

is greatly reduced. This makes it possible to separate zinc and cobalt by one precipitation. Experimental evidence indicates that acrolein reacts

with hydrogen sulfide on the surface of the zinc sulfide particles, thereby reducing post-precipitation.

COLUMBUS, OHIO

RECEIVED MAY 18, 1935

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

The Accuracy of the Titration of Thiocyanate with Mercuric Mercury

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

In a previous paper¹ it was shown that in the direct and the reverse titration of silver with thiocyanate nearly theoretical results are obtained, slight deviations being found as a result of side reactions occurring during the reaction of the silver and thiocyanate ions. It was thought of interest to test the accuracy of the titration of mercuric mercury with thiocyanate and the reverse titration, especially since it had been shown that the end-point could be determined with great precision. The titrations were made potentiometrically and also with ferric iron as indicator.

Materials and Apparatus

Pure potassium thiocyanate prepared as described in a previous paper¹ was used.

Mercury.—The metal was purified in the usual manner by bubbling hot air through it for several hours, followed by washing with dilute nitric acid and distillation in vacuum.

Mercuric Thiocyanate.—The salt was precipitated from a dilute potassium thiocyanate solution by adding a slight excess of mercuric nitrate solution. The crystalline precipitate was washed thoroughly with water, and was then recrystallized from a large volume of hot water.

Mercury Electrode.—The electrode shown in Fig. 1 was specially designed for this work, the electrode mercury being contained in the conical cup. Electrical connection between the mercury cup and the mercury column in the stem was made by means of a platinum wire, sealed solidly in the neck connecting the cup and stem. The cup had a diameter of 1 cm. at the top and was filled with pure mercury so that the level of the latter was slightly above the rim of the cup. The stem was filled with ordinary mercury, into which the copper wire potentiometer lead dipped.

This electrode was much more convenient than the conventional type, prepared by electrodeposition of mercury on a platinum electrode, and it eliminates the trouble of frequent replating necessary with the latter type.

Standard Solutions.—Standard stock solutions of potassium thiocyanate were prepared by weight according to the technique already described.¹ Standard mercuric nitrate solutions were prepared by dissolving carefully weighed samples (corrected to vacuum) of the pure metal in a moderate excess of 6 *N* nitric acid, boiling to remove oxides

of nitrogen, and diluting to a known weight. This solution was *ca.* 0.4 *N* (0.2 molar) by weight, and was *ca.* 0.02 *N* in free nitric acid. An exactly 0.05 *N* solution, for the finish of the titrations, was prepared by dilution of a weighed portion of the stock mercuric nitrate solution in a calibrated flask.

The total operative error involved in the preparation of the standard stock solutions (weighing materials and solutions) was probably less than 0.005%. The solutions were stored in the all-glass storage flasks previously described.¹

Procedure and Results of the Titrations

The general procedure of the titrations was as follows. A suitable portion of one of the stock solutions (*ca.* 50 g. of the potassium thiocyanate solution or 25 g. of the mercuric nitrate solution) was weighed into a 250-cc. beaker from a weight buret and diluted to 100-125 cc., with addition of sufficient nitric acid to make its concentration 0.1 *N* at the end of the titration. The mercury electrode, stirrer and salt bridge were then placed in the solution and the titrating solution was added from a weight buret with thorough stirring, until the measured e. m. f. indicated that either a slight excess or a slight deficiency had been added. The titration was then finished with the appropriate dilute solution from a calibrated 5-cc. microburet. The end-point was located in the usual way from the maximum in $\Delta E/\Delta V$. The final volume at the end of the titration was about 200 cc.

Titrations were made both at room temperature (*ca.* 23°) and at 0°, the titration beaker being placed in a jar of cracked ice for the latter titrations. Titration at 0° is preferable to titration at room temperature because the maximum in $\Delta E/\Delta V$ at the end-point is much more pronounced (change in solubility and dissociation with temperature). This is illustrated in Fig. 2, in which the data, in the region of the equivalence point, have been plotted for two typical titrations at 23 and at 0°.

Steady e. m. f. readings are obtained very quickly throughout the entire course of the titration, which is a marked advantage of the thiocyanate-mercury titration over the thiocyanate-silver titration.

The results obtained in ten titrations, given in Table I, have been expressed in terms of the ef-

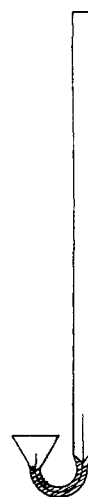


Fig. 1.—Mercury electrode for potentiometric titrations.

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

TABLE I
COMPARISON OF POTASSIUM THIOCYANATE AGAINST
MERCURY

Conditions	Effective strength of KCNS, %
1 Hg(NO ₃) ₂ to KCNS at R.T.; final titration with dilute Hg(NO ₃) ₂	99.93
2 As (1)	99.93
3 As (1)	99.94
4 As (1), except final titration with dilute KCNS	99.96
5 As (1), except titration at 0°	99.95
6 As (5)	99.95
7 As (5)	99.98
8 KCNS to Hg(NO ₃) ₂ at 0°; final titration with dilute Hg(NO ₃) ₂	100.02
9 As (8) except final titration with dilute KCNS	100.05
10 As (9)	100.04

of the solutions for titration and location of the exact equivalence point, were probably less than 0.01%.

In the first four titrations the standard mercuric nitrate solution was added to the potassium thiocyanate solution and the titrations were made at room temperature. In the first three titrations a slight deficiency of the mercuric nitrate was added and the titration was finished with the dilute mercury solution; in the fourth trial a slight excess of the mercuric nitrate solution was added and the excess was titrated back with the dilute thiocyanate solution. The remaining six titrations were all made at 0°. In experiments 5-7, the mercuric nitrate solution was added to the potassium thiocyanate solution, but in the

last three trials the reverse order of precipitation was employed.

The visual Volhard method for locating the end-point was compared with the potentiometric method as follows. The suspension remaining from a potentiometric titration, which contained a slight known excess of mercuric nitrate, was transferred to a glass-stoppered flask and after adding 2 cc. of saturated ferric alum as indicator, the solution was cooled to 12° and titrated with the dilute thiocyanate solution to the appearance of the first reddish-brown coloration.

A comparison flask was prepared which contained the same quantity of recrystallized mercuric thiocyanate and the same concentration of nitric acid, potassium nitrate and ferric alum at 12° as the solution titrated. In this way the end-point could be determined to within about 0.07 cc. of 0.01 N thiocyanate solution in a volume

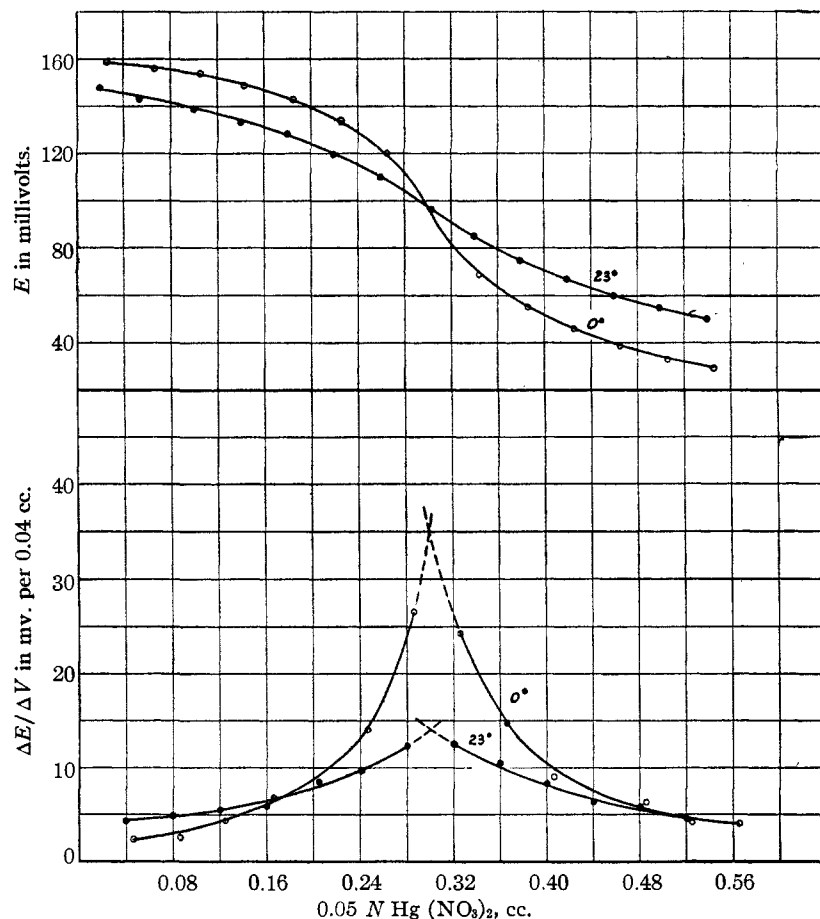


Fig. 2.—Curves of final titration of thiocyanate with mercuric nitrate in region of equivalence point at 0° and at 23°.

of 200 cc. corresponding to a titration error of 0.01%. effective strength of the potassium thiocyanate. In view of the careful technique employed in the comparisons, the total operative errors, including preparation of stock solutions, weighing portions

of 200 cc. corresponding to a titration error of 0.01%.

(2) I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **71**, 339 (1927).

In these titrations it was found that the Volhard end-point came 0.02% later than the potentiometric end-point, with respect to thiocyanate, or in other words, the effective strength of the potassium thiocyanate by the Volhard method was 0.02% less than the effective strength by the potentiometric method.

Discussion of Results

The data in Table I show that the reaction between mercuric mercury and thiocyanate is not exactly stoichiometric. When the mercury solution was added to the thiocyanate the effective strength of the potassium thiocyanate was found to be 99.94% at 25° and 99.96% at 0°. However, when the titration was carried out in the reverse way an effective strength of 100.03% was found at 0°. Although the deviation from the theoretical value is within the limits of an accurate analytical determination, it is greater than corresponds to the experimental error. The deviation found indicates that in the reaction between mercuric mercury and thiocyanate slight side reactions occur similar to those in the thiocyanate-silver titration.¹

By using the same technique described in the latter case we were able to detect small, but definite, quantities of fixed ammonia in the supernatant solutions after precipitation, whereas no trace of ammonia could be detected in the original mercuric nitrate and potassium thiocyanate solutions, or in any of the reagents and water used.

The presence of ammonia in the final solutions is definite proof that side reactions, probably involving the intermediate formation of cyanic acid and its subsequent decomposition to ammonium ion and carbon dioxide, take place during the precipitation of mercuric thiocyanate.

The occurrence of these side reactions is a serious objection to the use of potassium thiocyanate as a primary standard substance in mercurimetry, in extremely precise work. However, the errors caused by the side reactions are small (-0.05 to $+0.05\%$, depending on the order of precipitation), so that the salt should be a useful standard substance in work not requiring an accuracy better than $\pm 0.05\%$.

Acknowledgment.—We wish to express our appreciation to the Graduate School of the University of Minnesota for financial assistance during the course of the work described in this paper.

Summary

1. The effective strength of potassium thiocyanate as found by titration with mercuric mercury solution depends upon the order of precipitation, being an average of 99.95% when the mercury is added to the thiocyanate solution and 100.03% when the reverse order of precipitation is used. The effective strength is 0.02% lower by the visual Volhard method than by the potentiometric method when the solution at the end-point has a temperature of 12°.

2. The slight deviations from the theoretical value are attributed to the occurrence of side reactions; the presence of ammonium ion was detected in the solution at the end of the reaction.

3. In the potentiometric titration a much sharper break is found at 0° than at room temperature.

4. Potassium thiocyanate can be recommended as a standard substance in mercurimetry for work not requiring an accuracy greater than $\pm 0.05\%$.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 25, 1935