Accuracy of Two Generalized Compressibility Correlations

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NUMEROUS investigators have suggested that the accuracy of the familiar generalized compressibility correlations could be improved by another parameter in addition to reduced temperature and reduced pressure. Two of these proposed third parameters, the critical compressibility and a vapor pressure function, have been discussed by Lydersen, Greenkorn, and Hougen (*18*) and by Pitzer (*31*). In these articles, compressibility charts using these parameters are shown to provide substantial accuracy improvements over two-parameter correlations.

The correlating variable used by Lydersen and others was the critical compressibility, z_c. This factor varies widely among compounds, and charts which allow only a single value for it must be considerably in error in the region near the critical point. In 1951 Meissner and Seferian (*22*) correlated the deviation between observed and predicted compressibilities with the critical compressibility. Lydersen and coworkers extended this work to a greater number of compounds and prepared compressibility data in a tabular form in which $z = f(T_r, P_r, z_c)$. Tables of derived properties based upon the z_c correlation were also given.

The compressibility relationships developed by Pitzer and coworkers use "ω," termed acentric factor and defined as $\omega = -\log P_{rs} - 1$, where P_{rs} is the reduced vapor pressure at $T_r = 0.7$. Selection of this parameter arose from extensive statistical mechanics studies. A series of tables expresses the function $z = (P_r, T_r, \omega)$. Curl and Pitzer (*10*) have applied this correlation to the prediction of several thermodynamic properties.

Edmister (*11*) presented Pitzer's correlation in graphical form and showed that because the logarithm of vapor pressure is linear in reciprocal temperature for a substance, ω can be readily calculated from the atmospheric boiling point. This convenience, the abundance of boiling data, and the good accuracy of vapor pressure measurements (particularly by comparison with critical volume determinations) make this correlation attractive for normal engineering use.

It would be expected from the definition of each parameter that use of z_c would be particularly advantageous in improving compressibility prediction in the region near the critical point. The acentric factor, ω, would be expected to give greater accuracy in describing the vapor pressure curve, because the curve is predicted with the aid of two data points: the critical point where $P_{rs} = 1.0$ and at $T_{rs} = 0.7$ where $P_{rs} = 10^{-\omega-1}$. Ability to predict the critical region and vapor pressure is essential to an accurate equation of state, the generalized charts of which are a graphical form. The accuracy which one can expect from Lydersen's and Pitzer's charts has been explored in a comparison of predicted and observed compressibilities and vapor pressures for several systems.

Substances whose data were used in this study were selected to cover a broad range of types. They include three normal paraffins (methane, pentane, and heptane), three branched paraffins [single-branched 2-methylpropane (isobutane), double-branched 2,2-dimethylpropane (neopentane, and triple-branched 2,2,4-trimethylpentane (isooctane)], one olefin (ethylene), one aromatic compound (benzene), two organic halides (fluorobenzene and Freon 12), one alcohol (methanol), one monoatomic gas (argon), one diatomic gas (nitrogen), one triatomic gas (carbon dioxide), and one tetratomic gas (ammonia).

Critical constants, calculated acentric factors, and *P-V-T* data references for these systems are listed in Table I. Substances are listed in order of increasing critical compressibility. Critical temperatures range from 126° to 563° K., critical pressures from 25 to 111 atm., critical compressibilities from 0.22 to 0.29, and acentric factors from −0.002 to 0.556.

Uncertainties exist in some critical data, particularly critical compressibilities. Where literature values differed significantly, the review by Kobe and Lynn (*17*) was accepted as the final authority.

The correlations of Lydersen and of Pitzer and their coworkers were tested by their ability to predict vapor pressure, compressibilities of superheated and saturated gas, and density of saturated liquid over the T_r range 0.55 to 4.00 and P_r range up to 1.2. At this pressure and above, the tables of Lydersen, Greenkorn, and Hougen list columns only for $z_c = 0.23$ and 0.29. Interpolation and extrapolation above $P_{rs} = 1.2$ risk large errors. Vapor pressure comparisons included only P_{rs} greater than 0.1, because the acentric factor correlation was the more accurate below this level (*18*).

ACCURACY OF CORRELATIONS

The data summary of Table II shows that Pitzer's acentric factor correlation predicts vapor pressure with good accuracy. The maximum absolute deviation was 6.6%, and the largest average absolute deviation for a substance only

Table I. Critical Constants

	T_c, ° K.	P_c, Atm.	Z_c	ω	*P-V-T* Data
Methanol	513	78.5	0.220	0.556	(*34*)
Ammonia	405.5	111.3	0.242	0.249	(*1, 5, 15-17, 23*)
n-Heptane	540.2	27.0	0.260	0.352	(*4, 17, 31, 35*)
Fluorobenzene	559.7	44.7	0.264	0.253	(*30*)
2,2,4-Trimethylpentane	543.8	25.3	0.267	0.304	(*14*)
2,2-Dimethylpropane	433.8	31.57	0.269	0.195	(*2, 3*)
n-Pentane	469.8	33.31	0.269	0.233	(*6, 17, 33*)
Ethylene	283.1	50.5	0.269	0.090	(*1, 19, 26, 36, 37*)
Freon-12	384.8	39.6	0.273	0.167	(*1, 9, 17*)
Carbon dioxide	304.2	72.85	0.275	0.225	(*1, 24, 25, 28, 29*)
Benzene	562.7	48.66	0.276	0.215	(*12*)
2-Methylpropane	408.1	36.00	0.283	0.188	(*1, 7, 33*)
Nitrogen	126.2	33.54	0.288	0.037	(*8, 33*)
Methane	191.1	45.8	0.290	0.004	(*21, 31-33*)
Argon	151	48.0	0.290	−0.002	(*17, 18, 27, 31*)

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2.2%. Average deviations for a single substance were as high as 10.7% for Lydersen's correlation and the maximum was 29%.

In predicting the compressibility of saturated vapors, the correlations are comparable in accuracy, as indicated by the calculation summary in Table III. A small advantage for Pitzer's prediction method exists for seven of the ten substances, however. Except for methanol, the average deviation from Pitzer's correlation is less than 3%.

As expected, Lydersen's correlation is more accurate near the critical point. The advantage conferred by z_c, however, does not extend to regions much removed from the critical point, as indicated below.

	Average Deviation, %	
T_r	Pitzer	Lydersen
0.96	2.6	2.7
0.90	1.5	2.1

Below $T_r = 0.96$ saturated vapor compressibilities for most compounds were predicted with better accuracy by the acentric factor correlation.

Density data for saturated liquids are predicted better by Lydersen's correlation. Table IV shows average deviations of 3.3% or less.

The calculated absolute deviations in compressibilities of superheated gases, summarized in Table V, show a degree of accuracy sufficient for most engineering purposes. The average deviations from Pitzer's correlation were 2% or less. There were, however, instances where much greater errors have been calculated. Pitzer's predictions of ammonia compressibilities were in error by up to 12% in the region near the saturation curve. Both correlations give rise to large deviations at T_r between 1.0 and 1.1 when P_r is at or above 1.0. In this region most of the maximum deviations occur.

This survey found the acentric factor correlation *(31)* more accurate for vapor pressure predictions and compressibilities of nonpolar or slightly polar saturated vapors. It was also somewhat the better for most superheated gases. The critical compressibility correlation *(18)* was more accurate for saturated liquids and highly polar saturated vapors. This result was expected, because Pitzer and coworkers stated *(31)* that highly polar or hydrogen-bonding compounds would require representation by a fourth parameter.

FOUR-PARAMETER EQUATIONS

The occasionally large deviations indicate the need for further improvements in the generalized correlations. Several possibilities exist. Pitzer has suggested the development of a fourth parameter to characterize polar compounds; however, errors encountered in predicting z_c by the

Table II. Saturation Pressure

					Absolute Deviation, %			
	Data	T_r Range		No. of	Maximum		Average	
Compound	Source	Min.	Max.	Points	Pitzer	Lydersen	Pitzer	Lydersen
Methanol	*(34)*	0.80	0.98	7	0.8	29	0.5	10.7
Ammonia	*(16)*	0.75	0.98	8	0.3	16	0.1	6.1
Fluorobenzene	*(30)*	0.75	0.98	8	6.6	6.5	2.2	3.5
2,2,4-Trimethylpentane	*(14)*	0.75	0.98	8	0.7	6.2	0.3	4.2
n-Pentane	*(6)*	0.75	0.98	8	2.1	3.0	1.1	1.7
Ethylene	*(1)*	0.75	0.98	8	1.4	25	0.6	9
	(37)	0.75	0.98	8	1.7	25	0.9	9
Freon 12	*(1)*	0.75	0.85	3	1.5	9.7	0.8	6.7
Carbon dioxide	*(1)*	0.75	0.98	8	1.0	3.8	0.6	1.8
Benzene	*(12)*	0.75	0.98	8	1.7	4.5	0.5	1.9
2-Methylpropane	*(31)*	0.75	0.98	8	1.8	6.4	1.0	3.4
Nitrogen	*(8)*	0.75	0.98	8	1.1	8.4	0.3	2.0
Methane	*(21)*	0.75	0.98	8	0.6	9.3	0.3	2.5

Table III. Saturated Vapor Compressibility

					Absolute Deviation, %			
	Data	T_r Range		No. of	Maximum		Average	
Compound	Source	Min.	Max.	Points	Pitzer	Lydersen	Pitzer	Lydersen
Methanol	*(34)*	0.60	1.00	12	11.9	5.0	6.2	2.2
2,2,4-Trimethylpentane	*(14)*	0.88	1.00	7	1.7	3.4	0.5	1.0
n-Pentane	*(33)*	0.65	1.00	11	2.5	3.7	0.9	0.9
Ethylene	*(1, 37)*	0.60	1.00	12	3.7	6.0	2.7	3.9
Freon 12	*(1)*	0.60	1.00	7	3.0	2.1	2.3	1.0
Carbon dioxide	*(1)*	0.75	1.00	9	1.8	1.8	0.8	0.7
Benzene	*(12)*	0.92	1.00	5	2.3	3.1	0.8	1.3
2-Methylpropane	*(33)*	0.80	1.00	7	7.1	7.3	2.7	2.2
Nitrogen	*(8)*	0.60	1.00	12	1.1	3.0	0.5	1.7
Methane	*(21)*	0.55	1.00	10	3.1	3.1	0.8	1.6

Table IV. Saturated Liquid Density

					Absolute Deviation, %			
	Data	T_r Range		No. of	Maximum		Average	
Compound	Source	Min.	Max.	Points	Pitzer	Lydersen	Pitzer	Lydersen
Methanol	*(34)*	0.60	1.00	12	100	2.9	36.8	1.4
2,2,4-Trimethylpentane	*(14)*	0.70	1.00	10	4.2	0.5	2.3	0.15
n-Pentane	*(33)*	0.65	1.00	11	17.4	0.8	3.8	0.3
Ethylene	*(1, 37)*	0.60	1.00	12	16.6	9.9	3.8	7.6
Freon 12	*(1)*	0.60	1.00	7	30.3	1.4	11.4	0.7
Carbon dioxide	*(1)*	0.75	1.00	9	2.7	2.8	1.8	1.4
2-Methylpropane	*(33)*	0.80	1.00	8	4.3	6.6	2.4	3.3
Nitrogen	*(8)*	0.60	1.00	12	5.7	1.2	1.6	0.5
Methane	*(21)*	0.55	1.00	13	5.0	3.0	2.1	1.8

Table V. Superheated Gas Compressibility

Compound	Data Source	T_r Range		P_r Range		No. of Points	Absolute Deviation, %			
							Maximum		Average	
		Min.	Max.	Min.	Max.		Pitzer	Lydersen	Pitzer	Lydersen
Ammonia	*(5)*	0.85	1.50	0.20	1.15	50	12.0	1.4	1.2	0.3
n-Heptane	*(35)*	1.00	1.15	1.00	1.15	4	1.8	1.9	1.2	0.7
2,2-Dimethylpropane	*(3)*	1.00	1.20	0.80	1.20	11	2.2	7.7	0.8	2.0
n-Pentane	*(33)*	0.85	1.10	0.20	1.20	24	8.1	3.4	1.1	0.9
Ethylene	*(37)*	0.90	1.80	0.20	1.15	70	6.9	7.8	0.5	0.9
	(36)	0.95	1.10	0.20	0.80	14	0.7	1.7	0.4	0.6
	(26)	1.05	1.50	1.00	1.00	7	1.1	1.5	0.4	0.9
Freon 12	*(9)*	0.90	1.00	0.20	0.40	5	2.1	2.1	1.5	1.5
Carbon dioxide	*(1)*	0.90	1.60	0.20	1.20	49	1.7	2.7	0.5	0.5
	(28, 29)	0.90	1.40	0.40	1.20	42	3.5	6.7	0.8	0.9
Benzene	*(12)*	0.95	1.10	0.60	1.20	11	2.1	1.7	0.8	0.7
2-Methylpropane	*(33)*	0.90	1.25	0.20	1.15	40	5.4	8.7	0.5	0.7
	(7)	1.05	1.40	0.80	1.15	11	1.3	2.0	0.4	0.5
Nitrogen	*(8, 33)*	0.80	4.00	0.20	1.15	92	1.1	2.8	0.2	0.8
Methane	*(21)*	0.80	2.00	0.20	1.15	75	2.1	3.9	0.2	1.0
	(33)	1.60	2.00	0.20	1.15	30	0.7	2.2	0.1	1.1
Argon	*(27)*	1.80	2.00	1.00	1.15	6	0.2	1.9	0.1	1.5

acentric factor correlation do not correlate with dipole moment. Further developments in generalized compresibility charts may also improve the representation of nonpolar compounds.

Four-parameter generalized equations of state have been developed by Martin and Hou *(20)* and by Hirschfelder, Buehler, McKee, and Sutton *(13)*. These employ both z_c and the logarithmic temperature derivative of vapor pressure at the critical point (equivalent to ω). These equations have the virtue of avoiding the large errors in predicting vapor pressure, or gas compressibility near the critical point, which have been found when only one of these factors is included.

Figure 1 suggests a good possibility for improving generalized compressibility prediction. Data representing 37 substances are plotted along with curves relating ω with z_c as predicted by Lydersen and by Pitzer in their correlations. The scatter of points from the line representing Lydersen's correlation indicates the deviation in predicting saturation pressure at a reduced temperature of 0.7. The scatter from the other line indicates the deviation between observed critical compressibilities and those predicted by Pitzer's correlation.

This graph shows that an equation of state which attempts to predict both vapor pressure and gas compressibility data probably must include four parameters, because compounds may be equal in z_c and have different vapor pressure curves.

Similar substances follow a characteristic relationship between z_c and ω. Normal paraffins, for example, follow a line closely approximating that predicted by Pitzer. Similar curves are observed with other types of substances. A study of group contributions might be able to describe the varying shapes of the characteristic curves. A factor representing the type of substance would reduce what errors remain in Pitzer's prediction of compressibilities in the critical region. While this approach would be tantamount to a correlation of the type presented by Martin and Hou and by Hirschfelder and others, it may have advantages in dealing with mixtures, particularly mixtures of similar types of compounds, such as natural gas. This would satisfy Kammerlingh Onnes' requirement of "mechanical equivalence" by a factor more directly related to molecular structure than is z_c.

NOMENCLATURE

P = pressure
T = temperature
V = volume
z = compressibility
ρ = density
ω = acentric factor

Subscripts

c = at critical point
r = reduced
s = saturated

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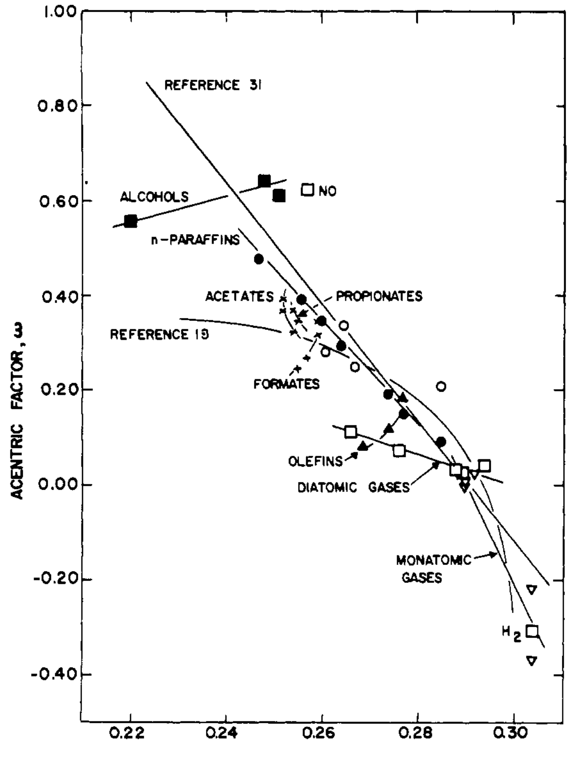

Figure 1. Various types of substances have characteristic relationships between acentric factor and critical compressibility

●	*n*-Paraffins	×	Esters
■	Alcohols	▽	Monatomic gases
▲	Olefins	□	Diatomic gases
○	Ethers		

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Effect of Hydrocarbon Types on Solvency and Burning Characteristics of Petroleum Naphthas

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PETROLEUM naphthas are selected for specific applications largely on the basis of empirical tests that have been related to end-use properties—viz., various types of octane tests, etc. The relationship to actual hydrocarbon composition has been largely qualitative. This article provides a quantitive relationship between hydrocarbon types and boiling range on the contribution of each hydrocarbon type towards solvency or burning quality.

BACKGROUND

The solvent naphthas usually boil in the range of 100° to 400° F. Most have a boiling point spread of 50° to 150° F. They are virgin cuts which contain paraffins, naphthenes, and aromatics; olefins are generally absent or present only in trace quantities. Solvency is often measured by the kauri butanol (K B) test (*1*). High values indicate high solvency power, and low values indicate low solvency power. The contention always was that aromatics control solvency; not much is generally said about the role played by naphthenes and/or paraffins. Because of the lack of adequate and accurate analytical techniques, no attempts were made to correlate solvency, measured by some empirical test such as the K B value, as a function of hydrocarbon types. Published data which relate the K B value to other tests such as the aniline point, the mid-boiling point, or A.P.I. gravity (*3*), only predict solvency from other easily determined and standardized physical tests. From a processing standpoint, these correlations are of no great value, because they shed no light on schemes that should be used to convert a naphtha of a known composition to another in order to meet a certain specification. If, on the other hand, the individual effects of different hydrocarbons on solvency are known, processing schemes could be chosen to change the composition of a naphtha to meet a certain specification.

Kerosine and kerosine-type jet fuels are usually virgin naphthas which boil in the range of 300° to 550° F. Most have a boiling point spread of 150° to 250° F. The required high boiling quality of kerosines and jet fuels is measured by the smoke point. This test (*4*) is designed to evaluate a product in respect to its ability to burn without smoke. High values indicate good burning characteristics, and low values indicate poor burning characteristics. Here again, the contention always was that the burning quality of a naphtha, as measured by the smoke point, improves by decreasing the aromatics content, but not much is generally said about the role of naphthenes and/or paraffins. Hunt (*5*) measured the smoke point of hydrocarbon compounds of different structures and molecular weights. His measurements were generally made on pure aromatics, naphthenes, or paraffins. Some measurements were made on pure aromatics blended with *n*-dodecane. Hunt, however, did not make measurements on mixtures of aromatics, naphthenes, and paraffins to evaluate the effects of blending these three hydrocarbons on smoke point. Nelson (*6*) attempted to describe quantitatively the effect of aromatics, naphthenes,