

Citation:

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Eleventh Series (Au, Hg, Tl, Pb, Bi). χ for Hg between -170° and -150° was approximately constant, and afterwards underwent a gradual numerical increase: at the melting point (-39°) it suffered a sudden change. The susceptibility of Tl numerically decreased between -170° and $+18^\circ$. The same was true for Pb, the change in this case being very slight. For Bi, $\chi = -1,58$ at -175° , a value which agrees well with that found by FLEMING and DEWAR ($-1,61$ at -182°)¹). With regard to some colloidal specimens of this series, χ for Hg was throughout constant: that of Au was constant between -170° and $+50^\circ$, afterwards decreasing slightly numerically. The character of the (χ, θ) curve for colloidal Bi was very peculiar.

Twelfth Series. (Th, U). The susceptibility of Th increased with the temperature. The value for U on the other hand decreased.

On the whole, we may say that the curves $\chi = \text{funct.}(\theta)$ show most varied aspects. Roughly, the elements are more or less distributed over the six possible classes, viz. para- or diamagnetic, each constant, increasing or decreasing as the temperature rises. Only seven diamagnetic elements do not vary within the whole temperature range, amongst them the three that CURIE happened to investigate. The thermomagnetic properties also show a certain correlation with the periodic system.

Physics. — *“Investigations concerning the miscibility of liquids.”*

By Prof. J. P. KUENEN.

Several years ago I began a systematic experimental investigation of the miscibility of liquids, in particular as regards the influence of temperature and pressure, or to express it differently an investigation into the shape and the change of shape of the projected liquid plait of the ψ surface and its position relatively to the vapour-liquid plait²).

A fertile combination and one which turned out interesting in many respects was found in the saturated hydrocarbons with the lower alcohols. The investigation of these and other mixtures which was discontinued from various causes was recently taken up again and I

¹) J. A. FLEMING and J. DEWAR, Proc. Roy. Soc., **63**, p. 311, 1898.

²) I take this opportunity to say that in my communication of October 28 on the geometrical properties of these plaits I did not wish to imply anything but what I thought I had distinctly expressed and that the implications which are attributed to me by Prof. VAN DER WAALS in his paper of November 25 are entirely outside my meaning.

propose to communicate the results to the Society from time to time.

A decided gap in the research was the absence in the series of hydrocarbons of a term with four carbon atoms and in one of my last papers on the subject¹⁾ I stated, that the preparation of normal butane had been tried and that it had not met with the desired success. The method was by electrolysis of sodium propionate, which yields a very impure gas, the chief products being carbon dioxide and ethylene. The treatment with bromine for the absorption of ethylene showed that bromine acts on butane and a repeated attempt to procure pure butane by this method did not succeed.

Better methods were not then available. In the mean time two new methods of preparing hydrocarbons from bromides or iodides have been published: one by the action of sodium dissolved in liquid ammonia (LEBEAU) and the other (GRIGNARD) with magnesium. Butane has been prepared by the first method by LEBEAU himself²⁾ and by the second method by OUÉDINOFF³⁾.

The results obtained by them do not agree accurately. I have applied both methods and again obtained results which do not quite agree either with each other or with those of the other investigators. I subjoin a table of the critical constants and boiling points.

Normal Butane.

Observer	Method of preparation	Crit. Temp.	Crit. press.	Boiling point
Lebeau	Lebeau	151—152		0.5
Ouédinoff	Grignard	146.5		0.6
Kuenen	Electrolysis	158.5		
"	"	145.5		— 1.7
(a) "	Lebeau	148.7	± 39	
(b) "	Grignard	150.8	37.5	— 0.1

The experiments communicated below were made with the two samples of butane indicated as (a) and (b)⁴⁾.

In the mean time some observations have been made by TIMMERMANS

¹⁾ J. P. KUENEN. Phil. Mag. (6) 6 p. 647. 1903.

²⁾ P. LEBEAU. Bull. Ac. R. de Belg. 1908 p. 300—304.

³⁾ OUÉDINOFF. Bull. Soc. Chim. de Belg. (23) Juin 1909.

⁴⁾ Later on I hope to communicate a set of physical constants of butane obtained with sample (b), mainly determined by S. H. VISSER, science student at Leiden.

and KOHNSTAMM¹⁾ on mixtures of butane with a few other substances, butane having been given to them by OUEÏDINOFF.

I begin by communicating a few critical endpoints²⁾ which I have determined.

Critical endpoints.

methylalcohol	+ isopentane	10.5
„	+ <i>n.</i> pentane	19.4 ³⁾
„	+ <i>n.</i> butane (<i>b</i>)	17.0 (<i>T.</i> and <i>K.</i> 16.6 ⁴⁾)
aethylalcohol	+ isopentane	—30
„	+ <i>n.</i> butane (<i>a</i>)	+ 37.5.

The critical end-point for methylalcohol and normal butane agrees well with the result of the other observers.

Very unexpectedly an entirely different result was obtained when use was made of butane (*a*), although in its constants but little differing from butane (*b*). This difference must be due to some impurity and although I cannot throw any light on the nature or action of this impurity, I will describe the observations, as they have brought to light a new phenomenon, which appears to be of interest.

When a mixture of butane (*a*) and methylalcohol was heated in a compression tube (Cailletet) in the presence of the vapour, the surface between the liquid layers disappeared about 22°, a somewhat higher temperature than for a mixture of butane (*b*) (17°.0). When however the temperature was further raised the meniscus soon reappeared and the definite critical end-point was not reached till 38°. Beyond 38° no separation of two liquids took place. The application of pressure revealed a similar abnormality: at temperatures above 22° a gradual increase of the pressure always had the effect of making the meniscus grow faint and disappear and afterwards permanently reappear.

It is not difficult to see what shape has to be attributed to the liquid plait in the *v-x* diagram in order to represent the above phenomena. The fact that pressure ultimately produces separation

¹⁾ J. TIMBERMANS and PH. KOHNSTAMM. Proc. XII 1909—10, p. 234 table on page 239.

²⁾ By critical end-point is meant the critical point of the liquid layers in the presence of vapour, i.e. the point where the liquid plait touches the vapour-liquid plait. In former papers I have usually called this point the critical mixing-point.

³⁾ Determined by me on a previous occasion (l. c. p. 647) and erroneously attributed by TIMBERMANS and KOHNSTAMM (l. c.) to isopentane instead of normal pentane.

⁴⁾ l. c. p. 239.

of the two liquids shows that the plait is open towards the x -axis. This is in accordance with the result obtained by TIMMERMANS¹⁾, that the critical temperature of the liquids is in this case raised by pressure, which means that beyond the critical end-point the liquid plait lies outside the vapour-liquid plait with its plaitpoint turned towards the latter. But the abnormal phenomenon was not noticed by him, nor have I been able to reproduce it with mixtures of butane (*b*).

If the liquid surface temporarily disappears as described, the plait would have to consist of two parts as shown in fig. 1 where the

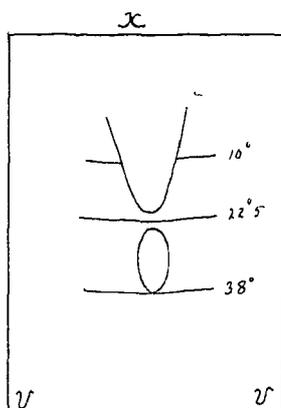


Fig. 1.

relative position with respect to the liquid branch of the vapour-liquid plait is also indicated. It seems unnecessary to show in detail, that the behaviour of the mixture under changes of pressure or temperature agrees with the assumed diagram. In itself a diagram of this nature is by no means improbable. In this connection it is important to consider the behaviour of a mixture of methylalcohol with isobutane as observed by TIMMERMANS. The critical end-point is in that case very near a point where the liquid plait divides and it would be quite possible for the plait in the case of the nearly allied normal butane to be divided in the manner assumed in fig. 1.

Further investigation of the phenomenon showed however that the assumption was incorrect. It may be remarked that the observations were extremely difficult owing to the great indistinctness of the liquid surface compared to other mixtures (TIMMERMANS notes the same peculiarity for mixtures of methylalcohol and isobutane). When I repeated the observation under the most favourable conditions with regard to illumination I found that the meniscus did not really

¹⁾ J. TIMMERMANS. Thèse Bruxelles 1911, p. 82.

disappear when it seemed to do so temporarily before, but as a rule remained just visible in the form of a dark and sometimes slightly coloured horizontal line near the axis of the-tube.

The moment of minimum distinctness could be observed with fair accuracy; in the table are given the observed pressures as also some three-phase pressures. The readings were not more accurate than to about $\frac{1}{2}$ atmosphere.

Temp.	Least distinctness at	Three phase pressure:
14.0	— atm.	$1\frac{1}{2}$ atm.
22.5	2	2
22.8	$3\frac{1}{2}$	—
24.2	$9\frac{1}{2}$	$2\frac{1}{4}$
25.0	$13\frac{1}{2}$	—
25.5	16	—
26.3	$21\frac{1}{2}$	$2\frac{1}{2}$
27.2	$25\frac{1}{2}$	—
28.5	33	—
29.3	$36\frac{1}{2}$	—
31.0	43	—
32.4	$53\frac{1}{2}$	3
33.7	$62\frac{1}{2}$	$3\frac{1}{2}$
36.8	75	—
37.0	78	—
38.1	—	$4\frac{1}{4}$
38.2	—	Cr. end-point
38.6	84	—

The plait cannot therefore be divided as in fig. 1 and our supposition has to be modified in the sense that the plait is only strongly contracted as in fig. 2.

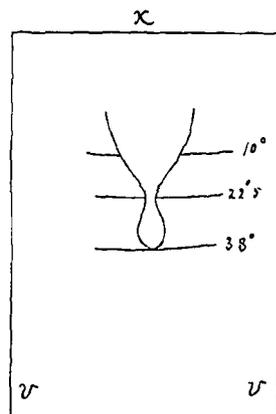


Fig. 2.

But the facts speak against this supposition too; for with fig. 2

one would expect phenomena which also occur near a critical point e.g. a distinct change in the relative volumes of the two phases (at 38° this phenomenon was very marked) and a slow settling down of the liquids after having been stirred up. This was not what happened at the points of indistinctness: in so far as the meniscus was visible at all, it reappeared (after stirring) comparatively quickly as if there was a difference in density between the liquids of the same order as at other points of the plait.

The only explanation which remains is that the refractive indices of the liquids become equal: the plait need not have any abnormal shape, but at some distance from the plaitpoint there is a point where the two coexisting liquids have the same index, which point, if outside the vapour liquid plait i.e. above 22° , may be reached by change of pressure. Though this phenomenon cannot but be very rare, it is not by any means impossible even with two pure substances. When the indices of the components differ little, there is a chance that the phenomenon may occur: there will be a maximum or minimum in the indices in that case for one particular proportion. Probably the index of butane is not much higher than that of methylalcohol (this question is being investigated): the indistinctness of the surface between the liquids even at a distance from the critical region makes this probable.

The question remains what impurity may have occasioned the difference in the behaviour of the two samples of butane in this respect ¹⁾. I am inclined to think, that butane (b) was purer than butane (a), especially as the experiments were made with the last remaining fraction of the butane (a) available, in which an admixture of higher boiling point may have been concentrated and during the operation of introducing the substances into the compression tube some moisture may also have got into the tube. However that may be it is very remarkable that an impurity which cannot have been large, as appears from the constants of the substance, can have had such a strong effect on the mixing phenomena, shifted the critical end-point from 17° to 38° and moreover produced the abnormality in the refractive index.

Finally it may be remarked, that the probable conclusion with respect to the impurity of the butane (a), raises some doubt as to the accuracy of the critical end-point for mixtures of ethylalcohol and butane. I hope shortly to be able to throw more light on the questions raised by these observations.

¹⁾ If the mixture contains a third substance it is properly speaking no longer possible to represent the phenomena with the aid of a $v x$ diagram, unless the admixture is so slight that it may be disregarded for the purpose of the graphical representation.