$H_4P_2O_7$) and suggests absence of appreciable amounts of a monobasic acid (HPO_3).

The relative stability at room temperature of this peracid in acetonitrile is remarkable in comparison with that of solutions of permonosulfuric acid in acetonitrile (*cf.* preceding paper). Since the peroxygen of H_3PO_5 is more active than that of H_2SO_5 it appears likely that the difference in stability is due to catalytic effects of the accompanying acids, inasmuch as H_3PO_4 is a weak acid compared with H_2SO_4. Just as permonosulfuric acid (*cf.* preceding paper), so also permonophosphoric acid can be kept in isoamyl alcoholic solution, the stability being of a similar order. Dilutions of the first two acetonitrile solutions described here with 10 volumes of isoamyl alcohol showed, in terms of the yields reported above, after three days at −11°, the presence of 51 and 50.5% (instead of initially 56 and 57%) of peracid and of 71.5% of peroxygen (instead of 76.5%) in both cases.

When instead of acetonitrile, ether or isoamyl alcohol was used as the medium for the interaction between hydrogen peroxide and phosphoric anhydride, the results were as follows. An ether solution, about 2.8 *M* in hydrogen peroxide and 0.85 *M* in water, left in contact, for twenty-four hours at room temperature, with an amount of phosphoric anhydride corresponding to the hypothetical reaction

$$P_2O_5 + H_2O_2 \longrightarrow HPO_3 + HPO_4 \qquad \text{(II)}$$

showed little action upon the solid phase. Analysis of the whole reaction mixture showed 2.5% of the hydrogen peroxide as such, 17% as peracid and a total peroxygen recovery of 26%. When the components were used in ratios corresponding to reaction (I) (2.5 *M* H_2O_2, 1.2 *M* H_2O) the phosphoric anhydride went into solution within two hours, forming an oily layer. Analysis showed a total recovery of 9.4% as peracid and 68% as hydrogen peroxide. After twenty hours the corresponding figures were 14 and 44% showing that formation of additional peracid proceeds much slower than loss of hydrogen peroxide. In similar experiments using isoamyl alcohol as the medium less than 2% of the hydrogen peroxide was converted into peracid.

Summary

A convenient method for the preparation of solutions of permonophosphoric acid, based on the heterogeneous interaction between phosphoric anhydride and hydrogen peroxide in acetonitrile, has been described and it has been shown that such solutions, even at room temperature, are relatively stable. When instead of acetonitrile, ether or isoamyl alcohol is used as the medium, the reaction between hydrogen peroxide and phosphoric anhydride is of negligible extent.

PHILADELPHIA, PENNA. RECEIVED NOVEMBER 12, 1936

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

A Comparison of Hydrogen, Quinhydrone and Glass Electrodes in Magnesium Sulfate Solutions

BY E. S. AMIS AND J. L. GABBARD

The error of the glass electrode compared with that of the hydrogen electrode in solutions of various ions has received much attention,[1-8] and the rapid increase in its use in various *p*H studies and industrial processes justifies further investigation. Therefore, the authors have made a direct comparison of the hydrogen, quinhydrone and glass electrodes in buffered and unbuffered, except for small quantities of hydrochloric acid, magnesium sulfate solutions.

Apparatus and Materials

The glass electrodes having a resistance of the order of 10^7 ohms were blown of Corning 015 glass in the form of a thin bulb[1,9] on the end of a tube of ordinary soft glass and aged for at least twenty-four hours before using. The silver–silver chloride electrode of the reduced oxide type[10] was placed in the 0.1 *N* hydrochloric acid inside the glass electrode and served as the reference electrode. The hydrogen electrodes were made in the usual manner and the quinhydrone electrodes were made and cleaned as recommended by Morgan, Lammert and Campbell.[11] The hydrogen electrodes were also cleaned in this manner before being platinized. This cleaning process was repeated and the hydrogen electrodes were newly platinized before each series of measurements. The platinum black was removed from the hydrogen electrodes by the use of hot aqua regia. Two hydrogen and two quinhydrone electrodes were used in making the measurements. If the difference in potential between the two respective electrodes was not less than 0.2 mv., a new pair of electrodes was selected. The calomel electrode was prepared from the Leeds and Northrup chemicals especially purified for the purpose. Commercial tank hydrogen was purified as described by Dole.[4] Since

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(1) W. S. Hughes, *J. Chem. Soc.*, 491 (1928).

(2) F. Quittner, *Ann. Physik*, [4] **35**, 745 (1928).

(3) D. A. MacInnes and D. Belcher, THIS JOURNAL, **53**, 3315 (1931).

(4) M. Dole, *ibid.*, **53**, 4260 (1931).

(5) M. Dole, *ibid.*, **54**, 3095 (1932).

(6) M. Dole, *J. Phys. Chem.*, **36**, 1570 (1932).

(7) M. R. Thompson, *Bur. Standards J. Research*, **9**, 833 (1932).

(8) G. Buchbock, *Z. physik. Chem.*, **A156**, 232 (1931).

(9) G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).

(10) G. Jones and M. Hartmann, THIS JOURNAL, **37**, 752 (1915).

(11) J. L. R. Morgan, O. M. Lammert and M. A. Campbell, *ibid.*, **53**, 454 (1931).

only comparative results were being sought, the solutions were made of commercial c. p. salts without further purification by accurately weighing the salts on an analytical balance, dissolving and diluting in a calibrated flask. The weaker solutions were made by diluting the stronger ones. The buffered solutions were made according to the directions given by Clark,[12] and standardized with the hydrogen electrodes. The quinhydrone was prepared by the Eastman Kodak Company.

The electrode vessel for the buffered solutions was similar to that used by Hovorka and Dearing,[13] consisting of four cylindrical separatory funnels of 80-ml. capacity sealed together and holding, respectively, the hydrogen, the glass and the quinhydrone electrodes and the connecting arm of the calomel electrode. The vessel for the unbuffered solutions was a 250-ml. Pyrex beaker containing the glass and the quinhydrone electrodes and the connecting arm of the calomel electrode.

The circuit used in the construction of the vacuum tube potentiometer was that described by DuBridge and Brown[14] modified to measure small potentials and to meet other requirements. The sensitivity of the potentiometer was 0.05 mv. and since there was no perceptible drift during the time required to make a measurement and neither body capacity nor external electrostatic fields had any effect upon its operation, the measurements could be repeated easily with a precision of 0.2 mv.

Experimental Procedure

The experiments consist of a direct comparison of the glass, hydrogen and quinhydrone electrodes in buffered magnesium sulfate solutions of various concentrations and slightly differing *p*H values, and also a comparison of glass and quinhydrone electrodes in unbuffered, except for very small quantities of dilute hydrochloric acid, magnesium sulfate solutions of various concentrations but of constant *p*H values. However, in the latter, different series at different *p*H values were studied, providing a means of observing the effect upon the electrode potentials caused by changing both the concentration and the *p*H values of the solutions.

With the glass, hydrogen, calomel and quinhydrone electrodes immersed in the same solutions connected by stopcocks as in the case of the buffered solutions, the following cells could be formulated

(A) Hydrogen–Quinhydrone Pt, H_2/soln., H^+ (a), Quinhydrone/Au

(B) Hydrogen–Glass Pt, H_2/soln./glass/0.1 *N* HCl/AgCl/Ag

(C) Glass–Quinhydrone Ag/AgCl/0.1 *N* HCl/glass/soln., H^+ (a), Quinhydrone/Au

(D) Hydrogen–Calomel Pt, H_2/soln.//sat. KCl/HgCl/Hg

(E) Calomel–Quinhydrone Hg/HgCl/sat. KCl//soln., H^+ (a), Quinhydrone/Au

(F) Glass–Calomel Ag/AgCl/0.1 *N* HCl/glass/soln.//sat. KCl/HgCl/Hg

The values for all these cells were obtained where possible for each solution and the values of D, E and F used to check the direct readings of A, B and C. The procedure followed in the actual measurement of the cells in the buffered solutions was similar to that used by Hovorka and Dearing,[13] with the exception that in this work the vacuum tube potentiometer was used for measuring all potentials. The quinhydrone electrodes were very unstable in the solutions of *p*H 7 or above.

In the solutions where a constant *p*H based on the readings of the quinhydrone electrodes was maintained, the quinhydrone electrodes were allowed to come to equilibrium in the unbuffered solutions and the e. m. f. of cell E noted. Then dilute (0.0101 *N*) hydrochloric acid was added dropwise, with stirring after each addition, until the e. m. f. corresponding to the desired *p*H was obtained, the glass electrodes were placed in the solution and the readings made. The hydrogen electrodes were unstable in these solutions, particularly those of higher *p*H values.

Results and Discussion

It is noted by observing cells A, B and C that as long as the quinhydrone and glass electrodes act as perfect hydrogen electrodes the values of the respective cells will remain constant and independent of the *p*H of the solutions. The potential of cell A is

$$(1)\quad E = E_h + E_q = -RT/F \ln a\mathrm{H}^+ + E_0 - RT/2F \ln ah/aq + RT/F \ln a\mathrm{H}^+$$

$$(2)\quad = E_0 - RT/2F \ln ah/aq$$

where ah, aq and $a\mathrm{H}^+$ are the activities of the hydroquinone, quinone and hydrogen ions, respectively. E_0 is the normal potential of the quinhydrone electrode (0.69938 v. at 25°).[18] Since the presence of dissolved substances may cause the value of the second term of equation (2) to vary due to the alteration of the activity ratio of the hydroquinone to the quinone, it is expected that the constant value of cell A should be slightly different from 0.69938 v., the actual value depending upon the kind of salts present and their con-

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[12] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1927, p. 106.

[13] F. Hovorka and W. C. Dearing, This Journal, **57**, 446 (1935).

[14] L. A. DuBridge and H. Brown, *Rev. Sci. Instruments*, **4**, 532 (1933).

TABLE I

DATA SHOWING THE QUINHYDRONE ELECTRODE ERROR (QE), THE GLASS ELECTRODE ERROR (GE) AND THE GLASS–QUINHYDRONE ERROR (GQ) IN MILLIVOLTS IN BUFFERED[a] MAGNESIUM SULFATE SOLUTIONS

			Temperature, 29°					Temperature, 25°	
			Cell B constants		Cell C constants			Cell B constants	
M	pH	Cell A constant 0.6979 v. QE	Glass No. 1 0.3651 v. GE	Glass No. 2 0.3574 v. GE	Glass No. 1 0.3328 v. GQ	Glass No. 2 0.3405 v. GQ	pH	Glass No. 6[b] 0.3540 v. GE	Glass No. 9[b] 0.3543 v. GE
0.1	4.15	−0.2	0.0	−0.4	−0.2	0.2	7.71	0.1	0.2
.2	3.98	.3	− .1	.0	.4	.0			
.5	3.77	− .3	− .2	− .2	.0	− .2	7.42	− .3	− .1
1.0	3.44	− .1	.0	− .1	.1	.2	7.23	.1	− .1
2.0	3.01	1.0	−1.4	− .7	2.6	1.7	6.96	−1.1	−1.3

[a] The buffered solutions used in preparing the solutions of lower pH contained 0.05 M potassium acid phthalate and 0.004 M NaOH while the buffer used for the higher pH solutions contained 0.05 M H_3BO_3, 0.05 M KCl and 0.004 M NaOH. [b] The Dole–MacInnes type of glass electrode. M Molar concentration.

TABLE II

DATA SHOWING GLASS–QUINHYDRONE ERRORS (GQ) IN MAGNESIUM SULFATE SOLUTIONS OF DIFFERING pH VALUES

	pH 5.88 and 27°			pH 5.21 and 27°			pH 4.30 and 26°	
	Constants			Constants			Constants	
M	Glass No. 5 0.3444 v. GQ	Glass No. 4 0.3461 v. GQ	M	Glass No. 3 0.3326 v. GQ	Glass No. 7 0.3355 v. GQ	M	Glass No. 5 0.3444 v. GQ	Glass No. 6 0.3395 v. GQ
1.87	8.9	9.3	2.09	9.8	9.9	2.05	4.7	5.1
1.25	5.4	5.8	1.53	6.5	6.6	1.53	3.4	3.8
0.63	1.4	1.6	1.04	3.7	3.9	1.02	2.4	2.2
.5	0.5	0.8	0.52	1.2	1.3	0.51	1.0	1.0
.25	.5	.7	.26	0.3	0.4	.25	0.1	0.1
			.21	.5	.6	.20	− .1	− .1
.13	.3	.3	.10	.2	.2	.10	.2	.2

centrations. However, as long as the value remains constant with change of magnesium sulfate concentration, it is evident that the ah/aq ratio is remaining constant and the quinhydrone electrode is functioning as a perfect hydrogen electrode.

The value of cell B has been discussed by Dole[4] (p. 4064). The value of cell C should be the value of cell A minus the value of cell B (0.6994 − 0.3524 = 0.3470 v. at 25°). Therefore, the constant value of this cell varies with each particular series of experiments. The constant values for cells A, B and C were obtained for each series of experiments by taking the values of the cells in the solutions of increasing concentration, plotting these values against the concentration, and extrapolating for the value of the cell at zero concentration. Any deviation of the cells from their constant values in each series of experiments is termed, respectively, the "quinhydrone electrode error," the "glass electrode error" and the "glass-quinhydrone error" and shown in Tables I and II. From Table I it is observed that neither the glass nor the quinhydrone electrodes show an appreciable error in 1 M concentration or less of buffered magnesium sulfate solutions below pH 4.15, but in the 2 M concentrations it is seen that each electrode has an appreciable error. The "glass–quinhydrone error" is, as would be expected, in close agreement with the numerical sum of the errors, disregarding sign, of the two electrodes.

The error of the glass electrode is negative, which means that the error is not a function of the positive magnesium ions. If the positive magnesium ions were entering or being adsorbed by the glass membrane of the glass electrode, it is easily seen by observing cell B that the error would be positive, in agreement with the observations of other investigators upon other positive ions.[3,4,6] If the equation (3) $\Delta E = S\, RT/F \ln a\mathrm{H_2O} = RT/F \ln \dfrac{p\ \mathrm{H_2O\ in\ MgSO_4}}{p\ \mathrm{H_2O}}$ derived by Dole[5] for the glass electrode functioning as a water electrode is used, letting $S = 1$, and using the vapor pressure of water and of water in magnesium sulfate solution at 50° as given in the "International Critical Tables," −1.2 mv. is obtained for the error in 2 M solution and −0.5 mv. in 1 M solution. The temperature interval of 21° (50 to 29°) would cause little change in the calculated error since Carpenter and Jette[15] have shown that the

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(15) C. D. Carpenter and E. R. Jette, THIS JOURNAL, **45**, 578 (1923).

p H_2O in $MgSO_4/p$ H_2O ratio for a saturated solution of magnesium sulfate is practically constant with change of temperature. In a trial calculation ΔE changed less than 0.2 mv. in going from 50 to 70° where the greatest change in the ratio as influenced by temperature is observed. Assuming that the concentration of the buffers in the solutions would have very little effect upon the total water vapor pressure, -1.2 mv. is in excellent agreement with the observed values except the value for the glass electrode No. 2. Therefore, it is felt that the observed error of the glass electrodes is due to the water error of the glass electrode.

The "quinhydrone error" is due to the "salt error"[13,16–18] of the quinhydrone electrode. From equation (2) it is seen that $E_s = -RT/2F \ln ah/aq$ where E_s is the "salt error" or the deviation of potential produced by the change of the activity coefficient ratio of the hydroquinone to quinone. Kiss and Urmanczy[18] showed that this error in salt concentrations above 1 N could be expressed by the linear relation (4) $E_s = C\mu + D$ where μ is the ionic strength of the solution and C and D are constants characteristic of the salt ($C = 0.300$ and $D = 1.3$ for magnesium sulfate). Hovorka and Dearing[13] have more recently shown that the error can be expressed by the more simple linear relation (5) $E_s = AN$ with A being a constant characteristic of the salt (0.00122 for magnesium sulfate) and N the normality of the solution. The data reported by these investigators were obtained by dissolving magnesium sulfate in 0.01 N hydrochloric acid. Table III contains a comparison of the data taken with the magnesium sulfate solutions at pH 4.30 in this investigation with theirs. When corrections are made for the water error of the glass electrodes in the higher concentrations it is seen that the data agree closely.

TABLE III

THE "SALT ERROR" OF THE QUINHYDRONE ELECTRODE IN MAGNESIUM SULFATE SOLUTIONS OF VARIOUS CONCENTRATIONS FROM DIFFERENT INVESTIGATIONS

	Kiss and Urmanczy MgSO₄ in 0.01 N HCl		Hovorka and Dearing MgSO₄ in 0.01 N HCl		This investigation Pure MgSO₄ brought to pH 4.30 by use of dilute HCl			
					Glass No. 5		Glass No. 6	
M	E_m, mv.	E_c, mv.	E_m, mv.	E_c, mv.	E_m, mv.	$E_{corr.}$	E_m, mv.	$E_{corr.}$
0.25	1.0	1.6	0.68	0.61	0.1		0.1	
.5	1.7	1.9	1.32	1.22	1.0		1.0	
1.0	2.4	2.5	2.40	2.44	2.4		2.2	
1.25	2.8	2.8						
1.5	3.1	3.1			3.4	2.6	3.8	3.0
2.0	4.0	3.7			4.7	3.5	5.1	3.9

E_m = measured errors; E_c = calculated errors and $E_{corr.}$ = corrected errors.

The data in Table II show that the "glass-quinhydrone errors" in the unbuffered solutions of higher pH, particularly in the higher concentrations, are much larger than in the solutions of lower pH. They are also much larger than those calculated by equations (4) and (5), even after corrections are made for the water error of the glass electrode. This is to be expected when it is considered that the pH of quinhydrone in pure water is about 5.85[19,20] which means that in the solutions of higher pH considerable ionization of the hydroquinone is taking place. This may affect the electrode potential as shown by La Mer and Parsons[21] by changing the electrode reaction from

$$C_6H_4O_2 + 2H^+ + 2e \rightleftharpoons C_6H_4(OH)_2 \text{ to } C_6H_4O_2 + 2e \rightleftharpoons C_6H_4O_2^{--}$$

or it may affect the actual pH of the solution by taking part in the acid base equilibrium by removing OH^- ions.

Kolthoff and Bosch[20] found close agreement between the quinhydrone and hydrogen electrodes in weakly buffered solutions ranging in pH from 3.6 to 7.2, which would indicate that the buffered solutions not only hold the activity coefficients of the hydrogen ion constant, but also tend to hold the ratio of the activity coefficients of the hydroquinone to the quinone constant thus preventing the "salt error." This would explain the absence of any appreciable "salt error" for the quinhydrone electrodes in the buffered solutions below one molar concentrations.

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(16) S. P. L. Sørensen, M. Sørensen and K. Linderstrøm-Lang. *Ann. Chim.*, **16**, 283 (1921).

(17) A. Urmanczy, *Magyar Chem. Folyoirat*, **39**, 1925 (1933).

(18) A. V. Kiss and A. Urmanczy, *Z. physik. Chem.*, **A169**, 31 (1934).

(19) R. J. Best, *J. Phys. Chem.*, **34**, 1815 (1930).

(20) Kolthoff and Bosch, *Biochem. Z.*, **183**, 435 (1927).

(21) V. K. La Mer and T. R. Parsons, *J. Biol. Chem.*, **57**, 613 (1923).

Summary

1. It has been shown that the presence of magnesium ions to the extent of two moles per liter does not affect the potential of the glass electrode.

2. The water error of the glass electrode in magnesium sulfate solutions has been found to conform well with the equation $\Delta E = S\,RT/F \ln a'H_2O$ as derived by Dole.

3. It has been shown that the glass electrode is suitable for measuring the "salt error" of the quinhydrone electrode in solutions buffered with only traces of hydrochloric acid, and that this error depends upon the pH of the solution.

LEXINGTON, KY. RECEIVED NOVEMBER 25, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Water from the Third Law of Thermodynamics. The Dissociation Pressure and Calorimetric Heat of the Reaction $Mg(OH)_2 = MgO + H_2O$. . The Heat Capacities of $Mg(OH)_2$ and MgO from 20 to 300°K.

BY W. F. GIAUQUE AND R. C. ARCHIBALD

The thermodynamic properties of water are sufficiently important and interesting to invite the fullest possible investigation. The present work was undertaken because it had been shown(1) that the experimental $\int_0^T C_p \, d \ln T$ for water does not give the correct entropy. This quantity is accurately known from the band spectrum data.

It seemed desirable to perform at least one experiment in which the third law of thermodynamics would give the entropy of water accurately and in a straightforward manner. The reaction $Mg(OH)_2 = MgO + H_2O$ was selected for this purpose for several reasons. First, a measurable dissociation occurs at a rather low temperature, although not at as low a temperature as we were led to expect from the erroneous available data. Second, the identity of the water molecule should be very completely lost in magnesium hydroxide and such difficulties as are present in ice, or conceivably in water of crystallization, should not be present. Third, the reaction is one which is well adapted to an accurate calorimetric investigation of the heat of reaction. Fourth, the atoms in the substances concerned are all of low atomic weight, which makes the measured and extrapolated quantities of entropy low, with a corresponding increase in the accuracy of the entropy of water derived from the experimental data.

The entropy of water was obtained from the thermodynamic relation

$$S_T(H_2O) = S_T(Mg(OH)_2) - S_T(MgO) + (\Delta H_T/T) + R \ln P_T \quad (1)$$

where ΔH_T and P_T are the heat and pressure of dissociation, respectively, at temperature T. It safely may be assumed that the fugacity is equal to the pressure at the low pressures and high temperatures of the experiment. We may state at once that complete agreement was found between the entropy value obtained as above and that derived from the molecular spectrum of water.

Since this research was undertaken the heat capacity of ice has been reinvestigated accurately by Giauque and Stout.[2] They have shown that the entropy discrepancy is in very exact agreement with the quantitative predictions of Pauling,[3] who bases his calculation on false equilibrium at low temperatures with respect to the random orientation of hydrogen bonds in ice.

More recently Long and Kemp[4] have made similar measurements on deuterium oxide. They have shown that a similar discrepancy exists in this case and find that it also is in quantitative agreement with the calculated discrepancy of Pauling.[3]

While there is no reason to doubt the reliability of the entropy of water as deduced from the accurately known band spectrum, and although this value is strongly supported by the above investigations, we believe that it is very desirable to have one or more third law checks on this important quantity.

Preparation and Purity of Magnesium Hydroxide and Magnesium Oxide.—Crystalline magnesium hydroxide was prepared by the method of de Shulten.[5] A wide-mouthed platinum bottle of one liter capacity was used. This fitted closely inside a well-insulated vertical tubular

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(1) Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

(2) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

(3) Pauling, *ibid.*, **57**, 2680 (1935).

(4) Long and Kemp, *ibid.*, **58**, 1829 (1936).

(5) De Schulten, *Compt. rend.*, **101**, 72 (1885).