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Potassium Iodide as a Primary Standard Substance in Permanganimetry

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It was shown in a previous paper from this Laboratory[1] that the potentiometric iodide–silver titration is capable of giving results accurate to within 0.02%, under the proper conditions. The purpose of the present study was to investigate the accuracy of several iodide-permanganate titration methods, with a view to using potassium iodide as a primary standard substance in permanganimetry. For this purpose we have compared the results obtained by standardizing solutions of potassium permanganate against potassium iodide, with those obtained using arsenious oxide and sodium oxalate as standard substances.

Materials

Potassium Iodide.—The potassium iodide used in this work was synthesized from purified potassium bicarbonate and pure hydriodic acid. The hydriodic acid was synthesized directly from purified iodine and hydrogen, using platinized asbestos as catalyst, in the all-glass apparatus shown in Fig. 1. All joints in this apparatus were of ground glass lubricated with a minimal amount of phosphoric acid, except the joint at the absorption bulbs, D, which was sealed with a drop of water. Iodine, purified by repeated sublimation from potassium iodide, was placed in the bulb A and volatilized by immersing the bulb in an electrically heated glycerol bath at 150 to 180°. The iodine vapor and an excess of pure hydrogen, introduced through the short arm, then passed through the porous platinized asbestos plug at B, which was heated to about 400° by a burner at the end close to the bulb while the other end was left unheated. The resulting hydrogen iodide passed through the trap C, which was immersed in a freezing ice–salt mixture to condense a small amount of unreacted iodine, and the gas was then absorbed in conductivity water in the absorption bulbs D to give a concentrated hydriodic acid solution.

Before starting a run and before the catalyst was heated, the apparatus was flushed out with nitrogen for a few minutes to prevent explosive reaction of hydrogen with oxygen from the air at the surface of the platinized asbestos. Hydrogen was then passed through the apparatus for a few minutes before the heating was started, and the rate of hydrogen flow during a run was so adjusted that about 2–3 bubbles per second escaped from the absorption bulbs. The rate of the reaction was controlled easily by regulating the temperature of the iodine bulb A and the rate of flow of hydrogen. In a typical run, 180 g. of iodine was converted to hydriodic acid in six hours with a yield better than 95%.

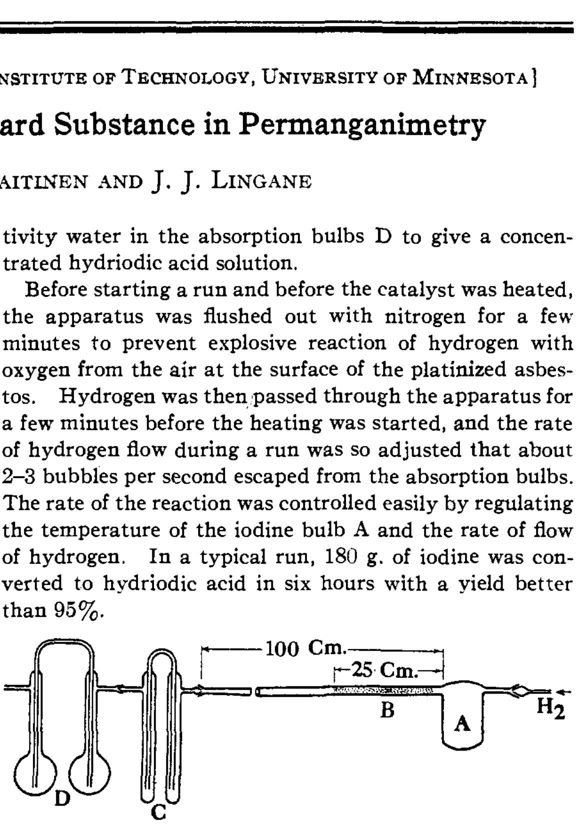

Fig. 1.—All glass apparatus for synthesis of hydriodic acid.

The hydriodic acid solution was treated with a slight deficiency of potassium bicarbonate which had been recrystallized repeatedly from water at 70° in an atmosphere of carbon dioxide, and the resulting solution of potassium iodide containing excess hydriodic acid was filtered and evaporated to crystallization on an electric hot-plate in an Erlenmeyer flask through which a rapid stream of hydrogen was bubbled. The potassium iodide obtained on cooling the solution was filtered off on a sintered glass funnel, freed from excess mother liquor by suction, and finally dried and stored in a desiccator over fused potassium hydroxide.

The salt was prepared for weighing by fusion in a platinum boat in an atmosphere of pure, dry hydrogen, under which conditions there was no trace of decomposition[1]

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(1) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, 58, 1524 (1936).

This method of obtaining very pure potassium iodide will be described in greater detail in a forthcoming volume of "Inorganic Syntheses."

Arsenious Oxide.—Bureau of Standards arsenious oxide was dried in a desiccator over concentrated sulfuric acid to constant weight. A sample of antimony-free arsenious oxide kindly furnished by Professor Foulk[2] was dried similarly.

Sodium Oxalate.—Bureau of Standards sodium oxalate was dried to constant weight at 105°.

Potassium Permanganate Solution.—Stock solutions of potassium permanganate, approximately 0.1 and 0.4 *N*, were prepared from reagent quality potassium permanganate, allowed to stand for two weeks, and filtered through a sintered glass filtering funnel. The stock solutions were checked at regular intervals by potentiometric titration of fused potassium iodide samples. Approximately 0.01 *N* solutions were prepared by diluting weighed portions of the stock solutions in a calibrated volumetric flask. A fresh 0.01 *N* solution was prepared every five days.

Experimental Technique.—The titrations were performed by adding the major portion of the stock solution from a weight buret until an end-point was closely approached, after which the titrations were finished by the use of 0.01 *N* solution delivered from an ordinary volume buret.

Weights and volumetric apparatus were calibrated carefully by standard methods. Weighings were corrected to vacuum using the following densities: brass weights 8.4, potassium iodide 3.13, arsenious oxide 3.86, and air 0.0012 g. per cc.

1. Iodide–Permanganate Titration According to Andrews.[3]—This titration is based upon the oxidation of iodide to colorless iodine monochloride in strong hydrochloric acid medium, the end-point being determined by the use of carbon tetrachloride.

About 25 ml. of water was introduced into a 500-ml. iodine flask and about 1 ml. of concentrated hydrochloric acid was added. Pure potassium bicarbonate was added in small portions until a slight excess was present and most of the air in the flask was replaced by carbon dioxide. A weighed sample of fused potassium iodide in a platinum boat was then introduced, and after solution of the salt was complete, the platinum boat was removed by means of a suitably bent glass rod and washed thoroughly with water. Sufficient concentrated hydrochloric acid (13.3 *N*) was added to obtain the desired acid concentration at the end-point given in Table I, assuming a final volume of 325–350 ml. The solution was cooled in an ice-bath and 6 ml. of carbon tetrachloride was added. The titration was then carried out with 0.4 *N* potassium permanganate from a weight buret until within a few drops of the end-point, and then finished with the 0.01 *N* solution, the end-point being detected by the disappearance of the iodine color from the carbon tetrachloride upon thorough stirring.

The results of titrations carried out at various acidities of hydrochloric acid are given in Table I, and the normality found compared with that obtained in the standardization against pure potassium iodide according to the potentiometric method by oxidation to iodine. It will be shown later in this paper that the latter method gives exact results.

TABLE I

TITRATION OF POTASSIUM IODIDE WITH POTASSIUM PERMANGANATE ACCORDING TO ANDREWS

No.	Final concn. HCl, *N*	KI (vacuum), g.	Total $KMnO_4$ soln. added, g.	Normality of $KMnO_4$, g.	Normality of $KMnO_4$ (potentiometrically)	Error of Andrews method, %
1	3.1	1.09311	28.761	0.45783	0.45753	+0.066
2[a]	3.3	1.23485	32.054	.46401	.46460	− .130
3	3.7	1.37193	36.118	.45756	.45753	+ .007
4	3.8	1.35017	35.027	.46433	.46460	− .058
5	4.3	0.99039	26.070	.45762	.45753	+ .020
6	5.1	1.09551	28.421	.46432	.46460	− .060
7	5.8	1.37068	35.564	.46415	.46460	− .097
8[a]	8.2	1.23690	32.490	.45858	.45768	+ .197
9	8.9	1.25115	32.864	.45859	.45768	+ .199
10	9.0	1.07241	28.180	.45841	.45768	+ .160

[a] Titration carried out rapidly (*ca.* 30 ml./min.). In the other cases the titrations were carried out no more rapidly than 10–15 ml./min.

2. Potentiometric Titration of Potassium Iodide by Oxidation to Iodine.—The fused sample of potassium iodide was dissolved in about 50 ml. of water in a wide-mouthed bottle. One ml. of concentrated sulfuric acid was added from a pipet, and a stream of purified nitrogen was bubbled through the solution to provide stirring. The final volume was about 100 ml., and the final sulfuric acid concentration was about 0.36 *N*. The usual potentiometric apparatus with a bright platinum indicator electrode was employed. Care was taken to wait for a steady e. m. f. after each addition of reagent. The end-point, found from the maximum value of $\Delta E/\Delta V$, could be determined with a precision of ±0.005%.

3. Titration According to the Iodocyanide Method of Lang.[4]—In this titration the iodide is oxidized to colorless iodine cyanide in dilute acid solution in the presence of hydrocyanic acid. The accurately weighed sample of potassium iodide (1 to 1.3 g.) was dissolved in an iodine flask in 25 ml. of water and 50 ml. of 4 *N* sulfuric acid and 30 ml. of 0.5 *N* potassium cyanide were added. The mixture was titrated with permanganate until near the end-point. Then 20 ml. of 0.2% starch solution was added and the titration continued with 0.01 *N* permanganate until the solution was colorless. In all titrations this end-point appeared 0.07% too early due to the fact that part of the iodine is present as iodine cyanide which is not reactive with starch and to the limited sensitivity of the iodine starch reaction. After the starch end-point had been reached, 2 drops of 0.025 *M* ferrous phenanthroline indicator were added and the titration continued until the color went from red to practically colorless. The ferrous phenanthroline must not be added before the starch iodine end-point as the indicator reacts with the iodine.

4. Titration by the Acetone Method of R. Berg.[5]—This titration is based upon the fact that the iodine first formed reacts with acetone present in the solution to give colorless iodoacetone.

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[2] See C. W. Foulk and P. G. Horton, THIS JOURNAL, **51**, 2416 (1929).

[3] L. W. Andrews, *Z. anorg. allgem. Chem.*, **36**, 76 (1903); THIS JOURNAL, **25**, 756 (1903).

[4] R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922).

[5] R. Berg, *Z. anal. Chem.*, **69**, 369 (1926); compare also D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **8**, 199 (1936).

Instead of using potassium iodate as recommended by Berg, potassium permanganate was used in the following titrations.

The fused sample of potassium iodide was dissolved in 25 ml. of water and 50 ml. of redistilled acetone, 20 ml. of 9 *N* sulfuric acid and water were added to give a volume of 200 ml. Near the end-point either 5 drops of 0.2% diphenylamine sulfonate or 2 drops of 0.025 *M* ferrous phenanthroline were added as indicators. The titrations were not well reproducible, indicating an average normality which was 0.55% low. For this reason the results are not tabulated. The poor results are probably due to a low rate of reaction between acetone and iodine.

5. Standardization of Potassium Permanganate with Arsenious Oxide. **(a) Potentiometrically.**—The sample of arsenious oxide (0.8 to 1 g.) was dissolved in 10 ml. of 6 *N* sodium hydroxide, which was free of reducing agents. Ten ml. of concentrated hydrochloric acid and 100 ml. of water were then added, the solution at the start of the titration thus being about 0.5 *N* in hydrochloric acid. One drop of 0.0025 *M* potassium iodate was added as catalyst, together with 1.0 g. of sodium chloride. The titrations with potassium permanganate were carried out using nitrogen for stirring, with care to wait for equilibrium, and the end-point determined from the maximum value of $\Delta E/\Delta V$.

(b) Visually.—The titrations were performed as in (a) above but with titration to the point where the first permanganate color was visible. This end-point appeared 0.012% later than the potentiometric end-point. Using ferrous phenanthroline as indicator, the end-point coincided to within 0.003% with the potentiometric end-point.

The results of the various titrations are given in a condensed form in Table II. In the last column the error in the normality is referred to the value obtained by the potentiometric iodide titration.

TABLE II

STANDARDIZATION OF 0.46 *N* POTASSIUM PERMANGANATE WITH POTASSIUM IODIDE AND ARSENIOUS OXIDE

No.	Standard substance	Method	Detns.	Average normality found	Av. dev. from mean, %	Diff. in normality related to (1), %
1	KI	Potentiometric	5	0.45753	±0.004	(0.00)
2	KI	Lang[a]	5	.45771	± .03	+ .04
3	As_2O_3[b]	Potentiometric	3	.45737	± .017	− .034
4	As_2O_3[c]	Potentiometric	3	.45740	± .015	− .028

[a] Ferrous phenanthroline end-point. [b] Bureau of Standards product (99.97% pure). [c] Product from Professor Foulk.

6. Standardization of Potassium Permanganate with Sodium Oxalate.—Since the procedures described for the standardization of potassium permanganate with sodium oxalate are given for 0.1 *N* solutions, permanganate solutions of the latter strength were prepared and standardized potentiometrically against pure potassium iodide. In the standardization with oxalate the procedures of McBride,[6] of Kolthoff,[7] and of Fowler and Bright[8] were followed closely. In all cases the end-point was found potentiometrically by finishing the titration with 0.01 *N* permanganate. The calculation of the results is based upon a purity of 99.96% as stated by the Bureau of Standards. The results are given in Table III.

TABLE III

STANDARDIZATION OF 0.09573[a] *N* POTASSIUM PERMANGANATE AGAINST SODIUM OXALATE

Method used	Differences in normality found, %				Average error
McBride	+0.31	+0.15	+0.16		+0.21
Kolthoff	+ .13	+ .05	+ .22		+ .13
Fowler and Bright	+ .09	+ .09	+ .06	+0.04	+ .07

[a] Normality determined by potentiometric titration against potassium iodide.

Discussion

1. It is known that dependent upon the acidity the results of the Andrews method may be high or low.[9] At a final acidity between 3.7 and 5.5 *N* the permanganate normality found was on an average 0.04% smaller than that found by the direct potentiometric titration. At the specified acidities the reproducibility is very good. At acidities between 8 and 9 *N*, the normalities found were about 0.2% too high, indicating that too little permanganate was used for a given amount of iodide. This may be due to an induced air oxidation of potassium iodide during titration or to a slow reaction near the end-point. It may be mentioned that a solution of potassium iodide in 7–8 *N* hydrochloric acid could be allowed to stand for a considerable time before an iodine color was noticed in the carbon tetrachloride layer upon shaking.

2. The potentiometric titration of iodide with potassium permanganate in dilute sulfuric acid gives exact and precise results, easily reproducible to within ±0.01%. The normality of the permanganate found by this method agreed within 0.03% with that obtained in the standardization with Bureau of Standards arsenious oxide, and with the antimony-free sample of arsenious oxide obtained from Professor Foulk. The titration of iodide according to Lang also gives satisfactory results and can be recommended with the Andrews titration for the standardization of potassium permanganate.

In order to avoid the troublesome fusion of

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(6) R. S. McBride, THIS JOURNAL, **34**, 393 (1912).

(7) I. M. Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

(8) R. M. Fowler and H. A. Bright, *Bur. Standards J. Research*, **15**, 493 (1935).

(9) E. H. Swift, THIS JOURNAL, **52**, 894 (1930); Swift and Garner, *ibid.*, **58**, 113 (1936); F. A. Philbrick, *J. Chem. Soc.*, 2254 (1930).

potassium iodide in a hydrogen atmosphere, experiments were performed using samples dried simply at 200–225°. The normalities obtained with the unfused salt were 0.02 to 0.03% higher than with the fused salt, indicating the retention of a very small amount of occluded water.

3. Although sodium oxalate and oxalic acid are classical primary standards, they are not suitable for the highly exact standardization of potassium permanganate solutions because of side reactions. Theoretical results can be found only by a compensation of errors. In agreement with Fowler and Bright[8] we found in the present work that McBride's procedure gives high normalities (average +0.20%), the precision of the titration being not greater than ±0.1% The procedure recommended by Kolthoff[7] gives slightly better results, although the average error was still +0.13%. The best results were obtained by Fowler and Bright's procedure, although even in this case the average error amounted to +0.07% as referred to potassium iodide. Therefore, potassium iodide and arsenious oxide fulfill the rigid requirements of primary standard substances better than sodium oxalate.

Acknowledgment.—We express our appreciation to the Graduate School of the University of Minnesota for financial aid which enabled us to do this work.

Summary

1. Potassium iodide and arsenious oxide are more suitable for the exact standardization of potassium permanganate than sodium oxalate.

2. The results obtained by the potentiometric titration of pure potassium iodide and of Bureau of Standards arsenious oxide with potassium permanganate agreed within 0.03%.

3. Potassium permanganate may be standardized against potassium iodide by Andrews' method or by Lang's method under the specified conditions. The results were accurate within 0.05%.

4. The results obtained with potassium iodide dried at 200–225° were 0.025% higher than with fused samples of the salt.

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[CONTRIBUTION FROM THE LABORATORY OF LIQUEFIED GASES OF THE KARPOV INSTITUTE FOR PHYSICAL CHEMISTRY]

A Study of Acid Catalysis in Liquid Ammonia

BY A. I. SHATENSHTEIN

Brönsted's work cleared up the concept of the acid–base equilibrium in any solvent. The solvent participates together with the dissolved substance in a double buffer equilibrium

$$\mathrm{acid}_1 + \mathrm{base}_2 \rightleftarrows \mathrm{acid}_2 + \mathrm{base}_1 \qquad (1)$$

This unified point of view enables one to correlate phenomena observed in different solvents, and in particular the catalysis of solvolysis reactions in aqueous and ammoniacal solutions.

From experimental results obtained in the catalysis of sugar inversion by concentrated aqueous solutions of acids it is evident[1] that the specific catalytic activity (ratio of the reaction velocity constant to the equivalent concentration of the acid) rises (as the concentration of the acid increases) in the case of perchloric, hydrobromic, hydrochloric and nitric acids (acids given in descending order of specific catalytic activity). This ratio remains constant in a solution of trichloroacetic acid and in solutions of the weaker acids the lower the dissociation constant of the acid the lower it falls.

The sequence of acids shown corresponds to the increasing firmness with which the proton is held in the molecule of acid and at the same time corresponds (for the so-called "strong" acids) to the increase of the interionic forces in their ionized solutions.

The rise in the specific catalytic activity can be attributed[2] to the primary salt effect, which may be more correctly described as the primary autosalt effect. This is really the influence of the field of forces of the ions surrounding the solvatized protons $(H_3O{\cdot}nH_2O)^+$ and the reacting molecules. The increase in the concentration of the ionized acid corresponds to an increase in the strength of the field and the decrease in the degree of solvatization of the ions.

Assuming equally complete ionization in concentrated aqueous solutions of all "strong" acids, one might expect greater catalytic activity of

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(1) A. Hantzsch and A. Weisberg, *Z. physik. Chem.*, **125**, 251 (1927).

(2) J. Brönsted and Bell, THIS JOURNAL, **53**, 2478 (1931).