

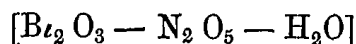
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On the system [formula], in:

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**Chemistry.** — “*On the system: [B<sub>2</sub>O<sub>3</sub>—N<sub>2</sub>O<sub>5</sub>—H<sub>2</sub>O]*”. By Prof. J. M. VAN BEMMELLEN.

Dr. G. M. RUTTEN has occupied himself in the Inorganic chemical Laboratory of the University of Leiden with the investigation of the system



according to the phase rule. He also has, when studying the solid phases, subjected the observations of former investigators (HEINTZ, GLADSTONE, BECKER, JANSSEN, RUGE, YVON, LUDDECKE, DITTE and others) on the basic nitrates and the so-called “Magisterium Bis-muthi” to a critical investigation.

His results were as follows:

#### A. *The solid phases.*

1. *The neutral salt B<sub>2</sub>O<sub>3</sub>. 3 N<sub>2</sub>O<sub>5</sub>. 10 H<sub>2</sub>O* (in future called briefly Z<sub>10</sub><sup>1)</sup>). This formula accepted of late years has been found correct. The salt does not possess a true melting point as formerly stated (72°), but it decomposes at 75°,5 into a liquid and the basic salt B<sub>2</sub>O<sub>3</sub>. N<sub>2</sub>O<sub>5</sub>. H<sub>2</sub>O (B<sub>1-1-1</sub>).

The prismatic, triclinic crystals exhibit an angle of extinction of 26°.

Two further hydrates of the neutral salt were discovered: Z<sub>4</sub> and Z<sub>3</sub>.

II. *The neutral salt Z<sub>3</sub>* (with 3 Mols. of H<sub>2</sub>O). It was obtained at the ordinary temperature from Z<sub>10</sub>, or from B<sub>2</sub>O<sub>3</sub> by addition of anhydrous nitric acid, in regular crystals as beautifully formed rhombic dodecahedrons. It should be mentioned that its composition could not be determined directly, because it was not possible to separate the crystals completely from the syrupy mother liquor. The composition was deduced by means of SCHREINEMAKERS' method of calculating, from the graphical construction in an equilateral triangle of the compositions: 1<sup>st</sup> of two different mother liquors which were in equilibrium with crystals of Z<sub>3</sub>, and 2<sup>nd</sup> of the crystals themselves with some of the mother liquor still adhering. The same applies to the salts presently to be described Z<sub>4</sub> and B<sub>1-2-1</sub>, which also could not be separated from the adhering mother liquor.

III. *The neutral salt Z<sub>4</sub>* (with 4 mols. of H<sub>2</sub>O). A definite mode

<sup>1)</sup> In future the salts which contain 1 mol. of B<sub>2</sub>O<sub>3</sub>, 3 Mol. N<sub>2</sub>O<sub>5</sub> and 10 or 4 or 3 Mol. H<sub>2</sub>O will be briefly called Z<sub>10</sub>, Z<sub>4</sub>, Z<sub>3</sub>; similarly the basic salts will be written B<sub>n<sub>1</sub>-n<sub>2</sub>-n<sub>3</sub></sub> if they contain n<sub>1</sub> Mol. of B<sub>2</sub>O<sub>3</sub>, n<sub>2</sub> Mol. N<sub>2</sub>O<sub>5</sub> and n<sub>3</sub> Mol. H<sub>2</sub>O

of preparing this cannot yet be given. The salt was accidentally discovered when making efforts to realize points of a quadruple line in the system  $[Z_{10}, Z_3, L, G]$  <sup>1)</sup>. The crystals differ from  $Z_3$  and  $Z_{10}$  as they are not regular and have an angle of extinction of  $90^\circ$ .

IV. *Hydrate of Z in a colloidal state.* This was discovered when anhydrous nitric acid was dropped into a mixture of  $Z_{10}$  with a strong solution of Bismuth nitrate. A salt was deposited in the form of transparent jelly which enclosed all the mother liquor. The colloidal state lasted, however, but a short time. Very soon small crystals were deposited which made the impression of octahedrons, perhaps  $Z_3$  or another hydrate. They have not yet been investigated.

V. *The basic salt  $B_{1-2-2}$ .* In one experiment  $Z_{10}$  was decomposed at  $75^\circ$  (which gave rise to the formation of  $B_{1-1-1}$ ), then mixed with  $Z_3$ , heated to  $80^\circ$  and cooled down to  $68^\circ$ . A crystalline salt was produced which differed in form from  $Z_{10}$  and  $Z_3$ , had an angle of extinction of  $40^\circ$ , and the composition  $B_{1-2-2}$ . More analyses are however desirable.

VI. *The basic salt  $B_{1-1-2}$ .* The investigation and the analysis confirmed the fact that this salt is the first product of the action of cold water on  $Z_{10}$ ; also of cold dilute nitric acid containing less than 6 pCt. of  $N_2O_5$  on  $Z_{10}$ ; or of cold water on a not too acid solution of bismuth nitrate. It forms small scales, exceedingly thin crystalline plates without a definite shape and showing double refraction. They are not permanent when they remain in contact with the mother liquor but gradually become converted into another basic salt. It cannot even be dried over sulphuric acid without decomposition. No nitric acid is expelled but it loses water until 0.7 mol. of this is left. This behaviour is not yet explained since  $B_{1-1-1}$  does not lose water over sulphuric acid. The velocity of change and the composition of the basic salt both depend on the concentration of the mother liquor and the temperature. As such basic salts have been found:  $B_{1-1-1}$ ,  $B_{10-9-7}$ ,  $B_{6-5-8(9)}$ . It has not yet been ascertained at what dilution and temperature between  $20^\circ$  and  $75^\circ$  the formation of  $B_{1-1-2}$  by the action of water on  $Z_{10}$  ceases and  $B_{1-1-1}$  is formed (or  $B_{10-9-7}$  or  $B_{6-5-8}$ ).

VII. *The basic salt  $B_{1-1-1}$ .* This salt is formed from  $B_{1-1-2}$ ,

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<sup>1)</sup> L = Solution, G = Vapour.

when this remains in contact with a solution containing more than 1 pCt.  $N_2O_5$ . If the nitric acid amounted to a few percent only the change required some months at the ordinary temperature. When a few more percent were present the time was reduced to a few weeks. The more the strength of the acid approaches the point where the existence of  $Z_{10}$  becomes possible, namely 24.83 pCt. of  $N_2O_5$  with 32.9 pCt. of  $B_2O_3$  at  $20^\circ$ , the more quickly the change will take place. For instance, if it contains 21 pCt. (with 27.15 pCt. of  $B_2O_3$ ) the change only takes a few hours at  $20^\circ$  <sup>1)</sup>. At higher temperatures — between the limits  $9^\circ$  and  $75^\circ$  — the change proceeds proportionally more rapidly.

The crystals thus formed are probably monoclinic and have an angle of extinction of  $10^\circ$ — $15^\circ$ . Their composition was determined by analysis, which had not been done as yet.

When  $Z_{10}$  decomposes at  $75.5^\circ$ , the same salt is formed, but it then has another crystalline form. It forms hexagonal thin prisms which are apparently isotropic but extinguish to the right if they lie on a side plane (salt  $\beta$ ). Analysis gave the composition  $B_{1-1-1}$ . It is also formed, together with the first form (salt  $\alpha$ ), at lower temperatures, such as  $65^\circ$ , from  $Z_{10}$  and a solution. The salt  $\beta$  seems to be more stable than the salt  $\alpha$ ; since in a solution from which the salt  $\alpha$  had first deposited, this was after some time converted into the salt  $\beta$ , the liquid having undergone no perceptible change in composition <sup>2)</sup>.

VIII. *The basic salt*  $B_{6-5-9(8)}$ . This salt is formed (as shown by very concordant analyses) at the ordinary temperature from  $B_{1-1-2}$ , when this remains for some months in contact with a very dilute solution ( $< 1$  pCt. of  $N_2O_5$  and  $< 0.33$  pCt. of  $B_2O_3$ ).

It also crystallises out when  $Z_{10}$  is decomposed by water, and the solid salt which is formed is dissolved in much water. This solution after a short time deposits  $B_{6-5-9(8)}$ . Even when the scales ( $B_{1-1-2}$ ) are left for a long time over water so that they attract moisture and become covered with a layer of liquid, this salt is gradually formed. In one experiment, they were completely converted after the lapse of one year <sup>3)</sup>.

The crystals are bi-axial, optically negative and belong to the

<sup>1)</sup> The crystals of  $B_{1-1-2}$  were shaken in a shaking-apparatus with the solutions for 5 hours.

<sup>2)</sup> Some difference must exist, though a very small one.

<sup>3)</sup> For instance, a dilution obtained by adding 1 part of  $Z_{10}$  to 24 parts of  $H_2O$ .

rhombic system and consequently extinguish to the right. Placed over sulphuric acid they behave like  $B_{1-1-1}$  losing neither nitric acid nor water.

They are also formed at higher temperatures from  $B_{1-1-2}$  or  $B_{1-1-1}$ , even when the solution is still more concentrated, but they then appear as small right — angled rhombic crystals. They are very stable, for they may be boiled for a considerable time with water without losing their transparency. A portion, however, dissolves but again deposits on cooling as  $B_{6-5-9(s)}$ . Larger crystals of the same composition are also formed. When heated for some hours on the boiling waterbath, the crystals become opaque; they have then disaggregated to a minute crystalline powder of  $B_{2-1-1}$ .

The number of mols. of water in the salt  $B_{6-5-9(s)}$  is not yet quite fixed. It varies from 8—9 and it remains possible that there exist two hydrates with 8 and 9 mols. of  $H_2O$  respectively, and that this may account for the small difference in the crystalline form noticed in different preparations. A further investigation must decide.

IX. *The basic salt*  $B_{10-9-7}$ . This compound is nearer to  $B_{1-1-1}$  than the preceding one. By treating  $Z_{10}$  with water a salt answering to this composition was obtained occasionally. The crystals extinguish to the right like  $B_{6-5-8}$ , but still they make another impression; they also exhibit a weaker double-refraction.

On treating  $Z_{10}$  with warm water, not only  $B_{6-5-9(s)}$  but also  $B_{1-1-1}$  and  $B_{10-9-7}$  made their appearance and this appeared to depend on the quantity of water present.

$B_{1-1-1}$	with a quantity of	1—about 3	parts of water to 1 part of $Z_{10}$
$B_{10-9-7}$	> > >	about 3—	> 20 > > > > > >
$B_{6-5-8(9)}$	> > >	20—25 or more	> > > > > $Z_1$

An investigation was instituted to see whether  $B_{10-9-7}$  represented merely a state of transition between  $B_{1-1-1}$  and  $B_{6-5-8}$ , and whether crystals were obtainable which stood nearer to  $B_{1-1-1}$  or to  $B_{6-5-8}$ , but this investigation has not as yet given any positive results.

X. *The basic salt*  $B_{2-1-1}$ . As already stated above this salt was obtained in a crystalline condition as the final product of the action of boiling water on the neutral salt. This is in agreement with the experience of former investigators. The crystals were too small to permit their shape to be properly observed.

XI. *The basic salt*  $B_{5-4-9}$ ,  $B_{4-3-9}$ ,  $B_{5-3-8}$ ,  $B_{5-3-6}$  described by JANSSEN, BECKER, DUFLOS and HERBERGER do not exist. *Following their methods of preparation no other salt than*  $B_{6-5-9}$  (s), *could be obtained* as shown by the crystalline form and the analysis. As the analytical process used by these investigators was faulty as regards the nitric acid, we may assume that they have found too little nitric acid. By a too prolonged washing with hot water (DUFLOS and HERBERGER) they may have had to deal with mixtures of  $B_{6-5-9}$  and  $B_{2-1-1}$ . The said basic salts must therefore, be rejected as long as there is no better proof of their actual existence.

XII. *Magisterium Bismuthi.* The preparation of this pharmaceutical preparation is differently described in the pharmacopaea and chemical manuals and its composition is given wrongly. As all the pharmacopaea direct the decomposition of  $Z_{10}$  with about 20 parts of hot or boiling water, it cannot consist of  $B_{1-1-2}$  or  $B_{1-1-1}$ , but must contain  $B_{6-5-9}$  (s) or  $B_{10-9-7}$ , or a mixture of both, sometimes even  $B_{2-1-1}$ . An investigation showed that different Dutch pharmaceutical preparations answered to the composition  $B_{6-5-9}$  (s) and others to a mixture of this salt with  $B_{10-9-7}$ .

B. EQUILIBRIUMS IN THE SYSTEM [ $B_{12}O_3-N_2O_5-H_2O$ ]  
WITH SOLID AND LIQUID PHASES.

The vapour phase has been altogether left out of consideration so that all results relate to the ordinary atmospheric pressure.

The course of the Isotherms, which indicate the composition of the liquid phases which were in equilibrium with the different solid phases, was totally or partially determined for three temperatures:  $20^\circ-30^\circ-65^\circ$ . Some few points were also determined at  $9^\circ$ ,  $11^\circ$  and temperatures between  $65^\circ$  and  $80^\circ$ .

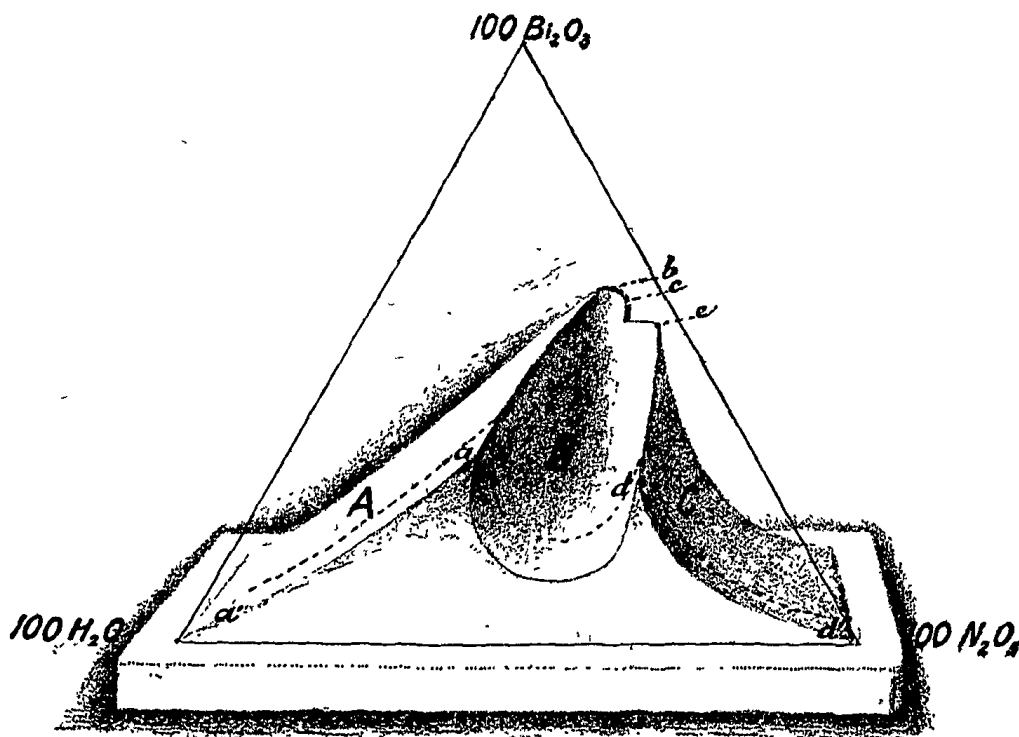
These isotherms were graphically represented in the well-known manner in equilateral triangles; with the aid of these a regular prism was constructed, the length of which answers to the temperature axis <sup>1)</sup>.

In this way a figure in space was formed of which I now present to the meeting a plaster cast, with the following perspective drawing of the same.

The triangle in the front surface of the figure corresponds to a

<sup>1)</sup> The points at the angles of each equilateral triangle (therefore the long sides of the prism) answer to the compositions 100 parts of  $H_2O$ , 100 parts of  $N_2O_5$ , 100 parts of  $B_{12}O_3$ . (See figure.)

temperature of  $9^\circ$ . The point  $b$  which lies furthest-back is situated in the triangle of  $75^\circ.5$ . The equilibria of the system which are possible at these temperatures in the most dilute and the most concentrated solutions, and also the equilibria at temperatures below  $9^\circ$  and above  $76^\circ$  are as yet entirely wanting.



On the isotherm at  $20^\circ$ , the course of the branches was determined where the salts  $B_{6-5-9}$ ,  $B_{1-1-2}$ ,  $Z_{10}$  and  $Z_3$  occur as solid phases in the system. In the figure it is shown by a dotted line. The branch with  $Z_{10}$  is determined at  $30^\circ$ , the branches with  $B_{1-1-1}$ ,  $Z_{10}$  and  $Z_3$  as solid phases are determined at  $65^\circ$ . The courses of two quadruple lines<sup>1)</sup> were also determined.

1. The one ( $a b c$  in the figure) which has the solid phases  $B_{1-1-1}$  and  $Z_{10}$  has been determined between the temperatures  $9^\circ$  ( $a$ ) and  $75^\circ.5$  ( $b$ ) and further back to  $72^\circ$  ( $c$ ). This line shows a temperature maximum at  $75^\circ.5$ , where  $Z_{10}$  is decomposed into  $B_{1-1-1}$  and liquid (p. 198). It then rebends itself. Its backward course has been examined up to  $72^\circ$  ( $c$  in the fig.).

2. The quadruple line which has the solid phases  $Z_{10}$  and  $Z_3$

<sup>1)</sup> The quadruple lines separate the triple surfaces formed by the different isothermal curves of different temperatures.

has been determined between  $9^\circ$  and  $65^\circ$  (points *d* and *e* in the fig.). The region of  $B_{1-1-1}$  (*A* in the fig.) between  $9^\circ$  and  $75^\circ.5$  has been to a great extent explored, but its boundary with the region  $B_{1-1-2}$  and of  $B_{6-5-9(8)}$  is not yet known. The regions of  $B_{1-1-2}$  and of  $B_{6-5-9(8)}$  are situated near the low concentrations. They partly cover or practically coincide with the region of  $B_{1-1-1}$  or with each other, because  $B_{1-1-2}$ , which is the more labile phase, can change in presence of the same liquid into the more stable phases  $B_{1-1-1}$  or  $B_{6-5-9}$ , which causes but very little change in the liquid phase.

The region of  $Z_{10}$ , as a solid phase (*B* in the fig.), has been explored between  $9^\circ$  and  $75^\circ.5$ ; except a small portion at the right of the figure between  $65^\circ$  and  $72^\circ$ , where the region is probably bounded by that of  $B_{1-2-2}$  and that of  $Z_4$ . The missing part lies between *c* and *e* as indicated in the figure by a right angle.

Of the region of  $Z_3$  as a solid phase (*C* in the fig.) only a portion is known: 1<sup>st</sup>. because the quadruple line with  $Z_3$  and  $Z_4$  as solid phases, which must bound it on one side, has not yet been determined 2<sup>nd</sup> because it has not been determined how far the isotherms with  $Z_3$  extend to the right. These have not been continued further than the point, where the liquid phase reaches the strength of 1 mol. of  $N_2O_5$  on 1 mol. of  $H_2O$ . It remains possible that with solutions, which contain less water still,  $Z_3$  is not capable of existence, but that a neutral salt with less than 3 mols. of  $H_2O$ , or an anhydrous salt or a salt with more than 3 mols. of  $N_2O_5$  takes its place. In each case the region of  $Z_3$  must end and pass into another one before the system is reached which consists entirely of  $B_{2O_3}$  and  $N_2O_5$  <sup>1)</sup>.

From this it is evident that the solubility of  $B_{1-1-1}$  increases pretty regularly between the said temperatures with the amount of nitric acid in the liquid phase, but that it again slightly decreases after the temperature maximum of  $75^\circ.5$ . The solutions which are in equilibrium with  $B_{1-1-1}$  differ (as above mentioned) very little from those which belong to  $B_{6-5-9(8)}$ , at least at  $20^\circ$ . The solubility of  $Z_{10}$  between  $9^\circ$  and  $75^\circ$  first decreases rapidly with the increase of nitric acid in the liquid phase, then passes through a minimum and then again increases until  $Z_3$  becomes the solid phase. The solubility of  $Z_4$  decreases rapidly with the increase of the strength of the nitric acid. It is not known whether it also passes through a minimum.

<sup>1)</sup> These systems lie in the graphic representation on the right side plane of the regular triangular prism.



The graphic representation of the experimentally found triple-planes and quadruple-lines in an equilateral triangle (in the well-known manner) allows of the prediction of quite a series of cases of equilibrium. So for example it may be concluded what will happen when a certain quantity of  $Z_{10}$  is treated at a certain temperature (within the observed limits) with increasing quantities of water, i. e. which solid phases are formed and what composition the liquid phase possesses. Also what will happen when a certain quantity of the basic salt  $B_{1-1-1}$  (with or without motherliquor) is treated with increasing quantities of nitric acid of a certain strength, or when the strength of the acid is increased. It may also be concluded which mixtures of  $B_{12}O_3$ ,  $N_2O_5$  and  $H_2O$  may lead at a certain temperature to the formation of one of two above mentioned solid phases, and which changes that mixture will undergo at increasing or decreasing temperatures. And so on.

The isothermal curves at temperatures above  $75.5^\circ$  are not yet determined. This determination will present great difficulties in its execution, particularly in the separation of the solid phases.

The agreement in form of the triple-lines in this system with those of  $[HgO-SO_3-H_2O]$  as determined by C. HOITSEMA (*Zeitschr. physik. Chem.* 1895, 17, 651) is worthy of notice.

**Chemistry.** — Prof. A. P. N. FRANCHIMONT presents to the library of the Academy the dissertation of Dr. L. VAN SCHERPENZEEL entitled: "*The action of hydrogen nitrate (real nitric acid) on the three toluic acids and some of their derivatives*", the contents of which he explains as follows:

The research of Dr. VAN SCHERPENZEEL is connected with that of Dr. MONTAGNE about which I reported last January and was undertaken at the same time. It required the knowledge of a twenty new compounds which have been prepared by Dr. VAN SCHERPENZEEL and are described in his dissertation.

Following up the researches of VAN ROMBURGH in 1885 and of TAVERNE in 1897 and 1898 on the action of nitric acid on benzoic acid and some of its derivatives, such as the methyl ester, the amide and both the methylamides, the question arose what influence would be exercised on the action of the nitric acid by the introduction of an atomic group in different positions into the benzene nucleus. Whilst MONTAGNE had chosen the monochlorinated derivatives and thus