ChE *class and home problems*

The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

BEWARE OF BOGUS ROOTS WITH CUBIC EQUATIONS OF STATE

RONALD M. PRATT
National University of Malaysia • Bangi, Selangor, Malaysia 43600

The Peng-Robinson equation of state and its close kin, the Soave-Redlich-Kwong equation, are simple yet very effective tools for solving phase equilibria problems involving hydrocarbons and other nonpolar and slightly polar species. Being cubic equations, when solved for the compressibility factor, Z, they will either yield three real roots or a single real root and a complex pair. It would be most convenient and is sometimes believed that one single root implies a single phase while three real roots imply liquid and vapor phases are in equilibrium. Sadly, such is not the case. Care must always be taken to extract the correct root. Major blunders can be made, as we will show in the following problem.

PROBLEM STATEMENT

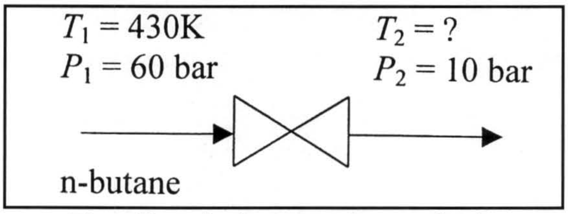

***Figure 1.** Throttling of n-butane to known final pressure.*

Pure n-butane at 430K and 60 bars is throttled to a final pressure of 10 bar, as shown in Figure 1. What is the temperature of the stream as it exits the valve? Use the Peng-Robinson equation of state to model the PVT behavior of n-butane.

***Ronald M. Pratt** is a lecturer in the engineering department at the National University of Malaysia. He obtained his BS in mathematics and in chemical engineering at the Colorado School of Mines, his MS in mathematics at the Fuxin Mining Institute in Liaoning Province, China, and his PhD in chemical engineering at the Colorado School of Mines. Research interests involve molecular dynamics and fractal modeling, and his teaching responsibilities have included undergraduate, graduate, and statistical thermodynamics courses and molecular simulation.*

SOLUTION

The Peng-Robinson equation is written as

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

where

R	universal gas constant
T	absolute temperature
v	molar volume
a	$a_c\left[1+m\left(1-\sqrt{T/T_c}\right)\right]^2$
a_c	$0.45723553\ R^2T_c^2/P_c$

m $0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$
b $0.077796074\,RT_c/P_c$
T_c critical temperature = 425.1K for n-butane[1]
P_c critical pressure = 37.96 bar for n-butane[1]
ω pitzer acentric factor = 0.200 for n-butane[1]

It is common to rewrite the Peng-Robinson equation as a cubic polynomial,

$$f(Z) = Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \tag{2}$$

where

$\alpha \equiv B-1$
$\beta \equiv A-2B-3B^2$
$\gamma \equiv B^3 + B^2 - AB$

and

$A \equiv aP/(RT)^2$
$B \equiv bP/RT$

Since an energy balance written across the valve (assuming residence time of the fluid in the valve is so short that heat loss through the valve casing is negligible) states that $\Delta H = 0$, we therefore need to find the exit temperature, T_2, that satisfies this condition. This requires that we be able to calculate the enthalpy change across the valve, ΔH. We will consider ΔH to be the sum of two parts, an ideal gas contribution and a residual correction for non-ideal behavior,

$$\Delta H = \Delta H^{ID} + \Delta H^{R} \tag{3}$$

The ideal gas contribution is determined from ideal gas (low pressure) heat capacity data:

$$\Delta H^{ID} = \int_{T_1}^{T_2} C_P^{ID}\,dT \tag{4}$$

Heat capacities for gases in the ideal gas state are functions of temperature only and are usually given by correlations. A common correlation[1] is

$$C_P^{ID} = R\left(A + BT + CT^2 + DT^{-2}\right) \tag{5}$$

Table 1 shows the coefficients for n-butane in the ideal gas state.

The residual contribution is calculated using standard equations[2,3] derived from the Peng-Robinson equation of state,

$$\Delta H^{R} = H_2^{R} - H_1^{R} \tag{6}$$

where

$$H^{R} = \frac{Ta' - a}{b\sqrt{8}}\,\ell n\left[\frac{Z + B\left(1+\sqrt{2}\right)}{Z + B\left(1-\sqrt{2}\right)}\right] + RT(Z-1) \tag{7}$$

and

$$a' \equiv \frac{da}{dT} = \frac{-ma}{\left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]\sqrt{TT_c}}$$

TABLE 1
Ideal Gas State Heat Capacity Coefficients for n-butane

	n-butane
A	1.935
B	36.915×10^{-3}
C	-11.402×10^{-6}
D	0

TABLE 2
Enthalpy Changes

T_2(K)	ΔH(J/mole)
400	1810.13
375	5508.98
350	2394.94
325	-683.42
330.531	0.00

H_1^R and H_2^R are evaluated from Eq. (7) using the compressibility factors corresponding to the initial and final states, respectively.

A temperature for the stream leaving the valve may be guessed and ΔH calculated as indicated above. Proceeding by trial and error (the secant method[4] could be used to impose self-consistency and avoid a trial-and-error solution), we obtain Table 2. We see that a value of T_2 = 330.531K gives a ΔH equal to zero (within two decimal places accuracy).

The "solution" is that the exit stream is n-butane vapor at 330.531K. All done, right? Not quite. Everything seems well until one looks at a phase diagram for n-butane or notices that the temperature is well below its boiling point at 10 bar pressure (T^{sat}=352.475K), and therefore at these exit conditions (10 bar, 330.531K) n-butane is a subcooled liquid. This is shown in Figure 2. The actual state of n-butane at 10 bar

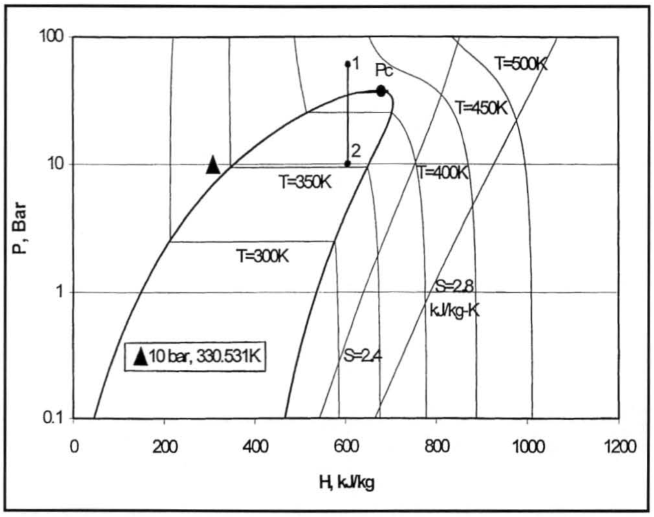

Figure 2. Pressure-enthalpy diagram for n-butane.

and 330.531K is shown by the m in Figure 2, obviously far from the correct solution (Point 2 in Figure 2), which indicates that the exit stream is a mixture of vapor and liquid.

The calculation has been deceiving us with bogus quasi-vapor roots. Vapor roots can only be used for temperatures above the boiling point. Below this temperature, liquid roots must be used. Therefore, to proceed with the solution to this problem, we should first determine the boiling point, T^{sat}, for n-butane at 10 bar. Since at the boiling point, liquid and vapor phases must be in equilibrium, we must find the temperature at which the chemical potentials of both phases are equal. For a pure component, this is equivalent to saying that the Gibbs free energies must be equal for the two phases. Since the ideal gas contribution to the Gibbs free energy is the same for each phase, we only need concern ourselves with the residual contribution. At the boiling point we require that

$$G_V^R = G_L^R \tag{8}$$

The residual Gibbs free energies are calculated from the Peng-Robinson equation of state using the standard derived formula[2,3]

$$G^R = -\frac{a}{b\sqrt{8}}\ell n\left[\frac{Z+B\left(1+\sqrt{2}\right)}{Z+B\left(1-\sqrt{2}\right)}\right] - RT(Z-B) + RT(Z-1) \tag{9}$$

The vapor G^R in Eq. (8) is computed from Eq. (9) using the largest compressibility factor root. Similarly, the liquid G^R should be calculated using the smallest root. Different temperature values may be selected on a trial-and-error basis until the equivalence of Eq. (8) is satisfied to within some tolerance. (Again the secant method can be used to facilitate coding of this algorithm.) Proceeding in this manner, we find that at 352.475K, $G^R = G^L = -540.28$ J/mole, and therefore $T^{sat} = 352.475$K.

For this problem, one will find that ΔH is positive when using the vapor roots at T^{sat}, and ΔH is large and negative when using the liquid root at T^{sat}. Therefore, the exit stream is a mixture of liquid and vapor in just the right combination to make $\Delta H = 0$. Equation (6) must be modified to include both a vapor and liquid contribution to the enthalpy of the exit stream,

$$\Delta H^R = xH_{2V}^R + (1-x)H_{2L}^R - H_1^R \tag{10}$$

TABLE 3
Computed Compressibility Factors

T	Z_L	Z_{middle}	Z_V	v_L(m^3/kmol)	v_{middle}(m^3/kmol)	v_V(m^3/kmole)
280	**0.03982**	none	none	**0.09270**	none	none
293	**0.03907**	0.44221	0.48898	**0.09617**	1.07724	1.19116
352.475	**0.03880**	0.13666	**0.79982**	**0.11370**	0.40048	**2.34383**
396	0.05482	0.05694	**0.86624**	0.18048	0.18746	**2.85197**
600	none	none	**0.96897**	none	none	**4.83360**

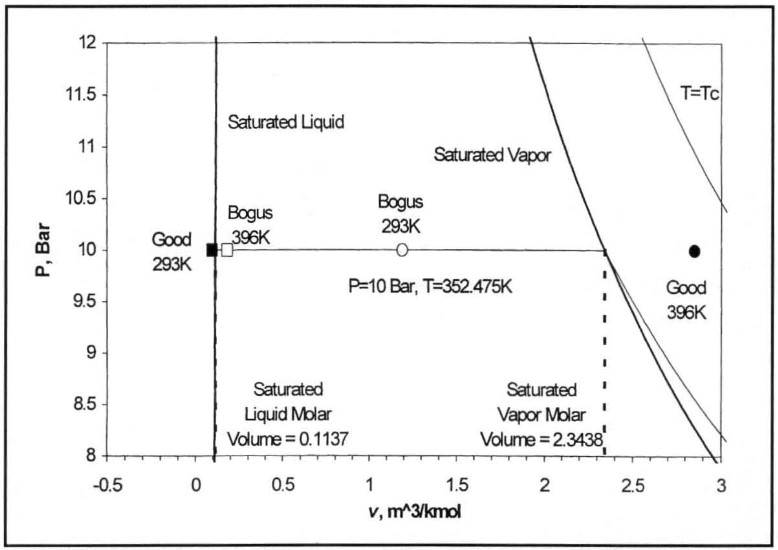

Figure 3. *Magnified pressure-volume diagram in the region P=10 bar for n-butane*

where x is the quality or percent vapor in the two-phase exit stream. When the calculation is made using Eq. (7), the exit stream is found to have a quality of 0.8434. Therefore, the correct solution to the problem is that the exit stream is at its saturation temperature of 352.475K and consists of 84.34% vapor and 15.66% liquid (as shown in Figure 2).

DISCUSSION

To illustrate more clearly what has happened here, we will look at solutions of the Peng-Robinson equation for Z (and v) at 10 bar at various temperatures. Obviously, at 10 bar, n-butane exists as a superheated vapor above T^{sat} and as a subcooled liquid below T^{sat}. At various temperatures at P=10 bar, we obtain Table 3 from Eq. (2).

Which roots are valid? Certainly we can rule out all of the intermediate or middle values. (These intermediate roots that lie within the saturation envelope are of use in stability analysis,[5] something we are not concerned with here.) Also, any liquid roots above the boiling point must be ruled out, and any vapor roots below the boiling point must be eliminated. Only the values in bold print hold any physical significance for us. (The Peng-Robinson equation is not recommended for calculating subcooled liquid values, but values are physically significant even if they are of low accuracy.)

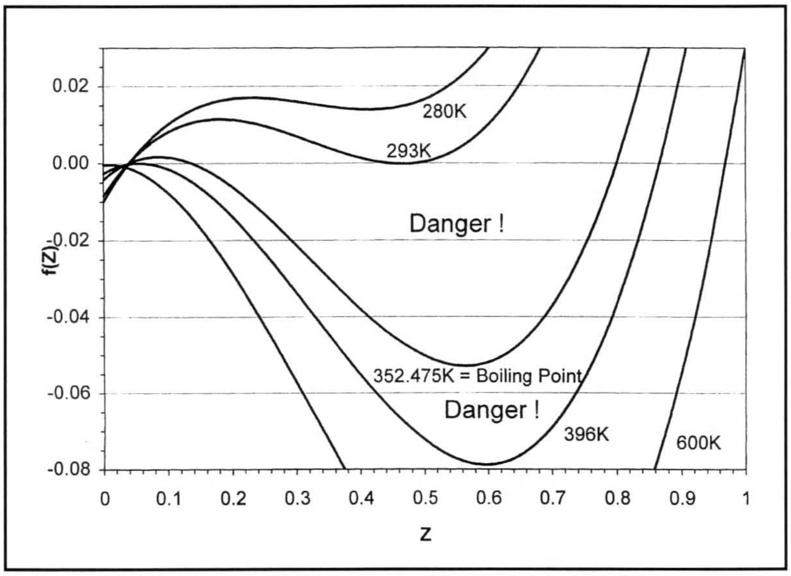

Figure 4. *The Peng-Robinson polynomial*

$$f(Z) = Z^3 + \alpha Z^2 + \beta Z + \gamma$$

as a function of Z for n-butane at 10 bar for various temperatures.

Figure 3 is a magnified PV diagram in the region of 10 bar and shows the bogus liquid root at 396K (0.18048 m^3/kmol) and the bogus vapor root at 293K (1.19116 m^3/kmol). Their respective valid superheated vapor and subcooled liquid volume roots are also shown. The saturated molar volumes are also indicated in Figure 3. Note that the bogus roots lie within the phase envelope.

The danger is that we obtain what appear to be liquid and vapor roots in regions quite far from the boiling point. A value of 293K is the minimum temperature (rounded to a whole number) that will still yield a bogus vapor root. At temperatures lower than this, the Peng-Robinson equation will provide just one real (liquid) root, and there is no danger. In this region between the boiling point and 293K (about a 60K spread), bogus vapor roots will appear. This is illustrated in Figure 4, which shows the cubic polynomial in Z (Eq. 2) as a function of Z. This area is marked "Danger!" in Figure 4. The polynomial crosses the zero horizontal axis three times within the danger region $293K \leq T \leq T^{sat}$. Therefore, in our example above, at 330.531K, the Peng-Robinson equation cheerfully provided an erroneous vapor root that gave us a nonsense solution to the problem.

A similar situation exists at temperatures above the boiling point. Between the boiling point and temperatures as high as 396K (a 43K spread), bogus liquid roots are calculated. This dangerous region is also marked on Figure 4. At temperatures over 396K, only a single (vapor) root is calculated, and there is no danger of bogus roots.

The key point is that before we can decide which roots are valid and which are bogus, we must already know the boiling point. An equivalent procedure would be to select the value of Z that corresponds to the lowest residual Gibbs free energy or fugacity[6] since the liquid and vapor free energy curves cross at the boiling point. Without taking these steps, it is easy to end up in big trouble.

CONCLUSION

In conclusion, it is not possible to assume simply that large roots of Eq. (2) are vapor values and that small roots are for the liquid. There is a large margin on both sides of the boiling point where bogus liquid or vapor roots are calculated. Selection of the correct root requires additional information, and considerable care must be taken.

REFERENCES

1. Smith, J.M., H.C. Van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics,* 5th ed., McGraw-Hill, New York, NY (1996)
2. Sandler, S.I., *Chemical and Engineering Thermodynamics,* John Wiley & Sons, New York, NY (1999)
3. Kyle, B.G., *Chemical and Process Thermodynamics,* Prentice Hall, Englewood Cliffs, New Jersey (1992)
4. Carnahan, B., H.A. Luther, and J.O. Wilkes, *Applied Numerical Methods,* John Wiley & Sons, New York, NY (1969)
5. Walas, S.M., *Phase Equilibria in Chemical Engineering,* Butterworth-Heinemann, Boston, MA (1985)
6. Savage, P.E., "Spreadsheets for Thermodynamics Instruction," *Chem. Eng. Ed.,* **29**, 262 (1995) ■