(I'') satisfus the well known thermo-dynamic relation

$$\frac{dlg\,K}{dt} = \frac{Q}{RT^2}.$$

HEMPTINNE and BEKAERT [1]) have observed a velocity constant for the reaction $(C_2H_5)_3N + C_2H_5Br \rightarrow (C_2H_5)_4 NBr$.

Here they found a dependence on the temperature which can be represented by a formula as (III''), but not by one as (III').

The same holds for a reaction investigated by von HALBAN [2]). KRÜGER [3]) proceeds in a calculation as we did in the first part of this paper; he thus finds temperature functions as in (I'), (II'), (III'). His model is therefore too limited. The purpose of this paper is to show how this may easily be avoided by inventing a somewhat wider model.

KRÜGER however thought the idea absolutely to be rejected, that for a combination a certain minimal velocity should be required [4]).

Of course I do not pretend that in any case a formula as (II'') or (III'') will hold. To be able to calculate a right formula, we must of course know the mechanism and as, even for the most simple dissociation, for that of hydrogen this is not the case, we shall have to content ourselves with an image.

When VAN DER WAALS derives his equation of state considering the molecules as perfectly elastic particles, he uses an image certainly not corresponding with reality. But still BOHR is of opinion that $\frac{1}{2}b$, may be compared approximately with the radius of a ring. Just as well as nobody will deny the quantitative insight given us by the considerations of VAN DER WAALS, notwithstanding the special image, I think that the above formulae when they shall have been sufficiently tested by the experiment, will also give to some extent a quantitative insight into this phenomenon.

The above considerations have of course no relation to the theory of quanta. The specific heat corresponds to that with 6 degrees of liberty.

Physical Laboratory, Delft.

[1]) HEMPTINNE und BEKAERT, Zeitschr. f. physik. Chem. **28**, 236 (1898)

[2]) HANS VON HALBAN ib. LXXVII 6. p. 731—733.

[3]) F. KRÜGER, Göttinger Nachrichten, 1908, pag 318 seq.

[4]) See further: K. F. HERZFELD, "Zur Theorie der Reaktionsgeschwindigkeiten" Ann. der Phys. 59, p. 635.

Chemistry. — *"The influence of different substances on the decomposition of monoses by an alkali and on the inversion of cane sugar by hydrochloric acid."* By Prof. H. I. WATERMAN and J. GROOT. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of January 31, 1920).

When the strength of the acid and of the alkali, from which the salt is formed, are known as well as the nature of the ions, we can calculate the percentage of the hydrolysis. The decomposition of monoses by an alkali can be controlled polarimetrically, so that this method as well as the often used inversion of cane sugar gives us a sensitive means to determine the percentage of the hydrolysis. [1])

Applying the law of mass-action to the electrolytic dissociation-equilibria that occur in such a solution, we can calculate the hydrolysis. Using

$$K_{phenol} = \frac{[H^{\cdot}][C_6H_5O']}{[C_6H_5OH]} = 1,3.10^{-10} \quad \text{and} \quad [H^{\cdot}][OH'] = 1,2.10^{-14}$$

and assuming the hydrolysis to be weak and the non hydrolized sodium-phenolate to be perfectly dissociated, we find for $\frac{1}{10}$ N sodium-phenolate solution, $[OH'] =$ rather more than 3.10^{-3}. [2])

When the hydrolysis of the sodium-phenolate in a $\frac{1}{10}$ N solution were perfect, then $[OH']$ would be 10^{-1}. From this we learn, that of the sodium-phenolate only $\frac{100}{10^{-1}} . 3.10^{-3} = 3 \%$ is hydrolized.

For more diluted solutions the percentage of this hydrolysis is higher. For $\frac{1}{10}$ N potassium-phenolate at 25° the hydrolysis is 3,1 %. [2])

These results are in agreement with the experiments on phenol, which taught that in an alkalic medium phenol practically behaves like a monobasic acid.

In this way the hydrolysis of many of the compositions treated up till now in the above mentioned investigations could be calculated when only enough data were at our disposition with regard to the strength of the respective acids and bases expressed in the well-known units.
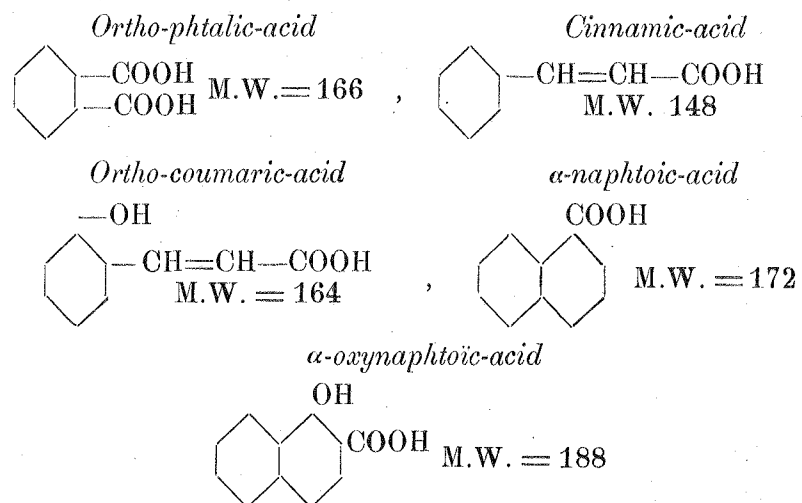
[1]) H. I. WATERMAN, These Proceedings XX (1917) p. 88, 382, 581.

[2]) J. WALKER, Introduction to physical chemistry 1919, p. 330 and 336.

A condition for the calculation is, that the nature of the ions and in general the constitution of the used compositions are known. When this is not the case the method of investigation followed by us may still give some indications. Before applying this method to the investigation of the acid or alkalic properties of organic dyes, we investigated a number of intermediate products. The investigation was also extended over several more or less strongly coloured substances. It was found possible to take away the colour just before the polarimetric measurements by means of norit or of bone-coal without lessening the accuracy of the method. In other cases alcohol was added sometimes. This changed somewhat the nature of the medium, but several compositions that could not be investigated owing to their weak solubility, could now be treated.

Most of the investigated compositions were obtained from KAHL-BAUM at Adlershof (near Berlin). When this is not the case it will be mentioned. As further different solutions were primarily coloured we paid little attention to the intensity of the darkening caused by the action of the hydroxylions on the glucose. The obtained analysis numbers will be given here only partly, elsewhere completely.

The *naphtyl-amines*. The melting-point of the used α-naphtyl-amine was 50°, that of the β-naphtyl-amine 112°. Hydrochloric compounds of these amines too were used. The experiment in an alkalic medium taught that neither α- nor β-naphtyl-amine bound an alkali, so that they do not influence the decomposition of a glucose in alkalic solution. In hydrochloric solution the amines in question behaved approximately as monovalent bases.

Ortho-phtalic-acid

—COOH
—COOH M.W. = 166 ,

Cinnamic-acid

—CH=CH—COOH '
M.W. 148

Ortho-coumaric-acid

—OH
— CH=CH—COOH ,
M.W. = 164

α-naphtoic-acid

COOH
M.W. = 172

α-oxynaphtoïc-acid

OH
COOH M.W. = 188

The melting-point of the investigated ortho-phalic-acid was 200°,

while for this substance is given e. g. 203°; a titration of the acid with $\frac{1}{10}$ N. KOH and phenolphtaleïn as indicator gave the percentage 99,8.

The melting-point of the cinnamic-acid that was present in the laboratory was 133°, of the ortho-coumaric-acid 205°. The α-naphtoïc-acid and the α-oxy-naphtoïc-acid melted respectively at 159° and at 187°.

It was found, that in diluted alcoholic solutions these compounds practically did not hinder the inversion of cane sugar (Table I); Table IV refers to the naphtoïc-acid. From the tables II and III we see, that in alkalic solution the behaviour of ortho-phtalic-acid is dibasic, of α-naphtoïc-acid monobasic, of cinnamic-acid monobasic and finally of coumaric-acid dibasic.

This might have been expected from the above given structural formulae.

We further investigated: *α-naphtol* (M.W. 144, melting-point 96°), *β-naphtol* (M.W. 144, melting-point 122°), 2.3. oxy-naphtoïc-acid (melting-point 217°)

OH
COOH M.W. = 188
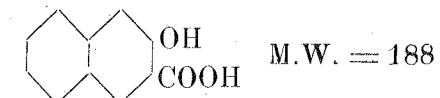
and *β-naphtoic-acid* (melting-point 185°, M.W. 172).

From the experiments made with a nearly 50 °/₀-alcoholic solution we learned, that α- and β-naphtol, α-naphtoïc-acid and 2.3. oxy-naphtoïc-acid practically do not influence the inversion of cane sugar by hydrochloric-acid (Table IV).

The behaviour of α- and β-naphtol in alkalic solution was approximately monobasic just as of β-naphtoïc-acid; *the 2.3. oxynaphtoic-acid behaved in an alkalic medium as a monobasic acid; this was also the case with the 1.2. oxynaphtoic-acid* (Tables V and VI).

In the same way as has been done for the salicylic-acid, led by analogous experiments [1]), we are now inclined to assume also for the mentioned oxynaphtoïc-acids, at least in alkalic media, a "ketoformula", e.g. as follows:

H_2
C=O
C—COOH

2. 3. oxynaphtoïc-acid
(ketoformula)

O
∥
C
C$<^H_{COOH}$

1. 2. oxynaphtoïc-acid
(ketoformula)
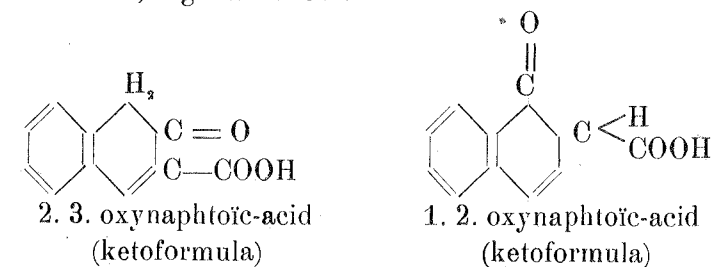
[1]) H. I. WATERMAN, These Proc. XX, 581 (1917).

TABLE I.

Influence of α-oxynaphtoïc-acid, cinnamic-acid, ortho-coumaric-acid, ortho-phtalic-acid on the inversion of saccharose by hydrochloric-acid.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		75 cm³ "96%" technical alcohol										The given time-interval is that of the standing in the thermostat. The readings were made, when the fluids had assumed about the temperature of the polarimeter space. At 35° the α-oxynaphtoïc-acid was just quite dissolved.
added					1162 milligr. phtalic-acid	752 milligr. α-oxynaphtoïc-acid	1036 milligr. cinnamic-acid	656 milligr. o. coumaric-acid				
		50 cm³ of a cane-sugar solution										
Number of cm³ hydrochloric-acid 1,005 N.		0	9	10	10	10	10	10	10	11	12	
		After filling to 150 cm³ placed in the thermostat at a temperature of 35°.										
Polarisation in Ventzke degrees (tube length 2 dm)	After ± 19 hours	+ 31.0	− 0.4	− 1.3	− 1.9	− 1.5	− 1.5	− 1.5	− 1.5	− 2.3	− 3.3	
	After ± 22½ hours	+ 31.0	− 2.0	− 2.8	− 3.3	− 3.3	− 3.0	− 3.0	− 2.8	− 3.6	− 4.2	
	After ± 41 hours	+ 31.1	− 5.9	− 6.3	− 6.4	− 6.5	− 6.3	− 6.3	− 6.2	− 6.5	—	

TABLE II.

Influence of ortho-phtalic-acid on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	Remarks.
		50 cm³ of a ± 3% glucose-solution									After addition of the alkali the ortho-phtalic-acid was quite dissolved.
added									581 milligr. o. phtalic-acid		
Number of cm³ potassium hydroxide 0,924 N.		0	2	3	4	5	6	7	10	10	
		Filled to 100 cm³ and placed in the thermostat (33°).									
Polarisation in Ventzke degrees (2 dm tube)	At the beginning	+ 4.6	+ 4.4	+ 4.2	+ 4.1	+ 4.0	+ 3.9	+ 3.8	+ 4.3	+ 3.7	
	After ± 2¼ hours	+ 4.6	+ 3.3	+ 3.0	+ 2.6	+ 2.4	+ 2.1	+ 1.8	+ 3.2	+ 1.3	
	After ± 3¼ hours	+ 4.6	+ 3.1	+ 2.5	+ 2.2	+ 1.8	+ 1.5	+ 1.2	+ 2.9	+ 0.7	

TABLE III.

Influence of α-naphtoïc-acid, cinnamic-acid and ortho-coumaric-acid on the decomposition of glucose by an alkali.

	A	B	C	D	E	F	G	H	I	Remarks.
	50 cm³ of a ± 3⁰/₀ glucose-solution									By heating the substances were dissolved in the glucose solution. At cooling crystallization took place. By the alkali however all was dissolved again. The solution I was coloured yellowish green after addition of the alkali.
added							344 milligr. α-naphtoïc-acid = 2 m.gr. mol.	1036 milligr. cinnamic-acid = 7 milligr. molecule	328 milligr. cumaric-acid = 2 milligr. molecule	
Number of cm³ potassium-hydroxide 0,929 N.	0	2	3	4	5	10	6	10	6	
	After filling to 100 cm³ placed in the thermostat (36°)									
Polarisation (V. degrees) 2 dm tube — After ± 1½ hours	+ 4.3	+ 3.3	+ 3.0	+ 2.6	+ 2.3	+ 1.4	—	+ 3.1	+ 3.4	
Polarisation (V. degrees) 2 dm tube — After ± 3 hours	+ 4.4	+ 2.8	+ 2.3	+ 1.7	+ 1.3	+ 0.5	+ 1.7	+ 2.5	+ 3.0	

TABLE IV.

Influence of α-naphtol, β-naphtol, α-naphtoïc-acid and β-oxynaphtoïc-acid on the inversion of saccharose by hydrochloric-acid.

	A	B	C	D	E	F	G	H	I	K	Remarks.
	75 cm³ "96 ⁰/₀" technical alcohol										The readings were made at room temperature.
dissolved					576 milligr. α-naphtol = 4 milligr. molecules	576 milligr. β-naphtol = 4 milligr. molecules	516 milligr. α-naphtoïc-acid = 3 m.gr. mol.	752 milligr. 2.3oxynaphtoïc-acid = 4 m.gr. mol.			
	50 cm³ cane-sugar solution (concentration 250 Gr./L.)										
Number of cm³ hydrochloric-acid 1,005 N.	0	7	8	9	10	10	10	10	10	10	
	Filled to 150 cm³ and placed in the Thermostat of 35°.										
Polarisation in Ventzke degrees (2 dm tube) — At the beginning	+ 31.6				+ 31.5	+ 31.5	+ 31.5	+ 31.5	+ 31.5		
After ± 4 hours	+ 31.5	+ 22.5	+ 21.4	+ 20.3	+ 19.2	+ 18.9	+ 18.5	+ 18.7	+ 18.9	+ 19.2	
After ± 24 hours	+ 31.5	+ 0.1	− 1.3	− 2.6	− 3.3	− 3.5	− 3.8	− 3.6	− 3.6	− 3.6	
After ± 28 hours	+ 31.6	− 1.6	− 2.6	− 3.5	− 4.4	− 4.5	− 4.6	− 4.5	− 4.4	− 4.4	
After ± 50 hours	+ 31.6	− 5.3	− 5.7	− 5.8	− 6.2	− 6.2	− 6.2	− 6.2	− 6.2	− 6.2	

TABLE V.

Influence of β-naphtoïc-acid and β-oxynaphtoïc-acid (2:3) on the decomposition of glucose by an alkali.

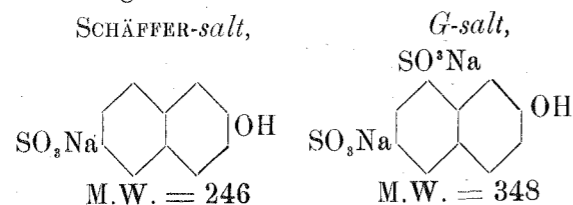|		A	B	C	D	E	F	G	H	I	K	Remarks.
		50 cm³ of a ± 3 % glucose solution										β-naphtoïc-acid was dissolved in the potassium hydroxide rather quickly, the β-oxynaphtoïc-acid only after long shaking with a yellow colour. The solid acid itself was also yellow.
dissolved									602 milligr. β-naphtoïc-acid = 3,5 m.gr. mol.		1316 m.gr. β-oxynaphtoïc-acid = 7 m.gr. mol.	
Number of cm³ potassium-hydroxide 0,929 N.		0	2	3	4	5	6	7	10	10	10	
		Filled to 100 cm³ and then placed in the thermostat (34°)										
Polarisation in VENTZKE degrees (2 dm tube)	At the beginning	+ 4.4	+ 4.1	+ 3.9	+ 3.8	+ 3.8	+ 3.7	+ 3.7	+ 3.7	+ 3.5	+ 4.0	
	After ± 2¼ hours	+ 4.4	+ 3.2	+ 2.7	+ 2.3	+ 2.1	+ 1.7	+ 1.5	+ 1.6	+ 1.0	+ 3.0	
	After ± 3¼ hours	+ 4.4	+ 2.8	+ 2.3	+ 1.7	+ 1.5	+ 1.1	+ 0.9	+ 1.0	+ 0.3	+ 2.6	

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TABLE VI.

Influence of α-oxynaphtoïc-acid (1,2) and β-oxynaphtoïc-acid (2,3) on the decomposition of glucose by an alkali.

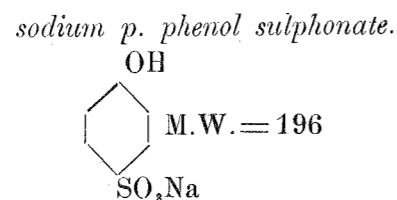|		A	B	C	D	E	F	G	H	I	K	Remarks.
		25 cm³ 96 % alcohol										The addition of alcohol was necessary to dissolve the α-oxynaphtoïc-acid.
dissolved									589.6 milligr. 1.2 oxynaphtoïc-acid = 0,896.3,5 m.gr. mol.		1179,1 milligr. 2.3 oxynaphtoïc-acid = 0,896.7 m.gr. mol.	
Number of cm³ sodium hydroxide 0,896 N.		0	2	.3	4	5	6	7	10	10	10	
		50 cm³ of a glucose solution. After filling to 100 cm³ placed at 35°.										
Polarisation (V. degrees 2 dm tube)	After ± 1½ hours	+ 6.8	+ 5.5	+ 4.8	+ 4.5	+ 4.0	+ 3.6	+ 3.3	+ 3.4	+ 2.4	+ 4.8	
	After ± 4 hours	+ 6.8	+ 4.5	+ 3.6	+ 2.9	+ 2.3	+ 2.0	+ 1.7	+ 1.8	+ 0.9	+ 3.6	
		Further the solutions remained at room temperature.										
	After ± 19 hours	+ 6.8	+ 4.0	+ 3.0	+ 2.4	+ 1.7	+ 1.4	+ 1.1	+ 1.3	+ 0.4	+ 3.1	

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Similar ketoformulae for the 2.3 oxynaphtoïc-acid are already found in the literature [1]).

Further we investigated still:

SCHÄFFER-*salt*,   *G-salt*,

SO₃Na

SO₃Na⎿⎾OH   SO₃Na⎿⎾OH

M.W. = 246   M.W. = 348

and also

sodium p. phenol sulphonate.

OH

M.W. = 196

SO₃Na

The sodium 2.6. naphtol sulphonate has been investigated as technical SCHÄFFER-salt and also as a purified one prepared in the laboratory by sulphonation of β-naphtol.

To determine the percentage of the technical product this was titrated by means of diazotated p. nitraniline according to the method in use in the technical control-stations of the dye-manufacturies [2]). In this way we found the percentage 76.4. The purified preparation when dried gave a loss in weight of 11,4 %. In the dried substance we made a sulphate-ash-determination. Having made the calcutation for Na, we found from this 9,1 %. (Theor. 9.35 %).

From the observations combined in table VII we see, that 4 milligram-molecules of the pure SCHÄFFER-salt bind just as much alkali as the corresponding quantity of the technical product.

If the pure salt behaved as a monobasic-acid, just $\frac{88,6}{100} . 4 = 3,5$ cm³

N. KOH would have been found. In reality we find 3,7 cm³ 0,93 N. KOH = 3,4 cm³ N. As the titration gave for the percentage of the technical product 76,4, it is probable, that the technical product in question is made impure by substances which can bind alkali, but which under the circumstances of the titration with diazo-solutions, cannot form colours. As might be expected the SCHÄFFER-salt could not bind an acid in a hydrochloric medium.

[1]) R. MÖHLAU, Berichte d. Deutsch Chem. Gesellsch. **28**, 3100 (1895);

M. SCHÖPF, Idem **29**, 265 (1896); F. FRIEDL, Sitzungsber. der Akad. der Wissenschaften, Mathematisch-Naturwissensch. Klasse, Wien, **119**, 731(1910).

[2]) R. MÖHLAU and H. BUCHERER, Farbenchemisches Praktikum.

TABLE VII.

Influence of Schäffer-salt (purified) and of Schäffer-salt (technical) on the decomposition of glucose by an alkali.

	A	B	C	D	E	F	G	H	I	K	Remarks.
Dissolved				50 cm³ of a ± 3% glucose solution							The substances were dissolved by heating. After cooling the alkali was added. With the potassium-hydroxide the solution H gave a blue fluorescence, while the solution I was coloured brownish green. Before the readings they had to be decoloured by means of norit.
								984 milligr. pure sodium SCHÄFFER-salt	984 milligr. technical SCHÄFFER-salt		
Number of cm³ potassium-hydroxide 0,93 N.	0	1	2	3	4	5	6	6	6	6	
				After filling to 100 cm³ placed in the thermostat (temperature 35°).							
Polarisation in V. degrees (tube length 2 dm)	After ± 2¼ hours	+ 4.3	+ 3.7	+ 3.2	+ 2.8	+ 2.4	+ 2.1	+ 1.8	+ 3.1	+ 3.1	+ 1.9
	After ± 3½ hours	+ 4.3	+ 3.4	+ 2.8	+ 2.2	+ 1.8	+ 1.4	+ 1.0	+ 2.5	+ 2.6	+ 1.0
					Further left at room temperature.						
	After totally ± 22 hours	+ 4.3	+ 3.2	+ 2.5	+ 1.8	+ 1.4	+ 0.9	+ 0.6	+ 2.3	+ 2.3	+ 0.6

TABLE VIII.

Influence of sodium para phenol sulphonate (technical) and of G salt (technical) on the decomposition of glucose by an alkali.

	A	B	C	D	E	F	G	H	I	K	Remarks.
	50 cm³ of a ± 5% glucose solution										The G-salt is dissolved with a brown colour which makes the readings very difficult. After treatment with norit the fluid is green fluorescent after the filtration, but can be read very well in a 2 dm. tube.
Dissolved								1568 mgr.sodium p.phenol-sulphonate 8 mgr. mol.	2436 mgr. G. salt =7 milligr. molecules	As sub I	
Added number of cm³ potassium-hydroxide 0.92 N.	0	1	2	3	4	5	10	10	10	10	
	After filling to 100 cm³ placed at 35°.										
Polarisation in V. degrees (tube length 2 dm) — After ± 2½ hours	+ 7.4	+ 6.5	+ 5.8	+ 5.2	+ 4.6	+ 4.1	+ 2.3	+ 5.4	norit + 4.4	2. 2.2 = + 4.4	
After ± 4 hours	+ 7.4	+ 6.2	+ 5.2	+ 4.3	+ 3.6	+ 3.0	+ 1.2	+ 4.5	norit + 3.6 + 3.5	2. 1.8 = + 3.6	
After ± 5½ hours	+ 7.4	+ 5.8	+ 4.7	+ 3.7	+ 3.0	+ 2.3	+ 0.6	+ 4.0	—	norit 2.1.5 = + 2.9 + 3.0	

The percentage of the sodium 2.6.8 naphtol disulphonate (G-salt) was determined in an analogous way as that of the Schäffer-salt by means of diazotated para-nitraline. The result was 82 %.

For the sodium para phenolsulphonate (technical product) we also found 82 %. The percentage for the dry substance was 87 %. In reality the percentage of sodium in the dry substance (calculated 11,7 %) was 11,3 % (determined with the sulphate-ash method).

The results with G-salt and sodium para phenolsulphonate in alkalic solution are to be found in table VIII. From these investigations we see, that 7 milligrammolecules of the technical G-salt have bound 6 cm³ KOH (0,92 N.) = 5,5 cm³ N. potassiumhydroxide.

When we suppose that because of the formula

$$SO_3Na \quad SO_3Na \quad OH$$
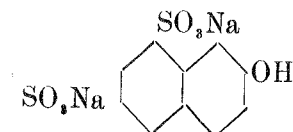
the G-salt behaves like a monobasic acid and at the same time that the admixtures, such as the inorganic salts, have no influence and that admixtures as other β-naphtolsulphonates have the same influence as the G-salt, we should conclude to a percentage of $\frac{5,5}{7} \cdot 100$ i.e. of nearly 80 % of constituents that can be bound to dyes.

By titration with diazotated paranitroaniline was found 82 %, so that in fact it is nearly sure, that in an alkalic solution the G-salt behaves like a monobasic acid.

In an analogous way we may deduce from the observations that in alkalic solution the sodium para phenolsulphonate behaves as a monobasic acid.

Delft, Jan. 1920.   *Laboratory of Chemical Technology Delft.*