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A Generalized Correlation for the Compressibilities of Normal Liquids

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Much attention has been given to the volumetric properties of normal fluids in the gas phase and it is now possible to estimate with good accuracy the compressibility of nonpolar (or slightly polar) gases. In this work we report a correlation for the compressibilities of normal liquids.

The compressibility β is defined by

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad (1)$$

For a given liquid, β is a function of both temperature and pressure (or density). As suggested by Wada (*6*) the effect of density ρ is given to a good approximation by

$$\rho\ \beta^{1/n} = \rho^s\ (\beta^s)^{1/n}$$

$$= \text{constant which depends on temperature} \qquad (2)$$

where superscript s stands for saturation and where n is an empirical constant. Substituting Equation (2) into Equation (1), we obtain

$$-\frac{d \ln v}{dP} = \beta^s \left(\frac{v}{v^s}\right)^n \qquad (3)$$

Rewriting and integrating Equation (3) we have

$$\int_{y^s}^{y} \frac{dy}{y^2} = -n\frac{\beta^s}{y^s}\int_{P^s}^{P} dP \qquad (4)$$

where $y = v^n$.

From Equation (4) we finally obtain

$$\rho^n = (\rho^s)^n\,[1 + n\ \beta^s\,(P - P^s)] \qquad (5)$$

The compressibility of saturated liquid, β^s, depends only on temperature. To obtain a generalized correlation, we reduced experimental compressibility data for argon (*7*), methane (*7*), nitrogen (*7*), benzene (*7*), and *n*-heptane (*3*). From these data we obtain the empirical reduced equation

TABLE 1. LIQUID VOLUME OF ARGON

Temp., °K.	Pressure, atm.	Vol.,* cc./g.mole	% Dev. $V_{\text{calc.}}$
110	100	31.1	—1.4
	500	28.7	—2.5
	1,000	26.9	—2.0
120	50	33.5	—0.9
	500	29.5	—2.5
	1,000	27.5	—2.1
130	50	36.4	—1.9
	500	30.3	—2.6
	1,000	28.1	—2.3
	2,000	25.4	—0.4
140	50	40.5	—2.4
	500	31.1	—2.6
	1,000	28.6	—2.0

* Experimental data from Din (*2*).

TABLE 2. LIQUID VOLUME OF CARBON DIOXIDE

Temp., °K.	Pressure, atm.	Vol.,* cc./g.	% Dev. $V_{\text{calc.}}$
273.16	50	1.059	1.7
	500	0.901	1.7
	1,000	0.837	2.1
283.16	50	1.147	1.0
	500	0.925	1.1
	1,000	0.854	1.7
293.16	60	1.276	—0.1
	500	0.950	2.0
	1,000	0.871	2.8

* Experimental data from Din (*2*).

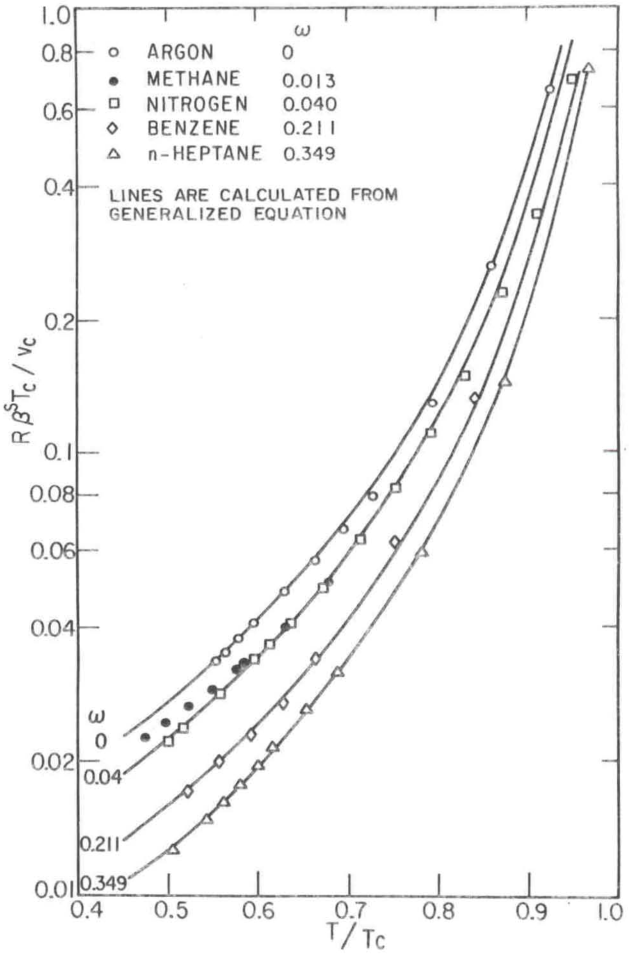

Fig. 1. Reduced compressibilities for saturated liquids.

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$$\frac{R\ \beta^s T_c}{v_c} = [1.0 - 0.89\ \omega^{1/2}][\exp(6.9547$$

$$- 76.2853\ T_R + 191.3060\ T_R^2$$

$$- 203.5472\ T_R^3 + 82.7631\ T_R^4)] \quad (6)$$

where $T_R = T/T_c$, T_c is the critical temperature, v_c is the critical volume, ω is Pitzer's acentric factor and R is the gas constant. Equation (6) holds for the interval $0.4 \leq T_R \leq 0.98$.

Figure 1 compares experimental compressibilities with those calculated from Equation (6).

To calculate densities (or volumes) of compressed liquids we use Equations (5) and (6) together with the correlation of Lyckman and Eckert (*1, 5, 6*) for the volumes of saturated liquids. Wada (*9*) has suggested that for normal fluids $n = 7$. However, our studies suggest that somewhat better results are obtained with $n = 9$. We can see that ρ is not strongly sensitive to n if we rewrite Equation (5) in logarithmic form:

$$\log \rho = \log \rho^s + \frac{1}{n} \log [1 + n\ \beta^s (P - P^s)] \quad (7)$$

Tables 1, 2, 3, and 4 compare observed liquid volumes at high pressures with those calculated from Equation (5). Figure 2 presents calculated and observed molar volumes for liquid butane. In all cases agreement between calculated and observed results is gratifying. For *n*-heptane at 523°K. somewhat larger deviations are observed because of proximity to the critical temperature (540°K.).

Because of their simplicity, Equations (5) and (6) are particularly useful for engineering calculations. They appear to give results at least as accurate as those obtained by other methods (*4*).

TABLE 3. LIQUID VOLUME OF *n*-BUTANE

Temp., °F.	Pressure, lb./sq.in.abs.	Vol.,* cu.ft./lb. mole	% Dev. $V_{calc.}$
130	80.6	1.734	—0.1
	1,000	1.688	—0.1
	5,000	1.574	—0.4
	10,000	1.497	—0.6
190	173.3	1.908	0.3
	1,000	1.824	0.3
	5,000	1.652	—0.5
	10,000	1.550	—0.5
250	327.7	2.202	—0.2
	1,000	2.021	—0.5
	5,000	1.736	—1.4
	10,000	1.606	—1.1
280	436.0	2.501	—1.3
	1,000	2.162	0.3
	5,000	1.782	—0.1
	10,000	1.636	0.6

* Experimental data from Sage and Lacey (*8*).

TABLE 4. LIQUID VOLUME OF *n*-HEPTANE

Temp., °K.	Pressure, bars†	Vol.,* cc./g.	% Dev. $V_{calc.}$
303.16	50	1.470	0.3
	500	1.400	0.1
	1,000	1.351	—0.1
	2,000	1.285	—0.2
	5,000	1.180	0.0
323.16	50	1.506	—0.2
	500	1.425	—0.5
	1,000	1.370	—0.7
	2,000	1.300	—0.8
	5,000	1.189	—0.5
373.16	50	1.610	—0.6
	500	1.491	—1.0
	1,000	1.420	—1.2
	2,000	1.336	—1.2
	5,000	1.211	—0.5
423.16	50	1.747	—0.4
	500	1.562	—0.8
	1,000	1.471	—0.8
	2,000	1.371	—0.5
	5,000	1.230	0.8
473.16	50	1.944	—0.5
	500	1.639	—0.9
	1,000	1.524	—0.6
	2,000	1.405	0.2
	5,000	1.248	2.1
523.16	50	2.224	2.9
	500	1.724	1.7
	1,000	1.578	2.7
	2,000	1.438	4.3
	5,000	1.268	6.9

* Experimental data from Doolittle (*3*).
† 1 bar = 14.504 lb./sq.in.abs.

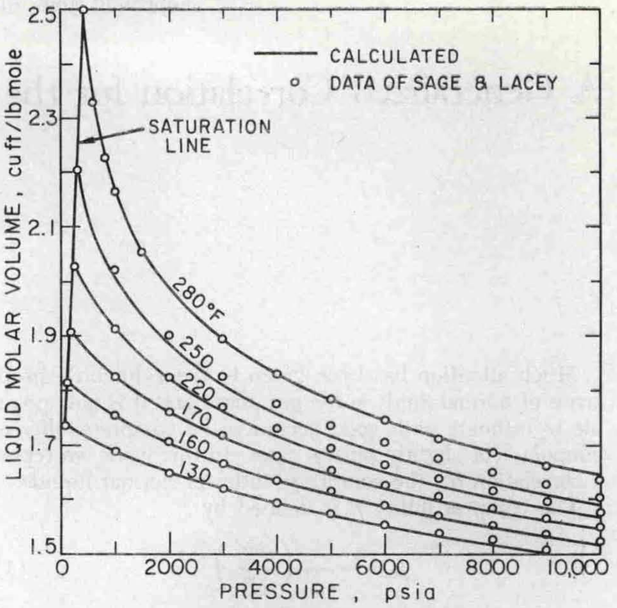

Fig. 2. Liquid molar volumes of *n*-butane at high pressures.

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