Experiments on the Condensation and Critical Phenomena of some Substances and Mixtures

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these reflexion coefficients would be precisely equal to unity and the first of them practically so.

I have to thank Mr. H. A. Ratcliff for help at the beginning of this work, and especially Mr. R. S. Willows for his valuable assistance at the later experiments and their reduction.

University College, Nottingham,
May, 1897.

XXI. *Experiments on the Condensation and Critical Phenomena of some Substances and Mixtures.* By Dr. J. P. KUENEN*.

1. THE investigation contained in this paper is a continuation of a research on "The Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide," which was read before the Physical Society some time ago†. The results arrived at in the latter paper were stated as follows:—

(1) All mixtures of C_2H_6 and N_2O which contain more than 0.1 of C_2H_6 have critical temperatures lying beneath the critical temperature of C_2H_6 .

(2) The vapour-pressures of the mixtures lie partly above those of N_2O , and accordingly show a maximum situated near 0.2 of C_2H_6 .

(3) This maximum does not disappear with rise of temperature, but remains up to the critical region; the maximum-curve reaches the plaitpoint-curve.

(4) The mixtures ranging between 0.2 and 0.5 of C_2H_6 have retrograde condensation of the second kind, all the others retrograde condensation of the first kind.

I have now discovered two more instances of mixtures with similar properties, viz. mixtures of ethane and acetylene, and mixtures of ethane and carbonic acid. I will begin by

* Read June 25, 1897.

† Kuenen, Proc. Phys. Soc. vol. xiii. pp. 523-548.

relating some experiments which were made in connexion with the former paper, and afterwards give an account of the results obtained with those mixtures.

A. On Ethane prepared by different methods.

2. The ethane used in my former experiments had been prepared from sodium acetate by electrolysis. Its vapour-pressures and critical constants, especially the latter, were different from those given by other observers. The different values are the following, p being expressed in atmospheres:—

	Dewar*.	Olszewski †.	Haenlen ‡.	Kuenen §.
t_c . . .	35°	34°	34·5°	32·05°
p_c . . .	45·2	50·2	50	48·8

Ethane from Ethyl Iodide.

3. In order to ascertain the probable reason of this divergence I prepared some ethane from ethyl iodide, the method used by Haenlen, and investigated its properties. The results have been communicated to the Royal Society of Edinburgh. I will therefore simply state my conclusions here so far as they bear upon the point in question.

Ethane from ethyl iodide contains a variable quantity which may go up to several per cent. of an admixture of higher critical temperature and higher density than ethane, probably butane. This impurity raises both the critical temperature and pressure, and lowers its vapour-pressures. Pure ethane is difficult if not impossible to obtain by this method.

This result accounts for Haenlen's critical values being higher than mine (and probably also for Olszewski's figures), and it shows at the same time the greater purity of my ethane. Even this was not absolutely pure, as shown by some change of the vapour-pressure with volume. But whatever the admixture may be that this was due to, it was probably too

* Phil. Mag. (5) xviii. p. 214.

† *Bulletin Ac. des Sciences de Cracovie*, 1889, p. 27.

‡ *Lieb. Ann.* cclxxxii. p. 245.

§ *Proc. Phys. Soc.* xiii. p. 533.

small to affect the critical temperature by more than a few tenths of a degree and the critical pressure by more than some tenths of an atmosphere.

Ethane from Sodium Acetate.

4. In order to confirm my results, and at the same time to obtain some more pure ethane for further experiments, I repeated the preparation of ethane from sodium acetate. The anode, consisting of two pieces of platinum foil (joint surface 150 cm.²), was placed inside a good-sized porous pot, care being taken to obtain a high current-density*. A current of about 15 amperes was used. Special precaution was required to prevent the indiarubber stopper which closed the porous pot from being burnt by the heat developed. A glass tube, passing through the stopper, was bent into a U-shape outside and contained some mercury. The contact with the platinum foil was made by platinum wires soldered to the foil.

The gas was washed in sodium hydrate, fuming sulphuric acid, and potash, and collected in a gasometer which was filled with a solution of potash. This gasometer consisted of two carboys, closed with indiarubber stoppers and connected by a wide glass tube. The yield of ethane was very high, very little oxygen being formed. The oxygen was moreover absorbed by introducing a piece of phosphorus into the gasometer.

5. In order to purify the gas further, it was compressed by means of a Natterer pump into a small copper cylinder fitted with high-pressure stopcocks†. In this process it was once more washed in potash and subsequently dried by calcium chloride and phosphorus pentoxide. Pump and cylinder were previously exhausted by a mercury air-pump. During the compression the copper cylinder was placed in solid carbonic acid. The pressure required to liquefy the gas was pretty high: this shows that it contained a considerable

* Murray, Journal Chem. Soc. lxi. pp. 10-36.

† Most of my high-pressure apparatus are manufactured by Giltay, Delft, Holland, and are of the same type as those used in the Physical Laboratory at the University of Leyden (Director, Prof. Kamerlingh Onnes).

quantity of some permanent gas ; this may have been air which in some unknown manner had got into the gas. By thoroughly boiling the ethane, as much of this admixture was removed as possible. The results obtained with this ethane show that some admixture was left, of about the same amount as in the gas which I used in my former experiments. It is noteworthy that with other substances, such as carbonic acid and nitrous oxide, I always succeeded in removing practically all impurity by this process ; for some reason the same thing seems more difficult with ethane. It is not impossible that ethane forms a mixture of constant boiling-point with the admixture, whatever it may be.

6. The apparatus which was used for filling the compression-tubes with the gases consisted almost of one piece of glass. The mercury air-pump was sealed to the double mercury gasometer which I used for preparing the mixtures (see below). This was connected at the other side with a tube leading to the compression-tube, and another tube through which the purified gas was supplied from the compression cylinder. The connexion with the cylinder was made by means of a copper tube, sealed with sealing-wax into a glass tube, the connexion with the compression tube being made by a ground joint. This was so adjusted, that the tube after being filled could be turned upright without being detached, by which manipulation the tube was shut off at the bottom by some mercury. There are two reasons why I prefer this manner of filling the tubes to sealing them off. In the first place many gases are more or less decomposed at the temperature of softened glass, and in the second place the sealing place is apt to end in a sharp point, while for the proper action of the little iron stirring-rod which I use inside the tubes, a rounded top is absolutely necessary. It need hardly be added that the apparatus was fitted with a certain number of safety-tubes dipping in mercury. I found that the amount of spring in the apparatus was quite sufficient, and that special glass springs were superfluous.

7. For the observations properly speaking, I used Ducretet's apparatus. The temperatures of air-manometer and gas-tube were kept constant with the running water of the supply. A constant water-pressure was obtained by means of an overflow

arrangement, and the current before passing round the gas-tube was heated by a long coil in warm water. A sufficiently constant temperature was obtained in this manner.

TABLE I.

Ethane from Sodium Acetate (April 1897).

$t.$	$p_b.$	$p_c.$	$v_b.$	$v_c.$
5.55	26.90	27.42	231.2	33.0
14.5	32.91	33.52	177.1	35.6
15.0	33.23	33.77	176.1	35.5
23.05	39.74	40.27	130.9	39.0
30.2	46.35	46.72	94.5	46.2
32.2	48.64		C	61.5

8. Table I. gives the results obtained: p_b and v_b are the pressures and volumes when the condensation begins, p_c and v_c when the whole substance is liquefied; p is expressed in parts of an atmosphere, the v 's in this and in all the other tables are expressed in an arbitrary unit, but reduced to the same initial volume at 0° and 1 atmosphere. C indicates the critical point. The experimental determination of the p_c 's gives no difficulty if the stirring-rod is continually used. For p_b this is not always the case, because stirring is not so effective when the volume is much larger. In cases of doubt p_b and v_b were therefore determined graphically as the points of intersection in the p - v diagram of the two parts of the isothermal, the part where the substance (mixture) is homogeneous and the part where there are two phases. Another advantage in drawing the latter part of the isothermal is that from its shape and the direction of its curvature some idea may often be obtained as to the nature of the admixture*.

9. Tables II. and III. contain values obtained for two samples of ethane on a former occasion. The pressures as shown by a comparison of the p - t curves are this time slightly

* Compare a paper on ethane in the Proc. R. S. of Edinburgh, 1897. I thought it unnecessary to publish the p - v diagrams as they offer no special interest.

TABLE II.
Ethane. (April 1895.) 1st sample.

$t.$	$p_b.$	$p_c.$
5.85	27.38	27.92
10.65	30.45	31.11
15.4	33.84	34.48
22.4	39.73	40.25
29.35	45.94	46.25
31.0	47.64	47.95
31.95	48.81 C	

TABLE III.
Ethane. (April 1895.) 2nd sample.

$t.$	$p_b.$	$p_c.$
3.95	26.17	26.89
15.4	34.11	34.66
22.4	39.89	40.32
29.3	45.89	46.19
32.05	48.91 C	

lower and the critical temperature a little higher. Absolutely pure ethane would probably have pressures slightly lower even and a slightly higher critical temperature. The p - t curves in the diagrams for ethane and the other single substances are drawn with p_b ; as this value is probably nearer the true value of p than p_c .

B. *Mixtures of Carbonic Acid and Acetylene.*

10. In my former paper I gave a first instance of mixtures having critical temperatures below those for the component substances. The only instance of critical temperatures above those of the components seemed to be that of mixtures of carbonic acid and acetylene. According to an observation of Dewar's*, a mixture of $\frac{1}{2}$ CO₂ and $\frac{1}{2}$ C₂H₂ has a critical temperature of 41° C., those for carbonic acid and acetylene being 31° and 37° respectively. It seemed necessary to try the experiment, because experiments on mixtures have always

* Proc. R. S. of London, xxx. p. 542.

to be accepted with caution, unless it appears that exceptional precautions have been taken to avoid retardation and impurities*. The phenomenon, if confirmed, would have been worth completely investigating. The results which I have obtained contradict Dewar's experiment.

Preparation of Carbonic Acid.

11. Both carbonic acid and acetylene were prepared before I was in a position to apply the method of purification described for ethane by condensation and distillation. I had therefore to resort to chemical methods of purifying the gases. Carbonic acid was made from sodium bicarbonate and sulphuric acid. The acid was contained in a boiling-flask provided with a dropping-funnel with the sodium bicarbonate solution. All solutions used were previously boiled and cooled in a current of carbonic acid. The gas passed through sulphuric acid and phosphorus pentoxide. Before the solution was admitted the whole apparatus had been exhausted with a mercury air-pump.

12. The purity of the carbonic acid was first tested in the compression-apparatus and appeared to be quite satisfactory.

TABLE IV.
Carbonic Acid.

t .	p_b .	p_c .	Amagat.
14.95	50.02	50.24	50.0
20.5	57.16		57.0
25.85	64.92	65.06	64.5
31.1	73.26		C

Amagat's values for the critical point are $31^{\circ}35$, 72.9 atm. The agreement is very close, the deviations of my values

* Prof. Dewar, on learning that I had repeated this experiment of his (forming part of an essentially qualitative investigation carried out in 1880), told me that his acetylene contained C_2H_3Br . This accounts for the high critical temperature and low vapour-pressures observed by him.

being probably due to a slight admixture of permanent gas. This would, in fact, make the vapour-pressures and critical pressure higher and the critical temperature lower. Similar deviations will be noticed by comparing some of Andrews's values with Amagat's, the former having been reduced to atmospheres.

<i>t.</i>	Andrews.	Amagat.
13.09	48.05-49.50	47.6
21.46	58.94-61.35	58.2

Andrews's critical constants are $30^{\circ}.9$ and about 73 atmospheres. The deviations are in the same direction, only much more pronounced. Andrews's carbonic acid contained about $\frac{1}{500}$ of air.

Preparation of Acetylene.

13. This gas was prepared in the same apparatus as carbonic acid, from calcium carbide and water. The water had been previously saturated with carbonic acid. The gas was washed in silver nitrate to absorb the phosphoretted hydrogen and sulphuretted hydrogen which it contained. It was freed from carbonic acid by soda-lime and dried in sulphuric acid and phosphorus pentoxide. Two samples were obtained. The first probably contained some air and also some phosphoretted hydrogen. In preparing the gas for the second time, a second washbottle with silver nitrate was introduced, and this bottle was only just beginning to get blackened, when the acetylene was collected. The only possible impurity of this sample is therefore a trace of air.

Some of this sample was used in making the mixture with CO_2 , the results for which are communicated below. Some mixtures of the first sample with CO_2 gave, however, similar results. The results obtained with the purer sample are contained in Table V.

14. Evidently the gas contained an admixture of some other substance. If this admixture is air, the vapour-pressures are slightly higher than for pure acetylene, and the critical

temperature a few tenths of a degree too low. In this case also the p_b 's were used in drawing the vapour-pressure curves in the diagrams.

TABLE V.
Acetylene.

$t.$	$p_b.$	$p_c.$
14.95	38.09	38.66
20.15	43.18	43.75
26.8	50.29	50.85
27.1	50.55	51.12
30.8	55.05	
35.25	61.02 C	

The pressures agree very well with those given by Villard *, who finds 37.9 at 15° C., and 42.8 at 20° 2. Ansdell's † values are a good deal different, his pressures being 32.77 at 13° 5, 39.76 at 20° 15, 48.99 at 27° 55, 56.20 at 31° 6. For the critical point he found 68.0 atmospheres and 36° 9 C. As to Pictet's ‡ values, they show no resemblance whatever with the others. His pressures were : 29.0 at 14° 1, 33.5 at 19° 5, 38.5 at 27° 6, and 48.0 at 36° 5 (critical point).

Mixture of Carbonic Acid and Acetylene.

15. The mixture was made in a mercury gasometer consisting of two parallel wide glass tubes of 300 c.c. each, provided at the bottom with a tap, an indiarubber tube, and a funnel with mercury sufficient to fill up the whole of the tubes. At the top the tubes ended in threeway stopcocks communicating together, the whole, as described before, connected on one side with the pump, and at the other side with the rest of the apparatus. The mixture contained $\frac{1}{2}\text{C}_2\text{H}_2$ and $\frac{1}{2}\text{CO}_2$.

* *Ann. de Chimie et Physique*, March 1897.

† *Proc. R. S. of London*, xxix. p. 211 (1879).

‡ *Zeitschrift Compr. und flüssige Gase*, i. p. 32 (1897).

16. The results obtained are the following :—

TABLE VI.
Mixture $0.5 \text{ C}_2\text{H}_2 - 0.5 \text{ CO}_2$.

t .	p_b .	p_c .
7.35	35.98	36.90
14.95	43.46	44.62
20.15	49.54	
24.75	55.18	56.10
26.15	57.10	57.95
31.55	64.79	65.17
32.55	66.52 C	

The differences between p_b and p_c (fig. 1), the pressures at the beginning of the condensation and at the end, are somewhat larger than for acetylene, as might be expected. It would be possible to make an allowance for the impurity of the component gases, and in that manner obtain approximate corrected values for the pressures. This would, however, be a rather uncertain calculation, and in drawing the border-curve for this mixture I have preferred to use the direct experimental values. Obviously, though the slight impurities of the CO_2 , and specially of the C_2H_2 , also affect the values for the mixture, the divergence from the true values can only be of the same order of magnitude as for the components.

17. The diagram (fig. 1) shows that the plaitpoint curve is a line with small curvature and that mixtures of carbonic acid and acetylene have critical temperatures between those for the pure gases. The border-curve for the mixture investigated is relatively narrow. This entails small differences in composition between the coexisting phases, the vapour containing only a little more carbonic acid than the liquid. It also follows that the critical phenomena will closely resemble those of a pure substance. This was found to be the case, the plaitpoint temperature and critical temperature nearly coinciding.

18. An instance of a critical temperature above those for the components has therefore not been discovered as yet. From the theory it may be deduced that this phenomenon

Fig. 1.
(Vide Tables IV., V., VI.)

Fig. 2.
(Vide Tables I., V., VII.-XI.)

will probably occur for mixtures which have a minimum vapour-pressure at low temperature; in the same way as the critical temperatures below those for the components seem to occur for mixtures which have a maximum vapour-pressure (as for nitrous oxide and ethane).

The law of the connexion between the two phenomena will be again referred to in connexion with the application of Prof. van der Waals's theory.

C. *Mixtures of Acetylene and Ethane.*

19. The relative position of the vapour-pressure curves and critical points in the t - p diagram of these gases was such as to promise interesting results for mixtures of them: in fact the same reasoning holds for this combination which led me originally to the choice of nitrous oxide and ethane. If we consider the curves for the four gases the critical temperatures of which are between 30° and 40° — CO_2 , C_2H_6 , C_2H_2 , and N_2O —we find that besides with the combinations C_2H_6 - N_2O and C_2H_6 - C_2H_2 we may expect similar phenomena with C_2H_2 - N_2O , a combination which I have not been able to try. Results obtained with the couple C_2H_6 - CO_2 will be described later on. They agree with those of N_2O - C_2H_6 , and C_2H_2 - C_2H_6 . The case C_2H_2 - CO_2 was discussed above. The combination CO_2 - N_2O offers no interest *a priori*. Moreover, some time ago I investigated a mixture of these two gases, but did not obtain any remarkable results.

Mixtures of some of these four gases with hydrochloric acid (51°) or methyl fluoride ($44^\circ.9$) also promise new results. Mixtures of hydrochloric and carbonic acids were investigated by Dewar * and Ansdell †. Their figures differ from each other, but the plaitpoint curve does not seem to offer any peculiarities. It is hardly necessary to add, that a number of combinations of substances at other temperatures might be mentioned which would probably display similar phenomena.

20. I began by preparing two mixtures of acetylene and ethane containing 0.68 and 0.27 of the latter gas respectively.

* Proc. R. S. of London, xxx. p. 543.

† *Ibid.* xxxiv. pp. 113-119.

After having got the constants for these two and not having any more acetylene available at the time, I made new mixtures by partly exhausting the compression-tube containing the 0.27 C_2H_6 mixture and introducing fresh quantities of ethane. In this manner four more mixtures were obtained. Though great care was taken not to introduce any traces of air into the tubes by this repeated process, it is not a safe method, and the results seem to show, that some impurity must have got into the mixture. Moreover, the calculation of the composition of each fresh mixture was again somewhat uncertain. The consequence is, that the last mixture prepared in this manner, which, according to the calculations, contained 0.76 C_2H_6 , showed higher changes of vapour-pressure ($p_e - p_b$) than the first mixture ($x = 0.68$), and at the same time a slightly lower critical temperature and higher critical pressure. All this does not agree with the position and shape of the plaitpoint curve. The results for this mixture had therefore to be rejected. This also makes the values for the other three mixtures (especially the last one) doubtful. It must, however, be understood that this small uncertainty does not make the general result in the least doubtful, only the curves would be slightly different for the mixtures if pure.

TABLE VII.

Mixture 0.68 C_2H_6 -0.32 C_2H_2 .

t .	p_b .	p_e .	v_b .	v_e .
6.97		39.48		33.9
7.05	34.1		172.5	
13.95	40.35	45.25	134.3	37.2
22.2	49.17	51.83	88.2	46.5
23.05		52.35		50.2
23.15		52.40	} M	50.7
23.35		52.41		54.3
23.4		52.32 P		57.4 P
23.45	51.31		72.9	
23.5	51.33		72.9	
23.55		52.29		59.1
23.6		52.22		60.2
23.65	51.72	52.16	67.2	60.3
23.75		52.06 C	65.1	

TABLE VIII.
Mixture 0.61 C_2H_6 -0.39 C_2H_2 .

t .	p_b .	p_c .	v_b .	v_c .
8.85	39.6	44.04	136.6	34.3
13.97	44.6	48.42	112.9	37.3
20.15	52.10	53.68	74.6	48.4
20.55	52.61	53.68	70.6	52.4
20.75	53.06	53.47 P	67.5	59.5
20.77		53.4? C		62.5

TABLE IX.
Mixture 0.51 C_2H_6 -0.49 C_2H_2 .

t .	p_b .	p_c .	v_b .	v_c .
8.4	40.87	45.60	130.4	33.1
14.0	46.4	50.50	106.3	36.1
19.35	53.27	55.02	73.2	46.1
19.75	54.10	55.02	65.2	51.2
19.85		54.87 P		54.4
19.9	54.24		64.4	
19.95	54.57	54.72	60.7	57.7
19.96		54.65? C		58.2

TABLE X.
Mixture 0.41 C_2H_6 -0.59 C_2H_2 .

t .	p_b .	p_c .	v_b .	v_c .
7.95		42.70		31.4
8.0	39.95		136.2	
14.0	46.1	48.19	107.3	34.6
19.35	52.0	53.67	83.1	40.6
20.95	54.50	55.11	67?	47.9
21.0	54.62	55.12		50.0
21.05		55.12		50.6
21.1		55.05 P		53.7
21.12		55.02		55.2
21.15		54.99 C		55.1

TABLE XI.
Mixture 0.27 C_2H_6 -0.73 C_2H_2 .

t .	p_b .	p_c .	v_b .	v_c .
7.6	38.25	39.61	148.4	29.7
13.95	44.63	45.64	114.5	31.7
22.2	53.9	54.55	75.7	39.0
23.75	56.05	56.27	61.7	47.7
23.8		56.25		51.1
23.85		56.23 C		55.4

21. The Tables VII.-XI. contain the results for the five mixtures; the diagram (fig. 2) shows the relative position of the vapour-pressure curves for the pure substances, the border-curves for the mixtures, and the plaitpoint curve which envelops the border-curves. Only two of the border-curves, for mixtures 0.68 and 0.27, have been drawn in order not to make the diagram too complicated.

The diagram is qualitatively the same as that for nitrous oxide and ethane: quantitatively there is a difference in the circumstance that the mixture of minimum critical temperature and the mixture of maximum vapour-pressure are much nearer to each other than in the other case. Mixture 0.51 was about the mixture of maximum pressure (point B), while the minimum critical temperature (point A) occurs for a mixture containing only a little more ethane ($x=0.53$ or 0.54). The same points B and A were much farther apart for $N_2O-C_2H_6$, where they belonged to mixtures $x=0.2$ and 0.5 respectively.

22. It was stated in my former paper that the critical phenomena of the mixtures of N_2O and C_2H_6 are little marked. Between C and A, and also between C and B, the condensation should be retrograde of the first kind between the two critical temperatures t_p and t_c ; between A and B the condensation should be retrograde of the second kind. The latter phenomenon has never yet been observed owing to disturbing circumstances such as gravitation and small impurities. For $C_2H_2-C_2H_6$ the chances of observing special critical phenomena between A, B are obviously even smaller than for $N_2O-C_2H_6$.

I succeeded this time in observing critical phenomena of the first kind with all five mixtures. This is chiefly owing to the temperatures being more constant than formerly. The phenomena were very marked for the mixtures 0.68, 0.61, and 0.51, much less marked with mixtures 0.41 and 0.27. Though the relative position of P (plaitpoint) and C (critical point) is the same along the curves C_1B and C_2A , this is not the case as regards the point of maximum pressure M. Between B and C_1 , M is between P and C; along AC_2 , P is between M and C. The results with mixtures 0.68, 0.61, and 0.27 are in accordance with this rule; mixture 0.41 shows M

to be near P but on the wrong side ; mixture 0.51, which is about the mixture of maximum vapour-pressure, should have one critical point ; evidently it contained some other admixture. Moreover, the differences between p_b and p_c are considerable for this mixture, while they should be very small, not larger than for the components used. Altogether the results show that at least some of the mixtures contained a small admixture of air. The figures are therefore less trustworthy than those for $N_2O-C_2H_6$ or those for $CO_2-C_2H_6$, the combination to be described presently.

The $v-x$ curves have the same character as those for $N_2O-C_2H_6$: it seems therefore unnecessary to publish them.

D. Mixtures of Carbonic Acid and Ethane.

23. The ethane used in these experiments was the same as for the mixtures with acetylene. The carbonic acid was taken from an ordinary carbonic-acid cylinder, after having been distilled and purified in a small high-pressure cylinder in the way as described for ethane (see § 5).

TABLE XII.
Mixture 0.50 C_2H_6 -0.50 CO_2 .

$t.$	$p_b.$	$p_c.$	$v_b.$	$v_c.$
8.8		47.47		32.2
8.85	45.74		113.8	
9.05	45.94		111.8	
9.1		47.74		32.4
14.95	52.94	54.10	82.6	37.1
17.55	56.63	57.18	62.4	44.8
17.75	56.90	57.24	60.8	51.4
17.85	56.99	57.15	59.9	55.9
17.88	57.10		57.4	

TABLE XIII.
Mixture 0.43 C_2H_6 -0.57 CO_2 .

$t.$	$p_b.$	$p_c.$	$v_b.$	$v_c.$
8.95	47.27	48.46	106.8	30.7
14.95	54.50	55.30	77.4	35.5
17.55		58.42		44.8
17.58	58.18		57.9	
17.62	58.37		52.7	

<i>t.</i>	<i>p_b.</i>	<i>p_e.</i>	<i>v_b.</i>	<i>v_e.</i>
8.05	48.58	49.07	106.0	28.8
14.95	55.82	56.28	79.8	32.2
17.28	59.02	59.31	66.9	35.0
18.68		61.19		41.4
18.69	61.14		53.3	
18.73		61.28		42.8
18.75	61.21	61.31	52.5	46.1
18.77		61.29		
18.80	61.26		48.5	

<i>t.</i>	<i>p_b.</i>	<i>p_e.</i>	<i>v_b.</i>	<i>v_e.</i>
10.35	48.84	49.46	111.2	25.4
16.0	55.72	56.32	90	27.2
23.15		66.32		37.7
23.2	66.15		52.9	
23.35	66.44	66.52	49.6	41.8
23.37		66.57		43.2
23.4	66.54		47.6

24. These mixtures (Tables XII.-XV., fig. 3) show again the phenomena of minimum critical temperature and maximum vapour-pressure which had been found with mixtures of ethane with N_2O and C_2H_2 . The minimum critical temperature occurs for a mixture $x=0.45$ about (A), the maximum vapour-pressure for $x=0.30$ approximately (B). These compositions are nearer together than for $\text{N}_2\text{O}-\text{C}_2\text{H}_6$, but not so near as for $\text{C}_2\text{H}_2-\text{C}_2\text{H}_6$.

25. Again, the critical phenomena characteristic of mixtures were very little marked. As just stated, mixtures containing ethane between the limits 0.30 and 0.45 ought theoretically to show the critical phenomena of the second kind. For mixture 0.43 points P and C were, however, so near together that I could not observe a difference. For mixture 0.50 P is between M and C; for mixture 0.30 M and P coincide, and very nearly also with C; for mixture 0.15 M seems to lie between P and C. All this agrees with the rules given above. The differences between p_b and p_c are very small, especially for the maximum mixture. This also is in accordance with theory. The results for this combination are more trustworthy than those for $\text{C}_2\text{H}_2-\text{C}_2\text{H}_6$, and as good or better than those for $\text{N}_2\text{O}-\text{C}_2\text{H}_6$.

The v - x diagram (not published) has the same character as for the two other combinations.

E. *Application of Van der Waals's Theory*.*

26. If taken as generally as possible, van der Waals's theory of mixtures depends on the assumption of the existence of a relation between p , v , and t for a mixture of the same character as for pure substances. The p - v curve must be supposed to have an unstable part below a certain temperature, and in changing the composition of the mixture gradual changes in the relation between p , v , and t should take place. The laws of the condensation, the critical phenomena, in general of the coexistence of phases are then found by an application of thermodynamics in one of its many forms: van der Waals

* *Archives Néerl.* xxiv. pp. 1-56; *Zeitschrift physik. Chemie*, v. pp. 133-173; *Kon. Akad. van Wet. Amsterdam*, Nov. 24, 1894, pp. 133-137; *ibid.* Mei 25, 1895, pp. 20-30; Juni 29, 1895, pp. 1-12.

used the ψ function ($\psi = \epsilon - T\eta$). (T = absolute temperature.) In fact wherever thermodynamics is used for purposes of this kind, the existence of a similar equation of condition must be presupposed, though the actual form of this equation can only be given in the simplest cases, and even then only qualitatively. It is well known that the theoretical equation for single substances given by van der Waals does not agree with the results of experiments, and the same is true for the analogous equation for mixtures of two substances which he uses in his theory. It is well, however, to bear in mind that a number of the results which he arrives at are independent of the form of the equation. Even those results which are not, still may have a resemblance to actual phenomena in the same manner as for single substances.

In the following account of some of the theoretical results I will only consider the case of the coexistence of vapour and liquid, *i. e.* a separation of the liquid into two will be excluded from the consideration.

I shall sometimes follow a method different from van der Waals's, chiefly for the sake of shortness and simplicity.

27. Let us suppose a set of isothermal curves (p - v diagram) to be drawn for the mixture as determined by observations of p , v , and t in homogeneous states, and completed by partly unstable interpolation-curves joining the curves in the homogeneous gaseous and liquid condition.

Suppose we forget for a moment that the substance is a mixture, and apply the Maxwell-Clausius criterion for finding the coexisting phases in the usual manner. We should then get the border or saturation-curve separating the homogeneous states from those where these are unstable or less stable than the separated states. The diagram thus obtained gives us the condensation-pressures, the vapour- and liquid-densities, and the critical point for the mixture, if supposed to behave like a pure substance, *i. e.* not dividing into phases which have a different composition. The real border-curve can only be found by a more complicated application of thermodynamics: still we may easily see one thing, that the real border-curve would lie entirely outside the hypothetical one just obtained. Instead of the horizontal line cutting off equal areas from the isothermal, we get a sloping line: this

line has again to cut off equal areas. Obviously this is only possible by making it start lower and finish higher than the straight line. This is true at all temperatures, and the conclusion is, as stated, that the border-curve will be entirely outside the hypothetical one. From this it follows, *e. g.*, that the real critical temperature is higher than the critical temperature for the undivided mixture; also that the critical isothermal does not touch the border-curve at the top M but at a point to the right C, where $\frac{dp}{dv} < 0$ instead of $= 0$ as for a single substance. The volume in the critical point is obviously larger and the pressure smaller than the same quantities at the top of the border-curve.

28. The last fact about the critical pressure (point C) not being the maximum pressure (point M) for the mixture on the border-curve was pointed out above with reference to the *p-t* diagram. In fact the loops for the mixtures are nothing but the real border-curves represented in a different manner. The third point P which we considered in that case (plait-point), the point of contact of the loop and the enveloping curve (plaitpoint curve), cannot be found by a simple geometrical construction in the *p-v* diagrams. The connexion between the latter diagrams for different mixtures is not so simple as the connexion between the loops (border-curves) in the *p-t* diagram. A point of intersection of two loops gives the pressure and temperature at which the two mixtures to which the loops belong will coexist as vapour and liquid*. The enveloping-curve contains the points of intersection of loops infinitely near each other; in other words, it gives the conditions of pressure and temperature of the coexistence of identical phases: at those points the mixtures are therefore in the critical condition, and will display the critical phenomenon. Evidently these points P do not in general coincide with either M or C. At the critical point C the mixtures do not show the critical phenomenon, the latter belonging to P, where the temperature is lower. This was fully explained on former occasions.

* This is not so when a mixture of maximum or minimum pressure is between the two mixtures.

29. The properties of the v - x diagram were sufficiently discussed in my previous paper. Also its meaning as projection on the v - x plane of curves on the ψ surface studied by van der Waals. It was found in the first place that the maximum mixture in its critical point behaves entirely as a single substance; this fact would appear in the p - v diagram by the critical isothermal touching the border-curve at the top, and by points M, P, and C coinciding. If the maximum mixture is the same at all temperatures (as is approximately realized by $\text{N}_2\text{O}-\text{C}_2\text{H}_6$ within the limits of temperatures used), the real border-curve coincides entirely with the hypothetical border-curve examined above. If the maximum mixture changes with temperature the two curves coincide at the top only.

30. The consequence of this coincidence is that the critical point of the maximum mixture may be determined in exactly the same way as for a single substance: the conditions being

$$\frac{dp}{dv} = 0, \quad \frac{d^2p}{dv^2} = 0.$$

The direction of the vapour-pressure curve of the maximum mixture at B (*i. e.* the direction of the maximum-curve at that point) is also the same as for a single substance. This direction may be easily proved to satisfy the equation

$$\left(\frac{dp}{dt}\right) = \left(\frac{\partial p}{\partial t}\right)_v^*,$$

* This equation is true for single substances at the critical point, and for the maximum mixture at B; for other mixtures it would hold at the hypothetical critical point for the homogeneous mixture. The hypothetical vapour-pressure curve for a mixture lies in between the two branches of the loop in the p - t diagram, and comes to an end at this hypothetical critical point at some distance from the plaitpoint-curve. The equation consequently does not hold for a mixture at its plaitpoint.

It seems therefore impossible to identify the expression $\left(\frac{\partial p}{\partial t}\right)_{vx}$ with the $\frac{dp}{dt}$ of the hypothetical vapour-pressure curve at the plaitpoint of an arbitrary mixture, although this is done by van der Waals in his interpretation of the equation which gives the difference of the value of $\left(\frac{dp}{dt}\right)_p$ and $\left(\frac{\partial p}{\partial t}\right)_{vx}$ (*Kon. Ak. Amsterdam*, Mei 25, 1895, pp. 13, 30; Juni 29, 1895, p. 3, form. (5)).

the index indicating the quantity which is kept constant in the differentiation. Van der Waals* has discovered that for single substances $\frac{T}{p} \frac{dp}{dt}$ is approximately equal to 7 at the critical point. It is an interesting confirmation of the theory that my maximum-curves also give a value about equal to 7 at point B.

31. An important question in connexion with this is, What is the direction of the plaitpoint-curve at B? In my former paper this point was left undecided. In the meantime Prof. van der Waals, to whom I showed my results, has published two papers† in which the properties of both points B and A are completely discussed. I will deduce here some of his results, sometimes using his equations in a different manner.

32. For $\frac{dp}{dt}$ of the plaitpoint-curve the following may be written:—

$$\left(\frac{dp}{dt}\right)_P = \left(\frac{\partial p}{\partial t}\right)_{vx} + \left(\frac{\partial p}{\partial v}\right)_{tx} \left(\frac{dv}{dt}\right)_P + \left(\frac{\partial p}{\partial x}\right)_{vt} \left(\frac{dx}{dt}\right)_P.$$

At B both $\frac{\partial p}{\partial v}$ and $\frac{\partial p}{\partial x}$ will be seen to be $=0$. This follows immediately from the conditions of the v - x diagram, $\frac{\partial p}{\partial v}$ being $=0$, because the line of equal pressure always touches the connodal curve at the plaitpoint, and is therefore parallel to the v -axis in this particular case; while $\frac{\partial p}{\partial x} = 0$, because the point has still the properties of a maximum pressure-point. Neither $\frac{dx}{dt}$ nor $\frac{dv}{dt}$ can be ∞ along the plaitpoint-curve at B, because that would mean that the temperature went through a maximum or minimum. The result is that at B

$$\left(\frac{dp}{dt}\right)_P = \left(\frac{\partial p}{\partial t}\right)_v = \text{(see above)} \left(\frac{dp}{dt}\right) \text{ along maximum curve,}$$

i. e. the maximum curve touches the plaitpoint-curve at B.

* "Continuity" &c., Supplementary Notes; *Kon. Ak. Amsterdam*, Mei 25, 1895, p. 27.

† *Kon. Ak. Amsterdam*, Mei 25, 1895, pp. 20-30; Juni 29, pp. 1-12.

The diagram in my former paper is therefore incorrect, as the plaitpoint-curve was drawn with a break at B.

33. As to point A, it may be proved that $\left(\frac{dp}{dt}\right)_P$ is infinite there. We must use for this the conditions which hold for the point where a plait is split up. A plaitpoint is a point of the connodal curve on the ψ surface, but at the same time of the spinodal curve. The connodal curve is the curve traced out by the double tangent-plane: the spinodal curve, which is inside the connodal curve, separates the part of the surface where the substance is stable from the unstable part. The equation of this curve is

$$A = \frac{\partial^2 \psi}{\partial v^2} \frac{\partial^2 \psi}{\partial x^2} - \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 = 0.$$

Inside the curve $A < 0$, outside $A > 0$.

Applying the condition that $A=0$ in the plaitpoint, we have

$$\left(\frac{dA}{dt}\right)_P = \left(\frac{\partial A}{\partial t}\right)_{vx} + \left(\frac{\partial A}{\partial x}\right)_{vt} \left(\frac{dx}{dt}\right)_P + \left(\frac{\partial A}{\partial v}\right)_{xt} \left(\frac{dv}{dt}\right)_P = 0.$$

Now at A $\frac{\partial A}{\partial t}$ is > 0 , because just before the division of the plait $A < 0$ in that point, and just after $A > 0$ *.

Moreover we have at point A $\left(\frac{\partial A}{\partial x}\right)_{vt} = 0$, and $\left(\frac{\partial A}{\partial v}\right)_{xt} = 0$.

This will be seen to be true on considering that in the direction of the x -axis A passes from negative through 0 back to negative, in the direction of v from positive through 0 back to positive. The conclusion we come to is that either

$\frac{dx}{dt}$ or $\frac{dv}{dt}$, or both, are infinite at A. The last alternative is the true one; but either of the three is sufficient for our purpose.

If we put in the general equation for $\left(\frac{dp}{dt}\right)_P$ in (32)

$\left(\frac{dx}{dt}\right)_P = \infty$, we find $\left(\frac{dp}{dt}\right)_P = \infty$, because at A neither $\frac{\partial p}{\partial x}$ nor $\frac{\partial p}{\partial v}$ is 0, the direction of the p line not coinciding with either the v or the x axis.

* A more rigorous proof may be given by working out $\frac{\partial A}{\partial t}$: compare van der Waals, *l. c.* Juni 29, p. 2.

34. From $\left(\frac{dp}{dt}\right)_p = \infty$ at A it follows, that the plaitpoint curve has a vertical tangent at A and the loop for the mixture of minimum critical temperature touches the plaitpoint curve at A in the ordinary manner. In my former paper I drew the plaitpoint curve with a break at A, as suggested by the experimental data, and drew some conclusions from this which now appear to have been erroneous. The two branches of the connodal curve at the moment of the division of the plait intersect as two straight lines. This was not sufficiently brought out in the diagram (fig. 11) *. Moreover the curves were drawn in such a manner, that a line parallel to the v -axis had, under certain circumstances, four points of intersection. This was an unnecessary assumption which, in cases of splitting up of the first plait, is not a probable one. Altogether the paragraphs 40-42 with the figures 7, 11, and 12 should be withdrawn.

35. All these results are entirely independent of the form of the equation between p , v , and T for the mixtures. We will now apply van der Waals's equation for some calculations regarding the mixtures investigated.

The equation between p , v , and T has the form

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

in which a_x and b_x depend on the composition of the mixture x in the following manner:—

$$\begin{aligned} a_x &= a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2, \\ b_x &= b_1(1-x)^2 + 2b_{12}x(1-x) + b_2x^2 \quad \dagger; \end{aligned}$$

a_1, b_1 being the constants for the first and a_2, b_2 for the second substance; a_{12} is the attraction-constant between the two substances, b_{12} the volume-constant for the combination. According to the simple suppositions underlying the deduction of the formula, we should have:

$$\sqrt[3]{b_{12}} = \frac{1}{2} \{ \sqrt[3]{b_1} + \sqrt[3]{b_2} \}.$$

36. Now the three combinations investigated offer a good opportunity for calculating a_{12} and b_{12} . We saw that the

* Kuenen, Proc. Phys. Soc. xiii. p. 545.

† Lorentz, Wied. Ann. xii. p. 134.

same formulæ hold for the critical point of the max. mixture as for a single substance. From the T and p in the maximum point B we can therefore calculate a_x and b_x and deduce from these the a_{12} and b_{12} . The values of a_{12} will give some idea of the relative attraction of the two kinds of molecules, probably quite as accurate an idea as the ordinary a gives of the mutual attraction of the same molecules. The b_{12} obtained may be compared with the theoretical value.

37. The results of my calculations are the following :—

TABLE XVI.

	t_c .	p_c .	a .	b .
N_2O	309	71.9	0.00753	0.00197
C_2H_2	308.25	61.02	0.00881	0.00231
CO_2	304.1	73.26	0.00714	0.00190
C_2H_6	305	48.8	0.01078	0.00286
			a_{12} .	b_{12} .
$N_2O-C_2H_2$ ($x=0.18$) ...	302.8	65.3	0.00859	0.00239
$C_2H_2-C_2H_6$ ($x=0.51$) ...	292.96	54.7	0.00789	0.002295
$CO_2-C_2H_6$ ($x=0.30$) ...	291.8	61.3	0.008076	0.002357
$CO_2-C_2H_2$ ($x=0.50$) ...	305.55	66.5	0.00792	0.00210

I have added to the table calculated values of a_{12} and b_{12} for the combination $CO_2-C_2H_2$. The mixture of these two gases was proved to have a very narrow border-curve, and consequently the critical point observed cannot have been very much above the hypothetical critical point. The calculation of a_{12} and b_{12} from the critical constants, though not legitimate, must have given values for a_{12} and b_{12} not very far wrong.

The values of b_{12} calculated from the formula in § 35 coincide with the values in Table XVI. in the case of $N_2O-C_2H_2$ and of $CO_2-C_2H_6$: for $C_2H_2-C_2H_6$ b_{12} is even smaller than b for C_2H_2 . a_{12} is in all cases smaller than the mean of the a 's, and for $C_2H_2-C_2H_6$ even smaller than a for C_2H_2 . It is chiefly on this smallness of a_{12} that the existence of a minimum critical temperature depends.

38. Knowing a_{12} and b_{12} , we may calculate the critical

constants for the other mixtures, if supposed to remain undivided. It is with the temperature that we are chiefly concerned.

TABLE XVII.

$\text{N}_2\text{O}-\text{C}_2\text{H}_6.$		
$x.$	$273 \frac{8}{27} \frac{a}{b}.$	$T_c.$
0.18	302.8	302.8
0.43	299.0	299.05
0.55	298.7	299.05
0.76	300.5	300.85
$\text{C}_2\text{H}_2-\text{C}_2\text{H}_6.$		
0.27	296.7	296.8
0.41	293.1	294.15
0.51	293.0	293.0
0.61	293.6	293.8
0.68	294.8	296.75
$\text{CO}_2-\text{C}_2\text{H}_6.$		
0.15	296.1	296.4
0.30	291.8	291.8
0.43	290.7	290.62
0.50	290.8	290.88

Table XVII. gives the calculated values of the hypothetical critical temperature as compared with the real critical temperature. The former is found to be everywhere lower than the latter (except for mixture 0.43 $\text{CO}_2-\text{C}_2\text{H}_6$, where the calculated value is 0.08 above the observed T_c , a difference almost within the limits of experimental errors): for the maximum mixture the two naturally coincide. The differences are very small, especially with $\text{N}_2\text{O}-\text{C}_2\text{H}_6$ and $\text{CO}_2-\text{C}_2\text{H}_6$. For $\text{C}_2\text{H}_2-\text{C}_2\text{H}_6$ they are somewhat higher for mixtures containing more C_2H_6 : this is in agreement with the fact that the critical phenomena were more marked for those mixtures than for the others. In plotting the values of Table XVII. against the x 's, two curves are obtained, connecting the same points C_1 and C_2 and touching at a point corresponding to B. The curves are close together and the minimum of a/b

should belong to approximately the same value of x as the minimum T_c . The existence of a minimum for a/b depends on a_{12}/b_{12} being smaller than both a_1/b_1 and a_2/b_2 *. Table XVIII. gives the values of x for the minimum of a/b and for the observed minimum critical temperature (point A). The two sets agree very closely.

TABLE XVIII.

	Min. a/b .	Min. T_c . : A.	Max. pressure.	
			Calculated.	Observed : B.
$N_2O-C_2H_6$...	$x=0.52$	0.50	0.01	0.20
$C_2H_2-C_2H_6$...	$x=0.50$	0.53	0.36	0.51
$CO_2-C_2H_6$...	$x=0.48$	0.45	0.10	0.30

39. In Table XVIII. are also given the mixtures of maximum pressure as observed and as calculated from the theory. The latter calculation is simple. In coexisting phases we have the three conditions that $\frac{\partial \psi}{\partial v}$, $\frac{\partial \psi}{\partial x}$, and $\psi - v \frac{\partial \psi}{\partial v} - x \frac{\partial \psi}{\partial x}$ are equal. Now ψ may be found from the equation $p = v T$, because $\frac{\partial \psi}{\partial v} = -p$. This leads to

$$\psi = -RT \left\{ (v - b_x) - \frac{a_x}{v} + \phi(x) \right\}.$$

The two first conditions mentioned lead immediately to

$$\left(\frac{1}{v_1} + \frac{1}{v_2} \right) \frac{\partial b_x}{\partial x} = \frac{1}{a_x} \frac{\partial a_x}{\partial x} \dagger,$$

remembering that x is the same in the two phases ; v_1 and v_2 are the volumes of the coexisting phases. At the critical point : $v_1 = v_2 = 3b_x$, and the equation becomes

$$\frac{2}{3b} \frac{\partial b_x}{\partial x} = \frac{1}{a_x} \frac{\partial a_x}{\partial x}.$$

There is not a very good agreement between the values

* Van der Waals, *Arch. Néerl.* xxiv. p. 23.

† Van der Waals, *l. c.* p. 23.

calculated from this formula and those observed. The points of agreement are that both sets of x 's are smaller than the x 's for the min. cr. temp., and that the smaller the x observed, the smaller also is the x calculated.

Considering how insufficient van der Waals's formula is, we should not expect a better agreement; still the equation seems to give correct indications as regards the relative position of the two points A and B. This connexion may be better shown in the following manner: the condition for the min. of a_x/b_x may be written thus:—

$$\frac{1}{a_x} \frac{\partial a_x}{\partial x} - \frac{1}{b} \frac{\partial b_x}{\partial x} = 0,$$

and the condition for point B

$$\frac{1}{a_x} \frac{\partial a_x}{\partial x} - \frac{2}{3b_x} \frac{\partial b_x}{\partial x} = 0.$$

When $\frac{\partial b_x}{\partial x} > 0$ (in which case also $\frac{\partial a_x}{\partial x} > 0$), as is the case in the three combinations investigated, the first equation gives a higher value of x than the second*.

40. But another question arises—What happens to the maximum at very low temperatures? This can be found from the same equation given above (in 39) by putting v_1 (volume of the liquid) equal to b_x and neglecting $1/v_2$. The result is the same equation as holds for the min. cr. temperature. Probably therefore, if the equation does not mislead us here too much, approximately the same mixture which has a min. cr. temp. will be the mixture of maximum vapour-pressure at low temperatures. We may therefore expect the mixtures of C_2H_6 with N_2O , C_2H_2 , and CO_2 which contain about 0.5 of each to have a max. vapour-pressure at low temperatures. By raising the temperature this maximum moves towards the substance of higher vapour-presures (N_2O , C_2H_2 , and CO_2). As we saw for $C_2H_2-C_2H_6$, this motion has been very small, the points B and A almost coinciding. It is not impossible that for other mixtures which have a max. pressure at low temperature the maximum reaches one of the components at higher temperature and thus disappears. Those

* Van der Waals, *Kon. Ak.* 29 June, 1895, pp. 11-12.

mixtures would still have a minimum for a_x/b_x and, if the real critical temperatures are not too much above the hypothetical ones, they would also show a minimum critical temperature.

Instances of maximum vapour-pressures are :—ethyl alcohol and carbon disulphide (Berthelot *), chloroform and carbon bisulphide (Guthrie †), ether and carbon disulphide (Guthrie), propyl alcohol and water (Konowalow ‡). Some of these combinations would be worth investigating at higher temperatures up to the critical condition.

41. Similar considerations hold for maximum critical temperature and minimum vapour-pressure. A minimum vapour-pressure at low temperature means, according to the equation, a maximum for a/b ; and a maximum of a/b is the same as a maximum of the hypothetical critical temperature, and therefore *a fortiori* of the *real* critical temperature. The minimum pressure will move towards the substance of lower vapour-pressure, with rise of temperature, and may either disappear or else exist up to the critical region. It is easy to understand what the p - t diagram would be like in this case. But the case has not been observed yet. A minimum vapour-pressure was found by Roscoe and Dittmar § for hydrochloric acid and water and for nitric acid and water, by Konowalow || for formic acid and water, by Friedel ¶ for hydrochloric acid and methyl ether. I hope to have an early opportunity of trying the latter combination, which will not require temperatures as high as the combinations with water.

42. One remark may be added. In the condensation of some substances it is assumed that an association takes place of molecules to more complicated systems. Substances with which that happens do not obey the laws of corresponding states, and van der Waals's formula would be even more inadequate in those cases than otherwise. We may expect similar phenomena to occur in the liquefaction of some

* Berthelot, *Comptes Rendus*, lxvii. p. 430.

† Guthrie, *Phil. Mag.* (5) xviii. p. 513.

‡ Konowalow, *Wied. Ann.* xiv. p. 34.

§ Roscoe & Dittmar, *Lieb. Ann.* cxii. p. 327, cxvi. p. 327.

|| Konowalow, *Wied. Ann.* xiv. p. 34.

¶ Friedel, *Comptes Rendus*, lxxxi. p. 152.

mixtures. An association of that kind one would feel inclined to identify with what is called the formation of molecular compounds. This would naturally have a great influence on the vapour-pressure, and it is not unlikely, that rules like those given above and deduced from van der Waals's formula would fail entirely in those cases. But these considerations can only be tested by experiment.

University College, Dundee.

DISCUSSION.

Dr. S. P. THOMPSON asked whether diagrams characteristic of cyanogen had been obtained. Its remarkable polymerism suggested an interesting case for critical phenomena.

Dr. KUENEN thought such a substance might be worth investigating.

XXII. *On the Steady Motion of an Electrified Ellipsoid.*

By G. F. C. SEARLE, M.A., *Demonstrator in Experimental Physics, Cavendish Laboratory, Cambridge* *.

AT the Meeting of the Royal Society on 19th March, 1896, I read a paper on "Problems in Electric Convection." The first part of the paper is printed in the 'Philosophical Transactions of the Royal Society' †, and contains the principles which are required in the solution of any problems about moving charges. The second part of the paper, which deals with the motion of a charged ellipsoid, was not published by the Royal Society. A few of the results are, however, stated in an abstract published in the 'Proceedings' ‡. By the permission of the Royal Society I now publish my results for a moving ellipsoid. As frequent reference to my paper in the 'Philosophical Transactions' will be necessary, I shall use the notation §§ 5 and {(9)} to indicate the paragraph or equation referred to in that paper.

* Read June 25, 1897.

† Phil. Trans. vol. 187 (1896) A. pp. 675-713.

‡ Proc. Roy. Soc. vol. lix. p. 343.