For the pressure coefficient E. Lisell [1]) gives

$$\gamma = -1{,}44 \cdot 10^{-5} \text{ at } T = 273° \text{ K.}$$

From our measurements we find

$$\gamma = -2{,}25 \cdot 10^{-5} \text{ at } T = 90° \text{ K.}$$

and

$$\gamma = -1{,}7 \cdot 10^{-5} \text{ at } T = 20°{.}3 \text{ K.}$$

so that the pressure coefficient has become somewhat greater at the lower temperatures. The increase obtained between 273° K. and 90° K. changes again to a diminution. The accuracy of the measurements is still too small to allow us to attribute any significance to this diminution at the lowest temperatures.

If we consider the decrease — Δw in the resistance for $p = 100$ atm., we find that it approximates to zero at the lower temperatures. Thus we find for Pb_f:

$$273° \quad \text{K.} \quad \text{for} \quad p = 100 \text{ atm.} \quad -\Delta w = 0{,}017 \ \Omega$$
$$90° \quad \text{K.} \quad ,, \ \ldots ,, \quad ,, \quad -\Delta w = 0{,}008$$
$$20°{.}3 \text{ K.} \quad ,, \quad ,, \quad ,, \quad -\Delta w = 0{,}001.$$

Physics. — "*Isotherms of monatomic substances and of their binary mixtures.* XIV. *Calculation of some thermal quantities for argon*". By H. Kamerlingh Onnes and C. A. Crommelin. Comm. N°. 133c from the Physical Laboratory at Leiden.

(Communicated in the meeting of November 30, 1912).

The empirical reduced equation of state for argon, VII. A. 3, published some time ago [2]), enables us to calculate a number of thermal quantities which are essential to a knowledge of monatomic substances in general and of argon in particular. These quantities may also be obtained graphically. Calculation by means of an equation which fits the experimental results over the whole region of observation allows, however, a much greater accuracy to be attained.

In the present paper [3]) we give values of $\left(\dfrac{\partial p}{\partial T}\right)_v$, $\left(\dfrac{\partial^2 p}{\partial T^2}\right)_v$, $\left(\dfrac{\partial \gamma_v}{\partial v}\right)_T = T\left(\dfrac{\partial^2 p}{\partial T^2}\right)_v$, $\left(\dfrac{\partial u}{\partial v}\right)_T = T\left(\dfrac{\partial p}{\partial T}\right)_v - p$, (Amagat's pression inté-

[1]) E. Lisell : Upsala Univ. Årsskrift 1903.

[2]) H. Kamerlingh Onnes and C. A. Crommelin, Proc. June 1912, Comm. N°. 128.

[3]) Already indicated in Suppl N°. 23, note 492, p. 146. Preliminary values obtained by C. A. Crommelin for some of the quantities here discussed have already been published by E. H. Amagat. C. R 9 April, 1912.

rieure [1])), and of REINGANUM's a, $a_R = \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] v^2$, calculated as functions of the temperature and of the density from equation VII. A. 3 [2]). The temperature is expressed in KELVIN degrees and is calculated from 0° C.; the pressure is expressed in international atmospheres [3]).

The importance of a knowledge of these quantities especially as functions of the temperature has already been repeatedly insisted upon [4]) so that we need say nothing further here upon that point. We shall only say that according to the chief VAN DER WAALS equation with constant a_w, b_w and R_w $\left(\frac{\partial p}{\partial T} \right)_v$, $\left(\frac{\partial u}{\partial v} \right)_T$ and a_R should be independent of the temperature, and consequently $\left(\frac{\partial^2 p}{\partial T^2} \right)$ should vanish, so that the deviations which they all show may be taken as a measure of the degree to which argon deviates from the simple assumptions regarding molecules accepted by VAN DER WAALS in developing his principal equation.

Agreement, at least approximate, with the chief VAN DER WAALS equation would first be expected in the monatomic substances, and therefore the investigation of these quantities for argon as well as a comparison of the results with those for substances of more complex molecular structure is of the greatest importance.

Consideration of the quantity introduced by REINGANUM [5]).

$$ a_R = v^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] = - \left(\frac{\partial u}{\partial \varrho} \right)_T $$

enables us to see that, as far as the mutual actions of the molecules is concerned, the assumptions upon which VAN DER WAALS founded his chief equation with constant a_w, b_w, and R_w must undergo some modification such as has recently been introduced by VAN DER WAALS in the various developments of the consideration of apparent association. If we retain for the moment the most immediate assumption suitable for monatomic substances such as argon, that the atoms are incompressible, then changes in a_R would be wholly due to deviations of the molecular

---

[1]) E. H. AMAGAT, numerous papers in the C. R. collected in "Notes sur la physique et la thermodynamique". Paris 1912.

[2]) For the notations used in this paper see Enc. math. Wiss. V. 10. Suppl. N⁰. 23.

[3]) Enc. math. Wiss. V. 10. Einheiten. a.

[4]) M. REINGANUM, Diss. Göttingen 1899, Ann. d. Phys. (4), 18 (1905) p. 1008. Suppl. N⁰. 23, p. 140 sqq.

[5]) M REINGANUM. Diss. Göttingen 1899.

TABLE I.

$$\left(\frac{\partial p}{\partial T}\right)_v$$

ρ_N	$+20°$	$0°$	$-20°$	$-40°$	$-60°$	$-70°$	$-80°$	$-90°$	$-100°$	$-110°$	$-113°$	$-116°$	$-119°$	$-122°$
20	+0.0764	+0.0766	+0.0768	+0.0770	+0.0773	+0.0775	+0.0777	+0.0779	+0.0781	+0.0784	+0.0785	+0.0786	+0.0787	+0.0788
40	1589	1595	1603	1612	1624	1630	1638	1646	1655	1665	1669	1672	1676	1680
60	2471	2485	2501	2521	2545	2559	2575	2593	2614	2637	2644	2652	2660	2668
80	3409	3431	3457	3490	3531	3556	3584	3615	3650	3690	3703	3717	3731	3745
100				4517	4578	4615	4657	4704	4759	4821	4841	4861	4883	4904
120							5790	5857	5934	6022	6051	6080	6110	6141
140									7173	7292	7331	7371	7411	7453
160									8473	8627	8678	8730	8783	8837
180										1.0030	1.0093	1.0159	1.0227	1.0296
200											1580	1662	1747	1833
220											3142	3243	3348	3455
240												4913	5041	5172
260												6683	6839	6998
280												8568	8757	8951
300												2.0589	2.0817	2.1053
320												2769	3044	3329
340												5136	5467	5810

TABLE II.

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

ϱ_N	+20°	0°	−20°	−40°	−60°	−70°	−80°	−90°	−100°	−110°	−113°	−116°	−119°	−122°
20	−0.00001	−0.00001	−0.00002	−0.00001	−0.00002	−0.00001	−0.00003	−0.00002	−0.00002	−0.00003	−0.00002	−0.00003	−0.00003	−0.00003
40	3	3	4	3	6	6	8	9	10	11	11	12	12	13
60	6	7	9	10	14	15	17	19	21	24	26	26	27	28
80	10	12	15	18	24	25	30	35	37	43	43	46	47	48
100				27	35	39	44	51	58	66	68	69	72	74
120							63	73	82	93	97	100	102	106
140									111	126	130	135	138	141
160									144	165	171	175	179	182
180										210	216	223	228	232
200											271	279	285	288
220											334	344	353	358
240												420	432	438
260												512	526	536
280												620	640	653
300												748	775	795
320												899	935	963
340												1079	1125	1165

TABLE III

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

ρ_N	+ 10°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	+ 1.150	+ 1.198	+ 1.254	+ 1.314	+ 1.381	+ 1.417	+ 1.454	+ 1.494	+ 1.533	+ 1.579	+ 1.593	+ 1.604	+ 1.620	+ 1.635
40	4.525	4.703	4.905	5.134	5.388	5.523	5.670	5.826	5.990	6.163	6.218	6.273	6.331	6.387
60	9 996	10.37	10.79	11.27	11.82	12.12	12.43	12.77	13.14	13.52	13.64	13.76	13.89	14.01
80	17.44	18.05	18.75	19.55	20.46	20 98	21.53	22.11	22 74	23.42	23.63	24.84	24.06	24.27
100				29.79	31.15	31.92	32.75	33.65	34.62	35.65	35.98	36.31	36.64	36.97
120							45.91	47.18	48.55	50.03	50.49	50 95	51.42	51.90
140									64.38	66.38	67.00	67.63	68.27	68.90
160									81.94	84.54	85.35	86.18	87.00	87.83
180										104.4	105.4	106.5	107.6	108.6
200											127 2	128 5	129.8	131.1
220											150.5	152.2	153.8	155.4
240												177.4	179.4	181.4
260												204.4	206.9	209.3
280												233.2	236.1	239.1
300												263.8	267.4	270.9
320												296.5	300.7	305.1
340												331.3	336.4	341.7

TABLE IV.

$$a_{RN} = \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} v'_N$$

ρ_N	$+20°$	$0°$	$-20°$	$-40°$	$-60°$	$-70°$	$-80°$	$-90°$	$-100°$	$-110°$	$-113°$	$-116°$	$-119°$	$-122°$
20	+0.002875	+0.002996	+0.003134	+0.003285	+0 003453	+0.003541	+0.003636	+0.003735	+0.003833	+0.003946	+0.003983	+0.004011	+0.004050	+0.004088
40	2828	2940	3066	3208	3367	3452	3543	3641	3743	3852	3886	3921	3957	3992
60	2777	2880	2997	3131	3282	3366	3454	3548	3649	3756	3789	3823	3857	3803
80	2725	2821	2930	3054	3197	3278	3363	3455	3554	3659	3692	3725	3759	3793
100				2979	3115	3192	3275	3365	3462	3565	3598	3631	3664	3697
120							3188	3276	3372	3474	3506	3539	3571	3604
140									3285	3387	3418	3451	3483	3516
160									3201	3302	3334	3366	3399	3431
180										3223	3255	3287	3319	3352
200											3180	3212	3245	3278
220											3110	3144	3177	3211
240												3081	3115	3150
260												3024	3060	3096
280												2974	3012	3050
300												2931	2971	3011
320												2895	2937	2979
340												2866	2910	2956

TABLE V.

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

ϱ_N	+20°	0°	−20°	−40°	−60°	−70°	−80°	−90°	−100°	−110°	−113°	−116°	−119°	−122°
20	−0.00293	−0.00273	−0.00506	−0.00233	−0.00426	−0.00203	−0.00579	−0.00366	−0.00346	−0.00489	−0.00320	−0.00471	−0.00462	−0.00453
40	879	819	1012	699	1279	1219	1543	1648	1731	1794	1761	1885	1849	1964
60	1759	1912	2278	2331	2983	3046	3283	3479	3635	3914	4162	4084	4160	4231
80	2931	3277	3796	4196	5114	5077	5793	6408	6404	7013	6884	7226	7242	7252
100				6293	7458	7921	8496	9338	0.10039	0.10764	0.10886	0.10839	0.11094	0.11181
120							0.12165	0.13366	14193	15167	15529	15709	15717	16016
140									19213	20549	20812	21207	21264	21304
160									24925	26910	27375	27491	27582	27498
180										34249	34579	35031	35133	35053
200											43384	43828	43916	43514
220											53470	54039	54394	54090
240												65978	66567	66177
260												80430	81051	80984
280												97396	98618	98662
300												1.1750	1.1942	1.2012
320												1.4122	1.4407	1.4550
340												1.6950	1.7335	1.7602

forces from the simple initial assumptions made by VAN DER WAALS. Such changes in a_R might originate from three causes: change in the a_w, in the b_w or in the R_w of the chief equation, as a result of the radius of the sphere of action being but slightly greater than that of the molecule, a circumstance [1] revealed in apparent association.

Since

$$T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial \gamma_v}{\partial v}\right)_T$$

the question as to whether $\left(\frac{\partial p}{\partial T}\right)_v$ is independent of the temperature and therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$, is most intimately connected with the question as to whether $\left(\frac{\partial \gamma_v}{\partial v}\right)_T = 0$ or not. For a long time this question remained undecided on account of the lack of experimental data. We now know that, at least for a number of substances, $\left(\frac{\partial p}{\partial T}\right)_v$ is in general a function of the temperature, and that therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ does not vanish.

If we now compare the behaviour of argon with respect to $\left(\frac{\partial p}{\partial T}\right)_v$ with that of isopentane we find correspondence in many respects.

YOUNG [2] [3] deduced from his observations upon isopentane that $\left(\frac{\partial p}{\partial T}\right)_v$ decreases with falling temperature for $v_r < 4.6$ c.c.; at greater volumes up to $v_T = 400$ c.c. it increases with falling temperature, while it remains practically constant at still greater volumes. For argon, for which the volumes are expressed in terms of the normal volume as unit, if the law of corresponding states were accurately obeyed these volumes would correspond to $v_N = 0.00377$ and $v_N = 0.328$ or $\varrho_N = 265$ and $\varrho_N = 3.05$.

The argon observations embraced by VII. A. 3 lie entirely within these limits, and from Table I we see that argon agrees with isopentane within the region of observation. Over the entire region $\left(\frac{\partial p}{\partial T}\right)_v$ falls with increasing temperature. At the lowest argon density

[1] This circumstance causes a change in b_w also, cf. H. KAMERLINGH ONNES and W. H. KEESOM, Suppl. N° 23, Nr. 47.

[2] M. REINGANUM, Diss. Göttungen. 1899, pg. 42.

[3] S. YOUNG, Proc. phys. soc. London 13 (1895), p. 602.

$\varrho_N = 20$ the diminution becomes extremely small, pointing to constancy at still lower densities. Argon differs from isopentane, however, in this respect that with argon at higher densities far above $\varrho_N = 265$, the increase becomes still more rapid, while the behaviour of isopentane would lead one to expect a diminution in the rate of increase.

From his observations upon isopentane YOUNG[1]) deduced the following rule for the behaviour of $\left(\dfrac{\partial^2 p}{\partial T^2}\right)_v$:

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v < \pm v_k} > 0 \quad \Big\rangle$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v > \pm v_k} < 0 \quad \Big\rangle$$

This rule has already been confirmed for a variety of substances, and is, as far as its second part is concerned, also obeyed by argon.

For carbon dioxide, ethylene and isopentane, REINGANUM found that the quantity $a_R = \left[T\left(\dfrac{\partial p}{\partial T}\right)_v - p \right] v^2$ is a minimum for v about $\dfrac{3}{4} v_k$ and at temperatures about $10°$ above t_k. If the law of corresponding states were strictly true this minimum for argon should be at $\varrho_N = 380$, and therefore outside the region of experiment. Nothing can be done consequently beyond trying to judge from extrapolation, if, and where, the minimum exists. If for this purpose we graph a_R as a function of ϱ_N at $-122°$ and $-116°$, then extrapolation towards higher densities shows that it is probable that these curves would also exhibit a minimum for argon at $v = \dfrac{3}{4} v_k$.

Physics. — *"On the rectilinear diameter for argon."* By E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN. Comm. 131*a* from the physical Laboratory at Leiden. (Continued).

(Communicated in the meeting of November 1912).

§ 5. *Results.* The results obtained are given in the following table[2]) (p. 961):

The calculated values of the ordinates of the diameter given in this table have been obtained from the equation

$$D_{\varrho\Gamma} = 0.20956 - 0.00\,26235\, t_{(K)}.$$

---

[1]) l. c.

[2]) For the notations, see Suppl. No. 23.