[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

# The Accuracy of the Potentiometric Iodide–Silver Titration

BY I. M. KOLTHOFF AND J. J. LINGANE

This study of the potentiometric iodide–silver titration was undertaken with a three-fold purpose: (a) to determine the accuracy of the titration, (b) to locate the isoelectric point of freshly precipitated silver iodide, and (c) to study the adsorption of silver and iodide ions by flocculated silver iodide, at extremely low concentrations. A knowledge of the accuracy of the iodide–silver titration was necessary before the required data for topics b and c could be obtained. The present paper contains the results of the experiments made to determine the accuracy of the titration, and subjects b and c will be discussed in a subsequent communication.

Although the *precision* of the potentiometric iodide–silver titration has been studied exhaustively by Lange and Berger,[1] these authors did not establish the *accuracy* of the titration since they worked with solutions of potassium iodide and silver nitrate whose concentrations were not exactly known. In lieu of direct experimental evidence of the accuracy of the titration, they studied the adsorption of silver and iodide ions on silver iodide, and concluded from the data so obtained that the titration should give results accurate to at least ±0.01%, when performed under the most favorable conditions. They found that titration at room temperature was impractical because of the strong adsorption of silver and iodide ions by the precipitate with consequent slow attainment of steady e. m. f. They found that the deleterious effects of adsorption were practically eliminated when the titration was performed at 90°, and they showed that the results were highly precise under these conditions.

Unfortunately, Lange and Berger did not pay particular attention to the purity of the materials which they used. Since commercial samples of potassium iodide almost invariably are contaminated by traces of bromide and chloride, this neglect casts some doubt on their conclusions. In the present study we have taken special care to use materials of a high degree of purity. Instead of working in neutral solution, as Lange and Berger did, we performed all titrations in the presence of a small amount of nitric acid, since adsorption of silver ions on the glass wall of the container is eliminated under such conditions.

### Materials Used

**Potassium Iodide.**—Since potassium iodide is not easily purified by usual recrystallization methods, because of its great solubility in water and because of the doubtful removal of possible traces of chloride and bromide, we prepared the salt from pure hydriodic acid and purified potassium bicarbonate. Hydrogen iodide was synthesized directly from purified iodine and hydrogen by the classical method in which platinized asbestos is used as catalyst, and the gas was dissolved in water to give a concentrated solution.[2] The solution of hydriodic acid was nearly neutralized with purified potassium bicarbonate, and evaporated in a hydrogen atmosphere until a considerable quantity of potassium iodide separated out, which was filtered off and dried.

**Silver.**—The preparation of the pure silver used in this study has been described in a previous paper from this Laboratory.[3]

**Nitric Acid.**—The nitric acid used in this work was obtained by distilling C. P. concentrated acid in an all-glass still, the middle fraction only being collected.

**Water.**—Conductivity water was used in all preparative work and in the preparation of all solutions.

**Apparatus.**—A silver iodide electrode was used as indicator electrode in the titrations, and a saturated calomel electrode was used as reference electrode. The silver iodide electrodes were prepared by plating platinum gauze electrodes (cylinders 1 cm. in diameter and 1 cm. long) with silver from a 10% potassium argentocyanide solution at low current density. The silver electrodes were then iodized by making them anodes in the electrolysis of a dilute potassium iodide solution for a few minutes at low current density, followed by thorough washing with water.

The titration vessel consisted of a one-liter beaker, painted black on the outside, and provided with a tightly fitting bakelite cover with suitable holes for the buret-tip, salt bridge, electrode, thermometer and stirrer. This arrangement provided efficient light protection. A saturated solution of potassium nitrate, free from chloride, was used in the salt bridge, which was filled with fresh solution for each titration. For the hot titrations, the titration beaker was placed in an electrically heated water-bath whose temperature could be held constant to ±0.5°.

Weights and volumetric apparatus were calibrated carefully by standard methods. Weighings were corrected to vacuum on the following density basis, weights (brass) 8.4, silver 10.5, potassium iodide 3.12 and air 0.0012 g. per cc.

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[1] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930).

[2] We are indebted to E. R. Caley and M. G. Burford (private communication) for suggesting the apparatus for this synthesis. Details of the methods of preparation are described by the authors in Volume I of "Inorganic Syntheses."

[3] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

**Preparation of Potassium Iodide for Weighing.**—Potassium iodide decomposes slightly when fused in air or nitrogen,[4] and the fused salt is strongly alkaline. We have found, however, that the salt may be melted in pure dry hydrogen with no trace of decomposition. Solutions of the salt which had been fused in hydrogen were always perfectly colorless, and showed no trace of alkalinity. Portions of the salt were prepared for weighing by melting for ten minutes at 700–725° in pure dry hydrogen in a platinum boat. The fused sample was allowed to cool to below 200° in hydrogen, and was then removed to a desiccator containing fused potassium hydroxide, where it remained until weighed.

### Technique of the Titrations

Separate samples of silver and potassium iodide were weighed out for each titration, the silver being in the form of buttons weighing from 1.0 to 1.5 g. each. A silver button was first carefully weighed and transferred to a small Kjeldahl flask in which it was dissolved in 3 cc. of concentrated nitric acid with gentle heating. The solution was then heated to remove oxides of nitrogen, the heating being continued for at least fifteen minutes after the disappearance of brown fumes. The solution was cooled, transferred to the titration beaker, and diluted to approximately 500 cc. The resulting solution was approximately 0.02 $N$ in silver and 0.04 $N$ in nitric acid.

The carefully weighed sample of potassium iodide was dissolved in approximately 100 cc. of water in a special dropping funnel previously described,[3] and the solution was mixed thoroughly. The potassium iodide solution was run dropwise into the silver solution with constant mechanical stirring, from ten to fifteen minutes being required for the addition. The funnel and platinum boat were rinsed out with eight to ten portions of water, which brought the total volume of solution to between 750 and 850 cc., after which the bakelite cover was placed on the beaker. The beaker was placed in the water-bath, the electrode, stirrer, thermometer and salt bridge were put in place, and after heating to the desired temperature, the titration was completed with 0.01 $N$ potassium iodide solution added from a microburet. Efficient mechanical stirring was employed, and the titrations were carried out in very faint diffuse daylight in a room with closely drawn shades, although this latter precaution was probably unnecessary because the titration vessel itself served as an efficient protection against light.

Titrations were made at room temperature, at 70 and at 90°, and some experiments were also made in which the precipitate was digested for some time at 95 to 100° before finishing the titration. A reflux condenser was used in the long digestion experiments to prevent evaporation of the solution.

In the majority of the titrations the end-point was found in the classical way from the maximum in $\Delta E/\Delta V$. However in the titrations at room temperature (without digestion) the maximum in $\Delta E/\Delta V$ was not well defined, and in these titrations the end-point was found by titrating to the equivalence potential.[5,3] The equivalence potential was determined by titrating very small amounts of silver with the dilute potassium iodide solution under the same conditions of acidity, temperature, and volume as in the actual titrations. At room temperature the equivalence potential found in this way was +0.098 volt against the saturated calomel electrode, in a 0.035 $N$ nitric acid solution. The average solubility product of silver iodide in 0.035 $N$ nitric acid, calculated from the data of several such "dilute" titrations, was $2.18 \times 10^{-16}$ at 25°. Titration at room temperature is not practical because of the long time required for the e. m. f. to reach steady values, and furthermore (Table II) the error of the titration is greatest at this temperature. As long as an hour is required to obtain steady e. m. f. readings between each addition of reagent at 25°. The drift is particularly bad in the immediate vicinity of the end-point, and the exact position of the maximum in $\Delta E/\Delta V$ is difficult to locate. Under the conditions described, the end-point determined by titrating to the equivalence potential agreed within the limits of the experimental error with that determined from the maximum in $\Delta E/\Delta V$. This was no longer true when the titration was performed in the more usual manner, by taking e. m. f. readings five minutes after each addition of reagent without waiting until the potential had attained constant values. By titrating to the equivalence potential, exactly the same result was obtained as in the slow titration; however, the values of $\Delta E/\Delta V$ changed in an irregular way in the neighborhood of the equivalence potential and two maxima were found. For this reason, fast titration at room temperature is not recommendable.

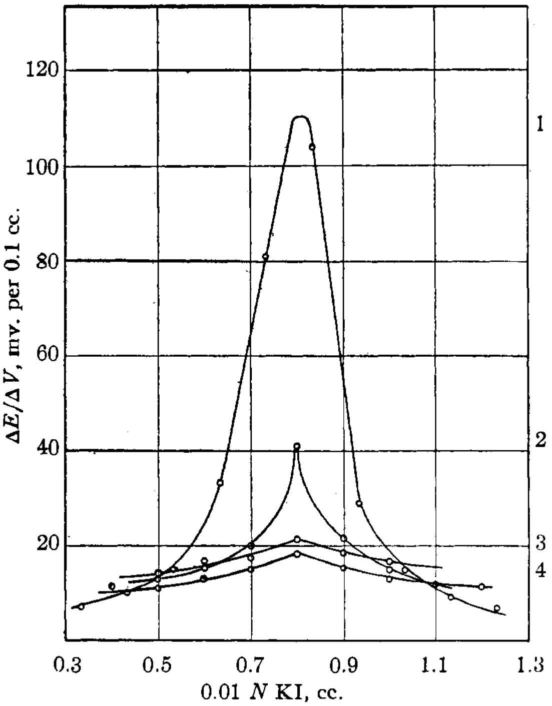

Fig. 1.—$\Delta E/\Delta V$ curves in region of equivalence point under various conditions: (1) digested 40 hours at 95°, titrated at room temp.; (2) direct titration at 70°; (3) direct titration at room temperature; (4) direct titration at 90°.

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[4] G. P. Baxter and F. N. Brink, THIS JOURNAL, **30**, 46 (1908).

[5] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1932, p. 100.

Constant e. m. f. readings can be obtained in a relatively short time at 70 or 90°, except in the immediate vicinity of the end-point where fifteen to thirty minutes are required. The same is true when the precipitate is digested previous to titration at room temperature. Under the latter conditions the most pronounced break in the potential is found, since the adsorptive properties of the precipitate have become extremely small, and the solubility is much smaller than at higher temperatures (Curve 1, Fig. 1).

In Fig. 1 the change of $\Delta E/\Delta V$ in the region of the equivalence point is plotted against the volume of 0.01 $N$ potassium iodide solution, under various conditions of titration. To simplify comparison the curves have been drawn so that the maximum value of $\Delta E/\Delta V$ came at the same point on the abscissa in each case. The numerical values of the volumes are thus without significance.

The final volume of the solutions varied between 750 and 850 cc., and the final concentration of nitric acid was 0.03 to 0.04 $N$.

## Data of the Titrations

The data of a typical titration at 90° are given in Table I, which is self-explanatory. Table II contains a summary of all the various titrations. The values of the atomic weights given at the head of Table II were taken from the International Table of Atomic Weights for 1935.

TABLE I

DATA OF A TYPICAL TITRATION AT 90°

1.33153 g. of silver (vacuum) dissolved in 3 cc. of concd. nitric acid and diluted to 500 cc. 2.04659 g. potassium iodide (vacuum) dissolved in 100 cc. of water and added to silver solution at room temperature. Mixture heated to 90 ± 0.5°, and titrated at this temperature with 0.01036 $N$ potassium iodide from microburet.

| 0.01036 $N$ KI, cc. | $E$, volts | $\frac{\Delta E}{\Delta V}$ | $\frac{\Delta^2 E}{\Delta V^2}$ |
|---|---|---|---|
| 0 | +0.2218 | | |
| 1.0 | .1964 | | |
| 1.4 | .1657 | | |
| 1.5 | .1548 | 109 | |
| 1.6 | .1413 | 135 | +40 |
| 1.7 | .1238 | 175 | −52 |
| 1.8 | .1115 | 123 | |
| 1.9 | .1015 | 100 | |

$V = 1.6 + \frac{40}{92} \times 0.1 = 1.64$ cc. Correction to KI = 2.82 mg. Total KI = 2.04659 + 0.00282 = 2.04941 g. Ratio KI/Ag = 2.04941/1.33153 = 1.53913. Theory = 1.53889, Error = +0.016%.

## Discussion of Results

A comparison of curves 2 and 4 in Fig. 1 shows that the magnitude of the break decreases with increasing temperature above about 70°, due to an increase in the solubility of silver iodide with increasing temperature. However, if the titration is made at a lower temperature, the magnitude of the break again decreases because of the increased adsorptive power of the precipitate. Curve 3 was obtained by performing the entire titration at room temperature, and it furnishes a striking illustration of the way in which the maximum is depressed by adsorption effects. Comparison of curves 1 and 3 illustrates the drastic decrease in the adsorptive power of silver iodide on aging. Although the solubility product of silver iodide at 70° is several hundred times greater than at room temperature, the adsorptive power of the precipitate as a result of aging is much less at the higher temperature, and hence the maximum is much more pronounced than that obtained in a titration carried out at room temperature in which the precipitate is not digested.

Although curves 3 and 4 of Fig. 1 indicate that the magnitude of the break is about the same at room temperature (without digestion) as at 90°, the e. m. f. readings obtained at the higher temperature are much more reliable, and hence the end-point can be accurately found from the location of the maximum in $\Delta E/\Delta V$ (Table I). In the titration at room temperature without digestion, the end-point can be found much more accurately by titrating to the equivalence potential than from the maximum in $\Delta E/\Delta V$.

An inspection of the data of Table II shows that the precision (reproducibility) of the titrations is very good; the average deviation from the mean of all the experiments at 70 and 90° is only ±0.005%. Titration at 90° gives the most accurate results, and the accuracy decreases in a very regular manner as the temperature of titration decreases. Digestion of the precipitate at 90°, and finally finishing the titration at room temperature, gives results almost as accurate as those at 90°. Furthermore, the e. m. f. in the final titration at room temperature after digestion, becomes steady more quickly than under any of the other conditions of titration.

A critical survey of the analytical data reported in Table II reveals that in the slow titration at room temperature the precipitate contains 0.1% of iodide in excess at the equivalence potential. In subsequent work it could be shown that this excess of iodide was present in the adsorbed state. On the basis of their study of electrodialyzed silver iodide sols, Verwey and Kruyt[6] predicted that the potentiometric iodide–silver titration should be in error by some tenths of a per cent. at

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(6) E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933); see also Verwey, *Kolloid Z.*, **72**, 187 (1935).

TABLE II

RESULTS OF POTENTIOMETRIC COMPARISON OF POTASSIUM IODIDE AND SILVER

Ag = 107.880, I = 126.92, K = 39.096. Theoretical Ratio KI/Ag = 1.53889

| No. | Ag (vacuum), g. | KI (vacuum), g. | Additional KI, g. | Total KI, g. | Ratio KI/Ag | Error, % | Conditions of titration, at |
|---|---|---|---|---|---|---|---|
| 1 | 1.19100 | 1.82934 | 0.00370 | 1.83304 | 1.53907 | +0.012 | 90° |
| 2 | 1.33153 | 2.04659 | .00282 | 2.04941 | 1.53913 | + .016 | 90° |
| 3 | 1.15309 | 1.76976 | .00498 | 1.77474 | 1.53911 | + .014 | 90° |
| 4 | 1.14648 | 1.76258 | .00215 | 1.76473 | 1.53925 | + .023 | 90° |
| 5 | 1.16336 | 1.78937 | .00106 | 1.79043 | 1.53902 | + .008$^a$ | 90° |
| 6 | 1.01570 | 1.56214 | .00135 | 1.56349 | 1.53932 | + .028$^a$ | 90° |
| 7 | 1.19303 | 1.83414 | .00213 | 1.83627 | 1.53916 | + .018$^a$ | 90° |
| | | | | Av. | 1.53915 | + .017 | |
| Av. deviation from mean = ±0.005%. | | | | | | | |
| 8 | 1.32755 | 2.03139 | 0.01260 | 2.04399 | 1.53967 | +0.051 | 70° |
| 9 | 1.41576 | 2.16939 | .01040 | 2.17979 | 1.53966 | + .050 | 70° |
| 10 | 1.23658 | 1.90227 | .00144 | 1.90371 | 1.53950 | + .040 | 70° |
| 11 | 1.13746 | 1.74996 | .00139 | 1.75135 | 1.53970 | + .053 | 70° |
| | | | | Av. | 1.53963 | + .048 | |
| Av. deviation from mean = ±0.005%. | | | | | | | |
| 12 | 1.18840 | 1.82652 | 0.00276 | 1.82928 | 1.53928 | +0.025 | Digested 30 hrs. at 95–100°. Final titration at room temp. |
| 13 | 1.21629 | 1.86862 | .00370 | 1.87232 | 1.53937 | + .031 | |
| | | | | Av. | 1.53933 | + .028 | |
| 14 | 1.29978 | 1.99741 | 0.0046 | 2.0020 | 1.5402 | +0.08 | Slow titration at room temp. |
| 15 | 1.05426 | 1.61901 | .0051 | 1.6241 | 1.5404 | + .10 | |
| 16 | 1.08617 | 1.66334 | .0100 | 1.6733 | 1.5405 | + .10$^b$ | Fast titration at room temp. |

$^a$ Digested for twenty hours at 95 to 100° before finishing titration at 90°. $^b$ Waited only five minutes between each addition of dilute potassium iodide solution.

room temperature, since they deduced from their data that aged silver iodide at the equivalence potential ($C_{Ag^+} = C_{I^-}$) will contain adsorbed iodide. Under the experimental conditions described in this study it has been found that in the direct titration at room temperature the error due to the asymmetric location of the isoelectric point amounts to 0.10 ± 0.02%.

When the titration is carried out at 70° the precipitate is subjected to a fairly drastic aging process, consequently the error due to adsorption decreases to 0.05%. The error decreases to 0.017% when the titration is carried out at 90°. Under these conditions the aging is so drastic that the adsorptive power of the precipitate becomes virtually negligible. The error found at 90° is greater than the experimental error, and may be attributed to an extremely slight adsorption of iodide at the equivalence potential or to a slight error in the atomic weight of iodine, since the second decimal place in the latter is still somewhat uncertain.[7]

The fact that the error increases from 0.017 to 0.028% when the precipitate is titrated at room temperature after a drastic aging at 90°, lends support to the former assumption. Actually it could be shown that such a precipitate at room temperature exerted a slight adsorptive power toward silver and iodide ions.

**Acknowledgment.**—We wish to express our appreciation to the Graduate School of the University of Minnesota for a grant which enabled us to pursue this study.

## Summary

1. Pure potassium iodide has been synthesized from hydriodic acid and potassium bicarbonate. The salt can be melted in a hydrogen atmosphere without decomposition.

2. The accuracy of the potentiometric iodide-silver titration has been investigated in a precise manner. The results show that in the slow titration of silver with iodide, the error at room temperature amounts to 0.1%, at 70 to 0.048% and at 90° to 0.017%. When the precipitate was digested at 90° near the equivalence point, and the titration finished at room temperature, the error was 0.028%. In all cases the precipitate contained an excess of iodide at the equivalence potential.

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(7) G. P. Baxter, O. Hönigschmid, P. LeBeau and R. J. Meyer, THIS JOURNAL, **57**, 787 (1935).

3. The errors found in the titration are caused by adsorption of iodide ions by the precipitate, and the error (adsorption) can be reduced to a very small value by titrating at 90°, or by digesting the precipitate at 90° in the presence of a slight excess of silver previous to finishing the titration at room temperature.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

# The Adsorption of Silver and Iodide Ions by Freshly Precipitated Silver Iodide. The Isoelectric Point of the Fresh Precipitate

BY I. M. KOLTHOFF AND J. J. LINGANE

In a previous communication,[1] we described the results of an investigation of the accuracy of the potentiometric iodide–silver titration. It was found that when the titration was performed at room temperature, to the equivalence potential, approximately 0.10% too much potassium iodide was required. In this paper we present experimental evidence which proves that the excess requirement of potassium iodide at room temperature is due to an adsorption of iodide ions by the fresh precipitate at the potentiometric end-point.

We have also directly determined the "isoelectric point" of freshly precipitated silver iodide. The isoelectric point, or "zero-point charge," is defined as the silver-ion concentration at which neither silver nor iodide ions are adsorbed by the precipitate.

In their study of the precision of the potentiometric iodide–silver titration, Lange and Berger[2] determined the adsorption of silver nitrate and potassium iodide on freshly precipitated silver iodide at various temperatures. They found that the adsorption of the "potential determining" silver and iodide ions agreed with the expression, $\Delta X = K \Delta \log C$; in which $X$ is the amount adsorbed, $K$ is a constant and $C$ is the equilibrium concentration of the ion being adsorbed. They found that this relation was valid at temperatures between 30 and 90°. It is very doubtful, however, whether the values of $X$ determined at the higher temperatures are really significant, because the fresh precipitate ages quite rapidly at higher temperatures, causing a continuous decrease in its adsorptive power with resultant continuous desorption of the ion initially adsorbed. We have found that this desorption process is very slow at room temperature in the presence of an excess of silver, but is greatly accelerated at the higher temperatures.

Lange and Berger concluded from their experiments that silver ions are adsorbed more strongly than iodide ions at equal equilibrium concentrations. Their conclusion was based on the erroneous assumption that neither adsorption of silver nor iodide ions occurs at the potentiometric end-point, or "equivalence potential," where $c\text{Ag}^+$ in solution is equal to $c\text{I}^-$. Actually, as will be shown in the present paper, the isoelectric point of freshly precipitated silver iodide at room temperature is found at a silver ion concentration of approximately $10^{-6}$ molar, the silver ion concentration thus being nearly 10,000 times as great as the iodide-ion concentration.

In agreement with Lange and Berger, Verwey and Kruyt[3] found in their work with well aged electrodialyzed silver iodide *sols* that the adsorption of iodide ions follows the expression $\Delta X = K \Delta \log C$. They could not determine the location of the isoelectric point directly without flocculating the sols, but with the aid of the foregoing expression they extrapolated to the point of zero adsorption (isoelectric point), and found that this point corresponded to a silver-ion concentration of $10^{-6}$ molar. This value agrees very well with the value we determined directly with a fresh *precipitate.*

Gorochovsky[4] found that the isoelectric point of silver iodide sols depended greatly on the silver iodide concentration of the sols. The results of his experimental work, however, are inconclusive since he did not correct for adsorbed silver or iodide ions on the surface of the silver iodide.

Lange and Berger mention the possibility of an

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

[2] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930).

[3] E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933).

[4] G. N. Gorochovsky, *J. Phys. Chem.*, **39**, 465 (1935); see also G. N. Gorochovsky and J. R. Protass, *Z. physik. Chem.*, **A174**, 122 (1935).