Physics. — *Vapour tensions, critical point and triple-point of carbon monoxide.* By C. A. CROMMELIN, W. J. BIJLEVELD and E. G. BROWN. (Communication No. 217b from the Physical Laboratory of the University of Leiden.) (Communicated by Prof. W. H. KEESOM.)

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Comparativily little is known about the vapour pressures of carbon monoxide, especially at the higher pressures. There are observations of many years ago by OLSZEWSKI [1]), by BALY and DONNAN [2]), by ESTREICHER and BOBOTEK [3]) and by CARDOSO [4]), more recent ones by CLUSIUS and TESKE [5]) and by VERSCHOYLE [6]). The subject appeared to us an interesting one for further research.

A very pure preparation of carbon monoxide was made in an all glass apparatus from anhydrous sodium formiate and dilute sulphuric acid. Impurities produced during the reaction (water vapours, acid fumes) were removed by cooling the gas to a temperature of about —90° C. (alcohol, cooled with liquid air). Finally the gas was compressed in a small steel cylinder of one liter capacity.

The measurements at high pressures were made in a glass tube with electromagnetic stirrer, those at lower pressures in a vapour pressure apparatus, described by CATH and KAMERLINGH ONNES [7]). The pressures from 2 to 12 atm. were measured by means of the standard open manometer, the higher ones by the closed manometer M_{60}. The temperatures were determined by means of one or two platinum thermometers calibrated with the helium-thermometer.

Corcerning the purity of the carbon monoxide we can mention, that we made repeated measurements at the same temperature but with different quantities of the phases. The slight differences found were within the limits of experimental errors.

The results of our measurements, which were made in the spring of 1929 are given in the following tables. The temperatures are given in Kelvin degrees on the Celsius and on the Avogadro scale, — 273.09° C. being assumed as the absolute zero, the pressures in international atmospheres, these being at Leiden aequivalent to 75.9529 cm.

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1) C. R. **99** (1884) p. 706.
2) J. Chem. Soc. (1902) p. 902.
3) Anz. Ak. Wiss. Krakau **7** (1913) p. 461.
4) J. de chimie phys. **13** (1915) p. 213.
5) Zeitschr. f. phys. Chemie (B) **6** (1929) p. 135.
6) Trans. R. Soc. (A) **230** (1931) p. 189.
7) Leiden, Comm. No. 152a.

We have tried to represent the vapour pressures in the liquid region by the following equation

$$\log p_{atm.} = -\frac{544.66}{T} - 10.217 \log T + 24.45338 + 0.02178\, T. \quad (1)$$

The deviations of the thus calculated values from the observed ones are given in Table I.

TABLE 1.

Liquid region vapour pressures of carbon monoxide			
Temperature		Pressure	
Celsius	absolute	int. atm.	$\Delta \log p$
—140.62	132.47	33.902	0.00000
—141.27	131.82	32.911	— 21
—143.86	129.23	29.184	— 96
—143.86	129.23	29.160	— 131
—147.13	125.96	25.014	— 58
—149.63	123.46	22.152	+ 2
—160.89	112.20	12.072	+ 165
—165.47	107.62	9.082	+ 23
—169.61	103.48	6.922	+ 160
—178.75	94.34	3.473	— 263
—185.48	87.61	1.8833	+ 17
—191.64	81.45	0.98131	— 39
—195.13	77.96	0.64566	+ 1
—199.24	73.85	0.37197	— 10
—199.24	73.85	0.37198	— 09
—199.23	73.86	0.37237	— 44
—204.92	68.17	0.15387	+ 93
—204.95	68.14	0.15292	+ 144

The critical temperature was determined by making a number of observations immediately above and below that point and by including in this way the temperature sought within a small region of $^1/_{50}°$. For the true value we took the middle of this region. The critical pressure was found

by plotting a number of vapour pressures immediately below the critical point and extrapolating to the critical temperature over a very small interval.

The boiling point is calculated from formula (1).

The triple-point has been realised for nearly an hour without any change.

Solid region vapour pressures of carbon monoxide		
Temperature		Pressure
Celsius	Absolute	int. atm.
—205.02	68.07	0.15119
—205.19	67.90	0.14566
—205.95	67.14	0.12866
—206.46	66.33	0.10663
—207.42	65.67	0.092847
—208.13	64.96	0.079931
—210.41	62.68	0.048003
—216.23	56.86	0.009493

Fundamental points of carbon monoxide			
Temperature		Pressure	
Celsius	Absolute	int. atm.	
—140.21 [2]	132.88 [2]	34.529 [2]	Critical point
—191.475	81.615 [1]	1.0000	Boiling point
—204.99 [3]	68.10 [3]	0.15146 [3]	Triple-point

[1]) This value agrees perfectly with the one of CLUSIUS and TESKE and the one of VERSCHOYLE.

[2]) For the critical constants CARDOSO gives: $t_k = -138°.7$, $T_k = 134°.3$ ($\pm$ 0°.10), $p_k = 34.60$ atm. ($\pm$ 0.10).

[3]) These values are in fairly good agreement with those of VERSCHOYLE, viz. —205.03° and 11.504 cm, the latter values being very slightly lower.

Summary.

A quantity of very pure carbon-monoxide was prepared. With this substance we accurately determined:

the vapour pressures liquid-gas from —141° to —205° C.;

the vapour pressures solid-gas from —205° to —216° C.;

the triple-point;

the critical point and the boiling point.

The vapour pressures in the liquid region are represented by a formula.