An Analysis of Ishikawa's Equation of State as Applied to the Critical Region of Isopentane

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In the last report of this series of study[1], one of the present authors (Ishikawa) made a close investigation of his equation of state: for one mole of gas

$$p+\frac{a}{V^{2-\varepsilon}}=\frac{RT}{V-b}$$

$a=3p_cV_c^2$, $b=V_c/3$ and ε is an empirically determinable parameter which depends upon molecular association, its factor, A, being defined by him as the ratio of observed P_cV_c/RT_c to its van der Waals' value 8/3, or $A=(1+3V_c^{\varepsilon})/4$ at the critical point. He remarked that ε varies but little with the volume and that ε-V curves of xenon and neopentane, $C(CH_3)_4$, in the critical region appear alike to

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[1] T. Ishikawa, This Bulletin, 26, 78, 530 (1953); ibid., 27, 226, 570 (1954); ibid., 28, 89, 515 (1955); T. Ishikawa and M. Ikeda, ibid., 26, 516 (1953).

consist of three parts, the first part being concave up to the critical point, or more precisely speaking, at first probably showing a minimum which is situated at the volume corresponding to the minimum of p-V curve plotted by his equation, taking ε to be that at the critical point, and finally a nearly straight line, the second part being undoubtedly a long straight line starting from the critical point; or, at the critical point the second and higher derivatives of ε with respect to the volume appear to be zero, and the third part being convex upward to the maximum which may correspond to the volume at which the other form of van der Waals' equation ($b=V_c/3$) takes the critical pressure. This paper is intended to analyze the ε-V curve by making use of Young's precise PVT-measurements on

TABLE I. CRITICAL ISOTHERM OF ISOPENTANE, 187.8°C

V cm^3 g^{-1}	p atm.	ε_{obs}	$\varepsilon_{obs} V^{1/3}$	ε_1	$\varepsilon_1+\varepsilon_{obs}$	ε_g	$\varepsilon_1+\varepsilon_g$	ε_{calcd}	n	p_{calcd} atm.	Deviation %
2.4	64.58	0.08025	0.44730	0.07993				0.07993		65.35	+1.19
2.5	53.37	0.07890	0.44580	0.07885				0.07885		53.48	+0.21
2.6	46.03	0.07769	0.44470	0.07782				0.07782		45.77	−0.56
2.7	41.14	0.07665	0.44434	0.07685				0.07685		40.73	−1.00
2.8	38.08	0.07567	0.44401	0.07592				0.07592		37.68	−1.18
2.9	36.08	0.07483	0.44424	0.07504				0.07504		35.75	−0.91
3.0	34.82	0.07460	0.44791	0.07420				0.07420		34.77	−0.14
3.2	33.54	0.07323	0.4455 mean	0.07262	0.14585	0.06779	0.14041	0.07323		33.54	±0.00
3.4	33.07	0.07270		0.07117	0.14387	0.06917	0.14034	0.07277		33.11	+0.12
3.6	32.96	0.07227		0.06982	0.14209	0.07050	0.14032	0.07236		32.88	−0.24
3.8	32.93	0.07308		0.06858	0.14166	0.07179	0.14037	0.07312		32.89	−0.12
4.0	32.92	0.07366		0.06741	0.14107	0.07302	0.14043	0.07364		32.94	+0.06
4.3	32.91	0.07479		0.06581	0.14060	0.07481	0.14062	0.07458		33.09	+0.55
4.6	32.89	0.07609		0.06434	0.14043	const. range		0.07607		32.91	+0.06
5.0	32.88	0.07782		0.06258	0.14040			0.07783		32.87	−0.03
5.5	32.82	0.07978		0.06062	0.14040			0.07979		32.81	−0.03
6.0	32.68	0.08146		0.05889	0.14035	0.08359		0.08144	4	32.68	±0.00
6.5	32.45	0.08284		0.05734	0.14018	0.08585		0.08289		32.43	−0.06
7.0	32.11	0.08404		0.05594	0.13998	0.08800		0.08402		32.12	+0.03
7.5	31.67	0.08513		0.05467	0.13980	0.09005		0.08510	3	31.68	+0.03
8.0	31.20	0.08597		0.05351	0.13948	0.09200		0.08599		31.19	−0.03
8.5	30.70	0.08663		0.05244	0.13907	0.09388		0.08667		30.69	−0.03
9.0	30.17	0.08717		0.05145	0.13862	0.09569		0.08714		30.17	±0.00
9.5	29.61	0.08765		0.05053	0.13818	0.09743		0.08755	2	29.63	+0.07
10.0	29.00	0.08822		0.04967	0.13789	0.09911		0.08816		29.01	+0.03
11.0	27.84	0.08894		0.04819	0.13713	0.10231		0.08906		27.82	−0.07
12.0	26.71	0.08947		0.04674	0.13621	0.10532		0.08956		26.70	−0.04
13.0	25.66	0.08955		0.04551	0.13506	0.10817		0.08967		25.64	−0.08
14.0	24.63	0.08965		0.04440	0.13405	0.11087		0.08941		24.66	+0.12
15.0	23.66	0.08971		0.04339	0.13310	0.11345		0.08977	4/3	23.65	−0.04
16.0	22.71	0.09018		0.04247	0.13265	0.11592		0.09011		22.71	±0.00
17.0	21.84	0.09029		0.04161	0.13191	0.11828		0.09030		21.84	±0.00
18.0	21.04	0.09019		0.04083	0.13102	0.12056		0.09036		21.03	−0.05
19.0	20.26	0.09046		0.04010	0.13056	0.12275		0.09030		20.27	+0.05
										mean	±0.21
20.0	19.53	0.09067				0.12487		0.09027	1	19.56	+0.15
30.0	14.41	0.08848				0.14294		0.09103		14.33	−0.56
40.0	11.28	0.09049				0.15732		0.08811		11.32	+0.35
50.0	9.30	0.08897				0.16947		0.08912	2/3	9.30	±0.00
60.0	7.90	0.08878				0.18009		0.08935		7.90	±0.00
80.0	6.07	0.08766				0.19822		0.08830		6.07	±0.00
90.0	5.44	0.08790				0.20615		0.08725		5.44	±0.00
100.0	4.93	0.08720				0.21352		0.08597		4.93	±0.00
										total mean	±0.20

isopentane at the temperature range of 170～200°C, the critical temperature being 187.8°C⁽2⁾.

Analysis of ε-V Curves

For the estimation of ε at each isotherm of isopentane, we take the following values: $T_c=187.8+273.16$°K, $p_c=25000$ mmHg (32.89 atm.), $d_c=0.2343\ \mathrm{cm^3\,g^{-1}}$, these values being quoted from the same observer's values on the border curve of this substance⁽3⁾, $M=72.151$, $R=82.06\ \mathrm{cm^3\,atm.\,deg^{-1}\,mol^{-1}}$, $\log a=6.9711254$, and $b=102.68\ \mathrm{cm^3\,mol^{-1}}$.

In the liquid portion below the critical temperature, it is highly probable as estimated that $\varepsilon\times V^{1/3}$ is constant at each isotherm, the mean values being 0.4674 (2.4～2.5), 0.4564 (2.4～2.7), 0.4513(2.4～2.8) and 0.4472(2.4～3.0) at 170, 176, 180 and 185°C, respectively, the numbers in the parentheses showing volume ranges in $\mathrm{cm^3\,g^{-1}}$, and so we have conducted similar operation on the ε values at and above the critical temperature, 187.8, 190, 195 and 200°C, their mean values being 0.4455(2.4～3.0), 0.44305(2.4～3.0), 0.4376(2.4～2.8) and 0.4320 (2.5～2.6), respectively. These constants are denoted by c_1's.

All these values except that at 170°C, multiplied by each temperature in the absolute scale T, gave a constant value 204.89 ± 0.34 (0.17% probable error), and therefore each value can be written as $204.89/T$. Let ε in the liquid portion be denoted by ε_1, then ε_1 is the product of the above obtained value at each isotherm by $V^{-1/3}$ or is briefly expressed by $204.89/TV^{1/3}$. In the region of liquid and gaseous coexistence, however, ε may become very complicated as supposed from the critical isotherm stated above, so we will make trial by taking the sum of ε_1 and ε in this region to search for ε in gaseous form in this region which is denoted ε_g. Unfortunately as Young's data are lacking in this region, we are obliged to study the functional form of ε_g in the isotherms of from 187.8 to 200°C, above which the constant range of $\varepsilon\times V^{1/3}$ in the liquid portion apparently disappears.

As seen from Table I, the values of $(\varepsilon_1+\varepsilon_{\mathrm{obs}})$ decrease at first, then approach nearly a constant, and again decrease.

For a supplementary test we will quote from the later PVT-measurements⁽4⁾ on neopentane by Beattie, Douslin and Levine together with their earlier measurements⁽5⁾ at 160.50～160.70°C, the critical temperature being 160.60°C already treated (see Table II). The constancy of $\varepsilon\times V^{1/3}$ in the liquid portion, $V=142.9\sim222.2\ \mathrm{cm^3\cdot mol^{-1}}$, is not so good as those which appeared in Table I, yet we dare take their geometric mean values as 0.4246. The constant range in the region of coexistence distinctly occurs between 304.9 and $400\ \mathrm{cm^3\,mol^{-1}}$, their mean value being 0.13721, the range of which is a little beyond the upper limit of coexistence at 160.00°C as referred to Fig. 1 in the earlier paper of these observers.

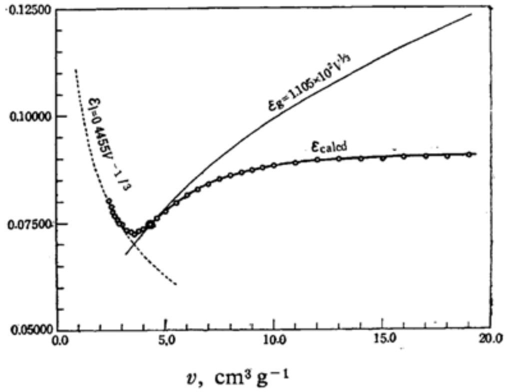

Fig. 1. ε-v Diagram of isopentane at 187.8°C.

The existence of a constant range of $(\varepsilon_1+\varepsilon_{\mathrm{obs}})$ as observed in this example has given us a clue for analyzing the first decreasing range up to a constant range: Putting the value $\varepsilon_{\mathrm{obs}}-\{(\varepsilon_1+\varepsilon_{\mathrm{obs}})-0.13721\}$, where $\varepsilon_1=0.4246V^{1/3}$, to be the form c_2V^n, n and c_2 being constants, we have obtained $n=1/3$ and $c_2=1.106\times10^{-2}$. Similar calculations have given us the respective values for isopentane as follows: $n=1/3$ for all the cases and c_2's are 1.105, 1.097, 1.081 and 1.064×10^{-2} at 187.8, 190, 195 and 200°C, respectively, and $c_2=1.1145\times10^{-2}$ at 185°C has been graphically obtained from the preceding values which are quite linear against temperature. At the critical temperature where $V=V_c$, for neopentane $1.106\times10^{-2}\ V_c^{1/3}$ ($V_c=303.0\ \mathrm{cm^3\,mol^{-1}}$) $=0.07429$, which is fairly coincident with the observed $\varepsilon=0.07411$, for isopentane $1.105\times10^{-2}\ V_c^{1/3}$ ($V_c=4.268\ \mathrm{cm^3\,g^{-1}}\times72.151=307.94$) $=0.07479$, which is also coincident with the observed $\varepsilon=0.07486$. Thus it is highly probable that the common form of $c_2V^{1/3}$ obtained above is no other than the required ε_g in each isotherm. This result shows us that in the critical isotherm $\varepsilon_1+\varepsilon_g=$ a constant for the volume range up to the critical volume, or in other words, the molecular complexities of liquid and gaseous states are in equilibrium for this range.

In the isotherms above the critical temperature, the same phenomenon is also observed,

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2) S. Young, *Proc. Roy. Dub. Soc.*, **12**, 374 (1910).

3) "International Critical Tables", Vol. III (1928), p. 244.

4) J. A. Beattie, D. R. Douslin and S. W. Levine, *J. Chem. Phys.*, **20**, 1619 (1952).

5) J. A. Beattie, D. R. Douslin and S. W. Levine, ibid., **19**, 948 (1951).

TABLE II. ISOTHERM OF NEOPENTANE, 160.50~160.70°C

V cm³ mol⁻¹	ε_{obs}	$\varepsilon_{obs} V^{1/3}$	ε_1	$\varepsilon_1+\varepsilon_{obs}$	$c_2\times10^2$	ε_g	$\varepsilon_1+\varepsilon_g$
142.9	0.06630	(0.3466)					
166.7	0.07382	0.4063					
200.0	0.07356	0.4302					
222.2	0.07231	0.4380					
		0.4246 geom. mean					
250.0	0.07210		0.06740	0.13950	1.108	0.06967	0.13707
259.7	0.07224		0.06655	0.13879	1.108	0.07056	0.13711
266.7	0.07242		0.06596	0.13838	1.107	0.07124	0.13720
270.3	0.07255		0.06565	0.13820	1.107	0.07151	0.13716
277.8	0.07283		0.06507	0.13790	1.106	0.07217	0.13724
285.7	0.07319		0.06447	0.13768	1.104	0.07284	0.13731
292.4	0.07352		0.06397	0.13749	1.103	0.07341	0.13738
298.5	0.07385		0.06353	0.13738	1.102	0.07392	0.13745
304.9	0.07421		0.06308	0.13729	1.106 mean		
312.5	0.07466		0.06257	0.13723			
319.5	0.07508		0.06211	0.13719			
328.8	0.07565		0.06152	0.13717			
333.3	0.07592		0.06124	0.13716	mean		
340.1	0.07634		0.06083	0.13717	0.13721		
357.1	0.07733		0.05985	0.13718			
363.6	0.07771		0.05949	0.13720			
370.4	0.07812		0.05912	0.13724			
377.4	0.07846		0.05875	0.13721			
400.0	0.07961		0.05763	0.13724			
500.0	0.08331		0.05349	0.13680			
666.7	0.08585		0.04860	0.13445			
1000.0	0.08701		0.04246	0.12947			

but the constant range becomes short and shifts to greater volume than the critical volume.

In these ranges ε_{calcd} can be estimated from a transformed relation: $\varepsilon_{calcd}=\varepsilon_{obs}-(\varepsilon_1+\varepsilon_g-\text{a constant})$, without doing the direct analysis of ε_{obs}. Next we consider ε-V curve beyond the critical volume. Since in the critical isotherm of isopentane $\varepsilon_g=1.105\times10^{-2}V^{1/3}$ coincides numerically with the observed ε in case $V=V_c$ and so $\varepsilon_1=0.4455\,V^{-1/3}$ vanishes as would be expected, we may put the change in molecular complexity in gaseous state to be the difference between the thus computed ε_g and ε_{obs} at the same volume, and assume that this difference is proportional to V^n, or $\varepsilon_{obs}=\varepsilon_g-c_3V^n$, n and c_3 being constants. This calculation necessitates dividing the ε-V curve into at least six parts: $n=4$ and $c_3=6.115\times10^{-14}$ (6.0~7.0), $n=3$ and $c_3=3.124\times10^{-11}$ (7.5~9.0), $n=2$ and $c_3=2.103\times10^{-8}$ (9.5~14), $n=4/3$ and $c_3=2.131\times10^{-6}$ (15~19), $n=1$ and $c_3=2.398\times10^{-5}$ (20~40), and $n=2/3$ and $c_3=3.416\times10^{-4}$ (50~100), the parentheses being volume range in cm³ g⁻¹. Similarly n's and c_3's of other isotherms have been obtained with expected results. For an example of the above results, we adopt from Table I (critical isotherm) with Fig. 1, in which ε_{obs} is denoted by ○, ε_{obs} at the critical point by ◎, ε_{calcd} by a thick line, $\varepsilon_1=0.4455\cdot V^{-1/3}$ and $\varepsilon_g=1.105\times10^{-2}V^{1/3}$ by dotted and fine lines respectively.

Discussion of the Results

Ishikawa's equation of state, though it is superior to most of the hitherto published equations of state, does not hold quantitatively in the critical region, so long as ε is assumed to be a constant throughout the whole range of volume. However, if we consider it to consist of sets of volume functions having one (c_1 for the liquid portion) or two (c_1 and c_2, c_2 and c_3 for the coexistence and gaseous portions) constants analytically obtained from ε_{obs}, his equation holds for a certain range of volume during which the same molecular complexity continues.

In the liquid portion the increase in $V^{1/3}$ or in average molecular distance (if it is assumed that a molecule is spherical with a diameter σ, $V=\pi\sigma^3N/6$ where N=Avogadro's number, and average molecular distance is the distance between the centers of the nearest molecules) causes the decrease in ε, this being consistent with the ordinary physico-chemical conception, whereas in the liquid and gaseous coexistence portion up to the critical volume the increase in average molecular distance causes the decrease in ε of liquid form, ε_l, and at the same time the increase in ε of gaseous form, ε_g, this being a case which is usually explained by the LeChatelier principle of mobile equilibrium. In the gaseous portion the decreasing rate from ε_g is propotional to the nth power of average molecular distance thus: $n=12$ for 1.15～1.18 times, $n=9$ for 1.21～1.28 times, $n=6$ for 1.31～1.45 times, and $n=4$ for 1.50～1.67 times the average molecular distance at the critical point (9.95 Å according to the above assumption).

According to Warren's study[6] from Stewart's X-ray diffraction measurements on normal paraffins from pentane to pentadecane[7], the long-chain molecules are straight in liquids and neighboring molecules are roughly parallel, 5.65 Å apart from each other, as if it were the diffraction of diatomic molecules, and also according to Müller the diffraction ring in normal paraffins observed by Stewart is due to assemblages of molecules (cybotactic groups), the average distance of the nearest approach near their melting points being 4.5～5.0 Å[8]. As computed from the relation $A=(1+3V_c^{\iota})/4$, the molecular association factors of neopentane, isopentane and n-pentane at their critical points are estimated to be 1.395, 1.402 and 1.471, respectively, the last being the value quoted from the critical constants measured by Beattie, Levine and Douslin[9]. These values are near to slightly polar substances such as methyl acetate (1.45), ethyl acetate (1.46) and propyl acetate (1.47) than to diatomic molecules such as nitrogen (1.29), oxygen (1.20), chlorine (1.35) and bromine (1.30). As a summery of the present analyses, we give in columns 10 and 11 in Table I the thus computed pressures, p_{calcd}, and their percentage deviations from the observed pressures, p_{obs}. On the whole, these deviations are so small that they are supposed to be experimental errors, since they are within less than 0.27% on the average up to 19～20 cm^3g^{-1}.

It is worth mentioning that Ishikawa's equation of state to which the thus suitable analyses are applied yields no such discrepancy from experiments in the critical region as all other equations of state generally do. Fig. 2 shows the comparison of Ishikawa's equation adopted from Table I (thick line, 0.21% deviation up to 19 cm^3g^{-1}) with Katayama's equation[10] (fine line, 1.81% deviation up to 20 cm^3g^{-1}) and Baba's equation[11] (dotted line, 1.96% deviation up to 19 cm^3g^{-1}) which were applied by themselves to the same Young's data of isopentane.

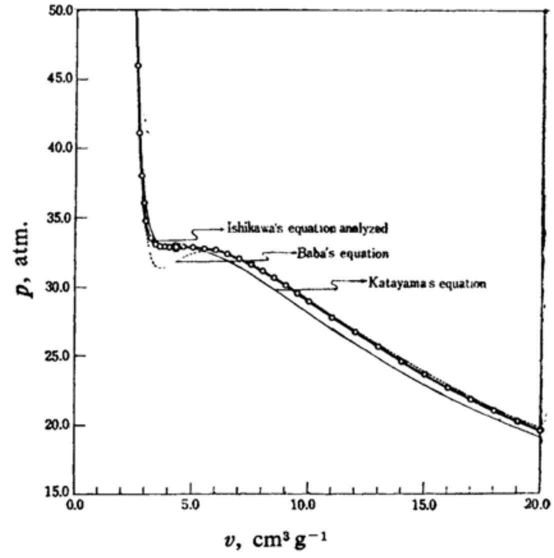

Fig. 2. Critical isotherm of isopentane.

Conclusion

The above results lead to the following conclusions (1) that liquid associated molecules still exist at least 12°C above the critical temperature, and that they are assembled up to the critical volume, as judged from the coexistence condition for liquid and gaseous states: $\varepsilon_l+\varepsilon_g=$ a constant, where $\varepsilon_l=c_1V^{-1/3}$ and $\varepsilon_g=c_2V^{1/3}$, the former corresponding to the functional form of ε for liquid assemblages and the latter to the base functional form of ε for gaseous assemblages, (2) that gaseous associated molecules exist from the lower point on the border curve to the gaseous region, and are disassembled from the base functional form proportional to the average distance stepwise with volume increase by van der Waals' forces of the 12th, 9th, 6th, 4th, 3rd and 2nd powers of average distance for their respective volume ranges, and therefore (3) that the nature of the p-V curve is, from the analytical standpoint of view, not continuous but discontinuous, and a clear difference in the functional forms between ε_l and ε_g, and

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6) B. E. Warren, *Phys. Rev.*, **44**, 969 (1933).

7) G. W. Stewart, *Proc. Natl. Acad. Sci.*, **13**, 787 (1927); *Phys. Rev.*, **31**, 174 (1928).

8) A. Müller, *Trans. Faraday Soc.*, **29**, 990 (1933).

9) J. A. Beattie, S. W. Levine and D. R. Douslin, *J. Am. Chem. Soc.*, **74**, 4778 (1952).

10) M. Katayama, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **43**, 609 (1922).

11) T. Baba, *J. Technol. Res. Kantogakuin Univ.*, **5**, 1 (1960).

the disappearance of the former at the critical volume is a strong proof contrary to the hitherto accepted conception of continuity of liquid and gaseous states.

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