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Physics. — “*On unmixing in a binary system for which the three-phase pressure is greater than the sum of the vapour tensions of the two components.*” By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Sept. 26, 1914).

1. In my investigation on the system hexane-water the remarkable phenomenon presented itself that the three-phase tension of the two liquid layers by the side of gas appeared to be greater than the sum of the vapour tensions of pure hexane and pure water¹⁾. When the tensions of the pure substances at a definite temperature are denoted by P_1 and P_2 , the three-phase pressure by P , then for temperatures which are not too far from the critical end-point

$$P > P_1 + P_2.$$

If we could speak of “partial pressures” for such an equilibrium, this result would be impossible. A proof of this is found in VAN DER WAALS—KOHNSTAMM’S “*Thermodynamik*”, which however is only valid when the gas-laws²⁾ hold for the saturate vapours. When the gas-laws do not hold for the gas phases, in other words if the gases possess surface layers, the proof is not valid, and the statement that the three-phase pressure must always be smaller than the sum of the vapour tensions of the components, holds therefore only for rarefied saturate vapours.

In my paper on the system hexane-water I have shown that the contradiction with the second law of thermodynamics, which at first sight may be supposed to exist in the observed phenomenon, is only an apparent one. We might, namely, be inclined to reason as follows: If the three-phase mixture possesses such a high pressure, the pressure exerted by the water and hexane molecules, or at least that of one of them will have to be greater than the pressure of water vapour, resp. hexane vapour over the pure components. If we therefore bring the three-phase mixture by means of a semi-permeable membrane into contact with pure hexane and with pure water under their own vapour pressure, hexane or water will pass through the semi-permeable membranes from the three-phase mixture towards the pure liquid. We should then get splitting up of the three-phase mixture, whereas just on the contrary the so high three-phase pressure sets in of its own accord from pure water and pure hexane. This is in conflict with the second law of thermodynamics.

¹⁾ These Proc. 16. 404. (1913).

²⁾ *Thermodynamik*. II. S. 476.

I have shown in the cited paper that the conclusion that the three-phase mixture will expel water through a membrane permeable to water, is really correct, and that probably *mutatis mutandis* the opposite thing will apply to hexane. The error in the above reasoning lies therefore only in the very last conclusion. I have pointed out *loc. cit.* that it is, indeed, possible that two liquids, each under its own vapour pressure, mix to a three-phase mixture that possesses the property to get unmixed again into the pure components through semi-permeable membranes; that this is not in contradiction with the second law of thermodynamics, but that on the contrary this phenomenon will be frequently met with in my opinion, also for systems which do not present the special behaviour mentioned at the head of this paper. Thus solutions of gases which are but sparingly soluble in water will certainly expel water, when they are osmotically brought in contact with pure water of the saturate tension. The observed phenomenon is therefore not in conflict with our theoretical considerations.

2. To get an answer to the question whether the system hexane-water presents an exceptional behaviour in the appearance of a three-phase pressure which is greater than the sum of the vapour tensions of the components, I have investigated a number of other systems in the hope of finding the remarkable phenomenon there too. First of all I have chosen the system pentane-water. The pentane which I had at my disposal, was however KAHLBAUM's "normal pentane", which is no pure normal pentane, but a mixture of normal and isopentane, which can only be separated with great loss of substance and time, as the boiling-points of the two substances lie near room-temperature, and differ only little (slightly more than 8 degrees). This slight difference of boiling-point involves that the pentane mixture behaves pretty well as a pure simple substance; the isothermal pressure ranges for condensation are slight. I have therefore given up the separation of the two pentanes, and compared the vapour tensions of the pentane mixture and of pure water with the three-phase tension of a pentane-water mixture. It is clear that both the pentane mixture and the three-phase mixture must possess a tension dependent on the volume at constant temperature, but also the three-phase tension appeared to be only little dependent on the volume. To execute this comparison of the pressures as exactly as possible I have determined the pressures for final condensation and for about equal volumes of gas and liquids both of the pentane mixture and of the three-phase mixture.

TABLE I.

Pentane mixture.		
Tem- perature.	Pressure (atm.)	
	End- condensation	$V_L = V_G$
151.3	17.65	
151.9		17.8
161.1		20.6
161.45	20.8	
169.95	23.7	
170.1		23.7
180.1		27.6
180.3	27.8	
190.25	32.15	
190.3		32.05
193.3		33.6

TABLE II.

Threephase mixture.		
Tem- perature.	Pressure (atm.)	
	End- condensation	$V_L = V_G$
150.15	22.45	
150.7		22.7
160.6		27.25
160.7	27.35	
166.5		30.3
170.25	32.55	
170.35		32.65
180.3		39.0
180.5	39.25	
187.1		44.1

When the values of pressure and temperature indicated in the above tables are graphically represented, it appears that the line for the end-condensation coincides fairly well with that which holds for equal liquid and vapour volume both for the pentane mixture and for the three-phase mixture; the difference is nearly everywhere smaller than 0.1 atmosphere, and is therefore of about the same value as the errors of observations. When the pressure values are read for definite temperatures from the graphical representation, the values of table 3 are found.

TABLE III.

Temperature	Three-phase pressure	Pentane pressure	Waterpressure	Difference
150	22.4	17.3	4.7	0.4
160	27.0	20.3	6.05	0.65
170	32.4	23.7	7.8	0.9
180	38.8	27.6	9.8	1.4
187.1	44.1	30.7	11.6	1.8

The values for the vapour tension of water have not been derived from earlier observations, but determined by myself to prevent an eventual deviation of the thermometer from vitiating the comparison. All the observations have been carried out with a normal thermometer, and with an Anschützthermometer verified by the boiling point of pure aniline.

We draw the conclusion from the last column of table 3 that the three-phase tension is again greater than the sum of the vapour tensions of the pentane mixture and of pure water. The difference appears again to be greatest at the critical endpoint — in all the tables the critical values are printed in bold type —; with decrease of temperature the difference decreases rapidly, and according to the theory it must reverse its sign at temperatures where the saturate vapours follow the gas laws.

The above described example shows therefore again a case of very high three-phase pressure. Though these experiments would have to be repeated with the pure substances to get perfect certainty about the behaviour of the binary systems, the conclusion that the pentanes and hexane behave analogously with respect to water, seems yet sufficiently certain to me. Also the relative situation of the critical end point with respect to the critical points of the components is the same as for the hexane-water mixtures.

Finally I will still point out that the above only proves that there exists a pentane-water mixture that possesses the repeatedly mentioned remarkable property, and this suffices also for my purpose; other proportions of pentane mixture and water will probably give rise to some change in the three-phase tensions because the pentane mixture is not a simple substance; for the solubilities of the two pentanes in water will probably not be in the same proportion as the quantities of the pentanes in the pentane mixture; the difference in the fifth column can therefore undergo some modification for another ratio of the two "components".

§ 3. The experiments of § 2 confirming my supposition that the abnormal value of the three-phase pressure would be a phenomenon of frequent occurrence, I thought I had a great chance to find the same peculiarity also for other binary systems. I have therefore looked for binary systems of which it was known that for low temperatures the three-phase pressure lies higher than the vapour tensions of the pure components separately and is about equal to the sum. Dr. BÜCHNER drew my attention to the systems carbon tetrachloride-water and benzene-water, which possess three-phase

tensions according to REGNAULT, which deviate little from the sum of the vapour tensions of the pure substances. REGNAULT even asserted that the tension of carbon tetrachloride-water mixtures is somewhat higher than the sum, and thought he had to ascribe this to slight contaminations; GERNEZ has shown later that the three-phase tension is really slightly smaller than the sum of the vapour tensions, which is therefore in harmony with the theory. I have now tried to investigate the two systems at higher pressure; I have, however, not succeeded in doing so with the system carbontetrachloride-water, as the components act on each other at higher temperatures. The investigation is possible for the system benzene-water, and also this system appeared really to furnish an example of the remarkable phenomenon.

Benzene free from thiophene (negative isatine reaction) was distilled from phosphorus pentoxide; the boiling point under normal pressure was $80^{\circ}.2$, and was therefore in perfect concordance with the value given by YOUNG. The vapour tension line of this benzene was determined, and then the three-phase tensions of a benzene-water mixture were measured and compared with the vapour pressure line of water, which was also determined by the aid of the same thermometers. To avoid corrections I have measured the three pressure values

T A B L E IV.

Temperature	Three-phase pressure	Waterpressure	Benzene pressure	Difference
150.0	10.6	4.7	5.9	0
160.0	13.2	6.05	7.1	0.05
170.0	16.4	7.8	8.5	0.
180.0	20.1	9.8	10.2	0.1
190.0	24.6	12.35	12.15	0.1
200.0	29.8	15.3	14.3	0.2
210.0	35.9	18.75	16.7	0.45
220.0	42.9	22.8	19.45	0.65
230.0	50.9	27.5	22.5	0.9
240.1	60.35	33.0	25.95	1.4
250.2	70.65	39.1	29.55	2.0
260.1	82.15	46.1	33.7	2.35
267.8	92.7	calc.(52.4)	calc.(37.35)	2.95
268.2	—	52.6	37.5	—

always at the same temperatures; if a slight error should occur in the absolute value of the given temperatures, this has no influence on the pressure differences. The thermometers which I used in this investigation, have been tested by a resistance thermometer, the resistance of which was determined for boiling water, naphthaline, benzophenon, and sulphur. The obtained results are given in table 4, the pressures are given in atmospheres.

It appears from the last column of table 4 that the difference at 150° to 200° is only slightly greater than the errors of observation, that the three-phase tension becomes appreciably greater than the sum of the vapour tensions at 210° , and that this difference rapidly increases with ascending temperature.

4. When we combine the results of the system hexane-water and those of § 2 and 3, it appears that in the three systems the three-phase tension is always greater than the sum of the vapour tensions of the components in the neighbourhood of the critical endpoint. Moreover these three systems present the same shape of the plaitpointline in the T - x -projection; the upper critical endpoint always lies lower than the critical points of the two components; the plaitpoint line presents therefore a minimum temperature in the T - x -projection (homogeneous double plaitpoint). Though in my opinion it is probable that the systems will behave perfectly analogously, a further investigation would have to decide whether for all this homogeneous double plaitpoint lies in the metastable region; I have shown this for the system hexane-water in my cited paper. It is remarkable that in the system ether-water the homogeneous double plaitpoint appears in the immediate neighbourhood of the ether axis or would perhaps lie outside the figure, so that the critical endpoint in contrast with the above discussed systems lies between the critical points of the components. In this system the said peculiarity does not occur. Accordingly I think I have to conclude that the systems which present critical endpoints which lie lower than the critical temperatures of the two components possess three-phase pressures which are higher at high temperatures than the sum of the vapour tensions of the pure substances, whereas the opposite is the case for systems for which the critical endpoint lies between the critical temperatures of the components. Perhaps this conclusion may contribute to account for this remarkable phenomenon.

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*Anorg. Chem. Laboratory of the
University of Amsterdam.*