Saturated Enthalpies for Mixtures of Propane and Propene

DAVID B. MANLEY and GEORGE W. SWIFT

Department of Chemical and Petroleum Engineering
University of Kansas, Lawrence, Kansas 66044

The isobaric general coexistence equation has been suggested by Tao (5) as a rigorous method of calculating the heats of vaporization of mixtures. Lee and Edmister (2) have applied this method to two systems and indicate that the greatest source of error lies in the method of smoothing and differentiating the isobaric temperature-composition data. In this work a rigorous form of the isobaric general coexistence equation is developed, and a method of correlating the temperature-composition data is derived which minimizes the errors involved and insures that the results are thermodynamically consistent.

THEORY

The starting point for the derivation is taken from Van Ness (6). For a single phase binary system

$$\frac{\Delta H'}{RT_a^2}\, dT = z_1 d(\ln \hat{f}_1) + z_2 d(\ln \hat{f}_2) \tag{1}$$

at constant pressure where

$$\Delta H' = H^{id} - H \tag{2}$$

is the enthalpy deviation from ideal gas behavior. Since the vapor and liquid fugacities are equal at equilibrium, writing Equation (1) for both phases and subtracting gives

$$\frac{\Delta' H}{(y-x)} = \frac{d[\ln(\hat{f}_2/\hat{f}_1)]}{dT} \tag{3}$$

where

$$\Delta' H = \frac{\Delta(\Delta H')}{RT_a^2} = \frac{1}{RT_a^2}\,[(\Delta H')^V - (\Delta H')^L] \tag{4}$$

Expanding the right-hand side of Equation (3) gives

$$\frac{\Delta' H}{(y-x)} = \left\{\frac{\partial[\ln(\hat{f}_2/\hat{f}_1)]}{\partial T}\right\}_y + \left\{\frac{\partial[\ln(\hat{f}_2/\hat{f}_1)]}{\partial y}\right\}_T \left(\frac{dy}{dT}\right) \tag{5}$$

where the ordinary derivative is constrained to saturation, but the partial derivatives are not. Define

$$\hat{f}_i = \hat{\phi}_i y_i P \tag{6}$$

and

$$\Gamma = \ln(\hat{\phi}_2/\hat{\phi}_1). \tag{7}$$

Then substituting into Equation (5) and rearranging gives the isobaric general coexistence equation

$$\frac{\Delta' H}{(y-x)} = \left(\frac{\partial \Gamma}{\partial T}\right)_y + \left[\left(\frac{\partial \Gamma}{\partial y}\right)_T + \left(\frac{1}{y(1-y)}\right)\right]\left(\frac{dy}{dT}\right) \tag{8}$$

In order to evaluate Equation (8) from the correlations already developed for the propane-propene system (3) and to evaluate dy/dT with as little error as possible the following change in variables was effected

$$\frac{dy}{dT} = \frac{dy}{dx}\,\frac{dx}{dT} \tag{9}$$

at constant pressure and saturation. Also under these conditions

$$\alpha = [y(1-x)]/[x(1-y)] \tag{10}$$

and consequently it can be shown that

$$\frac{dy}{dx} = y(1-y)\,\frac{d(\ln\alpha)}{dx} + \frac{y(1-y)}{x(1-x)} \tag{11}$$

Substituting into Equation (8) gives

$$\frac{\Delta' H}{(y-x)} = \left(\frac{\partial \Gamma}{\partial T}\right)_y + \left[\left(\frac{\partial \Gamma}{\partial y}\right)_T + \frac{1}{y(1-y)}\right]\left(\frac{dx}{dT}\right) [y(1-y)]\left[\frac{d(\ln\alpha)}{dx} + \frac{1}{x(1-x)}\right] \tag{12}$$

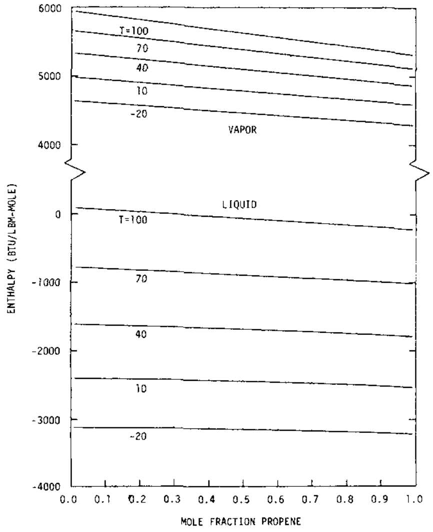

Fig. 1. Saturated enthalpies for the propane-propene system.

Correspondence concerning this communication should be addressed to G. W. Swift. D. B. Manley is at the University of Missouri-Rolla, Rolla, Missouri 65401.

Table 1. Constants for Relative Volatility Correlation

$0.0 \leq x \leq 1.0;\ -20 \leq T \leq 100$

C_{ij}

i \ j	1	2	3	4	5
1	5.3477933$E-01$	−6.2943642$E-02$	1.0166224$E+00$	−3.9297979$E+00$	2.7766818$E+00$
2	−1.2135190$E-01$	−1.1981030$E-01$	−1.0690262$E+00$	3.6228312$E+00$	−2.5104115$E+00$
3	3.0524790$E-02$	5.2702310$E-02$	3.6819313$E-01$	−1.2569626$E+00$	8.7610066$E-01$
4	−5.5703472$E-03$	−8.4538150$E-03$	−5.3536964$E-02$	1.9241811$E-01$	−1.3602916$E-01$
5	3.2059418$E-04$	5.3411150$E-04$	2.8398149$E-03$	−1.0909691$E-02$	7.8301447$E-03$

where the ordinary derivatives are constrained to saturation but the partial derivatives are not.

The advantage of Equation (12) is that dx/dT can be evaluated from the vapor pressure correlation

$$P = F(x, T) \tag{13}$$

already developed and only the second-order effect $d(\ln\alpha)/dx$ must be cross correlated from the isothermal $\alpha - x$ data. If Equation (8) were used to evaluate dy/dT it would be necessary to cross correlate the isothermal $P - y$ data which would lead to the same numerical problems encountered by Lee and Edmister (*2*).

METHOD OF CALCULATION

In Equation (12), $(\partial\Gamma/\partial T)_y$ and $(\partial\Gamma/\partial y)_T$ were evaluated analytically from the Redlich-Kwong equation of state and dx/dT was evaluated analytically from the vapor pressure correlation developed previously (3). $d(\ln\alpha)/dx$ was calculated from the empirical correlation

$$\ln\alpha = \sum_{i=1}^{5}\left[\left(\sum_{j=1}^{5} C_{ij}\,x^{j-1}\right)(\ln P)^{i-1}\right] \tag{14}$$

The constants C_{ij} in Equation (14) were evaluated by least square analysis of the isothermal $\alpha - x - P$ data previ-

Table 2. Saturated Enthalpies for the Propane-Propene System

$T = -20$

$H_1^{id} = 4777$ $H_2^{id} = 4445$

x	y	H_L	H_V
0.0	0.0	−3119	4641
0.1	0.1296	−3119	4595
0.2	0.2478	−3117	4552
0.3	0.3566	−3117	4513
0.4	0.4581	−3121	4477
0.5	0.5540	−3129	4443
0.6	0.6459	−3141	4411
0.7	0.7353	−3155	4380
0.8	0.8236	−3172	4349
0.9	0.9116	−3195	4319
1.0	1.0000	−3221	4289

$T = 10$

$H_1^{id} = 5223$ $H_2^{id} = 4850$

x	y	H_L	H_V
0.0	0.0	−2400	4994
0.1	0.1259	−2412	4942
0.2	0.2421	−2416	4894
0.3	0.3503	−2421	4849
0.4	0.4520	−2428	4808
0.5	0.5487	−2439	4769
0.6	0.6418	−2453	4731
0.7	0.7326	−2471	4695
0.8	0.8220	−2491	4660
0.9	0.9110	−2520	4625
1.0	1.0	−2539	4591

Table 2. (cont.)

$T = 40$

$H_1^{id} = 5697$ $H_2^{id} = 5274$

x	y	H_L	H_V
0.0	0.0	−1618	5335
0.1	0.1225	−1633	5276
0.2	0.2368	−1644	5221
0.3	0.3442	−1655	5170
0.4	0.4461	−1667	5121
0.5	0.5436	−1682	5075
0.6	0.6378	−1700	5032
0.7	0.7297	−1722	4989
0.8	0.8203	−1747	4949
0.9	0.9102	−1775	4909
1.0	1.0	−1803	4869

$T = 70$

$H_1^{id} = 6199$ $H_2^{id} = 5716$

x	y	H_L	H_V
0.0	0.0	−780	5656
0.1	0.1193	−804	5589
0.2	0.2318	−825	5525
0.3	0.3385	−844	5466
0.4	0.4404	−865	5409
0.5	0.5385	−886	5356
0.6	0.6337	−909	5304
0.7	0.7268	−934	5255
0.8	0.8184	−962	5207
0.9	0.9093	−991	5160
1.0	1.0	−1023	5115

$T = 100$

$H_1^{id} = 6728$ $H_2^{id} = 6177$

x	y	H_L	H_V
0.0	0.0	99	5951
0.1	0.1163	63	5874
0.2	0.2271	30	5801
0.3	0.3330	0	5732
0.4	0.4350	−30	5666
0.5	0.5336	−59	5603
0.6	0.6297	−89	5543
0.7	0.7238	−119	5485
0.8	0.8165	−150	5429
0.9	0.9084	−184	5375
1.0	1.0	−218	5322

ously published (3), and the constants are given in Table 1. Equation (14) fits the isothermal $\alpha - x - P$ data within 0.0003 units of relative volatility over a temperature range of −20 to 100°F.[*]

To evaluate the saturated enthalpies from $\Delta' H$ it was first necessary to calculate the ideal gas enthalpies for both the vapor and liquid phases. This information was correlated from the data given in API Research Project 44 (*1*) pages 582 and 594 where the standard states are ideal gases at 0°R. H^V was calculated from Equation (2) using the Redlich-Kwong equation of state to determine the enthalpy deviation for the gas, $(\Delta H')^L$ was determined from Equation (4) where $\Delta' H$ was calculated from Equation (12). Finally, H^L was calculated by applying Equation (2) to the liquid phase.

RESULTS AND CONCLUSIONS

The calculated saturated enthalpies are given in Table 2 and are shown graphically in Figure 1. Obviously, the effect of mixing on the heat of vaporization is quite small and for practical purposes can be ignored. Probably the major source of error in these data is the equation to correlate the isothermal $P - x$ data. Although the use of Equation (12) to calculate $\Delta' H$ eliminates numerical differentiation problems, errors in Equation (13), whether due to the form of the equation or to the experimental data on which it is based, will be reflected in the resulting enthalpies. The results of this work and also the work on relative volatilities indicate that when applying the general coexistence equation to calculate thermodynamic properties of close boiling mixtures the greatest effort should be expended on the accurate measurement of vapor pressure.

NOTATION

C_{ij} = constants for relative volatility correlation
F = function representing vapor pressure correlation
$\hat{f}_i$ = fugacity of component *i* in solution, lb./sq.in.abs.
H = enthalpy, B.t.u./lb.$_m$-mole
H^{id} = ideal gas enthalpy, B.t.u./lb.$_m$-mole
$\Delta H'$ = $H^{id} - H$, B.t.u./lb.$_m$-mole
$\Delta' H$ = $[(\Delta H')^V - (\Delta H')^L]/RT_a^2$, °R.$^{-1}$
P = pressure, lb./sq.in.abs.
R = ideal gas constant, B.t.u./lb.$_m$-mole°R.
T = temperature, °F.
T_a = temperature, °R.
x = mole fraction propene in liquid
y = mole fraction propene in vapor
z_i = mole fraction component *i*
α = relative volatility, $[y(1 - x)]/[x(1 - y)]$
Γ = $\ln(\hat{\phi}_2/\hat{\phi}_1)$
$\hat{\phi}_i$ = fugacity coefficient of component *i* in solution

Superscripts

L = liquid phase
V = vapor phase

Subscripts

1 = propane
2 = propene

LITERATURE CITED

1. API Research Project No. 44, A&M College of Texas, College Station, Texas (1953-date).
2. Lee, B., and W. E. Edmister, *AIChE J.*, **15**, 615 (1969).
3. Manley, D. B., and G. W. Swift, *J. Chem. Eng. Data*, **16**, 301 (1971).
4. Reamer, H. H., and B. H. Sage, *Ind. Eng. Chem.*, **43**, 1628 (1951).
5. Tao, L. C., *AIChE J.*, **14**, 988 (1968).
6. Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions," p. 137, MacMillan, New York (1964).

---

[*] Reamer and Sage (*4*) have measured the vapor-pressures, compositions, and specific volumes of mixtures of propane and propene at 100°F. and 160°F.; and these data were used by Manley and Swift (*3*) to help calculate the relative volatility of propene to propane at 130°F. However, since the original data of this study were limited to 100°F., and since the primary purpose of this paper is to demonstrate one method of calculating heats of vaporization, no effort was made to extend the enthalpy data to 130°F.

Estimation of Effective Molecular Quadrupole Moments

P. T. EUBANK

Department of Chemical Engineering
Texas A&M University, College Station, Texas 77843

Quadrupole-dipole interactions can produce important contributions to the second virial coefficient B (*1, 2*) and compressibility factor Z_c of highly dipolar gases such as water, ammonia, the alcohols, and the ketones. The importance of quadrupole interactions in quadrupole gases such as N_2, O_2, NO, CO, CO_2, C_2H_2, C_2H_4, and F_2 is well known (*3, 4*). Although for dipolar gases B^* $(\sigma, y, \tau, \gamma, q)$ and $Z_c(T_r, P_r, \tau, \gamma, q)$, the dependency of the critical constants on τ, γ and q should be recognized in corresponding states correlations of the compressibility factor.

Quadrupole moments can be estimated from quantum mechanics (based on an assumed form of the wavefunction) or extracted from microwave line broadening, pressure-induced infrared absorption, nuclear spin relaxation, induced birefringence, anisotropy in diamagnetic susceptibility, and other measurements. A comprehensive survey of literature values before 1966 is available (*5*). Except for water, few references as yet pertain to molecules which are not cylindrically symmetric. Differences of the order of 2×10^{-26} esu-cm^2 or more are still common although values for several axially symmetric molecules such as O_2, N_2, and CO_2 are known with greater certainty. A simple