

the fluorochlorates, BrF_3 from the fluorobromates and IF_5 from the fluoriodates. The order of stability seems to be $\text{Cs} > \text{Rb} > \text{K}$. The order of reactivity with water is $\text{Cl} > \text{Br} > \text{I}$.

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MOLAR REFRACTION AS AN INDEX OF PROTON TRANSFER: AN ESTIMATE OF THE ACID STRENGTH OF *p*-TOLUENESULFONIC ACID

Sir:

p-Toluenesulfonic acid is strong in water but largely un-ionized in 100% sulfuric acid.¹ We

medium effects for salts or strong acids even up to rather high ionic concentrations.⁵⁻⁸ Thus, if we ascribe the medium effect on *R* entirely to proton transfer, the ratio $c_{\text{C}_7\text{H}_7\text{SO}_3^-}/c_{\text{C}_7\text{H}_7\text{SO}_3\text{H}}$ is unity at about 43 wt. % H_2SO_4 . Using this datum, we could estimate pK_A of *p*-toluenesulfonic acid if the appropriate acidity function, H_- , were known.⁹ Unfortunately, this function is not known for arylsulfonic acids in 43 wt. % H_2SO_4 . We may, however, approximate its value by using recent data for the ionization of nitric acid,^{10,11} as shown in equation (1). On this basis, pK_A for *p*-toluenesul-

$$pK_A(\text{C}_7\text{H}_7\text{SO}_3\text{H}) = pK_A(\text{HNO}_3) + \left[\log \left(\frac{c_{\text{NO}_2^-}}{c_{\text{HNO}_3}} \right) \right]_{43\% \text{H}_2\text{SO}_4} \quad (1)$$

fonic acid is estimated as -1.3 at 25° . For comparison, pK_A for methanesulfonic acid has been

TABLE I
DATA AT 25.0°

Wt. % H_2SO_4	d_0	$n_0^{a,b}$	$10^3 K_d$	$10^3 K_n^a$	R (cc./mole)
0	0.997075	1.33256	72.1 ± 0.2	32.04 ± 0.10	43.11 ± 0.06
20	1.13647	1.35611	45.9 ± 0.2	$26.61 \pm .15$	$43.21 \pm .09$
40	1.29906	1.38069	17.9 ± 0.2	$20.30 \pm .27$	$42.50 \pm .16$
60	1.49398	1.40632	-12.0 ± 2.0	$14.69 \pm .24$	$41.75 \pm .39$
80	1.7216	1.43280	-43.4 ± 1.5	$10.58 \pm .16$	$41.39 \pm .30$

^a Refractive index data for the helium D_3 line, 5870 Å. ^b By interpolation from data of reference 5.

have measured the apparent molar refraction, R , of sodium *p*-toluenesulfonate in sulfuric acid-water mixtures, in the hope that proton transfer from the medium might be detected by a characteristic reduction in R .^{2,3}

Experimental values of several functions of the solvent composition are listed in Table I: the solvent density, d_0 ; the refractive index, n_0 ; the initial slopes, $K_d = (d - d_0)/c$ and $K_n = (n -$

estimated recently as -0.6 by a quite different method.¹²

(5) K. Fajans, H. Kohner and W. Geffcken, *Z. Elektrochem.*, **34**, 1 (1928).

(6) H. Kohner and M. L. Gressmann, *Z. physik. Chem.*, **A144**, 137 (1930).

(7) W. Geffcken and A. Kruis, *ibid.*, **B23**, 175 (1933).

(8) A. E. Brodskii, *Trans. Faraday Soc.*, **33**, 256 (1937).

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 269.

(10) N. C. Deno, H. J. Peterson and E. Sacher, *J. Phys. Chem.*, **65**, 199 (1961).

(11) G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **22**, 2067 (1954).

(12) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(13) Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

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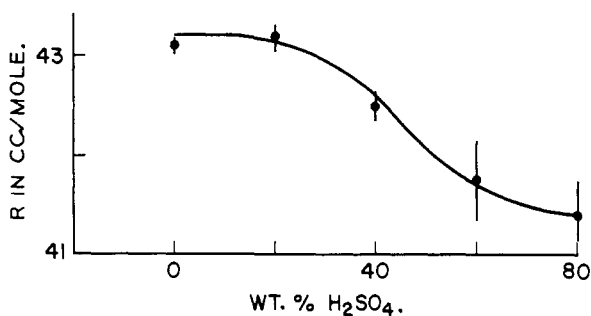


Fig. 1.—Apparent molar refraction of sodium *p*-toluenesulfonate vs. wt. % H_2SO_4 ; data at 25° .

$n_0)/c$, where c is the formal concentration of sodium *p*-toluenesulfonate; and R , computed from these quantities in the standard way.⁴ The plot of R vs. wt. % H_2SO_4 has an inflection at about 43 wt. %, as shown in Fig. 1.

The relatively large decrease in the value of R and particularly the inflection are almost certainly the result of proton transfer, since such behavior has no analogy in any of the previously published

(1) A. Hantzsch, *Z. physik. Chem.*, **65**, 41 (1908).

(2) K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).

(3) K. Fajans, *Z. physik. Chem.*, **B24**, 103 (1934).

(4) N. Bauer, in "Physical Methods of Organic Chemistry," A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 2nd ed., 1949, p. 1160.

MOLECULAR GEOMETRY AND THE VAPOR PRESSURE OF ISOTOPIC MOLECULES. THE EQUIVALENT ISOMERS *cis*-, *gem*- AND *trans*-DIDEUTERIOETHYLENES¹

Sir:

We wish to report a difference in vapor pressure of isotopic molecules which is associated with molecular geometry. The vapor pressure of *trans*-dideuterioethylene has been found to be larger than that of either *cis*- or *gem*-dideuterioethylene. Initial experiments were made in an efficient packed column of about 80 plates on mixtures of *cis*- and *trans*-dideuterioethylene, monodeuterioethylene and ethylene. These results now have been confirmed and extended by manometric measurements over the temperature range $130-180^\circ\text{K}$. on highly purified samples. The samples were purified by low temperature gas chromatography and contained less than 10^{-2} mole per cent. chemical impurities.

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.