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
COLUMBIA UNIVERSITY
NEW YORK CITY
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

Ag, AgCl, HCl (0.01 M), Quinhydrone ($Q.QH_2$), Pt (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	$E_{0.0\,m}$ 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, $QD_2 + H_2 = QH_2 + D_2$.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY
VICTOR K. LA MER
SAMUEL KORMAN

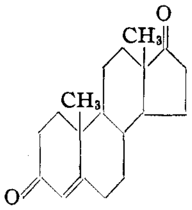
RECEIVED JULY 22, 1935

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.

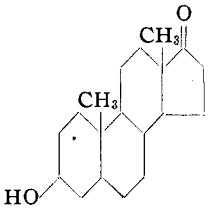
This similarity in behavior suggests that the testicular hormone may possess in a portion of its molecule a structure closely related to that which is present in the corpus luteum hormone. Therefore it seemed important to us to prepare a compound structurally related to both the corpus luteum hormone and to androsterone. Such a substance would be the unsaturated diketone, Δ^4-etio-cholen-dione-3,17. (I)



I

This compound has now been prepared in this Laboratory by oxidation of the dibromide of dehydroandrosterone (the dehydroandrosterone used in these experiments was prepared by Francis B. Cramer according to our method [Wallis and Fernholz, THIS JOURNAL, **57**, 1379 (1935)] with chromic acid by a method similar to that used in the preparation of the corpus luteum hormone [Fernholz, *Ber.*, **67**, 1855, 2027 (1934)]. It melts at 170° (uncorr.), $[\alpha]^{30}_D$ +199° in chloroform. Physiological investigations are being made to determine whether it possesses properties similar to the active principle occurring in testicular extracts.

We have also carried out experiments on the hydrogenation of dehydroandrosterone, and have found that in alcoholic solution, under proper conditions, 3-hydroxy-etioallocholanone-17 (II) is easily obtained by hydrogenation with palladium black. This product melts at 172° (uncorr.), $[\alpha]^{26}_D$ +88.6° in methyl alcohol. A mixed melting point with an authentic specimen of the hydroxy ketone showed no depression. In acetic acid solution both the double bond and the ketone group in dehydroandrosterone are hydrogenated. This also occurs when platinum black is used as the catalyst.



II

The experimental details of the preparation of these compounds together with the results of the physiological tests will be reported at a later date.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.

EVERETT S. WALLIS
E. FERNHOLZ

RECEIVED JULY 15, 1935

NEW BOOKS

Dictionnaire de la Chimie et de ses Applications. (Dictionary of Chemistry and its Applications.) By CLÉMENT DUVAL, Docteur ès Sciences physiques, RAYMONDE DUVAL, Docteur ès Sciences physiques, and ROGER DOLIQUE, Dr. ès Sciences phys. Pharmacien. Preface by H. Luc, Directeur général de l'Enseignement technique. Hermann & Cie., 6 Rue de la Sorbonne, Paris, France, 1935. xxxii + 747 pages. 13.5 × 19 cm., paper covers, price, 90 francs.

This excellent little dictionary provides the reader of French scientific literature with brief guiding definitions of about 20,000 terms in chemistry and related fields, including a number of French trade names not easily found elsewhere. Named types of apparatus are defined by use only and are not described. The list of names of minerals appears to be especially complete.

The modernity of the work is indicated by the inclusion of deuterium but not tritium. No etymological information is given nor is the correct syllabification or pronunciation indicated. It is obviously a book to be consulted by the reader who wishes to acquaint himself with the meaning of an unfamiliar term and for this reason alone deserves a place on the shelf of a reference library.

WILLIS A. BOUGHTON

The Application of Absorption Spectra to the Study of Vitamins and Hormones. By R. A. MORTON, D.Sc., Ph.D., F.I.C., The University of Liverpool. Published by Adam Hilger, Ltd., 98 Kings Road, Camden Road, London, N. W. 1, England, 1935. 73 pp. 25 figs. 16 × 25.5 cm. Price, per copy including postage, 10s./4d.

This little book consists of eight essays, seven dealing with specific vitamins, and one with a few hormones. It seems to furnish the text for an unwritten sermon extolling the possibilities of the spectroscopic method in organic