Summary

Measurements have been made of the sorption of hydrogen on platinum and on cobalt in both the massive and the supported states under conditions in which the temperature was varied from -78.5 to 0° and back to $-78.5°$. The results, pointing to a distinction between adsorption and a second factor, apparently solution, indicate that the sorptive process is largely confined to straight adsorption only when the sorbent is spread almost wholly as surface. With massive metals the secondary action assumes a role some five or ten times as great as with supported sorbents.

Poughkeepsie, N. Y. Received August 18, 1941

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

The Molecular Weight of Potassium Bromide and the Atomic Weights of Silver, Bromine and Potassium

By R. K. McAlpine and Edward J. Bird[1]

Although oxygen is the standard for atomic weights, the values for most of the elements have been determined, not by direct comparison, but indirectly by the use of secondary standards. In the experimental studies typified by the work of Stas, Richards, Baxter and Hönigschmid the importance of the atomic weight of silver is well recognized. There are, however, relatively few sets of data in the literature which permit the atomic weight of silver to be calculated without reference to a third element. An important recent piece of work in this field is that of Hönigschmid,[2] in which the ratios $Ba(ClO_4)_2:BaCl_2$ and $BaCl_2:2Ag$ were determined, leading to a calculated ratio of $Ag:4O$.

The present research was suggested in connection with the drying of potassium bromate for use as an analytical reagent. The direct thermal decomposition of potassium bromate as a basis for a new determination of the atomic weights of silver, bromine and potassium seemed feasible because of its slow decomposition at moderately elevated temperatures. Potassium bromate was particularly suitable for such determinations for the following reasons: (1) it crystallizes without water of hydration; (2) it has a very favorable temperature coefficient of solubility and is easily freed from bromide and chloride by recrystallization with centrifugal drainage; (3) it decomposes directly into potassium bromide and oxygen on heating; (4) the decomposition can be carried out at a low enough temperature so that no fusion occurs with its resultant loss of spray as bubbles of oxygen break at the surface. Its main defect is that it cannot be dried completely without some decomposition. Therefore, it is necessary to make a moisture determination, and the true weight of potassium bromate is obtained by subtracting the moisture correction from the weight of the original sample.

Preparation and Purification of Materials

All the materials for this work were carefully purified before use. The chemicals used as the starting point were reagent quality and met A. C. S. specifications. Water, nitric acid, hydrochloric acid and ammonium hydroxide were purified by well-known distillation methods. Potassium permanganate was purified by recrystallization; pure hydrogen by electrolysis.[3] The phosphorus pentoxide was sublimed in a current of oxygen. The sulfuric acid was fumed twice with a few crystals of potassium permanganate to remove halides and to destroy traces of organic matter. The potassium hydroxide used, although a commercial preparation, was shown by direct tests with hydrogen sulfide and silver nitrate to contain a negligible amount of heavy metals and less than 0.01% of chloride. The latter was adequately removed from the potassium bromate by recrystallization.

The preparation of pure silver, pure bromine and pure potassium bromide followed well-known methods in atomic weight work. In the case of silver, after preliminary recrystallization of silver nitrate, reduction to metallic silver by ammonium formate and fusion of the silver, the large buttons were subjected to electrolytic purification, and the crystals then fused in hydrogen on a lime support. After etching with dilute nitric acid and washing, the buttons were dried in hydrogen at 400° and stored in small petri dishes over fused potassium hydroxide. The bromine was dissolved in hot potassium hydroxide solution, followed by evaporation to crystallize out a mixture of potassium bromide and bromate. The crystals were converted to potassium bromide by heating at 500°, and the

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[1] This paper contains material from a dissertation presented to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

[2] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **178**, 1-32 (1929).

[3] J. P. Cooke and T. W. Richards, *Am. Chem. J.*, **10**, 102 (1888).

bromine was recovered from the residue by treatment with dilute sulfuric acid and less than an equivalent weight of potassium permanganate, and distillation. The pure potassium bromide, to check the composition of the residue from decomposition of the final potassium bromate, was prepared[4] by the reaction of the purified bromine in excess with recrystallized potassium oxalate, the potassium bromide being crystallized out, dried and finally fused in an atmosphere of nitrogen in a platinum crucible immediately before use.

The purity of the silver was checked by three syntheses of silver chloride according to the method of Richards and Wells.[5]

TABLE I

SYNTHESIS OF SILVER CHLORIDE

Cor. Ag in vac., g.	6.95254	7.03045	6.63263
Cor. AgCl in vac.	9.23774	9.34116	8.81249
Ratio AgCl: Ag	1.32869	1.32867	1.32866

The average ratio AgCl:Ag is 1.32867, which agrees exactly with that obtained by Richards and Wells.

The pure potassium bromate was prepared from the purified bromine and potassium hydroxide according to the reaction

$$3Br_2 + 6KOH(hot) \longrightarrow 5KBr + KBrO_3 + 3H_2O$$

The bromine was added slowly with stirring to a solution of potassium hydroxide until a slight excess was present, as shown by the color of the solution. The potassium bromide–potassium bromate solution, containing an excess of bromine, was boiled for some time to remove the excess of bromine and to complete the reaction. This treatment removes carbonates and traces of iodine. The hot solution was poured through a Jena glass filter of fine porosity. The clear solution was cooled below 5° and the potassium bromate crystals separated, using a centrifuge with a porcelain basket. This potassium bromate was then recrystallized eight times. The final product was placed in quartz beakers in vacuum desiccators containing fused potassium hydroxide and allowed to stand for several weeks or longer under a partial vacuum to dry. Tests showed the presence of less than 0.003 mg. of potassium bromide per gram of the potassium bromate. Spectroscopic tests for sodium showed less than 0.001 mg. per gram of sample.

In the purifications, centrifugal drainage was used in the separation of the mother liquor from the crystals. Electrical heating was generally applied. Quartz and platinum dishes were used in the final stages of purification. The work, as far as possible, was carried out under glass to minimize contaminations from dust particles.

Weighings.—The weighings were made on a Troemner number 10 balance, sensitive to 0.02 mg. The weights were carefully calibrated by the "double weighing" or "transposition" method.[6] The method of double weighing, using counterpoises of the same material, was employed throughout the work. A small amount of radium bromide was kept inside the balance to prevent the objects from retaining electric charges. Vacuum corrections were applied, taking into consideration the densities of the materials, the temperature, pressure and humidity. Weighings were reproducible to 0.02 to 0.03 mg.

The Decomposition Apparatus.—In Hönigschmid's work on barium perchlorate, the material was placed in a boat and heated in a long horizontal tube while being reduced to barium chloride. Such an arrangement places on the process stringent requirements of non-volatility and freedom from mechanical ejection of fine particles of material. Since in thermal decomposition it was recognized that some formation of dust was very likely to occur, it seemed much more suitable to attempt to carry the reaction out in a flask with comparatively long inlet and outlet arms. The decomposition flask J (Fig. 1) was made of transparent quartz and the ground joints connecting it with the rest of the apparatus were lubricated with a thin layer of graphite.[7] The outlet arm of the original flask was left open with the expectation that the mechanical carrying of potassium bromate dust out of the heated portion could be made negligible, but the preliminary experiments showed this would be extremely difficult if not impossible. The flask was therefore modified by having a quartz filter disk of fine porosity sealed in the lower part of the outlet arm, well within the heating zone when the flask was in the furnace. The flask had a capacity of approximately 40 ml. and a weight of about 47 g. Two counterpoises were made and the inlet and outlet arms were provided with ground-in stoppers.

The electric furnace (Fig. 1) was a Hoskins F. D. crucible type, which had three external resistances connected with it in series. Two of these served to make the coarse adjustments and the third, a set of six parallel resistances ranging from 37.5 to 400 ohms, enabled one to make the fine adjustments over the large temperature range used. The thermoregulator was made up as follows. (1) An air-bath, made by sealing a 600-ml. quartz beaker to a 400-ml. beaker at the edges, was connected by a quartz tube and ground joint to a glass barometric J-tube containing mercury. (2) To make the air-bath more sensitive, the outer beaker was wound with resistance wire and set on a resistance pad, both of which were connected in series to the furnace windings. (3) Two electrodes were sealed into the short arm of the J-tube, one above the mercury and the other below the surface, and connected to an Aminco supersensitive relay. Most of the heating was done by an uninterrupted source of current while the remainder was cared for by an intermittent source whose operation was controlled by the temperature of the furnace.

This arrangement was accomplished by means of a fairly high resistance in parallel with the main circuit and control of this with the relay. By a proper setting of the external resistances and adjustment of the level of the mercury column by means of stopcocks, it was possible to obtain any temperature in the desired range (85–550°) and to maintain this over long periods of time within ±2°. Temperatures were recorded by means of a Leeds and Northrup potentiometer indicator. The hot junction of the thermcouple was placed adjacent to the lower third of the decomposition flask.

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[4] Richards and Mueller, THIS JOURNAL, **29**, 644 (1907).

[5] T. W. Richards and R. C. Wells, *Carnegie Inst. Wash. Pub.*, No. **28**, 57–66 (1905).

[6] Circular of the Bureau of Standards Bulletin, No. 3, p. 37; P. F. Weatherill, THIS JOURNAL, **52**, 1938 (1930).

[7] R. K. McAlpine, "Study of Moisture Blanks in Thermal Decomposition Work," unpublished.

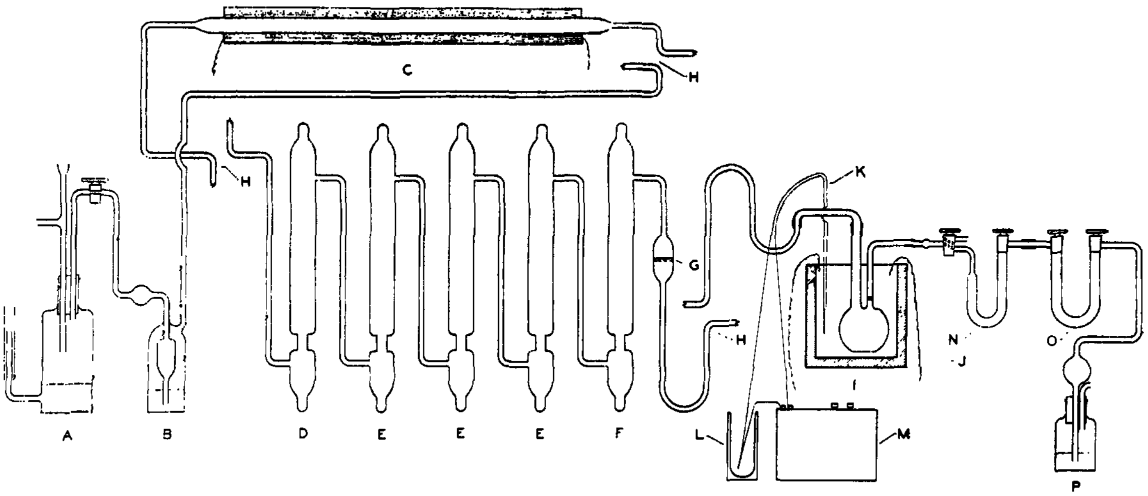

Fig. 1.—Apparatus for the thermal decomposition of potassium bromate: A, bottle and suction pump for obtaining washed air; B, sulfuric acid wash bottle and bubble counter; C, copper oxide furnace; D, soda lime tower; E, fused KOH towers; F, P_2O_5 tower; G, Jena glass filter; H, glass grids; I, Hoskins electric pot furnace; J, quartz $KBrO_3$ decomposition flask; K, thermocouple; L, cold junction; M, L and N, potentiometer; N, anhydrone and P_2O_5 tube; O, protection tube of P_2O_5; P, H_2SO_4 bubble counter.

The Absorption Apparatus and Apparatus for Obtaining Pure, Dry Air.—An aspirator bottle (A) (Fig. 1) of about 4 l. capacity was fitted with a filter pump to bring in washed air. The outlet tube was provided with a stopcock to control the rate of flow of air. A wash bottle (B) filled one-third with sulfuric acid (1:1) was used to indicate the rate of flow of air and also to remove some of the moisture. Glass grids at (H), not shown in the figure, gave flexibility to the system. The air was then passed through (1) the copper oxide furnace (C) (3 ft. by 1 in. (91 × 2.5 cm.)) at 400° to oxidize traces of organic matter, (2) the soda lime tower (D) to remove carbon dioxide and more moisture, (3) the fused potash towers (E) and the phosphorus pentoxide tower (F) to remove moisture and (4) the filter disk (G) to retain any dust particles.

The absorption apparatus (N) (Fig. 1) was a Pyrex U-tube, the outlet end of which was equipped with a ground-glass stopper and the inlet with a three-way stopcock. This stopcock permitted the air to be swept out of the apparatus without passing through the absorbent. The stopcock and stopper were lubricated with a thin film of special high-vacuum stopcock grease. The absorption tube was cooled by means of a copper coil surrounding the U-tube through which cold water was allowed to flow. The moisture absorbent used was anhydrous magnesium perchlorate followed by phosphorus pentoxide. The absorption tube (N) was followed by a protecting U-tube (O) filled with phosphorus pentoxide and this was connected to the sulfuric acid bubble counter (P).

Thermal Behavior of Potassium Bromate.—Exploratory experiments were carried out to determine the necessary procedure for moderately rapid but controlled decomposition. These experiments showed that there was a very slight decomposition (less than 0.01% of potassium bromate) in the temperature range from 85–120°, a very little decomposition (greater than 0.01%) above 150° but the decomposition was very slow until a temperature of approximately 365° was reached. As the temperatures were elevated above 365°, the rate of decomposition increased until near 385°, where it accelerated to such an extent that it became too rapid to permit effective control. It was found possible to decompose a large portion of the potassium bromate by slowly increasing the temperature in steps from 365 to 382° and the remainder with the exception of a trace could then be decomposed by continuing to increase the temperature in about 2-degree steps until a temperature of 388° was reached and holding there for about two hours. The last trace was decomposed by increasing the temperature to 525–550° and holding it at this point for two hours. The residues in these decomposition experiments were analyzed for undecomposed bromate as follows. Twenty-five milliliters of hot water was added to the potassium bromate residue to dissolve it. This solution was then transferred to a 250-ml. Erlenmeyer flask, carbon dioxide was passed into the cooled solution and flask to displace the air and 2 g. of potassium iodide was added, then 2 ml. of concentrated hydrochloric acid, diluted to 25 ml. The potassium bromate, if present, liberated an equivalent amount of iodine from this acid solution, and this was titrated with standard sodium thiosulfate solution about 0.02 *N*, using starch-iodide solution as indicator.

Determination of Moisture.—It was already well-known that potassium bromate could not be dried completely without undergoing some decomposition. Therefore, preliminary experiments were conducted to find suitable drying conditions so as to obtain a potassium bromate which would not change in moisture content while weighing or while sweeping out the apparatus preparatory to the decomposition operation. It was necessary to reduce the moisture content to about 0.1%, so that the residual moisture could be determined accurately during the decomposition by absorbing the water liberated in suitable absorbents and weighing it. A range of temperatures from 270 to 85° was covered. At 270° decomposition of the bromate was significant as shown by a marked test for bromide ion, but as the temperature was reduced, the decomposition decreased, and at temperatures less than 120°, the decomposition was less than 0.01%. At temperatures of 85-95°, the material could be heated for a twelve-hour period with only negligible decomposition. By using the material which had been partly dried in a vacuum desiccator, at reduced pressure, over fused potassium hydroxide for several weeks, it was found possible to obtain a satisfactory preparation of potassium bromate by heating in the decomposition apparatus at a temperature of 90-95° for two to four hours while a current of pure dry air was passed over it at the rate of 2-3 l. per hour. Samples of potassium bromide dried in this way were found to contain approximately 0.1% residual moisture.

Moisture Blanks.—Experiments were carried out to determine the amount of moisture collected by the absorbents due to diffusion of water vapor into the apparatus during the long-drawn-out decomposition and to determine the most suitable length of time to sweep out the apparatus with pure dry air before starting a determination. During the first series of experiments, the moisture blanks were found to be large and the apparatus was improved and corrected for leaks. In a second series of seven experiments, several of which were run in between the final series of decomposition experiments, the amount of water absorbed varied from 0.02 to 0.06 mg. over periods of eight and one-half to forty-two hours. Therefore, it seemed reasonable to take the average value of 0.04 mg. as a correction to the weight of water absorbed.

In earlier studies it was observed that all but a fraction of a milligram of the residual moisture was liberated below 380°, the oxygen formed in the decomposition of the potassium bromate and escaping from the interior of the crystals probably playing an important part in this result. Further, the loss in weight of the potassium bromide residue on being reheated at 500-550° was seldom greater than 0.02 mg. providing the first heating had been continued for at least two hours. This indicated that the last portion of water must have been removed in the first heating period. Therefore, the weight of the absorption tube was taken after the first period of heating at 500°.

Identity of the Residue from the Potassium Bromate Decomposition.—In determining the molecular weight of potassium bromide from the ratio of potassium bromate to the residue resulting from the thermal decomposition of the potassium bromate, it was necessary to prove that the residue was really pure potassium bromide. It was essential, then, to show that the potassium bromate had been completely decomposed and that no bromine had been lost by hydrolysis or other chemical reaction. The freedom of the residue from potassium bromate has already been considered, the tests for its presence being entirely negative. Bromine, however, might have been lost through reaction of potassium bromide with water vapor at higher temperatures or by direct decomposition of the bromate. These possible reactions may be represented by the equations

$$2KBr + H_2O \longrightarrow K_2O + 2HBr$$
$$4KBrO_3 \longrightarrow 2K_2O + 2Br_2 + 5O_2$$

It is to be noted, however, that the residue in both these cases would react alkaline in aqueous solution. Therefore, it was possible to test for such loss of bromine by examining the neutrality of the residue. Another searching test for the composition of the residue consists in determining its ratio to metallic silver and comparing this with the corresponding data from a pure sample of potassium bromide. If this last test were satisfactory, it would be evident that no free oxygen or water vapor had been trapped in the interior of the potassium bromide.

A number of residues from the potassium bromate decomposition were tested for neutrality using brom thymol blue as indicator. In carrying out this test the residue was dissolved in 50-75 ml. of redistilled water, transferred to a 100-ml. flask with a long neck, and treated with 0.5 ml. of the indicator. The flask was then connected to a water pump and heat applied, the solution boiling vigorously for several minutes. Without releasing the vacuum the solution was then cooled and its color compared with the green observed by looking through two layers of a corresponding solution, one layer being acid, the other alkaline. The water solutions of these residues gave neutral tests and thus indicated that no bromine was lost as free bromine or by hydrolysis during the slow decomposition of the potassium bromate.

The Ratio of Potassium Bromide to Silver.—Pure potassium bromide prepared from potassium oxalate and pure bromine was dried and compared with pure silver by methods[8] already well established. The average ratio of the KBr:Ag for eleven determinations was found to be in excellent agreement with the ratio obtained by using the residues from the potassium bromate decompositions. The results are discussed in more detail in another part of this paper. The results also were in excellent agreement with the values obtained by Richards and Mueller[9] and with that of Hönigschmid and Sachtleben.[10] From the results of the above tests, it is believed that the residues from the thermal decompositions of the potassium bromate samples consisted of pure potassium bromide.

Procedure.—(1) The decomposition flask was dried for two hours at 160° followed by two hours in the furnace at 550°, with pure dry air flowing through. The empty flask as well as the counterpoise were wiped with a moist cloth to establish reproducible water films and allowed to stand at least forty-five minutes to come to equilibrium. The weighings were then made using the usual precautions in atomic weight work, including adequate adjustment of air in vessels to atmospheric pressure. (2) Seven to twelve grams of potassium bromate was added to the flask, which was returned to the furnace and dried at 85-95° for two to four hours, with pure dry air flowing through at a rate of 2-3 l. per hour. The flask was allowed to cool to room temperature, stoppered, one stopper being grooved slightly to establish atmospheric pressure while weighing, removed to the balance room, wiped, allowed to reach equilibrium conditions and weighed. (3) The material was returned to the furnace, air passed over the potassium bromate in the decomposition flask at room temperature, but not through the absorption tube, for forty minutes. (4) The air was then turned through the absorption tube

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[8] Richards and Mueller, *Carnegie Inst. Wash. Pub.* No. **69**, p. 36; Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, **177**, 102-108 (1929).

[9] Richards and Mueller, THIS JOURNAL, **29**, 652 (1907).

[10] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933).

by means of the three-way stopcock, and the furnace allowed to heat up gradually for two to four hours until the temperature reached 374°. The stopcock opening the air-bath to the air remained open during this period. (5) The external resistances were adjusted and the mercury level in the thermoregulator was set to maintain this temperature and the stopcock closed. (6) The temperature was then increased in two-degree steps every two hours until a temperature of 378 to 380° was reached. This temperature was held constant overnight or for a longer convenient period of time, for the major decomposition to take place. (7) The temperature was again stepped up in two-degree units in two-hour periods until a temperature of 388° was obtained. (8) The temperature was then increased gradually to 550°, the stopcock leading to the air being open during this period. The thermoregulator was set to hold this temperature, which was maintained for two hours. (9) The furnace was then allowed to cool down with the stopcock of the air-bath open and the stopcocks in the absorption tube closed, allowing the air to by-pass out the side arm. The decomposition flask was then disconnected while the air was still flowing through and the flask immediately stoppered. (10) The decomposition flask and absorption tube were placed in desiccators and removed to the balance room. These were allowed to cool to balance room temperature, wiped and hung in the balance case for at least forty-five minutes and then weighed. (11) The flask was returned to the furnace and heated in two-hour periods at 550° until constant weight had been attained.

Results

The results are shown in Tables II, III and IV. The weights have been corrected to a vacuum basis. The moisture correction of 0.04 mg. has been applied to the vacuum weight of the water absorbed to get the true weight of the residual water in the partially dried potassium bromate. Run number 6 in the final series of decompositions was discarded because the rate of decomposition got out of control and fusion and spattering occurred.

Table II

The Thermal Decomposition of Potassium Bromate and the Molecular Weight of Potassium Bromide

Run no.	Hrs. heated	$KBrO_3$ in vac., g.	H_2O from $KBrO_3$ in vac., g.	$KBrO_3$, cor.	KBr in vac., g.	Mol. wt. of KBr
1[a]	48	10.69236	0.01540	10.67696	7.60833	119.011
2	51	7.55060	.00781	7.54279	5.37493	119.010
3	47	7.45585	.00767	7.44818	5.30753	119.011
4	48	9.73313	.00741	9.72572	6.93055	119.015
5	48	9.63561	.01551	9.62010	6.85524	119.012
7	50	8.51185	.01178	8.50007	6.05711	119.012
8	28	10.70737	.01376	10.69361	7.62021	119.012
9	53	10.38108	.01584	10.36524	7.38620	119.011
10	52	9.77644	.01293	9.76351	6.95738	119.009
11	57	9.79917	.01436	9.78481	6.97233	119.012
					Av.	119.011

[a] $KBrO_3$ sample B used in this run; sample C in all other runs.

Table III

Ratio of Potassium Bromide to Silver and the Atomic Weights of Silver, Bromine and Potassium

Run no.	KBr from $KBrO_3$ (vac.)	Ag (vac.)	Ratio KBr:Ag	At. wt. of Ag	At. wt. of Br from known ratio Br:Ag[a] = 0.740786	At. wt. of K[a]
2	5.37498	4.87217	1.103200	107.877	79.914	39.096
3	5.30758	4.81110	1.103195	107.876	79.913	39.098
4	6.93122	6.28281	1.103204	107.881	79.917	39.098
5	6.85536	6.21410	1.103194	107.880	79.917	39.095
7	6.05813	5.49155	1.103173	107.881	79.917	39.095
8	7.62092	6.90813	1.103181	107.882	79.915	39.097
9	7.38622	6.69531	1.103193	107.878	79.915	39.096
10	6.95738	6.30663	1.103185	107.878	79.914	39.095
11	6.97265	6.32040	1.103197	107.879	79.915	39.097
		Av.	1.103191	107.879	79.915	39.096

[a] The values in columns 6 and 7 are calculated from the corresponding values in column 5 and the molecular weights of KBr in Table II.

Table IV

Ratio of Potassium Bromide to Silver Using Potassium Bromide Made from Purified Bromine and Potassium Oxalate

Run no.	KBr in vac., g.	Ag in vac., g.	Ratio KBr:Ag
1	5.08563	4.60984	1.103211
2	4.94988	4.48694	1.103175
3	5.64545	5.11714	1.103200
4	5.38516	4.88142	1.103195
5	5.92139	5.36755	1.103184
6	4.62504	4.19245	1.103183
7	5.30793	4.81142	1.103193
8	4.50218	4.08093	1.103222
9	4.34549	3.93902	1.103191
10	5.25160	4.76034	1.103198
11	5.06778	4.59372	1.103197
		Av.	1.103195

The molecular weight of potassium bromide was calculated from the relation

mol. wt. KBr : 3 × 16 :: wt. KBr : wt. $KBrO_3$ − wt. KBr

Ten determinations give an average value of 119.011.

The atomic weight of silver was obtained from the proportion

at. wt. Ag : mol. wt. KBr :: wt. Ag : wt. KBr

In Table III nine determinations give an average value of 107.879, while in Table IV eleven determinations based on an independent preparation of potassium bromide yield practically an identical ratio for KBr:Ag.

The individual values for the atomic weight of bromine were calculated from the corresponding values for silver by using the well established[11] ratio, Br:Ag = 0.740786. The average for bro-

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(11) Baxter, *Carnegie Inst. Wash. Pub.*, No. **135**, p. 58; Hönigschmid and Zintl, *Ann.*, **433**, 201–230 (1923).

mine, 79.915, necessarily has the same ratio to silver, 107.879, as the international values 79.916 and 107.880, since the same ratio is used in both sets of calculations.

By subtracting the values for the atomic weight of bromine from the molecular weight of potassium bromide, the atomic weight of potassium was obtained. The results are recorded in column 7, Table III. The atomic weight of potassium was found to agree exactly with the accepted value of 39.096, which adds more evidence in favor of this as opposed to the higher value of 39.104 obtained by Hönigschmid and Goubeau[12] and of 39.100 obtained by C. R. Johnson.[13] The work of Richards and Stähler,[14] of Baxter and MacNevin,[15] and of Hönigschmid and Sachtleben[16] agrees with the value of 39.096.

Summary and Conclusions

1. Potassium bromate has been accurately converted to potassium bromide by thermal decomposition.
2. A precise correction has been applied for the moisture content of each portion used of the recrystallized and incompletely dried potassium bromate.
3. New values have been obtained for the molecular weight of potassium bromide and the atomic weight of silver, and from these, by application of the ratio of bromine to silver (available from the work of Baxter and Hönigschmid), new values for the atomic weights of bromine and potassium have been calculated referred to the new value for silver.
4. The experimental data may be summarized as follows: Ten determinations of the ratio $KBrO_3$: KBr give a mean value of 119.011 for the molecular weight of potassium bromide. Nine determinations of the ratio KBr : Ag, using the residue from decomposition of potassium bromate, give an average value of 1.103191 and eleven determinations of the same ratio using a fused salt obtained from the reaction of pure bromine on pure potassium oxalate give an average value of 1.103195. The atomic weight of silver obtained from this ratio is 107.879.
5. The value 107.879 for the atomic weight of silver agrees within one part in 100,000 with the present accepted value, and offers an important check on the work of Hönigschmid and Sachtleben in which the absence of moisture in the initial barium perchlorate and in the final barium chloride was assumed, but only proved indirectly.
6. The atomic weights of bromine and potassium calculated from these data and the ratio Br : Ag = 0.740786 become 79.915 and 39.096, respectively.
7. If the present international value for the atomic weight of bromine (based on Ag = 107.880) is subtracted from the new value for the molecular weight of potassium bromide, the corresponding atomic weight of potassium would be 39.095.

ANN ARBOR, MICH.

RECEIVED MARCH 31, 1941

[12] Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, **163**, 93 (1927); **177**, 102 (1929).

[13] C. R. Johnson, *J. Phys. Chem.*, **39**, 781 (1935).

[14] Richards and Stähler, THIS JOURNAL, **29**, 623 (1907).

[15] Baxter and MacNevin, *ibid.*, **55**, 3185 (1933).

[16] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Catalytic Effect of Water on the Aminolysis of Ethyl Phenylacetate in *n*-Butylamine

BY PAUL K. GLASOE, L. D. SCOTT AND L. F. AUDRIETH

In a series of publications from this Laboratory it has been shown that the solvolysis of esters in ammonia[1] and in amines[2] is catalyzed markedly by the addition of ammonium and amine salts, respectively. These findings have been interpreted as possible examples of acid catalysis, since "onium" salts are known to behave as acids not only in their respective parent solvents, but also in the fused state.

In view of the fact that water might also be expected to act as an acid in solvents more protophyllic than itself, care was always taken to ensure the use of absolutely anhydrous materials. It was to have been predicted that water might also

[1] (a) Slobutsky and Audrieth, *Proc. Natl. Acad. Sci.*, **23**, 611 (1937); (b) Fellinger and Audrieth, THIS JOURNAL, **60**, 579 (1938); (c) Audrieth and Kleinberg, *J. Org. Chem.*, **3**, 312 (1938); (d) Balaty, Fellinger and Audrieth, *Ind. Eng. Chem.*, **31**, 280 (1939).

[2] (a) Glasoe and Audrieth, *J. Org. Chem.*, **4**, 34 (1939); (b) Glasoe, Kleinberg and Audrieth, THIS JOURNAL, **61**, 2387 (1939).