

down by manganese dioxide. The color obtained from this precipitate is entirely pure.

0.2 grams platonic chloride (10% solution from Kahlbaum) gave 0.0205 mg. Fe, or 0.01025 per cent. Fe.

20 cc. 10 per cent. platonic chloride solution was freed from iron by alumina, a definite amount of iron was added to the filtrate and concentrated as before.

mg. Fe added	mg. Fe found
0.0150	0.0161
0.0150	0.0150

## SUMMARY.

1. The ferric sulphocyanate is extracted from its aqueous solution with a mixture of amyl alcohol and ether, using two cylinders, one of which contains the iron to be determined; a standard iron solution is then added to both cylinders from two burettes, the difference of the readings indicating the amount of iron sought. The final result is reached by averaging a series of readings.

2. A form of colorimeter is described, adapted to the use of extracting liquids.

3. The iron is concentrated and freed from all interfering substances by evaporation, or by precipitation as hydroxide or sulphide, using a suitable substance to collect and carry down the trace of precipitate; it is then dissolved in free sulphocyanic acid.

4. The fading out of the color of the ferric sulphocyanate is prevented by the use of persulphate, and the formation of discolored amylic solutions is prevented by saturating the sulphocyanic acid with mercuric sulphocyanate.

5. Special directions are given for concentrating traces of iron from various substances, with analytical data.

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CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS, NO. 2]

## ON SULPHOCYANIC ACID.

BY H. N. STOKES AND J. R. CAIN.

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An aqueous solution of sulphocyanic acid may be prepared by distilling an acidified solution of a sulphocyanate, by decomposing the barium or lead salts with sulphuric acid, or by decomposing the lead<sup>1</sup> or mercuric<sup>2</sup> salts under water with hydrogen sulphide and removing the excess of the latter by a stream of air or carbon dioxide. All these methods have their drawbacks, involving either distillation or the use of salts which are no

<sup>1</sup> Zimmermann, Ann. 204, 226 (1880).

<sup>2</sup> Rosenheim and Cohn, Z. anorg. Chem. 27, 288, note (1901).

to be found in every laboratory, and which are expensive and not to be depended on for purity. The decomposition of the lead salt by hydrogen sulphide is slow and the removal of the excess of the latter tedious.

In connection with our work on the colorimetric determination of iron<sup>1</sup>, we have employed a process by which any desired amount of aqueous sulphocyanic acid, free from iron and all other non-volatile impurities, may be prepared in a few minutes and which, in view of the increasing importance of this body as an analytical reagent, we communicate under a separate heading, together with a few observations on its properties and those of some of its derivatives.

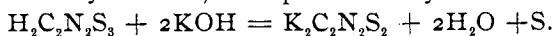
100 parts coarsely powdered ammonium sulphocyanate, which need not be free from iron, are dissolved in a stoppered graduated cylinder in a cool mixture of 65 parts by weight of concentrated sulphuric acid with 100 parts water. These correspond approximately to the equation  $2\text{NH}_2\text{SCN} + \text{H}_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 + 2\text{HSCN}$ . There is a marked fall of temperature. After noting the volume, the solution is transferred without delay to a separating funnel and shaken out once with three-fourths its volume of amyl alcohol. We here notice the peculiar phenomenon that iron, if present, remains entirely in the acid layer, which is usually colored pink, while the amylic layer is colorless. In order to obtain this result, however, it is necessary to adhere to the proportions given. If a more concentrated acid is used, there is considerable decomposition of the sulphocyanic acid, while, if as much as an equal volume of amyl alcohol be employed, some of the iron passes over into the latter. The amylic solution, which is found by titration with silver nitrate to contain 20-21 per cent. sulphocyanic acid, is unstable and soon becomes yellow, with ultimate deposition of isopersulphocyanic acid. It is, therefore, at once shaken out twice with an equal volume of water. As we have determined, sulphocyanic acid distributes itself about equally between water and amyl alcohol; the first aqueous extract, therefore, contains about 10 per cent., and the second 5 per cent., or the united extracts about 7.5 per cent., while the amyl alcohol retains about 5 per cent., in which concentration it is relatively stable and may be kept or used for making a weaker aqueous acid; it gradually turns yellow from formation of isopersulphocyanic acid, but this is entirely retained on extraction with water.

The aqueous acid thus prepared contains about one-fortieth of amyl alcohol, which, however, is without significance for most purposes. The 7.5 per cent. acid generally becomes yellowish, but the color may be removed by shaking with a small quantity of amyl alcohol. In this strength it is used in the colorimetric iron determination as prescribed in the preceding paper, after saturating with mercuric sulphocyanate.

<sup>1</sup> See the preceding paper.

Aqueous sulphocyanic acid prepared by the action of mineral acids on an alkali sulphocyanate, is a substance of very varying properties, depending on its age and concentration. It contains, as does also a freshly acidified solution of alkali sulphocyanate, a small quantity of a substance which increases on keeping, which rapidly gives, with hydrogen peroxide, bromine, or persulphate, a yellow amorphous oxidation product scarcely soluble in water but easily soluble in amyl alcohol, thus interfering seriously with colorimetric iron determinations. This substance, which appears to be colorless, can be removed for the greater part by shaking out with a small quantity of amyl alcohol. It appears to be absent at first in acids prepared by decomposing the silver salt with hydrogen sulphide; but in this, too, it gradually makes its appearance. It differs from isodisulphocyanic acid, which is also present, as the latter gives an oxidation product insoluble in amyl alcohol. Normal sulphocyanic acid is likewise rapidly oxidized by hydrogen peroxide, with marked rise of temperature, and also by bromine water; but the oxidation products are soluble and colorless. Judging from the analogous behavior of the unknown body and isodisulphocyanic acid, it may be the as yet unisolated isosulphocyanic acid  $\text{NH}:\text{CS}$ . The formation of yellow oxidation products by persulphate is entirely prevented by saturating the acid with mercuric sulphocyanate.

*Isodisulphocyanic Acid*,  $(\text{HN}:\text{CS})_2$ , is one of the products of the action of mineral acids on sulphocyanates or sulphocyanic acid<sup>1</sup> and of the spontaneous change of sulphocyanic acid itself. Hence it is present in both aqueous sulphocyanic acid and in the acidified sulphocyanate solutions used in colorimetric iron determinations. Our experiments show that to this substance, in part at least, is to be attributed the gradual bleaching of the color of ferric sulphocyanate so often referred to by writers on this subject, and also the formation of a precipitate in the ether solution of the same. We prepared this acid by decomposing isopersulphocyanic acid crystallized from amyl alcohol, with potassium hydroxide.<sup>2</sup>



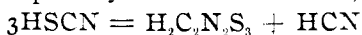
On acidifying, the amorphous yellow acid is obtained, which is slightly soluble in water and easily soluble in amyl alcohol, giving a yellow solution. It is distinguished from isopersulphocyanic acid by giving, with stannous chloride, an amorphous yellow precipitate, which does not turn red and crystalline, is soluble in amyl alcohol, dissolves in boiling water, and does not separate on cooling. Its behavior towards ferric salts is also characteristic. Its aqueous solution is colored red-brown by a small amount of ferric salt, but the intensity of the color is by no means comparable with that of ferric sulphocyanate. The color is partly taken up by amyl alcohol, giving a red-brown solution, but its solubility in this does

<sup>1</sup> Klason, J., pr. Chem. (2) 38, 383 (1888).

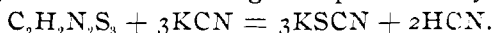
<sup>2</sup> Fleischer, Ann. 179, 204 (1875).

not seem to exceed that in water. Peculiarly noteworthy is it, that the color of either the aqueous or the amylic solution of the ferric salt fades out in a few minutes, and, if a little ferric sulphocyanate be present, this is bleached at the same time. Addition of a trace of persulphate instantly restores the color temporarily. Isodisulphocyanic acid is very rapidly oxidized by persulphate, hydrogen peroxide, or bromine water, giving a pulverulent yellow body, which is insoluble in and separates from either water, amyl alcohol, or ether. The properties of this substance agree with those of pseudosulphocyanogen.

*Isopersulphocyanic Acid*,  $H_2C_2N_2S_3$ , which is formed by the decomposition of sulphocyanic acid, especially when concentrated, after the equation



is frequently met with. It imparts a yellow color to the amylic or aqueous solutions, and is deposited as yellow needles. It is not always distinguished from pseudosulphocyanogen or other yellow oxidation product referred to above, nor from isodisulphocyanic acid, all of which are yellow and which may be encountered in the course of analytical operations with sulphocyanic acid. Isopersulphocyanic acid is not in itself an oxidation product, although it may accompany these. It may be recognized by its giving sulphocyanic acid on warming with potassium cyanide.<sup>1</sup>



A further characteristic reaction which we have observed is its behavior towards stannous chloride.<sup>2</sup> An amylic solution, shaken with a few drops of 10 per cent. stannous chloride solution, becomes of a stronger yellow and soon, or at once, according to the concentration, deposits a yellow precipitate. This rapidly becomes darker and denser, and soon turns to a dark-red, heavy, crystalline sediment. This redissolves in amyl alcohol on heating, forming a yellow solution which on cooling may give either the red or yellow form, the latter, however, soon turning red. This change is promoted by gentle warming. The salt is decomposed by much acid, but may be regenerated by further addition of stannous chloride. Impure material shows the same behavior, but the change to red is slower. Isopersulphocyanic acid may be detected in aqueous sulphocyanic acid by extracting with a small amount of amyl alcohol and treating the latter as above.

#### SUMMARY.

1. A rapid method of preparing pure sulphocyanic acid.
2. Some properties of the solution.
3. Isodisulphocyanic acid, its occurrence in sulphocyanic acid, its be-

<sup>1</sup>Steiner, Ber. 15, 1603 (1882).

<sup>2</sup>Völckel (Ann. 43, 76) states that it gives a yellow precipitate with stannous chloride.

havior towards oxidizing agents, and its agency in the bleaching of ferric sulphocyanate.

4. Isopersulphocyanic acid, its occurrence in sulphocyanic acid, and a characteristic reaction.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

## THE DETERMINATION OF ANIONS IN THE ELECTROLYTIC WAY.<sup>1</sup>

By JOEL H. HILDEBRAND.

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The negative groups in salts—the anions—have in the period of metal determination received scant attention from the electro-analyst. The few observations of Vortmann<sup>2</sup> and Specketer<sup>3</sup> have attracted little attention, and only since Smith<sup>4</sup> by the use of a mercury cathode and a silver anode made successful estimation simultaneously of both components in sodium chloride, barium chloride, strontium bromide, etc., has the idea of estimating anions electrolytically become a subject of serious thought. The experiments of Withrow (thesis 1905) were directed to this end. They, however, showed that ultimate and most complete success would probably come only by the use of the combined anode and mercury cathode. The present investigation was begun with this thought constantly in mind. The results clearly prove that it is now possible to determine not only halogens, but even anions such as CO<sub>3</sub>, CNS, Fe(CN)<sub>6</sub>, and others. Salts that are analyzed with difficulty by time honored methods are now electrolyzed most easily and with exceeding accuracy in exceedingly short periods of time. That separations of anions will also be made in the same manner appears certain, although the present study has been restricted to their determination alone, and to the perfection of the apparatus necessary for that purpose.

### Results with Stationary Anode.

*Apparatus.*—The mercury cathode cell as described by Myers<sup>5</sup> was used to contain the solution to be electrolyzed. Three platinum gauzes (5 by 10 cm.) attached to stiff platinum wires and rolled into cylinders with the shorter dimension as axis and of such diameter as to be suspended readily in the cell were the anodes. These gauzes were plated with silver, the coating being made as heavy as possible. After washing with water, alcohol and ether, the deposits were carefully brushed with a soft camel's hair brush to remove all loosely adherent silver and then weighed.

<sup>1</sup> From author's Ph. D. thesis, 1906.

<sup>2</sup> *Monatsh.* 15, 280; 16, 674. *Electrochem. Z.* (1894) 1, 137. *Akad. d. Wissenschaft. Wein.*, 11 7, 95.

<sup>3</sup> *Z. Electrochem.*, 4, 539.

<sup>4</sup> *This Journal*, 25, 890 (1902).

<sup>5</sup> *This Journal*, 26, 1124.