EVALUATION AND MAINTENANCE OF AN ENTHALPY DATABASE

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NOMENCLATURE

a, b, c, d	Correlation constants in Equation (2.7)
A	Helmholtz energy
$A\text{-}A^o$	Helmholtz energy departure function from ideal gas state
B, C, D	Virial coefficients in Equation (2.15)
C_p	Specific heat capacity at constant pressure
C_v	Specific heat capacity at constant volume
$g\Delta z$	Potential energy difference for a unit mass
G	Gibbs free energy
$G\text{-}G^o$	Gibbs free energy departure from ideal gas state
Δh	Enthalpy difference
h^E	Excess enthalpy
H^o	Ideal gas enthalpy
$H\text{-}H^o$	Enthalpy departure function from ideal gas state
ΔH_{vap}	Latent heat of vaporization
$\dot{m}$	Mass flow rate of fluid
p	Absolute pressure
Q	Heat input into the system
R	Universal gas constant
S	Entropy
$S\text{-}S^o$	Entropy departure function from ideal gas state
T	Absolute temperature
ΔU	Change in internal energy
$U\text{-}U^o$	Internal energy departure from ideal gas state
v	Volume

W_s	Work extracted by the fluid per unit mass
z	Component Mole fraction
Z	Compressibility factor
RMSE	Root-mean-squared error
%AAD	Average absolute percent deviation

Greek Symbols

Δ	Change in property
ρ	Density
ω	Acentric factor

Subscripts

c	Critical number
r	Reduced number
Dep	Departure
calc	Calculated
meas	Measured
Len	Lenoir
API	American Petroleum Institute

Superscripts

o	Standard state
ig	ideal gas
m	mixture
E	Excess number

CHAPTER I

INTRODUCTION

In the United States, there are a number of cooperative research organizations sponsored by industry. In the thermodynamic and physical properties areas, there are three trade organizations or engineering society groups of interest to the energy sector. The Gas Processors Association (GPA) conducts research on gases, light hydrocarbons, and process solvents for the recovery and purification of natural gasoline, liquefied petroleum gas (LPG) and on substitute gas (1). The American Petroleum Institute (API) Subcommittee for Technical Data, in its Refining Department, conducts research on petroleum and synthetic crude refining. The Design Institute for Physical Property Data (DIPPR), under American Institute of Chemical Engineers (AIChE), conducts research for the chemical/petrochemical area.

Cooperative research of this kind involves participation and sponsorship by industrial companies. Some of the advantages accruing to participating organizations include the availability of research results in a timely fashion. Data used in process design are obtained at a fraction of the cost of internal or contract measurement. In addition, when industry and the participants operate from a common database, plant design and construction is rendered more efficient. In other cases, cooperative data supplement internal research and also serve as calibration data for such research.

Rationale

Enthalpies are required for economic evaluation and design of chemical processes. In the chemical process industry, enthalpy data are used in designing separation units, reactors, heat exchangers, refrigerators, humidifiers, etc. Thus, accurate enthalpy data are needed for efficient process design and optimization purposes. Inaccurate thermodynamic properties such as the enthalpy values can lead to inoperative plants, or more likely, to over-design and superfluous capital investment.

The Gas Processors Association (GPA) maintains an extensive compilation of enthalpy departure data, among other kinds of thermodynamic data, of use to the natural gas processing industry in a "databank." The goal of the GPA Project 921, Enthalpy Database Development and Maintenance, is to compile, evaluate, and maintain experimental enthalpy, heat of solution, and isothermal enthalpy departure data for pure components and mixtures of known composition that address the technical needs of the gas processing industry. In this context, the database is used primarily to (1) evaluate enthalpy prediction methods and computer models, (2) develop new or system-specific correlations, and (3) identify experimental measurements for direct application (interpolation) in process engineering calculations.

Owing to the practical importance of enthalpy data in the process industry and its importance in model development efforts, it is essential that such data be accurate. Thus, the database must be free of data-entry errors, and probable errors in the experimental measurements must be noted.

The current enthalpy data in the GPA database are in the form of enthalpy departure values, which have been generated from experimental enthalpy data reported in the literature (24). Over the years, different techniques were employed to determine the enthalpy departure entries, since the experimental data were based to different reference states. Consequently, assessing the accuracy of the database departure values by direct comparison with the original enthalpy records in the literature is not possible.

Research Objectives

The goal of this work was two-fold.

- First, to evaluate the ability of the Peng-Robinson equation of state (EOS) for predicting the enthalpy departure values of natural gas systems maintained in the GPA databank.
- Second, to use the Peng-Robinson EOS enthalpy departure model to screen the enthalpy entries and help assess the quality of data in the GPA databank.

The thesis is organized into six chapters. Chapter II describes the basic experimental apparatus for enthalpy measurements. It discusses the formulation of enthalpy departure functions, ideal gas enthalpy correlations, and the reference states used for enthalpy determination. It includes a literature review of enthalpy departure function estimation using different equations of state and also discusses the reasons for choosing the Peng-Robinson equation of state for purposes of data evaluation.

A description of the GPA enthalpy database format and its holdings is given in Chapter III. The literature sources of the data in the database and the experimental techniques employed by the investigators are discussed in this chapter. Methodologies for smoothing of raw data and for data quality checks are also reviewed.

Chapter IV presents the model evaluations for all the enthalpy data in the database. The tables include the liquid-phase and vapor-phase predictions for the pure components and binary, ternary, and multicomponent mixtures.

The issues pertaining to enthalpy data quality assurance are dealt with in Chapter V. The methodology used for identifying data discrepancies and data meriting further examination, based on the EOS model evaluations, is demonstrated with the help of three sample test case systems.

Finally, Chapter VI contains the conclusions of this study and recommendations for future work.

CHAPTER II

LITERATURE REVIEW

In this chapter, background concepts which include the thermodynamic definition of enthalpy, its representation in terms of intrinsic variables, and the basic procedure for experimental determination of enthalpy are discussed. A pertinent literature review of the ideal gas enthalpy determination, enthalpy departure functions from equations of state, and the reference states used for calorimetric measurements are presented. The reasons for choosing the Peng-Robinson equation of state for data evaluation purposes are also discussed.

Definition of Enthalpy

For a closed system, i.e., a system which does not exchange mass with its surroundings, the first law of thermodynamics may be mathematically expressed as:

$$\Delta U = Q - W \tag{2.1}$$

where

U = internal energy

Q = heat input into the system

W = work done by the system

In addition to internal energy, another thermodynamic function, known as enthalpy is commonly used owing to its practical importance. For any system, enthalpy, H, may be mathematically expressed as:

$$H \equiv U + pV \tag{2.2}$$

where

p = absolute pressure

V = volume

The units of H, as seen from Equation (2.2) given above, are those of energy.

Enthalpy, H, is an example of a *state function*. Thermodynamically, a *state function* is a quantity which does not depend upon the past history of the substance nor the path employed to reach that condition or *state*. Internal energy, U, pressure, p and volume, V are all examples of state functions.

The general first law expression for *steady-state* fluid flow across any two sections, is given as (55):

$$\dot{m}\Delta h + \dot{m}\frac{\Delta u^2}{2} + \dot{m}g\Delta z = \dot{Q} - \dot{W}_s \tag{2.3}$$

where

Δh = enthalpy difference between the sections

$\dot{Q}$ = heat added to the fluid between the sections per unit time

$\dot{W}_s$ = work extracted by the fluid per unit time

$\dot{m}$ = mass flow rate of the fluid

$\frac{\Delta u^2}{2}$ = kinetic energy difference of the fluid between the sections per unit mass of fluid

$g\Delta z$ = potential energy difference between the sections per unit mass of fluid

Some of the terms in Equation (2.3) are expressions for energy per unit mass of fluid; in the SI system of units, energy is expressed in joules or in some multiples of joules. For most thermodynamic applications, the kinetic and potential energy terms are negligibly small and may, therefore, be omitted. In such a case, Equation (2.3) reduces to:

$$\Delta h = Q - W_s \tag{2.4}$$

where Δh, Q and W_s are per unit mass of fluid.

Experimental Determination of Enthalpy

Enthalpies are almost always determined experimentally using a flow calorimeter (55). A simple schematic for a calorimeter is given in Figure 1. The main feature of a flow calorimeter is an electric heater immersed in a flowing fluid. The flow setup is designed so that the kinetic and potential energy changes of the fluid between Sections '1' and '2' of Figure 1 are negligible. This requirement is met by ensuring that the two sections are at the same elevation, the velocities of flow are small, and that no shaft work is done between Sections '1' and '2.' Hence Equation (2.4) reduces to

$$\Delta h = h_2 - h_1 = Q \tag{2.5}$$

The electric resistance is used to add heat to the flowing fluid, where the rate of energy input is determined from the resistance of the heater and the current passing

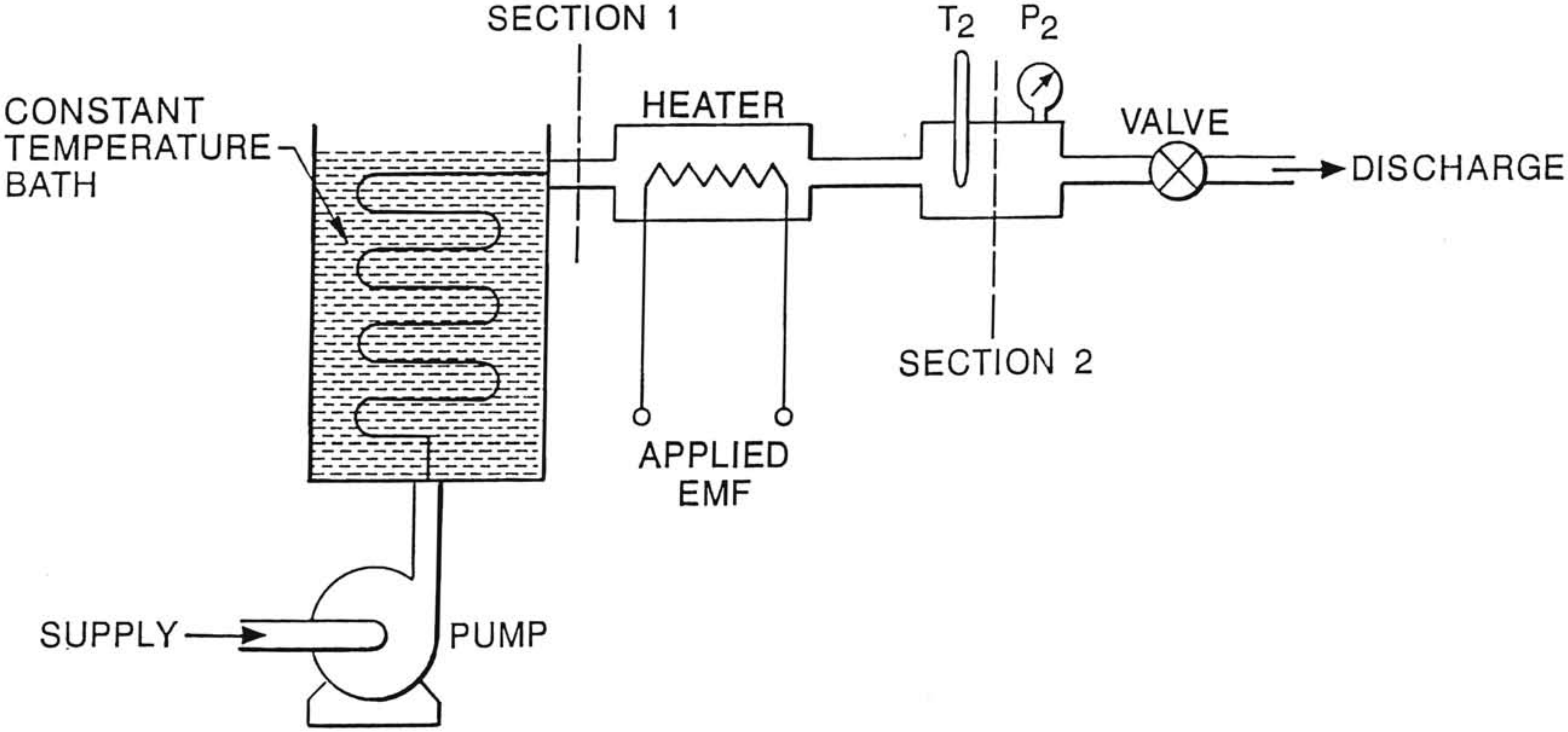

Figure 1. A Simple Schematic of a Flow Calorimeter

through it. The entire apparatus must be kept well insulated. In practice, there are a number of details that demand careful attention, but in principle the operation of the calorimeter apparatus is simple. Measurements of the heat input rate and the rate of fluid flow allow calculation of Δh between the Sections '1' and '2.' Equation (2.5) reveals that differences in enthalpy rather than absolute values of enthalpy are determined experimentally. In reference to Figure 1, the enthalpy difference is between the fluid entering at Section '1' and exiting at Section '2,' $h_2 - h_1$. If enthalpy of the fluid at Section '1' is arbitrarily taken as zero, then $\Delta h = h_2 = Q$ as indicated by Equation (2.5). Hence, the choice of a reference state assumes importance when dealing with enthalpy measurements. Generally, all enthalpies are based to an arbitrarily chosen reference state. Thus, when making comparisons between different enthalpy values, the reference states to which the values are based should be the same.

The Enthalpy Equation

According to the phase rule, for a homogeneous substance of constant composition, fixing the values of two intensive properties establishes its state. The molar or specific enthalpy of a substance may, therefore, be expressed as a *function* of two other state variables. The two state variables are, for convenience, chosen as temperature and pressure. Therefore,

$$H = H(T, p)$$

The enthalpy of a compound can be expressed as a summation of three quantities (53):

$$H(T,p) = [H(T,p) - H(T,p^o)] + [H(T,p^o) - H(T^o,p^o)] + H(T^o,p^o) \quad (2.6)$$

where

$H(T,p)$ = enthalpy of a pure fluid or a mixture

$H(T,p) - H(T,p^o)$ = enthalpy departure function

$H(T,p^o) - H(T^o,p^o)$ = ideal gas enthalpy difference

$H(T^o,p^o)$ = enthalpy at the reference state

$H(T^o,p^o)$ is the enthalpy of formation of the compound from the elements at T^o and p^o, or the reference state chosen for enthalpy calculations. The quantity $[H(T,p^o) - H(T^o,p^o)]$ is the difference in the enthalpy of the compound in the ideal gas state at the temperature of interest and the reference state of T^o. $[H(T,p) - H(T,p^o)]$ is called the enthalpy departure function and is the difference in the enthalpy of the compound at the temperature-pressure condition of interest and the enthalpy of the compound in the ideal gas state at the same temperature. For notational convenience, the enthalpy departure function and the ideal gas enthalpy difference will, hereafter, be denoted as $H - H^o$ and H^o, respectively. Enthalpy departures are also termed as residual enthalpies, and symbolically denoted as H^R.

Ideal Gas Enthalpy Determination

The ideal gas enthalpy function is calculated using an exact relation of type given below.

$$H^o = \int C_p^o dT$$

where H^o is the ideal gas enthalpy, C_p^o the ideal gas heat capacity at constant pressure, and T the absolute temperature. The choice of the functional form of heat capacity in most correlations is of a polynomial type (2, 3).

$$C_p^o = a + bT + cT^2 + dT^3 + ... \qquad (2.7)$$

In the United States, and for substances of interest to the energy sector, the parameters (a, b, c, d, ...) in most cases are regressed from C_p^o data of the API Research Project 44 and the Thermodynamic Research Center (TRC) Data Project (2, 3). These equations are derived using conventional least-squares method, minimizing the sum of the squares of either the absolute deviations or percentage deviations with respect to reported C_p^o data. The reference base used was 0 Btu/lb at 0 °R for the enthalpy computations - the same as those used for the API Research Project 44 tables (2, 3).

Heat capacity correlations of the polynomial form are, by far, the most popular means of computing ideal gas enthalpy values. This is because they are reasonably accurate and afford an easy means of ideal gas enthalpies computation by way of analytical integration. The accuracy of the equations can be improved by increasing the number of constants in the correlation.

A drawback of the polynomial form of heat capacity correlations is that even though greater accuracy in fitting of the individual property may be achieved, it is at the expense of being thermodynamically inconsistent (6). This is so because actual heat capacity behavior is not constrained to follow any particular polynomial.

Some of the more elaborate choices for heat capacity correlations have the form (4, 5) shown below :

$$C_p^o = a + b\exp(-c/T^n) \tag{2.8}$$

This form is derived from theoretical considerations, but it is not readily amenable to integration, i.e., a series expansion or a numerical integration procedure is required. However, the predicted values of C_p^o are more accurate than those calculated from the polynomial equation with four constants (4).

More complex equations for calculating the ideal gas heat capacity and enthalpy have been proposed (6). These equations are more rigorous in form since they are derived based on statistical mechanical formulae for the heat capacity of an ideal gas (7-9). Comparison with existing heat capacity correlations shows that these equations are more accurate for most cases.

Enthalpy Departure Function Estimation

The enthalpy departure function, $[\,H(T,p) - H(T,p^o)\,]$, is obtained from the pressure-volume-temperature (pvT) properties of the fluid under study. An equation of state (EOS) capable of describing the pvT behavior of the fluid offers the most efficient means for determining enthalpy departure functions.

For a pressure-explicit EOS, the departure function for the Helmholtz energy, A, is developed first using the appropriate fundamental property relations. Then, all the other departure functions are readily obtained (53), as shown below:

$$A - A^o = -\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV - RT\ln\frac{V}{V^o} \tag{2.9}$$

$$S - S^o = \int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{R}{V}\right]dV + R\ln\frac{V}{V^o} \tag{2.10}$$

$$H - H^o = (A - A^o) + T(S - S^o) + RT(Z - 1) \tag{2.11}$$

$$U - U^o = (A - A^o) + T(S - S^o) \tag{2.12}$$

$$G - G^o = (A - A^o) + RT(Z - 1) \tag{2.13}$$

It is worthwhile to note here that the departure functions ($H - H^o$) and ($U - U^o$) do not depend upon the value of the chosen reference state p^o (or V^o) while ($A - A^o$), ($S - S^o$), and ($G - G^o$) depend upon p^o (or V^o).

For the specific EOS, the right-hand side expressions of the above equations have to be evaluated. A detailed derivation of the enthalpy departure function using the Peng-Robinson equation of state is given in Appendix A.

Overview of Volumetric Equations of State

Equations of state play a central role in chemical engineering. Equations of state (EOS) that represent relations between the pressure, p, molar volume, v, absolute temperature, T, and compositions are referred to as volumetric EOS. A volumetric EOS in conjunction with interrelationships provided by classical thermodynamics can be used for estimating enthalpy departure functions from the ideal gas and for calculating phase equilibria.

Since equations of state are so important in engineering, the literature on the subject is vast. Literally, hundreds of variations of equations of state exist. However, most of the accurate volumetric equations of state may be classified according to their origin. The groups of equations may be classified as the van der Waals family of cubic equations, the family of extended virial equations, corresponding states equations, and those equations derived from statistical thermodynamics based on lattice models, perturbation and integral equation theories, or from fitting computer simulation data.

The van der Waals family of cubic equations of state have been the subject of much attention and research since the famous cubic equation of van der Waals (vdW) was proposed in 1873:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \tag{2.14}$$

where b is the excluded volume and a, the cohesion parameter. While the vdW equation of state is of historical interest, it is not quantitatively accurate. Other, more accurate equations of state are those of Redlich and Kwong (RK) (62), Wilson-Redlich-Kwong (63), Soave-Redlich-Kwong (SRK) (64), Peng-Robinson (PR) (51), Schmidt and Wenzel (SW) (65), Harmens and Knapp (HK) (66), Patel and Teja (PT) (67), Adachi-Lu-Sugie (ALS) (68) and recently Trebble and Bishnoi (TB) (69). This list is by no means exhaustive, but it does represent some of the major milestones along the path of cubic EOS development.

The virial equation of state is an infinite-power series in inverse molar volume, as given by Equation (2.15) below. This equation, first proposed by Thiesen (20), represents the volumetric behavior of real fluids as a departure from the ideal gas equation,

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots \qquad (2.15)$$

Z is the compressibility factor. The coefficients B, C, D, etc., are called "virial coefficients"; B is the second virial coefficient, C is the third coefficient, and so on. From statistical mechanics, these coefficients are related to the forces between the molecules; i.e., the second virial coefficient represents the interactions between two molecules, the third virial coefficient reflects the simultaneous interaction among three molecules, etc.

The Beattie-Bridgeman truncated virial equation (70), a variation of the virial equation of state, was the first satisfactory equation of state for the quantitative description of real-gas volumetric behavior. This equation was widely used for the representation of gaseous pvT behavior until it was replaced by the Benedict-Webb-Rubin (BWR) equation (71).

Benedict and coworkers (71) modified the Beattie-Bridgeman equation to yield the BWR equation:

$$Z = 1 + \left[\frac{B_o - (A_o/RT) - (C_o/RT^3)}{v}\right]$$

$$+ \left[\frac{b - (a/RT) + (c/RT^3)}{v^2}\right] - \frac{\gamma c}{RT^3 v^4} \qquad (2.16)$$

The BWR EOS fits the pvT data of methane, ethane, propane, and *n*-butane; and helped calculate density and other derived properties, such as enthalpy, fugacity, vapor pressure, and latent heat of vaporization to high accuracy. The equation was initially applied to mixtures of these four light components, and in 1951 was extended further to include eight additional hydrocarbons up to *n*-heptane. In fact, since the BWR equation is specialized (fine tuned for lower weight hydrocarbons), it is one of the more accurate equations of state for these mixtures. For this reason, there are many variations for the BWR equation; Cooper and GoldFrank (72), Orye (73), Morsy (74), Starling (75), Nishiumi and Saito (76), Schmidt and Wagner (77), and the AGA natural gas equation by Starling et al. (78). The AGA natural gas equation is a high precision EOS represented by two sets of 52 terms, one set for pure gases and the other for mixtures. Each expression is intended for custody transfer of pure gases or mixtures containing paraffins (methane through n-decane, i-butane, i-pentane), nitrogen, oxygen, argon, carbon dioxide, carbon monoxide, hydrogen, helium, and/or hydrogen sulfide.

Enthalpy Departures from Equations of State

A literature overview of enthalpy departure predictions using various equations of state is presented in this section. The enthalpy departure predictions using BWR EOS were compared to the Peng-Robinson EOS for a mixture of ethane and methane at 38.61 °C (10). The BWR equation gave superior results upon comparison with experimental measurements (11). A modified BWR equation was compared in its enthalpy predictive capability against RK, Beattie-Bridgeman and Lee-Edmister for a limited database of methane, water and ammonia systems (12). The BWR equation was the most successful. Enthalpy departure predictions are made for eleven nonpolar fluids using the most general cubic EOS of Kumar and Starling. The equation was compared with the PR equation and the three-parameter corresponding states Modified BWR (3PCS-MBWR) equation of state (13). According to those comparisons, the most general cubic EOS is more accurate than the PR equation and compares quite well with the three-parameter corresponding states modified BWR (3PCS-MBWR) equation of state.

An evaluation of enthalpy departure prediction methods for nonpolar and polar fluids was performed by Toledo et al. (14). The SRK, Mathias-SRK, PR, Ploecker-Lee-Kesler (PLK), and the GCEOS (Skjold-Jorgensen, 1984) equations of state were tested against a set of eleven-thousand experimental data points comprising 18 pure components, 23 binaries, and 5 ternaries. The evaluation shows that the PLK and GCEOS methods are significantly superior to the SRK and PR methods for single-phase, nonpolar fluids, particularly in the vapor phase. These models perform similarly for polar fluids but show larger deviations. The GCEOS model has been found to be a promising method for both nonpolar and polar fluids. The predictions in the two-phase region by any of these methods show higher deviations.

Similarly, enthalpy departure predictions were compared for a database comprising four pure substances and two binary mixtures; the pure substances represented by cyclohexane, nitrogen, octane and pentane; the binaries were varying compositions of *n*-pentane - cyclohexane and *n*-pentane - *n*-octane mixtures (15). The van der Waals (vdW)-711 EOS was compared to the PR equation. The PR EOS yielded much better results. The explanation for the differences in performance may be attributed to the presence of the covolume parameter, b, in the PR equation. Adachi and Sugie (16) conclude that the covolume parameter is the controlling factor in enthalpy calculations. According to their study, a cubic EOS which gives good *pvT* predictions is found to be able to predict enthalpy departures well, and PR EOS is a good choice for this purpose.

A fairly comprehensive study involving the comparative capabilities of eleven cubic equations of state was carried out for a representative sample of 2640 points for paraffins ranging from methane to *n*-decane by Adachi, Sugie, and Lu (17). The PR EOS gave lower deviations for enthalpy departure values compared to SW, SRK, HK, and ICL (Ishikawa-Chung-Lu) equations of state. The PR EOS predictions were similar to those of KS EOS. However, the ALS EOS yielded best enthalpy departure prediction results.

The TB EOS was compared in its enthalpy predictive capabilities to PR EOS using a database involving methane, carbon dioxide, ammonia, and water (18). The PR EOS proved to be more accurate than the TB EOS for all three components other than water. In fact, for carbon dioxide the predicted values between the two equations of state differed by almost 100%. The PR EOS gave superior enthalpy predictions when compared to the Trebble-Bishnoi-Salim, TBS EOS (19) for a database similar to the one used by Trebble and Bishnoi (18).

It is evident from the above discussion that the modified BWR type equation is a viable tool for calculating vapor-liquid equilibrium and departure functions for nonpolar mixtures. However, since the middle 1970s, the SRK and PR equations have dominated VLE and departure function calculations in the hydrocarbon industry. These equations are surprisingly good for thermal property calculations, except in the critical region (20). Albeit, the extended BWR equations are still preferred when volumetric and other thermodynamic information of high accuracy are needed, since the cubic equations of state do not represent volumetric data well.

Despite its success in correlating both gas and liquid light hydrocarbon mixtures, the BWR equation poses certain disadvantages. The constants of BWR and its related equations of state have been tabulated by a number of authors for various compounds (57). These constants were mostly obtained from fitting experimental data at low to moderate pressures, thus they cannot be easily extended to high pressure without verification. Furthermore, these equations cannot be employed if the required pure component constants are not available.

The equations of state described thus far are of an empirical nature and at best semiempirical. Empirical equations are often useful; albeit, limited in their application. Such equations must be applied in the range of temperature, density and composition where experimental data exist; when empirical equations are extrapolated into regions where no data are available, poor estimates often result. Further, since the equation-of-state parameters have little or no physical significance, it is often difficult to estimate parameters for other fluids, and especially for mixtures. Theoretically based equations of state address some of the problems mentioned above. Based on statistical thermodynamics, these modern equations of state result from lattice models, perturbation and integral equation theory, or from fitting computer simulation data. Among the theoretically based equations, the perturbed-hard-chain theory in its various forms has been in general use (58, 59). However, none of these equations have received the acceptance of the simpler cubic equations of state, such as those of the Soave and Peng-Robinson equations.

The simplified perturbed-hard-chain theory (SPHCT) EOS, the modified SPHCT EOS and the PR EOS were evaluated for the prediction of calorimetric properties (60). The results indicate that the abilities of the PR EOS, the original SPHCT EOS and the modified model to predict calorimetric properties are similar to their comparative abilities to predict volumetric properties. The evaluations were conducted using six pure fluids covering the two-phase and the single-phase regions. The fluids considered were methane, ethane, propane, benzene, carbon dioxide and water. These evaluations were limited in scope and further examination will be required to assess the potential of these equations.

Daubert (54) used the PR EOS for enthalpy departure predictions and comparisons against selected enthalpy values in the GPA databank. The databank has since been continually added to and maintained. The model predicted enthalpy departures very well for light hydrocarbons and gases, although, the accuracy decreased for the heavier hydrocarbons - pentane and above.

Similary, in this work it was decided to use the PR EOS enthalpy departure model for data evaluation purposes and to study its predictive capabilities against the enthalpy departure values in the GPA databank. The advantages of the PR enthalpy departure model, which suited our requirements, are several. Specifically, the model is:

- Capable of handling multiphase natural gas systems over a wide range of temperature and pressure conditions.
- Generalized and applicable to multicomponent systems with established mixing rules.
- Reasonably accurate with an acceptable speed of computation.

Excess Enthalpies and Equations of State

Thus far, enthalpy departure functions, which represent enthalpy changes as a result of deviation from ideal gas behavior, have been discussed. It is a common occurrence that when two or more pure compounds mix, 'excess' enthalpy is produced owing to molecular interaction. Excess enthalpies are commonly denoted as h^E, where the superscript 'E' signifies 'excess' property. At the same temperature and pressure, the enthalpy of a binary "ideal mixture" would be:

$$h^{ig} = y_1 h_1 + y_2 h_2 \tag{2.17}$$

where y_1 and y_2 are the mole fractions for the pure components '1' and '2,' respectively; and h_1 and h_2 are the molar enthalpies of the two components (55). On mixing, excess enthalpy, h^E is expressed as:

$$h^E = h^m(p,T,y) - y_1 h_1 - y_2 h_2 \tag{2.18}$$

where $h^m(p,T,y)$ is the enthalpy of the resulting mixture at the same temperature and pressure. In an ideal mixture, the excess enthalpy, also known as heat of mixing, is zero. An ideal mixture is to be expected only when the molecular interaction, mass, and size are sufficiently similar. Excess enthalpies are usually determined from calorimetry data.

The excess enthalpies of gaseous mixtures are, at times, correlated by means of equations of state (20). The modified Martin-Hou (MH) EOS (1981) was used to correlate the excess enthalpy of binary gaseous mixtures at pressures up to 100 atm (22). Equations of state have also been used to correlate h^E in the liquid region. For instance, Adachi and Sugie (1988) correlated h^E of the water-acetone system by means of a cubic equation of state; Casielles et al. (1989) predicted h^E of a ternary system from binary experimental data using the PR equation.

Reference States for Enthalpy Data

It is important to note the reference states employed in reporting enthalpy data. No uniform reference states are currently used for reporting calorimetric property data. Different sources employ different reference states. A discussion of the reference states employed and the calculation paths used by two organizations respected for the integrity of their compilations is given below. The GPA reference states and enthalpy departure methods are discussed in Chapter III.

National Institute of Standards and Technology (NIST)

NIST (formerly NBS) uses non-analytic equations of state (25, 26) to derive thermophysical data of pure fluids for a wide range of pressure and temperature conditions. The general form of the equation of state is the same for all pure hydrocarbons, but the density and temperature-dependent functions are substance-specific. The constants in the equation of state are obtained by fitting the equation specifically to available pressure-density-temperature ($p\rho T$) data for the fluid.

The calorimetric properties determination involves the computation of both the ideal gas enthalpy difference and the enthalpy departure function. For ideal gas enthalpy difference, an equation is developed to fit the available data on a given calorimetric property as a function of temperature, T. The property chosen depends on the availability of consistent data. From the equation for the chosen property, the other ideal gas functions are evaluated by using the appropriate thermodynamic formulae.

The departure function expressions for change in internal energy, ΔU, change in specific heat at constant volume, ΔC_v, and related quantities are first evaluated along an isotherm from zero density to the required $\rho - T$ state. Then, ΔH and ΔC_p are computed using the appropriate formulae. For the vapor phase, including saturated vapor, the above method is used to evaluate the departure function. For the liquid phase, including saturated liquid, ΔH_{vap} is subtracted from the saturated vapor value and integration is performed similar to the vapor phase.

The reference state chosen by NIST is $U = 0$ at the liquid triple point, obtained by use of an arbitrary value for $U\,(T^o, p^o)$. For instance, according to Goodwin (25), n-butane is assigned an internal energy $U =$ 22644.306 J/mol at 0 K and 0 Pa, to accommodate a triple point $U\,(T^o, p^o)$ of zero.

Thermodynamic Research Center-American Petroleum Institute
TRC-API 44

According to TRC "Thermodynamic Tables-Hydrocarbons" (27), the ideal gas enthalpy difference is computed by resorting to statistical mechanics. Statistical thermodynamics along with spectroscopic data are used for the calculation of specific heats. Specific heats, in turn, yield enthalpy values and other thermodynamic functions. The predicted values are checked, when possible, against experimental data and, in some cases, adjustments are made to achieve better agreement.

The departure functions estimation techniques have not been indicated. The tabulated values are based on experimental measurements, estimation procedures or a combination of both. The reference state used in computing the ideal gas thermodynamic functions is a temperature of 0 K and a pressure equal to 1 bar.

The ideal gas thermodynamic properties for the elements used by TRC-API 44 are similar to those in the JANAF Thermochemical Tables (28). Also, TRC-API 44 has used symbols, units for thermodynamic properties and atomic masses of elements based on the International Union of Pure and Applied Chemists (IUPAC) review of 1983 (29).

The literature review revealed that a consensus seems to have emerged for the need to standardize the reference states employed for thermodynamic functions in general, and enthalpy values in particular. Since 1975, all tabulated values are given in terms of International System (SI) of units. Temperature and pressure values of 0 K and 1 bar (or 1 atm) appear to be emerging as *defacto* standard reference states for thermodynamic function computations. However, large volumes of enthalpy data still remain which are based on different reference states.

CHAPTER III

GAS PROCESSORS ASSOCIATION (GPA) ENTHALPY DATABASE

The GPA Enthalpy database contains enthalpy departure data for pure components and mixtures of materials that include the following: paraffins to C_{16}; alkyl naphthenes to C_9; aromatics to C_{10}; and nonhydrocarbons include nitrogen, carbon monoxide, carbon dioxide, hydrogen sulphide, hydrogen, and water. The systems in the database and the temperature and pressure conditions at which data are reported are of particular interest to the natural gas processing industry. In this chapter, the GPA enthalpy database format and holdings are presented. The sources of experimental data and the experimental techniques employed by the investigators are discussed. Issues involving thermodynamic consistency checks, smoothing of enthalpy data, and departure conversion techniques are also reviewed.

GPA Enthalpy Database Format

The database format includes identification of the components, the mole fraction of each component for each composition and the temperature, pressure, enthalpy, phase (liquid, vapor, or two-phase), and the literature reference number for each data point (24).

The compound identification numbers follow the method used in the GPSA Engineering Data Book. The database uses a single set of consistent units for reporting temperature, pressure and enthalpy departure values. The unit for temperature is '°F', the pressure values are reported in 'psia', and the enthalpy departures have units of 'Btu/lb.' Each data record also includes the phase code, departure method, literature reference number, and a code identifying whether the data point is raw or smoothed.

The phase code specifies whether the point is in the liquid phase, vapor phase, or the two-phase region. These are denoted by: 1 = liquid; 2 = vapor; 3 = two-phase; 4 = liquid/two-phase and 5 = vapor/two-phase. Although, five different phase codes in the database are used to describe all the data records, in reality only three phases are present. These are: the liquid region (represented by phase codes '1' and '4'), vapor phase (phase codes '2' and '5') and the liquid-vapor region denoted by phase code '3.' The departure method is indicated by a letter (A, B, C, D), each of which denotes a procedure used to process the original enthalpy values to their departure values. The four departure methods are described in a later section in this chapter. For any data record, 'R' and 'S' are used to indicate raw or smoothed experimental values, respectively.

GPA Enthalpy Database Holdings

The enthalpy database holdings include twenty pure fluids, twenty-nine binary mixtures, five ternary mixtures, one quaternary mixture and two multicomponent natural gas systems at various compositions. Tables 3, 4, 5 and 6 in Chapter IV give a complete listing of the current holdings in the database along with the molar compositions of all systems and the temperature and pressure ranges for the systems. The tables also include the number of data points for each of the three phases and the corresponding literature reference numbers. The listing of the reference numbers and the literature sources are given in Appendix B.

Source of Enthalpy Data in the Database

All the enthalpy departure data in the database are based on experimental data collected and compiled over a period extending almost twenty five years (mid 1960's to 1990). A fair amount of the data in the database was acquired through projects sponsored by the GPA (Projects 661, 722, 731, 741, 742, 792, 811). However, the database also draws heavily upon the extensive compilations of enthalpy data that were experimentally obtained by Lenoir et al. (1967-1972) at the University of Southern California, Los Angeles. The database also includes enthalpy data selected from other literature sources (Appendix B has a complete listing).

Lenoir's Reference State for Calorimeteric Measurements

Lenoir et al. (1967-1972) used a reference state of 75 °F and the liquid-phase condition while carrying out their experiments. This was accomplished by ensuring that the hydrocarbon leaving the calorimeter was at 75 °F and in the liquid state. The fluid flows through the calorimeter apparatus at a constant flow rate and has an inlet temperature in the range of 150-700 °F. The upper range of the inlet temperature may be lower or higher depending upon the specific hydrocarbon being used. The pressure was usually varied from 0-1400 psia for all fluids in the flow calorimeter experiments. The change in enthalpy was measured by the quantity of Freon-11 evolved as heat transferred in the calorimeter from the hydrocarbon fluid to the surrounding Freon-11, which was maintained precisely at its boiling point and 75 °F.

All of the calorimetric experimental data collected by Lenoir et al. were rebased from the reference state of 75 °F, liquid-phase condition to the API Data Book (1966) enthalpy datum level of saturated liquid at -200 °F. This was accomplished by adding a constant value of enthalpy to the experimentally-obtained enthalpy values for each system. This constant value of enthalpy for each system was determined by subtracting the latent heat of vaporization from the ideal gas state at 75 °F. The enthalpy value at the ideal gas state at 75 °F is taken relative to the API reference state of -200 °F from the API Data Book (1966). The latent heats of vaporization data were referenced to different sources for different compounds (30-33). In certain cases, for instance, the cis-2-pentene calorimetric measurements, instead of using the API Data Book value for ideal gas enthalpy and the heat of vaporization data, the rebasing from 75 °F to the -200 °F state was carried by graphical integration of heat capacity values from Todd et al. (34). For the binary mixtures, ideal gas enthalpies from the API Data Book were computed as a weighted average of the two pure component values. Also, heats of mixing data were used where applicable. The heats of mixing data, in turn, were referenced to different sources (35-37).

The original enthalpy measurements, relative to 75 °F and the associated pressures, are deposited with the American Society of Information Science (ASIS). Having converted all experimental enthalpy data to the -200 °F basis, the data were plotted on large-scale cartesian coordinate graph paper, and smoothing was performed by visually drawing an appropriate average curve through the plotted values (38). The final smoothed enthalpy values were presented in tabular form.

GPA Reference States for Enthalpy Data

Prior to 1974, GPA enthalpy research projects have resulted in the publication of experimental pure component and mixture enthalpies for systems of interest to the gas industry (39, 40). However, most of the published data were based on different reference states. To eliminate this variation in the reported data, the GPA enthalpy data were converted to two common reference states: the ideal gas state at 0 K, and the elemental states at 25 °C. In 1974, Cochran and Lenoir (GPA Project 733) devised techniques for data conversion to the above two reference states (23). All the GPA sponsored enthalpy projects from 1974 on have reported experimental enthalpy values referred to the above two states (41-46).

Thermodynamic Consistency Checks for GPA Enthalpy Data

GPA reports (39, 40, 41, 47) have presented experimental enthalpy values as isothermal and isobaric enthalpy differences. This means of compiling data aided in testing for thermodynamic self consistency. Isothermal enthalpy differences were measured at two temperatures on each system studied. Measurements at the second temperature were made to permit an evaluation of the data around closed loops. Since the enthalpy is a state property, the sum of all changes around a closed loop should add to zero. Experimental measurements will not close perfectly due to experimental uncertainties, and the lack of closure is a measure of the accuracy of data. For comparitive purposes, the lack of closure is calculated as percentage error by dividing the residual difference times 100 by the sum of the absolute value of all the enthalpy changes around the closed loop. As an example, Figure 2 gives a pictorial representation of loop closure for experimental enthalpy data on 50 mole % hydrogen - 50 mole % ethane (40).

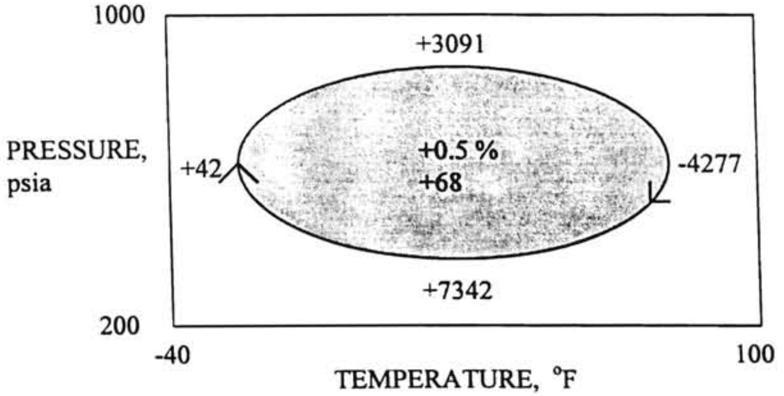

Figure 2. Pictorial Representation of loop closure for enthalpy data on 50-50 mole% H_2S-Ethane

The isothermal and isobaric data were tested for consistency by making loop checks between temperature and pressures. From Figure 2 above:

a) At 200 psia, from 100 °F to -40 °F $(\Delta H)_{p1}$ = - 7342 Btu/lb-mole
b) At -40 °F, from 200 to 1000 psia, $(\Delta H)_{T1}$ = + 42 Btu/lb-mole
c) At 1000 psia, from -40 °F to +100 °F, $(\Delta H)_{p2}$ = + 3091 Btu/lb-mole
d) At 100 °F, from 200 to 1000 psia, $(\Delta H)_{T2}$ = + 4277 Btu/lb-mole

Summation around the closed loop = + 68 Btu/lb-mole

Out of a total enthalpy change around the loop of 14,752 Btu/lb-mole, + 68 Btu/lb-mole represents an error of + 0.5%. Such loop closures were performed on GPA enthalpy data, wherever possible. Set criterion was employed to accept or reject the enthalpy data analyzed. Typical values of absolute errors in the loop closure calculations for all the smoothed enthalpy data (39, 40, 41, 47) were between 0 - 1%. A negative value for the error % indicated a lack of closure while a positive value represented "excess of closure."

Smoothing of GPA Enthalpy Data

The GPA reports most of its enthalpy measurements on isotherms and isobars (39, 40, 41, 47). These data provide direct isothermal information for checking and evaluating new or existing equations of state or other correlations for predicting enthalpy. Isothermal data are best suited for this because an equation of state predicts the deviation from ideal gas behavior as a function of pressure at the system temperature. Isothermal data can be compared directly with the equation of state predictions.

Smoothing of experimental data can be carried out using several methods. One would be to plot the data directly on a grid and to smooth it graphically. Indeed, this was the method employed by Lenoir et al. (38) to perform smoothing of their data. However, the drawback to this method is that it is difficult to plot data on a reasonable scale with an accuracy much better than ± 1%; thus, this procedure suffers from lack of precision, both in plotting the experimental data and in reading the smoothed data from the plot.

Another method would be to select an analytical function which approximates the data; plot deviations between the measured and calculated data; draw a smooth curve through the deviations; and then correct the calculated data by means of the smoothed deviation curve. This method has the advantage in that the deviations can be plotted on a much larger scale, so that plotting and reading errors become insignificant compared to scatter in the experimental data. The GPA relied on this method due to its inherent advantages.

The GPA chose a modified Redlich-Kwong (RK) equation-of-state (MARK V program) as the analytical function for smoothing the individual isotherms. The ideal gas heat capacity constants used were taken from the API Data Book (1966, 1982). Deviation plots were prepared showing deviation in Btu/lb versus pressure (in psia) for the different systems. The correction factor was then applied to the calculated enthalpies by use of the following relationship:

$$H_{smooth} = H_{calc} + \left(H_{meas} - H_{calc}\right)_{smoothed} \tag{3.1}$$

Conversion of GPA Enthalpy Data to the Standard GPA Reference State

The GPA research report RR-11 (23) describes the two standard GPA reference states for enthalpy data. The datum levels chosen were:

a) the ideal gas state at absolute zero, and

b) the elemental states at 25 °C.

All the GPA enthalpy data (39, 40, 41, 47), including both raw and smoothed, had to be adjusted to the above two reference states. The original GPA data obtained were referred to different temperature and pressure states. For instance, the reference states used while obtaining experimental enthalpy data for certain systems in RR-6 (39) are presented in Table 1.

As observed, not only different systems. but the same system with different compositions are each based to a different reference state. To convert all of these data to the ideal gas state at absolute zero involved rebasing on both the pressure and temperature axes.

Table 1
Experimental Enthalpy Reference States
for Systems in GPA-RR 6

System	Mol. Fraction	Phase	Temperature (°F)	Pressure (psia)
Methylcyclohexane	1.0	liquid	-100	50
Methane	0.25	liquid	-100	200
n-Heptane	0.75			
Methane	0.5	liquid	-100	600
n-Heptane	0.5			
Methane	0.95	liquid	-100	2500
n-Heptane	0.05			

All of the enthalpy data were translated from their original pressure states to the zero-pressure ideal gas state. GPA RR-11 (39) describes the conversion of enthalpy data for gases to the zero pressure level. The relation used for rebasing enthalpy data for pressures up to 50 psia to the ideal gas state involved the use of virial coefficients documented in the literature (48). The relation used was:

$$H - H_o = \left(B - T\frac{dB}{dT} \right) P \tag{3.2}$$

where B is the second virial coefficient. Experimental values were not available for all components, nor for all needed temperature ranges, so an alternative general correlation for predicting B was needed. The correlation of Pitzer and Curl (49) was selected.

$$B = \frac{RT_c}{P_c}\left[0.1445 - \frac{0.33}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} \right.$$

$$\left. + \omega\left(0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8} \right) \right] \tag{3.3}$$

Equation (3.3) is quite accurate except at very low reduced temperatures, and it can be reliably used to 50 psia. Having rebased enthalpy data up to 50 psia accurately, the measured enthalpies were based further on the ideal gas, 0 K basis. The API-44 heat capacity constants were used for computing ideal gas enthalpies based to the 0 °R state. These values, in turn, were used to perform the rebasing to the 0 K state.

For data tabulations that use a pressure reference state higher than 50 psia, Starling (50) extrapolated the highest temperature isotherm to zero psia; this extrapolated zero psia value was then used as the basis for calculating ideal gas enthalpy values at all other temperatures using ideal gas enthalpies from the API Research Project 44 values.

Once all the data were converted to a single standard reference state, the tabulated enthalpy departure values in the GPA enthalpy database result as the difference between the enthalpy value at a particular pressure coordinate for an isotherm and the ideal gas (zero-pressure) value for the same isotherm.

GPA Departure Conversion Techniques

GPA converted its entire database of experimental enthalpy values, related to different reference states, to departure values in 1989-1992 (GPA Project 822). This section summarizes the four departure calculation techniques that were employed by the investigators for enthalpy data conversions (24).

Method A

This method is used to convert Lenoir's (23) data. The departure function H_{Dep} is defined as:

$$\begin{aligned} H_{Dep} &= H(T,p) - H(T,p^o) \\ &= H(T,p)Len + [\, H(T,p^o)API - H(T,p^o)Len \,] - H(T,p^o)API \end{aligned}$$

where

$H(T,p)Len$ = Lenoir's experimental value

$[H(T,p^o)API - H(T,p^o)Len]$ = enthalpy difference between Lenoir's experimental base and the API base of -200 °F, saturated liquid

Method B

This method is used for data requiring only the ideal gas enthalpy $H(T, p^o)$ for determining the departure value, i. e., $H(T^o, p^o) = 0$. $H(T, p^o)$ is either given by the author or calculated from the API Technical Data Book ideal gas enthalpies.

Method C

This method is used for trans-decalin, cis-decalin and tetralin. H_{Dep} is defined as:

$$H_{Dep} = [H_T - H_{75L}] + [H_{75V} - H^o_{75}] - [H_{75V} - H_{75L}] - H^o_T + H^o_{75}$$

where

$[H_T - H_{75L}]$ = experimental value

$[H_{75V} - H^o_{75}]$ = pressure effect at 75 °F

$[H_{75V} - H_{75L}]$ = heat of vaporization at 75 °F

H^o_T = ideal gas value at T

H^o_{75} = ideal gas value at 75 °F

Method D

This method is same as Method C, except for the way the ideal gas values are calculated. It is used for only cis-2-pentene.

CHAPTER IV

EQUATION-OF-STATE ENTHALPY DEPARTURE MODEL EVALUATIONS

This chapter includes a description of the Peng-Robinson (PR) equation of state (EOS), and the enthalpy departure expression derived from it. The reasons for choosing the PR EOS for this study were discussed in Chapter II. The model evaluations performed along with the database holdings are presented in tabular form.

The Equation-of-State Model

The PR EOS was used in this study (51):

$$p = RT/(v-b) - a_c\alpha/(v^2+2bv-b^2) \tag{4.1}$$

where

$$b = 0.07780\ RT_c/p_c \tag{4.2}$$

$$a_c = 0.45724\,(RT_c)^2/p_c \tag{4.3}$$

$$\alpha = [1 + m(1-T_r^{0.5})]^2 \tag{4.4}$$

$$m = 0.37464 + 1.54226\ \omega - 0.26992\ \omega^2 \tag{4.5}$$

The mixing rules employed are:

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{4.6}$$

$$b = \sum_{i} \sum_{j} z_i z_j b_{ij} \tag{4.7}$$

where

$$a = a_c \cdot \alpha \tag{4.8}$$

$$a = (a_{ii} a_{jj})^{0.5} (1 - C_{ij}) \tag{4.9}$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj}) \tag{4.10}$$

C_{ij} and D_{ij} are adjustable, empirically-determined binary interaction parameters which characterize the binary formed by component i and component j.

Peng-Robinson Equation-of-State
Enthalpy Departure Function

From exact thermodynamics, the difference between the enthalpy of a pure compound fluid and the enthalpy of an ideal gas at the same temperature is given by

$$H - H^o = \int_{v}^{\infty} \; [p - T(\partial p/\partial T)_v]\, dv \; + \; pv \; - \; RT \tag{4.11}$$

Equation (4.11) is also obtained by adding Equations (2.9, 2.10 and 2.11) presented in Chapter II, and substituting for the compressibility factor, $Z = \frac{pv}{RT}$, in Equation (2.11).

When the PR equation is used to determine the integral of Equation (4.11), we obtain,

$$\begin{aligned} H - H^o = \; & a_c \; [(\alpha - T\, d\alpha/dT)/2\sqrt{2}b\,] \ln [(v - 0.414b)/(v + 2.414b)] \\ & + \; pv \; - \; RT \end{aligned} \tag{4.12}$$

with

$$d\alpha/dT = (-\alpha/T_c)\,(mT_r^{-0.5})\,/\,[\,1 + m\,(1 - T_r^{0.5})] \tag{4.13}$$

Equations (4.12) and (4.13) are easily extended for multicomponent mixtures when used in conjunction with Equations (4.9) and (4.10). For a multicomponent system,

$$H - H^o = \left[\left(\sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j \gamma_{ij} T - a\right) \Big/ \; 2\sqrt{2}b\right] \ln\,[(v - 0.414b)/(v + 2.414b)]$$

$$+ \; pv \; - \; RT \tag{4.14}$$

with

$$\gamma_{ij} = a_{ij}\;\{(-0.5m_i T_{ri}^{-0.5}\,/\,T_{ci}\,[\,1 + m_i\,(1 - T_{ri}^{0.5})]$$

$$- \,(-0.5m_j T_{rj}^{-0.5})/\,T_{cj}\,[\,1 + m_j\,(1 - T_{rj}^{0.5})]\} \tag{4.15}$$

A detailed derivation for the PR departure functions is given in Appendix A.

Pure Fluid Properties

The pure component properties which include the critical temperature T_c, critical pressure p_c, and the acentric factor ω constitute the input variables for the PR equation enthalpy departure model. Also, the molecular weights of the substances were needed to report enthalpy departures on a unit mass basis. The pure fluid values of T_c, p_c, and ω used are those given by Daubert (24). However, the pure fluid properties for cis-2-pentene, ethylcyclohexane, cis-decalin and trans-decalin, tetralin, and hexadecane were taken from Reid et al. (53). Appendix C contains a listing of the pure fluid properties used for the present study.

Software Used

The enthalpy departure model was incorporated into the 'GEOS' program; GEOS is an elaborate thermodynamic software for calculating volumetric, phase equilibrium and calorimetric properties (52). The software has the capability to handle multiple systems simultaneously.

The program inputs needed for performing the enthalpy departure predictions and making comparisons with the experimental enthalpies included the pure fluid critical properties, temperature, pressure, feed composition, experimental enthalpy departures as reported in the GPA database, and the option to calculate vapor or liquid enthalpy. The GPA database phase codes discussed in Chapter III are used for determining liquid or vapor enthalpy options. In the enthalpy departure predictions carried out, the "raw ability" of the PR EOS was employed, in that, the mixing rules with no interaction parameters were used ($C_{ij} = 0,\ D_{ij} = 0$).

To validate the accuracy of the GEOS software, enthalpy departures generated by GEOS were compared to similar predictions by the ASPEN PLUS™ simulator. A test system involving the ethane-propane mixture (76.3 mol % ethane) was selected from the GPA database for the purpose. The results are shown in Table 2.

As observed from Table 2, the predicted enthalpy values obtained using GEOS to those generated by ASPEN PLUS were almost identical. The slight differences, which are generally within 0.1%, may be attributed to differences in the pure fluid critical properties employed by ASPEN PLUS™ for purposes of enthalpy departure prediction.

Table 2
Enthalpy Departure Comparisons

Pt. No.	Temp. °F	Pressure psia	Exp. Btu/lb	Cal. (ASPEN™) Btu/lb	Cal. (GEOS) Btu/lb	Phase
1	-280.0	250.0	-244.5	-236.93	-237.09	liq
2	-200.0	250.0	-225.2	-221.19	-221.32	liq
3	68.0	500.0	-151.7	-149.46	-149.56	liq
4	80.0	500.0	-146.0	-142.17	-142.27	liq
5	115.0	716.0	-125.3	-118.04	-118.24	liq
6	-40.0	2000.0	-183.0	-183.41	-183.50	liq
7	80.0	250.0	-17.7	-17.71	-17.74	vap
8	240.0	250.0	-9.8	-10.70	-10.72	vap
9	152.0	500.0	-30.1	-30.96	-31.02	vap
10	251.0	1000.0	-43.3	-47.15	-47.23	vap

Model Evaluations

Tables 3, 4, 5 and 6 give summary reports of error statistics for the PR EOS data screening results, along with the GPA enthalpy database holdings. The model evaluations encompassed twenty pure fluids, thirty binary mixtures, five ternary mixtures and three multicomponent enthalpy systems. In all, around fifteen-thousand data records were included in the evaluations. For each system considered, the absolute average deviation (AAD) and the root mean square error (RMSE), both expressed in Btu/lb, is given for the vapor and liquid phases.

Daubert (24) had used the PR model to predict enthalpy departure functions and make comparisons with the enthalpy departure values in the GPA databank. However, the mixing rules employed in his evaluations were different from those used for the present study. Daubert relied on pseudo-critical fluid properties, derived using Kay's mixing rules for the critical properties (56), for binary and multicomponent natural gas systems. In this study, pure fluid properties in conjunction with mixing rules, specified earlier in this chapter, were used to calculate fluid mixture properties. The model statistics resulting from this work are similar to Daubert's work for a fairly large number of gas systems in the GPA databank. Therefore, Kay's pseudo-component mixing rules and the mixing rules used in this chapter result in comparable predictions.

The results obtained indicate that the accuracy of enthalpy predictions is superior for lower molecular weight hydrocarbons. For example, ethane (liquid-phase AAD = 2.1 Btu/lb, vapor-phase AAD = 1.8 Btu/lb) had lower deviations compared to propane (liquid-phase AAD = 2.6 Btu/lb, vapor-phase AAD = 4.1 Btu/lb).

There is no apparent difference in the ability of the PR model to predict vapor-phase and liquid-phase enthalpy departure values. For certain systems, the liquid-phase predictions might be marginally better than the vapor-phase, and for others the opposite may be true. For example, n-octane displays an AAD of 1.7 Btu/lb and RMSE of 2.4 Btu/lb in the liquid-phase; and for the vapor-phase it shows an AAD and RMSE of 3.4 Btu/lb and 4.0 Btu/lb, respectively. In contrast, benzene has a liquid-phase AAD of 4.0 Btu/lb and a RMSE of 4.7 Btu/lb; and in its vapor-phase, 1.4 Btu/lb and 2.2 Btu/lb are the observed AAD and RMSE values.

The evaluations revealed that the PR enthalpy departure model, in general, performed similarly for the pure fluids, binary fluid systems and other multicomponent systems. The model statistics (RMSE and AAD values) reported in Tables 3, 4, 5 and 6 for the various systems in the liquid and vapor phases support these observations.

Again, there was no difference in the PR model's ability to predict enthalpy departures based on the temperatures. Depending upon the pure fluid system or mixture under consideration, the deviations were lower for lower temperature isotherms and, at other times, the opposite was true.

Also, on examining the point-by-point error analyses for each data set, it was observed that the predictions, as expected, were not accurate in the critical region. This was true of almost all the enthalpy systems in the database.

Table 3
Peng-Robinson EOS Error Analyses: Pure Fluids

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb) AVE	Absolute Deviation (Btu/lb) RMSE	Departure Method	References Raw	References Smooth
1	Methane	1.0	-250.0	250.0	L[a]	14	1.4	1.8			
			50.0	2000.0	V[b]	25	2.5	3.1			578
					L-V[c]	0				NRD[d]	573
2	Ethane	1.0	-250.0	200.0	L	41	2.1	2.8			
			-50.0	3000.0	V	28	1.8	2.3			
					L-V	0				NRD	592
3	Propane	1.0	-250.0	200.0	L	40	4.1	5.5			
			400.0	2000.0	V	21	2.6	4.4			564
					L-V	0				NRD	590
4	n-Pentane	1.0	95.9	15.2	L	142	2.4	3.4			
			691.5	1400.0	V	253	1.7	2.4		458	
					L-V	14				663	585
5	n-Heptane	1.0	361.8	50.0	L	105	7.1	7.6			
			548.6	100.0	V	52	2.8	3.4			556
					L-V	157				665	666
6	n-Octane	1.0	150.8	15.2	L	162	1.7	2.4			
			600.3	1400.0	V	85	3.4	4.0			
					L-V	7			A, B	663	586
7	iso-Octane	1.0	188.4	290.0	L	18	1.6	1.8			
			476.4	1450.0	V	0					
					L-V	0			B	NRD	687

Table 3
Peng-Robinson EOS Error Analyses: Pure Fluids (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb) AVE	Average Deviation (Btu/lb) RMSE	Departure Method	References Raw	References Smooth
8	n-Hexadecane	1.0	199.5	25.0	L	82	2.3	4.2			
			657.0	1400.0	V	21	4.3	4.6			
					L-V	5				584	583
9	Cyclohexane	1.0	117.0	15.4	L	133	2.2	2.8			
			689.0	1400.0	V	181	2.4	3.1			
					L-V	8				584	677
10	Methyl- Cyclohexane	1.0	176.0	17.0	L	122	6.4	7.2			
			464.0	1365.0	V	46	5.5	6.2			
					L-V	0				592	676
11	Ethyl- Cyclohexane	1.0	224.4	290.0	L	21	8.2	9.4			
			584.4	1450.0	V	0					
					L-V	0			B	NRD	687
12	cis-2-Pentene	1.0	159.8	20.0	L	69	2.7	3.3			
			448.7	1400.0	V	210	2.5	3.6			
					L-V	26				581	678
13	Benzene	1.0	200.0	100.0	L	118	4.0	4.7			
			696.5	1400.0	V	243	1.4	2.2		584	
					L-V	14				581	679
14	Toluene	1.0	140.0	17.0	L	107	2.9	3.3			
			464.0	1365.0	V	38	2.3	2.6			
					L-V	0				592	676

Table 3
Peng-Robinson EOS Error Analyses: Pure Fluids (continued)

Sys. No	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
15	Ethyl-Benzene	1.0	350.4	22.0	L	33	1.5	2.1			
			485.4	80.0	V	12	0.8	0.9			
					L-V	0			B	NRD	687
16	cis-Decalin	1.0	149.0	25.0	L	44	7.1	7.9			
			595.9	1400.0	V	32	3.2	3.8			
					L-V	6				580	582
17	trans-Decalin	1.0	120.1	22.0	L	124	3.2	4.5			
			644.2	1400.0	V	50	3.9	4.5			
					L-V	14				580	582
18	Tetralin	1.0	101.1	25.0	L	90	3.3	4.9			
			677.3	1400.0	V	36	1.4	1.6			
					L-V	58				580	675
19	H_2S	1.0	80.3	145.0	L	0					
			440.3	4351.0	V	61	1.0	1.4			
					L-V	0			B	NRD	686
20	Nitrogen	1.0	-250.0	200.0	L	7	0.8	1.0			
			-50.0	3000.0	V	48	1.1	1.2			
					L-V	0				NRD	587

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a 'L' refers to data points represented by phase code = 1 & 4 in the database
b 'V' refers to data points represented by phase code = 2 & 5 in the database
c 'L-V' refers to data points represented by phase code = 3 in the database
d 'NRD' = No raw data

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures

Sys. No	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
1	Methane	0.948	-280.0	14.7	L[a]	167	1.3	1.5			
	Propane	0.052	230.0	2000.0	V[b]	252	2.4	2.9			
					L-V[c]	57			B	NRD[d]	570
2	Methane	0.883	-280.0	250.0	L	191	1.6	2.0			
	Propane	0.117	300.0	2000.0	V	213	3.0	3.2			
					L-V	65			B	NRD	661
3	Methane	0.72	-280.0	250.0	L	210	2.1	2.6			
	Propane	0.28	300.0	2000.0	V	175	2.2	2.5			
					L-V	84			B	NRD	573
4	Methane	0.494	-280.0	250.0	L	252	3.6	4.6			
	Propane	0.506	300.0	2000.0	V	136	0.9	1.0			
					L-V	84			B	NRD	588
5	Methane	0.234	-280.0	250.0	L	322	3.4	4.5			
	Propane	0.766	300.0	2000.0	V	103	1.1	1.3			
					L-V	47			B	NRD	590
6	Methane	0.949	90.0	500.0	L	0					
	Propane	0.051	200.0	2000.0	V	12	4.8	5.3			
					L-V	0			B	NRD	591
7	Methane	0.874	90.0	500.0	L	0					
	Propane	0.126	200.0	2000.0	V	12	3.7	3.9			
					L-V	0			B	NRD	591

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (^{o}F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
8	Methane	0.951	-100.0	50.0	L	6	9.1	8.8			667
	n-Heptane	0.049	500.0	2000.0	V	79	1.1	1.6			592
					L-V	50				NRD	666
9	Methane	0.491	-100.0	50.0	L	15	5.4	6.1			667
	n-Heptane	0.509	600.0	2500.0	V	44	2.9	4.7			592
					L-V	76				NRD	666
10	Methane	0.249	-100.0	50.0	L	90	3.7	11.7			667
	n-Heptane	0.751	600.0	2500.0	V	35	3.7	4.1			592
					L-V	10				NRD	666
11	Ethane	0.763	-280.0	250.0	L	60	3.0	3.9			
	Propane	0.237	251.0	2000.0	V	37	1.5	1.9			592
					L-V	17			B	NRD	671
12	Ethane	0.498	-280.0	250.0	L	48	3.2	4.7			
	Propane	0.502	300.0	2000.0	V	28	2.3	4.6			592
					L-V	15			B	NRD	671
13	Ethane	0.276	-280.0	500.0	L	26	2.4	2.5			
	Propane	0.724	300.0	2000.0	V	23	1.9	2.3			592
					L-V	10			B	NRD	671
14	Propane	0.43	111.0	65.0	L	14	4.3	5.3			
	iso-Pentane	0.57	358.0	1400.0	V	21	7.2	8.4			
					L-V	20			A	579	NSD[e]

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
15	n-Pentane	0.809	75.0	200.0	L	34	2.3	3.0			
	n-Octane	0.191	605.1	1400.0	V	81	2.9	3.5			
					L-V	22			A, B	663	663
16	n-Pentane	0.597	75.0	200.0	L	53	3.0	3.4			
	n-Octane	0.403	605.1	1400.0	V	75	4.0	4.6			
					L-V	34			A, B	663	663
17	n-Pentane	0.392	75.0	15.2	L	53	2.5	3.1			
	n-Octane	0.608	601.7	1400.0	V	64	4.4	5.0			
					L-V	21			A, B	663	663
18	n-Pentane	0.218	75.0	15.2	L	67	1.9	2.4			
	n-Octane	0.782	605.1	1400.0	V	81	3.0	3.4			
					L-V	14			A, B	663	663
19	n-Pentane	0.167	198.6	25.0	L	28	3.4	4.0			
	n-Hexadecane	0.833	618.8	1400.0	V	2	2.9	2.9			
					L-V	32			A, B	584	583
20	n-Pentane	0.386	148.0	25.0	L	39	3.0	3.5			
	n-Hexadecane	0.614	619.2	1400.0	V	16	3.0	3.3			
					L-V	78			A, B	584	583
21	n-Pentane	0.587	138.6	25.0	L	41	102.8	632.5			
	n-Hexadecane	0.413	625.5	1400.0	V	16	1.6	1.8			
					L-V	101			A, B	584	583

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Average Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
22	n-Pentane	0.794	117.0	25.0	L	60	2.6	2.4			
	n-Hexadecane	0.206	625.1	1400.0	V	31	2.4	8.1			
					L-V	152			A, B	584	583
23	Methane	0.5	-100.0	50.0	L	68	8.0	14.1			
	Methyl-	0.5	600.0	2500.0	V	36	3.5	4.1			667
	Cyclohexane				L-V	3				NRD	592
24	n-Pentane	0.197	122.6	15.4	L	102	2.8	3.2			
	Cyclohexane	0.803	696.0	1400.0	V	177	2.7	3.7		580	
					L-V	28			A, B	584	677
25	n-Pentane	0.385	119.9	100.0	L	102	1.6	2.0			
	Cyclohexane	0.615	704.7	1400.0	V	176	2.2	2.8		580	
					L-V	25			A, B	584	677
26	n-Pentane	0.612	127.4	100.0	L	92	2.6	3.1			
	Cyclohexane	0.388	695.8	1400.0	V	197	2.1	2.9		580	
					L-V	23			A, B	584	677
27	n-Pentane	0.793	141.4	25.0	L	85	2.6	3.3			
	Cyclohexane	0.207	696.0	1400.0	V	244	2.1	2.9		580	
					L-V	24			A, B	584	677
28	n-Pentane	0.502	331.3	300.0	L	43	3.6	4.4			
	cis-2-Pentene	0.498	450.2	1400.0	V	116	1.7	2.4			
					L-V	12			B, C	581	678

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
29	Methane	0.5	-100.0	50.0	L	40	21.9	24.1			
	Toluene	0.5	600.0	2500.0	V	33	0.8	1.1			667
					L-V	62			B	NRD	592
30	Propane	0.252	200.0	200.0	L	9	4.0	4.5			
	Benzene	0.748	400.0	1000.0	V	2	3.7	4.8			
					L-V	2			B	564	NSD
31	Propane	0.498	200.0	200.0	L	7	3.3	3.4			
	Benzene	0.502	400.0	1000.0	V	2	0.9	1.2			
					L-V	5			B	564	NSD
32	Propane	0.797	200.0	200.0	L	3	4.6	6.0			
	Benzene	0.203	400.0	1000.0	V	5	2.3	2.9			
					L-V	4			B	564	NSD
33	n-Pentane	0.186	152.0	15.2	L	68	2.4	3.5			
	Benzene	0.814	694.1	1400.0	V	210	2.1	2.7		581	
					L-V	40			A, B	584	681
34	n-Pentane	0.4	150.0	25.0	L	98	2.0	2.5			
	Benzene	0.6	695.0	1400.0	V	257	2.9	3.9		581	
					L-V	48			A, B	584	681
35	n-Pentane	0.594	152.5	25.0	L	69	2.9	3.5			
	Benzene	0.406	695.0	1400.0	V	234	2.9	3.8		581	
					L-V	43			A, B	584	681

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb) AVE	Absolute Deviation (Btu/lb) RMSE	Departure Method	References Raw	References Smooth
36	n-Pentane	0.801	151.8	25.0	L	60	2.1	2.8			
	Benzene	0.199	692.9	1400.0	V	234	2.5	3.1		581	
					L-V	34			A, B	584	681
37	n-Pentane	0.322	149.6	20.0	L	85	4.3	4.8			
	trans-Decalin	0.678	597.8	1400.0	V	45	4.8	5.7			
					L-V	112			D, B	580	582
38	n-Pentane	0.561	148.9	20.0	L	64	3.5	4.3			
	trans-Decalin	0.439	599.3	1400.0	V	41	4.6	5.7			
					L-V	154			C, B	580	582
39	n-Pentane	0.725	118.9	30.0	L	60	2.8	3.5			
	trans-Decalin	0.275	598.6	1400.0	V	78	3.1	3.5			
					L-V	136			C, B	580	582
40	n-Pentane	0.884	100.0	20.0	L	76	2.3	2.6			
	trans-Decalin	0.116	599.4	1400.0	V	88	1.8	2.5			
					L-V	134			C, B	580	582
41	n-Pentane	0.197	100.9	25.0	L	82	4.3	5.7			
	Tetralin	0.803	696.0	1400.0	V	77	21.8	38.8			
					L-V	89			C, B	580	675
42	n-Pentane	0.399	148.1	25.0	L	40	4.1	5.2			
	Tetralin	0.601	676.9	1400.0	V	46	4.8	5.8			
					L-V	125			C, B	580	675

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
43	n-Pentane	0.588	122.5	25.0	L	39	5.7	6.2			
	Tetralin	0.412	636.0	1400.0	V	59	5.3	6.1			
					L-V	146			C, B	580	675
44	n-Pentane	0.795	120.0	25.0	L	50	4.2	4.4			
	Tetralin	0.205	639.6	1400.0	V	104	4.0	4.6			
					L-V	138			C, B	580	675
45	n-Pentane	0.893	119.9	25.0	L	79	2.4	2.6			
	Tetralin	0.107	638.0	1400.0	V	158	3.6	4.9			
					L-V	108			C, B	580	675
46	Benzene	0.93	367.2	200.0	L	71	4.2	5.1			
	n-Octane	0.07	596.5	1400.0	V	88	3.5	13.4			
					L-V	36			A, B	581	679
47	Benzene	0.857	179.2	20.0	L	97	4.8	5.8			
	n-Octane	0.143	596.6	1400.0	V	103	2.8	3.4			
					L-V	44			A, B	581	679
48	Benzene	0.771	368.5	200.0	L	56	4.6	5.6			
	n-Octane	0.229	596.5	1400.0	V	78	2.6	3.5			
					L-V	23			A, B	581	679
49	Benzene	0.446	158.5	20.0	L	132	4.0	5.0			
	n-Octane	0.554	598.2	1400.0	V	89	4.2	4.9			
					L-V	53			A, B	581	679

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (^{o}F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
50	Benzene	0.271	157.6	20.0	L	100	1.6	3.4			
	n-Octane	0.729	598.7	1400.0	V	100	3.8	4.5			
					L-V	46			A, B	581	679
51	Benzene	0.963	150.2	20.0	L	84	6.2	6.9			
	n-Hexadecane	0.037	597.1	1400.0	V	124	5.5	6.9			
					L-V	71			A, B	580	682
52	Benzene	0.92	150.8	20.0	L	65	8.6	9.6			
	n-Hexadecane	0.08	595.0	1400.0	V	69	6.9	7.9			
					L-V	103			A, B	580	682
53	Benzene	0.814	150.7	20.0	L	64	10.2	11.4			
	n-Hexadecane	0.186	595.4	1400.0	V	20	9.6	10.1			
					L-V	120			A, B	580	682
54	Benzene	0.67	151.8	20.0	L	66	10.9	12.4			
	n-Hexadecane	0.33	594.0	1400.0	V	9	10.2	10.4			
					L-V	97			A, B	580	682
55	Benzene	0.419	148.2	20.0	L	60	7.6	9.1			
	n-Hexadecane	0.581	601.5	1400.0	V	8	6.3	6.4			
					L-V	62			A, B	580	682
56	Benzene	0.211	470.2	400.0	L	59	2.0	2.8			
	Cyclohexane	0.789	579.2	1400.0	V	152	3.2	4.5			
					L-V	37			A, B	581	680

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
57	Benzene	0.334	193.6	20.0	L	68	1.2	1.5			
	Cyclohexane	0.666	578.7	1400.0	V	128	3.0	4.5			
					L-V	37			A, B	581	680
58	Benzene	0.812	447.2	400.0	L	80	1.6	1.8			
	Cyclohexane	0.188	581.7	1400.0	V	172	3.2	4.4			
					L-V	57			A, B	581	680
59	Benzene	0.613	444.0	400.0	L	71	1.6	2.2			
	Cyclohexane	0.387	577.1	1400.0	V	121	3.3	4.3			
					L-V	43			A, B	581	680
60	Methane	0.566	-280.0	250.0	L	7	2.4	2.2			
	Nitrogen	0.434	40.0	2000.0	V	369	1.8	2.0			667
					L-V	95			B	NRD	591
61	H_2	0.5	-200.0	500.0	L	0					
	CO	0.5	-150.0	2500.0	V	66	1.8	2.5			
					L-V	0				NRD	667
62	H_2	0.75	-250.0	750.0	L	0					
	CO	0.25	-200.0	2500.0	V	70	3.0	4.2			
					L-V	0				NRD	673
63	H_2	0.5	-250.0	20.0	L	0					
	Methane	0.5	0.0	2500.0	V	82	2.7	4.0			
					L-V	13			B	NRD	673

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
64	CO_2	0.447	-63.7	72.5	L	0					
	Nitrogen	0.553	116.3	2900.8	V	190	1.0	1.3			
					L-V	1			B	NRD	688
65	CO_2	0.4761	-63.7	72.5	L	0					
	Methane	0.5239	116.3	7252.0	V	187	5.0	6.2			
					L-V	0			B	NRD	688
66	CO_2	0.5	-50.0	100.0	L	0					
	Methane	0.5	200.0	2000.0	V	40	5.0	6.2			
					L-V	8				NRD	667
67	CO_2	0.5	-50.0	100.0	L	31	13.1	13.4			
	n-Pentane	0.5	250.0	2000.0	V	28	4.1	7.1			
					L-V	14			B	NRD	685
68	H_2S	0.5	-110.0	1000.0	L	6	7.2	7.4			
	Methane	0.5	0.0	2000.0	V	25	3.5	7.0			
					L-V	17			B	NRD	670
69	H_2S	0.4927	80.3	145.0	L	0					
	Methane	0.5073	440.3	5076.4	V	81	11.4	14.4			
					L-V	0			B	NRD	686
70	H_2S	0.5	-120.0	20.0	L	25	5.0	6.3			
	Ethane	0.5	200.0	2000.0	V	18	1.3	1.8			
					L-V	4			B	NRD	670

Table 4
Peng-Robinson EOS Error Analyses: Binary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
71	H_2S	0.8933	170.3	145.0	L	0					
	Methyl-	0.1067	440.3	6526.5	V	67	11.2	13.8			
	Cyclohexane				L-V	19			B	NRD	686
72	H_2S	0.9184	215.3	145.0	L	0					
	Toluene	0.0816	440.3	9427.5	V	96	8.0	10.9			
					L-V	25			B	NRD	686
73	H_2S	0.5141	125.3	145.0	L	0					
	CO_2	0.4859	440.3	8702.4	V	79	6.2	8.0			
					L-V	5			B	NRD	686

a 'L' refers to data points represented by phase code = 1 & 4 in the database
b 'V' refers to data points represented by phase code = 2 & 5 in the database
c 'L-V' refers to data points represented by phase code = 3 in the database
d 'NRD' = No raw data
e 'NSD' = No smooth data

Table 5
Peng-Robinson EOS Error Analyses: Ternary Mixtures

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
1	Methane	0.366	-240.0	250.0	L[a]	19	5.4	6.5			
	Ethane	0.311	300.0	2000.0	V[b]	12	1.7	1.9			
	Propane	0.323			L-V[c]	0				NRD[d]	574
2	Methane	0.3702	-240.0	250.0	L	140	2.4	3.4			
	Ethane	0.3055	300.0	2000.0	V	24	1.1	1.3			
	Propane	0.3243			L-V	76				NRD	671
3	H_2S	0.333	-110.0	20.0	L	12	24.4	24.7			
	Methane	0.334	200.0	2000.0	V	27	2.9	5.1			
	Ethane	0.333			L-V	9				NRD	670
4	CO_2	0.3333	-50.0	100.0	L	5	3.4	4.4			
	Methane	0.3333	300.0	2000.0	V	38	2.2	2.6			
	Ethane	0.3333			L-V	3				NRD	672
5	n-Pentane	0.2	350.2	400.0	L	70	7.8	8.6			
	Cyclohexane	0.202	600.0	1400.0	V	135	5.9	6.3		581	
	Benzene	0.598			L-V	81			A,B	665	683
6	n-Pentane	0.333	348.4	20.0	L	76	1.9	2.2			
	Cyclohexane	0.334	600.0	1400.0	V	139	2.6	3.1		581	
	Benzene	0.333			L-V	66			A, B	665	683
7	n-Pentane	0.601	351.5	40.0	L	92	2.1	2.6			
	Cyclohexane	0.199	600.0	1400.0	V	154	2.0	2.4		581	
	Benzene	0.20			L-V	52			A, B	665	683

Table 5
Peng-Robinson EOS Error Analyses: Ternary Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
8	Benzene	0.333	201.3	40.0	L	87	2.7	3.1			
	n-Octane	0.334	600.0	1400.0	V	25	2.6	3.9			
	Tetralin	0.333			L-V	50			C, B	581	684
9	Benzene	0.45	201.3	40.0	L	84	3.5	4.2			
	n-Octane	0.45	600.0	1400.0	V	48	3.1	4.4			
	Tetralin	0.10			L-V	85			C, B	581	684

a 'L' refers to points represented by phase code = 1 & 4 in the database
b 'V' refers to points represented by phase code = 2 & 5 in the database
c 'L-V' refers to points represented by phase code = 3 in the database
d 'NRD' = No raw data

Table 6
Peng-Robinson EOS Error Analyses: Multicomponent Mixtures

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb) AVE	Absolute Deviation (Btu/lb) RMSE	Departure Method	References Raw	References Smooth
1	H_2S	0.3037	80.3	145.0	L	0					
	Methylcyclohexane	0.0986	440.0	4351.2	V	66	10.1	11.6			
	Toluene	0.1031			L-V	14					
	Methane	0.4946							B	NRD	686
2	Methane	0.84352	391.8	22.79	L	0					
	CarbonDioxide	0.04054		2383.35	V	13	8.9	13.6			
	Water	0.05509			L-V	0					
	Nitrogen	0.00038									
	Propylene	0.00009									
	Carbonyl-Sulphide	0.00009									
	H_2S	0.02882									
	2-Methylpropane	0.00009									
	Ethane	0.02136									
	Propane	0.01002								NRD	674
3	Methane	0.85791	409.8	136.76	L	0					
	Ethane	0.02841		2110.46	V	8	3.7	5.5			
	Water	0.05000			L-V	0					
	Hydrogen	0.00010									
	Helium	0.00133									
	Nitrogen	0.01587									
	CarbonDioxide	0.00285									

Table 6
Peng-Robinson EOS Error Analyses: Multicomponent Mixtures (continued)

Sys. No.	Components	Mole Fractions	Temp. Range (°F)	Press. Range (psia)	Expt. Phase	No. of Points	Absolute Deviation (Btu/lb)		Departure Method	References	
							AVE	RMSE		Raw	Smooth
3	Propane	0.01900									
	Propylene	0.00010									
	2-Methylpropane	0.00922									
	n-Butane	0.00922									
	2-Methylbutane	0.00295									
	n-Pentane	0.00304								NRD	674

CHAPTER V

ENTHALPY DATA
QUALITY ASSURANCE

The main goal of the model evaluations was to provide an EOS-based screening tool to audit the current GPA enthalpy database and establish the validity of the current entries. As described in Chapter III, there was no direct method of ascertaining the validity of the entries in the database by comparing records with the original sources of data. This is because the original enthalpy data have been manipulated to generate enthalpy departure values, which are entered into the GPA database. Thus, transcription errors and gross outliers are identified based on "higher-than-expected" deviations between the reported and predicted values for any data set.

Data-Entry Checks

As a first step toward assessing the validity of the records in the database, data-entry checks were performed, which involved visual inspection of database records for typographical errors and omissions relating to temperature, pressure, composition, and phase-code entries. The data-entry errors were detected by comparing database records with the original sources of data. Following are examples of some of the observations made while checking the pure fluid enthalpy data.

- Incorrect references; e.g., for *n-heptane* the data points 25-130 have 556 listed incorrectly as the reference number. Reference number 556 is for the VLE data of *n-heptane*.
- Incorrect and/or extraneous records; e.g., *cyclohexane* has two different records for enthalpy departure values at 620 °F and 300 psia, both from the same reference source. In this case, either one of the references is wrong, or one of the data entries is extraneous and should be deleted.
- Redundant information; e.g., data points 266 and 267 for *cyclohexane* are identical.
- Omission of records; e.g., for *tetralin* the enthalpy departure values corresponding to the isobar of 20 psia are not included in the database.
- Incorrect entries; e.g., for *trans-Decalin* the data points 1-24 correspond to the isobar of 22 psia, and not 20 psia as is incorrectly tabulated in the database.

EOS-Based Data Screening

The PR enthalpy model statistics and the detailed point-by-point output analyses were used to screen and evaluate the GPA enthalpy data. In all, around fifteen-thousand data records in the single phase region (i.e., data represented by phase codes '1' and '2', respectively) were scrutinized for possible outliers using the EOS data screening procedure. To achieve those objectives, certain criteria were used to help identify data points showing deviations between the reported and predicted enthalpy departure values that were larger than expected. The data records noted were:

1. Data-entry errors not noted by inspection.
2. Data points exhibiting deviations in calculated enthalpy departure values that are greater than twice the root-mean-squared error (RMSE) for the entire data set. Near-critical data points were given special attention.
3. Data points showing an abrupt change in the deviation sign.
4. Data values showing gross systematic errors; these are identified by the disagreement in the deviations among reported data sets for the same system at identical or similar conditions.

Test Cases

The following section describes the methodology applied and the analyses used to identify data records meriting further examination. Three test cases involving an alkane (n-pentane), a cycloalkane (cyclohexane), and an aromatic (benzene) are presented.

n-Pentane

For the n-pentane system, the point-by-point analysis revealed data entry errors that were not detected by visual inspection of the data records in the database. The output file statistics of the liquid-phase enthalpy departure function show that there are two different isotherms for identical isobars and identical enthalpy departure functions. Also, both database records are from the same reference source. The two records are 193.8 °F, 200.0 psia and 194.0 °F, 200.0 psia; both of these have the enthalpy departure function equal to -144.4 Btu/lb. The isotherms of 205.2 °F and 205.3 °F at 200.0 psia also have an identical enthalpy departure value of -138.7 Btu/lb. It would appear that one of the records in each case is a typographical error and needs to be deleted from the records. But on verifying with the original reference source (663 in Appendix B), it becomes clear that the records do not represent a data-entry error. Indeed, the reference source reports an identical enthalpy value (not the departure) for the two different isotherms.

Again, for the liquid enthalpy departure functions, most of the isotherms at the 400 psia isobar show a consistently high deviation, which exceeds the value of twice the RMSE for the entire data set (6.8 Btu/lb). The 300 - 400 °F isotherms at the 600 psia isobar also display "higher-than-usual" deviations and have, therefore, been flagged. The two individual enthalpy records at 405.9 °F, 1000 psia and 361.9 °F, 1400 psia have been flagged for showing deviations exceeding twice the RMSE value for the entire data.

For the vapor-phase enthalpy predictions, the individual enthalpy records at 600.3 °F, 200.0 psia and 400.0 °F, 500.0 psia have been marked for showing abrupt change in deviation signs and also for having deviations in excess of those for the neighboring points. For this data set, two records at 400 °F, 800 psia are reported with two different enthalpy departure values of -102.0 Btu/lb and -96.5 Btu/lb, respectively. But on further inspection, it is revealed that one record represents raw experimental data while the other represents smoothed data.

The data meriting further analysis for n-pentane is given in Table 7. Figures 3 and 4 show deviation plots which represent enthalpy departure deviations against corresponding temperature values. These plots give a visual representation for the flagged data records. As shown in the figures, the majority of the flagged records show

Table 7
Flagged Data Records for n-Pentane

Data Record No.	Temp. (F)	Press. (psia)	Enth. Dept (Btu/lbm)	Exp. Phase	Raw/Smooth data	Reference No.	Criteria for Outliers
28	193.8	200.0	-144.4	1	R	663	1
29	194.0	200.0	-144.4	1	R	663	1
30	205.2	200.0	-138.7	1	R	663	1
31	205.3	200.0	-138.7	1	R	663	1
76	600.3	200.0	-2.7	2	R	663	2&3
86-96	280.1 -353.8	400.0	-------	1	R	663	4
120	250.0	500.0	-130.0	1	R	458	4
121	300.0	500.0	-122.0	1	R	458	4
122	350.0	500.0	-113.0	1	R	458	4
127	400.0	500.0	-53.0	2	R	458	2&3
134-142	300.0 -406.0	600.0	-------	1	R	663	4
143	426.0	600.0	-59.7	2	R	663	2
158	400.0	700.0	-100.0	2	R	458	2
164	450.0	900.0	-83.0	2	R	458	2
177	405.9	1000.0	-103.6	1	R	663	2
178-187	450.0 -690.6	1000.0	------	2	R	663	4
189	450.0	1100.0	-92.0	2	R	458	2
198	361.9	1400.0	-118.0	1	R	663	2
200-213	402.5 -689.9	1400.0	------	2	R	663	4

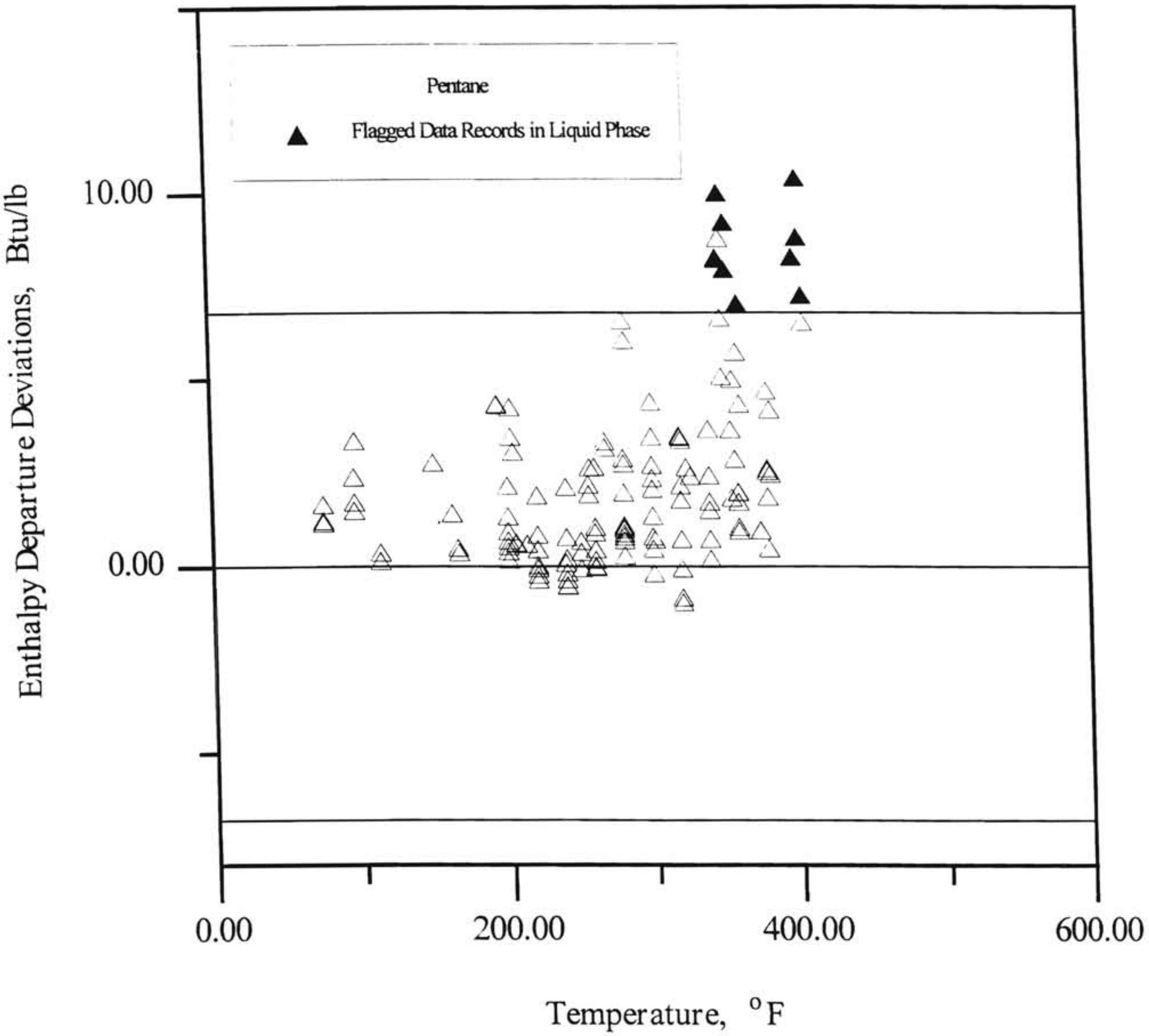

Figure 3. Liquid-Phase Enthalpy Departure Deviations for n-Pentane

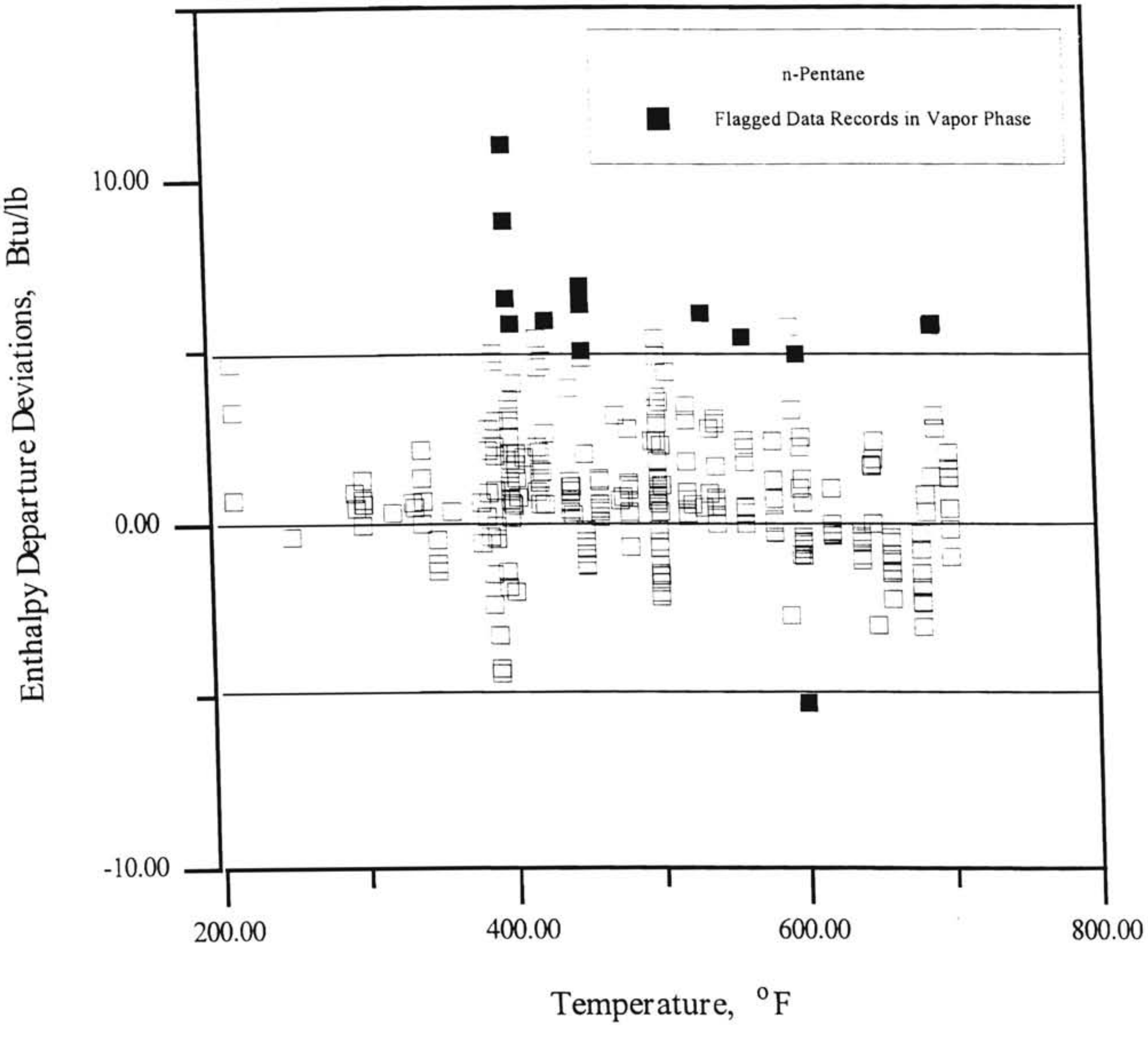

Figure 4. Vapor-Phase Enthalpy Departure Deviations for n-Pentane

enthalpy departure deviations greater than twice the RMSE. However, most of the flagged records result as a part of a systematic trend in deviations; an observation not evidenced by the plots. As discussed later, only a few of these flagged data records eventually are identified as "possible" outliers.

Cyclohexane

For the liquid-phase enthalpy departure predictions, the data record at the temperature of 181.8 °F, 15.4 psia was flagged since it showed a deviation of -4.7 Btu/lb compared to similar isotherms at the 15.4 psia isobar, which have a consistent deviation of around 2.7 Btu/lb. The raw data record at 471.2 °F, 400.0 psia was highlighted for showing a deviation of 8.5 Btu/lb, which is in excess of twice the RMSE of 3.0 Btu/lb for the entire data set. The smoothed data points at 520.0 - 530.0 °F, 588 psia and 540.0 °F, 700 psia were flagged due to the high deviations between the reported and predicted departure values (almost 9 Btu/lb).

For vapor-phase predictions, the raw data record at 199.4 °F, 15.4 psia was flagged for showing an abrupt change in the deviation sign (deviation = 0.2 Btu/lb) while similar isotherms (194.5 °F, 196.8 °F, 205.2 °F) at 15.4 psia have deviations equal to -2.5 Btu/lb. Two records at 671.9 °F, 15.4 psia and 686.1 °F, 15.4 psia, respectively were flagged for displaying deviations which are greater than twice the RMSE for the entire data set (3.15 Btu/lb). The two raw data records at 497.7 °F, 300 psia and 518.8 °F, 300 psia, both of which are from the same reference source, were marked for reporting identical enthalpy departure values at -21.2 Btu/lb. Indeed, one of these entries is wrong, for on verifying with the reference source, different values of enthalpies are recorded for 497.7 °F, 300 psia and 518.8 °F, 300 psia data records. Table 8 presents a listing of the flagged records for cyclohexane. Figures 5 and 6 depict the deviation plots for cyclohexane in the liquid and vapor phases, respectively. Similar to the n-Pentane system, most of the flagged records display deviations greater than twice the RMSE.

Benzene

The point-by-point analysis of the system revealed that the raw data in the database for the enthalpy departures for the liquid-phase showed a consistent deviation of 6-7 Btu/lb for isobars ranging from 500 - 800 psia. Although, the deviations are high, when compared to the absolute average deviation of 4 Btu/lb for the entire data set, the data points are not flagged. First, because the records represent raw experimental data; second, the deviations are consistently of the same order. One would assume that the deviations would be lower, if the data set had been smoothed using an equation of state or some other means. For this raw data set, it was also observed that certain data records corresponding to the 1000 and 1400 psia isobars, showed deviations of the order of 1.5 Btu/lb and 0.3 Btu/lb, respectively. This is contrary to what one would expect, since deviations between reported and calculated departures are lower for high pressure values. This may indicate the possibility for systematic errors in the original enthalpy measurements. Further, in this data set, the data record corresponding to 439 °F, 1000 psia showed an abrupt change in deviation sign. This record has, therefore, been identified for further examination.

Table 8
Flagged Data Records for Cyclohexane

Data Record No.	Temp. (F)	Press. (psia)	Enth. Dept (Btu/lb)	Exp. Phase	Raw/Smooth data	Reference No.	Criteria for Outliers
9	181.8	15.4	-147.2	1	R	584	3
14	199.4	15.4	-1.5	2	R	584	3
21	377.0	15.4	0.1	2	R	584	3
25	671.9	15.4	11.8	2	R	584	2
26	686.1	15.4	8.2	2	R	584	2
35-42	350.4- 684.8	-----	-----	2	R	584	4
66	497.7	300.0	-21.2	2	R	584	1
67	518.8	300.0	-21.2	2	R	584	1
76	471.2	400.0	-103.2	1	S	677	2
104	531.1	588.0	-91.3	1	R	584	2
119	561.2	700.0	-76.3	2	R	584	2
135	512.1	1000.0	-113.9	1	R	584	2
144	598.5	1200.0	-91.1	2	R	584	2
237	500.0	500.0	-103.2	1	S	677	2
249	520.0	588.0	-98.1	1	S	677	2
250	530.0	588.0	-92.3	1	S	677	2
260	530.0	700.0	-97.7	1	S	677	2
261	540.0	700.0	-95.0	1	S	677	2
262	560.0	700.0	-78.1	2	S	677	2
298	620.0	1000.0	-75.5	2	S	677	2
299	640.0	1000.0	-67.7	2	S	677	2
319	620.0	1400.0	-90.5	2	S	677	2

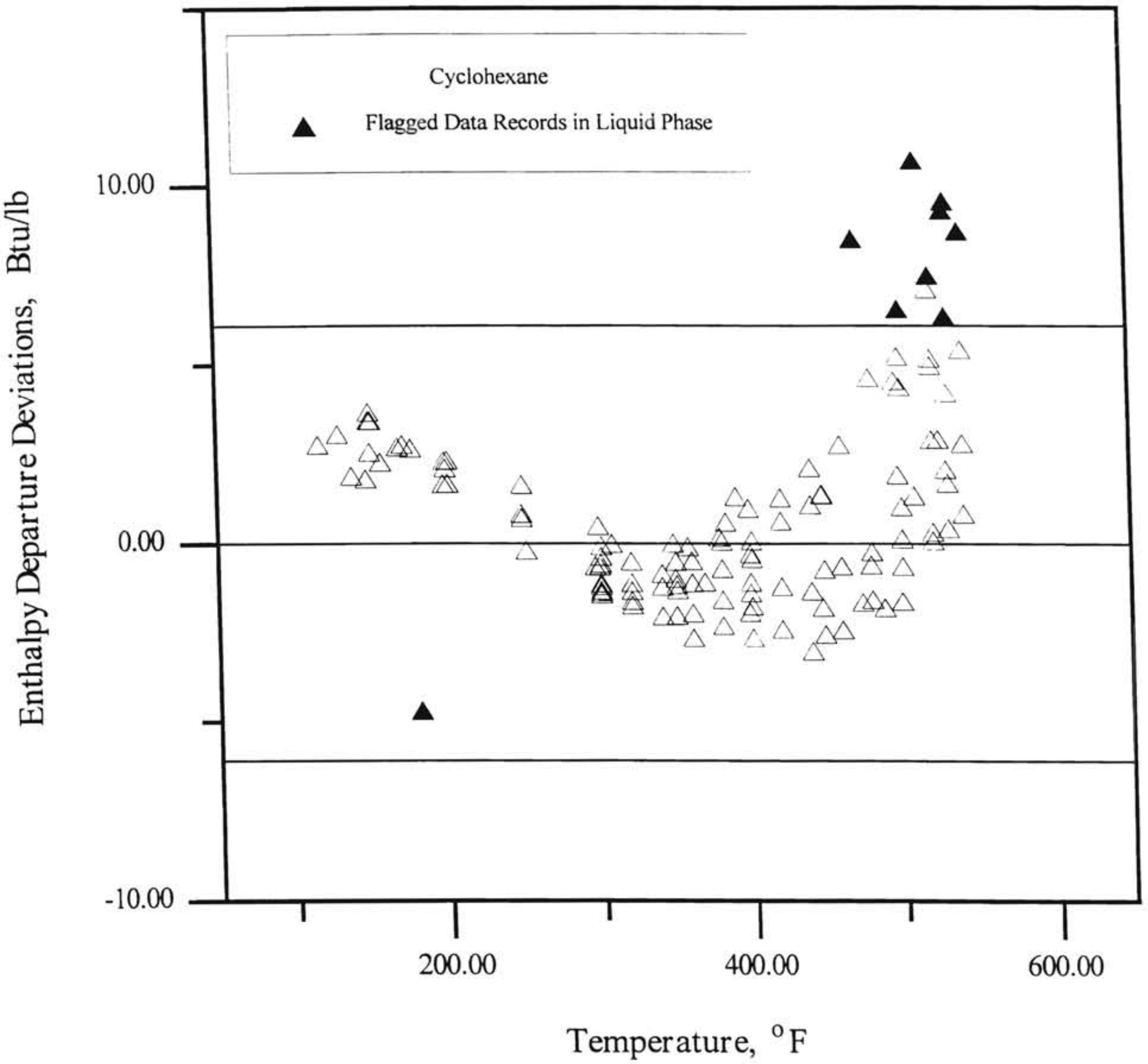

Figure 5. Liquid-Phase Enthalpy Departure Deviations for Cyclohexane

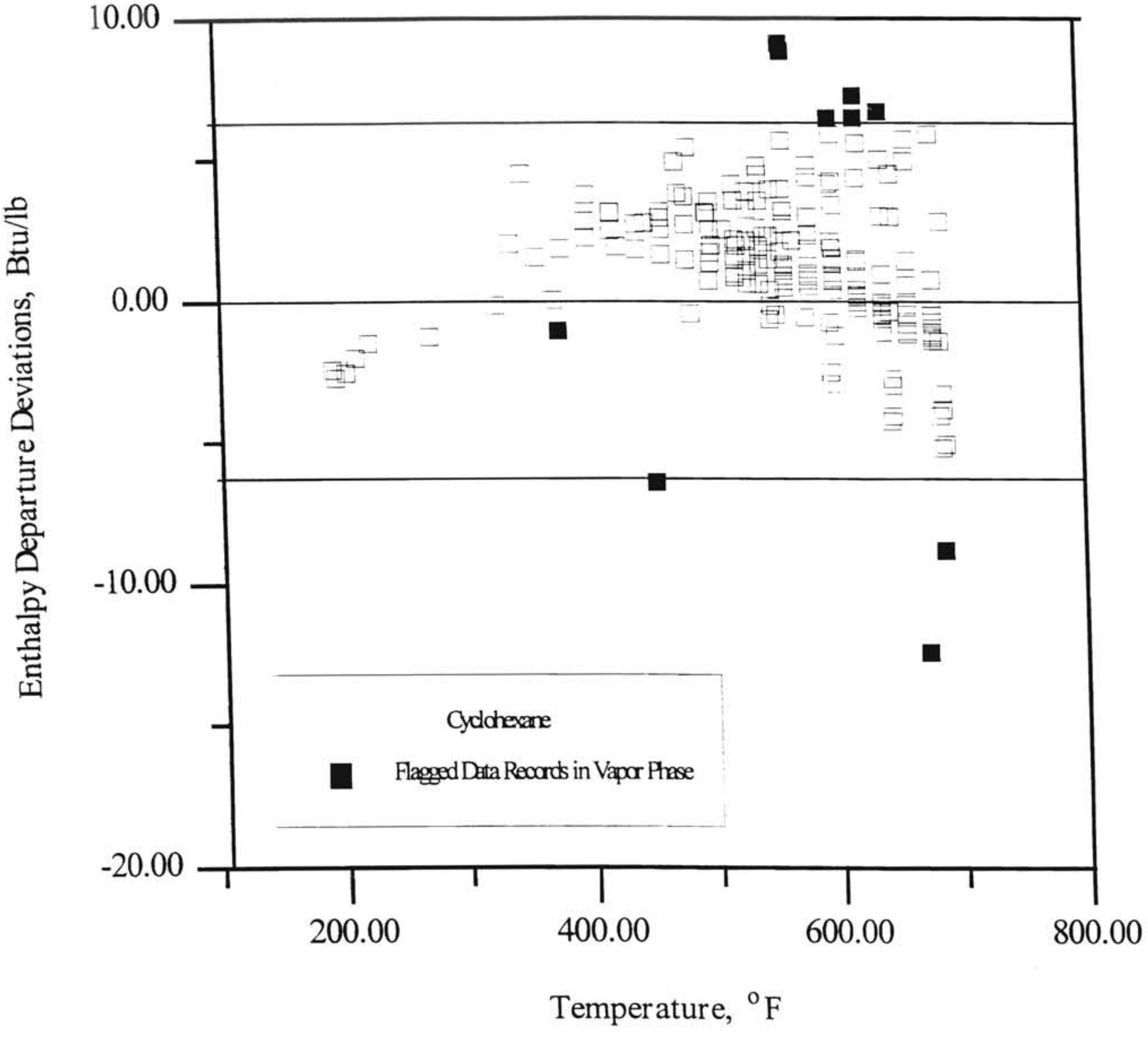

Figure 6. Vapor-Phase Enthalpy Departure Deviations for Cyclohexane

For the vapor-phase enthalpy departure predictions, the raw enthalpy record corresponding to the temperature of 553.6 °F and a pressure of 750.0 psia was flagged since the deviation of the predicted and reported value equals +7 Btu/lb. This value is quite high when compared to the average deviation for the other isotherms at 750.0 psia (from the same original reference) which show an average deviation of -2 Btu/lb. Some of the smoothed data points corresponding to the 750 psia isobar were flagged since the deviations between the reported and predicted values were not consistent. The deviations ranged in sign and magnitude from +7 Btu/lb to -5 Btu/lb. The 800 psia isotherm for the smoothed enthalpy data contains possible outliers, since the deviations were about 7 Btu/lb for six consecutive data records and -2.5 Btu/lb for the six records which follow it. For this isobar, not only are the deviations not consistent, they are fairly high when compared to the absolute average deviation (AAD) for the entire data set of the vapor-phase enthalpies (1.45 Btu/lb). For similar reasons, both raw and smoothed data records corresponding to the 1000 psia isobar have been marked as data requiring further analysis. The possible outlier candidates for the benzene system are listed in Table 9. The enthalpy departure deviation plots for benzene are given in Figures 7 and 8. The plots depict deviation trends similar to those given earlier for n-pentane and cyclohexane.

Discussion

The analysis presented above for the three case studies highlights the methodology adopted for assessing the quality of data in the GPA enthalpy database. A treatment similar to that for n-pentane, cyclohexane and benzene was employed to identify possible outliers for all the pures, binaries, ternaries and multicomponent systems in the enthalpy database. It is evident from the discussion presented that each system has to be treated on an individual basis and examined for possible outliers. Upon closer inspection of the enthalpy deviations for the above mentioned sample systems, it was observed that a very large number of records that were flagged for displaying higher-than-usual deviations (greater than twice the RMSE) are actually a part of a systematic trend in deviation for the particular data set. Consequently, the deviations exhibited by these data may be a result of model-lack-of-fit, and therefore these records may not qualify as outliers. The deviation plots given in Figures 3 - 8 present a graphical depiction of the possible outliers for the test systems considered based on the set criteria; however, these plots do not indicate the trends in deviations for a given isotherm or isobar, and as such, they are inadequate for identifying trends in deviations.

Tables 10, 11 and 12 present a summary of the possible outliers in enthalpy data of the pure fluids, binaries and the ternaries and multicomponent systems, respectively. As documented in these tables, the data screening have resulted in the following outlier ratios: For pure components, OR = 21/1625; for binary systems, OR = 122/5814; and for ternary systems, OR = 2/276. It is important to note here that the assessments made on the data quality are based on the relative comparisons generated by the EOS screening procedure employed for this purpose. Therefore, data records have been marked as "possible" outliers. Consequently, further analysis and examination, which includes comparisons with predictions against other enthalpy models, is required for a more accurate assessment for probable errors in the experimental enthalpy measurements.

Table 9
Flagged Data Records for Benzene

Data Record No.	Temp. (F)	Press. (psia)	Enth. Dept (Btu/lb)	Exp. Phase	Raw/Smooth data	Reference No.	Criteria for Outliers
22	345.9	100.0	-11.0	2	R	581	2
77	535.9	600.0	-47.6	2	R	584	2
137	553.6	750.0	-94.7	2	R	581	2
153	439.4	1000.0	-128.6	1	R	584	3
157	559.1	1000.0	-104.0	2	R	584	2
158	581.1	1000.0	-94.9	2	R	584	2
159	600.7	1000.0	-81.4	2	R	584	2
309	554.0	750.0	-93.6	2	S	679	2
310	556.0	750.0	-88.6	2	S	679	2
312	560.0	750.0	-68.1	2	S	679	2
322	554.0	800.0	-99.4	2	S	679	4
323	556.0	800.0	-97.7	2	S	679	4
324	558.0	800.0	-96.1	2	S	679	4
325	560.0	800.0	-93.7	2	S	679	4
326	565.0	800.0	-87.6	2	S	679	4
327	570.0	800.0	-79.8	2	S	679	4
344	556.0	1000.0	-105.2	2	S	679	2
347	565.0	1000.0	-101.5	2	S	679	2
348	570.0	1000.0	-99.8	2	S	679	2
354	700.0	1000.0	-38.5	2	S	679	2

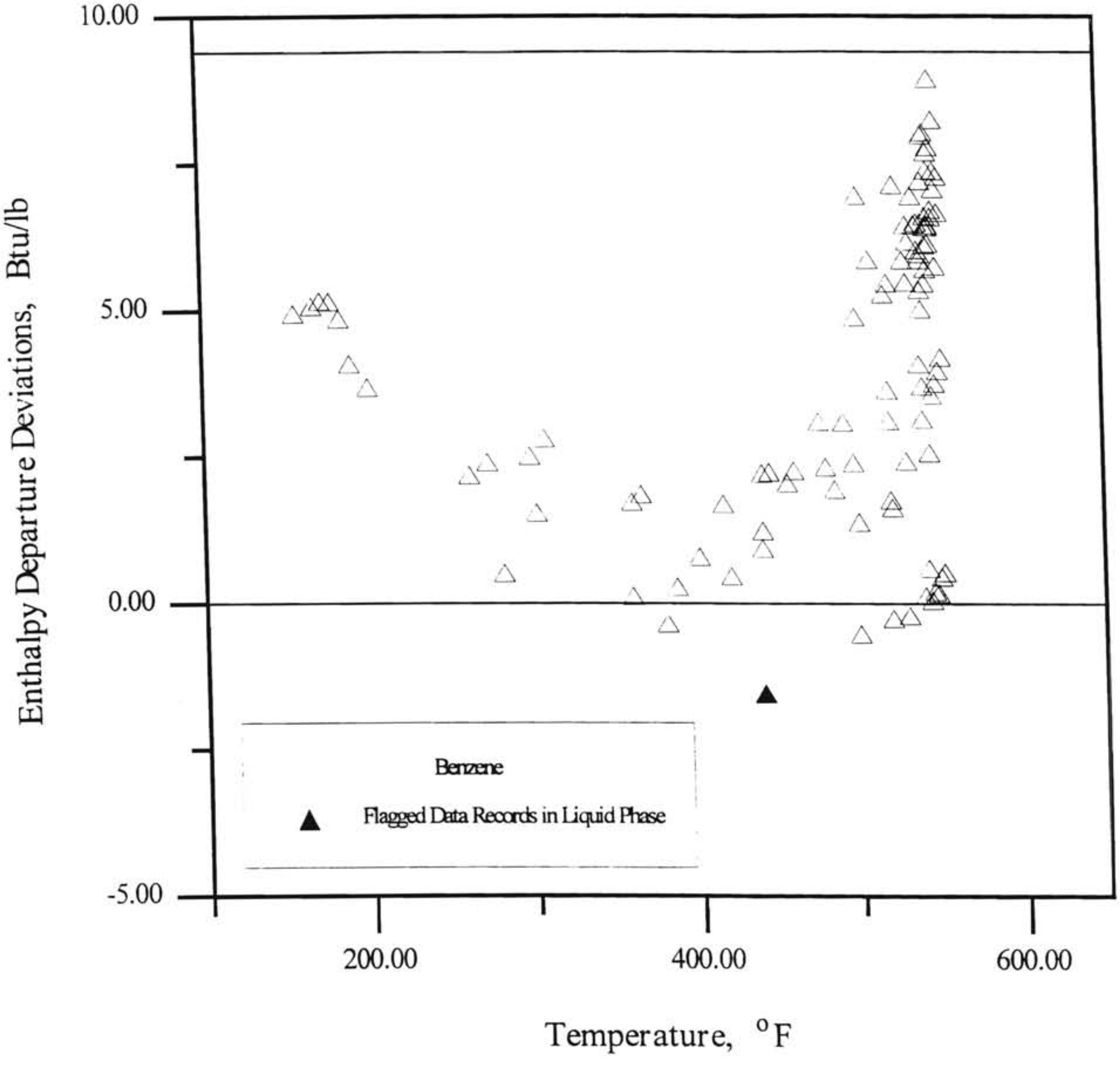

Figure 7. Liquid-Phase Enthalpy Departure Deviations for Benzene

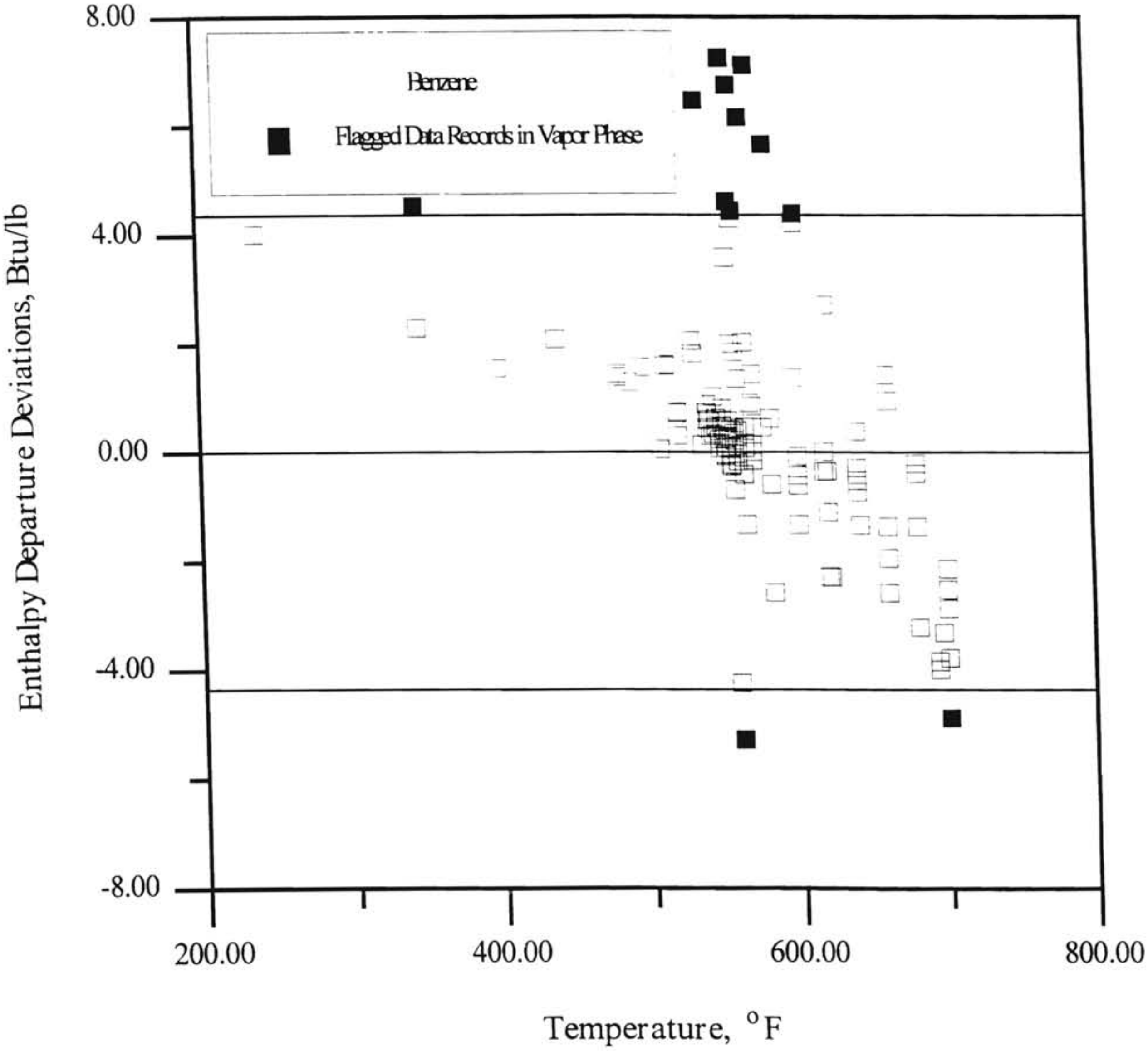

Figure 8. Vapor-Phase Enthalpy Departure Deviations for Benzene

Table 10
Summary of Possible Outliers in Enthalpy Data
for the Pure Fluids

No.	System	Exp. Phase	No. of outliers	Outlier Ratio, OR	Total OR
1	Methane	1	2	2/14	3/39
		2	1	1/25	
2	Ethane	1	0	0/41	1/69
		2	1	1/28	
3	Propane	1	0	0/40	1/61
		2	1	1/21	
4	n-Pentane	1	0	0/141	1/390
		2	1	1/249	
5	n-Octane	1	1	1/159	1/244
		2	0	0/85	
6	iso-Octane	1	1	1/18	1/18
7	n-Hexadecane	1	1	1/81	1/101
		2	0	0/20	
8	Cyclohexane	1	3	3/128	7/304
		2	4	4/176	
9	cis-2-Pentene	1	0	0/50	4/243
		2	4	4/193	
10	trans-Decalin	1	0	0/120	1/153
		2	1	1/33	

Total Outlier Ratio for Pure Fluids = 21/1625

Table 11

Summary of Possible Outliers in Enthalpy Data for the Binary Mixtures

No.	System	Mole Fraction	Exp. Phase	No. of Outliers	Outlier Ratio, OR	Total OR
1	Methane	0.951	1	0	0/6	1/85
	n-Heptane	0.049	2	1	1/79	
2	Methane	0.491	1	0	0/15	3/59
	n-Heptane	0.509	2	3	3/44	
3	Methane	0.249	1	4	4/90	4/125
	n-Heptane	0.751	2	0	0/35	
4	Ethane	0.498	1	0	0/48	2/76
	Propane	0.502	2	2	2/28	
5	Propane	0.43	1	0	0/0	2/21
	iso-Pentane	0.57	2	2	2/21	
6	n-Pentane	0.587	1	1	1/41	1/57
	n-Hexadecane	0.413	2	0	0/16	
7	n-Pentane	0.794	1	1	1/60	2/91
	n-Hexadecane	0.206	2	1	1/31	
8	Methane	0.5	1	1	1/68	1/104
	Meth-Cylohex	0.5	2	0	0/36	
9	n-Pentane	0.197	1	1	1/97	2/267
	Cyclohexane	0.803	2	1	1/170	
10	n-Pentane	0.385	1	0	0/96	1/263
	Cyclohexane	0.615	2	1	1/167	
11	n-Pentane	0.612	1	1	1/89	5/279
	Cyclohexane	0.388	2	4	4/190	
12	n-Pentane	0.793	1	0	0/82	6/315
	Cyclohexane	0.207	2	6	6/233	
13	n-Pentane	0.502	1	0	0/43	1/159
	cis-2-Pentene	0.498	2	1	1/116	

Table 11
Summary of Possible Outliers in Enthalpy Data
for the Binary Mixtures (continued)

No.	System	Mole fraction	Exp. Phase	No. of outliers	Outlier Ratio, OR	Total OR
14	Methane	0.5	1	6	6/40	6/73
	Toluene	0.5	2	0	0/33	
15	Propane	0.252	1	0	0/9	1/11
	Benzene	0.748	2	1	1/2	
16	Propane	0.797	1	1	1/3	1/8
	Benzene	0.203	2	0	0/5	
17	n-Pentane	0.186	1	2	2/64	5/266
	Benzene	0.814	2	3	3/202	
18	n-Pentane	0.4	1	1	1/93	5/341
	Benzene	0.6	2	4	4/248	
19	n-Pentane	0.801	1	0	0/84	1/278
	Benzene	0.199	2	1	1/224	
20	n-Pentane	0.725	1	2	2/60	2/138
	trans-Decalin	0.275	2	0	0/78	
21	n-Pentane	0.561	1	1	1/64	1/105
	trans-Decalin	0.439	2	0	0/41	
22	n-Pentane	0.884	1	1	1/76	1/164
	trans-Decalin	0.116	2	0	0/88	
23	n-Pentane	0.197	1	0	0/82	20/159
	Tetralin	0.803	2	20	20/77	
24	n-Pentane	0.795	1	0	0/50	1/154
	Tetralin	0.205	2	1	1/104	
25	n-Pentane	0.893	1	1	1/79	1/237
	Tetralin	0.107	2	0	0/158	
26	Benzene	0.93	1	0	0/71	1/159
	n-Octane	0.07	2	1	1/88	

Table 11
Summary of Possible Outliers in Enthalpy Data for the Binary Mixtures (continued)

No.	System	Mole fraction	Exp. Phase	No. of outliers	Outlier Ratio, OR	Total OR
27	Benzene	0.857	1	0	0/97	1/132
	n-Octane	0.143	2	1	1/103	
28	Benzene	0.771	1	1	1/56	1/132
	n-Octane	0.229	2	0	0/76	
29	Benzene	0.271	1	15	15/100	15/200
	n-Octane	0.729	2	0	0/100	
30	Benzene	0.963	1	1	1/83	1/207
	n-Hexadecane	0.037	2	0	0/124	
31	Benzene	0.92	1	1	1/65	3/134
	n-Hexadecane	0.08	2	2	2/69	
32	Benzene	0.67	1	2	2/66	2/75
	n-Hexadecane	0.33	2	0	0/9	
33	Benzene	0.211	1	2	2/59	4/211
	Cyclohexane	0.789	2	2	2/152	
34	Benzene	0.334	1	3	3/67	9/195
	Cyclohexane	0.666	2	6	6/128	
35	Benzene	0.812	1	0	0/80	1/252
	Cyclohexane	0.188	2	1	1/172	
36	Benzene	0.613	1	0	0/71	3/192
	Cyclohexane	0.87	2	3	3/121	
37	CO_2	0.5	1	0	0/31	1/59
	n-Pentane	0.5	2	1	1/28	
38	H_2S	0.5	1	0	0/6	3/31
	Methane	0.5	2	3	3/25	

Total Outlier Ratio for Binaries = 122/5814

Table 12
Summary of Possible Outliers in Enthalpy Data for the Ternary Mixtures

No.	System	Mole Fraction	Exp. Phase	No. of Outliers	Outlier Ratio, OR	Total OR
1	Methane	0.3702	1	1	1/140	1/164
	Ethane	0.3055	2	0	0/24	
	Propane	0.3243				
2	Benzene	0.333	1	0	0/87	1/112
	n-Octane	0.334	2	1	1/25	
	Tetralin	0.333				

Total Outlier Ratio for Ternaries = 2/276

Beyond the EOS comparative studies conducted here, it would have been useful to evaluate the thermodynamic consistency of enthalpy data. In this case, however, it was not possible to devise thermodynamic consistency tests of the Gibbs-Duhem type for evaluating the enthalpy data quality in the GPA database. This is because experimental volumetric and entropy data were not available for the systems at the required temperature and pressure conditions. Also, all GPA enthalpy values analyzed are single-phase data. To apply the Gibbs-Duhem analysis, vapor-liquid equilibrium (VLE) measurements are required for successfully implementing the thermodynamic consistency checks.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The Peng-Robinson EOS was used to predict enthalpy departure functions for natural gas systems in the GPA enthalpy database. The predicted departures were then compared against the departure values generated from experimental enthalpy values in the database. The model evaluations revealed that the PR EOS provides reasonably accurate predictions for the enthalpy departures. Typical average deviations of 2-6 Btu/lb were observed for all the systems considered; this was true for both the liquid and vapor phase predictions.

For the homologous series of alkanes, alkyl naphthenes or aromatics, the lower molecular weight hydrocarbons, in general, gave superior enthalpy predictions. Moreover, the PR model did not show any apparent difference in its ability to predict enthalpy departures in the liquid and vapor phases. Similar results were obtained by Daubert (54) using pseudo-pure component mixing rules.

The model evaluations were used to help screen enthalpy data entries in the GPA database. Data points exhibiting "higher-than-usual" deviations were marked as possible outliers and were identified for further examination and analyses. For all systems considered, on an average, one to two percent of the total records analyzed each for the pures, binaries and ternaries were marked as possible outliers. Under the enthalpy data quality assurance procedure, the temperature, pressure, and composition records were also visually inspected for data-entry errors.

It was not possible to devise thermodynamic consistency checks of the Gibbs-Duhem type for evaluating the enthalpy data quality in the GPA database. This is because experimental volumetric and entropy data were not available for the systems at the required temperature and pressure conditions. Also, most of the enthalpy data in the database are in the single-phase region.

For future work, graphical deviation plots should be made to help analyze the systematic trends in deviation displayed between the EOS departure function predictions and the experimentally obtained enthalpy departure entries in the GPA database. Also, other enthalpy prediction models should be evaluated against the experimental enthalpy departure values in the database. The other models could include a variation of the BWR EOS and the currently popular cubic EOS amended by volume translation and/or equipped with different mixing rules. Theoretically based modern equations of state, which include the SPHCT and its variations, should be tested for their enthalpy departure prediction capabilities. Such models could be of help in assessing the quality of enthalpy data identified as displaying systematic trends in deviations.

Techniques should be devised to establish smoothing procedures for the raw enthalpy data in the database. Equations of state or other means could be employed for this purpose.

Finally, enthalpy data reported in the literature for natural gas systems after 1990 should be added to the GPA enthalpy database. Such data would serve as an excellent complement to the existing enthalpy entries in the database and would better define the need for additional experimental measurements.

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APPENDIX A

A DETAILED DERIVATION OF PENG-ROBINSON EQUATION OF STATE ENTHALPY DEPARTURE FUNCTION

The expression for the PR EOS enthalpy departure model is derived below. Similar derivations for the PR EOS are given by Edmister and Lee (61). From exact thermodynamics, isothermal definition of enthalpy departure is given as:

$$H - H^0 = \int_v^\infty \left[P - T\left(\frac{\partial p}{\partial T}\right)_v \right] dv + pv - RT \tag{4.11}$$

The Peng-Robinson equation is given as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{4.1}$$

$$a(T) = a_c \cdot \alpha(T) \tag{4.8}$$

$$\alpha(T) = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \tag{4.4}$$

Using the volume integral equation,

$$T\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{v-b} - \frac{T}{v(v+b)+b(v-b)} \cdot \frac{\partial a(T)}{\partial T}$$

$$p - T\left(\frac{\partial p}{\partial T}\right)_v = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} - \frac{RT}{v-b} + \frac{T}{v(v+b)+b(v-b)} \cdot \frac{\partial a(T)}{\partial T}$$

$$\int_\infty^v \left[p - T\frac{\partial p}{\partial T}_v \right] dv = \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \cdot \int_\infty^v \frac{dv}{(v+b)^2 - 2b^2}; \qquad \text{@ const. } T:$$

$$\int_\infty^v \frac{dv}{(v+b)^2 - 2b^2} = \int_\infty^v \frac{dv}{(v+b)^2 - \left(\sqrt{2}b\right)^2} = \frac{1}{2\sqrt{2}b} \ln \frac{v + b\left(1-\sqrt{2}\right)}{v + b\left(1+\sqrt{2}\right)}\Bigg|_\infty^v$$

$$H - H^o = \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \frac{1}{2\sqrt{2}b} \ln \left. \frac{v + b\left(1-\sqrt{2}\right)}{v + b\left(1+\sqrt{2}\right)} \right|_{\infty}^{v} + pv - RT$$

$$\lim_{v \to \infty} \ln \frac{v + b\left(1-\sqrt{2}\right)}{v + b\left(1+\sqrt{2}\right)} = \ln 1.0 = 0.0$$

$$H - H^o = \frac{1}{2\sqrt{2}b} \ln\left(\frac{v + b\left(1-\sqrt{2}\right)}{v + b\left(1+\sqrt{2}\right)} \right) \cdot \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} + pv - RT \qquad \text{(A.1)}$$

$$H - H^o = \frac{1}{2.828b} \ln\left(\frac{v - 0.414b}{v + 2.414b} \right) \cdot \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} + pv - RT \qquad \text{(A.2)}$$

$$a(T) = a_c \cdot \alpha(T) \qquad \text{(4.8)}$$

$$= a_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$$

$$\frac{\partial a(T)}{\partial T} = 2 \cdot a_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right] \cdot m \cdot \frac{\partial}{\partial T}\left[1 - T_r^{0.5}\right]$$

$$= -a_c \cdot m \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \cdot \frac{T_r^{-0.5}}{T_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]}$$

$$\frac{\partial a(T)}{\partial T} = \frac{-m \cdot T_r^{-0.5}}{T_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]} \cdot a_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$$

$$\frac{\partial a(T)}{\partial T} = \frac{-m \cdot T_r^{-0.5}}{T_c \cdot \left[1 + m\left(1 - T_r^{0.5}\right)\right]} \cdot a(T) \qquad \text{(A.3)}$$

This is the form for a_{ii}, hence for a pure substance, it becomes

$$\frac{\partial a(T)}{\partial T} = \frac{-m_i \cdot T_{ri}^{-0.5}}{T_{ci} \cdot \left[1 + m_i\left(1 - T_{ri}^{0.5}\right)\right]} \cdot a_i(T) = \frac{-m_i \cdot T_{ri}^{-0.5}}{T_{ci} \cdot \left[1 + m_i\left(1 - T_{ri}^{0.5}\right)\right]} \cdot a_{ci} \alpha_i(T)$$

$$T \cdot \frac{\partial a(T)}{\partial T} = \frac{-m \cdot T_r^{0.5}}{\left[1 + m\left(1 - T_r^{0.5}\right)\right]} \cdot a(T) \qquad \text{(A.4)}$$

Substituting (A.4) in (A.2) :

$$H - H^{o} = \frac{1}{2.828b}\ln\left(\frac{v - 0.414b}{v + 2.414b}\right)\cdot\left\{\frac{-m\cdot T_r^{0.5}}{\left[1 + m\left(1 - T_r^{0.5}\right)\right]}\cdot a(T) - a(T)\right\}$$

$$+\,pv - RT \tag{A.5}$$

$$H - H^{o} = \frac{a_c}{2.828b}\left[\left(\alpha - T\frac{d\alpha}{dT}\right)\right]\ln\left[\frac{(v - 0.414b)}{(v + 2.414b)}\right] + pv - RT \tag{4.12}$$

with

$$\frac{d\alpha}{dT} = \frac{-\alpha}{T_c}\left[\frac{mT_r^{-0.5}}{1 + m\left(1 - T_r^{0.5}\right)}\right] \tag{4.13}$$

Equations (4.12) and (4.13) are used to determine the PR enthalpy departure function for a pure component.

Mixture Departure Function

For mixtures,

$$a = \sum_{i}^{n}\sum_{j}^{n} z_i z_j a_{ij} \tag{4.6}$$

where $a_{ij} = \left(1 - C_{ij}\right)a_i^{0.5}a_j^{0.5}$ (4.9)

Expanding for a binary,

$$a = z_1^2 a_{11} + 2z_1 z_2 a_{12} + z_2^2 a_{22}$$

$$= z_1^2 a_{11} + 2z_1 z_2\left(1 - C_{12}\right)a_{11}^{1/2}\cdot a_{22}^{1/2} + z_2^2 a_{22}$$

$$= z_1^2 a_{c1}\alpha_1 + 2z_1 z_2\left(1 - C_{12}\right)a_{c1}^{1/2}\cdot a_{c2}^{1/2}\cdot \alpha_1^{1/2}\cdot \alpha_2^{1/2} + z_2^2 a_{c2}\cdot \alpha_2 \tag{A.6}$$

Note that $a_{11} \equiv a_1$ and $a_{22} \equiv a_2$

$$\frac{\partial a}{\partial T} = z_1^2 a_{c1}\frac{\partial \alpha_1}{\partial T} + 2z_1 z_2 a_{c1}^{1/2} a_{c2}^{1/2}\left(1-C_{12}\right)\cdot\frac{\partial\left(\alpha_1^{1/2}\cdot\alpha_2^{1/2}\right)}{\partial T} + z_2^2 a_{c2}\frac{\partial \alpha_2}{\partial T} \tag{A.7}$$

From (A.3)

$$\frac{\partial a_i}{\partial T} = a_{ci}\cdot\frac{\partial \alpha_i}{\partial T} = \frac{-m_i\cdot T_{ri}^{-0.5}}{T_{ci}\cdot\left[1+m_i\left(1-T_{ri}^{0.5}\right)\right]}\cdot a_{ci}\cdot\alpha_i(T) \tag{A.3}$$

$$\frac{\partial\left(\alpha_1^{1/2}\cdot\alpha_2^{1/2}\right)}{\partial T} = \alpha_2^{1/2}\cdot\frac{\partial\alpha_1^{1/2}}{\partial T} + \alpha_1^{1/2}\cdot\frac{\partial\alpha_2^{1/2}}{\partial T} \tag{A.8}$$

$$\alpha^{1/2} = \left[1+m\left(1-T_r^{0.5}\right)\right] = \left[1+m\left(1-\frac{T^{0.5}}{T_c^{0.5}}\right)\right]$$

$$\frac{\partial\alpha^{1/2}}{\partial T} = \frac{-m}{T_c^{0.5}}\cdot 0.5T^{-0.5} = \frac{-0.5mT_r^{-0.5}}{T_c}$$

$$\frac{\partial\alpha_i^{1/2}}{\partial T} = \frac{-0.5m_i T_{ri}^{-0.5}}{T_{ci}} \tag{A.9}$$

Substituting (A.9), (A.8), (A.5) into (A.7), one gets

$$\frac{\partial a}{\partial T} = \frac{z_1^2 a_{c1}\alpha_1}{T_{c1}}\left[\frac{-m_1 T_{r1}^{-0.5}}{1+m_1\left(1-T_{r1}^{0.5}\right)}\right] + \frac{z_2^2 a_{c2}\alpha_2}{T_{c2}}\left[\frac{-m_2 T_{r2}^{-0.5}}{1+m_2\left(1-T_{r2}^{0.5}\right)}\right]$$

$$+\ 2z_1 z_2 a_{c1}^{1/2} a_{c2}^{1/2}\left(1-C_{12}\right)\left[\alpha_2^{1/2}\frac{-0.5m_1 T_{r1}^{-0.5}}{T_{c1}} + \alpha_1^{1/2}\frac{-0.5m_2 T_{r2}^{-0.5}}{T_{c2}}\right]$$

$$= \frac{z_1^2 a_{c1}\alpha_1}{T_{c1}}\left[\frac{-m_1 T_{r1}^{-0.5}}{1+m_1\left(1-T_{r1}^{0.5}\right)}\right] + 2z_1 z_2 a_{c1}^{1/2} a_{c2}^{1/2}\alpha_1^{1/2}\alpha_2^{1/2}\left(1-C_{12}\right).$$

$$\left\{\left(\frac{-0.5m_1 T_{r1}^{-0.5}}{\left[1+m_1\left(1-T_{r1}^{0.5}\right)\right]T_{c1}}\right) + \left(\frac{-0.5m_2 T_{r2}^{-0.5}}{\left[1+m_2\left(1-T_{r2}^{0.5}\right)\right]T_{c2}}\right)\right\}$$

$$+\frac{z_2^2 a_{c2}\alpha_2}{T_{c2}}\left[\frac{-m_2 T_{r2}^{-0.5}}{1+m_2\left(1-T_{r2}^{0.5}\right)}\right] \tag{A.10}$$

So, in general, for a multicomponent mixture,

$$\frac{\partial a}{\partial T}=\sum_i\sum_j z_i\cdot z_j\cdot a_{ci}^{1/2}\cdot a_{cj}^{1/2}\cdot\alpha_i^{1/2}\cdot\alpha_j^{1/2}\left(1-C_{12}\right)\cdot\left\{\frac{-0.5m_i T_{ri}^{-0.5}}{T_{ci}\left[1+m_i\left(1-T_{ri}^{0.5}\right)\right]}\right.$$

$$\left.-\frac{0.5m_j T_{rj}^{-0.5}}{T_{cj}\left[1+m_j\left(1-T_{rj}^{0.5}\right)\right]}\right\} \tag{A.11}$$

Substituting (A.10) into Equation (4.12):

$$H-H^{o}=0.3536\left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n}z_i z_j\gamma_{ij}T-a}{b}\right]\cdot\ln\left(\frac{v-0.414b}{v+2.414b}\right)+pv-RT \tag{4.14}$$

where

$$\gamma_{ij}=a_{ij}\left\{\frac{-0.5m_i T_{ri}^{-0.5}}{T_{ci}\left[1+m_i\left(1-T_{ri}^{0.5}\right)\right]}-\frac{-0.5m_j T_{rj}^{-0.5}}{T_{cj}\left[1+m_j\left(1-T_{rj}^{0.5}\right)\right]}\right\} \tag{4.15}$$

Equation (4.14) is the required expression for a multicomponent mixture.

APPENDIX B

LITERATURE REFERENCES IN THE GPA ENTHALPY DATABASE

A listing of the literature reference numbers along with their corresponding literature sources for all the enthalpy data in the GPA Enthalpy Database is presented in this appendix.

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APPENDIX C

THE PURE FLUID CRITICAL PROPERTIES USED FOR THE PENG-ROBINSON ENTHALPY DEPARTURE FUNCTION MODEL EVALUATION

Table 13
Pure Fluid Critical Properties Used in Evaluations

No.	Compound	Formula	Mol. wt.	Pressure (psia)	Temp. (F)	Acentric Factor, ω
1	Methane	CH_4	16.043	666.4	-116.67	0.0104
2	Ethane	C_2H_6	30.070	706.5	89.92	0.0979
3	Propane	C_3H_8	44.097	616.0	206.06	0.1522
4	iso-butane	C_4H_{10}	58.123	527.9	274.46	0.1852
5	n-Butane	C_4H_{10}	58.123	550.6	305.62	0.1995
6	Isopentane	C_5H_{12}	72.150	490.4	369.10	0.2280
7	n-Pentane	C_5H_{12}	72.150	488.6	385.8	0.2514
8	n-Heptane	C_7H_{16}	100.204	396.8	512.7	0.3494
9	n-Octane	C_8H_{18}	114.231	360.7	564.22	0.3977
10	iso-octane	C_8H_{18}	114.231	372.4	519.46	0.3035
11	n-Hexadecane	$C_{16}H_{34}$	226.448	205.7	830.93	0.742
12	Cyclohexane	C_6H_{12}	84.161	590.8	536.6	0.2096
13	Methylcyclohexane	C_7H_{14}	98.188	503.5	570.27	0.2358
14	Ethylcyclohexane	C_8H_{16}	112.216	439.4	636.5	0.243
15	Propene	C_3H_6	42.081	668.6	197.17	0.1356
16	cis-2-Pentene	C_5H_{10}	70.135	529.05	397.13	0.240
17	Benzene	C_6H_6	78.114	710.4	552.22	0.2093
18	Toluene	C_7H_8	92.141	595.5	605.57	0.2633
19	Ethylbenzene	C_8H_{10}	106.167	523.0	651.29	0.3027
20	Tetralin	$C_{10}H_{12}$	132.206	509.9	834.5	0.303
21	cis-Decalin	$C_{10}H_{18}$	138.254	455.6	804.3	0.230
22	trans-Decalin	$C_{10}H_{18}$	138.254	455.6	782.3	0.27
23	Carbon monoxide	CO	28.010	507.5	-220.43	0.0484
24	Carbon dioxide	CO_2	44.010	1071.	87.91	0.2667
25	Hydrogen Sulfide	H_2S	34.08	1300.	212.45	0.0948
26	Sulfur dioxide	SO_2	64.06	1143.	315.8	0.2548
27	Carbonyl Sulfide	COS	60.07	852.37	215.33	0.099
28	Hydrogen	H_2	2.0159	188.1	-399.9	-0.2202
29	Nitrogen	N_2	28.0134	493.1	-232.51	0.0372
30	Water	H_2O	18.0153	3198.8	705.16	0.3443
31	Helium	He	4.0026	32.99	-450.31	0.

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