Adaptation of van der Waals Equation to Describe Enthalpy Behavior of Gaseous Propane

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The enthalpy of pure substances and their mixtures continues to be of primary importance in the design calculations of petroleum and chemical processes. Common methods of obtaining enthalpies are presented elsewhere (*4*) and may involve reading values from pure component enthalpy charts or calculating them using adequate equations of state or generalized corresponding state correlations.

Common equations of state employ the intensive parameters pressure and temperature and the fundamental quantity volume. For example, the Benedict-Webb-Rubin equation of state (*2*) adequately describes the PVT behavior of those substances for which the necessary eight constants are available. The application of this equation to obtain enthalpy departures from ideal gas behavior involves partial differentiation and subsequent integration consistent with the thermodynamic relationship

$$(H^* - H)_T = \int_v^\infty \left[v \left(\frac{\partial P}{\partial v} \right)_T + T \left(\frac{\partial P}{\partial T} \right)_v \right] dv \quad (1)$$

Regardless of the pressure explicit equation of state that is used, the resulting enthalpy departure expression will always be an equation involving temperature and volume as independent variables. The usual situation encountered is that of estimating enthalpy departures for a given temperature and pressure; volume is only of secondary importance. To obtain these departures using the integrated form of Equation (1), however, molar volumes must first be calculated from the original equation of state by an iterative technique. This approach places the prime focus of attention upon procuring an accurate value for volume, which in turn determines the accuracy of the enthalpy departure. Furthermore, any inadequacies in the functional form of the original equation of state are magnified in the resulting expression for enthalpy departure, due to the differentiation and integration associated with Equation (1). These arguments point to the desirability of bypassing volume altogether by establishing a relationship capable of defining enthalpy departure directly in terms of temperature and pressure. Consequently, the aim of this study centers on investigating a possible analogy between density and enthalpy departure, with the objective of replacing density by enthalpy departure in an equation of state.

Figure 1 shows isothermal relationships of P versus $1/(H^* - H)$ for propane. The behavior of these isotherms is very similar to that observed on a plot of P versus v, indicating an analogy between $1/v$, or density, and enthalpy departure. If this analogy is valid, it should be possible to involve the quantity $1/(H^* - H)$ in an equation of state in the same manner as volume. Examination of a low pressure isobar, however, quickly reveals that simply replacing v with $1/(H^* - H)$ in the familiar expression $Pv = RT$ fails to reflect the proper temperature dependence. In fact, the exponent on T appears to be very close to 2. Combination of these observations leads to the postulation of the following relationship for the dilute gaseous state

$$\frac{P}{H^* - H} = \kappa T^2 \quad (2)$$

where κ is a constant. To extend the applicability of Equation (2) to higher pressures and lower temperatures, a simple van de Waals type model is proposed of the form

$$[P + a(H^* - H)^2] \left[\frac{1}{H^* - H} - b \right] = \kappa T^2 \quad (3)$$

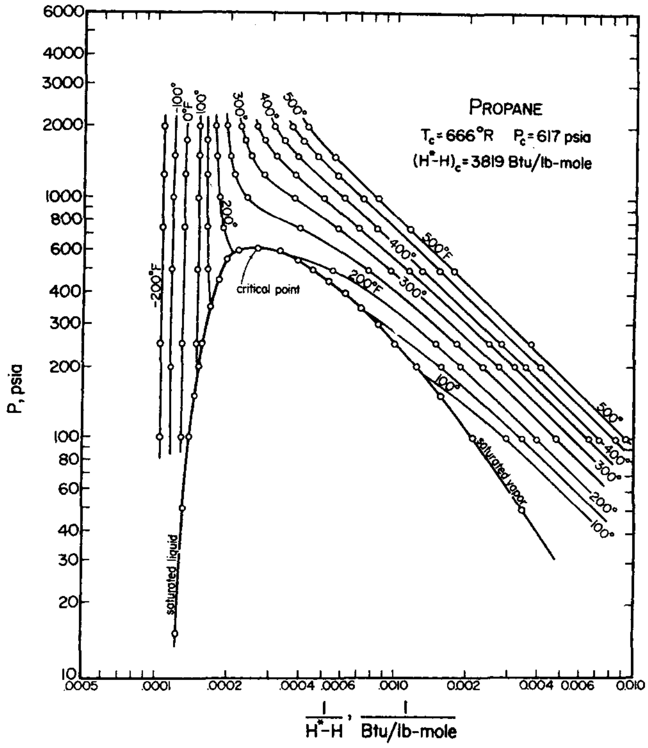

Fig. 1. Isothermal relationships of P versus $1/(H^* - H)$ for propane.

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where a and b are constants analogous to those of the van der Waals equation of state. The estimation of the constants a, b, and κ can be obtained by applying boundary conditions at the critical point in the same manner as outlined by van der Waals for his equation of state (5).

ESTIMATION OF CONSTANTS a, b, AND κ

The boundary conditions to be employed at the critical point are

$$\left[\frac{\partial P}{\partial\left(\frac{1}{H^* - H}\right)^2}\right]_{T_c} = 0 \qquad (4)$$

and

$$\left[\frac{\partial^2 P}{\partial\left(\frac{1}{H^* - H}\right)^2}\right]_{T_c} = 0 \qquad (5)$$

Using Equations (3), (4), and (5) results in the following relationships:

$$a = \frac{3P_c}{(H^* - H)_c^2} \qquad (6)$$

$$b = \frac{1}{3(H^* - H)_c} \qquad (7)$$

$$\kappa = \frac{8}{3}\frac{P_c}{(H^* - H)_c T_c^2} \qquad (8)$$

It should be noted that κ is not a universal constant as is R in the van der Waals equation of state.

For pure components, values of $(H^* - H)_c$ may be obtained directly from available enthalpy data or may be estimated from values of $(H^* - H)/T_c$ at the critical point for different values of z_c as presented by Hougen, Watson, and Ragatz (3).

TEST OF MODEL VALIDITY

Of the several light hydrocarbons, tabulated values of enthalpy for propane reported by Yesavage (6) are perhaps the most reliable from the standpoint of being actual calorimetric data which have been tested for internal thermodynamic consistency. The propane data reported extend to pressures of 2,000 lb./sq. in. abs. and cover a range in temperature from −280° to +500°F. Because of these considerations, propane has been chosen to test the validity of Equation (3). The values of a, b, and κ as calculated from Equations (6), (7), and (8) are as follows:

$$a = 1.2694 \times 10^{-4}$$

$$b = 8.7292 \times 10^{-5}$$

$$\kappa = 9.7173 \times 10^{-7}$$

The internal pressure term, assumed to be of the form

$$\pi = a(H^* - H)^2 \qquad (9)$$

may be analyzed to determine whether the squared dependence on enthalpy departure is consistent with actual behavior. Using the values of b and κ from Equations (7) and (8), π values may be calculated from the rearranged form of Equation (3) using experimental enthalpy departures, temperatures, and pressures:

$$\pi = \frac{\kappa T^2}{\dfrac{1}{H^* - H} - b} - P \qquad (10)$$

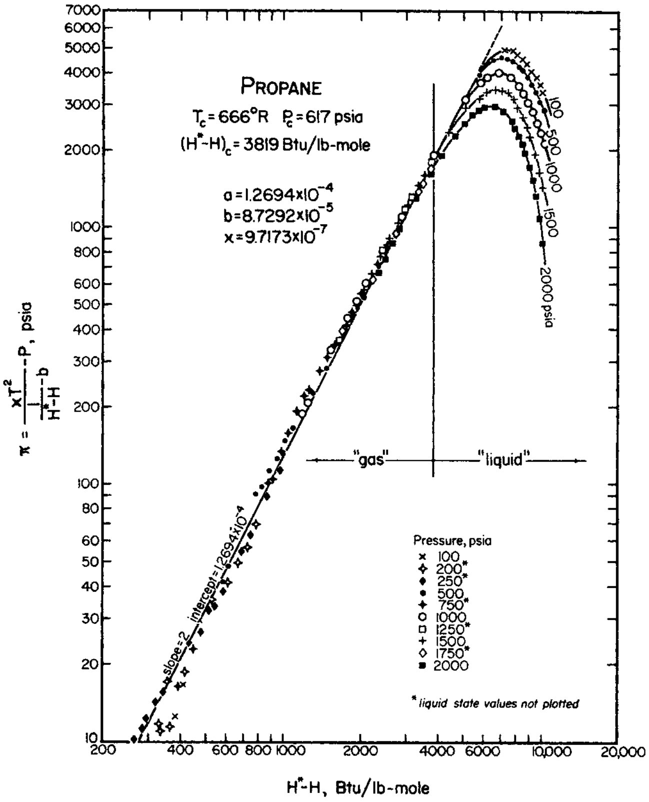

Fig. 2. Plot showing squared dependency of π versus $H^* - H$ for the gaseous state of propane, $H^* - H < (H^* - H)_c$.

If Equation (3) is a valid representation of the behavior of substances, then values of π obtained from Equation (10) should produce a straight line of slope two and intercept a when plotted against $H^* - H$ on log-log coordinates. Values of π calculated for propane were plotted against $H^* - H$ as shown in Figure 2. For the gas phase $H^* - H < (H^* - H)_c$, all of the pressures produced a single straight line whose slope and intercept are surprisingly close to 2 and a, respectively. For values of $H^* - H > (H^* - H)_c$, it is clear that Equation (9) no longer holds and that a more complex, pressure-dependent function would be necessary to describe the behavior in the liquid state.

APPLICATION OF MODEL TO GASEOUS PROPANE

The results of the preceding section confirm the validity of Equation (3) for propane in the gaseous state. To test the accuracy of this equation, enthalpy departures were calculated from Equation (3) using Newton's method and compared with the experimental values reported by Yesavage (6). The greatest deviations from experimental values were observed in the critical region where they became as high as 8.1 B.t.u./lb. For conditions removed from the critical region, the accuracy improves and at low pressures the deviations become essentially zero. Table 1 presents a summary of deviations of calculated enthalpy departures from corresponding experimental values. The conditions include temperatures that extend from the saturated vapor state to 500°F. for enthalpy departures, $H^* - H < (H^* - H)_c$. For the range considered, an average deviation of 0.96 B.t.u./lb. (n = 280 points) resulted.

COMPARISON OF RESULTS WITH BWR EQUATION

A critical review of methods available for the estimation of enthalpy departures, $H^* - H$, has been presented in a study sponsored by the American Petroleum Institute (4). In that study, both equations of state and generalized correlations were considered. For light hydrocarbons, methane through *n*-butane, it was found that the BWR equation yields the most accurate enthalpy departures. For this reason, and the fact that an analytical expression is better suited for computational purposes, the BWR equation was selected to compare the accuracy of Equation (3) with a proven method of predicting enthalpy departures. Consequently, the values of enthalpy departure calculated from Equation (3) were compared with those obtained for the same conditions using the method outlined by Benedict, Webb, and Rubin (2). The deviations of the enthalpy departures from experimental values are also presented in Table 1. The average deviation for the range considered is 0.76 B.t.u./lb. ($n = 280$ points) with a maximum deviation of 2.26 B.t.u./lb.

While the average deviation for the BWR method is not significantly better than that produced by Equation (3), the BWR method is nevertheless more consistent and produces a significantly lower maximum deviation. Furthermore, the consistently negative bias of the BWR deviation indicates that the equation of state constants could stand improvement.

Equation (3) produces reasonably accurate enthalpy departures, particularly below the critical pressure. The fact that the equation is relatively simple, involving only three constants, and yet produces average deviations comparable to those of the BWR method, lends further credence to the analogy between density and enthalpy departure.

While solving Equation (3) for enthalpy departure still involves an iterative technique, its solution is far simpler than the corresponding BWR method. For example, it is not difficult to program an electronic calculator with only six storage locations to perform a linear iterative solution of Equation (3) for enthalpy departure. In fact, presuming its applicability to other hydrocarbons, Equation (3) may prove attractive as a desk method for calculating gaseous enthalpy departures.

The inadequacy of Equation (3) in the liquid state is not surprising when one considers the similar tendency of the van der Waals equation in PVT behavior. To handle the enthalpy departure in this region, a more sophisticated equation is necessary, just as for PVT behavior the van der Waals equation of state has been followed by the Beattie-Bridgeman (1), the Benedict-Webb-Rubin (2), and other equations of state.

OPTIMIZED CONSTANTS a, b, AND κ

An attempt was made to refine the values of a, b, and κ by using a search technique to minimize enthalpy departure deviations according to the criterion $\sum_{i=1}^{n} D_i^2 =$ minimum, where D = experimental minus calculated values of $H^* - H$. A mapping of the response surface showed it to be unimodal over a domain of a, b, and κ close to the values predicted by Equations (6), (7), and (8). The search converged to the values

$$a = 1.2942 \times 10^{-4}$$

$$b = 9.2052 \times 10^{-5}$$

$$\kappa = 9.5686 \times 10^{-7}$$

For the same conditions outlined previously, these optimized constants produced an average deviation of 0.85 B.t.u./lb. ($n = 280$ points) and a maximum deviation of 8.3 B.t.u./lb.

For the purposes of optimizing a, b, and κ, it is clear that Equations (6), (7), and (8) produce values that are very good first approximations.

CONCLUSIONS

The adequacy of Equation (3) for predicting gas phase enthalpy departures of propane confirms the existence of an analogy between density and enthalpy departure. Furthermore, presuming Equation (3) may be applied to other hydrocarbons, the accuracy obtained from this relatively simple relationship makes it attractive to consider as a desk method for calculating enthalpy departures of gases.

The analogy exhibited by Equation (3) suggests that more sophisticated relationships could be developed to improve the accuracy and to extend its application into the liquid region.

Table 1. Comparison of Accuracy of Equation (3) and BWR Method: Deviations of Calculated Enthalpy Departures from Experimental Measurements of Gaseous Propane

Pressure lb./sq.in.abs.	Lowest temperature examined, °F.	Number of data points	Deviations, B.t.u./lb.											
			Equation (3) with a, b, and κ from Equations (6), (7), and (8)				BWR method				Equation (3) with optimized a, b, and κ			
			Avg.	RMS	Bias	Maximum	Avg.	RMS	Bias	Maximum	Avg.	RMS	Bias	Maximum
100	60	45	0.21	0.32	−0.19	−0.90	0.54	0.73	−0.54	−1.71	0.29	0.41	−0.29	−1.09
200	110	40	0.31	0.48	−0.31	−1.61	0.77	0.95	−0.77	−2.26	0.52	0.74	−0.52	−2.42
250	130	38	0.32	0.44	−0.32	−1.51	0.84	0.97	−0.80	−1.92	0.59	0.78	−0.59	−2.62
500	190	32	0.46	0.61	0.28	−2.31	0.68	0.77	−0.67	−1.40	0.58	1.60	−0.45	−8.27
750	230	28	1.75	2.45	1.71	8.09	0.70	0.81	−0.67	−1.56	0.97	1.32	0.84	4.42
1,000	270	24	2.03	2.55	2.03	5.73	1.03	1.09	−1.03	−1.86	1.30	1.76	1.26	4.39
1,250	290	22	2.12	2.47	2.12	4.16	0.77	0.80	−0.77	−1.40	1.51	1.86	1.48	3.30
1,500	320	19	1.34	1.48	1.30	2.20	0.67	0.68	−0.67	−0.90	0.82	0.97	0.78	1.56
1,750	340	17	0.79	1.40	−0.66	−4.37	1.02	1.04	−1.02	−1.49	0.99	1.37	−0.99	−3.83
2,000	360	15	2.50	2.98	−2.50	−6.70	0.82	0.83	−0.82	−1.15	2.63	2.92	−2.63	−5.93
		280	0.96	1.58	0.34	8.09	0.76	0.87	−0.75	−2.26	0.85	1.35	−0.14	−8.27

$D = (H^* - H)_{\text{exptl}} - (H^* - H)_{\text{calc}}$

$\text{Avg.} = \frac{1}{N}\Sigma|D|$

$RSM = \sqrt{\frac{\Sigma D^2}{N}}$

$\text{Bias} = \frac{1}{N}\Sigma D$

N = number of data points

NOTATION

a, b = constants, Equation (3)
H^* = enthalpy of ideal gas, B.t.u./lb.-mole
H = enthalpy, B.t.u./lb.-mole
P = pressure, lb./sq. in. abs.
R = gas constant
T = absolute temperature, °R.
v = molar volume
z = compressibility factor

Greek Letters

κ = constant, Equation (3)
π = internal pressure, lb./sq. in. abs.

Subscripts

c = critical
T = constant temperature
v = constant volume

LITERATURE CITED

1. Beattie, J. A., and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).
2. Benedict, M., G. B. Webb, and L. C. Rubin, *Chem. Eng. Progr.*, **47**, 419 (1951).
3. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," 2nd edit., Vol. II, Wiley, New York (1959).
4. Thompson, W. H., W. G. Braun, and M. R. Fenske, Documentation of the Basis for Selection of the Contents of Chapter 7, "Technical Data Book-Petroleum Refining," American Petroleum Institute, New York (1966).
5. van der Waals, J. D., dissertation, Leiden (1873).
6. Yesavage, V. F., Ph.D. dissertation, Univ. Michigan, Ann Arbor (1968).

Heat and Mass Transfer for Turbulent Pipe Flow

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Heat and mass transfer coefficients for turbulent flow in smooth circular pipes have been represented by empirical equations of the form

$$N_{Nu} = a\,(N_{Re})^b\,(N_{Pr})^c \qquad (1)$$

with various values of the constants a, b, and c to correlate experimental data.

EARLY RESEARCH

The equations of Colburn (*1*), Dittus and Boelter (*2*), Drexel and McAdams (*3*), and Sieder and Tate (*4*) are representative of the significant differences in the constants for Equation (1). These constants represent data for fluids with Prandtl numbers with the approximate range of 1 to 100. Interest in liquid metals as heat transfer media resulted in experimental data which showed that these data for very low Prandtl number fluids could not be predicted by correlations of the form of Equation (1). This difference occurs because the wall region, with characteristics of laminar flow, provides the resistance for heat transfer with Prandtl numbers greater than one, but the fully turbulent core region represents much of the resistance for the liquid metals.

The velocity profile was subdivided by von Karman (*5*) into three regions: laminar, buffer, and turbulent core. The velocity data of Nikuradse (*6*) were used to determine the eddy diffusivity for momentum as a function of the dimensionless radial distance, and an equation was derived to relate the Stanton number to the friction factor and Prandtl number. Martinelli (*7*) extended the concept of von Karman to include the core region and to use the velocity profile to obtain temperature profiles at uniform flux to predict heat transfer coefficients. Martinelli's assumptions were:

1. The "laminar sublayer" corresponds to y^+ from 0 to 5 and $\epsilon_H = 0$.
2. A buffer layer for y^+ from 5 to 30 and $\epsilon_H = \epsilon_v$.
3. The turbulent core for y^+ greater than 30 and $\epsilon_H = \epsilon_v$.

Inclusion of the core region provided the basis for prediction of heat transfer coefficients for liquid metals in addition to the Prandtl number range of 1 to 10 that was adequately represented by the von Karman equation. Experimental data for mass transfer showed that the von Karman equation underestimates the transfer rate because turbulence exists in the laminar sublayer. Lin, Moulton, and Putnam (*8*) recognized this sublayer turbulence and suggested introduction of an eddy of magnitude $\epsilon/\nu = 0.00033\,(y^+)^3$ into the laminar sublayer. Kropholler and Carr (*9*) used this eddy representation with a four-region velocity profile to develop a heat and mass transfer correlation. Equal diffusivities were assumed for momentum,

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