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Physics. — Communication N^o. 71 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES : "*Expression of the equation of state of gases and liquids by means of series.*"

§ 1. I have followed in this communication a different method in considering the equation of state than has been done up to now. Various methods have been tried to empirically derive functions of v and t for VAN DER WAALS' a and b by means of kinetic or thermodynamic considerations, but without obtaining a good agreement with the observations over the whole range of the equation of state. Neither was I successful in similar attempts which were repeatedly occasioned by my continued research on the corresponding states and other investigations resulting from them at the Leiden laboratory. Whenever I seemed to have found an empirical form, I discovered after having tested it more closely that it appeared useful only within a limited range to complete what had been found in a purely theoretical way by VAN DER WAALS and BOLTZMANN. Hence it appeared to me more and more desirable to combine systematically the entire experimental material on the isothermals of gases and liquids as independently as possible from theoretical considerations and to express them by series. The idea of making this attempt and executing the elaborate calculations required ripened gradually on talking the matter over with my friend Dr. E. F. VAN DE SANDE BAKHUIZEN, and many thanks are due to him for his advice in arranging and executing all the stages of those calculations.

§ 2. My calculations, in so far as they are given in this paper comprise AMAGAT's observations¹⁾ relating to hydrogen, oxygen, nitrogen and carbon dioxide.

Although I had in mind the development of the equation of state $p = f(v, T)$ in a convergent double infinite series in terms of the molecular density $\frac{1}{v}$ and the absolute temperature, it follows from the nature of the subject that we can only obtain a representation by a polynomial of a limited number of terms, and we need not wonder that this polynomial does not even converge for all densities. Each co-efficient of such a polynomial can be determined for an individual isotherm only when the polynomial consists of a moderate number of terms. Only in this way we can obtain a good agreement at the first calculation. Therefore the polynomial must be derived

¹⁾ Ann. de Ch. et de Phys. 6e Sér. t. XXIX, 1893.

rom the infinite series not only by approximate combination of the remainder to some terms, but also through suitable omission of intermediate terms.

It must be borne in mind, that the co-efficients of each of the remaining terms will have to be also expressed by a contracted series in terms of the temperature and hence it is obvious that we must try in the first place to bring about an agreement with a number of terms as small as possible but equal for all temperatures.

But for this it is not sufficient to pay attention to one substance only. The range of temperatures for which precise observations have been made in the case of single substances, is too limited for each of those substances to derive from them the way in which the co-efficients of the terms of an isothermal are dependent on the temperature. We are still far from having realised the idea which has occupied me for many years viz. that of the precise determination of the isothermals of hydrogen at temperatures going down to its boiling point and lower. To a certain extent it is possible to substitute for the investigation of one single substance over the whole range of the equation of state, that of several others within different limits, namely when we combine by means of the law of corresponding states the portions of the ranges of reduced temperature and density given by each of the substances investigated.

It is true that the various substances are not rigidly mechanically similar. Some time ago VAN DER WAALS has especially made clear how the different degrees of compressibility of the molecules (in connection with the number of degrees of freedom) will show themselves by a difference in the equations of state of various substances. And instead of neglecting the deviations in order to arrive at the general equation of state we should be inclined to do the reverse and start from the complete equation of state of each substance, in order to express the deviations from the law of the corresponding states as functions of reduced temperature and pressure, these deviations being small for substances belonging to one group, and somewhat larger for substances belonging to different groups¹⁾ consisting of mutually almost mechanically similar substances. But so long as the observations have not proceeded further the method described will be the only way to determine as function of the temperature the coefficients of the simple terms in an isothermal developed with regard to density, which I will call *virial co-efficients*, and to form a

¹⁾ KAMERLINGH ONNES, Proceedings Royal Acad. of Science 1881, p. 11.

representation of the equation of state, given by the observations.

I will not enlarge on the way in which the differences in the combined reduced equations of state will show themselves in the variation of the reduced virial co-efficients with the reduced temperature. We will only remark here that the number of terms in our polynomials must be chosen so that all the isothermals of the different substances which we consider in our calculations can be represented by means of co-efficients, each of which can be taken as derived from the observations.

The more substances are considered the more difficulties arise. Therefore besides hydrogen, oxygen and nitrogen we have taken only carbon dioxide, and so the range covered does not extend far below the critical temperature.

From the standpoint I have chosen the results obtained are to be considered only as the first preliminary data in our method of investigation. A similar calculation will I dare say be required for any investigation. And even if my further calculations would fall short of my expectations the results obtained will be valuable for further investigations by others on the equation of state. They will represent the observations over which they extend in a concise and easily handled form. This is the reason that I no longer delay the publication.

§ 3. For the development in series the following form was chosen :

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} \quad (1)$$

where p represents the pressure in atmospheres (45° northern latitude), v the volume of the molecular weight ¹⁾ the unit being chosen so that v is expressed in the theoretical normal volume ²⁾ and the value for A at 0°C. is

$$A_0 = 1 \quad (1)$$

(I) can also be considered as the series

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + Z$$

¹⁾ Verh. Kon. Akad. v. Wet. 1881, p. 5—7.

²⁾ Comp. Communication No. 47 cont § 2 Febr. '99.

with the remainder ¹⁾)

$$Z = \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8}.$$

The case of the densities at which Z may be neglected is sufficiently important to direct special attention to the co-efficients B and C .

With regard to a term $\frac{F}{v^8}$, it appeared that for the isothermals of 60° C. (and less decisively for those of 10° C.) of carbon dioxide the best agreement was obtained when $F = 0$. This also decided the choice of even or odd terms either of which could be kept in the remainder. At first it seemed as if with great densities and low temperatures a further addition of $\frac{G}{v^{16}}$ could give a better agreement, but afterwards this was found to be unnecessary.

After

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} + \frac{G}{v^6} \quad . \quad . \quad (40^\circ V)$$

were investigated a large number of forms at 40° C.

$$pv = A + \frac{B}{v} + \frac{C}{v(v-\gamma)} + \frac{D}{v(v-\gamma)^2} + \frac{E}{v(v-\gamma)^3} + \frac{F}{v(v-\gamma)^4} \quad . \quad (40^\circ I)$$

$$pv = A + \frac{B}{v} + \frac{C}{v(v-\gamma)} + \frac{D}{v(v-\gamma)^3} + \frac{E}{v(v-\gamma)^5} + \frac{F}{v(v-\gamma)^7} \quad . \quad (40^\circ II)$$

¹⁾ It will also be possible to write VAN DER WAALS' original equation of state:

$$pv = RT + \frac{RTb-a}{v} + \frac{RTb^2}{v^2} + Z$$

$$\text{with } Z = \frac{RTb^3}{v^2(v-b)}.$$

$$pv = A + \frac{B}{v} + \frac{C}{v(v-\gamma)} e^{\frac{\gamma}{v-\gamma}} + \frac{D}{v(v-\gamma)^2} e^{\frac{2\gamma}{v-\gamma}} +$$

$$+ \frac{E}{v(v-\gamma)^3} e^{\frac{3\gamma}{v-\gamma}} + \frac{F}{v(v-\gamma)^4} e^{\frac{4\gamma}{v-\gamma}} \dots \quad (40^\circ \text{ III})$$

$$pv = A + \frac{B}{v} + \frac{C}{v^3} + \frac{D}{v^5} + \frac{E}{v^7} + \frac{F}{v^9} \dots \quad (40^\circ \text{ VI})$$

$$pv = A + \frac{B}{v} + \frac{C}{v^2} e^{-\frac{v}{\gamma}} + \frac{D}{v^3} e^{-\frac{2v}{\gamma}} + \frac{E}{v^4} e^{-\frac{3v}{\gamma}} + \frac{F}{v^5} e^{-\frac{4v}{\gamma}} \dots \quad (40^\circ \text{ VII})$$

The reasons for trying all of which in connection with VAN DER WAALS' equation may easily be seen, but they proved less suitable for the calculations than (I) and (40° V) while at a nearer investigation (I) appeared to be the most suitable.

It is remarkable that whereas our theoretical representations would lead us to forms as (40° I, II, III, IV), the calculation of differences requires a form as (I).

The development in series (I) relates to the theoretical normal volume as unit of volume. AMAGAT gives the volume expressed in the normal volume; if we call this v_N and that given by AMAGAT v_A then

$$v = v_A v_N \dots \dots \dots (2)$$

If we apply AMAGAT's results to

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

then we have

$$A = A_A v_N, \quad B = B_A v_N^2, \quad C = C_A v_N^3, \quad D = D_A v_N^5 \dots \dots (3)$$

further for $t = 0^\circ \text{ C.}$

$$v_N = A_0 + \frac{B_0}{v_N} + \frac{C_0}{v_N} + \dots = \frac{A_0}{A_{A0}} = \frac{1}{A_{A0}} \dots \dots (4)$$

and

$$A_{A_0} = 1 - (B_{A_0} + C_{A_0} + D_{A_0} + E_{A_0} + F_{A_0}) \cdot \dots \quad (5)$$

We put as condition $\frac{A_T}{A_0} = 1 + 0.0036625 t^1$ (where $A_0=1$) or in other words we assume that formula (I) would show that at infinite volume the ideal gaseous state would exist. Hence follows with (3) and (1)

$$A_{AT} = A_T \quad A_{A_0} = A_{A_0} (1 + 0.0036625 t) \quad \dots \quad (6)$$

The calculations were begun with preliminary approximations; at the second approximation we worked with

	Carbon dioxide	Oxygen.	Nitrogen.	Hydrogen.
$A_{A_0} =$	1.00706	1 00092	1 00038	0 99932

The co-efficients B_A, C_A, D_A, E_A, F_A , for each isotherm were now found to first approximation by solving the 5 equations following from 5 well-chosen observations, and then by successive calculation of differences without using least squares, were corrected as much as possible. The results obtained in this way individually for all the isothermals investigated are combined in the following table.

The first column gives the substance and the temperature, for which AMAGAT has measured the isothermal. The second column indicates the solution for the five co-efficients, which gave the best agreement with this isothermal. Co-efficients which had to be assumed in those cases where the range of densities was not sufficient to determine 5 co-efficients individually are placed in brackets; this was the case with the higher temperatures for hydrogen, nitrogen, oxygen, where the pressures do not reach 3000 atm. as with the lower temperatures, but go only up to 1000 atm., and with temperatures below the critical temperature of carbon dioxide where the labile region occasions a similar uncertainty.

¹⁾ In comparing with Comm. N^o. 60 on the co-efficient of pressure variation of hydrogen it must be remembered that the calculations were begun before that communication.

The isothermals gave special difficulties below the critical temperature. Here one of the equations was obtained by means of MAXWELL's criterium. Let p_m be the maximum vapour-pressure, v_v the liquid volume and v_d the vapour volume under this pressure then

$$\begin{aligned}
 p_m (v_d - v_v) = & A \left(\log v_d - \log v_v \right) - B \left(\frac{1}{v_d} - \frac{1}{v_v} \right) \\
 & - \frac{1}{2} C \left(\frac{1}{v_d^2} - \frac{1}{v_v^2} \right) - \frac{1}{4} D \left(\frac{1}{v_d^4} - \frac{1}{v_v^4} \right) \\
 & - \frac{1}{6} E \left(\frac{1}{v_d^6} - \frac{1}{v_v^6} \right) - \frac{1}{8} F \left(\frac{1}{v_d^8} - \frac{1}{v_v^8} \right) \quad (7)
 \end{aligned}$$

AMAGAT gives for carbon dioxide the following densities δ (in G. per c.c.) and maximum vapour pressures in atmospheres (Table N^o. 28).

	δ_v		δ_d		p_m
0°	0.914	[0.921]	0.096	[0.098]	34.3
10°	0.856		0.133		44.2
20°	0.766		0.190		56.3
30°	0.598	[0.607]	0.334	[0.312]	70.7

In order to arrive at a good representation with a constant p_m it appeared to be desirable in some cases to modify δ_v and δ_d a little; the values used are added in this table between brackets.

The calculations were made by means of the equation obtained from (7) by using v_d ; the reduction of δ to v_d was carried out (comp. Communication N^o. 47 cont. § 2. Febr. '99) with

$$v_d = \frac{10^{-3}}{\delta} 1.9771.$$

Virial coefficients for individual isothermals. First approximation.							
		$10^3. B_A$	$10^6. C_A$	$10^{12}. D_A$	$10^{18}. E_A$	$10^{24}. F_A$	
Hydrogen 200° 25	IV	+ 1.3417	+ 0.80723	+ 2.1460	[- 1.5000]	[+ 0.5000]	
	99.25	III	+ 1.0572	+ 0.60637	+ 1.9865	[- 1.5000]	[+ 0.5000]
	47.3						
	15.4	II	+ 0.75371	+ 0.54346	+ 1.8251	- 1.9387	+ 0.86681
	0.	IV	+ 0.66815	+ 0.67030	+ 1.2958	- 1.0448	+ 0.36485
Nitrogen 199.5	$\frac{V + VI}{2}$	+ 1.1952	+ 4.5383	+ 15.318	[+ 2.5000]	[0.0000]	
	99.45	$\frac{IV + V}{2}$	+ 0.44303	+ 3.5048	+ 13.955	[+ 2.5000]	[0.0000]
	43.6						
	16.0	III	- 0.24806	+ 2.7636	+ 11.090	+ 4.7792	+ 0.28505
	0.	II	- 0.37215	+ 2.6217	+ 9.7771	+ 10.016	- 7.3740
Oxygen 199.5	$\frac{II + III + IV + V}{4}$	+ 0.47351	+ 2.9417	+ 7.3280	[+ 2.5000]	[0.0000]	
	99.5	$\frac{V + VI}{2}$	- 0.12073	+ 2.4644	+ 5.7202	[+ 2.5000]	[0.0000]
	15.6	II	- 0.78278	+ 2.1925	+ 3.3320	+ 7.5866	- 5.2394
	0.	III	- 0.92953	+ 2.2931	+ 2.2395	+ 9.1032	- 6.3161
Carb. dioxide 258	198	II	- 2.9653	+ 8.7762	- 4.4031	+ 125.15	- 117.00
	187	4	3.8567	8.7740	7.2828	90.025	12.416
	100	1	4.4621	9.4540	15.612	103.27	26.442
	90	1	4.6981	10.004	22.078	134.75	94.265
	80	2	4.9027	10.338	24.517	136.57	92.657
	70	$\frac{I + II}{2}$	5.0997	10.554	24.677	124.37	68.432
	60	2	5.3396	11.159	29.716	137.98	85.546
	50	2	5.6011	11.747	31.681	124.58	43.496
	40	IV 4	5.8506	12.192	33.234	121.52	- 39.039
	35						
	32						
	30	VIII	6.2334	13.712	41.372	[120.00]	+ 25.012
	20	IV	6.4155	13.585	38.984	[119.72]	- 30.025
	10	VII	6.6896	14.109	45.860	[120.00]	- 57.765
0	X	- 7.0409	- 14.904	- 43.362	[+ 120.00]	- 32.645	

These virial coefficients relate to the normal volume as unit.

In order to judge of the agreement the differences of the observed (O.) and the computed (C.) pv_A are given here in units of the fourth decimal and in percents of pv_A for carbon dioxide at 60° C. and hydrogen at 15° 4 C.

CARBON DIOXIDE 60°.						HYDROGEN 15° 4.					
Tab. N°. 14 AM			Tab. N°. 13 AM.			Tab. N°. 8 AM			Tab. N°. 4 AM.		
P.	O.-C.	In pCt.	P.	O.-C.	In pCt.	P.	O.-C.	In pCt.	P.	O.-C.	In pCt.
45	- 8	- 0 1	50	- 9	- 0 1	100	+ 17	+ 0.1	700	+ 27	+ 0.2
48	- 8	- 0 1	75	+ 27	+ 0 3	150	+ 1	0.0	800	+ 24	+ 0.1
50	- 9	- 0.1	100	0	0	200	- 5	0.0	900	- 42	- 0.2
53	- 4	0.0	125	- 1	0	250	+ 11	+ 0.1	1000	- 35	- 0 2
55	- 2	0.0	150	+ 9	+ 0.2	300	- 17	- 0 1	1100	+ 41	+ 0 2
60	- 1	0.0	175	- 25	- 0 5	350	- 12	- 0 1	1200	+ 63	+ 0.3
65	0	0.0	200	+ 2	0	400	- 16	- 0.1	1300	+ 48	+ 0.3
68	+ 2	0.0	225	- 1	0	450	- 8	- 0 1	1400	+ 48	+ 0.2
70	+ 1	0.0	250	+ 10	+ 0 2	500	- 3	0.0	1500	+ 36	+ 0.2
75	- 4	0.0	275	+ 3	0 0	550	+ 1	0 0	1600	+ 19	+ 0.1
80	- 5	- 0 1	300	- 26	- 0.4	600	+ 3	0 0	1700	- 34	- 0.2
85	- 4	- 0 1	350	+ 27	+ 0.4	650	+ 7	0.0	1800	- 26	- 0 1
90	- 2	0.0	400	+ 21	+ 0.2	700	- 5	0.0	1900	+ 10	0.0
95	0	0 0	450	+ 3	0	750	- 8	- 0.1	2000	- 9	0.0
100	0	0.0	500	+ 29	+ 0.3	800	- 26	- 0.2	2100	+ 6	0.0
110	+ 8	+ 0.1	550	0	0	850	- 50	- 0 3	2200	+ 53	+ 0.2
			600	- 40	- 0.3	900	- 40	- 0.2	2300	+ 77	+ 0.3
			650	- 33	- 0 3	950	- 59	- 0.3	2400	+ 113	+ 0.4
			700	- 10	- 0.1	1000	- 65	- 0.4	2500	+ 89	+ 0 3
			750	+ 50	+ 0.4				2600	+ 149	+ 0.5
			800	+ 42	+ 0.3				2700	+ 71	+ 0.3
			850	+ 43	+ 0.3				2800	+ 2	0.0
			900	- 32	- 0 2				2900	- 85	- 0.3
			950	- 194	- 1.1				3000	- 146	- 0.5
			1000	- 444	- 2 4						

There are some cases that are less favourable, but considering the agreement with the isothermals which are represented by the system of co-efficients, B_A, C_A, D_A, E_A, F_A , the regular course of these co-efficients with the temperature may be adduced as a proof that the co-efficients obtained have not only importance for the calculations but have also a physical meaning. Even if some difficulties remain as with the densities of carbon dioxide at pressures above 850 atm. and with the densities in the neighbourhood of saturation, the choice of six terms in the polynomial appears in reasonably good agreement with the nature of the problem and the accuracy of the observations.

§ 4. In order to express the virial co-efficients as functions of temperature we introduce the reduced quantities:

$$p = \frac{p}{p_k} , \quad v = \frac{v}{v_k} , \quad t = \frac{T}{T_k} \dots \dots \dots (8)$$

where k relates to the critical state.

Then (I) changes into:

$$\lambda p v = \mathfrak{A} + \frac{\mathfrak{B}}{\lambda v} + \frac{\mathfrak{C}}{\lambda^2 v^2} + \frac{\mathfrak{D}}{\lambda^4 v^4} + \frac{\mathfrak{E}}{\lambda^6 v^6} + \frac{\mathfrak{F}}{\lambda^8 v^8} \dots \dots \dots (III)$$

where $\mathfrak{A}, \mathfrak{B}, \mathfrak{C}, \mathfrak{D}, \mathfrak{E}$ and \mathfrak{F} are functions of t and

$$\lambda = \frac{p_k v_k}{T_k} \dots \dots \dots (9)$$

while

$$\left. \begin{aligned} \mathfrak{A} &= \frac{A}{T_k} , \quad \mathfrak{B} = \frac{B}{T_k^2} p_k , \quad \mathfrak{C} = \frac{C}{T_k^3} p_k^2 \\ \mathfrak{D} &= \frac{D}{T_k^5} p_k^4 , \quad \mathfrak{E} = \frac{E}{T_k^7} p_k^6 , \quad \mathfrak{F} = \frac{F}{T_k^9} p_k^8 \end{aligned} \right\} \dots \dots \dots (10)$$

or with (3)

$$\left. \begin{aligned} \mathfrak{A} &= \frac{A_A}{T_k} v_N, & \mathfrak{B} &= \frac{B_A}{T_k^2} p_k v_N^2, & \mathfrak{C} &= \frac{C_A}{T_k^3} p_k^2 v_N^3 \\ \mathfrak{D} &= \frac{D_A}{T_k^5} p_k^4 v_N^5, & \mathfrak{E} &= \frac{E_A}{T_k^7} p_k^6 v_N^7, & \mathfrak{F} &= \frac{F_A}{T_k^9} p_k^8 v_N^9 \end{aligned} \right\} \dots (11)$$

gives on the one hand the connection of the reduced virial co-efficients with the virial co-efficients expressed with regard to the theoretical normal volume as unit, on the other hand with the virial co-efficients expressed with regard to the normal volume as unit.

We attribute to λ the same value for all substances, which gives the advantage that in the reduction calculations the p_k and T_k , which generally are much more accurately known than v_k , can be used.

The calculations are made with the following

Data and reduction factors.				
	Hydrogen.	Nitrogen.	Oxygen.	Carbon dioxide.
T_k	38.5 OLSZ.	127 OLSZ.	154.2 OLSZ	304.45 AM.
p_k	20 OLSZ.	35 OLSZ.	50.7 OLSZ.	72.9 AM.
$\log \mathfrak{B} - \log B_A + 5$	3 13070	2.33614	2.32890	1 88988
$\log \mathfrak{C} - \log C_A + 5$	2.84657	1.77625	1.84628	1.26619
$\log \mathfrak{D} - \log D_A + 6$	3 27830	1 65646	1.88105	1.01880
$\log \mathfrak{E} - \log E_A + 7$	3.71003	1.53667	1.91581	0.77141
$\log \mathfrak{F} - \log F_A + 8$	4 14176	1.41688	1 95057	0.52402

The reduced virial co-efficients of all the substances together found in this way show already in their relation to the reduced temperature (rounded off in the following table) the same regularity as we found for the non-reduced numbers for a single substance, another proof, that the virial co-efficients have a real meaning.

In the following table, in which the reduced virial co-efficients are combined I have omitted those which would be obtained from the assumed co-efficients [] in the table of § 3

9*

Reduced virial co-efficients from individual isotherms to first approximation.						
t		10 ⁸ . B	10 ¹¹ . C	10 ¹⁸ . D	10 ²⁵ . E	10 ³² . F
12.29	Hydrogen 200°.25	+ 1812.76	+ 566.98	+ 4073.1		
9.67	99.25	+ 1428.43	+ 425.90	+ 3770.4		
8.32	47.3					
7.49	15.4	+ 1018.38	+ 381.72	+ 3464.1	- 9943	+ 12014
7.09	0	+ 902.78	+ 470.79	+ 2459.5	- 5359	+ 5057
3.72	Nitrogen 199.5	+ 259.16	+ 271.11	+ 694.46		
3.06	Oxygen 199.5	+ 100.98	+ 206.48	+ 557.22		
2.93	Nitrogen 99.45	+ 96.07	+ 209.36	+ 632.69		
2.49	» 43.6					
2.42	Oxygen 99.5	- 25.75	+ 172.98	+ 434.96		
2.28	Nitrogen 16.0	- 53.79	+ 165.09	+ 502.81	+ 164.4	+ 7.4
2.15	» 0	- 80.70	+ 156.61	+ 443.27	+ 344.6	- 192.6
1.87	Oxygen 15.6	- 166.93	+ 153.89	+ 253.36	+ 625.0	- 467.6
1.77	» 0	- 198.23	+ 160.95	+ 170.29	+ 749.9	- 563.7
1.745	Carbon dioxide 258					
1.548	198	- 210.11	+ 162.00	- 45.98	+ 739.4	- 391.0
1.347	137	- 299.30	+ 161.96	- 76.05	+ 531.8	- 41.5
1.226	100	- 346.27	+ 174.51	- 163.02	+ 610.1	- 88.4
1.193	90	- 364.59	+ 184.65	- 230.54	+ 796.1	- 315.0
1.160	80	- 380.46	+ 190.82	- 256.01	+ 806.8	- 309.7
1.127	70	- 395.77	+ 194.81	- 257.69	+ 734.7	- 228.7
1.094	60	- 414.37	+ 205.97	- 310.30	+ 815.1	- 285.9
1.061	50	- 434.67	+ 216.83	- 330.83	+ 736.0	- 145.4
1.028	40	- 454.02	+ 225.05	- 347.03	+ 717.9	- 130.5
1.012	35					
1.002	32					
0.996	30	- 483.74	+ 253.09	- 432.02		- 83.6
0.963	20	- 497.85	+ 250.76	- 457.07		- 100.3
0.930	10	- 519.13	+ 260.43	- 458.00		- 193.1
0.897	0	- 546.37	+ 275.09	- 452.79		- 109.1

§ 5. Because of the approach to the ideal gas-state at high temperatures, it is desirable in developing the reduced virial co-efficients with regard to \bar{t} , to start from t and to take polynomials of $\frac{1}{t}$

The linear form in t is insufficient. It is obvious that for instance $\mathfrak{C} = \mathfrak{C}_1 t + \mathfrak{C}_2$ is altogether unsatisfactory. Some calculations made us suppose that by means of such terms as $t e^{\frac{c}{t}}$ some peculiarities in the course of the functions could be represented, and that then c might be chosen nearly equal to 1. Such terms (giving also after the development terms in $1/t$) can easily be brought into connection with the idea of the collisions as dissociation phenomenon, and as in a development in series of an equation of state which takes this into account, terms $t e^{\frac{2}{t}}$ could also be expected, a term of this form was immediately taken into consideration. Although for the representation of \mathfrak{B} and \mathfrak{C} the three terms considered were sufficient, for \mathfrak{D} it was necessary to introduce still more terms and we returned to $\frac{1}{t}$; this was also used with \mathfrak{E} and \mathfrak{F} . So the first approximation for the reduced virial co-efficients was obtained.

$$10^8. \mathfrak{B} = + 499.79 t - 297.66 t e^{\frac{1}{t}} - 21.74 t e^{\frac{2}{t}}$$

$$10^{11}. \mathfrak{C} = + 141.725 t - 149.828 t e^{\frac{1}{t}} + 67.367 t e^{\frac{2}{t}}$$

$$10^{18}. \mathfrak{D} = + 587.74 t - 313.26 t e^{\frac{1}{t}} + 139.87 t e^{\frac{2}{t}} - 1145.93 \frac{1}{t}$$

$$10^{25}. \mathfrak{E} = - 8448.85 t + 6594.51 t e^{\frac{1}{t}} - 8793.16 \frac{1}{t}$$

$$10^{32}. \mathfrak{F} = + 9067.14 t - 7116.56 t e^{\frac{1}{t}} + 10152.19 \frac{1}{t}$$

In the following table are combined the deviations between the virial co-efficients derived from these reduced virial co-efficients with regard to the normal volume and those immediately derived from the observation in the table of § 3.

Deviations of the virial coefficients in first approximation.					
	$10^3 \Delta B$	$10^6 \Delta C$	$10^{12} \Delta D$	$10^{18} \Delta E$	$10^{24} \Delta F$
Hydrogen 200°.25	- 0.0348	- 0.2161	- 0.4765	[+ 1.7441]	[- 0.7546]
99.25	+ 0.0343	- 0.19782	- 0.0518	[+ 0.8185]	[- 0.3955]
47.3					
15.4	+ 0.02623	- 0.08029	+ 0.2780	- 0.3770	+ 0.2642
0.	- 0.00466	+ 0.07947	- 0.1601	+ 0.3798	- 0.1849
Nitrogen 199.5	- 0.0591	+ 0.7382	- 12.134	[+ 51.807]	[- 69.735]
99.45	- 0.07318	+ 0.3502	- 4.843	[+ 19.304]	[- 26.879]
43.6					
16.0	- 0.09586	+ 0.0417	+ 0.189	- 0.9606	+ 1.690
0.	- 0.08145	- 0.0398	+ 0.5035	+ 0.713	- 1.799
Oxygen 199.5	- 0.17991	+ 0.1707	- 4.770	[+ 11.6517]	[- 9.806]
99.5	- 0.11754	+ 0.0815	- 1.8276	[+ 1.8991]	[- 1.110]
15.6	- 0.15608	+ 0.0003	+ 0.0504	+ 0.9331	- 1.522
0.	- 0.17291	+ 0.1079	- 0.1803	+ 1.6533	- 2.089
Carbon dioxide 258					
198	- 0.0236	+ 0.2977	- 7.489	+ 3.73	+ 9.81
137	- 0.0115	- 0.2973	+ 3.615	- 37.58	+ 104.08
100	+ 0.0310	- 0.3335	+ 4.141	- 23.11	+ 71.33
90	- 0.0116	- 0.046	+ 0.095	+ 9.33	- 3.29
80	- 0.0133	- 0.014	+ 0.079	+ 12.35	- 9.22
70	+ 0.0029	- 0.144	+ 2.333	+ 1.61	+ 6.78
60	- 0.0113	+ 0.067	- 0.309	+ 16.86	- 19.30
50	- 0.0339	+ 0.202	+ 0.088	+ 5.27	+ 13.21
40	- 0.0286	+ 0.125	+ 0.851	+ 4.11	+ 7.58
35					
32					
29	- 0.1393	+ 1.045	- 5.057	[+ 4.52]	+ 61.13
20	- 0.0279	+ 0.220	- 0.536	[+ 6.07]	- 4.74
10	+ 0.0153	- 0.066	- 3.432	[+ 7.99]	- 43.35
0	+ 0.0093	- 0.219	- 1.162	[+ 9.21]	- 28.90

§ 6. Starting from the first approximation for the virial coefficients given in § 5 we looked now for small variations in the virial coefficients so that the latter while keeping the agreement with the isothermal, which they have to represent, allow of a better development in terms of the reduced temperature. And so the isothermals were mutually smoothed. The weak point in this method, when it is extended over more substances is the imperfect agreement of the reduced equations of state, further increased by uncertainty in the critical data. But it is important to see how far we can advance under these circumstances.

In calculating the variations $\Delta B_A, \Delta C_A, \Delta D_A, \Delta E_A, \Delta F_A$ which had each to satisfy each of the isothermals and which therefore had to be mostly sought out in the same way as B_A, C_A, D_A, E_A, F_A were calculated, it appeared desirable also to modify slightly the form of the development in series with regard to the reduced temperature.

We put:

$$\begin{aligned}
 \mathfrak{B} &= b_1 t + b_2 t e^{\frac{1}{t}} + b_2 t e^{\frac{2}{t}} + b_3 \frac{1}{t} \\
 \mathfrak{C} &= c_1 t + c_2 t e^{\frac{1}{t}} + c_2 t e^{\frac{2}{t}} + c_3 \frac{1}{t} \\
 \mathfrak{D} &= d_1 t + d_2 t e^{\frac{1}{t}} + d_3 \frac{1}{t} + d_4 \frac{1}{t^2} \\
 \mathfrak{E} &= e_1 t + e_2 t e^{\frac{1}{t}} + e_3 \frac{1}{t} + e_4 \frac{1}{t^2} \\
 \mathfrak{F} &= f_1 t + f_2 t e^{\frac{1}{t}} + f_3 \frac{1}{t} + f_4 \frac{1}{t^2}
 \end{aligned}
 \quad \left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} \dots (IV)$$

We find for the 20 coefficients, which cover the range of the 4 substances the following

Coefficients of temperature of the reduced virial coefficients.				
	1	2	3	4
$10^8 b^{(IV)}$	+ 564.78	- 339.79	- 40.56	+ 186.71
$10^{11} c^{(IV)}$	+ 197.677	- 190.441	+ 61.328	+ 100.102
$10^{18} d^{(IV)}$	+ 669.98	- 204.92	- 866.31	+ 391.12
$10^{25} e^{(IV)}$	- 8546.45	+ 6655.21	- 8628.76	- 128.93
$10^{32} f^{(IV)}$	+ 9772.71	- 7729.47	+11653.22	- 527 02

From this follow immediately with (IV) and the reduction factors of § 4 the virial coefficients in the development of series (II), which gives the value calculated for the pv_A observed by AMAGAT.

The following tables show the deviations between observation and calculation for all the observations. If we examine them, it appears that the deviations must be chiefly attributed to the difference of the substances which we have combined, and might also be partly due to the uncertainty of the critical data.

O—C. HYDROGEN (Tab. N ^o . 8 Am. and N ^o . 4 Am.)								
P.	0°	15°.4	99°.25	∞00° 25	P.	0°	15°.4	47°.3
1	0				1	0		
100	+ 0.3	+ 0.5			100	+ 0.3		
150	+ 0.3	+ 0.4	+ 0.2	- 0.1	200	+ 0.4		
200	+ 0.4	+ 0.4	+ 0.2	- 0.3	300	+ 0.4		
250	+ 0.4	+ 0.6	+ 0.1	- 0.5	400	+ 0.6		
300	+ 0.4	+ 0.3	0.0	- 0.7	500	+ 0.6		
350	+ 0.5	+ 0.4	- 0.1	- 0.8	600	+ 0.8		
400	+ 0.6	+ 0.3	- 0.2	- 0.9	700	+ 0.7	+ 0.4	
450	+ 0.7	+ 0.3	- 0.3	- 1.0	800	+ 0.4	+ 0.3	
500	+ 0.6	+ 0.4	- 0.4	- 1.1	900	+ 0.6	- 0.2	
550	+ 0.6	+ 0.4	- 0.5	- 1.3	1000	+ 0.7	- 0.3	- 1.5
600	+ 0.7	+ 0.3	- 0.6	- 1.4	1100	+ 1.2	+ 0.1	- 1.6
650	+ 0.7	+ 0.3	- 0.8	- 1.6	1200	+ 1.0	+ 0.1	- 1.8
700	+ 0.6	+ 0.2	- 1.0	- 1.8	1300	+ 1.0	0.0	- 1.9
750	+ 0.5	+ 0.1	- 1.0	- 2.0	1400	+ 0.8	- 0.1	- 2.0
800	+ 0.5	0.0	- 1.2	- 2.1	1500	+ 0.6	- 0.2	- 2.1
850	+ 0.5	- 0.2	- 1.3	- 2.3	1600	+ 0.5	- 0.4	- 2.1
900	+ 0.4	- 0.2	- 1.5	- 2.5	1700	+ 0.6	- 0.7	- 2.1
950	+ 0.4	- 0.3	- 1.7		1800	+ 0.5	- 0.7	- 2.3
1000	+ 0.2	- 0.4	- 1.7		1900	+ 0.5	- 0.6	- 2.4
					2000	+ 0.5	- 0.7	- 2.6
					2100	+ 0.4	- 0.6	- 2.7
					2200	+ 0.4	- 0.4	- 2.8
					2300	+ 0.5	- 0.3	- 2.6
					2400	+ 0.7	- 0.2	- 2.5
					2500	+ 0.9	- 0.2	- 2.3
					2600	+ 1.0	+ 0.1	- 2.4
					2700	+ 1.1	- 0.1	- 2.2
					2800	+ 0.9	- 0.2	- 2.2
					2900		- 0.4	- 2.1
					3000		- 0.4	

O.—C. NITROGEN (Tab. N ^o . 9 Am. and N ^o . 5 Am.)									
P.	0°	16°	99°.45	199°.50	P.	0°	16°	45°.6	
1	+ 0.0				1	0			
100	+ 0.2	+ 0.0			100	+ 0.2			
150	+ 0.4	+ 0.3	+ 0.7	+ 0.9	200	+ 0.4			
200	+ 0.4	+ 0.4	+ 0.7	+ 0.8	300	+ 0.8			
250	+ 0.5	+ 0.5	+ 1.0	+ 0.9	400	+ 1.1			
300	+ 0.8	+ 0.8	+ 1.3	+ 1.1	500	+ 1.5			
350	+ 1.0	+ 0.9	+ 1.4	+ 1.2	600	+ 1.7			
400	+ 1.1	+ 1.0	+ 1.5	+ 1.3	700	+ 1.8			
450	+ 1.3	+ 1.3	+ 1.5	+ 1.4	800	+ 2.2	+ 0.8		
500	+ 1.5	+ 1.2	+ 1.4	+ 1.5	900	+ 2.3	+ 1.7	+ 1.4	
550	+ 1.7	+ 1.3	+ 1.3	+ 1.4	1000	+ 2.3	+ 1.5	+ 0.3	
600	+ 1.7	+ 1.4	+ 1.2	+ 1.4	1100	+ 2.5	+ 1.7	+ 0.7	
650	+ 1.6	+ 1.4	+ 1.2	+ 1.4	1200	+ 2.6	+ 1.8	+ 1.2	
700	+ 1.6	+ 1.3	+ 1.1	+ 1.2	1300	+ 2.7	+ 1.7	+ 1.3	
750	+ 1.7	+ 1.4	+ 1.1	+ 1.0	1400	+ 2.8	+ 1.5	+ 1.3	
800	+ 1.7	+ 1.5	+ 1.1	+ 0.8	1500	+ 2.8	+ 1.4	+ 1.0	
850	+ 1.8	+ 1.5	+ 1.0	+ 0.8	1600	+ 2.8	+ 1.6	+ 1.1	
900	+ 1.9	+ 1.6	+ 1.1	+ 0.6	1700	+ 2.5	+ 1.6	+ 1.0	
950	+ 2.0	+ 1.7	+ 1.2	+ 0.6	1800	+ 2.2	+ 1.3	+ 0.7	
1000	+ 2.1	+ 1.7			1900	+ 2.2	+ 1.4	+ 0.8	
					2000	+ 2.1	+ 1.5	+ 0.7	
					2100	+ 2.1	+ 1.4	+ 0.6	
					2200	+ 2.1	+ 1.4	+ 0.5	
					2300	+ 2.2	+ 1.3	+ 0.3	
					2400	+ 2.3	+ 1.5	+ 0.5	
					2500	+ 2.7	+ 1.6	+ 0.5	
					2600	+ 3.0	+ 1.6	+ 0.6	
					2700	+ 3.3	+ 1.8	+ 0.4	
					2800	+ 3.4	+ 2.0	+ 0.5	
					2900	+ 3.6	+ 2.2	+ 0.6	
					3000	+ 3.6	+ 2.2	+ 0.7	

O.—C. OXYGEN. (Tab No. 7 Am. and No. 4 Am.)							
P.	0°.	15°.6	99°.50	199°.5	P.	0°.	15°.6
1	0				1	0	
100	- 1.2	- 0.5	+ 0.4		100	- 1.3	
150	- 1.3	- 1.1	0.0	+ 0.3	200	- 1.7	
200	- 1.7	- 1.5	0.0	- 0.1	300	- 1.9	
250	- 1.9	- 1.5	0.0	- 0.3	400	- 1.6	
300	- 1.9	- 1.7	- 0.1	- 0.4	500	- 1.3	
350	- 1.7	- 1.7	0.0	- 0.4	600	- 1.0	- 1.4
400	- 1.6	- 1.7	+ 0.2	- 0.5	700	- 0.6	- 0.9
450	- 1.5	- 1.5	+ 0.2	- 0.6	800	- 0.1	- 0.9
500	- 1.5	- 1.5	+ 0.2	- 0.5	900	+ 0.1	- 0.5
550	- 1.3	- 1.4	0.0	- 0.7	1000	+ 0.4	- 0.2
600	- 1.2	- 1.4	0.0	- 0.9	1100	+ 0.6	- 0.1
650	- 0.9	- 1.2	0.0	- 1.0	1200	+ 0.6	- 0.1
700	- 0.8	- 1.1	0.0	- 1.2	1300	+ 0.4	- 0.1
750	- 0.6	- 1.2	0.0	- 1.3	1400	+ 0.1	- 0.4
800	- 0.3	- 1.1	- 0.3	- 1.6	1500	+ 0.2	- 0.4
850	- 0.1	- 1.0	- 0.5	- 1.7	1600	0.0	- 0.5
900	+ 0.1	- 0.8	- 0.7	- 2.0	1700	0.0	- 0.3
950	+ 0.2	- 0.7	- 0.9	- 2.3	1800	- 0.1	- 0.3
1000	+ 0.4	- 0.5	- 1.1		1900	- 0.2	- 0.5
					2000	- 0.1	- 0.5
					2100	+ 0.1	- 0.7
					2200	0.0	- 0.7
					2300	0.0	- 0.6
					2400	0.0	- 0.6
					2500	0.0	- 0.4
					2600	0.0	- 0.4
					2700	0.0	- 0.7
					2800	0.0	- 0.8
					2900	- 0.1	- 1.0
					3000	- 0.4	- 0.9

O.—C.		CARBON DIOXIDE. (Tab. No. 14 Am.)											
P.	0°	10°	20°	30°	32°	35°	40°	50°	60°	70°	80°	90°	100°
31	+ 0.5												
33	+ 0.4	0.0											
34	+ 0.4	0.0											
35	-14.5*	0.0	0.0										
37	-18.5*	0.0	0.0	- 0.1									
40		- 0.1	0.0	- 0.1	+ 0.1	- 0.0	- 0.1						
44		+ 0.1	0.0										
45		+16.5*	- 0.1	- 0.1	+ 0.0	- 0.0	- 0.2	- 0.1	- 0.1	- 0.2			
48			+ 0.1	0.0			- 0.1	- 0.2	- 0.1	- 0.2			
50	-21.6* + 6.5*	0.0	0.0	+ 0.0	0.0	- 0.1	- 0.1	- 0.1	- 0.1	- 0.2	0.0	+ 0.1	
53			- 0.1	0.0			0.0	- 0.1	- 0.1	- 0.1	- 0.2	0.0	+ 0.1
55			- 0.1	0.0	+ 0.0	0.0	- 0.1	- 0.1	0.0	- 0.1	- 0.2	0.0	+ 0.1
56			- 0.1										
57			+10.1*										
60		+ 5.9*	- 0.1	+ 0.1	0.0	- 0.1	0.0	0.0	- 0.1	- 0.2	- 0.1	+ 0.1	
65			- 0.2	- 0.2	- 0.1	- 0.2	0.0	0.0	0.0	- 0.1	- 0.1	+ 0.1	
68			- 0.3	- 0.3	- 0.1	- 0.2	- 0.1	0.0	- 0.1	- 0.1	- 0.1	+ 0.1	
70			- 0.6	- 0.3	- 0.2	- 0.2	- 0.1	0.0	0.0	- 0.1	- 0.1	+ 0.1	
71			+ 4.1										
72			+ 3.6	- 0.3									
73				0.0									
74			+ 2.7	+ 0.3	- 0.2								
74.5				+ 1.8									
75			+ 2.1	+ 3.9	- 0.2	- 0.4	- 0.1	- 0.1	0.0	0.0	0.0	+ 0.2	
76				+ 3.8	- 0.1								
78			+ 2.1	+ 3.5	+ 0.4								
80			+ 1.5		+ 2.1	- 0.5	0.0	- 0.1	0.0	+ 0.1	0.0	+ 0.2	
82					+ 2.6	- 0.1							
85					+ 2.1	+ 0.2	- 0.1	0.0	+ 0.1	+ 0.1	0.0	+ 0.3	
90					+ 1.7	+ 0.9	- 0.1	0.0	0.0	0.0	0.0	+ 0.3	
95							+ 0.9	- 0.1	0.0	0.0	+ 0.1	+ 0.1	+ 0.3
100							+ 0.7	- 0.1	0.0	0.0	+ 0.1	+ 0.1	+ 0.3
110							- 0.5	- 0.2	- 0.2	0.0	0.0	+ 0.1	+ 0.4

O.—C.		CARBON DIOXIDE. (Tab. No. 13 Am.)													
P.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	137°	198°	258°	
50	-21.6*	+ 6.4*	+ 0.2	0.0	- 0.3	- 0.2	- 0.1	- 0.1	- 0.3	0.0	+ 0.1	- 0.2			
75	-31.4*	-12.7*	+ 0.9	+ 3.0	+ 0.2	+ 0.3	+ 0.3	+ 0.1	0.0	- 0.1	+ 0.2	0.0	+ 0.1	- 0.6	
100	-14.1*	- 5.2*	+ 1.5	+ 2.5	+ 0.7	- 0.1	0.0	0.0	+ 0.1	+ 0.1	+ 0.3	+ 0.1	+ 0.3	- 0.5	
125	-11.0*	- 0.2	+ 2.7	+ 0.5	+ 0.2	- 0.8	- 0.4	- 0.3	- 0.1	+ 0.1	+ 0.4	+ 0.2	+ 0.5	- 0.3	
150	- 9.7*	- 0.2	+ 2.5	- 0.6	+ 0.4	- 0.7	- 0.5	- 0.7	- 0.1	- 0.1	+ 0.3	+ 0.3	+ 0.8	- 0.2	
175	- 7.7*	- 0.3	+ 1.9	+ 0.2	+ 0.6	- 0.7	- 1.0	- 0.5	- 0.6	- 0.2	+ 0.2	+ 0.4	+ 0.9	0.0	
200	- 7.5*	+ 1.2	+ 2.8	+ 1.5	+ 1.4	- 0.1	- 0.3	- 0.7	- 0.4	- 0.6	+ 0.1	+ 0.4	+ 1.1	+ 0.2	
225	- 2.9	+ 0.4	+ 4.5	+ 3.9	+ 1.9	- 0.6	- 0.1	- 0.6	- 1.0	- 0.5	0.0	+ 0.3	+ 1.4	+ 0.4	
250	- 3.0	+ 0.9	+ 3.9	+ 4.9	+ 2.0	- 0.5	+ 0.3	- 0.4	- 1.9	- 1.1	0.0	+ 0.1	+ 1.6	+ 0.6	
275	- 3.3	+ 1.3	+ 4.1	+ 4.1	+ 3.3	+ 1.3	+ 0.4	- 0.4	- 0.9	- 1.0	- 0.3	- 0.2	+ 1.5	+ 0.7	
300	- 3.7	+ 1.5	+ 4.0	+ 4.8	+ 3.4	+ 1.0	+ 0.1	- 0.3	- 1.0	- 1.0	- 0.8	0.0	+ 1.4	+ 0.8	
350	- 2.3	+ 2.8	+ 3.8	+ 4.0	+ 3.7	+ 1.9	+ 1.1	- 0.4	- 0.7	- 1.5	- 1.1	- 0.5	+ 1.3	+ 0.9	
400	- 1.6	+ 1.8	+ 4.6	+ 4.1	+ 3.9	+ 2.1	+ 1.2	- 0.2	- 0.7	- 1.2	- 1.6	- 1.3	+ 1.0	+ 0.8	
450	- 2.8	+ 2.3	+ 4.6	+ 4.3	+ 3.5	+ 1.9	+ 1.1	+ 0.2	- 0.7	- 1.6	- 1.8	- 1.9	+ 0.7	+ 0.6	
500	- 2.0	+ 2.4	+ 4.6	+ 3.9	+ 2.6	+ 2.1	+ 1.5	+ 0.3	- 0.6	- 1.5	- 2.0	- 2.3	+ 0.3		
550	- 2.5	+ 1.9	+ 4.7	+ 4.6	+ 3.2	+ 1.7	+ 1.2	+ 0.5	- 0.2	- 1.8	- 2.1	- 2.6	+ 0.1		
600	- 2.1	+ 1.4	+ 3.6	+ 4.2	+ 3.7	+ 2.0	+ 0.9	+ 0.2	- 0.6	- 1.6	- 2.0	- 3.0	- 0.7		
650	- 2.4	+ 2.0	+ 3.9	+ 3.8	+ 3.3	+ 2.0	+ 1.0	+ 0.2	- 0.5	- 1.6	- 2.1	- 3.6	- 1.2		
700	- 2.1	+ 2.2	+ 3.6	+ 4.6	+ 3.9	+ 2.5	+ 1.2	+ 0.1	- 0.7	- 1.7	- 2.3	- 3.9	- 1.9		
750	- 3.0	+ 2.7	+ 4.7	+ 5.5	+ 4.5	+ 3.1	+ 1.6	+ 0.4	- 1.0	- 1.8	- 2.1	- 4.0	- 2.1		
800	- 2.9	+ 2.1	+ 4.4	+ 4.9	+ 4.4	+ 3.0	+ 1.5	+ 0.2	- 0.9	- 1.9	- 2.6	- 4.3	- 2.7		
850	- 2.8	+ 1.3	+ 3.9	+ 4.5	+ 4.2	+ 2.7	+ 1.5	+ 0.2	- 1.2	- 2.4	- 2.8	- 4.5	- 2.9		
900	- 2.9	+ 1.2	+ 3.0	+ 3.6	+ 3.2	+ 2.0	+ 1.0	- 0.3	- 1.3	- 2.5	- 3.2	- 4.8	- 3.7		
950	- 3.4	- 0.1	+ 2.1	+ 2.4	+ 1.9	+ 1.0	+ 0.1	- 1.1	- 2.0	- 2.9	- 3.7	- 5.1	- 4.3		
1000	- 4.2	- 1.0	+ 0.9	+ 1.5	+ 0.8	+ 0.1	- 1.3	- 2.1	- 3.1	- 3.8	- 4.1				

The deviations asterisked in the tables of carbon dioxide are in the neighbourhood of the state of saturation. Owing to the great variation of p with a small variation in v , the agreement cannot be judged from the deviation from pv , and for this we might with more

(146)

advantage consider the deviation which v would have to undergo in order to yield this variation in pv .

At 0° C. for instance instead of the percent deviation in pv_{Δ} at

$P = 35, 37, 50, 75, 100, 125, 150, 175, 200$ atm.

$-14.5^*, -18.5^*, -21.6^*, -31.4^*, -14.1^*, -11.0^*, -9.7^*, -7.7^*, -7.5^*$

we have to put

$-0.6, -0.8, -1.0, -1.7, -0.9, -0.7^s, -0.7, 0.6, -0.6$

percent variation in v_{Δ} .

Also at 10° C. and $P = 45, 50, 75, 100$ atm.

instead of $+16.5^*, +6.5^*, -12.7^*, -5.2^*$ percent of pv_{Δ}

$+1.5, +0.6, -1.1, -0.5$ percent of v_{Δ}

and at 20° and $P = 57, 60$ atm.

instead of $+19.1^*, +5.9^*$ percent of pv_{Δ}

$+2.6, +1.2$ percent of v_{Δ}

The criterium of MAXWELL expressed in $\frac{1}{10000}$ parts of the unit of pv_{Δ} agrees to

$+157$ at 0°

$+113$ at 10°

$+71$ at 20°

$+36$ at 30°

Both the deviation just considered and this latter, would be considerably smaller if we had only employed carbon dioxide.

§ 7. Finally a similar calculation to that used for form IV was carried out with polynomials

$$\begin{aligned}
 \mathfrak{B} &= b_1 t + b_2 + b_3 \frac{1}{t} + b_4 \frac{1}{t^3} \\
 \mathfrak{C} &= c_1 t + c_2 + c_3 \frac{1}{t} + c_4 \frac{1}{t^3} \\
 \mathfrak{D} &= d_1 t + d_2 + d_3 \frac{1}{t} + d_4 \frac{1}{t^3} \\
 \mathfrak{E} &= e_1 t + e_2 + e_3 \frac{1}{t} + e_4 \frac{1}{t^3} \\
 \mathfrak{F} &= f_1 t + f_2 + f_3 \frac{1}{t} + f_4 \frac{1}{t^3}
 \end{aligned}
 \left. \vphantom{\begin{aligned} \mathfrak{B} \\ \mathfrak{C} \\ \mathfrak{D} \\ \mathfrak{E} \\ \mathfrak{F} \end{aligned}} \right\} \dots (V)$$

It gives for the required values

Temperature coefficients of the reduced virialcoefficients.				
	1	2	3	4
$10^8 b^{(V)}$	+ 183.212	- 405.612	- 127.258	- 122.435
$10^{11} c^{(V)}$	+ 67.880	- 62.647	+ 131.275	+ 97.211
$10^{13} d^{(V)}$	+ 474.172	- 306.627	- 657.471	+ 126.641
$10^{25} e^{(V)}$	- 1871.27	+ 6426.11	- 4651.33	+ 781.52
$10^{32} f^{(V)}$	+ 2002.92	- 7272.08	+ 6331.42	- 1170.45

Although I thought at first that a good representation of the observations could best be attained by IV, it appeared that the representation by means of the more simple form V almost entirely corresponds to this. The reduced virial coefficients calculated according to V correspond so closely to those calculated according to IV that it was entirely superfluous to separately calculate another equation for all observations by means of this form (V) as was done for IV (again using the reduction factors in § 4 in order to find the virial coefficients in the development in series II).