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Author

Redlich, Otto.

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Otto Redlich

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On the Three-Parameter Representation of the Equation of State

Otto Redlich
Inorganic Materials Research Division, Lawrence
Berkeley Laboratory, and Department of Chemical
Engineering, University of California, Berkeley, 94720

Abstract

Almost all small, nonpolar molecules satisfy the theorem of corresponding states; their P-V-T-relation is quite well represented by a two-parameter equation proposed in 1949. A third individual parameter is known to be required for long chains and polar molecules.

The quality of the three-parameter representation has been examined by means of an equation of state based solely on the critical constants. The equation is reasonably convenient for practical applications, including the derivation of the fugacity coefficient.

Mean deviations for 13 widely different substances confirm a fairly satisfactory algebraic representation by three individual parameters. A few exceptions, such as water, hydrogen and helium, are well known.

1. Introduction

The practical interest in an equation of state rests preponderantly in the various thermodynamic properties that are derived from it, especially the fugacity coefficient. It has been pointed out long ago that we measure almost always the P-V-T-relations but actually need the fugacity coefficient. For this reason and also for convenient use with computers an adequate algebraic representation is desired.

The problem seemed to be close to its solution 25 years ago when a simple equation of state was proposed[1]. From the beginning it was manifest that the "old equation" could not constitute a really satisfactory solution because it contained only two individual parameters; thus it was in accord with the theorem of corresponding states, which had been known to be deficient. In fact, the old equation was surprisingly satisfactory for a large group of small, nonpolar molecules, but it did not well represent long chains and polar molecules. Moreover, the work of Pitzer[2] and his coworkers and of Riedel[3] showed that three individual parameters are necessary and sufficient for a good representation of all substances with the exception of very few, such as hydrogen, helium and water. It was obvious to hope that the reasonable introduction of a third parameter into a suitable modification of the old equation would solve the problem. Horvath's review[4] of the old equation contains 34 references to attempts at improving its accuracy without too great a loss of simplicity and convenience. So far none of the results has been generally adopted. Perhaps it may be concluded that we should search more systematically for a new approach to this problem.

Unquestionably the most difficult part is the representation of the critical point and its neighborhood. It occurred to us that the most promising way might be to catch the bull by its horns, i.e., to start by constructing a three-parameter equation with the critical compressibility ratio as one parameter. The two other parameters are determined, as before, by the critical data. One cannot expect, of course, that a reasonably simple equation of this kind will result in sufficient accuracy. But one may hope to obtain a "main term" which reproduces approximately the peculiarities of the problem. The remaining discrepancies must then be eliminated as far as possible by additional terms. As a matter of course, these terms must not contain any new individual parameters.

In the following only the reduced temperature, pressure and volume will be introduced; they will be denoted by T, P and V. The critical temperature and pressure will not explicitly appear and only the critical compressibility factor will.

Since most applications will be carried out by automatic computation, it will be convenient to make a concession to computer language in order to deal with the shortcoming of our usual language, namely, the lack of suitable symbols. We shall therefore write two (and occasionally even three) capital letters for a single quality, e.g., ZC for the critical compressibility factor. Multiplication will be indicated by a dot when necessary to avoid ambiguity.

The choice of ZC as the third parameter is not seriously different from the use of Pitzer's acentric factor ω since there exists a fairly good relation

$$ZC = 0.291 - 0.082\omega \qquad (1)$$

between the two quantities.

The primary basis of observed data was given by Pitzer's tables, supplemented by Lu and coworkers[5] for the reduced temperatures 0.5 to 0.8. An array of 288 data was prepared according to the schedule:

Reduced Temperatures	Reduced Pressures	Critical Compressibility Factors
0.5	0.2	0.291
0.6	0.4	0.250
0.7	0.6	
0.8	0.8	
0.9	1.0	
1.0	1.2	
1.1	1.6	
1.2	2.0	
1.6	3.0	
2.0	5.0	
3.0	7.0	
4.0	9.0	

It will be seen that the "difficult" critical region is most closely covered; this should be taken into account in judging the magnitude of deviations.

2. The Main Term

For the development of the main term Z of the compressibility factor, one will of course follow the general guidelines that have been useful for the old equation. In other words, one concludes from Wegscheider's discussion[6] that only a cubic equation with a reduced limiting volume B is acceptable. Thus the search for the term can start from an equation of the van der Waals type. The (reduced) relation

$$P \cdot ZC = \frac{T}{V - B} - \frac{QQ}{V^2 + F \cdot V + G} \qquad (2)$$

containing a function QQ of the temperature and the constants B,F and G is general enough to serve as a starting point.

In the critical conditions

$$ZC = \frac{1}{1 - B} - \frac{Q}{1 + F + G} \qquad (3)$$

$$0 = \frac{1}{(1 - B)^2} - \frac{Q(2 + F)}{(1 + F + G)^2} \qquad (4)$$

$$0 = \frac{1}{(1 - B)^3} - \frac{Q(3 + 3F + F^2 - G)}{(1 + F + G)^3} \qquad (5)$$

we have written Q for the value of the function QQ at the critical temperature. The conditions (3), (4),(5) are satisfied if the constants conform with the relations

$$F = 1/ZC - 3 + B \tag{6}$$

$$G = B(3 - 2B - 1/ZC) + ZC(1 - B)^3 \tag{7}$$

$$Q = [1 - ZC(1 - B)]^3 . \tag{8}$$

This leaves only the value B of the limiting volume open. In the old equation we had chosen the value 0.26, which is a fair average of individual values (Kuenen[7] quotes values between 0.242 and 0.282). The satisfactory behavior of the old equation at very high pressures is a consequence of the choice of the value of B.

Unfortunately the value 0.26 did not give good results in the equation (2). A series of systematic tests led to the value

$$B = 0.352 \tag{9}$$

which is significantly higher. But the difference is expected to be harmful only at extreme pressures.

For the representation of the temperature function QQ and other functions, we introduce a number of abbreviations. The symbols

$$AT = 1, \quad \text{if} \quad T < 1 \tag{10}$$

$$AT = 0, \quad \text{if} \quad T \geq 1 \tag{11}$$

$$AP = 1, \quad \text{if} \quad P < 1 \tag{12}$$

$$AP = 0, \quad \text{if} \quad P \geq 1 \tag{13}$$

help in a concise notation. We write

$$TS = T^{-0.5} \quad ; \quad TD = 1 - TS \tag{14}$$

$$AU = 0.291 - ZC \, . \tag{15}$$

With the auxiliary function

$$QW = 1 - 0.26TD + 1.60TD^2 - AV \cdot TD(13.7 + 1.60TD^2) + 16.0 \cdot AT \cdot AU \cdot TD^2 \tag{16}$$

the best representation turned out to be

$$QQ = QW[1 - ZC(1 - B)]^3 TS/ZC \, . \tag{17}$$

Introducing relations (6) to (17) into (2), we obtain a reduced equation of state which contains (in addition to the critical temperature and pressure) only the single individual parameter ZC.

The comparison of this equation (Main Term) with the old equation by means of two sets of 144 points from the tables of Pitzer and of Lu is shown in Table 1. The old equation (R and K) furnishes for small, non-polar molecules (ZC = 0.291) a representation that is nearly the best one can expect. Actually only the isotherms for $T = 0.5$ and 0.6 show serious discrepancies; if we restrict the temperature range to 0.7-4.0, the root of the mean square deviation drops from 0.0132 to 0.0097. But the old equation fails for less "normal" substances as shown for the example with ZC = 0.250.

The main term is better for this case, but still by no means satisfactory. Additional terms are required to reduce the deviations.

Table 1. Deviations in Z

ZC	Maximum Deviation			Mean Deviation		
	R and K	Main Term	Final	R and K	Main Term	Final
0.291	0.066	0.071	0.030	0.013	0.022	0.011
0.250	0.381	0.350	0.044	0.102	0.058	0.011

3. Additional Terms

A plot of the deviations from the main term reveals a picture of such capriciousness that we have not even tried to take account of them by means of a single, comprehensive function. Instead, a number of additional functions was devised, each of which covered only part of the T-P range.

This method has some advantages. The additional terms can be simple, well-behaving functions, which can be fairly easily constructed and adjusted. If an improvement is later found to be desirable, an amendment can be easily introduced.

The selection of the proper function for each partial range by the computer does not present any serious difficulty. Moreover, non-automatic computation is by no means impossible. Often only a small range of the independent variables need be covered; one can then restrict the number of additional functions and also dispense with the computer. In this case, one evades solving the cubic equation (2) by plotting P as a function of Z at given T.

The various ranges are indicated in Table 2. A distinction must be made at subcritical temperatures between gas and liquid; the computer recognizes the phase by the magnitude of the solution Z of the main term (higher or lower than ZC). Some auxiliary functions are defined in Table 3, in which the symbols (10) to (15) are used. With all these abbreviations, the additional terms are given in Table 4. The main term Z is converted to the final value ZF by addition of the terms given.

The additional functions have been chosen such that their first derivatives with respect to temperature and pressure are continuous (except for some breaks at T = 1.0 and 1.6). No attempt, however, has been made to avoid discontinuity in the second derivatives.

Neither the calculation of the fugacity coefficient nor that of the first derivatives presents any difficulties. But numerical differentiation may be taken into consideration as a more convenient method for obtaining the derivatives.

Table 2. Ranges for the Additional Terms

Range	T	P	Z	State
A	$T \leq 1.0$	≤ 1.0	$\geq ZC$	Gas
B	$T < 1.0$		$< ZC$	Liquid
C	$1.0 < T \leq 1.12$	≤ 4.0		
D	$1.12 < T \leq 1.6$			
E	$1.6 < T \leq 4.0$	≤ 1.0		
F	$1.6 < T \leq 4.0$	$1.0 < P \leq 4.0$		

Table 3. Auxiliary Functions

$TL = (T-1)/0.12; \quad TJ = (T-1.12)/0.48; \quad TK = (1-T^{-0.5})^2$

$PL = [(1-P)/(1-0.85P)]^3; \quad PK = (1-P^{-1})^3$

$GA = 0.128 - 0.226TD + AU(1.44 + 4.3TD)$

$GB = -(0.0518 + 6.61AU)(1 - T)^3$

$GC = 0.128 + 1.44AU$

$GD = 0.081 + 0.98AU$

$GE = -0.0085 - 0.382AU$

$GF = -0.070 - 1.85AU$

$GG = -0.029 + 0.22AU$

$GH = 0.200 + 1.20AU + (3.38 - 80.8AU)TK + (-9.5 + 262.0AU)TK^2$

$GJ = 0.071 - 9.74AU + (-2.62 + 262.0AU)TK + (8.65 - 803.0AU)TK^2$

$HL = AP \cdot GC \cdot P \cdot PL$

(For $P \leq 1.38$) $HM = GD(1.38 - P)P$

(For $P > 1.38$) $HM = GE(1 - 1.38/P)(26.4/P - 290.0AU/P - 1)$

$HU = (1 - AP)(GF \cdot PK + GG.PK^2)$

Table 4. Additional Terms

Region	Additional Term (ZF - Z)
A	$GA \cdot PL$
B	$GB \cdot P$
C	$[1 + 4TL(1 - TL)][HL(1 - TL)^2 + HM \cdot TL^2]$
D	$[1 + 4TJ(1 - TJ)][HM(1 - TJ)^2 + HU \cdot TJ^2]$
E	0.0
F	$GH \cdot PK + GJ \cdot PK^2$

4. Computing

For the solution of a cubic equation a SHARE-program, VIETA (A,Y,MTYPE), has been convenient. It solves the equation

$$A(1)\cdot Y^3 + A(2)\cdot Y^2 + A(3)\cdot Y + A(4) = 0 \qquad (18)$$

according to Cardan's procedure and furnishes three values for Y and one of the values -1, 0, 1 for MTYPE, indicating the case of three real roots, the case of two roots equal, and the case of a real root Y(1) and a complex root. The program has been modified in the case of three real roots by ordering the solutions according to magnitude.

The old equation as well as relation (2) furnishes solutions for both the gaseous and the liquid phases in a range in which one of the two phases is metastable. The stability determination requires the calculation of the fugacity coefficient. In the modified VIETA-program Y(1) represents the result for the gaseous phase and Y(3) for the liquid phase if three real roots are found.

Table 5 shows the essential steps of the computer program used. The individual parameter ZC must be introduced at the start of the "substance cycle", the (reduced) temperature for the section "T-functions", and the pressure for the section "R and K", in which the results of the old equation are computed for a comparison. The subroutine VIETA is used in this section for the computation of the compressibility factor ZK and, if two phases are indicated, of

Table 5: Essential Computing Steps

```
      A(1)=1.0
      B=0.352
C SUBSTANCE CYCLE
      ZR=1.0/ZC
      AU=0.291-ZC
C T-FUNCTIONS
   36 TS=1.0/SQRT(T)
      TD=1.0-TS
      F=ZR-3.0+B
      G=B*(3.0-2.0*B-ZR)+ZC*(1.0-B)**3
      QU=1.0-ZC*(1.0-B)
      QW=1.0-0.26*TD+1.60*TD*TD-AU*TD*(13.7 +173.2*TD)
      IF (T.LT.1.0) QW=QW+16.0*AU*TD**2
      QQ=ZR*TS*QW*QU**3
      GA=0.128-0.226*TD+AU*(1.44+4.3*TD)
      IF (T.GT.1.0) GO TO 38
      GB=-(0.0518+6.61*AU)*(1.0-T)**3
      GO TO 39
   38 IF (T.GT.1.6) GO TO 40
      GC=0.128+1.44*AU
      GD=0.0810+0.98*AU
      GE=-0.0085-0.382*AU
      GF=-0.070-1.85*AU
      GG=-0.029+0.22*AU
      TL=(T-1.0)/0.12
      TJ=(T-1.12)/0.48
      GO TO 39
   40 TK=TD**2
      GH=-0.200+1.20*AU+(3.38-80.8*AU)*TK+(-9.5+262.0*AU)*TK**2
      GJ=0.071-9.74*AU+(-2.66+262.0*AU)*TK+(8.65-803.0*AU)*TK**2
   39 CONTINUE
C R AND K
      A(2)=-1.0
      AK=0.4278*P*TS/(T*T)
      BK=0.086667*P/T
      A(3)=AK-BK*(1.0+BK)
      A(4)=-AK*BK
      CALL VIETA(A,Y,MT)
      ZK=Y(1)
      ZKL=0.0
      IF (MT.GT.-1) GO TO 33
      ZKL=Y(3)
   33 CONTINUE
```

```
C MAIN TERM
      PP=ZR/P
      A(2)=F-B-T*PP
      A(3)=G-B*F+PP*(QQ-F*T)



      A(4)=-G*B-PP*(B*QQ+G*T)
      CALL VIETA(A,Y,MT)
      Z=ZC*P*Y(1)/T
      ZL=0.0
      IF (MT.GT.-1) GO TO 34
      IF (Y(3).LE.0.0) GO TO 34
      ZL=ZC*P*Y(3)/T
   34 CONTINUE

C ADDITIONAL TERMS
      PK=(1.0-1.0/P)**3
      PL=0
      IF (P.LT.1.0) PL=P*((1.0-P)/(1.0-0.85*P))**3
      IF (T-1.0) 41,42,43
   42 IF (P.GE.1.0) ZF=Z
      IF (P.LT.1.0) ZF=Z+GA*PL
      GO TO 49
   41 IF (P.GE.1.0) GO TO 44
      IF (Z.LT.ZC) GO TO 44
      ZF=Z+GA*PL
      GO TO 49
   44 ZF=Z+GB*P
      GO TO 49
   43 IF (T.GT.1.6) GO TO 46
      HL=0.0
      IF (P.LT.1.0) HL =GC*PL
      HM=(0.081+0.98*AU)*(1.38-P)*P
      IF (P.GT.1.38) HM=-(0.0085+0.382*AU)*(1.0-1.38/P)*((26.4-290.0*AU)
     2/P-1.0)
      HU=0.0
      IF (P.GT.1.0) HU=(GF+GG*PK)*PK
      IF (T.GT.1.12) GO TO 45
      ZF=Z+(1.0+4.0*TL*(1.0-TL))*(HL*(1.0-TL)**2+HM*TL**2)
      GO TO 49
   45 ZF=Z+(1.0+4.0*TJ*(1.0-TJ))*(HM*(1.0-TJ)**2+HU*TJ**2)
      GO TO 49
   46 CONTINUE
      ZF=Z
      IF (P.GT.1.0) ZF=Z+(GH+GJ*PK)*PK
   49 CONTINUE
```

ZKL for the liquid. In the section "Main Term" the solutions Y(1) and Y(3) furnish the reduced volumes, from which the corresponding compressibility factors Z and ZL are computed.

The final results ZF and ZFL are obtained by addition of the appropriate additional terms to Z and ZL.

The program can be looped for pressure inside a temperature-loop inside a substance-loop.

5. Results

As indicated in Table 1, the mean deviation of the final results is reduced to 0.011.

Table 6 summarizes the deviations for 13 substances ("Mean Deviation" is the root of the average deviation square).

It is very difficult to furnish a "true" picture of the quality of an equation of state. There are extended ranges in which any reasonable equation leads to very small errors. On the other hand, the accuracy of the best equation cannot be high near the critical point since here dZ/dP is infinite. The choice of Z as a function of P may be questioned for judging the deviations; percentage deviations would furnish a somewhat different picture. But the main difficulty lies in the "unbiased" selection of observed data; a constant interval in P, for instance, certainly would not lead to a true picture. The "maximum deviations" in Table 6 occurred for the final equation almost always near the critical point.

The results for the final equation are believed to indicate the limits of accuracy for a three-parameter relation. Most of the deviations in the last column of Table 6 are not much larger than the mean deviation 0.011 for the tables of Pitzer and of Lu. The differences can be interpreted as illustrating the efficiency of the three-parameter representation.

Replacing the critical compressibility factor by the acentric factor does not, in general, appreciably change the

Table 6. Examples of Deviations

Substance	ZC	Temperature		Pressure	No. of	Maximum Deviations		Mean Deviations	
		from	to	to	Points	R and K	Final	R and K	Final
Methane[8]	0.2881	1.63	2.68	10.40	19	0.026	0.025	0.012	0.015
Pentane[8]	.2745	.94	1.09	10.12	51	.099	.027	.049	.012
Nonane[8]	.254	.52	0.86	9.04	28	.299	.049	.118	.015
Decane[8]	.2473	.50	0.83	9.81	21	.374	.068	.182	.026
Propylene[9]	.2730	.75	1.57	1.80	55	.058	.063	.025	.016
1-Butene[8]	.279	.74	1.51	8.50	27	.056	.040	.026	.017
Benzene[8]	.274	.55	0.91	7.00	14	.087	.018	.051	.008
Xenon[10]	.2926	1.00	1.98	7.02	20	.045	.071	.027	.030
Oxygen[11]	.2921	1.77	2.09	2.46	16	.009	.020	.006	.016
Hydrogen Sulfide[8]	.2833	.74	1.19	7.66	25	.035	.016	.018	.010
Carbon Dioxide[8]	.2745	.91	1.68	9.35	29	.068	.046	.028	.014
Sulfur Dioxide[12]	.2697	.75	1.22	3.86	19	.066	.047	.031	.015
Ammonia[13]	.2425	.78	1.48	0.97	23	.065	.040	.026	.023

deviations. Only for ammonia the mean deviation is reduced from 0.023 to 0.015 if the acentric factor (corresponding to a fictitious value ZC = 0.2707) is introduced.

It does not appear to be likely that a fourth parameter would result in a considerable improvement.

Relations containing more than three parameters are in general overdetermined. They may be very useful in representing data within a limited range of observation. Beyond this range great caution is advisable.[14].

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720