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

THE ACTIVITY OF HYDROBROMIC ACID IN PURE AQUEOUS SOLUTION AND IN SOLUTIONS CONTAINING SULFATES

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RECEIVED JULY 29, 1925 PUBLISHED JANUARY 8, 1926

The only determinations of the activity of hydrobromic acid previous to this investigation,[1] were those based upon the electromotive-force measurements of Lewis and Storch[2] and the vapor-pressure measurements of Bates and Kirschman.[3] The former covered the field 0.01 M to 0.10 M, and the latter the field 6 M to 11 M.

The present investigation includes a series of electromotive-force measurements which determine the activity of hydrobromic acid over the range 0.08 M to 1.55 M. The cells measured were of the same type as those used by Lewis and Storch[2] and may be represented as follows: $H_2 \mid HBr(xM) \mid AgBr \mid Ag$. The main purpose of this investigation, however, was the determination of the mean activity of hydrobromic acid in the presence of sulfates at a variety of concentrations, which data were necessary for the complete interpretation of certain reaction-rate data.[4]

In connection with this work, there has been suggested a semi-empirical extension of the ionic-strength principle[5] to solutions containing weak electrolytes, with or without a common ion, which may be applied whenever the activity coefficient of the strong electrolyte in pure aqueous solution and the ionization constant of the weak electrolyte are known.

Experimental Methods

The hydrobromic acid solutions were prepared by dilution of a constant-boiling mixture with "conductivity" water. The distillations, which were conducted in an all-Pyrex still in an atmosphere of nitrogen, were repeated several times, the middle fractions only being retained. The sulfuric acid solutions were prepared from a sample of C. P. concentrated solution which had been heated for several hours to drive off volatile impurities, such as sulfur dioxide. The potassium bromide and sodium sulfate used were purified by repeated recrystallization from distilled water.

The acid concentration (molality) was determined by titrating samples, weighed in air, with standard hydroxide solution; the reference substance was sodium carbonate,

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[1] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 519.

[2] Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917).

[3] Bates and Kirschman, *ibid.*, 41, 1991 (1919).

[4] (a) Bray and Livingston, *ibid.*, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923).

The interpretation of the rate data, given in these two papers, will be presented very shortly in terms of the activity data as given in this paper.

[5] Ref. 1, Chap. XXVIII.

the indicator methyl orange. The bromide concentration was determined gravimetrically, as silver bromide. Those solutions which contained sodium sulfate were prepared from a definite weight of hydrobromic acid, of known strength, and of pure anhydrous sodium sulfate; the sulfate concentration was not checked analytically.

The mechanical construction of the hydrogen-electrode vessels and of the hydrogen generators was similar to that described by Lewis, Brighton and Sebastian.[6] The hydrogen electrodes were of the platinized platinum type.

The silver bromide electrodes were of the Jahn[7] electroplated type. The method of preparation was similar to that outlined by MacInnes and Beattie[8] for silver chloride electrodes. The electrodes were prepared in lots of five, and were kept and compared in a five-branched vessel containing 0.1 *M* hydrobromic acid. When in use, one or more of the electrodes was transferred directly to the cell vessel, which was a side tube sealed to the hydrogen electrode vessel. They were checked against one another before and after each measurement. When the cell electrolyte was dilute hydrobromic acid or a mixture of sulfuric acid and potassium bromide, the silver electrodes nearly always gave the same reading before and after being transferred to the cell vessel. When placed in relatively concentrated hydrobromic acid (above 1.0 *M*), they changed rapidly, and did not return to their original values when replaced in the comparison cell. This effect was probably due to the increased solubility of the silver bromide.[9]

The cells were kept in an oil thermostat, which was constant within 0.06°.

The potentiometer was of the type described by Lewis, Brighton and Sebastian.[6] A Weston standard cell was substituted for the saturated standard cells used by them. In order that the total working resistance of the two resistance boxes might be still kept at 9999 ohms, the constant resistance of 182 ohms was replaced by one of 187 ohms. The standard cell was checked at intervals against several similar standards. The resistances of the potentiometer were checked under the conditions of actual use (compare Ref. 6).

Summary of Measurements and Calculations

By using the data of Lewis and Storch[10] we are able to avoid the necessity of carrying our measurements into very dilute solution and of comparing our electroplated silver electrodes with the more reproducible finely divided silver electrodes.[11] In practice each silver electrode was measured against a hydrogen electrode in 0.10 *M* hydrobromic acid, the observed electromotive force was compared with that given by Lewis and Storch,[2] and a correction, sufficient to make the values identical, was applied to the single electrode potential of the silver electrode. This correction was then applied to all electromotive-force measurements involving this electrode. As was stated before, these silver electrodes were checked against one another at frequent intervals, and against the hydrogen electrode in 0.10 *M* hydrobromic acid solution frequently enough to show that the five electrodes were not all changing in a uniform manner.

[6] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[7] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

[8] MacInnes and Beattie, THIS JOURNAL, **42**, 1118 (1920).

[9] Compare Pearce and Fortsch, *ibid.*, **45**, 2853 (1923).

[10] Ref. 2, Table III, p. 2550.

[11] Ref. 1, p. 407.

We have taken a value for E^0 of 0.0734, consistent with the data compiled by Lewis and Randall.[12]

In correcting the total hydrogen pressure to one atmosphere, it has been assumed that the total vapor pressure of the hydrobromic acid used was equal to that of pure water at the same temperature. For the more concentrated sulfuric acid solutions we have utilized the aqueous tension measurements of Brönsted.[13]

In calculating the values of the activity coefficients from the electromotive-force measurements, we have used the familiar formula,

$$0.1183 \log \gamma = E^0 - (E + 0.1183 \log m_{\pm}) \qquad (1)$$

In the following table, the values of *m*, the concentration of hydrobromic acid in moles per thousand grams of water (*i. e.* molality) are given in the second column; the measured values of the electromotive force, corrected to unit hydrogen pressure, in the third; and the corresponding values of the activity coefficient, in the fourth. These data are represented graphically (as circles) in a γ - $\mu^{1/2}$ plot, Fig. 2.

TABLE I

THE ACTIVITY COEFFICIENTS OF HYDROBROMIC ACID IN AQUEOUS SOLUTION

No.	m	E	γ	No.	m	E	γ
1	0.0850	0.2101	0.824	7	0.4970	0.1214	0.791
2	.1086	.1982	.812	8	.755	.0980	.822
3	.1878	.1812	.796	9	1.010	.0804	.864
4	.1878	.1814	.793	10	1.505	.0537	975
5	.2400	.1585	.795	11	1.505	.0534	.980
6	.3075	.1463	.787				

With the possible exception of the last two experiments, we believe that the measured values of the electromotive force are not in error by more than 0.2 or 0.3 mv. at most. While the values of E listed represent single experiments, each experiment involved measurements with from two to five different silver electrodes over a period of at least three days. If the electromotive force did not remain practically constant during this time, or if the (corrected) measurements with the several silver electrodes were not identical, the results were discarded. In the last two experiments, however, the electromotive force showed a gradual drift from the time the silver electrode was introduced into the solution. This made it impossible to obtain measurements in more concentrated solution. A

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[12] Ref. 1, pp. 334–336.

Values for E^0 obtained by combining the known values of γ_{HBr} (for (HBr) $\leqq 0.1\ M$) with our measured values of the e.m.f., uncorrected except for hydrogen pressure, always agreed with that derived from the values of Lewis and Storch within a few tenths of a millivolt. It therefore seems certain that there is a large error in the value for E^0 recently computed by Gerke [*Chem. Rev.*, 1, 337 (1925)] from the work of Pearce and Hart [THIS JOURNAL, **43**, 2483 (1921)].

[13] Brönsted, *Z. physik. Chem.*, **68,** 693 (1910).

similar effect was noticed at much lower concentrations by Pearce and Fortsch,[9] who studied the analogous cell with hydriodic acid.

To avoid confusion in interpreting the data presented in Table I the following values (Table II) of the activity coefficient of hydrobromic acid at round concentrations are given. These values were read from a smooth curve drawn through the points determined experimentally. They are probably accurate within 2–3%, but should be considered as preliminary values only. For purposes of comparison, the corresponding values of the activity coefficient of hydrochloric acid, taken from the averaged values of Lewis and Randall,[14] are also given.

TABLE II

THE ACTIVITY COEFFICIENTS OF HYDROBROMIC ACID IN AQUEOUS SOLUTION

m	0.01	.05	.10	.20	.30	.50	.75	1.00	1.50
HBr	0.924	.860	.814	.793	.786	.792	.821	.864	.977
HCl	0.924	.860	.814	.783	.768	.762	.788	.823	(.924)

The results of the experiments performed with solutions containing sulfates are listed in Tables III, IV and V. Since it was deemed more important to make these experiments comprehensive than to make them exact, no great effort was made to improve the accuracy of the individual experiments, and although the values of the activity coefficient derived from them may in some cases be in error by as much as 5%, the average error is very probably much smaller.

Table III shows the effect of varying the ratio of potassium bromide to sulfuric acid, while the total ionic strength remained constant. The data given in the seventh column, under the heading νH_2SO_4 are values of what we shall call the "ionic fraction." It may be defined as the ratio of the contribution of sulfuric acid to the ionic strength to the total ionic strength, that is,

$$\nu_{H_2SO_4} = \mu_{H_2SO_4}/\mu_{total} = 3(H_2SO_4)/[3(H_2SO_4) + (KBr)] \qquad (2)$$

The data given in the last column of this table, and the two following, will be referred to later.

TABLE III

THE ACTIVITY OF HYDROBROMIC ACID IN SOLUTIONS OF POTASSIUM BROMIDE AND SULFURIC ACID AT CONSTANT IONIC STRENGTH, 0.200

No.	H_2SO_4	KBr	$m_\pm$	E (corr.)	γ	$\nu_{H_2SO_4}$	$\gamma_{calcd.}$
1	0.01341	0.1603	0.0656	0.2318	0.699	0.201	0.684
2	.02330	.1300	.0777	.2243	.683	.349	.671
3	.0368	.0894	.0811	.2246	.650	.553	646
4	.0462	.0610	.0751	.2292	.641	.695	.638
5	.0587	.0231	.0521	.2481	.640	.894	.640

In Fig. 1, the activity coefficient of hydrobromic acid, Col. 6, is plotted against the "ionic fraction" of sulfuric acid. It should be noted that the

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[14] Ref. 1, Table 4, p. 336.

activity coefficient increases as the ionic fraction of sulfuric acid decreases below 0.60, but is practically constant for all values above this. This ionic fraction of 0.60 corresponds to a solution in which the molal concentration of bromide is twice that of the acid.[15]

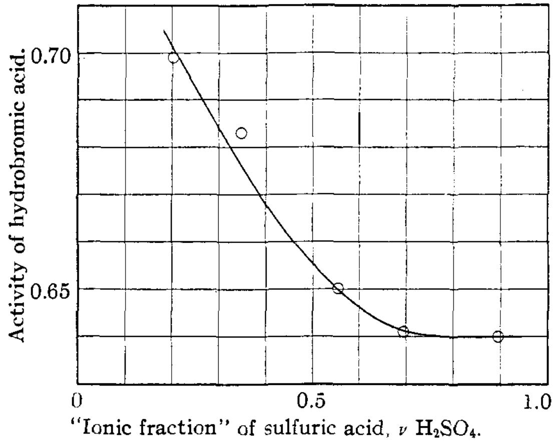

Fig. 1.—The activity of hydrobromic acid in solutions of potassium bromide and sulfuric acid at constant ionic strength.

In the experiments at varying ionic strength all solutions were made up so that the "ionic fraction" of sulfuric acid was greater than 0.6. These experiments were performed because they were necessary for the interpretation of existing rate data,[4a,b] not because they were thought particularly well adapted to the study of the general problem of activities in mixed electrolytes.

Table IV

The Activity of Hydrobromic Acid in Solutions of Potassium Bromide and Sulfuric Acid at Various Ionic Strengths

No.	(H_2SO_4)	(KBr)	$m_\pm$	E (corr.)	γ	μ	γ calcd.
1	0.02285	0.0402	0.0428	0.2540	0.695	0.108	0.683
2	.0379	.0177	.0366	.2628	.684	.132	.675
3	.0379	.0800	.0778	.2284	.629	.194	.652
4	.0545	.0341	.0610	.2393	.649	.197	.635
5	.1161	.1000	.1524	.1961	.603	.449	.621
6	.3180	.1003	.2526	.1739	.560	1.055	.583
7	.681	.1000	.3691	.1512	.596	2.14	.601
8	1.025	.1000	.4528	.1363	.649	3.18	.645
9	1.909	.1000	.6185	.1156	.711	5.83	...

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[15] It is interesting to note that this is in agreement with the prediction of Livingston and Bray, based upon rate measurements [This Journal, **45**, 2056 (1923)]. "The activity coefficient so obtained is practically independent of variations in the ratio (KBr)/(H_2SO_4) from 2.0 to 0.035."

In Fig. 2 these values of the activity coefficient are plotted against the square root of the ionic strength: they are represented as branched circles. The crosses in this figure represent the values of the activity coefficient of hydrobromic acid in potassium bromide-sulfuric acid solutions, obtained by Livingston and Bray from reaction rate measurements.[4b] For ionic strengths between 0.1 and 2.0, they are in good agreement with the values presented here. As far as we know, they constitute the first successful attempt to obtain activities from reaction rate measurements.

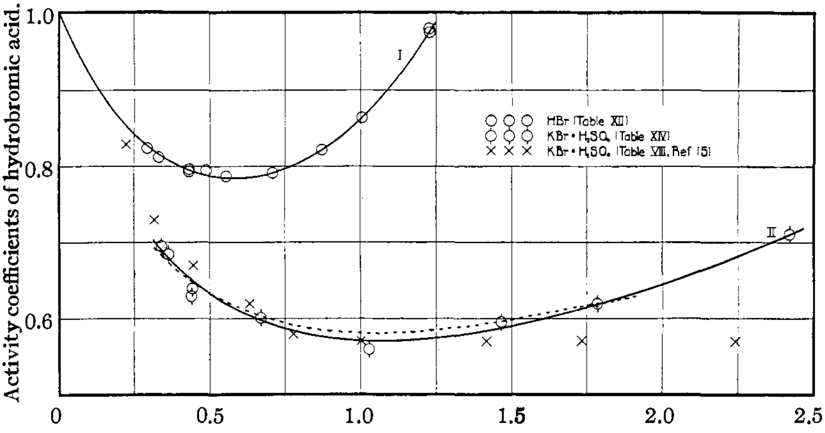

Fig. 2.—The activity coefficient of hydrobromic acid.

To obtain some measure of the relation between the activity coefficient of hydrobromic acid and the ratio $\Sigma(H^+)/\Sigma(SO_4^{--})$, a few experiments were performed in solutions containing 0.1039 *M* hydrobromic acid and various concentrations of sodium sulfate. These results are listed in Table V.

TABLE V

THE ACTIVITY OF HYDROBROMIC ACID IN SOLUTIONS OF HYDROBROMIC ACID AND SODIUM SULFATE

No.	Na_2SO_4	HBr	$m_\pm$	E (corr.)	γ	μ	γ calcd.
1	0.0500	0.1039	0.1039	0.2122	0.645	0.254	0.648
2	.1000	.1039	.1039	.2222	.531	.404	.515
3	.3000	.1039	.1039	.2412	.367	1.004	.295

These data demonstrate that sulfate ion greatly depresses the mean activity of hydrobromic acid. Since hydrosulfuric ion is known to be a moderately weak acid,[16] it is very probable that the observed effect is due to a decrease in the hydrogen-ion activity. It is apparent that the ionic-strength principle, as defined by Lewis and Randall,[17] does not

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[16] (a) Kolthoff, *Rec. trav. chim.*, **43**, 207 (1924). (b) Noyes and Stewart, THIS JOURNAL, **32**, 1133 (1910).

[17] Ref. 1, Chap. XXVIII, pp. 364–385.

hold even approximately for these results, or for those given in Tables III and IV. This deviation is not surprising, for the definition of the ionic strength involves the assumption of complete ionization of all electrolytes present.

A more obvious case, which does not differ fundamentally from those presented in Table V, is that of a solution A molal in respect to hydrobromic acid and B molal in respect to sodium hydroxide, where A is greater than B. Here, water would be regarded as a non-electrolyte, and the ionic strength (μ) would not be taken as (A + B), but rather as $^1/_2$ (A + A − B + B) or A; and the mean molality of the hydrobromic acid ($m\,\pm$) would not be taken as A, but rather as $\sqrt{(A - B)A}$. Although it would be entirely logical to interpret all measurements involving weak electrolytes in a similar fashion, we believe that it will prove more convenient to express them as usual, in terms of the stoichiometrical molalities, and to use our knowledge of the degree of ionization of the weak electrolyte involved to predict the approximate value of the activity coefficient in any given solution.

As an illustration of this method of prediction, let us compute the value of the activity coefficient of hydrobromic acid for a solution made up as acetic acid 0.1515 *M* and potassium bromide 0.150 *M*. Using the round value,[18] 1.8×10^{-5}, for the ionization constant of acetic acid, and assuming all other electrolytes present to be completely ionized, we may compute the following values for the several ion concentrations: $(H^+) = (Ac^-) = 0.00165\ M$, $(K^+) = (Br^-) = 0.150\ M$. To avoid confusion let us introduce two new functions, the "effective ionic strength" (μ') and the "effective mean molality" ($M\pm'$), which are defined for this case by the following equations.

$$\mu' = {}^1/_2[(H^+) + (Ac^-) + (K^+) + (Br^-)] = 0.15 \qquad (3)$$

$$m\pm' = \sqrt{(H^+)(Br^-)} = 0.0158 \qquad (4)$$

On the assumption of complete ionization,

$$\mu = [\Sigma(HAc) + \Sigma(KBr)] = 0.30 \qquad (5)$$

$$m\pm = \sqrt{\Sigma(KBr) \times \Sigma(HAc)} = 0.1508 \qquad (6)$$

Since we have placed the blame for the observed deviation entirely on the formation of undissociated acetic acid, it follows that the activity coefficient of 0.150 *M* hydrobromic acid ($\gamma_{\mu'\,\mathrm{pure}}$) should be equal to the mean activity (as determined by the electromotive-force measurements) divided by the "effective mean molality" of the solution.

$$\gamma_{\mu'\,\mathrm{pure}} = a\pm/m\pm' \qquad (7)$$

The activity coefficient of hydrobromic acid in the mixed solution is by definition,

$$\gamma_{\mu} = a\pm/m\pm \qquad (8)$$

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[18] Ref. 1, p. 310.

Combining Equations 7 and 8, and substituting a value (0.800) interpolated from Table II for $\gamma_{\mu'\,\text{pure}}$, we obtain

$$\begin{aligned}\gamma_{\mu} &= \gamma_{\mu'\,\text{pure}}\, m_{\pm}'/m_{\pm} \\ &= 0.800 \times 0.0158/0.1508 = 0.084\end{aligned} \qquad (9)$$

To obtain a corresponding experimental value we have used a solution of the same composition[19] as the electrolyte for a cell of the hydrogen-silver bromide-silver type. The mean value, corrected to atmospheric pressure, of two separate determinations of the electromotive force of the cell is 0.2934 volt. The corresponding value for the activity coefficient of hydrobromic acid is 0.092. These results are in sufficiently close agreement to demonstrate the value of this method of prediction. The difference between the observed and computed values is probably due chiefly to the increase of the ionization constant of acetic acid because of the added electrolyte.[20]

If we make some arbitrary or empirical assumption in regard to the ionization of sulfuric acid, we can apply this same treatment to our measurements of hydrobromic acid in the presence of sulfates. We shall assume that the first ionization of sulfuric acid is complete, and that the equilibrium constant for the second ionization has the value[21] 3.0×10^{-2}. A value of the activity coefficient has been computed, by means of this assumption, corresponding to each measured value. These values are given in the last columns of Tables III, IV and V. It is surprising to note that for these experiments this relation seems to hold over a much wider range than the ionic-strength principle, as applied to strong electrolytes, usually does. In Fig. 2 the dotted line was not drawn through the experimental points (crosses), but was determined directly from the solid line (for pure hydrobromic acid) by means of this principle. Its agreement with the experimental points needs no comment.

Summary

1. The mean activity of hydrobromic acid has been determined over the range 0.10 *M* to 1.5 *M*, by means of electromotive-force measurements of cells free from liquid junctions.

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[19] The acetic acid was purified by Dr. Webb of this Laboratory by repeated distillation and crystallization.

[20] Compare Brönsted, *J. Chem. Soc.*, [I], **119**, 574 (1921). Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

[21] This value was chosen empirically to fit the e.m.f. measurements presented in Table IV. It should be noted, however, that it is identical with the value obtained by Noyes and Stewart (Ref. 16 b) from conductivity measurements, and by Kolthoff (Ref. 16 a) from experiments with indicators.

It seems worth while to point out that the principle outlined here offers a new method for the determination of the degree of ionization of weak electrolytes, by means of e.m.f. measurements. It should be particularly valuable in the study of polybasic acids or of weak acids in the presence of "inert" salts.

2. The activity of hydrobromic acid has been determined in a variety of solutions containing sulfates, and these results have been compared with those of Livingston and Bray,[4b] which were based upon reaction-rate measurements.

3. A method for the prediction of the mean activity of strong electrolytes in the presence of weak electrolytes has been suggested, and has been tested with certain data presented here.

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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION. III. THE INTERPRETATION OF RATE MEASUREMENTS AS A FUNCTION OF THE ACTIVITY PRODUCT OF HYDROBROMIC ACID

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RECEIVED JULY 29, 1925 PUBLISHED JANUARY 8, 1926

That the steady-state rate of decomposition of hydrogen peroxide in a bromine-bromide solution is proportional to the activity product of the hydrobromic acid, has already been demonstrated by Livingston and Bray.[1] The evidence presented by them applies only to reaction mixtures of ionic strength less than 0.25, which do not contain sulfate. Because of the lack of activity data, they found it necessary to make the somewhat uncertain assumption that the activities of hydrobromic and hydrochloric acids are identical at identical concentrations.

Recently published values of the activity of hydrobromic acid in pure aqueous solutions, and in solutions containing sulfates,[2] make it possible to correct these computations, of Livingston and Bray, and to extend them to include solutions of higher ionic strength as well as to solutions containing sulfates.[3]

The Steady-State Rate in Terms of the Activity Product of Hydrobromic Acid

The existing rate data,[1,3] for solutions of hydrobromic acid and of potassium bromide and sulfuric acid, have been interpreted in terms of the recently published activity data, in Tables I and II. The steady-state concentrations of acid and bromide are given in the second and third columns, respectively; the first-order rate constant (k) in the third; and the "concentration" rate constant (K), as defined by Equation 1, in the fourth.

$$-d(H_2O_2)/dt = K(H_2O_2)(H^+)(Br^-) \qquad (1)$$

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[1] Livingston and Bray, THIS JOURNAL, **45**, 2048 (1923).

[2] Livingston, *ibid.*, **48**, 45 (1926).

[3] Compare Bray and Livingston, *ibid.*, **45**, 1251 (1923).