**Determination of stability when searching for entropy values.**

Often when solving process problems, the entropy and pressure of a state are known, and the remaining state variables are to be found. If this is the case, it is helpful to keep in mind the behavior of the isobars. Whenever multiple real roots exist, the fugacity is used to determine which root is stable as will be explained in this handout.

Figure 1 shows the behavior of the entropy values for ethane at 0.1 MPa as calculated by the Peng-Robinson equation of state using a real gas reference state of \( T = 298.15 \text{K} \) and \( P = 0.1 \) MPa. The figure was generated from the spreadsheet PREOS.xls by adding the formula for entropy departure for the center root and then changing the temperature at a fixed pressure of 0.1 MPa. The corresponding values of \( S \) were recorded and plotted.

![Figure 1. Entropy values for ethane calculated from the Peng-Robinson equation along an isobar at 0.1 MPa. The largest Z root is shown as diamonds, the smallest Z root is shown as triangles, and the center root is shown as open squares. The stable behavior is indicated by the solid line.](image)

Suppose a process problem requires a state with \( S = -18.185 \) J/mol-K. At 200K, the largest Z root has this value. The corresponding values of the fugacities from largest to smallest Z are 0.0976 MPa, 0.652 MPa, 0.206 MPa, indicating that the largest root is most stable, so the largest root will give the remainder of the state variables.
Suppose a process problem requires a state with $S = -28.35$ J/mol-K. At 150K, the largest $Z$ root has this value. The corresponding values of the fugacities from largest to smallest $Z$ are 0.0951 MPa, 0.313 MPa, 0.0099 MPa, indicating that the smallest root is most stable. Even though the largest $Z$ root has the correct value of $S$, the root is not the most stable root, and must be discarded.

Further exploration of roots would show that the desired value of $S$ cannot be obtained by the middle or smallest roots, or any most stable root. Usually if this behavior is suspected, it is quickest to determine the saturation conditions for the given pressure and compare the saturation values to the specified value. The saturation conditions at 0.1 MPa can be found by adjusting the $T$ until the fugacities become equal for the large $Z$ and small $Z$ root, which is found to occur at 184.2K. At this condition, the corresponding values of the fugacities from largest to smallest $Z$ are 0.0971 MPa, 0.524 MPa, 0.0971 MPa, indicating that largest and smallest $Z$ roots are in phase equilibrium, and the center root is discarded as before. The corresponding values for saturated entropy are $S = -21.3021$ J/mol-K for the vapor phase and -100.955 J/mol-K for the liquid phase. For any condition at 0.1 MPa, any value of $S$ between these two values will fall in the two-phase region. Therefore the desired state of $S = -28.35$ J/mol-K is two-phase, with a quality calculated using

$$S = S_{satL} + q \left(S_{satV} - S_{satL}\right)$$

$$-28.35 \text{ J/mol-K} = -100.955 + q(-21.3021 + 100.955) \quad \Rightarrow \quad q = 0.912$$

The cautions highlighted in the example also apply when searching for specific values of other state properties by adjusting $P$ and/or $T$. For example, it is also common to search for a state with specified values of $\{H, P\}$ by adjusting $T$. The user must make sure that the root selected is a stable root, or if the system is two-phase, then a quality calculation must be performed.