

yield is due to the elimination of side reactions by precipitating the potassium salt of hydroxylamine disulfonic acid and separating it from the excess sulfite before hydrolysis.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 275]

## THE COMPARATIVE IONIZATION OF SELENIC AND SULFURIC ACIDS

BY M. S. SHERRILL AND E. H. LYONS, JR.

RECEIVED NOVEMBER 6, 1931

PUBLISHED MARCH 5, 1932

### Introduction

There is much evidence to indicate that sulfuric acid in moderately dilute aqueous solution is substantially completely ionized with respect to its first hydrogen, but only partly with respect to its second. Thus, Sherrill and Noyes,<sup>1</sup> by combining conductance and transference data of sulfuric acid at different concentrations, have estimated the ionization of  $\text{HSO}_4^-$  ion in sulfuric acid solutions at 25° to vary from 96% at an acid concentration 0.0005 normal to 34.5% at 0.1 normal. The corresponding value of the ionization constant of the  $\text{HSO}_4^-$  ion was computed to be 0.0115. In making these calculations, it was assumed that the mobility and the activity coefficient of any given ion is, at a definite temperature, determined solely by the ionic strength of the solution.

It is generally assumed that selenic acid closely resembles sulfuric acid in its ionization relations. The physico-chemical evidence of this is very limited, but certain approximate conclusions may be drawn from a comparison of the equivalent conductances of the two acids and their acid salts shown in the following table.<sup>2</sup>

TABLE I  
EQUIVALENT CONDUCTANCES AT 25°

Substance	0.002	0.005	0.01	0.02	0.05	0.1	0.20	0.5
$\text{Na}_2\text{SO}_4$	122.1	117.3	112.4					
$\text{Na}_2\text{SeO}_4$	117.3	113.7	109.4					
$\text{H}_2\text{SO}_4$	390.3	364.9	336.4	308.0	272.6	250.8	234.3	222.5
$\text{H}_2\text{SeO}_4$	384	366	349	328	295	272	253	233

These values indicate that the mobilities of the sulfate ion and selenate ion are approximately the same, and that in dilute solution the hydrogen-ion concentrations in sulfuric acid and selenic acid solution of the same normality are nearly identical, whereas at higher concentrations, such as 0.2 *N*, the hydrogen-ion concentration is slightly greater in the selenic

<sup>1</sup> Sherrill and Noyes *THIS JOURNAL*, **48**, 1870 (1926).

<sup>2</sup> "International Critical Tables." Vol. VI, pp. 242, 236, 247.

acid solutions, assuming the mobilities of  $\text{HSO}_4^-$  and  $\text{HSeO}_4^-$  to be the same.

In order to confirm these conclusions and to compare the activities of hydrogen ion in solutions of selenic acid and sulfuric acid of the same concentration, Small<sup>3</sup> measured the electromotive force at 25° of cells of the type,  $\text{H}_2$ ,  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{SeO}_4$  (*c* formal), satd. KCl,  $\text{Hg}_2\text{Cl}_2 + \text{Hg}$ . The apparatus consisted of a Leeds and Northrup student type potentiometer, with a desk galvanometer, and the Clark<sup>4</sup> form of cell with a specially designed shaker to rock the hydrogen half-cell.

The results of this investigation are summarized in Table II.

TABLE II  
ELECTROMOTIVE FORCE AT 25°

Form. wt. acid in 1000 g. of $\text{H}_2\text{O}$	$\text{H}_2\text{SO}_4$ -Cell $E_1$	$\text{H}_2\text{SeO}_4$ -Cell $E_2$	Difference $E_1 - E_2$
0.1000	0.3014	0.3001	0.0013 volt
.2000	.2859	.2850	.0009
.5000	.2644	.2628	.0016
1.000	.2469		

The values for the electromotive force correspond to a barometric pressure of 754 mm. At concentrations of selenic acid above 0.5 formal no reliable results could be obtained owing to reduction of selenic acid by hydrogen at the platinized electrode. The differences in electromotive force, recorded in the last column, can be regarded as a measure of the difference in the electrode potentials only under the assumption that the two liquid potentials counterbalance each other. As this assumption is approximately correct, the small differences of only about one millivolt indicate that the activities of hydrogen ion in solutions of selenic and sulfuric acid of the same concentration are substantially equal.

In the present investigation, which was a continuation of Small's work, the electromotive force of cells of the following type was measured

Pt, Quinhydrone (Satd.) +  $\text{H}_2\text{SO}_4$ (*c* formal),  $\text{H}_2\text{SeO}_4$ (*c* formal) +  
Quinhydrone (Satd.), Pt.

In some cases the solution at the electrode was saturated not only with quinhydrone, but also with quinone, thus converting the quinhydrone electrode into the quino-quinhydrone electrode of Biilmann.<sup>5</sup>

In such a cell, with the two acids at the same concentration, the liquid potential is practically equal to zero, so that the electromotive force of the whole cell may be considered equal to the difference between the two electrode potentials. Since each of these, as shown below, is practically determined by the activity of the hydrogen ion in the solution,

<sup>3</sup> Small, Thesis M. I. T., 1927, unpublished.

<sup>4</sup> Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 2d ed., 1923, pp. 180-185.

<sup>5</sup> Biilmann, *Bull. soc. chim.*, 41, 151 (1927).

the observed electromotive force furnishes a measure of the relative hydrogen-ion activities in sulfuric acid and in selenic acid solutions of the same concentration.

The exact expression for the electrode potential is given by the well-known equation

$$E = E_0 + \frac{RT}{F} \ln [H^+] - \frac{RT}{2F} \ln \frac{[C_6H_4O_2]}{[C_6H_4(OH)_2]}$$

in which  $E_0$  is a constant, the molal electrode potential of the reaction of oxidation,  $C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2E^-$ , and the symbols  $[H^+]$ ,  $[C_6H_4(OH)_2]$ , and  $[C_6H_4O_2]$  represent the activities of the hydrogen ion, of hydroquinone and of quinone, respectively, in the solution at the inert metal electrode. With the quinhydrone electrode, the last term is practically zero, since hydroquinone and quinone are produced in the solution in equimolar quantities and have therefore almost equal activities. With the quino-quinhydrone electrode this term has a constant value, since the activity of the hydroquinone and also that of the quinone becomes definitely fixed by the presence of the two solids in contact with the solution.

In this investigation the acid concentration was varied from 0.01 to 0.8 formal. As will be shown later, the hope of obtaining with such electrodes reliable results at concentrations above 0.5 formal was not realized. The extension of the work to concentrations below 0.1 formal is of importance, since, as already pointed out, the ionization of the second hydrogen of sulfuric acid changes rapidly with the concentration in these more dilute solutions.

**Preparation of Materials and Solutions.**—The selenic acid was prepared from a sample of commercial selenium. Following the method of Dennis and Koller<sup>6</sup> the crude selenium was dissolved in an excess of concentrated nitric acid, the solution was evaporated to dryness, the residue moistened with water and the liquid again evaporated to remove the excess of nitric acid. The selenous acid thus obtained was recrystallized six times from water. Selenic acid was prepared from this pure selenous acid by the method of Meyer and Moldenhauer.<sup>7</sup> This consists in oxidizing the selenous acid to selenic acid by means of chloric acid, prepared by the interaction of barium chlorate and sulfuric acid, and then concentrating the resulting solution *in vacuo*. The final product showed no test for selenous or sulfuric acid.

A stock solution of selenic acid was made from this concentrated acid, and standardized against sodium carbonate, using methyl orange as indicator. The solutions used in the cells were prepared from the stock solution by suitable dilution with water. All concentrations are expressed as formula weights of selenic acid,  $H_2SeO_4$ , per 1000 g. of water.

<sup>6</sup> Dennis and Koller, *THIS JOURNAL*, **41**, 952 (1913).

<sup>7</sup> Meyer and Moldenhauer, *Z. anorg. allgem. Chem.*, **116**, 192-200 (1921).

The solutions of sulfuric acid of known concentration were prepared from concentrated c. p. sulfuric acid by the procedure just described for selenic acid.

The quinhydrone was obtained from the Eastman Kodak Co. It melted at 168–170°.

**Apparatus and Method of Measurement.**—The potentiometer was a Leeds and Northrup student type with a desk galvanometer. It was standardized through the use of a carefully calibrated Weston standard cell.

The electrode vessels were of the usual calomel cell type, 25 mm. in diameter, 90 mm. long, with side arms of 8-mm. tubing constricted at the tip to 5 mm. Each half-cell was fitted with a rubber stopper bearing three electrodes, two of platinum foil, 10 mm. by 20 mm., and one of gold foil, 8 mm. by 25 mm. Each platinum electrode was welded to a short platinum wire and sealed to a glass tube. The connection to the potentiometer was made by means of mercury and copper wire. The gold electrode was welded to a longer gold wire, which was sealed into an open glass tube by means of sealing wax, and connected to the potentiometer by copper wire.

Various methods of cleaning the electrodes were tried before reproducible values of the electromotive force could be obtained. Biilmann's method<sup>8</sup> of heating the electrodes to redness in an alcohol flame was the one finally adopted. When by this procedure the potential difference between each pair of electrodes immersed in the same acid solution was reduced to a value less than a tenth of a millivolt, the electrodes were considered to be satisfactory for use.

In preparing the quinhydrone half-cells a small quantity of quinhydrone (10–50 mg.) was stirred with the solution to form a paste, which was then shaken with more of the solution in the electrode vessel. With the metal electrodes inserted, the vessel was approximately half filled with solution. For the quino-quinhydrone half-cells a similar procedure was followed, using an excess of one part of quinhydrone to five parts of quinone. With these cells only the platinum electrodes were used. They were bent upward in the shape of a hook so as to catch and hold some of the two solid phases at the metal surface, thus insuring saturation.

The liquid junction in the cell was made as follows. The half-cells with the side arms projecting into an empty 50-cc. beaker were immersed, as far as such an arrangement would permit, in a water thermostat at 25°, within 0.05°. A drop was formed at the tip of each side arm and then removed by touching it with a clean stirring rod. The bridge solution of selenic acid, which was slightly more dense than the sulfuric acid solution of equal concentration, was flowed into the beaker until it rose

<sup>8</sup> Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

above the tips of the side arms. To minimize convection currents in establishing the liquid junction, the one side arm was protected by a small glass tube which acted as a collar.

In measuring the electromotive force readings were taken for each possible combination of electrode pairs. Thus, with three electrodes in each quinhydrone half-cell, nine different combinations were possible, and correspondingly nine separate readings were taken. The electromotive force recorded in the tabulation of results represents in each case the average of a number of such measurements with freshly made solutions in the cells.

**Results of the Electromotive Force Measurements.**—The results of the measurements with cells of the type Pt, Quinhydrone- $\text{H}_2\text{SO}_4$  (*c* formal),  $\text{H}_2\text{SeO}_4$  (*c* formal)—Quinhydrone, Pt are shown in Table III.

TABLE III  
ELECTROMOTIVE FORCE OF CELLS CONTAINING BOTH SULFURIC AND SELENIC ACIDS AT  
25° IN MILLIVOLTS

Formal concn. acid ( <i>c</i> )	Quinhydrone electrodes	Quino-quinhydrone electrodes	Formal concn. acid ( <i>c</i> )	Quinhydrone electrodes	Quino-quinhydrone electrodes
0.0100	0.08	..	0.4000	0.40	0.01
.0250	.15	..	.5000	.00	.11
.0500	.39	..	.6000	...	(1.0)
.1000	.02	..	.7000	...	(3.3)
.2000	.30	..	.8000	...	(1.4)
.3000	.06	0.23			

Very reproducible results for the electromotive force were obtained with quinhydrone electrodes up to an acid concentration 0.5 formal. The results recorded represent not only an average of the separate values of electromotive force obtained with the different electrode pair combinations, but also an average of the final values thus obtained with freshly made solutions in the cells. The electromotive force differed from zero seldom by more than one or two tenths of a millivolt; and though these small values were almost all positive it is doubtful whether the deviation from zero is really significant.

At higher concentrations the results were less reproducible, particularly with the gold electrodes. For this reason a series of measurements was made with quino-quinhydrone electrodes. It was still found impossible with acid concentrations above 0.5 formal to obtain results reproducible to less than several millivolts. The values recorded in parentheses, though representing averages, are accordingly to be regarded as unreliable.

These results indicate that for the range of concentration from 0.01 to 0.5 formal the activities of hydrogen ion in solutions of selenic acid and of sulfuric acid of the same concentration are very nearly equal. It is correspondingly probable that for this concentration range the ionization re-

lations of selenic acid are almost identical with those of sulfuric acid. Hence, accepting the estimates of Sherrill and Noyes<sup>1</sup> in the case of sulfuric acid as applicable to selenic acid, the statement may be made that selenic acid at a concentration 0.5 formal exists mainly in the form of the ions,  $H^+$  and  $HSeO_4^-$ , whereas, at a concentration 0.01 formal, the ion  $HSeO_4^-$  is about 67% dissociated into  $H^+$  and  $SeO_4^{2-}$  ions. As the ionization constant of  $HSO_4^-$  was found to be 0.0115, that of  $HSeO_4^-$  is of nearly the same magnitude.

### Summary

The electromotive force of cells of the type, Pt, Quinhydrone  $H_2SO_4$  (*c* formal),  $H_2SeO_4$  (*c* formal) Quinhydrone, Pt, was measured at 25° and found to be substantially equal to zero over a range of acid concentration in the cell from 0.01 to 0.5 formal. At higher acid concentrations, 0.6 to 0.8 formal, reproducible results could not be obtained. The conclusion was drawn that in dilute solution the ionization relations of selenic acid are almost identical with those of sulfuric acid.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE  
COLLEGE OF NEW YORK UNIVERSITY]

## AN EXTENSION OF THE ISOAMYL ALCOHOL SEPARATION OF THE ALKALI AND ALKALINE EARTH METALS TO THE LESS COMMON ALKALIES, LITHIUM, RUBIDIUM AND CESIUM

BY HERMAN YAGODA<sup>1</sup>

RECEIVED NOVEMBER 7, 1931

PUBLISHED MARCH 5, 1932

Gooch has shown that isoamyl alcohol can be applied to the quantitative separation of lithium from sodium and potassium by its solvent action upon the chlorides,<sup>2</sup> and Browning has used the same alcohol for bringing about a separation of calcium from barium and strontium using the nitrates<sup>3</sup> and of strontium from barium using the bromides.<sup>4</sup> Detailed schemes for the qualitative analysis of the entire alkali group have been developed by Ato and Wada,<sup>5</sup> and Noyes and Bray.<sup>6</sup> These methods were designed to detect small quantities of any one of the alkalies when present in admixture with large amounts of the others. Because of the similar solubilities of the salts of potassium, rubidium and cesium, the

<sup>1</sup> Formerly a fellow at the University.

<sup>2</sup> F. A. Gooch, *Am. Chem. J.*, **9**, 33 (1887).

<sup>3</sup> P. E. Browning, *Am. J. Sci.*, **43**, 50 and 314 (1892).

<sup>4</sup> P. E. Browning, *ibid.*, **44**, 459 (1892).

<sup>5</sup> Sunao Ato and Isaburo Wada, *Sci. Papers Inst. Phys. Chem. Research*, **4**, 261 (1926), in English; *Z. anal. Chem.*, **72**, 50 (1927).

<sup>6</sup> Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," 1927, p. 246.