

Citation:

J.J. van Laar, Some remarks suggested by a paper by Messrs. Timmermans and Kohnstamm, in: KNAW, Proceedings, 12, 1909-1910, Amsterdam, 1910, pp. 454-457

piperazino N(di) acetamide by applying HOFMANN's original method or the modified process and therefore chose another way, namely, the reduction of the corresponding nitrile with sodium and alcohol. This nitrile was still unknown, although we were acquainted with the co-related amide the dicarbamino-piperazine or piperazino N₂di carbonylamide (piperazyldi-urea) and the esters of the correlated acid dicarboxyalkyl-piperazine (piperazyldiurethane). The sought nitrile is N(di) cyanopiperazine or *piperazino N(di) formonitrile*. It was prepared from bromocyanogen and piperazine in aqueous solution with addition of alkali. It is sparingly soluble in cold water, but more readily so than its homologue, and insoluble in ether. It crystallises from alcohol in leaflets m.p. 168°, which shine like mother of pearl; from water it is deposited in long flat crystals with a strong lustre resembling in form the well known Gypsum troins. This nitrile, like its homologue gives, in benzene solution, a white hygroscopic precipitate with dry hydrogen chloride, which is no doubt a combination with HCl.

It does not combine with methyl iodide and (unlike its homologue) not with benzene either. In water, no compound is formed with oxalic acid.

By reduction of this nitrile with sodium and alcohol we have obtained the desired-amine, which crystallises beautifully with water. The compounds with hydrogen chloride, picric acid and oxalic acid have been prepared, and also the picryl and benzoyl derivative and will be described later on in the "Recueil des Travaux chimiques."

We may state here, however, that the amine is not decomposed on boiling with dilute sulphuric acid; in any case it does not yield ammonia and formaldehyde as might have been expected from a derivative of methylenediamine (which it certainly is).

Physics. — "*Some remarks suggested by a paper by Messrs. TIMMERMANS and KOHNSTAMM.*" By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

In these Proceedings Vol. XII, p. 234 in a paper by Messrs. TIMMERMANS and KOHNSTAMM some remarks occur in reference to my former papers on plaitpoint lines etc., which remarks, in my opinion, rest on a misunderstanding.

I hope later on to collect the papers published by me on the subject mentioned in a book, but I may be allowed already now briefly to refute Messrs. T. and K.'s ideas concerning the results obtained by me theoretically.

a. On p. 235 T. and K. call it a "serious objection" to my investigations "that starting from a special case (the supposition $a_{12} = \sqrt{a_1 a_2}$ is probably referred to) they represent it as the general one and *therefore*¹⁾ must pronounce as abnormal a type occurring for normal substances."

Here I must remark that I have *never* represented the special case $a_{12} = a_1 a_2$ — from which I only started to make the *calculations* feasible — as the general case. Cf. my paper of March 1905 p. 650, where it distinctly says: "The *suppositions*¹⁾, on which the following calculations are based, are consequently the following." Etc. (Cf. there 3).

Nor have I ever *on account of this supposition* pronounced type II occurring for *normal* substances (fig. 3a of the paper of June 1905; afterwards I called this type III) with two cusps R_1 and R'_2 in the plaitpointline (which *also* occurs for $C_2H_6 + C_2H_5OH$, etc.) to be abnormal. I have simply kept the existing nomenclature and spoken of an abnormal *type*, "abnormal", because the plaitpoint line does not run directly from C_1 to C_2 as for type III (fig. 2a loc. cit.; later type II), and because it had first been supposed that this so-called "abnormal" type could only occur for abnormal substances.

The result of my observations was exactly that this "abnormal" type might very well occur for *normal* substances.

So far I had not yet got, however, in my paper of May 1905. The investigation begun there was only completed in a subsequent paper. Therefore I only wrote on p. 29 loc. cit. (line 9 from the top): "At all events the anomaly of one of the components *can*¹⁾ give rise to the occurrence of this second principal type." This refers, of course, to KUENEN's well-known experimental investigation concerning $C_2H_6 + C_2H_5OH$, etc.

But in a later paper (evidently overlooked by T. and K.) viz. in These Proc. Vol. IX Sept. 1906 (The longitudinal plait) I stated on p. 227 as a *result* of my investigations (four papers in these Proc. and two in the Arch. Teyler — see p. 227, line 2—3 from top): "So it appeared that *all* the abnormal cases found by KUENEN may already appear for mixtures of *perfectly normal* substances". (The italics are already found in the quoted place).

This was founded on the investigation, published by me in the Arch. Teyler (2) T. XI première partie, 1902: Les courbes de plissement etc. et sur le pli longitudinal. This paper begins with § 1.

¹⁾ The italics are ours.

La possibilité du type III (before called type II by me). On p. 4 of this paper in Teyler in fig. 2 the *coexistence region* of this type is graphically represented, viz. the region *PBQB*. This figure has been reproduced in the paper in These Proc. of Sept. 1906 (see the Plate, fig. 1). In this paper on p. 225—231 I gave a *recapitulation* of *all* my previous papers. Compare particularly p. 230: "It is now of the greatest importance," etc. "This investigation forms the conclusion of the last paper in the Arch. Teyler." And on p. 231: "In any case the investigations described in the Arch. Teyler have *proved* that this very abnormal type III is *possible for mixtures of normal substances*" etc. (The italics are already found in the original paper).

b. Further T. and K. object to my investigations (p. 235 of their paper) that they, "very onesidedly, lay the stress on the existence of open plaits, a circumstance, which by no means can be considered as a *result*, as it immediately follows from the arbitrary, if not erroneous *supposition* of the linear dependence of *b* and *x*."

Now I have never asserted that $\frac{d^2b}{dv^2} = 0$ would always agree with what actually happens; again I have simply *assumed* this, in order to make the *calculations* possible. (See p. 649 of the paper of March 1905 under 2).

c. The remark on p. 235. "For the case at last that one of the components is *abnormal*, VAN LAAR arrives at saturation lines of a very complicated form", etc. — this remarks seems very strange to me. I do not remember having ever theoretically treated the case that one of the components is abnormal. The papers, viz. published by me before the paper of March 1905 cannot be considered as belonging to the series which begins with this paper, in which for the first time the problem of the *plaitpoint lines*, and everything in connection with it, was strictly treated. And I never published anything concerning anomalous substances in this series of papers either. I hope to do this perhaps on a future occasion.

d. In connection with p. 236 of T. and K's paper I only mention that it was by no means generally doubted up to now that for perfectly normal substances *non-miscibility* can occur. VAN DER WAALS himself already stated the conditions of non-miscibility for normal substances in his Continuitat II, p. 43. But it was only doubted whether some "abnormal" *forms* of non-miscibility (Type I and III,

occurring among others for $C_2H_6 + CH_3OH$, C_2H_5OH , etc.) could occur for perfectly normal substances.

e. In T. and K's paper it says in a footnote on p. 242 that in later papers I should have left out a dotted line, occurring on the plate of an earlier paper, "*probably* because the special suppositions of VAN LAAR render the occurrence of the required homogeneous double plaitpoints impossible for normal substances."

I have only omitted the case represented by this line because the different course (either to the left or to the right) of the p - T -line was totally unessential for my investigations. But by no means because my special suppositions would render the occurrence of these double plaitpoints impossible for *normal* substances. On the contrary!

f. The inaccurate remark on p. 242 at the bottom of T. and K's paper beginning: "In VAN LAAR's later paper" will not call for any further refutation after the above remarks. Of the *seven* papers published by me on this subject, Mr. T. and Mr. K. seem to have read only two, those of March and May 1905. All the following papers, in which the investigation of the first two was continued, have apparently escaped their notice, particularly the papers mentioned above under a.

In conclusion I will only remark that type II has by no means been modified by me, and that I have *proved* (TEYLER loc. cit.) that such an intricate system of plaits is certainly possible on my "*simple*" suppositions, and that I have nowhere thought I had to ascribe the occurrence of this type to *abnormality* (See above sub a). On the contrary I asserted the very *opposite*, as clearly appears from the above quotation from my paper of Sept. 1906 These Proc. "So it appeared" etc. p. 227.

And this, I think, refutes sufficiently all Messrs. TIMMERMANS and KOHNSTAMM's remarks in reference to me.

Baarn, Nov. 15, 1909.

(December 23, 1909).