An Equation of State in Analytical Form (Continued)

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In the previous paper[1] one of the authors (Ishikawa) proposed an equation of state slightly differed in its form from van der Waals' equation, but greatly improved in having a quantitative nature, i.e., for 1 mole of a gas the state is expressed by

$$p+\frac{a}{V^{2-\varepsilon}}=\frac{RT}{V-b},\ a=3p_cV_c^2,\ b=V_c/3,$$

in which ε is an **analytically** determinable constant at each isotherm.

As clearly understood from the derivation of the equation, a and b are not the constants which satisfy $(\partial p/\partial V)_{\mathrm{T}}=0$ and $(\partial^2 p/\partial V^2)_{\mathrm{T}}=0$, so that at critical isotherm, the equation

$$p+\frac{a}{V^{2-\varepsilon}}=\frac{RT_c}{V-b},\ a=3p_cV_c^2,\ b=V_c/3 \qquad (1)$$

should be combined with its critical condition:

$$p_c=\frac{3RT_c}{2V_c(1+3V_c^{\varepsilon})} \qquad (2)$$

where ε is not the value at the critical point, but the mean at the critical isotherm, or ε_c as denoted in the foregoing paper.

From the standpoint of the continuity of state, the unstable region of state at temperatures below the critical temperature has been supposed to consist of three portions of superheated liquid, supersaturated vapour and $\partial V/\partial p>0$, the first and second portions being realizable, but the third being never realizable. Actually in the stable state these three

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[1] Tetsuya Ishikawa: This Bulletin. **26**. 78 (1953).

portion coincide on a horizontal straight line corresponding to a given temperature to realize a liquid-vapour coexistence region expressed by a well known relation:

$$\log_e \frac{p}{p_c} = A - B\frac{T_c}{T} \qquad (3)$$

A and B being constants of nearly equal magnitude, so that the state may be fully expressed by this relation in combination with an equation of state in a van der Waals' form which holds true even at temperature below the critical temperature.

We are fortunate to find the recent measurements done by Oliver and his collaborators on monomer of chlorotrifluoroethylene, C_2ClF_3, having average purity of 99.84%[2].

The molecular volumes of this substance at 25.0°C under high pressure range are all less than $b_{corr.} = b.(3RT_c/8p_cV_c) = RT_c/8p_c$, hence van der Waals' equation should be rejected.

Tests for the new equation are diagrammatically shown in Fig. 1, in which the curves in full and their connecting broken lines are plotted by taking $2-\varepsilon = 1.861$, 1.879, 1.903 and 1.920 as the mean values at 25, 50, 75 and 100°C respectively, excluding the values in parentheses in Table I, which are far from having uniform pressures in unstable portions and those probably due to errors coming from the samples of different purity as noticed by the experimenters. These values together with the value at the critical point, 1.925, directly calculated by means of formula (2), are on a straight line as expected from the previous study. This proposition, therefore, serves as a supplemental test for estimating a probable value of $(2-\varepsilon)$.

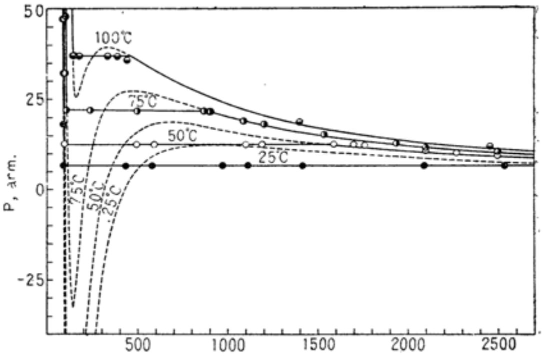

Fig. 1. Isotherms of C_2ClF_3.

TABLE I

$(2-\varepsilon)$ Values of C_2ClF_3 ($t_c = 105.8$°C, $p_c = 40.1$ atm., $d_c = 0.55$ g./cc.)

$b = 70.59$, $\log a = 6.732021$

25.0°C		2—ε	50.0°C		2—ε	75.0°C		2—ε	100.0°C		2—ε
p(atm.)	V(cc./mol.)		p(atm.)	V(cc./mol.)		p(atm.)	V(cc./mol.)		p(atm.)	V(cc./mol.)	
47.29	89.34	1.862	47.30	95.74	1.908	47.91	105.88	1.902	37.05	142.92	1.923
32.26	89.57	1.861	12.81	99.01	1.888	32.27	108.67	1.904	37.02	150.02	1.925
18.24	89.80	1.860	12.73	99.36	1.889	22.14	111.70	1.907	36.93	179.77	1.927
6.774	90.97	1.866	12.66	497.71	1.868	22.20	112.05	1.907	36.91	335.80	1.915
6.796	91.78	1.871	12.53	594.27	1.857	22.06	241.69	1.918	36.82	389.97	1.915
6.766	94.93	1.888	12.50	1100.01	1.844	21.85	501.55	1.883	35.86	444.01	1.914
6.689	433.64	1.877	12.53	1190.04	1.848	21.74	868.57	1.900	18.80	1401.68	(1.941)
6.608	581.57	1.851	12.41	1591.31	1.882	21.61	902.00	1.904	11.91	2455.10	(1.995)
6.608	970.25	1.814	12.44	1705.22	1.904	21.58	905.03	1.904	8.629	3490.35	(2.038)
6.564	1109.56	(1.807)	12.42	1705.92	1.904	19.02	1088.82	(1.902)	6.650	4520.70	(2.015)
6.563	1418.57	(1.798)	12.16	1763.00	(1.906)	18.19	1200.76	(1.910)			
6.526	2093.09	(1.803)	10.68	2101.36	(1.913)	15.26	1535.98	(1.916)			
6.488	2537.80	(1.820)	10.05	2269.79	(1.916)	12.75	1935.38	(1.923)			
			9.311	2497.38	(1.920)	10.52	2498.66	(1.953)			
	mean	1.861		mean	1.879		mean	1.903		mean	1.920

The fair coincidences between the observed points denoted by ●, ○, ◑ and ◒ at 25, 50, 75 and 100°C respectively and the calculated curves outside of liquid-vapour coexistence regions are quite satisfactory.

The liquid-vapour coexistence regions can be represented by the following relation with less than 1.6% error:

$$\log_e \frac{p}{p_c} = 6.743 - 6.729\frac{T_c}{T},$$

which fits better than $\log p_{mm} = 7.75412 - 1392.82/(t+319.70)$ proposed by the same experimenters.

Next we shall consider critical isotherms with two examples of hydrogen and carbon dioxide[3]. According to the classical theory, the critical point has been treated as a mathematical point of inflexion, e.g., applying van der Waals' equation, the condition of it is

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[2] G. D. Oliver, J. W. Grisard. C. W. Cuningham: *J. Am. Chem. Soc.*, **73**, 5719 (1951).

[3] Adopted from "International Critical Tables" III, p. 5, 12.

$(8p_cV_c-3RT_c)^3=0$, or $V_c=3RT_c/8p_c$. The actual volume range at the critical pressure, however, is always found to be appreciably longer than that in the neighbourhood of this point, or diagrammatically, the curve of the liquid portion calculated from van der Waals' equation is situated farther from p-axis than the observed points (see Fig. 2 and 3, in which dotted curves are van der Waals' equation and ○ are observed points). This divergency needs another reasonable explanation.

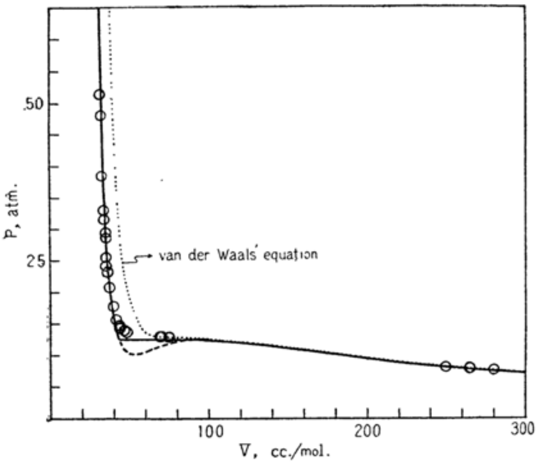

Fig. 2. Critical isotherm of H_2.

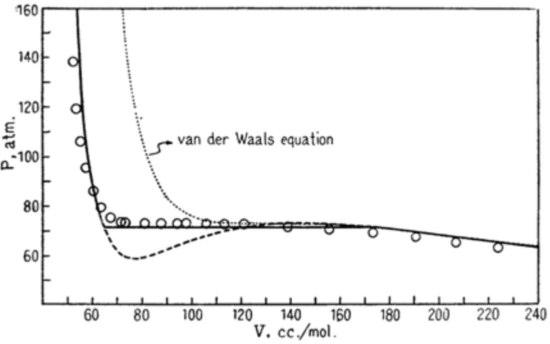

Fig. 3. Critical isotherm of CO_2.

Draw a horizontal straight line passing through the critical condition, $p_c=3RT_c/2V_c(1+3V_c^{\varepsilon})$, where ε is taken to be ε_c as stated above, i.e., $2-\varepsilon=1.928$ for H_2 and 1.912 for CO_2 (compare with Table 4 in the preceding paper). We see that experimental points lie near the line, and that by so doing the portion of supersaturated vapour almost disappears but a realizable portion of superheated liquid still remains. Further tests at other temperatures show that similarity though flat in its form happens even at a few or a few tens degrees above the critical temperature.

The above elucidation is no other than an extension of the already explained liquid-vapour coexistence to a critical region where p must tend to p_c, but $\log_e p/p_c=A-BT_c/T$ fails since A is not exactly equal to B.

The indefiniteness of the critical state (which means that even after the meniscus has disappeared, the density of the system is not uniform) since 1904, has long been the subject of investigation and the present recognition is that there exists a critical region between the temperature at which the meniscus disappears and that at which liquid can no longer exist[4].

Taking this recognition into account, the conception of combination of equation (1) with p_c from formula (2) which is elongated horizontally as a limiting case of relation (3) for the volume range between two portions of liquid and vapour states may be permissible.

Trials show that the calculated curve by use of the new equation passes on or by the observed points in both portions of liquid and vapour states (full line and its connecting broken line in Fig. 2 and 3 denote the calculated curves taking the same values of $(2-\varepsilon)$ as above).

This and foregoing results lead to the conclusion that the new equation of state, which is valid for gases, is also available for liquids.

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[4] e. g., S. Glasstone "Textbook of Physical Chemistry", p. 433 (2nd Edition).