to within 0.05 mv. for two to four hours, followed by a slow drift. The micro results are as reproducible as with the macro technique, the average value being only 0.01 mv. less than that computed from the Harned and Wright empirical eq. (2); namely, for $m = 0.01$; $E = 0.23549$ v.

Type	HCl. M	$E_{0.01}$, mv.
A	0.01002	0.23552 ± 0.07
	.01002	.23545 ± .04
	.01008	.23544 ± .03
B	.01006	.23550 ± .06
	.01006	.23548 ± .03

DEPARTMENT OF CHEMISTRY
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VICTOR K. LA MER
MARION H. ARMBRUSTER

RECEIVED MAY 23, 1935

THE E. M. F. OF THE QUINHYDRONE ELECTRODE IN HEAVY WATER. THE ACIDIC DISSOCIATION OF DEUTEROQUINONE

Sir:

By measuring the e. m. f. of the cell

$$\text{Ag, AgCl, HCl } (0.01\ M), \text{ Quinhydrone } (Q.QH_2), \text{ Pt} \qquad (I)$$

corresponding to the processes

$$2HCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QH_2;\ E_H \quad (1)$$
$$2DCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QD_2;\ E_D \quad (2)$$

when carried out in ordinary and heavy water, we obtain the free energy of the exchange process

$$2DCl(0.01\ M) + QH_2 = 2HCl(0.01\ M) + QD_2;\ E_D - E_H \quad (3)$$

If we assume that the activity of the chloride ion is the same in both waters, equation (3) may be considered as the difference of the dibasic acid dissociations

$$QH_2 = Q^{=} + 2H^+ \text{ (in } H_2O);\ K_H \quad (4)$$
$$QD_2 = Q^{=} + 2D^+ \text{ (in } D_2O);\ K_D \quad (5)$$

where K_H, the average dissociation constant, equals $K_1K_2 = (1.75 \times 10^{-10})(4 \times 10^{-12}) = 2.64 \times 10^{-11}$ for ordinary water [S. E. Sheppard, *Tr. Am. Electrochem. Soc.*, Preprint 39 (1921); La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923)].

Extrapolation to pure D_2O indicates that $E_D - E_H = 0.0345$ v. Hence $\log K_H/K_D = 0.0345/0.05911 = 0.5837$, or $K_H/K_D = 3.84$, a result which accords with the decrease in acidic dissociation of other weak acids in D_2O; *e. g.*, deutacetic acid [Lewis and Schutz, THIS JOURNAL, **56**, 1002 (1934)], chloroacetic acid [*ibid.*, **56**, 1913 (1934)].

N_{D_2O}	Molality HCl	$E_{0.01m}$ mole/1000 g.	$E_{0.01m}$ mole/55.5 moles
0	0.011182	0.23548	0.23548
	.010855	.23541	.23541
0.103	.01192	.23736	.23677
.3454	.013576	.24604	.24409
	.00880	.24614	.24419
.5109	.01127	.25301	.25016
	.01018	.25306	.25021
.6925	.008844	.26173	.25770
	.009718	.26169	.25766
.9240	.010446	.27190	.26685
	.009991	.27195	.26690
(1.0000)		(.2752)	(.2700)

The measurements were made at 25° with Type B micro cells as described [La Mer and Armbruster, THIS JOURNAL, **57**, 1510 (1935)] where the reliability of the micro technique is established. In the last column of the table the e. m. f. is corrected to exactly 0.01 mole HCl/55.5 moles solvent for purposes of comparison. The normal potential is 0.4774 volt, but in heavy water the value extrapolated linearly would be 0.5119 v. if we make the highly plausible assumption that the activity coefficients in D_2O and H_2O are identical. N_{D_2O}, the mole fraction of heavy water was computed from density measurements using the formula of La Mer and Baker [*ibid.*, **56**, 2641 (1934)]. Both curves deviate from linearity at low D_2O concentrations. Experiments are in progress to check the reliability of extrapolation. The investigation is being continued, using the deuterium gas electrode to study the reaction, $QD_2 + H_2 = QH_2 + D_2$.

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SAMUEL KORMAN

RECEIVED JULY 22, 1935

THE OXIDATION AND REDUCTION OF DEHYDROANDROSTERONE

Sir:

It has been shown by Gallagher and Koch [*J. Biol. Chem.*, **104**, 611 (1934)] that highly active testicular extracts are sensitive to hydrogen-ion concentration, and show a decided decrease in their activity when boiled with alkalies, whereas active extracts obtained from male urine do not show this behavior. This fact strongly indicates that the active compound present in the testes is different in structure from that of androsterone. It is also known that this instability toward alkalies is a characteristic property of the corpus luteum hormone.