Fugacity and Vapor Pressure of Nonpolar Liquids at Low Temperatures

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Available generalized correlations of fugacity coefficients of nonpolar liquids are reexamined in their lower temperature ranges, and these correlations are extended to a reduced temperature of 0.35. Generalized functions are constructed from literature data on vapor pressures and liquid densities. Two sets of functions are presented with ω and z_c, respectively, as third parameter. The results fulfill a need for basic information in the engineering of cryogenic systems.

The same vapor pressure data are correlated in a generalized form down to $T_r = 0.35$ to give a one-parameter family of reduced vapor pressures curves. The correlation is compared with data on simple fluids, normal fluids, polar substances, and quantum fluids.

The principal objective of this paper is to generalize fugacity coefficients of nonpolar liquids at low temperatures to provide a norm of comparison for nonideal solution behavior and to provide a basis for phase equilibrium calculations. Correlations at high temperatures are available from other investigations (*1* to *3*). We collected vapor pressure data at low temperatures and calculated fugacity coefficients from these data. The fugacity coefficient was then correlated as a function of reduced temperature and pressure with either ω or z_c as third parameter. The low temperature fugacity coefficients were integrated with high temperature correlations. Finally we used the vapor pressure data to generalize the vapor pressure at low temperatures. The results reported fulfill a need for basic information in the engineering of cryogenic systems.

The fugacity of the saturated liquid is calculated from vapor pressure using Martin's equation for the second virial coefficient (*9*). The fugacity coefficient is determined as a combination of the saturated liquid fugacity and a pressure correction determined from liquid volume data at saturation pressure.

Vapor pressure which is frequently as useful because of its direct relationship to fugacity is also correlated for nonpolar liquids with either ω or z_c as third parameter. The correlation provides a basis for an exploration of the limit of applicability of three-parameter correlations.

CALCULATION OF FUGACITY

Fugacity of liquids has been included in previous generalized correlations of thermodynamic properties. For instance, the reduced states correlation of Pitzer et al. (*1*) employs the acentric factor ω for a third parameter extending down to a lower limit of $T_r = 0.8$. The reduced states correlation of Lydersen, Greenkorn, and Hougen (*2*), based on the use of z_c for a third parameter, covers reduced temperatures down to 0.5. Chao and Seader (*3*) gave equations for fugacity coefficients at values of $T_r > 0.50$. The present work reexamines these correlations at their lower temperature ranges and extends them to a reduced temperature of 0.35.

The calculation of fugacity of liquids starts with vapor pressure data. The American Petroleum Institute Project 44 tables (*4*) contain a wealth of information on vapor pressure of normal paraffin hydrocarbons. The range of pressure is from 10 to 1,500 mm. Hg. These values generally fall in the range of reduced temperature from 0.5 to 0.8. They provide the basis for the present work in this temperature range.

At reduced temperatures below 0.5 the vapor pressures are so low that special experimental techniques are required for their accurate determination. Hence there is a correspondingly smaller quantity of data at these low temperatures. Tickner and Lossing (*5*) employed mass spectrometer for the determination of very small vapor pressures. We depend on their data for reduced temperatures below 0.5. We also used vapor pressure of n-octane down to $T_r = 0.4$ taken from reference *6*.

Liquid fugacity is calculated from vapor pressure data according to

$$\ln \nu = \ln\left(\frac{p^0\phi^0}{p}\right) + \frac{\tilde{V}_L{}^0(p - p^0)}{RT} \tag{1}$$

where ν denotes the fugacity coefficient of the liquid and is defined by

$$\nu = f/p \tag{2}$$

The derivation of Equation (1) may be found in standard texts (*7*). The superscript 0 in Equation (1) denotes properties of a saturated fluid. Thus p^0 stands for vapor pressure and ϕ^0 is the fugacity coefficient of the saturated vapor

$$\phi^0 = \frac{f^0}{p^0} \tag{3}$$

Equation (1) is rigorous except for the assumption that the liquid is incompressible. This is an excellent simplifying assumption at low temperatures, which is the scope of this work. However at progressively higher temperatures real liquids become increasingly more compressible. Possible errors resulting from the assumed incompressibility of liquids in Equation (1) can be estimated by considering the isothermal compressibility β_T, defined as

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{4}$$

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TABLE 1. $\nu^{(0)}$ AT VARIOUS T_r AND P_r

T_r	$\nu^{(0)}$						
	$P_r = 0.1$	0.3	0.5	1.0	3.0	5.0	10.0
0.35	0.00035	0.000112	0.000075	0.000042	0.000025	0.000025	
0.40	0.0030	0.000107	0.000725	0.000380	0.000209	0.00020	
0.45	0.013	0.00465	0.0031	0.0016	0.00087	0.00080	
0.50	0.054	0.0177	0.0109	0.00604	0.00316	0.00286	0.00410
0.55	0.132	0.0447	0.0282	0.0155	0.00794	0.00682	0.00980
0.60	0.288	0.1048	0.0631	0.0339	0.01660	0.0142	0.01820
0.65	0.549	0.1998	0.1260	0.0661	0.0331	0.0276	0.0345
0.70	0.934	0.311	0.204	0.1149	0.0549	0.0430	0.0541
0.75	1.447	0.49	0.324	0.1738	0.0794	0.0635	0.0805

Integration of Equation (4) from saturation gives

$$\frac{V}{V^0} = \exp\{-\beta_T (p - p^0)\} \tag{5}$$

Expanding Equation (5) in a power series, ignoring higher order terms, one gets

$$\frac{V}{V^0} = 1 - \beta_T (p - p^0) \tag{6}$$

Now we evaluate

$$\text{Error } (\ln \nu) = \int_{p_0}^{p} \frac{\tilde{V}^0}{RT} \beta_T (p - p^0)\, dp \tag{7}$$

Integrating

$$\text{Error } (\ln \nu) = \frac{1}{2} \frac{\tilde{V}^0 \beta_T}{RT} (p - p^0)^2 \tag{8}$$

We evaluate this error for the highest pressure of the correlation $P_r = 10.0$ at $T_r = 0.75$ with values of β taken from Rowlinson (*8*). These calculations show the maximum error in ν is of the order of 1%.

In addition to vapor pressure data, which is the most important part, the use of Equation (1) for the calculation of ν requires two additional pieces of data: ϕ^0 and $\tilde{V}_L{}^0$.

For the calculation of ϕ^0 we chose to use Martin's equation (*9*) for the second virial coefficients:

$$\frac{P_c B}{RT} = \frac{0.188}{T_r} - \frac{0.468}{T_r^2} - \frac{8.87}{T_r^2} \exp\{-5\, T_r\} \tag{9}$$

The formula for the calculation of ϕ^0 with the use of B is

$$\phi^0 = z^0 \tag{10}$$

The compressibility of z^0 is related to B by

$$z^0 = \frac{p^0}{\rho^0 RT} = 1 + B\rho^0 \tag{11}$$

Equation (11) determines ρ^0 and z^0 for known values of B.

The fugacity coefficient of the saturated vapor ϕ^0 is never far from 1 at all the conditions studied, because of the low vapor pressures. Its deviation from 1 tends to be the largest at the highest temperatures where it amounts to about 2%. It can be concluded that the effect of imperfection of saturated vapor is small for the purpose of this work.

Molal volumes of the liquid $\tilde{V}_L{}^0$ are derived from density values contained in the American Petroleum Institute Project 44 tables (*4*). These tables adequately cover the substances selected for developing the present correlations.

CORRELATION OF LIQUID FUGACITY

Substances are selected for their varying values of acentric factor ω and critical compressibility factor z_c. In the range of reduced temperatures from 0.5 to 0.8, we chose to use the n-paraffins from methane up to C_{20} covering values of ω up to about 0.8 and values of z_c from 0.23 to 0.29. In the range of reduced temperatures below 0.5 the values of ω extend to 0.4 and the values of z_c from 0.26 to 0.29. The substances studied are n-paraffins from methane to pentane, n-octane, ethene, propene, iso-butane, and 1-butene.

Fugacity coefficients calculated in the manner described in the preceding section are used to determine values of the functions $\nu^{(0)}$ and $\nu^{(1)}$ in the reduced states equations:

$$\log \nu = \log \nu^{(0)} + \omega \log \nu_\omega{}^{(1)} \tag{12}$$

and

$$\log \nu = \log \nu^{(0)} + (z_c - 0.293) \log \nu_{z_c}{}^{(1)} \tag{13}$$

The three functions $\nu^{(0)}$, $\nu_\omega{}^{(1)}$ and $\nu_{z_c}{}^{(1)}$ depend only on reduced temperature and reduced pressure. According to Equation (12), at a fixed value of reduced temperature and reduced pressure a plot of $\log \nu$ at various values of ω should follow a straight line. The intercept of the line at $\omega = 0$ determines $\log \nu^{(0)}$ and the slope determines $\log \nu_\omega{}^{(1)}$. Graphs were constructed at various T_r and p_r. The results obtained are presented in Tables 1 and 2.

TABLE 2. $\log \nu_\omega{}^{(1)}$ AT VARIOUS T_r AND P_r

T_r	$-\log_{10} \nu_\omega{}^{(1)}$						
	$P_r = 0.1$	$P_r = 0.3$	$P_r = 0.5$	$P_r = 1.0$	$P_r = 3.0$	$P_r = 5.0$	$P_r = 10.0$
0.35	6.260	6.35	6.410	6.49	6.529	6.67	
0.40	4.67	4.76	4.79	4.85	4.91	5.074	
0.45	3.70	3.72	3.740	3.86	3.90	4.02	
0.50	2.890	2.870	2.970	3.015	3.120	3.162	3.399
0.55	2.150	2.180	2.264	2.361	2.410	2.420	2.729
0.60	1.721	1.780	1.795	1.800	1.860	1.920	2.094
0.65	1.316	1.325	1.350	1.375	1.490	1.529	1.732
0.70	0.950	0.960	1.012	1.040	1.095	1.111	1.490
0.75	0.675	0.688	0.718	0.740	0.78	0.829	1.050

TABLE 3. $\log \nu_{zc}^{(1)}$ AT VARIOUS T_r AND P_r

T_r	$\log_{10} \nu_{zc}^{(1)}$ at various T_r and P_r $P_r = 0.1$	$P_r = 0.3$	$P_r = 0.5$	$P_r = 1.0$	$P_r = 3.0$	$P_r = 5.0$	$P_r = 10.0$
0.35	66.80	67.2	67.49	69.10	71.20	71.50	
0.40	50.40	50.8	51.0	52.20	53.25	54.60	
0.45	39.40	39.82	40.7	40.85	41.35	42.90	
0.50	30.20	30.4	30.6	31.39	32.20	33.42	35.10
0.55	22.79	22.9	23.6	23.7	24.95	25.13	28.45
0.60	18.09	18.15	18.20	18.29	18.91	19.58	21.85
0.65	13.39	13.69	13.91	14.01	15.15	15.61	17.85
0.70	9.90	10.25	10.49	10.70	11.52	11.72	15.30
0.75	6.96	7.04	7.36	7.42	7.64	8.32	10.85

Equation (12) was derived by Pitzer and co-workers (*1*). Equation (13) results from the observation that for simple fluids $z_c = 0.293$. The use of z_c in association with the correction function $\nu^{(1)}$ follows the scheme of Lydersen, Greenkorn, and Hougen (*2*). We also can plot Equation (13) according to which the logarithm of ν for various values of z_c should follow a straight line. The intercept of this line at $z_c = 0.293$ determines $\log \nu^{(0)}$ and the slope determines $\log \nu_{z_c}^{(1)}$. Graphs were constructed at various T_r and p_r. The values of $\nu^{(0)}$ thus obtained were found to coincide with those presented in Table 1. The values of $\nu_{z_c}^{(1)}$ are presented in Table 3.

Ethene and propene were found to deviate substantially from the linear relation of Equation (13). Their z_c values of 0.27 and 0.274, respectively, also deviate substantially from Lydersen's correlation of critical properties (*10*), which places them at 0.286 and 0.282, respectively. Because of this discrepancy, data for ethene and propene were not used in the development of values of $\nu_{z_c}^{(1)}$.

The present values of $\nu_{z_c}^{(1)}$ show some disagreement with the values given by Lydersen, Greenkorn, and Hougen (*2*) at T_r below 0.8. At a reduced temperature of 0.5, which is the lowest temperature studied by Lyderesn et al., the uncertainty in ν caused by this difference can amount to 15% for a substance with a z_c of 0.25.

Our new values of $\nu^{(0)}$ are in substantial agreement with Chao and Seader's (*3*) equation at the higher temperatures. However, there is some disagreement at the lower temperatures. Figure 1 shows a comparison at $T_r = 0.5$, which is the lowest limit for Chao and Seader's equation. The maximum deviation taking place at $P_r = 1.0$ amounts to about 20%. The deviation appears to be systematic. Chao and Seader (*3*) obtained their liquid fugacity values from processing of mixture data with selected equations to represent nonideal liquid solution behavior and vapor imperfection. For the heavy substances the vapor imperfection calculations played a dominant role. The systematic deviation in ν at the low reduced temperatures appears to be caused by the use of the Redlich and Kwong equation of state [which was used by Chao and Seader (*3*) to represent vapor imperfection]. The new values of ν of the present correlation should be considered for mixture calculations when an accurate equation of state is used for the reliable calculation of vapor imperfection.

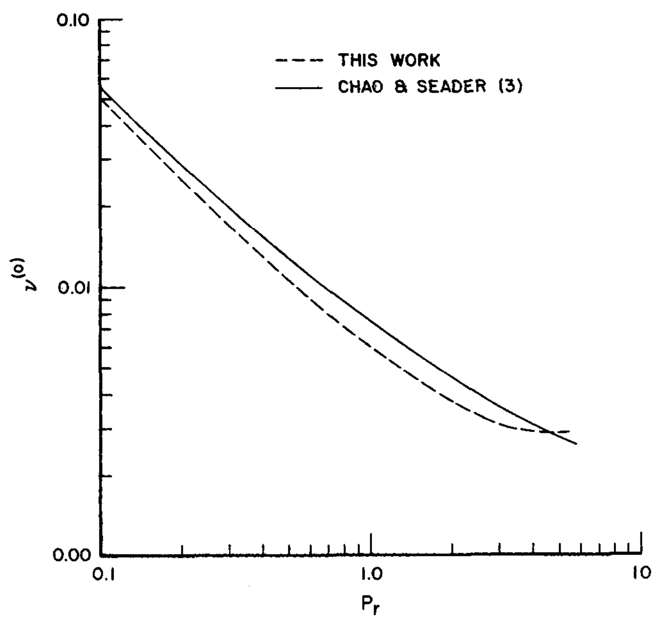

Fig. 1. Comparison of $\nu^{(0)}$ at $T_r = 0.5$.

VAPOR PRESSURE AT LOW TEMPERATURES

Vapor pressure data from the same sources described above were used to develop a generalized correlation of vapor pressure at the lower reduced temperatures. For this purpose we adopt, similar to Equations (12) and (13)

$$\log p_r = \log p_r^{(0)} + \omega \log p_{r\omega}^{(1)} \qquad (14)$$

and

$$\log p_r = \log p_r^{(0)} + (z_c - 0.293) \log p_{r\,z_c}^{(1)} \qquad (15)$$

Equation (14), based on the use of ω for third parameter, follows the scheme of Pitzer and co-workers (*1*). They have tabulated values of $p_r^{(0)}$ and $p_{r\omega}^{(1)}$ down to $T_r = 0.56$. Halm and Stiel (*11*) extended the tables down to $T_r = 0.44$. In Table 4 we show our new values of $\log p_r^{(0)}$, $\log p_{r\omega}^{(1)}$, and $\log p_{rzc}^{(1)}$ for values of T_r from 0.55 to 0.35. Our values of $\log p_r^{(0)}$ and $\log p_{r\omega}^{(1)}$ agree closely with Halm and Stiel's results (*11*), where the temperatures coincide except for $\log p_{r\omega}^{(1)}$ at T_r of 0.44.

Table 4 essentially defines a one-parameter family of reduced vapor pressure curves. The parameter can be either ω or z_c. Since the table values are functions of T_r only, interpolation can be readily carried out in electronic computers by means of Lagrange's formula (*12*). We have

TABLE 4. GENERALIZED VAPOR PRESSURE FUNCTIONS

T_r	$\log p_r^{(0)}$	$\log p_{r\omega}^{(1)}$	$\log p_{r\,z_c}^{(1)}$
0.550	−1.91	−2.24	23.8
0.525	−2.11	−2.53	27.0
0.550	−2.33	−2.91	30.7
0.475	−2.59	−3.32	35.0
0.450	−2.88	−3.75	40.0
0.425	−3.21	−4.34	45.3
0.400	−3.58	−4.94	51.8
0.375	−4.03	−5.46	57.7
0.350	−4.52	−5.93	62.9

used a fourth-degree interpolation formula to make comparisons of the ω correlation with vapor pressure data in the literature.

Reduced vapor pressures at low T_r are sensitively dependent on the individual substances, that is, on the value of ω. This is evident from the large absolute values of $\log \nu^{(1)}$ at low T_r. It becomes of interest to find out if one value of ω, suitably determined, should be adequate to represent the entire reduced vapor pressure behavior of a substance. Since the value of $\log p_{r\omega}{}^{(1)}$ at $T_r = 0.70$ is relatively small, the reduced vapor pressure is not sensitively dependent on ω at this T_r. Therefore it appears that one would not obtain the most dependable determination of ω by using vapor pressure at $T_r = 0.7$ as required in Pitzer's original definition of ω. A lower value of T_r, for instance 0.6, should probably serve better.

We have determined values of ω in the least squares sense for the best representation of reduced vapor pressures according to the formula

$$\omega = \frac{\Sigma \log p_{r\omega}{}^{(1)} \left(\log p_{r,\,\mathrm{exp}} - \log p_r{}^{(0)}\right)}{\Sigma \left(\log p_{r\omega}{}^{(1)}\right)^2} \qquad (16)$$

The summation is taken over the collection of vapor pressure points.

Vapor pressure data were collected to extend over the widest possible temperatures but to emphasize the low temperature range. They were used in Equation (16) to determine values of ω for substances of diverse types, including simple fluids, normal fluids, polar substances, and quantum fluids. Table 5[*] shows the deviations of the calculated vapor pressures from the experimental values using the ω values determined in this manner for a few representative substances. Methane and xenon are probably good approximations of simple fluids. Their vapor pressure behaviors are represented by the present correlation to generally within 1% with maximum deviation of about 2%. The normal fluids as represented by *n*-pentane and *n*-octane follow the correlation to about 4% with maximum deviations of about 8%. Strongly polar and associated substances are represented by water and ethanol. Of all the substances studied, water shows the largest deviation, with a maximum of about 10% at the triple point. Ethanol shows about half as much deviation. The deviations of polar substances from the generalized functions of this work are higher than those for Halm's work (*11*) which employs a fourth parameter. Nevertheless the present deviations are tolerable for some purposes.

The quantum fluids, para-hydrogen, and helium 3 assume negative values of ω, a reflection of the fact that at the same T_r their reduced vapor pressures are higher than those of all other substances. Their vapor pressures follow the correlation about as closely as the simple fluids. This description must be qualified for helium, inasmuch as its liquid shows a second-order transition as the temperature is lowered. Only the high temperature liquid phase follows the generalized correlation.

DISCUSSION

The principal objective of this paper—to generalize fugacity coefficients of low temperature nonpolar liquids—has been accomplished. Two equivalent sets of generalized functions are presented, one based on the use of ω and the other on z_c. The accuracy and applicability of the correlations have been explored in terms of a study of vapor pressures.

Our vapor pressure studies indicate that a single third parameter can be used for the correlation of thermodynamic properties of simple fluids, normal fluids, polar substances, and quantum fluids. The best accuracy can be expected for simple fluids and quantum fluids. Results for normal fluids and polar substances are less accurate at low reduced temperatures.

It is of interest that no qualitative differences are observed in the vapor pressure behaviors of fluids of such diverse types examined here, in spite of profound differences in the molecular mechanisms that differentiate fluids of these categories. It seems that the vapor pressure would make an unsuitable basis for the differentiation of the mechanism of molecular interactions.

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NOTATION

B = second virial coefficient
f = fugacity
p = pressure
R = universal gas constant
T = absolute temperature
V = volume
z = compressibility factor, pV/RT

Greek Letters

β = isothermal compressibility as defined by Equation (14)
ν = fugacity coefficient of a liquid, f/p
ρ = density
ϕ = fugacity coefficient of a gas, f/p
ω = acentric factor

Superscripts

(0) = simple fluids
(1) = deviation from simple fluid
0 = saturated fluid

Subscripts

c = critical state
r = reduced quantity

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[*] Table 5 has been deposited as document 01321 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 909 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $6.50 for photocopies.