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**Chemistry.** — “*On Phenyl Carbaminic Acid and its Homologues*”.

By Prof. F. E. C. SCHEFFER. (Communicated by Prof. BÖESEKEN.)

(Communicated in the meeting of September 29, 1918).

1. *Introduction.*

It was observed by DITTE in 1887 that under high pressure and at temperatures lower than room temperature aniline with carbonic acid can react under formation of a solid compound which consists of equal molecular quantities of aniline and carbonic acid <sup>1)</sup>. It may besides be inferred from his paper that unmixing takes place at ordinary temperature. Some years ago Dr. J. J. POLAK carried out a number of experiments with the same system of substances in the organic chemical Laboratory of the Amsterdam University <sup>2)</sup>; he too succeeded in ascertaining the existence of a compound, and the result of his analysis pointed to the same composition as was given by DITTE. It further appeared in his researches that the compound melts on being heated in the presence of a liquid and a vapour rich in carbonic acid, before the meniscus liquid-vapour disappears, with formation of a second liquid layer; this suggested the thought to me that the system aniline-carbonic acid would present an analogy in its behaviour with BAKHUIS ROOZEBOOM's gas-hydrate systems and with the system sulphuretted hydrogen-water, the phenomena of which I have fully described in These Proceedings <sup>3)</sup>. It will appear from the below-mentioned observations that the compound, which in my opinion is to be considered as a carbaminic acid, gives rise in the P-T diagram to the appearance of a quadruple point, where solid compound, two liquid layers, and gas coexist, and that the three-phase lines which intersect in this quadruple point, can be determined with sufficient accuracy. This system also furnishes a new application of the quadruple point rule, drawn up by me in 1912 <sup>4)</sup>, which was described by SCHREINEMAKERS in the Zeitschrift für physikalische Chemie almost at the same time <sup>5)</sup>.

<sup>1)</sup> Compt. rend **105**. 612. (1887).

<sup>2)</sup> Not published. The results of his research have been kindly put at my disposal by Dr. POLAK, for which I gladly express my indebtedness to him here.

<sup>3)</sup> These Proc. **13**. 829 (1910/11) and **14**. 195 (1911/12)

<sup>4)</sup> These Proc. **15**. 389 (1912/13).

<sup>5)</sup> Zeitschr. f. physik. Chem. **82**. 59 (1913).

I further extended this investigation to the three toluidines, and I have succeeded in determining the limits of existence of three compounds. I have determined the composition of two of these compounds by analysis; the composition of the third had already

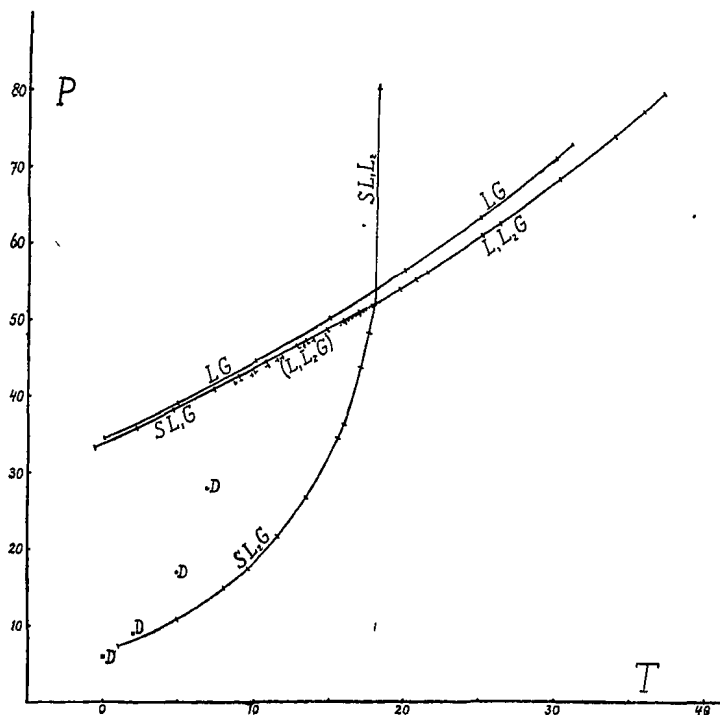


Fig. 1.

been found by DITTE. The great analogy between the three systems will probably justify the conclusion that these compounds are the three isomer tolyl carbaminic acids.

2. *The system aniline-carbonic acid; the phenyl carbaminic acid.*

From "anilin purissimum" of MERCK coloured red by contact with the air a middle fraction was separated by fractionation; a slight quantity of this was put into the Cailletet tube by the aid of a long glass capillary. As a test tube I used a tube with a widened upper end of the same shape as in my researches on the systems ether-water and hexane-water<sup>1)</sup>. For the filling with carbonic acid the test tube was connected with a ground piece to an apparatus consisting of a generating apparatus for carbonic acid, which was obtained from diluted sulphuric acid and sodium bicarbonate, and was dried with phosphorus pentoxide,

<sup>1)</sup> These Proc. 15. 380 (1912/13),

<sup>2)</sup> These Proc. 16. 404 (1213 14).

an apparatus for a high vacuum, consisting of a vessel with cocoa-nut carbon and a GEISSLER tube, a tube for condensation of the carbonic acid (by the aid of liquid air) and a vessel of about  $\frac{1}{2}$  liter capacity as carbonic acid reservoir<sup>1)</sup>. As it was exclusively my purpose in these experiments to determine three-phase pressures, a determination of the concentration of the mixtures used was superfluous. For the first observation I used a mixture with great excess of carbonic acid. When the test tube had been screwed on to the pressure cylinder after the filling, and the mixture had been heated to the ordinary temperature, it appeared that the solid substance could be kept at ordinary temperature only under high pressure. When the available volume was so small that there was only a small quantity of gas present, then a three-phase equilibrium of compound by the side of a thinly liquid layer (rich in carbonic acid) and gas occurred at the ordinary temperature at a pressure of about 50 atmospheres. When the pressure was diminished, the liquid vanished with violent boiling, and solid remained by the side of gas. Below 30 atmospheres the solid substance decomposed with formation of a liquid rich in aniline, a strong generation of gas being perceptible in this layer. Accordingly the solid compound is decomposed into liquid and gas on decrease of pressure. It is clear that the pressure at which this decomposition just sets in indicates the three-phase coexistence of compound, liquid rich in aniline, and gas. On increasing enlargement of the volume there remains coexistence of liquid by the side of gas. At the ordinary temperature the existence of phenyl carbaminic acid is, therefore, only possible at pressures above about 30 atmospheres. Hence in perfect analogy with the gas hydrates the dissociation tensions of this compound are three phase equilibria. This applies also to the determinations which DITTE carried out by observation of the pressure at which gas begins to form from the crystals, or of the pressure at which this generation ceases, which are of course theoretically the same, but practically different according to DITTE<sup>2)</sup>. DITTE ascribes the latter to inaccuracies of the temperature determination, in my opinion the slowness of the transformation  $S \rightarrow L + G$  is undoubtedly responsible for this. In my former researches on the system sulphuretted hydrogen-water I have also been able to observe such a slow transformation<sup>3)</sup>.

In order to be able to determine the three-phase pressures

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<sup>1)</sup> Cf. also These Proc. 13. 830 (1910/11).

<sup>2)</sup> loc. cit.

<sup>3)</sup> loc. cit.

accurately, I have adjusted a wide cylindrical vessel narrowed at the lower end round the test tube, in which vessel alcohol was stirred by means of vertically moving leaden plates; the heating took place electrically; cooling was effected by introduction of solid carbonic acid. In the observations with small volume it now appeared that the maximum temperature at which the compound can exist by the side of gas, is about  $18^{\circ}$ . The quadruple point lies at this temperature; the pressure is about 52 atmospheres. In this point there is intersection of the three-phase lines S (compound),  $L_1$  (liquid rich in carbonic acid), and G (gas), which is stable at temperatures below the quadruple point, and cannot be prolonged above the quadruple point,  $S + L_1 + G$ , which exhibits a value of  $\frac{dp}{dT}$  which rapidly increases with the temperature in the neighbourhood of the quadruple point,  $L_1 + L_2 + G$ , which indicates stable equilibria above the quadruple point, but can also be easily determined below the quadruple point; then these equilibria are, however, metastable with respect to the solid phase. The fourth three-phase line  $S + L_1 + L_2$  rapidly moves from the quadruple point to higher pressure. The situation of the three-phase lines is indicated in fig. 1 by the letters given above; the quantitative data have been collected in table 1; they have been obtained with two mixtures; one contained a great, the second a small excess of carbonic acid; the determinations carried out with the two mixtures, are in good agreement. When the figure is consulted the phenomena described in the beginning of this paragraph will be clear. As long as gas is present, the solid compound can only exist for pressures which are higher than the three-phase line  $SL_2G$ . DITTE's determinations, which are indicated both in the figure and in the table by the symbol D, appear to depart perceptibly from mine; only in the neighbourhood of  $0^{\circ}$  do the observations agree fairly well. It makes the impression that DITTE has determined the points where solid substance is formed on increase of pressure, and that the pressures have been found much too high through the retardation of the transformation  $L + G \rightarrow S$ , though DITTE mentions that he observed the pressures at which the generation of gas ceased. In this respect the phenomena are again in perfect analogy with the system sulphuretted hydrogen-water, where CAILLETET and BORDET's observations present analogous deviations with mine. <sup>1)</sup> DITTE does not lay claim, however, to great accuracy for his observations; he states that his determinations give

<sup>1)</sup> These Proc. 13. 833, fig. 2 and table on p. 834. (1910/11).

only rough values, but that they may yet give an impression of the way in which "aniline carbonate" dissociates.

TABLE 1.

LG(CO <sub>2</sub> )		L <sub>1</sub> L <sub>2</sub> G		SL <sub>2</sub> G	
T	P	T	P	T	P
0	34.4	8.7	41.8	0	6 D
5.0	39.0	9.8 <sup>5</sup>	42.8	0.9 <sup>5</sup>	7.4
10.1	44.6	10.0	43.2	2	9 D
15.0	50.2	10.9	43.9	5.0	10.9
20.0	56.6	11.5	44.8	5	17 D
25.0	63.4	11.8 <sup>5</sup>	45.1	7	28 D
30.0	71.1	13.2 <sup>5</sup>	46.6	8.1	15.0
31.1	72.9	13.9 <sup>5</sup>	47.4	9.7	17.5
SL <sub>1</sub> G		16.0	49.7	11.6	21.7
		16.9 <sup>5</sup>	50.8	13.5	26.7
T	P	17.8	51.8	15.5	34.6
		19.7	54.1	15.9	36.4
-0.6	33.3	20.7	55.4	17.1	43.8
+2.2	35.7	21.5	56.3	17.6	48.3
4.7	38.1	25.1 <sup>5</sup>	61.1	SL <sub>1</sub> L <sub>2</sub>	
7.4	40.8	26.3	62.7		
9.0	42.5	30.2 <sup>5</sup>	68.4	T	P
10.8	44.4	33.9	74.0		
12.8	46.5	35.8	77.1	18.0	52
13.4	47.3	37.1 <sup>5</sup>	79.5	18.2	80
14.8	48.6				
15.9	49.8				
16.9 <sup>5</sup>	50.9	Quadruple point		18.0°	52.0 atm.

When we pursue the three-phase line L<sub>1</sub>L<sub>2</sub>G towards higher temperature, the fluidity of the upper layer becomes greater and greater, and at 37° the critical phenomenon presents itself; the critical end-point lies 6° and about 7 atmospheres higher than the critical point of carbonic acid. We further derive from the figure that the three-

phase tension  $L_1L_2G$  begins to depart more from the carbonic acid tension with increasing temperature; at the quadruple point the deviation amounts almost to 2 atmospheres; at the critical point of carbonic acid to about  $3\frac{1}{2}$  atmospheres.

It follows from the already mentioned quadruple rule, which I formulated before as follows: *The region that does not possess metastable prolongations of threephase lines in the P.-T.-projection, is that of coexistences of phases of consecutive concentration*<sup>1)</sup>, that the region between  $SL_1G$  and  $SL_2L_2$  satisfies the above mentioned condition. In this region, which besides by the two mentioned three-phase equilibria is also bounded by  $SL_1G$  and  $L_1L_2G$  resp. by  $SL_1L_2$  and  $SL_2G$ , the coexistences occur of the two phases which the adjoining three-phase equilibria have in common, hence in this case  $S + L_1$ ,  $L_1 + G$ , and  $S + L_2$ . As these coexistences according to the rule mentioned must refer to phases which succeed each other in concentration, the succession is  $GL_1SL_2$ ; the concentration of the compound lies, therefore, between that of the two coexisting liquid layers. Hence the transformation  $S \rightleftharpoons L_1 + L_2$  takes place on the three-phase line  $SL_1L_2$  in the neighbourhood of the quadruple point.

3. In order to get acquainted with the concentration of the compound Dr. POLAK has caused a weighed quantity of aniline to act on an excess of carbonic acid in a fused-to tube at the ordinary temperature. After the compound had been formed the tube was opened again at  $-80^\circ$ , and placed in a bath of about  $-60^\circ$ ; after half an hour the tube was again fused to, and weighed after having been heated to the ordinary temperature. This analysis yielded the concentration  $C_6H_5NH_2 \cdot 1.01 CO_2$ .

I have carried out three analyses in a way that differs but little from that described here; the method of investigation was the same as that which I have described in my second paper on the system sulphuretted hydrogen-water<sup>2)</sup>; the excess of carbonic acid was sucked off at  $-80^\circ$  by means of a waterjet pump. For the quantity of carbonic acid in gramme-molecules which combines with one mol. of aniline, was found successively 0.98, 0.99, and 0.98. The compound consists, therefore, of an equal number of molecules of aniline and carbonic acid.

#### 4. *The system o-toluidin-carbonic acid; the o-tolyl-carbaminic acid.*

Also in the system o-toluidine-carbonic acid I have been able to ascertain the formation of a compound; the quadruple point lies here,

<sup>1)</sup> loc. cit.

<sup>2)</sup> loc. cit.

however, at lower temperature. As the inquiry into the equilibria

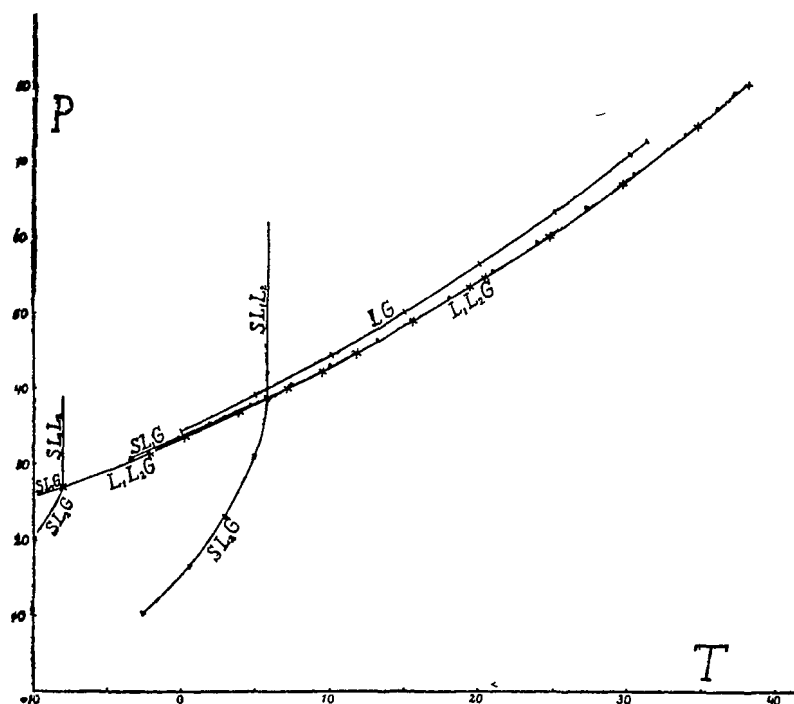


Fig. 2.

at low temperatures is attended with experimental difficulties, I have rested satisfied with the determination of the quadruple point and of the three-phase line  $L_1L_2G$  with the critical end point. The found three-phase pressures are recorded in table 2 and indicated in fig. 2

TABLE 2.

$L_1L_2G$			
T	P	T	P
-2.1	31.5	19.4	53.5
+0.3	33.6	20.4	54.8
3.9	36.8	24.7	60.1
7.3	40.1	29.6	67.1
9.5	42.3	34.5	74.9
11.8	44.7	38.1	80.8
15.6	49.0		
Quadruple point		-7.5°	27.5 atm.



by crosses. At temperatures below the quadruple point a compound again occurs, which has also already been observed by DITTE, and which according to him consists of equal molecular quantities of o-toluidine and carbonic acid. I myself have not determined the concentration of this compound; the application of the above described method of analysis is accompanied with pretty great difficulties at the low temperatures. The possibility that the solid substance should be pure o-toluidine is excluded, because the quadruple point lies at higher temperature than the melting-point of the pure substance. (Cf. table 5).

5. *The system m-toluidine-carbonic acid, the m-tolyl carbaminic-acid.*

There occurs a quadruple point  $SL_1L_2G$  in the system m-toluidine-carbonic acid at a temperature which lies between that of o-toluidine-carbonic acid and that of aniline-carbonic acid. The three-phase lines have again the same relative situation as was described above. The observations referring to the three-phase lines  $L_1L_2G$ ,  $SL_1G$  and  $SL_2G$  are recorded in table 3 and indicated in figure 2 by triangles. In this figure are also found the vapour tensions of pure carbonic acid (see table 1).

6. The analysis of the compound according to the method

TABLE 3.

$L_1L_2G$		$SL_2G$		$SL_1G$	
T	P	T	P	T	P
7.5	40.5	-2.6	10.4	-3.4	30.8
10.0	43.1	+0.6	16.5	-0.2	33.4
13.2	46.4	2.9	23.1	+1.9	35.3
15.5	49.2	5.0	31.5	2.9	36.2
18.0	52.1			4.7	37.7
20.9	55.7			5.7	38.6
23.9	59.5				
27.3 <sup>5</sup>	64.2				
30.3	68.5				
33.7	73.8	Quadruple point		6.3 <sup>o</sup>	39.2 atm.
35.8 <sup>5</sup>	77.4				
37.2	79.6				

mentioned in § 3 yielded varying values in contrast to those of aniline and of p-toluidine, as will appear in § 8. For the quantity of carbonic acid which combines with one molecule of m-toluidine, was found successively 0.76, 0.79, 0.85, 0.86, 0.88, 0.88, 0.93, 0.89, 0.86, 0.92, and 0.89 mol. These values for the carbonic acid content are most probably all too small. The cause of this deviation is in my opinion the following: Liquid carbonic acid and m-toluidine are little miscible. Accordingly the formation of the compound on cooling takes chiefly place on the boundary of the two layers. In consequence of this a partition of solid substance is continually formed, separating the two layers. Part of the toluidine can, therefore, be withdrawn from the action of carbonic acid. It is clear that after the excess of carbonic acid has been sucked off, the quantity of bound carbonic acid is found too small. In order to render the formation as complete as possible, the tubes were kept in ice for several days; in the successive determinations this period increases from 2 to 10 days. It appears, therefore, that the time has not much influence on the result of the analysis. In the last determination the tube was cooled for 7 hours with ice and salt ( $-15$  to  $-20^{\circ}$ ); it also yields too low a result. The supposition that the m-toluidine should be impure, appeared erroneous, as the correct value of  $65^{\circ}$  was found for the melting-point of the acetate compound. I think I am justified in concluding from the above-mentioned determinations that the compound likewise consists of equal molecular quantities of toluidine and carbonic acid.

7. *The system p-toluidine-carbonic acid; the p-tolyl carbaminic acid.*

In the P-T-diagram the system p-toluidine-carbonic acid yields a three-phase line  $L_1L_2G$ , which deviates little from that of the said systems. (Cf. fig. 3). The quadruple point  $SL_1L_2G$  lies here at higher temperature; the four three-phase lines which intersect in this quadruple point, are indicated in fig. 3; the quantitative data in table 4. The relative situation of the four phases is the same here as in the preceding systems. The stable part of the three-phase line  $SL_2G$  terminates at lower temperature in a second quadruple point  $SS_BL_2G$  ( $S_B$  is solid p-toluidine). In the preceding systems the corresponding quadruple point lies at lower temperature and pressure; in this system the temperature of the two quadruple points differs little from the critical temperature of carbonic acid. The three-phase lines  $SL_2G$  and  $S_BL_2G$  are easy to determine, when we heat at constant pressure and read the temperature at which liquid is formed. Without further examination we may state about the three-phase

line  $SS_B L$ , that the slope will be steep. Of three of the three-phase lines that pass through the quadruple point  $SS_B L_2 G$  the situation

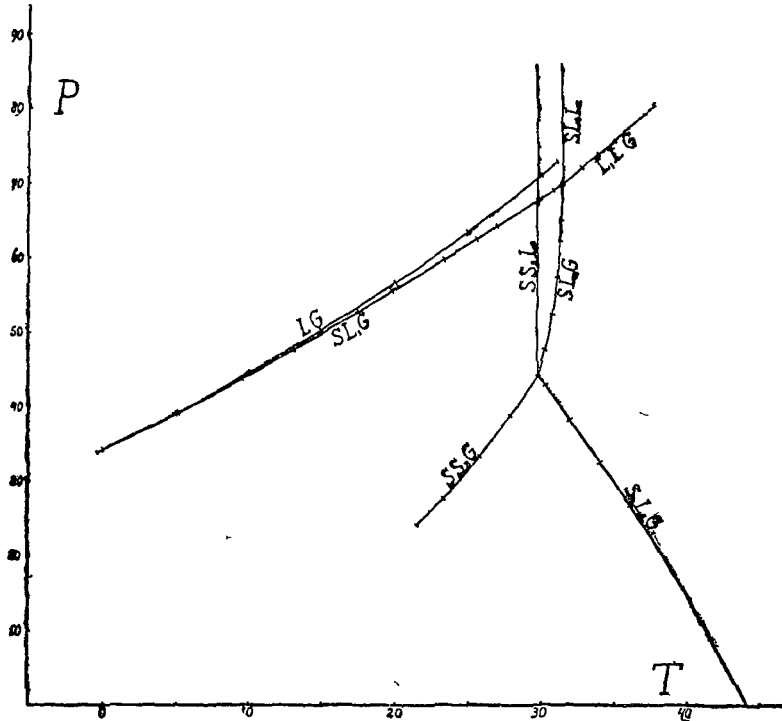


Fig. 3.

could, therefore, easily be given. The fourth three-phase line  $SS_B G$  was, however, difficult to find. The quadruple point rule mentioned, however, gave me an indication where it was to be found. There exist two possibilities for the situation of this fourth three-phase line, which are represented by fig. 4a and b. The three-phase line

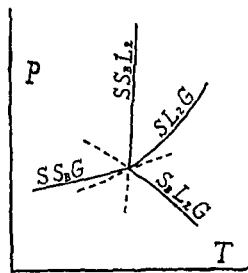


Fig. 4a.

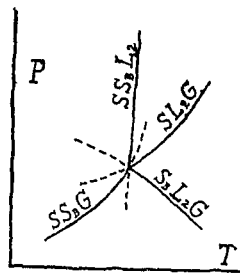


Fig. 4b.

$SS_B G$  must namely lie between the metastable prolongations of  $SL_2 G$  and  $S_B L_2 G$  (fig. 4a) or between those of  $SL_2 G$  and  $SS_B L_2$  (fig. 4b). Other situations are impossible, because else two-phase coexistences

would occur with an angle larger than  $180^\circ$ ; I have set forth in the mentioned paper that this is impossible. When with the aid of the quadruple point rule we examine what succession of the phases would appear according to fig. 4a, it appears that no metastable prolongations occur between  $SS_B L_2$  and  $SL_2 G$ , that the two-phase coexistences in this region are:  $G + S$ ,  $S + L_2$  and  $L_2 + S_B$  and that the succession of the phases is given by  $GSL_2 S_B$ .

In an analogous way it would follow from fig. 4b that the order of the phases would be  $SGL_2 S_B$ . This order indicates diminishing carbonic acid content, because  $S_B$  represents solid p-toluidine. That the compound  $S$  would be richer in carbonic acid than the gas phase, which practically consists of pure carbonic acid, is excluded; p-toluidine has a very slight vapour tension (b.pt.  $200^\circ$ ) at this temperature, and the content of p-toluidine in the vapour is, therefore, very small. The only possibility is, therefore, given by fig. 4a. I have, therefore,

TABLE 4.

$SL_1 G$		$L_1 L_2 G$		$SL_2 G$	
T	P	T	P	T	P
-0.4	33.9	32.8	72.0	30.2	47.7
+5.1	39.1	33.9	73.9	30.8	52.5
9.6	43.6	35.0 <sup>s</sup>	75.7	31.1	57.3
13.1	47.6	37.7 <sup>s</sup>	80.4	31.3	62.2
17.5	52.7	SSB G		31.4	65.0
19.8	55.5			S <sub>B</sub> L <sub>2</sub> G	
23.3	59.8	T	P		
25.6	62.4	21.5	24.2		
27.0	64.3			23.3	27.6
29.7	67.7	25.8	33.4	32.0	38.2
30.8	69.0	27.9	38.8	34.0	32.5
				36.2	26.8
Quadruple point		$SL_1 L_2 G$		31.5°	70 atm.
		$SS_B L_2 G$		29.7°	44 atm.

tried to find the required three-phase equilibrium in the region between

the metastable prolongations of  $SL_2G$  and  $S_B L_2G$ . The determinations were difficult; the only way to find the equilibria was by examining whether rise of pressure or descent of pressure takes place at constant temperature after some lapse of time. It is clear that below the three-phase line  $SS_B G$  (fig. 4a) the two-phase coexistence  $S_B + G$  is found, and above it  $S + G$  and  $S + S_B$ , because  $S$  with regard to its concentration lies between  $G$  and  $S_B$ , and the coexistence of the two solid substances will extend towards higher pressure<sup>1)</sup>. Hence the transformation  $S_B + G \rightleftharpoons S$  occurs on the three-phase line. The upper arrow indicates the conversion on diminution of volume, the lower one on expansion. When at a definite temperature a fall of the pressure takes place, we are above  $SS_B G$ ; when the pressure increases, we are below  $SS_B G$ . In this way an upper and a lower limit was found, which were no further apart than one atmosphere, sometimes some tenths of an atmosphere. The slowness of the transformation rendered this method of working necessary; the lower limit was found to yield values which were better reproducible than the upper one. The explanation of this is in my opinion to be found in the fact that the transformation  $S \rightarrow S_B + G$  takes place more easily than the opposite one. This is self-evident, as the action of  $G$  on  $S_B$  can exclusively take place on the boundary of the two phases, and formation of a phase  $S$  can stop the action. Accordingly the values of the lower limit are recorded in table 4; besides, the upper limit often differs no more than a fraction of an atmosphere from the lower one, as has been said. The relative situation of the three-phase lines is actually that which was predicted with the aid of the quadruple point rule.

8. The analysis of the compound did not present any difficulties. The results of the analyses were resp. 1.00, 0.97, and 0.99 mol.  $CO_2$  to 1 mol. p-toluidine. Hence the compound contains equal molecular quantities of the two components.

#### 9. Summary of the results.

The four examined systems yield pretty well coinciding three-phase lines  $L_1 L_2 G$ . The critical end-points lie close together. The great difference between the systems consists only in the situation of the quadruple points. In table 5 the four systems are arranged

<sup>1)</sup> This can also be immediately derived from the relative situation of the three-phase lines in fig. 4a.

according to ascending quadruple point temperatures. The order in temperature is the same as that in pressure.

TABLE 5.  
Quadruple points  $SL_1L_2G$ .

o-toluidine		m-toluidine		aniline		p-toluidine	
T	P	T	P	T	P	T	P
-7.5	27.5	6.3	39.2	18.0	52.0	31.5	70
Melting points.							
m-toluidine		o-toluidine		aniline		p-toluidine	
-30		-15		-7		44	

This is indeed also necessary on account of the coincidence of the  $L_1L_2G$  lines.

The order of the melting-points of the pure components deviates from this only in so far that *m*-toluidine and *o*-toluidine have exchanged places. I have determined the four melting-points given in table 5 myself. That of *m*-toluidine was not known, as far as I could find out; that of *o*-toluidine agrees with the observation by KNOEVENAGEL<sup>1)</sup>. For the melting-point of aniline we find  $-8^\circ$  given; my value lies somewhat higher; TIMMERMANS' value lies again higher than mine<sup>2)</sup>. I think, however, that I may conclude from the small melting-range presented by my preparation, that the substance was pure. We find  $45^\circ$  for the melting-point of *p*-toluidine in the handbooks; my value is lower, and agrees with HULETT's very carefully executed determination ( $43, 9^\circ$ )<sup>3)</sup>.

The compounds that occur in these systems, contain the components in the ratio 1: 1. I think, therefore, that I have to consider them as carbaminic acids. These compounds were still unknown, only DITTE has evidently observed two of them in his experiments. It is clear from the limits of stability of the compounds, why they have not been found; at ordinary temperature only two of these compounds are possible (phenyl- and *p*-tolylcarbaminic acid). The first decomposes directly into liquid and gas, the second into solid *p*-toluidine and gas, when the tubes are opened.

<sup>1)</sup> Ber 40. 517. (1907). KNOEVENAGEL finds besides the melting-point of  $-15.5^\circ$  another belonging to a metastable modification ( $-21^\circ$ ). TIMMERMANS' determination ( $-24.4^\circ$ ) may refer to this metastable modification.

<sup>2)</sup> TIMMERMANS. Bull. Soc. Chim. Belg. 27. 334. (1914).

<sup>3)</sup> HULETT. Zeitschr. physik. Chem. 28. 650. (1899).

At low temperature they can all exist at ordinary pressure, but the formation will be hampered by the afore-said reason that the compound can put a stop to the action of the two phases (gas and solid) on each other by separation.

It is worthy of note that evidently through the action of aromatic amines on carbonic acids free acids are formed in contrast with ammoniac and the aliphatic amines, which form salts.

Of the said carbaminic acids a few salts are known. When it is tried to obtain the free acids by double conversion with acid, they split up into carbonic acid and the free amines; only at high pressure or low temperature could the free carbaminic acids be formed. Yet it is possible, and even probable that these acids, though they are durable at the ordinary temperature only under increased pressure, occur in the liquids L<sub>1</sub>. The assumption that for certain reactions the carbaminic acids can act as intermediate product, is therefore certainly not to be deemed impossible.

It appears from the P-T-diagrams that the quadruple point of p-tolylcarbaminic acid lies higher than that of phenylcarbaminic acid. Possibly the quadruple point of one of the xylylcarbaminic acids lies at still higher temperature. The as-o-xylylidine certainly invites to further investigation, the quadruple point will probably have shifted here to higher temperature, as the melting-point lies higher than that of p-toluidine. It is possible that for this system the quadruple point has already disappeared; we should then pass to another type of binary systems; in this case the behaviour will become analogous to that of sulphuretted hydrogen-ammoniac, the particulars of which I described on an earlier occasion.<sup>1)</sup>

When we think the quadruple point gradually removed to higher temperature, it will disappear when it coincides with the critical end-point. A gradual change is not to be realized, as the change in constitution takes place discontinuously. It is here, however, possible that by suitable choice of the homologues the displacement takes place in small leaps, and the transition of the type presented by these systems into that of sulphuretted hydrogen-ammoniac appears very clearly.

In his thesis for the doctorate BUCHNER already pointed out the existence of such a transition for systems without compound. I shall describe the phenomena which present themselves in these transformations in a later treatise.

*Delft, August 30<sup>th</sup> 1918.*

*Technical University.*

<sup>1)</sup> Thesis for the Doctorate (1909). Zeitschr. physik. Chemie. 71. 214 and 671. 1910).