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.

The Activity Coefficients and Activity Product of Potassium Metaperiodate[1]

BY JAMES HOMER JONES AND NORMAN HECKMAN[1a]

Previous work on the solubility of potassium metaperiodate in water and aqueous solutions includes Hill's[2] on the solubility in water, aqueous potassium hydroxide and aqueous periodic acid; and Pederson's[3] 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 metaperiodate[4] and sodium chloride[5] 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.

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

Apparatus.—A water thermostat with a temperature control of ±0.03° 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.

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

(1a) Present address: St. Joseph's of Indiana, Collegeville, Indiana.

(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).

Data

The solubility of potassium metaperiodate in water and in aqueous solutions of sodium chloride, lithium nitrate and potassium nitrate are tabulated in Table I and shown graphically in Fig. 1.

TABLE I

SOLUBILITY OF POTASSIUM METAPERIODATE AT 25°

| M_{KIO_4}	M_{NaCl}	M_{KIO_4}	M_{LiNO_3}	M_{KIO_4}	M_{KNO_3}
0.02248	0.0000	.....	.....	......	.....
.02441	.04955	0.02397	0.03075	0.01404	0.02552
.02561	.1024	.02465	.05361	.01004	.05120
.02654	.1536	.02564	.09232	.006407	.1028
.02724	.2025	.02813	.2039	.004130	.2074
.02923	.4054	.02955	.3089	.003247	.3114
.03040	.6096	.03046	.4112	.002768	.4138
.03155	.8202	.03190	.5928	.002285	.6161
.03204	1.0289	.03353	.8179	.002058	.8230
.03288	1.2825	.03433	.9567	.001933	1.0275
.03304	1.5394				
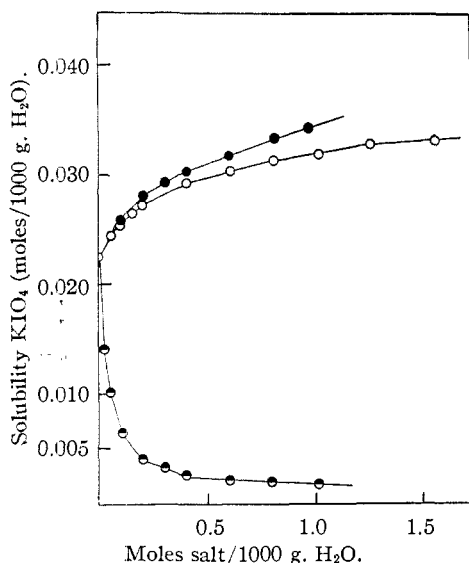
Fig. 1.—Solubility of potassium metaperiodate in salt solutions: ●, LiNO₃; O, NaCl; ◓, KNO₃.

Discussion of Data

The activity coefficients of potassium metaperiodate in the presence of sodium chloride or lithium nitrate may be evaluated from the increase in solubility provided some suitable value for the solubility at zero ionic strength can be obtained. The extrapolation to zero ionic strength can be made conveniently by using a Debye–Hückel relation modified by introducing an average ionic diameter $å$ (equation 1).

$$\log m = \log m_0 + \frac{0.5085\mu^{1/2}}{1 + 0.3281 \times 10^8 å\mu^{1/2}} \quad (1)$$

In equation 1, m_0 refers to the solubility in terms of moles per 1000 g. of water at zero ionic strength, μ refers to the ionic strength and $å$ to the ionic diameter parameter. Suitable values of $å$ for each salt used were determined by combining in turn each solubility determination with the solu-

bility in pure water and solving each pair simultaneously for $\log m_0$ and $å$. Some typical values for these two quantities are summarized in Table II.

TABLE II

	NaCl			LiNO₃	
$\mu^{1/2}$	m_0	$å$	$\mu^{1/2}$	m_0	$å$
0.2719	0.01947	4.50	0.2339	0.01938	3.73
.4244	.01945	4.30	.3435	.01938	3.82
.6592	.01943	4.11	.6646	.01931	3.24
1.1445	.01942	4.11	.9955	.01931	3.13

The m_0 values are in molalities and $å$ values in ångströms. By selecting the values of $m_0 = 0.01945$ as representing the sodium chloride data, and $m_1 = 0.01938$ as representing the lithium nitrate data, the activity coefficients are readily obtained from the relation $\gamma = m_0/m$. From the average of the two values for m_0, it is possible to compute a mean value of the activity product constant for potassium metaperiodate. Since the activity coefficients are unity at infinite

TABLE III

ACTIVITY COEFFICIENTS OF POTASSIUM METAPERIODATE

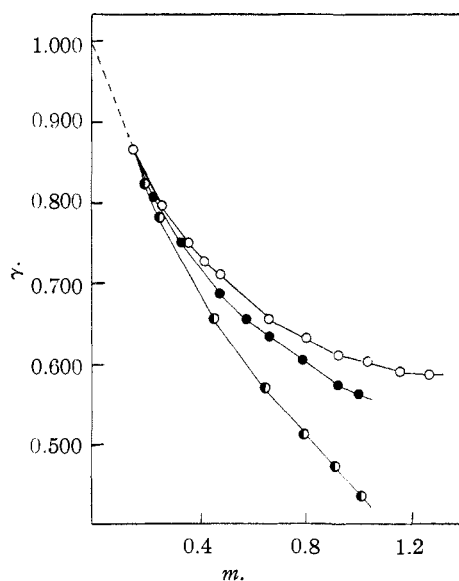| NaCl		LiNO₃		KNO₃	
μ	γ	μ	γ	μ	γ
0.02248	0.866	0.02248	0.866	0.02248	0.864
.07396	.798	.05472	.809	.03956	.824
.1280	.760	.07826	.786	.06124	.783
.1801	.734	.1180	.754	.2115	.657
.2297	.715	.2320	.689	.4166	.572
.4346	.666	.3384	.656	.6184	.517
.6400	.640	.4417	.636	.8251	.472
.8518	.617	.6247	.608	1.0294	.436
1.061	.608	.8514	.578		
1.315	.592	.9910	.565		
1.572	.589				

Fig. 2.—Activity coefficients of potassium metaperiodate in salt solutions: O, NaCl; ●, LiNO₃; ◑, KNO₃.

dilutions, $K_{sp} = m_0^2 = (0.01942)^2 = 3.77 \times 10^{-4}$. Using this value for K_{sp} and the solubility data in potassium nitrate solutions, the activity coefficients of potassium metaperiodate in potassium nitrate solutions may be calculated from the relation

$$\gamma = \sqrt{K_{sp}/[IO_4^-][K^+]}$$

The values for the activity coefficients are collected in Table III, and shown graphically in Fig. 2.

It should be noted that within our experimental error, the γ values in potassium nitrate solutions having concentrations higher than 0.2 m are the same as the γ values for potassium nitrate of the same total molality.

Our values for the solubility of potassium metaperiodate is 0.02248 molal compared to Hill's value of 0.0223. The other values recorded in

Seidell[6] and in the "International Critical Tables[7]" at 13° are over 20% higher and are certainly in error. Pederson's[3] value at 18° of 0.01618 mole liter is a much more reasonable value.

Summary

The solubility of potassium metaperiodate in water and in aqueous solutions of lithium nitrate, sodium chloride and potassium nitrate have been determined at 25° up to ionic strengths of approximately one.

The activity coefficients of potassium metaperiodate have been computed for the saturated solution in water and the various salt solutions.

The activity product has been calculated.

(6) Seidell, "Solubilities of Inorganic and Metal Organic Compounds," p. 825.

(7) "International Critical Tables," Vol. 4, p. 239.

The Reactions of the Hydroxyl Radical[1]

By W. H. Rodebush, C. R. Keizer, Frances S. McKee and J. V. Quagliano

Numerous investigators[2-5] have studied the reactions of the products of the glow discharge in water vapor. It is agreed that the principal dissociation products are hydrogen atoms and hydroxyl radicals. If the products of the discharge are conducted immediately into a liquid air trap considerable yields of hydrogen peroxide are obtained. If Dry Ice is substituted for liquid air no hydrogen peroxide is obtained and frequently very little water is condensed. Attempts to measure the concentration of the hydroxyl radical in the vapor from the discharge by spectroscopic or other means have always indicated that the hydroxyl radicals disappear rapidly by some sort of reaction (presumably a homogeneous one) but it has not been clear just what this reaction or reactions might be.

Recently we have had occasion to repeat some of these experiments in this Laboratory and it appears worthwhile to report some additional results which were obtained and the conclusions which may be drawn from them.

Experimental

The glow discharge operates at a much lower voltage in water vapor than in hydrogen (1000 volts at 60 cycles will maintain a good discharge in a 30-mm. tube, 2 meters in length). As is well known, the actual voltage drop varies only slightly with the length of tube but markedly

with the diameter. So far as yield of hydrogen peroxide is concerned the optimum conditions appear to be a pressure of 0.1–0.2 mm. of water vapor in the discharge tube with as rapid a throughput as possible under the low pressure conditions.

Arrangement of Condensation Traps.—The prime factor in the variation of products and yields of the reaction is the arrangement and temperature of the condensation traps. Three different arrangements were studied.

A. A liquid-air cooled trap was placed in the closest possible position adjacent to the discharge tube.

B. The trap in arrangement A was cooled with Dry Ice and a second trap cooled with liquid air was placed immediately behind it.

C. The liquid air trap in arrangement A was moved to a distance of 1 meter from the discharge tube with a connecting tube of 25 mm. diameter.

In every case careful tests were made by means of additional traps to prove that products were not passing through the traps because of too rapid flow.

Products of the Reaction.—The products and yield obtained from the glow discharge vary greatly with the location and temperature of the condensation traps. If the discharge products are pumped rapidly through a liquid air trap placed in the closest possible position to the discharge (A) the maximum yield of peroxide is obtained. The condensate will show on analysis more than 60% hydrogen peroxide the remainder, of course, being water. Furthermore, practically all of the oxygen which entered the discharge tube as water is recovered in the form of water or hydrogen peroxide.

If Dry Ice is substituted for the liquid air as a cooling agent, arrangement B, no peroxide and only a small amount of water is collected. If a second trap cooled with liquid is placed beyond the Dry Ice trap no hydrogen peroxide and very little water is condensed.

Finally, if the products of the discharge are conducted through a meter length of tube and then into a liquid air no peroxide and practically no water is condensed in the trap.

Interpretation of Experimental Results.—The results obtained with the various arrangements described above can be accounted for if one makes the following postulates.

(1) This article is based upon work performed for the Office of Scientific Research and Development under Contract OEMsr 1452.

(2) K. F. Bonhoeffer and T. G. Pearson, Z. physik. Chem., **B14**, (1931).

(3) W. H. Rodebush and R. W. Campbell, J. Chem. Phys., **4**, 293 (1936).

(4) A. A. Frost and O. Oldenberg, ibid., **4**, 642 (1936).

(5) W. V. Smith, ibid., **11**, 110 (1943).