

Dr. J. P. KUENEN. *Measurements concerning the surface of VAN DER WAALS for mixtures of carbonic acid and methyl chloride.*

The appearing of VAN DER WAALS's theory ¹⁾, for the application of which experimental material is wanting, suggested to me to determine a series of isothermal lines for three mixtures of carbonic acid and methyl chloride between 25° C. and 160° C. in order to calculate the constants, which VAN DER WAALS uses, and with them to execute the construction of the surface of free energy, which was introduced by him. However it was impossible to use the characteristic equation of VAN DER WAALS, which, as is well-known, can, with simple substances even, represent the observations within narrow limits only. With the first equation of CLAUSIUS ²⁾ the isothermals for methyl chloride and one of the mixtures could be rendered very well, for the other two approximately only. The constants calculated are the following (the letters are those of CLAUSIUS) ³⁾:

¹⁾ Arch. Néerl. 24 p. 1—56. Zeitschr. Phys. Chem. 5. p. 133—173.

²⁾ Wied. Ann. 9. p. 14.

³⁾ The values are slightly modified according to later results;

	K	β	b	R
CH ₃ Cl	6.555	0.00165	0.00135	0.003750
$\frac{3}{4}$ CH ₃ Cl	(4.94)	0.00138	0.00110	0.003738
$\frac{1}{2}$ CH ₃ Cl	4.020	0.00163	0.00098	0.003721
$\frac{1}{4}$ CH ₃ Cl	(2.86)	0.00117	0.00085	0.003705
CO ₂	2.116	0.00095	0.00087	0.003684

The values in brackets for two of the mixtures are only mean values of those, which hold good for the different temperatures ¹⁾.

By using these equations we can calculate the lines of free energy for the different temperatures and so execute approximately the construction of VAN DER WAALS's surface; in order to obtain some accuracy it will be necessary to extend the observations over further intervening mixtures, since the manner in which in CLAUDIUS's equation the constants depend upon the constitution of the mixture is not known. The knowledge of such a thermodynamical surface for a mixture is of the greatest importance for the study of the coëxistence of two or three phases. These phenomena (condensation) were studied qualitatively only as yet; the results partly agree with those of former investigators, ANDREWS and others.

The great influence of retardation, also in the homogeneous condition (imperfect mixing), was investigated

cf. Arch. Néerl. 26 p. 61, 68, 69. In the equations for methyl chloride and for carbonic acid some more small modifications have been made.

¹⁾ See my treatise in Arch. Néerl. l. c.

at large and at last for the greater part neutralised by the application of a stirring-apparatus, consisting in a small piece of iron within the tube, in which the mixtures were investigated, which piece could be moved during the experiments by an electromagnet gliding round the tube. Thus agreeing results were obtained and the experiments did not take more time than was necessary.

The flattening and disappearing of the liquid surface, which at definite temperatures was observed by former experimenters, was also seen by me. However from VAN DER WAALS'S theory we may conclude another way of condensation, which must take the place of the disappearing of the liquid surface and which may be called *retrograde condensation*; with it the quantity of the denser phase at first increases till a maximum is attained, and then diminishes and at length disappears. The fact, that observation has given the disappearing of the surface instead of this retrograde condensation till now, can be explained by the retardation, which in the case of two phases becomes of important influence. I am going to test this explanation by aid of my stirring-apparatus mentioned above, and, as independent from this theoretical reasoning I sometimes observed the diminishing of the fluid phase by compression, I soon hope to be able to obtain all the successive stages of the phenomenon as described above.

The critical temperatures of the mixtures investigated do not agree with PAWLEWSKI'S law, as indeed was not to be expected.

The following values were found:

	Obs.	Calc.
$\text{CH}_3 \text{Cl}$	143.0	143.0
$\frac{3}{4} \text{CH}_3 \text{Cl}$	123.0	117.8
$\frac{1}{2} \text{CH}_3 \text{Cl}$	97.1	90.9
$\frac{1}{4} \text{CH}_3 \text{Cl}$	65.4	62.0
$\frac{1}{9} \text{CH}_3 \text{Cl}$	46.0	45.1
CO_2	31.0	31.0

At last from the equations some Tables were calculated for the deviations from DALTON's law and for the increase of pressure by mixing at constant volume.
