Each point on the graph is marked by means of an arrow to indicate whether the equilibrium is approached from the increasing or decreasing urea side of the reaction. The temperature in the experiments varied between 154 and 155.6°.

Excess Carbon Dioxide.—The conversion obtained with no excess ammonia is very close to 44%. This is in agreement with the finding of other investigators as already noted. Several experiments with an excess amount of carbon dioxide were also made. Since they are not shown on the graph they are given in Table III.

TABLE III

EXCESS CARBON DIOXIDE (TEMP., 155.6°)

Expt.	Starting materials	Carbon dioxide, % of combined CO_2 in starting material	Conversion to urea
1C	Carbamate + carbon dioxide	97.0	44.35
2C	Urea + water	100.0	44.0
3C	Carbamate + carbon dioxide	61.2	44.3
4C	Urea + water + carbon dioxide	61.2	45.7

Conclusion

The experimental results show that an excess amount of ammonia over that combined as carbamate acts as a dehydrating agent, removing the water from the active mass, thus preventing its reaction with urea and thereby shifting the equilibrium toward the urea side. Carbon dioxide does not show this effect. The slope of the conversion curve at 300% excess ammonia is such that a complete dehydration is not to be expected with more ammonia, under the conditions here considered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE IODIMETRIC DETERMINATION OF SMALL AMOUNTS OF ZINC

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It has been shown by Spacu[1,2] and his co-workers, that zinc can be very accurately determined by precipitating the zinc as zinc pyridine thiocyanate, which may be weighed as such or ignited and weighed as zinc oxide. By employing special apparatus Spacu and Ripan[3] extended their method to the gravimetric determination of as low as 12 mg. of zinc. Unlike most very insoluble zinc compounds, zinc pyridine thiocyanate precipitates in a distinctly crystalline form which transfers and filters perfectly. The precipitate is definite in composition and has the formula,

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[1] G. Spacu, *Z. anal. Chem.*, **64**, 338 (1924).

[2] G. Spacu and J. Dick, *ibid.*, **73**, 356 (1928).

[3] G. Spacu and R. Ripan, *ibid.*, **64**, 338 (1924).

$ZnPy_2(SCN)_2$. Apparently no one has attempted the iodimetric determination of the thiocyanate in this precipitate as the basis of the volumetric determination of small amounts of zinc.

In slightly alkaline solution iodine reacts with thiocyanate according to the reaction

$$NCS^- + 4I_2 + 8OH^- \longrightarrow SO_4^= + 7I^- + 4H_2O + ICN \qquad (A)$$

Upon acidification the iodocyanogen again reacts instantly and quantitatively with iodide to form iodine and cyanide, giving the final quantitative relation

$$NCS^- + 3I_2 + 4H_2O \longrightarrow SO_4^= + 8H^+ + 6I^- + CN^- \qquad (B)$$

On the basis of the above reactions, it was found in this Laboratory that alkali thiocyanate can be very accurately determined iodimetrically by adding a moderate excess of standard iodine solution to a thiocyanate solution made alkaline with the proper amount of borax, and then acidifying the reaction mixture and titrating the excess iodine with standard thiosulfate, using starch as indicator. A. Schwicker,[4] who also recently worked on the iodimetric determination of alkali thiocyanates, states that borax is unsatisfactory as a buffer for the oxidation reaction. His failure to obtain satisfactory results was undoubtedly due to the use of an insufficient amount of borax.[5]

Since alkali thiocyanate can be accurately determined by the method referred to above, the same method was applied directly to the zinc pyridine thiocyanate precipitate. In order to establish this, about a gram of the precipitate was specially prepared by adding the calculated amounts of the precipitating agents to a very dilute boiling hot solution of zinc sulfate and allowing the solution to cool slowly without disturbance. In this way large needle-like crystals (about 2 cm. in length) were obtained. These were filtered and washed several times with anhydrous methyl alcohol and then dried at room temperature in vacuo. Weighed portions of this material were dissolved in hot water, and borax was then added and the mixture boiled to expel the pyridine. After cooling, the determination was carried out according to the principle stated above, for the determination of alkali thiocyanate. The removal of the pyridine by boiling in the presence of borax insured a very sharp end-point in the residual titration with thiosulfate. In the presence of borax the zinc is precipitated as a flocculent basic zinc borate. It might seem that this precipitate would occlude considerable thiocyanate. This, however, is not the case, for the results given in Table I show excellent agreement with the theoretical.

Apparatus and Reagents

Bureau of Standards certified burets, pipets and volumetric flasks were used in all precision measurements. A 25-cc. buret was used for the

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[4] A. Schwicker, *Z. anal. Chem.*, **77**, 278 (1929).

[5] Pagel and Ames, THIS JOURNAL, **52**, 2698 (1930).

residual titration with thiosulfate. Conductivity water prepared with a large specially constructed all-pyrex still was used throughout. Highest purity chemicals were used with the exception of borax ($Na_2B_4O_7 \cdot 10H_2O$) which was Mallinckrodt C. P. grade. Samples of the recrystallized material, however, gave identical results. Standard zinc solutions were prepared from U. S. Bureau of Standards stick zinc (Sample No. 43a) containing less than 0.01% total of detected impurities. Accurately weighed portions of this zinc were placed in a 2-liter volumetric flask with a slight calculated excess of dilute sulfuric acid. While the zinc was dissolving the flask was kept in cold water to insure very slow reaction in order to eliminate any losses due to spray. Pipetted portions of the standard zinc solution were used in the determinations. Where very small amounts of zinc were desired, aliquot parts of the standard solution were again accurately diluted, and pipetted portions of the latter again taken. Standard 0.1 *N* potassium iodate solution (used as a source of free iodine) was prepared directly by dissolving and diluting the calculated weight of the pure dried salt. The ratio of the 0.1 *N* thiosulfate to the iodine liberated from the iodate was determined under the same conditions that were present in the actual determinations. Temperature corrections for the standard solutions were taken into account.

Experimental

Weighed portions of the pure zinc pyridine thiocyanate were transferred into a 500-cc. wide-mouthed conical flask. About 125 cc. of water was added and the contents of the flask heated nearly to boiling, until the precipitate dissolved. Six grams of borax was then added and the mixture gently boiled for about ten minutes. After allowing to cool somewhat, the flask was stoppered with a clean rubber stopper (previously cleaned thoroughly by boiling in dilute alkali) and thoroughly cooled with tap water. In a second 500-cc. flask, a 50-cc. pipetted portion of the iodate solution was treated with 2 g. of potassium iodide and 10 cc. of 1 *N* hydrochloric acid. The cold borax reaction mixture was then immediately transferred, and thoroughly rinsed with water, into the flask containing the liberated iodine. After rinsing down any drops on the sides, the flask was stoppered and allowed to stand for ten or fifteen minutes to insure complete oxidation. The total volume at this stage was about 150 cc. Ten cc. of 6 *N* hydrochloric acid was then added and the excess iodine immediately slowly

TABLE I

RESULTS WITH PURE $ZnPy_2(SCN)_2$

	Iodine, 0.1000 *N*		
$ZnPy_2(SCN)_2$, g.	Calcd., cc.	Reduced, cc.	Error, %
0.0849	30.00	30.02	+0.1
.0849	30.00	30.04	+ .1
.0900	31.80	31.83	+ .1

titrated to almost colorless with standard thiosulfate before adding starch indicator.

The following procedure and technique was found to give very satisfactory results for the determination of various small quantities of zinc, ranging from 3 to 33 mg. in a volume of 100 cc. The technique is not difficult; nevertheless, every detail given is essential for accurate results.

One gram of solid potassium thiocyanate is dissolved in the zinc solution, followed by 1 cc. of pyridine, which is added drop by drop while stirring. This is then allowed to stand for one hour, with occasional stirring to insure complete precipitation of the zinc in the supernatant liquid. During this time the temperature of the precipitation mixture should not be allowed to rise above 20°. Filtration is then effected by using a snugly fitting disk of filter paper in a clean 25-cc. capacity Gooch crucible. This disk of paper, of such size that the edges will be slightly turned up against the inside walls of the crucible, is best prepared by tracing the circumference with a knife and tearing along the mark to produce a smoothly frayed edge. The crucible is forced into a rubber ring (Bailey crucible holder) until the bottom protrudes at least 1 cm. through the ring. The ring is then placed in a clean funnel fitted into a suction flask. A transfer solution is prepared by dissolving 10 g. of potassium thiocyanate and 10 cc. of pyridine in a liter of water. After wetting the filter with this solution and sucking down firmly, the precipitate is filtered with gentle suction and quantitatively transferred with the transfer solution. The precipitate is then washed with not more than 10 cc. of a solution of anhydrous ether containing 1% of pyridine by volume, cooled to 20° or lower. The greater part of the ether wash solution should be directed down the sides of the crucible in a very fine stream. The crucible is then removed and the outside wiped clean with a damp towel. The crucible is then inverted over a 500-cc. wide-mouthed conical flask, and the filter paper together with nearly all of the precipitate is dislodged by thrusting a fine wire through the bottom of the crucible. The crucible is washed thoroughly with boiling water and the volume of solution increased to approximately 150 cc. This is heated until the precipitate is completely dissolved, ignoring the slight amount of flocculent zinc hydroxide which may form. After adding 6 g. of borax, the determination is completed according to the procedure given above, in the analysis of the weighed portions of the pure precipitate. A minimum excess of 5 cc. of 0.1 *N* iodine, over that required for reaction (A), is essential for the complete oxidation of the thiocyanate in ten minutes, in a volume of 150 cc. This excess is estimated with sufficient accuracy by comparing the color of the oxidation mixture (after standing for two minutes) with the color produced by the iodine, liberated under the same conditions, from 5 cc. of 0.1 *N* iodate in 150 cc. of water. If the excess iodine found is less than that specified, a second pipetted portion of iodate is treated as before and the