

## **Selected Equation of State in the Acentric Factor System<sup>1</sup>**

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A new equation of state in the acentric factor system is developed on the basis of high-precision data. The region in  $T_r$ ,  $\rho_r$  space where there is good agreement is identified, as well as the regions of significant departures. The equation fits very well in the critical region.

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**KEY WORDS:** acentric factor; corresponding states; equation of state; virial coefficient.

### **1. INTRODUCTION**

The acentric factor has proven to be very useful in the representation or estimation of fluid properties. In comparison with earlier three-parameter systems extending corresponding states, there were two important advances. The first was the use of theory [1] to indicate the characteristics of molecules which could be expected to follow accurately a pattern of behavior defined by  $T_c$ ,  $P_c$ , and a third parameter. The second was the choice of an easily and accurately measurable quantity, the slope of the vapor pressure curve, as the basis for the third parameter [2]. Initially, the  $P$ - $V$ - $T$  and other properties were given in the form of tables [2, 3], although an analytical equation was soon developed for the second virial coefficient [4].

At the time of the original work, the best analytical equation of state failed to represent the experimental  $P$ - $V$ - $T$  behavior within experimental uncertainty [5]. Advances in electronic computers soon made it feasible, however, to use more complex equations, and various investigators have presented equations of state using the acentric factor. Some of these

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equations have limited ranges of validity or were intentionally simplified for convenience. But others do provide analytical equations of good accuracy and wide applicability, and of these we take that of Yamada [6] as the best example for comparison.

It is our purpose to revisit this subject with recognition of recent investigations of high precision. It was never pretended that an acentric factor equation would express the true equation of state of a particular fluid exactly. In 1955, however, the apparent discrepancies were within the experimental uncertainties for most, if not all, of those fluids expected to conform. It is now possible to determine the accuracy of conformity to the acentric factor theory, since the discrepancies exceed the uncertainties of recent measurements. Also, an equation can be selected which represents fluid behavior to the accuracy to which various individual fluids conform to the three-parameter acentric factor system.

Full details and references exceed the limit for this report and will be given elsewhere in a full account. The primary results and the selected equation are given below.

## 2. DATA SELECTION

From the theoretical analysis for the second virial coefficients [1], it was shown that most nonpolar molecules of various shapes and sizes conformed to three-parameter system. The very light gases  $H_2$ , He, and Ne had to be excluded because of quantum effects on their translational motion. Dipolar effects follow a somewhat different pattern. Molecules interacting primarily by dispersion (London) forces can be included, however, if their dipole or quadrupole moments are small. Excluded are strongly polar or hydrogen bonding molecules such as  $H_2O$ , alcohols, acids, etc.

For the present research, we included Ar, Kr, Xe, and all of the normal paraffins through octane together with a selection of other fluids of different molecular types within the criteria given above for which there were data of high precision.

Wherever there were recent critical compilations, the recommended values were adopted, e.g., those of Dymond and Smith [7] for second virial coefficients, of Rabinovich et al [8] for Ar, Kr, and Xe, and of Younglove and Ely [9] for the paraffins through butane. For several other fluids, original literature values were used. Table I lists the critical constants and acentric factors.

The acentric factor definition is

$$\omega = -\log P_r(\text{at } T_r = 0.7) - 1.000 \quad (1)$$

**Table I.** Critical Properties, Acentric Factors, and References for the Fluids Included in this Research

Fluid	$T_c$ (K)	$P_c$ (bar)	$\rho_c$ (mol · dm <sup>-3</sup> )	$\omega$
Argon	150.86	48.979	13.41	-0.004
Krypton	209.39	54.96	10.87	-0.002
Xenon	289.74	58.40	8.370	0.002
Methane	190.53	45.9797	10.15	0.011
Nitrogen	126.20	34.00	11.21	0.037
Ethylene	282.3452	50.403	7.634	0.087
Ethane	305.34	48.7143	6.875	0.100
Propylene	365.57	46.646	5.3086	0.141
Propane	369.85	42.4766	5.000	0.153
Tetrafluoromethane	227.527	37.45	7.1096	0.177
Neopentane	433.75	31.963	3.214	0.197
Butane	425.16	37.96	3.920	0.200
Sulfur hexafluoride <sup>a</sup>	318.70	37.590	5.067	0.208
Carbon dioxide	304.21	73.825	10.59	0.223
Pentane	469.69	33.64	3.215	0.252
Hexane	507.85	30.58	2.7105	0.303
Heptane	540.15	27.36	2.345	0.350
Octane	568.76	24.87	2.031	0.398

<sup>a</sup> Used only for the second virial coefficient calculation.

where  $P_r$  is the reduced vapor pressure at  $T_r = 0.7$ , but  $\omega$  can be evaluated from any vapor pressure datum well removed from the critical point. Also needed was a "best" expression for the compressibility factor as a function of the acentric factor. A linear expression sufficed:

$$z_c^* = 0.2905 - 0.0787\omega \quad (2)$$

The asterisk is added to remind one that this is the value from the equation rather than the value calculated from the reported critical parameters of the particular fluid. The individual values of the critical compressibility factor and the line for Eq. (2) are shown in Fig. 1.

### 3. CHOICE OF FORM FOR REDUCED DENSITY

While the usual definition of reduced density is the simple ratio to the experimental critical density  $\rho_r = \rho/\rho_c$ , the latter quantity is not directly measured and is subject to considerably greater uncertainty than either  $T_c$  or  $P_c$ . Thus, there is a significant advantage in the use of a reduced density

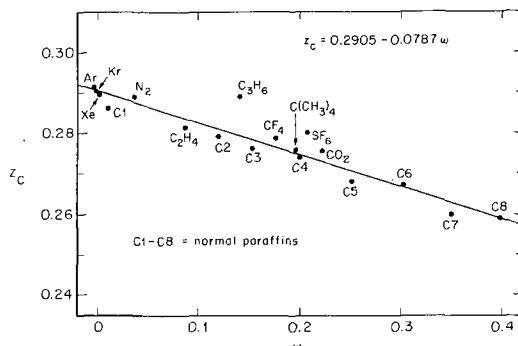


Fig. 1. Individual critical compressibility factors as a function of acentric factor. The line is the linear fit of the data [Ed. (2)].

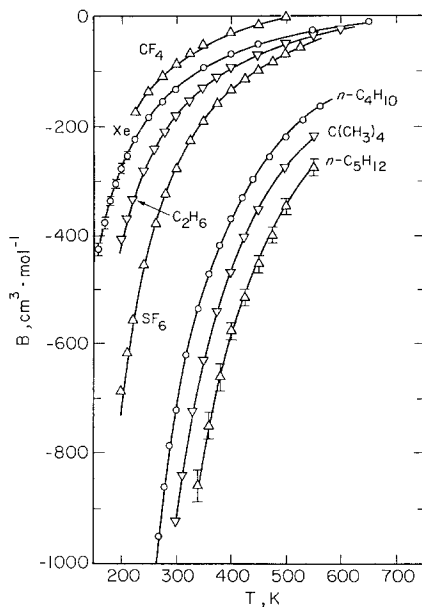
based on  $T_c$  and  $P_c$  instead  $\rho_c$ . The original presentation of the acentric factor system was in terms of the compressibility factor as a function of  $T_r$  and  $P_r$  which avoided the use of  $\rho_r$ . But we now wish to use  $\rho_r$  along with  $T_r$  as independent variables in our equation. We considered the alternative forms  $\rho_r = \rho(RT_c/P_c)$  and  $\rho_r = \rho(z_c^* RT_c/P_c)$ . In the latter,  $z_c^*$  is the "standard" value of the compressibility factor for the acentric factor of the particular fluid from Eq. (2). The second form has the advantage of giving values approximately equal to those obtained from  $\rho_r = \rho/\rho_c$ . Thus, no gross error will arise if one uses the ordinary  $\rho_r$  instead of the one here defined. Hence, we adopt the definition

$$\rho_r^* = \rho(z_c^* RT_c/P_c) \quad (3)$$

and the asterisk can be added to distinguish this quantity from  $\rho/\rho_c$ .

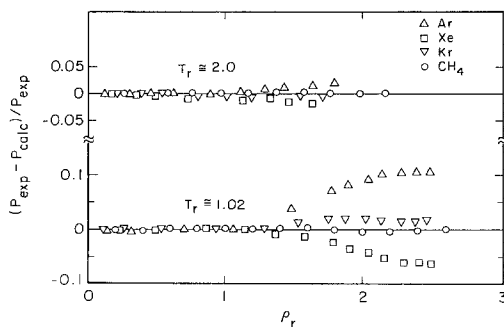
#### 4. EQUATION OF STATE

An extended Benedict-Webb-Rubin (eBWR) equation as developed by Jacobsen [10] was selected as the complete equation of state. Since wide-ranging  $PVT$  data of numerous substances had been previously fit to this particular eBWR, we felt that it was flexible enough for our purposes. The second virial coefficient was first fitted, and the resulting terms were held fixed thereafter (Fig. 2). We then fitted the complete equation and eliminated terms that were not significant. In each case, we first fit the simple fluids.



**Fig. 2.** Second virial coefficient data as a function of temperature for several substances. The lines represent our calculated values [Eq. (4a)].

A careful review of the data on a corresponding-states basis for the simple fluids Ar, Kr, Xe, and CH<sub>4</sub> showed excellent conformity at low densities but significant deviations at reduced densities above 1.5, especially at low reduced temperatures. In that region argon showed the highest reduced pressures and xenon the lowest, with krypton and methane intermediate.



**Fig. 3.** Deviations of our calculated pressures [Eq. (4)] from the Ar, Kr, Xe, and CH<sub>4</sub> data for two reduced-temperature isotherms.

After exploring various methods for the derivation of a specific numerical equation, we chose methane as a model simple fluid. This resolved fitting problems in the dense fluid region. The resulting equation after elimination of unnecessary terms was

$$Z = 1 + B_r \rho_r + C_r \rho_r^2 + D_r \rho_r^3 + E_r \rho_r^5 + F_r \rho_r^7 + G_r \rho_r^8 + H_r \rho_r^{10} + I_r \rho_r^{12} \quad (4)$$

$$B_r = c_1 + c_2/T_r + c_3/T_r^2 + c_4/T_r^6 \quad (4a)$$

$$C_r = c_5 + c_6/T_r + c_7/T_r^3 + (c_8/T_r^4) \exp(-\rho_r^2) \quad (4b)$$

$$D_r = c_9 + c_{10}/T_r + c_{11}/T_r^2 \quad (4c)$$

$$E_r = c_{12}/T_r^2 + c_{13}/T_r^3 \quad (4d)$$

$$F_r = c_{14}/T_r^2 + c_{15}/T_r^3 \quad (4e)$$

$$G_r = c_{16}/T_r^3 + (c_{17}/T_r^3 + c_{18}/T_r^5) \exp(-\rho_r^2) \quad (4f)$$

$$H_r = (c_{19}/T_r^3 + c_{20}/T_r^4) \exp(-\rho_r^2) \quad (4g)$$

$$I_r = (c_{21}/T_r^3 + c_{22}/T_r^4) \exp(-\rho_r^2) \quad (4h)$$

with  $\rho_r = \rho_r^*$  throughout and

$$c_i = c_{i,0} + c_{i,1}\omega + c_{i,2}\omega^2 \quad (5)$$

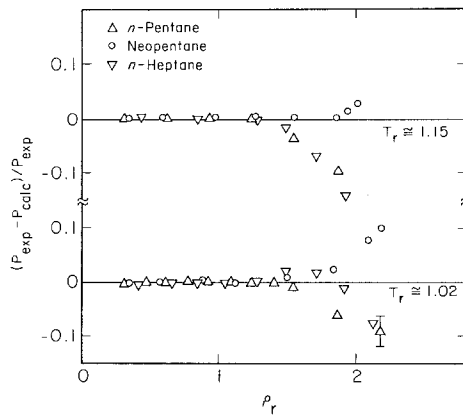
Figure 3 shows deviations of the data from our calculated values for two isotherms for Ar, Kr, Xe, and CH<sub>4</sub>. The deviations from the near-critical isotherm become significant above a reduced density of 1.5. Although these deviations seem large, it should be noted that the  $\partial \ln P_r / \partial \ln \rho_r$  is about 6 in this region. Thus, if one considers deviations in  $\rho_r$  at given  $P_r$ , they are only about -1.6% for argon and about +1.0% for xenon.

The simple fluid equation was used in the overall fit without further refinement, and the overall equation was developed by the addition of acentric factor-dependent terms. Thus, the  $c_{i,0}$  terms were those for methane, while the rest were evaluated from a fit of the entire data base. Terms that were not significant were then eliminated from the equation, removing the quadratic acentric factor-dependent terms first. Increased uncertainties were assigned to the pressure values at high reduced densities, as seemed appropriate for these incompressible regions. The final values of the parameters of the resulting equation are listed in Table II.

As was the case with simple fluids, significant deviations from the fit appear in the dense fluid region. Those for the paraffins (Fig. 4) start at approximately the same reduced density as for the simple fluids and are the

Table II. Coefficients for Eq. (4)

	$c_{i,0}$	$c_{i,1}$	$c_{i,2}$
$c_1$	0.442259	0.725650	—
$c_2$	-0.980970	0.218714	—
$c_3$	-0.611142	-1.24976	—
$c_4$	-0.00515624	-0.189187	—
$c_5$	0.1513654	2.306706	-10.41174
$c_6$	-0.04382625	-4.696068	15.14146
$c_7$	1.102699	3.129384	-9.521409
$c_8$	-0.6361056	0.3266766	2.904622
$c_9$	0.008759626	-3.204099	8.002338
$c_{10}$	0.3412103	8.872169	-14.40386
$c_{11}$	-0.8842722	-6.687471	11.76854
$c_{12}$	0.1375109	-0.2432806	-0.5515101
$c_{13}$	-0.1443457	1.286932	-2.180988
$c_{14}$	-0.005969554	0.04541961	—
$c_{15}$	0.02450537	-0.4158241	0.7914067
$c_{16}$	-0.00419959	0.0910596	-0.1786378
$c_{17}$	0.0004665477	-1.262028	-2.826772
$c_{18}$	-0.01945101	0.7812220	4.190046
$c_{19}$	0.04083643	1.398844	—
$c_{20}$	-0.03546917	-1.456041	—
$c_{21}$	-0.002877955	-0.2104505	—
$c_{22}$	0.005896265	0.2191255	—

Fig. 4. Deviations, as in Fig. 3, for *n*-pentane, neopentane, and *n*-heptane.

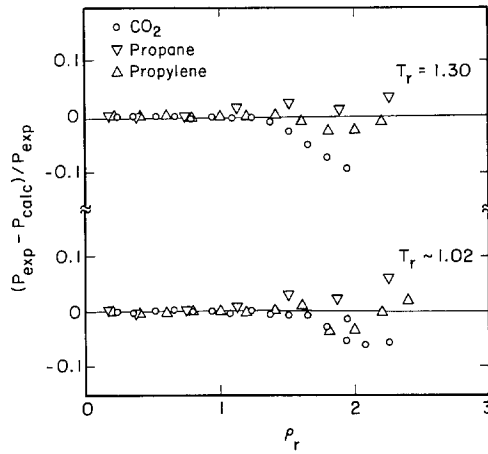


Fig. 5. Deviations, as in Fig. 3, for  $\text{CO}_2$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_3\text{H}_8$ .

Table III. Comparison of Equations of State with the Data Base

Fluid	Number of data	Avg. abs. dev. in pressure (%)	
		This work	Yamada [6]
Argon	260	0.456	0.711
Krypton	149	0.355	0.274
Xenon	233	0.342	0.647
Methane	208	0.291	0.783
Ethylene	231	0.336	0.648
Ethane	281	0.353	0.609
Propane	178	0.396	0.205
Carbon tetrafluoride	139	2.152	3.007
Neopentane	306	0.588	1.364
Butane	223	0.406	0.573
Carbon dioxide	273	0.547	1.647
Pentane	140	0.983	1.109
Hexane	51	2.378	2.527
Heptane	54	0.833	1.133
Propylene	99	0.699	0.827
Total	2825	0.584	0.969



opposite sign for the two pentane isomers. It is interesting to note that the agreement for propylene (Fig. 5), which was not used in the fit, is within the range seen for other substances.

## 5. DISCUSSION

A comparison of our fit with that for the 44-parameter equation of Yamada [6] is shown in Table III for a number of fluids using our data base. In general, we include a wider temperature and density range in our data base than did Yamada, as well as including some near critical data. We adopted Yamada's reduced density limit of 1.8 for the comparison. Yamada does not give a temperature limit, but guided by his data base, we have limited the comparison to reduced temperatures less than 3.0. Our equation, in general, does better for our data base over this range. Our equation showed a significant improvement over Yamada's for fluids where our data covered a much larger temperature range. That Yamada's equation does slightly better for a few fluids with data of limited temperature ranges is not disturbing, since our intent was to develop an equation that could be used over a wide range of reduced temperature and density.

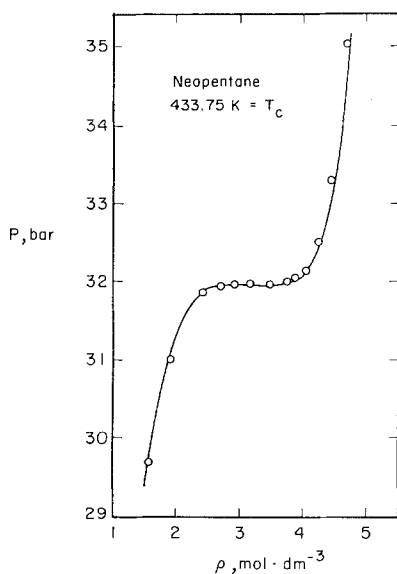


Fig. 6. Comparison of Eq. (4) with the experimental  $\text{C}(\text{CH}_3)_4$  pressure data for the critical isotherm.

The other area in which we hoped to improve a generalized equation of state was in the critical region. Our use of many near-critical data enabled us to obtain a good fit in the critical region; this is shown for neopentane in Fig. 6. This aspect will be discussed fully in an expanded paper to be published soon.

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## REFERENCES

1. K. S. Pitzer, *J. Am. Chem. Soc.* **77**:3427 (1955).
2. K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.* **77**:3433 (1955).
3. R. F. Curl, Jr., and K. S. Pitzer, *Ind. Eng. Chem.* **50**:265 (1958.)
4. K. S. Pitzer and R. F. Curl, Jr., *J. Am. Chem. Soc.* **79**:2369 (1957).
5. J. B. Opfell, B. H. Sage, and K. S. Pitzer, *Ind. Eng. Chem.* **48**:2069 (1956).
6. T. Yamada, *AIChE J.* **19**:286 (1973).
7. J. C. Dymond and E. B. Smith, *The Second Virial Coefficients of Gases: A Critical Compilation* (Clarendon, Oxford, 1980).
8. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton, and Xenon* (English translation) (Hemisphere, Washington, D.C., 1988).
9. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* **16**:577 (1987).
10. R. B. Jacobsen, Ph.D. thesis (Washington State University, Pullman, 1972).