

Reprinted from: VOLUME 63 (1973) No. 3

PHYSICA

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EUROPHYSICS JOURNAL

NORTH-HOLLAND AMSTERDAM

AN EQUATION FOR THE CRITICAL ISOTHERM OF REAL GASES

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Received 27 April 1972

Synopsis

Modern ideas about the behaviour of fluids near the critical point lead to a description of the nonanalytic character of that point as an approximation in terms of an expansion around it. In this paper an extension for the equation of the critical isotherm from the critical point to the ideal gas and up to high densities is proposed. The exponent δ_0 and the coefficient D_0 of the critical isotherm are related to the second virial coefficient and to the real-gas factor. These relations are compared with experimental values of several substances. Special calculations are made in the pressure range from zero to 1000 bar for water and up to 1400 bar for CO_2 .

Recently there has been some interest in the equation of state describing not only the nonanalytic asymptotic scaling behaviour very near the critical point but also giving higher-order corrections important further away from the critical point^{1,2}). The scaled equation of state has been used successfully to describe the critical region of several substances³). However, this description is valid only within a range of 30 per cent of the reduced density $(\varrho - \varrho_c)/\varrho_c$ and 1 to 3 per cent of the reduced temperature $(T - T_c)/T_c$. For theoretical and practical purposes it would be desirable to have an equation of state valid in the whole fluid range from the ideal gas to high densities and giving the nonanalytic scaling behaviour near the critical point as a first approximation in terms of an expansion around it. As a first step, in the present paper a simple formula is proposed for the pressure as a function of density at the critical isotherm from zero density up to the critical and higher densities. The asymptotic exponent δ_0^* of the critical isotherm is related to the second virial coefficient and to the real-gas factor $\sigma = \varrho_c T_c R/P_c$.

The critical isotherm in the neighbourhood of the critical point is given by:

$$\Delta p = D_0 |\Delta \varrho|^{\delta_0 - 1} \Delta \varrho, \quad (1)$$

* In this paper we use the index 0 for the critical exponent exactly at T_c and ϱ_c .

with the reduced pressure difference $\Delta p = (P - P_c)/P_c$ and the reduced density difference $\Delta \varrho = (\varrho - \varrho_c)/\varrho_c$. In the usual way the critical exponent δ_0 is defined as:

$$\delta_0 = \lim \left(\frac{d(\ln \Delta p)}{d(\ln \Delta \varrho)} \right) \quad \text{for} \quad \Delta \varrho \rightarrow 0. \quad (2)$$

This exponent is only valid in a range very near the critical density and it should not be expected that δ_0 is constant over a larger density range. Therefore one can define more generally a density-dependent exponent and propose this equation for the critical isotherm:

$$\delta(\Delta \varrho) = \frac{d(\ln \Delta p)}{d(\ln \Delta \varrho)} = \frac{\Delta \varrho}{\Delta p} \frac{d\Delta p}{d\Delta \varrho}. \quad (3)$$

As is known⁶), a plot of $\ln \Delta p$ versus $\ln \Delta \varrho$ yields approximately straight lines over a large density range, therefore one should expect that $\delta(\Delta \varrho)$ is a simple function of the density.

As a limiting value at zero density, $\Delta \varrho = -1$, from the ideal-gas law in reduced form one finds:

$$\Delta p + 1 = (\varrho_c T_c / P_c) R (\Delta \varrho + 1) (\Delta T + 1), \quad \text{with} \quad \Delta T = (T - T_c) / T_c. \quad (4)$$

At the density $\Delta \varrho = -1$, $\Delta p = -1$ and at the critical isotherm $\Delta T = 0$ we get:

$$\delta(\Delta \varrho = -1) = (\varrho_c T_c / P_c) R = \sigma. \quad (5)$$

For most fluids the real-gas factor σ is between the value 3.3 for He and 4.28 for H_2O . Using, for low densities, the equation of state in virial expansion:

$$p = \varrho RT (1 + B_r \varrho + C_r \varrho^2 + \dots), \quad (6)$$

we get for $\Delta T = 0$ the first and second derivatives of $\delta(\Delta \varrho)$ at $\Delta \varrho = -1$:

$$\left(\frac{d\delta}{d\Delta \varrho} \right)_{\Delta \varrho = -1} = \sigma (2B_c \varrho_c + \sigma - 1), \quad (7)$$

and

$$\left(\frac{d^2 \delta}{d\Delta \varrho^2} \right)_{\Delta \varrho = -1} = \sigma [3C_c \varrho_c + B_c \varrho_c (3\sigma - 2) + \sigma (\sigma - 1)], \quad (8)$$

with B_c and C_c as the second and third virial coefficients at the critical temperature.

To get more information about $\delta(\Delta \varrho)$, for CO_2 δ was calculated from the data of refs. 4 and 5 and the values obtained were plotted in fig. 1. Very near the critical

point the values are uncertain because Δp goes to zero and the possible error in Δp could be as large as its value. In the range $-0.05 < \Delta \varrho < 0.05$ there are values from optical measurements⁶⁾ of density *versus* height at the critical temperature. In this figure, for densities between $\Delta \varrho = -1$ and the critical value, $\delta(\Delta \varrho)$ is well approximated by a straight line fulfilling condition (5):

$$\delta(\Delta \varrho) = \delta_0 + (\delta_0 - \sigma) \Delta \varrho. \quad (9)$$

Assuming that eq. (9) is correct, with the help of eqs. (9) and (3) an equation for the critical isotherm is obtained which is valid from the ideal-gas state to the critical density:

$$\Delta p = \text{sign}(\Delta \varrho) \Delta \varrho^{\delta_0} \exp[(\delta_0 - \sigma)(\Delta \varrho + 1)]. \quad (10)$$

So the asymptotic coefficient D_0 of the critical isotherm (1) is given by

$$D_0 = \exp(\delta_0 - \sigma). \quad (11)$$

In table I D_0 is determined from eq. (11) and compared with values obtained for several fluids from various analyses of the experimental data. The agreement is good for the simple fluids ^3He , ^4He , Xe, CO_2 and the polar fluid H_2O . Any change of δ_0 will cause a corresponding change in D_0 .

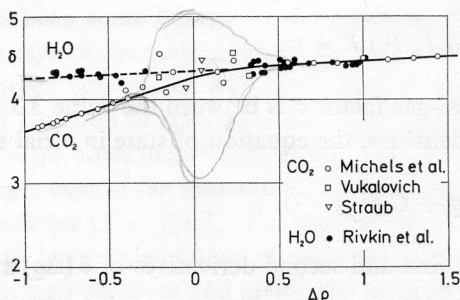


Fig. 1. "Exponent" $\delta(\Delta \varrho) = d(\ln p)/d(\ln \Delta \varrho)$ *versus* $\Delta \varrho$ for CO_2 and H_2O .

Assuming that $\delta(\Delta \varrho)$ is linear in the range $-1 \leq \Delta \varrho \leq 0$ with the slope $(\delta_0 - \sigma)$, the second virial coefficient at T_c follows from eq. (7):

$$B_c = (1/2\varrho_c) [(\delta_0/\sigma) - \sigma]. \quad (12)$$

Likewise, we find for the critical exponent:

$$\delta_0 = \sigma(2B_c\varrho_c + \sigma). \quad (13)$$

TABLE I

Comparison of the critical coefficient $D_0 \text{ exp.}$ with values calculated from eq. (11).

Substance	σ	δ_0	$D_0 \text{ exp.}$	$D_0 \text{ eq. (11)}$	Refs. for δ_0 and $D_0 \text{ exp.}$
^3He	3.297	4.23	2.77	2.54	7
		4.16	2.42	2.37	2
^4He	3.306	4.45	3.2	3.15	8
		4.44	3.14	3.12	3
Xe	3.452	4.6	3.3	3.16	8, 3
CO_2	3.636	4.6	2.60	2.61	8
		4.47	2.32	2.30	3
H_2O	4.28	4.324	1.046	1.046	9

If the last assumption is correct, with the help of eq. (8) the third virial coefficient for T_c can be expressed by:

$$C_c = (1/3\varrho_c^2) [B_c\varrho_c (2 - 3\sigma) - \sigma(\sigma - 1)]. \quad (14)$$

Eqs. (12) and (13) are tested with virial coefficients for a number of fluids at T_c as reported by Straub^{10,11}). The critical exponent δ_0 calculated by eq. (13) is between 4 and 4.3 for most fluids (table II). Only for H_2 , N_2 and H_2O are the deviations greater. The real-gas factor σ depends on the critical values T_c , P_c and ϱ_c . The uncertainty in the density is up to 5% in some cases. The second virial coefficient is uncertain within a few per cent. Table II shows also the comparison of the second virial coefficient B_c of several fluids with coefficients calculated with eq. (12) by assuming a "universal" critical exponent $\delta_0 = 4.2$. The deviations are within a range of 2% except for H_2 , N_2 , C_7H_{12} and H_2O . For some fluids the third virial coefficient C_c is available¹⁰) and the deviations from eq. (14) are for most fluids within a 10% limit. The accuracy of C_c from theoretical calculations or from measurements is in most cases not better than the values obtained by eq. (14).

For H_2O a special calculation was made with the experimental data^{12,13}). The exponent $\delta(\Delta\varrho)$ is also plotted *versus* $\Delta\varrho$ in fig. 1 and one obtains a straight line between the ideal-gas state and high densities. With $\delta_0 = 4.324$ and $\sigma = 4.28$ the critical isotherm can be represented with eq. (10) from the ideal-gas state up to 1000 bar⁹). This result is in good agreement with the skeleton tables for water¹⁴). The coefficient D_0 is in this case 1.046. For the exponent of the coexistence curve we found $\beta_0 = 0.35$ and for the exponent of the compressibility along the critical

TABLE II

Calculation of the second and third virial coefficient and the critical exponent δ_0 with eqs. (12), (13), (14) and comparison with experimental values from ref. 10

Substance	T_c (K)	P_c (bar)	ρ_c $\left(\frac{\text{mol}}{\text{cm}^3} \times 10^{-3}\right)$	σ	$-B_{c \text{ exp.}}$ from ref. 10 (cm^3/mol)	$-B_{c \text{ cal.}}$ from eq. (12) with $\delta_0 = 4.2$ (cm^3/mol)	$\frac{B_{\text{exp.}} - B_{\text{cal.}}}{B_{\text{exp.}}}$ (%)	δ_0 from eq. (13)	$C_{c \text{ exp.}}$ from ref. 10 (cm^6/mol^2)	$C_{c \text{ cal.}}$ from eq. (14)
⁴ He	5.1983	2.27464	17.399	3.306	59.2	58.5	1.2	4.12	1160	586
n H ₂	33.250	12.970	15.385	3.279	69.4	64.9	6.4	3.75	1540	1260
p H ₂	32.976	12.928	15.59	3.306	69.5	65.3	6.0	3.77	1527	1311
N ₂	126.15	34.05	11.1	3.419	103.5	98.7	4.7	3.84		
Ar	150.65	48.55	13.317	3.435	85	83.1	2.2	4.03	2220	1946
Xe	289.74	58.40	8.416	3.471	138.6	134.4	3.0	3.95		
CH ₄	190.7	46.07	10.14	3.486	114	112.5	1.3	4.09		
C ₂ H ₆	305.40	48.839	6.929	3.602	177	175.81	0.7	4.14		
C ₂ H ₄	282.65	50.640	7.699	3.573	158	155.7	1.5	4.07		
C ₄ F ₈	388.48	27.78	3.099	3.586	395	389.6	1.3	4.07	7800	7943
C ₃ H ₈	369.96	42.57	5.006	3.617	242	245.3	-1.4	4.33	46400	50506
SF ₆	318.71	37.60	5.15	3.623	241	239.2	0.7	4.14		
N ₂ O	309.57	72.55	10.28	3.646	122	121.4	0.5	4.16	5300	4887
C ₂ F ₃ Cl ₃	487.25	34.15	3.08	3.638	406	403.2	0.7	4.14		
CO ₂	304.19	73.81	10.63	3.636	118	117.1	0.8	4.14	4070	4608
n-C ₄ H ₁₀	425.16	37.97	3.928	3.657	321	319.3	0.5	4.20	31200	33312
neo C ₅ H ₁₂	433.76	31.57	3.25	3.663	383	387.1	-1.0	4.16		
SO ₂	430.65	78.84	8.173	3.711	156	157.8	-1.2	4.31		
n-C ₅ H ₁₂	469.77	33.75	3.20	3.704	400	401.8	-0.4	4.21		
C ₆ H ₅ F	560.19	44.91	3.69	3.802	360	365.5	-1.5	4.38	48000	44303
n-C ₇ H ₁₂	540.2	27.0	2.34	3.844	566	587.9	-3.9	4.6		
H ₂ O	647.06	220.89	17.6	4.28	84.2	93.5	-10	5.6	1570	2167

isochore $\gamma_0 = 1.16$. These values fulfil the scaling relation:

$$\gamma_0 = \beta_0 (\delta_0 - 1). \quad (15)$$

For fluids with a smaller value of σ the slope of $\delta(\Delta\varrho)$ changes at the critical density to a smaller but seemingly constant value. Actually one might assume $\delta(\Delta\varrho)$ to be a hyperbolic function which can be approached by two straight lines with different slopes. Indeed, we get the best least-squares fit of the CO_2 data with separate exponents and coefficients for the low- and high-density range. This must not be in conflict with scaling. For the range $-1 \leq \Delta\varrho \leq 0$ we use eq. (10) with $\delta_0 = 4.2$ and $\sigma = 3.6362$ and for the range $0 \leq \Delta\varrho \leq 1.52$ we use

$$\Delta p = |\Delta\varrho|^{\delta_0} \exp(\delta_1 + \delta_2 \Delta\varrho), \quad (16)$$

with $\delta_0 = 4.425$, $\delta_1 = 0.9705$ and $\delta_2 = 0.05$. The standard error in this case is 1.5%. If one uses one equation for the whole density range, $-1 \leq \Delta\varrho \leq 1.52$, in which $\delta(\Delta\varrho)$ is expanded in a series, one gets the following expression for the critical isotherm:

$$\Delta p = \text{sign}(\Delta\varrho) |\Delta\varrho|^{\delta_0} \exp\left(\sum_{i=0}^n \delta_i \Delta\varrho^i\right). \quad (17)$$

In this case n must be 8 to get the same standard error as with eqs. (10) and (16).

It seems that for CO_2 the real value for the critical exponent δ_0 is between 4.2 and 4.4. If we choose $\delta_0 = 4.3$ and $\beta_0 = 0.348$ from ref. 15, we get, with the scaling relation (15) the compressibility exponent $\gamma_0 = 1.15$. This value is in agreement with the experimental value of White and Maccabee¹⁶⁾ who found $\gamma_0 = 1.17$, but lower than most published values. From the scaling relation

$$\beta_0 (\delta_0 + 1) = 2 - \alpha_0, \quad (18)$$

one gets the exponent of the isochoric specific heat $\alpha_0 = 0.155$. Buckingham *et al.*¹⁷⁾ found $\alpha_0 = 0.125$ and our own measurements¹⁸⁾ of the specific heat of CO_2 yield a value of $\alpha_0 = 0.14$. So a value of δ_0 near 4.3 is consistent with other measurements and the scaling law.

If the exponential function of eq. (17) is expanded in a series we find the higher-order terms of the critical isotherm to be $\delta_0 + 1$, $\delta_0 + 2$ and so on. Green, Cooper and Sengers¹⁾ found for the first term $\delta_0 + 1.6$ to $\delta_0 + 2.4$, Wallace and Meyer²⁾ $\delta_0 + (2 \pm 0.5)$. Assuming that the critical exponent δ_0 is for many substances between 4.0 and 4.4 we found that in the pressure-density plane the symmetry of the critical isotherm at the low- and high-density side depends on the critical real factor σ . So the symmetry for H_2O with a higher σ value is better than for CO_2 or ^4He with a lower value of σ . Eq. (10) appears to be a law of

corresponding states for the critical isotherm in the range from zero density to the critical density.

Acknowledgements. We would like to thank Dr. B. Widom for an invitation to a Gordon Conference last summer and the fruitful discussions there; and Dr. C. S. Kiang, Dr. D. Stauffer and J. Wise for useful suggestions and the hospitality during a visit to Clark College, Atlanta. Also Dr. J. M. H. Levelt-Sengers is kindly acknowledged for the revision of the manuscript.

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