a level with S when the porous cylinder is inserted. The porous cylinder is then inserted and filled to the top with hydrochloric acid. After the cathode is inserted the apparatus is ready for electrolysis.

The current may be taken from a 120 volt direct current, lighting circuit with a number of incandescent lamps in parallel with each other and in series with the cell. The cell may be run continuously on 8-10 amperes. The current is used quantitatively in dissolving platinum. During a run of four and a half hours at 8 amperes, 64 grams of platinum were dissolved. The theoretical quantity for 36 ampere hours is 65 grams. While the apparatus is in operation the hydrochloric acid travels from the cathode cell to the anode under the influence both of gravity and electric endosmoses. With the proper adjustments of height of hydrochloric acid in the anode cell, the heavy layer of chlorplatinic acid solution is delivered at the tip of the siphon S, drop by drop. If the flow of concentrated solution ceases for any reason it may again be started by gentle suction at S. For this purpose it is best to have the siphon tip S connected with a receiving flask by means of a double perforated stopper. The acid in the cathode chamber is replenished from time to time as it becomes necessary.

If towards the end of the operation, when the amount of platinum remaining upon the perforated disk becomes small, bubbles of chlorine commence to rise through the liquid, it is an indication that the current density is becoming too great. In this case, bringing fresh acid into the neighborhood of the platinum black and decreasing the current will remedy the chlorine evolution.

In concentrating the solution of chlorplatinic acid after it is so prepared, chlorine is passed through it for a short while. This insures freedom from platinous compounds in case any have been formed during the electrolysis.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 20.]

THE THEORY AND PRACTICE OF THE IODOMETRIC DETERMINATION OF ARSENIOUS ACID.

BY EDWARD W. WASHBURN.

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1. Introduction.—The first application of arsenious acid solution in titrametric analysis was made by Gay Lussac,[1] who used it in chlorimetry with an indigo indicator. Penot[2] later improved the method by the use of strips of starch iodide paper as the indicator and the use of caustic soda as the solvent for the arsenious acid, instead of hydrochloric acid,

[1] Gay Lussac, Ann., **18**, 18.

[2] Penot, Dingl. Pol. J., **127**, 134 and **129**, 286.

which had been used by Gay Lussac. Friedrich Mohr[1] still further improved the process and brought it into its present form by using standard iodine solution instead of chlorine water as the titrating agent and adding the starch indicator directly to the solution. In the earlier editions of his "Titrirmethode" Mohr directs that the arsenious acid solutions be made up with sodium carbonate and that this substance be present in excess during the titration. In the later editions, however, he recommends the substitution of ammonium carbonate as the neutralizing agent, since he finds it to give "a more permanent end-point." Most of the modern text books on analytical chemistry, however, have adopted sodium bicarbonate for this purpose and this is the custom among chemists in this country.

A critical study of this analytical method particularly from the standpoint of the equilibria involved, seems not to have been made, although all of the data necessary for this purpose are now available in the literature of physical chemistry. In fact many of the latest editions of the standard text books on analytical chemistry including Fresenius, Classen, Sutton and Mohr contain incomplete or misleading statements in regard to the theory of the method and the precautions to be observed in applying it. For example to quote from Sutton's "Volumetric Analysis," (1904): "The principle upon which this method of analysis is based is the fact that when arsenious acid is brought in contact with iodine in the presence of water and *free alkali* it is converted into arsenic acid. The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of bicarbonate since monocarbonated alkalies *interfere with the color of the blue iodide of starch used as an indicator.*" It might be inferred that the normal carbonate or even the hydroxide would not be objectionable if the use of starch as an indicator were dispensed with.

The development of this method seems to have been purely on empirical grounds and the conditions existing in the solution at the end-point, particularly the conditions necessary for securing a "permanent end-point" are not clearly understood. Owing to this rather unsatisfactory condition of the literature on the subject and in view of the fact that under proper conditions this method is one of the most accurate in the field of analytical chemistry, the following treatment of the subject will be made somewhat detailed. The equilibria involved in the method will first be considered and the calculation of the proper conditions to be observed at the end-point as well as the methods for securing these conditions will be given in detail. The preparation and preservation of standard solutions and the operations and precautions to be observed in applying the method will then be described.

2. *Theory of the Method.*—When a solution of iodine in potassium iodide is added to a solution containing arsenious acid the reaction which takes place may perhaps best be expressed as follows:

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \qquad (1)$$

or in words, arsenious acid reacts with triiodide ion and water to produce arsenic acid, hydrogen ion and iodide ion (the "free iodine" in a 0.1 N iodine solution being practically all in the state of triiodide). This reaction is reversible and can be made to go *completely*[1] in *either* direction according to conditions. The reaction from left to right is made use of in determining arsenious acid, while that from right to left is the basis of a method for determining arsenic acid. We shall consider here only the former case and will proceed to determine the conditions necessary to make the reaction go quantitatively from left to right.

In general an equilibrium can be displaced from left to right by increasing the concentration of the substances on the left-hand side of the equation, or decreasing the concentration of those on the right, or by combining both. In the present instance it is obvious that the concentration of the arsenious acid cannot be increased since the object of the titration is to secure its complete oxidation, and for a similar reason the concentration of the arsenic acid cannot be decreased. The concentration of the I_3-ion must not exceed the first recognizable amount since this determines the end-point. The concentration of the water is, of course, a constant. We are therefore reduced to regulating the hydrogen ion or iodide ion concentration, or both, in order to effect our purpose. Since considerable amounts of iodide are introduced with the free iodine, to keep the latter in solution, and since moreover the presence of iodide ion is necessary to give the proper colored end-point, if starch is used as the indicator,[2] it would be inconvenient to attempt to reduce the iodide ion concentration to a small value. It is obvious, therefore, that the success of the whole titration will depend upon the possibility of maintaining the hydrogen ion concentration at a sufficiently small value.

The most obvious method of reducing the hydrogen ion concentration of a solution is to add an alkali and, since[3] $(H^+)\cdot(OH^-) = K$, by adding sufficient alkali the hydrogen ion concentration can be made as small as desired, the hydroxyl ion concentration, of course, increasing proportionally. In the present case we are, however, limited to a very small value of the hydroxyl ion, since iodine reacts in alkaline solution to form iodide and hypoiodous acid and eventually iodate, as expressed by the following reactions,

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[1] By "completely" or "quantitatively" is meant to such a degree that the amount of the substance to be determined, remaining unchanged shall be negligibly small.

[2] See Section 13, Note 6.

[3] Expressions of the form (X) will be used to indicate formula weights of the sub

$$OH^- + I_3^- = HIO + 2I^- \qquad (2)$$

and

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O. \qquad (3)$$

It is thus evident that the hydrogen ion concentration must be kept small enough to allow reaction (1) to proceed quantitatively and yet large enough so that reactions (2) and (3) shall not take place to an appreciable extent. These two conditions might, of course, be mutually contradictory, depending upon the values of the equilibrium constants of the reactions in question.

3. Calculation of the Upper Limit of Hydrogen Ion Concentration.—The equilibrium equation for reaction (1) is

$$\frac{(H_3AsO_4)\cdot(H^+)^2\cdot(I^-)^3}{(H_3AsO_3)\cdot(I_3^-)} = K. \qquad (4)$$

The value of this constant is not known very accurately but a value sufficiently exact for the present purpose can be calculated from the data of J. R. Roebuck.[1] From the data in Roebuck's second paper for the experiments made without sulphuric acid (Table 38), the value $K = 3 \cdot 10^{-2}$ for 0° has been calculated. From the experiments made in the presence of sulphuric acid (which greatly complicates the calculation) Luther[2] has recently computed the value $K = 3.3 \cdot 10^{-2}$. For 25° the value would be $K = 7 \cdot 10^{-2}$.

Assuming a desired accuracy of 0.001 per cent. in the titration, which, as will be shown later, it is possible to approach, the calculation of the upper limit of the hydrogen ion concentration is made as follows: 100 cc. of a 0.1 N arsenious acid solution and 100 cc. of a 0.1 N iodine solution are used in the titration, the total volume when the end-point is reached being *250 cc.* The standard iodine solution contains also 0.12 mol. of potassium iodide per liter. The following relations, therefore, exist: 100 cc. of 0.1 N iodine solution give 0.005 mol of triiodide and 0.012 mol. of potassium. 100 cc. of 0.1 N arsenious acid solution give 0.005 mol. of H_3AsO_3. Together they produce 0.01 mol. of iodide to which should be added 0.012 mol., giving 0.022 mol. of iodide present at the end of the titration. There are also produced 0.005 mol. of arsenic acid ($H_3AsO_4 + H_2AsO_4^-$), and 0.01 mol. of hydrogen ion, the latter, however, being neutralized as far as necessary by the presence of some neutralizing agent. These amounts are present in a volume of 250 cc. Assuming the iodide to be 98 per cent. ionized we have

$$(I^-) = 0.022 \cdot 0.98 \cdot 4 = 8.6 \cdot 10^{-2}.$$

Since only 0.001 per cent. of the arsenious acid is to remain at the end of the titration, we have

$$(H_3AsO_3) = 0.00001 \cdot 0.005 \cdot 4 = 2.0 \cdot 10^{-7}.$$

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[1] Roebuck, J. Phys. Chem., 6, 395, and 9, 756.

[2] Luther, Z. Elektrochem., 13, 289.

For the concentration of the triiodide we shall assume the amount of free iodine necessary to give the color of the end-point in a volume of 250 cc. As will be explained later,[1] this is found by experiment to be $(I_3^-) = 2.0 \cdot 10^{-7}$.

To obtain the value of (H_3AsO_4) it will be necessary to know the ionization constant for arsenic acid. This can be readily calculated from the conductivity data of Walden[2] in the usual manner and is found to be $4.8 \cdot 10^{-3}$.[3] We have therefore the two equations

$$\frac{(H^+) \cdot (H_2AsO_4^-)}{(H_3AsO_4)} = K = 4.8 \cdot 10^{-3}$$

and

$$(H_2AsO_4^-) + (H_3AsO_4) = 0.005 \cdot 4 = 2.0 \cdot 10^{-2},$$

from which (H_3AsO_4) can be readily obtained in terms of (H^+). Substituting the foregoing values in the equilibrium equation

$$\frac{(H_3AsO_4) \cdot (H^+)^2 \cdot (I^-)^3}{(H_3AsO_3) \cdot (I_3^-)} = 7 \cdot 10^{-2}, \qquad (4)$$

and solving for (H^+) we obtain the result $(H^+) = 1.0 \cdot 10^{-4}$ as the upper limit of the hydrogen ion concentration.[4]

4. Calculation of the Lower Limit of the Hydrogen Ion Concentration.—To find the concentration of hydroxyl ion which will produce an error of 0.001 per cent. due to the formation of iodate according to the reaction

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O,$$

it is necessary to know the equilibrium constant for this reaction. This constant can be obtained from the following data:

$$\frac{(H^+)^6 \cdot (IO_3^-)(I^-)^5}{(I_2)^3} = 2.8 \cdot 10^{-47} \text{ (Sammet).}^5 \qquad (5)$$

$$(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14} \qquad (6)$$

and

$$\frac{(I_2) \cdot (I^-)}{(I_3^-)} = 1.3 \cdot 10^{-3} \text{ (Noyes and Seidensticker).}^6 \qquad (7)$$

Dividing equation (5) by equation (6) raised to the sixth power and then multiplying by equation (7) cubed we get

$$\frac{(IO_3^-) \cdot (I^-)^8}{(OH^-)^6 \cdot (I_3^-)^3} = 6 \cdot 10^{28}, \qquad (8)$$

which is the constant desired. As before, we have total triiodide used

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[1] See Section 13, Note 6.

[2] Walden, Z. physik. Chem., 2, 49.

[3] See also Luther, Z. Elektrochem., 13, 297.

[4] It is worth noting that if an accuracy of only 0.1 per cent. is required, this value is still $5 \cdot 10^{-4}$.

[5] Sammet, Z. physik. Chem., 53, 640.

[6] Noyes and Seidensticker, Z. physik. Chem., 27, 357

0.005 mol. Of this 0.001 per cent. = $5.0 \cdot 10^{-8}$ mol. will produce $1/3 \cdot 5.0 \cdot 10^{-8} = 1.67 \cdot 10^{-8}$ mol. of IO_3^-.

We have therefore

$$\begin{aligned} (IO_3^-) &= 4 \cdot 1.67 \cdot 10^{-8} = 6.7 \cdot 10^{-8}, \\ (I^-) &= 8.6 \cdot 10^{-2}, \\ (I_3^-) &= 2 \cdot 10^{-7}, \\ (OH^-) &= x. \end{aligned}$$

Substituting in the equilibrium equation (7) above and solving for (OH^-), we find $(OH^-) = 10^{-4}$, a value which, if exceeded, will cause an error of 0.001 per cent. due to the formation of iodate.

The equilibrium constant for reaction (2)

$$OH^- + I_3^- = HIO + 2I^-,$$

is obtained from the following data:

$$\frac{(HIO^-) \cdot (I^-) \cdot (H^+)}{(I_2)} = 10^{-9} \ \text{(Sammet),[1]} \tag{8}$$

$$(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14}, \tag{9}$$

$$\frac{(I_2) \cdot (I^-)}{(I_3^-)} = 1.3 \cdot 10^{-3}. \tag{10}$$

Multiplying (8) by (10) and dividing by (9) gives

$$\frac{(HIO)(I^-)^2}{(I_3^-) \cdot (OH^-)} = 1.3 \cdot 10^{2} \tag{11}$$

for the value of this constant. Solving as before for (OH^-) we find $(OH^-) = 10^{-5}$ which is a smaller value than that obtained for reaction (2).

Therefore, since $(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14}$, we get for the *lower* limit of the hydrogen ion concentration the value $(H^+) = 10^{-9}$. We therefore conclude that if an accuracy of 0.001 per cent. is desired in this titration, the hydrogen ion concentration in the solution when the titration is finished, must lie between the limits, $(H^+) = 10^{-4}$ and $(H^+) = 10^{-9}$. The best value will evidently be the geometrical mean of these two which is $3 \cdot 10^{-7}$. This differs very little from the concentration of hydrogen ion in pure water so that we may state as the final conclusion of the preceding calculations, that, *at the completion of the titration of an arsenious acid solution with standard iodine, the solution should be neutral.*

5. *Solutions of Constant Hydrogen Ion Concentration.*—A solution will automatically keep itself at any desired hydrogen ion concentration even though small quantities of acid or base be added to it, provided it contains something which will remove both hydrogen and hydroxyl ions when acid or alkali are added to the solution. A solution which contains the salt of a weak acid (or base) together with an excess of the acid (or base) has this property of automatically maintaining itself at a practically constant hydrogen ion concentration. If for example acid be

added to a solution containing sufficient amounts of the weak acid HA and its salt MA in the proper proportions, hydrogen ion will be immediately removed by the reaction,

$$H^+ + A^- = HA,$$

and in a similar manner alkali will be neutralized according to the reaction,

$$HA + OH^- = H_2O + A^-.$$

The proper porportions of acid (or base) and salt to use in order to keep the solution at any desired hydrogen ion concentration are readily calculable from the ionization constant of the acid (or base). If the mixture is to be equally efficient in the removal of hydrogen and hydroxyl ions, it is evident that the concentration of the acid (HA), should be equal to that of the ionized salt (A^-), *i. e.*

$$(HA) = (A^-) = \gamma(S) \qquad (a)$$

where γ is the degree of ionization and (S) the total molar concentration of the salt. Combining this relation with the equilibrium equation for the ionization of the acid,

$$\frac{(H^+) \cdot (A-)}{(HA)} = K, \qquad (b)$$

we obtain the result $K = (H^+)$.

That is, *the ionization constant of the acid should be numerically equal to the desired hydrogen ion concentration.* In case no suitable acid can be found which exactly fulfils this condition, one is chosen which most nearly does so. Suppose its constant is

$$K = n(H^+), \qquad (c)$$

then if n is not too large, this acid can be used, provided the ratio of salt (S), to acid (HA), is changed. By combining equations (*a*), (*b*) and (*c*), it is evident that this ratio must have the value,

$$\frac{(S)}{(HA)} = \frac{n}{\gamma}. \qquad (d)$$

In applying these considerations to the problem in hand, since the solution is to be kept neutral, *i. e.*, $(H^+) = (OH^-) = 10^{-7}$, it is evident that the acid chosen should have an ionization constant not far from 10^{-7}. Of the numerous acids which might be used for this purpose we shall consider here only the following acids and their salts.

Acid.	Salt.
NaH_2PO_4	Na_2HPO_4
H_2CO_3	$NaHCO_3$
H_3BO_3	Na_3BO_3

Phosphoric Acid.—The ionization constants of the three hydrogens of this acid are given by the following equations:[1]

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[1] The values of these constants have been recently determined in this laboratory by Mr. G. A. Abbott in an investigation which will be published shortly

$$\frac{(H^+)\,(H_2PO_4^-)}{(H_3PO_4)} = 1 \cdot 10^{-2}.$$

$$\frac{(H^+)\,(HPO_4^{--})}{(H_2PO_4^-)} = 2.1 \cdot 10^{-7}.$$

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = 5.6 \cdot 10^{-13}.$$

The first hydrogen is a strong acid but the salt of this acid, NaH_2PO_4, acts as a weak acid with the ionization constant 2.10^{-7} and is therefore suitable for the purpose in hand. The ionization constant of the third hydrogen is so small that the ionization of HPO_4^{--} will be entirely negligible. We have, therefore, $(S) = C_{Na_2HPO_4}$, and $(HA) = (H_2PO_4^-) = \gamma_1 C_{NaH_2PO_4}$ where $C_{NaH_2PO_4}$ is the total molar concentration of NaH_2PO_4 and γ_1 its degree of ionization as a salt. Substituting these values in equation (*d*) above we obtain the result

$$\frac{C_{Na_2HPO_4}}{C_{NaH_2PO_4}} = \frac{n\gamma_1}{\gamma}$$

and since γ_1 can be assumed equal to γ, we conclude that the solution at the end of the titration should contain about two mols of Na_2HPO_4 for every mol of NaH_2PO_4 in order to preserve neutrality.

Calculation for Carbonic Acid.—This acid is in general not adapted for the purpose of maintaining a constant hydrogen ion concentration because, being a gas, it escapes gradually from the solution so that its concentration and consequently that of the hydrogen ion is an uncertain quantity. Only when the solution is kept saturated with carbon dioxide at a definite temperature and pressure is the concentration of the carbonic acid in the solution of a definite known quantity. For our present purpose therefore it is necessary to know what concentration of sodium bicarbonate must prevail in a solution *saturated* with carbon dioxide if the concentration of the hydrogen ion is to be 10^{-7}. We have the following ionization equations for the acid.[1]

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = 3.04 \cdot 10^{-7}.$$

$$\frac{(H^+) \cdot (CO_3^{--})}{(HCO_3^-)} = 6.04 \cdot 10^{-11}.$$

Here also the dissociation of the second hydrogen in a neutral solution is negligible. In a solution saturated with carbon dioxide at 25° and 1 atmosphere $(H_2CO_3) = 0.0338$. Substituting in equation (*d*) again we obtain

$$\frac{(S)}{0.0338} = \frac{3.04}{\gamma} \text{ which gives } C_{NaHCO_3} = 0.12.$$

Therefore in a 0.12 molar solution of sodium bicarbonate, saturated with

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[1] McCoy, Am. Chem. J., 29, 437.

carbon dioxide the hydrogen ion concentration will be about 10^{-7}. The ratio between acid and salt (1:4) is not so favorable as in the case of the phosphate. Owing to the relatively small concentration of the acid, the hydrogen ion concentration will be rather sensitive to the escape of CO_2 from the solution, since to offset this loss, carbonic acid is being continually produced at the expense of the hydrogen ions according to the reaction,

$$H^+ + HCO_3^- = H_2CO_3 = H_2O + CO_2.$$

Boric Acid.—Sammet[1] by the measurement of the E. M. F. of a hydrogen electrode, has determined the hydrogen ion concentration in a solution saturated with respect to both borax and boric acid and found it to be $(H^+) = 6 \cdot 10^{-7}$.

We have therefore three combinations which theoretically should be equally suitable for keeping the solution neutral during the titration.

6. Test of the Conclusions.—The conclusions of the foregoing considerations were tested by standardizing an approximately 0.1 normal iodine solution against a 0.1 normal arsenious acid solution. About 100 cc. of the iodine solution were used in each case. The solutions were weighed instead of measured, the end-point being reached by using a very dilute arsenious acid solution, the procedure being that described in the following sections. It will be noticed that the conclusions of the foregoing calculations are completely justified. These results will be discussed later when the procedure has been described.

	$NaHCO_3 +$ H_2CO_3	$Na_3BO_3 +$ H_3BO_3	$Na_2HPO_4 +$ NaH_2PO_4	KI alone.
Value of 100 grams of iodine solution in terms of As_2O_3.	0.48737	0.48733	0.48735	—
	0.48736	0.48733	0.48736	—
	0.48738	—	—	—
	0.48736	—	—	—
	0.48735	—	—	—
Blanks in same unit.............	0.000078	0.000078	0.000078	0.000073

Mean, 0.487354.
a. d., 0.000012 = 0.0025 per cent.
A. D., 0.0000040 = 0.00082 per cent.
Max. d., 0.000056 = 0.01 per cent.

7. Titration by Weight.—For the most accurate work in titrametric analysis it is necessary to weigh all the solutions used instead of measuring them, and the solutions are conveniently made up on the weight standard system, that is, so that 1000 grams of a normal solution contain one equivalent weight of the substance. Indeed even for work in which only 0.1 per cent. accuracy is required, this method possesses several advantages over the volumetric method and need consume very little

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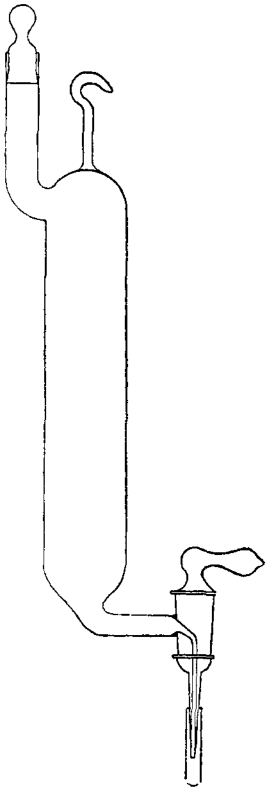
[1] *Loc. cit.*

more time. Its principal advantages are: (1) since graduated vessels are not used, no time need be spent in calibration and no errors are introduced from this source; (2) frequent cleaning of the burettes is not necessary as drops clinging to the sides of the burette do not affect the result; (3) the result is independent of the temperature of the solutions; (4) no time is consumed in allowing the burette to drain, in fact the weight-burette can be weighed in the time usually consumed in drainage.



A convenient form of a weight-burette, devised by Mr. C. A. Kraus, of this laboratory, is shown in the figure. The stopcock and glass cap for the tip are very carefully ground so as to insure a tight joint. The opening for filling the burette is placed at the side so that none of the solution can come in contact with the stopper which is hollow and open at the bottom. In order to permit the entrance of air during the titration, the stopper and the side of the socket are provided with two small holes which can be made to coincide by turning the stopper in its socket. In weighing, the burette is suspended from the balance arm by the hook, a similar burette suspended from the other arm serving as a counterpoise. For most work a suitable weight-burette can also be readily made from a separatory funnel by cutting off the stem, drawing it down to a point, and grinding on a glass cap. Previous to filling the burette, a small quantity of the solution is shaken in it and then allowed to run out. This insures the saturation of the air in the burette by the vapor of the solution.

8. Preparation of Standard Iodine Solutions.—To prepare a liter of approximately 0.1 N iodine solution, 12.7 grams of resublimed iodine are weighed into a small beaker, about 20 grams of pure potassium iodide added, and the whole covered with water and allowed to stand with occasional stirring until solution is complete. The solution is then filtered through an asbestos filter into the stock bottle and sufficient water (best distilled) added to make the volume about 1 liter. The statement is frequently made that iodine solutions cannot be kept very long unchanged and require frequent standardization. In the experience of the author, however, an iodine solution properly prepared and used is one of the most stable of standard solutions. The chief causes of change in titer are losses from evaporation, from particles of dust which may get into the solution, and from impurities in the water used in preparing the solution. With proper precautions these losses are, however, inappreciable. The neck of the bottle should be kept covered with a beaker to exclude dust, and when the solution is shaken to mix it, care should be taken to avoid wetting the stopper. The solution should always be removed with a pipette, *never by pouring*. It is advisable to allow a newly-prepared solution to stand a few days previous to standardizing and the stock bottle should be kept in a dark place. The following results were obtained for the standardization of an iodine solution at an interval of two months, the solution being in frequent use meanwhile.

November 5th, 1 gram I solution = 0.0048504 gram As_2O_3.
January 8th, 1 gram I solution = 0.0048505 gram As_2O_3.

9. *Preparation of Tenth-Normal Arsenious Acid Solution.*—The arsenious oxide is purified by recrystallization from hot water and by sublimation. After drying in a vacuum over sulphuric acid, about 5 grams of the crystals are placed in a small weighing tube and about 4.95 grams are accurately weighed out into a glass stoppered liter flask which has been previously cleaned, dried and weighed to centigrams. Ten to 12 grams of pure caustic soda are then dissolved in about 30 cc. of water, which has been freshly distilled from an alkaline permanganate solution to insure absence of organic matter and dissolved oxygen. After filtering through asbestos it is added to the flask which is then allowed to stand until solution is complete. The chief impurity which it is necessary to guard against in the caustic soda is *iron*. The grade known as "purified by alcohol" is usually satisfactory for this purpose as it gives a very small blank.

When solution of the arsenious acid is complete (about half an hour), 100 cc. of water are added and a delivery tube is inserted in the flask below the level of the liquid. The delivery tube is connected with a generator supplying carbon dioxide and the gas is allowed to bubble slowly through the solution until saturation is reached. After removing and washing the delivery tube the solution is diluted to nearly a liter with the freshly distilled water. The flask is then placed on the balance pan and water added from a dropper until the weight of the solution is 206.73 times the weight of the As_2O_3 used. After thorough mixing, the solution is ready for use and will preserve its titer almost indefinitely. One thousand grams of the solution correspond to 0.1 equivalent of arsenious acid.

Instead of the above method of preparing the solution with sodium bicarbonate, the following method in which sodium phosphate is used gives fully as satisfactory results and possesses certain advantages as will be pointed out later. In this method the arsenious acid is weighed out as before but is dissolved by adding a strong solution of sodium hydroxide of known strength, the amount added containing 12 grams of NaOH.

When solution of the arsenious acid is complete a solution of pure phosphoric acid containing 0.15 mol of H_3PO_4 is added and the whole made up to the final weight as before.

10. Preparation of the Starch Solution.—This solution, prepared as directed in Treadwell's "Analytical Chemistry,"[1] and preserved in small bottles, is eminently satisfactory. A large supply should be prepared at one time, as solutions prepared at different times are liable to give somewhat different colored end-points. When properly prepared, the first color obtained with iodine should be *pink*. Starch solution which gives a blue or greenish-blue color as the first shade should be rejected. The "soluble starch" of commerce is not to be recommended for the finest work. Two cc. of the starch solution are used in each titration.

11. Standardization of the Iodine Solution against the Arsenious Acid Solution.—About 100 cc. of the arsenious acid solution are removed with a pipette and transferred to a carefully tared Erlenmeyer flask of 500 cc. capacity provided with a rubber (or better, glass) stopper.[2] The weight of the solution to the nearest milligram is then determined, and the flask is placed upon a large sheet of white paper in a good light (preferably north). The weight pipette is then filled with the iodine solution as previously described and is weighed to the nearest milligram. The pipette is placed in its support and the flask containing the arsenious acid solution is held in the hand so that the tip of the pipette touches the inside of the neck of the flask. About 100 cc. of the iodine solution are added and the flask is stoppered lightly and rotated until the yellow color of the iodine disappears. If the arsenious acid solution was prepared with bicarbonate the solution will effervesce, and during the effervescence the flask should be held in a slanting position so that the walls of the flask and not the stopper receive the fine spray thrown up by the effervescence. The titration is continued slowly until finally one drop of the iodine solution produces a permanent yellow color. The flask is then stoppered and allowed to stand while the weight burette is weighed again.

The titration is completed by using a dilute arsenious acid solution. This is prepared by diluting 25 grams of the 0.1 normal solution to a volume of a liter. This 0.0025 N arsenious acid solution is kept in a bottle with a burette permanently attached to it. A titration is finished by adding this dilute solution drop by drop until the yellow color has almost disappeared. Two cc. of the starch solution are then added and the addition of the arsenious acid solution continued until the blue color

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[1] Analytical Chemistry, Treadwell-Hall, Vol. 2, p. 513 (1904).

[2] It is convenient to have a number of these flasks ready for use. The lightest flask in the set is used as a partial counterpoise, and the weights of the others are marked on their stoppers. The flasks should be kept in the balance room so as to be under the same conditions of temperature and humidity as the balance.

gives way to a rose color which just matches the color of flask No. 2, of a set of color standards whose preparation will be described below. Before adding the last two or three drops it is best to wait ten or fifteen minutes to insure the completion of the reaction and the attainment of equilibrium. The flask should be protected from the light during this interval. *This end-point when reached (if the flask is kept stoppered and protected from the light) is permanent both in shade and intensity of color for several weeks, and the end-point is sensitive to two drops of the dilute arsenious acid solution, that is, to less than 0.002 per cent.*[1]

12. Preparation of Permanent Color Standards.—A flask containing a solution, the titration of which has just been completed, is made just colorless by the addition of a few drops of the dilute arsenious acid solution. It is then placed under a burette containing a 0.005 N iodine solution and iodine added until a faint permanent yellowish-pink color is produced. In a second flask a solution is made up which exactly matches this color. This is color standard No. 1. It can be made by combining solutions of ferric chloride, copper nitrate and cobaltous nitrate in the proper proportions. Another drop of the dilute iodine solution is then added and a second color standard made up to match this color, which is more of a pink shade. A third drop of iodine solution is then added and the third color standard made to match this color. In titrating a solution the end-point is always taken as the color corresponding to the middle flask in the set of color standards. This shade of pink, which is close to what is known as the "sensitive tint" in polarimetry, is much more sensitive to small changes than are the blue tints obtained by the further addition of iodine.

13. Notes on the Process.—(1) In titrations with the use of sodium bicarbonate as the neutralizing agent it is *absolutely essential* that the solution be kept saturated with carbon dioxide as the calculations indicate; consequently the titration should never be made in a beaker but always in a stoppered flask.[2] This is a precaution which is not mentioned in the text books, but its importance is readily shown by the following experiment. The titration as described above was made in a beaker. When the end-point was reached the solution was stirred for thirty seconds. At the end of this time the solution had become completely colorless. That this was not due to the slowness of the reaction was made evident by

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[1] It is best to avoid unnecessary exposure to strong light, especially direct sunlight, since light catalyzes the reaction

$$O_2 + 4H^+ + 4I^- = 2I_2 + 2H_2O$$

which may take place to a slight extent, even in neutral solution, in case dissolved oxygen is present. See Plotnikow, Z. physik. Chem., **58**, 214.

[2] The author has found nothing superior to Erlenmeyer flasks for *all* titrametric analyses. They are much more reliable and convenient than the beaker and stirring-rod so frequently used.

adding a few drops of hydrochloric acid to the solution. This caused the evolution of carbon dioxide and the color immediately returned to fade away again on further stirring and consequent escape of carbon dioxide. Unless sufficient free carbon dioxide be present the concentration of hydroxyl ion becomes sufficiently large to cause the formation of an appreciable amount of hypoiodous acid and a consequent fading of the end-point.

Some authors recommend cooling the solution to 0° with cracked ice as giving a more delicate end-point. This is not to be recommended, however, as the reaction is too slow at this temperature. The observed increase in the delicacy of the end-point in the cold solution is simply due to the greater solubility of carbon dioxide at this temperature, so that a solution open to the air does not become alkaline so rapidly as at a higher temperature. *At room temperature and in a closed flask the delicacy and permanency of the end-point are all that could be desired.*

(2) The use of the sodium phosphate has the advantage that the acid is not a gas and its concentration in the solution can be controlled by the operator. Since there is no effervescence when it is used, mechanical loss from this source is impossible. It is to be recommended in preference to the bicarbonate.

(3) The use of the borax-boric acid mixture, while it gives accurate results, is not convenient and has no advantage over the other two. The use of ammonium carbonate as directed by Mohr in his last edition, is still less to be recommended, since owing to the volatility of both the acid and base, the concentration of hydrogen ion is still less under the control of the operator.

(4) In titrating an unknown solution of arsenious acid, the solution, if alkaline, is made neutral with hydrochloric acid; if acid, it is neutralized with sodium hydroxide, using *phenolphthalein* as the indicator. The neutralizing agent, bicarbonate or phosphate, is then added from time to time during the titration and when the titration is nearly completed more of the neutralizing agent is added until the total quantity added amounts to about 5 grams of $NaHCO_3$ or 11 grams of $Na_2HPO_4.12H_2O$ for every 100 cc. of 0.1 N iodine solution required in the titration. The volume at the end of the titration should be about 250 cc. for every 100 cc. of the 0.1 N iodine solution used. Under these conditions the acid produced by the reaction is enough to saturate the solution with carbon dioxide or to produce NaH_2PO_4 in the proper amount to give the molar ratio $\frac{Na_2HPO_4}{NaH_2PO_4} = 2$, at the end-point. The Na_2HPO_4 should be added, in solution, from a burette.

(5) For the determination of small quantities of arsenious acid a 0.01 N iodine solution is used and in this case it is necessary to add the proper

amount of hydrochloric acid to insure saturation with carbon dioxide or to produce the proper amount of NaH_2PO_4, since the acid produced by the reaction is not sufficient. The amount of hydrochloric acid to use in the case of the phosphate has to be obtained by calculation for each case if the highest accuracy is required, so that the use of the bicarbonate is more convenient in this instance. Potassium iodide must also be added to give the proper color for the end-point.

(6) The necessity of the presence of sufficient iodide in the solution to develop the proper color with the starch indicator has been emphasized by Treadwell. If a dilute iodine solution be added to water containing starch, a considerable amount of solution is required before the blue color is produced. The presence of an iodide in the solution causes the color to appear when only a small amount of the iodine has been added. Other salts have a similar effect in developing the color. In order to compare the effect of different salts, the following experiment was made. To a flask containing 250 cc. of water, 3 grams of potassium iodide, and 2 cc. of starch solution, the dilute iodine solution was added until the end-point color was reached. A set of flasks containing 250 cc. of 0.1 molal solutions of the substances named below was then prepared and after the addition of 2 cc. of starch solution, the dilute iodine solution was added to each until the same depth of color was produced as in the first flask. The amounts of iodine solution required in each case is shown in the table.

0.1 molal solution of	cc. of I solution used.
KI	5.5
KCl	17.0
NaCl	17.0
$MgSO_4$	16.0
$Ba(NO_3)_2$	13.0
$(NH_4)_2SO_4$	14.0
(Pure water)	45.0

The color of the end-point in the case of the iodide is of a different shade than the others and is probably due to a different effect. It is usually attributed to the formation of a compound, the statement being made that its presence is essential to the production of the "blue compound" with starch. That this may not be the whole explanation is shown by the effect of the other salts.

14. Determination of Blanks.—In making a blank the solution is made up to correspond exactly to the solution to be titrated but with the omission of the arsenious acid. In addition, it is necessary to add pure potassium iodide (3 grams per 250 cc.) for the reason mentioned in the preceding note. Pure hydrochloric acid is used, if necessary, to insure saturation with CO_2 or to produce the proper amount of NaH_2PO_4. The blanks are made by using an 0.005 N iodine solution whose ratio to the dilute arsenious acid solution has been determined. With pure materials the blanks, which are purely volume corrections, should be very small, never exceeding a value equivalent to 0.0001 gram As_2O_3. The author has obtained blanks as low as 0.00004 gram As_2O_3, which in an analysis requiring 100 cc. of 0.1 N iodine solution amounts to only 0.008 per cent. The blank is always subtracted in calculating an analysis.

15. Applications of the Method.—It is evident from the preceding calculations and experiments that under the proper conditions iodine can be quantitatively reduced to iodide by arsenious acid and that a *definite, permanent and exceedingly delicate end-point* is obtained. The accuracy and definiteness of the end-point makes this method a valuable and convenient one for determining the atomic ratio between arsenious acid and iodine since the materials necessary for the determination can be readily purified and the method is free from any sources of error due to side reactions, adsorption, presence of water, etc., which have to be corrected for in many precipitation methods in atomic weight work. The accurate knowledge of this ratio is important to the analytical chemist since arsenious acid is the most convenient and accurate standard for iodimetry.

BOSTON, November 1, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SPECIFIC GRAVITIES OF THE IODIDES OF SODIUM, POTASSIUM, RUBIDIUM, CAESIUM, CALCIUM, STRONTIUM AND BARIUM.

BY GREGORY PAUL BAXTER AND FRANCIS NEWTON BRINK.

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Attention has been recently called by various authors to large discrepancies and inaccuracies in the present tables of specific gravities.[1] If for no other reason, the interest attached to molecular volume[2] makes the accurate knowledge of specific gravities of considerable importance. Since the specific gravities of the chlorides and bromides of the alkali and alkaline earth metals have already been determined with care,[3] the present research is concerned with the iodides of these elements. Lithium iodide was not investigated because its density has recently been found by one of us.[4]

Among the chief sources of error in specific gravity determinations may be mentioned imperfect drying of the substances and inclusion of mother-liquor by crystals. Both these difficulties were avoided in the

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[1] Proc. Am. Acad., **31**, 163; Am. Chem. J., **31**, 220, 229, 558; Trans. Chem. Soc., **91**, 56.

[2] See especially Richards, Proc. Am. Acad., **37**, 3, 399; **38**, 293; **39**, 581.

[3] Landolt-Börnstein-Meyerhoffer.

[4] Baxter, Am. Chem. J., **31**, 558.