

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@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

# THERMODYNAMIC PROPERTIES INVOLVING DERIVATIVES

## *Using the Peng-Robinson Equation of State*

R.M. PRATT

*The National University of Malaysia • Bangi, Selangor, 43600, Malaysia*

Equations of state are among the marvels of chemical engineering. Though simple and convenient, they may be used to model both liquid and vapor behavior for non-polar and low-polar mixtures.<sup>[1,2]</sup> Consequently, such methods are the preferred tools of the hydrocarbon processing industry. It is not often, especially in thermodynamics, that you can do so much with so little. In this article, we calculate thermodynamic properties that contain derivatives, a topic not normally found in textbooks.

There are two motivations for presenting this material. First, the calculations are simple, requiring no iteration or trial-and-error solutions. They are, however, useful items to add to the engineer's toolkit, and they require only critical property and ideal-gas heat-capacity data. Second, it enables the student to use some seemingly abstract equations of thermodynamics to directly make numerical calculations. It is rewarding to see these relationships used to make actual calculations and to observe relative magnitudes of various quantities.

To illustrate the methods, we use the Peng-Robinson equation of state applied to a binary vapor hydrocarbon mixture. There is an almost endless number of derivatives that can be calculated—we will consider only a few of the more commonly encountered ones. It is trivial to simplify the ensuing equations for the special case of a pure component or to apply the equations to any number of components. The equations are valid for both liquid and vapor phases.

### PROBLEM STATEMENT

Using the Peng-Robinson equation of state, calculate the

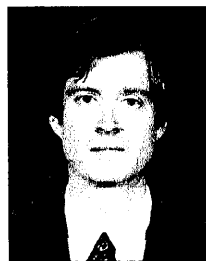
1) Joule-Thompson coefficient,  $J \equiv \left( \frac{\partial T}{\partial P} \right)_H$

2) Fluid sonic velocity,  $c \equiv \sqrt{\left( \frac{\partial P}{\partial \rho} \right)_S}$

for a binary vapor mixture of n-butane and n-pentane at 390K and 11 bar that consists of 35.630 mole % n-butane. Take  $k_{ij}$  for this binary pair to be zero.

### SOLUTION

We will solve this problem in three steps. First, we will use the Peng-Robinson equation of state to evaluate the three derivatives involving  $P$ ,  $v$ , and  $T$ , i.e.,  $(\partial P / \partial v)_T$ ,  $(\partial T / \partial P)_v$ ,



**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.

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and  $(\partial v / \partial T)_P$ . Then we will find the real fluid heat capacities,  $C_v$  and  $C_p$ , and finally we will apply these results to calculate the two thermodynamic derivatives indicated above.

### Solution of the Peng-Robinson Equation of State for $(\partial P / \partial v)_T$ , $(\partial T / \partial P)_v$ , and $(\partial v / \partial T)_P$

The Peng-Robinson equation is written as

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

where

- R universal gas constant
- T absolute temperature
- v molar volume
- a  $a_c \left[ 1 + m \left( 1 - \sqrt{T/T_c} \right) \right]$
- $a_c$   $0.45723553 R^2 T_c^2 / P_c$
- m  $0.37464 + 1.54226 \omega - 0.26992 \omega^2$
- b  $0.077796074 RT_c / P_c$
- $T_c$  critical temperature
- $P_c$  critical pressure
- $\omega$  pitzer acentric factor

The critical properties for the two components of our system are taken from Smith and Van Ness (Table 1).<sup>[3]</sup>

For convenience, the Peng-Robinson equation is often written in a cubic polynomial form for the compressibility factor  $Z = Pv / RT$

$$f(Z) = Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \quad (2)$$

where

$$\begin{aligned} \alpha &\equiv B - 1 \\ \beta &\equiv A - 2B - 3B^2 \\ \gamma &\equiv B^3 + B^2 - AB \end{aligned}$$

and

$$\begin{aligned} A &\equiv aP / (RT)^2 \\ B &\equiv bP / RT \end{aligned}$$

For an N-component fluid with composition,  $\{w_i\}$ , we calculate the mixture parameters, a and b, from the empirical relations:

$$a = \sum_{i=1}^N \sum_{j=1}^N w_i w_j \sqrt{a_i a_j} (1 - k_{ij}) \quad \text{and} \quad b = \sum_{i=1}^N w_i b_i \quad (3)$$

The binary interaction coefficient,  $k_{ij}$ , is exactly zero for  $i=j$ ; for  $i \neq j$ ,  $k_{ij}$  is close to zero for hydrocarbons. Values of  $k_{ij}$  for many component pairs are available in the literature,<sup>[4]</sup> although for most hydrocarbon pairs it is safe to take  $k_{ij}=0$ . We will henceforth use values without subscripts to refer to

quantities applied to the mixture as a whole, and subscripted values for pure component quantities. From Eq. (1), we calculate the pure component parameters using  $R=83.14 \text{ cm}^3\text{-bar/mol-K}$ :

$$\begin{aligned} a_1 &= 15911115 \text{ cm}^6\text{-bar/mol}^2 & a_2 &= 23522595 \text{ cm}^6\text{-bar/mol}^2 \\ b_1 &= 72.43235 \text{ cm}^3/\text{mol} & b_2 &= 90.14847 \text{ cm}^3/\text{mol} \end{aligned}$$

and then, from Eq. (3), we find that

$$a = 20631852 \text{ cm}^6\text{-bar/mol}^2 \quad b = 83.836216 \text{ cm}^3/\text{mol}$$

We now solve Eq. (2) for the compressibility factor, Z. This equation is easily solved using Newton-Raphson iteration<sup>[5]</sup> or by using the cubic formula.<sup>[11]</sup> In either case we calculate the vapor phase compressibility factor (largest of the three real roots) to be 0.7794 for the vapor. Consequently, the molar volume, v, of the vapor mixture is  $ZRT/P = 2297.54 \text{ cm}^3/\text{mol}$ .

With knowledge of the molar volume and compressibility, we now calculate the three PVT derivatives, which follow directly from the equation of state. Knowledge of these quantities is prerequisite to finding most any derivative thermodynamic property. We know that these three derivatives must satisfy the "cyclical rule," which may be written as

$$\left( \frac{\partial P}{\partial v} \right)_T \left( \frac{\partial T}{\partial P} \right)_v \left( \frac{\partial v}{\partial T} \right)_P = -1 \quad (4)$$

Therefore, once we have values for any two of the three PVT derivatives, the third may be calculated from Eq. (4). We will evaluate each derivative independently, however, and use Eq. (4) to check our work.

The first derivative in Eq. (4) is found by direct differentiation of Eq. (1),

$$\left( \frac{\partial P}{\partial v} \right)_T = \frac{-RT}{(v-b)^2} + \frac{2a(v+b)}{[v(v+b)+b(v-b)]^2} \quad (5)$$

Substituting in the values determined above, we find that

$$\left( \frac{\partial P}{\partial v} \right)_T = -0.0035459 \text{ bar} / (\text{cm}^3 / \text{mol})$$

The second derivative in Eq. (4) is also found by direct differentiation of Eq. (1),

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{v-b} - \frac{a'}{v(v+b)+b(v-b)} \quad (6)$$

and is found to be 0.0434866 bar/K. Therefore,

$$\left( \frac{\partial T}{\partial P} \right)_v = 22.99558 \text{ K} / \text{bar}$$

The third derivative in Eq. (4) is a bit trickier since Eq. (1) is not readily explicit in volume or temperature. It is therefore found implicitly, using Eq. (2),

$$\left( \frac{\partial v}{\partial T} \right)_P = \frac{R}{P} \left[ T \left( \frac{\partial Z}{\partial T} \right)_P + Z \right] \quad (7)$$

where

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{\left(\frac{\partial A}{\partial T}\right)_P (B-Z) + \left(\frac{\partial B}{\partial T}\right)_P (6BZ + 2Z - 3B^2 - 2B + A - Z^2)}{3Z^2 + 2(B-1)Z + (A - 2B - 3B^2)}$$

and

$$\left(\frac{\partial A}{\partial T}\right)_P = \frac{P}{R^2 T^2} \left(a' - \frac{2a}{T}\right) \quad \left(\frac{\partial B}{\partial T}\right)_P = \frac{-bP}{RT^2}$$

The derivative term,  $a' = da/dT$ , may be evaluated directly from Eq. (3) as

$$a' = \frac{da}{dT} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N w_i w_j (1 - k_{ij}) \left( \sqrt{\frac{a_j}{a_i}} a_i' + \sqrt{\frac{a_i}{a_j}} a_j' \right) \quad (8)$$

where

$$a_i' = \frac{da_i}{dT} = \frac{-m_i a_i}{\left[1 + m_i \left(1 - \sqrt{T/T_{c_i}}\right)\right] \sqrt{TT_{c_i}}} \quad (9)$$

The pure component parameters are found from Eq. (9) as

$$a_1' = -25547.0 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}$$

$$a_2' = -38460.2 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}$$

and  $da/dT$  for the mixture is found from Eq. (8) to be

$$a' = -33543.8 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}.$$

Substituting known values in to Eq. (7), we find that

$$\left(\frac{\partial v}{\partial T}\right)_P = 12.26396 \text{ cm}^3 / \text{mol} \cdot \text{K}$$

If we multiply the three numbers together we will see that we have satisfied Eq. (4).

### Calculation of the Heat Capacities $C_v$ and $C_p$

We first find  $C_v$ . We will consider this real fluid property to be a sum of an ideal gas contribution and a residual correction for non-ideal behavior:

$$C_v = C_v^{\text{ID}} + C_v^{\text{R}} \quad (10)$$

The ideal-gas contribution is found using heat-capacity data applicable to gases at very low pressures, which are available in many thermodynamics textbooks. We will use the simple correlation in Smith and Van Ness<sup>[3]</sup>

$$C_v^{\text{ID}} = R(A + BT + CT^2 + DT^{-2} - 1) \quad (11)$$

which is not recommended for temperatures below 298K nor valid for temperatures over 1500K. For n-butane and n-pentane, the coefficients are given in Table 2.

The ideal gas contribu-

	n-butane	n-pentane
A	1.935	2.464
B	$36.915 \times 10^{-3}$	$45.351 \times 10^{-3}$
C	$-11.402 \times 10^{-6}$	$-14.111 \times 10^{-6}$
D	0	0

tion for the mixture is a mole fraction weighted average of the pure component values, i.e.,

$$C_v^{\text{ID}} = \sum_{i=1}^N w_i C_{v_i}^{\text{ID}} \quad (12)$$

Inserting the known temperature of 390K into the above equations, we calculate for each component

$$C_{v_1}^{\text{ID}} = 113.050 \text{ J/mol} \cdot \text{K}$$

$$C_{v_2}^{\text{ID}} = 141.376 \text{ J/mol} \cdot \text{K}$$

and for the mixture

$$C_v^{\text{ID}} = 131.283 \text{ J/mol} \cdot \text{K}$$

To calculate the residual contribution to Eq. (10), we use the standard equation found in many textbooks<sup>[4,6]</sup> for the residual internal energy derived from the Peng-Robinson equation of state

$$U^{\text{R}} = \frac{Ta' - a}{b\sqrt{8}} \ln \left[ \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right] \quad (13)$$

The value of  $C_v^{\text{R}}$  is calculated from its definition

$$C_v^{\text{R}} = \left( \frac{\partial U^{\text{R}}}{\partial T} \right)_v$$

Evaluation of the partial derivative of Eq. (13) with respect to temperature yields

$$C_v^{\text{R}} = \frac{Ta''}{b\sqrt{8}} \ln \left[ \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right] \quad (14)$$

with the temperature derivative of Eq. (8) yielding

$$a'' = \frac{d^2 a}{dT^2} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N w_i w_j (1 - k_{ij}) \left[ \frac{a_i' a_j'}{\sqrt{a_i a_j}} + \frac{a_i'' \sqrt{a_j}}{\sqrt{a_i}} + \frac{a_j'' \sqrt{a_i}}{\sqrt{a_j}} - \frac{1}{2} \left( \frac{a_i'^2 \sqrt{a_j}}{\sqrt{a_i^3}} + \frac{a_j'^2 \sqrt{a_i}}{\sqrt{a_j^3}} \right) \right] \quad (15)$$

where

$$a_i'' = \frac{d^2 a_i}{dT^2} = \frac{da_i'}{dT} = \frac{a_{c_i} m_i \sqrt{\frac{T_{c_i}}{T}} (1 + m_i)}{2 T T_{c_i}} \quad (16)$$

These equations appear complicated, but the calculation is straightforward, albeit tedious. Pure component parameters for  $a''$  are found from Eq. (16) to be

$$a_1'' = 53.2619 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}^2$$

$$a_2'' = 80.7496 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}^2$$

and  $a''$  for the mixture is found from Eq. (15) to be

$$a'' = 70.2732 \text{ cm}^6 \cdot \text{bar/mol}^2 \cdot \text{K}^2$$

If doing hand calculations, very little error (usually less than 2%) is introduced by using the mole fraction weighted average in calculating  $a''$ . In this case, we would calculate  $a''$  to be  $70.9557 \text{ cm}^6\text{-bar/mol}^2\text{-K}^2$ . Substituting the above mixture quantities into Eq. (14) (using  $Z_L=0.779438$ ) gives  $C_V^R=1.152 \text{ J/mol-K}$ .

Using Eq. (10), we now obtain  $C_V=132.436 \text{ J/mol-K}$ .

We will use an equation analogous to Eq. (10) to calculate  $C_P$ ,

$$C_P = C_P^{ID} + C_P^R \quad (17)$$

and since  $C_P^{ID} = C_V^{ID} + R$ , we readily calculate  $C_P^{ID}$  to be  $139.597 \text{ J/mol-K}$ . The residual contribution may be calculated from the general relationship between  $C_V$  and  $C_P$ ,

$$C_P^R = C_V^R + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial v}{\partial T} \right)_P - R \quad (18)$$

The two partial derivatives are already calculated above and can be substituted into Eq. (18); we find that  $C_P^R = C_V^R + 124.85 \text{ cm}^3\text{-bar/mol-K}$  and therefore  $C_P^R = 136.37 \text{ cm}^3\text{-bar/mol-K}$ , or  $13.637 \text{ J/mol-K}$ . Adding the ideal gas and residual contributions according to Eq. (17) yields

$$C_P = 153.235 \text{ J/mol-K}$$

### Calculation of Thermodynamic Properties J and c

Now that we have values for the three PVT derivatives as well as the two heat capacities,  $C_V$  and  $C_P$ , we can calculate a large number of thermodynamic derivatives. We will only evaluate two of the more commonly encountered ones, the Joule-Thompson coefficient,  $J$ , and the speed of sound in a fluid,  $c$ .

It is simple to calculate the Joule-Thompson coefficient,  $(\partial T / \partial P)_H$ , using the working equation<sup>[6]</sup>

$$J = \frac{1}{C_P} \left[ T \left( \frac{\partial v}{\partial T} \right)_P - v \right] \quad (19)$$

since all the required values have been calculated. Substituting into Eq. (19), we obtain

$$J = 1.62195 \text{ K/bar}$$

The fluid sonic velocity  $\sqrt{(\partial P / \partial \rho)_S}$  is calculated from the working equation<sup>[6]</sup>

$$c = v \sqrt{-\frac{C_P}{C_V} \left( \frac{\partial P}{\partial v} \right)_T} \quad (20)$$

All the required values have been calculated. Substituting into Eq. (20) yields  $c=147.164 \text{ (cm}^3\text{-bar/mol)}^{0.5}$ . Since these

are unusual velocity units, some units conversion is in order. The average molecular weight of the vapor mixture is  $67.152 \text{ g/mol}$  and we find that the sonic velocity is

$$c^2 = 21657 \frac{\text{cm}^3\text{-bar}}{\text{mol}} \cdot 100000 \frac{\left( \frac{\text{kg-m}}{\text{s}^2} \right)}{\text{bar}} \cdot \frac{\text{m}}{100\text{cm}} \cdot \frac{1000\text{g}}{\text{kg}} \cdot \frac{1\text{mol}}{67.152\text{g}} = 3.2251 \times 10^8 \frac{\text{cm}^2}{\text{s}^2}$$

$$\text{or } c = 179.586 \text{ m/s} = 646.5 \text{ km/hr}$$

We can compare this result with the low pressure (ideal gas) limiting value

$$c_{ID} = \sqrt{\frac{C_P^{ID}}{C_V^{ID}}} RT = 185.683 (\text{cm}^3\text{-bar/mol})^{0.5} = 226.590 \text{ m/s}$$

## DISCUSSION

Calculation of derivative properties is easy if there is an equation of state available to model the PVT behavior of the fluid. Two such properties have been evaluated here using the Peng-Robinson equation of state. It is trivial to evaluate a large number of other derivative properties once we know the three PVT derivatives and the two heat capacities. In this age of computers, it is worthwhile for the student to develop a spreadsheet or set of computer subroutines to calculate thermodynamic properties of hydrocarbons and hydrocarbon mixtures.<sup>[7]</sup> Including these and other thermodynamic derivatives would be very easy, indeed.

It is interesting to estimate some of these derivatives by using their finite-difference approximations and to compare these estimates with results using the equations discussed above. For example,  $C_P$  is approximated by evaluating the enthalpy  $H=H^{ID}+U^R+RT(Z-1)$  at two nearby temperatures at 11 bar (and same composition)

$$C_P \equiv \left( \frac{\Delta H}{\Delta T} \right)_P = \frac{30012.449 - 29705.977}{391 - 389} = 153.236 \text{ J/mol-K}$$

which is essentially the same as the result obtained above, with any error due to the finite-difference approximation.

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