

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

The Potentiometric Iodide-Silver Titration at Extreme Dilutions

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

In a study of the solubility of slightly soluble (10^{-3} to $10^{-5} N$) silver salts in solutions of various electrolytes and in water it was necessary to develop an accurate method for the determination of very small amounts of dissolved silver. We have found that the potentiometric titration of silver with iodide is very suitable for this purpose, and as little as one part of silver in twenty million parts of solution ($5 \times 10^{-7} N$) may be titrated with an accuracy of a few per cent. when 500 ml. of the solution is taken for analysis. At this high dilution the potentiometric method is more accurate than any other method of analysis, especially in the presence of large amounts of indifferent electrolytes.

Experimental

Apparatus and Materials.—The potentiometric apparatus and the general technique of the iodide-silver titration have been described already.¹ Silver iodide electrodes were used, since our experience has shown that these are somewhat more satisfactory than plain silver electrodes. A saturated calomel electrode, with a saturated potassium nitrate bridge, was used as reference electrode. Titrations were performed in the absence of light in the one liter titration beaker previously described.¹ The potassium iodide titrating solution was delivered from a 10-ml. microburet, with which volumes could be read easily to ± 0.005 ml.

The nitric acid, water and salts were purified carefully by the usual methods. Mallinckrodt reagent quality potassium iodide (ground and dried at 200°) was used in most of the experiments since in titrating the very dilute silver solutions it gave the same results as the carefully synthesized salt.¹

Approximately $0.01 N$ stock solutions of silver nitrate and potassium iodide were prepared by weighing out the dried salts. The more dilute solutions were prepared by diluting the stock solutions in carefully calibrated volumetric apparatus. The potassium iodide titrating solutions varied in concentration from 10^{-3} to $5 \times 10^{-6} N$, depending on the concentration and volume of silver solution to be titrated. These solutions were stable for several weeks when made up in pure water that was entirely free from traces of copper and stored in the dark. The concentrations of the various solutions were known to $\pm 0.1\%$.

Data of the Titrations.—For the purpose of illustrating a typical titration we may consider the case of the most dilute silver solution that was titrated, which was only $5.15 \times 10^{-7} N$ in silver. The data obtained in this titration are given in Table I and Fig. 1. These data show that the

TABLE I

DATA OF TYPICAL TITRATION AT EXTREME DILUTION

500 ml. of $5.15 \times 10^{-7} N$ silver nitrate, containing 2 ml. of concd. nitric acid, titrated with $4.99 \times 10^{-6} N$ potassium iodide at room temperature in presence of air.

$4.99 \times 10^{-6} N$ KI, ml.	E, v.	$\Delta E/\Delta V$, mv. per 0.4 ml.
0	+0.1824	
1.0	.1766	
2.0	.1695	
3.0	.1600	
3.8	.1490	
4.2	.1412	78
4.6	.1307	105
5.0	.1138	169
5.4	.0882	256
5.8	.0648	234
6.2	.0505	143
6.6	.0410	95
7.0	.0330	80
8.0	.0203	
9.0	.0115	

$$V = 5.0 + \frac{256 - 169}{(256 - 169) + (256 - 234)} \times 0.4 = 5.32$$

ml.; calcd. = 5.16 ml. Error, +3.2%.

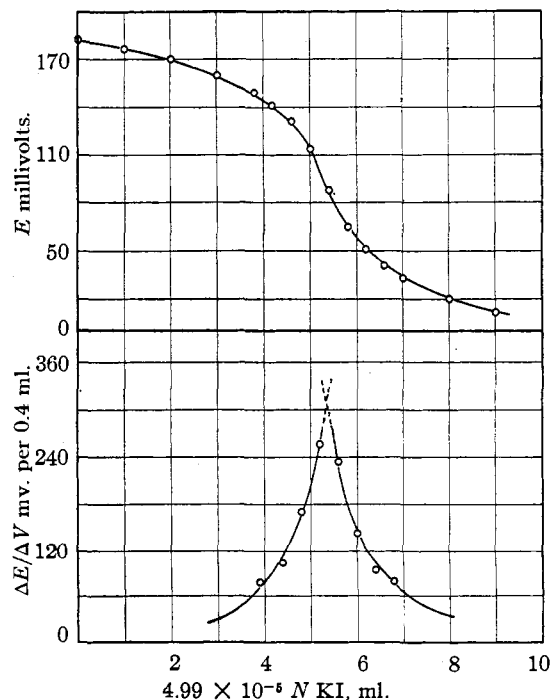


Fig. 1.—Titration of 500 ml. of $5.15 \times 10^{-7} N$ silver nitrate with $4.99 \times 10^{-6} N$ potassium iodide (data from Table I).

(1) I. M. Kolthoff and J. J. Lingane, *THIS JOURNAL*, **66**, 1524 (1936).

TABLE II
 SUMMARY OF TITRATIONS

Series no.	Concn. of AgNO ₃ , <i>N</i>	No. of titrations	Other salts, g.	Av. error, %	Av. E _{E. P.} , v.	Remarks ^a
1	1.029 × 10 ⁻⁵	6	±0.14	0.099	R. T. in air
2	1.029 × 10 ⁻⁵	1	-.64	.097	R. T. in CO ₂
3	1.030 × 10 ⁻⁶	3	+2.3	.095	R. T. in air
4	1.030 × 10 ⁻⁶	5	+1.2	.095	R. T. in CO ₂
5	1.030 × 10 ⁻⁶	2	20 g. Ba(NO ₃) ₂	+1.0	.096	R. T. in CO ₂
6	1.030 × 10 ⁻⁶	2	10 g. Ba(NO ₃) ₂	±1.3	.098	R. T. in CO ₂
7	1.030 × 10 ⁻⁶	1	20 g. K ₂ SO ₄	+8.1	.090	R. T. in CO ₂
8	5.15 × 10 ⁻⁷	1	+3.2	.093	R. T. in air
9	2.058 × 10 ⁻⁵	1	-0.32	.098	60° in air
10	1.029 × 10 ⁻⁵	2	-.25	.097	60° in air
11	9.41 × 10 ⁻⁶	1	+.51	.097	60° in air
12	9.41 × 10 ⁻⁶	1	+.06	.099	55° in CO ₂

^a R. T. = room temperature.

end-point of the titration (maximum value of $\Delta E/\Delta V$) is still well defined at this extreme dilution, and the error of +3.2% is remarkably small when it is realized that the total amount of silver titrated was only 0.028 mg. in a volume of 500 ml.

A summary of the results obtained in twenty-six titrations in which the concentration of silver titrated was varied between 5×10^{-7} and 10^{-5} *N*, is given in Table II. Some of these titrations were carried out in the absence of air, by bubbling a rapid stream of carbon dioxide through the solution, in order to see whether atmospheric oxygen had any influence on the accuracy of the titration. Titrations were also made in solutions that contained large amounts of very pure barium nitrate and potassium sulfate. A few titrations were also made at 60°.

The column headed "av. E_{E. P.}" in Table II, contains the average values of the e. m. f. at the end-point of the titrations (equivalence potential); the significance of these values will be explained later.

Discussion

Steady e. m. f. readings are obtained relatively rapidly in these "dilute" titrations, except in the immediate vicinity of the end-point where ten to fifteen minutes are required between each addition of the potassium iodide solution. The e. m. f. becomes steady more quickly in these "dilute" titrations than in titrations of ordinary amounts of silver because the amount of solid silver iodide present is so extremely small that adsorption effects are negligible. The time required for the e. m. f. to become steady simply corresponds to the time required to re-establish solubility equilibrium after each addition of potassium iodide. This is substantiated by the fact that the direction of the drift is toward decreasing values of the e. m. f., *i. e.*, toward decreasing silver ion activity.

When the titration is carried out at 60° the e. m. f. becomes steady more quickly, because

solubility equilibrium is attained more rapidly at the higher temperature. A titration at room temperature requires about one to one and one-half hours, but at 60° this time is reduced to about one-half. In titrating a 10^{-5} *N* silver solution at 60° the maximum value of $\Delta E/\Delta V$ is only about one-third as great as at room temperature, but is still sufficiently sharp to allow an accurate determination of the end-point.

An inspection of the data of Table II shows that a 10^{-5} *N* silver solution can be titrated at room temperature with an accuracy of at least ±0.2%, a 10^{-6} *N* solution can be titrated with an accuracy of about 1-2% and a 5×10^{-7} *N* solution with an accuracy of about 3%. Since the percentage error is a linear function of the amount of silver titrated, it is evident that the absolute error is constant and independent of the amount of silver titrated in this range of concentrations.

The data also show that air has no marked effect on the accuracy of the titration, although a comparison of series nos. 3 and 4 and nos. 11 and 12 indicate that somewhat better results are obtained in the presence of carbon dioxide when titrating very small amounts of silver or when titrating at 55-60°.

Large amounts of barium nitrate have no influence on the results. Potassium sulfate (sulfate ion) in large amounts on the other hand causes a large positive error (no. 7). The deleterious influence of the sulfate ion on the behavior of silver electrodes appears to be rather general; it has been observed previously in work with the silver electrode.²

The interference of large amounts of sulfate

(2) I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **119**, 202 (1921); **132**, 117 (1923).

ion at these high dilutions is to be attributed to the reaction



which results in a decrease of the silver ion activity, an increase in the solubility of silver iodide, and an asymmetric location of the equivalence point; *i. e.*, the equivalence point no longer corresponds exactly to the maximum value of $\Delta E/\Delta V$.

We have also found that the titration can be carried out with the same degree of accuracy in dilute potassium bicarbonate medium (pH about 8.3) as in dilute nitric acid.

The titration may be simplified and made more convenient by simply titrating to the equivalence potential instead of recording the data of the entire titration curve.³ The average value of the equivalence potential found was $+0.097 \pm 0.005$ v. against the saturated calomel electrode, as shown by the data of Table II. This value is in excellent agreement with that found in the titration of ordinary amounts of silver.¹ We have found that the value of the equivalence potential is practically the same (within ± 5 mv.) in dilute potassium bicarbonate medium as in dilute nitric acid, and it is evident from Table II that it is also practically independent of temperature, and the presence of large amounts of barium nitrate. Titrations to the equivalence potential gave identically the same results as by the ordinary method, and are more convenient because the constant attention of the operator is not required.

(3) I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928); I. M. Kolthoff and J. J. Lingane, *THIS JOURNAL*, **57**, 2126 (1935).

It is evident from these results that this titration should be a valuable analytical method of investigating the solubility and activity relations of slightly soluble silver salts. We are using the method in a study of the activity of silver chloride and silver iodate in various salt solutions. Obviously the method could also be applied to the determination of very small amounts of iodide by adding an excess of silver nitrate solution to the unknown iodide solution and back-titrating the excess silver.

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Summary

1. The accuracy of the potentiometric iodide-silver titration at extreme dilutions has been investigated. Using a 500-ml. sample, a 10^{-5} *N* silver solution can be titrated with an accuracy of $\pm 0.2\%$, a 10^{-6} *N* solution with an accuracy of 1–2% and a 5×10^{-7} *N* solution with an accuracy of about 3% at room temperature. Large amounts of barium nitrate have no influence on the results, but a large positive error was found in the presence of high concentrations of sulfate ions.

2. The titration is recommended as an analytical tool in investigations of the solubility and activity relations of slightly soluble silver salts.

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The Structure of Crystalline Bromine

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Introduction

There is very little crystallographic information available concerning crystalline bromine. The material melts at -7.3° and single crystals are readily obtained from the vapor. It would be expected that the crystalline structure of bromine should be very similar to that of orthorhombic iodine.¹ This has turned out to be the case, and the structure analysis has been considerably simplified by making comparison with the known structure of iodine.

(1) Harris, Mack and Blake, *THIS JOURNAL*, **50**, 1583 (1928).

Experimental

Bromine crystals were formed from the vapor on the surface of a round-bottomed flask filled with dry ice and placed over the mouth of a beaker containing liquid bromine. The crystals showed a pronounced elongation along the direction of the *c*-axis, and were thus readily oriented for rotation and oscillation patterns about *c*. They were mounted by being placed upon a smooth surface of dry ice, and cemented to a fine glass rod with a soft vaseline which froze upon cooling. The crystal was maintained at about -150°