Correlation Method for Determining Compressed Liquid Densities

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A method is presented to calculate compressed liquid densities with a minimum of data. Data required are the critical values of pressure and temperature, and saturated liquid densities. The correlation predicts densities with less than 5% error in a region where few data are available.

FOR CALCULATIONS involving the handling and storage of cryogenic liquids under pressure, heat transfer to pressurized liquids, etc., accurate thermodynamic data are needed for compressed liquids. Such data can be computed if saturated liquid properties are known, together with P-ρ-T data on the compressed liquid. Unfortunately, experimental data are available for only a relatively few compressed liquids. Furthermore, most equations of state are limited by their developers to densities only slightly greater than the critical value. Thus, the Martin-Hou equation of state (*7*),

$$P = \sum_{i=1}^{5} f_i\,(V-b)^{-i} \qquad (1)$$

where the f's are temperature dependent, $f_i = A_i + B_iT + C_ie^{(K'T\ T)}$ is recommended for use at densities up to 1.5 times the critical density.

At higher densities, the generalized correlation of Lu (*5*) is often used. This correlation,

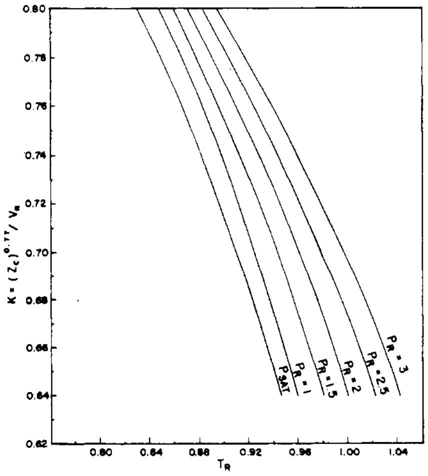
$$K = K(T_R, P_R) \qquad (3)$$

is graphical, using T_R as the independent variable and P_R as the parameter, with the dependent function, K, being a function of reduced volume and Z_c.

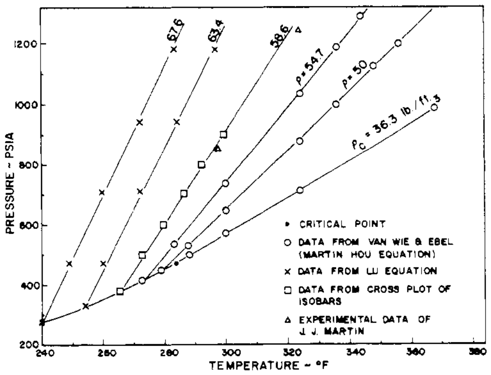
$$K = \frac{(Z_c)^{0.77}}{V_R} \qquad (3)$$

It is therefore a three-parameter correlation based on the work of Lydersen, Greenkorn, and Hougen (*6*).

In this paper a method is presented for determining compressed liquid densities, making use of data correlation based on the linearity of isometrics. This method was suggested by the fact that the Martin-Hou equation predicts essentially linear isometrics up to the maximum density for which it is recommended, and an inspection of the Lu chart showed, from the spacing of the parametric variable P_R along the isometrics, that Lu had based his diagram on linear isometrics. Although Obert states (*11*) that at high density the isometrics possess a degree of positive curvature, experimental data for several fluids indicate that the curvature, if any, is small and of the same order of magnitude as the experimental uncertainty.



◄ Figure 1. Lu chart for estimating liquid densities



► Figure 2. Isometrics of Freon-114

It was therefore possible to redraw the Lu chart to an expanded scale, restricting the range to $P_r < 3.0$, $T_r > 0.76$, and add parametric lines for $P_R = 1.5$ and $P_R = 2.5$. Within its range, the chart is identical with that originally prepared by Lu. The modified chart is shown as Figure 1, and is available in an enlarged version from the authors.

Since accurate saturated liquid densities were available for Freon-114 from Van Wie and Ebel (*15*), the modified Lu chart was used in the following manner. A liquid density was selected whose isometric was desired. The saturation temperature for this saturation density was determined from vapor pressure data, and interpolated as necessary. The value of T_R was then calculated, based on $T_c = 754°$R. The intersection of this value of T_R with the saturation line on the Lu chart identified the particular isometric. A horizontal line from this point then intersected the lines of constant P_R at particular values of T_R. These points were then plotted on a P-T diagram to obtain the isometric lines. This method is considered more accurate than the alternative method of calculating a value of K from given values of pressure, density, and temperature and entering the chart directly, since computing errors are eliminated, and saturated liquid properties have usually been more thoroughly investigated and are known with more accuracy than properties of the compressed liquid near the critical point.

Figure 2 is a plot of the isometrics of Freon-114, a portion of the data being taken from the Van Wie and Ebel tabulation and a portion from the Lu charts. Figure 3 is a cross-plot of the data of Figure 2 showing isobars as the parameter and density as the dependent function. Figure 2 shows that the data from the Lu chart do not overlap the data from the Martin-Hou equation. Rather, there

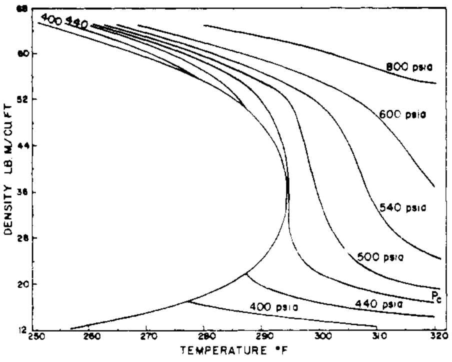


Figure 3. Isobars of Freon-114

is a gap between the values of 54.7 and 63.4 pounds per cubic foot. This has been filled with an isometric at 58.6 pounds per cubic foot based on the data read from Figure 3. The gap arises from the fact that the lowest value of K computed by Lu was 0.62. A chart correlating K down to 0.58 would be required to close the gap completely. Since the curvature of the isobars is not excessive at this density, the 58.6 pounds per cubic foot isometric represents the interface between the two sets of data. Both the linearity of the resulting isometric and the regularity of increase in slope of the lines indicate that the Martin-Hou equation and the Lu chart represent a similar approach to the correlation of density data and that no discontinuities occur at the interface.

The density value of 58.6 was chosen, since this represents the highest density at which Martin (*8*) obtained experimental density measurements. The triangle-shaped points in Figure 2 represent two samples of these experimental data and show that the correlation is at least as good as the fit of the Martin-Hou equation, from which a portion of the data of Figure 2 was derived. The equation of state shows errors of as much as 6% from the experimental values at this density, and neither of these points is as much in error as that value.

Enthalpy and entropy corrections from the saturated liquid values can be calculated from the density data of Figure 3, utilizing the Maxwell relations, thus completing the thermodynamic data required for this region.

Based on the encouraging results with Freon-114, the authors decided to determine if the method was generally applicable. Therefore, the best experimental data available were collected for the additional materials of carbon dioxide (*4, 9, 10*), propane (*12*), water (*1, 3, 14*), *n*-pentane (*12*), and sulfur dioxide (*2*). Included in this group are nonpolar materials, a material with a large dipole moment and an idiosyncratic value of Z_c, and a material with a quadrapole moment. The data have all been converted to reduced properties to determine if they would follow a single type of correlation based on the theory of corresponding states.

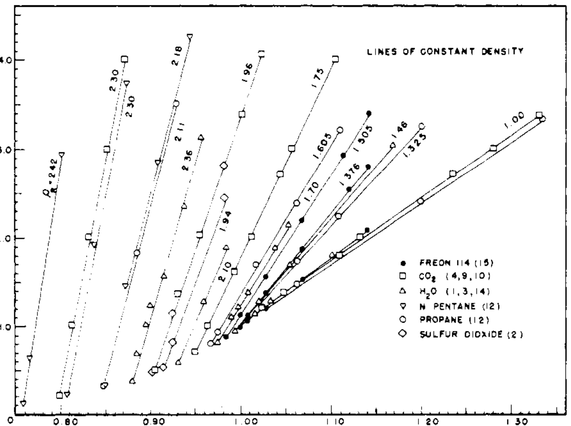


Figure 4. Reduced isometrics for a variety of experimental data

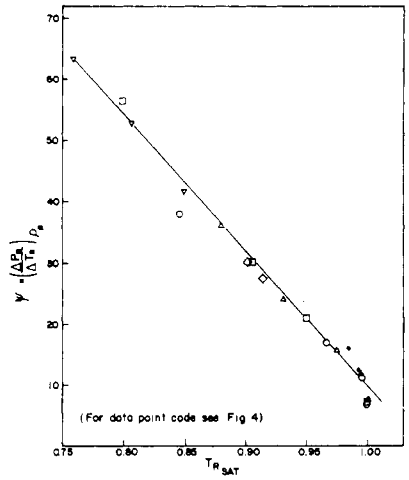


Figure 5. Slope of reduced isometrics as a function of reduced boiling point

The values are plotted as Figure 4, and the generality of the correlation is self-evident.

When reasonable amounts of experimental data are available as is the case with these specific materials, no more generalization is required. As was the case with Freon-114, it is merely necessary to plot those data which are available from experiment or from an equation of state in the region for which its validity has been established. These data can then be connected by straight lines with the equivalent saturated liquid density, to obtain the isometrics, the isobars then being drawn by cross-plotting the data.

For materials where experimental data are either scanty or entirely lacking (usually the more common case), a chart has been prepared based on the law of corresponding states. This correlation assumes that not only are the isometrics linear, but also that their slopes are a linear function of the reduced boiling point (saturation temperature). That this is qualitatively true can be seen from Figure 4. The slopes of the various isometrics have been calculated from Figure 4, and are plotted *vs.* $(T_R)_{\text{sat}}$ as Figure 5.

The slopes of the reduced isometrics have been computed from Figure 4, and are listed in Table I in order of decreasing reduced boiling point.

A brief examination of the data of Table I makes it clear that although the reduced isometrics are linear (Figure 4), reduced density is not a good correlating factor. However, the reduced saturation temperature appears to

Table I. Slopes of the Reduced Isometrics of Various Materials

Material	Source	ρ_R	$T_{R_{\text{sat}}}$	$\Delta P_R/\Delta T_R$	ψ = Slope Factor
Freon-114	(*15*)	1.00	1.00	1.08/0.141	7.66
Carbon dioxide	(*4*)	1.00	1.00	2.39/0.330	7.20
Water	(*3*)	1.00	1.00	1.08/0.140	7.70
Propane	(*12*)	1.00	1.00	2.35/0.334	7.05
Water	(*1, 3*)	1.46	0.995	2.08/0.174	11.9
Propane	(*12*)	1.32	0.995	2.29/0.205	11.2
Freon-114	(*15*)	1.38	0.993	1.86/0.148	12.6
Freon-114	(*15*)	1.505	0.985	2.50/0.156	16.0
Water	(*14*)	1.70	0.975	1.34/0.085	15.9
Propane	(*12*)	1.605	0.967	2.41/0.142	17.0
Carbon dioxide	(*4, 9, 10*)	1.75	0.950	3.30/0.156	21.1
Water	(*1, 3*)	2.10	0.931	1.30/0.054	24.1
Sulfur dioxide	(*2*)	1.94	0.914	1.93/0.070	27.6
Carbon dioxide	(*4, 9, 10*)	1.96	0.905	3.57/0.118	30.3
Sulfur dioxide	(*2*)	1.98	0.902	3.57/0.118	30.3
Water	(*3, 14*)	2.36	0.880	2.75/0.076	36.2
n-Pentane	(*12*)	2.18	0.849	3.96/0.095	41.7
Propane	(*12*)	2.11	0.846	3.19/0.084	38.0
n-Pentane	(*12*)	2.30	0.807	3.52/0.067	52.5
Carbon dioxide	(*9, 10*)	2.30	0.799	3.80/0.067	56.7
n-Pentane	(*12*)	2.42	0.759	2.83/0.044	63.4

Table II. Computation of Densities from Linear Isometrics as Compared with Observed Densities

Material	T	P	T_R	P_R	$T_{R\text{sat}}$	Density		Source	Error, %
						Calcd.	Exptl.		
Freon-114	320° F.	760 p.s.i.a.	1.034	1.61	0.977	56.7 lb./ft.^{3}	53.8	(*15*)	5.4
Freon-114	294.3° F.	500 p.s.i.a.	1.00	1.06	0.986	52.3 lb./ft.^{3}	53.3	(*15*)	1.9
Water	790° F.	8000 p.s.i.a.	1.072	2.49	0.970	34.6 lb./ft.^{3}	33.8	(*1*)	2.4
Propane	100° F.	2000 p.s.i.a.	0.841	3.23	0.786	31.6 lb./ft.^{3}	31.6	(*12*)	0.0
Propane	190° F.	2000 p.s.i.a.	0.976	3.23	0.893	27.1 lb./ft.^{3}	27.4	(*12*)	1.1
Hydrogen chloride	50° C.	141.7 kp./sq. cm.	0.995	1.67	0.946	0.758 g./ml.	0.760	(*13*)	0.1
Hydrogen chloride	60° C.	146 kp./sq. cm.	1.026	1.72	0.968	0.694 g./ml.	0.700	(*13*)	0.9
n-Butane	340° F.	1500 p.s.i.a.	1.092	2.91	0.959	2.45 ft.^{3}/mole	2.46	(*12*)	0.4
n-Butane	190° F.	2000 p.s.i.a.	0.887	3.88	0.815	1.83 ft.^{3}/mole	1.83	(*12*)	0.0

be satisfactory and does, in fact, show a linear correlation with a negative slope (Figure 5). Although two points show large deviations, the degree of agreement is very good in view of the wide range of material types and experimental sources from which the data points were derived. The linear equation for the data is,

$$\psi = 65.25 - 221.2\ (T_{R\text{sat}} - 0.75)$$

This equation has a useful range from $(T_R)_{\text{sat}}$ of 0.995 to 0.75. At the low end, it correlates the data satisfactorily, but the authors were not able to find valid experimental data to extend the equation to a lower range. At the upper end, the case is different. There seems to be no doubt that the correlation becomes nonlinear in the vicinity of $(T_R)_{\text{sat}} = 0.995$, and that the linear equation produces results that are 25 to 30% high at the critical point. Since this is the region in which the isotherms are essentially of infinite slope, and data are both scanty and widely varying, the authors have not been able to determine the nature of this nonlinearity. Therefore, at present, the region between 0.995 and 1.00 is essentially undefined, and subject to interpolation error of 10 to 20%.

A generalized plot of linear isometrics is shown in Figure 6, which is usable with an absolute minimum of available data, merely requiring critical values and saturated liquid densities. To determine density at any particular temperature and pressure, only two steps are required: Compute the reduced pressure and temperature for the material; locate this point on Figure 6 and determine the reduced saturation temperature for the material by following the isometric line to its intersection with the saturation curve. The saturation density at this temperature is also the density of the material at the desired temperature and pressure.

Since reduced densities do not correlate with reduced saturation temperature, if density and temperature (or pressure) are known, a trial and error technique is required to determine the dependent variable.

The results of such computations are given in Table II, for materials where precision *PVT* data are available. The density so calculated is then compared with an experimental density determined by graphical interpolation of the reported data.

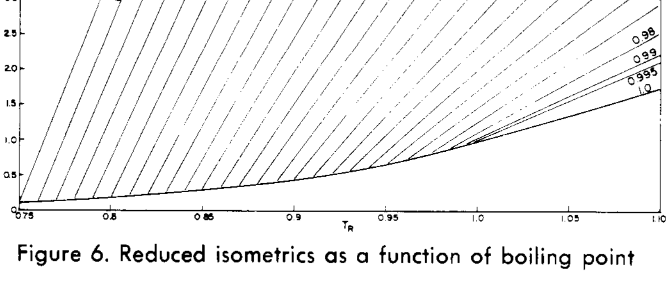


Figure 6. Reduced isometrics as a function of boiling point

The correlation has thus been tested utilizing both polar and nonpolar materials over a range of isometrics from 0.786 to 0.995 and shows a maximum deviation of 5.4%, with a root mean square deviation of 2.26%. The authors feel that 95% confidence can be given that the chart will predict liquid densities within its usable range with an error not greater than 4.5%. This is equivalent to assuming that the errors are due to random causes and are equally likely to be plus or minus.

Based on these data, the authors believe that a new and useful correlation has been developed, utilizing a minimum of available data and predicting densities with less than 5% error in a region where little experimental evidence is presently found in the literature.

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