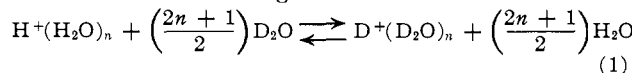


### HYDROGEN ISOTOPE FRACTIONATION IN ACIDIFIED SOLUTIONS OF PROTIUM AND DEUTERIUM OXIDE<sup>1</sup>

Sir:

The equilibrium constant for hydrogen isotope fractionation between solvent and acid species in aqueous solutions of strong mineral acid has never been



measured directly. And yet this fractionation factor is of primary importance to any comparison of rates or equilibria of acid-base reactions in protium and deuterium oxides. We wish here to report the preliminary results of a method we have employed to measure this equilibrium constant directly for the first time.

Our method is based on the fact that the position of the proton n.m.r. signal from an aqueous solution of strong acid is a measure of the fraction of protons in the

traditionally has been considered to exist as the monohydrate,  $\text{H}_3\text{O}^+$ , in aqueous solution, but recent evidence indicates that the aggregate  $\text{H}_9\text{O}_4^+$  may be more stable.<sup>3</sup> In such a large aggregate it is very likely that different protons will have different chemical shifts. But the structure of water and the solvated proton is constantly changing by very rapid proton jumps, and it is convenient to treat such a system of several different kinds of rapidly interchanging protons in terms of protons with only two different chemical shifts. Rather than assume a specific model, we have used data obtained as outlined above to calculate  $K$  for a number of integral values of  $q$ , the number of hydrogens in the solvated proton aggregate ( $q = 2n + 1$  where  $n$  is that used in eq. 1) with the weighted-average chemical shift  $\delta_{\text{H}^+}$ . Table I shows that  $l$ , the  $q$ th root of  $K$ , is not very sensitive to changes in  $q$ : there is a regular decrease in  $l$  with increasing  $q$ , but the change

TABLE I

CALCULATED ISOTOPE FRACTIONATION CONSTANTS FOR PROTIUM AND DEUTERIUM OXIDE SOLUTIONS OF PERCHLORIC ACID

Mole fraction perchloric acid	% Deuterium <sup>a</sup>	$\delta$ (c.p.s.) <sup>b</sup>	$l^c$						
			$q = 1$	2	3	4	5	7	9
0.0540	83.9	41.7	0.683	0.674	0.665	0.655	0.645	0.622	0.597
.105	67.9	75.5	.718	.702	.685	.665	.643	.589	.516
.105	52.5	71.9	.716	.701	.684	.666	.646	.596	.530
.168	46.8	115.2	.742	.717	.689	.652	.608	.469	.182
.0541	0.0	31.1	...	...	...	...	...	...	...
.105	0.0	61.4	...	...	...	...	...	...	...
		Av.:	0.715	0.699	0.681	0.660	0.636	0.569	0.456
		Std. dev.:	.024	.018	.011	.007	.018	.068	.186
		$100 \times (\text{Std. dev.})/\text{Av.}$ :	3.4	2.6	1.6	1.1	2.8	12.	41.

<sup>a</sup> Atom % deuterium in system (100 D/(D + H)). <sup>b</sup> Measured at 40 Mc. with respect to an external  $\text{H}_2\text{O}$  standard and corrected for differences in bulk susceptibilities between  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures (susceptibility corrections for the presence of perchloric acid are negligible) but not corrected for the effect of the anion (J. C. Hindman, *J. Chem. Phys.*, **36**, 1000 (1962); A. J. Kresge, to be published). <sup>c</sup>  $(K)^{1/q}$ , where  $K$  is that in eq. 4.

acid species.<sup>2</sup> Rapid exchange of hydrogen between the solvated proton and the solvent—the phenomenon which prohibited direct measurement of this equilibrium constant before—does not permit observation of separate n.m.r. signals from the solvent and the solvated proton. Instead, a composite signal ( $\delta$ ) is seen in these solutions whose position is the number average of the signals ( $\delta_{\text{H}^+}$  and  $\delta_{\text{H}}$ ) from the individual species

$$\delta = p\delta_{\text{H}^+} + (1 - p)\delta_{\text{H}} \quad (2)$$

where  $p$  is the atom fraction of protons in the acid species. If  $\delta$  is measured with respect to  $\delta_{\text{H}}$ , the chemical shift of the solvent, this relationship simplifies to

$$\delta = p\delta_{\text{H}^+} \quad (3)$$

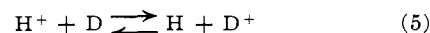
Since  $\delta$  is a function of  $p$ , it can be used to measure the effect of a perturbation of the system on  $p$ . In the present case, for example, introduction of deuterium into a system consisting of strong acid and protium oxide will change the ratio of protium in the acid species to protium in the solvent. The change in this ratio can be related to a change in  $p$  and can be measured by the change in  $\delta$ . This, together with mass balance relationships, provides sufficient information to calculate the equilibrium constant for eq. 1

$$K = \frac{[\text{D}^+(\text{D}_2\text{O})_n][\text{H}_2\text{O}]^{(2n+1)/2}}{[\text{H}^+(\text{H}_2\text{O})_n][\text{D}_2\text{O}]^{(2n+1)/2}} \quad (4)$$

The stoichiometry of eq. 1 is dependent on the extent of solvation of the proton in water. The proton

is not large. The value of  $q$  which best fits the data (smallest spread in  $l$ ) is 4, with 3 not much worse.

The best value of  $l$  based on this preliminary work is 0.67 (average of values for  $q = 3$  and  $q = 4$ ). This is the isotope effect for converting one hydrogen in the solvated proton aggregate to one solvent hydrogen



The value of 0.67 is consistent with an early estimate which put this constant at 0.63,<sup>4</sup> and a later revision which raised it to 0.67.<sup>5</sup> More recently,  $l$  was calculated to be 0.704 from observed infrared and Raman frequencies of acid solutions in protium and deuterium oxides.<sup>6</sup>

We are also applying this method to protium and deuterium oxide solutions of strong base. These experiments give a tentative value of 0.8 for the isotope effect on changing one O-H<sup>-</sup> bond in the solvated hydroxide ion to one O-H bond in water.

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

(3) M. Eigen and L. De Maeyer, "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 5.

(4) W. E. Nelson and J. A. V. Butler, *J. Chem. Soc.*, 957 (1938).

(5) E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

(6) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).