180 Messrs. J. P. Kuenen and W. G. Robson on
therefore from 10 *,

$$C_s' = \frac{\mu p(2n+1)}{(n+1)k_1 a \sigma} \frac{r f_n(kr)}{f_n(ka)} \frac{d\Omega_n}{ds} e^{ipt}$$

$$= \frac{\sqrt{2}k_1(2n+1)}{4\pi(n+1)} \left(\frac{a}{r}\right)^n e^{-k_1(a-r)} \left\{ 1 - \frac{n(n+1)(a-r)}{4k_1 a r} \right\}$$

$$\times \cos \{pt - k_1(a-r) + \chi\} \frac{d\Omega_n}{ds}, \quad . \quad . \quad . \quad (30)$$

where $\tan \chi = \frac{1}{\frac{2k_1}{n(n+1)(a-r)} - \frac{1}{4k_1 a r}}$

Hence $\tan \chi = 1$ approximately,

therefore $\chi = \frac{\pi}{4}$.

Hence when the inducing system is the circular circuit before mentioned, $ds = r d\theta$, and we find

$$C' = \frac{\sqrt{2} \gamma k_1}{2} e^{-k_1(a-r)} \cos \left\{ pt - k_1(a-r) + \frac{\pi}{4} \right\}$$

$$\times \sum_1^{\infty} \frac{\sin^2 \alpha \sin \theta}{r} \left(\frac{a}{c}\right)^n \frac{2n+1}{n(n+1)} \left\{ 1 - \frac{n(n+1)(a-r)}{4k_1 a r} \right\} P_n'(\alpha) P_n'(\theta). \quad (31)$$

XVII. *On the Mutual Solubility of Liquids.—Vapour-pressure and Critical Points.* By J. P. KUENEN and W. G. ROBSON*.

THE experiments recorded in this paper have reference to the equilibrium between liquid and vapour, for two substances which, in the liquid state, do not mix in all proportions at all temperatures. Our attention has been especially directed to the equilibrium-pressure of some of these mixtures at different temperatures, and to the nature of the critical phenomena which may occur in different cases. Regnault† measured the vapour-pressures of two mixtures of this kind—carbon disulphide and water, and ether and water. The vapour-pressures for the first pair were found to be only a little less than the sum of the vapour-pressures of the components; and Regnault rightly connected this fact with the

* Communicated by the Authors.

† Regnault, *Relation des expériences*, t. xxvi.

other, that these two substances are mutually almost insoluble, in contrast to liquids like ether and water. There is, however, no reason to make, as Regnault did, this difference the basis of a division into two groups, because it is now known that almost every degree of mutual solubility occurs, and that the solubility sometimes changes rapidly with the temperature. Regnault's measurements of the vapour-pressures of mixtures of ether and water tended to show that what we shall call the pressures of the three phases were practically equal to those of pure ether between 15°C . and 33°C . The same conclusion is arrived at from some determinations, due to Marchis*, of the boiling-points of these mixtures. Later experiments by Linebarger†, Konowalow‡, Beckmann§, and others prove, however, that up to the boiling-point the pressure of the three phases exceeds by a few millimetres the pressure of ether. For this pair of liquids, therefore, the equilibrium-pressure was higher than that of either substance, though much less than the sum of the vapour-pressures of the pure substances.

Konowalow, in his investigation on mixtures, found a combination of partial miscibility—water and isobutyl alcohol||. The pressures of the three phases were in this case also higher than for water, the more volatile of the two components, and nearly equal to the sum of the pressures of the pure substances, this combination approaching the case of carbon disulphide and water. For bromine and water, a combination investigated by Bakhuis Roozeboom¶, the pressures are higher than for pure bromine. Konowalow** was also the first to point out the theoretical possibility of a second case, in which the pressure of the three phases would be between the pressures of the components, and the impossibility of the three-phase pressure being less than the vapour-pressure of either component.

The first instance of Konowalow's second group was discovered by Bakhuis Roozeboom ††—sulphur dioxide and water. Bancroft in his book, 'The Phase Rule,' gives two more instances—sulphur and xylene, and sulphur and toluene.

We are aware of no other experiments regarding the equilibrium-pressure of three phases; all other investigations

* Marchis, *Compt. Rend.* cxvi. p. 358.

† Linebarger, *Chem. News*, vol. lxx. p. 52.

‡ Konowalow, *Wied. Ann.* xiv. p. 223.

§ Beckmann; comp. Nernst, *Zeitschrift Phys. Chem.* viii. p. 134.

|| Konowalow, *Wied. Ann.* xiv. p. 42.

¶ Bakhuis Roozeboom, *Zeitschrift Phys. Chem.* ii. p. 453.

** Konowalow, *Wied. Ann.* xiv. p. 222.

†† Bakhuis Roozeboom, *Zeitschrift Phys. Chem.* ii. p. 450.

have regard to the compositions of the two liquids which are in equilibrium. The most important of these are by Guthrie *, Alexejew †, and quite recently Rothmund ‡. The paper of the last named, which appeared after the completion of our experiments, contains a very full account of former experiments on the same subject. By these investigations the following facts have been established. The mutual solubility of two liquids changes considerably with temperature. In the large majority of cases, the mutual solubility increases with rise of temperature, the two phases approaching each other and finally becoming identical. Above the temperature at which this occurs the liquids are consolute, *i. e.* they mix in all proportions. In some cases, this temperature was not reached, but the changes in composition tended to show that a further rise of temperature would have made them also consolute. In other cases, ether and water for example (Klobbie §), the change of composition of the liquids was so small that no definite conclusion could be arrived at. In several cases the mutual solubility, instead of increasing regularly with rise of temperature, began by diminishing, *i. e.* the composition of the phases receded from each other, but beyond a certain point they approached again, and ultimately the phases coincided. In one case (water and secondary butyl alcohol, Alexejew) the phases first approached, then receded, and finally approached again and coincided. It is different with diethylamine and water (Guthrie ||), triethylamine and water (Guthrie and Rothmund), β -collidin and water (Rothmund ¶), and also with the bases of the pyridin and chinolin series and water. For these mixtures the mutual solubility increases on lowering the temperature, until at a certain temperature the phases become identical; below this temperature they are consolute. What happens to these mixtures on their temperature being raised has not as yet been settled.

In order to represent the behaviour of liquids with respect to their mutual solubility, the temperature-composition diagram is used. The curve in this diagram, which we shall call the solubility-curve, gives the compositions of the two liquids which are in equilibrium at each temperature. Orme Masson** approached the problem from the theoretical side; he was one of the first to point out the resemblance

* Guthrie, *Phil. Mag.* 5th ser. xviii. pp. 22, 495.

† Alexejew, *Wied. Ann.* xlvi. p. 305.

‡ Rothmund, *Zeitschrift Phys. Chem.* xxvi. p. 433.

§ Klobbie, *Zeitschrift Phys. Chem.* xxiv. p. 615.

|| Guthrie, *l. c.*

¶ Rothmund, *l. c.*

** Orme Masson, *Zeitschrift Phys. Chem.* vii. p. 500.

of the condition where the liquids become identical to the critical point where a liquid and its vapour become identical. This resemblance makes him suppose that any pair of liquids is bound to reach a similar critical point with rise of temperature, in the same way as every pure substance has a critical point. Rothmund agrees with Masson; he even goes so far as to admit the possibility of every combination having a lower critical point of complete miscibility and a higher one, between which two liquids would be possible. Or, putting it in terms of the solubility-curve, this curve might be found to be a closed curve, if only the limits of temperature were taken wide enough.

There is, however, another possibility with regard to the solubility-curve which Masson and Rothmund seem to have overlooked, viz. :—That on heating, the vapour and one of the liquids may become identical in density and composition, *i.e.* may reach a critical point, before the two liquids become identical. It is often not sufficiently remembered that the equilibrium between two liquids is not properly defined unless the liquids are in contact with the third phase, the vapour. If the vapour is not present, the composition and density of the coexisting liquids depend on the pressure, as well as on the temperature. As a matter of fact, in the experiments as they are usually made, there *is* a vapour phase above the two liquid layers, and the pressure which establishes itself at each temperature is the true equilibrium-pressure of the three phases (if we neglect the influence of the small quantity of air which is usually present in the vapour). The fact, however, that increase of pressure *above* the three-phase pressure has a very small effect on the composition (and also on the density) of the liquids under ordinary conditions * has led to the view, which seems common among workers in this field, that the influence of the vapour is of little account. Although this view is correct, in so far as increase of pressure above the three-phase pressure has as a rule a very small effect, it is not true in so far as the pressure at which the two liquids coexist cannot be less than this three-phase pressure. The importance of this will be seen at once, if the case in which the temperature is higher than the critical temperature of the upper liquid layer and the vapour is considered. Here no such lower limit for the pressure of the two remaining phases exists. The pressure, and therefore also the composition and density of the two phases, may be varied within wide limits; and it depends

* Instances will be given below where this influence was very prominent. A very small pressure was sufficient to make the two liquids mix, so that the rule that this influence may be neglected is not a general one.

entirely on the proportion in which the two substances are mixed, between what limits of pressure the phases may exist, and (this is of especial importance) at what temperature the phases become identical. In other words, above the critical point for the upper liquid and the vapour the solubility-curve does not exist, in the same way as the curve does not exist beyond a critical point of the two liquids.

The character of the solubility-curve cannot therefore be ascertained without taking into account the vapour. Let us consider the nature of the solubility-curve from this point of view.

The complete solubility-curve consists of *three* branches, two of which represent the compositions of the liquids, the third that of the vapour. The vapour branch may be either between or outside the liquid branches, according as the three-phase pressure is higher than or between the pressures of the pure substances *. Of these three branches, with rise of temperature two will reach a critical point: either the two liquid branches, as was the case with most of the mixtures examined by Alexejew and Rothmund; or one of the liquid branches and the vapour branch. Moreover, cases occur (see above) where the liquid branches form a critical point with *fall* of temperature. We shall call such a point a lower critical point. It will be seen that a number of combinations, some of which are represented in the diagrams 1-4, is possible.

Figs. 1 and 2 are the solubility-curves for liquids which have an upper critical point. The dotted curve representing the composition of the vapour is outside the liquid curves in fig. 1, between them in fig. 2. In both cases it stops suddenly at the critical temperature of the liquids. The case represented in fig. 2 is in many respects a remarkable one. It has the peculiarity that the composition of the vapour is the same as that of the liquids at their critical point. And it may be proved that, above this critical temperature, there is a maximum vapour-pressure or minimum boiling-point. We have ascertained by some rough measurements that several mixtures belong to this type. Examples of such mixtures are methyl alcohol and carbon disulphide, ethyl alcohol and carbon disulphide, water and phenol †, water and aniline. These mixtures, however, require further investigation, so that we will not discuss them at present.

* Konowalow, *l. c.*

† This combination has since been fully investigated by van der Lee (Dissertation, Amsterdam, November 1898), and also by Lehfeldt (Phil. Mag. [5] xlvii. p. 284).

Fig. 1.

Fig. 2.

Fig. 3 (p. 186) represents a case in which the vapour and one of the liquids have a critical point. This is the complete solubility-curve for ether and water, as will appear from the measurements given in this paper. Here the water and ether branch stops abruptly at the temperature (201°C.) at which the upper liquid and the vapour reach their critical point. The composition of the vapour is between the compositions of the liquids, and accordingly the three-phase

Fig. 3.

pressure is higher than the vapour-pressure of ether at all temperatures. The analogy between figs. 1 and 3 is evident.

In fig. 4 the vapour branch is outside the liquid branches,

Fig. 4.

and again a critical point for the vapour and upper liquid exists. Moreover, the liquids have a lower critical point, the consequence being that the solubility-curves only exist between two definite temperatures. It will be shown below

that this diagram holds for mixtures of ethane with ethyl, propyl, isopropyl, and normal butyl alcohols. For ethane and methyl alcohol the lower critical temperature, if it exists, was not reached in our experiments. Very probably fig. 4 is also the true diagram for some of the mixtures mentioned above which have a lower critical point, although they may equally well belong to the type of fig. 3, with the addition of a lower critical point for the liquids.

The solubility-curve does not completely represent the phenomena with which we are dealing, so that it is necessary to use other diagrams, especially the p - t and v - x . We shall use these later, particularly the v - x diagram, because it is the one that is used in the theory of van der Waals regarding mixtures of two substances. In all our experiments we have been guided by this theory. Its value, it seems to us, is largely independent of the special form of the equation of condition on which it is based. For the purpose of disentangling the complicated relations between composition, pressure, volume, and temperature, the ψ -surface with its plaits and plait-points is an indispensable guide; and, so far no phenomena have been discovered which are not fully accounted for by the possible position, growth, and decay of the plaits.

Our first experiments were made with ether and water. The questions we wished to solve for this combination were:—What are the pressures of the three phases at temperatures above the boiling-point? And secondly, Do the liquids mix at a certain temperature, or is a critical point between the vapour and the upper liquid reached? In order to obtain correct values for the vapour-pressures it was necessary to mix pure water and pure ether, and to exclude all other substances, such as air. The water used was distilled, free from organic matter, and left no residue on evaporation. The ether was from Kahlbaum, and was always freshly distilled from sodium before being used. It did not act on mercury even when wet. It did not give iodoform with caustic potash and iodine, nor did it dissolve fuchsin; the boiling-point was constant at $34^{\circ}35$ C. (760 mm.). The mercury was treated with nitric and sulphuric acids, and distilled *in vacuo*. In order to introduce the liquids air-free into the compression-tube, the principle of the method used by Ramsay and Young was applied. Our arrangement was as follows:—The tube of a Cailletet apparatus, but with a narrow tube at the bottom instead of a wide one, had sealed to it, at this end, a bulb, and to this bulb a second one at right angles to the direction of the tube. Into the former bulb some

mercury was introduced, and the tube and bulb were then filled with liquid. All air was then expelled by continued boiling under reduced pressure. The liquid was boiled away from the narrow compression-tube until the required amount was left, when a sudden tilting of the tube caused the mercury to fill the vapour-space. The second bulb prevents the liquid, while boiling is going on, from getting into the tubes leading to the air-pump.

The bulbs were then cut off and the tube introduced into the compression apparatus. In the case of water and ether it was necessary to introduce some water, boil out the air, and then as quickly as possible fill the tube with ether and proceed in the manner described. In the time occupied by the introduction of the ether, there is some chance of a little air dissolving in the water. Precaution was therefore taken after filling with ether to boil away a layer of some millimetres of the watery liquid. A stirrer, consisting of a piece of iron wire provided with enamel knobs, was used inside the compression-tube. We experienced a good deal of trouble on account of the action of the water on the glass tube. This action began at a temperature of about 160°C ., and at 200°C . gradually made the tube opaque. The action on the enamel knobs was even stronger; for our later experiments on ether and water we therefore enclosed the iron wire in a little glass tube. Even this precaution did not remove the difficulty, for when the experiments were nearly finished, the water had eaten a hole into this little tube. By prolonged heating of the mixture at 235°C ., under a pressure of 100 atmospheres, the watery layer diminished rapidly, and finally disappeared while a thick white coating was formed on the glass. Curiously enough, the vapour-pressures at lower temperatures were not much affected by this action on the glass, except of course after the lower layer had entirely disappeared. Notwithstanding these difficulties, the pressures which we found from independent observations with different fillings, before and after the application of the high temperature, agree very well, and may therefore be considered quite trustworthy. Some results obtained near the critical point, which we have difficulty in reconciling with the theory, have been probably occasioned by an impurity produced by the action of the water on the glass. These irregularities consist in the appearance of the critical phenomena, not at the real critical point for the upper liquid and the vapour (201°C .), but also at temperatures down to 198°C . This may be explained by the presence of a third substance in small quantity. We never noticed this irregularity with pure substances; but

similar results were afterwards obtained with ethane and isopropyl alcohol, the latter substance being used as it came from Kahlbaum, as the quantity was too small to admit of efficient purification.

The temperatures up to 50° C. were usually obtained by means of a water-jacket. For higher temperatures, and also sometimes for the lower ones (down to 30° C.), a vapour-jacket was used. The electromagnet which moves the stirrer is outside this jacket. The boiling-substances used were carbon disulphide, alcohol, chlorobenzene, aniline, and quino-line. Aniline is the only one of these liquids that we had difficulty in obtaining pure. Its boiling-point rose gradually during distillation, and it was not easy to know which fraction to select. There was, in consequence, some uncertainty as to the relation of our aniline to that used by Ramsay and Young in obtaining their pressure-temperature tables. We therefore always used a small Geissler thermometer (Jena glass) in the vapour-jacket, and were thus able to read the temperature directly. Unfortunately the discrepancy between this direct reading and the temperature as obtained from the tables of Ramsay and Young is sometimes considerable. In some cases there is no doubt that the direct reading is the correct one, as, for instance, at 100° C., for the thermometer could be tested at that temperature. In the tables which follow the temperatures are those read on the thermometers.

The pressures were read (1) on an open mercury-manometer up to 4.5 atmospheres, (2) on a closed air-gauge reading from 3 to 30 atmospheres, and (3) on a closed air-gauge giving readings above 25 atmospheres. The second gauge was graduated by means of the first at a low pressure. A comparison made between gauges 2 and 3 showed a difference of about $\frac{3}{4}$ of an atmosphere. This difference we have since found is due to the gradual oxidation of the mercury in the third gauge.

The irregularities in the differences near 130° C. and 150° C. are due to the difference between the gauges, and probably also to the already mentioned uncertainty of the temperatures. It will be seen from the table and the curves in the diagram, that the pressure of the three phases is everywhere higher than for ether at the same temperature. The difference is very small at the boiling-point, but increases rapidly as the temperature rises. The three-phase pressure remains, however, well below the sum of the vapour-pressures of water and ether. Our result near the boiling-point agrees with that obtained by Beckmann*. For the pressure at

* Nernst, *Zeitschrift phys. Chem.* viii. p. 134.

TABLE I.—Ether and Water.

Temp.	Ether and Water. Three-phase pressure.	Ether. Vapour-press (Ramsay & Young).	Water. Vapour-press. (Regnault).	Sum of Vap.-pressures of Ether and Water.	Sum— three-phase pressure.
34.15	764.3 mm.				
40	1.250 atmo.	1.212	.073	1.285	.035
50	1.744	1.679	.121	1.800	.056
60	2.381	2.274	.196	2.470	.089
70	3.195	3.018	.306	3.324	.129
80	4.229	3.935	.467	4.402	.173
90	5.514	5.040	.691	5.731	.217
100	7.04	6.39	1.00	7.39	.35
110	8.95	7.98	1.41	9.39	.44
120	11.27 } 11.30 } 14.00 } 14.03 }	11.28 ^s	1.98	11.84	.55
130	14.01 ^s	12.05	2.67	14.72	.71
150	21.50	17.48	4.71	22.19	.69
160	26.08	20.78	6.12	26.90	.82
170	31.12	24.50	7.84	32.34	1.22
180	36.93	28.69	9.92	38.61	1.68
201	52.03 } 51.96 }	52.00 Crit.	—		

Fig. 5.

34°15 C. we found 764·3 mm. As the change of the vapour-pressure of the three phases at the boiling-point is practically the same as for pure ether, *i. e.* 26·7 mm. per degree, a pressure of 760 mm. would have been obtained at a temperature of 35°99 C. The boiling-point of our ether was 34°35 C. at 760 mm., so that the three-phase boiling-temperature was 0°36 lower than for pure ether. Beckmann found 0°32. The agreement is very close, especially considering the absolutely different methods by which the results were obtained. We take this agreement as one of the proofs of the purity of the substances used.

Another test of purity is the comparison of the pressures at the same temperature, but at different volume. In most cases the pressure was lower at small than at large volume; this may be accounted for by a small fall in temperature in the vapour-jacket in going up. We did not succeed in getting rid of this fall; the constant use of the electromagnet prevented our protecting the tube as well as we might otherwise have done. The differences in pressure are accounted for by a fall in temperature of about 0°13 C.

The existence of a critical point for the upper liquid layer and the vapour at 201° C. has already been mentioned. The critical phenomena are very simple when two of three phases become identical. There is one temperature, and one only, where this can happen, and the critical phenomena are therefore almost identical with those of a single substance, and not with those of a mixture of two substances, when there is not a second liquid. It was pointed out, however, that ether and water showed some irregularity in the critical phenomena appearing at temperatures below 201° C. down to 198°. The influence of gravitation is of rather an intricate character in the case of three phases, and we will not attempt to discuss it on this occasion; but the absence of similar irregularities with other mixtures of pure substances which we investigated, makes us think that the reason of the irregular behaviour must be looked for in some impurity caused by the action of the water on the glass, and not in gravitation.

Above 201° C. there are only two phases left; the phenomena now are the ordinary phenomena of mixtures. A critical point, different for each mixture, may be looked for, above which no condensation is possible, retrograde condensation at lower temperatures, and finally a temperature (plait-point temperature) where the two remaining phases become identical. None of these phenomena could be observed with ether and water, as the opacity of the tube made

all observation impossible; and also the pressures required to reach the critical points are very high, the critical pressure of water itself being 190 atmospheres.

For further experiments our attention was directed to combinations of hydrocarbons and alcohols. In order to get the phenomena for which we were looking within easy reach of temperature we selected ethane, and we have combined this substance with a number of the lower alcohols.

A compression-tube was filled with ethane prepared from sodium acetate by electrolysis, and purified in the manner described in a former paper by one of us*. The substance to be introduced into the ethane was poured on the top of some mercury in a beaker, and boiled for some time in order to expel dissolved air. The beaker was then quickly cooled, the tube placed in the mercury, and by expelling some of the ethane and lifting the tube a few drops of the liquid were readily introduced without any chance of air getting in.

The methyl and ethyl alcohols were dried by boiling with finely powdered calcium carbide. After distillation the alcohols were treated with anhydrous copper sulphate, and finally, just before use, they were distilled from a flask with Wurtz head. The boiling-points, which were quite constant during this last distillation, were for methyl alcohol $64^{\circ}49$ C. at 760 mm., and for ethyl alcohol $78^{\circ}15$ C. at 760 mm.

The propyl alcohol was similarly treated with calcium carbide and copper sulphate. It was then fractionated, a long still-head containing platinum-gauze being used. The portion boiling at $96^{\circ}65$ (at 760 mm.) was used for the mixtures. The amyl alcohol was purified by repeated distillation, the distilling-flask being fitted with the deflegmator described by Young and Thomas. The boiling-point of the portion used for making the mixtures was $129^{\circ}23$ – $129^{\circ}28$ C. at 760 mm.

The isopropyl and butyl alcohols were used as they came from Kahlbaum. Their boiling-points were respectively $80^{\circ}2$ – $81^{\circ}3$ C. and $113^{\circ}6$ – $116^{\circ}8$ C. (both at 760 mm.).

The ethane was first tested. The values of the vapour-pressures and critical constants (Table II.) agree with those obtained on former occasions, and the small increase of pressure required for the total liquefaction ($p_b - p_a$) shows that the ethane was very pure.

* Kuenen, *Zeitschrift phys. Chem.* xxiv. p. 694; *Phil. Mag.*, Aug. 1897, p. 175.

TABLE II.—Ethane.

Temp. Centigrade.	p_a .	p_b .
10.98	30.83	31.02
14.95	33.62	33.91
22.95	40.13	40.37
32.16	C.	48.86

p_a = the pressure at which liquid appears.

p_b = the pressure at which vapour disappears.

Our first experiment with methyl alcohol made us think that it mixed with ethane in all proportions (Table III.). After expelling some of the alcohol, however, we obtained two liquid layers at all temperatures up to the critical temperature of the ethane layer and the vapour (Table IV.).

TABLE III.—Ethane and Methyl Alcohol (I.).

t .	p_b .	
14.95	33.62	Two phases.
31.95	50.99	" "

Vapour disappears at the pressures p_b . Normal condensation.

TABLE IV.—Ethane and less Methyl Alcohol (II.).

t .	p_a .	p_b .	
15.1	33.44	33.77	Three phases.
22.9	39.45		"
22.95		39.91	"
31.55	47.16	47.48	"
	p .		
31.75		47.46	"
34.2		49.81	"
35.1		50.76	"
35.37	C.	51.99	"

At p_a second liquid appears. At p_b vapour disappears. Normal condensation.
 p is a mean pressure.

The former result was therefore due to the proportion of alcohol being too large. In order to ascertain whether a lower critical temperature for the two liquids existed we cooled some methyl alcohol to -78°C . in solid carbonic acid, and distilled some ethane into it. The two layers appeared again quite distinctly, without any indication of a critical point.

The pressures of the three phases (Table IV.) will be seen to be smaller than those for pure ethane. The pressures indicated by p_b are those registered when the last trace of vapour was just disappearing. That these are somewhat higher than the pressures read at a larger volume is due to the slight impurity in the ethane (see Table I.). From the theory it follows that if the pressure of the three phases is between the vapour-pressures of the pure components, and no maximum vapour-pressure exists, then the composition of the vapour is not between but outside the compositions of the two liquids.

Fig. 6.

Fig. 6 shows diagrammatically the relative position of the three points (a, b, c) representing the three coexisting phases in the v - x diagram in this case. The dotted curves are the plait-point curves of the two halves of the vapour-liquid plait and the liquid plait. The straight lines connect the coexisting phases, and show by their position in which direction

the pressure increases—here from the alcohol towards the ethane on both sides of the vapour-liquid plait. The pressure for mixtures containing so much alcohol that no second liquid layer is formed must therefore be lower than the three-phase pressure at the same temperature. The pressure of the first mixture at $14^{\circ}95$ C is 33.62 atmospheres (which would have been 33.74 at $15^{\circ}1$ C.), and thus indeed slightly lower than the corresponding pressure of the three phases at the end of the condensation of mixture II. The pressure at $31^{\circ}95$ C., on the other hand, is much higher than the corresponding three-phase pressure. The explanation of this divergence from theory is probably simply this: that near the end of the condensation a second layer, which escaped our notice, had actually been formed, and the high pressure required was really a pressure on the two-liquid plait, and not on the vapour-liquid plait.

With rise of temperature the points *b* and *c* approach each other. At $32^{\circ}16$ C., the critical temperature of ethane, a plait-point appears on the surface on the ethane side. This plait-point approaches *cb*, and at $35^{\circ}37$ C. the two phases become identical, and the plait-point disappears. Above $35^{\circ}37$ there is only one plait left, the plait-point of which in the case of methyl alcohol could not be reached, as the pressure and temperature became too high. We will defer further consideration of the phenomena above the critical point to the cases of propyl and butyl alcohol, where the second plait-point belonging to the liquid plait was thoroughly investigated.

The next three higher alcohols differed from methyl alcohol in having a lower critical point. Ethane and ethyl alcohol, for instance, at the ordinary temperature mix in all proportions. At $31^{\circ}9$ C. (Table V.) the liquid, after showing the charac-

TABLE V.—Ethane and Ethyl Alcohol (I.).

<i>t.</i>	<i>p_b.</i>	
14.97	32.97	Two phases.
	<i>p.</i>	
31.90	C. 46.25	Three phases.
31.95	46.34	"
32.15	46.49	"
32.55	46.90	"
34.85	49.05	"
39.15	53.23	"
40.67	C. 54.90	"

teristic blue colour which always precedes critical phenomena, suddenly separates into two liquids. Below $31^{\circ}9$ C., therefore, the points *a* and *b* do not exist: at the moment of their

TABLE VI.—Ethane and more Ethyl Alcohol (II.).

<i>t.</i>	<i>p.</i>	
32.65	C. 47.12	Three phases.
32.75	47.16	„
32.95	47.30	„
40.75	C. 54.68	„

appearance a small plait is formed, the plait-point of which, so to speak, lies between *a* and *b*, which are still close together. With rise of temperature this liquid plait becomes broader and longer, *a* and *b* receding from each other. The other plait-point has now (at $32^{\circ}16$, the critical temperature of ethane) also made its appearance, and gradually approaches the three-phase triangle. The pressures will be seen to be related to each other as in the case of methyl alcohol and

TABLE VII.—Ethane and still more Ethyl Alcohol (III.).

<i>t.</i>	<i>p_b.</i>	
14.95	32.81	Two phases.
	<i>p.</i>	
32.75	C. 47.04	Three phases.
32.95	47.26	„

ethane. For instance, at $14^{\circ}95$ (Table VII.) the two-phase pressure of $32^{\circ}81$ is less than the pressure in Table V. for a mixture containing less alcohol.

At 35° C., say, the *v-x* diagram has the appearance shown in fig. 7. No difficulty will be found in imagining the gradual diminution of the plait *P*₁ with further rise of temperature and its disappearance at $40^{\circ}7$. [The two critical points $31^{\circ}9$ and $40^{\circ}67$ are somewhat different from those obtained with more alcohol in the mixtures Tables VI. and VII., a difference due probably to the introduction of impurity.]

Above $40^{\circ}7$ there is only one plait left, the plait-point of which is not P_1 (as is the case with ordinary mixtures) but P_2 . For ordinary mixtures the plait-point lies near the left-hand edge of the plait. Here it is turned much further towards

Fig. 7.

the x -axis, the consequence being that the critical temperature and the plait-point temperature differ much more than they do in other cases. Instances of this will be given for ethane and propyl alcohol, for which combination the v - x diagram has the same character as for ethyl alcohol and ethane. The critical temperatures for propyl alcohol and ethane are $38^{\circ}67$ and $41^{\circ}7$. The two critical temperatures approach each other as we ascend the alcohol series. For butyl alcohol and ethane we find $38^{\circ}1$ and $39^{\circ}8$.

Tables VIII. and IX. for propyl alcohol and ethane are again in full concordance with the diagrams.

In fig. 8 (p. 199) the following curves have been drawn:—The vapour-pressure curve for ethane (that for propyl alcohol is not shown); the three-phase curve which starts at $38^{\circ}7$ and ends at $41^{\circ}7$ C.; the plait-point curve $C_1 C_4$ of the plait-point P_1 connecting C_1 the critical point of ethane with C_4 the end

TABLE VIII.—Ethane and Propyl Alcohol (I.).

<i>t.</i>	<i>p.</i>	
38.67	C. 52.78	Three phases.
38.75	52.85	"
38.95	53.12	"
39.95	54.09	"
41.7	C. 56.01	"
39.55	54.22	} By compression after the vapour has disappeared, the quantity of liquid at the bottom diminishes and disappears at these pressures; retrograde condensation.
39.75	54.47	
40.35	55.39	
41.75	57.43	
42.2	58.22	
43.35	59.81	

TABLE IX.—Ethane and more Propyl Alcohol (II.).

<i>t.</i>	<i>pb.</i>	
14.96	32.76	Vapour disappears. Two phases
31.8	46.17	" " } Normal
31.96	46.35	" " } Condensation.
38.05	52.25	" "
38.75	53.03	Vapour disappears. Three phases
38.85	53.09	" " } Normal
39.65	53.91	" " } Condensation.
38.82	53.14	} By compression, after the disappearance of the vapour, the liquids approach each other in composition and mix, displaying critical phenomena at these pressures.
38.95	53.27	
39.65	54.29	
40.55	55.70	
43.35	59.76	
43.47	59.90	
49.75	68.83	
55.95	75.76	
82.1	103.2	} Lower liquid disappears by pressure; retrograde condensation.
91.4	106	

of the three-phase curve; the plait-point curve C_2C_3 of the plait-point P_1 starting at C_2 , the critical point of propyl alcohol (not shown), and after a long detour (not completely investigated) reaching C_3 , the beginning of the three-phase curve.

It is impossible to give a full account of the phenomena which occur at different temperatures with different quantities of alcohol. They may all be read directly from the $v-x$ or $p-t$ diagrams. One point, however, may be specially mentioned,

namely, the possibility of making the two liquids mix by pressure at temperatures above the lower critical temperature. It depends on the proportion of alcohol in the mixture whether this will be possible, or whether either the one or the other liquid will gradually diminish in quantity and disappear.

Fig. 8

With a suitable proportion the plait-point P_2 may be reached by the application of pressure. If the composition of the mixture does not correspond accurately with the composition of the plait-point P_2 , the critical phenomena of the liquids are obtained either near the top or near the bottom of the column of substance. Thus, with one particular mixture (Table IX.) several points of the plait-point curve $C_2 C_3$ could be determined*.

* The explanation of this is to be found in the action of gravitation. See Kuenen, *Communications Phys. Lab. Leiden*, No. 17.

For instance (Table IX.), at $38^{\circ}82$ C. the two liquids become identical and mix at a pressure of 53.14 atmospheres, while the three-phase pressure (measured at the moment of the disappearance of the vapour) is 53.07 atmospheres. The pressure over and above the three-phase pressure required for the mixing is only .07 of an atmosphere. At the critical temperature itself ($38^{\circ}67$) no pressure would be required at all. As the temperature rises the excess of pressure required increases. At $40^{\circ}55$ the three-phase pressure is 54.75 atmospheres (as calculated from Table VIII.), while the plait-point pressure on the liquid plait is 55.70 atmospheres, *i. e.* almost an atmosphere more. These examples show sufficiently that the excess of pressure required is small at temperatures only slightly above $38^{\circ}67$ C.

The first mixture (Table VIII.) contained so little alcohol that at no temperature could critical phenomena of the liquids be observed, the lower liquid layer disappearing before the plait-point was reached. The pressures at which this happens are lower than the pressures at which the second mixture shows plait-point phenomena as they should be.

Just above the critical point for this mixture (and the same holds for the other alcohols) the influence of pressure is very marked indeed, and the same thing *may* be true for many other mixtures in the neighbourhood of a critical point for two liquids.

The tables for butyl alcohol do not require any further explanation, the phenomena being very much the same as for propyl alcohol.

TABLE X.—Ethane and Butyl Alcohol (I.).

<i>t.</i>	<i>p.</i>	
14.95	32.86	} Vapour disappears by compression; two phases.
22.9	38.88	
31.95	46.66	
33.35	48.04	
41.23	56.55	
50.15	68.49	

TABLE XI.—Ethane and less Butyl Alcohol (II.).

<i>t.</i>	<i>p.</i>	
15.3	33.48	} Vapour disappears by compression; two phases.
22.95	39.36	
31.95	47.07	
38.1	C.	} Three phases.
38.55	53.67	
38.75	53.97	
39.8	C. 55.04	
38.75	54.22	} Compression of the liquids gives critical phenomena and mixing; at 38°·75 near the top and at higher temperatures nearer and nearer to the bottom of the tube.
39.75	55.81	
39.95	56.19	
50.0	70.04	
60.0	81.78	

With isopropyl alcohol we did not obtain such good results as with the other alcohols, probably owing to its impurity. It gives three phases, between two limits of temperature, just as the other alcohols do, the upper critical temperature being about 44° C. The lower critical point could not be determined with any accuracy as critical phenomena of the liquids in the presence of vapour were observed between wide limits of temperature (38° to 42°) instead of at one temperature only. Also at temperatures below 38° (down to about 25°) three layers were still formed, and retrograde condensation was observed—all this pointing to the presence of a third substance. Though the butyl alcohol also was not very pure (as shown by the boiling-point), its impurity appeared to have a much smaller effect on the phenomena than in the case of isopropyl alcohol.

With the mixture of isoamyl alcohol and ethane, the last one we tried, no three phases were observed, although three decreasing proportions of alcohol were used. The plait-point, however, still retains the same character as with the other alcohols, that is, it is turned considerably towards the x -axis, as will be seen from Table XIV. This particular mixture displayed plait-point phenomena at 45° C. ; up to 107°·6 C., the highest temperature we could apply with safety on account of the high pressures, it still showed (retrograde) condensation. With this mixture therefore the plait-point temperature and the critical temperature, which with such mixtures as carbon dioxide and methyl chloride, carbon dioxide and air, &c. are almost identical, differ considerably. The same thing

will probably often be found when the critical temperatures of the two components differ largely.

TABLE XII.—Ethane and Amyl Alcohol (I.).

<i>t.</i>	<i>p.</i>	
14.95	31.78	} Vapour disappears. Normal condensation.
31.95	46.12	
52.55	68.85	

TABLE XIII.—Ethane and less Amyl Alcohol (II.).

<i>t.</i>	<i>p.</i>	
14.95	33.34	} Vapour disappears; normal condensation. At the last three temperatures the surface between the two phases was faint; and there were indications of critical phenomena.
31.95	47.16	
41.95	57.99	
59.5	80.13	
69.9	93.12	
78.15	101.0	

TABLE XIV.—Ethane and less Amyl Alcohol (III.).

<i>t.</i>	<i>p.</i>	
14.95	33.59	} Vapour disappears. Normal condensation.
31.95	47.37	
43.15	59.91	} Critical phenomena at 43°·15 near the top, at 44°·95 near the middle, and at high temperatures near the bottom of the tube.
44.95	62.40	
45.75	63.46	
50.35	69.56	
55.77	75.27	
100.0	115.6	} Liquid disappears. Retro-grade condensation.
107.6	118.2	

Mixtures of ethane and ether were tried, but three phases were never obtained, the two liquid components mixing in all proportions. Ethane and water do not mix in all proportions. Measurements showed that for this combination (Table XV.)

TABLE XV.—Ethane and Water.

<i>t.</i>	<i>p_a.</i>	<i>p_b.</i>	
14.95	33.59	34.00	Three phases.
22.95	40.07	40.46	"
32.15	C. 48.81		"

the pressures and critical constants differed very slightly from those of pure ethane (Table II.). The difference $p_b - p_a$ is more than for ethane, which may, however, be due to a difference in the purity of the ethane itself. The pressures are so nearly the same as those for pure ethane that we cannot say whether the three-phase pressures are greater or less than the pressures for ethane. Probably, as for the alcohol mixtures, the three-phase pressure is less than the pressure of the ethane. Table XVI., in which are given a few not very accurate measurements made by one of us a few years ago, shows that for

TABLE XVI.—Carbon Dioxide and Water.

<i>t.</i>	<i>p.</i>	Amagat, CO ₂ .
18.85	54.4	} Three phases.
31.2	72.4	
31.5	C.	

mixtures of carbonic acid and water the three-phase pressure is probably less than the pressure of carbonic acid. For this mixture the critical temperature was found to be above the critical temperature of carbonic acid, as was to be expected.

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