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The Behavior of the Glass Electrode in Hydrogen Peroxide Solutions

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Glass electrode pH sets are shown to behave in a reversible and reproducible manner in hydrogen peroxide solutions of all strengths. The low apparent pH values which are observed appear to be due to a simple shift in the E_0 values for the electrode system in this new environment. Corrections are supplied by which the observed pH values can be converted to numbers having the same significance as pH values in ordinary water solutions. Comparison is made with a previous theory of glass electrode deviations. A possible explanation for the observed deviations is advanced. These results shed considerable light on the properties of hydrogen peroxide as an ionizing solvent.

Introduction

The properties of hydrogen peroxide reaction systems are greatly affected by additions of acid and alkali. The glass electrode has been much used in peroxide solutions in an attempt to measure acidity and alkalinity in this very convenient and rapid fashion. As a matter of actual practice such measurements are almost always made by simply immersing commercial glass-calomel electrode sets in the solution and then reading the dial as in the case of aqueous solutions. This procedure is defensible for very dilute peroxide solutions but not for concentrated solutions.

One way to deal with the problem is to dilute strong solutions to some arbitrary low concentration. This method is widely used, but it often measures the purity of the diluting water more than anything else. On the other hand, direct measurement in concentrated solutions gives quite unexpected results.

A few investigations have been made on the behavior of the glass electrode in strong hydrogen peroxide solutions. Regardless of the theoretical complications, it has been found that the glass electrode can behave in a reversible and reproducible manner in peroxide solutions.¹ We have found that commercial glass electrode sets as supplied for use in aqueous systems will function at all hydrogen peroxide concentrations. The results presented here permit one to interpret the readings in straightforward fashion and to obtain corrected pH values which appear to have a connection with hydrogen ion activity.

Materials. Hydrogen Peroxide.—The starting material was a specially purified solution containing about 99.8% hydrogen peroxide.

Water.—Distilled water was further purified by passing through a mixture of ion-exchange resins, Amberlite IR-120 and Amberlite IR-410.

Perchloric Acid.—Baker analyzed reagent grade acid was used without further purification in the preparation of 0.1 *N* perchloric acid solutions. The perchloric acid titrants were prepared in solutions of the same hydrogen peroxide concentration as that to which they were to be added.

Sodium Hydroxide.—J. T. Baker analyzed reagent grade pellets were used to prepare a 20% solution. This solution was further purified by the addition of magnesia, 4% with respect to the sodium hydroxide. After stirring for one hour, the solution was centrifuged and ready for use. This treatment provided a caustic solution which could be added to hydrogen peroxide with a minimum of decomposition. Ordinary reagent grade sodium hydroxide causes fairly vigorous decomposition of hydrogen peroxide solutions.

(1) A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **51**, 1690 (1955).

(B) **Apparatus.**—A Beckman model G pH Meter was used in all pH measurements. It was equipped with Beckman calomel electrode #4970 and Beckman glass electrode #1190-80.

Parallel investigation with asbestos junction and palladium junction calomel electrodes showed that only the asbestos junction type gave reproducible results in the higher concentration range.

(C) **Procedure.**—Solutions of hydrogen peroxide of approximately 25, 50, 70, 80, 90 and 99.8% were prepared. Acid and alkaline titrating solutions, 0.1 *N* $HClO_4$ and 0.1 *N* $NaOH$, were made by volumetrically diluting 70% $HClO_4$ and 20% $NaOH$ solutions with each of the above hydrogen peroxide solutions.

The electrodes were immersed in a 100-ml. sample of the peroxide solution to be investigated and the "apparent pH " measured. (The term "apparent pH " will be used to designate the pH as read on the meter.) Increments of 0.1 *N* $HClO_4$ were then added with pH measurement after each addition until the acid concentration in the titrated solution was 0.016 *N*. This procedure was repeated with a fresh portion of peroxide, using 0.1 *N* $NaOH$ as the titrant.

The curves obtained by plotting these data are shown in Fig. 1. These comprise a family of typical titration curves,

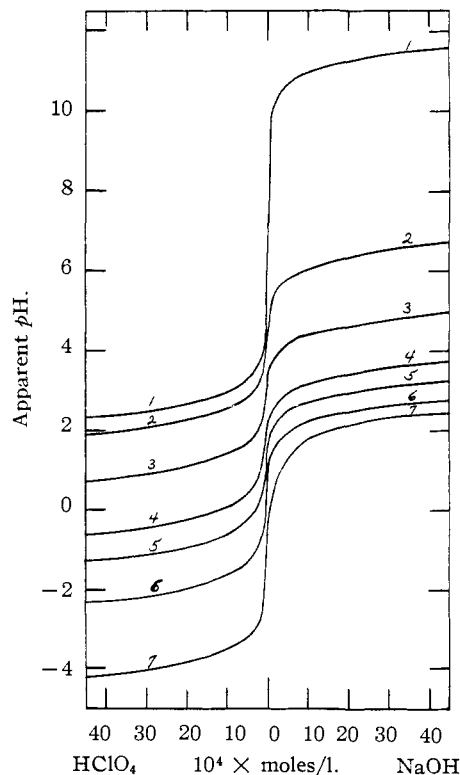


Fig. 1.—Titration curves in hydrogen peroxide solutions: 1, water; 2, 24.8% H_2O_2 ; 3, 49.6% H_2O_2 ; 4, 71.3% H_2O_2 ; 5, 79.2% H_2O_2 ; 6, 88.8% H_2O_2 ; 7, 99.8% H_2O_2 .

TABLE I

H ₂ O ₂ concn. →	E.M.F. vs. -LOG C _{H+} FOR VARIOUS HYDROGEN PEROXIDE SOLUTIONS—TEMPERATURE 27 ± 1°													
	0%		24.8%		49.6%		71.3%		79.2%		88.8%		99.8%	
	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.	-log C _{H+}	E.m.f., mv.
4.16	217	4.31	231	4.23	305	4.30	350	4.31	407	4.31	465	4.31	573	
3.90	233	4.00	256	4.00	322	4.00	377	4.01	430	4.01	488	4.01	609	
3.64	248	3.70	275	3.70	347	3.70	410	3.71	456	3.71	518	3.71	634	
3.48	258	3.53	285	3.53	355	3.53	425	3.54	468	3.53	530	3.49	648	
3.28	270	3.31	296	3.31	368	3.31	440	3.32	481	3.31	544	3.31	659	
3.10	281	3.13	304	3.13	375	3.13	452	3.14	491	3.14	554	3.14	670	
3.00	286	3.01	312	3.01	383	3.01	461	3.02	499	3.01	561	3.01	678	
2.69	305	2.71	329	2.71	399	2.71	480	2.72	519	2.72	580	2.72	696	
2.51	316	2.53	340	2.53	410	2.54	492	2.55	530	2.54	590	2.54	706	
2.32	327	2.33	353	2.33	423	2.32	503	2.34	543	2.33	603	2.33	719	
2.02	345	2.05	373	2.05	440	2.04	522	2.06	562	2.05	620	2.05	734	
1.76	361	1.77	393	1.77	455	1.78	535	1.79	576	1.79	638	1.79	751	
Slope	0.0602		0.0604		0.0566		0.0648		0.0631		0.0616		0.0606	
Intercept (E ₀), mv.	-467		-495		-554		-643		-690		-747		-860	
Correlation coeff., r	1.000		0.998		0.999		0.996		0.999		1.000		1.000	

with the equivalence points displaced to lower and lower apparent pH values as the peroxide concentration is increased. In 70% and stronger solutions, the apparent pH becomes negative. A known bias voltage was added to the calomel electrode side of the circuit in order to shift these values to the range covered by the meter scale.

Results

By short circuiting the pH meter, one can determine the dial setting that corresponds to e.m.f. = 0. It is then possible to calculate the e.m.f. corresponding to any dial setting. In this manner, the apparent pH values for acid solutions were converted to e.m.f. In Table I these e.m.f. values are listed against the corresponding values of -log C_{H+} obtained by assuming complete dissociation of the perchloric acid. This assumption is supported by the fact that hydrogen peroxide solutions have dielectric constants almost the same as that of water.² The slope and intercept for each set of data were obtained by fitting a straight line to the experimental points *via* least squares. The first two points in each titration curve were omitted from consideration because the titrant additions (0.05 and 0.10 ml.) were so small as to introduce considerable uncertainty. The correlation coefficients, *r*, show the excellent fit obtained with the remaining 10 points.

The corrected pH of any peroxide solution at room temperature can be estimated by proper use of the equation, $pH = (E - E_0)/0.060$, using the appropriate value for E₀. It is even more convenient to read the apparent pH from the meter and then add a correction depending upon the hydrogen peroxide concentration only. Appropriate corrections are shown in Fig. 2. These corrections should be valid for any glass electrode system using a saturated KCl salt bridge which behaves reversibly in hydrogen peroxide solutions.

The ionic strength varied during these titrations, reaching a maximum of about 0.016. The expected effect on the activity is such as to cause a deviation of about 0.1 pH unit in the most concentrated solutions. An actual set of experiments was carried out in 50% hydrogen peroxide in which the ionic strength was varied from 0 to 0.023. The

apparent pH at the equivalence point was shifted by about 0.2 unit by this change. In view of these facts, it was considered best to avoid the complications involved in maintaining constant ionic strength and to accept instead this relatively small uncertainty in the measurements.

The cell used in these studies involved a liquid junction between saturated aqueous potassium chloride and the peroxide solution under test. The unknown potential difference at this junction is included in the E₀ values above. There is no way to measure this junction potential but there is reason to believe that it may have been relatively small. In the first place, the cell e.m.f. was very stable with time and easily reproducible upon reforming the junction. Also, the substitution of hydrogen peroxide for water in a solution of a neutral salt has little effect on the electrical conductance, leading to the supposition that ion mobilities (except hydrogen ion) are about the same in hydrogen peroxide as in water.³

Curve 1 in Fig. 3 shows the apparent pH at the equivalence point of the titration curves. Curve 2 shows the corrected equivalence point pH. In effect these two curves represent the apparent pH and corrected pH of solutions made up from pure hydrogen peroxide and pure water.

Curve 2 indicates that pure hydrogen peroxide is more dissociated than pure water, but less so than its aqueous solutions. This is in accord with other evidence. For example, the conductance of pure aqueous peroxide solutions varies in the same manner.⁴

The effect of dissolved carbon dioxide on the apparent pH of hydrogen peroxide solutions of several concentrations was investigated. After the apparent pH was measured, the solution was subjected to vacuum and warmed in order to expel the carbon dioxide. The pH was again measured. Carbon dioxide was then bubbled through the solution, after which time the pH was remeasured. In dilute peroxide, the apparent pH was depressed by CO₂ exposure, as in the case of aqueous solutions. In solutions containing about 90% hydrogen peroxide

(3) E. S. Shanley, *et al.*, *ibid.*, **78**, 5190 (1956).

(4) W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publ. Corp., New York, N. Y., 1955.

(2) P. M. Gross and R. C. Taylor, *THIS JOURNAL*, **72**, 2075 (1950).

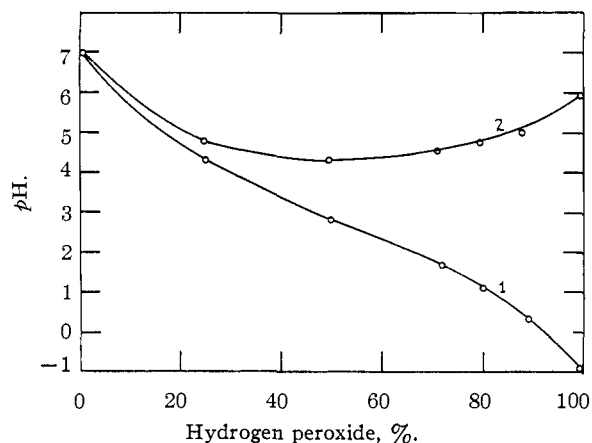


Fig. 2.—Equivalence point pH : 1, apparent pH ; 2, corrected pH .

and upward, CO_2 was without effect, even at a partial pressure of one atmosphere.

The ion product for the various peroxide solutions can be calculated from these data. One method is simply to double the pH at the equivalence point in order to obtain values for pK . An alternate method is to extend the curves of $\log C_{H^+}$ vs. e.m.f. into the region of alkaline additions. One then estimates C_{H^+} from this curve and the corresponding e.m.f. readings while assuming C_{OH^-} equal to the concentration of sodium hydroxide added. The ion product K_w is the product of C_{H^+} and C_{OH^-} . Table II below contains pK values obtained in these two ways.

TABLE II
 pK VALUES FOR HYDROGEN PEROXIDE SOLUTIONS

% H_2O_2	$2 \times$ equivalence point pH	pK	$C_{H^+} \times C_{OH^-}$
0	14.0	14.0	14.0
24.8	9.7	9.5	9.5
49.6	8.7	9.0	9.0
71.3	9.0	8.8	8.8
79.2	9.5	9.0	9.0
88.8	10.0	9.5	9.5
99.8	11.0	10.8	10.8

The agreement is good considering the assumptions involved, and considering the different methods of calculation. The first method depends upon the end-point data from the titration curves, while the second weights the data considerably removed from the end-points.

The data obtained in this experiment can be used to test Dole's theory of glass electrode behavior.⁵ This theory predicts that at constant hydrogen ion activity, the potential of the glass electrode will vary with the activity of the water in the solution under test, as shown by eq. 1

$$E = RT/F \log a_{H_2O} \quad (1)$$

Hydrogen peroxide is an especially interesting diluent for the water, since it affects the dielectric constant of the solvent only a little and leaves the

(5) M. Dole, *THIS JOURNAL*, **54**, 3095 (1932).

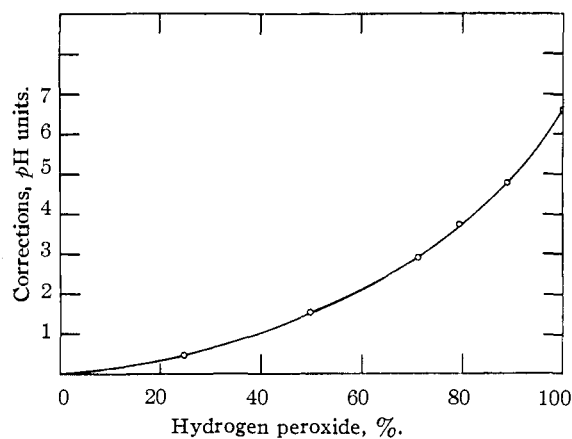


Fig. 3.—Corrections to be added to the glass electrode apparent pH .

ionic strength the same. Table III shows a comparison between the predictions of the above equation and the observed voltage changes.

TABLE III
GLASS ELECTRODE DEVIATIONS IN HYDROGEN PEROXIDE SOLUTIONS

% H_2O_2	H_2O activity	E , v. predicted by eq. 1	E , v. obsd.
0	55.5	-0.000	0.000
24.8	43.8	-.006	.028
49.6	28.1	-.018	.087
71.3	14.5	-.034	.176
79.2	8.3	-.047	.223
88.8	3.4	-.069	.280
99.839

It is obvious that the behavior of the glass electrode in this case does not conform even in sign to the prediction of eq. 1. These data do not exclude the possibility that water is transferred through the glass membrane along with the proton, but some other process must also occur to account for the observed potential changes.

The glass electrode process involves transfer of the proton from one solution to another, so that appreciable energy differences are not surprising if the solutions are different in character. In the present case, the maximum voltage difference at the same hydrogen ion concentration proved to be about 0.39 v. This corresponds to a free energy change of about 9 kcal./mole. It is quite possible that this represents the difference in free energy of solvation of the proton in water and in nearly anhydrous H_2O_2 . The free energy of hydration of the proton has been estimated at 249.6 kcal./mole,⁶ so that a difference of 9 kcal./mole could easily arise between the two solvents. The difference is in the direction indicating the proton to be more firmly bound to the water. Acids are known to have low heats of dilution in strong hydrogen peroxide, a fact which probably reflects this same lower energy of solvation of the proton.

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(6) T. J. Webb, *ibid.*, **48**, 2589 (1926).