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THE SOLUBILITY PRODUCT OF BARIUM MANGANATE AND THE EQUILIBRIUM BETWEEN MANGANATE AND PERMANGANATE IONS[1]

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The reaction between manganates and water to give permanganates, manganese dioxide and a base, as illustrated by the equation

$$3K_2MnO_4 + 2H_2O \rightleftarrows 2KMnO_4 + MnO_2 + 4KOH \qquad (1)$$

is reversible.[3] Sackur and Taegner,[4] after unsuccessful attempts to determine the equilibrium constant for the reaction by chemical means, turned to electrochemical methods. Their calculations involve the use of the degree of ionization of various substances and of transference numbers in solutions of high concentration of alkali. The quantities in question are not known with any degree of accuracy and their results are therefore only in the nature of rough approximations. While the work to be described in this paper was in progress, an article was published by Ruby[5] dealing with the equilibrium in question. As pointed out by Ruby, the analytical methods employed were subject to errors of several per cent. For this reason considerable uncertainty is attached to the results. Finally, the work was carried out at 45° because at lower tem-

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[1] Part I of this paper was presented at the meeting of the National Academy of Sciences, held in December, 1921, in Chicago. Part III was presented at the Intersectional Meeting of the American Chemical Society held May 4, 1923, at Urbana, Illinois.

[2] The material of this paper is taken from a thesis presented by H. B. Siems to the faculty of the Ogden Graduate School of Sciences of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Diefenbach, Ger. pat., 195,323, **1908.**

[4] Sackur and Taegner, *Z. Elektrochem.*, **18,** 718 (1912).

[5] Ruby, This Journal, **43,** 294 (1921).

peratures equilibrium was reached too slowly. The method employed by us is entirely different from those employed by the preceding workers in the field; it avoids most of the difficulties encountered by them and can be used satisfactorily at ordinary temperatures.

Our method is based on the fact that barium manganate is very insoluble, but that it nevertheless reacts with water to give barium permanganate, barium hydroxide and manganese dioxide. With this material as source of manganate ion the concentration of all of the components of the system is so low that 100% ionization may be safely assumed. The concentration of manganate ion can be determined by calculation from the solubility product of the barium manganate—a procedure which avoids the difficulty of determining the concentration of this ion in the presence of permanganate. The amount of manganate ion present is too small to affect the color of the permanganate, and the latter can therefore be determined colorimetrically. Finally, the danger of errors due to decomposition of manganate or permanganate is avoided because these ions are in equilibrium with solid barium manganate and decomposition in solution is compensated by further reaction of the solid with water.

Before proceeding to the solution of the main problem by this method, it was necessary to determine the solubility product of barium manganate. In this part of the work, data were obtained of interest in connection with the question of the validity of the solubility-product relationship in solutions containing moderately high concentrations of an electrolyte which yields no ion common to the slightly soluble salt. In the second place, a method for determining very small concentrations of hydroxide ion in the presence of the highly colored, strongly oxidizing permanganate ion had to be developed. This paper is therefore divided into three sections; the first two dealing with the two problems just mentioned and the third with the determination of the equilibrium between manganate and permanganate ion.

I. The Solubility Product of Barium Manganate

The solubility product of barium manganate cannot be determined directly from measurements of the concentration of a saturated solution of the salt in water for two reasons. In the first place, the solubility of the salt is too small for accurate measurement; in the second place, water decomposes the dissolved barium manganate very extensively according to an equation analogous to Equation 1. The desired solubility product was determined indirectly by measuring equilibrium concentrations in the reaction

$$BaMnO_4 + K_2CO_3 \rightleftharpoons BaCO_3 + K_2MnO_4 \qquad (2)$$

in mixtures prepared by shaking solutions of various amounts of potassium carbonate and potassium hydroxide with a considerable excess of solid barium manganate and solid barium carbonate.[6] Potassium hydroxide is added to prevent decomposition of the potassium manganate and hydrolysis of carbonates. Application of the solubility-product principle leads to the equation,

$$\frac{[MnO_4^{--}]}{[CO_3^{--}]} = \frac{K_{BaMnO_4}}{K_{BaCO_3}} \qquad (3)$$

for the equilibrium state. Concentrations are expressed by the customary symbols; K_{BaMnO_4} is the solubility product of barium manganate and K_{BaCO_3} the solubility product of barium carbonate. The latter has the value,[7] 8.1×10^{-9} at 25°. The source of manganate ion is the potassium manganate and of carbonate ion, potassium carbonate. Hence we may write,

$$K_{BaMnO_4} = 8.1 \times 10^{-9} \times \frac{\gamma_1\,[K_2MnO_4]}{\gamma_2\,[K_2CO_3]} \qquad (4)$$

In Equation 4, γ_1 is the activity coefficient, or degree of ionization, of potassium manganate and γ_2 that of the potassium carbonate in the mixture. These degrees of ionization are not known, nor is there any reliable method for obtaining them because of the presence of the third electrolyte, potassium hydroxide. Potassium manganate and potassium carbonate are, however, salts of the same ionic type and the maximum total concentration employed is approximately 0.1 M. With these considerations in mind we may provisionally assume that the activity coefficients of the two salts are identical in the solution in which both are present. The equation then becomes,

$$K_{BaMnO_4} = 8.1 \times 10^{-9} \times \frac{[K_2MnO_4]}{[K_2CO_3]} \qquad (4a)$$

Application of this equation to the experimental data (Table II) gives constant values for K_{BaMnO_4}. If we admit that the solubility-product relationship, expressed in the terms herein used, is applicable, constant values for K_{BaMnO_4} can be obtained from Equation 4a only if $\gamma_1 = \gamma_2$ or if the ratio γ_1/γ_2 has a constant value. On the other hand, it is extremely probable that at very low concentrations the activity coefficients of these two salts of the same ionic type are identical. If therefore the ratio γ_1/γ_2 is constant, the activity coefficients must also be equal up to concentrations of 0.1 M which is the highest value for which the constancy of K_{BaMnO_4} holds. In order to test these possibilities further, we varied not only the concentration of the two salts but that also of the potassium hydroxide. Finally also we substituted for the potassium salts and for potassium hydroxide the corresponding sodium compounds (Table

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[6] Theoretically it might seem unnecessary to add solid barium carbonate, since it is formed during the course of the reaction. We found, however, that reproducible equilibrium constants could not be obtained unless the solid is added—unquestionably because of the formation of supersaturated solutions.

[7] McCoy and Smith, THIS JOURNAL, **33**, 468 (1911).

IIa). In spite of all of these changes the value of K_{BaMnO_4} remains constant. It would require what seems to us an improbable cancellation of errors to bring about the constancy observed unless the assumptions herein made are actually correct to within the experimental error of the experiments.

Preparation and Analysis of Barium Manganate.—Fusion of barium salts with manganese dioxide and barium hydroxide[8] yields a green, very impure product. Reduction of barium permanganate with hydrogen peroxide[9] did not give barium manganate of high enough purity. Treatment of potassium manganate with barium chloride[10] yields a product which is relatively pure, but which contains traces of chloride. The latter is objectionable in our work. Modifications of this method proved very time-consuming. The following procedure was finally adopted.

A boiling, saturated solution of barium hydroxide is filtered through a hot-water funnel into a hard glass round-bottom flask, from which steam is escaping in order to reduce to a minimum possible contamination with carbon dioxide. To the boiling solution small amounts of a saturated solution of potassium permanganate are added at short time intervals.[11] The solution is kept boiling for four hours. The amount of potassium permanganate used is such that, at the end of this time, barium hydroxide is slightly in excess of the amount required for the reaction $4Ba(OH)_2 + 4KMnO_4 \longrightarrow 4KOH + 4BaMnO_4 + 2H_2O + O_2$. The blue-black barium manganate is allowed to settle and is then washed with large amounts of conductivity water until the supernatant liquid gives only a faint test for barium. As much water as possible is then removed by decantation and by distillation under reduced pressure. The residual solid is dried in an electric oven at 110°, the drying is completed in a vacuum desiccator over phosphorus pentoxide and the material is finally stored over potassium hydroxide.

The usual method for analyzing manganates[12] cannot be used for barium manganate because the presence of sulfuric acid causes deposition of barium sulfate on the material which has not yet reacted, and thus prevents complete interaction. The following procedure gives excellent results.

The solid barium manganate is suspended in an excess of phosphoric acid and is thereby decomposed according to the reaction, $3BaMnO_4 + 4H_3PO_4 \longrightarrow 2Ba(H_2PO_4)_2 + Ba(MnO_4)_2 + MnO_2 + 2H_2O$. To the mixture of suspended manganese dioxide and dissolved barium permanganate an excess of a standardized, approximately 0.1 N solution of ferrous phosphate is added. Both manganese dioxide and the permanganate react with this solution. The excess is then titrated back with potassium permanganate. The end-point is sharp and the titration can be carried out at room temperature. This procedure gives the total oxidizing power of the material. To determine how much of this is due to barium manganate and how much to manganese dioxide, present in the sample as an impurity, another portion is analyzed. In this analysis, the mixture ob-

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[8] Rosenstiehl, *Dingl. Polytech. J.*, **177**, 409 (1864). The compound obtained is said to have the composition $3BaO.2MnO_3$.

[9] Gorgeau, *Compt. rend.*, **110**, 958 (1890).

[10] Kassner and Keller, *Arch. Pharm.*, **239**, 473 (1901).

[11] Oxygen is given off on the addition of potassium permanganate to barium hydroxide and the mixture may be ejected from the flask with almost explosive violence if too large an amount of the permanganate is added at once.

[12] Askenasy and Klonowski, *Z. Elektrochem.*, **16**, 108 (1910).

tained by treatment with phosphoric acid is filtered and only the dissolved barium permanganate is titrated. From the titration the amount of manganate originally present is readily calculated. Application of this procedure to a sample of the barium manganate showed that it consisted of 92.04% of barium manganate and 2.74% of manganese dioxide. The remaining 5.22% was barium carbonate, as is shown by the fact that the total barium was found to be 52.94% while the value calculated on the assumption that the undetermined 5.22% is barium carbonate is 52.97%.[13]

The barium manganate, prepared as described above, is a very fine powder. It is therefore quite possible that adsorption of ions by the solid might sufficiently change the concentrations of solutions to affect the correctness of the method of calculation. In order to avoid uncertainty due to this possibility, the following experiments were carried out. Several 250cc. glass-stoppered bottles[14] containing solutions of known content of potassium hydroxide and potassium carbonate, 0.3 g. of barium carbonate and various amounts of solid barium manganate were shaken for four days in a thermostat kept at 25 ± .01°. The concentration of the manganate ion was then determined by the ordinary method of titration which could here be employed because the barium concentration was very low. Row 1 of Table I gives the amount of solid barium manganate added to 80 cc. of the solution used and Row 2 the concentration of manganate in the equilibrium mixture.

TABLE I

EFFECT OF VARIATION OF THE AMOUNT OF SOLID BARIUM MANGANATE ON ITS APPARENT SOLUBILITY IN SOLUTIONS OF POTASSIUM CARBONATE

Barium manganate added to 80 cc. of solution

$BaMnO_4$, mg.	85	95	185	235	275	305	666
K_2MnO_4, moles per l.	0.00104	110	130	123	156	146	177
$BaMnO_4$, mg.	2360	2890	2940	3205	3705	...	...
K_2MnO_4, moles per l.	0.00255	256	255	256	255	...	...

Since the concentration of the original solution was the same in all of the experiments recorded in Table I, one would expect the amount of solid barium manganate added to have no influence on the final concentration of the solution. The fairly steady increase in the manganate concentration might seem to indicate a disturbing influence of adsorption, if it were not for the fact that when the amount of solid added reaches a certain value further addition produces no further increase in the concentration of manganate. The phenomenon may therefore be explained on purely mechan-

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[13] The solution of ferrous phosphate used in these analyses was prepared by treating pure "reduced" iron powder with 30% phosphoric acid. The reaction was carried out in a flask stoppered with a Bunsen valve. After all of the iron had dissolved, more phosphoric acid was added and the solution titrated roughly with 0.1 *N* potassium permanganate. The solution was then diluted with freshly boiled conductivity water to 0.1 *N* strength and its factor accurately determined. Such solutions change their factors rather slowly when kept in dark bottles and away from sunlight. A solution which was 0.1092 *N* was kept in a dark bottle for 119 hours. During this time the factor had changed to 0.101 *N*. Another sample, kept in an ordinary bottle in diffused sunlight, had fallen to 0.07485 *N* in the same length of time. In all experiments, the factor of the ferrous phosphate solution was determined shortly before use.

[14] The stopper and neck of the bottles were covered with a rubber cap to prevent contamination of the contents of the bottles with the water from the bath.

ical grounds—when the amount of solid manganate is small, the barium carbonate precipitated during the course of the reaction completely coats it and prevents attainment of equilibrium. But when barium manganate is present in great excess, its surface is so large that it cannot be completely coated by the barium carbonate which is precipitated.[15]

The actual determinations of the solubility product of barium manganate were made in a manner quite similar to that just described. The amount of barium manganate used was in excess of the minimum quantity shown to be necessary in Table I; 0.3 g. of barium carbonate was again added, but the concentrations of potassium carbonate and of potassium hydroxide were varied in the different experiments. The carbonate contained in the solutions of potassium hydroxide was determined by the method of Küster[16] and enough potassium carbonate was then added to bring the total carbonate concentration to the desired value. The mixtures were shaken for from 6 to 32 days in a thermostat at 25°. After equilibrium was thought to have been reached, the solutions were filtered through several layers of very fine asbestos in a special filtering device which made possible exclusion of atmospheric carbon dioxide. In the analyses, sulfuric acid, from which reducing material had been removed by treatment with potassium permanganate, was used.

The first column of Table II contains the carbonate concentration. This is obtained by subtracting from the original concentration of carbonate

TABLE II

SOLUBILITY PRODUCT OF $BaMnO_4$ AT 25°

Concn. K_2CO_3	Concn. K_2MnO_4	Concn. KOH	$K_{BaMnO_4} \times 10^{10}$
0.0246[a]	0.0007525[b]	0.982	2.48
.0255[a]	.0007575[b]	.982	2.44
.03692	.001102	.662	2.42
.05080	.001565	.662	2.44
.06918	.002125	.982	2.49
.07318	.002250	.662	2.49
.08126	.002482	.662	2.47
.08533	.002605	.982	2.47
.08538	.002565	.982	2.43
.09579[a]	.002890	.982	2.44
.09736	.003010	.662	2.50
.10142	.003100	.982	2.48
.10141	.003107	.982	2.48

[a] The carbonate was determined gravimetrically.

[b] Equilibrium was reached from the manganate side.

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[15] The data on the minimum quantity of barium manganate required in these experiments can be used to obtain information concerning the thickness of the deposit of barium carbonate. Since some uncertainty is attached to these calculations they are not reproduced here.

[16] Küster, *Z. anorg. Chem.*, **13,** 127 (1897).

that of the manganate in the equilibrium mixture. This method of calculation is based on the fact that in the reaction one mole of manganate is formed from one of carbonate, as shown in Equation 2.[17] In the second column are given the concentrations of potassium manganate determined by titration or colorimetrically. The third column contains the concentration of the potassium hydroxide and the fourth the values of the solubility product of barium manganate, calculated according to Equation 4a. Concentrations are expressed in terms of moles per liter.

It is seen from these data that the solubility product of barium manganate is constant over a moderately wide range of concentrations of the two common ions and in the presence of varying amounts of potassium hydroxide. Its value is 2.46×10^{-10} at 25°. It should be added, however, that when the concentration of potassium carbonate is increased materially above the highest value recorded in the table, the value of the solubility product gradually rises. Similar effects have been noted by others in similar work.[18] In the range of concentrations used in the determination of the equilibrium between manganate and permanganate, for which this solubility product is necessary, the concentrations involved are always far below the maximum value mentioned.

While the fact that changes in the concentration of potassium hydroxide do not affect the solubility product, as shown in Table II, makes fairly certain the correctness of the assumption that the presence of this electrolyte does not influence the absolute value of the constant, it was thought best for the reasons given in the theoretical discussion to corroborate this conclusion by making a few determinations in which potassium hydroxide and carbonate are replaced by the corresponding sodium compounds. Sodium manganate is far less stable than potassium manganate and the results in these mixtures are therefore not quite as uniform as those in which potassium compounds were used. It will be noted that those ex-

TABLE IIa

SOLUBILITY PRODUCT OF $BaMnO_4$ AT 25°

Concentration of NaOH, 0.7176

Concn. Na_2CO_3	0.02614	0.04295[a]	0.08467	0.04572
Concn. Na_2MnO_4	0.0007612	0.001272	0.002330	0.001185
$K_{BaMnO_4} \times 10^{10}$	2.36	2.40	2.13	2.10

[a] The carbonate was determined gravimetrically.

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[17] This method of calculation leads to incorrect results if any of the dissolved manganate decomposes during the course of the experiment. The final carbonate concentration was, therefore, actually determined in a few experiments, by acidifying the solutions and weighing the liberated carbon dioxide in the usual way. The calculated and observed values invariably checked in the experiments in which potassium salts were used. Sodium salts are discussed below.

[18] See, for example, Noyes and Kohr, *Z. physik. Chem.*, **42,** 336 (1903). Foote, *ibid.*, **33,** 740 (1900). Meyerhofer, *ibid.*, **53,** 513 (1905).

periments in which the carbonate was determined gravimetrically, most closely reproduce the value of the constant as found in Table II. This is to be expected, since calculation of the carbonate from the manganate concentration leads to erroneous results unless the manganate is perfectly stable.

In view of the instability of sodium manganate, the agreement in the values of the solubility product obtained in the potassium and in the sodium salts solutions is satisfactory. We may therefore calculate the value of the manganate ion concentration from that of barium ion by the use of the value for the solubility product of barium manganate as given in Table II.

II. Determination of Very Small Concentrations of Hydroxide Ion in the Presence of Permanganate

Several methods for the determination of hydroxide ion in the presence of permanganate are mentioned in the literature. Craig[19] reduces the permanganate and manganate to manganese dioxide by means of hydrogen peroxide. The alkali originally present and that liberated in the course of the reduction are titrated with standard acid using phenolphthalein as indicator. Two sources of inaccuracy were found when the method is applied to solutions of low hydroxide-ion content. In the first place, it is very difficult to remove the last traces of hydrogen peroxide from the mixture[20] and these small traces destroy the sharpness of the end-point of the indicator. In the second place, manganese dioxide absorbs alkali[21] to such an extent that the accuracy of titrations in solutions from which manganese dioxide has been freshly precipitated is greatly impaired. A similar method employed by Ruby[5] is fairly reliable when the hydroxide-ion concentration is high, but is not accurate for low concentrations. Reduction of the permanganate by oxalic acid in solutions to which a known amount of sulfuric acid had been added and titration of the acid after removal of permanganate, likewise proved unsatisfactory because end-points in the presence of manganese salts are not sharp enough to be satisfactory for the analysis of very dilute solutions. The reason for this is that manganous compounds are oxidized by air as the solution approaches neutrality and the color changes which accompany this oxidation mask the end-point of the indicator. Determination of the alkalinity by means of the hydrogen electrode is not feasible because of the presence of permanganate.[22]

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[19] Craig, *J. Soc. Chem. Ind.*, **38**, 96 (1919).

[20] Lottermoser and Lehmann [*Kolloid Z.*, **29**, 251 (1921)] have shown that the rate of decomposition of hydrogen peroxide in weak alkaline solutions is very low.

[21] See, for example, Abegg, "Handbuch der Anorganischen Chemie," S. Hirzel, Leipzig, **1913**, vol. IV, part 2, p. 822.

[22] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Co., Baltimore, **1923**, p. 265.

The minimum in the conductivity of mixtures of solutions of an acid and of a base, which occurs at the neutral point, has frequently been used as a means of determining the end-point of titrations. The usefulness of this method, particularly when colored substances such as permanganates are present, has been pointed out by Küster.[23] Harned[24] showed the necessity of removing carbon dioxide. For this purpose he made the alkaline solutions slightly acid with a known amount of standard acid and boiled the mixture at reduced pressure. Application of Harned's method to the extremely dilute solutions employed by us did not give satisfactory results, probably because of slight losses of acid by spraying. We therefore made use of a titration vessel whose construction is made clear in Fig. 1. Carbon dioxide is removed by passing a carefully purified stream of air through the acidified solutions. The design of the apparatus is such that after approximately 80 cc. of solution has been put into the vessel, the cell constant is not affected by the addition of further amounts.

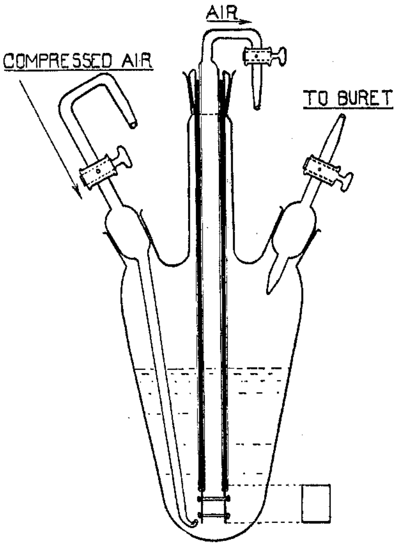

Fig. 1.

In applying the conductivity method of titration to very dilute solutions, difficulties are encountered which are not noticed when solutions of ordinary concentrations are employed, as will be pointed out below. The titrations were made with 0.01 *N* barium hydroxide solution, protected from carbon dioxide in the usual way. The solution to be analyzed was diluted in the conductivity vessel with conductivity water to about 150 cc. to avoid variation in the cell constant. The alkali was added in small portions and after each addition the vessel was thoroughly shaken and a moderately vigorous stream of air passed through it to ensure thorough mixing. The conductivity of the solution was then measured.[25] As long as the solutions contain an appreciable excess of acid, the readings of the conductivity are found to be constant immediately after mixing.

[23] Küster, *Z. anorg. Chem.*, **42,** 229 (1904).

[24] Harned, THIS JOURNAL, **39,** 256 (1917).

[25] The method of conductance measurement was that described by Washburn, THIS JOURNAL, **38,** 2431 (1916) and **39,** 235 (1917), and by Schlesinger and Reed, *ibid.*, **41,** 1727 (1919). It was found unnecessary to keep the conductivity vessel in a constant-temperature bath since, with the relatively large amounts of solution used (150 cc.), temperature changes were too slow to influence the minimum point.

But as the neutral point is approached, this is no longer the case. The conductivity gradually changes, sometimes over a period of half an hour or more, even though mixing has been adequate. Evidently a small amount of hydrogen ion is adsorbed in the electrodes and is released by them very slowly to neutralize the alkali added. This condition persists until a considerable excess of alkali has been added. The condition appears in exaggerated form when the acid is added to alkaline solutions. The difficulty can be reduced to a minimum if, when the end-point has been nearly reached, from 0.4 to 0.5 cc. of alkali is added at a time. In this way constancy of reading is attained in a few minutes, but it is always necessary by repeating the readings to make sure that constancy has been attained. The last few points of the curve on the acid side and the first few on the alkali side need not be used in determining the end-point, as the latter can be found by graphical extrapolation. On the other hand, points taken too far from the end-point must likewise not be used, since in these the effect of dilution plays a disturbing role. We employed points lying

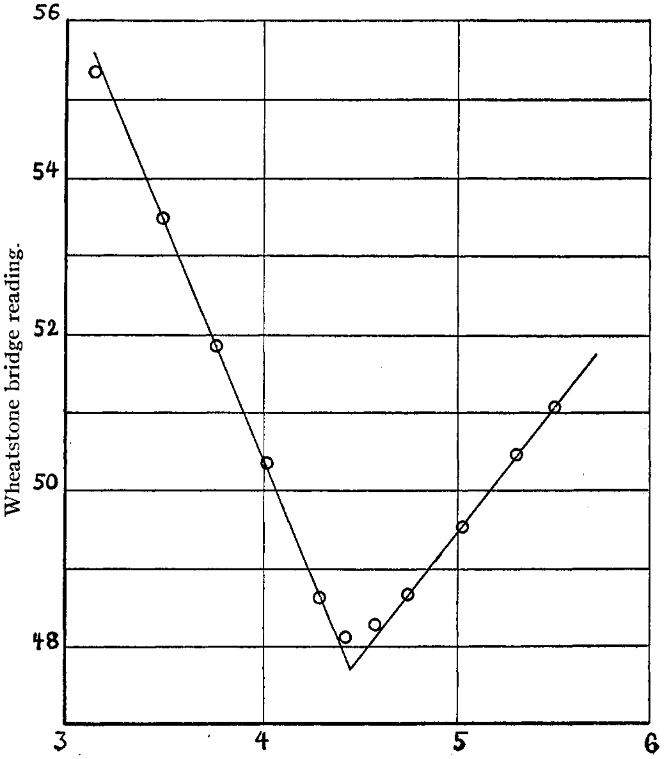

Fig. 2.

at positions corresponding to between 1 and 2 cc. of 0.01 *N* solution from the end-point. (See Fig. 2.) With these precautions we found it possible to make titrations of solutions as dilute as 0.00005 *N* after dilution with an accuracy of approximately 0.4% and with much higher accuracy for somewhat more concentrated solutions.

III. The Equilibrium between Manganate and Permanganate Ions

The equilibrium between manganate and permanganate ions was determined by studying the reaction

$$3BaMnO_4 + 2H_2O \rightleftarrows Ba(MnO_4)_2 + MnO_2 + 2Ba(OH)_2 \qquad (5)$$

The barium manganate is extremely slightly soluble, as shown in the first part of this paper. As a result, the concentrations of all of the other substances are so small that complete ionization may be safely assumed to occur. Manganese dioxide is present as a solid and its concentration is therefore to be considered constant.[26] We may therefore write for the equilibrium condition

$$\frac{[MnO_4^-]^2\ [OH^-]^4}{[MnO_4^{--}]^3} = K_{eq.} \qquad (6)$$

Concentrations, in moles per liter, are expressed by the bracketted symbols, and $K_{eq.}$ is the equilibrium constant. The concentration of permanganate ion can be determined colorimetrically and that of hydroxide ion by the method described in Part II of this paper. The concentration of the manganate ion is calculated according to the equation $[MnO_4^{--}] = 2.46 \times 10^{-10}/[Ba^{++}]$ as shown in Part I. Since the sources of barium ion are the barium permanganate and barium hydroxide formed in the reaction, it was hoped that its concentration could be calculated from the concentrations of the permanganate and the hydroxide ions. Unfortunately, this did not prove possible. Even though Pyrex or Jena glass bottles were used as reaction vessels, soluble matter from the glass reacted with the solutions and caused precipitation of some of the barium, probably as silicate. It therefore became necessary to determine the barium analytically. After trying several methods described for this purpose in the literature, we found the precipitation of barium as sulfate the most reliable. The solutions to be analyzed were so dilute that the weight of barium sulfate obtained from 100 cc. varied between 0.016 and 0.0016 g. and, although every precaution was of course taken, these quantities are so small that the experimental error involved in the determination of the barium was far greater than that of the other quantities involved. Since the concentration of the barium enters into Equation 6 raised to third power, a weighing error of 0.1 mg. may produce an error of from 15 to 20% in

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[26] It is possible that barium manganite ($BaMnO_3$) is formed in the reaction. It can be shown that the equilibrium equation would be unchanged, even if that were true, on the very reasonable assumption that barium manganite is hydrolyzed—even though the assumed hydrolysis proceeds only to the slightest extent.

the apparent value of the constant. Of course, this error was somewhat cut down by using as large amounts of solution as possible, but the necessity of using the sulfate method for barium materially decreased the accuracy of our results.[27]

The solutions for the determination of the equilibrium were made up in glass-stoppered Jena "resistenz" bottles. To 150 cc. of conductivity water and 2.5 g. of solid barium manganate, 0.5 g. of a mixture of solid barium manganate and a small amount of a paste containing manganese dioxide[28] was added. The bottles were then fitted with rubber caps and rotated in a thermostat at 25 ± 0.01°. The bottles were kept in the thermostat for from six to thirty-six days; equilibrium seems, however, to have been attained in the shorter interval. The equilibrium concentrations were altered by using in some experiments the suspensions in water, by adding nitric acid to others in order to decrease the hydroxide-ion concentration and by adding various small amounts of barium hydroxide to another set. In the latter, equilibrium is attained from the permanganate side, since permanganate is formed immediately on suspending the manganate in water and the addition of barium hydroxide causes a very noticeable decrease in the permanganate color. When the solutions were ready for analysis, they were removed from the bottles by means of a special filtering device in which they were filtered out of contact with atmospheric carbon dioxide and in which changes in temperature were reduced to a minimum.

Table III gives the results of analyses carried out as described above.[29] The data for the concentration of manganate ion are calculated from the solubility product of barium manganate as described above. All concentrations are expressed in moles per liter. The last column gives the value of the equilibrium constant calculated according to Equation 6.

[27] Use of microchemical methods might have improved the results, but the equipment for such work was not at hand. Experiments are under way on the development of a more accurate method for the determination of minute amounts of barium and it is hoped to repeat the determinations of the constant with a higher degree of accuracy at a later date.

[28] The manganese dioxide paste was prepared by passing carbon dioxide for four hours through a suspension of barium manganate in boiling water. The solid material was allowed to settle and the supernatant liquid was removed by decantation. The solid was then repeatedly washed with boiling conductivity water. In this way manganese dioxide in the form which is obtained in the course of the reaction is added to the mixture. Attainment of equilibrium seems to be hastened by this procedure.

[29] A slight correction is applied to the concentration of hydroxide ion as obtained by the conductivity titration. The solutions are saturated with barium carbonate which reacts with the nitric acid of which a known amount is added to the solution before titration. The carbonate therefore appears as hydroxide in the titration. From the solubility product of barium carbonate (8.1×10^{-9}) and the concentration of barium ion, determined by analysis, the amount of barium carbonate in the solutions can be calculated. The concentration of hydroxide ion in some of the solutions is so small that the amount of barium carbonate contained in them causes an appreciable, although not very large, error if the correction is not applied.

TABLE III

EQUILIBRIUM CONSTANT OF THE REACTION BETWEEN MANGANATE, PERMANGANATE AND HYDROXIDE IONS

$[OH^-] \times 10^3$	$[MnO_4^-] \times 10^3$	$[Ba^{++}] \times 10^3$	$[MnO_4^{--}] \times 10^7$	Days in thermostat	$K_{eq.}$
4.131	0.0331	1.06	2.32	9	25.5
2.715	.0709	1.11	2.22	7	24.6
1.957	.1848	0.69	3.56	6	11.1
2.077	.3466	.43	5.72	31	12.0
1.297	.3839	.72	3.42	36	10.5
0.957	.4613	1.03	2.39	9	13.8
1.082	.8714	0.69	3.57	6	22.9
0.848	.8742	.71	3.46	17	9.5
				Mean	16.2

The values for the constant show very considerable variation, but in judging the results one must bear in mind that the concentration of hydroxide ion appears in the equation for the constant raised to the fourth power, that of the permanganate ion raised to the second and that of the manganate raised to the third powers. Relatively small errors are therefore greatly magnified. When our results are compared with those of previous investigators,[4,5] it will be seen that the deviations in the values of the constants are much smaller than in the work of the others. In addition, our value of the constant is the first which is at all reliable for ordinary temperatures. That the deviations in our results are due to small experimental errors in determining the various quantities involved is shown by the fact that the variations in the constants are not related in any way to systematic changes in any of the factors.

Some conclusions might be drawn with regard to the heat of the reaction by using our values for the constant at 25° and those of Ruby[5] at a higher temperature, but owing to the large deviations from constancy in both sets of values, little importance would be attached to such a calculation. It is intended at some future time to repeat our work at other temperatures and to avoid the difficulty caused by the uncertainty in the determination of barium.[30]

Summary

1. A method is described of preparing barium manganate of a fairly high degree of purity and a method of analysis of the substance has been worked out. The method of analysis involves the use of ferrous phosphate as a reducing agent, which may be of value in other connections.

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[30] This can be done in two ways: by finding a more accurate method for the determination of barium, and by avoiding the introduction of soluble material from the reaction vessel. The use of quartz may be of value although the solutions are slightly alkaline. We attempted to avoid the difficulty by coating the glass. Coatings of wax, paraffin and manganese dioxide did not withstand the rotating of the vessels. Coatings of silver are rapidly attacked and other coatings seemed to contain enough pores to make them useless.

2. The solubility product of barium manganate has been calculated on the assumptions that the solubility-product relationship is applicable to moderately dilute solutions of two salts in contact with the solid phases of both and that the two salts, potassium manganate and potassium carbonate, which are of the same ionic type, are ionized to the same extent in solutions containing both of them. The value of the solubility product calculated on these assumptions has been found to be 2.46×10^{-10} when the value 8.1×10^{-9} is used for the solubility product of barium carbonate. The fact that the values for the solubility product thus calculated are actually constant over fairly wide ranges of concentration of the two salts and of the potassium hydroxide present to prevent hydrolysis, and that they are unaffected by substituting sodium for potassium compounds has been taken to lend a considerable degree of plausibility to the assumptions made.

3. The conductivity method for determining the end-point of an acidimetric titration has been applied to extremely dilute solutions. Special precautions necessary under these conditions are pointed out and a convenient apparatus is described.

4. The equilibrium between manganate and permanganate ions has been studied at 25°. The preliminary value for the equilibrium constant,

$$K_{\text{eq.}} = \frac{[\text{MnO}_4^-]^2\,[\text{OH}^-]^4}{[\text{MnO}_4^{--}]^3}$$

has been found to be 16 ± 7.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF SODIUM BARIUM AND CADMIUM DITHIONATES IN WATER SOLUTION[1]

BY JACOB CORNOG AND W. E. HENDERSON

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In several places in the literature[2] may be found the statement that solutions of dithionate salts when heated decompose according to the general reaction

$$\text{MS}_2\text{O}_6 = \text{MSO}_4 + \text{SO}_2 \tag{1}$$

where *M* is any metal coming above hydrogen in the displacement series. Yet nowhere can be found record of quantitative investigation of the end products of decomposition nor is there any record indicating that solutions of alkali or alkali earth dithionates have thus been decomposed.

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[1] Abstract of a part of a thesis submitted in 1922 to the Graduate School of the Ohio State University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Welter and Gay Lussac, *Ann. chim. phys.*, **10**, 312 (1819). Heeren, *Pogg. Ann.*, **7**, 55, 171 (1826). Klüss, *Ann.*, **246**, 179 (1888).