Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"On the relation between the sulphur modifications."* By Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of September 28, 1912).

Prof. SMITS has authorised me to criticise a recently published report of a lecture by KRUYT delivered before the Deutsche Bunsen Gesellschaft (Z. f. Elektr. Chem. 1912, 10, 581) and to make use for this of the experimental data obtained during a research conducted by me as private assistent. Before proceeding to this it seems to me desirable to mention very briefly some points in historical order.

SMITH and his coadjutors were the first to assume dynamic isomery with sulphur. They determined the course of the equilibrium line $S_\lambda - S_\mu$ and also the solidification line of the monoclinic sulphur. KRUYT, in addition, determined the initial melting points of rhombic sulphur which, at different temperatures, had got into equilibrium with S_μ, the melting point line of SMITH being used as the method of analysis. Moreover, he concluded to the existence of a metastable region of demiscibility contrary to SMITH and his co-workers who rejected this.

By Prof. SMITS it was pointed out already in 1910 that the results of the sulphur investigation contain data which support his theory of allo-tropy. KRUYT, for instance, had stated that when starting with rhombic sulphur, which has placed itself in equilibrium at 90° and then determining the melting point of the sulphur in this condition, according to SOCH's method, 110°.9 was found whereas, in the same method of working, a melting point of 111°.4 was observed when the S had come into equilibrium at 65°. From this result it, of course, follows that we are dealing here with an inner equilibrium in the solid state, therefore with mixed crystals, and that the line for the inner equilibrium in the solid condition proceeds on increasing the temperature, to a greater S_μ content, as in the liquid. Prof. SMITS therefore changed the T, x-figure (fig. 1) into that indicated in fig. 2.

Afterwards, A. SMITH and CARSON (Z. f. phys. Chem. 1911, **77,** 661) have determined the solidification line of S_{Rh} also making use of the lines determined previously. This line differs a little with the curve of KRUYT. Moreover, they also found a third melting point line, that of the "soufre nacré". In the same time KRUYT (Chem. Weekblad 1911, 647) announced that all the values of the transition temperature $(T \rightarrow)$, with varying quantities of S_μ are situated lower than REICHER's value (95°.6) and also that the dimensions of the mixed crystal-region are not such that the influence thereof on his calculations exceeds the experimental errors.

In the meanwhile it had been pointed out by Prof. SMITS that the theory of the allotropy leads us to expect that the previous history
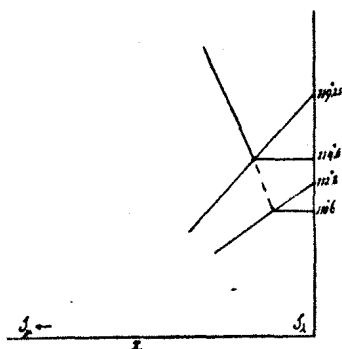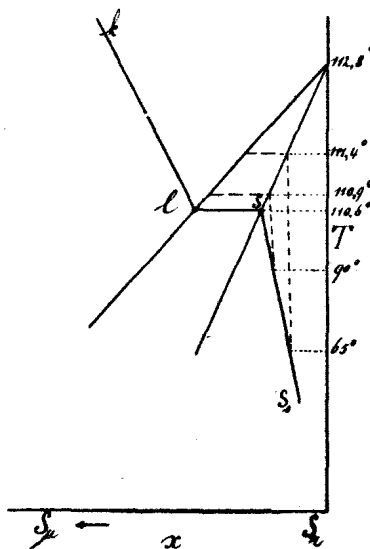

Fig. 1.   Fig. 2.

might exert an influence on the situation of the transition point. Specially conducted experiments confirmed this surmise completely (A. SMITS and H. L. DE LEEUW, On the system sulphur, Proc. 1911). The $T \rightarrow$ was determined according to REICHER's method with this modification that the upper end of the dilatometer was not sealed. The transition temperature was consequently determined at 1 atm. pressure, whereas with REICHER the pressure amounted to 4 atm. The influence which the pressure exerts on the transition temperature is calculated by REICHER to be equal to $^1/_{30}°$ rise per atm. pressure increase. This tallies, as instead of 95°.6 observed by REICHER, I found 95°.45.

Now in order to find $T \rightarrow$ when S_μ was present the sulphur was heated to boiling in the dilatometer and then rapidly cooled so that a great part of the S_μ formed remained intact. Then the dilatometer liquid (a mixture of 9 vol. of turpentine and 1 vol. of CS_2 which had been boiled for a long time with sulphur and showed no longer an evolution of gas) was added and the transition point determined by ascertaining at which temperature one was *above* and when one was *below* $T \rightarrow$. In the first case the level of the liquid rises at a constant temperature (conversion $S_{Rh} \rightarrow S_M$), in the second case it falls (conversion $S_M \rightarrow S_{Rh}$).

Here it was shown that already at a much lower temperature than

$95°,45$ could be observed a conversion of rhombic into monoclinic sulphur, *which could be made reversible by lowering the temperature*; hence there must be a transition point. A conversion of S_μ into crystalline S could not account for that reversible behaviour as then either S_M or S_{Rh} was formed owing to which the volume ought to always decrease and no temperature should be found at which the volume increased. As stated in the communication from Prof. Smits and myself, the S_μ present in the mixed crystals will be converted *continuously* into S_λ, from which it follows that when an increase in volume is noticed, the conversion $S_{Rh} \rightarrow S_M$ predominates [1]. So as to make sure that the phenomena observed were not due to the not yet complete equalization (after about 10 minutes) of the each time differently chosen temperature of the thermostat, a second dilatometer containing S which had been in equilibrium for weeks and gave a $T \rightarrow$ of $95°.45$ was placed in these experiments, by way of a check, next to the dilatometer, which contained sulphur with much S_μ. Below follows with full details the result of one of the experiments. In the first column is given the temperature of the thermostat. The second column gives the time elapsed after placing the dilatometer in the thermostat. In the third column is found, first the change in the dilatometer with the S_μ and below that in the control dilatometer.

From this we see that $2^1/_4$ hours after the heating the control dilatometer at $71°$ did not further rise in 15 minutes, but the other one did, showing that a conversion took place with change in volume, which can never be explained by conversion of S_μ into S_{Rh} or S_M as this causes the volume to decrease. The only possible thing, therefore, is that $S_{Rh} \rightarrow S_M$, that is to say the transition point has been lowered by S_μ to below $71°$. This fall depends on the quantity of S_μ which will decrease gradually. The processes which take place in presence of each other are $S_\mu \rightarrow S_{Rh}$, $S_\mu \rightarrow S_M$ and $S_M \rightleftarrows S_{Rh}$. The decrease of S_μ may be seen from the rise in $T \rightarrow$. After $4^1/_1$ hours, no more change in volume at $71°$ could be observed, whilst after $6^2/_2$ hours the liquid in the dilatometer distinctly fell. The transition temperature then appeared to lie between $71°$ and $72°$ [2]. In this way

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[1] The forming or augmentation of a second phase rich in S_μ should also cause the volume to increase. Whether a part of the depression in this manner has to be explained, is on trial. It is however sure, that even when it were so, the lowering of the transition point by S_μ, has to be considered as certain.

[2] This is not quite correct on account of the always continuing conversion $S_\mu \rightarrow$ crystalline S in consequence of which, on decrease of the volume, a slight conversion of $S_{Rh} \rightarrow S_M$ can take place. For the sake of brevity we will disregard this, however.

Temperature of bath	Total lapse of time after placing in the thermostat	Rise in mm.	Time in which the rise was observed.
71°	2¹/₄ hours	+2 0	15 min.
	4¹/₄ „	0 0	10 „
	6¹/₂ „	−1¹/₂ 0	12 „
76°	23¹/₂ „	+¹/₂ after 12 m. 0	10 „
78°	24¹/₄ „	+2¹/₂ after 15 m. 0	12 „
	24³/₄ „	+3¹/₂ 0	20 „
	28 „	+1¹/₂ 0	18 „
	29 „	+¹/₂ 0	15 „
	29³/₄ „	−¹/₂ 0	12 „
	47¹/₂ „	−2¹/₂ 0	15 „
86°	48¹/₂ „	−1 after 12 m. 0	15 „
86°	49¹/₄ „	+2 after 15 m. 0	10 „
87.5°	52 „	+2¹/₂ 0	12 „
	53¹/₂ „	+1 0	10 „
	72 „	−2 0	10 „
91.5°	73 „	+1 after 14 m. 0	12 „
	73¹/₂ „	+1 0	18 „
	75¹/₄ „	0 0	15 „
	76¹/₄ „	−1 0	18 „
	78 „	−2 0	15 „
94°	78¹/₂ „	+1¹/₂ after 12 m. 0	20 „
	168 „	−1¹/₂ 0	25 „
95.2°	168¹/₂ „	+1 0	20 „
	169 „	+1 0	22 „
95.3°	169¹/₂ „	somew. falling 0	14 „
95.4°	169³/₄ „	0 0	12 „
	170 „	0 0	12 „
95.6°	170¹/₄ „	+¹/₂ 0	18 „
	172 „	+1 +¹/₂	20 „

the rise of $T \rightarrow$ could be readily traced, from which it appeared that this, with ever decreasing velocity, rose until 95.45° was reached, which temperature is the true unary transition temperature. Hence, we see that $T \rightarrow$ can be lowered by S_μ fully 20°. In harmony therewith is also the fact that starting from S_μ-free sulphur, REICHER (Dissertation) obtained, as he thought, diverging results, namely first a transition temperature of 97° which temperature he found in course of time on the decrease until the unary transition temperature 95°,45 was reached at which S_μ is present.[1])

Simultaneously with the result mentioned above several experiments were communicated which contrary to KRUYT's investigation (Z. f. phys. Ch. **64** 513) removed all grounds for the assumption of a metastable region of demiscibility in the pseudo system. It appeared that the occurrence of two layers is due to the difference in temperature which between the two layers may amount to even from 10 to 30°. When the heat conductivity was improved by the introduction of platinum wire or small gauze this phenomenon occurred less distinctly or not at all. Quite in harmony therewith is also the influence which an alteration in the diameter of the sulphur tubes exerts on the appearance of two layers. That we are not dealing here with a metastable region of demiscibility appeared, contrary to KRUYT, also from the fact that in the presence of NH_3, which is a positive catalyst, that apparent unmixing occurred still better, notwithstanding we now follow the equilibrium line. While KRUYT believed that there existed a constant three-phase temperature S_μ with two liquid layers at 110° (intersecting point of the solidifying line of S_M with the region of demiscibility, point d of Fig. 4), this also did not prove correct as, on inoculation with monoclinic sulphur, solidification temperatures of 108° and 109° were observed and, when starting from pure S_μ, even 106°.

As the last publication I mention KRUYT's lecture which contains pretty well the same as the article in the Chem. Weekblad except that Fig. 3 occurs also.[2]) From this we notice that KRUYT now assumes that C ($T \rightarrow$ of S_μ-free sulphur) lies at 94°.8, GH at 95°.6 (unary temp. really 95°.45). In what manner these experiments have been carried out, is, however, not communicated. They must be faulty or

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[1]) GERNEZ also gives too high values (97°.6—98°.4). As GERNEZ only observed $SRh \rightarrow SM$ and not $SM \rightarrow SRh$ his figures are likely to be too high and do not prove much.

[2]) In the Fig. KRUYT draws the S_μ to the right. The reason that I always place it to the left is that I do not want to depart from the custom to place the substance with the lowest m.p., therefore, presumably S_μ, to the left.

interpreted wrongly for it is a fact that addition of S_μ lowers the transition point. The highest point given by KRUYT for the metastable equilibrium $S_R \rightleftarrows S_M$ is 96°. Above this, S_R when passing into S_M,
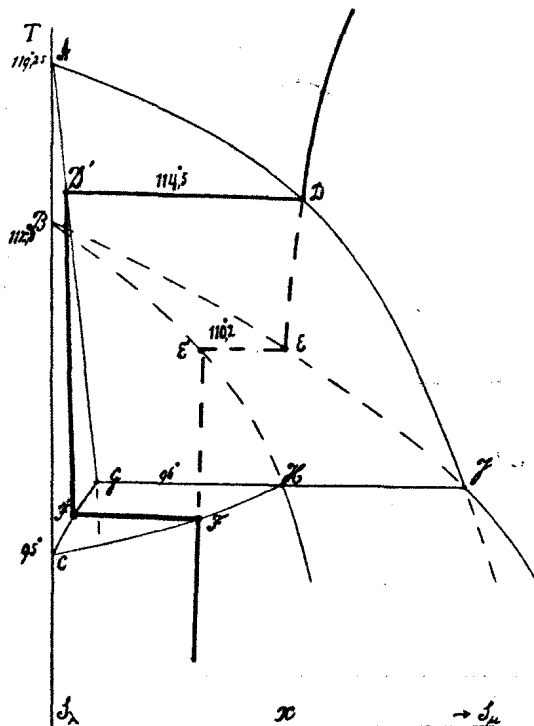

Fig. 3.

ought to begin to melt. This statement is rather remarkable when we read that KRUYT in the Chem. Weekbl. 648, (1911) actually states that all values for the $T \rightarrow$, on change of S_μ-content, lie *lower* than 95°.6. I should like to ask, how that temperature has been found? Also, the high values (97°.6 and 97°), determined by GERNEZ and REICHER, find no room in KRUYT's Figure.

Hence, it is faulty without any doubt to let CG proceed to higher temperatures; this line falls. If, however, we draw CG sinking we obtain a Figure which is identical with a figure previously given by Prof. SMITS (Proc. 1911, 264) and represented here by Fig. 4. This identity becomes perfect if we leave out the dissociation region drawn therein (which as stated in a note ought to be discarded as not a single experimental fact points to its existence). In this way we obtain Fig. 5. What KRUYT (fig. 3) calls CG is in fig. 4 and 5 op etc.

The deduction of the transition point of the sulphur with the aid of the equilibria lines of the solid substance is therefore not due to KRUYT.
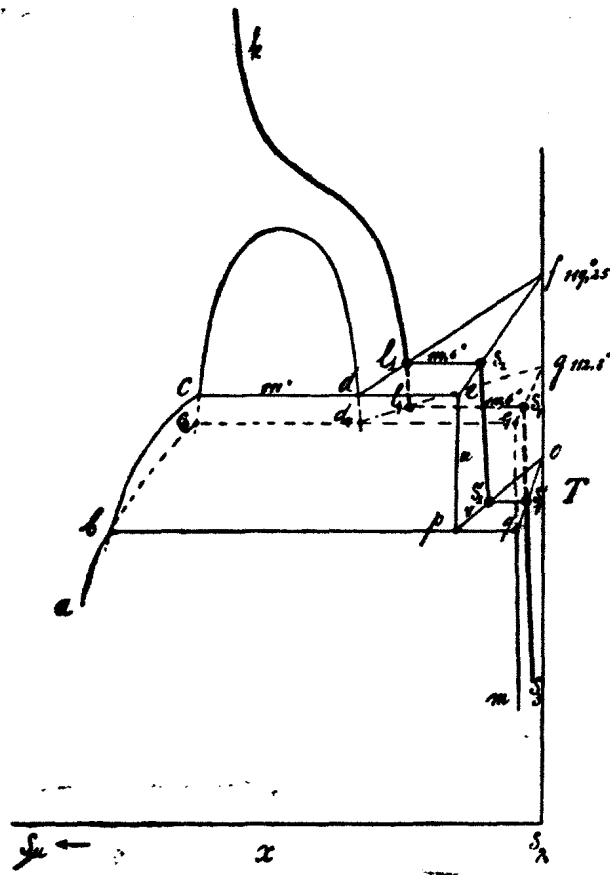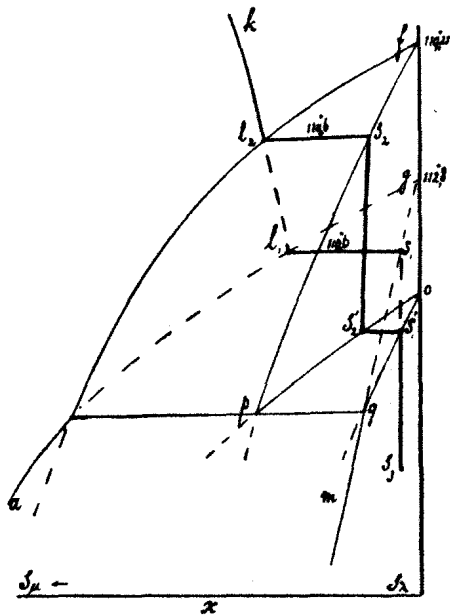
Fig. 4.

Fig. 5.

Kruyt draws no region of demiscibility, but states that for *the sake of brevity he discards the probable occurrence of the region of demiscibility.* It would have been more correct to state that *nothing pleads for its existence and that therefore it was omitted.* In connection herewith I will observe the following. If we prolong the lines AD and BE, as indicated by Kruyt (Zt. phys. Chem. 64, 513) they intersect each other at about 106°, so far above 96°. GHI would then lie at 106° which cannot be. If now we call to our aid a region of dissociation (see Fig. 2) this difficulty, of course, does not occur, but this alone does not justify the assumption of a region of demiscibility, particularly if we remember that the mode of representation is not correct.

The matter may indeed be explained readily when, as required by Prof. Smits's theory, we not merely assume two kinds of sulphur S_λ and S_μ, but (at least) *three* kinds of molecules which we will indicate briefly by S_μ, S_M, and S_{Rh}. Because there exists a transition point $S_M \rightleftarrows S_{Rh}$ we must also assume a pseudobinary system $S_{Rh} - S_M$. The whole S-diagram then becomes ternary of which already a schematic figure has been constructed (Proc. XIV, 266) Prof. Smits has now modified the former ternary figure by omitting the region of demiscibility and keeping account with the third crystallised modification, the *soufre nacré*[1]). This drawing is given in Fig. 6. The above mentioned difficulty does not arise here at all. The lines AD and BE from Fig. 3 are lines which in the ternary figure run over the surfaces $l_2 S_2 LS$ and $l_1 S_1 L^1 S^1$ and therefore are spacial curves which may deviate much from the right ones. If we assume that the equilibrium $S_M \rightleftarrows S_{Rh}$ sets in with infinite velocity there is formed from the pseudo ternary figure the pseudobinary Fig. 5, in which the curves justmentioned have undergone an intricate projection, whereby a *crossing* may turn into an *intersection* so that the above mentioned intersection at 106° need not signify anything.

Hence, it is incorrect to assume, as Kruyt, Smith, and others, that we can deduce from the unary solidification temperature of the S_{Rh} the S_μ-content with the aid of the line of equilibrium, since in the projection the situation of the lines in regard to each other is totally changed. Also it is not permissible, as Kruyt has done, to first determine the melting point of the rhombic modification and then to determine the composition with the aid of the melting point when the substance has become monoclinic, for AD and BE need not, of course, be situated in *one* plane. Kruyt's experiments on the melting point of rhombic sulphur clearly indicate this.

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[1]) See These Proceedings XV p. 369.

Kruyt has, in fact, not determined BE, but BE', that is to say the *initial temperatures of fusion*[1]). The line BE has been determined
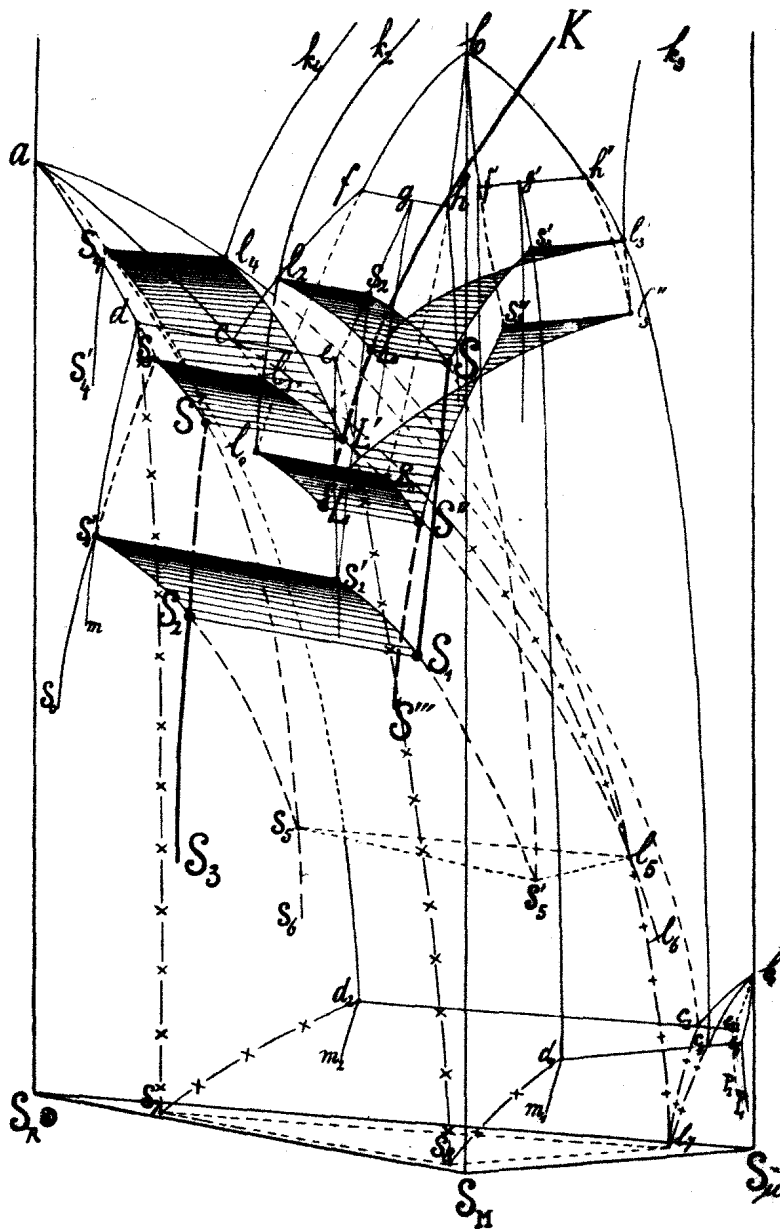
by SMITH; it differs somewhat and ought to lie somewhat higher [1]). Now, KRUYT allows the sulphur to become monoclinic and then again determines the initial melting point, but according to his figure, this is totally impossible, when we notice that BE' is situated nearly totally between $AD'G$ and ADJ, so that, starting from points of BE we arrive into the region monoclinic sulphur-liquid, owing to which the substance must be partly melted and consequently no initial melting point can be observed.

This is the result of the incorrect assumption that CG rises, owing to which AG nearly always gets situated quite to the left of BA. If CG is drawn falling (lowering of the transition point) in which case we again obtain Fig. 5 this difficulty does not arise.

Summarising, I arrive at the following conclusions which differs case we from that of KRUYT:

1st The modifications introduced by KRUYT in the previous Fig. of Prof. SMITS (Proc, XIV, 264) are incorrect.

2nd By addition of S_μ the transition temperature $S_\mu \gtrless S_{Rh}$ is *lowered*.

3rd Fig. 3 (from KRUYT) is not in harmony with the phenomena observed (also see ad 7). Even KRUYT's own experiments are in disaccordance with it.

4th KRUYT has determined not the line BE from Fig. 3, but the line BE'.

5th The system sulphur is not pseudobinary, but at least pseudo-ternary.

6th In consequence of this, the true direction of the lines from figs. 3, 4, and 5 is another one than that assumed by KRUYT. The significance of the intersecting points of the lines drawn by KRUYT also differs from that attributed to them by that investigator.

7th There exist no grounds for the assumption of a region of demiscibility.

*Inorg. Chem. Lab. University.*
Amsterdam, September 1912.

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[1]) The difference has to be explained by the different method of working. Freezing points are easily found too low, melting points too high especially in the case of mixed crystals.

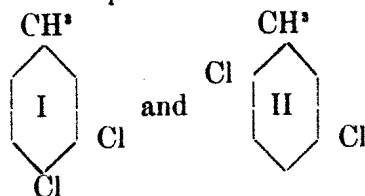**Chemistry.** — *"On the nitration of the chlorotoluenes"*. By Prof. A. F. Holleman and Dr. J. P. Wibaut.

When two substituents are present in the benzene nucleus, both have a certain influence on the place where a third substituent enters. Which of the possible trisubstituted isomers will be obtained in a larger quantity depends, as I have shown elsewhere, on the velocity of substitution which both of the groups cause.

If we consider for instance a monochlorophenol, the new entering substituent places itself nearly exclusively on the ortho- and para-places with regard to hydroxyl and not on these places with regard to chlorine, because the velocity of substitution, which OH causes is much larger than that caused by chlorine.

By considering all the cases of substitution in the bisubstituted benzene derivatives, I found, that the velocity of substitution to meta-places is always much slower than that to para-ortho-places, and that the substituents that direct a new substituent to the latter places cause a velocity of substitution which decreases in the following order:

$$OH > NH_2 > halogens > methyl$$
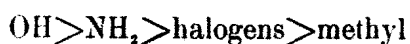
As the halogens and methyl cause no large difference in the velocity of substitution, it should be expected, that the entrance of a third group takes place para-ortho as well to the halogen as to methyl. Indeed, Cohen and Dakin proved in an excellent and very laborious research that in the chlorination of orthochlorotoluene all the four possible chloro-*o*-chlorotoluenes are formed and in the chlorination of *p*-chlorotoluene the two possible dichlorotoluenes, whereas with meta-chlorotoluene the same operation procured the isomers I and II, but not the symmetrical dichlorotoluene, just as might be expected, because neither chlorine nor methyl direct a substituent to meta-places.

In order to get an insight in the ratio of these velocities, it is necessary quantitatively to determine the proportions in which the isomers are formed; and as nitrations are generally not attended with production of secondary products, we resolved to study again the nitration of the monochlorotoluenes. Through former investigations it was known, that *o*-chlorotoluene yields the product $CH_3,Cl,NO_2 = 1,2,5$ (Goldschmidt, Hönig, B. **19**, 2440), *m*-chlorotoluene yields the isomers $CH_3,Cl,NO_2 = 1,3,4$ and 1,3,6 and para-chlorotoluene yields the isomers $CH_3,Cl,NO_2 = 1,4,2$ and 1,4,3. The latter nitration had been