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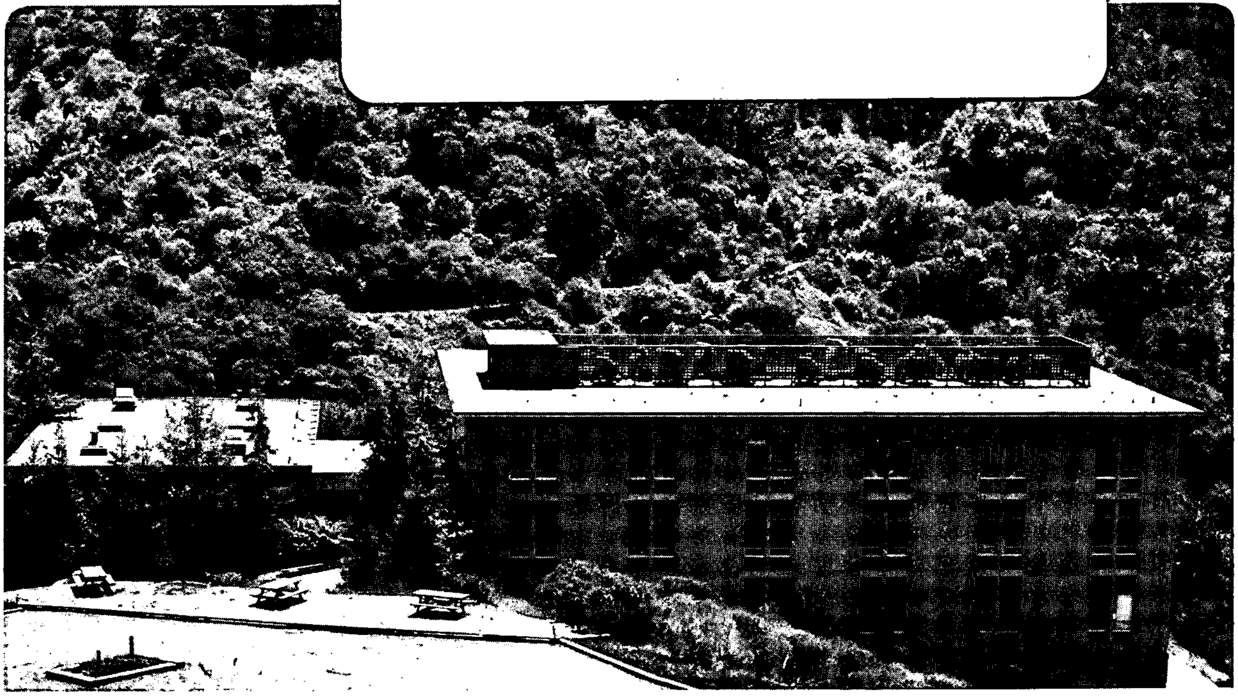

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SELECTED EQUATION OF STATE IN THE ACENTRIC FACTOR SYSTEM

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Abstract:

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

Key Words: equation of state, acentric factor, corresponding states, 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 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 coefficient [1], it was shown that most non-polar molecules of various shapes and sizes conformed to a 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, 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

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

where P_r is the reduced vapor pressure at $T_r = 0.7$, but ω 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:

$$z_c^* = 0.2905 - 0.0787\,\omega \tag{2}$$

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 significant advantage in the use of a reduced density based on T_c and P_c instead of ρ_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 ρ_r. But we now wish to use a ρ_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 ρ_r instead of the one here defined. Hence, we adopt the definition

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

and the asterisk can be added to distinguish this quantity from ρ/ρ_c.

4. EQUATION OF STATE

An extended Benedict-Webb-Rubin (eBWR) equation as developed by Jacobson [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 it was flexible enough for our purposes. The second virial coefficient was first fitted and the resulting terms held fixed thereafter. We then fitted the complete equation and eliminated terms that were not significant. In each case, we first fit the simple fluids.

A careful review of the data on a corresponding states basis for the simple fluids Ar, Kr, Xe, CH_4 showed excellent conformity at low densities but significant deviations at reduced densities above 1.5, especially at low reduced temperature. In that region argon showed the highest reduced pressures and xenon the lowest, with krypton and methane intermediate. 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

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

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

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

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

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

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

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

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

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

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

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

Figure 3 shows deviations of the data from our calculated values for two isotherms for Ar, Kr, Xe, and CH_4. 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 ρ_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 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 density, 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 opposite sign for the two pentane isomers. The significant deviations for SF_6 and CO_2 (Fig. 5) appear at lower reduced densities. SF_6 had significant deviations from the 1.48 reduced temperature isotherm at reduced density as low as 0.6. While these low density deviations cannot be attributed to incompressibility, neither do we believe that they are simply a fitting problem. Therefore, any attempt to force better agreement with these data will only cause problems with other fluids.

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 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.

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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ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Individual critical compressibility factors as a function of acentric factor. Line is linear fit of the data (Eq. 2).

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

Figure 3. Deviations of our calculated pressures (Eq. 4) from the Ar, Kr, Xe, and CH_4 data for two reduced temperature isotherms.

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

Figure 5. Deviations, as in Fig. 3, for CO_2, C_3H_8, and SF_6.

Figure 6. Comparison of Eq. 4 with the experimental $C(CH_3)_4$ pressure data for the critical isotherm.

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

Fluid	T_c	P_c	ρ_c	ω
	K	bar	$mol \cdot dm^{-3}$	
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	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

Table II. Coefficients for Equation 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	2.213693	-9.598692
c_6	-0.04382625	-4.671259	13.32762
c_7	1.102699	4.520863	-8.917107
c_8	-0.6361056	-0.6065285	3.142454
c_9	0.008759626	-3.401562	8.038689
c_{10}	0.3412103	10.11966	-13.58086
c_{11}	-0.8842722	-8.968310	11.38057
c_{12}	0.1375109	-0.2214839	-0.5157391
c_{13}	-0.1443457	1.694982	-2.497557
c_{14}	-0.005969554	0.05297974	-
c_{15}	0.02450537	-0.5180199	0.8662445
c_{16}	-0.004199589	0.1105148	-0.1932394
c_{17}	0.0004665477	-0.9976422	-3.441064
c_{18}	-0.01945101	0.1485973	4.972850
c_{19}	0.04083643	1.128021	-
c_{20}	-0.03546917	-1.071834	-
c_{21}	-0.002877955	-0.1932453	-
c_{22}	0.005896265	0.1704968	-

Table III. Comparison of Equations of State with Database

Fluid	Number of Data	Avg. abs. dev. in pressure %	
		This Work	Yamada [6]
Argon	260	0.457	0.711
Krypton	149	0.356	0.274
Xenon	233	0.342	0.647
Methane	208	0.292	0.783
Ethylene	231	0.391	0.648
Ethane	281	0.402	0.609
Propane	178	0.464	0.205
Carbon Tetrafluoride	139	1.972	3.007
Neopentane	306	0.446	1.364
Butane	223	0.510	0.573
Sulfur Hexafluoride	167	1.153	2.776
Carbon Dioxide	273	0.589	1.647
Pentane	140	1.166	1.109
Hexane	51	2.413	2.527
Heptane	54	0.939	1.133
Propylene	99	0.677	0.827
Total	2292	0.628	1.070

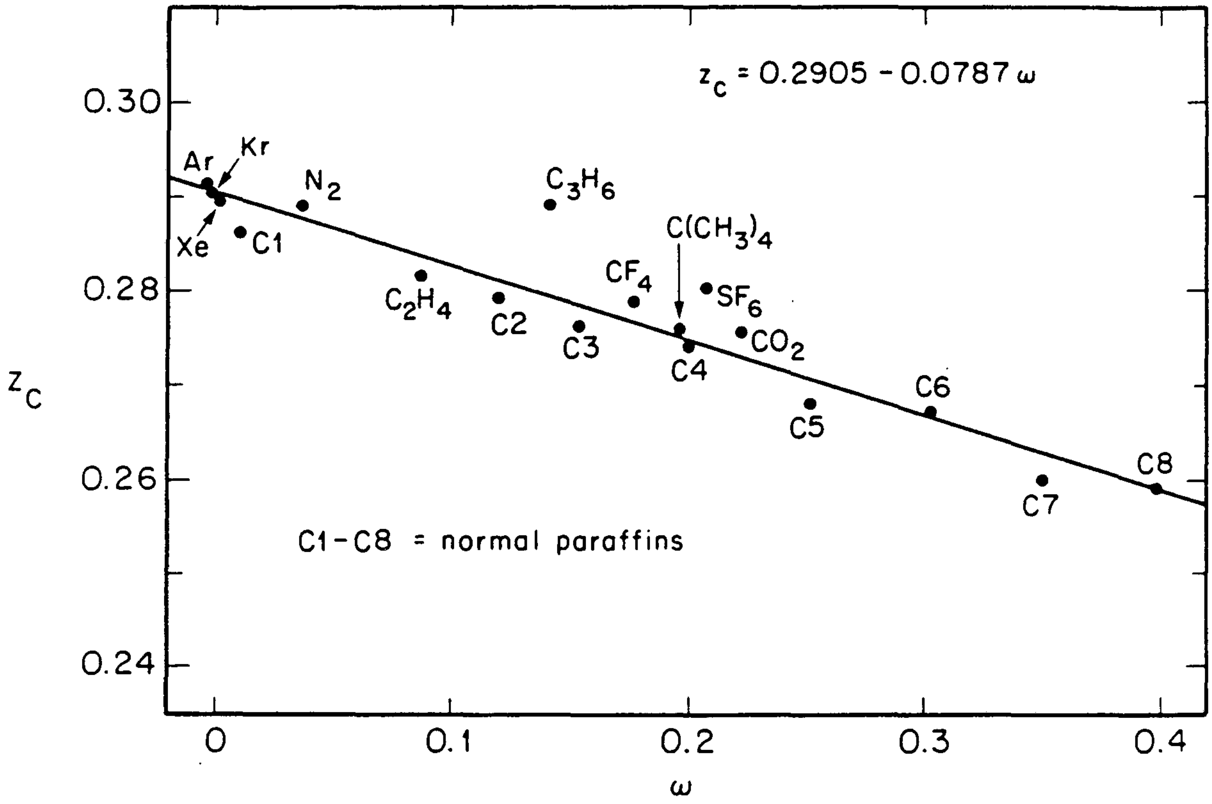
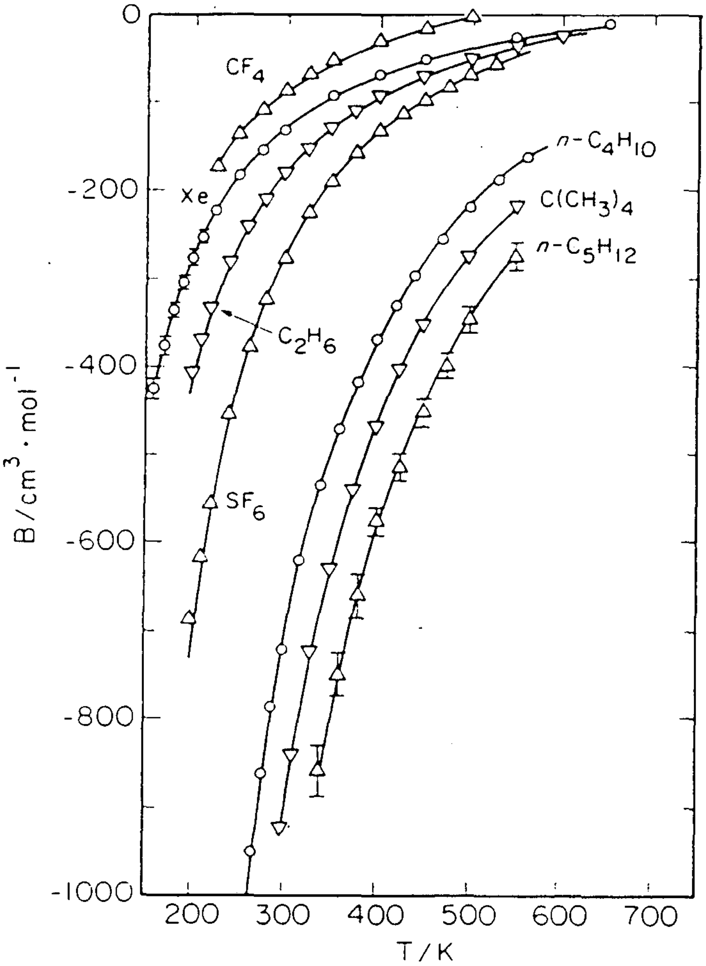


Figure 1.



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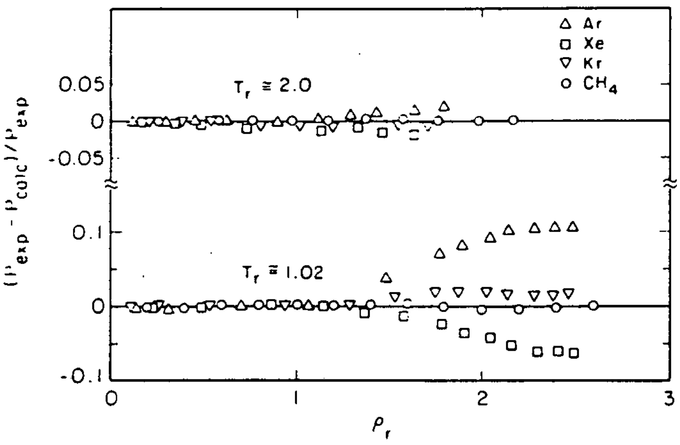
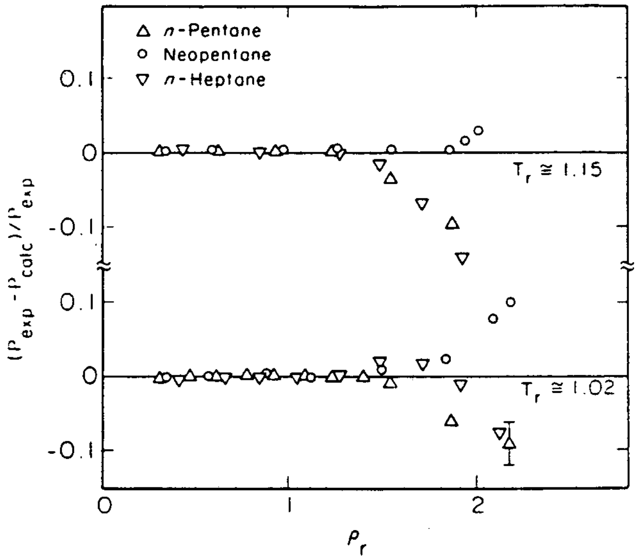


Figure 3.



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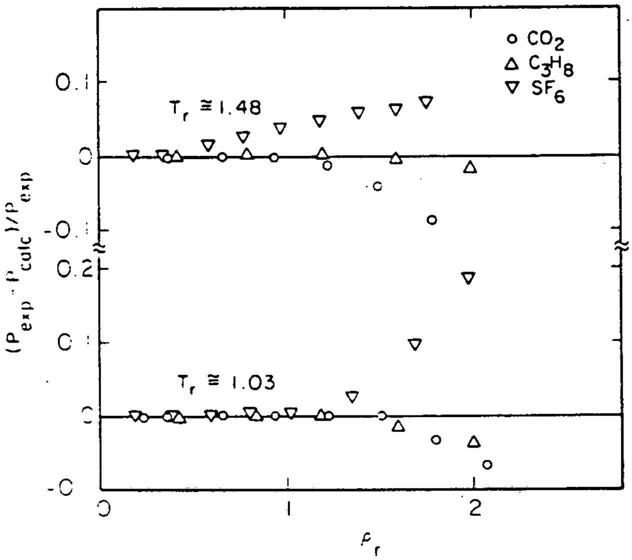

Figure 5.

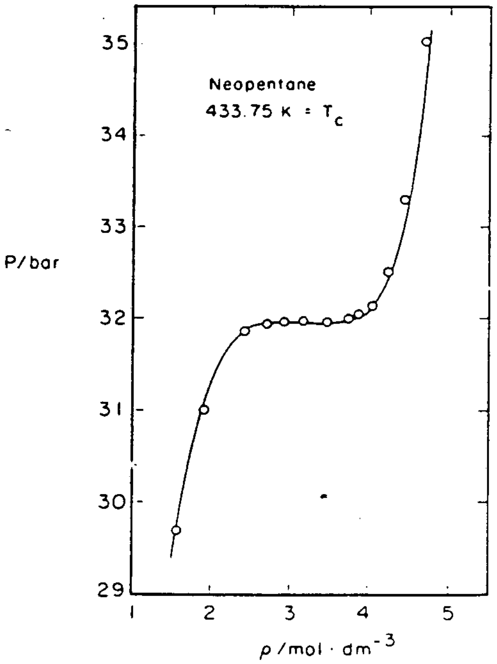

Figure 6.

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