

Citation:

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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

becomes clear, small bubbles or drops are seen to move from below and from above towards a certain point in the tube. At last a meniscus appears there. This remains at that place. The temperature at which these phenomena were observed was adopted as the plaitpoint-temperature of the mixture considered, the volume and the pressure as plaitpoint volume and pressure.

If the temperature is a little higher, the meniscus appears lower in the tube. The exact point where it appears cannot be observed with certainty: drops are seen to move from above to below, and bubbles from below to above more and more regularly towards one place; at this place the meniscus will appear, but this place is rising already before the meniscus has properly formed itself. When it is formed, it generally still rises. If the temperature is still higher the meniscus is distinctly seen to rise from the bottom of the tube. At the lower end a quantity of liquid is gathered by the drops which fall from the top to the meniscus. The same holds, mutatis mutandis, for temperatures below the plaitpoint temperature.

Of the data about the point of contact only the temperature could accurately be (to within $0^{\circ}.01$) derived from the experiment. To determine the pressure some points at the beginning and at the end of the condensation to within $0^{\circ}.1$ of the point of contact were observed; they were drawn and the point where the tangent is at right angles with the axis of temperature was found. This gave the pressure of the point of contact with sufficient accuracy. Then the point of contact volume was deduced from the isothermal.

The molecular proportion of oxygen will be represented by x , V_{thN} is the theoretical normal volume, for the meaning of ΔK_{20} comp. this Comm. II p. 552.

§ 2. *First mixture of carbon dioxide and oxygen.*

$$x = 0.1047.$$

Before the measurements: $V_{thN} = 69.743$ cc.

After ,, ,, 69.725 ,,
 mean: $\overline{69.734}$,,

a. Border curve.

Beginning condensation.

Temp	v	p
17.53 ^s	0 008552	66.08
17.63	8483	66.40
19.48	7708	69.48
20.19	7362	71.59
20.28	7288	71.94
21.48	6709	74.85
22.06	6456	76.24
22.38	6098	77.85
22.83	5860	79.14
22.87	5822	79.26
22.98	5697	79.95
23.23	5366	81.46

End condensation.

Temp.	v	p
11.68	0 002597	85.52
14.78	2757	87.09
17.52 ^s	2949	88.25
17.68	2986	88.29
19.38	3195	88.46 ^s
20.19	3292	88.35
20.28	3323	88.35
21.48	3664	87.35
22.09	3880	86.58
22.43	4069	86.03
22.80	4301	85.34
22.88 ^s	4324	85.12
22.98	4441	84.90
23.18	4663	84.16

b. Isothermal of 17°.60 C.

No.	v	p	pv	$v_{big.}$
1	0.011384	58.35	0.6642	
2	10605	60.46	0.6412	
3	0 009826	62.62	0.6153	
4	9047	64.84	0.5866	
5	8503	66.24	0.5632 ^s	<i>bc</i>
6	7489 ^s	67.85	0.5182	0 000338
7	6712 ^s	69.54	0.4668	571
8	6108	71.12	0.4344	826
9	5935	71.65	0.4252 ^s	879
10	5385	73.39	0.3952	0.001105
11	5157	74.26	0.3830	1194
12	4486 ^s	77.12	0.3460	1502
13	4379 ^s	77.68	0.3402	1556
14	3482	83.35	0.2902	2189
15	2954	88.30	0.2608	<i>ec</i>
16	2848	91.71 ^s	0.2612	
17	2719 ^s	97.38	0.2648	
18	2572	109.13	0.2807	
19	2466	123.34	0.3042	

c. Isothermal of 20°.29 C.

No.	v	p	pv	$v_{liq.}$
1	0.011699	58.86	0.6886	
2	11384	59.72	0.6798	
3	10605	61.94	0.6569	
4	0.009826	64.31	0.6319	
5	9047	66.62	0.6027	
6	8900	67.15	0.5976	
7	8269	69.04	0.5709	
8	7490	71.41	0.5348	
9	7291	71.98	0.5248	<i>bc</i>
10	6713	73.07	0.4905	0.000267
11	5935	75.32	0.4470	596 ^s
12	5157	77.94	0.4019 ^s	968
13	4468	80.88	0.3614	0.001360
14	4379	81.39	0.3564	1445
15	3640	85.85	0.3125	2230
16	3501	86.91	0.3043	2540
17	3335	88.28	0.2944	<i>cc</i>
18	3132	91.50	0.2866	
19	2959	95.64	0.2830	
20	2897	97.76	0.2832	
21	2759	104.46	0.2882 ^s	
22	2613	114.89	0.3002	
23	2527	125.12 ^s	0.3162	

d. Plaitpoint isothermal (21°.99 C.).

No.	v	p	pv	$v_{liq.}$
1	0.012159	58.36	0.7096	
2	11384	60.52	0.6889	
3	0.009826	65.32	0.6419	
4	8269	70.37	0.5819	
5	6713	75.37	0.5059 ^s	
6	6400	76.42	0.4891	<i>bc</i>
7	5935	77.64	0.4608	0.000210
8	5157	80.34	0.4143	638
9	4379	83.76	0.3668	0.001169
10	3878	86.60	0.3358	<i>pp</i>
11	3613	88.74	0.3206	
12	3054	97.11 ^s	0.2966	
13	2769	109.26	0.3025	
14	2598	123.75	0.3215	

e. Isothermal of 22°.68 C.

No.	v	p	p^v	v_{liq}
1	0.012159	58 63	0 7129	
2	11384	60 90	0 6933	
3	10605	63 29	0 6712	
4	0.009826	65 76	0.6461 ⁵	
5	9047	68 28 ⁵	0.6178	
6	8269	70 92	0 5865	
7	7489 ⁵	73 49	0 5504	
8	6712 ⁵	76 09	0 5108	
9	5913	78 74	0 4656	<i>bc</i>
10	5546	79 97	0 4435	0.000198 ⁵
11	5157	81.33	0.4194	400
12	4768	82 89	0 3952	597 ⁵
13	4379	84 73 ⁵	0 3711	709
14	4309	85.05	0 3664 ⁵	591
15	4278	85.22	0 3646	625
16	4258	85.35	0 3634	288
17	4243	85.40	0 3623 ⁵	95 ¹⁾
18	4219	85.54	0 3609	125
19	4218	85 53	0 3608	<i>ec</i>
20	3991 ⁵	87 03	0 3474	
21	3604	90 23	0 3252	
22	3049	99 19	0 3025	
23	2752	112 67	0 3101	
24	2612	124 50	0 3252	

¹⁾ To explain the irregular course of v_{liq} here, we refer to this Comm. III, p. 562, while we remark that the variations of v_{liq} with the temperature and with the volume become very large in this area, so that a small error in the latter may give rise to a large error in the value of v_{liq} .

f. Point of contact isothermal (23°.29 C.). *g.* Isothermal of 25°.20 C.

No.	v	p	pv	No.	v	p	pv
1	0.012159	58.95	0.7168	1	0.012159	59.81	0.7272 ^s
2	11785	60.04	0.7075 ^s	2	11384	62.14	0.7074
3	11384	61.21	0.6968	3	10605	64.59	0.6850
4	10605	63.59	0.6744	4	0.009826	67.23	0.6606
5	0.009826	66.09	0.6494	5	9047	69.97	0.6320
6	9047	68.70	0.6215	6	8869	72.78	0.6018
7	8269	71.34	0.5899	7	7490	75.69	0.5669
8	7480	74.04	0.5545	8	6712 ^s	78.59	0.5276
9	6712 ^s	76.71	0.5149	9	5935	81.69	0.4848
10	5935	79.48	0.4717	10	5156 ^s	84.85	0.4376
11	5546	80.80	0.4431	11	4768	86.61	0.4130
12	5157	82.23	0.4241	12	4379	88.70	0.3885
13	4768	83.78	0.3995	13	391 ^s	91.40	0.3648
14	4379	85.88	0.3761	14	3609	94.97	0.3427
15	3991	87.97	0.3511	15	3229	101.13	0.3266
16	3605	91.26	0.3290	16	2846	114.98	0.3273
17	3046	101.03	0.3077	17	2710	124.35	0.3370
18	2791 ^s	112.40	0.3138				
19	2646	124.08	0.3283				
Point of contact:							
	0.005005	82.83					

This mixture has been prepared in a simpler mixing apparatus than that referred to in this Comm. II § 3, and the pressures are measured with an air manometer and then reduced to the indications of the hydrogen manometer used later, as said in III § 3.

Of the border curve it may be remarked that below 19°.38 C. the end condensation pressure decreases at a falling temperature, which has not been observed by VERSCHAFFELT in mixtures of carbon dioxide and hydrogen at the temperatures at which he observed.

Between the plaitpoint- and the point-of-contact-temperature there was retrograde condensation of the first kind (temporary liquid phase).

§ 3. *Second mixture of carbon dioxide and oxygen.*

$$x = 0.1994$$

$$A_{K_{20}} = 1.00413.$$

Before the experiments: $V_{thN} = 69.608 \text{ cc}^3$.After " " " " 69.555 " "mean: 69.581^s " "*a.* Border curve.

Beginning condensation.

No.	Temp.	v	p
1	10.06	0.009233 ^s	66.35
2	12.15 ^s	8190 ^s	71.57
3	14.12 ^s	7125 ^s	77.29
4	16.01	5803	86.02
5	16.23	5530	87.84

End condensation.

No.	Temp.	v	p
1	10.09	0.003205	102.48 ^s
2	12.20	3633	100.05 ^s
3	14.11	3994 ^s	97.37 ^s
4	16.00	4784	92.57
5	16.22	5156	90.55

b. Isothermal of 9°.62 C.

No.	v	p	pv	$v_{liq.}$
1	0.009795	64.05	0.6274	
2	9412	65.36	0.6152	<i>bc</i>
3	8742	66.89	0.5881	0.000124
4	7948	69.16	0.5497	308
5	7147	71.79	0.5131	470
6	6404	74.92	0.4798	672
7	5500	79.65	0.4381	909
8	4811	84.23	0.4052	0.001122
9	4022	91.55	0.3682	1464
10	3338	100.07	0.3340	2221
11	3164	102.67	0.3248	<i>cc.</i>
12	2874	112.50	0.3233	
13	2742	121.35	0.3327	
14	2699	125.18	0.3379	
15	2632	129.33	0.3404	
16	2581	135.67	0.3502	

c. Isothermal of 11°.35 C.

Nc.	v	p	pv	v_{liq}
1	0.010341	63.46	0.6562	
2	0.009505	66.25	0.6298	
3	8763	68.90 ^s	0.6038	
4	8629	69.37	0.5986	<i>bc</i>
5	7950	70.95	0.5640 ^s	0.000217
6	7203 ¹	73.53 ^s	0.5297	384
7	6396	77.02	0.4926	573
8	5608	81.14	0.4550	781
9	4829	86.40	0.4172	0.001097
10	4097	92.84	0.3804	1376
11	3712	96.79	0.3593	1707
12	3446	100.08	0.3449	2336
13	3397	100.89	0.3427	<i>ec</i>
14	3280	103.21	0.3385	
15	3028	110.48	0.3345	
16	2853	119.11	0.3398	
17	2718	128.44	0.3491	
18	26.1	137.56	0.3605	

d. Plaitpoint isothermal (12°.51 C.).

No.	v	p	pv	v_{liq}
1	0.010259	64.42	0.6609	
2	0.009570	66.77	0.6390	
3	8741	69.74	0.6096	
4	8040	72.27	0.5811	<i>bc</i>
5	7197	75.16	0.5409	0.000201
6	6378	78.56	0.5010 ^s	439
7	5597	82.66	0.4627	674
8	4772	88.24	0.4211	0.001041
9	3981	95.61	0.3806	1360
10	3606	99.65	0.3593	<i>pp</i>
11	3299	105.38	0.3476 ^s	
12	3057	112.34	0.3434	
13	2870	121.71	0.3493	

e. Isothermal of 14°.04 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	<i>v</i> _{liq.}
1	0.010318	65.06	0.6713	
2	0.009504	67.91	0.6454	
3	8726	70.87	0.6184	
4	7926	74.06	0.5870	
5	7272	76.79	0.5584	<i>bc</i>
6	7095	77.46	0.5496	0.000043
7	6337	80.59	0.5107	0.000265
8	5694	84.05	0.4786	457
9	4761	90.15	0.4292	786
10	4402	93.16	0.4101	888
11	4066	96.35	0.3918	933
12	3947	97.55	0.3850	<i>cc</i> 1)
13	3700	100.97	0.3736	
14	3287	109.15	0.3588	
15	3002	118.66	0.3562	
16	2823	128.20	0.3619	

f. Isothermal of 15°.41 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	<i>v</i> _{liq.}
1	0.010276	66.02	0.6784	
2	0.009515	68.77	0.6543 ^s	
3	8763	71.71	0.6284	
4	7991	74.91	0.5986	
5	7159	78.62	0.5628	
6	6435	82.05	0.5280	<i>bc</i>
7	5971	84.32 ^s	0.5035	0.000139
8	5604	86.34	0.4838	228
9	5229	88.71	0.4639	327
10	4997	90.31	0.4515	367
11	4844	91.44	0.4429	387
12	4667	92.81	0.4331	361
13	4538	93.84	0.4258	273
14	4460	94.43	0.4211 ^s	164
15	4419	94.87	0.4192	<i>cc</i>
16	4045	98.88	0.4000	
17	3692	103.36	0.3816	
18	3253	113.06	0.3678	
19	3008	122.03	0.3671	
20	2821	133.17	0.3757	
21	2732	141.72	0.3872	

1) Here we also had retrograde condensation of the first kind, although this does not appear from the values given.

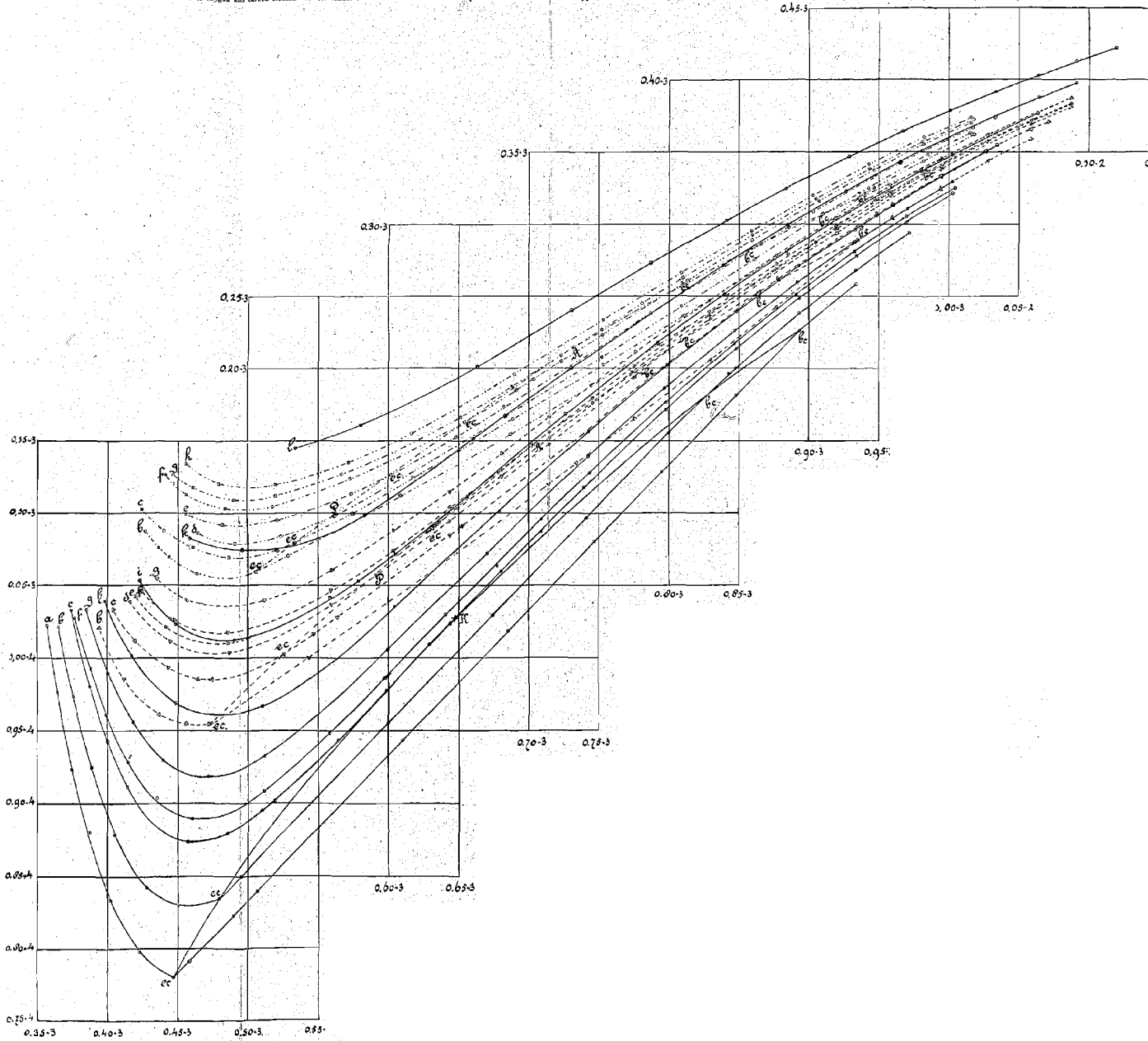
g. Point of contact isothermal (16°.27 C.). h. Isothermal of 17°.66 C.

No.	v	p	pv
1	0.010312	66.34 ^b	0.6841 ^b
2	0.009519	69.28	0.6595
3	8701	72.58	0.6315
4	7955	75.77	0.6028
5	7163	79.37	0.5685
6	6389	83.20	0.5316
7	5934	85.31	0.5105
8	5592	87.57	0.4897
9	5228	89.80	0.4695
10	4824	92.72	0.4473
11	4434	96.05	0.4259
12	4031	100.54	0.4053
13	3647	106.62	0.3888
14	3284	114.28	0.3753
15	3053	122.29	0.3734
16	2857	133.27 ^b	0.3808
17	2759	140.71	0.3832
Point of contact:			
	0.005322	89.20	

No.	v	p	pv
1	0.010273	67.26	0.6910
2	0.009510	70.17	0.6673
3	8683	73.60	0.6391
4	7920	76.98	0.6097
5	7161	80.58 ^b	0.5771
6	6359	84.77	0.5390 ^b
7	5610	89.15	0.5001
8	4843	94.59	0.4581
9	4087	102.08	0.4172
10	3688	108.02	0.3984
11	3280	117.36	0.3849
12	2973	129.44	0.3848
13	2816	141.18	0.3976

§ 4. *Comparison of the mixtures according to the law of corresponding states with carbon dioxide.* In Comm. N°. 59, Proc. Sept. 1900 methods are discussed for a graphical comparison of isothermals of mixtures with those of a simple substance. Here as well for carbon dioxide as for the two mixtures $\log \frac{pv}{T}$ ¹⁾ was drawn as a function of $\log v$ for the different temperatures. (For the absolute zero we accepted — 273°.04 C.). If the law of corresponding states also holds for mixtures of normal substances it must be possible to

¹⁾ As the temperatures are so high that in the theoretical isothermals no negative pressures occur, the drawing of $\log \frac{pv}{T}$ offers no difficulty.



make the corresponding isothermals of the different diagrams coincide by shifting them only in the direction of the $\log v$ -axis.

I found that it was not possible to place the diagrams in such a way over each other that the isothermals of the whole system coincided; I, however, succeeded for the large volumes. According to KAMERLINGH ONNES this signifies that in the mixture the coefficients A, B, C, D, E, F of his series do not hang together with the coefficients of the pure substance at corresponding temperatures in such a manner as would follow from the law of corresponding states, but that for the volumes where the terms with D, E, F in comparison with the others are still so small that we may neglect the differences between these terms and those given by coefficients which would obey the law of corresponding states, the diagrams will coincide over such a large range of temperature that B and C may still be regarded as corresponding functions of temperature, hence a critical temperature and a critical pressure holding for this range of volume and temperature may be deduced from the law of corresponding states.

On the plate the diagrams are placed over each other so as to give the best agreement for the larger volumes. In the horizontal direction $\log v$ is drawn, in the vertical $\log \frac{pv}{T}$. The complete lines refer to carbon dioxide, the dash lines to the first mixture, the dash-dots lines refer to the second mixture. The points for carbon dioxide are enclosed in circles, those for the first mixture in triangles, for the second in squares. The different isothermals are indicated by the letters a, b , etc., with which they are communicated in IV § 2 and V §§ 2 and 3. The points at the beginning and the end of the condensation are marked by $b.c.$ and $e.c.$; they are connected by curves which thus separate the homogeneous area from the area where separation occurs. Finally the plaitpoints and the points of contact are indicated by P and R , K is the point adopted according to IV § 5 for the critical point of carbon dioxide.

It appears that the agreement for volumes larger than the critical is very satisfactory. In the smaller volumes, however, considerable systematic deviations from the law of corresponding states occur. We have already used these diagrams to determine the critical temperature, pressure and volume in the sense as explained above for the different mixtures. Although these results are satisfactory they will not be given here, as more accurate results may be expected from the same operations with diagrams projected on double the scale for the part concerned.

If on a pT -diagram we draw the point of contact- and the plait-

point curves, they are seen to touch each other at the end (critical point of pure carbon dioxide) in agreement with Comm. N^o. 81 §§ 9 and 14 (Proc. Oct. 1902). In the investigated part the curves do not show the point of inflection found by VERSCHÄFFELT with mixtures of hydrogen and carbon dioxide (Comm. N^o. 47 Proc. Feb. 1899); they are always concave towards the T -axis.

Physics. — “*Isothermals of mixtures of oxygen and carbon dioxide.*”

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(Communicated in the meeting of November 28. 1903).

§ 5. According to § 4 (p. 586) the observations allowed of a more accurate determination of the data for the critical point of the mixtures for the range of the larger volumes and the range of temperatures over which the observations have been made, in the sense as it has been explained there, than it was possible from the drawing given there. To this end diagrams were projected on double the scale for the points in the homogeneous area for which the volume is larger than 0.005; in these diagrams 0.0005 is represented by 1 mm. both for $\log \frac{pv}{T}$ and for $\log v$. To determine the relation of the critical pressures independently and to test the relation of the critical temperatures of mixtures to that of pure carbon dioxide, diagrams were constructed for the same area, where $\log \frac{pv}{T}$ is drawn as a function of $\log p$; here 1 mm. represents: on the $\log p$ -axis 0.00025, on the $\log \frac{pv}{T}$ -axis 0.0005.

§ 6. The diagram for the mixture which had been transferred on tracing paper and in the middle of which a cross of axes was drawn in order to permit an accurate judgment of the agreement of the systems of axes for the two diagrams, was placed over the diagram for carbon dioxide, so that the $\log v$ -, and $\log p$ -axes respectively coincided, and then they were shifted until to the eye the isothermals of the mixture coincided with the system for carbon dioxide.