

$$\log \frac{x}{(1-x)^n} = (n-1) \{ \mu - x\mu' \} - \mu'_x + B + \frac{A}{T}.$$

This last equation yields the results we have obtained, in a still simpler way than that which we have made use of originally. It has moreover the advantage, that the usual signification of x and μ , as it is established in the theory of a binary system, may be kept unchanged.

Reactions like that of acetaldehyde and paraldehyde, reactions which we can bring about at pleasure by means of a catalyzer and in which the composition may be determined experimentally are of course of the highest importance for the investigation of the course of the molecular transformation. For reactions as that of acetic acid the density is the only criterion for the degree of the transformation; and this criterion fails as soon as we work in circumstances in which the deviations from the laws for the perfect gases are considerable. The experimental investigation will therefore not be able to prove the occurrence of a minimum in the number of the double molecules in the saturated vapour of acetic acid. At the temperature at which the theory predicts that minimum and which lies probably between $0.8 T_{cr}$ and $0.9 T_{cr}$, the density of the saturated vapour is already so great that it is nearly impossible to deduce reliable conclusions concerning the course of the transformation.

Physics. — "*Critical phenomena in partially miscible liquids.*" By Prof. J. D. VAN DER WAALS.

I have read with great interest the communication of Prof. KUENEN under the above title, which occurs in the Proceedings of the previous session, and it induces me to draw attention to the following considerations.

In my paper of March 25th 1899 I started from the thought, that the series of plaitpoints, which may occur at different temperatures, whether we arrange them to a plaitpoint curve or assign a place to them in the x, v plane, must form one or more continuous curves — of course continuous in the mathematical sense.

When therefore the experiment yielded, e.g. for ethane and ethyl-alcohol two separate plaitpoint curves, I have connected them by means of a theoretical part.

If we wish to connect the two pieces of curves found to one curve, we may perform this in two simple ways. In the first place we may connect them in such a way that the curve is con-

tinuous also as to its direction. In the second place we may, between the ends of the pieces which are experimentally determined, trace a curve which presents in those ends abrupt changes of direction and which has about the same course as the three-phase pressure, though it lies everywhere lower than that pressure.

I then thought that the two pieces of the plaitpoint curve were to be connected in the first manner. The experiment had shown that the peculiarities which must then occur, namely the existence of a minimum and of a maximum temperature, were possible and really occurred in nature; at any rate the minimum temperature. The peculiarity, on the other hand, which occurs, if we make the connection in the second manner, namely the abrupt change of the direction, was never observed.

Now when we have made a choice and when we wish to examine its meaning, all conclusions must of course be in accordance with the choice we have made. Here I will mention the following conclusions from the first way of bringing about the connection: 1st. A mixture with minimum critical temperature exists. 2nd. A mixture with maximum critical temperature exists. 3rd. Plaitpoints occur outside the borders of the three-phase temperature, which cannot be observed, as they lie above the empirical ψ -surface.

In this case a plait must necessarily at a certain temperature be separated from the principal plait, which at higher temperature (the maximum critical temperature) has contracted to one point. In short then the phenomenon quite corresponds to the description I have given Cont. II, p. 187. If therefore KUENEN accepts the way in which the connection of the two pieces of the plaitpoint curve he has determined experimentally, is brought about, then I cannot but consider it to be inconsistent, if he raises objections to the interpretation.

But more important is the question whether the choice we have made is the right one; whether, therefore, the connection between the two pieces of the curve should not rather be brought about with two abrupt changes in the direction. This has at the same time the following meaning. Is the plaitpoint the course of which is indicated by the theoretic curve, perhaps quite another plaitpoint as that whose course is indicated by the experimental curve? Now I read in the paper of KUENEN p. 321 that he has obtained the figure I have originally given, with the aid of other curves. But I think that this must be understood in such a way that he has succeeded in pointing out, that the two ends of the experimental branches may be connected. The way in which the connection must be established can here, after my opinion, not be decided. I have already doubted some time as to

this question. The first way of connecting requires that as well a mixture with a maximum, as a mixture with a minimum critical temperature occurs. And though I expressed in my paper of 1899 the expectation, that it would be possible to account for this, yet I must acknowledge, that a further investigation has made me consider the occurrence of a maximum critical temperature more and more improbable.

After my opinion the question is decided by that part of the plaitpoint curve KUENEN has determined experimentally, which starts at the critical point of methylalcohol and which indicates the course of a plaitpoint belonging to a plait which has its summit towards the side of the small volumes. The fact that $\frac{dp}{dT}$ is negative or at any rate smaller than $\left(\frac{\partial p}{\partial T}\right)_v$ quite agrees with the circumstance, that $\left(\frac{d^2v}{dx^2}\right)$ is positive.

If this plait had its summit on the side of the large volumes, then it would be possible to explain the course also for the case of ethane and methylalcohol by admitting the existence of a maximum and a minimum T_{cr} . As this is however not the case it seems to me that we cannot but assume with KUENEN, that the theoretical part of the plaitpoint curve indicates the course of a point, drawn i. a. by KORTEWEG (Archives Néerl. XXIV, p. 305, fig. 12) and which belongs to a sideplait if we trace the connodal curve of the sideplait also in the unstable region. The discontinuity in the direction of the curve ensues then from the fact that the theoretic part represents the course of another plaitpoint than the experimental part.

If we return to the case of ethane and methylalcohol then we must admit that above T_B the spinodal curve possesses a protuberance towards the side of the small volumes, accompanied by a new connodal curve, which if we trace it also in the unstable region, presents a new plaitpoint. Or, what comes to the same: the existing plaitpoint splits up into two plaitpoints. This second plaitpoint lies on the side of ethane and in the beginning it will move with great velocity. At higher values of T the sideplait extends and in consequence thereof that part of the principal plait which has a plaitpoint on the side of ethane contracts. At the moment that that part would vanish the second plaitpoint has coincided with the plaitpoint which is indicated by the point A (see fig. (1) of p. 319). This description differs in details from that of KUENEN, but a great number of figures would be required

in order to show this difference clearly, but then also in order to bring us into agreement.

For the case of ethane and methylalcohol the theoretical plaitpoint belonging to the sideplait of the side of alcohol coincides at T_A (see fig. 2, p. 326) with the practical plaitpoint of the side of ethane. At lower value of T it is displaced in the p, v -plane towards the side of alcohol and when the temperature continues to decrease it approaches asymptotically to the plaitpoint with which it forms a "système double hétérogène" (after the terminology of KORTWEG). If we draw this series of points in the plaitpoint diagram, it must of course satisfy the condition which follows from the fact, that they lie below the three-phase triangle, namely on the side of the small pressures. At low temperatures it lies even in the region of the negative pressures.

Fig. 2 of KUNEN p. 326 must therefore be completed with a theoretic curve which starts at point A , retrogrades immediately to lower temperatures and lies below the curve of the three-phase pressure. The theoretic branch approaches to the same asymptote as the highest branch that starts at C_2 . For the theoretic branch also $\left(\frac{d^2v}{dv^2}\right)$ must be positive, and therefore we have:

$$\frac{dp}{dT} < \left(\frac{\partial p}{\partial T}\right)_v$$

The rapid rising of this branch at low values of T seems to be contradictory to this explanation. But if we take into account that also $\left(\frac{\partial p}{\partial T}\right)_v$ approaches to an infinitely great value for values of v which approach to the limiting volume, this apparent contradiction disappears.

What is surprising, at least to me, is that these theoretic plaitpoints serve to make the course of the practical plaitpoints continuous. But on the other hand the circumstance, that also for the course of these theoretic plaitpoints a so important and at the same time a so simple meaning has been found, confirms my opinion that now the true description of the phenomenon has been given, at least for those cases, in which the longitudinal plait has its summit on the side of the small volumes.

But though the accuracy of the description of the phenomenon has increased, we must acknowledge that the chance to find a satisfactory explanation for the phenomenon is not greater than before; on the contrary it has diminished. The circumstance in which a mixture of two substances has a maximum and a minimum critical temperature needs now no longer be inquired into. The question whether the

size of the molecule of the normal substance has influence on the course, has also lost its direct importance. For mixtures of ethane with an alcohol the separation between the two types lies between methyl- and ethylalcohol; the question whether this separation takes place between two higher terms of the alcohol series, if we take instead of ethane a higher term of the series of carbonhydrogene compounds, which seemed very important before is now no longer of primary interest¹⁾. It seems to me that I have to return in many respects to my original meaning, namely that we have to inquire after the circumstance which causes the spinodal curve to show a protuberance towards the side of the small volumes. In mixtures of a normal substance with an associating one this cause can perhaps be found in the circumstance that the quantity $\left(\frac{\partial p}{\partial x}\right)_v$ can obtain abnormous high values for such a mixture. As the equation:

$$-\frac{\partial p}{\partial v} \frac{\partial^2 \psi}{\partial x^2} = \left(\frac{\partial p}{\partial x}\right)^2$$

applies to the spinodal curve, the value of $-\frac{\partial p}{\partial v}$ may also be abnormally high in this case. If this is really the case an explanation for the protuberance is given which is certainly satisfactory. Yet a great distance exists between this observation and an adequate calculation.

In any case these experiments of KUENEN, to which I hope that he will add many others, are an important contribution to our knowledge of the critical phenomena of not miscible substances.

Physics. — "*The influence of variation of the constant current on the pitch of the singing arc.*" By J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. P. ZEEMAN).

In the course of some experiments on the physiological action of alternating currents of very high frequency, I tried the currents generated by means of DUDDELL'S singing arc. A constant current arc between solid carbons shunted by a self-inductive resistance and a condenser emits a note, the pitch of which corresponds with the frequency of the alternate current generated in the condenser-circuit.

¹⁾ An experiment in order to investigate whether for propane the limit lies between ethyl- and propylalcohol was already in preparation for a long time in the laboratory of Amsterdam. But other labour which could not be delayed prevented each time those who would undertake the investigation.