the cells, whereas exclusively the Na Cl-solution exercises an in-
fluence on the volume in consequence of its concentration.

This does not seem to be in accordance with the function of
the bladder as a reservoir for the refuse products, of which the urea
constitutes an important, and for the organisation a very injurious part.

There must be factors then, which counteract the resorption of
urea in the wall of the bladder.

Physics. — *"An anomaly in the course of the plaitpointcurve in
a mixture of anomalous substances."* By Prof. J. D. VAN
DER WAALS.

In the „Zeitschrift für physikalische Chemie XXVIII Heft 2"
KUENEN and ROBSON have communicated observations on the mutual
solubility of liquids, which give occasion for a short remark. In
mixtures of ethane and ethylalcohol or one of the following alcohols
they found, that the plaitpointcurve consists of two isolated bran-
ches, which intersect, and end on the curve which indicates the
pressure of the three phases. In the following figure their result
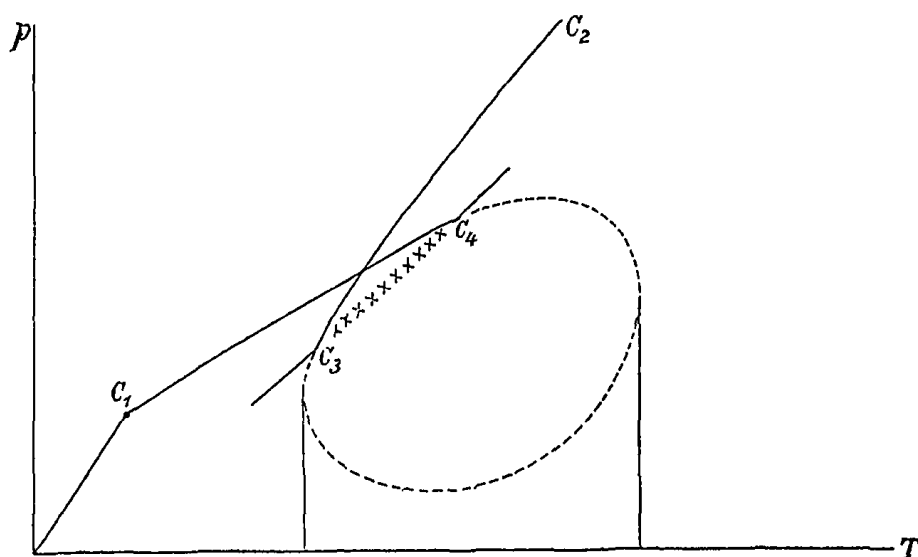has been represented schemetically.

Fig. 1.

Let C_1 be the critical point of ethane, C_2 that of alcohol, then
C_4 indicates the point, in which the plaitpoint, originating in C_1
can be observed no longer and it seems to serve as terminating point
of the pressure of the three phases. Then C_3 indicates the point,
in which the plaitpoint, originating in C_2 cannot be observed any

longer, because it disappears there above the triangle of the three phases-pressure. It appears then as the beginning point of the three phases-pressure.

Led by the thought that if the temperature rises a plaitpoint can only appear on the surface ψ, if a plait splits into two parts or can disappear, if two plaitpoints fall together, and that therefore a branch of a plaitpointcurve can never end in any other point than in the critical points of the components or in a point at an infinite distance. I have occupied myself with the question how the two separate branches can be joined into one curve. The simplest way of doing this is by joining the two branches, as is indicated by the dotted line in the figure.

The vertical lines, between which the closed part of the curve lies, represent then a maximum and a minimum temperature. The minimum temperature is the temperature at which the transverse plait splits into two parts and from which a plaitpoint starts to the right and to the left towards the critical point of the components. The greatest irregularity of the point, going towards C_2, the critical point of alcohol, is that in its course it approaches a little nearer to the side of the small volumes. But the point, describing its way to C_3 has greater irregularities. At the maximum temperature it meets another, which has come from the opposite direction, starting from C_1 and at their meeting its movement ends. The three branches mentioned however, form a continuous curve on the vx-plane.

At a given temperature, between the minimum and the maximum temperature, the projection of the spinodal curve consists of two separate parts. One part forms a small closed curve round the point where the meeting will take place; the other part has an almost regular form.

But the two plait-points, which belong to the first part, are quite covered by the ruled surface of the connodal curve of the second part. Moreover the peculiarity presents itself that there is a great distance between the spinodal and the connodal curve- a distance great enough to contain the closed branch of the spinodal curve. After I had convinced myself that an exact description of the phenomenon has been given in what I have said before, the question was to be solved, how this would agree with the fact, which I had remarked before. I have remarked (Molekulartheorie V 2) that for a mixture of two substances there can only be question of a maximum or of a minimumtemperature, but that the existence of the two at once is excluded. I think that we must look for the explanation of this in the fact that in the experiments of KUENEN and

Robson one of the components is an anomalous substance. It is almost generally accepted, especially because they do not follow the law of the correspondent states, that alcohols when in the liquid state possess complex molecules. At $x = 1$, i. e. for pure alcohol, the association into complex molecules is perfect or maximum. But when x is very small the dissociation into simple molecules is nearly perfect. Under these circumstances the critical temperature is not determined by the course of $\frac{a_x}{b_x}$ alone.

The critical temperature would be proportional to this quantity, if the molecules of alcohol also in a rarefied solution continued to be, what they were in the dense state when the substance is taken pure.

Now in general the critical temperature of smaller molecules will be lower than that of more complex molecules. Starting from ethane the temperature would have to rise considerably till it reached that of alcohol according to the course of $\frac{a_x}{b_x}$. In consequence of the dissociation of the alcohol molecules the course will be determined by $f \frac{a_x}{b_x}$, where f is smaller than unity. If x is near unity this factor too will not differ much from unity. For values of x which do not exceed $\frac{1}{2}$, an idea of the value of this factor is obtained by equating it to $\frac{1}{1 + x}$. Now it is easy to see that even if $\frac{a_x}{b_x}$ had no minimum or maximum, there would be numerous cases, in which the factor f causes such a maximum, and this would involve that there was also a minimum.

If the true interpretation of the phenomenon is to be found in this, a course such as Kuenen and Robson have found for mixtures of alcohol, can never be found if the substances do not associate But the reverse may not be stated. What appeared as a longitudinal plait in Kuenen and Robson's experiments, was in reality nothing but a somewhat modified transverse plait. The following phrase already refers to such a modification : (Mol. Theorie p. 172) „Es zeigt sich dann aber, dass in diesem Falle die beiden Falten auf ihre Bildungsweise anders angesehen werden müssen u. s. w." In the figure on p. 173 the spinodal curve has, however, not been traced correctly. The bulging to the right of P should not be there. It should be replaced by a small isolated closed curve, which has separated from the other parts at the minimum temperature.

It is not without interest to remark that the mixture of ethane and methylalcohol behaves so differently. To find the probable cause

of this deviation I have construed the locus of the point for which $\dfrac{dp}{dv}$ and $\dfrac{d^2p}{dv^2} = 0$, as has been done in "Een benaderde loop voor de plooipuntslijn van een mengsel" (Verslag der vergadering Kon. Akad., 27 Nov. 1897). Now we had also to take into consideration, that one of the substances is abnormal. The influence of this property can only be calculated in a very incomplete manner. because the way in which association of the molecules takes place in such an abnormal substance, is not known. In consequence the result which I have obtained by this wholly approximative calculation may only be accepted with great reserve.

The locus mentioned may occur in two different forms, which depend on the fact whether in the gaseous state the molecules of the abnormal substance are larger or smaller than the molecules of the substance with which they are mixed. If they are larger the curve has a loop which hangs down as in the figure (1). That the molecules of $C_2 H_6 O$, $C_3 H_8 O$, etc. are greater than that of $C_2 H_6$ will not be doubted. If on the other hand the molecules of the abnormal substance in the gaseous state are smaller, the loop is turned upwards. To all probability, however, the molecules of $C H_4 O$ will be smaller than those of $C_2 H_6$. In this case the following schematical figure may make clear the probable course.
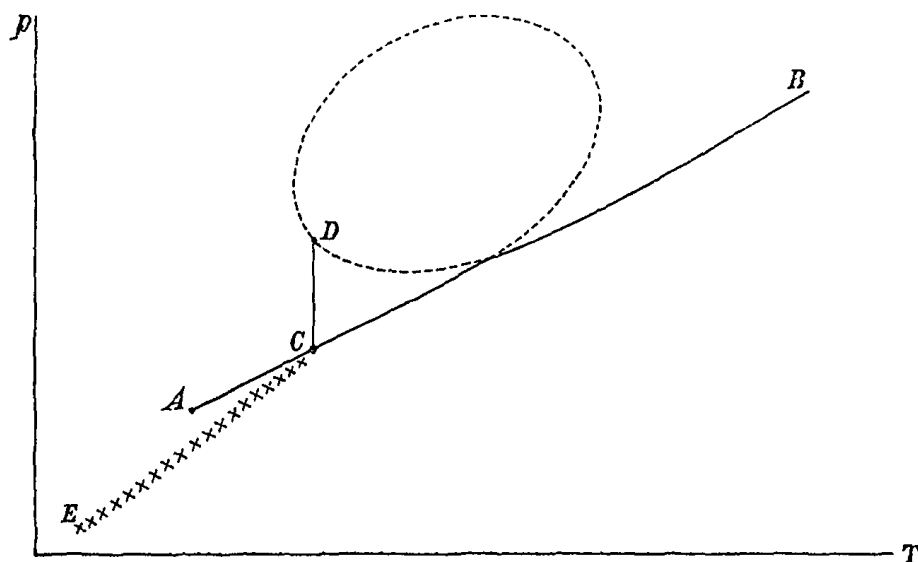

Fig. 2.

Let A be the critical point of ethane, B that of methylalcohol. Let EC be the pressure-curve of the three phases and C the point, in which the plaitpoint-curve, originating in A, meets the three-phase-

pressure-curve. In this case point D, which lies on that branch of the plaint-curve that originates in B above C, is the last of the plait-points that may be realized if the phenomena of retardation are excluded. From this follows, that however much we may lower the temperature, the pressure of the three phases will continue to exist. The points between C and D, marked on the curve, indicate plait-points of such values of x, at which they lie above the derived surface, resting on the connodal line which encloses the two separate branches of the spinodal line. From the phrase of KUENEN and ROBSON, p. 357 : "Oberhalb 35,37° ist nur eine Falte vorhanden, deren Faltenpunkt wir bei Methylalcohol nicht erreichen konnten, weil Druck und *Temperatur* zu hoch waren" seems to follow, that point D of our figure 2 must not lie above C, but that it would have to be taken more to the side of B. As there remain so many uncertainties, it is to be regretted, that in the case of methylalcohol they have not been able to carry out their investigation. We must not attach greater value to fig. 2 than that it has led to the supposition' that the cause of the difference in behaviour for mixtures of ethane and methylalcohol must be found in the smallness of the methyl molecules [1]).

I shall avail myself of this opportunity to make the following remark about what is really properly to be called "longitudinal plait."

In a mixture of normal substances a relation may exist between the quantities a_1, a_{12}, a_2, b_1, b_{12} and b_2, of such a nature that there actually exist two plaits, each of which possesses a connodal curve of its own. At a same temperature both may be proved experimentally. Then the principal direction of the transverse plait is // v-axis and the principal direction of the longitudinal plait is // x-axis. But in this case the plaitpoint of the longitudinal plait lies on the side of the large volumes. This has been proved theoretically by Prof. KORTEWEG in the special case of symmetry and a similar case has been worked out experimentally by Mr. VAN DER LEE. (Proc. Royal Acad. 1898). Theory has not yet been able to decide whether this plait may be again closed if the volumes are much smaller still, or whether it continues to diverge, even when the limiting volumes are reached. If the latter should

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[1]) The geometrical locus of the points, for which $\dfrac{dp}{dv}$ and $\dfrac{dp^2}{dv^2}$ is equal to 0, cannot teach anything about the plaitpoints of the real longitudinal plait. Moreover I do not share Mr. KUENEN's expectation that also for methylalcohol the plait is the same as for the following alcohols. I expect that the course of the plaitpoint-curve of a mixture of methylalcohol and ethane shows great resemblance to that of a mixture of water and ether.

be the case, a plait, which appears as a longitudinal plait, but which has its plaitpoint on the side of the small volumes, as in the observations of K UENEN and ROBSON, is not a longitudinal plait, but a somewhat modified transverse plait. If then in the liquid state complete mixture does not take place under all circumstances, the phenomenon is to be ascribed to other causes than in case of a real longitudinal plait.

If further investigations confirm what has been said, we should have to find the cause in this case in the fact that at least one of the substances is abnormal.

Physics. — *"On variation of volume and of pressure"*. III. By Prof. J. D. VAN DER WAALS.

In order to be able to judge about the extent of the variation of volume and of pressure in mixtures of two substances, it will be necessary, to find for the different proportions of mixing the pressures at which the number of the molecules is the same for the two substances, if the volume and the temperature are also the same. If there were no deviations from the law of BOYLE, the pressures required would be equal. Assume that for a mixture the characteristic equation is :

$$\left(p + \frac{a_x}{v^2}\right) \left(v - b_x\right) = MRT ,$$

at a given temperature the 2nd member of this equation has a constant value for mixtures with the same number of molecules, and so we may find the pressure which satisfies the preceding condition in solving the value of p from this equation, if the value of v is constant. Take as unity of pressure 1 atmosphere and as unity of volume, the volume occupied by a molecular quantity of the mixture under that pressure. The value of the second member is then

$$(1 + a_x) (1 - b_x) (1 + \alpha t) ,$$

for which we may write with a sufficient degree of approximation

$$(1 + a_x - b_x) (1 + \alpha t) .$$

If we write p_0 for the value of the pressure taken as unity, and