

HOW TO ESTIMATE THERMODYNAMIC VALUES OVER THE V-L INTERPHASE

John J. Carroll, P.Eng.*

The tables of Lee and Kesler [1] are useful for calculating the thermodynamic properties of fluids. The tables are so important that they have been reproduced in many standard references, including Reid et al. [2] and Perry's Handbook [3].

The tables include compressibility factors, enthalpy departures, entropy departures, fugacity coefficients and heat capacity (both C_p and C_v departures). For each property there are two tables, one for the simple fluid and the other for the deviation.

Thus, a fluid property, say, compressibility factor, z , can be calculated as a linear combination of two functions, using an acentric factor, ω , for weighting:

$$z = z^{(0)} + \omega z^{(1)}$$

Here, $z^{(0)}$, the compressibility factor of the simple fluid, and $z^{(1)}$, the deviation, are listed in the appropriate tables as functions of the reduced temperature, T_R , and reduced pressure, P_R .

In the tables given by Reid et al for compressibility factors and other functions, there is a solid line that staircases down from low reduced temperature and low reduced pressure to the critical point. This line demarcates the liquid phase (low temperature and high pressure) and vapor phase (high temperature and low pressure).

Extreme care must be taken to not interpolate across this vapor-liquid (V-L) interphase line. In fact, the line does not appear in the original Lee-Kesler tables, and so it is quite easy to make this mistake when using them.

*Mr. Carroll is a simulation specialist with SACDA Inc. (343 Dundas St., Suite 500, London, Canada N6B 1V5). He has a Ph.D. in chemical engineering from the University of Alberta. He is a member of the Canadian Soc. of Chemical Engineering.

Don't interpolate

Take, for example, a calculation for the density of *n*-butane at 10°C and 380 kPa ($T_c = 425.2$ K, $P_c = 3,800$ kPa, $M = 58.124$ kg/kmol, and $\omega = 0.193$), using the Lee-Kesler tables. At these conditions, *n*-butane is a liquid (the vapor pressure at 10°C is about 150 kPa). To start, one should calculate the reduced temperature and pressure:

$$T_R = (10 + 273.15) / 425.2 = 0.666, \\ \text{and } P_R = 380 / 3,800 = 0.100$$

From the Lee-Kesler tables, at $T_R = 0.65$, $z^{(0)} = 0.0178$ and $z^{(1)} = -0.0078$; at $T_R = 0.7$, $z^{(0)} = 0.8958$, $z^{(1)} = -0.1161$. By interpolation, at $T_R = 0.666$, $z^{(0)} = 0.2988$, $z^{(1)} = -0.0425$, $z = 0.2988 + 0.193(-0.0425) = -0.2906$, and the density ($\rho = MP/zRT$) is 32.3 kg/m³.

The values for reduced temperatures of 0.65 and 0.70 at a reduced pressure of 0.1 are on opposite sides of the solid line. Thus, one is a liquid-phase compressibility factor and the other is for a gas. Therefore, this interpolation and, hence, the density is incorrect.

A better approach is to use only values for the liquid and extrapolate. At $T_R = 0.65$, $z^{(0)} = 0.0178$, $z^{(1)} = -0.0078$, and at $T_R = 0.6$, $z^{(0)} = 0.0186$, $z^{(1)} = -0.0082$. By linear extrapolation, at $T_R = 0.666$, $z^{(0)} = 0.0175$, $z^{(1)} = -0.0077$, $z = 0.0160$, and a density of 586 kg/m³.

The density calculated by the second method is closer to 589 kg/m³, the density of saturated liquid *n*-butane at 10°C [4]. Although the calculated and reported values are at slightly different pressures, the agreement is excellent.

As another example, calculate the density of saturated-vapor and saturated-liquid propane ($T_c = 369.2$ K, $P_c =$

4,245 kPa, $M = 44.097$ kg/kmol and $\omega = 0.153$) at 22.7°C. The vapor pressure of propane at 22.7°C is 902 kPa. To start, $T_R = (22.7 + 273.15) / 369.8 = 0.8$, while $P_R = 902 / 4,245 = 0.2125$.

From the tables, at $P_R = 0.2$, $z^{(0)} = 0.8539$ and $z^{(1)} = -0.116$; at $P_R = 0.4$, $z^{(0)} = 0.0661$ and $z^{(1)} = -0.0272$. By linear interpolation, at $P_R = 0.2125$, $z^{(0)} = 0.7879$, $z^{(1)} = -0.1105$, $z = 0.7711$, and the density is 2.1 kg/m³.

Now, the question arises: Is this the density for a vapor or for a liquid? From the magnitude of the compressibility factor, it appears to be for vapor. If so, then how do we calculate the density of the liquid? According to this approach, the two phases would have to have the same density. Again, we have interpolated across the solid line and, therefore, the result is questionable.

However, if for the vapor, only values representing the vapor phase are selected, then at $P_R = 0.1$, $z^{(0)} = 0.9319$, $z^{(1)} = -0.0487$, and at $P_R = 0.2$, $z^{(0)} = 0.8539$ and $z^{(1)} = -0.1160$. Extrapolation to P_R at 0.2125 yields $z^{(0)} = 0.8442$, $z^{(1)} = -0.1244$ and $z = 0.8253$, along with a density of 19.6 kg/m³.

Similarly, for the liquid, selecting only values representing liquid-phase compressibilities, at $P_R = 0.4$, $z^{(0)} = 0.0661$, $z^{(1)} = -0.0272$, and at $P_R = 0.6$, $z^{(0)} = 0.0985$, $z^{(1)} = -0.0401$. By linear extrapolation, at $P_R = 0.2125$, $z^{(0)} = 0.0357$, $z^{(1)} = -0.0151$, $z = 0.0334$, and the density is 484 kg/m³. These compare quite well with values in literature [4] of 20.2 kg/m³ for vapor and 496 kg/m³ for liquid.

Thus, the principle is to extrapolate, using only liquid values from the table for liquid calculations, and only vapor values for vapor calculations. ■

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