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phenomena of retardation, the experimental investigation of the critical phenomena in mixtures has led to reliable results. That phenomena of retardation give rise to important deviations is shown by the fact that CAILLETET has observed condensation at  $25^{\circ}$ , whereas my experiments show that the critical point of contact of his mixture after equilibrium of the phases has been obtained, ought to be found at about  $23^{\circ}$ .

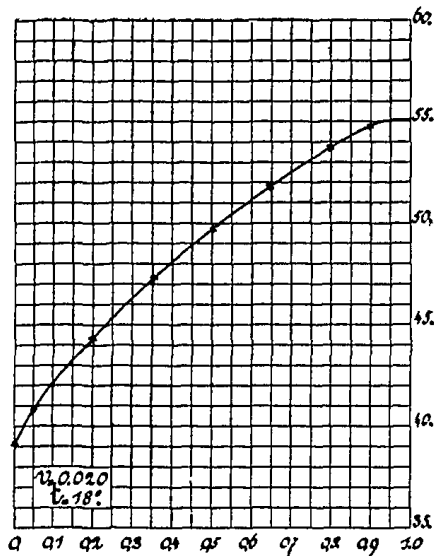
**Physics.** — „*Measurements on the change of pressure by substitution of one component by the other in mixtures of carbonic acid and hydrogen*”. By Dr. J. VERSCHAFFELT. (Communication N<sup>o</sup>. 47 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES. (*Continued.*))

### § 1. *Change of pressure by substitution.*

Tables VI—X contain the results of the determination of isothermals in mixtures with a still larger quantity of hydrogen than those treated of in the former communications. In these mixtures no condensation-phenomena appeared in the area observed; and so they cannot reveal to us anything more about the further course of the plaitpoint-curve, but in connection with the results communicated before, they show us in what way, at a given temperature and a given volume, the pressure of the mixture depends on its composition.

With the aid of all the determinations communicated we have first calculated the coefficients of pressure, the values of which for different compositions and volumes are given in Table XI. Then we have calculated for one and the same temperature ( $18^{\circ}$  C.) the isothermals of the different mixtures and represented them in a new diagram, the  $p-v-x$  diagram. On this diagram we have read the pressures belonging to one and the same volume for different mixtures: table XII contains the values read in this way for some volumes.

As will be explained in § 2 we have chosen the units of volume for the different mixtures so that 1 c.m.<sup>3</sup> of each mixture contains the same number of molecules, when the volumes of these mixtures expressed in the units accepted for this purpose, have the same value. Table XII therefore shows the change in pressure when, starting from one of the two substances in pure condition, we gradually substitute the molecules of this substance for an equal number of molecules of the other substance.



by an equal number of carbonic acid molecules hardly any change in the pressure takes place.

Table XII shows clearly that neither the coefficients of pressure undergo any material change, when the number of hydrogen molecules substituted by carbonic acid molecules is only a small fraction of the whole number of hydrogen molecules.

## § 2. *The unit of volume.*

It was desirable to express the volume for each mixture in a special unit of volume, chosen so that one c.m.<sup>3</sup> of each of the mixtures contains the same number of molecules when its volume, expressed in this unit, has the same value. We can do this by taking for each mixture as unit of volume: the volume which the quantity of substance used would occupy at 0° C. and 1 atm., if the mixture behaved like a perfect gas. This volume I will call the *theoretically normal volume*; it is obtained by multiplying the volume generally called the *normal volume* viz. the volume which is actually occupied by the substance at 1° C. and 1 atm., by a factor expressing the deviation from AVOGADRO's law.

In connection with AVOGADRO's law this measure for pure substances has been proposed by KAMERLINGH ONNES in 1881. At the same time he pointed out the desirability of expressing henceforth the molecular quantities also in absolute measure. In order to determine the deviation of the normal volume of hydrogen from that which is to be used in applying AVOGADRO's law, he employed VAN DER WAALS's law and the value 0,00050, deduced by VAN DER

WAALS for  $a-b$  (Continuiteit p. 91) from REGNAULT's observations. And so he obtained in K.G. M. S. the equation

$$\left(p + \frac{A}{v^2}\right)(v-b) = 2262000 (1+at) ,$$

which he thought fit for determining the deviation of the gases from AVOGADRO's law<sup>1)</sup>.

In the case of hydrogen we shall however use AMAGAT's observations below 200 atm., which we have also used in determining the pressures. With sufficient approximation they yield for the isothermal of 0° C.

$$p(v - 0,000690) = 0,99931^2),$$

when the normal volume is chosen as unit. Hence in order to obtain the theoretically normal volume we must multiply the volume at 0° and 1 atm. by 0,99931.

From the weight of 1 liter of hydrogen: 0,08955 gramme at 0° and 760 m.m. mercury, 0° C. and 45° latitude and the molecular weight of CO<sub>2</sub>: 43,89, we deduce the weight of a liter carbonic acid to be 1,9652 gramme under the same circumstances; REGNAULT found for this 1,9771, which means a deviation of 0,0060 from the theoretical value with respect to hydrogen. The density of carbonic acid is therefore 0,0053 higher than the theoretically normal density, so that in order to find the theoretically normal volume of pure carbonic acid we must multiply the volume at 0° and 1 atm. by 1,0053.

An observation made by BRAUN<sup>3)</sup> gives us some information on the deviations of AVOGADRO's law shown by mixtures of carbonic acid and hydrogen. He has found that when we mix two equal volumes of hydrogen and carbonic acid under a pressure of about 71 c.m. mercury, the pressure rises 0,097 c.m. thus 0,0014. And so we may accept that when taking two equal volumes of hydrogen and carbonic acid we obtain by mixing a

<sup>1)</sup> The problem in general has been treated by v. D. WAALS in his communications "On the accurate determination of the molecular weight of gases from their density." Proc. Nov. '98 and "Variation of volume and of pressure in mixing II." Proc. Dec. '98

<sup>2)</sup> See KAMERLINGH ONNES. Verh. Kon. Akad. v. Wet. 1881. Algemeene theorie der vloeistoffen, p. 5-7. Abstract: Arch. Néerl. t. XXX.

<sup>3)</sup> Wied. Ann., 34, p. 948, 1888. KUENEN has pointed out a similar change of pressure in mixing compressed gases by stirring.

double volume under a pressure of 1.0014 atm. Let  $n$  be the number of molecules which one volume of a perfect gas would contain at  $0^\circ$  and 1 atm., so that  $0,99931 n$  is the number of molecules of hydrogen and  $1,0053 n$  the number of molecules of carbonic acid, then it is easy to see that one volume of the mixture at  $0^\circ$  and 1 atm. must contain  $1,0009 n$  mol. And so in order to find the theoretically normal volume of a mixture consisting of an equal number of molecules of hydrogen and carbonic acid we must multiply the volume at  $0^\circ$  and 1 atm. by 1,0009.

Let, as in v. D. WAALS's paper,  $x$  be the proportion of the number of hydrogen-molecules to the whole number of molecules, then we can represent the deviation from AVOGADRO's law by the numbers: 1,0053 for  $x=0$ , 1,0009 for  $x=0,5$ , and 0,99931 for  $x=1$ . The deviation for intermediate mixtures can be found with sufficient approximation by applying a parabolic formula of the form  $y = a + bx + cx^2$ ; and then we find that the deviation may be represented by

$$y = 0,99931 + 0,0060 (1-x)^2 .$$

According to this formula the influence of small admixtures of carbonic acid with the hydrogen is very small, a fact to which the attention will be drawn later on.

For the reduction to  $0^\circ$  C. we had to use the coefficients of expansion of the mixtures. As a first approximation I might have calculated the coefficients of expansion with the aid of a linear formula from the coefficients of expansion of the pure substances: 0,00366 for  $H_2$ , 0,00371 for  $CO_2$ . But led by the previous result regarding the deviations from AVOGADRO's law I thought it probable that the dependence of the coefficient of expansion on the composition  $x$  would show the same characteristics; and so I was obliged to put it thus:

$$a_p = 0,00366 + 0,00005 (1-x)^2 .$$

In determining the theoretically normal volume of hydrogen it was mentioned that by starting from different experimental data we arrive at different deviations from AVOGADRO's law.

This is even more so in the case of carbonic acid. If by the side of the number 0,99950 for hydrogen formerly accepted by KAMERLINGH ONNES we also borrow from v. D. WAALS's *Continuïteit* (p. 76) the number 1,00646 for carbonic acid (deduced from REGNAULT's isothermal lines) and if we substitute this for REGNAULT's determination

of the density of carbonic acid we should find for the mixture  $\frac{1}{2}$  hydrogen— $\frac{1}{2}$  carbonic 1,00158, whence :

$$y = 0.99950 + 0.00136(1-x) + 0.00560(1-x)^2 .$$

From the point of view of a consistent application of VAN DER WAALS'S law a calculation of the theoretically normal volume of the carbonic acid from the normal volume and the compressibility would be preferable to the method of calculation followed by me. But then the proportion of the weights of one volume of carbonic acid and hydrogen in the state of perfect gases and the molecular weights would be discordant, and it are the latter which we want as a basis for our choice of units of volume (with a view to V. D. WAALS'S theory of mixtures). The influence of the differences yielded by the calculations from the different data is not such as to render doubtful the character of the change of pressure when substitution takes place, but still in my determinations the discrepancies differ little from the errors of observation. From this we see once more the necessity of accurate observations with perfectly pure substances in order to make progress in the knowledge of the laws which govern the gaseous state.

TABLE VI.  $x = 0.3528$ .

Volume 0,0	$P_{18}^{\circ.00}$	$P_{31}^{\circ.60}$
2810	34.44	36.85
2585	37.17	39.80
2442	39.15	41.96
2299	41.38	44.38
2159	43.77	46.95
2014	46.54	49.99
1869	49.70	53.45
1724	53.35	57.40
1587	57.35	61.80
1480	60.90	65.75
1340	66.35	71.75
1207	72.40	78.45
1067	80.30	87.25
09255	89.90	98.30
07940	101.60	112.0
06510	115.3	

TABLE VII.  $x = 0.4993$ .

Volume 0,0	$P_{18}^{\circ.00}$	$P_{33}^{\circ.00}$
3168	32.11	33.84
2975	34.09	35.95
2825	35.78	37.78
2667	37.85	39.97
2512	40.08	42.36
2355	42.60	45.07
2206	45.34	47.97
2045	48.71	51.55
1889	52.35	55.50
1736	56.80	60.20
1624	60.45	64.05
1468	66.35	70.40
1323	73.05	77.65
1172	81.85	87.10
1017	93.15	99.50
08694	107.3	114.9

TABLE VIII.

 $x=0,6445.$ 

Volume 0,0	$P_{16^{\circ}\cdot 80}$	$P_{24^{\circ}\cdot 20}$	$P_{31^{\circ}\cdot 00}$
2979	34.85	35.82	36.85
2746	37.76	38.79	39.95
2600	39.90	41.00	42.13
2446	42.35	43.53	44.80
2294	45.10	46.34	47.88
2143	48.21	49.60	51.00
1989	51.90	53.35	54.95
1836	56.05	57.60	59.35
1686	60.90	62.65	64.55
1576	65.20	67.05	69.05
1433	71.45	73.60	75.80
1284	79.50	82.00	84.55
1140	89.25	92.05	94.85
09935	102.2	105.5	108.9
08495	119.2		

TABLE IX.

 $x=0,7963.$ 

Volume 0,0	$P_{18^{\circ}\cdot 30}$
3293	32.61
2999	35.81
2723	39.47
2474	43.49
2253	47.78
2032	53.00
1840	58.60
1630	66.20
1484	72.95
1335	81.35
1212	89.65
1090	100.1
09650	113.2

TABLE X.

 $x=0,8972.$ 

Volume 0,0	$P_{17^{\circ}\cdot 10}$
3234	33.46
2989	36.29
2840	38.15
2692	40.31
2532	42.94
2384	45.72
2217	49.22
2076	52.65
1904	57.50
1764	62.25
1635	67.40
1485	74.55
1336	83.15
1173	95.20
1028	109.5

TABLE XI. Coefficients of tension. (15°—30° C.)

Volume 0,0	Compositions $x =$									
	0.0000	0.0491	0.0995	0.1990	0.3528	0.4993	0.6445	0.7963	0.8972	1.0000
30	0.162	0.159	0.156	0.150	0.142	0.134	0.130	0.127	0.126	0.126
28	175	172	168	163	155	146	141	138	136	135
26	190	186	183	177	168	159	154	150	148	146
24	209	204	199	193	183	174	168	163	161	159
22	229	223	218	211	201	191	185	179	176	173
20	257	249	242	234	223	212	204	197	194	192
18	295	285	276	265	250	237	227	221	216	214
16	346	333	321	306	286	270	256	249	244	242
14	412	395	381	360	331	312	296	286	281	278
12	503	481	461	431	395	373	353	339	331	327
10	620	590	566	433	495	464	436	415	405	397

TABLE XII. Pressures at 18°.

Volume 0,0	Compositions $x =$									
	0.0000	0.0494	0.0995	0.1990	0.3528	0.4993	0.6445	0.7963	0.8972	1.0000
30	28.90 <sup>1)</sup>	29.68	30.37	31.33	32.70	33.81	34.77	35.80	36.19	36.31
29	29.73	30.43	31.33	32.25	33.75	34.92	35.95	37.09	37.46	37.59
28	30.58	31.35	32.25	33.24	34.85	36.12	37.19	38.43	38.83	38.97
27	31.45	32.32	33.23	34.34	36.04	37.39	38.56	39.81	40.29	40.45
26	32.40	33.33	34.28	35.53	37.32	38.80	40.05	41.33	41.87	42.04
25	33.36	34.40	35.37	36.77	38.64	40.23	41.64	42.98	43.62	43.77
24	34.38	35.53	36.54	38.04	40.12	41.80	43.33	44.80	45.48	45.65
23	35.47	36.73	37.78	39.43	41.72	43.57	45.17	46.73	47.48	47.70
22	36.55	38.00	39.11	40.91	43.40	45.46	47.18	48.90	49.67	49.94
21	37.75	39.40	40.55	42.50	45.26	47.50	49.39	51.20	52.15	52.40
20	39.03	40.85	42.10	44.26	47.30	49.65	51.80	53.75	54.80	55.10
19	40.40	42.40	43.76	46.15	49.49	52.10	54.45	56.65	57.80	58.10
18	41.90	44.02	45.56	48.22	51.90	54.05	57.45	59.85	61.15	61.50
17	43.43	45.70	47.47	50.40	54.60	58.00	60.75	63.45	64.90	65.25
16	45.00	47.52	49.55	52.80	57.50	61.30	64.55	67.45	69.10	69.50
15	46.64	49.45	51.85	55.45	60.80	65.00	68.75	72.10	73.85	74.35
14	48.35	51.65	54.30	58.40	64.60	69.30	73.35	77.50	79.25	79.95
13	50.05	54.00	56.00	61.75	68.80	74.30	78.80	83.55	85.65	86.45
12	51.85	56.40	59.85	65.60	73.60	80.00	85.30	90.85	93.10	94.10
11	53.65	59.00	63.05	69.75	79.10	86.75	93.00	99.25	102.0	103.1
10	55.50	61.65	66.55	74.25	85.40	94.40	102.1	109.6	112.9	114.3

**Chemistry.** — „*On the velocity of electrical reaction*”. By Dr. ERNST COHEN, (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. If two elements, arranged as follows.

Electrode, reversible with respect to the anion.	Saturated solution of a salt <i>S</i> in presence of the stable solid phase of the salt.	Electrode, reversible with respect to the cathion.
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and

<sup>1)</sup> This column has been deduced from isothermal determinations of pure carbonic acid, not yet published.