One of us has previously deduced the rule [1]) that the metastable continuations of the branches *ac* and *bc* must fall both together either within or without $\angle Cu_2 . c . HgCl_2$. Which case occurs here is difficult to prove experimentally as both branches, in the vicinity of point *c* practically coincide with the sides of the angle $Cu_2 . c . HgCl_2$. Moreover, the saturation line *bc* of the $HgCl_2$ exhibits a very peculiar form. The metastable continuation must, of course, terminate somewhere on the side $HgCl_2$—$CuCl_2$ of the triangle; from the course of the stable part in the vicinity of *c*, it appears, however, that this will not be possible without a point of inflexion appearing somewhere on the metastable part or on the stable part situated in the vicinity of *c*.

Chemistry. — "*The system Tin-Iodine*". By Prof. W. REINDERS and S. DE LANGE. (Communicated by Prof. SCHREINEMAKERS.)

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

1. Of tin and iodine two compounds are known, stannous and stannic iodide. As regards the preparation and properties of these compounds there exist in the literature different conflicting statements. By the older investigators [2]), for instance, it is stated that on heating tin with iodine, stannous iodide is formed. HENRY [3]), however finds a mixture of SnI_2 and SnI_4 and PERSONNE [4]) SnI_4 only. The melting point of SnI_4 is given by PERSONNE [5]) as 145° (solidifying point 142°), by EMICH [6]) 143°. The boiling point according to PERSONNE is at 295°, EMICH finds 341°. HENRY, however, states that it sublimes at 180°.

Of SnI_2 the melting point is given both at 246 [7]) and at a dull red heat (PERSONNE) and the boiling point both at 295° [7]) and at the temperature of molten glass (PERSONNE).

For the knowledge of the binary systems of a metal and a metalloid a renewed investigation was therefore desirable.

2. SnI_4 was prepared in two ways, *a*. by treating granulated tin for some days with a solution of iodine in carbon disulphide and

[1]) F. A. H. SCHREINEMAKERS, Die heter. Gleichg. von BAKHUIS ROOZEBOOM. III'. 268.
[2]) I. a. BERZELIUS, Traité de chimie; RAMMELSBERG, Pogg. Ann. **48**, 169.
[3]) Phil. Trans. **135**, 363 (1845).
[4]) Compt. rendus. **54**, 216 (1862).
[5]) l. c.
[6]) Sitzungsber. der K. Ak. v. W. Wien **113**, II*b*, 535 (1904) (Monatshefte **25**, 907.
[7]) COHEN, Abegg's Handbuch d. anorg. Ch. III. 2, 571.

evaporating the solution obtained, *b.* by melting iodine with a small excess of tin. The weighed out quantities were introduced in small portions into a glass tube and if necessary, heated a little to start the reaction; the tube was then sealed, heated for some time at 250°, then placed vertically and cooled slowly. The orange-red crystalline mass obtained was then separated from the tin and the bottom layer of crystals and reduced to a fine powder. Both methods gave according to analysis, pure SnI_4 without any SnI_2 whatever. Found: 18,95—18,99 % of Sn; theory 18,99 %.

For the preparation of SnI_2 is recorded *a.* addition of $SnCl_2$-solution to KI-solution [1]) *b.* dissolution of tin in concentrated hydriodic acid [2]).

The first method seems the most simple one. It has the disadvantage however, that in this reaction besides the red SnI_2, double salts with KI may be formed also, whilst it is still uncertain whether a protochloro-iodide (HENRY), or mixed crystals with $SnCl_2$ are perhaps obtained in addition. The first method was, therefore, abandoned and the second process used instead. The action of tin on HI proceeds slowly and was carried out in a round bottomed flask attached to a refluxcondenser. The red crystals obtained were dried in a vacuum desiccator, first for a few weeks over sticks of KOH, then for a few months over P_2O_5. Found 31,83 and 31,87 % of Sn; theory 31,92 %.

Another mode of preparation will be mentioned presently.

3. The melting point of SnI_4 was found 143,°5, therefore in agreement with EMICH, who gives 143°.

The solidifying point determinations of I-SnI_4-mixtures took place in the usual manner by cooling in the apparatus VAN EIJK. In order to prevent strong undercooling we constantly stirred with the thermometer during the cooling.

The results are united in the subjoined table (p. 476) and represented graphically in Fig. 1.

Hence we have a simple melting point line with a eutecticum at 79°,6 and 60 % by weight of SnI_4 (12,06 at. % Sn).

4. In the preparation of SnI_4, it had already been shown that SnI_4 could be heated for a considerable time with Sn at 250° without any perceptible reaction setting in with formation of SnI_2.

The possibility had, therefore, to be considered whether Sn and

[1]) BOULLAY, Ann. d. phys. et chim. (2) **34**, 337 (1827); PERSONNE, l. c.

[2]) PERSONNE l. c.

Composition of the liquid		Initial Solidifying point	
gr. SnI_4 per 100 gr. $SnI_4 + I$	at. Sn per 100 at. Sn + I		
0	0	113°.2	
10	2.02	109.0	
20	4.04	104.7	
30	6.05	99.7	
40	8.06	94.7	
50	10.06	87.6	
55	11.06	83.0	
60	12.06	79.6	
65	13.05	83.5	(eutecticum 79°.6)
70	14.05	89.8	
80	16.04	108.4	
90	18.02	127.0	
100	20.00	143.5	

$Sn I_4$ might not really be in stable equilibrium with each other and that $Sn I_2$ might be at high temperature a labile compound that would dissociate into $Sn + Sn I_4$. Looking at the fact that the number of halogen atoms, capable of combining with an element, generally decreases with the atomic weight of the halogen, the probability of this was not great, and it was even to be expected that SnI_2 would be very permanent.

In order to decide this, weighed quantities of Sn, $Sn I_4$, and $Sn I_2$ were heated in a sealed tube during 14 hours at 360°. Starting from 12.5 grams of $Sn I_4$, 7.7 grams of $Sn I_2$ and 2.4 grams of Sn there were obtained about 9.6 grams of $Sn I_4$, 10.5 grams of $Sn I_2$ and 1.6 gram of Sn. Consequently, there was a very appreciable decrease of Sn and $Sn I_4$ and an increase of $Sn I_2$.

The reaction $Sn + Sn I_4 \rightarrow 2 Sn I_2$, therefore, actually does take place, although very slowly. The contradiction between the statement of PERSONNE that from Sn + I no $Sn I_2$ is formed and that of HENRY, who states that a mixture of $Sn I_4$ and $Sn I_2$ is formed, is now explained. HENRY has evaporated $Sn I_4$ with an excess of fine tin powder and so obtained a partial conversion into $Sn I_2$ which was

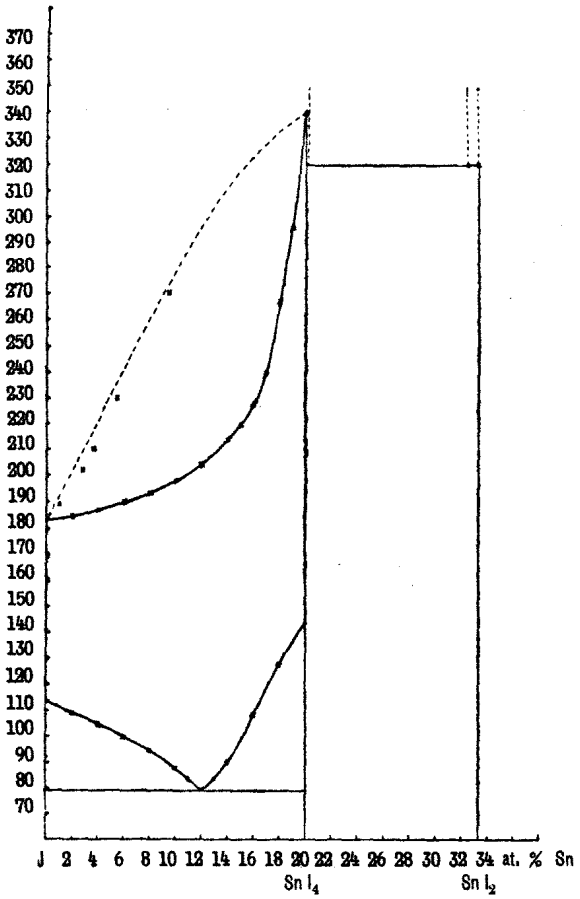

Fig. 1.

left on evaporation. PERSONNE allowed but a short time for the reaction and took no particular care to accelerate the same by addition of an excess of fine tin powder, and so he got no appreciable quantities of $Sn I_2$.

By this conversion is now indicated also another method for the preparation of $Sn I_2$, namely, prolonged heating of $Sn + Sn I_4$ in a sealed tube at a high temperature (360°).

It appears that $Sn I_2$ and $Sn I_4$ then form two liquid layers, a bottom layer of $Sn I_2$ and an upper layer of $Sn I_4$. In order to promote the reaction it is, therefore, necessary to keep on shaking the tube so as to bring the $Sn I_4$ into contact with the Sn. By placing the tube, at the end of the heating operation, in a vertical position, and then allowing it to cool, we obtain, after solidification a crystalline stick which can be readily removed from the tube and breaks up along a fairly sharp meniscus into a SnI_2 and a SnI_4 piece. By strongly heating in a test tube of hard glass, the $Sn I_2$ can be freed from the adhering $Sn I_4$.

The analysis of the SnI_2 thus prepared gave 31.6 and 31.2 % of tin instead of the theoretical quantity (31.9).

5. The melting point of SnI_2 was determined by heating and cooling in a small electric furnace consisting of a cylindric little pot of porous earthenware, surrounded by a nickel heating wire and placed in a similar larger pot which was then filled up with asbestos. **The melting point was found at 319°—320°.**

The boiling point of SnI_2 was determined in a 25 cm. long hard glass tube 3—4 cm. in diameter, the upper part of which was thoroughly isolated by a thick layer of asbestos and could be heated electrically by a nickel wire, whilst the lower part, which contained the SnI_2 was heated strongly either electrically or with the blow-pipe. The temperature was measured with a standard Pt-PtRh thermocouple.

The mean of many determinations was 720°.

6. Addition of SnI_4 or Sn had no perceptible influence on the melting point of SnI_2. These substances, when by the side of SnI_4, form a second liquid phase, so that above 320° there are two regions of decomposition, one between SnI_4 and SnI_2 and one between SnI_2 and Sn. The fused SnI_2 lies in a narrow region of homogeneous mixing.

In order to determine the limits of these regions of decomposition, SnI_2 and SnI_4 were heated in a narrow sealed tube and shaken for an hour at 350° in an electric tube furnace. The apparatus was then placed in a vertical position, the tube was removed and rapidly cooled in a current of air. The solidified SnI_2 and SnI_4 layers were separated from each other, well scraped and then analysed.

The SnI_4 layer. The total tin content was 18.95 and 19.02, mean 18.99, which corresponds to pure SnI_4. The solubility of SnI_2 in SnI_4 is therefore, practically *nil.* This result was confirmed by dissolving a portion of the upper layer in carbon disulphide and after adding iodine, titrating the excess of the latter with sodium thiosulphate; only 0,06 % of SnI_2 was thus found.

The SnI_2 layer. The total tin content amounted to 31.2 and 30.9 %, mean 31.1 %; SnI_2 requires 31.9 % of tin. This analysis therefore points to a 6 % SnI_2 content. This figure must probably be considered as a maximum. During the fusion the SnI_4 penetrates between the glass and the SnI_2 layer so that after cooling, this is enveloped by a thin layer of SnI_4 which might be not completely removed in some places. The fact that addition of SnI_4 does not

perceptibly affect the melting point of SnI_2 shows that the solubility of SnI_4 in this layer is very trifling.

The SnI_2 layer saturated with Sn. SnI_2, prepared by shaking molten SnI_4 with Sn, did not differ in colour from that which had been prepared by the net process and fused afterwards. A solubility of Sn in SnI_2 did not make itself conspicuous by a darker colour, or as LORENZ [1]) describes it by a "Metallnebel". The analysis of fused SnI_2 which had been heated with Sn for some time at 350°—400° and then poured off from the molten metal, also did not differ perceptibly from that of pure SnI_2. The solubility of Sn in SnI_2 is, therefore, exceedingly small. This is in agreement with the determinations of the solubility of Sn in SnI_2 by R. LORENZ [2]), who found that at 629° this is only 0.13 % more than at 400°, so that, at 350°, it may be safely taken as practically *nil.*

7. The boiling point of SnI_4 was determined at 340°; EMICH has stated it to be at 341°. These determinations therefore tally, and the previous statement by PERSONNE (295°) must be rejected as being inaccurate.

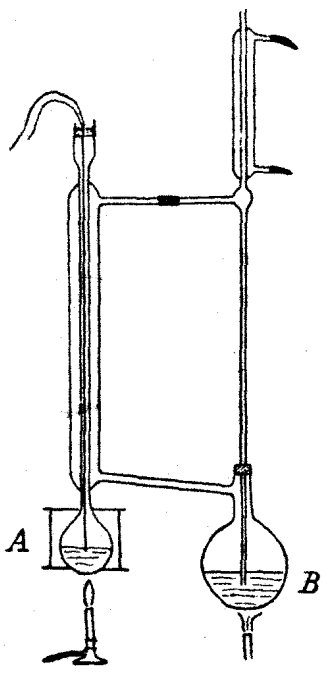

Fig. 2.

8. The boiling points of mixtures of I and SnI_4 were determined in the apparatus drawn in Fig. 2. This consisted of a round-bottomed flask A of ± 100 cc capacity, half way filled with the boiling mixture and protected by an asbestos case in the bottom of which a circular opening was made. The boiling flask can then be heated over the naked flame without danger of superheating.

To the flask was sealed a vertical tube surrounded by a jacket which was heated up to 140° by xylene vapour from B. This prevented the vapour from A from forming a solid deposit in the tube; it condensed to liquid and was collected again in A.

If, after long boiling, the iodine vapour had diffused too much towards the upper part of the apparatus, the heating of A was suspended and all the iodine reentered the flask. The apparatus

[1]) R. LORENZ. Die Elektrolyse geschmolzener Salze.
[2]) R. LORENZ. Die Elektrolyse geschmolzener Salze II, 77.

gave great satisfaction. Not a trace of vapour was lost and by adding every time weighed quantities of SnI_4 or I and starting from the pure components or of a mixture of known composition, a whole series of determinations could be carried out.

The temperature was recorded by means of a previously standardised thermo-couple of silver-constantan which was plunged into the boiling liquid.

The results are united in the following table.

Composition of the liquid.		Boiling point.
gr. SnI_4 per 100 gr. SnI_4+I	at. Sn per 100 at. Sn+I	
0	0	183
10	2.02	184
20	4.04	187
30	6.05	190
40	8.06	193
50	10.06	198
60	12.06	204
70	14.05	214
75	15.05	219.5
80	16.04	228
85	17.03	240
90	18.02	267
95	19.01	296
100	20.00	340

9. Finally, we endeavoured to determine the composition of the saturated vapour which coexists with the different SnI_4 – I mixtures.

For this purpose the liquid was heated to boiling in a 25 c.m. long circular tube surrounded at its upper end by a thick asbestos jacket. In the vapour space was then placed a long suction tube with a pipette-like enlargement of 1—2 c.c., capillarily drawn out and bent upwards at the lower end. By means of this tube some vapour close above the surface of the boiling liquid was withdrawn; this condensed for the greater part in the pipette and was then

analysed. Although these determinations have only a qualitative value, we still think it worth while to communicate the result.

Boiling point	Composition of the liquid.		Composition of the vapour.	
	in % SnI_4 by weight	in at. % Sn	in % SnI_4 by weight	in at. % Sn
185	13	2.6	2	0.4
189	27	5.4	5	1.0
201	55	11.0	14	2.8
210	66.5	13.3	18	3.6
230	81	16.2	28	5.6
270	91	18.2	48	9.6

Summary of results.

1. The melting point of SnI_4 is 143,°5, the boiling point 340°. The melting point of SnI_2 is 320°, the boiling point 720°.

2. In the action of Sn on I, there is at first an exclusive formation of SnI_4. The reaction $SnI_4 + Sn = 2\,SnI_2$ takes place with extreme tardiness and even at 350° it still proceeds at a very slow rate.

3. The melting point line of mixtures of SnI_4 and I consists of two branches with a eutecticum at 79°,6 and 60 % by weight of SnI_4 (12,06 at. % Sn). The boiling point line takes a regular course without a maximum or a minimum.

4. Fused SnI_2 and SnI_4 form two liquid layers, the composition of which at 350° is: SnI_4 with traces only of SnI_2 and SnI_2 with at most 6 % of SnI_4. As Sn also is not perceptibly soluble in molten SnI_2, this lies in a very narrow region of homogeneous mixing which, at 350°, extends from 33,3 at. % Sn (pure SnI_2) to 32,5 at. % Sn (SnI_2 + 6 % by weight of SnI_4).

Inorg. Chem. Laboratory
Technical High School.

Delft, June 1912.

Chemistry. — *"The distribution of dyestuffs between two solvents. Contribution to the theory of dyeing."* By Prof. W. REINDERS and D. LELY Jr. (Communicated by Prof. F. A. H. SCHREINEMAKERS.)

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

For the explanation of the absorption and retention of dyestuffs by fibres there exist three theories; the chemical theory, the theory of solid solution, and the mechanical or adsorption theory.

According to the first theory [1]) the colouring matter enters into a chemical reaction with a constituent of the fibre with formation of an insoluble product, which is retained in the fibre. This constituent — according to KNECHT, lanolinic acid in wool and sericinic acid in silk — is supposed to have the character of an amphoteric electrolyte and, therefore, to be capable of forming a salt with the base of the basic dyestuffs as well as with the acid of the acid dyestuffs.

An important argument in favour of this theory is the observation that when dyeing with basic dyestuffs there first occurs a dissociation into base and acid, the former then being absorbed by the fibre and the latter retained in the bath.

But it appears, however, that this dissociation also takes place in the absorption of dyestuffs by cotton, by pure cellulose [2]) and by inorganic matters such as glass, asbestos, silicates [3]), and carbon [4]) in which substances we surely cannot assume the presence of an acid capable of forming a salt with the dissociated base.

Moreover, the occurrence of such a dissociation in the case of acid dyestuffs is still doubtful [5]), and it also does not take place with the substantive colouring matters which are absorbed in their entirety. The chemical method of explanation is here a complete failure.

We also might be led to expect that the amount of colouring matter that can be absorbed by a certain fibre would be determined by the quantity of acid or base in that fibre. Only so much colouring matter ought to be taken up as is equivalent to this content in acid or base and a further addition of colouring matter to the bath should not cause any further absorption of the dyestuff by the fibre. More-

[1]) KNECHT, Berl. Ber. **21**, 1556, 2804; **22**, 1120 (1889). SUIDA, Sitzungsber. der K. Akad. d. Wiss. Wien. **113** II_B, 725 (1904); Z. f. angew. Chem. 1909, 2131.

[2]) KNECHT, Färberzeitung **18**, 22 (1893/94).

[3]) GEORGIEVICS, Färberzeitung **19**, 9, 129, 188, 286 (1894/95).

[4]) FREUNDLICH und LOSEV. Z. f. physik. Chem. **59**, 284 (1907); LOSEV, Inaug Dissert. Leipzig 1907, p. 45.

[5]) LOSEV, l. c. p. 67.