The solution of the nickel salt was an intense green and that of the cobalt a deep blue. In every case there was some evolution of gas at the cathode.

A number of experiments were performed using hydrated salts of the metals given in Table II and unpurified acetamide that contained considerable water. The deposition was good in each case. When 1 cc. of water was added to the solution of $Zn(CN)_2$ in the purified acetamide, an excellent deposit was obtained.

Summary

1. Zinc, cadmium, lead, tin, cobalt and nickel were deposited electrolytically from solutions of their salts in formamide. Current densities were of the order of 0.02 to 0.04 amp. sq. cm. The temperature was 100°.
2. Zinc, cadmium, tin, lead, cobalt, nickel and thallium were deposited from solutions of their salts in acetamide, under similar conditions.
3. Metals higher than zinc in the electromotive series were not deposited from solutions in either solvent.

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

THE VOLUMETRIC DETERMINATION OF THIOCYANATE WITH IODINE AND WITH IODATE

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It has long been known that the quantitative oxidation of thiocyanate with iodine is extremely slow in neutral or in acid solution. The reaction is

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

In slightly alkaline solution the above reaction is comparatively rapid, and a consecutive reaction occurs, $I_2 + CN^- \longrightarrow ICN + I^-$, giving the final quantitative relation

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

Upon acidification the iodocyanogen again instantly and quantitatively reacts with iodide to form free iodine and cyanide. In the presence of a suitable buffer, Reaction B should go to completion rapidly with a moderate excess of iodine. Upon acidification the iodine in excess of that required for Reaction A may then be determined by back titration with standard thiosulfate, using starch as indicator.

During the past year we have investigated the iodimetric determination of zinc as zinc pyridine thiocyanate. Since pyridine interferes with the iodine titration it was hoped that a suitable non-volatile buffer might be found which would expel the pyridine on boiling and subsequently serve as a buffer for the oxidation reaction. Disodium hydrogen phosphate proved somewhat unsatisfactory, but borax served both purposes admirably. The suitability of borax as a buffer was studied with respect to time required for complete oxidation, the quantity of borax required and the minimum of excess iodine permissible for quantitative oxidation. Tables I and II show the results of this study. Table III shows the results obtained by using iodine liberated from standard iodate solution. While this work was in progress, Alfred Schwicker[1] published a paper in which he showed that ammonium borate is a very desirable buffer for the oxidation reaction. Schwicker gives a review of the proposed methods; therefore these will be omitted in this paper. Although ammonium borate would be unsuitable for our work, we have nevertheless very carefully checked his work and found it to be sound in principle, but certain details have undoubtedly been overlooked. Schwicker carried out his oxidation reactions using 5 to 10 cc. of 1 *N* ammonium borate with a considerable excess of free iodine, in total volumes apparently ranging from 20 to 90 cc. The amount of ammonium borate required for larger volumes and the means of judging the minimum excess of iodine when the quantity of thiocyanate is not known, are not given. We have found that 10 cc. of 1 *N* ammonium borate in 150 cc. of reaction mixture is sufficient, provided that 4 or 5 cc. of iodine is added in excess of the amount required for Reaction B. This excess can easily be determined with sufficient accuracy by adding 5 cc. of the iodine solution to a volume of water equal to that of the oxidation mixture and comparing the colors. Unless this precaution is taken, errors may arise due to coincidence, for if the calculated amount of iodine is added, the solution still remains very distinctly colored with free iodine, even at the end of three minutes (Schwicker states that one to two minutes is sufficient), giving all appearances of the reaction being complete. Upon acidifying and determining the excess iodine, the results may be nearly 2% low. Table IV shows the results of various amounts of excess iodine. Schwicker seems to have attempted the use of borax, and states that two hours is required for complete reaction. His experience is probably explained by Table I, since we likewise found that insufficient borax gave low results.

Materials and Apparatus

Bureau of Standards certified burets, pipets, and volumetric flasks were used in all precision measurements. A 25-cc. buret was used for the thiosulfate back titrations. The oxidation reactions were carried out in 250-cc. glass-stoppered pyrex Erlenmeyer flasks. Conductivity water prepared with a large, specially constructed all-pyrex still, was used throughout. Highest purity chemicals were used, except the borax ($Na_2B_4O_7 \cdot 10H_2O$) which was Mallinckrodt c. p. grade. Samples of the recrystallized material, however, gave identical results. All standard solutions were kept in opaque bottles fitted with buret supports which permitted automatic filling by suction. To reduce errors, pipetted portions were used wherever possible. Eighteen liters of 0.1 *N* iodine (in 0.2 *N* potassium iodide) was prepared in a 20-liter bottle. This solution remained unusually constant in strength; nevertheless, it was standardized daily with arsenious oxide. The iodine solution was tested for iodate and cyanogen with negative results.

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[1] Alfred Schwicker, *Z. anal. Chem.*, **77**, 278 (1929).

Approximately 0.1 N potassium thiocyanate was volumetrically standardized with 0.1 N silver nitrate, using ferric alum as indicator. The silver nitrate was gravimetrically standardized as silver chloride, both at the beginning of the work and again at the close. Likewise, the silver nitrate–thiocyanate ratio was redetermined, both with identical results. The different strengths of thiocyanate given in the tables were prepared by diluting measured amounts of the 0.1 N solution (actual 0.1010 molar or 6 × 0.1010 N as reducer in Reaction A). Standard potassium iodate solution was prepared by dissolving and diluting the calculated weight of the pure dried salt. The thiosulfate–iodine ratios were run under the same conditions that were present in the actual determinations—that is, the thiosulfate into the measured portion of iodine with corresponding acidity. It was noticed, however, that identical results were obtained in neutral solution. Starch indicator was used throughout. Temperature corrections for the standard solutions were taken into account.

Procedure

In all data given in Tables I and II, the iodine was added to pipetted portions of thiocyanate to which had been added the given amounts of borax dissolved in sufficient water to give a volume of 150 cc. during the oxidation reaction. After the addition of the iodine the containers were placed in a dark cupboard until the reaction was thought to be complete. The solution was then acidified with 10 cc. of 6 N hydrochloric acid and the excess iodine immediately titrated slowly with thiosulfate until almost colorless, before the starch indicator was added. The time given in these tables excludes the time required for adding the iodine. The normality of thiocyanate is given as reducer in acid solution (Reaction A). Iodine in excess to Reaction B is the difference between "iodine added" and $^4/_3$ times the "calcd. iodine."

TABLE I

EFFECT OF TIME AND THE QUANTITY OF BORAX

0.06733 N KSCN, cc.	Borax, g.	Time, min.	Iodine, 0.1008 N Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
50	1	10	50.00	31.52	33.40	−5.6
50	3	10	49.52	33.26	33.40	−0.4
50	3	30	50.00	33.36	33.40	− .1
50	3	30	50.00	33.38	33.40	− .1
50	5	5	49.50	33.10	33.40	− .9
50	5	5	49.50	33.06	33.40	−1.0
50	5	10	49.50	33.37	33.40	−0.1
50	5	30	50.00	33.38	33.40	− .1
50	5	105	50.00	33.37	33.40	− .1
25	5	3	27.30	16.65	16.70	− .3
25	5	5	27.30	16.67	16.70	− .2
25	5	5	27.31	16.66	16.70	− .2
25	5	11	27.30	16.67	16.70	− .2
25	5	30	27.32	16.68	16.70	− .1

These results show that with 5 to 5.5-cc. excess iodine in a volume of 150 cc., it is necessary to use 5 g. of borax to insure complete reaction in ten minutes. With smaller amounts of thiocyanate the reaction is complete in five minutes but ten minutes is recommended in all cases. The following table shows the consistency of results obtained under the above conditions, and also that larger excess of iodine causes no error on long standing.

TABLE II

EXPERIMENTAL RESULTS

0.06733 *N* KSCN, cc.	Time, min.	Iodine, 0.1008 *N* Added, cc.	Excess, cc.	Reduced, cc.	Calcd., cc.	Error, %
50	10	49.52	5.0	33.38	33.40	−0.1
50	10	49.50	5.0	33.39	33.40	.0
50	10	50.00	5.5	33.39	33.40	.0
50	10	50.00	5.5	33.38	33.40	− .1
25	10	27.30	5.0	16.66	16.70	− .2
25	10	27.27	5.0	16.65	16.70	− .3
25	30	50.00	27.7	16.66	16.70	− .2
(0.08657 *N*)						
25	45	40.00	11.3	21.45	21.47	− .1
50	30	65.00	7.7	42.86	42.94	− .2
50	30	65.00	7.7	42.89	42.94	− .1

A reference solution for judging the minimum excess of iodine should be prepared before starting the titration. A 5-cc. portion of iodine is added to a volume of water about equal to that of the solution to be titrated. During the early stages of the titration the iodine is reduced almost instantly, but later the color begins to fade slowly. At this point about 10 cc. more should be added. If at the end of two minutes the color is as dark or darker than that of the reference solution, the mixture is allowed to stand for at least eight minutes longer to insure complete oxidation; otherwise, more iodine is added until the proper excess is assured.

Instead of using 0.1 *N* iodine solution, the equivalent amount of 0.1 *N* iodate solution may be treated with 2 g. of potassium iodide followed by 10 cc. of 1 *N* hydrochloric acid. The thiocyanate solution containing 6 g. of borax is then added. The regular procedure as given for iodine is then followed. If the reaction mixture shows less than the required excess of iodine at the end of two minutes, a second portion of iodate is treated as above and the oxidation mixture is poured into the latter. It is advisable to add another gram of borax if a second portion of iodate is required.

Table III shows the accuracy of this modification.

TABLE III

RESULTS USING STANDARD IODATE

KSCN, cc.	Iodate, 0.1000 *N* Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
25 (0.06733 *N*)	25	16.81	16.83	−0.1
50 (0.06733 *N*)	50	33.70	33.66	+ .1
50 (0.06733 *N*)	50	33.66	33.66	.0
25 (0.06060 *N*)	25	15.14	15.15	− .1
50 (0.06060 *N*)	(25 + 25)[a]	30.35	30.30	+ .2
50 (0.06060 *N*)	(25 + 25)[a]	30.33	30.30	+ .1

[a] Indicates a second portion of iodate.

Table IV shows the possible errors that may arise from coincidence, due to insufficient excess of iodine in following Schwicker's procedure. To 50-cc. portions of thiocyanate, the indicated amounts of iodine in excess for Reaction B were added and the mixture was diluted to 140 cc. Ten cc. of the ammonium borate (prepared according to Schwicker) was then added and the reaction allowed to proceed for two minutes before acidification, as Schwicker directs.

Table IV

Excess iodine, cc.	0.0	0.0	0.2	0.5	2.0	4.0	4.0	5.0
Error, %	−1.7	−1.2	−0.9	−0.7	−0.3	−0.2	−0.2	−0.2

The possibility of this error has already been discussed in the introduction of this paper. The results were found to be quite accurate with very slight excess of iodine in the presence of 15 instead of 10 cc. of ammonium borate in a 150-cc. volume. A minimum of 4 to 5 cc. of excess iodine is, nevertheless, recommended.

Summary

It has been shown that under suitable conditions borax gives the proper alkalinity for the rapid volumetric determination of thiocyanate with iodine.

Lincoln, Nebraska

[Contribution from the Chemical Laboratory of the University of California]

THE EXISTENCE OF ELECTRONIC ISOMERS IN THE SOLID STATE AND IN SOLUTION. THE MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$ AND ITS VARIATION WITH THE TEMPERATURE

By Simon Freed

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The quantum theory of Bohr and also the quantum mechanics[1] lead to the following relation connecting the paramagnetic susceptibility of a monatomic gas with the temperature

$$\chi = \frac{B^2g^2j(j+1)}{3RT} \qquad \text{I}^2$$

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[1] Sommerfeld, "Atombau," 4th ed., pp. 630–648; Van Vleck, *Phys. Rev.*, **31**, 604 (1928).

[2] Formula I is the quantum analog to the formula derived by Langevin on the classical theory

$$\chi = M^2/3RT = C/T$$

where M is the magnetic moment generated by the unbalanced electrons in their orbits. $C = M^2/3R$ is known as Curie's constant. This formula expresses Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. The magnetic field is more effective in orienting the elementary magnets when the thermal agitation is less violent.