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rimentally to agree with that deduced from (59) one could get a fair conception of the molecule which would at least give this law of dependence upon temperature by calculating v from the temperature of the BOYLE point (if within the specified region) and σ from the terms in the expression for B which are independent of T, and then m_e, the moment of the doublet; from this one could, for instance, calculate the distance of the electron from the centre in the case of the molecular representation indicated at the beginning of this section. Further discussion of experimental results, however, must be postponed till a later paper.

Physics. — *Isotherms of monatomic substances and of their binary mixtures. XIII. The empirical reduced equation of state for argon.* By Prof. H. KAMERLINGH ONNES and Dr. C. A. CROMMELIN. Comm. N°. 128 from the physical laboratory at Leiden.

In a previous paper [1]) we indicated the desirability of obtaining from the mean reduced empirical equation of state for a number of normal substances which we have called VII. 1.[2]), a mean reduced empirical group-equation applicable to the monatomic substances. As a first step in that direction we now give a special reduced empirical equation for argon which we shall call VII. A. 3. and which embraces data obtained from observations made in both vapour and gaseous states. [3])

In previous communications similar special equations have been published, viz. one for carbon dioxide [4]) in gas, vapour, and liquid states, and one for hydrogen [5]) which embraced all available observations on the gaseous state. The important part as convenient summaries of all available experimental data played by such special

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increase of temperature undergone by a quantity of gas contained under high pressure on the addition of a measured quantity of heat showed that even at 200° K. γ_{vA} is for hydrogen considerably below $^5/_3 R$, while at 60° K. the value obtained was $^3/_2 R$. It was mentioned during the discussion at the Conseil SOLVAY, Nov. 1911, that Professor KAMERLINGH ONNES and myself had undertaken an investigation of γ_{vA} by KUNDT's method for hydrogen at temperatures down to that of liquid hydrogen, but this investigation has not yet been completed.

[1]) Proc. March 1911. Comm. N°. 120a.

[2]) Suppl. N°. 19 p. 18.

[3]) Proc. Dec. 1910, Comm. N°. 118b and C. A. CROMMELIN, Thesis for the doctorate, Leiden, 1910.

[4]) Arch. néerl. (2). 6. 874. 1901, Comm. N°. 74.

[5]) Proc. April 1909, Comm. N°. 109a.

equations in all sorts of thermodynamical calculations concerning the particular substance within the limited range through which the equation holds, makes it essential to obtain the best possible agreement between the equation and the results yielded by experiment. As the form VII. 1. was chosen for this equation with a view to its relationship to other investigations concerning the equation of state, it was fortunate that, for the comparatively small region of temperature covered by the argon observations, there were still the same number of coefficients available for the equation as had been found required to give good average agreement over the whole region covered by the equation of state for various different substances.

In the paper [1]) which contained the isotherm determinations for argon we have already given preliminary values for the individual virial coefficients A_A, B_A, etc. of the equation

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A{}^2} + \frac{D_A}{v_A{}^4} + \frac{E_A}{v_A{}^6} + \frac{F_A}{v_A{}^8}$$

as directly calculated from the observations for each individual isotherm.

The reduced virial coefficients $\mathfrak{B}$, $\mathfrak{C}$, etc. have now been calculated from the virial coefficients B_A, C_A etc. as functions of the reduced temperature t, which comes to the same as the evaluation of the constants in the equations

$$\left.\begin{array}{l} \mathfrak{B} = b_1 t + b_2 + \dfrac{b_3}{t} + \dfrac{b_4}{t^3} + \dfrac{b_5}{t^5} \quad [2]) \\[4mm] \mathfrak{C} = c_1 t + c_2 + \dfrac{c_3}{t} + \dfrac{c_4}{t^3} + \dfrac{c_5}{t^5} \end{array}\right\}\ \text{etc.} \qquad \ldots \ldots \ (I)$$

By this the coefficients are adjusted to the observations with respect to both temperature and density.

We may here give a short résumé of the manner in which these calculations were carried out.

As in the present instance the final terms of the polynomial $pv_A = A_A + \dfrac{B_A}{v_A} +$ etc. exert but a slight influence and therefore can be calculated only approximately from the observations, it was

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[1]) Proc. Dec. 1910. Comm. N⁰. 118*b* and C. A. CROMMELIN, Thesis for the doctorate, Leiden 1910.

[2]) Proc. June 1901, Comm. N⁰. 71 and Arch. néerl. (2) 6. 874 1901, Comm. N⁰. 74.

As can be seen a 5th term has been added to the equations there given. For the formulae connecting B_A and $\mathfrak{B}$, C_A and $\mathfrak{C}$, etc., reference may be made to the former paper. In the present paper we shall use chiefly the reduced virial coefficients which are to be preferred for the adjustment of the values of the coefficients.

best to begin with the adjustment of these terms. The fairly great changes which these terms as a rule undergo, have but a slight influence upon the values of the initial coefficients, while, on the other hand, small changes made in the initial coefficients in the process of adjustment occasion appreciable alterations in the coefficients of the final terms, and so the adjustment of the values of the final coefficients would become more difficult than it is as a rule at small densities.

In the case of argon the coefficients $\mathfrak{E}$ and $\mathfrak{F}$ need not be taken into account, for their values have been adopted from VII. 1.[1]) and consequently they have already been adjusted to the observations. Our calculations therefore began with the adjustment of $\mathfrak{D}$, which, as a glance at the values of D_A already published[2]) will clearly show, had to be done in a somewhat arbitrary manner. Some of these D_A's have been taken from VII. 1. The values of D_A at the lower temperatures, which were very irregular, were now plotted, while for $\mathfrak{t} = 6$ the D_A value from VII. 1 was included. In this way values of D_A or $\mathfrak{D}$ were graphically smoothed, and then the deviations of these smoothed values from VII. 1. were represented as functions of the reduced temperature by a linear equation

$$\Delta\mathfrak{D} = \Delta\mathfrak{b}_1 \mathfrak{t} + \Delta\mathfrak{b}_2$$

(in which

$$\Delta\mathfrak{D} = \mathfrak{D}_a - \mathfrak{D}_{VII.1.}$$
$$\Delta\mathfrak{b}_1 = \mathfrak{b}_{1.a} - \mathfrak{b}_{1.VII.1.}$$
$$\Delta\mathfrak{b}_2 = \mathfrak{b}_{2.a} - \mathfrak{b}_{2.VII.1})$$

In this way $\mathfrak{b}_{1.a}$ and $\mathfrak{b}_{2.a}$ were calculated as functions of the reduced temperature, while $\mathfrak{b}_{3.a}$, $\mathfrak{b}_{4.a}$ and $\mathfrak{b}_{5.a}$ were taken from VII.1.

The values of $\mathfrak{D}$ adjusted in this way were then converted into D_A and were used in the first place to get an idea of the magnitude of the corrections to be applied to the values of $\mathfrak{B}$ and $\mathfrak{C}$ so as to give the best possible agreement with the observations. When this was done we could then proceed to the adjustment proper of the values of B_A and C_A, or rather of $\mathfrak{B}$ and $\mathfrak{C}$ according to the formulae (I).

As can be seen from what follows, this process yielded values of the coefficients which, especially as regards the $\mathfrak{B}$ coefficient, did not differ much from those of VII.1. while, at the same time, a comparison with the experimental data of the reduced equation of state

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[1]) Suppl. N⁰. 19 p. 18.
[2]) Proc. Dec. 1910, Comm. N⁰. 118b.

thus obtained gave thoroughly satisfactory results. The results of all these calculations viz. the coefficients b_1, b_2, b_3, b_4, b_5, c_1, c_2 etc., of the equation VII. A. 3., the virial coefficients obtained from these, and finally, the comparison of VII. A. 3. with the experimental data are given in the following tables.

The figures italicised in the tables are those which have been taken from VII. I.

TABLE I. Coëfficients of the equation VIII. A. 3.

	1	2	3	4	5
$b \times 10^3$	+ 137.193	− 146.732	− 505.734	+ 94.358	− 17.8488
$c \times 10^{11}$	+ 97.9740	− 528.608	+ 836.166	− 315.182	+ 77.4006
$b \times 10^{18}$	+ 236.30	+ 421.825	− *903.004*	+ *367.7055*	− *178.5625*
$e \times 10^{25}$	−*1588.948*	+*5725.652*	−*4331.720*	+ *864.610*	+ *40.449*
$f \times 10^{32}$	+*1685.000*	−*6477.876*	+*6019.629*	−*1512.028*	+ *144.537*

TABLE II. Virial coëfficients of equation VII. A. 3.

ϑ	A_A	$B_A \times 10^3$	$C_A \times 10^6$	$D_A \times 10^{12}$	$E_A \times 10^{18}$	$F_A \times 10^{24}$
+ 20.39	+ 1.07545	− 0.60178	+ 0.76768	+ 6.78079	+ *7.6045*	− *4.35430*
0.00	+ 1.00074	− 0.76763	+ 0.91203	+ 5.93894	+ *8.7321*	− *4.98937*
− 57.72	+ 0.78922	− 1.30257	+ 1.50907	+ 3.28679	+ *10.5255*	− *5.02409*
− 87.05	+ 0.68174	− 1.62411	+ 1.92013	+ 1.18908	+ *10.5566*	− *3.93044*
− 102.51	+ 0.62511	− 1.81201	+ 2.16108	+ 0.72267	+ *10.4013*	− *3.10842*
− 109.88	+ 0.59810	− 1.90692	+ 2.28115	+ 0.20350	+ *10.3251*	− *2.69045*
− 113.80	+ 0.58372	− 1.95896	+ 2.34653	− 0.09396	+ *10.2947*	− *2.47655*
− 115.86	+ 0.57617	− 1.98675	+ 2.38134	− 0.25708	+ *10.2877*	− *2.35600*
− 116.62	+ 0.57340	− 1.99711	+ 2.39431	− 0.31873	+ *10.2806*	− *2.31432*
− 119.20	+ 0.56393	− 2.03255	+ 2.43867	− 0.53362	+ *10.2759*	− *2.17669*
− 120.24	+ 0.56012	− 2.04701	+ 2.45677	− 0.62312	+ *10.2764*	− *2.12239*
− 121.21	+ 0.55658	− 2.06056	+ 2.47376	− 0.70808	+ *10.2783*	− *2.07246*
− 130.38	+ 0.52296	− 2.19283	+ 2.64178	− 2.10863	+ *10.3966*	− *1.66293*
− 139.62	+ 0.48909	− 2.33484	+ 2.83477	− 2.41358	+ *10.8045*	− *1.42979*
− 149.60	+ 0.45252	− 2.50118	+ 3.10431	− 2.78849	+ *11.8440*	− *1.53961*

TABLE III. Comparison of equation VII. A. 3 with observation.

| d_A	O–C in %	d_A	O–C in %	d_A	O–C in %	d_A	O–C in %
+ 20°.39		**0°.00**		**– 57°.72**		**– 87°.05**	
20.499	– 0.07	2).877	+ 0.05	23.509	+ 0.11	25.152	+ 0.17
25.759	+ 0.01	26.581	– 0.02	[28.575	– 0.16]	34.467	+ 0.02
32.590	+ 0.14	32.302	+ 0.05	33.793	– 0.05	55.822	– 0.10
35.330	– 0.09	37.782	– 0.06	48.116	0.00	71.444	– 0.06
35.759	– 0.13	51.840	– 0.15	64.948	+ 0.06	94.625	– 0.14
47.319	– 0.04	65.325	– 0.21	90.695	+ 0.11	119.84	+ 0.19
59.134	+ 0.07						
59.250	– 0.06						
– 102°.51		**– 109°.88**		**– 113°.80**		**– 115°.86**	
25.571	+ 0.19	26.242	+ 0.14	67.078	– 0.16	69.947	– 0.23
35.077	0.00	34.807	+ 0.26	88.889	– 0.13	91.308	– 0.18
[47.893	+ 0.47]	65.142	– 0.54	106.68	– 0.34	108.02	– 0.35
[53.752	+ 0.48]	66.530	– 0.29	129.17	– 0.25	131.51	– 0.38
62.240	– 0.05	87.176	+ 0.01	152.71	– 0.14	155.12	– 0.27
[69.954	+ 0.50]	102.76	– 0.20	155.40	– 0.07	179.94	– 0.06
84.002	– 0.08	125.56	– 0.09	182.13	+ 0.37	[183.35	+ 2.40]
95.802	– 0.17	148.32	+ 0.03	184.82	+ 0.27	235.47	+ 1.16
115.88	– 0.17	152.79	– 0.26	212.99	+ 1.02	319.52	+ 0.20
135.65	– 0.01	180.84	+ 0.37				
158.01	+ 0.13						
– 116°.62		**– 119°.20**		**– 120°.24**		**– 121°.21**	
26.480	+ 0.25	26.871	+ 0.24	72.627	– 0.04	27.326	+ 0.24
34.939	– 0.01	34.965	+ 0.24	82.816	+ 0.10	35.283	+ 0.25
68.630	– 0.13	[70.314	– 0.25]	99.246	+ 0.03	71.459	– 0.10
90.563	– 0.21	70.481	– 0.66	118.51	– 0.10	85.580	– 0.05
110.19	– 0.46	70.580	– 0.56	136.31	– 0.02	100.33	– 0.03
133.69	– 0.39	83.257	– 0.63	165.79	– 0.09	[123.85	– 0.19]
159.71	– 0.25	96.834	– 0.31	206.57	+ 0.82	148.95	– 0.10
161.75	– 0.35	98.863	– 0.83	280.25	+ 3.22	170.05	– 0.16
[186.15	+ 0.13]	124.97	– 1.10	338.95	+ 0.89	234.13	+ 1.73
210.02	+ 0.64	[143.71	– 0.44]			333.75	+ 1.93
[260.61	+ 1.74]	156.36	– 1.07				
331.29	– 0.46	[172.25	+ 0.07]				
		222.69	– 0.04				
		275.02	+ 1.11				
		336.89	– 1.72				
– 130°.38		**– 139°.62**		**– 149°.60**			
27.394	+ 0.30	28.122	+ 0.12	29.183	– 0.03		
[31.583	– 0.44]	35.573	– 0.10	34.646	– 0.14		
34.726	+ 0.24						
55.807	+ 0.20						
65.125	+ 0.14						
77.821	+ 0.77						
[101.71	– 0.81]						

The accompanying diagrams exhibit the reduced coefficients $\mathfrak{B}$ and $\mathfrak{C}$ as functions of the reduced temperature t within the region of observation for argon, that is, from $t = 2$, to $t = 0.8$. The curves drawn through the circles refer to the special argon equation VII. A. 3, those through the triangles to the mean reduced equation VII. 1. and those through the squares to the special equation for carbon dioxide, V. S. 1. [1])

As the experimental data at present employed are very limited in scope we must, in the meantime, be somewhat chary of drawing conclusions as to the mutual actions of molecules when they come within each other's immediate neighbourhood from a comparison of VII. A. 3. with the equations for the other substances shown in our diagrams. In the case of the $\mathfrak{B}$ coefficient the absence of data at small values of t is specially felt [2]), while as far as $\mathfrak{C}$ and the special argon equation are concerned it is the absence of data towards the side of high densities. Equation VII. A. 3 can, therefore, be regarded only as a first step towards the formation of *the* empirical equation of state for argon.

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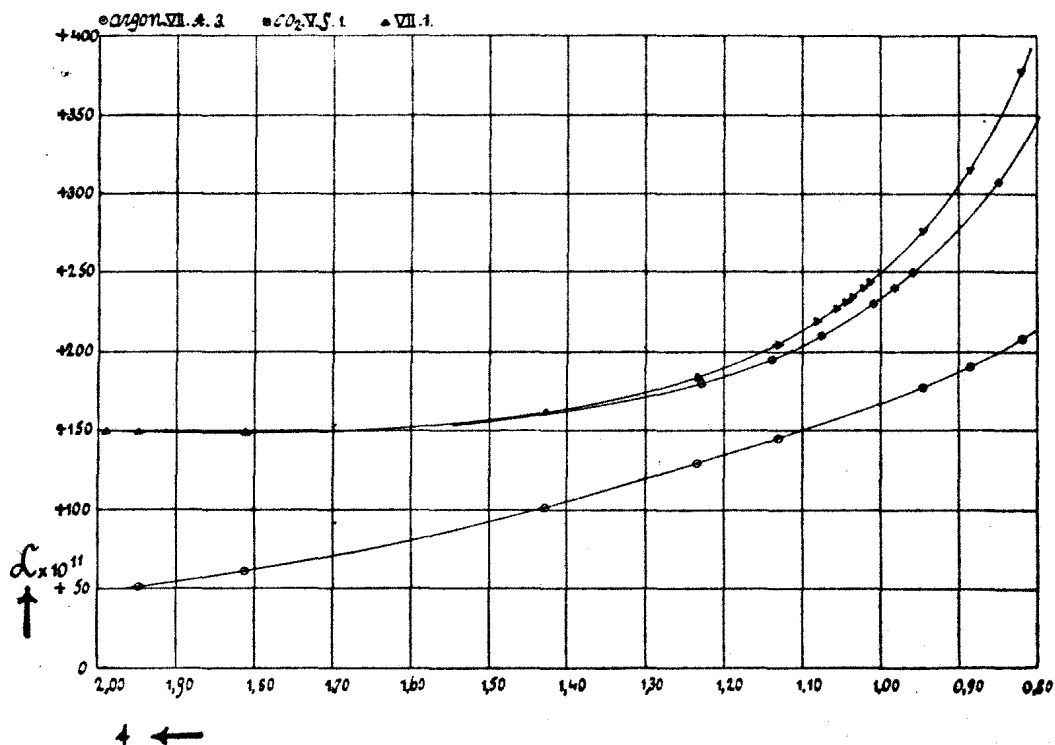
[1]) Arch. Neérl. (2), 6, p. 874, 1901. Comm. N⁰. 74.

[2]) We hope to be able to publish shortly some experimental results to supply this deficiency.
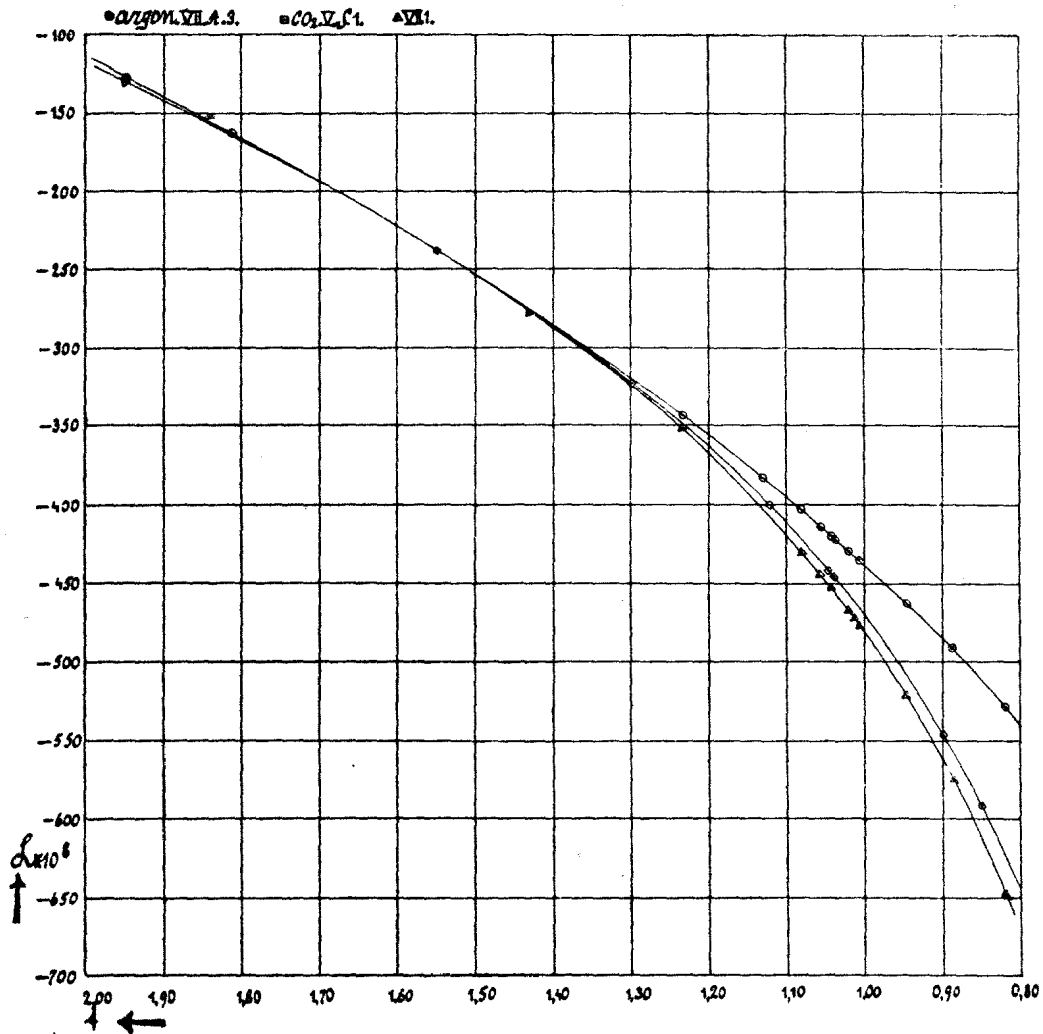
We may still take it, however, that we have advanced a step since our previous papers [1]). It was there found that deviations of the isotherms in the gas state were systematically connected with deviations of the diameter and of the vapour pressure curves (with which the deviations of the latent heat of vaporization etc., are connected by thermodynamical formulae), while in the present case a much simpler survey is obtained of the deviations of the isotherms at densities at which the virial coefficient D need not be taken into account. These are shown in the two curves for $\mathfrak{B}$ and $\mathfrak{C}$, which therefore play pretty much the same part in this particular region as the boundary curve for equilibrium between liquid and vapour. And it is again striking how the various substances arrange them-

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[1]) Proc. March 1911, Comm. N⁰. 120b and Proc. July 1911, Comm. N⁰. 121b.

selves as far as these deviations are concerned according to the more or less complicated structure of their molecules. The curves for VII. 1 in the region of reduced temperature to which the diagrams refer are obtained chiefly from isopentane and ether, substances which have very complex molecules; after these come, in the order given, carbon dioxide, with an undoubtedly less complex molecule, and finally argon. Clearly, just as was the case with the deviations which were encountered in a previous paper [1]), one must look for the explanation of this in a real or apparent compressibility which diminishes in magnitude as the molecule becomes less complex in shape or structure, or in a characteristic behaviour of the attraction potential determined by this peculiarity.

We hope to present further communications shortly giving results of calculations of various thermodynamical quantities which may be made from the equation now given within the limited region for which it holds.

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[1]) Proc. July 1911. Comm. N°. 121b.

(September 2, 1912).