211. *Spectrophotometric Determination of the Dissociation Constant of Hydrogen Peroxide.*

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The ultraviolet absorption spectra of hydrogen peroxide have been determined in aqueous buffers of different pH by spectrophotometry. The value $(2{\cdot}63 \pm 0{\cdot}12) \times 10^{-12}$ at 30° for the dissociation constant of hydrogen peroxide has been derived.

AQUEOUS solutions of hydrogen peroxide absorb continuously[1] in the range 3750—2150 Å, the extinction being a maximum at 2150 Å but decreasing continuously at longer wavelengths. Progressive addition of sodium hydroxide to aqueous hydrogen peroxide strongly displaces the absorption curves towards longer wavelengths.[2] This indicates that at a particular wavelength the optical density of hydrogen peroxide solution increases with increasing amounts of added alkali, pointing to a relation between optical density and pH. Our results confirm the observation by Bredig and his coworkers[2] and also lead to the conclusion that the optical density of aqueous hydrogen peroxide depends on the proportions of the molecular form H_2O_2 and of the anion HO_2^-: $H_2O_2 + H_2O = H_3O^+ + HO_2^-$.

By measuring the molar extinction coefficients at a given wavelength in acid solution (ε_1), alkaline solution (ε_3), and buffer solution (ε_2) of known pH, it is possible to calculate the value of pK from the equation[3] $\mathrm{p}K = \mathrm{pH} + \log_{10}[(\varepsilon_2 - \varepsilon_3)/(\varepsilon_1 - \varepsilon_2)]$. When all measurements are carried out with the same cell and solutions of the same concentration, the optical density or absorbance values can be used in place of molar extinction coefficients.

In Stenström and Goldsmith's method,[4] adopted by us, the use of the above equation is simplified by plotting absorbance against pH. At the midpoint of the break in the curve pH = pK, since at this point the log term is zero.

EXPERIMENTAL

The absorption spectra were measured with a Unicam quartz photo-electric spectrophotometer (Model SP 500) and a hydrogen lamp operated from a stabilised power supply. Both cells, of fused silica and of 1 cm. optical path, matched perfectly. pH measurements were taken with a Leeds and Northrup pH indicator having a glass electrode which was previously standardised.

Phosphate buffers (pH 2·0—12) were made up from solutions of 0·1M-phosphoric acid in 0·1N-potassium hydroxide. 0·1N-Potassium hydroxide solution was used as a solution of pH 13. All reagents were Merck's analytical grade.

All measurements were carried out at 30° ± 0·5° (room temperature).

Hydrogen peroxide (Merck) was purified by two distillations under reduced pressure. The concentration of the aqueous distillate was measured photometrically with use of a Beer's law graph obtained for the system H_2O_2–$Ti(SO_4)_2$.[5] The distillate was then diluted with conductivity water to give a 0·04M-solution. 1 c.c. of this was diluted to 25 c.c. with the buffer of known pH; thus the hydrogen peroxide concentration for absorption measurements was $1{\cdot}6 \times 10^{-3}$M. Solutions for use in the blank cell of the spectrophotometer contained 24 c.c. of buffer and 1 c.c. of water.

Fig. 1 contains the plots against wavelength of the absorbance of hydrogen peroxide in

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[1] Urey, Dawson, and Rice, *J. Amer. Chem. Soc.*, 1929, **51**, 1371; Allmand and Style, *J.*, 1930, 596.

[2] Bredig, Lehman, and Kuhn, *Z. anorg. Chem.*, 1934, **218**, 16.

[3] Hammett, Dingwall, and Flexser, *J. Amer. Chem. Soc.*, 1935, **57**, 2103.

[4] Stenström and Goldsmith, *J. Phys. Chem.*, 1926, **30**, 1683; see also DeVries and Gantz, *J. Amer. Chem. Soc.*, 1954, **76**, 1008.

[5] Snell and Snell, " Colorimetric Methods of Analysis," Van Nostrand, New York, 1949, p. 882.

solutions of pH 5·95, 11·23, 11·80, and 13·00. Beyond 2600 Å the absorption drops to very low values in dilute solutions.

The plot of absorbance against pH (not shown) at 2200 Å gives pK = 11·40.

To reduce the absorbance to zero ionic strength, corrections were made in the apparent or measured pH of the buffers by using the relation $(\text{pH})_0 = (\text{pH})_a + 0{\cdot}51\, \mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})$, where $(\text{pH})_0$ is the pH of the buffer at zero ionic strength, $(\text{pH})_a$ the apparent or measured pH of the same and μ is the ionic strength. The Table contains the compositions, ionic strengths, and corrected pH values of the buffers used.

	Composition (mmoles)				
$(\text{pH})_a$	H_3PO_4	KOH	$\mu^{\frac{1}{2}}$	$\dfrac{0{\cdot}5\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$	$(\text{pH})_0$
4·44	49·90	50·10	0·2243	0·0935	4·53
5·95	48·08	51·92	0·2361	0·0974	6·05
7·10	38·47	61·53	0·2909	0·1150	7·22
7·70	35·21	64·79	0·3072	0·1199	7·82
8·25	34·02	65·98	0·3130	0·1215	8·37
9·00	33·35	66·65	0·3161	0·1225	9·12
10·50	32·26	67·74	0·3262	0·1255	10·63
11·23	29·44	70·56	0·3514	0·1326	11·36
11·80	25·00	75·00	0·3874	0·1424	11·94
13·00	—	100·00	0·3162	0·1201	13·12

FIG. 1.

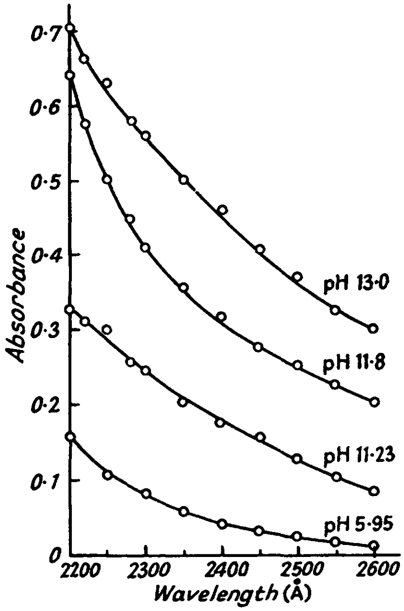
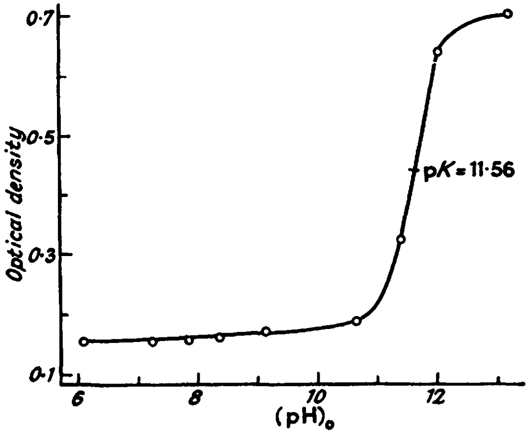


FIG. 2.



The plot of absorbance (Fig. 2) against these corrected pH values gives pK_a as 11·56 at 2200 Å. Similar treatment of results at 2220 and 2250 Å gives the pK values 11·58 and 11·60. The mean of these three is 11·58, which corresponds to a value of $K = (2{\cdot}63 \pm 0{\cdot}12) \times 10^{-12}$ at 30 ± 0·5° and shows fair agreement with the value of $(2{\cdot}82 \pm 0{\cdot}1) \times 10^{-12}$ at 30° obtained by Evans and Uri from an E.M.F. method.[6]

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[6] Evans and Uri, *Trans. Faraday Soc.*, 1949, **45**, 224.