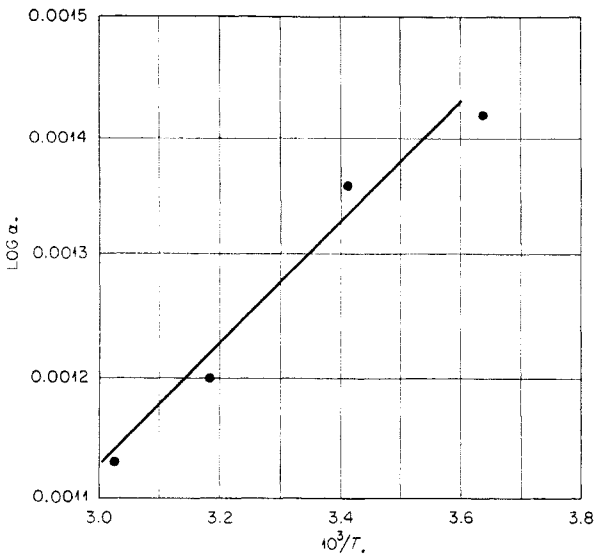

Fig. 1.—The log of α as a function of $10^3/T$.

Results and Discussion

The results of these experiments are summarized in Table I. The uncertainty in the isotopic equilibrium constants is estimated to be less than one digit in the last decimal place shown. As expected, the data show an inverse dependence upon temperature.

By plotting log α *vs.* $1/T$, a straight line was obtained, as shown in Fig. 1. The heat of exchange calculated from the slope of this line was 2.26 cal./mole and $-\Delta S$ was 1.81×10^{-3} cal./mole degree at 25°. These results are slightly higher than those given by Glueckauf[3] for the Na^{22}–Na^{24} exchange, and doubtless reflect the greater mass difference ratio ($\Delta M/M$) which exists between the isotopes of lithium as compared to Na^{22} and Na^{24}.

USE OF GLASS ELECTRODES TO MEASURE ACIDITIES IN DEUTERIUM OXIDE[1,2]

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Received August 26, 1959

Recent studies have shown that a conventional glass electrode apparatus can be used to give fairly precise values of acidity in aqueous solutions, particularly when only relative values of the acidity are needed.[4,5] One situation where it would be helpful to have additional data on relative acidities is for solutions of weak acids and bases in the solvents D_2O and H_2O. We have therefore investigated the applicability of the glass electrode to measurement of acidity in D_2O solutions. A general study is already available on some of the properties of glass electrodes in D_2O,[6] but it does not give much consideration to the measurement of acidity in D_2O with ordinary electrodes. We have recently learned that this latter problem was considered some time ago by Hart, and by R. B. Fischer and R. A. Potter but the results are available only in special publications.[7,8]

Experimental

All measurements were made with a Beckman Model G *p*H meter at 25°. The Beckman No. 39166 (old No. 19166) glass electrode and saturated calomel electrode combination was used for all measurements, unless otherwise noted. The *p*H meter was standardized with conventional buffer mixtures chosen to be close to the range of the *p*H measurements. Reagent grade chemicals were used without further purification. Formic acid was redistilled and maleic acid, aniline hydrochloride and pyridinium perchlorate were recrystallized. The D_2O was 99.5 atom % deuterium. Solutions of NaOD were made by passing water vapor over sodium. Other solutions in D_2O were made by dissolving the anhydrous hydrogen compound (except for hydrochloric acid where a concentrated aqueous solution was diluted). For the low concentrations studied, this did not change the deuterium content by a significant amount. All concentrations are in moles (or equivalents) per liter.

Results and Discussion

Glass Electrode Measurements in Solutions of Strong Acids.—Solutions of roughly 0.01 *M* hydrochloric acid in H_2O and in D_2O were prepared by dilution and the exact concentration of acid was determined by titration with standard base. The averages of several *p*H meter readings with the standard electrode combination are given under (a) of Table I. For solutions of comparable acidity

TABLE I

GLASS ELECTRODES IN SOLUTIONS OF HYDROCHLORIC ACID IN H_2O AND IN D_2O

Solutions are 0.00976 *M* HCl in H_2O and 0.00983 *M* DCl in D_2O; *p*H meter standarized with *p*H 4.00 phthalate buffer

		Av. rdgs. H_2O soln.	Av. rdgs. D_2O soln.	Difference
(a)	Standard glass electrode—Beckmann No. 39166; 39168 calomel	2.08	1.69	0.40
(b)	Beckmann 1190-80 glass electrode; 1170 calomel	2.08	1.69	.39
(c)	Beckmann type E glass electrode; 1170 calomel	2.02	1.62	.40
(d)	"Synthetic" 1190-80 glass electrode; 1170 calomel	2.13	1.73	.40

the *p*H meter reading in D_2O solution is 0.40 *p*H unit lower than in H_2O solution. To determine whether this difference was characteristic only of this particular electrode system, these same solutions were measured using various glass electrode–calomel electrode combinations. The results are given in (b), (c) and (d) of Table I. It is apparent that the difference is constant for the different electrodes, within the error of reading the meter. The "synthetic 1190–80" electrode in (d), Table I, is an ordinary Beckman 1190–80 electrode from which the internal solution was poured out and replaced with a solution of 0.100 *M* HCl in H_2O. The

(1) Supported in part by a grant from the Atomic Energy Commission.

(2) Presented at the 136th meeting of the American Chemical Society, Atlantic City, September, 1959.

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TABLE II

MEASUREMENTS WITH GLASS ELECTRODE FOR STRONG BASES IN H_2O AND IN D_2O

	Base	Acidity: $-\log C_{H^+}$	Acidity: $-\log C_{D^+}$	Δ calcd.	pH Reading: In H_2O	pH Reading: In D_2O	Δ exp.	ΔpD: (Δcalcd. − Δexp.)
(a)	NaOH NaOD	12.00	12.86	0.86	11.83	12.21	0.38	0.48
(b)	NaOH NaOD	12.00	12.86	.86	12.00[a]	12.47[a]	.47	.39
(c)	$Ba(OH)_2$ $Ba(OD)_2$	12.46	13.29	.83	12.38	12.82	.44	.39
(d)	$Ca(OH)_2$ $Ca(OD)_2$	12.28	13.14	.86	12.22	12.67	.45	.41

[a] Measurements made with type E (low sodium ion error) electrode.

actual potential of this electrode was markedly different from a normal 1190–80 electrode but even so the difference for the two solvents remains at 0.40 *p*H unit.[9]

These measurements indicate that the difference of 0.40 *p*H meter unit is not dependent on the particular type of glass electrode and that the *p*D of a solution in D_2O can be determined by use of the equation

$$p\mathrm{D} = p\mathrm{H} \text{ meter reading} + 0.40 \qquad (1)$$

where the "*p*H meter reading" is obtained with an apparatus standardized to read *p*H in H_2O solutions. For convenience, we shall refer to the difference, *p*D minus *p*H meter reading, in this case 0.40, as $\Delta p\mathrm{D}$.[10]

Fisher and Potter[7] made studies of a glass electrode system using buffer solutions in D_2O and concluded that an equation like 1 could be used to give *p*D. However, they proposed a numerical constant of 0.25 rather than 0.40. Hart[8] did a similar study with solutions of hydrochloric acid in the two solvents and also with phosphate buffers (*p*H of from 5 to 7). He found values for the constant of equation 1 which range from 0.40 to 0.47. Hart also gave further consideration to the Fisher and Potter results and noted difficulties in the latters' work, both in the extrapolations and in the calculation of ionic strength. We conclude that the value of 0.40 for the constant of equation 1 agrees within experimental error with all of the earlier results.

Glass Electrode Measurements in Solutions of Strong Bases.—*p*H meter readings using the standard electrodes were made on solutions of 0.001009 *M* NaOH in H_2O and 0.001104 *M* NaOD in D_2O. The resulting average values are given under (a) in Table II. Calculation of the value of $-\log C_{D^+}$ or $-\log C_{H^+}$ for solutions of known concentration of hydroxide ion involves the ion product of water. This was taken to be 0.15×10^{-14} and 1.01×10^{-14} for D_2O and H_2O, respectively.[11]

The value of $\Delta p\mathrm{D}$ of 0.48 for the sodium hydroxide solutions is significantly higher than that obtained for acid solutions. However, it is well known that the sodium ion error of the standard glass electrode depends on the *p*H at a fixed concentration of sodium ion. From the Beckman chart of sodium ion error it is found that for 0.01 *M* sodium ion at 25° the correction is 0.13 *p*H unit at *p*H 12.80 and 0.05 unit at *p*H 12.00. The value of $\Delta p\mathrm{D}$ taking this into account is 0.48–0.08 = 0.40 *p*H unit, the same as the value for acid solutions. In agreement with this, a $\Delta p\mathrm{D}$ value of 0.39 (Table IIb) was found for these same solutions with the Beckman type E electrode which has a negligible sodium ion error at these concentrations. Further confirmation of the similarity of $\Delta p\mathrm{D}$ in acid and in base solutions is given by the results obtained with solutions of approximately 0.029 *N* barium hydroxide and 0.02 *N* calcium oxide in H_2O and D_2O (Table II, (c) and (d). These solutions would be expected to show an insignificant cation effect at these low concentrations. In both cases the $\Delta p\mathrm{D}$ is 0.40 *p*H unit, within experimental error.

K_H/K_D Ratios for Some Weak Acids and Bases.—To determine whether the correction term 0.40 is applicable in the *p*H range between the extremes of strong acids and strong bases, the pK_a values for some weak acids were determined in H_2O and in D_2O using the glass electrode to measure *p*H and *p*D. For every acid, values of pK_H' or pK_D' (where K' is the concentration equilibrium constant) were calculated from the *p*H or *p*D value and the molar ratio of acid and conjugate base for each of several buffer ratios. Values of $\Delta pK'$, defined as $pK_D' - pK_H'$ were always calculated from pK_D' and pK_H' values for solutions of equal ionic strength. In most measurements the ionic strength was less than 0.10. Values of pK_H or pK_D were calculated from pK' using the activity coefficient expression

$$-\log f\pm = \frac{0.509\sqrt{I}}{1 + \sqrt{I}}$$

where I is ionic strength for molar concentrations. It made no difference, within experimental error, whether the K_H/K_D ratio was calculated from the average of the $\Delta pK'$ or the ΔpK values.

Table III summarizes the values of K_H/K_D obtained for a variety of weak acids. In general the agreement between the K_H/K_D ratios from glass electrode studies and from other methods of measurement is quite satisfactory, and it seems safe to conclude that the factor of 0.40 for $\Delta p\mathrm{D}$ is applicable to measurements at intermediate acidities.

(9) In view of the frequent recommendation that a glass electrode should be equilibrated in water for several hours before use, it is worth noting that when a glass electrode was transferred from a water solution to a D_2O solution (or *vice versa*) the "*p*H" difference of 0.40 appeared to be established as rapidly as measurements could be made.

(10) As is well known, the definition of *p*H is somewhat fuzzy. One can assume that the definition of *p*D is equally so. Our implicit definition of *p*D is that it "means the same thing for solutions in pure D_2O that *p*H does for H_2O."

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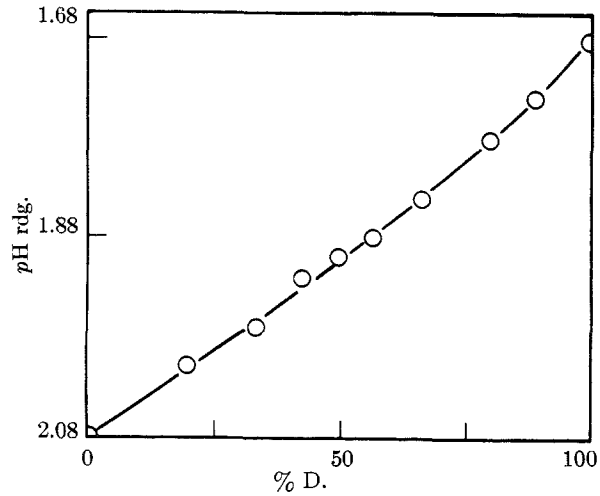

Fig. 1.—Dependence of pH meter reading for 0.01 M hydrochloric acid on atom per cent. deuterium of the aqueous solvent. Meter standardized to read pH for H_2O solutions.

TABLE III

K_D/K_H FROM MEASUREMENTS OF pH AND pD WITH GLASS ELECTRODE

Acid	pK^H	pK^D	ΔpK^a	K^H/K^D	K^H/K^D other
Acetic	4.73	5.25	0.52	3.3	3.33[12]
Formic	3.75	4.20	.45	2.8	2.5[13]; 2.7[14]
Aniline·HCl	4.55	5.13	.58	3.8	3.1[13]
Maleic, pK_1	1.98	2.53	.55	3.6	4.2[15]
Maleic, pK_2	6.28	6.61	.33	2.1	2.4[15]
Phosphoric, pK_1	2.11	2.31	.20	1.6	1.6[13]
Carbonic, pK_2	10.33	10.96	.63	4.3	4.4[16]
m-Nitroaniline·HCl	2.48	2.96	.48	3.0	3.8[17]

[a] Values of $\Delta pK'$, calculated from measurements of similar ionic strengths are the same, within experimental error.

Dependence of ΔpD on Deuterium Content of Solution.—Varying quantities of 0.010 M HCl in H_2O and 0.010 M DCl in D_2O were mixed to form a series of solutions of the same acid concentration but with different deuterium content. The "pH's" of these solutions were measured with the standard glass electrode. As Fig. 1 shows the reading of the pH meter is very nearly a linear function of the atom per cent. deuterium.

Source of Potential Difference Giving Rise to ΔpD.—The correction term ΔpD could arise from a change of potential in D_2O compared to H_2O for either or both the glass electrode and the calomel electrode. In an exploratory experiment on this point, after the pH meter was standardized with the standard electrodes, the calomel electrode was replaced by one containing a saturated solution of potassium chloride in D_2O. There was no significant change in the meter reading. It thus appears that the potential change is due solely to the glass electrode.

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THE NATURE OF THE S–O BOND IN DISULFUR MONOXIDE

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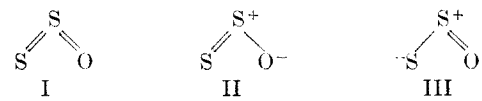
Received October 14, 1959

Recently Meschi and Myers[1] have reported the detailed microwave spectrum and molecular structure of disulfur monoxide, S_2O. Mass spectrometric and other measurements[2] had previously led them to positive identification of that unstable compound, which at one time[3] was mistaken for dimeric sulfur monoxide, $(SO)_2$. From analysis of the spectra they found for the molecule a bent S–S–O structure with the following parameters: S–S distance, 1.884 Å.; S–O, 1.465 Å.; S–S–O angle, 118 ± 0.5°. The authors also concluded: "the S–O bond is probably fairly close to a single bond." However, this view is not supported by the existing data. A single covalent S–O bond should be appreciably longer than the above, namely, 1.70 Å., from the sum of the covalent radii of the S and O atoms.[4] (The revised values corrected for partial ionic character of the bond[5] lead to nearly the same bond length, 1.69 Å.) The distance 1.51 Å. quoted by Meschi and Myers for the single S–O bond is in fact the interatomic distance in the tetrahedral SO_4^{--} ion where considerable double bond character is expected.

As for the double-bond radii of the atoms, their "normal" values are much more uncertain that those of the single bonds. At any rate the S–O bonds in SO_2, 1.432 Å., are definitely shorter than the sum of the Pauling's double-bond radii, 1.49 Å. The explanation for this has been given by Moffitt[6] who analyzed the electronic structure of various sulfoxides and sulfones by means of his self-consistent LCAO method and showed that in these molecules the S–O bonds are largely double, with the 3d orbitals of sulfur contributing appreciably to the π-bonding. The resulting hybrid bond is stronger than one involving a pure p- or d-bonding orbital of sulfur. Obviously, such is the case for disulfur monoxide where the central S atom can use its 3d orbital in hybridization (form I) rather than forming so-called coördinate bonds with large formal charge separation as in the canonical forms II and III



From the known vibrational frequencies of the S_2O molecule[7] the force constant for the S–O bond may be estimated roughly at 9.3×10^5 dynes cm.$^{-1}$

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