

0.005% gelatin are accurately proportional to the concentration of +5 antimony.

The ratio of the average observed diffusion current constants, 7.50/3.00, agrees exactly with the theoretical value 2.50 for successive 2- and 5-electron reduction reactions. The observed diffusion current constants correspond to a value of 0.61×10^{-5} cm.²/sec. for the diffusion coefficient of the hexachloroantimonate ion under these conditions. By means of relations that have been described elsewhere (ref. 6, p. 45), it follows from these data that the equivalent conductance of the SbCl_6^- ion at infinite dilution at 25° is in the neighborhood of 23 ohm⁻¹ cm.².

Summary

From its solutions in 4 to 6 *N* hydrochloric acid, or in 6 *N* perchloric acid containing 0.2 *N* hydrochloric acid, +5 antimony undergoes stepwise re-

duction at the dropping electrode, first to the +3 state and then to the metal. The reducible species is the SbCl_6^- ion. Both diffusion currents of the resulting double wave are very well developed.

In 6 *N* hydrochloric acid containing 0.005% gelatin the first wave starts at zero applied e.m.f., and the half-wave potential of the second wave is -0.257 v. vs. the saturated calomel electrode. Both diffusion currents are directly proportional to the concentration of +5 antimony, and the diffusion current constants $i_d/(C m^{2/3} t^{1/6})$ are equal to 3.00 and 7.50 microamp./millimole/liter/mg.^{2/3}/sec.^{1/2} at 25°.

Solutions of +5 antimony in 6 *N* perchloric acid in the absence of chloride ion show no indication of a reduction wave before reduction of hydrogen ion.

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The Effect of the Hydrogen Ion Concentration upon the "Salt Error" of the Quinhydrone Electrode

BY JAMES L. GABBARD¹

Introduction

In a previous investigation data were obtained indicating that the "salt error" of the quinhydrone electrode, which has been investigated by a number of workers,²⁻⁸ is a function of the hydrogen ion concentration as well as the concentration of the salt present. In all previous investigations the solvent for the salt solutions was 0.01 *N* hydrochloric acid. This means that the *pH* of the solutions were low, and varied only slightly. Therefore, it was felt that a study of the "salt error" as a function of the hydrogen-ion concentration would be valuable.

Apparatus and Materials

The electrode vessel, shown in Fig. 1, consisted of three 2.5 × 6 cm. Pyrex tubes connected by a three-way stopcock and fitted, respectively, with a pair of hydrogen electrodes, a pair of quinhydrone electrodes, and the connecting arm of a calomel cell. A rubber stopper was fitted over the lower portion of the stopcock and sealed with picene.

The salt solutions of the various concentrations

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- (2) E. S. Amis and J. L. Gabbard, *THIS JOURNAL*, **59**, 557 (1937).
- (3) F. Hovorka and W. C. Dearing, *ibid.*, **57**, 446 (1935).
- (4) A. V. Kiss and A. Urmanczy, *Z. Physik. Chem.*, **A169**, 31 (1934).
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were made by diluting in volumetric flask concentrated stock solutions which were made by weighing and diluting commercial C.P. chemicals. Those of magnesium salts were quantitatively analyzed for their magnesium content. The solvent for the salt solutions was approximately 0.01 *N* acetic acid. However, to avoid fermentation the calculated amount of glacial acetic acid was added at the time of dilution and the exact acid strength determined by titration. The quinhydrone was obtained from the Eastman Kodak Company. The platinizing solution made by dissolving C.P. platinum in aqua regia, repeatedly evaporating to near dryness in hydrochloric acid, diluting to a strength of 2% and adding a trace of lead acetate. The hydrogen electrodes were made from thin sheet platinum in the usual manner while the quinhydrone electrodes were the regular L. and N. gold electrodes. Before each series of measurements the platinum black was removed from the hydrogen electrodes by dipping in hot aqua regia and with the gold electrodes placed in hot chromic acid cleaning solution (110-125°) and allowed to stand overnight. A series of experiments included all the measurements on any particular salt concentration at the various *pH* values. The electrolytic hydrogen was purified by passing it through bottles containing concentrated potassium hydroxide, water and cotton, and then over hot metallic copper (450-500°).

Experimental

A pair of clean, well-rinsed hydrogen electrodes were platinized for exactly one minute by use of a three-volt heavy duty dry cell, washed under the

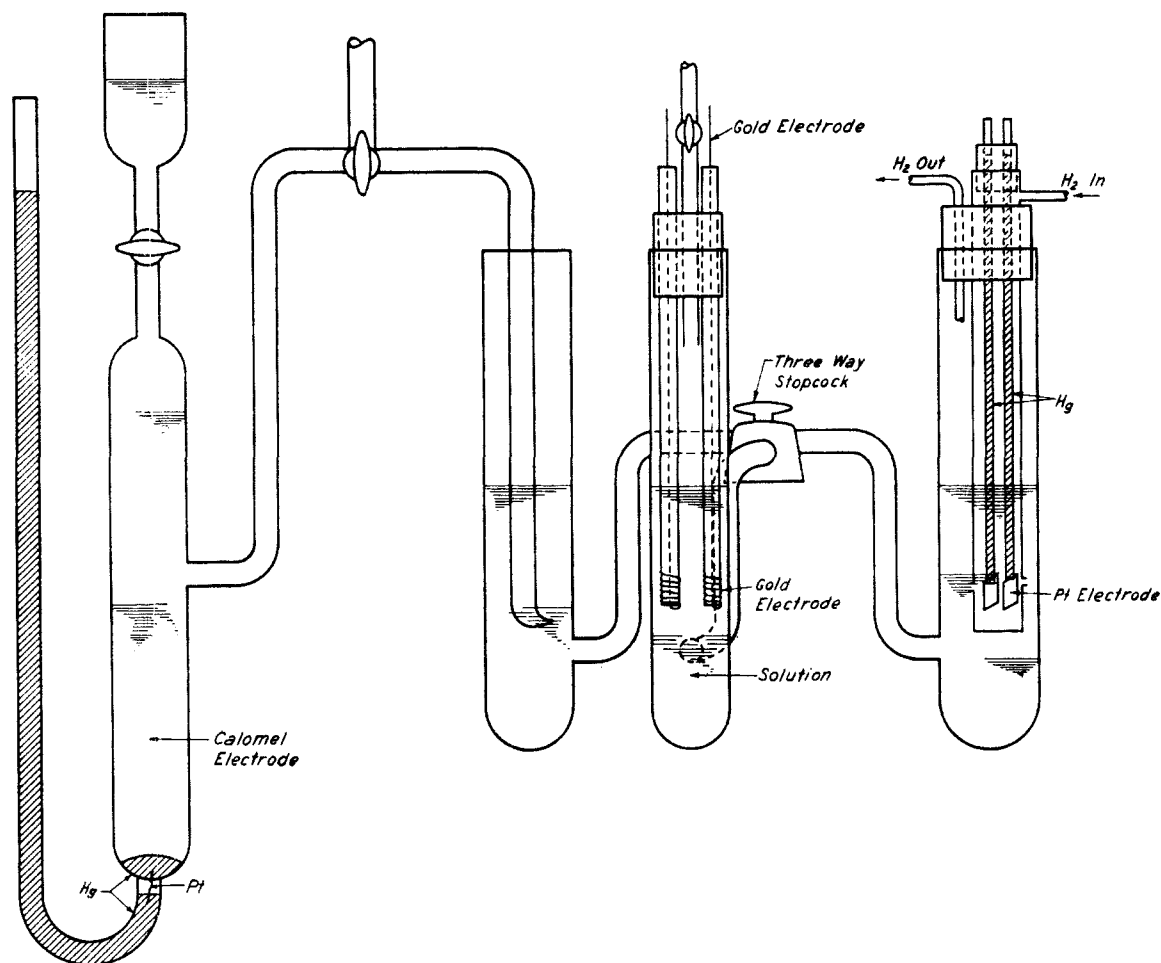


Fig. 1.—Electrode vessel.

tap with abundance of water, rinsed in distilled water, and made the cathode in a five per cent. solution of sulfuric acid under a potential of three volts while the electrode vessel was being prepared. A pair of quinhydrone electrodes were taken from the cleaning solution, similarly rinsed and placed in distilled water. A 150-ml. portion of the desired salt concentration was used in each measurement. Each tube of the thoroughly cleaned electrode vessel was rinsed in succession with three approximately 10-ml. portions of the solution. Each 10-ml. portion was subsequently used to rinse the electrodes as they were placed in the electrode vessel. The electrode vessel was filled to a level just below the connecting arms as indicated in Fig. 1, the rinsed electrodes introduced into the solution in the respective tubes, the solution then transferred from tube to tube by suction in order to ensure complete homogeneity, and the vessel placed in the thermostat with the water standing slightly above the connecting arms. The arm of the calomel cell was introduced and the stopcock turned to disconnect the respective tubes. The hydrogen after being passed through a few ml. of the same solution was passed into the hydrogen electrode

assembly at the rate of one pulsation per second, and the quinhydrone introduced and well stirred by use of the pair of gold electrodes. In the first experiments purified nitrogen was passed through the tube containing the quinhydrone for fifteen minutes before the electrode was introduced. This procedure was found unnecessary by actual experiment. The potential between the two hydrogen electrodes was measured until it became less than 0.2 mv. which was taken as a criterion that the electrodes were in perfect condition. This procedure was repeated for the quinhydrone electrodes. The respective pairs of electrodes were then shorted with each other and the potentials of the cells measured, thus

- A. Hydrogen-quinhydrone
Pt, H₂ | soln. α_{H⁺}, quinhydrone | Au
- B. Pt, H₂ | soln. α_{H⁺} || satd. KCl | Hg₂Cl₂ | Hg

The stopcock between the respective tubes was open during the actual measurements, which were repeated at fifteen-minute intervals until they reached a constant value ±0.2 mv. The potentials were corrected for the deviations of the hydrogen electrode from standard conditions.

While the potentials were reaching equilibrium, a second 150 ml. portion was taken and a calculated amount of 0.1 *N* potassium hydroxide (in case of potassium chloride) containing a concentration of the salt equal to that of the solution being measured, was added to increase the *pH* of the solution and the measurements as described repeated.

In case of the magnesium and barium salt solutions 1.0 *N* sodium hydroxide was added to change the *pH* of the solutions.

The *pH* of the solutions were obtained from the measured potential of cell B by use of the relation

$$pH = (E - E_0)/RT/F$$

where *E* is the measured potential of the cell, *E*₀ is a constant determined by the use of a potassium acid phthalate buffer made according to the directions given by the Bureau of Standards and the other symbols have their usual meaning.

Discussion of Data

The potential of cell A at 25° and 760 mm. pressure is given by the equation

$$(1) E = E_h - E_q = -RT/F \ln a_{H^+} + E_0 - RT/2F \ln \frac{a_h/a_q + RT/F \ln a_{H^+}}{a_h/a_q}$$

$$(2) E = E_0 - RT/2F \ln a_h/a_q$$

where *E*₀ is the normal potential of the quinhydrone electrode (0.69938 v. at 25°) *a*_h, *a*_q and *a*_{H⁺} are the activities of the hydroquinone, quinone and hydrogen ion, respectively. Since the salts present cause a change in the activity ratio of the hydroquinone to quinone in the second term of the equation (2), the constant value of the cell will be different from 0.69938 v. depending upon the concentration and kind of salt.

The deviation of cell A from this constant value is a measure of the change in the ratio of the activities to hydroquinone to quinone caused by the salt concentration and is a measure of the "salt error" of the quinhydrone electrode.

After measuring the potentials of cell A in the potassium chloride solutions and in the higher concentrations of magnesium sulfate solutions with a slow decrease of the hydrogen ion concentration, it became apparent that the potential of the cell remained constant and was independent of the hydrogen ion concentration provided the *pH* of the solution was less than 4.5. It was also observed that the constant values of the cell agreed within ± 0.2 mv. with the values obtained by Hovorka and Dearing³ for the same salt concentrations. This comparison is shown in Table I. Therefore, it was considered unnecessary to extend the study below a *pH* value of 5 and that the constant value of the cell below this *pH* value could be taken from the data of Hovorka and Dearing. It was also evident from the data that, while increased concentration of the salt caused deviations from the constant value to begin at a slightly lower *pH* value, the concentration was not the determining factor. Consequently in the case of the magnesium and barium chloride solu-

tions only the relatively high and low concentrations were investigated.

TABLE I
COMPARISON OF CELL A POTENTIALS IN SOLUTIONS OF LOW *pH* VALUE

<i>N</i>	Salt	—Potentials of cell A in volts—	
		Hovorka and Dearing (0.01 <i>N</i> HCl solvent)	This investigation (0.01 <i>N</i> in acetic acid)
0.25	KCl	0.6988	0.6986
1.0	KCl	.6972	.6974
2.0	KCl	.6950	.6948
1.0	MgSO ₄	.7007	.7006
2.0	MgSO ₄	.7018	.7016

The deviations of the potentials of cell A from the constant value, the potential of the cell in the salt solutions 0.01 *N* in acetic acid, as the *pH* value of the solution increased show the influence of the hydrogen-ion concentration upon the "salt error" of the quinhydrone electrode. Data showing these deviations in mv. for different salt solutions are given in Table II and are plotted *vs.* the *pH* values of the solutions in Fig. 2.

TABLE II
THE DEVIATION OF THE "SALT ERROR" OF THE QUINHYDRONE ELECTRODE IN MILLI-VOLTS AS A FUNCTION OF THE HYDROGEN ION CONCENTRATION

<i>N</i>	KCl		MgSO ₄		MgCl ₂		BaCl ₂	
	<i>pH</i>	mv.	<i>pH</i>	mv.	<i>pH</i>	mv.	<i>pH</i>	mv.
0.10			5.58	0.6	5.66	0.9	5.47	0.5
			5.68	.9	5.73	1.1	5.77	1.1
			6.00	1.9	5.95	2.2	5.94	1.5
			6.70	13.6			6.24	4.3
			7.85	55.9				
0.25	3.33	-0.4						
	3.35	-.1						
	3.39	.3						
	4.25	-.6						
	4.76	-.6						
	5.28	.4						
	5.65	.4						
	5.91	.1						
6.16	.7							
6.62	6.3							
0.5			5.49	0.5				
			5.71	1.0				
			5.87	1.8				
			6.25	6.0				
1.0	3.32	0.2	3.57	0.0				
	3.33	-.2	5.58	.9				
	5.69	.2	6.00	4.4				
	5.83	.6	8.11	39.1				
	6.05	2.5						
6.38	10.1							
2.0	3.34	0.0	3.52	0.0	5.18	-0.2	4.84	0.5
	5.63	1.1	4.67	.0	5.40	.1	5.58	2.5
	5.81	1.0	5.34	.5	5.46	.0	5.76	4.3
	6.10	2.2	5.61	2.0	5.61	3.5	6.62	21.7
					5.76	4.3		
	6.83	8.2	6.43	8.4	6.44	14.4		

These data show clearly the limitations of the quinhydrone electrode in measuring the *pH* of slightly buffered salt solutions. If the *pH* is less than 5, the "salt error" of this electrode is independent of the *pH* of the solution except at very high concentrations. At a *pH* of 5.5 the devia-

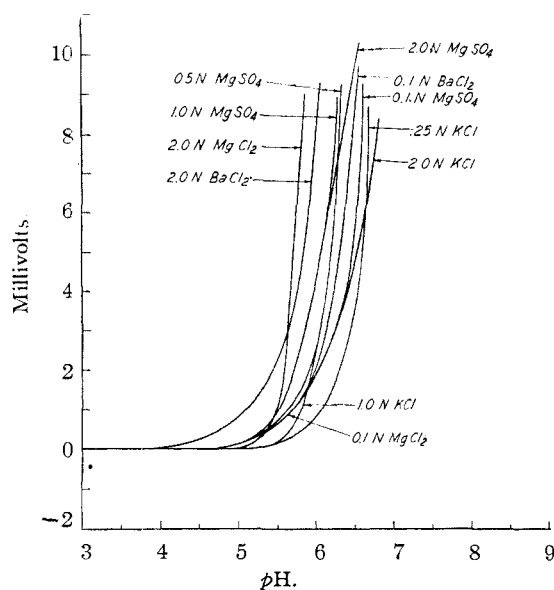


Fig. 2.—The deviation in millivolts of the salt error of the quinhydrone electrode as a function of pH .

tions in most cases amount to less than 0.02 pH units but increase rapidly above this value and indicate that the quinhydrone electrode is not to be trusted in measuring the pH of slightly buffered salt solutions above a pH value of 6.

Since the signs of the deviation are positive, the change in the ratio of the activities of the hydroquinone to the quinone is best explained by assuming that the quinhydrone takes part in the acid base reaction.

Summary

1. The "salt error" of the quinhydrone electrode in slightly buffered salt solutions increases rapidly with the decrease of the hydrogen ion concentration above a pH value of 5.5.

2. The deviations in the "salt error" of the quinhydrone electrode appears at a lower pH as the concentration of the salt solution increases.

3. The large "salt error" deviations of the quinhydrone electrode as the pH of the solution increases are apparently due to the acid base reaction of the hydroquinone.

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The Activity Coefficients and Activity Product of Potassium Metaperiodate¹

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Previous work on the solubility of potassium metaperiodate in water and aqueous solutions includes Hill's² on the solubility in water, aqueous potassium hydroxide and aqueous periodic acid; and Pederson's³ on the solubility in water, aqueous urea and aqueous dioxane. No computations of activity coefficients or of the activity product were attempted.

The present investigation determines the solubility of potassium metaperiodate at 25° in water and in aqueous solutions of sodium chloride, lithium nitrate and potassium nitrate. The results are used to compute the activity coefficients and activity product of the potassium metaperiodate.

Experimental

Purification of Materials.—The purification of potassium metaperiodate⁴ and sodium chloride⁵ have been described previously. Reagent grade lithium nitrate and potassium nitrate were recrystallized twice from a good grade of water and dried in platinum weighing boats before use.

(1) Taken from a thesis presented by Rev. Norman Heckman to the Graduate School of Indiana University in partial fulfillment for the A.M. degree, 1946.

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(2) Arthur E. Hill, *THIS JOURNAL*, **50**, 2670-2692 (1928).

(3) K. J. Pederson, *Kgl. Danske Videnskab. Selskab. Math. fys. Medd.*, **18**, No. 12 (1941).

(4) J. H. Jones, *THIS JOURNAL*, **68**, 240 (1946).

(5) *Ibid.*, **65**, 1353 (1943).

Preparation of Solutions.—All solutions were prepared by weighing the dry salts and water.

Apparatus.—A water thermostat with a temperature control of $\pm 0.03^\circ$ was used. Adequate stirring and agitation of the solutions were provided.

Procedure.—Potassium metaperiodate dissolves very slowly at 25° but more rapidly at elevated temperatures. A sample of potassium metaperiodate and water was agitated for three weeks in our thermostat, and analysis showed that its concentration was still somewhat lower than that obtained by crystallization from a supersaturated solution. The concentration of the solution obtained from the supersaturated side showed no change in composition after twenty-four hours. The solutions here used were made by weighing the predetermined amounts of salts into a tared equilibrium vessel and adding 100 ml. of preheated water. The vessel was shaken occasionally until the water had cooled to about 30°, then it was stoppered and weighed to determine the exact amount of water added. The vessels were placed in the thermostat and agitated for a period of twenty-four to forty-eight hours. The agitator was disconnected and three 25-ml. aliquots were removed for analysis. Each sample was accurately weighed to enable an approximation of its density to be made.

Each sample was analyzed for metaperiodate content by adding potassium iodide and hydrochloric acid and titrating the iodine liberated with sodium thiosulfate. The thiosulfate solution was standardized against the solid potassium metaperiodate and against a standard dichromate solution. The concentration of the foreign salt was determined from the known weights of salt and water added.

All solubilities were obtained by approach from the supersaturated side, but the reproducibility and consistency of results bear out the attainment of equilibrium. The potassium metaperiodate was always present in considerable excess.