

**Chemistry.** — “The Photochemical Decomposition of Potassium-cobaltioxalate and its Catalysis by Neutral Salts” by Prof. F. M. JAEGER and G. BERGER.

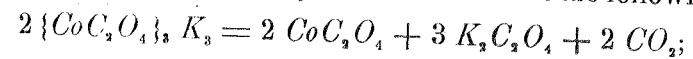
(Communicated at the meeting of May 29, 1920).

§ 1. With the intention of studying the photochemical action of dextro- and laevogyratory circularly polarized light upon both optical antipodes<sup>1)</sup> of *potassium-cobalti-oxalate*:  $K_3\{Co(C_2O_4)_3\} + 3H_2O$ , and with the purpose of proving the probable difference in speed of reaction with each component, if attacked by circularly polarized light of opposite direction, — we started a series of experiments, which were of a preliminary character as regards the specific peculiarities of the photochemical process itself.

Simultaneously we tried to find out, if it would be possible to regulate the speed of reaction by the addition of certain substances to the solution in such a way that the velocity became as favourable as possible to the purpose aimed at on starting these experiments. We give already here a review of the results obtained, which must be considered as the foundation of further investigations, because we found some remarkable facts, which in their turn might be of interest as startingpoints to some other research-work of a more general character.

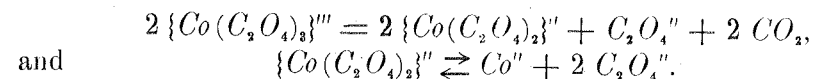
If all details are, for the moment, left aside, we can say that the photochemical decomposition of the complex *potassium-cobalti-oxalate* occurs in a way fully analogous to that observed in the case of the corresponding *ferric* salt of analogous constitution: in our case, *carbondioxide* is split off, and a pink coloured precipitate of *cobalto-oxalate*:  $CoC_2O_4$  is formed, while a gradually increasing quantity of *potassium-oxalate* goes into solution; this last salt may, for a small part, combine with some *cobalto-oxalate* formed, into a complex salt of the constitution:  $K_2\{Co(C_2O_4)_2\}$ , which, however, is almost completely dissociated in its components.

The reaction may principally be formulated in the following way:



<sup>1)</sup> F. M. JAEGER, *Recueil des Trav. des Chim. d. Pays-Bas*, **38**, 247—256, (1919); *idem*, *Lectures on the Principle of Symmetry and its Applications in All Natural Sciences*, 2nd Edit., Amsterdam, (1920), p. 216, 249, 250, 317.

or, — if the electrolytic dissociation of these salts is taken into account, perhaps better by the relations:



§ 2. The photochemical reaction mentioned was, for the first time, studied systematically in 1917 by VRÁNEK<sup>1)</sup>, under conditions of experiment very widely differing from ours. This author studied extremely dilute solutions of the salt, with concentrations ranging from 0,01 to 0,0001 mol. per Liter, and experimented always with very small volumes of the solution, — conditions made necessary by the optical method followed by him in this investigation. Nevertheless, the measurements were carried out with much care and a precision as great as possible, yet the results obtained give the impression that the reaction is in reality much more complicated than the author himself seems to believe. For, on the one hand, he thinks it probable with respect to the numbers obtained, that the reaction is a *bimolecular* one, in agreement with the ionic equation suggested above; but his absorption-measurements do not give any numbers, which might be looked upon as true reaction-“constants”, and it can be easily seen, that they do not agree really either with a *monomolecular* or with a *bimolecular* process, so that it were better to speak in this case of an accelerated bimolecular, or of a retarded monomolecular reaction. By spectrophotometric observation, he was, moreover, able to demonstrate, that the emeraldgreen solutions have two principal absorption-maxima, for  $\lambda = 4260$  A. U., and for  $\lambda = 6050$  A. U. respectively; and he stated, that the reaction goes on in darkness as well, light-radiation therefore chiefly acting as an accelerator. The temperature-coefficient of the dark reaction appeared to be rather great (4,56), but that of the photocatalysis, on the contrary, very small; finally an appreciable BECQUEREL-effect through the total volume of liquid is manifested, as soon as it is exposed to the light, which fact could be demonstrated by means of measurements of the electromotive force produced in mixed solutions of *cobalto-* and *cobalti-*salt with respect to a normal *calomel*-electrode, if the solutions are brought from the dark into the neighbourhood of a source of light. VRÁNEK could state as disturbing factors: 1. the slight solubility of the *cobalto-oxalate* formed in the solution of *potassium-oxalate*; 2. the retarding action exerted on the photocatalytic process by the *potassium-oxalate* formed in the reaction, — which influence, however,

<sup>1)</sup> J. VRÁNEK, *Zeits. f. Elektrochem.*, **23**, 336, (1917).

appeared to diminish gradually with increasing concentration of the catalyst; and 3. the tendency of *cobalto-oxalate* to form supersaturated solutions<sup>1)</sup>, instead of precipitating normally. Finally there is again a disturbing effect, because of the subsequent photochemical decomposition of the *oxalate*-ion and its transformation into a *formate*-ion, which reaction, as BERTHELOT and GAUDECHON<sup>2)</sup> had already demonstrated formerly, occurs chiefly under the influence of rays of *small* wave-lengths. All the different effects mentioned manifest their special influence in a more or less sensible degree, and they prove sufficiently, how very complicated indeed the whole mechanism of the process is.

The author could, however, not find a catalysing action by addition of acids, such as hydrochloric or sulphuric, under the conditions of his experiments<sup>3)</sup>.

§ 3. In contrast to those of VRÁNEK, our experiments were executed with much more concentrated solutions of the complex salt, while, after many trials, finally the direct gravimetric determination of the *cobalto-oxalate* generated was adopted as method of analysis; the cobalto-salt was determined as metallic *cobalt*, after reduction in a current of dry hydrogen. Even in the case of very concentrated solutions, the error resulting from the solubility of the precipitate in the solution containing *potassium-oxalate*, appeared to be small enough to neglect it in comparison with the other incertitudes of the experiment: in the most unfavourable circumstances the deviations caused by this factor did not surpass 1,5 %.

The dark green liquid was kept in a vessel of transparent quartz, surrounded by a quartz-mantle of greater diameter; in the space between the cylinders a current of water was continually passed, which was kept at an almost constant temperature by means of a metallic spiral-tube, placed in a thermostat; the temperature varied in our experiments between 21° and 23° C. As source of light a quartz-lamp (HERAËUS) was used, which was placed always at exactly the same distance (140 m.m.), and which sent its rays into the solution not before its current had reached a constant and always identical intensity, and also its radiating power had become constant. All the conditions of the experiments were, for the rest, in all cases as constant as possible; e.g. the volume of the solution was always the same, namely 50 ccm. Because also the

<sup>1)</sup> ST. DEAKIN, M. SCOTT and B. D. STEELE, Zeits. f. phys. Chemie, **69**, 126, (1909).

<sup>2)</sup> D. BERTHELOT and H. GAUDECHON, Compt. rend. de l'Acad. d. Sc., Paris **152**, 162, (1911).

<sup>3)</sup> J. VRÁNEK, loco cit., p. 350.

crystallised complex salt is decomposed very slowly, when preserved in darkness, the preparation used in our first experiments contained a very small quantity of the *cobalto*-salt; so that, after its quantity had been determined accurately, the necessary, and only very small correction of the results made necessary by it, was applied in the first series of measurements. The degree of accuracy of the method of analysis was tested beforehand by experiments with mixed solutions of known composition, and it was found really sufficiently great. The solutions were continually stirred by means of a current of *nitrogen*, regulated at about four bubbles every second; later-on stirring was brought about by a current of *carbon dioxide*, after it was found, that the reaction was not influenced by it in any respect. It is necessary to perform the analysis of the solutions in darkness, and to filter the precipitate as rapidly as possible, to wash it immediately, and to carry out all necessary manipulations in rapid succession. As long as the mother-liquor is adhering to the precipitate, all access of light must be carefully prevented, as well as all considerable increase of temperature.

In a first series of determinations, we thus obtained the following data:

Temperature in °C.:	Time of Exposure in minutes:	Corr. Weight of the Cobalti-Salt in 50 ccm.:	Corr. Weight of metallic Co. found:	Percentage of the Salt decomposed:
22°3	60'	0.7247 Gr.	0.0634 Gr.	73.34 %
22.2	60	0.9709	0.0665	51.41
22.2	60	1.2124	0.0695	48.05
22.5	60	1.4655	0.9694	39.70
21.7	60	1.7021	0.0686	33.78
21.9	60	1.9434	0.0699	30.16

Taking into account the unavoidable uncertainties, which always remain in the study of so highly complicated a reaction as this, and attributing only a moderate value to the small increase which the first four numbers apparently show with respect to each other, — it must be evident from these results, that the quantities of the salt decomposed within identical intervals of time are approximately independent of the initial concentration, and chiefly determined by the amount of light-energy absorbed during that time. The reaction-order is evidently zero, — a fact which may be used as an argument on behalf of the view, that the process is of a purely photocatalytic

character. It might be expected that also a true proportionality would exist between the time of exposure and the amount of decomposed substance, if the initial concentrations were the same in all cases. However, experience only partially confirms this conclusion; at least we found, for instance, the following data in a series of experiments:

Temperature in °C.:	Time of Exposure in minutes:	Corr. Weight of the Cobalti-Salt in 50 ccm.:	Corr. Weight of the metallic Co. found:	Percentage of the Salt decomposed:
23.2	30'	0.0803 Gr.	0.0310 Gr.	26.4 %
23.9	45	0.9017	0.0357	33.2
23.5	60	0.9902	0.0511	44.7

This divergence becomes somewhat intelligible if we remember that the medium is continually changing chemically and physically during the reaction; therefore, because it changes gradually as well in absorptive power as in concentration of the *cobalti-salt* or *potassium-oxalate*, the action of the light in 60 minutes e.g., can *not* be equivalent to twice the action in 30 minutes, etc. On the contrary, there is rather a cause for astonishment at the fact that the results of the first series of experiments were really so regular, while the initial concentrations in these experiments differed so appreciably from each other, and thus the same was true for the absorptive power of the solutions used. It may be, that the slight increase of the first four numbers mentioned above, finds its explanation also in this particular circumstance.

§ 4. Afterwards the experiments described above were again repeated, and now a specially purified salt, free from all *cobalto-oxalate* was made use of. It was freshly prepared and immediately used in the experiments, in which a lamp of somewhat smaller intensity was applied as source of light. For the numbers obtained, see the table on the following page.

From these measurements it appears that the speed of reaction is relatively greater with the smaller, than it is with the greater concentrations; that also in the most favourable circumstances disturbing influences seem to play a rôle, which have as a consequence some uncertainties of the analysis; and that, at least with respect to the last four numbers, the total decomposition may be supposed as *independent* of the original concentration. It must be remarked, that

Temperature in °C.:	Time of Exposure in minutes:	Weight of the Cobalti-Salt in 50 ccm.:	Weight of metallic Co. found:	Percentage of the Salt decomposed:
22° ± 1°	60'	0.750	0.0567	62.2 %
id.	60	1.000	0.0546	45.8
id.	60	1.250	0.0411	27.5
id.	60	1.500	0.0475	26.5
id.	60	1.750	0.0429	20.5
id.	60	2.000	0.0465	19.5

the mean decomposition in 60 minutes (ca. 0.0445 Gr. *Co*) is here only about  $\frac{2}{3}$  of that formerly observed, — which may be chiefly caused by the fact, that the intensity of radiation of the *quartz-lamp* was a smaller one than formerly, and by a somewhat modified form of the vessels employed. All these measurements have, therefore, not an absolute, but merely a *relative* significance.

§ 5. Results mutually agreeing much better, however, were obtained in the study of the influence, which the addition of certain electrolytes to the solution has upon the photocatalysis under consideration. For it had soon become evident by preliminary experiments, that, — in contrast to VRÁNEK'S negative results of the addition of acids, — a remarkably strong influence on the speed of reaction could be observed, if neutral salts were added to the concentrated solutions of the *cobalti-salt* used by us. An addition of *alcohol* had, however, no appreciable effect; but solutions of neutral salts, if added to the photosensitive solution, have immediately a very distinct influence, when the salts of strong bases and acids are used for this purpose.

Such a catalytic influence of salt-solutions on photochemical reactions has, indeed, been found already by some other authors, e.g. by JORISSEN and REICHER<sup>1)</sup> in the case of the photochemical oxydation of solutions of *oxalic acid* by free oxygen, and by ROLOFF<sup>2)</sup> in the case of EDER'S solution: the last mentioned investigator found even one case which seems to be of the same type as those described here.

Subsequently the influence was studied by us, which resulted from the addition of varying quantities of *potassium*, *sodium*, and *lithium chlorides*; in a second series of determinations the analogous influence

<sup>1)</sup> W. P. JORISSEN and L. TH. REICHER, Zeits. f. phys. Chemie, **31**, 142, (1899).

<sup>2)</sup> M. ROLOFF, Zeits. f. phys. Chemie, **13**, 327, (1894).

of magnesium, beryllium, and ferric chlorides was investigated. The choice of such salts is limited by the condition, that only salts of such cations can be used, whose oxalates are easily soluble. For in the case of only slight solubility of those oxalates, a part of the cation added would gradually be removed from the solution by precipitation with the potassium oxalate set free during the reaction. However, these investigations may be extended eventually by the use of ammonium, rubidium, and caesium salts, while, on the other hand, a wide variation of all kinds of anions will be possible here.

In all experiments the same volume of solution (50 ccm) was used, containing 0,0607 grammol. of the (anhydrous) complex salt per Liter. Moreover, the whole experimental arrangement was in all cases accurately the same, while the time of exposure was always

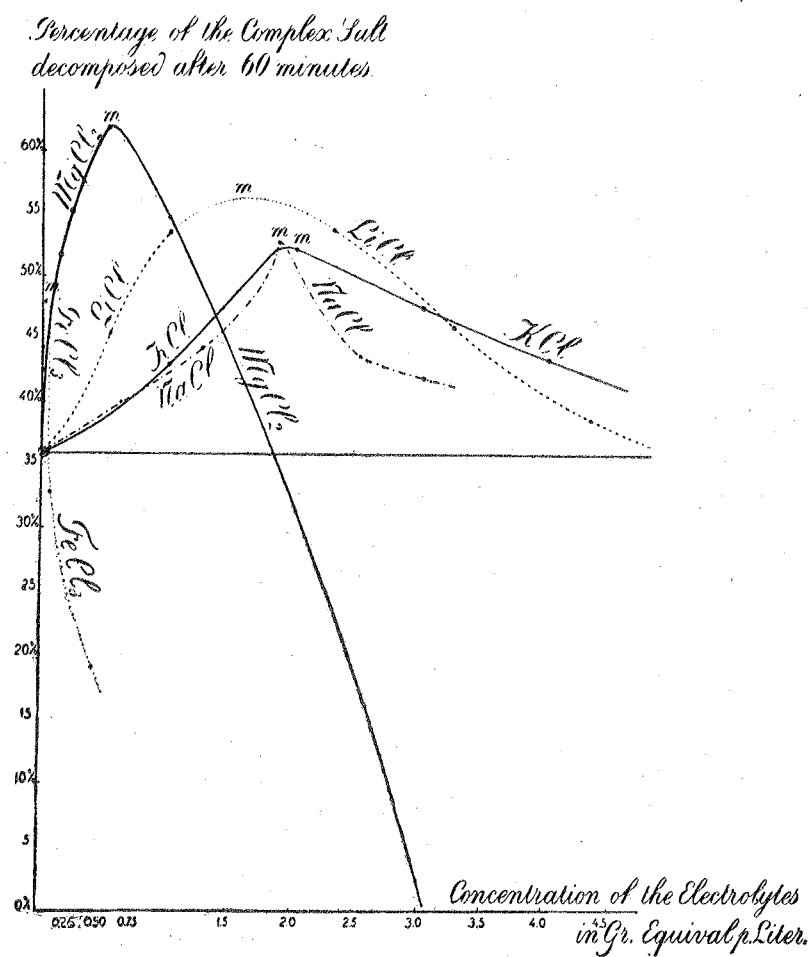


Fig. 1.

I. 50 ccm. of a 0,0607 mol. solution of  $K_3 \{Co(C_2O_4)_3\}$ ; KCl as catalyst; time of exposure = 60 minutes; temperature =  $21^\circ \pm 1^\circ C$ .

Weight of KCl in Grams in 50 ccm.:	Concentration of KCl in Equiv. per Liter:	Weight of Co found:	Weight of Salt decomposed in Gr.:	Percentage of Salt decomposed:
0	0	0.0648 Gr.	0.4833 Gr.	36.17 %
1.864	0.50	0.0696	0.5196	38.89
3.728	1.00	0.0771	0.5756	43.08
7.456	2.00	0.0935	0.6981	52.24
11.184	3.00	0.0856	0.6391	47.83
14.912	4.00	0.0781	0.5832	43.64

II. Conditions the same as before; NaCl as catalyst:

0	0	0.0648	0.4833	36.17 %
1.829	0.626	0.0715	0.5338	39.95
3.658	1.252	0.0792	0.5913	44.25
5.487	1.878	0.0946	0.7063	52.85
7.316	2.504	0.0783	0.5846	43.75
9.145	3.128	0.0752	0.5614	42.02

III. Conditions the same as before; LiCl as catalyst.

0	0	0.0648	0.4833	36.17 %
1.153	0.543	0.0816	0.6092	45.59
2.306	1.086	0.0962	0.7182	53.75
6.918	3.258	0.0827	0.6174	46.21
9.224	4.344	0.0685	0.5114	38.27
11.530		0.0609	0.4547	34.03

IV. Conditions the same as before;  $MgCl_2$  as catalyst.

0	0	0.0648	0.4833	36.17 %
0.299	0.125	0.0930	0.6943	51.96
0.599	0.251	0.0988	0.7376	55.20
1.198	0.503	0.1113	0.8310	62.19
2.396	1.006	0.0983	0.7339	54.92
4.792	2.012	0.0567	0.4233	31.68
7.188	3.018	0.0041	0.0306	2.29

60 minutes. The temperature was  $21^{\circ} \pm 1^{\circ}$  C.; the concentrations of the solutions of salts used were consecutively varied from 0,1 normal to full saturation. The complex salt used was carefully purified and did not contain any appreciable amount of *cobalto-oxalate*; moreover, the solutions were stirred by the aid of a current of *carbondioxide*, after it had been demonstrated, that this gas had no influence upon the speed of reaction.

Above we have given a review of the results obtained, while in fig. 1 these data are reproduced in graphs, in which the equivalent-concentrations of the electrolytes added are used as abscissae, while the percentages of the original salt transformed, are taken as ordinates in it.

The determinations with  $BeCl_2$  and  $Fe_2Cl_6$  are somewhat less accurate, as a consequence of secondary influences, as e.g. the strong hydrolysis of the *beryllium*salt, and perhaps the formation of complex compounds in the case of the *ferric* salt; by these factors the image may be somewhat less definite. The data obtained in these cases follow here :

V. Conditions the same as before; $BeCl_2$ as catalyst.				
Weight of $BeCl_2$ in Grams in 50 ccm.:	Concentration of $BeCl_2$ in Equiv. p. Liter:	Weight of Co found:	Weight of Salt decomposed in Gr.:	Percentage of Salt decomposed:
0	0	0.0648	0.4833	36.17 %
0.009	0.004	0.0383	0.2859	21.40
0.023	0.011	0.0536	0.4002	29.95
0.045	0.023	0.0511	0.3815	28.55
0.090	0.045	0.0404	0.3016	22.57
0.180	0.090	0.0332	0.2479	18.55
VI. Conditions the same as before; $Fe_2Cl_6$ as catalyst.				
0	0	0.0648	0.4833	36.17 %
0.035	0.013	0.0614	0.4584	34.31
0.087	0.032	0.0798	0.5958	44.59
0.119	0.045	0.0859	0.6413	48.10
0.174	0.065	0.0585	0.4368	32.69
1.044	0.390	0.0348	0.2576	19.28

§ 6. In these series of observations evidently we cannot speak of real reaction-constants: the data available do agree neither with the supposition of a monomolecular, nor of a bimolecular reaction-form.

But all curves of Fig. 1 manifest a clear and obvious *analogy* of shape: they rise evidently all to a steeper or flatter *maximum*, and then decline more or less rapidly. The addition of all these electrolytes thus involves an *acceleration* of the photochemical reaction in the case of smaller concentrations of them, *which, however, reaches a maximum at a certain concentration, characteristic of each salt, and which subsequently again diminishes*. In some cases this diminution may even change into a *retardation* of the process<sup>1)</sup> at concentrations, which are not even so very high; and finally in the case of  $MgCl_2$ , for instance, the reaction may be stopped even completely by it!

Another very remarkable fact is, *that the maxima are situated at smaller concentrations, as the valency of the cation, i.e. its electrostatic charge, is greater*: for the bivalent  $Mg$ -ion this maximum approaches much nearer to the ordinate-axis, than for the monovalent ions of the *alkali*-metals, while the maximum of the curve of the trivalent  $Fe$ -ion is situated in the immediate vicinity of the Y-axis. The *nearer* these maxima approach the ordinate-axis, the more *steeply* the curves will appear to decline after passing the maximum. However, not only the electric charges of the ions, but also their *specific* properties appear to play a part in this: thus, for instance, the three maxima of the curves of the *alkali*-metals do *not* coincide, although their charges are the same; but they approach the Y-axis the more closely, the smaller is the atomic weight of these elements. The respective concentrations of the solutions of these three electrolytes, at which the maxima are reached, are, if graphically interpolated, — for  $LiCl$ ,  $NaCl$ , and  $KCl$  respectively: 1,65 N. equiv., 1,88 N. equiv., and 1,96 N. equiv.; these concentrations may e.g. be considered as approximatively proportional (1 : 1,14 : 1,18) to the logarithms of the ionic velocities at  $18^{\circ}$  C. of the three kinds of ions, being here about: 1 : 1,06 : 1,17. Of course, we emphasize, that no especial significance should be attributed to such relations as suggested here, because the number of data is yet too small, and their accuracy not sufficiently great. But attention may be drawn to the fact only that the *specific* properties of the ions play also a rôle in this, and

<sup>1)</sup> It may be remarked here, that JORISSEN and REICHER (loco cit.), as well as ROLOFF, found instances of *positive* and *negative* photocatalysis under the influence of neutral salts, however, without making a general supposition about the possible shape of the respective curves. In ROLOFF's paper one case is mentioned, which is in full agreement with the data obtained by us, namely, where he used  $KNO_3$  as a catalyst, and found a maximum of its action at a certain concentration.

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 <sup>1)</sup>, GHOSH <sup>2)</sup>, NOYES <sup>3)</sup>, 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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Groningen, May 1920.

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

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

<sup>3)</sup> 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* <sup>1)</sup>, be it to the *sulphate*:  $Ru(SO_4)_2$ , or to a complex salt <sup>2)</sup> 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.

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

<sup>2)</sup> A. WERNER, Ber. d.d. chem. Ges., **40**, 2621, (1907).