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

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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.[1,2] 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, $J \equiv \left(\dfrac{\partial T}{\partial P} \right)_H$

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

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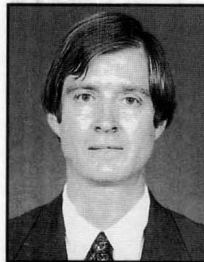
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and $(\partial v/\partial T)_P$. Then we will find the real fluid heat capacities, C_v and C_p, and finally we will apply these results to calculate the two thermodynamic derivatives indicated above.

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

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

where

R	universal gas constant
T	absolute temperature
v	molar volume

$a \qquad a_c\left[1+m\left[1-\sqrt{T/T_c}\right]\right]$

$a_c \qquad 0.45723553\ R^2T_c^2/P_c$

$m \qquad 0.37464 + 1.54226\ \omega - 0.26992\ \omega^2$

$b \qquad 0.077796074\ RT_c/P_c$

$T_c \qquad$ critical temperature

$P_c \qquad$ critical pressure

$\omega \qquad$ pitzer acentric factor

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

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

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

where

$\alpha \equiv B - 1$

$\beta \equiv A - 2B - 3B^2$

$\gamma \equiv B^3 + B^2 - AB$

and

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

$B \equiv bP/RT$

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

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

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

TABLE 1
Critical Property Data for n-butane and n-pentane

	n-butane	n-pentane
$T_c(K)$	425.1	469.7
$P_c(bar)$	37.96	33.7
ω	0.200	0.252

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 cm³-bar/mol-K:

$a_1 = 15911115$ cm⁶-bar/mol² $a_2 = 23522595$ cm⁶-bar/mol²
$b_1 = 72.43235$ cm³/mol $b_2 = 90.14847$ cm³/mol

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

$a = 20631852$ cm⁶-bar/mol² $b = 83.836216$ cm³/mol

We now solve Eq. (2) for the compressibility factor, Z. This equation is easily solved using Newton-Raphson iteration[5] or by using the cubic formula.[1] 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 cm³/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

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

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),

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

Substituting in the values determined above, we find that

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

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

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

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

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

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),

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

where

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

and

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

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

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

where

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

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

$$a_1' = -25547.0 \text{ cm}^6\text{-bar/mol}^2\text{-K}$$
$$a_2' = -38460.2 \text{ cm}^6\text{-bar/mol}^2\text{-K}$$

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

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

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

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

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:

$$C_V = C_V^{ID} + C_V^{R} \qquad (10)$$

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[3]

$$C_V^{ID} = R\left(A + BT + CT^2 + DT^{-2} - 1\right) \qquad (11)$$

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-

TABLE 2		
	n-butane	n-pentane
A	1.935	2.464
B	36.915×10^{-3}	45.351×10^{-3}
C	-11.402×10^{-6}	-14.111×10^{-6}
D	0	0

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

$$C_V^{ID} = \sum_{i=1}^{N} w_i C_{V_i}^{ID} \qquad (12)$$

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

$$C_{V_1}^{ID} = 113.050 \text{ J/mol} - \text{K} \qquad C_{V_2}^{ID} = 141.376 \text{ J/mol} - \text{K}$$

and for the mixture

$$C_V^{ID} 131.283 \text{ J/mol} - \text{K}$$

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

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

The value of C_V^R is calculated from its definition

$$C_V^R \equiv \left(\frac{\partial U^R}{\partial T}\right)_V$$

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

$$C_V^R \equiv \frac{Ta''}{b\sqrt{8}} \ln\left(\frac{Z + B\left(1 + \sqrt{2}\right)}{Z + B\left(1 - \sqrt{2}\right)}\right) \qquad (14)$$

with the temperature derivative of Eq. (8) yielding

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

where

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

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

$$a_1'' = 53.2619 \text{ cm}^6 - \text{bar/mol}^2 - \text{K}^2$$
$$a_2'' = 80.7496 \text{ cm}^6 - \text{bar/mol}^2 - \text{K}^2$$

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

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

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 cm^6-bar/mol^2-K^2. Substituting the above mixture quantities into Eq. (14) (using Z_L=0.779438) gives C_v^R=1.152 J/mol-K.

Using Eq. (10), we now obtain C_v=132.436 J/mol-K.

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

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

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

$$C_P^R = C_v^R + T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P - R \qquad (18)$$

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

$$C_P = 153.235 \, J/mol-K$$

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[6]

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

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

$$J = 1.62195 \, K/bar$$

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

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

All the required values have been calculated. Substituting into Eq. (20) yields c=147.164 (cm^3-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 g/mol and we find that the sonic velocity is

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

$$3.2251\times10^8\frac{cm^2}{s^2}$$

or $\qquad c=179.586 \, m/s = 646.5 \, km/hr$

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

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

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.[7] 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)

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

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

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