Summary

1.   Data have been presented in support of a theory of hydrolytic adsorption of electrolytes from solution by activated, ash-free sugar charcoal.

2.   It has been demonstrated that the adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali which remains in solution.

3.   The adsorption by this charcoal of a number of acids, bases and salts has been investigated.   It has been found that pure charcoal does not adsorb the strong inorganic bases.   The adsorption of a salt of a strong base and a readily adsorbed acid results in the liberation of free base.

4.   The effect, on adsorption, of the substitution of hydroxyl and amino groups in organic acids has been noted.   The introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending upon the nature of the acid into which it is introduced.   The introduction of the amino group decreases the adsorption of the acid, the extent also depending upon the nature of the acid into which it is introduced.   The effect of the amino group is considerably greater than that of the hydroxyl group.

5.   A number of the conflicting results of other investigators have been reproduced by means of neutral, activated, ash-free charcoal and an explanation of their causes have been offered.

6.   In an early paper a theory for hydrolytic adsorption will be presented in which it will be shown that we must consider that molecules become oriented at the interface as a result of adsorption.

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THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. I. THE STABILITY OF BROMIC ACID IN BOILING SOLUTIONS

By G. Frederick Smith

The use of bromic acid in volumetric analysis was first suggested by Kratschmer.[1]   The sodium salt was prepared and shown to be stable when dried at 180°.   The oxidation of potassium iodide to iodine in dil. hydrochloric, nitric, sulfuric and phosphoric acid solutions was shown to be quantitative.   Feit and Kubierschky[2] used 0.1 N solutions of potassium bromate acidified slightly with sulfuric acid, and stated that under ordinary conditions of storage such solutions were stable during quite long periods of time.   They suggested the use of this reagent in the oxidation

[1] Kratschmer, Z. anal. Chem., 24, 546 (1885).

[2] Feit and Kubierschky, Chem.-Ztg., 15, 351 (1891).

of ferrous salts, hydrosulfuric, nitrous and oxalic acids by the addition of an excess of bromate determined iodimetrically after boiling off the bromine formed during the reaction, but gave only a few determinations. Other applications of bromate as standard solution have since been developed, such as the procedure of Györy[3] in the oxidation and estimation of arsenic and antimony in hot hydrochloric acid solution. The use of bromic acid in volumetric analysis has heretofore been, in general, limited to those processes in which an excess of reagent is not employed.

During the study of a new method for the determination of manganese in its ores the following reaction was investigated: $5Mn(NO_3)_2 + 2KBrO_3 + 4H_2O \longrightarrow 5 MnO_2 + Br_2 + 2KNO_3 + 8HNO_3$. It was found desirable to use an excess of standard potassium bromate in acid solution with filtration of the manganese precipitated followed by an iodimetric determination of the excess, first boiling off the bromine formed during the oxidation of the manganese. As a necessary preliminary step a study of the stability of bromates in boiling acid solution was made.

The object of the present paper is to call attention to the unexpected stability of bromate in boiling acid solution. This fact will doubtless suggest additional volumetric methods. In addition to the work being carried out on the determination of manganese above mentioned, the use of bromic acid in the volumetric estimation of sulfides and of nitrites is under investigation in this Laboratory.

Comparison of Different Samples of Potassium Bromate.—Potassium bromate solutions may be standardized by either of two procedures. If the sample is of known purity it needs no standardization and portions may be dried at 110–120°, weighed and dissolved in the proper volumes of water. Samples of unknown purity may be standardized by the liberation of iodine from potassium iodide in dil. acid solution following the procedure of Kratschmer,[1] the liberated iodine being titrated with sodium thiosulfate solution in the usual manner. The strength of the potassium bromate solution may be determined directly by its reaction with pure arsenious oxide by the method of Györy.[3] In the present work comparative results only were desired and samples of potassium bromate from various representative sources were selected for test. In actual practice samples of bromate of unknown purity, if suitable otherwise, could be standardized by either of the methods mentioned above.

The materials selected for test were the following.

Sample 1 was furnished by the analytical laboratory of an industrial plant and was purified by repeated crystallization; Sample 2 was from ordinary c. p. stock material; Sample 3 was an old imported stock not guaranteed as to purity; Sample 4 was a c. p. material freed from potassium bromide by recrystallization and used in other work published from

[3] Györy, Z. anal. Chem., **32,** 415 (1893).

these Laboratories; it was dried at 110°; Sample 5 was a very old imported stock different from Sample 3; it was dried at 110°. Samples 1a, 2a, and 3a were the same as Samples 1, 2 and 3, respectively, except that they were dried for several hours at 110°.

The samples were analyzed to determine their bromide content by a procedure to be described later. Samples 1 and 4 were found to be free from bromide. Sample 2 contained 0.07% of bromide calculated as potassium bromide, Sample 3, 0.02% and Sample 5, 0.06%. Sample 5 was known to be more than 20 years old and contained the highest percentage of total impurity. All samples other than Sample 1 contained chloride in small amount.

The analyses reported in this paper were made with calibrated flasks, burets, and pipets and are thought to be accurate within 0.02 cc.

Method of Testing Stability

In most cases of oxidation without excess of bromate a bromide is formed. If an excess of bromate is added, bromine is evolved as follows: $KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3Br_2 + 3K_2SO_4 + 3H_2O$. Thus, in all reactions with excess of bromic acid as oxidizing agent in acid solution bromine is evolved and 5 equivalents of oxygen are made available. If the bromine formed can be boiled off without decomposing the excess of bromic acid, such excess can be determined very accurately by reaction with potassium iodide, since 6 equivalents of iodine are liberated for each molecule of bromate present.

Bromic acid is most effective as an oxidizing agent in acid solution. The common acids other than hydrochloric acid are available for bromate oxidations. The stability of potassium bromate in boiling nitric, sulfuric, perchloric, phosphoric and acetic acids of known strength was tested as follows.

25.00cc. portions of 0.1 N potassium bromate solutions were diluted to 100cc. after the addition of a known amount of the acids. Each solution thus obtained was transferred to a 500cc. round-bottom flask provided with a reflux condenser fitted to the flask by a ground-glass joint, and gently boiled during 5 minutes; the condenser was then drained, the contents of the flask cooled to room temperature and the bromate determined iodimetrically.

In all subsequent determinations of bromate iodimetrically, except with phosphoric and acetic acids, the solutions were made 0.3 N with respect to the acid and contained 2.5 g. of potassium iodide in 100 cc. With phosphoric acid the solutions were 0.33 M and with acetic acid 2 M. The iodine liberated was titrated at once against approximately 0.1 N sodium thiosulfate with freshly prepared starch solution added at the end of the reaction. With 2 N acetic acid 10 minutes was allowed for completion of the reaction. At the same time the sodium thiosulfate solution was compared with the untreated bromate solutions using hydrochloric acid, other conditions being as above stated.

The results with perchloric acid of different concentrations are given in Table I.

TABLE I

THE EFFECT OF BOILING, WITH VARIOUS CONCENTRATIONS OF PERCHLORIC ACID, UPON
THE OXIDIZING POWER OF POTASSIUM BROMATE

Time of boiling, 5 minutes.   Volume of solutions, 100 cc.   Each determination represents 0.06959 g. of $KBrO_3$.

Sample	Iodine value of untreated sample. Cc. of thiosulfate	$HClO_4$ N	Iodine value of boiled sample Cc. of thiosulfate	Difference Cc. of thiosulfate
1a	25.75	0.60	25.77	+0.02
	25.75	1.20	25.75	± .00
	25.75	2.00	25.72	— .03
1	25.66	0.15	25.66	± .00
	25.69	0.20	25.67	— .02
	25.69	0.30	25.65	— .04
2a	25.50	0.30	25.50	± .00
	25.50	0.60	25.50	± .00
	25.50	0.90	25.48	— .02
2	25.68	0.05	25.68	± .00
	25.70	0.30	25.65	— .05
	25.70	0.60	25.65	— .05
3a	25.72	0.60	25.72	± .00
	25.72	1.20	25.72	± .00
	25.74	2.00	25.48	— .26
3	25.72	0.30	25.70	— .02
	25.72	0.60	25.71	— .01
	25.72	0.90	25.70	— .02
	25.72	1.20	25.68	— .04
4	25.70	0.60	25.68	— .02
	25.70	0.90	25.65	— .05
5	25.22	0.60	25.23	+ .01
	25.22	1.20	25.23	+ .01
	25.21	2.00	24.38	— .83

The results of the experiments given in Table I show that, under the conditions observed, pure samples of potassium bromate are stable with 2 N acid, and the most impure sample tested was completely stable at 1.2 N acid concentration.

Similar tests using nitric acid are recorded in Table II.

TABLE II

THE EFFECT OF BOILING, WITH NITRIC ACID, UPON THE OXIDIZING POWER OF POTASSIUM
BROMATE

25.00 cc. of 0.1 N $KBrO_3$ used.   Time of boiling, 5 minutes.   Volume of solutions, 100 cc.

Sample	Iodine value of untreated sample Cc. of thiosulfate	HNO_3 N	Iodine value of boiled sample Cc. of thiosulfate	Difference Cc. of thiosulfate
1a	25.74	1.00	25.74	±0.00
	25.74	2.00	25.72	— .02
3a	25.76	1.00	25.77	+ .01
	25.76	2.00	25.74	— .02
5	25.21	1.00	25.21	± .00
	25.21	2.00	25.21	± .00

The results recorded in Table II show that nitric acid is superior to perchloric acid under the conditions observed.   Acid concentration greater than 2 N nitric was not investigated.   0.3 N nitric acid solutions did not liberate iodine from the potassium iodide added before titration.

The corresponding data for sulfuric acid are recorded in Table III.

TABLE III

THE EFFECT OF BOILING, WITH VARIOUS CONCENTRATIONS OF SULFURIC ACID, UPON THE OXIDIZING POWER OF POTASSIUM BROMATE

25.00 cc. of 0.1 N KBrO$_3$ used.   Time of boiling, 5 minutes.   Volume of solutions, 100 cc.

Sample	Iodine value of untreated sample Cc. of thiosulfate	Equivalent normal H$_2$SO$_4$	Iodine value of boiled sample Cc. of thiosulfate	Difference Cc. of thiosulfate
1a	25.74	0.25	25.68	−0.06
	25.74	.15	25.70	− .04
	25.74	.05	25.72	− .02
3a	25.74	.30	25.66	− .08
	25.74	.15	25.65	− .09
	25.74	.05	25.70	− .04
5	25.21	.50	25.09	− .12
	25.21	.25	25.16	− .05
	25.21	.05	25.17	−. .04

The results recorded in Table III show that other than very weak sulfuric acid concentrations measurably affect the stability of boiling bromate solutions.   With pure bromate the effect is inappreciable in 0.05 N acid. The effect of the sulfuric acid is not proportional to its concentration.

Substantially the same results obtained in Table III were found using Sample 1a and phosphoric instead of sulfuric acid.

The Influence of Bromine

The experiments reported in the first 3 tables do not exactly duplicate working conditions, due to the absence of bromine in the boiling solutions. Accordingly, mixtures of known amounts of pure potassium bromide and bromate were acidified with nitric, perchloric and acetic acids, and heated to boiling.   The bromine formed, according to the reaction given above, was liberated and a stream of air was passed to aid in the evolution of bromine.   The solutions were cooled, the acidity was adjusted, and the excess of bromic acid determined iodimetrically.

Although chloride in small amount was not expected to reduce bromic acid, this point was tested.   It was thought that bromine or bromide might bring about reaction between chloride and bromate.

The results of these experiments are given in Table IV.

Table IV shows that bromine does not affect the stability of hot acid solutions of potassium bromate.   Boiling, 2 N acetic acid solutions of potassium bromate are stable, but bromine apparently caused some reaction between the acetic acid and excess of bromate.   Small amounts of

TABLE IV

THE EFFECT OF POTASSIUM BROMIDE AND OF SODIUM CHLORIDE IN ACID SOLUTIONS OF
DIFFERENT CONCENTRATIONS AT THE BOILING TEMPERATURE UPON THE OXIDIZING
POWER OF POTASSIUM BROMATE

25.00 cc. of 0.1 N KBrO$_3$ used.   Time of heating, 5–10 minutes.   Volume of solutions, 100 cc.

KBrO$_3$ Sample	Iodine value of untreated bromate Cc. of thio-sulfate	0.01 N KBr added Cc.	Calc. value of KBrO$_3$+ KBr Cc. of thio-sulfate	Iodine value of boiled solution Cc. of thio-sulfate	Acid used and its normality	Difference Cc. of thio-sulfate
1a	25.76	25.00	22.68	22.67	HNO$_3$ 0.6	− 0.01
	25.76	25.00	22.68	22.69	HNO$_3$ 1.0	+ 0.01
1a^a	25.75	25.00	22.68	22.67	HClO$_4$ 1.0	± 0.00
	25.75	None	...	25.74	Acetic 1.0	− 0.01
	25.75	None	...	25.74	Acetic 2.0	− 0.01
1a^b	25.75	25.00	22.67	12.27	Acetic 2.0	− 10.39
		0.01 N NaCl				
1a	25.76	10.00	...	25.74	HClO$_4$ 0.5	− 0.02
	25.76	30.00	...	25.71	HClO$_4$ 0.05	− 0.05
1a^c	25.76	50.00–10.00	19.59	19.58	HClO$_4$ 0.05	− 0.01

^{a} New solution of KBrO$_3$.

^{b} Heated for 15 minutes to complete evolution of Br$_2$.

^{c} 50.00 cc. of 0.01 N KBr, 10.00 cc. of 0.01 N NaCl.

chloride are without effect on the hot bromate solutions.   The effect of 10 mg. of chlorine in 100 cc. becomes appreciable.[4]

The Analysis of Potassium Bromate for Bromide

Samples 1 to 5 inclusive were analyzed for their bromide content by determining the bromine evolved from a weighed sample upon acidifying and heating.   Half-gram samples were dissolved in 100 cc. of water in an evolution flask connected with a 10-bulb absorption tube containing 100 cc. of 0.3 N potassium iodide solution.   The acid was added and a current of air passed continuously during about 10 minutes while the solution was heated to the boiling point.   The iodine liberated in the 10-bulb tube was titrated with sodium thiosulfate solution after acidification.   The solution remaining in the flask served to test for chloride with silver nitrate. The presence of ferric iron did not decrease the stability of the bromate in these tests.   The results of the tests were given above.   (P. 1117.)

Barium Bromate Substituted for Potassium Bromate

Barium bromate is readily obtainable and in several ways seems to be useful as a substitute for potassium bromate.   It is considerably less soluble than potassium bromate.   It has a high temperature coefficient of solubility and crystallizes without water of hydration.   It compares favorably with potassium bromate in stability towards heat, and was therefore tested for stability.   The results of the experiments showed that barium bromate in boiling perchloric and nitric acid solution com-

[4] In this connection see Rupp, Z. anal. Chem., 57, 19 (1918).

pares well with potassium bromate solutions in stability. With sulfuric and phosphoric acids, barium bromate solutions are affected to the same extent as are potassium bromate solutions.

Neutral solutions of potassium and barium bromate were found to be perfectly stable over long periods of time. Acid solutions of potassium bromate are not correspondingly stable.

Summary

1. 0.025 N solutions of pure potassium bromate, 2 N with perchloric, nitric or acetic acid, are not decomposed after boiling for 5 minutes; sulfuric and phosphoric acid solutions are much less stable.

2. The presence of free bromine has no effect except with acetic acid, but 10 mg. of chloride exerts a very slight reducing action.

3. Bromide in bromate may be determined by acidifying the solution and distilling the bromine liberated.

4. Barium bromate may be substituted for potassium bromate with equally good results.

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THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTION[1]

BY R. F. SCHNEIDER[2] WITH S. A. BRALEY

In 1920 Braley and Hall[3] presented some preliminary experiments on the transference numbers of sodium and potassium in mixed chloride solution, which indicated, in equivalent chloride mixtures ranging from 0.2 N to 1.6 N total concentration, a relatively higher transference number for sodium than called for by calculation from the conductance data of the simple salt solutions. As this agreed so favorably with the work of Smith and his students[4,5] on heterogeneous equilibria between aqueous and metallic solutions, it seemed entirely advisable that a more extensive study should be made with the idea of throwing further light on the composition of salt solutions and their degree of association and dissociation, with special reference to the complete-dissociation theory and the application of the mass law.

[1] Read at the Pittsburgh meeting of the American Chemical Society, September, 1922.

[2] An abstract of a thesis presented to the Faculty of the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Braley and Hall, THIS JOURNAL, 42, 1770 (1920).

[4] Smith and Ball, ibid., 39, 179 (1917).

[5] Smith and Wells, ibid., 42, 185 (1920).