

## On the Light Absorption of Polychromates

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### *Introduction.*

The composition of chromate solutions was established by Jander and his coworkers (1). They have shown that the condensation reactions leading to the formation of oxygen bridges lead to characteristic changes in the absorption spectra. The greater the molecular weight of the resulting aggregates the flatter and smoother are the absorption curves and the beginning of the light absorption is shifted the more towards longer wave lengths. Characteristic extinction curves could be correlated with all different states of aggregation indicated by diffusion (1b). Biró (2) has measured the light absorption of polychromate solutions to elucidate the mechanism of light absorption.

The experimental methods and apparatus were earlier described (3). All the preparations used of analytical purity, and if necessary purified by further recrystallisation. The solutions were carefully filtered through Jena glass filters and their concentrations analytically controlled. All solutions were prepared with spectroscopically pure water distilled from Jena glass apparatus.

### *The extinction curves.*

In order to obtain comparable data, we have evaluated all the extinction curves with the same precision. The extinction curve of a 0,001 m  $K_2CrO_4$  solution in 0,01 m KOH (Fig. 1, Curv. 1 = 1/1) was used as reference (4). This curve is reproduced in all figures with dotted line.

0,001 m  $K_2CrO_4$  in 0,01 m KOH has two bands at 370 and 270  $m\mu$ , a rising absorption at 210  $m\mu$  and another maximum at 420  $m\mu$  (1/1). The band at the longer wave length shows a variation with the concentration (5). In 2,52 m solution the steeply descending absorption is shifted towards longer wave length 1/1a).

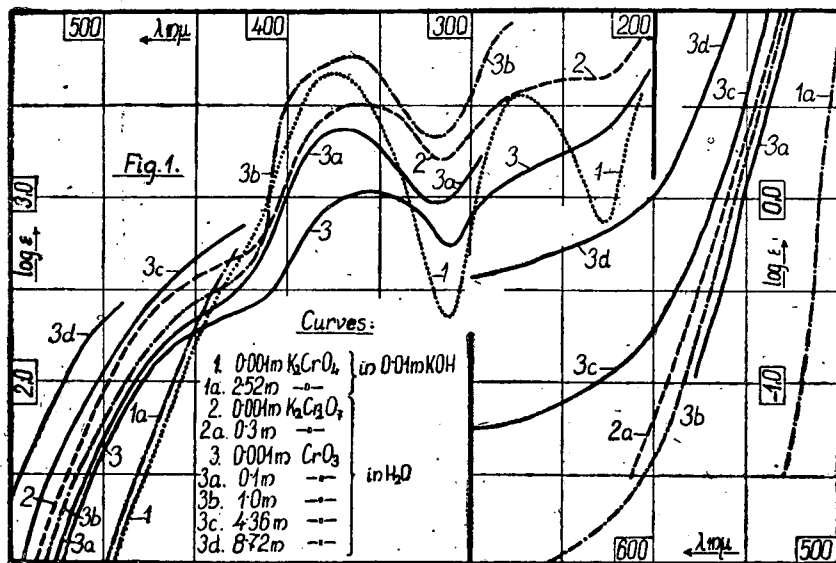
0,001 m  $K_2Cr_2O_7$  in water has one sharp and one less sharp band at 350 and 260  $m\mu$  respectively, a faint band at 440  $m\mu$ , furthermore a rising absorption at 210  $m\mu$  (2). This curve is changed with changing concentration (1/2a).

0,001 m  $CrO_3$  in water has an extinction curve (1/3) structure similar to that of a  $K_2Cr_2O_7$  solution, though it is lower (6a). The extinction curves of  $CrO_3$  solutions are strongly influenced by the concentration (1/3a-3d). With increasing concentration the extinction rises in the region of the first and second bands (1/3a-3b) of the reference curve (1/1). In concentrated (8,72 m) solutions a flat minimum is observed at 700  $m\mu$  (1/3d).

The maxima and minima of the reference curve (2/1) are smoothed in the presence of increasing  $HClO_4$  concentration (2/2-9). The second band disappears nearly completely already in presence of 0,01 m  $HClO_4$  and the first is shifted toward shorter wave lengths (2/4). The descending limb of the first band reaches into longer wave lengths and

a new flat band appears around  $430 \text{ m}\mu$  (2/4). In 0,1, 1,0, 3,0 and 5,0 m  $\text{HClO}_4$  the two bands of the reference curve (2/1) is shifted toward longer wave lengths (2/5-8). In 7,0 m  $\text{HClO}_4$  we obtain an almost structureless curve (2/9) with little intensity. The curves measured in different concentrated  $\text{HClO}_4$  have only in smaller concentration regions constant section points.

The changes produced by  $\text{HCl}$  in the reference curve 3/1) are similar 3/2-7). The reference curve (3/1) and the curves measured in different concentrated  $\text{HCl}$  (3/2-7) have only in smaller concentration regions constant section points. In concentrated  $\text{HCl}$  solutions the  $\text{Cl}_2$  formation troubles the extinction measurements.



Increasing concentration of  $\text{H}_2\text{SO}_4$  has a similar effect (4/2-6). Beginning from 12 m  $\text{H}_2\text{SO}_4$  the extinction increases slowly and the curves are almost structureless (5/4-7). The curves at corresponding  $\text{HClO}_4$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  concentrations are not identical. The common points of the curves at different  $\text{H}_2\text{SO}_4$  concentrations are not so constant as those at the presence of the other acids. The curve obtained in presence of concentrated  $\text{H}_2\text{SO}_4$  (5/7) shows a general rise towards the longer wave lengths and has flat bands at  $440, 390, 320$  and  $280 \text{ m}\mu$ .  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrO}_3$  have similar curves in concentrated  $\text{H}_2\text{SO}_4$ .

Due to the strong absorption of the nitrate ion it was not possible to evaluate the effect of nitric acid below  $350 \text{ m}\mu$  (6/2-7). The remaining less characteristic part of the curve shows the changes on the concentration of  $\text{HNO}_3$  as in the cases formerly discussed. This is the reason why the data of Jander and Spandau (1b) had to be complemented.

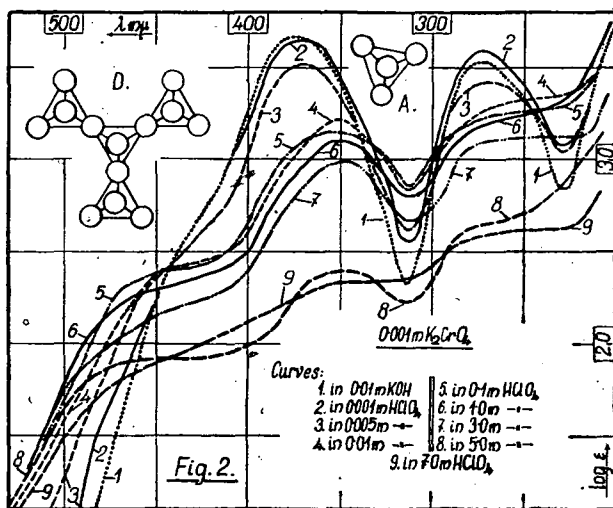
In the case of  $\text{K}_2\text{CrO}_7$  and  $\text{CrO}_3$  we obtained similar effects as in the case of  $\text{K}_2\text{CrO}_4$ .

#### *The constitution of chromate solutions.*

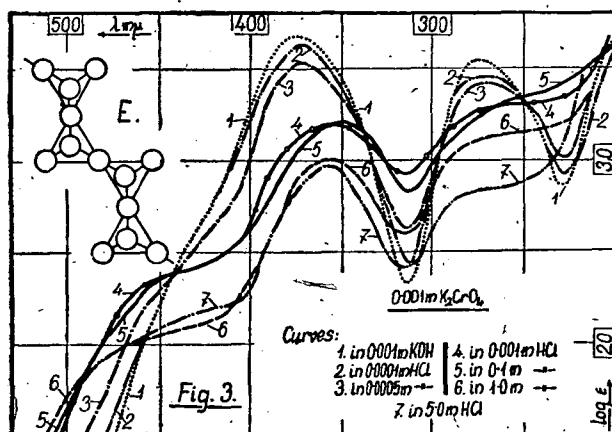
Alkaline chromate solutions contain mostly the  $\text{CrO}_4^{2-}$  ion. This is supported by the weak effect of concentration on the extinction curves

(1/1 and 1a). It is not possible to explain the failure of complying with Beer's law with the assumption of the formation of higher complexes (5).

Neutral chromate solutions contain, depending on the concentration, furthermore the ions:  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCr}_2\text{O}_7^-$  (6), and this is supported by the concentration dependence of the extinction curves.



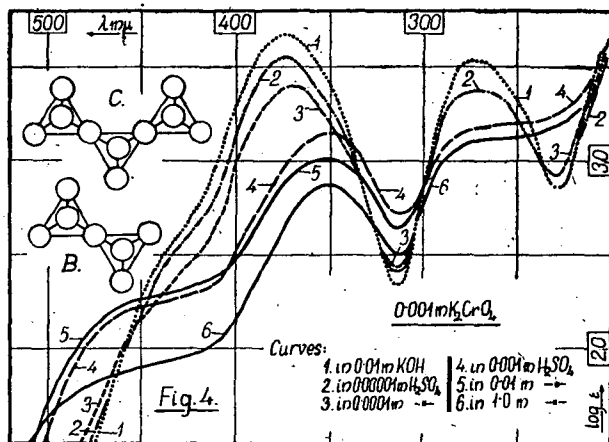
$\text{K}_2\text{Cr}_2\text{O}_7$  solutions have mostly the ion:  $\text{Cr}_2\text{O}_7^{2-}$ . At lower concentration the ions  $\text{HCr}_2\text{O}_7^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  are also present (7). Dichromate solutions show strong deviations from Beer's law (6), as the ions higher complexes. The distribution of charge and thus the extinction are thereby vastly influenced.



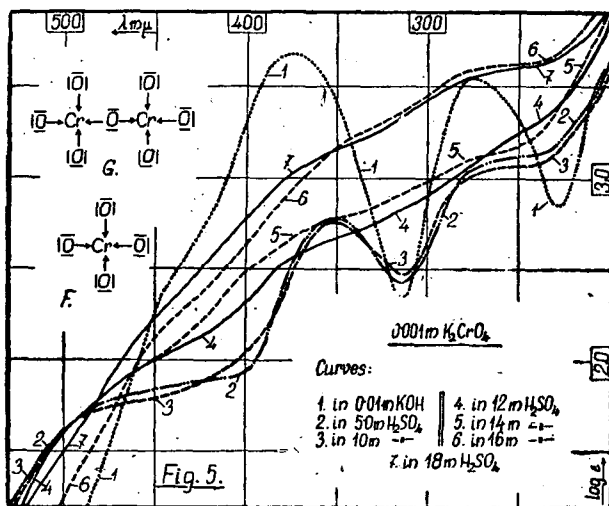
In the solution of  $\text{CrO}_3$  in water, the ion  $\text{CrO}_7^{2-}$  is dominating (8). However, other ions, like  $\text{HCr}_2\text{O}_7^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  have to be taken account. In more concentrated solutions of  $\text{CrO}_3$  higher polymers are formed.

Normal chromates crystallise from alkaline acid neutral solutions, bichromates from acetic acid solutions and tri- and tetrachromates from more acid solutions (a).

According to the results of diffusion experiments (1) the  $\text{CrO}_4^{2-}$  ion (diffusions coefficient  $D_{10} = 0.57$ ) is present in alkaline solutions. In the solutions containing 0.01–4.0 m  $\text{HNO}_3$  the  $\text{Cr}_2\text{O}_7^{2-}$  ion exists, it has a diff. coeff. of  $D^{10} = 0.635$ . The  $\text{Cr}_3\text{O}_{10}^{2-}$  ion is observed in 5.0–10.0 m  $\text{HNO}_3$  solutions, it has a diff. coeff.  $D_{10} = 0.58$ –0.59. The chromate ion being much smaller than the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Cr}_3\text{O}_{10}^{2-}$  ions, it is supposed, that it has to be hydrated with 12 molecules of water, and for similar reason the molecule of  $\text{Cr}_2\text{O}_7^{2-}$  should contain 3 molecules of water. Thus, the degree of hydration is diminishing with increasing aggregation.

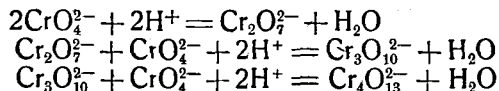


As the diff. coeff. is rather constant in the above mentioned intervals of hydrogen ion concentration, either one of the ions is always preponderantly present at the corresponding hydrogen ion concentration. The change from one type of ion to the other occurs in a sharp interval.



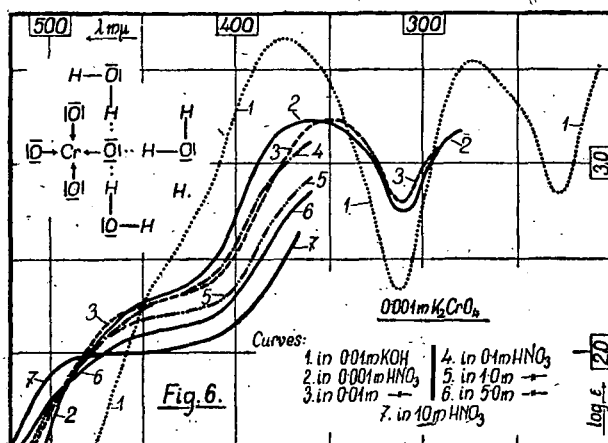
According to its Raman spectrum, the  $\text{CrO}_4^{2-}$  ion has a tetrahedral configuration. Polychromates form chains similar to the aliphatic hyd-

rocarbons. It follows from the condensations reactions with elimination of water :



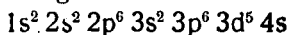
that the neighbouring tetrahedra joined through their corners (2/D, 3/E, 4/B and C). Condensation and chemical hydration are facilitated by the lone electron pairs of the oxygen atoms (5/F and G, 6/H). If they are all utilized the chromate ion is able to bind 12 molecules of water, which agrees with the results of the diffusion experiments (1b). The sharp decline in hydration is the result of the strong dehydrating effect of the acids.

In concentrated  $\text{CrO}_3$  solutions a quasi crystalline structure is obtained due to very strong aggregation, this is inferred from the dark red colour of  $\text{CrO}_3$  (10). In concentrated sulfuric acid the complex  $\text{HO}\cdot\text{SO}_2\text{OCrO}_2\text{OH}$  is formed (6a), this is shown by the atypical structure of the extinction curve. The formation of chromylsulfate  $\text{CrO}_2\cdot\text{SO}_4$  is also possible (6a).



#### *On the mechanism of the light absorption.*

The electron configuration according to Smith-Stoner in case of chromate ion is the following :



In the case of tetrahedral configuration the coordinative valence electrons would be  $3d^0 4s^2$ . As the aggregation through oxygen bridges admits lone electron pairs (5/g), there will be the same electron configuration around the chromic ion as around the chromate ion.

The light absorption results in the extinction of the electrons of the chromic ion and those of the coordinative valence electrons. The first band must be ascribed to the coordinative valence electrons as it reacts stronger to the state of aggregation (5). The second band corresponds to the excitation of the electrons of the chromic ions proper. The shift observed in the longer wave length portion of the first band and the appearance of a new band in the case of the polychromates must be attributed to the extension of the system of coordinative va-

lence electrons due to aggregation. It is remarkable that the aggregation of chromic ions through oxygen bridges and complex formation have a similar effect (i. e. a sharp rise in extinction in the visible part of the spectrum and in the near ultraviolet) (11). In the hope of obtaining better information about the mechanism involved, we have applied the method previously described (12) but we met no success.

From the constancy of the diffusion coefficients (1a) and the nearly constant crossing of the extinction curves it appears likely that an equilibrium exists between two successive states of aggregation of the chromate ion. Thus the extinction curve in dilute acids could be calculated from the extinction of the  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions. However, the calculated curve does not fit the experimental data. We have to suppose that apart from the equilibrium between the two above mentioned ions equilibria between other ions must exist, i. e. the extinction curve reacts a more sensitive way than the diffusion coefficient. It is for this reason that the absorption studies of Jander and Spandau (16) had to be extended through the present studies.

#### Summary.

The extinction curves of  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrO}_3$  in water and in different concentrations of  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  have been studied.

The formation of polychromates has a complicated and specific influence in the case of these acids. The extinction curves in dilute acid solution cannot be calculated from the other data by assuming that there is an equilibrium between two states of aggregation. In concentrated sulfuric acid solutions the formation of heteropoly acids has to be taken into account. Further investigations are in progress on these lines.

Szeged, (Hungary) August 1947.

#### References.

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