tion which might be put upon this divergence is that the cupric oxide begins to dissociate at about 900°. In the neighborhood of 1000° we are no longer measuring the vapor pressure of cupric oxide, but of cuprous oxide, or of a solution of cuprous and cupric oxides. Unfortunately for this interpretation, however, Smyth and Roberts have shown that solid solution of cuprous oxide in cupric oxide does not take place in the temperature range where both oxides remain solid. Furthermore, the same authors have shown that the dissociation temperature of cupric oxide in equilibrium with oxygen gas at a pressure of 750 mm. is about 1100°, instead of 900°.

It is hardly to be expected, however, that the method which we have described is reliable enough, especially at the higher temperatures, to justify conclusions of more than a qualitative nature.

Summary

1. Using a catalytic method of determining copper in extremely small concentrations, the vapor pressure of copper oxide has been determined by the dynamic method at four temperatures, and found to be about 1×10^{-7} mm. at 600°, 1×10^{-4} mm. at 800°, 7×10^{-4} mm. at 900°, and 1×10^{-4} mm. at 1000°.

2. The calculated heat of vaporization for copper oxide in the range 600–800° is 63,000 calories.

3. The vapor pressure of copper at 810°, almost 1200° lower than for any previously recorded data, is at least 5×10^{-7} mm.

Columbus, Ohio

[Contribution from the Chemical Laboratory of the University of Michigan]

THE ELECTROMETRIC TITRATION OF THE HALIDES IN THE PRESENCE OF ONE ANOTHER

By H. H. Willard and Florence Fenwick

Received October 25, 1922

I. The Determination of Total Halide by Titration with Silver Nitrate

The usual silver titration of the halides and thiocyanate can be made more accurate and simple by using the electrometric indicator.[1] The break at the end-point with the bimetallic electrode system previously described[2] decreases in magnitude as the solubility of the silver salt increases and is, therefore, poorest in the titration of chloride. The end-

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[1] Behrend, *Z. physik. Chem.*, **11**, 485, 466 (1893). Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2**, 672, 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, **1919**. Liebich, "Die potentiometrische Bestimmung von Chlor, Brom und Jod," *Dissertation*, Dresden, **1920**.

[2] This Journal, **44**, 2516 (1922).

point here is a slight rise followed by a slow fall in the potential difference between the 2 electrodes. The change is not as abrupt as in many cases but is perfectly distinguishable, especially after a little practice with it. Due to the very weak oxidizing potential of the solution to be titrated, the intial voltage is high and there is little change up to the immediate vicinity of the end-point. The electrodes should not be cleaned between titrations, as the inversion point increases in clarity with the first few successive titrations.

In order to test the accuracy of the electrometric method a strictly 0.1 *N* solution of chemically pure sodium chloride was titrated with a standard solution of silver nitrate, prepared from a nitric acid solution of pure metallic silver.[3] The electrode system consisted of 2 fine platinum thermocouple wires wound in a small, loose spiral and polarized with 0.5 volt through an external resistance of 100,000 ohms. Four 10.00cc. samples of the chloride solution were acidified with 5 to 10 drops of nitric acid, diluted to 80 cc. and titrated. The volumes of silver nitrate used were 18.59, 18.59, 18.58, 18.60 cc., or an average of 18.59 cc. The theoretical requirement was 18.59 cc.

With the reversed titration the end-point rise is more pronounced than the fall; 25.00cc. samples of the silver nitrate were diluted to 90 cc. and titrated with the standard chloride. Three titrations required 13.45, 13.45, 13.45 cc., or an average of 13.45 cc. which is the theoretical amount. Theoretical results are obtained regardless of the direction of approach.

II. The Direct Titration of Bromide

Norman McCulloch[4] developed a method for the determination of bromide in the presence of chloride based upon the selective oxidation of the former in the presence of hydrocyanic acid by manganic chloride, formed by adding a standard solution of potassium permanganate to a very large excess of manganous chloride. The excess of the manganic compound was reduced with potassium iodide and the excess of the latter titrated with potassium permanganate to the iodine chloride end-point, employing the usual chloroform indicator. Iodide, if present, is oxidized with the bromide.

In testing this method with a view to simplifying it, the iodide titration of the excess manganic chloride was found to give a good electrometric end-point, but the results were unsatisfactory. The reaction does not proceed regularly except under rigidly controlled conditions and the consumption of the oxidizing agent is in excess of that required by the simple reaction.

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[3] The silver used had been especially purified for atomic weight work.

[4] McCulloch, *Chem. News*, **60**, 259 (1889). Sutton, "Volumetric Analysis," J. and A. Churchill, London, 10th ed., p. 170.

In order to avoid the necessity of having the oxidizing agent present in excess it seemed desirable to attempt a direct titration with permanganate in the presence of hydrocyanic acid. It is evident that the success of the proposed method depends upon the relative velocities of the reactions: (1) $HCl + HCN + O \longrightarrow ClCN + H_2O$; (2) $HBr + HCN + O \longrightarrow BrCN + H_2O$; (3) $HI + HCN + O \longrightarrow ICN + H_2O$.

Pure potassium bromide was prepared by recrystallizing pure potassium bromate and fusing it in a platinum dish. A strictly 0.1 *N* (or 0.05 *M*) solution by weight was used in making the titrations recorded here. Hydrocyanic acid was obtained by adding a solution of chemically pure potassium cyanide (which gave no blank with permanganate), containing 100 g. of the salt per liter, to the acid halide solution prepared for analysis. Some of the titrations were carried out in an Erlenmeyer flask but the majority simply in an open beaker. The odor of hydrocyanic acid was distinctly noticeable but no serious discomfort was experienced during the course of a day's work.

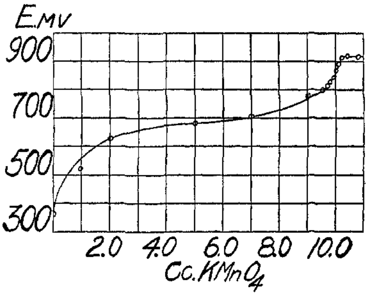

Fig. 1.—Titration of bromide in presence of chloride.

The first titrations were run on solutions having an initial volume of 100 cc. and containing 10.00 cc. of potassium bromide solution, 5 cc. of potassium cyanide and various amounts of sulfuric and hydrochloric acids, using the bimetallic electrode system. No satisfactory end-point was obtained. The second reaction was a little too slow, or the first reaction too fast, or a combination of both, to give a sufficiently sharp potential break. For this reason the silver chloride electrode previously described[5] was substituted for one of the platinum wires and the titration curve plotted. Fig. 1 shows a typical titration curve.

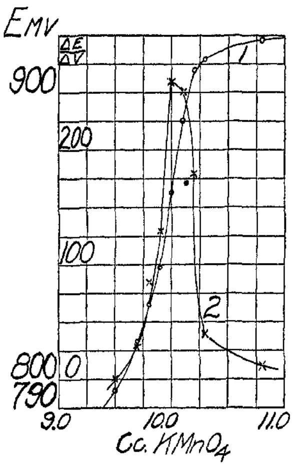

Fig. 2.—End-point in titration of bromide in presence of chloride.

The break is certainly not ideal, but offers distinct possibilities, particularly in a case such as this where there is no other method available. After each addition of permanganate there is a slight drag before equilibrium is reached but this is not serious although it is advisable to keep as uniform as possible the interval of time elapsing between adding the titrating solution and reading the buret. Ignition of the platinum electrode before each titration aids in keeping the end-point rise abrupt.

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[5] This Journal, **44**, 2508 (1922).

The data for the titration curve are given in Table I and the behavior in the near vicinity of the end-point is shown more in detail in Fig. 2.

TABLE I

TITRATION OF BROMIDE IN PRESENCE OF CHLORIDE

10.00 cc. of KBr; 5 cc. of KCN; 5 cc. of HCl (sp. gr. 1.19); 10 cc. of H_2SO_4 (sp. gr. 1.84). Total vol., 100 cc.

$KMnO_4$ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$	$KMnO_4$ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$	$KMnO_4$ added Cc.	E Mv.	$\frac{\Delta E}{\Delta V}$
0.0	360	...	9.00	772	0	10.00	865	260
1.0	520	...	9.50	796	48	10.10	890	250
2.0	625	...	9.70	813	85	10.20	908	180
5.0	681	...	9.80	826	130	10.30	912	40
7.0	706	..	9.90	839	130	10.80	918	12

Theor. requirement, 9.91 cc.

Curve 1 was obtained by plotting the readings of the potentiometer against the corresponding buret readings; Curve 2, by plotting $\Delta E/\Delta V$ against V, the volume of titrating solution delivered.[6] The potassium permanganate used was standardized against pure sodium oxalate. Its 0.1 N factor was 1.0095. The theoretical requirement for this titration was, therefore, 9.91 cc. As nearly as can be read from the curve the flex in Curve 1 is at 10.00 cc. The maximum in Curve 2 is at the same point. The error is, then, 0.09 cc., which corresponds to 0.36 mg. of bromine.

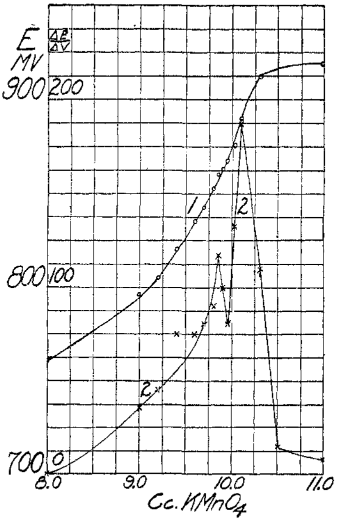

Fig. 3.—End-point in titration of bromide in presence of chloride.

Fig. 3 illustrates the end-point curve of a duplicate titration, which shows a different curve.

The results of several titrations are summarized in Table II.

The theoretical permanganate requirement was 9.91 cc. in the first 5 titrations and 19.81 in the last 2. Particular attention should be drawn to the occurrence of a submaximum in Curve 2 of Fig. 3, since this is not always found. The succeeding decrease in the rate of the potential rise was at the theoretical end-point in both cases. The flex in the E-V curve is not easy to read with great accuracy; the maximum in the second curve is more readily determined. It may be observed that if an arbitrary correction of —0.10 cc. is added to this last value the error in the titration is never greater than 0.42 mg. of bromine. The amount of hydrochloric acid was increased in the fourth and sixth titrations to 10 cc. and in the fifth

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[6] Hostetter and Roberts, THIS JOURNAL, 41, 1341 (1919).

and seventh to 20 cc. without affecting the results. No sulfuric acid was used in the seventh titration.

Table II

No.	Flex (Curve 1)	Maximum (Curve 2)	Minimum (Curve 2)
1 (Fig. 2)	10.00	10.00	..
2 (Fig. 3)	10.00	10.10	9.95
3	10.00	9.96	..
4	9.90	10.00	9.90
5	10.00	9.90	..
6	20.00	19.85	19.80
7	19.90	19.90	..

Effect of Iodide.—Iodide, if present, must obviously be titrated either with or before the bromide. A solution of potassium iodide was prepared and titrated with the standard permanganate. The end-point curve is shown in Fig. 4 and the data in Table III. This titration will be discussed more fully later.

Table III

Titration of Iodide in the Presence of Chloride

10.00 cc. of KI; 5 cc. of KCN; 10 cc. of HCl (sp. gr., 1.19); 10 cc. of H_2SO_4 (sp. gr., 1.84). Total vol., 100 cc.

$KMnO_4$ added Cc.	*E* Mv.	$KMnO_4$ added Cc.	*E* Mv.	$KMnO_4$ added Cc.	*E* Mv.
0.00	145	6.00	289	9.61[a]	773
1.00	236	8.00	308	9.65	827
2.00	251	9.00	324	9.70	844
4.00	272	9.50	349	9.90	880
5.00	281	9.58	370	10.10	885
				11.00	900

[a] End-point.

A duplicate titration gave identical results. When dealing with the pure iodide the break at the end-point is extremely great, about 400 mv.

Table IV

Titration of Bromide in Presence of Chloride and Iodide

10.00 cc. of KBr; 10.00 cc. of KI; 5 cc. of KCN; 10 cc. of HCl (sp. gr., 1.19); 10 cc. of H_2SO_4 (sp. gr., 1.84). Total vol., 100 cc.

$KMnO_4$ added Cc.	*E* Mv.	$KMnO_4$ added Cc.	*E* Mv.	$KMnO_4$ added Cc.	*E* Mv.	$\frac{\Delta E}{\Delta V}$
0.0	142	9.79	365	17.0	741	...
1.0	235	9.83	380	18.0	777	...
2.0	251	9.85	600	19.00	827	0
5.0	282	9.95	650	19.30	856	97
8.0	309	10.5	655	19.40	867	110
9.0	323	12.0	661	19.50	979	120
9.5	338	14.0	695	19.60	891	120
9.68	348	15.5	717	19.70	903	120
9.75	356	16.0	725	19.80	907	40
...	...	...	...	20.50	916	13

Theoret. requirement, 9.61 + 9.91 = 19.52 cc.

The next step was to add the standardized iodide solution to known amounts of bromide and titrate the mixtures. Fig. 5 shows the curve of such a titration and Fig. 6 the final end-point only. The data are given in Table IV.

A sharp break occurred at 9.85 cc., 0.24 cc. higher than the iodide requirement. The solution turned deep red-brown as the permanganate was added but faded slowly to colorless in the vicinity of the end-point. The effect of the presence of bromide on the oxidation of iodide will be taken up under the discussion of the titration of the latter.

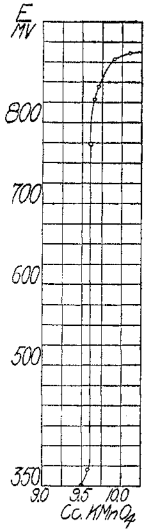

Fig. 4.—End-point in titration of iodide in presence of chloride.

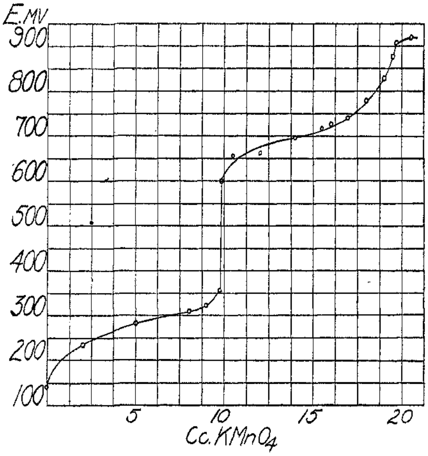

Fig. 5.—Titration of iodide and bromide in presence of chloride.

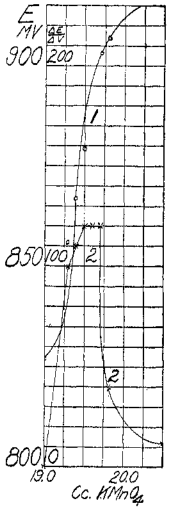

Fig. 6.—Final end-point in titration of iodide and bromide in presence of chloride.

A duplicate titration gave similar results but the curve showed a submaximum as in Fig. 3.

These last two titrations may be summed up as follows: the flex (Curve 1) 19.42, 19.45; maximum (Curve 2) 19.50, 19.60; minimum (Curve 2) 19.50; theoretical volume of potassium permanganate, 19.52 cc.

Much the same conclusions may be drawn as in the preceding titrations. There is a tendency for the maximum in Curve 2 to occur too late. The submaximum was met with in only one of the determinations but then very close to the theoretical end-point.

Effect of High Concentration of Chloride.—It was apparent from the work so far that the presence of considerable amounts of hydrochloric acid offered no difficulties. In order to insure the entire non-interference of chloride under all conditions the regular bromide titration was now carried out in the presence of a very high concentration of pure sodium chloride. The samples contained 10.00 cc. of potassium bromide, 25 g. of sodium chloride, 5 cc. of potassium cyanide solution, and 10 cc. of conc. sulfuric acid in a volume of 100 cc. The titration curves showed no essential difference from those previously obtained.

Summarizing the results of three titrations: the flex (Curve 1) 9.95, 9.90, 10.00; maximum (Curve 2) 10.10, 9.95, 9.90; minimum (Curve 2) 9.90, 10.00.

The results are but slightly more irregular than with less chloride. Averaging the values for the maximum in Curve 2 and applying the correction adopted, —0.10 cc. of 0.1 *N* solution, give a permanganate consumption of 9.88 cc. This means a deviation from the calculated result of —0.03 cc., which is equivalent to 0.12 mg. of bromine. The maximum single deviation is 0.36 mg. of bromine.

III. The Determination of Iodide

A. The Determination of Iodide by Selective Oxidation with Permanganate to Iodine Cyanide

It was noted in connection with the determination of bromide that the oxidation of iodide was not far from being selective when the iodide and bromide were present in equal parts.[7] The iodide end-point was so remarkably distinct that it seemed worth while to investigate the possibility of adapting the same method to the titration of iodides.

As indicated by the titration curves[8] the oxidation of iodide is more rapid, the end-point break far greater and sharper than with bromide. For this reason the bimetallic system is entirely satisfactory in this case and was used in all the titrations recorded here because of its greater simplicity. The break amounts normally to nearly 300 mv.

The first step was to determine the accuracy of the end-point inversion by titrating weighed samples of a standard solution of potassium iodide.

TABLE V

TITRATION OF IODIDE

Wt. of soln. G.	0.1 *N* $KMnO_4$ used Cc.	I per g. G.
18.8481	37.35	0.012576
9.0338	17.95	0.012612
10.6316	21.14	0.012618
		Av. 0.012602

The samples were diluted to about 100 cc. for titration and contained 15 to 20 cc. of conc. hydrochloric acid and 5 cc. of a 10% solution of potassium cyanide. The results of three titrations are recorded in Table V.

This solution, standardized gravimetrically by precipitation as silver

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[7] See p. 627.

[8] See p. 628, Fig. 5.

iodide, gave the value 0.012596, which shows that the reaction proceeds according to the equation, $HI + HCN + O = ICN + H_2O$, from which it follows that 1 cc. of 0.1 *N* potassium permanganate is equivalent to 6.346 mg. of iodine.

An approximately 0.1 *N* solution of potassium iodide was now prepared, standardized as above and samples of it were titrated in the presence of various amounts of the potassium bromide solution used in developing the preceding method. The acidity in all cases was 15% by volume of conc. hydrochloric acid.

Table VI

Titration of Iodide in Presence of Bromide

Expt.	KI Cc.	0.1 *N* KBr Cc.	Ratio Br:I	Final vol. Cc.	$KMnO_4$ used Cc.	Error Cc.
1	20.00	0	0	120	19.29	..
2	20.00	0	0	120	19.30	..
3	20.00	0.50	1:40	120	19.30	0.00
4	20.00	1.00	1:20	120	19.30	0.00
5	20.00	5.00	1:4	120	19.30	0.00
6	20.00	10.00	1:2	120	19.35	+0.05
7	20.00	20.00	1:1	120	19.48	+0.18
8	20.00	20.00	1:1	120	19.46	+0.16
9	10.00	10.00	1:1	120	9.75	+0.10
10	20.00	20.00	1:1	240	19.30	0.00
11	40.00	40.00	1:1	240	38.57	−0.01

Table VI clearly demonstrates that both the ratio of the concentrations of bromide and iodide and the absolute concentrations affect the accuracy of the titration. Until the ratio rose as high as 1:1 (Expt. 6) there was no interference in the titration of a 20.00cc. sample of the iodide. When the ratio reached unity the error was nearly four times as great (Expts. 7 and 8) but only twice as great as when the concentration was reduced by half (Expt. 9). Keeping other factors the same as in Expts. 7 and 8 but doubling the volume eliminated all error, while the error with this larger volume became negligible with the same absolute concentrations that in those experiments showed a large error.

It may be concluded that the selective oxidation of iodide to iodine cyanide by potassium permanganate in hydrocyanic acid solution is possible in all concentrations of chloride and in moderate concentrations of bromide, the magnitude of which is a function of the ratio of the concentration of bromide to the concentration of iodide and also of the absolute concentrations of each.[9] In cases where these factors are not known the

[9] After this work was ready for publication a paper appeared by R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922), in which he states that the oxidation of iodide to iodine cyanide in hydrocyanic acid solution is selective in the presence of chloride, bromide, and nitrate if the titrating solution is potassium iodate, but if potassium permanganate is used bromide interferes. It is desired to point out that Lang dealt with much higher concentrations of bromide than covered by our work.

proposed procedure is to titrate duplicate samples in dilutions varying by at least 100%. If the consumption of the oxidizing agent is the same in both solutions the results may be regarded as trustworthy.

Crotogino[10] and, later, Hendrixson[11] developed a method for the selective oxidation of iodide in the presence of bromide and chloride by potassium permanganate based on a control of the acidity of the solution. Serious interference was encountered in the presence of much smaller amounts of bromide and chloride than are permissible in the method outlined here. Also, the break in Hendrixson's titration was only 160 mv. as compared with 400 mv. by the iodine cyanide method.

B. The Determination of Iodide by Oxidation to Iodate with Hypobromite

A method for the determination of iodide involving oxidation to iodate is, theoretically at least, the ideal method since the oxidation change is the greatest possible, and the presence of bromide and chloride in any amount cannot interfere.

It was observed that when a hypobromite solution was added to a neutral or alkaline solution of an iodide no change occurred at first, but after considerable hypobromite had been added the yellow color of the solution instantly faded.

An electrometric titration of the iodide with hypobromite was attempted but no end-point obtained. The results seemed to indicate that the oxidation of the iodide was complete but too slow for electrometric work.

An arsenite solution has no reducing effect upon an alkaline solution of iodate. It would, therefore, seem to offer an excellent possibility for a back titration of excess hypobromite added to an iodide solution.

Table VII

Titration of Hypobromite with Arsenite

KBrO taken Cc.	$NaAsO_2$ req. Cc.	Average 0.1 *N* factor KBrO
5.00	4.20	....
	4.20	0.8400
10.00	8.40	..
	8.41	0.8400
		Av. 0.8400

An exactly 0.1 *N* solution of sodium arsenite was prepared by weight from pure arsenious oxide dissolved in sodium carbonate. A solution of potassium hypobromite was made by pouring 40 to 50 g. of bromine slowly into a solution of about 30 g. of potassium hydroxide in 250 cc. of water, kept at nearly 0°, and diluting to 5 liters. This solution was standardized by titrating electrometrically with the arsenite.

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[10] Crotogino, *Z. anorg. Chem.*, **24**, 255 (1899).

[11] Hendrixson, This Journal, **43**, 14, 859 (1921).

The end-point with both mono- and bimetallic electrode systems is excellent. The bimetallic was used throughout the work here because of its greater convenience. The potential difference between the polarized electrodes increases slowly with the approaching end-point, the inversion is sharp and the subsequent fall unmistakable.

Weighed samples of a standard potassium iodide solution previously used (Table V) were rendered strongly alkaline with 1 g. of potassium hydroxide, an excess of potassium hypobromite solution, newly standardized, was added, the solution diluted to 100 cc. and allowed to stand for 5 minutes before titrating the excess hypobromite with arsenite (Table VIII). It was found by preliminary experiments that when the excess was titrated immediately, the results indicated that the oxidation of the iodide, especially when present in large amounts, was sometimes incomplete.

TABLE VIII

DETERMINATION OF IODIDE

Wt. soln. G.	0.1 *N* KBrO added Cc.	0.1 *N* $NaAsO_2$ required Cc.	I per g. G.
7.9961	54.11	6.57	0.012574
5.2440	37.46	6.29	0.012571
6.4879	41.62	3.04	0.012577
7.2983	49.95	6.55	0.012577
6.6566	45.79	6.20	0.012579
2.8775	20.81	3.71	0.012569
			Av. 0.012575

The results in Table VIII agree well with those obtained gravimetrically, 0.012596, and by the iodine cyanide method, 0.012602 (Table V). Since 6 equivalents of oxygen are required in the oxidation to iodate, 1 cc. of 0.1 *N* hypobromite solution is equivalent to 2.115 mg. of iodine.

It is very evident that a solution of hypobromite can have no oxidizing action upon either a bromide or a chloride and exactly the same results were obtained in experiments in which 25 g. of sodium chloride and 10 g. of potassium bromide had been added.

The stability of a hypobromite solution depends largely upon the purity of the reagents used in its preparation.[12] A high concentration of alkali also tends to retard decomposition. Unless the rate of decomposition is accurately known it is necessary to standardize the solution twice daily.

Summary

1. The direct titration of bromide in hydrocyanic acid solution to bromine cyanide, BrCN, by potassium permanganate is too slow to be used with the bimetallic electrode system. If, however, the usual monometallic system is used and the titration curve plotted the end-point may be quite easily determined.

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[12] Willard and Cake, THIS JOURNAL, 43, 1610 (1921).

2. The oxidation takes place according to the theoretical requirement of 2 equivalents of oxygen, and the oxalate factor for the permanganate may be used. The maximum in the $\frac{\Delta E}{\Delta V} - V$ curve described usually lies a little too far to the right, but when a correction of —0.10 cc. of 0.1 N titrating solution is made the maximum error is less than 0.4 mg. of bromine.

3. A sub-maximum often precedes the end-point maximum in the $\frac{\Delta E}{\Delta V} - V$ curve and the intervening sub-minimum lies extremely close to the theoretical end-point. The sub-maximum does not always occur.

4. Iodide, if present, is oxidized to the corresponding iodine compound, ICN, but chloride in any quantity does not interfere. Since a selective determination of iodide is possible, the proposed method provides an excellent means for the rapid determination of bromide in the presence of any concentration of the other two halides.

5. Iodide may be accurately titrated electrometrically by oxidation to iodine cyanide with permanganate in hydrocyanic acid solution in all concentrations of chloride and in moderate concentrations of bromide.

The effect of bromide is a function of the ratio of its concentration to that of iodide and also of the absolute concentration of each.

6. A more accurate method is the oxidation of iodide to iodate by excess of alkaline hypobromite, the excess being titrated electrometrically with arsenite.

The presence of any amount of bromide or chloride is without effect.

Either the bimetallic or monometallic electrode system may be used in both methods.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS WESLEYAN UNIVERSITY]

THE SOLUBILITY RELATIONS IN MIXTURES CONTAINING POLAR COMPONENTS

BY F. SPENCER MORTIMER

Received October 27, 1922

In a recent paper the author[1] described a graphical method for calculating the ratio of the experimental to the ideal slope of the curves obtained by plotting the logarithm of the mole fraction of solute against the reciprocal of the absolute temperature of the solubility point of the mixture and, hence, for calculating the solubility in non-ideal solutions.

In applying this method the most serious difficulties are encountered in mixtures containing polar components. It is the purpose of this article

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[1] Mortimer, THIS JOURNAL, 44, 1416 (1922).