We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

## Summary.

In this paper the atomic weight of four different samples of radio-lead not hitherto tested, as well as one sample of ordinary lead (used to control the others) was determined. The results were as follows:

| | |
|---|---|
| Ordinary lead | 207.18 |
| Radio-lead (Colorado) | 207.00 |
| Radio-lead (Australia) | 206.34 |
| Radio-lead (obtained from bröggerite from Norway) | 206.12 |
| Radio-lead (obtained from cleveite from Langesund, Norway) | 206.08 |

That the most carefully selected sample should give the lowest result is strong evidence that the higher results obtained from other samples were due merely to the accidental admixture of ordinary lead. As before, no new lines were found either in the ultraviolet or visible spectrum of any of these samples. Hence the atom of lead may be supposed to have a dual structure. Each sample, except the ordinary lead, possessed radioactivity, but the magnitude of this radioactivity seemed to bear no relation to the lowering of the atomic weight.

CAMBRIDGE, MASS., 1914–1916.

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[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

# THE SYSTEMATIC DETECTION OF THIOCYANATES.

BY LOUIS J. CURTMAN AND BEN R. HARRIS.

Received September 23, 1916.

**Nature of the Problem.**—One of the most striking reactions in qualitative work, is the red color produced when ferric salts and thiocyanates are brought together in solution. While the production of this red color serves as an exceedingly sensitive test for iron, as a test for thiocyanates this reaction is not only of a much lower order of sensitiveness,[1] but is also interfered with by many acids. Arsenates, phosphates, oxalates, tartrates, fluorides[2] and borates[3] hinder the free course of the reaction; ferrocyanides mask the red color, while iodides, acetates and nitrites offer the most serious interferences by forming colorations with ferric salts similar to the color of ferric thiocyanate.

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[1] This was to be expected; for, Kruss and Moraht (*Ber.*, **22**, 2056 (1899)) have demonstrated that the maximum color is produced when ferric chloride and potassium thiocyanate are brought together in the proportion of 1 : 12, respectively, a condition that is not reproducible when unknown and minute amounts of thiocyanate have to be dealt with. Quantities of thiocyanates in excess of this ratio also produce the maximum color, so that in testing for iron it is always possible to produce the deepest color attainable in a given case.

[2] Stokes and Cain, *Bull. Bur. of Standards*, 3, No. 1, 115 (1907).

[3] Prescott and Johnson, *Qual. Chem. Anal.*, **1918**, p. 155.

**Determination of the Sensitiveness of the Test.**—To determine the sensitiveness of the test for thiocyanates, which depends upon the formation of ferric thiocyanate, a definite volume of a standard solution of potassium thiocyanate was treated in a test tube, with 0.5 cc. 2 *N* ferric chloride solution,[1] the whole diluted to 5 cc., shaken, allowed to stand one minute and observed. The results obtained are given in Table I.

TABLE I.

| No. | Mg. SCN. | Result. |
|---|---|---|
| 1–2 | 5–3 | Deep blood red |
| 3–4 | 1–0.5 | Deep red |
| 5–6 | 0.4–0.3 | Brownish red |
| 7 | 0.2 | Light brownish red |
| 8 | 0.1 | Reddish yellow (limit) |

An inspection of Table I will show that 0.1 mg. of thiocyanate may be detected with the ordinary amount of care.[2] The addition of three drops of concentrated hydrochloric acid had practically no effect on the color.

For a reason stated below,[3] numbers 1, 3 and 8 of Table I were repeated, using ferric nitrate and 3 drops of 10% nitric acid in place of ferric chloride and hydrochloric acid, respectively. Results identical with those recorded in Table I were obtained.

It may be of interest to state that while in the detection of minute amounts of iron, the test may be considerably intensified by extracting the ferric thiocyanate with ether, this procedure is of no value when conditions are reversed. In Experiments 3–8, Table I, colorless ether layers were obtained when the solutions were shaken first with 2 and then with 5 cc. of ether, the aqueous layers retaining their original colors. This is probably due to the fact that in the test for iron there is invariably added a large excess of thiocyanate, while in the experiments noted above this was not the case.

**Extent of Interferences.**—To determine the extent to which iodides, acetates and nitrites interfere with the test for thiocyanates, a series of experiments was conducted. The procedure was the same as that followed in the determination of the sensitiveness of the test. The results obtained are recorded below in Tables II, III and IV.

TABLE II.

Interference of Iodides.

| No. | Mg. I. | Result. |
|---|---|---|
| 1 | 30 | Blood red |
| 2–3 | 20–15 | Dark brownish red |
| 4–5 | 10 | Light brownish red |
| 6 | 8.5 | Light brownish red |
| 7–8 | 7 | Yellowish red (limit) |
| 9 | 0.0 | Very faint yellow |

TABLE III.

Interference of Acetates.

| No. | Mg. $C_2H_3O_2$. | Result. |
|---|---|---|
| 1–2 | 100–50 | Deep blood red |
| 3–4 | 30–25 | Reddish brown |
| 5–6 | 20 | Light reddish brown |
| 7–8 | 18 | Reddish yellow (limit) |
| 9–10 | 0.0 | Very pale yellow |

[1] This solution contained 0.5 cc. conc. HCl per liter.

[2] This figure is also given by A. A. Noyes, *Qual. Chem. Anal.*, **1915**, p. 101.

[3] See number eight under "Comments on the Procedure."

TABLE IV.

Interference of Nitrites.

| No. | Mg. $NO_2$. | Result. |
|---|---|---|
| 1 | 100 | Brownish red ppt. |
| 2–3 | 50–35 | Dark reddish brown |
| 4–6 | 25–17 | Brown |
| 7–8 | 14 | Light brown (limit) |
| 9–10 | 11 | Brownish yellow |

**Comments.**—It is evident that iodides rank first in the degree of interference. It may be of interest to note that the colorations produced both by large and small amounts of iodide are almost identical in tint with those produced by certain corresponding quantities of thiocyanate, whereas the colorations produced by small amounts of acetate and of nitrite resemble the color of ferric thiocyanate less closely. It is for this reason, that it was difficult to determine the "limit" interferences of these acids. The limit data, especially in Table IV, are therefore only approximate. In the tables, the limit of interference is that quantity of the substance which produces a coloration equivalent to that formed under similar conditions by 0.1 mg. of thiocyanate. The ferric chloride solution mentioned contained 0.5 cc. of concentrated hydrochloric acid per liter to retard hydrolysis. This free acid decomposed the nitrite, hence, a special, nearly neutral 2 *N* ferric chloride solution was used in the determination of the interference of nitrites. Even this solution caused a slight evolution of the oxides of nitrogen. The coloration given by iodides was unaffected by the addition of three drops of concentrated hydrochloric acid. The same quantity of acid, however, bleached to a greenish yellow, the coloration given by acetates.

**The Available Methods for the Detection of Thiocyanates in the Presence of Iodides.**—A search of the literature failed to disclose a direct method for the separation of iodides from thiocyanates.[1] The liberation of iodine and its removal by means of carbon disulfide or some similar solvent is the only means for this purpose. Of the many liberators of iodine, *e. g.*, $KMnO_4$, $H_2O_2$, $K_2Cr_2O_7$, $KNO_2$, Cl-water and $FeCl_3$, only the last named was suitable; for, while they all adequately liberated the iodine,

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[1] After the completion of this work, our attention was called to a paper by Benedict and Snell (THIS JOURNAL, **27**, 738), entitled "A Method for the Detection of the More Common Acids," in which the separation of thiocyanates from iodides is effected by digesting the precipitate of AgI and AgSCN "in the cold with a mixture of three volumes of 2 *N* sodium chloride and one volume of 5 *N* HCl." To determine whether this method possessed any advantage over the one proposed by us, test experiments were made, a description of which appears in Note 4, page 2625. While this paper was in press, Weber and Winkelman (THIS JOURNAL, **38**, 2000) published a paper in which the separation of I and SCN is effected by heating their silver salts with sodium formate in alkaline solution. By this process the AgSCN is reduced giving metallic silver and sodium thiocyanate while AgI is not reduced.

they also oxidized the thiocyanate to cyanide and sulfate, thus vitiating the subsequent ferric thiocyanate test. Even the use of ferric chloride did not yield satisfactory results, owing to the fact that the extraction with carbon disulfide was cumbersome and that the removal of the excess of iron which it was necessary to introduce at the beginning, entailed serious difficulties.

Advantage was also taken of the fact that nascent hydrogen reacts with thiocyanates to give hydrogen sulfide.[1] The evolution of hydrogen sulfide would thus serve as a suitable, though indirect, means for the detection of thiocyanates in the presence of iodides, acetates and nitrites, subsequent to the removal of all other sulfur compounds capable of liberating hydrogen sulfide under similar conditions. This method was tried but was abandoned on account of the excessive sensitiveness of the test and because of its inability to indicate the quantity of thiocyanate present.

The procedure finally adopted and described in detail below depends upon the fact[2] that silver iodide is for all practical purposes inert in a hot 5% sodium chloride solution, while silver thiocyanate is transposed to sodium thiocyanate and silver chloride[3] by this treatment.[4] Acetates and nitrites are held in solution by making the preliminary silver precipitation in a boiling, sufficiently dilute solution. The precipitate consisting of silver iodide and thiocyanate[5] is filtered and subjected to the sodium chloride treatment. Other interfering acids are previously removed by precipitating them with a solution of a mixture of barium and calcium nitrates[6] and a solution of cobalt nitrate.[7]

## Procedure.

The solution contained in a 200 cc. beaker is rendered *just* alkaline with sodium hydroxide. $Ba(NO_3)_2 + Ca(NO_3)_2$ and $Co(NO_3)_2$ are added in excess in the order named. About 3 g. of washed asbestos fiber are introduced, the mixture boiled for $^1/_2$ minute with stirring, filtered on a

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[1] Fresenius, "Manual of Qual. Chem. Anal.," Well's translation, p. 372 (1898).

[2] A number of experiments was made to test this point. See also Nos. 1 and 2, Table V.

[3] Some of the AgCl so formed is dissolved by the excess of NaCl.

[4] As this transposition was similar to that employed by Benedict and Snell (see Note 1, p. 2624) experiments were made to ascertain which of the two was the more efficient. Two separate precipitates each consisting of a mixture of 500 mg. of I as AgI and 1 mg. of SCN as AgSCN were treated, respectively, by the two procedures. The conditions were kept uniform as to volume and the quantity of $FeCl_3$ added. With the Benedict and Snell method a solution having an orange-yellow color was finally obtained; whereas our procedure gave as the final result a dark brownish red solution affording unmistakable evidence of the presence of SCN.

[5] Silver chloride and bromide are also filtered off at this point.

[6] 50 g. $Ca(NO_3)_2.4H_2O$ were dissolved in 100 cc. water. This solution was then saturated with $Ba(NO_3)_2$.

[7] This solution contained 25 g. $Co(NO_3)_2.6H_2O$ in 100 cc.

fluted filter and washed with hot water till the washings are only faintly pink. The filtrate and washings, received in a 150 cc. beaker, should have a volume of about 100 cc. The filtrate is rendered acid with 5 drops 10% $HNO_3$ and $AgNO_3$ solution[1] added in excess. The reaction mixture is boiled for one minute with stirring to prevent loss by bumping, filtered[2] and washed with hot water till the washings are no longer pink. The precipitate, together with part of the filter paper to which the precipitate adheres, is returned to the beaker in which the silver precipitation was made, 10 cc. of 5% NaCl solution are added, the mixture kept near the boiling point for 3 to 5 minutes with vigorous stirring, filtered on a very small filter and washed twice with hot water, catching filtrate and washings in a 50 cc. evaporating dish. The combined filtrate and washings are concentrated by evaporation to about 4 cc., transferred to a test tube, acidified with 1 drop 10% $HNO_3$ and finally treated with 0.5 cc. 2 *N* ferric nitrate.

**Comments on the Procedure.**—1. The $Co(NO_3)_2$ precipitates sulfides, cyanides, ferrocyanides and ferricyanides, thereby materially reducing the size of the silver precipitate and supplying a separation of thiocyanates from ferrocyanides. The nitrates of Co, Ba and Ca were employed in preference to the chlorides to render the silver precipitate as small as possible.

2. The asbestos fiber is added to facilitate the filtration of cobalt cyanide, ferrocyanide and ferricyanide. The asbestos also serves to indicate the presence of an excess of $Co(NO_3)_2$ which is not otherwise visible. If allowed to drop gently and float on the surface of the liquid, the asbestos will acquire a pink color when cobalt is present in excess. Furthermore the asbestos prevents bumping when the mixture is boiled.

3. The silver precipitate may well be washed by decantation, the bulk of the precipitate being retained in the beaker for the NaCl treatment.

4. In test analyses 12–24 where the silver precipitate consisted almost exclusively of 1 mg. of thiocyanate as AgSCN in a volume of 110 cc., there was visible only a faint opalescence which required a second filtration. Care should be taken always to obtain a perfectly clear filtrate from the silver precipitate, refiltering if necessary. It is safer in any case to refilter because the pink color resulting from the presence of Co, may mask the opalescence.

5. It is imperative that the silver precipitate be washed free of cobalt because the pink color of the latter may be mistaken for ferric thiocyanate in the final test.

6. A confirmatory test was always made with $HgCl_2$ solution. With small amounts of SCN, the decolorization with $HgCl_2$ is even a better indication of the presence of the acid than the original red or reddish color.

7. Since thiosulfates are only incompletely precipitated by barium, on the addition of silver nitrate, first a yellow and finally a black precipitate of $Ag_2S$ separates out. But as evidenced by test analyses 14, 30 and 32, Table V, this precipitate does not interfere with the general procedure.

8. The final test is made in a volume of 5–6 cc. Before the test can be made, however, the solution as a rule will have cooled sufficiently to cause some of the dissolved AgCl to separate out, thus causing the solution to become turbid. The addition

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[1] 6.45 g. $AgNO_3$ were dissolved in 100 cc. of water, yielding a solution containing 50 mg. Ag per cc.

[2] A 9 cm. S. & S. No. 590 filter is required for this purpose.

of $FeCl_3$ augments this turbidity; hence the use of $Fe(NO_3)_3$. The cloudiness, however, may be diminished and in most cases entirely removed by warming, the rise in temperature causing the AgCl to redissolve.

**Test Analyses.**—To test the efficiency of the method a large number of test analyses was made. The results are given in Table V.

**Comments on Table V.**—Following the procedure, thiocyanate was found in test analysis No. 26, although none was introduced. This result, however, does not militate against the method for the reason that thiocyanate, although not originally added, was nevertheless formed in solution from the interaction of sulfides and cyanides or of the polysulfide in the sulfide solution, and cyanides. It was therefore considered necessary to avoid the simultaneous presence of sulfides and cyanides in further experiments. The same may be said of thiosulfates as evidenced by the result obtained in test analysis 28. Prescott and Johnson[1] state that thiocyanate is formed in the fusion of cyanides with thiosulfates; and what holds true for a fusion may be supposed to take place also when the salts are boiled together in solution, though probably in a much lesser degree. The negative results obtained in test analyses 30 and 31, in which the above precautions were observed, showed the method to be thoroughly trustworthy.

**Approximation of the Quantity of Thiocyanate.**—In the course of the work it was observed that with amounts of thiocyanate greater than 4 or 5 mg., the depth of color was such as to make it impossible to approximately estimate with the naked eye the amount of thiocyanate present. Between the colors produced by 5 and 250 mg., there was only a very slight difference in opacity. Between 25 and 250 mg. of thiocyanate there was no discernable difference in the coloration. It was therefore deemed desirable to devise means whereby the quantity of ferric thiocyanate might be roughly estimated. The volume of mercuric chloride solution[2] required to discharge the red color affords such means. Attempts to bleach the color completely by comparison with a blank were unsuccessful because of the disproportionately large amount of mercuric chloride required to remove the last tinge of red. Mercuric chloride solution was therefore added only to the point when a certain brown tint was reached; beyond this stage, the bleaching was exceedingly slight with each addition of 0.3 cc. of mercuric chloride, whereas up to this point considerable changes in color were produced by the same small quantities of mercury solution. With very large amounts of thiocyanate the changes on first adding the mercuric chloride are not visible; but this state of no apparent change is easily distinguished from that alluded to above, by

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[1] "Qualitative Chemical Analysis," p. 272 (1908).

[2] It was found necessary to use a highly concentrated solution because dilution alone discharges the red color. To dissolve 27 g. $HgCl_2$ in 100 cc. of water, it was necessary to add 10 g. NaCl. The resulting solution contained 200 mg. Hg per cc.

TABLE V.—TEST ANALYSES.

| No. | SCN. | I. | $C_2H_3O_2$. | $NO_3$. | Cl. | Br. | F. | CN. | $Fe(CN)_6^{III}$. | $Fe(CN)_6^{IV}$. | S.[1] | $SO_3$. | $S_2O_3$. | $C_4H_4O_6$. | $PO_4$. | $SO_4$. | $CO_3$. | $SiO_3$.[2] | $AsO_4$. | $CrO_4$. | $B_4O_7$. | $ClO_3$. | $C_2O_4$. | Result. | Effect of $HgCl_2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1–1*a* | 0.0 | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 2 | 1.0 | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 3–3*a* | 0.0 | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 4 | 1.0 | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 5 | 0.0 | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 6 | 1.0 | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 7 | 0.0 | 200 | ... | ... | ... | ... | ... | ... | 50 | 50 | 200 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 8 | 0.0 | 200 | 100 | ... | ... | ... | ... | 50 | 100 | 50 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 9 | 1.0 | 300 | 50 | ... | ... | ... | ... | 50 | 50 | 50 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Distinct brownish red | Bleached to yellow |
| 10 | 1.0 | 250 | 50 | ... | ... | ... | ... | ... | 50 | 50 | 100 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Distinct brownish red | Bleached to yellow |
| 11 | 1.0 | 100 | 50 | ... | 100 | 150 | ... | ... | 50 | 50 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Distinct brownish red | Bleached to yellow |
| 12 | 1.0 | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 13 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 14 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 15 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 16 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 17 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 18 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 19 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 20 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 21 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | ... | Blood red | Bleached to yellow |
| 22 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | ... | Blood red | Bleached to yellow |
| 23 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | ... | Blood red | Bleached to yellow |
| 24 | 1.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 500 | Blood red | Bleached to yellow |
| 25 | 1.0 | 200 | 100 | 20 | ... | 20 | ... | ... | ... | 50 | 50 | 50 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 50 | Distinct red | Bleached to yellow |
| 26 | 0.0 | 100 | ... | ... | ... | ... | ... | 50 | 100 | 50 | 200 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Blood red | Bleached to yellow |
| 27 | 0.0 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | ... | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | Brown | Appreciably bleached |
| 28 | 0.0 | ... | ... | ... | ... | ... | ... | 200 | ... | ... | ... | ... | 300 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Deep blood red | Bleached to yellow |
| 29 | 0.0 | ... | ... | ... | ... | ... | ... | 200 | ... | ... | ... | 300 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | Negative | No change |
| 30 | 0.0 | 25 | 25 | 25 | 25 | 25 | 25 | ... | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | Negative | No change |
| 31 | 0.0 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | ... | 25 | ... | 25 | 25 | 25 | 25 | ... | 25 | 25 | 25 | 25 | 25 | Negative | No change |
| 32 | 1.0 | 25 | 25 | 25 | 25 | 25 | 25 | ... | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | Distinct red | Bleached to yellow |
| 33 | 1.0 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | ... | 25 | ... | 25 | 25 | 25 | 25 | ... | 25 | 25 | 25 | 25 | 25 | Distinct red | Bleached to yellow |

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[1] The solution used was prepared by saturating with $H_2S$ a definite volume of a standard solution of NaOH and then adding to the saturated solution an equal volume of the same NaOH solution.

[2] The silicate solution used was prepared by fusing a known quantity of C. P. silicic acid with sodium carbonate.

the presence of a blood red color in the latter as against a brown color in the former. The results recorded in Table VI show that the volume of mercuric chloride solution required to bleach the red color to the point when no further considerable change takes place on adding 0.3 cc., is roughly proportional to the quantity of thiocyanate present. This reaction therefore furnishes a basis for an approximate estimation of thiocyanates.

TABLE VI.

| No. | Mg. SCN. | Cc. $HgCl_2$ solution used. |
|---|---|---|
| 1 | 5 | 0.6 |
| 2 | 50 | 5.4 |
| 3 | 100 | 9.9 |
| 4 | 250 | 18.6 |

**Significance of the Results.**—It has been stated by Kern[1] and confirmed by us that in the presence of thiocyanates, palladium chloride may fail to give a reliable indication of the presence of iodides and that palladium nitrate may fail to give a reliable separation of iodides from chlorides and bromides. The need for a test for thiocyanates in the presence of iodides is therefore evident. Moreover, it is hardly necessary to state that in the presence of alkali halides only, the entire preliminary procedure may be dispensed with in testing for thiocyanates. To the solution, acid with dilute nitric acid, it is only necessary to add silver nitrate, and after filtering to treat the precipitate with sodium chloride solution.

## Summary.

1. The sensitiveness of the ferric thiocyanate test for thiocyanates has been determined.
2. Data are supplied showing the extent of the interference of iodides, acetates and nitrites.
3. A procedure has been devised for the systematic detection of thiocyanates depending upon the ability of a 5% sodium chloride solution to transpose silver thiocyanate.
4. Numerous tests analyses show the reliability of the method.

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# FREE ENERGY AND HEAT CAPACITY.

BY JAMES M. BELL.

Received November 20, 1915.

In a recent paper, T. W. Richards[2] writes as follows:

"I was able to show, in cases of certain typical reversible galvanic cells, that when free energy change increases with rising temperature, total energy change decreases, and *vice versa*."

And appended to this is a footnote as follows:

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[1] *Chem. News*, 32, 242 (1875).

[2] THIS JOURNAL, 36, 2433 (1914).