Some Remarks on the New Equation of State as Applied to the Critical Region

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The indefiniteness of the critical state has been an interesting question for as long a time as since 1880, but the exact nature of the critical point does not yet seem to be established. The shape and the degree of flatness of the isotherms in the critical region are not those predictable from a van der Waals' type of equation which is conditioned by $(\partial p/\partial V)_{T=T_c}=0$, $(\partial^2 p/\partial V^2)_{T=T_c}=0$, and $(\partial^3 p/\partial V^3)_{T=T_c}=0$, but could be reconciled with either of the current theories: (1) Mayer-Harrison's "derby hat" theory[1] which predicts below the true critical temperature, T, flat, horisontal isotherms above the temperature of meniscus disappearance, T_m; (2) Rice's modified "derby hat" theory[2] which predicts a flat, horizontal critical isotherm with linear but sloping isotherms immediately above T_c; and (3) Zimm's singular point theory[3] which describes the critical point as a singularity at which not only $(\partial p/\partial V)_{T=T_c}=0$, $(\partial^2 p/\partial V^2)_{T=T_c}=0$, but also all the higher derivatives are zero. The precise pVT measurements in the critical region of xenon done by Habgood and Schneider[4], however, offer no support for Mayer-Harrison's theory since there is no obvious region of flat, horizontal isotherms above T_m, and also for Rice's theory since the observed coexistence border curve appears to be definitely rounded at the apex.

The present author[5] put forward a modified form of van der Waals' equation available for both gaseous and liquid phases:

$$p+a/V^{2-\epsilon}=RT/(V-b),\ a=3p_cV_c^2,\ b=V_c/3,$$

where ϵ is a constant independent of pressure to the extent that the applied pressure affects no appreciable change in molecular association.

The introduction of ϵ into van der Waals' equation is sufficient to allow the critical factor, RT_c/p_cV_c, to be consistent with experiments, i.e., the reduced equation at the critical point, $RT_c/p_cV_c=2(1+3V_c^{\varepsilon})/3$, $\varepsilon=0.077\pm0.008$ when V is expressed in cc./mol., is valid for 66 kinds of normal and slightly polar substances, but such transformation of equation results in separating a simple van der Waals' critical point, which is conditioned by either of $b=V_c/3$ or $b=RT_c/8p_c$ with $a=27p_cb^2$, into a maximum and a minimum with never realizable portion, $\partial V/\partial p>0$, and with supersaturated vapour portion, the former being supposed to correspond with generally accepted phenomena in the liquid-vapour coexistence region. The divergency in the portion of $(\partial V/\partial p)_{T=T_c}>0$ may be saved, if the critical point is assumed to be the limiting case of liquid-vapour coexistence region by combining the equation of critical isotherm, $p+a/V^{2-\varepsilon}=RT_c/(V-b)$, with the horizontal line passing through the critical pressure, $p_c=3RT_c/2V_c(1+3V_c^{\varepsilon})$, where ε is not the value at the critical point, but the mean at the critical isotherm, provided that the continuity of state is true.

It is the fact, however, that there occurs no appreciable difference between ε at the critical point and the mean of ε values in the critical region, e.g., from Habgood and Schneider's data of xenon at the critical point, $t_c=16.590$°C, $p_c=57.636$ atm., and $d_c=1.099$ g./cc., ε is evaluated to be 0.06932, whereas the mean of ε values out of 29 measurements in their observed density range of 0.91503 to 1.30705 g./cc. is 0.06941; also from their preliminary data[6], the mean of ε values out of 16 measurements in the density range of 0.9934 to 1.2463 g./cc., for the range of which a meniscus is expected to disappear, is 0.06932; again from Beattie, Douslin, and Levine's data[7] for neopentane, $C(CH_3)_4$, ε at the critical point, $t_c=160.60$°C, $p_c=31.57$ atm., and $V_c=303$ cc./mol., is 0.07411, whereas the mean of ε values out of 17 measurements in their observed volume range of 259.7 to 377.4 cc./mol. is 0.07495.

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[1] T. E. Mayer and S. F. Harrison, *J. Chem. Phys.*, **6**, 87, 101 (1938).

[2] O. K. Rice, *J. Chem. Phys.*, **15**, 314 (1947).

[3] B. H. Zimm, *J. Chem. Phys.*, **19**, 1019 (1951).

[4] H. W. Habgood and W. G. Schneider, *Can. J. Chem.*, **32**, 98 (1954).

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

[6] W. G. Schneider and H. W. Habgood, *J. Chem. Phys.*, **21**, 2080 (1953).

[7] J. A. Beattie, D. R. Douslin and S. W. Levine, *J. Chem. Phys.*, **19**, 948 (1951).

In the present case, to evaluate p(atm.) against a given V(cc./mol.) from the new equation of state, we take ε's at the respective critical points: for Xe, $2-\varepsilon=1.93068$, $b=V_c/3=39.82$cc./mol., $\log a=6.3923491$, and $T_c=16.590+273.16$°K; and for $C(CH_3)_4$, $2-\varepsilon=1.92589$, $b=101.0$ cc./mol., $\log a=6.9392811$, and $T_c=160.60+273.16$°K, their results being illustrated (in full line) with the observed pressures (circles) in Fig. 1 and Fig. 2, in which are also shown, for the sake of comparison, the curves from van der Waals' equation (in dotted line) by putting $b=RT_c/8p_c=51.57$ cc./mol., $\log a=6.6168073$ for Xe, and $b=140.93$ cc./mol., $\log a=7.2286712$ for $C(CH_3)_4$.

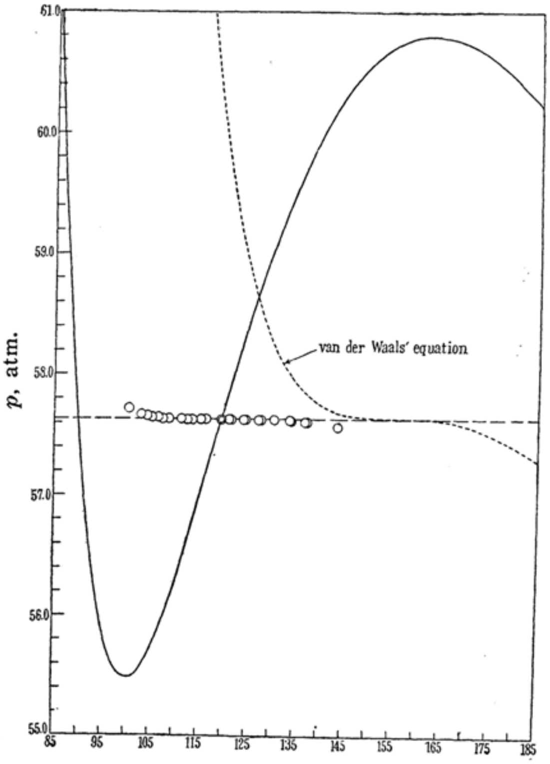


Fig. 1. p-V Diagram of xenon at the critical temperature.

As seen from Figs. 1 and 2, it can be acknowledged (1) that the inflection point in the portion of $(\partial p/\partial V)_{T=T_c}>0$ nearly coincides with the actual critical point (double circle), (2) that the minimum point is situated near the least volume in the liquid-vapour critical region, (3) that the maximum point is situated at the critical volume corresponding to van der Waals' equation ($b=RT_c/8p_c$), and (4) that the liquid-vapour critical region is the horizontal line which passes through the inflection point and ends close to the corresponding volumes of the maximum and the minimum.

With these consistent results for both cases, one is not able to deny the fact that the new equation has some intimate relationship with the actual state, but one can not elucidate any more, so long as $(2-\varepsilon)$ in the critical region is assumed to keep constant, so that, in the following case, we shall analyze the variation of ε with respect to the volume.

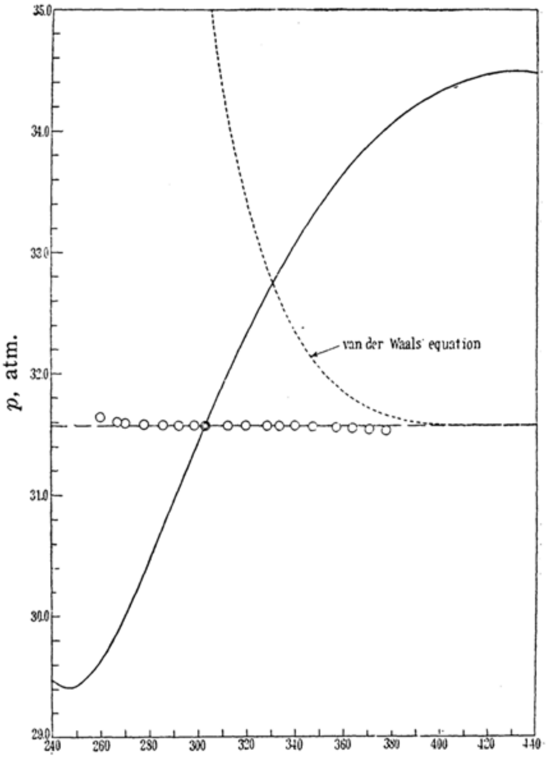
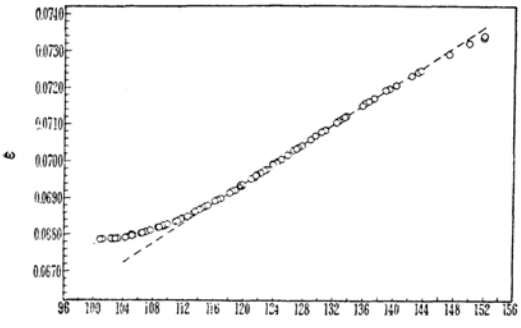


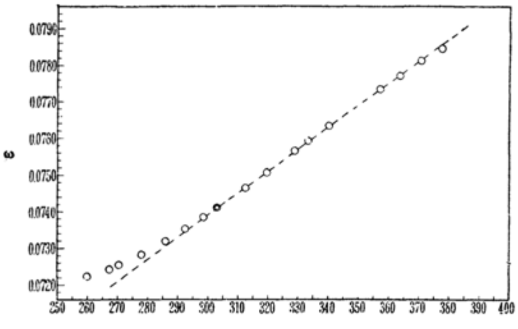
Fig. 2. p-V Diagram of neopentane at the critical temperature.

For each substance, isothermal ε values at the critical temperature and at most 0.10° above and below the critical temperature have been computed from the measurements of the same workers cited above (see Tables I and II), and are diagrammatically shown in Figs. 3 and 4. As seen from Figs. 3 and 4, ε values within these temperature ranges seem to converge upon the respective unique curves, which are quite similar with each other, and each curve appears to consist of three parts, the first part being concave up to the critical point (double circle), or more precisely speaking, at first horizontal, or probably a minimum which is situated at the corresponding volume of the minimum



V, cc./mol.

Fig. 3. ε-V Diagram of xenon in the critical region.



V, cc./mol.

Fig. 4. ε-V Diagram of neopentane in the critical region.

TABLE I

ISOTHERMAL ε VALUES OF XENON IN THE CRITICAL REGION

16.550°C		16.585°C		16.590°C		16.590°C	
V cc./mol.	ε	V cc./mol.	ε	V cc./mol.	ε	V cc./mol.	ε
102.27	0.06789	100.90	0.06787	100.46	0.06785	100.87	0.06786
104.33	0.06794	102.68	0.06789	104.30	0.06792	102.94	0.06787
106.44	0.06804	104.82	0.06793	106.48	0.06804	105.13	0.06797
108.62	0.06819	107.02	0.06807	108.74	0.06819	107.46	0.06811
110.94	0.06836	109.37	0.06825	111.16	0.06837	109.90	0.06828
113.36	0.06859	111.91	0.06847	113.50	0.06862	112.47	0.06849
115.87	0.06887	114.44	0.06872	116.18	0.06893	115.22	0.06879
118.49	0.06919	116.87	0.06900	118.83	0.06922	118.09	0.06914
121.13	0.06953	119.83	0.06937	121.61	0.06959	120.95	0.06950
123.94	0.06990	122.78	0.06973	124.40	0.06994	123.94	0.06989
126.75	0.07026	125.87	0.07014	127.33	0.07036	127.09	0.07032
129.65	0.07066	129.04	0.07056	130.30	0.07076	130.32	0.07076
132.66	0.07106	132.40	0.07102	133.58	0.07117	133.71	0.07120
135.80	0.07149	135.84	0.07148	136.64	0.07159	137.36	0.07168
138.95	0.07190	139.45	0.07194	143.49	0.07246		
		143.35	0.07244				
		147.20	0.07289				

16.600°C		16.620°C		16.490°C		16.690°C	
V cc./mol.	ε	V cc./mol.	ε	V cc./mol.	ε	V cc./mol.	ε
101.17	0.06787	103.27	0.06791	103.25	0.06790	103.25	0.06790
103.09	0.06789	105.32	0.06797	111.44	0.06844	111.44	0.06842
105.11	0.06798	107.43	0.06810	114.83	0.06877	114.83	0.06875
107.26	0.06808	109.61	0.06823	119.70	0.06937	119.70	0.06931
109.41	0.06824	111.97	0.06847	121.68	0.06961	121.68	0.06958
111.66	0.06842	114.39	0.06870	123.05	0.06979	123.05	0.06975
114.08	0.06867	116.90	0.06898	136.27	0.07156	136.27	0.07151
116.52	0.06895	119.53	0.06935	151.89	0.07336	151.89	0.07339
119.05	0.06926	122.21	0.06965	175.21	0.07563	175.21	0.07558
121.78	0.06960	125.04	0.07003				
124.53	0.06996	127.86	0.07040				
127.29	0.07034	130.69	0.07079				
130.12	0.07071	133.63	0.07119				
133.06	0.07112	136.82	0.07162				
136.03	0.07151	140.25	0.07204				
142.25	0.07230	143.21	0.07241				
		149.83	0.07320				

TABLE II

ISOTHERMAL ε VALUES OF NEOPENTANE IN THE CRITICAL REGION

V cc./mol.	160.50°C	160.58°C	160.60°C	160.62°C	160.70°C	mean
			ε			
259.7	0.07224	0.07224	0.07224	0.07223	0.07223	0.07224
266.7	0.07243	0.07243	0.07242	0.07242	0.07241	0.07242
270.3	0.07255	0.07255	0.07255	0.07355	0.07253	0.07255
277.8	0.07283	0.07283	0.07283	0.07283	0.07282	0.07283
285.7	0.07320	0.07319	0.07319	0.07318	0.07317	0.07319
292.4	0.07353	0.07353	0.07352	0.07352	0.07351	0.07352
298.5	0.07386	0.07385	0.07384	0.07385	0.07383	0.07385
304.9	0.07423	0.07422	0.07422	0.07421	0.07419	0.07421
312.5	0.07467	0.07467	0.07466	0.07466	0.07465	0·07466
319.5	0.07509	0.07509	0.07508	0.07508	0.07504	0.07508
328.8	0.07566	0.07566	0.07565	0.07565	0.07562	0.07565
333.3	0.07594	0.07593	0.07593	0.07592	0.07590	0.07592
340.1	0.07639	0.07635	0.07633	0.07633	0.07631	0.07634
357.1	0.07735	0.07735	0.07733	0.07731	0.07730	0.07733
363.6	0.07773	0.07772	0.07771	0.07770	0.07767	0.07771
370.4	0.07814	0.07813	0.07812	0.07811	0.07808	0.07812
377.4	0.07850	0.07847	0.07846	0.07845	0.07844	0.07846

of p-V curve, and finally a nearly straight line, the second part being undoubtedly a long straight line starting from the critical point, or in other words, at the critical point, the second, third, and higher derivatives of ε with respect to the volume appear to be zero, and the third part being convex up to the maximum corresponding to the volume at which the other form of van der Waals' equation ($b=V_c/3$) takes the critical pressure. The volume coincidences of the minimum with the minimum of p-V curve, and of the maximum with the inflection point of this form of van der Waals' equation have been confirmed by making use of Beattie, Barriault, and Brierley's data⁽⁸⁾ for Xe, and of Beattie, Douslin, and Levine's data⁽⁹⁾ for $C(CH_3)_4$. On the whole, it is clear that in the critical region $(\partial\varepsilon/\partial V)_T$ is always positive.

According to the Le Chatelier principle of mobile equilibrium⁽¹⁰⁾, if the volume occupied by the molecules is increased, the state will tend to occur in the direction of increased number of molecules, or, if molecular association⁽¹¹⁾ is taken into account, in the direction of diminishing the degree of molecular association which will result in pressure increase, whereas in the critical region where the pressure is, by experience constant over a finite volume range, the state will occur to increase the degree of molecular association, i.e., to increase ε which depends on molecular association, so as to annul, as far as possible, the effect of volume increase, and if so, so long as a differential shift of ε occurs to be proportional to a differential shift of V in the same direction, the pressure will continue to be constant, or in other words, $(\partial^2\varepsilon/\partial V^2)_T=0$, $(\partial^3\varepsilon/\partial V^3)_T=0$, and so on at the critical point should be the necessary condition that the pressure in the critical region is constant over a finite volume range.

That the above condition is satisfied can clearly be acknowledged by comparing the observed constant pressure range in Fig. 1 or 2 with the straight line portion in Fig. 3 or 4 for each substance, and at the same time, the fact that there occurs no change of ε with respect to the volume just above and below the critical temperature in each case is a strong proof of the existence of a critical region, at least, within 0.10°C above the critical temperature.

The maximum point of ε which appears in the supersaturated vapour portion has been estimated to have the value of 14.4% increase for Xe, and the value of 17.5% increase for $C(CH_3)_4$ as referred to the respective critical values, each maximum corresponding to $V=341.62$ cc./mol. and $V=975.3$ cc./mol. respectively as computed from van der Waals' equation ($b=V_c/3$).

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(10) H.L. Chatelier, *Compt. rend.*, **100**, 441 (1885).

(11) refer to T. Ishikawa, This Bulletin, **27**, 570 (1954).