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Some Peculiarities of Solutions of Ferric Sulphocyanate

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therefore, we are not at present justified in the assumption that elements at the moment of formation or liberation from their compounds possess properties in any way different from those they commonly exhibit.

SOME PECULIARITIES OF SOLUTIONS OF FERRIC SULPHOCYANATE

BY LAUNCELOT ANDREWS, PH. D.

The deep blood-red color of solutions of ferric sulphocyanate has frequently been taken advantage of for the determination of small quantities of iron in river or spring water, in blood, in alloys, in alumcake, etc.

The earliest method of this kind, so far as I have been able to ascertain, is due to T. L. Herapath, who proposed to determine minute quantities of iron by the addition of potassium sulphocyanate to the acidified solution containing an unknown amount of iron, and also to a standard iron solution of known strength, the latter being then diluted until both showed the same tint.

Very similar methods have been employed or devised by A. Thomsen (*Ch. Soc. Jour.*, 47, 493), Ad. Joles (*Arch. f. Hygiene*, XIII, 402), L. Lapique (*Bull. Soc. Chim.*, 2, 295, and by R. R. Tatlock (*Jour. Soc. Ch. Ind.* 6, 276).

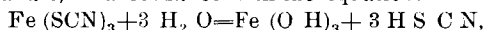
Vierordt (*Quant., Spektralanalyse*), suggested a fundamental modification of Herapath's colorimetric method, in that he dispensed wholly with a standard comparison solution, substituting for it a direct spectrophotometric determination of the amount of light of given wave length, transmitted by a layer of the ferric sulphocyanate solution one c. m. thick. In this method the assumption, based upon analogy, is made that the light absorbing power of the solution is directly proportional to the amount of iron contained therein; or in other words, *that the negative logarithm of the fraction of light transmitted is proportional to the concentration of the solution*, and the assumption seems to be confirmed by Vierordt's observations.

Subsequent investigations by Krüss and Moraht (*Lieb. Ann.*, 260, 193; *Kalorimetrie, u. Spektral analyse*, 1891, p. 125), and by Magnanini (*Zeit. phys. Ch.* 8,1) have shown the assumed proportionality to be non-existent in fact. If aqueous solution of ferric sulphocyanate be diluted its color fades away in a much more rapid ratio than corresponds to the diminishing concentration of the solution. The depth of color is much enhanced by an excess of either generatrix, *i. e.*, of KSCN or of FeCl_3 , and as Magnanini has shown the change follows the laws of mass action qualitatively and quantitatively.

Magnanini dismisses the affair at this point as a *res adjudicata* assuming that the sulphocyanate is subject, in its solution in water, to a progressive electrolytic dissociation in the ions, Fe and S C N. In accordance with well

known principles this dissociation must become more complete with increasing dilution, and of course the formation of colorless ions from the colored salt must result in a diminution of the intensity of the color.

There is, however, another explanation not only possible, but probable. Ostwald has shown that other salts of ferric iron undergo in dilute solution more or less complete hydrolysis into colloidal ferric hydrate and free acid. If this hydrolysis also occurs in solutions, as we have no reason to doubt, of the sulphocyanate, in accordance with the equation.



It would offer a complete explanation of the phenomena hitherto observed.

II. EXPERIMENTAL PART.

In order to obtain further insight into the nature of the changes occurring upon dilution of solutions of ferric sulphocyanate, and indirectly of solutions in general, it seemed advisable to operate in solutions containing no water.

In such solutions the hydrolysis called for by the second theory given above could not occur and the electrolytic dissociation called for by the first theory could occur only in a subordinate degree. Hence both theories would lead us to expect that a solution of stated concentration of $\text{Fe}(\text{SCN})_3$ in ether or in amyl alcohol or in absolute ethyl alcohol would have a much more intense color than a solution of the same strength in water, and second that the color would be proportional to the strength.

My observations have confirmed the first prediction, but not the second.

A solution in ether was first prepared containing 4.7 m. g. $\text{Fe}(\text{SCN})_3$ per cu. cm., both the iron and sulphocyanogen being directly determined and found in accordance. From this solution, which was kept in the dark, the other solutions were prepared and their absorption coefficients determined by repeated observations in a Vierordt spectroscope with double symmetrical slit.

First.—Comparison of absorbtive power in amyl alcohol and water solutions. A solution containing .0625 m. g. $\text{Fe}(\text{SCN})_3$ per c. c. of amyl alcohol transmitted 42 per cent of light of wave length 587, or about the same amount as an aqueous solution containing .247 m. g. per c. c., or nearly four times as strong.

I. Amyl alcohol containing .05 m. g. $\text{Fe}(\text{SCN})_3$ per c. c., $T=15^\circ$.

MIDDLE OF REGION.	PER CENT TRANSMITTED LIGHT.	EXTINCTION COEF.	ABSORPTION RATIO K.
617	84.0	.078	
589	56.2	.250	.200
564	42.5	.372	.184
517	19.1	.719	
501	16.0	.796	

II. Amyl alcohol containing .1 m. g. Fe (SCN)₃ per c. c. T=15°.

MIDDLE OF REGION.	PER CENT TRANS- MITTED LIGHT.	EXTINCTION COEF.	ABSORPTION RATIO K.
617	41.0	.377	
589	14.8	.830	.120
564	6.8	1.167	

III. Amyl alcohol containing .094 m. g. Fe (SCN)₃ per c. c. T=18°. Older solution, stood 48 hours.

MIDDLE OF REGION.	PER CENT TRANS- MITTED LIGHT.	EXTINCTION COEF.	ABSORPTION RATIO K.
623	61.0	.215	.436
599	42.9	.367	.263
568	12.2	.914	.104
556	9.0	1.045	.090

IV. Ethyl alcohol .094 m. g. Fe (SCN)₃ per c. c. T=18°.

MIDDLE OF REGION.	PER CENT TRANS- MITTED LIGHT.	EXTINCTION COEF.	ABSORPTION RATIO K.
568	21.6	.665	
556	12.7	.896	

Other series of experiments with ethyl alcohol, amyl alcohol and ether, demonstrated that the absorbent power of solutions of ferric sulphocyanate in these menstrua diminishes more rapidly than the concentration. The amyl alcohol was distilled from phosphoric acid to remove traces of organic bases and then thoroughly dried. Hydrolysis of the ferric salt can therefore not occur.

If electrolytic dissociation occurs, the molecular conductivity of these solutions must increase with diminishing concentration and in proportion to the diminishing light-absorbing power.

The electrical resistance of the same solutions which had been examined optically was therefore determined in a resistance cell of the form described by Arrhenius, by Ostwald's method with Kohlrausch-Wheatstone bridge and telephone. The specific resistance of the amyl alcohol employed was about 100,000,000 ohms per m. m. cube.

All the measurements showed that the molecular conductivity of the non-aqueous solutions examined diminished with increasing dilution and in about the same ratio as the reciprocal of the absorption coefficient, whereas the molecular conductivity should be greater at high dilutions than at low if the tapering off of the color of the former is due to electrolytic dissociation.

I am not prepared to present final quantitative results at present because my apparatus is not perfectly adapted to the measurements of such high resistances, but there is no reason to question the qualitative results nor the general character of the numerical data. A cell now in course of construction having a much smaller resistance constant than that heretofore in use is expected to furnish results of the desired accuracy.

Ivan Klobukoff (*Zeit. Phys. Chem.* IV, 429,) has observed that solutions of hydrochloric acid in ether and in amyl alcohol exhibit a diminution of molecular conductivity with increasing dilution of the solutions and has shown that it is not due to any chemical action of the acid upon the alcohol. This phenomenon evidently belongs in the same class with that which I have observed in the case of ferric sulphocyanate solutions.

Neither of the theories as yet advanced seems capable of explaining all the facts and more extended studies of the spectroscopic and electrical behavior of other colored salts in non-aqueous solvents must be made before any theory can be advanced with profit.

ELECTROLYSIS OF SILVER—LABORATORY NOTES.

W. S. HENDRIXSON.

(*Abstract.*)

The author exhibited some pieces of apparatus devised in connection with his work on the atomic weight of tin, and also a quantity of pure silver prepared by electrolysis of the pure silver of Stas in strong nitric acid solution. The method of electrolysis was essentially that of Abrahall* as modified by Richards†. By using a strong acid solution containing fifteen per cent of silver and a battery consisting of sixteen gravity cells the silver was obtained in large crystals and no peroxide was formed at the positive pole. Separate experiments showed that silver deposited under these conditions, from a solution to which copper had been added, contained no trace of the latter metal.

The apparatus exhibited included:

1. A platinum condenser for the preparation in pure condition of such substances as attack glass or metals other than platinum, viz, water, hydrochloric, hydrobromic and nitric acids. Cork or other connections are avoided by selecting a retort into the neck of which the condenser tube fits closely. The first portion of the vapor condenses between the glass and platinum and forms a seal. The condenser tube is bent so that the neck of the retort or flask may be inclined upward to secure a back flow and to avoid the mechanical carrying over of substances by the spray.

2. A separatory funnel having a doubly-bored stop-cock like that in the well-known Lunge's nitrometer. On turning the cock to arrest the flow of the liquid the column in the stem, which in the ordinary funnel remains in the stem, being held by atmospheric pressure, falls at once since it is replaced by air which enters the stem through the second hole in the stop-cock.

* *Journal Chem. Soc.*, 1892, p. 660.

† *Proc. Amer. Academy*, Vol. XXVIII, p. 22.