in Fig. 2 where A (Fig. 2) is 1 mm. capillary Pyrex tubing, B (Fig. 2) is a 2-way stopcock, one branch of which connects to a nitrogen reservoir maintained at one atmosphere pressure and the other branch connects to a reservoir maintained at partial vacuum by means of a water aspirator, and C (Fig. 2) is a mercury reservoir. A_5 is of sufficient height to shut off one atmosphere pressure and the other mercury shut off valves were of sufficient height to retard a pressure differential somewhat greater than the vapor pressure of the solvent at room temperature (about 13 cm.). B is a small Kjeldahl trap to retard the passage of liquid drops. C is a small water cooled condenser. D is the tube to hold the solute vial, and D_1 is a side tube at right angles to the figure that holds a glass enclosed piece of iron. E is the solvent container, and E_1 is the sealed capillary which when broken by the solenoid-activated glass-enclosed piece of iron releases the solvent vapors to the system. F is a bulb of 6.097-cc. capacity in which the initial solution is made, and G a mixing bulb of 5.107-cc. capacity between indicating marks on the tubing. The lower connection to both F and G is capillary tubing. H is a calibrated capillary tubing, and I and J are calibrated sections of 5-mm. tubing. K and L are lengths of capillary tubing. N was a liquid check valve that caused the solution to flow in one direction. O_1, O_2 and O_3 are connections to 3-way stopcocks, one branch of which leads to the vacuum reservoir and the other to the nitrogen pressure reservoir. P_1, P_2 and P_3 are mercury reservoirs with volumes sufficient to enable operation of the containers and calibrated tubes above them. Q is a trap used for a second distillation of the used solvent from T for reuse in those cases where a non-volatile solute was used and no contamination occurred. R is a short section of capillary tubing. S is the drain stopcock protected by mercury and lubricated with acid-treated hydrocarbon. T is the residue container. U is a 3-way stopcock, one branch leading to the dry nitrogen and the other to a high vacuum system evacuated by mechanical and diffusion pumps. V is the upper and W is the lower connections to the cell assembly. X is a 25-cc. Pyrex buret tube, and Y is a bulb of 39.02-cc. capacity. Z is the volume calibration mark below bulb Y.

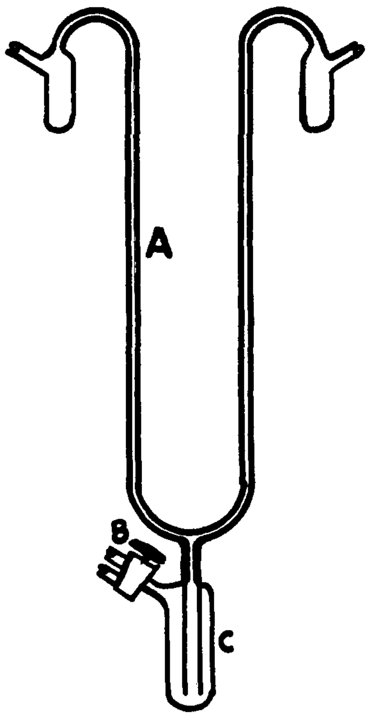

Fig. 2.—Shut-off valve.

Before describing the cell assembly, it is convenient to describe the cells. These are shown in detail in Fig. 3. Cell I is a Washburn type A cell,[10] and cells II, III and IV were designed from cells described by Jones and Bollinger.[11] Cells III and IV were similar in appearance but differed in cell characteristics. The cells were constructed to hold as small a volume as possible and to drain when supported in

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(6) Commercial bulletin. Trifluoroacetic acid, Minnesota Mining Mfg. Co., 1949.

(7) F. Swarts, *Bull. Classe. Sci. Acad. roy. Belg.*, **8**, 343 (1922).

(8) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1930 (1928).

(9) J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

(10) E. W. Washburn, THIS JOURNAL, **38**, 2431 (1916).

(11) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

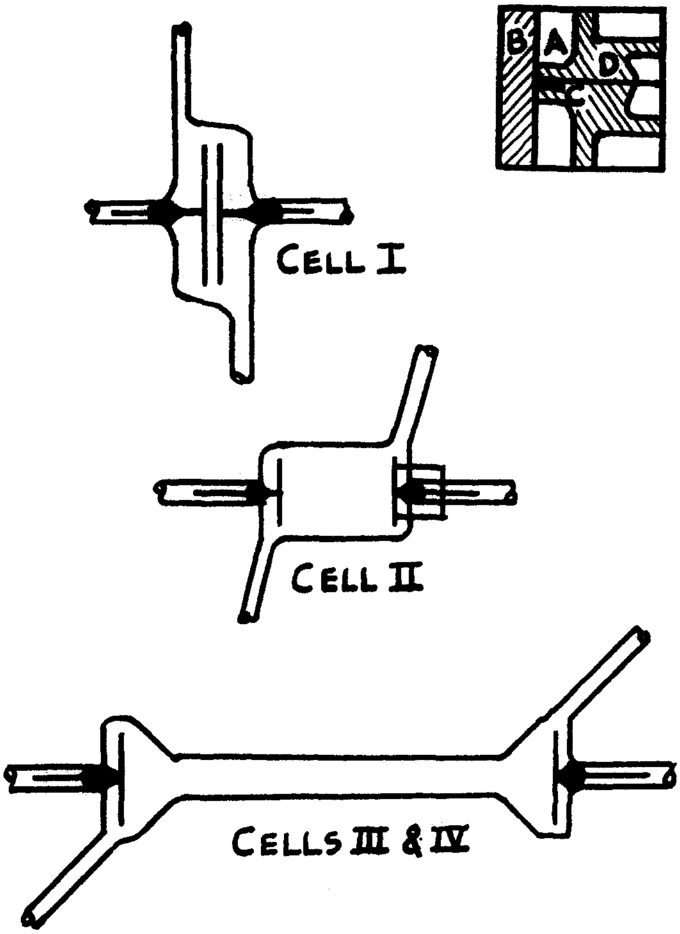

Fig. 3.—Conductivity cells.

the assembly. The electrodes were platinum alloyed with enough indium to make them stiff. Platinum rod C welded to the center of the electrode B was spot welded to a tungsten wire D. In sealing to the glass, the spot weld and platinum rod were covered with glass to prevent corrosion as well as to provide mechanical support. Electrodes of cells III and IV were platinized as described by Jones and Bollinger.[12] Electrodes of cells I and II were not platinized. All cells were calibrated with potassium chloride aqueous solutions. The cell diameter of the cells I, II, III and IV in this order were 4.0, 1.8, 1.0 and 0.33 cm.; the distance between electrodes 0.1, 1.2, 11.5 and 16.5 cm.; the diameter of the electrode 3.6, 1.4, 2.3 and 1.9 cm.; and the cell constants 0.00953, 0.4287, 12.78 and 125.4. The four cells covering a range of cell constants of over 10,000 enabled a wide range of conductivities to be determined.

The cell assembly shown in Fig. 4 is contained in a constant temperature air-bath. Air from the compressed air line was preheated by a copper coil immersed in a water-bath held 20 to 30°. It then passed through trap A heated with a 15-watt light bulb C. Asbestos shield B prevented heat loss. The light was operated by a relay controlled by a thermostat inside the air-bath. Temperature control was to ±0.1°. D is the upper connection to the dilution system, F is a 16-gallon galvanized trash can placed inside a wooden box E, the space between the two being filled with rock wool insulation. G's are openings in the air line set tangential to the circumference. H's are the contact tubes of cell P which form the support for the cell and are fastened to the wooden cover L by means of I, a short piece of pressure tubing. J is a wooden washer, and K a flat piece of soft rubber. M is a thermometer, and N the thermal regulator. O, P, Q and R are cells IV, III, II and I in that order. O and P are slanted at 45°, Q at 5°, and R at 0° from the vertical to ensure complete drainage. The horizontal axes are rotated 45° from cell to cell for special considerations. S is the lower connection to the dilution system.

The conductance bridge is similar to one described by Jones and Josephs.[13] The source was an audio oscillator at 500, 1000 and 2000 cycles. Wires connecting various elements are 15 cm. apart to prevent intercapacitance. Mercury cups provided connections to the cells.

Weighed quantities of solutes were sealed *in vacuo* in small thin wall bulbs. These were placed in the dilution system in tube D, Fig. 1.

Procedure.—Before beginning a series of measurements, bulb E was filled with recrystallized trifluoroacetic acid; and an air-free sample in a thin-walled glass bulb was placed in the tube D and sealed in. The entire system including both the dilution system and the cell assembly was evacuated through stopcock U.

The entire system was closed at A_5 and then filled with acid vapor and internally rinsed with the liquid acid. This was done by breaking the capillary E_1, condensing the vapor with Dry Ice externally applied to D, transferring this liquid to bulb G by lowering the mercury level to expose opening N, and then raising the mercury to drive the liquid through I and H. Similar operations transferred the liquid through J and K to X and Y. Raising and lowering the liquid completed the washing. A larger volume of liquid was then condensed into X and Y. These had a sufficient volume so that liquid contained in them would fill all the cells. This liquid was then pushed back and forth through the cells to constant resistance of the rinsing liquid. The mercury was then lowered below point Z, and the liquid allowed to flow into T. Stopcock S was closed, and the mercury from P_3 raised to Z so as to fill R and protect the solutions from stopcock grease.

In preparing a solution, bulb F of Fig. 1 was filled about three-fourths full of liquid; and valve A_2 closed. The solute sample in D was released by breaking the vial. It was rinsed into F and mixed by raising and lowering the mercury. Last traces of solute were washed from D by condensing vapor at the top of D with Dry Ice. Valve A_2 was opened and sufficient liquid added to F to bring it up to the calibrated volume. When the correct volume was present at room temperature, valve A_2 was closed.

The concentrated solution made in F was diluted in two stages by the addition of solvent. This was accomplished by mixing the concentrated solution made in F with solvent in G for the first step, and by mixing the result of the first dilution with more solvent in X and Y.

For the first dilution, bulb G was three-fourths filled with solvent liquid. A precalculated amount of solution from F was forced into G from the calibrated tube H, or if larger amounts were required into tube I also. To ensure complete transfer, a few drops of mercury were allowed to pass from H to G. The solution was then increased to the calibrated volume with additional solvent and thoroughly mixed.

Before the second dilution was made, a measured amount of liquid acid (40 to 50 cc.) was condensed into bulbs X and Y and run in and out of the cells. When a constant resistance was obtained, a precalculated amount of the solution in G was transferred to X for the second dilution, and pushed up and down in the cells to ensure adequate mixing. When the temperature and conductance readings had become constant, the conductance was recorded as determined from the cell from which the highest precision could be expected. A solution of higher concentration was prepared by adding more material from G. For the higher concentrations it was necessary to add more of the concentrated solution from F by transfers of a similar nature. After the concentration range had been covered, the used solution was transferred to reservoir T. The apparatus was then rinsed with pure solvent and this also run into T. It could then be filled with dry nitrogen, a new solute sample placed in D, and a new series of measurements taken.

Results

In Table I are shown the results of the conduct-

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[12] G. Jones and G. M. Bollinger, THIS JOURNAL, **57**, 280 (1935).

[13] G. Jones and R. C. Josephs, *ibid.*, **50**, 1049 (1928).

TABLE I

CONDUCTIVITIES IN CF_3CO_2H AT 25°

Solute, $(C_4H_9)_3N$			Solute, $(C_4F_9)_3N$		Solute, $(C_4N_9)_2O$		Solute, H_2O		Solute, CF_3CO_2K		
$K = 0.076 \times 10^{-6}$			$K = 0.0759 \times 10^{-6}$		$K = 0.0483 \times 10^{-6}$		$K = 0.0512 \times 10^{-6}$		$K = 0.0661 \times 10^{-6}$		
$C \times 10^4$	Λ	Λ'	$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ	Λ'
∞	36.2	38.8	∞	...	∞	...		...		29.4	38.5
0.563	31.6	32.9	0.2943	0.33	0.3322	0.29	0.3336	0.078	0.3110	16.9	19.1
0.834	30.1	31.0	0.764	.28	0.599	.27	0.638	.085	0.693	12.6	13.6
1.006	29.5	30.3	1.598	.22	1.219	.21	1.147	.072	0.991	11.1	11.7
2.005	25.9	26.3	2.906	.15	1.675	.196	1.483	.074	1.260	10.4	10.9
3.404	23.5	23.9	8.64	.068	2.060	.182	1.749	.082	1.609	9.16	9.57
5.21	21.5	21.8	29.14	.028	2.528	.170	2.047	.080	1.974	8.39	8.73
9.17	19.1	19.2	62.6	.015	3.203	.151	2.675	.071	2.431	7.72	7.99
16.86	16.6	16.7			4.046	.135	4.186	.056	4.162	6.19	6.35
43.03	12.9	12.9			6.33	.102	7.19	.040	6.95	4.99	5.09
100.0	11.5	11.5			11.55	.072	13.08	.028	13.24	4.45	4.50
128.8	10.8	10.8			24.87	.046	29.14	.017	32.36	3.43	3.46
					51.6	.031	59.1	.013	63.9	2.82	2.83
					100.9	.028	101.5	.010	112.4	2.04	2.06
							764.0	.007	152.9	1.65	1.66
									1140.0	1.52	1.53

ance measurements. Λ is the equivalent conductance of the solution at concentration, C, in moles per liter. K is the specific conductance of the solvent. Λ is obtained after correcting the measured specific conductance for the specific conductance of the solvent. Λ', where given, is calculated without making this correction. There is some uncertainty relative to making this correction in the two cases for which Λ' values are given. These solutes produce ions which would suppress the auto ionization of the solvent, but the extent of this is unknown. Extrapolation to infinite dilution was accomplished for these two cases by the method of Fuoss.[14] For this purpose the dielectric[7] constant of the solvent was taken as 40.7 at 25° and the viscosity as 0.00876 poise.[6] This method of Fuoss enables an equilibrium constant to be calculated of the solute taken as a weak electrolyte. It is interesting to compare such calculations with similar ones for comparable solutes in nitrobenzene, which has the same dielectric constant, and acetic acid. This is done in Table II.

TABLE II

COMPARABLE SALTS IN DIFFERENT SOLVENTS

Salt	Solvent	Λ_0	$K \times 10^5$	$\Lambda_0\eta_0$[15]
$(C_4H_9)_3NHI$	$C_6H_5NO_2$[16,17]	33.33[18]	9.5	0.603
$(C_4H_9)_3NHPi$	$C_6H_5NO_2$	28.85[18]	19	.523
$(C_4H_9)_3NHO_2CCF_3$	CF_3CO_2H	36.2	40	.317
		38.8[a]	31[a]	.340[a]
CF_3COOK	CF_3CO_2H	29.4	2.3	.258
		38.5[a]	1.4[a]	.337[a]
$(CH_3)_4NCl$	CH_3CO_2H[19,20]	13.3[21]	0.62	.148
KCl	CH_3CO_2H	10.0	0.10	.112

[a] No solvent correction applied. λ_0 = Equivalent conductivity at infinite solution, η_0 = viscosity of pure solvent, K = equilibrium constant.

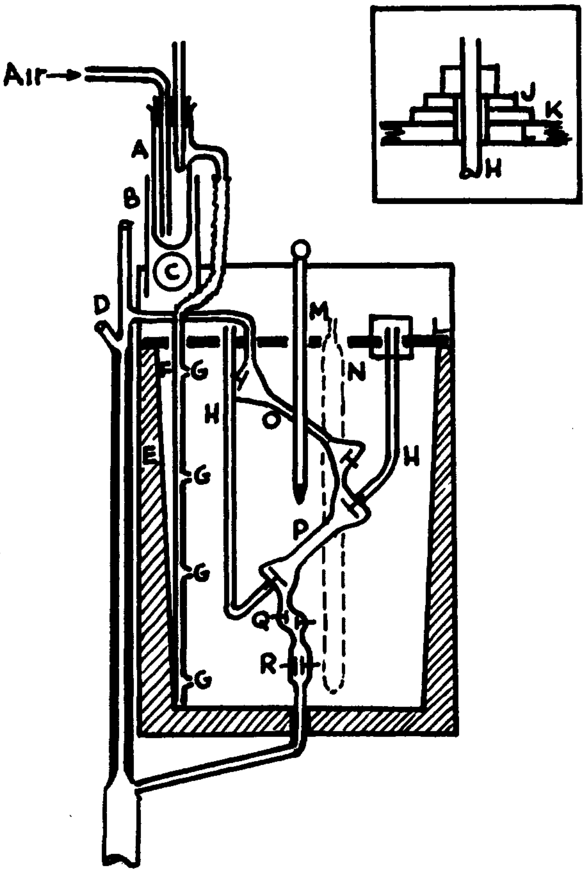

Fig. 4.—Cell assembly.

Discussion

It is seen from the results that water has a very low conductivity in trifluoroacetic acid in contrast to its high conductivity in liquid hydrogen fluoride. The reverse situation in water solutions is of interest for comparison, in that the conductance of trifluoroacetic acid is much higher than hydrogen fluoride.

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(14) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

(15) Waldens rule computation: P. Walden, *Z. physik. Chem.*, **55**, 207 (1906); P. Walden and H. Ulich, *ibid.*, **107**, 219 (1923); H. Ulich and E. J. Birr, *Z. angew. Chem.*, **41**, 443 (1928).

(16) Dielectric constant of nitrobenzene = 34.9: R. T. Lattey and O. Gattey, *Phil. Mag.*, [7] **7**, 985 (1929).

(17) Viscosity of nitrobenzene = 0.01811 poise; P. Walden and E. J. Birr, *Z. physik. Chem.*, **163A**, 281 (1932).

(18) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

(19) Dielectric constant of acetic acid = 6.2: R. P. Seward and C. H. Hamblet, *ibid.*, **54**, 544 (1932).

(20) Viscosity of acetic acid = 0.01121 poise: J. Kendall and P. M. Gross, *ibid.*, **43**, 426 (1921).

(21) B. V. Weidner, A. W. Hutchison and G. C. Chandlee, *ibid.*, **60**, 2877 (1938).

Both $(C_4F_9)_3N$ and $(C_4H_9)_2O$ give low conductivities, which is evidence of the formation in the solutions of few ions. As the only expected means of the production of ions from these solutes requires that they function as bases, it must be concluded that in this solvent they are extremely weak bases. In other words, the extent of the following reactions must be small

$$(C_4F_9)_3N + CF_3CO_2H \rightleftarrows (C_4F_9)_3NH^+ + CF_3CO_2^-$$

$$(C_4H_9)_2O + CF_3CO_2H \rightleftarrows (C_4H_9)_2OH^+ + CF_3CO_2^-$$

The potassium salt of the acid gives a moderate conductivity to its solution in the acid. $(C_4H_9)_3N$ in contrast to its fluorocarbon analog gives a relatively high conductance showing evidence of considerable basicity as per the reaction

$$(C_4H_9)_3N + CF_3CO_2H \rightleftarrows (C_4H_9)_3NH^+ + CF_3CO_2^-$$

There is also some evidence of the crystallization of the indicated salt, $(C_4H_9)_3NHCF_3CO_2$, as it was noticed on dissolving the amine in the acid that a white solid was first formed. This dissolved in larger quantities of the solvent on mixing.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE COLLEGE OF ENGINEERING, THE UNIVERSITY OF FLORIDA]

The Solubility of Organic Solids in Fluorocarbon Derivatives

BY J. H. SIMONS[1] AND M. J. LINEVSKY

RECEIVED APRIL 28, 1952

The solubility of naphthalene, *p*-nitrotoluene and hexachlorethane were determined in a fluorocarbon oxide, $(C_4F_9)_2O$ and a fluorocarbon nitride, $(C_3F_7)_3N$ at 25 and at 35°. Consistent with the concept of interpenetration as postulated by Simons and Dunlap, the first two substances were far below ideally soluble whereas the last was more nearly so. The temperature coefficient of solubility gives a heat of solution greater than the ideal heat of solution by an amount which gives a measure of the heat of interpenetration. The two solvents do not differ appreciably in solubility properties.

The demonstrated failure to even approach ideal solubility of fluorocarbons and hydrocarbons as illustrated in a recent paper,[2] increases the interest in the solubility properties of fluorocarbons and their derivatives. The availability of $(C_4F_9)_2O$ and $(C_3F_7)_3N$ from the operation of the electrochemical process[3] made possible the determination of the solubility of several organic solids in these liquids.

Materials and Apparatus.—Naphthalene, hexachlorethane and *p*-nitrotoluene were obtained as chemically pure reagents and were further purified by two recrystallizations from ethanol. The fluorocarbon derivatives were purified by distillation; the $(C_4F_9)_2O$ was taken from a cut boiling between 100.7 and 101.0°, and the $(C_3F_7)_3N$ was taken from a cut boiling between 128.1–128.5°.

The solubility vessel was a tube about 20 mm. in diameter about 8 cm. long with a sintered glass disk sealed in the center. The ends were drawn down and attached to 8 mm. ground glass joints. The female portions of these joints served as caps. With the 20-mm. tube vertical, the tube to the lower joint was bent 180° to bring the two joints parallel and level.

Procedure.—A weighed amount of solute and solvent was placed in the lower portion of the solubility vessels. This was then shaken in a constant temperature bath for 48 hours. The vessel was now inverted to the bath and the saturated solutions withdrawn by suction. The vessel with the undissolved solute was then weighed. As both solute and solvent are volatile, there is an uncertainty whether the weighed undissolved solute contains unevaporated solvent or whether some of the solute has evaporated. To obtain a reliable reproducible value, the following procedure was employed.

The first weight was taken as soon as the excess liquid had been removed. Air was then drawn through the vessel for a measured period of time (30 seconds). The vessel was then again weighed. This was repeated some ten times. By plotting the weight of the vessel against the time of air passage under a fixed set of conditions and extrapolating the linear portion of the curve back to zero time, a reliable reproducible value was obtained. The loss of weight for the first few measurements represented the loss of both absorbed solvent and evaporated solute. After the solvent had been lost, the loss of weight represented the evaporation of the solute under a fixed set of conditions for a determined period of time. This gave a straight line on the graph, the extrapolation of which to zero time gave the weight of the undissolved solute uncontaminated by absorbed solvent. From this weight, solubilities were readily calculated.

Results.—In Table I are shown the results of the measurements. The ideal solubility was calculated using the equation

$$\log_{10}\frac{1}{N_2} = (\bar{H}_2 - H_2)\,\frac{T_m - T}{4.575T_mT}$$

where

N_2 = ideal solubility in mole fraction

$\bar{H}_2 - H_2$ = difference in heat content of the solute in solution and as pure solid

T_m = melting point of solute in °K.

T = temperature in °K. at which solubility is taken

For naphthalene, the melting point is taken as 80.2° and $\bar{H}_2 - H_2$ in cal. per mole as the heat of fusion[4] 4580. For *p*-nitrotoluene, the melting point is taken as 51.8 and the heat of fusion[5] 4010. For hexachloroethane, the melting point is taken as 186.8 and $\bar{H}_2 - H_2$ as the sum of the heat of fusion[6] and the heat of transition[7] 4900.

Conclusions.—As can be readily seen from the table, the solubilities of both naphthalene and *p*-nitrotoluene are far below ideal at both temperatures in both fluorocarbon solvents. For comparison, the solubility of naphthalene in dibutyl ether was obtained from extrapolation of the data of Bennet and Philip.[8] At 25° it was 0.190 mole

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(1) The College of Engineering, The University of Florida, Gainesville, Florida.

(2) J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

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(4) M. F. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

(5) H. D. Crockford and N. L. Simmons, *ibid.*, **37**, 259 (1933).

(6) P. J. van der Lee, *Z. anorg. Chem.*, **223**, 216 (1935).

(7) Van de Vloed, *Bull. soc. chim. Belg.*, **48**, 229 (1939).

(8) M. G. Bennet and W. G. Philip, *Trans. Chem. Soc. Lond.*, 1937 (1928)