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H. Kamerlingh Onnes & Zakrzewski, C., The validity of the law of corresponding states for mixtures of methyl chloride and carbon dioxide, in: KNAW, Proceedings, 7, 1904-1905, Amsterdam, 1905, pp. 285-290					
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reticularis of the crossed side and ascending frontalwards are found in the same region up to their junction with the superior crus cerebelli.

My own sections suggest very strongly indeed, that these centrifugal (from the cerebellum, or rather from the nucleus dentatus) fibres, take their course by the superficial layers of the middle cerebellar peduncle and then can be followed right through the pyramidal bundles or partly winding around them to the reticular substance.

In different series it becomes clear that proceeding in the series of sections from below upwards there, where are found the first degenerate fibres in the reticular substance, also the first degenerate fibres appear in the middle peduncle. While by Thomas no sound reasons are given for his conception about the significance of this bundle, it pleads against the opinion of Probst that in the region of the vestibulary nuclei, no degenerate fibres are found.

Finely the sections show, compared with the sections gained by other experiments, that the ventral thalamic bundle originates for the greater part from the ventral portions of the cerebellum, especially of the flocculus. Sections of cats-brain after similar operations leave no doubt, that after lesion of more dorsal cerebellar portions, there exists a very marked contrast between the very pronounced degeneration of the crus cerebelli ad corpora quadrigemina and the very slight degeneration of the ventral thalamic bundle, whereas as well in the cat as in the rabbit after exclusive lesion of the flocculus, both bundles are affected about equally.

Physics. — "The validity of the law of corresponding states for mixtures of methyl chloride and carbon dioxide," by Prof. H. Kamerlingh Onnes and Dr. C. Zakrzewski. Communication Not. 92 from the Physical Laboratory at Leiden by Prof. Dr. H. Kamerlingh Onnes (continued).

(Communicated in the meeting of June 25, 1904).

§ 1. Introduction. In n°. IX of the "Contributions to the knowledge of van der Waals' \$\psi\$-surface" we have expressed the hope of giving an experimental contribution to the investigation of the co-existing mixtures of methyl chloride and carbon dioxide at low temperatures in connection with the test of the law of corresponding states for mixtures, which for many years has formed a subject of experimentation at Leiden. Of the extensive territory of reduced states, which

the mixtures of carbon dioxide and methyl chloride afford for measurements on either side of the critical state, (reason why in about 1890 it was chosen for the first investigations of the \psi-surface) a considerable portion round the critical state has been immediately investigated by Kuenen (Comm. No. 4, April '92). Hartman in Comm. No. 43, June '98 has added to this area that of the coexisting phases at 9.5 C. We have extended the area investigated in two directions, albeit only by a few preliminary researches.

The results of some of those measurements, though a few are only preliminary and served chiefly as a means for us to decide upon the method of investigation, seem important enough now that still so little is known about the different degrees of approximation to which the law of corresponding states holds for mixtures in diffe-

rent fields of reduced state
$$\left(v = \frac{v}{v_k}, t = \frac{T}{T_k}\right)$$
.

Our measurements refer in the first place to gaseous mixtures under almost normal conditions, in the second place to coexisting phases at low temperatures.

For the normal gaseous phase we found the law of corresponding states to be confirmed to a high degree of approximation. The virial coefficient B, which determines the deviation of mixtures of methyl chloride and carbon dioxide from Boyle's law at small densities, can be sufficiently derived by means of the law of corresponding states.

Greater deviations were found when we investigated the coexisting phases at low temperature. Here we have determined by means of the dew-point apparatus, described in the first part of this communication, the begin condensation pressure of the mixture $x = \frac{1}{2}$ at -25° C.: the temperature for which we have constructed the \psi-surface in Suppl. No. 8, Sept. '04. The deviations found are rather great, they point to an increase of the deviations from the law of corresponding states in the mixtures at low temperatures in the liquid state. The determination of the end condensation pressure for the same mixture $x = \frac{1}{2}$ at -25° C. with the piezometer of the first part of this communication would involve complications (comp. ibid. § 5). In order to obtain an idea of the deviations of the liquid branch of the binodal curve at x=1/2from that according to the law of corresponding states, we have investigated the condensation pressure for $x = \frac{1}{2}$ at a lower temperature, viz. — 38°.5 C. This corroborated the result of the investigation of the vapour phase at — 25° C.

- I. The compressibility in the neighbourhood of the normal state.
- § 2. Determination of the second virial coefficient. The mixtures

were prepared and the compressibility determined in the mixing apparatus and volumenometer described in Comm. No. 84, March '03. The method of observation and calculation has been treated in detail by Keesom, Comm. No. 88, Jan. '04.

The gases were prepared by distillation first in ice, subsequently in solid carbon dioxide. From previous communications it will appear that in this way pure carbon dioxide is obtained. Of methyl chloride the same will be proved in the continuation of this paper (§ 8).

The values found at the temperature t of the pressure p, volume V and molecular composition of methyl chloride, x are given in table I.

TABLE I. Compressibility of mixtures of carbon dioxide and methyl chloride.					
x = 1 (CH, Cl)					
N ₀	p in m m	V in c.c.	t		
I.	1137 33	537 67	20 05		
II.	593 69	1043 51	20 07		
Ш.	479.23	1296-33	20.07		
x = 0 6945					
Ι.	1200 32	537.49	20 09		
II.	624,45	1043 50	20 10		
III.	503 49	1297 01	20 08		
x = 0.5030					
ı.	1173.08	537 73	19 97		
II.	608.87	1043 66	19 87		
III.	400.88	1296 30	19 87		

The values for x = 0 may be borrowed from Comm. No. 88. For the calculation of these observations we shall use the empirical reduced equation of state of Comm. No. 71, June '01, which is particularly suited for the investigation of the degree of validity

of the law of corresponding states, in the form as laid down in § 4, which deviates little from that of Suppl. No. 8, Sept. '04.

In the first place the observed pressures must be reduced to the same temperature 20° C. For this purpose we have calculated the real coefficients of pressure-variation of carbon dioxide (0.003460) and methyl chloride (0.003586) with the equation of state mentioned and the coefficient of pressure-variation given below for ideal gases, and we have taken linearly interpolated values for the mixtures.

Owing to the small differences in temperature the errors ensuing from this remain below those of the observation.

Let v be the volume expressed in terms of the theoretical normal volume (introduced in Comm. N°. 47 Febr. '99), then we have approximately

$$pv = A + \frac{R}{v}$$
, where $A = 1 + \alpha_{\infty} t$

and α_{∞} the coefficient of pressure-variation of an ideal gas. One of the advantages of the empirical reduced equation of state is, that it teaches us the degree of approximation to which the higher terms in $\frac{1}{v}$ may be omitted. Then we have for the calculation of the second virial coefficient as a first approximation, if B^2 also is neglected (for further approximations see § 5):

and with $\alpha_{\infty} = 0.00366195$ (instead of 0.0036625 of Comm. N°. 71) we derive from table I:

TABLE II. Second virial coefficient for mixtures of carbon dioxide (x = 0) and methyl chloride (x = 1) to the first approximation.

composi- tion	$\frac{B}{A^2}$ from I and II	$\frac{R}{d^2}$ from I and III	$\frac{B}{A^2}$ mean	В	
4	0.01507	0.04900	0.01500	0.00071	
x=1	— 0.01797	0 01800	— 0.01798	-0.02071	
0 6945	- 0 01302	- 0 013 9	- 0.01310	<u>_0</u> 01509	
0 5030	- 0.01034	- 0.01005	- 0.0i019	0.01175	
0	Keesom, Comm. No. 88.			-0 00654	
1				1	

§ 3. The virial coefficient B as a quadratic function of the molecular composition x.

According to van der Waals' equation of state $B = RTb_{\nu\nu\nu} - a_{\nu\nu\nu}$, if $a_{\nu\nu\nu}$ and $b_{\nu\nu\nu}$ represent van der Waals' constants with regard to the theoretical normal volume. Hence, to the first approximation, we must have for the mixture with the composition x

(Cl Me. CO₂) (ClMe) (1 l Me. CO₂) (CO₂)
$$B = B x^2 + 2 {}_{(12)}B x (1 - x) + B (1 - x)^2$$

By means of least squares we found¹):

$$B_{20^0} = -0.020772$$
 $B_{20^0} = -0.010067$
 $B_{20^0} = -0.010067$
 $B_{20^0} = -0.006515$.

The agreement appears from the following table:

The deviations are less than $2^{\circ}/_{\circ}$, hence also less than the deviations of the single values of $\frac{B}{A}$ inter se. Thus the agreement with the quadratic form was sufficiently proved, so that for the time being measurements with other mixtures, not exceeding this accuracy, could be left off.

§ 4. Validity of the law of corresponding states for the virial coefficient B. According to the law of corresponding states the virial coefficients are derived from the coefficients of the reduced equation of state through multiplication by functions of T_k and p_k (comp. Comm. N°. 71 and also Suppl. N°. 8, Sept. '04, the first four sections).

As the critical data of mixtures of carbon dioxide and methyl chloride have been derived in Comm. N°.59b from Kurnen's experiments, we may determine B for a given temperature, for instance B_{20} by

$$B_{20} = \frac{T_k^2}{p_k} \, \mathfrak{D}_{\mathfrak{t}},$$

¹⁾ The coefficients given here have been derived from values for B which do not differ essentially from those given in table II.

where \mathfrak{V}_t is the value of the function \mathfrak{V} of the reduced temperature belonging to $t = \frac{293.04}{T_L}$.

For B we have used a function of a form differing slightly from the form VI.1, given in Suppl. N°.8, which did not only agree with hydrogen, oxygen and nitrogen but also with ether, viz. a form VI.2, which instead of agreeing with ether in the same way as VI.1, agrees with the average of ether and isopentane:

$$10^{8} \cdot \mathfrak{D} = +179,883 t -374,487 -181,324 \frac{1}{t} -110,267 \frac{1}{t3}$$

The agreement appears from the following table, where we find in the first column the values calculated according to the last formula, and in the second column those of the quadratic formula of § 3;

	according to	according to	difference
	corresponding states	quadratic formula	
1	0.021920	-0.020772	0.001148
1/2	0.016502	-0.015866	0.000636
3/4	0.012179	-0.011855	0.000324
0	0.006485	-0.006515	+0.000030

The deviations on the side of the methyl chloride are larger than those of the errors of observation and those of the quadratic formula. Methyl chloride, therefore, does not agree so well with ether and isopentane as carbon dioxide. This same result is also arrived at in another way. It appears, however, that the mixtures do not deviate more than the methyl chloride itself.

(To be continued).

Physics. — "On the measurement of very low temperatures. VII.

Comparison of the platinum thermometer with the hydrogen thermometer". (Continuation of Comm. N°. 77. Febr. 1902). By

B. Meilink. Communication N°. 93 from the Physical Laboratory at Leiden by Prof. H. Kamerlingh Onnes.

(Communicated in the meeting of June 25, 1904).

§ 5. The measurements at low temperatures. The thermometers were mounted as described by Kamerlingh Onnes in Comm. No. 83 Febr. 1903 § 5. During the first preliminary measurements, the hydrogen thermometer and the resistance thermometer (cf. Comm. No. 77 § 2) were placed in the cryostat (described in Comm. No. 51, Sept. 1899),