length 2537 Å. In the presence of oxygen, this irradiation has been found to produce reaction such that on subsequent hydrolysis equal numbers of equivalents of chloride, acid and oxidizing agent are found; the reaction is assumed to be $2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2$. Using a monochloroacetic acid actinometer, quantum yields of one carbon tetrachloride oxidized per quantum absorbed have been found.

PASADENA, CALIF. RECEIVED JANUARY 2, 1935

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The "Salt Error" and Normal Electrode Potential of the Quinhydrone Electrode at 25°

BY FRANK HOVORKA AND WILLIAM C. DEARING

The "salt error" of the quinhydrone electrode was recognized but neglected by Biilmann[1] in the initial study of the cell Pt/quinhydrone, $H^+(m)$, H_2(1 atm.)/Pt at 18 and 25°. From solubility measurements Sörensen, Sörensen and Linderström-Lang[2] showed the "salt error" to be due to a change in the activity ratio of hydroquinone and quinone, the dissociation products of quinhydrone. From similar measurements Linderström-Lang[3] calculated the potential corrections for the quinhydrone electrode. He also determined by extrapolation the value of E°_{KB}, the potential of the quinhydrone–hydrogen cell at 18° were water the experimental liquid. Kruyt and Robinson[4] confirmed the results of Linderström-Lang regarding the influence of salts on the solubilities of hydroquinone and quinone. Numerous factors which influence the potential of the quinhydrone–hydrogen cell were carefully studied by Biilmann and Jensen.[5] Tammann and Jenckel[6] and Čupr[7] determined the "salt error" of the quinhydrone electrode in a limited number of solutions, but measurements were made against the calomel electrode rather than against the hydrogen electrode in the same solutions. Harned and Wright[8] determined the normal electrode potential of the quinhydrone electrode at intervals from 0 to 40° by an indirect method which required the combining of data for two types of cells. In a similar manner Urmánczy[9] determined the "salt error" of the quinhydrone electrode against the hydrogen electrode for solutions of various salts, but with less precision due to uncertainties of the liquid junctions involved. For further papers dealing with the quinhydrone electrode and related subjects the reader is referred to a bibliography compiled by Morgan, Lammert and Campbell.[10]

In view of the increasing importance of the quinhydrone electrode in many fields it seemed advisable to study some of the fundamental properties of the electrode in a more systematic manner and with greater precision than heretofore attained. Foremost among the objectives was a study of the quinhydrone–hydrogen cell and a determination of the "salt error" of the quinhydrone electrode in solutions of a large number of electrolytes, each over such a range of concentration as to permit definite conclusions regarding the trend of the "salt error" and the possibility of making adequate corrections. As a corollary of this was the evaluation of E_0, the normal electrode potential of the quinhydrone electrode. Several secondary objectives developed in the course of the investigation. These will be discussed later.

Apparatus and Materials

Electrolytic hydrogen from a tank was washed with concentrated potassium hydroxide solution and water, then passed over platinum at 450°. Upon reaching the thermostat the hydrogen passed through a washing bottle containing the solution being studied and thence to the electrode vessel which was similar in some respects to that used by Linderström-Lang.[3] It consisted of two tubes, C and D, of 40-cc. capacity, and E with a capacity of 20 cc. These were connected through the three-way stopcock, F. A heavy rubber cap, G, was fitted tightly over the bottom of the stopcock. This was sealed with lacquer and furnished adequate insulation from the bath.

Two hydrogen electrodes of B. & S. No. 18 platinum wire and leads were sealed into a 5-mm. tube, leaving 17 mm. of the electrode wires exposed. This was fitted into a larger tube by means of a small rubber stopper. Two

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(1) Biilmann, *Ann. Chim.*, **15**, 109 (1921).

(2) Sörensen, Sörensen and Linderström-Lang, *ibid.*, **16**, 283 (1921).

(3) Linderström-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 4 (1924); **16**, No. 3 (1925).

(4) Kruyt and Robinson, *Verslag. Akad. Wetenschappen Amsterdam*, **35**, 812 (1926).

(5) Biilmann and Jensen, *Bull. soc. chim.*, **41**, 151 (1927).

(6) Tammann and Jenckel, *Z. anorg. allgem. Chem.*, **173**, 337 (1928).

(7) Čupr. *Pub. Faculté Sci. Univ. Masaryk*, No. 133 (1931).

(8) Harned and Wright, THIS JOURNAL, **55**, 4849 (1933).

(9) Urmánczy, *Magyar Chemiai Folyoirat*, **39**, 125 (1933).

(10) Morgan, Lammert and Campbell, *Trans. Am. Electrochem. Soc.*, **61**, 405 (1932).

holes for the escape of hydrogen were placed in this tube 1 cm. from the bottom. The exit tube, H, extended down the side of the thermostat.

Two gold wire electrodes, L. & N. No. 7701, were mounted in a rubber stopper and occupied the tube D of the electrode vessel. One arm of a small stopcock also passed through the stopper to permit the equalization of pressure within and without.

The electrode potentials were measured by means of a L. & N. type K potentiometer, type R galvanometer, and lamp and scale. The standard cell was of the unsaturated cadmium type, made by the Eppley Laboratories and certified by the Bureau of Standards. This was checked at frequent intervals against another certified Eppley cell. The system was shielded and free from appreciable stray currents.

The thermostat was held at 25 ± 0.01°.

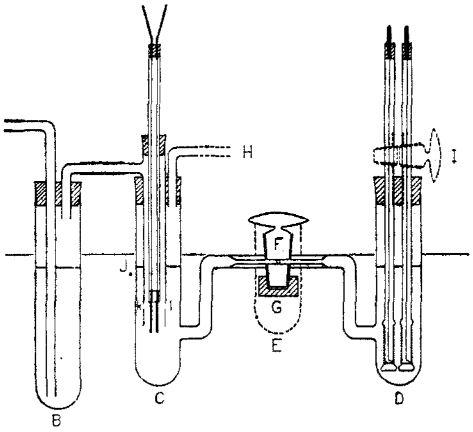

Fig. 1.

Preliminary work with the hydrogen electrode led to the following conclusions. (a) The deposition of gold plate prior to platinizing does not improve the electrode. The removal (by electrolysis in hydrochloric acid) of the platinum black deposit on such a base has no advantage over the method finally adopted. (b) Deposits from pure platinic chloride are less satisfactory than those from solutions containing lead acetate. (c) Electrolysis in sodium hydroxide solution following the platinizing has no advantage over sulfuric acid alone. (d) Reasonably thin deposits of black are more satisfactory than thick when used in solutions where there is little danger of poisoning, and when the electrodes are replatinized frequently. The procedure finally adopted was as follows. The old black was removed with a damp cloth and fine emery powder. This was followed by a similar polishing process employing alkaline scouring powder. Occasionally a final treatment in hot chromic acid or alcoholic potassium hydroxide was necessary to obtain even evolution of hydrogen when testing for cleanliness. The platinum black was deposited from a 2% solution of platinic chloride containing 0.02 g. of lead acetate per 100 cc. The electrodes were then electrolyzed in 7% sulfuric acid for about twenty minutes, rinsed thoroughly under the tap and with distilled water, and kept immersed in the latter when not in use.

Procedures such as flaming, washing in absolute alcohol, etc., were found to be entirely unnecessary with the gold wire quinhydrone electrodes used. They were cleaned occasionally in hot chromic acid, and their behavior was at all times quite regular. When not in use they were kept immersed in distilled water.

There has been considerable diversity of opinion as to the best method for the preparation of quinhydrone. The product of the Eastman Kodak Company has been widely used and recommended by recent workers.[10,11] A supply obtained from that company was compared with another sample from the same company which had been in the laboratory for some time, and they were found to agree to within 0.00002 v. However, a later comparison with two samples prepared by the method of Biilmann and Lund[12] and three samples prepared by the direct union of quinone and hydroquinone showed the Eastman product to give a distinctly negative potential with respect to the others. The above five samples agreed among themselves to within 0.00004 v., those prepared by direct union being more positive. Furthermore, the Eastman product after recrystallization from water gave a potential in excellent agreement with that prepared from quinone and hydroquinone. Equimolecular quantities of the compounds were dissolved in the minimum volumes of boiled distilled water at 65°, filtered and the solutions mixed while warm. After cooling with ice the quinhydrone was filtered on a Buchner funnel, washed four times with cold water and dried between filter papers at room temperature.

Constant boiling hydrochloric acid prepared according to Foulk and Hollingsworth[13] constituted the stock acid solution and from this a 0.5 *N* secondary stock solution was prepared. The latter was used in making up all solutions which were 0.01 *N* with respect to hydrochloric acid, the constant boiling acid being used for those of higher concentrations. Each solution was prepared by weighing out appropriate quantities of acid and salt and diluting in a calibrated flask at 25°. C. P. salts of the highest quality obtainable were employed, part being further purified by recrystallization. (It should be borne in mind that the measurements of the "salt error" which constitute this research are themselves differential in nature, and that any errors due to slight impurities are of second order. To illustrate: assuming that a sample of potassium chloride contains even 0.1% sodium chloride, it can be shown that for a 2 *N* potassium chloride solution, at which concentration the error would be greatest, this error is only 0.000001 volt, less than one-tenth the minimum experimental error.) The solutions were prepared from salts either in the anhydrous state or from concentrated stock solutions which were analyzed by standard quantitative procedures. The sulfuric acid solutions were likewise prepared by weighing appropriate quantities of an analyzed solution and diluting as stated above.

Experimental Procedure

The electrode vessel and electrodes were washed thoroughly with three portions of the solution being studied,

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[11] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

[12] Biilmann and Lund, *Ann. chim.*, **16**, 321 (1921).

[13] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

then solution was added until it stood at J in all three arms. C and D each contained about 20 cc. The unit was lowered in the thermostat until the cross arms were just submerged. Hydrogen was introduced, and the rate so adjusted as to give about eight pulsations in the electrode tube every five seconds. These alternately bathed and exposed to hydrogen the upper centimeter of the electrodes. As soon as hydrogen was introduced the stopcocks F and I were opened for a moment to allow for slight readjustment of the solution level, then F was closed. The potential between the two hydrogen electrodes was then followed. This fluctuated widely for a short period but soon began to drop steadily. Within fifteen minutes the difference was usually <0.00002 v. If the reading did not reach this value within a reasonable period the run was stopped, the electrodes cleaned and replatinized, and a fresh sample of solution taken. For steady readings between the electrodes it was desirable to have sufficient immersion to renew, with each pulsation, the film of solution on the glass at the base of the electrodes.

Having attained equilibrium between the hydrogen electrodes to the extent indicated above, approximately 100 mg. of quinhydrone was introduced into D and stirred with the electrodes for about ten seconds. The potential between these electrodes was then followed as above. Even if read immediately the difference was always <0.00005 v., and after stirring three or four times during the succeeding five minutes the potential invariably dropped at least to 0.00001 v.

It was found that the above equilibria were good criteria of near equilibrium between the hydrogen and quinhydrone electrodes. The two hydrogen electrodes were connected together and used as a single unit, likewise with the quinhydrone electrodes. The stopcock I was closed and the air cushion prevented fluctuations within the connecting tube when F was opened, thus eliminating the possibility of intermixing the solutions in C and D. The electrodes were widely enough separated to prevent complications due to ordinary diffusion of hydrogen and quinhydrone during the course of a run. The constancy of the potentials provided proof of this.

The stopcock F was turned to connect C and D, the potential read and the cock closed. Two or three preliminary readings were taken to assure attainment of equilibrium. The potentiometer circuit was always balanced immediately preceding a reading. Final readings were taken over a period of one-half to one and one-half hours. Any significant change in potential during this time was unusual (except in such cases as concentrated hydrochloric acid). All readings were taken with the stopcock open. Potentials with the cock closed were sometimes found to differ from the others as much as 0.00005 v.[3]

The hydrogen electrodes were replatinized before each series of runs as a precaution against possible accumulation of poison, and rarely did they give trouble. Barometric readings were checked two or three times during a run. Potentials were found to be independent of the rate of hydrogen flow, and the slight fluctuation in hydrogen pressure during pulsations at the electrode produced no detectable variation in potential.

Results and Discussion

The general plan included the study of 0.05, 0.5, 1 and 2 *N* solutions of salts, each solution also being 0.01 *N* with respect to hydrochloric acid. In addition, solutions of the following compositions were examined: 0.1 *N* salt + 1 *N* HCl, 0.5 *N* salt + 0.5 *N* HCl and 1 *N* salt + 0.1 *N* HCl. The significance of the latter will be discussed later. Mannitol was included to determine the "salt error" produced by a typical non-electrolyte. Series for hydrochloric and sulfuric acids completed the investigation.

All readings were reduced to a hydrogen pressure of 760 mm. at 0°. In addition to the usual barometric correction, this involved a consideration of the hydrostatic pressure due to immersion of the electrode, and the vapor pressure of the solution. In some of the more concentrated solutions the difference between the latter and pure water was equivalent to 0.00003 v. Potentials in some of the more concentrated solutions were inclined to drift, and more weight was given to the earlier readings. This drift was especially true of 2 *N* hydrochloric acid solutions, no doubt due to its reaction with quinone to form chlorohydroquinone.

On the basis of constancy and reproducibility of readings the average precision of the "salt error" measurements lies within the limits ±0.00002 v. However, the potential of the quinhydrone–hydrogen cell is dependent upon a number of factors, such as the preparation of the quinhydrone, the potential of the standard cell, the potentiometer, etc., and it is doubtful whether the cell is capable of general reproducibility exceeding ±0.00003 v. This may be considered the general accuracy of these results.

The free energy change of the reaction quinone $+ 2H^+ + 2e \rightleftharpoons$ hydroquinone determines the electrode potential of the quinhydrone electrode. When referred to the normal hydrogen electrode the potential is

$$E = E_0 - \frac{RT}{2F}\ln\frac{a_h}{a_q} + \frac{RT}{F}\ln a_{H^+} = E_0 - \frac{RT}{2F}\ln\frac{\gamma_h}{\gamma_q} + \frac{RT}{F}\ln a_{H^+} \qquad (1)$$

where E_0 is the normal electrode potential of the quinhydrone electrode and a_h, a_q, a_H, and γ_h, γ_q are the activities and activity coefficients of hydroquinone, quinone and hydrogen ion, respectively.[14]

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(14) Clark, "The Determination of Hydrogen Ions," 3d ed., p. 407.

When the hydrogen and quinhydrone electrodes are immersed in the same solution the cell can be formulated Pt/H_2, electrolyte, H^+ (a), quinhydrone/Au. The expression for the corresponding potential is

$$E = E_H + E_q = -\frac{RT}{F}\ln a_{H^+} + E_0 - \frac{RT}{2F}\ln\frac{\gamma_h}{\gamma_q} + \frac{RT}{F}\ln a_{H^+} \quad (2)$$

$$= E_0 - \frac{RT}{2F}\ln\frac{\gamma_h}{\gamma_q} \quad (3)$$

Although the use of quinhydrone assures equal concentrations of quinone and hydroquinone, the activity and activity coefficient ratios are altered by the presence of other dissolved substances. The resulting change in potential is termed the "salt error" of the quinhydrone electrode. It is with the evaluation of E_0 and this "salt error" that this research deals.

The potentials of the quinhydrone–hydrogen cell for solutions of hydrochloric acid are given in Table I, column 3. Since this acid was used to acidify all solutions (0.01 *N*) it is essential to determine the extent to which the "salt error" is due to the acid. In Fig. 2 the above potentials are plotted against normality. At low concentrations the deviation due to the acid is a linear function of concentration, and extrapolation to zero normality gives the value 0.69938 v. The cell

TABLE I

Normality	Runs	E	pH_{se}	γ_h/γ_q	E_{se} and pH_{se} constants
			HCl		
0.01	5	0.69935	−0.0005	1.002	
.04	3	.69926	− .0020	1.009	
.1	10	.69906	− .0054	1.025	$A = -0.00364$
.5	6	.69766	− .0291	1.143	$B = -\ .0616$
1	3	.69583	− .0601	1.319	
2	4	.69200	− .1250	1.776	
			LiCl		
0.05	2	0.69931	−0.0012	1.005	
.5	2	.69844	− .0159	1.076	$A = -0.00209$
1	2	.69742	− .0322	1.165	$B = -\ .0353$
2	4	.69507	− .0729	1.399	
			NaCl		
0.05	3	0.69927	−0.0019	1.009	
.5	2	.69824	− .0193	1.093	$A = -0.00244$
1	4	.69702	− .0399	1.202	$B = -\ .0413$
2	5	.69440	− .0843	1.474	
			KCl		
0.05	4	0.69926	−0.0020	1.009	
.09	15	.69918	− .0034	1.016	
.5	2	.69828	− .0186	1.089	$A = -0.00220$
1	2	.69718	− .0372	1.187	$B = -\ .0372$
2	5	.69495	− .0750	1.412	
			$MgCl_2$		
0.05	2	0.69928	−0.0017	1.008	
.5	3	.69843	− .0161	1.077	$A = -0.00205$
1	2	.69743	− .0330	1.164	$B = -\ .0346$
2	2	.69516	− .0714	1.389	
			$CaCl_2$		
0.05	2	0.69929	−0.0015	1.007	
.5	2	.69840	− .0166	1.079	$A = -0.00217$
1	2	.69736	− .0342	1.170	$B = -\ .0367$
2	2	.69490	− .0758	1.417	
			$SrCl_2$		
0.05	2	0.69930	−0.0014	1.006	
.5	4	.69840	− .0166	1.079	$A = -0.00224$
1	2	.69729	− .0354	1.177	$B = -\ .0379$
2	2	.69476	− .0782	1.433	
			$BaCl_2$		
0.05	2	0.69925	−0.0022	1.010	
.5	3	.69821	− .0198	1.095	$A = -0.00259$
1	3	.69690	− .0420	1.213	$B = -\ .0438$
2	2	.69408	− .0897	1.511	
			H_2SO_4		
0.05	2	0.69931	−0.0012	1.005	
.5	2	.69856	− .0139	1.066	$A = -0.00186$
1	2	.69765	− .0293	1.144	$B = -\ .0314$
2	2	.69552	− .0653	1.352	
			Li_2SO_4		
0.05	2	0.69944	+0.0010	0.995	
.5	3	.70023	.0144	.936	$A = 0.00159$
1	2	.70102	.0277	.880	$B = .0269$
2	2	.70248	.0524	.786	
			Na_2SO_4		
0.05	2	0.69943	0.0008	0.996	
.5	2	.70003	.0110	.951	$A = 0.00134$
1	4	.70072	.0227	.901	$B = .0227$
2	4	.70206	.0454	.812	
			K_2SO_4		
0.05	3	0.69943	0.0008	0.996	
.5	6	.70005	.0113	.949	$A = 0.00141$
1	3	.70079	.0238	.896	$B = .0238$
1.3	3	.70121	.0310	.867	
			$MgSO_4$		
0.05	2	0.69944	0.0010	0.995	
.5	3	.70003	.0110	.951	$A = 0.00122$
1	4	.70067	.0218	.904	$B = .0206$
2	4	.70175	.0401	.831	
			Mannitol		
0.05	4	0.69943	0.0008	0.996	
.125	4	.69953	.0025	.988	
.25	2	.69972	.0058	.974	$A = 0.00140$
.5	2	.70005	.0113	.949	$B = .0237$
1	2	.70080	.0240	.895	

1 *N* KCl + 0.1 *N* HCl

Ideal potential	0.69938 v.
1 *N* KCl deviation	− .00220 v.
0.1 *N* HCl deviation	− .00032 v.
Calculated	0.69686 v.
Observed	.69688 v.

potential when the solution is 0.01 *N* hydrochloric acid is 0.69935 v., hence the "salt error" for 0.01 *N* hydrochloric acid is −0.00003 v. If it is assumed that "salt errors" are additive, the various salt series can be corrected for the presence of 0.01 *N* hydrochloric acid by adding 0.00003 v. to the observed readings. That this additivity is true for mixtures of hydrochloric acid and chlorides was definitely proved, as will be shown later. In Table I, column 3, are given the potentials corresponding to the various chloride solutions, corrected for the 0.01 *N* hydrochloric acid. For mixtures of hydrochloric acid and sulfates a point of considerable interest arose. The basis for the corrected sulfate values in Table I will be discussed later.

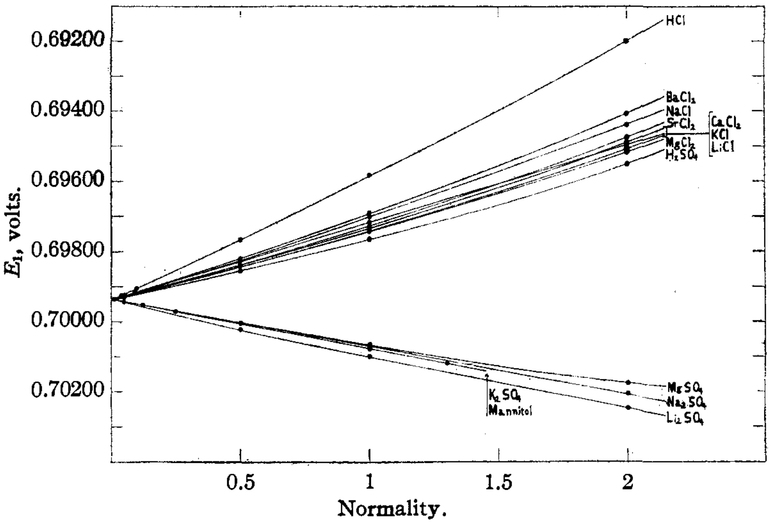

Fig. 2.

In Fig. 2 the potentials for all series are plotted as functions of concentration. It is at once apparent that there are two distinct groups of solutes, causing negative and positive deviations.[9] Moreover, within the limits of this investigation, these are composed of chlorides and sulfates, respectively, except that sulfuric acid is found with the chlorides. In no case is there marked departure from a linear relationship, which suggested the possibility of additivity of deviations. To test this the solutions given in Table IIA were examined. The observed values for the mixtures are given in column 2 and the values calculated on the basis of additivity in column 3. The tables show a typical calculation.

The agreement between calculated and observed values leaves no question as to the validity of the additive property with reference to hydrochloric acid and chlorides.

If the sulfate series are corrected for 0.01 *N* hydrochloric acid on the basis of such additivity (0.00003 v.), the extrapolated potential corresponding to zero concentration lies slightly below 0.69938 v., the value found from the hydrochloric acid, sulfuric acid and chloride curves. Moreover, examination of the mixtures of hydrochloric acid and sulfates given in Table IIB shows a wide discrepancy between "Calculated *A*" and observed values, those under "Calculated *A*" being derived in the manner that was so satisfactory for chlorides. This would indicate a complete breakdown of the additive principle. But mixtures of this type differ in one important respect. If complete ionization and a uniform distribution of ions prevailed, an explanation of the error in the calculations would seem impossible. But, with respect to molecules or their equivalent in terms of aggregates of ions, there is the possibility of forming new species. For example, assume the preparation of a solution 0.5 *N* with respect to both hydrochloric acid and sodium sulfate. The equilibrium could be represented

$$2HCl + Na_2SO_4 \rightleftharpoons HCl + NaCl + NaHSO_4 \rightleftharpoons 2NaCl + H_2SO_4$$

The potential calculated on the basis of 0.5 *N* HCl + 0.5 *N* Na_2SO_4 is in error 0.00087 v. A glance at the curves, Fig. 2, will show that on the basis of 0.5 *N* NaCl + 0.5 *N* H_2SO_4 both deviations are negative, and will lead to a radically different calculated value. This is found to be 0.69742 v., and the observed value is 0.69744 v. The agreement is as good as was found for mixtures of hydrochloric acid and chlorides. Values so calculated for the sulfates are given in Table IIB under "Calculated *B*." For such as 0.1 *N* Li_2SO_4 + 1 *N* HCl the reaction is assumed to be

$$0.1\ N\ Li_2SO_4 + 1\ N\ HCl \rightleftharpoons 0.1\ N\ LiCl + 0.1\ N\ H_2SO_4 + 0.9\ N\ HCl$$

For all mixtures of 0.1 *N* sulfate + 1 *N* HCl the values so obtained are in good agreement with the observed. Likewise with all mixtures of 0.5 *N* sulfate + 0.5 *N* HCl. The agreement in the series 1 *N* sulfate + 0.1 *N* HCl is not as good.

TABLE IIA

Mixture	E, obsd.	E, calcd. A
0.1 N LiCl + 1 N HCl	0.69562	0.69565
0.5 N LiCl + 0.5 N HCl	.69665	.69672
1 N LiCl + 0.1 N HCl	.69709	.69710
0.1 N NaCl + 1 N HCl	.69562	.69560
0.5 N NaCl + 0.5 N HCl	.69650	.69652
1 N NaCl + 0.1 N HCl	.69675	.69670
0.1 N KCl + 1 N HCl	.69561	.69560
0.5 N KCl + 0.5 N HCl	.69653	.69656
1 N KCl + 0.1 N HCl	.69688	.69686
0.1 N $MgCl_2$ + 1 N HCl	.69560	.69564
0.5 N $MgCl_2$ + 0.5 N HCl	.69666	.69671
1 N $MgCl_2$ + 0.1 N HCl	.69707	.69711
0.1 N $CaCl_2$ + 1 N HCl	.69563	.69563
0.5 N $CaCl_2$ + 0.5 N HCl	.69663	.69668
1 N $CaCl_2$ + 0.1 N HCl	.69705	.69704
0.1 N $SrCl_2$ + 1 N HCl	.69562	.69563
0.5 N $SrCl_2$ + 0.5 N HCl	.69666	.69668
1 N $SrCl_2$ + 0.1 N HCl	.69695	.69697
0.1 N $BaCl_2$ + 1 N HCl	.69559	.69559
0.5 N $BaCl_2$ + 0.5 N HCl	.69645	.69649
1 N $BaCl_2$ + 0.1 N HCl	.69660	.69658

TABLE IIB

Mixture	E, obsd.	E, calcd. A	E, calcd. B
0.1 N Li_2SO_4 + 1 N HCl	0.69581	0.69599	0.69587
0.5 N Li_2SO_4 + 0.5 N HCl	.69760	.69851	.69762
1 N Li_2SO_4 + 0.1 N HCl	.70030	.70070	.70051
0.1 N Na_2SO_4 + 1 N HCl	.69578	.69595	.69582
0.5 N Na_2SO_4 + 0.5 N HCl	.69744	.69831	.69742
1 N Na_2SO_4 + 0.1 N HCl	.70000	.70040	.70019
0.1 N K_2SO_4 + 1 N HCl	.69580	.69595	.69582
0.5 N K_2SO_4 + 0.5 N HCl	.69745	.69833	.69746
1 N K_2SO_4 + 0.1 N HCl	.70013	.70047	.70026
0.1 N $MgSO_4$ + 1 N HCl	.69581	.69595	.69586
0.5 N $MgSO_4$ + 0.5 N HCl	.69768	.69831	.69761
1 N $MgSO_4$ + 0.1 N HCl	.70008	.70035	.70019

Although considerably better than those calculated on the original basis, A, the values are still somewhat higher than the observed. This is of interest with respect to the correction of the sulfate series for the presence of 0.01 N HCl. The corrected values, E, given in Table I, column 3, are obtained by applying the above relationship. This yields a corrective term of 0.00005 v. for sulfate solutions in contrast to 0.00003 v. for chlorides. But the extrapolated zero for sulfates is still slightly lower (about 0.00003 v.) than that for chlorides, hydrochloric acid and sulfuric acid. In these sulfate series there is a predominance of sulfate over hydrochloric acid, and it is in the similar case of 1 N sulfate + 0.1 N HCl mixtures that the calculated potentials differ from the observed.

From equation (3) it is seen that

$$E_{se} = -\frac{RT}{2F}\ln\frac{\gamma_h}{\gamma_q} \qquad (4)$$

where E_{se} is the "salt error" or potential deviation. Values for E_{se} are obtained from the experimental data by the relationship $E_{se} = E - 0.69938$. The existence of positive and negative "salt errors" was indicated by the solubility measurements of Linderström-Lang[8] and upheld by experiment. Any deviation of γ_h/γ_q from unity must result in "salt error," as seen in equation (4). In Table I, column 5, are given the values of this ratio. They are also the values of the activity ratio, a_h/a_q, since the concentrations of quinone and hydroquinone from quinhydrone are equal. The near approach of the "salt error," hence $\ln \gamma_h/\gamma_q$, to linear is in keeping with the equation $\ln \gamma = kc$, where k is a constant characteristic of the salt and c is the concentration of the salt. Numerous investigations have shown it to hold approximately for the influence of salts on the activity coefficients of neutral substances.

For approximate pH work the neglect of the "salt error" of the quinhydrone electrode is justified. Furthermore, such measurements always involve a liquid junction with an uncertainty of at least 0.0001 v. This corresponds to about 0.002 pH and masks any small "salt error," even in the most accurate work. But in higher concentrations the "error" must be considered. As shown in Fig. 2, in no case up to 2 N concentration is the deviation from linear greater than 0.00015 v., and in most cases is less than 0.0001 v., the limit of accuracy for pH work. Therefore the "salt error" can be expressed by the simple linear equation

$$E_{se} = Ac \qquad (5)$$

where A is a constant characteristic of the salt and c is the normality of the solution. In terms of pH the "error" becomes

$$p\mathrm{H}_{se} = \frac{E_{se}}{0.05912} = \frac{Ac}{0.05912} = Bc \qquad (6)$$

where B is likewise a constant characteristic of the solute. The constants A and B are given in Table I, column 6, and the values for $p\mathrm{H}_{se}$ in column 4.

By an indirect method Urmánczy[9] determined the "salt error" for several salts from 0.5 N to higher concentrations. For all concentrations above 1 N, except for calcium chloride and nitrates, he found an approximately linear relationship following the equation $E_{se} = Cc + D$, where C and D are constants characteristic of the salt, and c the normality. Values calculated from the equation differ from the observed not more than 0.0003 v. His failure to find the more simple relationship, $E_{se} = Ac$, is due in the main to an incorrect value for the extrapolated zero. Urmánczy employed 0.6990 v. which he obtained with a 0.05 N hydrochloric acid solution. But this solution itself has a "salt error" of 0.00016 v. for which no allowance was made. The remaining difference between 0.6990 v. and 0.69938 v. may well be due to errors inherent in the method, such as liquid junction potentials. The use of 0.6990 v. not only contributes toward the D term in the equation but causes both the chloride and sulfate curves to show their greatest departure from linear over the extrapolated range from 0.5 N to zero concentration, whereas this is the region in which the curvature should be least. The use of 0.69938 v. eliminates this error.

For the chlorides the order of negative "salt error" is $Li < K < Na < H$ and $Mg < Ca < Sr < Ba$. Linderström-Lang[3] found quinone and hydroquinone to be salted out by the alkali chlorides in the order $K < Na < Li$. The lack of agreement between these Hofmeister series is understood when it is remembered that the "salt error" of the quinhydrone electrode is not determined by a change in the activity of either quinone or hydroquinone individually, but by a change in the ratio a_h/a_q. By using the data of the above author for solubilities in 2 N alkali chloride solutions at 18°, it was found that the calculated "salt errors" showed the same inverted order as found in this investigation from electromotive force measurements. Many attempts have been made to find a relationship between ionic size and salting-out effect, but as yet there is no general agreement among workers. The part which hydration plays in the salting-out process is little understood, although it is probably of less importance than formerly thought. The phenomenon cannot be approached purely from an ionic point of view, for non-electrolytes (mannitol) produce "salt errors" of the same type and order as electrolytes.

Frequent reference has been made to the extrapolated zero or ideal potential of the cell Pt/H_2, electrolyte, $H^+(a)$, quinhydrone/Au, which was found to be 0.69938 v. Equation (3) indicates that the potential of the above cell is independent of the hydrogen-ion activity, and depends only upon the ratio a_h/a_q. E will equal E_0 when this ratio is 1, a condition existing, in general, only when the concentration of the solution is zero. (The effect of the slightly soluble quinhydrone and its components upon their own activities is negligible.) Hence the extrapolated zero potential is equal to E_0, the normal electrode potential. The equation

$$E = E_0 - \frac{RT}{2F} \ln \frac{a_h}{a_q} + \frac{RT}{F} \ln a_{H^+}$$

is the accepted one for the quinhydrone electrode. There is, however, in a practical sense, no normal quinhydrone electrode. E_0 is the normal electrode potential of the system quinone–hydroquinone. In this system the ratio a_h/a_q can be adjusted arbitrarily to equal unity in any solution in which the hydrogen-ion activity is 1. In a solution of quinhydrone any such arbitrary adjustment is impossible.

Harned and Wright[8] determined the value of E_0 at intervals from 0 to 40°. However, their results are based on the combined data for two types of cells. The value so determined for E_0 at 25° was 0.69968 v., which differs from that obtained in the present investigation by 0.00030 v. No correction was made for the "salt error" due to the 0.01 N hydrochloric acid with which the runs were made. This would increase the difference by 0.00003 v. The value 0.69938 v. has been obtained by the extrapolation of curves for fourteen series of solutions, with a probable error of ±0.00003 v. The accuracy claimed by Harned and Wright is ±0.0001 v. When this is considered the difference between the two values is reduced to about 0.0002 v. Those authors state that "the normal electrode potential of the quinhydrone electrode can undoubtedly be found most accurately by the direct measurement of cell III," that being the quinhydrone–hydrogen cell on which the potential 0.69938 v. is based.[15]

Since this research was confined to 25°, it yields no data on the temperature coefficient of the quinhydrone electrode, but one point is deserving of brief discussion. Values in the literature range from −0.00074 volt/degree[16] to −0.00077 volt/degree.[17] Equation (3) indicates that the temperature coefficient of the quinhydrone–hydrogen cell, dE/dT, will equal dE_0/dT

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(15) In a recent private communication Wright points out a probable source of error in their procedure. A preliminary redetermination indicates a value for E_0 about 0.00018 v. lower than that published. If this is confirmed the agreement with 0.69938 v. will be much better.

(16) Biilmann and Krarup, *J. Chem. Soc.*, **125**, 1954 (1924).

(17) Schreiner, *Z. physik. Chem.*, **117**, 57 (1925).

only when the value of γ_h/γ_q is independent of temperature. The latter condition will prevail only when γ_h/γ_q equals unity, that is, when there is no solute present which produces a "salt error." The potential will then correspond to E_0. Therefore, although E_0 has a definite temperature coefficient, all other values of dE/dT will depend upon the nature and concentration of the cell solution.

In a Communication to the Editor[18] a report was made on some work dealing with the standard quinhydrone electrode. This was preliminary to the present investigation, and was carried out with the Eastman quinhydrone which, as already pointed out, was later found to be unsatisfactory. Two new series of runs, a total of twenty-four, were made with standard acid mixture, 0.01 N HCl + 0.09 N KCl, prepared (a) by mixing one part of 0.1 N HCl and 9 parts of 0.1 N KCl, and (b) by weighing out appropriate quantities of KCl and HCl solution and diluting at 25°. The method under (a) corresponds to general practice whereas (b) is in keeping with the present research. Although the mean potential for series (a) was again slightly higher than for (b), it is doubtful whether the difference is significant. The potentials of both series can be expressed by 0.69915 ± 0.00003 v., which supersedes the values previously published.[18] Due to its ease of preparation, reproducibility, constancy during a working day and freedom from temperature lag, this standard quinhydrone electrode has many advantages over the widely used calomel electrodes.

The quinhydrone–hydrogen cell has been the center of discussion up to this point. Tammann and Jenckel,[6] Čupr[7] and Urmánczy[9] have made measurements of the influence of neutral salts on the potential of the quinhydrone electrode when referred to the calomel electrode. Such measurements are of limited accuracy due to the necessity of using a salt bridge. Similar measurements were made during the present investigation, employing the standard quinhydrone electrode instead of the calomel electrode. The bridge connection was made through the arm E, Fig. 1. The results were in general agreement with the findings of the above workers. In such a cell the effect of the alkali chlorides is in the increasing order K < Na < Li. This is not, however, inconsistent with the order found for the quinhydrone–hydrogen cell. In the latter the change in hydrogen-ion activity due to the solute is balanced at the two electrodes, whereas, when a fixed half-cell is employed, the change in potential of the quinhydrone electrode is a composite of the "salt error" and the effect due to changing hydrogen-ion activity.

Summary

1. An improved method for the study of the quinhydrone–hydrogen cell has been developed.

2. The "salt error" of the quinhydrone electrode has been determined with an accuracy of ±0.00003 v. for fourteen solutes in concentrations from 0.05 to 2 N. All measurements were made at 25°.

3. It was shown that there exists a near linear relationship between "salt error" and concentration of solute. Constants to be used in the correction of pH values were derived.

4. "Salt errors" were found to be additive for many mixtures. Certain anomalies are exhibited by mixtures of sulfates and hydrochloric acid.

5. The relation of "salt error" to the ratio γ_h/γ_q was discussed.

6. The normal electrode potential, E_0, of the quinhydrone electrode, or more strictly of the system quinone–hydroquinone, was determined to be 0.69938 ± 0.00003 v. at 25°.

7. The standard quinhydrone electrode was studied and found to have a potential, with respect to the hydrogen electrode, of 0.69915 ± 0.00003 v. at 25°.

CLEVELAND, OHIO RECEIVED JANUARY 7, 1935

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[18] Hovorka and Dearing, THIS JOURNAL, 56, 243 (1934).