An Equation of State in Analytical Form (Continued)

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From the successive studies on this subject[1], the author is convinced that his equation of state is, among the hitherto pubished equations of state, the only one which has applicability to liquids as well as to vapours. As a supplementary example, it is necessary to add a comparison between his equation and Beattie-Bridgeman's equation, the latter having generally been accepted to hold with high accuracy for vapours. Fig. 1 shows a graphical comparison between these two equations by quoting gaseous neopentane, $C(CH_3)_4$, at the critical isotherm from Beattie, Douslin, and Levine's recent measurements[2] (the author's equation, full line; Beattie-Bridgeman's equation, broken line; observed values, ○). Their calculated values above 3.5 mole/l were not given, and they were computed by use of their determined constants: $A_0=23.3300$, $B_0=0.33560$, $a=0.15174$, $b=0.13358$, $c=400\times10^4$. For the author's curve $(2-\varepsilon)$ the value at the critical isotherm was taken to be 1.922, the mean of the values: 1.913, 1.914, 1.917, 1.920, 1.924, 1.927, 1.928, 1.928, 1.927, and 1.926 at 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 6.0 mole/l respectively.

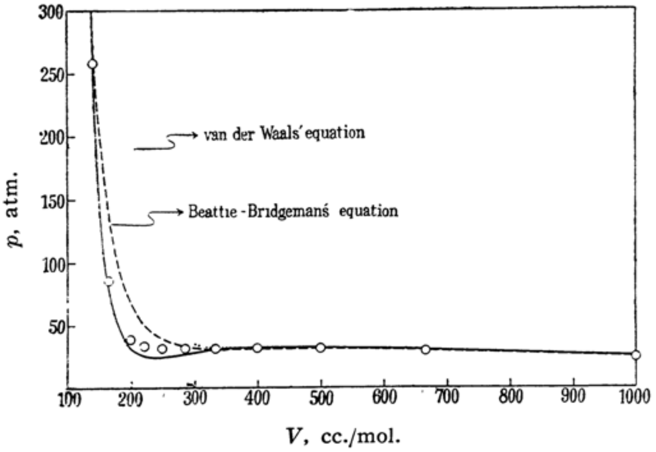

Fig. 1. Critical Isotherm of $C(CH_3)_4$

As seen from the figure in which van der Waals' equation is also shown by a dotted line, Beattie-Bridgeman's equation behaves like, but far better than, van der Waals' equation as reported in the latest paper. Similar facts are found for a certain range above the critical temperature and also in the case of normal pentane, whose data are quoted from the measurements of the same investigators[3], hence it appears that Beattie-Bridgeman's equation fails at pressures so high as to correspond to the liquid portion in the neighbourhood of the critical temperature. On the other hand, the author's equation, which is valid even at such high pressures as stated above, displays a signoidal curve (showing a maximum and minimum) still above the critical temperature, the reason being easily understood from its derivation from van der Waals' equation. In fact, such a signoidal curve occurs even at a temperature from a few (e. g. H_2) to a few tens degrees (e. g. CO_2, $C(CH_3)_4$, C_2H_4[4]) above the critical temperature, though its supersaturated vapour portion, including the maximum, nearly coincides with the observed values. The necessity of this discrepancy in analytical meaning will be elucidated hereafter.

Phillips[5] carried out interesting experiments on the viscosity of carbon dioxide under a wide range of pressures both above and below the critical temperature. His observed

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[1] T. Ishikawa, This Bulletin, **26**, 78, 530 (1953); T. Ishikawa, M. Ikeda, ibid., **26**, 516 (1953).

[2] J. A. Beattie, D. R. Douslin, S. W. Levine, *J. Chem. Phys.*, **20**, 1619 (1952).

[3] J. A. Beattie, S. W. Levine, D. R. Douslin: *J. Am. Chem. Soc.*, **74**, 4778 (1952).

[4] Adopted from "International Critical Tables", III, p. 15.

[5] P. Phillips, *Proc. Roy. Soc., London*, A**87**, 48 (1912).

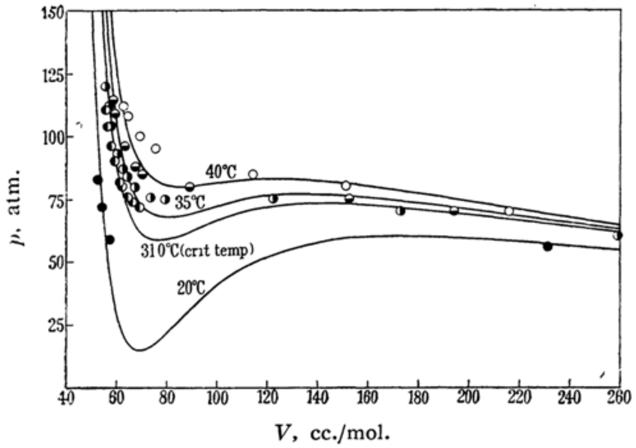

Fig. 2. Isotherms of CO_2

$p-V$ values at and above the critical temperature (denoted by ●, ◐, ◑, ◒, and ○ at 20, 30, 32, 35, and 40°C respectively in Fig. 2) lie fairly close to each isotherm except that which, if vapour and liquid still coexist, corresponds to the superheated liquid portion and the never realizable portion, $(\partial V/\partial p)>0$, of plots of the author's equation (full line), in which $(2-\varepsilon)$ values are computed from the previously obtained linearity, $2-\varepsilon=1.912+0.00028\,(T-T_c)$, except the value, 1.903 at 20°C, which is determined directly from Phillips' data for the reason that the availability of the linearity for vapour state down to a temperature below the critical temperature is at present questionable.

TABLE I

Tests for constancy of H (V-b) and of H $V^{2-\varepsilon}$ (H, poise; V, cc./mol.)

20°C		
p atm.	H (V-b)	H $V^{2-\varepsilon}$ $2-\varepsilon=1.903$
83	0.0171	1.56
72	0.0172	1.54
59	0.0177	1.55
mean	0.0173	1.55

30°C		
p atm.	H (V-b)	H $V^{2-\varepsilon}$ $2-\varepsilon=1.912$
110.5	0.0181	1.66
104	0.0179	1.64
96	0.0180	1.63
90	0.0172	1.58
82	0.0175	1.56
80	0.0172	1.53
76	0.0174	1.52
74	0.0170	1.51
73	0.0170	1.50
72	0.0171	1.52
mean	0.0174	1.57

32°C		
p atm.	H (V-b)	H $V^{2-\varepsilon}$ $2-\varepsilon=1.912$
120	0.0188	1.72
112	0.0183	1.67
104	0.0181	1.64
93	0.0179	1.60
87	0.0182	1.62
84	0.0183	1.62
80	0.0186	1.65
76	0.0187	1.67
75	0.0192	1.74
mean	0.0185	1.66

35°C		
p atm.	H (V-b)	H $V^{2-\varepsilon}$ $2-\varepsilon=1.913$
114.5	0.0183	1.64
109	0.0181	1.63
96	0.0184	1.63
88	0.0181	1.61
85	0.0175	1.56
mean	0.0181	1.61

40°C		
p atm.	H (V-b)	H $V^{2-\varepsilon}$ $2-\varepsilon=1.915$
112	0.0177	1.57
108	0.0176	1.56
100	0.0180	1.59
94	0.0181	1.62
mean	0.0179	1.59

Total average value of H (V-b), 0.0178 with 2.8% deviation; total average value of H $V^{2-\varepsilon}$, 1.60 with 2.7% deviation.

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[6] A. J. Batschinski, *Z. phys. Chem.*, **84**, 643 (1913).

According to Batschinski's formula[6] for normal liquids, the product of viscosity coefficient η by specific free volume $(v-\omega)$ is independent of temperature, where $M\omega$ (M= molecular weight) is nearly equal to van der Waals' b $(=V_c/3)$. His formula can be rewritten as follows: $\eta(V-b)$=a constant independent of temperature where V is the molecular volume. Applying the latter formula to Phillips' viscosity data, we find that the formula holds good at high pressures for the measured temperature even above the critical temperature, and further, a like constancy is also obtained if we assume η to be simply proportional to cohesive pressure, $a/V^{2-\epsilon}$, in the author's equation (see Table 1).

Moreover, between the constant range of $\eta(V-b)$ or $\eta V^{2-\epsilon}$ at each temperature (see Table 1) and its corresponding superheated liquid portion of the author's curve (see Fig. 2) there may exist a parallelism, or in other words, the lowest pressure limit of the former appears to come near the end point (close to the minimum) of the latter.

The above results lead to the conclusion that the occurrence of a superheated liquid portion above the critical temperature is necessary for elucidating the persistence of a liquid molecular state above the critical temperature, which no equation except the author's presents, this phenomenon being also in accord with the recent Swietoslawski and Markowska's observation on the critical region, that density difference between the lower and upper parts of the tube was still noticeable after the disappearance of the meniscus[7].

The author is indebted to Nagasaki American Cultural Center for furnishing him with American journals in which Beattie and his coworkers published their compressibility measurements.

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[7] W. Swietoslawski, H. Markowska, *Roczniki Chem.*, **26**, 207 (1952); *C.A.* **47**, 10302 (1953).