NOTES

A Supplementary Note on the Author's Equation of State

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Bentley's mass spectral study at room temperature of carbon dioxide gas[1] seems to give a concrete meaning to the ε of the author's equation of state: $p+a/V^{2-\varepsilon}=RT/(V-b)$, where $a=3p_cV_c^2$, $b=V_c/3$, and ε is a parameter depending upon molecular association[2]. Since ε is presumably the concentration of associated molecules (cybotactic groups) as judged from the deduction of the equation from the kinetic theory of gases[3], the $(2-\varepsilon)$ parameter should be the concentration of unassociated molecules. If this is really so, $\varepsilon/(2-\varepsilon)$ may correspond to the total intensities of CO_2^+, $(CO_2)_2^+$, $(CO_2)_3^+$, ……, and $(CO_2)_{23}^+$ relative to CO_2^+, which is numerically equal to 0.0442 as estimated from the graph given by Bentley. In his graph the point for $(CO_2)_{23}^+$ is lacking, probably because experimental errors for polymers above $(CO_2)_{22}^+$ become too great for actual values to be decided.

For the test of this postulation, the author has quoted PVT measurements on carbon dioxide at the critical temperature (30.98°C) from the I. C. T.[4] and those at 32.075, 31.037, 25.053 and 0°C from Michels and Michels' data[5], using 44.011 for the molecular weight and 1.9768 g. cm^{-3} for the density at 0°C.

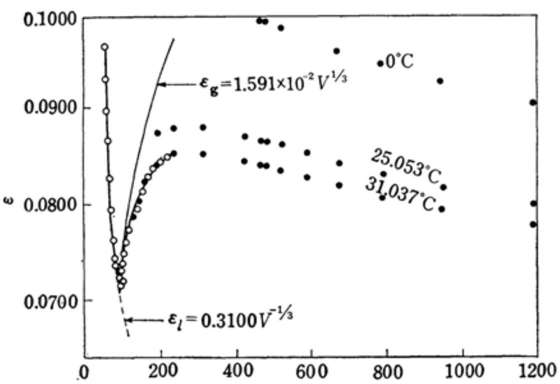

Fig. 1. ε-V Diagrams of carbon dioxide at 30.98, 31.037, 25.053 and 0°C.

ε-V relations are shown in Fig. 1, in which the values from the former data are denoted by white circles and those from the latter data by black circles. The analysis of ε at the critical temperature is quite similar to that already made in the case of isopentane[6].

We obtain for the liquid portion $\varepsilon=5.046\ V^{-1}$ (V=52.59～63.72) and $\varepsilon_l=0.3100\ V^{-1/3}$ (V=67.93～73.38); for the liquid and gaseous coexisting portion $\varepsilon_l+\varepsilon_g=0.1406$ (V=81.40～106.36) and $\varepsilon_g=1.591\times10^{-2}\ V^{1/3}$; and, for the gaseous portion, $\varepsilon=\varepsilon_g-cV^n$, $n=4$, $c=7.130\times10^{-12}$ (V=113.59～139.71), $n=3$, $c=1.116\times10^{-9}$ (V=156.54～190.63), and $n=2$, $c=2.284\times10^{-7}$ (V=207.37～224.15), the numbers in parentheses indicating volume ranges in cm^3 mol^{-1}. The calculated pressures from these values have an average deviation of $\pm0.52\%$ from the observed pressures[7].

Granting that the ε values at the lowest pressure, 16.5～19.0 atm., listed in Michels and Michels' data are not so much different from those for 5 atm., at which the pressure of the beam of gas molecules passing through a small orifice and a series of larger orifices from a reservoir was maintained in Bentley's measurements, we can guess at what temperature his measurements were made: Bentley's value, 0.0442, will lie on a straight line passing through the four values of $\varepsilon/(2-\varepsilon)$ at 32.075, 31.037, 25.053 and 0°C, namely, 0.0403 at 19.0843 atm., 0.0405 at 19.0023 atm., 0.0417 at 18.5374 atm., and 0.0474 at 16.5488 atm., if his measurements were made at 14.2°C. However, as Bentley remarked, cooling of the bulk gas occurs as a result of the Joule-Thomson effect, which is less than 6°C for 5 atm.; his so-called room temperature seems, therefore, to have been about 20°C.

In Bentley's reply to the author's request, he

1) P. G. Bentley, *Nature*, **190**, 432 (1961).
2) T. Ishikawa, This Bulletin, **26**, 78 (1953).
3) T. Ishikawa, ibid., **27**, 573 (1954).
4) "International Critical Tables", Vol. 3, McGraw-Hill Book Co., New York (1928), p. 12.
5) A. Michels and C. Michels, *Proc. Roy. Soc.*, **A153**, 201 (1935—6).
6) T. Ishikawa and M. Ikeda, This Bulletin, **34**, 1329 (1961).
7) Presented by T. Ishikawa and M. Ikeda at the Meeting of the Chemical Society of Japan, Tokyo, November, 1961.

said the room temperature was indeed about 20°C; it is difficult to give a more precise figure as the work was done over a long period during which the temperature altered by several degrees.

The above consideration leads us to the following conclusion: $\varepsilon/(2-\varepsilon)$ corresponds to the ratio of the total sum of ion intensities of polymers to that of monomers, at least so far as the present data are concerned.

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