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The temperature of the experimental tube was read with an eye-glass to within $0^{\circ}.01$ on an "Einschluss thermometer", divided into $0^{\circ}.1$, with a scale on milkglass. From time to time this was compared at different temperatures with a similar thermometer tested at the Reichsanstalt with the air thermometer, while the variation of the zero of the latter in the mean time was accounted for and also the temporary depression of the zero, which, after the thermometer had for a long time been heated at 48° C., amounted to $0^{\circ}.02^{\circ}$ C.

6. *Reduction of the observations.* In cases where, in contrast to the determination of the plaitpoint and the point of contact of the mixtures and the critical point of carbon dioxide, the greatest possible constancy of the temperature was not absolutely necessary, the temperature during the determination of an isothermal which lasted on an average from 3 to 4 hours was allowed to vary a few hundredths of a degree. For the reduction to one temperature, temperature coefficients for the different volumes were derived from the observations.

In the two series, one at an always increasing, the other at an always decreasing pressure, pressures were measured, corresponding to different volumes, which in the two series differed but little. Pressures were derived from them for the same volume and then the mean was found. When it appeared that these pressures agreed sufficiently (comp. § 4) we have afterwards simply taken for two corresponding points the mean of the volume and the pressure.

Physics. — "*Isothermals of mixtures of oxygen and carbon dioxide.*

IV. Isothermals of pure carbon dioxide between 25° C. and 60° C. and between 60 and 140 atmospheres." By W. H. KESOM. Communication N^o. 88 (4th part) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

§ 1. *Reason for the investigation of carbon dioxide.* Although the isothermals of carbon dioxide have been extensively investigated by AMAGAT, I have yet determined a number of isothermals together with its critical point. I was led to it by the following considerations:

1st. it was desirable that I should be able to judge of the purity of the carbon dioxide which I used for the preparation of the mixtures, and it seems that this judgment may best be derived from the increase of the vapour pressure with condensation at a stationary temperature¹⁾;

¹⁾ Comp. Comm. N^o. 79. Proc. April 1902.

2nd. difficulties had arisen about some quantities at the critical point of carbon dioxide, which are important for the theory of the mixtures. AMAGAT, for instance, had determined the critical pressure at 72.9 atm., while VERSCHAFFELT from AMAGAT's isothermals derived 73.6 atm.¹⁾ Obviously this may give rise to an error in the determination of the data of the critical point of the mixtures, if as in Comm. N^o. 59²⁾ the logarithmical systems of isothermals are shifted over each other. Moreover in Comm. N^o. 75, Proc. Dec. 1901 p. 299, for $\left(\frac{\partial \pi}{\partial \tau}\right)$ at the critical point from AMAGAT's isothermals: 7.3 had been derived; from his determinations of the saturated vapour pressures: 6.5. This points to an uncertainty in the determination of the critical volume. AMAGAT has determined the critical point and the vapour pressures in different apparatus and hence probably also with other carbon dioxide than the isothermals; by determining the two in the same tube with the same carbon dioxide I hoped to arrive at more certainty on these points.

3^d. By comparing the isothermals of the mixtures after RAVEAU's method with isothermals of carbon dioxide observed in the same experimental tube some systematical errors which might occur in the observations are eliminated from the determination of the critical data of the mixtures. In this way an error in the determination of the diameter of the graduated stem of the experimental tube would have no influence on the critical pressure and temperature of the mixture.

§ 2. In the following tables v is the volume expressed in terms of the theoretical normal volume, p the pressure in atmospheres (0° C., 45° Northern latitude), v_{liq} the volume of the liquid. The points of the beginning and the end of the condensation are marked by the letters bc and ec . For the point bc we adopted the point where after having decreased the volume there appeared for the first time with proper stirring a liquid "Schlier" on the wall, or after having increased the volume with proper stirring only such "Schlier" remained. These two points agreed sufficiently. The point ec could be observed sharply, as with a small variation of the volume the last part of the phase disappeared or reappeared. Especially here, however, phenomena of retardation had to be avoided by forcible stirring. $V_{th,N}$ stands for the theoretical normal volume, the meaning of $A_{K_{20}}$ is explained in the 2nd part of this Comm., p. 552.

1) Comp. Comm. N^o. 55. Proc. April 1900.

2) Proc. Sept. 1900.

*First carbon dioxide.*Before the measurements: $V_{thN} = 71.020^s$ c.c.

$$A_{K_{20}} = 1.00570$$

a. Isothermal of $25^{\circ}.55$ C.

No..	v	p	pv	v_{liq}
1	0.008573	63.12	0.5411 ^s	
2	7812	64.36	5028	<i>bc</i>
3	7046	64.42	4539	0.000420
4	6227 ^s	64.41	4011	859
5	5504	64.41	3545	0.001276
6	4837	64.40	3115	1664
7	4068	64.39	2619	2088
8	3205	64.42	2065	2597
9	3085	64.37	1986	2652
10	2869	64.41	1848	²⁾
11	2738	64.43 ¹⁾	1802 ^s	<i>cc</i>
12	2645	70.91	1876	
13	2520	80.65 ^s	2033	
14	2438	92.97	2267	
15	2366	105.79	2503	
16	2309	122.55 ^s	2830	
17	2270	138.42	3142	

¹⁾ We shall later revert again to the purity of the carbon dioxide, as it appears from the increase of pressure at the condensation.

²⁾ Here the liquid meniscus reached the part of the tube where through the sealing in the blow-pipe the marks no longer were visible.

b. Isothermal of 28°.15 C.

No.	v	p	pv	v_{liq}
1	0.009238	63.44	0.5924	
2	8565	65.19	5583	
3	7807 ^s	66.75 ^s	5212	
4	7030	67.99 ^s	4780	
5	6950	68.19	4739 ^s	
6	6673	68.39	4564	<i>bc</i>
7	6300	68.41	4310	0.00290
8	5502	68.41	3764	947
9	4712	68.43 ^s	3224 ^s	0.001625
10	3974	68.48	2721	2189
11	3119	68.45	2135	1)
12	3011	68.43	2060	<i>ec</i>
13	2813	72.40 ^s	2037	
14	2670	78.55	2097	
15	2546	89.54	2279	
16	2446	103.47	2531	
17	2367	119.61	2834	
18	2315	136.58	3161	

c. Bordercurve in the neighbourhood of the critical point.

Beginning condensation

Temp.	v	p
30.05	0.005594	71.47
30.82	4833	72.72 ^s

End condensation

Temp.	v	p
30.11	0.003328	71.53
30.81	3725	72.74

d. Critical point :

Temp.: 30.98 Pressure: 72.93 Volume: 0.00443 ²⁾.

1) Comp. footnote to the preceding table.

2) For the determination of this comp. § 5.

e. Critical isothermal : (30.98° C.)

No.	v	p	pv
1	0.010068	63.36	0.6379
2	0.009314	65.39	0.6090
3	8582	67.22	0.5769
4	7809	69.08 ^s	0.5395
5	7031	70.73	0.4973
6	6275	71.95	0.4515
7	5483	72.74 ^s	0.3988
8	5102	72.87	0.3718
9	4777	72.93	0.3484
10	4403	72.94	0.3211
11	4254	72.98	0.3104
12	3959	72.96	0.2888 ^s
13	3656	72.99 ^s	0.2669
14	3296	73.53	0.2423
15	3230	73.89	0.2387
16	3051	75.43	0.2302
17	2862	79.43	0.2273
18	2721	86.10	0.2343
19	2593	95.70	0.2482
20	2509	106.18	0.2664 ^s
21	2435	119.35	0.2906 ^s
22	2362	138.65	0.3275

f. Isothermal of 31.89° C.

No	v	p	pv
1	0.010086	63.87	0.6442
2	0.009314	65.99 ^s	0.6147
3	8570	67.94 ^s	0.5823
4	7771	70.03	0.5442
5	7017	71.68	0.5030
6	6267	73.03 ^s	0.4577
7	5528	73.94	0.4087
8	5117	74.24	0.3799
9	4742 ^s	74.44	0.3530
10	4364 ^s	74.56	0.3254
11	3942	74.69	0.2944
12	3610	75.00	0.2707
13	3228	76.20	0.2460
14	2883	82.02	0.2365
15	2717	89.90	0.2443
16	2593	99.77	0.2587
17	2503	111.45	0.2790
18	2439	122.79	0.2905
19	2377	136.71	0.3240

g. Isothermal of 34°.02 C.

No.	v	p	pv
1	0.010067	65.18	0.6562
2	0.009337	67.29 ^s	0.6283
3	8560	69.49	0.5948
4	7791	71.64	0.5581 ^s
5	7023 ^s	73.65	0.5173
6	6255	75.34	0.4712
7	5526 ^s	76.60 ^s	0.4236
8	4672	77.57 ^s	0.3624
9	3971	78.38 ^s	0.3113
10	3243	81.11	0.2630 ^s
11	2955	86.16	0.2546
12	2746	95.02	0.2609
13	2614	105.95	0.2770
14	2510	119.53	0.3000
15	2426	136.66	0.3316

h. Isothermal of 37°.09 C.

No.	v	p	pv
1	0 010863	64.56	0.7013
2	10093	66.10	0.6752
3	0 003339	69.29	0.6471
4	8554	71.73	0.6135 ^s
5	7810	74.11	0.5788
6	7059	76.40	0.5304
7	6287	78.58 ^s	0.4940
8	5525 ^s	80.47	0.4446
9	4770	82.11	0.3917
10	4011	83.89	0.3365
11	3230	88.89	0.2871
12	2799	103.08	0.2885
13	2609	119.27	0.3112
14	2495	136.01	0.3393

Second carbon dioxide ¹⁾.

Before the experiments: $V_{thN} = 69.647$ c.c., weight 2

After " " " " " " 69.629 " " 1

Mean 69.641 " "

i. Isothermal of 41°.95 C.

No.	v	p	pv
1	0.011546	64.85	0.7487
2	10794 ^s	67.28	0.7262 ^s
3	10047	69.81	0.7014
4	0 009211	72.78	0.6704
5	8486	75.48	0.6405
6	7640	78.57	0.6003
7	6915	81.31	0.5622 ^s
8	6181	84.04	0.5194 ^s
9	5320	87.18	0.4638
10	4530	90.13	0.4082 ^s
11	3778	94.10	0.3555
12	3087	105.01	0.3242
13	2817	117.96	0.3323
14	2642	134.85	0.3563

k. Isothermal of 48°.10 C.

No.	v	p	pv
1	0.012311	65.20	0.8027
2	11572	67.69	0.7833
3	10787 ^s	70.52	0.7607
4	0.009970	73.61	0.7339
5	9232	76.61	0.7073
6	8442	80.07	0.6760
7	7678	83.38	0.6402
8	6899	87.07	0.6007
9	6118	90.90	0.5561
10	5380	94.78	0.5099
11	4570	99.62	0.4552
12	3823	105.50	0.4033
13	3129 ^s	119.38	0.3736
14	2864	135.56	0.3883

¹⁾ Because the experimental tube has broken, the first quantity was lost. As, however, the fracture occurred below the graduated portion of the stem, the advantage mentioned in § 1, sub 3 remained.

l. Isothermal of 57°.75 C.

No.	v	p	pv
1	0.013174	66.27	0.8730
2	12356	69.20	0.8550
3	11586	72.18	0.8363
4	10807 ⁵	75.42	0.8151
5	10009 ⁵	78.99	0.7906
6	0.009271	82.49	0.7648
7	8482	86.62	0.7347
8	7668	91.16	0.6990
9	6930	95.73	0.6638
10	6113	101.32	0.6194
11	5372	107.06	0.5751
12	4596	114.45	0.5260
13	3795	126.10	0.4786
14	3421 ⁵	135.81	0.4647

§ 3. To simplify later calculations I have calculated for the isothermals e, f, g, h, i, k, l the values of pv for regularly increasing densities $\left(\frac{1}{v}\right)$. Therefor each value has been interpolated from 4 points derived directly from observation; only for the extreme values we have interpolated between 3 points¹⁾. So we find the values given

¹⁾ For this we used the formula of LAGRANGE, which may be easily written in the following form:

$$P = P_2 + (P_3 - P_2) \frac{d - d_2}{d_3 - d_2} + (P_1 - P_1') \frac{(d - d_2)(d - d_3)(d - d_4)}{(d_1 - d_2)(d_1 - d_3)(d_1 - d_4)} + \\ + (P_4 - P_1') \frac{(d - d_1)(d - d_2)(d - d_3)}{(d_4 - d_1)(d_4 - d_2)(d_4 - d_3)},$$

where

$$P_1' = P_2 + (P_3 - P_2) \frac{d_1 - d_2}{d_3 - d_2},$$

$$P_4' = P_3 + (P_3 - P_2) \frac{d_4 - d_3}{d_3 - d_2}.$$

P represents pv , while $\frac{1}{v}$ is represented by d . Supposing that d lies between d_2 and d_3 , the two last terms of P become relatively small and they may be easily calculated with a sliding-rule.

in table XX; the first column gives the different densities (expressed in terms of the theoretical normal density), the following columns the values of pv belonging to it, each time for the temperature mentioned at the head of the column.

TABLE XX.
Isothermals of carbon dioxide.

$\frac{1}{v}$	30 98°	31.89°	34.02°	37.09°	41.65°	48.10°	57 75°
80							0 8583
100	0.6355	0.6411	0.6538	0 6719	0.6997	0.7343	0.7703
120	0 5653	0.5715	0.5844	0.6036	0.6335	0 6712	0.7285
140	0.5037	0.5094	0 5240	0.5440 ^s	0 5746	0 6135	0 6743
160	0 4409	0.4566	0.4708	0.4918	0 5237	0 5640	0.6273
180	0.4039	0.4106 ^s	0.4254	0 4466	0 4796	0.5212	0.5864
200	0.3646	0 3716	0.3863	0.4081	0 4416 ^s	0 4847	0 5521
220	0 3314	0 3387	0 3491	0 3754	0 4094	0.4536	0 5226 ^s
240	0.3041	0.3109	0.3226	0.3477	0.3819 ^s	0.4264	0 4991
260	0.2806	0.2875	0.3021	0.3243 ^s	0.3567 ^s	0.4048	0 4812
280	0 2614	0.2680	0.2825 ^s	0.3052	0 3423 ^s	0.3872	0.4692
300	0.2448	0.2521	0.2677	0.2915 ^s	0.3302	0.3763	
320	0.2333	0 2410	0.2590	0 2835	0.3245 ^s	0.3737	
340	0.2273	0.2321	0.2554 ^s	0.2863	0.3255	0.3817	
360	0.2305	0 2401	0.2588	0.2900	0.3362		
380	0.2427	0 2530	0.2742	0 3073			
400	0 2690	0.2800	0.3031	0 3376			
420	0.3169 ^s	0.3230					

§ 4. $v_{liq.}$ was reduced to the same temperature for the isothermals a and b in the following way: From the height of the liquid meniscus we directly derived the volume of the vapour phase: $v_{vap.}$ If v_1 is the specific volume of the existent liquid phase, v_2 the specific volume of the vapour (as unity we always have here the theoretical normal volume), we find:

$$\frac{dv_{vap.}}{dT} = - \frac{v_{vap.}}{v_2 - v_1} \left(\frac{v_1}{v_2} \frac{dv_2}{dT} - \frac{v_2 - v}{v - v_1} \frac{dv_1}{dT} \right).$$

After the vapour volumes have thus been reduced to one temperature, the liquid volumes are derived from this. We have assumed in this that v_1 and v_2 are functions of the temperature T only and not also of v , as DE HEEN and others think. On this supposition we can derive v_1 and v_2 from each pair of observations of v_{liq} at different v and at the same temperature. The values calculated thus have been combined in table XXI together with those derived directly from observation.

TABLE XXI.

Isothermal of 25°.55 C.			Isothermal of 28°.15 C.		
Nrs.	v_1	v_2	Nrs.	v_1	v_2
2		0.07812	6		0.006673
3 and 7	0.002799	7736	7 and 9	0.003043	6680
4 and 8	2819	7722	8 and 10	2998	6709
5 and 9	2809	7747	12	3011	
11	2798				
mean	0.0028035	0.0077735	mean	0.003016	0.006684

We see that no regular variation in the values of v_1 and v_2 can be remarked, so that this justifies with regard to these experiments our assumption of the dependence of v_1 and v_2 on the temperature only.

In the calculation of the mean values of v_1 and v_2 in table XXI we have accorded the same weight to the value borrowed directly from observation as to the mean of the values derived from the other observations.

§ 5. For the determination of the critical point the following may serve: The thermostat was adjusted at a few hundredths of a degree below the critical temperature (the temperature above which no stationary meniscus is observed). By letting a small quantity of water of higher temperature into the mixing bath, the experimental tube was brought to a few hundredths of a degree above the critical temperature, and the substance was well stirred. Then the temperature falls very slowly. If the volume lies between certain limits, the following phenomena may be seen: A blue mist is formed which

at a definite place becomes denser and denser¹⁾. At a given moment "striae" appear, the substance boils and rains, a meniscus is formed. From the very first, the latter is perfectly sharp and flat, it remains at the same place also after stirring. The temperature was observed immediately after the appearance of the striae, then the pressure and the volume and then the temperature was determined again. So we obtain the pressure for one or a few hundredths of a degree below the critical temperature. For this a correction has been applied.

If we allow the temperature to rise, we still see a meniscus during a considerable length of time after the temperature in the bath has risen to a few hundredths of a degree above the critical temperature. It disappears immediately, however, when we stir. Hence this is no phenomenon of equilibrium.

So we could derive the temperature and the pressure directly from observation. For the volume this was not possible, as owing to the effect of gravitation the phenomena described above occur at different volumes, so for instance in my observations with a volume: 0.003924 (stirrer below), where the meniscus appeared in the immediate neighbourhood of the top of the tube, and with a volume 0.004281 (stirrer above) where the meniscus appeared 1 mm. above the mercury.

The method generally used for the determination of the critical volume consists in determining some liquid and vapour densities at temperatures below the critical, and then using the rule of the rectilinear diameter of CAILLETET and MATHIAS. To this end we have drawn on a diagram the densities resulting from the data of § 4, table XXI and § 2, c, as a function of the temperature, and the diameter has been drawn on it. A deviation from the rectilinearity could not be stated with certainty. For the critical density, expressed in terms of the theoretical normal density we derive from this diagram 239, hence for the critical volume 0.00418.

Another method is this: At the critical point $\left(\frac{dp}{dT}\right)_{\text{crit.}} = \left(\frac{\partial p}{\partial T}\right)_v$ (for the proof see for instance Comm. N°. 75).

To determine $\left(\frac{dp}{dT}\right)_{\text{crit.}}$ we have combined in table XXII under *O* the vapour pressures resulting from § 2; for the temperatures 25°.55 C and 28°.15 C we have taken the means from the different values for the pressure.

¹⁾ If the temperature is kept constant, the mist during a considerable length of time (say 10 minutes) does not change to the eye.

TABLE XXII.

Temp.	O.	C.	O—C.
25 55	64.40	64 41	+0 01
28.15	68.43	68 43	0 00
30.05	71 45	71.44	-0 01
30.82	72 72	72.67	-0 05
30 98	72.93		

If we calculate for the different values the coefficient f for VAN DER WAALS's formula¹⁾:

$$\log \frac{p}{p_k} = f \frac{T - T_k}{T},$$

we find with increasing temperature regularly decreasing values of f . If in the development in powers of $\frac{1}{T}$ we take one term more, so that we arrive at the formula:

$$\log \frac{p}{p_k} = \frac{T - T_k}{T} \left(f + g \frac{T_k - T}{T} \right),$$

and we calculate the values of f and g which give the best agreement, we find very nearly $g = f$. Then I have put:

$$\log \frac{p}{p_k} = f \frac{(T - T_k) T_k}{T^2}$$

and found $f = 2.914^5$. By means of this we obtain the values for p given in column C. The agreement is quite satisfactory, only for the temperature 30°.82 C. there is a considerable deviation: the same is also found in the comparison of the saturation volumes so that here we have probably to do with an error of observation.

From this we find at the critical point:

$$\left(\frac{dp}{dT} \right)_{\text{coex}} = 1.610.$$

From the determinations of the isothermals we cannot with certainty derive a definite variation of $\left(\frac{\partial p}{\partial T} \right)_v$ at the same volume with the temperature, as may be best derived from table XX. Therefore I have derived $\left(\frac{\partial p}{\partial T} \right)_v$ for the different densities from the isothermals of 30°.98 C. and 48°.10 C. and found the following values:

¹⁾ Continuität I p. 158.

TABLE XXIII.

$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$	$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$	$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$
100	0 581	200	1.403	300	2 304
120	0 742	220	1 570	320	2 624
140	0 898	240	1 715	340	3 066
160	1 066	260	1 886		
180	1.233	280	2 062		

If from this we interpolate in the same way as in § 3 we find that $\left(\frac{\partial p}{\partial T}\right)_v = 1.610$ for the density 225.50, to which belongs the volume: 0.00443.

This value does not agree with that derived above from the densities. The difference is larger than can be ascribed to the errors in the observation. The deviation is in the same sense as follows from AMAGAT's experiments. The following might serve as an explanation of this difference:

According to a remark of Prof. KÄMÉRLINGH ONNES from whom a new paper on the cause of the deviations near the critical point may be expected (comp. Comm. N^o. 74, Arch. Néerl. série II, t. VI, p. 887) the appearance of the mist in the neighbourhood of the critical point seems to indicate that a part of the substance condenses round numerous centres equally distributed over the whole space. That only in this area this appears so distinctly, might be ascribed to the circumstance that here small forces are sufficient to cause great variations of density. These condensations might have a perceptible influence for instance on the saturation volume although the variation of the pressure would not become perceptible in consequence of it.

In a comparison of mixtures with pure substances according to the law of corresponding states we must disregard those condensations, as they do not occur at corresponding points (in mixtures near the plaitpoint). Hence our purpose will probably be served best if we adopt for the critical volume: 0.00443, as this value according to a thermodynamical relation results from determinations not so near to the critical point, and where therefore particular phenomena which occur in its immediate neighbourhood have played no part.

The following quantities are further found at the critical point, which are necessary for the comparison of the observations with the theoretical results of Comms. N^o. 75 and N^o. 81 :

$$C_4 = \frac{T_k}{T_o p_k v_k} = 3.45.$$

$$\frac{T_k}{p_k} \left(\frac{dp}{dT} \right)_k = 6.712.$$

$$\left(\frac{\partial^2 p}{\partial T \partial v} \right)_k = -422, \text{ hence } C_4 \frac{v_k T_k}{p_k} \left(\frac{\partial^2 p}{\partial T \partial v} \right)_k = -26.9.$$

Here, in agreement with the value of the coefficient of expansion for the ideal gaseous state accepted in this Comm. III, p. 558 we have put: $T_o = 273.04$.

Physics. — “*Isothermals of mixtures of oxygen and carbon dioxide.*
V. *Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide*”. By W. H. KEESOM. Communication N^o. 88 (5th part) from the Physical Laboratory at Leiden by Prof. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903.)

§ 1. The following sections contain the tables about two mixtures of carbon dioxide and oxygen. For the meaning of v , p , v_{liq} and the determination of the *b.c.*- and the *e.c.*-points I refer to this Comm. IV § 2. Of the end condensation point it should be remarked that over a definite area below and above the plaitpoint temperature the meniscus, in consequence of the effect of gravitation, disappeared in the tube.

The data about the plaitpoint were derived directly from the experiment. On the phenomena near the plaitpoint I find the following remarks among my notes of the observations: When the volume increases from the homogeneous (liquid) state a blue mist gradually forms itself. As the volume increases (small variations at a time) this becomes denser. If the volume increases still more, layers of different degrees of refrangibility suddenly appear, which quickly move among themselves. When we stir, however, they still dissolve into the thickening blue mist. At a given moment, after the volume has been increased again a little, these layers begin to concentrate towards the middle of the tube, at the top and at the bottom it