

Citation:

F.A.H. Schreinemakers, Equilibriums in systems of three components. Change of the mixing-temperature of binary mixtures by the addition of a third component, in:
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me doubt; and that is, that according to the results obtained by me formerly (Verslag Kon. Akad. 27 Nov. 1897) $a_1 + a_2 - 2 a_{1,2}$ would be negative for CO_2 and CH_3Cl or $a_{1,2} > \frac{a_1 + a_2}{2}$, and this would require a greater value for $a_{1,2}$ than would be found from Mr. KUENEN's values for $-\Delta_p$. In order that $a_{1,2} > \frac{a_1 + a_2}{2}$ should hold good, e. g. at $T = 343^\circ$, $a_{1,2}$ would have to be greater than 0.00126, while from the calculation of $-\Delta_p$, $a_{1,2}$ is found to be at the utmost 0.0116. That from Mr. KUENEN's observations $a_{1,2} < \frac{a_1 + a_2}{2}$ follows, is confirmed by the observation, that mixing of CO_2 and CH_3Cl gives increase of volume.

If this is really the case, it would prove that I ought to have expressed myself with still greater reserve than I did in my: "Approximative rule for the course of the plait-curve of a mixture" ¹⁾. Though I have drawn the attention to the fact, that the real plait-curve will deviate from the curves drawn, yet I had thought, that the deviations would not be so great, as to make the different types no longer to be distinguished. Yet so great a deviation really occurred in this case.

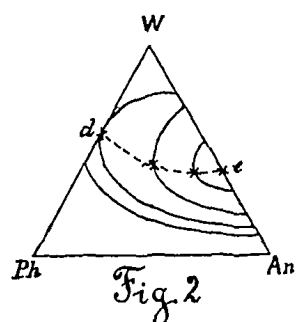
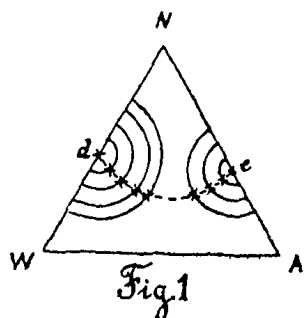
If we look back on the two rules discussed here: $\Delta_v = 0$ and $\Delta_p = 0$, we are induced to qualify the first rule as an approximative law. Throughout the course of the isotherme, from an infinite volume down to the smallest possible volume of the substance, there may be deviation, but the deviation remains within finite limits. The second rule holds perfectly good for infinite rarefaction, but it would be utterly impossible to apply it also to liquid volumes. Such a law may be qualified as a *loi-limite*. Considered from this point of view, the law of BOYLE too is not an approximative law, but only a *loi-limite*.

Chemistry. — Prof. VAN BEMMELEN reads a paper of Dr. F. A. H. SCHREINEMAKERS on: „*Equilibriums in systems of three components. Change of the mixing-temperature of binary mixtures by the addition of a third component.*”

Among the different systems composed of the components A , B and C we suppose the case, that in two of the binary systems f. i. $A-B$ and $A-C$ two liquid phases can appear, but not in the system $B-C$. An example of this we find f. i. in the system formed of:

¹⁾ Verslag Kon. Akad. Nov. 1897.

water, alcohol and succinonitrile, two liquid layers only appearing in the binary systems water-succinonitrile, and alcohol-succinonitrile but not in the system water-alcohol. A second example, which Dr. SCHREINEMAKERS has now subjected to an investigation is the system: water, phenol and aniline; in the system phenol-aniline there do not appear two liquid layers, in the systems water-phenol and water-aniline there do. Yet the isotherms acquired in both systems are entirely different as shown in figures 1 and 2. In fig. 1 the letters



W , A , N indicate the components water, alcohol, succinonitrile; in fig. 2 the components are water, aniline and phenol, indicated by the letters W , An and Ph . In both systems we shall only consider part of the appearing equilibria viz the appearing liquid phases that can be in equilibrium with each other; the equilibria in which solid phases appear are not considered here.

Let us begin with the system: water, alcohol, succinonitrile; at temperatures above 56.5 only homogeneous liquids are possible and no separation into two layers can appear. The ζ -surface in fig. 1 above the triangle $W A N$ is consequently in every point convex-convex downwards.

Here and in future we only consider the sheet of the ζ -surface that belongs to the liquid phase¹⁾. When the temperature falls there appears at 56.5 a plaitpoint and at lower temperatures a plait is developed ending on the plane $W N \zeta$ and continually extending in case of a fall in the temperature. In fig. 1 d is the projection of the plaitpoint at 56.5 ; the different lines drawn, each of them ending in two points of the line $W N$ are the connodal lines at the different temperatures; they are all situated in such a way, that those belonging to lower temperatures lie outside those of higher temperatures. In case of a fall in the temperature the plait from the side $W N$ extends more and more. At $\pm 32^\circ$ there appears however a second plait on the ζ -surface, originating in the plane $A N \zeta$, in a point, the projection of which is indicated by e ; consequently we now get at a lower temperature

¹⁾ Vid. J. D. VAN DER WAALS, Proceedings of the Royal Academy of Amsterdam 1897, 209.

besides the connodal lines ending on the side WN , also connodal lines ending on the side NA . Both plaits extend more and more when the temperature falls and the two connodal lines approach each other continually; the crosses on the dotted line de indicate the plait-points of the different connodal lines. We are therefore led to suppose that in the end the two plaits merge into each other; yet it was impossible to demonstrate this experimentally, because, in consequence of the appearance of the solid phase succinonitrile, the left connodal line below $\pm 5^{\circ}5$ and the right one below $\pm 4^{\circ}5$ indicate only less stable equilibriums.

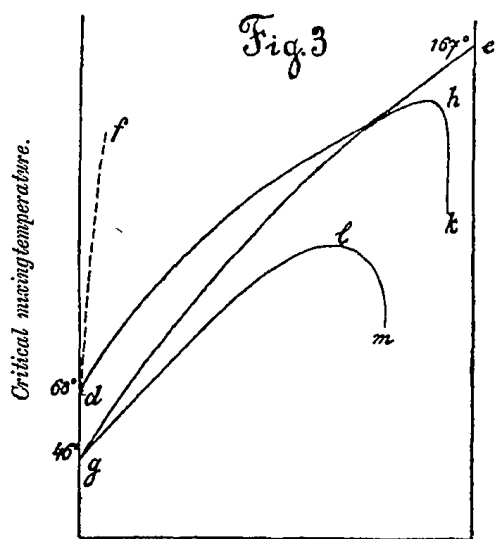
Quite different are the phenomena in the system water, anilin and phenol in fig. 2. Here there appears namely but *one* plait on the ζ -surface. Above 167° a separation of a liquid in two layers can never occur in this system; the ζ -surface is in every point convex-convex downwards. At 167° there appears a plait-point on the side $WAn\zeta$, its projection being e . As the temperature falls the plait extends and we get connodal lines as in fig. 2, in which the crosses again indicate the plaitpoints. The plait continues to extend and reaches at 68° the plane $WPh\zeta$ in a point, the projection of which is indicated by d ; the connodal line has a form like the one which in fig. 2 touches the side PhW in point d . At still lower temperatures the plaitpoint on the ζ -surface disappears; the plait extends from one side to the other, so that two entirely separate convex-convex parts are formed. The connodal line now has fallen into two parts, separated from each other, both ending on the sides PhW and AnW . At further lowering of the temperature the connodal line keeps its form; the two parts move however continually farther from each other and at last some of the points represent less stable states, as solid phases, viz phenol and a combination of phenol and aniline are formed.

The preceding investigations have led to a theoretical and experimental investigation of different curves; in these pages a survey is given of some of the experimental investigations.

Let us take the connodal lines of fig. 2; below 68° no plaitpoint appears on them; at 68° it appears in point d and the temperature rising it moves along the line de from d to e where it disappears at 167° . It is however very difficult to realize these plaitpointcurves experimentally; neither has this been done in the different systems investigated by Mr. SCHREINEMAKERS. He has however determined another curve, which will not much deviate from it in the two systems mentioned above. It is the line of the critical mixingtemperatures which coincides with the former in at least 2 points,

viz. in the points *d* and *e*: the critical mixing-temperatures of the binary systems.

If we start with a mixture of phenol and aniline, adding water to this binary mixture, two liquid phases are formed, passing into one when heated; this mixing-temperature depends upon the quantity of water added. The highest mixing-temperature we are able to reach by the addition of water, may be called the critical mixing-temperature of water with the said binary mixture. In varying the proportion of phenol and aniline in the binary mixture, another critical mixing-temperature will be obtained by the addition of water.



Molec. anilin on 100 Molec phenol + anilin.

In fig. 3 is shown on the X-axis the composition of the binary mixture; on the Y-axis the critical mixing-temperature of this binary mixture with water. We then get the line *de* in which *d* indicates the critical mixing-temperature of phenol with water, and *e* that of aniline with water. The line *de* may be drawn according to the table given below.

Composition of the binary mixture in Molec. aniline on 100 Molec. Phenol + Aniline	Critical mixing-temperature after the addition of water.
0	68°
11.58	95°
25.4	114°—115°
37.3	127°
50	139°—140°
62.8	148°
76.07	155°5
87.66	163°
100	167°

For each of the binary mixtures of phenol and aniline, given in the above table the mixing-temperature is determined by the addition of different quantities of water and the critical temperature deducted from it.

We see therefore that the critical mixing-temperature of the binary mixtures increases in proportion as they contain more aniline —

decreases on the contrary in proportion as they contain more phenol. The extreme limits are 68° and 167°.

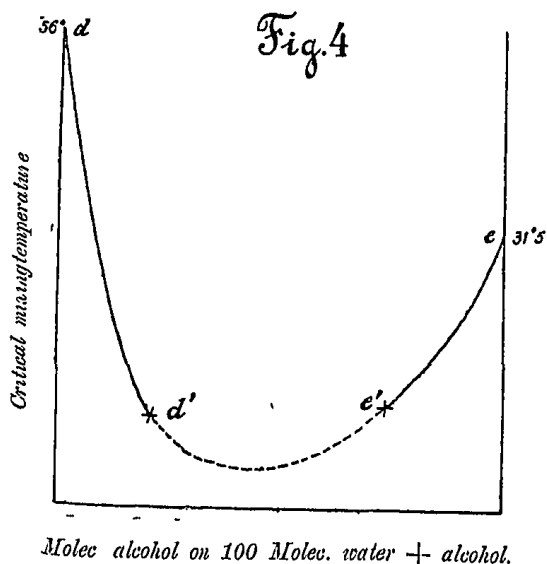
Dr. SCHREINEMAKERS has also investigated how the critical mixing-temperature of water with phenol is changed by the addition of sodiumchloride. In the following table the results are given.

Composition of the binary mixture in Molec. Na Cl on 100 Molec. (H ₂ O + Na Cl)	Critical mixingtemperatures after the addition of phenol.
0	68°
0.304	78°
1.579	123°
2.084	144°

If we now indicate in fig. 3 on the X-axis the binary mixture viz. Molec. Na Cl on 100 Molec. (Na Cl + H₂O), and on the Y-axis the critical mixingtemperature of those mixtures with phenol, we get the dotted line *df*, rising very quickly. A similar line also exists in the system investigated by SCHREINEMAKERS of water-succinonitrile and sodiumchloride.

By the addition of aniline or Na Cl we therefore get a rise in the critical mixingtemperature of phenol with water; the same occurs also if the pressure is augmented, as lately shown by Dr. N. J. VAN DER LEE¹⁾. A fall in the critical mixingtemperature can also occur, as Dr. SCHREINEMAKERS found with alcohol.

A line quite different from that in fig. 3 is found by SCHREINEMAKERS in the system: water, alcohol and succinonitrile.



If we start from the binary mixture water and alcohol, we can again get two liquid layers by the addition of succinonitrile. In fig. 4 the composition of the binary mixture: water and alcohol is read on the x-axis, while on the y-axis we find the critical mixingtemperature by the addition of succinonitrile. The course of the line *dd'e'e* is known from the following table:

¹⁾ Dissertation. The influence of pressure on the critical mixingtemperature. Amsterdam 1898.

Composition of the binary mixture in Molec. Alcohol on 100 Molec. Alcohol + water.	Critical mixingtemperature after the addition of succinonitrile.
0 Point <i>d</i>	56°
5.7	41°5
12.1	30°5
25.9	12°
30.1 Point <i>d'</i>	7°5
66.6 Point <i>e'</i>	8°5
70.4	11°
84.6	21°
100 Point <i>e</i>	31°5

Of the dotted line *d'e'* only a small part could be realized; the greater part it is however impossible to determine. Yet we are led to suppose that the line *d'e'* will run as drawn in the figure viz.: with a minimum-temperature at $\pm 3^\circ$ coinciding with the point in which in fig. 1 the two connodal lines merge into each other. The difficulty of determining the course of the curved line lies in the fact of the two liquid-phases presenting there less stable equilibriums; the few cases in which Dr. SCHREINEMAKERS succeeded in obtaining them, were insufficient to deduct the critical mixingtemperatures from.

Besides the question of the critical mixingtemperatures of ternary systems, we can set ourselves many other problems one of which I shall discuss.

Take a binary mixture viz. one of water and phenol; the mixing temperature of such a mixture depends upon its composition; f.i. the mixingtemperature of a mixture containing 10.9 pCt. of phenol is $\pm 46^\circ$. This mixingtemperature is altered not only by pressure, but also by the addition of a third component; it may be raised or depressed. An example of a rise Dr. SCHREINEMAKERS has determined experimentally by taking as a third component aniline; he found that the mixingtemperature began by rising from 46° to about 163° , to fall again after a further addition of aniline. In order to draw this line in fig. 3, only the components phenol and aniline of the ternary mixture are considered. Owing to the proportion of water and phenol being constant in all the mixtures, the entire composition is known. We have:

Molec. aniline on 100 Molec. phenol + aniline.	Mixingtemperature.
0	46°
46.57	127°
67.68	148°
79.99	157°
86.18	160°
89.9	162°
93.6	161°5
95.66	± 157°
97.47	± 142°

If in fig. 3 the number of Molec. aniline on 100 Molec. Phenol + aniline is indicated again on the X-axis, and on the Y-axis the mixingtemperature, we get a line ghk as is drawn in fig. 3 which: 1° starts from g to a higher temperature, 2° touches the line de 3° reaches its maximum temperature in h and 4° further on bends down to lower temperatures.

The preceding line ghk is for a mixture containing 10.9 pCt. Phenol and 89.1 pCt. water; for mixtures of other compositions we also get other lines. F. i. if we take a mixture of 63.7 pCt. phenol and 36.3 pCt. water, it has just like the former its mixingtemperature at $\pm 46^\circ$. When adding aniline we then get the following:

Molec. aniline on 100 Molec. phenol + aniline.	Mixingtemperature.
0	46°
21.64	90°
29.58	97°
43.72	107°
51.93	109°
60.48	108°5
71.97	102°
78.35	92°

These values are indicated in fig. 3 by glm , which like ghk begins at g , reaches its maximum temperature at l , and then bends down to lower temperatures.

So we have now got two lines, both starting from point *g* in fig. 3. From each point below *d* two more such lines may be drawn; but from *d* itself but *one*. To find this we must set out from the critical solution of water and phenol. But this is not exactly known. Dr. SCHREINEMAKERS took a solution, containing 35.77 pCt. phenol which certainly lies near the critical one. He found:

Molec aniline on 100 Mol phenol + aniline.		Mixingtemperature
0	± 68°
20.46	105°5
23.83	120°
50.68	135°
68.69	144°
76.88	145°
80.18	144°
87.20	± 137°

The line that may be deduced from this table is however not given in fig. 3; as far as it is continued, it is entirely above *glm* but intersects *ghk* in a point situated between *g* and the intersection of the two curves *ghk* and *de*.

Physics. — „On the accurate determination of the molecular weight of gases from their density.” By Prof. J. D. VAN DER WAAALS.

From the equation:

$$\left(p + ap_0 \frac{v_0^2}{v^2}\right) (v - b v_0) = \Sigma \frac{1}{3} m N s^2$$

follows

$$\Sigma \frac{1}{3} m N s_0^2 = p_0 v_0 (1 + a) (1 - b)$$

and

$$\Sigma \frac{1}{3} m N s^2 = p_0 v_0 (1 + a) (1 - b) (1 + \alpha t) .$$

If the quantity *N* is equal for two different gases, it follows from the thesis that at the same temperature $\frac{1}{2} m s^2$ is the same, that for the two gases $p_0 v_0 (1 + a) (1 - b)$ has also the same value, and therefore also $v_0 (1 + a) (1 - b)$.