

*Citation:*

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**Chemistry.** — "*The solubilities of the isomeric chromic chlorides*".

By Prof. H. W. BAKHUIS ROOZEBOOM and J. OLIE JR.

(Communicated in the meeting of May 27, 1905).

At the December meeting 1903, a communication was made by BAKHUIS ROOZEBOOM and ATEN as to the changes in form which may occur in the solubility-lines of binary mixtures in dependence on the quantities of the molecules of a compound which may be formed from the components in the liquid mixtures. This subject is only a part of a more extensive problem embracing the equilibria of phases in systems composed of three kinds of bodies between which a transformation is possible in liquid (or vapour). If that transformation takes place with greater velocity than the setting in of the equilibria of phases, the system will appear externally as a binary one, although it is in reality ternary, and in order to explain the course of the equilibria of phases we must take into account that ternary nature.

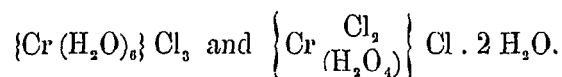
In those cases where the third kind of molecules consists of a combination of the two others no instance has, as yet, been noticed where a correct view could be formed with certainty as to the inner composition of the liquid phase.

We, however, came across an example where this is quite possible, namely in a case where two isomeric substances may be converted into each other by dissolving in a third substance. Similar cases may frequently occur with all kinds of organic isomers; but apart from the fact that their behaviour has been little investigated from the point of view of the equilibria of phases we often lack the means to determine the two kinds in solution. That possibility, however, presented itself with the isomeric chromic chlorides, which not only may be determined in each others' presence, but also require when in solution much more time to reach an equilibrium than is necessary to reach the equilibrium between solid matter and solution. This rendered it also possible to study the change of the solubility as a function of the progressive transformation in the solution. Finally, this research could also serve to elucidate the cause of the stability or instability of the isomers, and the most rational method of preparing the same from the solution.

It has long been known that all kinds of salts of trivalent chromium when in solution undergo molecular transformations depending on temperature and concentration which are shown by the change in colour of the solutions, which may vary from green to violet. Only of late this matter has been better understood when various

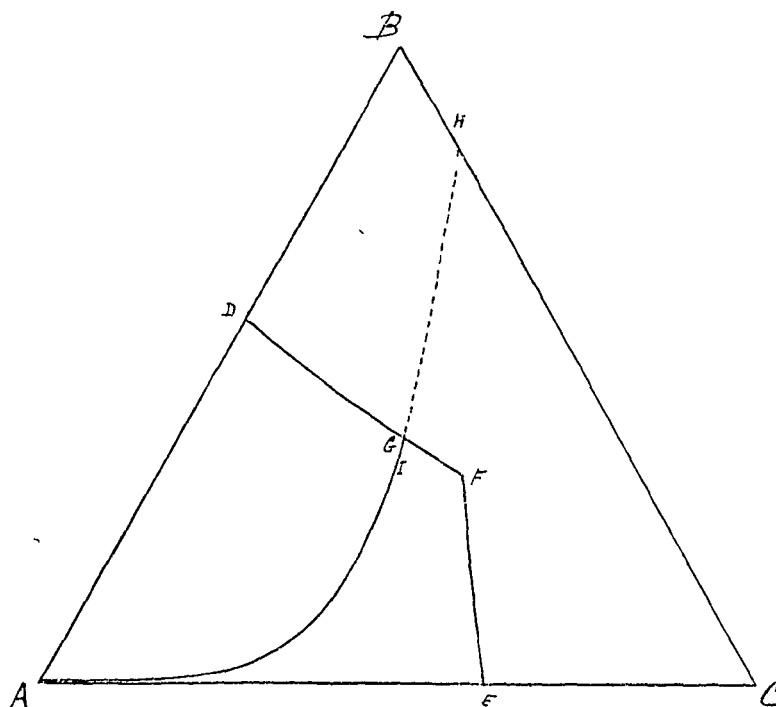
modifications of the same salt were successfully isolated in a solid condition.

In the case of chromic chloride two compounds were found to exist at the ordinary temperature with 6 H<sub>2</sub>O. In connection with his theory on complex compounds, WERNER proposed the following structural formulae:



The first salt is violet, the second one green. In the first salt the three chlorine atoms should be capable of ionisation; in the latter only one. If only these are precipitable by silver solutions<sup>1)</sup> the amount of each salt in a mixed solution may thus be quantitatively determined.

First of all measurements were made at 25° as to the velocity of the transformation of solutions with different contents of chromic chloride and as to the final condition which they attain.



The result of these last investigations is indicated in the Figure by the line AGH.

In this figure A stands for the solvent H<sub>2</sub>O, B for the green

<sup>1)</sup> We found this not to be absolutely correct but the precipitable chlorine could in any case be used as a measure for the two salts.

and  $C$  for the violet chromic chloride. Both are taken in the calculation as hydrates with  $6\text{H}_2\text{O}$  so that the sum of  $\text{H}_2\text{O}$  and the two hydrates is always taken as 100 (percentage by weight).

The line  $AGH$  first runs close to the axis  $AC$ . This means that in weak solutions a final condition is reached in which the chromic chloride occurs nearly exclusively in the violet modification.

Strictly speaking this means in the condition in which the violet chromic chloride finds itself the moment it has dissolved. Briefly, we will call this the violet condition. If, therefore, we make a solution of the green chloride of the same concentration the green chloride will be almost completely changed into the violet salt. This process proceeds slowly enough to admit of its course being studied, also to show that both green and violet lead to the same final condition.

If the amount of hydrated chromic chloride exceeds 20 % the line  $AI G$  begins to run perceptibly upwards and consequently the final condition in the solution shifts more and more towards green.

In the point  $I$  the final equilibrium is situated near an equal amount of green and violet. This corresponds with a total of 65 % of chloride<sup>1)</sup> of which 32.5 % is green and 32.5 % violet.

It will be noticed that we cannot go further than  $G$  because the solution there reaches its saturation. If crystallisation did not take place the prolongation of the line  $AI G$  could be determined. If this may be represented by  $GH$ , the terminal point  $H$  would indicate the amount of green and of violet chloride in liquid hydrate of chromic chloride (without excess of water); this point would therefore lie at about 15 % violet and 85 % green. Its determination is however impossible as the green hydrate melts at  $83^\circ$  and the violet one at  $92^\circ$ . Although the melted hydrates crystallise very slowly still it is difficult to keep them liquid down to  $25^\circ$ .

The final condition of solutions of different concentrations thus being known, the solubility of the two-hydrates at  $25^\circ$  was studied. The saturation was very soon accomplished,  $D$  and  $E$  represent the concentrations of freshly prepared saturated solutions of green and violet chloride.

These, however, soon undergo a modification. In the green solution violet chloride is formed and conversely. This causes a change in the solubility which runs along the lines  $DF$  and  $EF$  respectively. These show that the total solubility of both green and violet increases as the transformation of green into violet or the reverse proceeds in the solution.

<sup>1)</sup> This total amount may be read off on  $AC$  or  $AB$  if we draw from  $I$  a line parallel with  $BC$ .

The solutions of the green chloride do not however run further than  $G$ , where the solution saturated with green also attains the inner composition corresponding with the equilibrium at the total concentration. Solutions on  $GF$  could only be made by rapidly dissolving a mixture of green and violet in the desired proportion and then introducing some solid green chloride. These solutions would then, however, recede towards  $G$  as the point of final equilibrium of the liquid saturated with green chloride.

The solutions saturated with violet chlorid run along the line  $EF$ . The solution  $F$  might be at the same time in equilibrium with green chloride, but as soon as this occurred the violet would be completely converted into the green and then the solution containing the green would again shift to  $G$  as a terminal point.

As the line of equilibrium  $AGH$  intersects the solubility line for the green but not that for the violet chlorid, the latter cannot be definitely in equilibrium at  $25^\circ$  with any solution, consequently at this temperature the green chloride is the only stable one. Even outside the solution the violet changes, therefore, after a lapse of time, into the green; in contact with the solution this takes place more rapidly. This is the reason why the line  $EF$  cannot always be followed up.

The question now arises how it is possible to separate violet chloride in the solid condition. This is done by leading gaseous  $HCl$  into solutions containing at most 30% of green chloride and which have been recently heated to  $100^\circ$ .

Addition of  $HCl$  at  $25^\circ$  diminishes in a high degree the solubility of both chlorides.

The two lines  $DF$  and  $EF$  are shifted towards the left about parallel to their original positions and about to the same extent. It will be easily seen that the point of intersection  $G$  will also move towards the left and might finally arrive in the liquid region to the left of the equilibrium line. In that case this line would no longer intersect  $DF$  but  $EF$ ; a saturated solution of violet chloride would then be in inner equilibrium and the violet chloride could be separated in a stable condition.

This, however, is not the case, because the line  $AG$  also moves strongly towards the left on addition of  $HCl$  and consequently the equilibrium in the solution shifts towards the green side. The investigation showed that the violet chloride is still metastable in contact with the solutions rich in  $HCl$ ; the point of intersection  $F$  therefore remains, obviously, to the right of  $AG$  even on addition of  $HCl$ .

If, however, we heat to  $100^\circ$  before leading  $HCl$ , the line  $AG$  moves very considerably towards the violet side so that it now

intersects the solubility isotherm of the violet chloride at 25°. The receding of the solutions towards the green, on cooling, now proceeds with sufficient slowness to enable us to precipitate the violet chloride at 25° by means of a current of HCl, which diminishes its solubility.

**Chemistry.** — "*Nitration of symmetric nitrometaxylene.*" By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 27, 1905).

If symmetric dinitrophenol or symmetric dinitromethylaniline is treated with mixed nitric and sulphuric acids, pentanitrophenol or pentanitrophenyl-methylnitramine is formed <sup>1)</sup>. Consequently the presence of the two nitro-groups, which are in the *meta*-position with regard to the OH or NHCH<sub>3</sub> group does not prevent the introduction of another three nitro-groups in the *para*-position and *ortho*-positions in the benzene core. Symmetric dinitroanisole and phenetol yield, however, on nitration tetranitroanisole or tetranitrophenetol <sup>2)</sup>; the hydrogen atom in the *para*-position with regard to the oxyalkyl group is not replaced by NO<sub>2</sub> here. As the methyl group on substitution in the benzene core behaves in some respects analogous to the OH and NH<sub>2</sub> (or NH CH<sub>3</sub>) groups it seemed of importance to investigate the conduct of symmetric dinitrotoluene on nitration in order to ascertain what influence is exercised here by the NO<sub>2</sub>-groups in the *meta* position.

The symmetric dinitrotoluene was, therefore, heated with mixed nitric and sulphuric acid for two hours on the waterbath; the substance had not, however, undergone any change. The presence of the nitro-groups in the *meta*-position with regard to the CH<sub>3</sub> group consequently prevents the further introduction of nitro-groups in the positions 2, 4 and 6. If, however, one of the NO<sub>2</sub>-groups in symmetric dinitrotoluene is replaced by bromine, this substance may be successfully nitrated. Symmetric bromonitrotoluene yields on treatment with mixed nitric and sulphuric acids three isomeric trinitrobromotoluenes which it is, however, difficult to isolate.

The question now arose what result is obtained when one of the NO<sub>2</sub>-groups of symmetric dinitrotoluene is replaced by CH<sub>3</sub>, in other words what is the behaviour of symmetric nitro-*m*-xylene on nitration? For it is known that *m*-xylene readily yields 2-4-6-trinitro-

<sup>1)</sup> Recueil **21**, 254.

<sup>2)</sup> " **23**, 111; **24**, 40.