

that the characteristics of the added salts in this photocatalysis are evidently intimately connected with the electric charges of the ions and with their mutual electrostatic actions upon each other.

If the relations found here, should indeed appear to be generally valid after the investigations have been extended over a much greater number of cases of photocatalysis, it would perhaps appear to be possible to give a theoretical explanation of all these peculiarities and more particularly of the occurrence of a maximal catalysis by salts, starting with the views about the nature of strong electrolytes and their abnormal behaviour, as developed in recent times by BJERRUM ¹⁾, GHOSH ²⁾, NOYES ³⁾, and others; which views in every case, however, would involve a complete break with the electrolytic dissociation-theory of ARRHENIUS, at present still almost universally adopted.

Perhaps one of us will return to this question again in future, after a more detailed experimental investigation of this kind has been made.

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¹⁾ N. BJERRUM, Zeits. f. Elektrochemie, **24**, 321, (1918); Zeits. f. anorg. Chem. **109**, 275, (1919).

²⁾ I. C. GHOSH, Journ. Chem. Soc. London, **113**, 449, 627, 707, (1918).

³⁾ A. A. NOYES and MC. INNES, Journ. Amer. Chem. Soc. **42**, 239, (1920).

Chemistry. — “*Colloidal Sulphurcompounds of Ruthenium*”. By Prof. F. M. JAEGER and J. H. DE BOER.

(Communicated in the meeting of May 29, 1920).

§ 1. It was for the first time during the process of recovering *ruthenium* from residues, that we observed some phenomena indicating the existence of colloidal *sulphur*-compounds of that metal. The properties of the colloidal solutions thus obtained, appeared to be sufficiently interesting, to study the phenomena more in detail. The results of this investigation are accordingly summarized in the following paper.

If a solution of freshly prepared *ammonium-sulphide* be added to a *hot* solution of some salt of tetravalent *ruthenium* ¹⁾, be it to the *sulphate*: $Ru(SO_4)_2$, or to a complex salt ²⁾ like: $\left\{ Ru \begin{matrix} (HO) \\ (NO) \end{matrix} (NH_3)_4 \right\} Br_2$,

a brownish black precipitate of RuS_2 will be formed, which does not manifest any especially remarkable properties. Totally different, however, is the behaviour of these substances with respect to each other, if the experiment is carried out at *lower* temperatures, e. g. at 0° C.: under these circumstances a dark, greenish black precipitate is formed, while a dark green colloidal solution appears at the same time. This solution is very unstable: it rapidly becomes turbid, depositing greenish black flakes of the same kind as the original precipitate. For the green solution is nothing but a colloidal solution of the original precipitate, produced by the addition of ammonium-sulphide; it shows the TYNDALL-effect, and its dispersed particles appear to carry a *negative* electric charge, as follows from the electric cataphoresis of the solution. On being put into contact with the air for some hours, the solution is completely flocculated, and the supernatant liquid then shows only the yellow colour of the ammonium-polysulphides. The green solution is much more stable, if first strongly diluted with water; but even in these circumstances it appears to be flocculated completely after twenty-four hours. Neither an addition of gum arabic, nor that of gelatine, can increase the stability of the colloidal solution.

¹⁾ U. ANTONY and A. LUGHESSI, Gazz. Chim. It. **28**, (II), 139, (1898).

²⁾ A. WERNER, Ber. d.d. chem. Ges., **40**, 2621, (1907).

§ 2. If now the flocculated solution is quietly left standing during a couple of days, its colour becomes gradually pale pink; and after standing somewhat longer, finally a more or less intense reddish violet solution is obtained, while at the bottom of the vessel a precipitate of finely divided sulphur has accumulated. An analogous phenomenon is observed, when one tries to subject the original, dark green solution to dialysis: also in that case a pink solution is finally obtained after the flocculation of the original green one. This new red solution, into which the original green liquid is transformed, also appears to be a colloidal solution: both the original and the red liquid exhibit the TYNDALL-effect and on being examined with the ultra-microscope they both show the characteristic structure and the BROWNIAN motion of true colloidal solutions. The stability of the red solution appears, however, to be much greater than that of the dark green solution mentioned before.

Soon it became evident that for the change of the unstable green solution into the much stabler red solution, the presence of the free oxygen of the air is essential; that, in other words, an *oxydation*-process goes on, in which the greenish black precipitate originally formed is gradually dissolving under continuous absorption of oxygen, while a red colloidal solution is formed by it. This chain of events could be illustrated, leaving no doubt whatever about its truth, by the following series of experiments:

a. Greenish black *ruthenium-sulphide* freshly precipitated at 0° C. was first washed with icy-cold water, and subsequently dried after washing it with absolute alcohol and ether. Immediately it was mixed with water and shaken in a stoppered bottle; a suspension is formed of an originally bluish hue, the upper layer of which is, however, already after one and a half hour converted into a pale pink liquid. After a day the colour turns reddish violet, while the quantity of the precipitate is gradually diminished, the longer the contact of the different substances lasts. Simultaneously a slight precipitate of sulphur is deposited on the bottom of the flask.

b. At 0° C. freshly precipitated greenish black sulphide, treated as described above, was vigorously shaken with water, and a continuous current of pure air sucked through the liquid. Soon the solution turns reddish violet; after some days the original precipitate has completely disappeared, while some finely divided sulphur only remains, which can be easily removed by filtering. This is one of the best modes of preparing the red colloidal solutions.

c. On being exposed to the air for a long time, the dry greenish-

black sulphide gradually changes its colour, being converted into a reddish, dark coloured mass, which gives immediately the red solution, if shaken with water.

d. A piece of filter-paper soaked in the green colloidal solution, becomes very rapidly violet on being exposed to the air. If the oxygen of the air is first removed, *no* change of colour appears; the precipitate generated in flocculating the green solution gives, however, automatically the reddish violet liquid, when exposed to the atmosphere.

e. Whilst RuS_2 , precipitated from hot solutions is simply attacked by nitric acid (spec. grav.: 1.4) and oxydized to a brown solution, the greenish black sulphide is attacked by the same acid extremely vigorously, almost explosively: a red violet solution is formed, while, moreover, some sulphur is precipitated at the same time. The red-violet solution is, also after neutralisation of the acid in excess, slowly oxydized further, when in contact with the air; finally the solution becomes completely colourless, and the slightly acid liquid thus obtained appears to contain a *sulphate*. Not even a preliminary dilution of the red-violet liquid with water can prevent this oxydation to sulphate. The presence of mere traces of the unstable greenish black sulphide may be proved by this reaction of oxydizing the supernatant liquid by means of nitric acid¹⁾; and it is in this way, that we can demonstrate the fact, that the sulphides precipitated from *ruthenium* solutions by ammonium sulphide between 0° C. and boiling-temperature, are really mixtures of stable RuS_2 and the unstable greenish black sulphide, here described. It suffices to shake the precipitate simply with water, and to add strong nitric acid to this suspension: the red colour will then appear immediately.

§ 3. Because the new sulphide appeared to lose its characteristic properties, if heated even to only 110° C., it was necessary, under exclusion of the oxygen of the air as much as possible, to prepare it always at *lower* temperatures; also it must be rigorously purified for the purpose of analysis. In the process of precipitation, free sulphur is moreover always formed, — a fact also noticeable²⁾ in working with other ruthenium sulphides, — and therefore necessitating repeated

¹⁾ Already other investigators have occasionally had an opportunity to observe a pink coloration of the solutions obtained in their studies on *ruthenium sulphides*, without any attempt at an explanation of the said phenomenon, it was e.g. mentioned by ANTONY and A. LUCHESSI, loco cit 30, (II), 540, (1900).

²⁾ C. CLAUS, Ann. der Chem. u. Pharm., 59, 245, (1846); U. ANTONY and A. LUCHESSI, Gazz. Chim. Ital. 30, (II), 539, (1900).

extraction of the product by carbon disulphide at low temperatures. The substance was, therefore, rapidly put into a small ERLIENMEYER-flask, carbon bisulphide was poured upon it, the air driven out by carbon dioxide, and the flask shaken for some time at room-temperature. This treatment was repeated several times, till no sulphur was any more extracted; the carbon bisulphide was then washed out by a mixture of dry alcohol and ether, the product finally washed with absolute ether and carefully dried in an atmosphere of carbon dioxide. For the purpose of analysis a weighed quantity was put into a ROSE-crucible, which in its turn was hung inside a nickel crucible, and carefully roasted with access of the air; afterwards it was ignited in a current of dry hydrogen. All the determinations were made by means of a micro-balance.

Analysis: 12,33 m.Gr. of the greenish black sulphide gave 4,26 m.Gr. *Ru*; calculated for RuS_6 : 34,69% *Ru*; found: 34,55% *Ru*.

Because in the oxydation of this sulphide, as will be demonstrated below, there is formed a substance containing four atoms of sulphur, while simultaneously sulphur is set free, this high content of sulphur is perfectly in agreement with the whole chemical behaviour of the greenish black sulphide¹⁾, which has the character of a *ruthenium persulphide*.

§ 4. We must now first review the properties of the red-violet solution, which is formed by oxydation of the green solution described above. Its refractive index appeared to be practically identical with that of pure water; moreover, besides the TYNDALL-effect and the BROWNIAN movement, it manifests in a particularly beautiful way the phenomenon of electric cataphoresis: the dispersed particles possess, in contradistinction to those of the green colloidal solution, a *positive* charge. Although the solution is very stable, and may even be concentrated on the water-bath without coagulation, it can be flocculated by the addition of electrolytes, — be it only slowly. The pure solution was mixed with a small quantity of solutions of NH_4Cl , $CaCl_2$, Fe_2Cl_6 , K_2SO_4 and Na_2HPO_4 . Already after a day some precipitate was formed from each of these liquids, and the intensity of their colour diminished. If more of the electrolytes be added, the precipitate formed first again disappears, but after twenty-four hours a certain quantity is again deposited. After a couple of days the colour of the liquid has completely disappeared, and all of the dispersoid has been flocculated. Most rapidly this takes place, when *phosphate* is added,

¹⁾ It may be remarked here, moreover, that on heating this sulphide at the open air at 120° C., also SO_2 is formed; the sulphur seems to be partially more loosely bound than the remaining part of it.

the electrostatic charge of the anions, therefore, being decisive here, — a fact, which is in agreement with the stated positive charge of the dispersed particles. Such experiments were also carried out with a more concentrated solution, $CaCl_2$ being added to it. After one day already there appeared a precipitate, the colour of the solution being violet; after two days more precipitate was formed, while the colour became bluish violet; after five days the colour was dark bluish violet; after a fortnight it was similar and only a relatively small amount of precipitate was formed. In no case the colloidal solution was flocculated completely, it, therefore, appearing to be extremely stable. This follows also from the behaviour of the liquid, while being concentrated on the waterbath: even the last drops retain their bluish violet colour, and the amorphous reddish violet powder, which is continually deposited at the surface-border of the liquid, may be redissolved immediately into a colloidal solution of the same kind as the original liquid. This reversibility of the colloid corresponds also here with a smaller sensitiveness to electrolytes. On complete evaporation a violet and a grey powder are obtained; only the violet one is reversible. If heated for some time, it turns grey, afterwards black, and then it can no longer be dissolved. After being dried at 110° C. until the weight has become constant, the powder is black and possesses a metallic lustre.

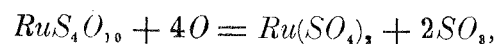
Of this product the content of *ruthenium* was determined in the way formerly described, and by the aid of the micro-balance.

Analysis: 17,23 mGr. of the powder contain 4,55 mGr. *Ru*. The amount of sulphur was determined by volumetric analysis: a solution, the *ruthenium* content of which was accurately known, was oxydized by a solution of potassium-permanganate of known strength, and the amount of sulphate afterwards estimated as $BaSO_4$. Such solutions were prepared from a known weight of the pure greenish black sulphide by oxydation of its solution by means of an air current.

Analysis: A quantity of the solution containing 2,40 mGr. *ruthenium*, gave 21,4 mGr. $BaSO_4$, corresponding with 2,93 mGr. *sulphur*, this being 32,18%. Therefore 41,42% of *oxygen* is present, corresponding with the formula: RuS_4O_{10} , which was afterwards confirmed by other tests.

Calculated for RuS_4O_{10} :	Observed:
<i>Ru</i> : 26,16 %	26,40 %
<i>S</i> : 32,82 %	32,18
<i>O</i> : 41,02 %	41,42 %

The oxydation of the solution to *ruthenium sulphate* and free *sulphuric acid* can, therefore, be expressed by the equation:



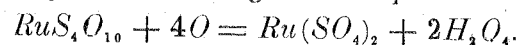
which was completely checked and confirmed by the determination of the oxygen liberated from the permanganate used and absorbed by the substance, as well as by the quantitative measurement of the amount of sulphuric acid formed. For this latter quantity is equal to the total amount of acid found, minus the acid added for the volumetric analysis, plus the quantity of acid used during the titration with $KMnO_4$.

Analysis: A quantity of the colloidal solution, containing 2,30 mGr. of *ruthenium* ($= 0,0225$ milli-mol. Ru) was titrated with 10 ccm. of a $\frac{1}{25}$ normal solution of sulphuric acid and 4,9 ccm. $KMnO_4$ of 0,09 normal, — if a normal solution be calculated as one containing 0,4 mol p. Liter, equivalent to 0,09 mGr. atom O p. ccm. Therefore, totally 0,0882 mGr. O , corresponding with $4O$ to 1 Ru were used. As there are used at the same time 2,65 ccm. H_2SO_4 of the strength mentioned above in this reaction, 7,35 ccm. sulphuric acid remain. As 38 ccm. of $\frac{1}{100}$ normal $NaOH$ -solution were necessary in the subsequent titration, and for 7,35 ccm. H_2SO_4 only 29,4 of this $NaOH$ -solution were necessary, it follows that 0,043 milli-mol. H_2SO_4 are formed in the reaction by oxydation of the sulphur. For every atom Ru there are thus formed 2 molecules H_2SO_4 , which data, with respect to the quantity of O absorbed in the process, demonstrate clearly the correctness of the equation just mentioned.

§ 5. Thus, while the original greenish black sulphide appeared to be RuS_6 , this is transformed by vigorous absorption of atmospheric oxygen into the reddish violet compound RuS_4O_{10} , with simultaneous splitting-off of free sulphur, according to the equation:



while the compound formed is afterwards further oxydized by the potassium permanganate according to the equation:



The red colloid is, therefore, by no means to be considered as the final oxydation-product of the greenish black sulphide, but it represents an intermediate stage on the way leading finally to *ruthenium sulphate*. This fact too could be confirmed by special reactions:

a. Strong nitric acid oxydizes the red coloured solution at low temperatures slowly, but on heating more rapidly, to a solution which appears to contain free sulphuric acid.

b. A solution of potassium permanganate makes the colour of the

colloidal solution and that of the permanganate rapidly disappear, while in the liquid SO_4 -ion becomes demonstrable.

c. Addition of H_2O_2 and some diluted acid soon makes the colour of the solution disappear, while sulphate is formed.

d. The red-violet powder obtained by evaporation from the solution, prepared by oxydation of the original green solution by the air, no longer gives a reddish violet colloidal solution, after being exposed to the air for three weeks; it gives a slightly greenish solution of acid reaction, containing a perceptible amount of SO_4 -ion.

These different reactions prove undoubtedly, that the violet RuS_4O_{10} is an intermediate product, which by further absorption of oxygen is transformed into the sulphate: $Ru(SO_4)_2$. The compound has the composition of a normal *ruthenium*salt of *pyrosulphurous acid*: $H_2S_2O_6$, and more particularly, of a *pyrosulphite* of *tetravalent ruthenium*. In this way the *pyrosulphite* appears as an intermediate product in the oxydation-process of *ruthenium-persulphide* to *ruthenium-sulphate*; most remarkable in it is, moreover, the colloidal nature of this intermediary *ruthenium-pyrosulphite*, the dispersed particles of which bear at the same time an electrostatic charge of opposite algebraic sign to those in the colloidal solution of the original *persulphide*.

Some other reactions of the colloidal *pyrosulphite* may be of interest here:

a. The colloidal solution of the salt is rapidly decolourized by strong *sulphuric acid*.

b. *Hydrochloric acid*, especially in higher concentrations and at higher temperatures, has the same effect, while sulphuric acid is formed simultaneously.

c. *Sodium hydroxide* (1 : 3) slowly decolourized the solution, but at higher temperatures even a more dilute solution does this rapidly.

d. On addition of *mercurous nitrate*, the violet colour disappears immediately; a brown turbidity appears, and, after some hours, a brownish black precipitate is formed, which is probably a sulphide of mercury.

e. *Ammonium sulphide* does not give a precipitate, but makes the colour disappear; *sulphur dioxide*, however, has no appreciable effect.

f. A solution of *silver nitrate* turns the colour slowly into a brown one, and a brownish black precipitate is gradually formed, which is soluble in ammonia.

g. On boiling the colloidal solution with *sodium carbonate*, the colour is rapidly changed into a pale green one.

h. A concentrated violet solution turns blue on addition of a dilute acid; but after neutralizing with a base, the red-violet colour is restored; etc.

SUMMARY.

In the above we were able to demonstrate, that the product of the precipitation of a salt of tetravalent *ruthenium* by *ammonium sulphide* differs with the temperature: at 100° C., brownish black RuS_2 is formed besides free sulphur, but at 0° C. greenish black RuS_6 is formed, which has the character of an irreversible colloidal substance, and which in the presence of ammonium sulphide in excess, gives a beautiful green, but unstable colloidal solution. At intermediate temperatures mixtures of both sulphides are formed besides free sulphur.

The dark green sulphide and the green colloidal solution of RuS_6 , the particles of which are negatively charged, rapidly absorbs free oxygen, and is transformed into a reddish violet solution of the reversible colloidal *ruthenium-pyrosulphite*: RuS_4O_{10} , the particles of which bear a positive electrostatic charge. This salt is, in its turn, changed by oxygen (air, nitric acid, permanganate) into *ruthenium sulphate* and free *sulphuric acid*. The properties and reactions of these different products were investigated on general lines.

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Anatomy. — “*On the Index cephalicus and the absolute Dimensions of the Head of the Population of Holland*” By Prof. L. BOLK.

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For a general anthropological characterization of a people or a race, one is generally restricted to the three following characteristics: the degree of pigmentation, the length of the body and the proportion of the greatest length of the head or skull to the greatest breadth, expressed in a proportionate number, the so-called Index cephalicus.

This is calculated according to the formula $\frac{100 \text{ breadth}}{\text{length}}$, and as the length always surpasses the breadth, the Index cephalicus will always be expressed by a number smaller than 100. When the Index cephalicus rises above 80, the head is called brachycephalic; when it falls below 75, the term dolichocephalic is applied to it. Indices between 75 and 80 are characterized as mesocephalic. The Index cephalicus — being a proportionate number — does not teach us anything about the real dimensions of the head or skull, every value of the Index may occur with larger and smaller skulls and heads.

Some time ago I communicated the result of very extensive investigations on the two first mentioned anthropological characteristics — the degree of pigmentation and the length of the body, so that I may assume a sufficient knowledge of this physical disposition of our population. Until now this was not the case with the third characteristic — the Index cephalicus — because it is not so easy to obtain data for this in sufficient number, as for the characteristics mentioned before. It is true that I previously communicated data¹⁾ on the Index cephalicus, but these were based on a comparatively small number of measurements and so they must be considered as provisional communications only.

I have gradually gathered a number of data, in my opinion sufficient, to be able to construct a reliable image of the Index cephalicus

¹⁾ De Bevolking van Nederland in hare anthropologische samenstelling, in ‘GALLÉE, Het Boerenhuis in Nederland en zijn Bewoners’, Utrecht 1909.