Chemistry. — *"On Metastable Unmixing and the Classification of Binary Systems."* By Prof. F. E. C. Scheffer. (Communicated by Prof. Böeseken).

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1. In the recently published work on systems with two liquid phases Büchner discusses in § 4 the different spacial figures of systems in which besides two liquid layers there also occur compounds.[1] He successively discusses there the systems with quadruple points, $VL_1 L_2 G$ (V = compound), and those which present analogy in behaviour with the system diphenylamine-carbonic acid, which was closely examined by Büchner.

In my recently published paper on the phenyl- and tolyl-carbaminic acids[2] I have pointed out that the systems aniline, resp. toluidine-carbonic acid belong to the category first discussed by Büchner, and that with a suitable choice of the homologues of aniline a transition can appear in the second case discussed by Büchner. The latter I have, however, indicated as the type sulphuretted hydrogen-ammoniac. In reference to this the following remarks may be made.

2. In all the systems in which a three phase line SLG intersects the critical line part of the latter is not stable, and if retardations are not possible, it is, therefore, not realizable. This not realizable part of the critical line can be either entirely metastable, or partly metastable, partly unstable. Neither possibility can be demonstrated directly experimentally.

In the system ether-anthraquinone examined by Smits it has always been assumed up to now that the critical line has no cusps, and that, therefore, no unmixing takes place in the unstable region[3]; it has, however, been assumed in the system diphenylamine-carbonic acid examined by Büchner that the critical line possesses two cusps in the unstable region. In the stable region the two systems exhibit, however, a perfectly analogous behaviour. The reason to assume that

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[1] Bakhuis Roozeboom, Heterogene Gleichgewichte. II 2. (1918) S 184. et seq

[2] These Proceedings. **21.** 644. (1919).

[3] Bakhuis Roozeboom. Heterogene Gleichgewichte II. 1. (1904). S. 378 et seq.

there is no unmixing in one system, whereas metastable unmixing is assumed to take place in the other case, lies in the shape of the critical line in the stable region, in one case it is possible to join the two stable parts of the critical line by a curve with a regular, continuous course; in the other case the critical line would have to present a peculiarly steep course with a strongly pronounced maximum. This latter is deemed less probable, and can also be explained in a plausible way by the assumption that the critical line has two cusps. I will, however, point out that also metastable unmixing in the unstable region is possible for the system ether-anthraquinone, and that for the system diphenylamine-carbonic acid the metastable unmixing has not been proved, but has only been rendered probable. Hence a sharp classification of these types of binary systems is impossible.

A similar case is offered by the system sulphuretted hydrogen-ammoniac[1]). In this investigation I have theoretically examined what phenomena occur in the stable region when a critical line intersects the three phase line VLG; it was not necessary to consider metastable unmixing in that case, because it is clear that all the phenomena in the stable region can be derived from a system without unmixing. When now the experimental results of this research are examined, it appears that the critical line, when it does not possess cusps in the unstable rigion, must have a very steep course, just as that in the system diphenylamine-carbonic acid. (I have expressed this graphically in my Thesis for the Doctorate) On the same grounds that lead us for the system diphenylamine carbonic acid to the conclusion of the existence of two cusps in the critical line, the system sulphuretted hydrogen-ammoniac may be counted among the systems with unmixing. As in my opinion this system would then be the most elaborately examined example of such systems, in which besides unmixing also a compound occurs, I have indicated the second case discussed by Büchner as the type sulphuretted hydrogen-ammoniac in the cited paper.

1 December 1918.   *Delft. Technical University.*

1) Disseitatie Amsterdam 1909. Zeitschr f physik. Chem **71** 214 and 671 (1910).