TABLE I

DENSITY AND REFRACTIVE INDEX OF URANYL FLUORIDE SOLUTIONS

	Density				Refractive index				Mole refraction (cc.) (25°)
	25°		30°		25°		30°		
Wt. % UO_2F_2	d	$\Delta d^a \times 10^4$	d	$\Delta d^a \times 10^4$	n^{25}_D	$\Delta n^a \times 10^5$	n^{30}_D	$\Delta n^a \times 10^5$	
1.002					1.33319	−1	1.33266	−4	17
2.495	1.0202[b]	0			1.33417	0	1.33366	−5	17.0
4.985	1.0443	0	1.0429	0	1.33586	0	1.33531	−2	17.0
5.025	1.0448	−1			1.33597	−8			17.1
7.481					1.33764	−2	1.33705	−2	17.1
9.607					1.33925	−10	1.33864	−7	17.2
10.20	1.0983	0	1.0967	0	1.33963	−5	1.33907	−7	17.1
15.01					1.34333	−6	1.34275	−7	17.04
20.09	1.2164	+2	1.2146	0	1.34756	−5	1.34692	−2	17.09
20.48	1.2219[b]	−2			1.34788	−2	1.34721	+3	17.01
24.89					1.35188	−1	1.35114	+9	17.06
30.10	1.3632	0			1.35705	0			17.09
30.18	1.3632	+13	1.3607	+15	1.35705	+6	1.35636	+11	17.21
33.39					1.36059	+1	1.35988	+5	17.09
40.30	1.5509	+4	1.5481	+6					
40.27					1.36888	−5	1.36825	−9	17.14
46.36					1.37726	−1	1.37647	+6	17.15
50.27	1.7893	+2	1.7859	+1	1.38316	+14	1.38239	+18	17.13
50.90					1.38439	−5	1.38370	−11	17.15
56.90					1.39503	+1	1.39418	+10	17.13
57.10					1.39542	0	1.39457	+9	17.13
61.12					1.40392	−26	1.40303	−15	17.14
61.63	2.1627	−1	2.1589	−15	1.40475	+2	1.40407	−9	17.11

[a] Δd and Δn are the differences: calculated values minus experimental values. [b] Measured by gradient tube method.

weight per cent. His densities agree with those calculated by equation 1 to *ca.* 0.1% except for the saturated solution, where his points scatter considerably more. Since his densities are reported to four significant figures, the agreement clearly is within his experimental error and indicates that there is no systematic error in the uranium analyses.

Assuming that the density of uranyl fluoride solutions follows equation 1, the apparent molal volume ϕ_V at 25° was computed by the equation

$$\phi_V = M_2(1/d_0 + a + bF_2) = 308.07(0.0909 + 0.0567F_2) = 28.0 + 17.5F_2 \quad (2)$$

where $M_2 = 308.07$ is the molecular weight of uranyl fluoride.

Since it had been shown earlier[3,5] that uranyl fluoride in the concentration range studied does not appreciably dissociate into ions (*i.e.*, essentially is a non-electrolyte under these conditions), the large variation of ϕ_V with concentration is surprising. For non-electrolytes ϕ_V would have been expected to change little with concentration.[6] It is of interest that extrapolation of ϕ_V to $F_2 = 1$ yields $\phi_V = 45.5$ cc. which may be compared with the molal volume $V = 48.3$ cc. of solid UO_2F_2 which was calculated from the crystallographic value of the density ($\rho = 6.38$).[7]

2. Refractive Index.—The results of the refractive index measurements are also listed in Table I. The refractive indices were fitted to the equation

$$n^t{}_D = n^{0t}{}_D + \alpha c + \beta c^{3/2} \quad (3)$$

where c is the concentration (molarity), α and β are constants, and where $n^t{}_D$ and $n^{0t}{}_D$ are the measured refractive indices of the solutions and of water at temperature t, respectively. Satisfactory fit of the data to equation 3 was obtained at 25° using $\alpha = 0.02055$ and $\beta = -0.00185$ and at 30° using $\alpha = 0.02049$ and $\beta = -0.00183$. The deviations between experimental and calculated values are shown in Table I. It is believed that the scatter is due, to a large extent, to the inaccuracies in the analyses of the uranium solutions.

Values of the mole refraction (R) of UO_2F_2 were calculated according to the equation[8]

$$R = \frac{(n^2 - 1)}{(n^2 + 2)} \times \frac{1}{d}\left(\frac{1000}{m} + M_2\right) - \frac{(n^0)^2 - 1}{(n^0)^2 + 2} \times \frac{1}{d_0} \times \frac{1000}{m} \quad (4)$$

where m is the molality of the solution. The results of the calculations are also listed in Table I. Within the accuracy of the data, R appears to be constant ($R = 17.1 \pm 0.1$ cc.) and hence does not reflect the considerable change in the degree of dimerization of uranyl fluoride which occurs in this concentration range.

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Preparation of β-H-Perfluoro Alkanesulfonic Acids

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The synthesis of β-H-perfluoroethanesulfonic acid by the reaction of sodium bisulfite with tetrafluoro-

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[5] J. S. Johnson and K. A. Kraus, unpublished.

[6] See for example, H. S. Harned and B. B. Owen, "Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 260.

[7] W. H. Zachariasen, *Acta Cryst.*, **1**, 277 (1948).

[8] W. Geffcken, *Z. physik. Chem.*, **B5**, 81 (1929).

TABLE I

β-H-PERFLUORO ALKANESULFONIC ACIDS

Sulfonic acid	Conv.,[a] %	Yield, %	B.p.		Neut. equiv.		Anal. of sodium salt			
							Na, %		S, %	
			°C.	Mm.	Calcd.	Found	Calcd.	Found	Calcd.	Found
$CF_3CFHCF_2SO_3H$	93	64	111-113	20	232	228	..	..	..	..
$C_3F_7CFHCF_2SO_3H$	83	79	119-120	14	332	317	6.50	6.55	9.04	9.19
$C_5H_{11}CFHCF_2SO_3H$	74	73	119-120	3	432	415	5.07	5.25	7.05	7.21

[a] Based on olefin reacted.

ethylene has been reported by Barrick.[1] Several higher molecular weight β-H-perfluoro alkanesulfonic acids have now been prepared in good yield by the reaction of sodium bisulfite with perfluoropropene, perfluoropentene-1 and perfluoroheptene-1. A summary of the preparation and properties of these sulfonic acids is presented in Table I.

These sulfonic acids are viscous liquids, soluble in both water and diethyl ether. They are very hygroscopic and form solid hydrates when exposed to moist air. They are strong acids as indicated by their reaction with NaCl to liberate HCl. The acids as well as their sodium salts are highly surface active in aqueous media, *e.g.*, a solution containing 1% by weight of $C_5F_{11}CFHCF_2SO_3H$ gave a surface tension of 38 dynes per centimeter at 25°. A preliminary investigation was made into the thermal and hydrolytic stability of the sodium salts. The dry salts are thermally stable up to 350° but undergo extensive decomposition in aqueous base at about 250°.

Experimental

Perfluoropropene, perfluoropentene-1 and perfluoroheptene-1 were prepared by the method of Hals, Reid and Smith.[2] Preparation of the β-H-perfluoro alkanesulfonic acids was carried out according to the following typical experiment: A mixture of 90 g. (0.6 mole) of perfluoropropene, 60 g. (0.5 mole) of sodium bisulfite, 27.4 g. of borax, 120 cc. of water and 0.8 g. of benzoyl peroxide was charged to a stainless steel autoclave. The contents of the autoclave were heated with agitation at 110-120° for nine hours. Ten grams of unreacted perfluoropropene was bled from the autoclave at room temperature. The reaction mixture was then evaporated to dryness and the resulting salts extracted with hot ethanol. There was isolated 115 g. of crude ethanol-soluble $CF_3CFHCF_2SO_3Na$. About 100 g. of this vacuum-dried salt was mixed with 150 g. of 95% H_2SO_4 and 40 g. of SO_3 (Sulfan β), and distilled under reduced pressure. Fractionation of the distillate gave 68 g. of $CF_3CFHCF_2SO_3H$ boiling at 111-113° (20 mm.).

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(1) P. L. Barrick, U. S. Patent 2,403,207 (July 2, 1946).

(2) L. J. Hals, T. S. Reid and G. H. Smith, THIS JOURNAL, **73**, 4054 (1951).

CENTRAL RESEARCH DEPARTMENT
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A Convenient Synthesis of 2-β-Hydroxyethylaminofluorene[1]

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The literature contains a method for the preparation of 2-β-hydroxyethylaminofluorene,[2,3] but it is troublesome and gives a poor yield of product. It has now been found that the compound can be obtained readily in high yield by the decomposition of β-chloroethyl N-2-fluorenylcarbamate in alkaline solution.

The infrared spectra of β-chloroethyl N-2-fluorenylcarbamate (I), 3-(2′-fluorenyl)-2-oxazolidone (II), 2-β-hydroxyethylaminofluorene (III) have been determined. The carbonyl band of II lies at 5.76μ while that of the starting carbamate lies at 5.72μ. As II has no O-H or N-H stretching vibration bands, the structure assignment of the compound as an oxazolidone is substantiated. III has no C=O stretching vibration band but has N-H and O-H bands at 2.93 and 2.77 μ, respectively. The starting carbamate has a N-H band at 2.90μ. This substantiates the structure of III as 2-β-hydroxyethylaminofluorene.

Experimental[4]

β-Chloroethyl N-2-Fluorenylcarbamate.—To an ice-cold stirred solution of 1.81 g. of 2-aminofluorene[5] in 10 ml. of pyridine was added dropwise 1.1 ml. of β-chlorethyl chlorocarbonate. The solution was stirred an additional half hour at 0-10° and then poured into 200 ml. of cold 25% sulfuric acid. An oil was formed which solidified after two hours. Crystallization from heptane gave 2.73 g. (95% yield) of colorless microneedles, m.p. 134-134.5°.

Anal. Calcd. for $C_{16}H_{14}ClNO_2$: C, 66.67; H, 4.86. Found: C, 67.05; H, 5.09.

3-(2′-Fluorenyl)-2-oxazolidone.—A solution of 1.6 g. of potassium hydroxide in 40 ml. of ethanol was added to 2.88 g. of β-chloroethyl N-2-fluorenylcarbamate dissolved in 150 ml. of hot ethanol. The stirred solution remained clear for a short time and then a thick crystalline precipitate was formed. The stirred mixture was immediately cooled to room temperature. Stirring was continued for an additional half hour. Excess water was added and then the white crystalline precipitate was filtered. Crystallization from methyl cellosolve gave 2.38 g. (95% yield) of colorless plates, m.p. 239-240°.

Anal. Calcd. for $C_{16}H_{13}NO_2$: N, 5.58. Found: N, 5.88.

2-β-Hydroxyethylaminofluorene.—A solution of 3.2 g. of potassium hydroxide in 80 ml. of ethanol was added to a hot solution of 2.88 g. of β-chloroethyl N-2-fluorenylcarbamate in 40 ml. of ethanol. A thick crystalline precipitate of the oxazolidone was formed which dissolved with decomposition on refluxing vigorously for two hours. Three-fourths of the alcohol was distilled off. Excess water was added to the residue. Crystallization from hexane gave 2.0 g. (89% yield) of colorless plates, m.p. 148-149°. Davis, *et al.*,[3] reported yellow plates, m.p. 150°.

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(1) This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) W. C. J. Ross, *J. Chem. Soc.*, 183 (1949).

(3) W. Davis, J. L. Everett and W. C. J. Ross, *ibid.*, 1331 (1950).

(4) All melting points are uncorrected. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 Infrared Spectrophotometer.

(5) W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 448.