

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

## NOTES ON SILVER BROMATE.

By J. H. REEDY.

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**Variation in Potential.**—In a study of silver electrodes which the writer made a few years ago, it was noticed that the potential of the electrode  $\text{Ag} | \text{solid AgBrO}_3 | 0.1 M \text{KBrO}_3$ , when freshly prepared, was not definite, but underwent a progressive change for some time. This change frequently amounted to more than 100 millivolts, and was always in the direction indicating a decrease in the solubility of the silver bromate. The silver bromate used was of "technical" grade, and according to the statement of the manufacturers, was made by the action of an excess of bromine on silver nitrate solution. Its composition was therefore a mixture of silver bromate and silver bromide in the molar ratio 1:5. Representative results (referred to the 0.1 *N* calomel electrode as +0.342 volt) are given in Table I, the temperature being 25°. In all cases, the electrode, upon standing, finally gave a value of +0.631 volt.

TABLE I.—VARIATION IN THE ELECTRODE  $\text{Ag} | \text{AgBrO}_3$  IN 0.1 *M*  $\text{KBrO}_3$ .

Time. days.	Electrode potential. Volt.
0	+0.795
1	+0.643
2	+0.641
3	+0.634
4	+0.631
5	+0.631

**Purification.**—To meet the possibility that this change of potential might be due to the presence of some metastable substance in the impure silver bromate, this material was purified by extraction with hot water, using the apparatus shown in Fig. 1. The recrystallized silver bromate was collected on a filtering plate P, washed several times with ice water, and finally dried in a vacuum desiccator. Silver bromate prepared in this way is pure white, and appears when dry to be wholly unaffected by light. The wet salt was not found to be so stable.<sup>1</sup> A portion of the pure material was placed in a carefully cleaned tube, covered with water, and the top of the tube sealed off. After standing several weeks, the side next to the window showed a slaty-gray color, while the rest was only slightly affected. To see if there was any change in volume during the darkening, due to the formation of an insoluble gas (oxygen, supposedly), some wet silver bromate was sealed in a tube with a manometer containing pure liquid paraffin attached. After standing for more than a year there was no displacement of the levels in the arms, as shown by a "blank"

<sup>1</sup> Cf. Stas, *Mem. de l'Acad. r. de Belgique*, 35, 82, 118.

apparatus alongside. This darkening effect is very marked when wet crystals are heated, though the dry salt seems to be quite stable. Instead of decomposing about  $150^{\circ}$ , as was reported by Stas, the carefully

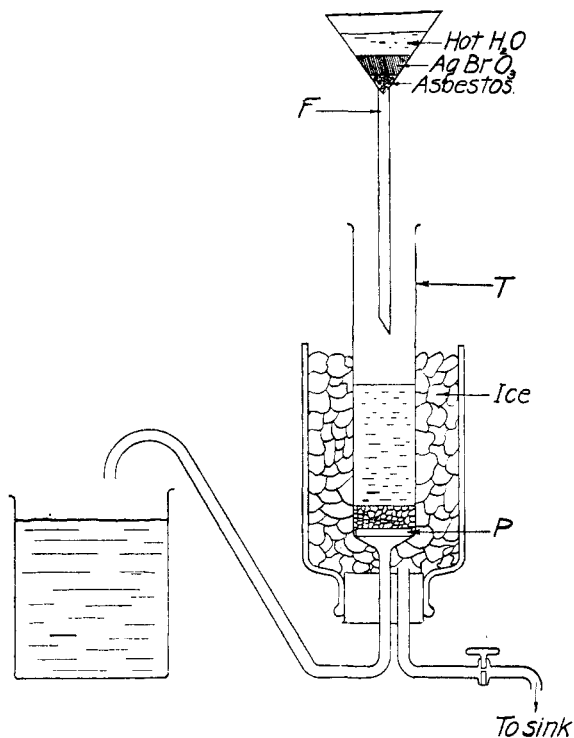


Fig. 1—Recrystallization of silver bromate.

purified salt was heated above its melting point ( $308$  to  $310^{\circ}$ ) without visible decomposition. The introduction into the heated salt of a foreign substance, as a little dust, was found to cause violent explosion.

The purity of the recrystallized product was determined as follows. Samples were weighed in evaporating dishes and converted into silver bromide by evaporation to dryness with an excess of pure hydrobromic acid solution and dried at  $120^{\circ}$  to  $125^{\circ}$ . The weight of the silver bromide residue indicated degrees of purity varying slightly with the batch of crystals used. The purity usually ranged from 99.6% to 99.8%, though in one case, when the sample had been heated to  $130$ – $135^{\circ}$  for several hours, a purity of 100% was found. This deviation from absolute purity might possibly be due to the presence of a small amount of the unknown silver perbromate; however, the most natural assumption is that the foreign substance is water. This was the opinion of Stas, who reported that the last traces of water in silver bromate could not be driven off below its decomposition point.

**Dimorphism.**—Potential measurements made on electrodes using the purified silver bromate gave even more erratic results than the crude

silver bromate-bromide mixture. On the other hand, silver bromate prepared by the interaction of silver nitrate and potassium bromate solutions at ordinary temperatures gave the potential of +0.631 volt immediately. It was noticed at this point that there was a difference in the crystalline form of the silver bromate prepared from hot and cold solutions. The crystals formed by sudden cooling were hair-like, while those from the cold solutions were tetragonal crystals. Figs. 2 and 3 are from microphotographs of these forms. The habit of the hair-form in

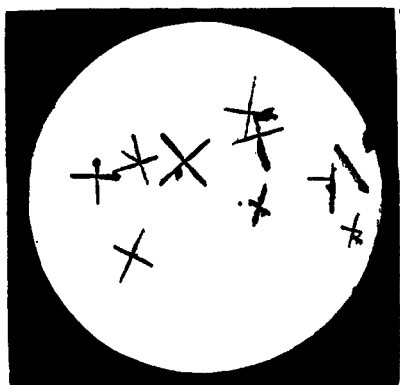


Fig. 2.—The hair form.

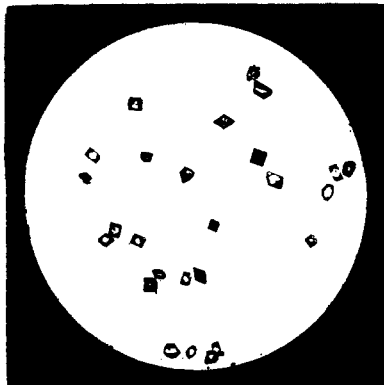


Fig. 3.—The tetragonal form.

forming crosses as shown in the figure is the frequent, but not the universal behavior of these crystals. Upon slow cooling of a hot saturated solution, however, the tetragonal form was the main product. While the hair-form is truly stable only at high temperatures, by sudden cooling (that is, "freezing the equilibrium") it may be carried over in a metastable condition into the region of the tetragonal form. In the dry condition this metastable form seems to persist indefinitely, and even in solution the reversion into the common form may be surprisingly slow. As a result of the greater solubility of the hair-form, electrodes whose solutions contain it show elevated potentials. The fact that Retgers<sup>2</sup> has already pointed out that silver chlorate shows the phenomenon of dimorphism had been assumed by the writer as presumptive evidence that the bromate also might crystallize in two forms.

**Solubility and Transition Point.**—At the suggestion of the writer, Mr. S. J. Gould has determined the solubility curve for silver bromate in water and the transition point of the two forms.

Samples of saturated solutions were taken at various temperatures between 25° and 100°, and weighed in glass-stoppered bottles. Due precautions were taken against change in concentration owing to cooling

<sup>2</sup> Retgers, *Z. physik. Chem.*, 5, 438 (1890).

during the transfer. After cooling and weighing, the amount of silver bromate was determined by adding an excess of potassium iodide solution, acidifying with dil. hydrochloric acid, and titrating the liberated iodine with standard thiosulfate solution. Table II shows the solubilities as

TABLE II.—SOLUBILITY OF  $\text{AgBrO}_3$ .

Temperature, ° C.	Solubility in 100 g. of $\text{H}_2\text{O}$ . G.
25	0.196
30	0.227
35	0.269
40	0.316
45	0.371
50	0.433
55	0.497
60	0.570
65	0.648
70	0.735
75	0.832
80	0.936
85	1.055
90	1.325

read from the curve and Fig. 4 the curve itself.

The solubility value for the stable form at 25° has been confirmed by e. m. f. measurements. Since there is some doubt as to the exact value of the normal silver electrode, a cell of the concentration type is desirable for this work. The combination used was  $\text{Ag} | \text{AgBrO}_3 | \text{solid } 0.1 M \text{ KBrO}_3 \text{ sat. w. AgBrO}_3 | \text{Conc. KNO}_3 | 0.1 M \text{ AgNO}_3 | \text{Ag}$ . This cell gave a potential of 0.1193 volt at 25°. Assuming that the onization of 0.1 *M* potassium bromate solution is 82.5%, and of saturated silver bromate solution in 0.1 *M* potassium bromate solution is 98% (the same as for potassium bromate and silver nitrate at the corresponding concentration), a solubility of 0.00827 mole per liter, or 0.1955 g. per 100 g. of water, is indicated.

No indication of a break in the solubility curve appears until near the boiling point of the

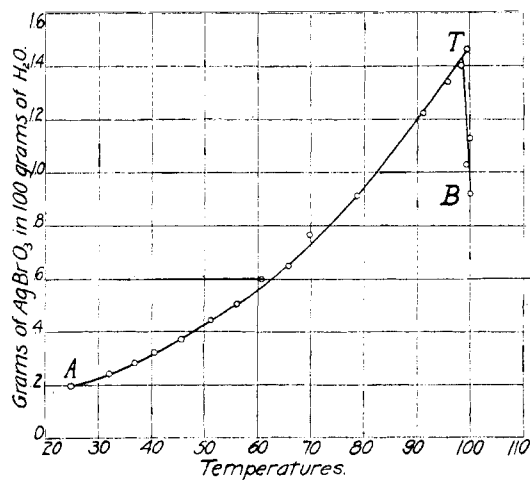


Fig. 4.—The solubility of silver bromate.

solution, where some apparently irregular values are found. The stations on the curve *BT* (Fig. 4) were obtained from solutions which had been allowed to boil for some time, the samples being taken after slight cooling. Evidently these values are somewhat uncertain. High confidence is placed in the values given in the curve *AT*. Solubility data may be said to indicate a transition point near  $98.5^\circ$ , with a possible error of  $0.5^\circ$ .

The dilatometer method gave practically the same value for the transition point. A saturated hydrocarbon oil of high boiling point, obtainable

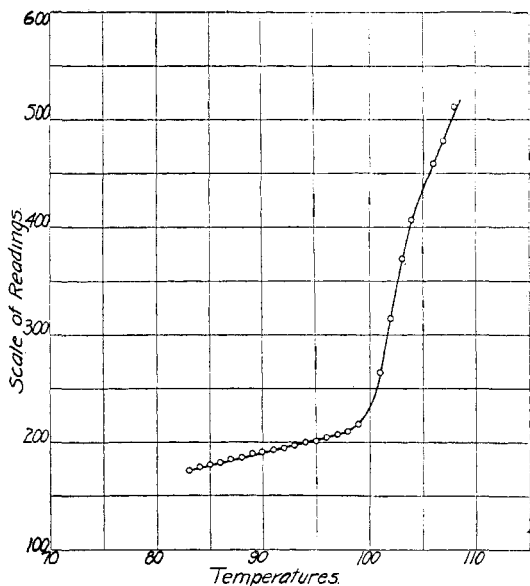


Fig. 5.—Dilatometer readings for silver bromate in "Nujol."

commercially, was used as the liquid. Readings are plotted in Fig. 5, and a transition point of about  $98.5^\circ$  is again indicated. The apparent break in the curve at about  $104^\circ$  is due to the fact that a gas begins to be evolved near that point.

**A Standard in Iodimetry.**—In view of the stability of silver bromate and the ready determination of its purity, its suitability as a standard in iodimetry suggests itself, and was investigated in the following way. The purity of the silver bromate used was determined by converting it into silver bromide by the hydrobromic acid treatment described above. Samples of approximately one g. each were weighed into 250 cc. volumetric flasks, 150 cc. of water and an excess of potassium iodide added and the mixture was heated for some time on a steam-bath. In this way the silver bromate is completely converted into silver iodide and potassium bromate. The contents of the flask were then cooled and made up to 250 cc. Samples of 25 cc. each were acidified with dil. hydrochloric acid and titrated with sodium thiosulfate solution. The usual arsenious oxide method, using the highest grade of arsenic trioxide available, gave a titer appreciably higher than the silver bromate, *viz.*, 0.2%. This indicated that the purity of the silver bromate was greater than that assumed, or that the purity of the arsenic trioxide was less than 100%. Later, after recrystallizing the arsenic trioxide from dil. hydrochloric acid solution and subliming

it very carefully at as low a temperature as possible so as to prevent decomposition into metallic arsenic and oxygen, results were obtained which checked with the silver bromate within 0.05%. This indicates that while silver bromate may have a somewhat higher oxygen equivalent than arsenic trioxide, this defect is fully compensated by its greater definiteness.

**Gas Evolved upon Heating.**—It was noticed that a gas was evolved when silver bromate was heated in contact with water to about 100°. The same thing was found in the dilatometer determination in which the liquid medium was a saturated paraffin oil. The gas was assumed at first to be oxygen in the first case, and oxygen or carbon dioxide in the second. The fact that there was no sensible change in the composition of the silver bromate led to a closer investigation of this phenomenon. An apparatus was devised for heating the salt in contact with these liquids and catching the gas evolved. An atmosphere of hydrogen was kept above the liquids so as definitely to exclude air. The gas in both cases turned out to be a mixture of oxygen and nitrogen in practically the proportion occurring in the atmosphere. Spectroscopic examination gave no evidence of anything else. In the case of water as the liquid, 1 gram of silver bromate yielded during heating for 3 or 4 weeks at 90 to 100° slightly more than 4 cc. of gas. With the oil it gave a little less. It is supposed that the air was occluded during the precipitation of the crystals, or else absorbed later. The latter supposition is favored by the fact that the silver bromate was always precipitated from hot solutions.

This absorbed air suggests an alternate theory for the deviation of the purified silver bromate from 100% purity. The weight of the 4 cc. of air absorbed by one gram of the salt would amount to an impurity of about 0.5%, just as found above.

### Summary.

1. Silver bromate exists in dimorphic forms, *viz.*, tetragonal pyramids, stable at ordinary temperatures, and hair-like crystals, stable near 100°.
2. The variations in the potential of silver bromate electrodes are due to the presence of the metastable hair-like form, which shows a higher solubility than the tetragonal form.
3. Dry silver bromate is stable toward light and heat, but in the presence of water darkens slowly at low temperatures, and rapidly at high temperatures.
4. Silver bromate may be used as a standard in iodimetry.
5. Silver bromate crystals absorb an appreciable amount of air which is slowly given up at high temperatures.