EVALUATION AND A NEW REPORTING METHOD FOR ENTHALPY DATA

By

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METHOD FOR ENTHALPY DATA

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NOMENCLATURE

a, b, c, d	Correlation constants in Equation (2.4)
A	Helmholtz energy
$A-A^{o}$	Helmholtz energy departure function from ideal gas state
c	Degree of freedom parameter
C	Virial coefficient
C_p	Specific heat capacity at constant pressure
G	Gibbs energy
$G-G^{o}$	Gibbs energy departure from ideal gas state
H^{o}	Ideal gas enthalpy
$H-H^{o}$	Enthalpy departure function from ideal gas state
m	Mass
N_A	Avogadro's number
p	Absolute pressure
Q	Conical partition function
R	Universal gas constant
S	Entropy
$S-S^{o}$	Entropy departure function from ideal gas state
T	Absolute temperature
T^*	Characteristic temperature
ΔU	Change in internal energy
$U-U^{o}$	Internal energy departure from ideal gas state
v	Volume
v^*	Characteristic volume
z	Mole fraction of component

Z	Compressibility factor
Z_M	Maximum coordination number
RMSE	Root mean squared error
AAD	Average absolute deviation

Greek Symbols

ω	Acentric factor

Subscripts

c	Critical number
r	Reduced number

Superscripts

o	Standard state

CHAPTER I

INTRODUCTION

The Gas Processors Association (GPA) is a cooperative research organization sponsored by a consortium of companies in the energy sector. The GPA conducts research in the thermodynamics and physical properties areas, specifically on gases, light hydrocarbons, and process solvents for the recovery and purification of natural gas, liquefied petroleum gas (LPG) and on substitute gas (1).

Sponsoring companies receive multiple economic benefits from cooperative research. By dividing the cost of research among several groups, each participating organization is able to acquire valuable research for a fraction of the cost of performing the research internally or by contract measurement. A common database for many industrial partners also prevents the need for multiple reproductions of the same research, since internal research in companies usually remains proprietary and is not shared with the rest of industry. The money saved on research can be invested in other areas, helping participating companies compete more effectively in the dynamic global economy.

The cooperative database is available to help produce more accurate and efficient equipment design. The economic benefits from improved design in industry can be staggering, not only yielding lower capital costs, but also reducing operating costs for the lifetime of the designed equipment. The data can also be applied to better simulate existing equipment for use in debottlenecking and efficiency improvements. The cooperative data can also serve to supplement internal research and also serve as calibration data for such research

BENEFIT OF ENTHALPY DATA

Accurate design of process equipment is no less than a requirement. Improper design of equipment will lead, at best, to over-expenditure of capital dollars and increased operating costs. Over time, a corporation will no longer be in a competitive position and will have to reevaluate the design of its equipment. On the other hand, improper design can lead to faulty equipment, causing process shutdowns or even incidents.

Accurate enthalpy data are necessary when performing energy balances on equipment units or processes. Many equations exist to predict enthalpy for different groups of fluids at different temperatures, pressures, phases and mixtures. Unfortunately, no equation exists to accurately predict the enthalpy of any fluid, or mixture of fluids, at any process conditions. Experimental enthalpy data are required to evaluate these equations, and to provide more exact data, when needed, than what the models are able to provide.

The GPA maintains an extensive compilation of thermodynamic data, including enthalpy departure data in a database. The GPA commissioned Project 921, Enthalpy Database Development and Maintenance, to compile, evaluate and maintain experimental enthalpy, heat of solution and isothermal enthalpy departure data for pure fluids and mixtures of interest to the gas processing industry. In this context, the database is used to primarily to: 1) evaluate enthalpy prediction methods and computer models, 2) develop new or system-specific correlations and 3) provide experimental measurements for direct application in process engineering calculations.

Direct comparisons of the current enthalpy data in the database to the values in the literature (2) would be ideal. Unfortunately, data has been compiled over several decades. Different techniques were employed to determine the enthalpy departure entries, since the experimental data were based on different reference states. Consequently, it is no longer pratical to compare the enthalpy departure data in the database to the literature values.

RESEARCH OBJECTIVES

Three main objectives were established for this work:

1. Use the Peng-Robinson Equation of State to evaluate
    - a) single-phase pure and multicomponent data in the GPA database, and
    - b) two-phase pure and multicomponent data in the GPA database.
2. Evaluate the modified form of Park-Gasem-Robinson (3) equation as it applies to enthalpy departure data
3. Develop a novel, more useful, reporting method for data evaluations.

Unfortunately, 1.b was not completed in the present work due to a lack of information in the database. This will be discussed in more detail in Chapter III

THESIS OVERVIEW

The thesis is organized into six chapters. Chapter II describes the equations of state used to evaluate the GPA database. This chapter begins with the Peng-Robinson equation of state, then covers the Park-Gasem-Robinson equation of state. Chapter II also covers information concerning the required physical properties and software used to complete the evaluations.

Chapter III explains the methodology used to evaluate the enthalpy departure data. Three main tools for evaluating enthalpy data are covered: 1) direct comparison to the original references, 2) equation-of-state evaluations and 3) graphical evaluation of enthalpy data. This chapter also gives some example cases of how to employ the three tools listed above.

Chapter IV describes the need for deviation plots. This chapter begins with the conventional methods of plotting deviations as functions of either temperature or pressure. Later, the chapter covers the evolution of the proposed three-dimensional temperature-pressure-deviation plots used throughout this work.

Chapter V covers the results of the GPA enthalpy database evaluation. First, the chapter explains the results from the Peng-Robinson equation of state. Then, the results from the Park-Gasem-Robinson equation of state are presented. The chapter finishes with a comparison between the two equations.

Finally, Chapter VI summarizes the conclusions for this study and recommendations for future work

CHAPTER II

EQUATION OF STATE ENTHALPY DEPARTURE MODEL EVALUATIONS

The contents of this chapter addresses five main goals:

- Explanation of enthalpy departure calculations for this work. The information for this objective was first presented by Rastogi (4). It is divided into three sections: the enthalpy equation, ideal gas enthalpy determination and enthalpy departure function estimation.
- Explain why the Peng-Robinson (PR) equation of state (EOS) was selected for the enthalpy evaluation of the Gas Processors Association database.
- Describe the PR EOS and the enthalpy departure function for this equation of state.
- Describe the Park-Gasem-Robinson (PGR) EOS and its enthalpy departure function.
- Provide an overview of the necessary tools to perform an analysis of the enthalpy data using the above equations of state.

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. Therefore, the molar or specific enthalpy of a substance may be expressed as a *function* of two other state variables. The two state variables are chosen as temperature and pressure. Therefore,

$$H = H(T, p) \tag{2.1}$$

The enthalpy of a compound can be expressed as a summation of three quantities (5):

$$H(T, p) = \left[H(T, p) - H(T, p^\circ)\right] + \left[H(T, p^\circ) - H(T^\circ, p^\circ)\right] + H(T^\circ, p^\circ) \tag{2.2}$$

WHERE

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

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

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

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

$H(T^\circ, p^\circ)$ is the enthalpy of formation of the compound from the elements at T° and p°, or the reference state chosen for enthalpy calculations. The quantity [$H(T, p^\circ) - H(T^\circ, p^\circ)$] 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°. [$H(T, p) - H(T, p^\circ)$] 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 $H - H^\circ$ and H°, 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.

$$H^{o} = \int C_{p}^{o} dT \tag{2.3}$$

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 (6, 7).

$$C_{p}^{o} = a + bT + cT^{2} + dT^{3} + \ldots \tag{2.4}$$

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 (6, 7) 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 (6, 7).

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 (8). 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 (9, 10) shown below :

$$C_p^o = a + b\exp(-c/T^n) \tag{2.5}$$

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 (9)

More complex equations for calculating the ideal gas heat capacity and enthalpy have been proposed (8). These equations are more rigorous in form since they are derived based on statistical mechanical formulae for the heat capacity of an ideal gas (8-10). 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 (5), as shown below:

$$A - A^o = -\int_{\infty}^{v} \left(p - \frac{RT}{v} \right) dv - RT \ln \frac{v}{v^o} \tag{2.6}$$

$$S - S^o = \int_{\infty}^{v} \left[\left(\frac{\partial p}{\partial T} \right)_v - \frac{R}{v} \right] dV + R \ln \frac{v}{v^o} \tag{2.7}$$

$$H - H^o = (A - A^o) + T (S - S^o) + RT (Z - 1) \tag{2.8}$$

$$U - U^o = (A - A^o) + T (S - S^o) \tag{2.9}$$

$$G - G^o = (A - A^o) + RT (Z - 1) \tag{2.10}$$

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 elsewhere (4)

SELECTION OF AN EVALUATION METHOD

The advantages and shortcomings of the PR EOS for enthalpy evaluation are presented in this section. Complete literature overviews of enthalpy prediction methods can be found elsewhere (4, 14).

Adachi (15) completed a reasonably comprehensive study involving the comparative capabilities of eleven cubic equations of state for paraffins ranging from methane to decane. The PR EOS (7) yielded lower deviations for enthalpy departure values than the Schmidt and Wenzel. (16). Soave-Redlich-Kwong (17) and Harmens and Knapp (18) equations of state. The PR EOS predictions were similar to those of Kumar and Starling (19). However. the equation of state of Adachi et al. (20) yielded best enthalpy departure prediction results.

In 1984. Daubert (2) used the PR EOS for enthalpy departure predictions and comparisons with selected enthalpy values in the GPA databank. The database has seen much growth and maintenance since that time. Daubert's evaluation no longer is comprehensive to all the systems in the GPA databank. However. Daubert showed the PR EOS predicted enthalpy departures very well for light hydrocarbons and gases. As the molecular weight increased. the accuracy decreased. specifically for pentane and heavier components

Although the equation shows limitations for heavier hydrocarbons, the PR EOS still has several advantages (4)

- 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 acceptable computational speed.

The shortcomings of the PR EOS are easily dealt with in the evaluation. The present work is more concerned with the deviation of data relative to data within the same system. The relative deviation between points becomes of greater importance than whether the PR EOS can predict precisely enthalpy departures over a range of temperatures and pressures.

PENG-ROBINSON EQUATION OF STATE

The PR EOS was used in this study is as follows (21):

$$p = \frac{RT}{(v-b)} - \frac{a_c \alpha}{(v^2 + 2bv - b^2)} \tag{2.11}$$

where

$$b = 0.07780 \frac{RT_c}{p_c} \tag{2.12}$$

$$a_c = 0.45724 \frac{(RT_c)^2}{p_c} \tag{2.13}$$

$$\alpha = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \tag{2.14}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{2.15}$$

The mixing rules employed are:

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{2.16}$$

$$b = \sum \sum z_i z_j b_{ij} \tag{2.17}$$

where

$$a = a_c \cdot \alpha \tag{2.18}$$

$$a_{ij} = \left(a_{ii} a_{jj}\right)^{0.5} \left(1 - C'_{ij}\right) \tag{2.19}$$

$$b_{ij} = \frac{1}{2}\left(b_{ii} + b_{jj}\right) \tag{2.20}$$

where C_{ij} is an adjustable, empirically-determined "binary interaction parameter" which characterizes the interactions between component i and component j.

Enthalpy Departure Function for the PR EOS

The enthalpy departure function [H(T,p) - H(T,p°)] as applied to the PR EOS is:

$$H - H^{\circ} = a_c\left[\left(\alpha - \frac{Td\alpha}{dT}\right)\Big/2\sqrt{2}b\right]\ln\left[\frac{v-0.414b}{v+2.414b}\right] + pv - RT \tag{2.21}$$

with

$$\frac{d\alpha}{dT} = \left(\frac{-\alpha}{T_c}\right)\frac{\left(mT_r^{-0.5}\right)}{1+m\left(1-T_r^{0.5}\right)} \tag{2.22}$$

To extend Equations (2.21) and (2.22) to multicomponent systems, mixing rules are applied. Using Equations (2.19) and (2.20), enthalpy departure equations for the PR EOS are easily obtained.

$$H - H^{\circ} = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j \gamma_{ij} T - a}{2\sqrt{2}b}\right]\ln\left[\frac{v-0.414b}{v+2.414b}\right] + pv - RT \tag{2.23}$$

with

$$\gamma_{ij} = a_{ij}\left[\frac{-0.5m_i T_{ri}^{-0.5}}{T_{ci}\left(1+m_i\left(1-T_{ri}^{0.5}\right)\right)} - \frac{-0.5m_j T_{rj}^{-0.5}}{T_{cj}\left(1+m_j\left(1-T_{rj}^{0.5}\right)\right)}\right] \tag{2.24}$$

A detailed derivation for the PR enthalpy departure has been outlined by Rastogi (4)

MODIFIED PARK-GASEM- ROBINSON EQUATION OF STATE

Recently, Row (14) proposed a modification to the equation of state proposed by Park (3). The Park-Gasem-Robinson (PGR) equation was based on the generalized van der Waals partition function for chain-like molecules. The PGR equation of state used an expression for the free volume of hard spheres in the repulsive term and an augmented generalized cubic equation of state attractive terms. A square-well potential was used to describe the attractive energy between segments of molecules. Row modified the PGR to provide simplicity and flexibility as well as more accurate prediction capability. The modified PGR equation of state is

$$Z = 1 + c\left(\frac{\beta_1 \tau}{v_r - \beta_2 \tau} - \frac{\alpha Y v_r}{v_r^2 + u v_r + w} - \frac{Q_1 \alpha Y}{v_r + Q_2}\right) \tag{2.25}$$

where

$$\alpha Y = Z_M \left[\exp(F_t) - 1\right] \tag{2.26}$$

$$F_t = \omega_1\left(\frac{1}{2\tilde{T}}\right)^{1/2} + \omega_2\left(\frac{1}{2\tilde{T}}\right) + \omega_3\left(\frac{1}{2\tilde{T}}\right)^{3/2} + \omega_4\left(\frac{1}{2\tilde{T}}\right)^2 \tag{2.27}$$

and $\tau = 0.7402$, $\beta_1 = 4$, $\beta_2 = 1.9$, $v_r = v/v^*$, $\tilde{T} = T/T^*$, and Z_M, ω_1, ω_2, ω_3, and ω_4 are universal constants.

The enthalpy departure function as applied to the PGR EOS is:

$$H - H^{\circ} = RT\left[Z - 1 - Z_M cT\left(\frac{da}{dT}\right)_{v} \Omega\right] \tag{2.28}$$

where

$$\Omega = \frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right)-\frac{Q_1}{Q_2}\ln\left|\frac{v_r-\beta_2\tau}{v_r}\right| \tag{2.29}$$

and

$$\left(\frac{da}{dT}\right)_v = -\frac{1}{T}\left[\begin{array}{l}\frac{\omega_1}{2}\left(\frac{T^*}{2T}\right)^{1/2}+\omega_2\left(\frac{T^*}{2T}\right)+\frac{3\omega_3}{2}\left(\frac{T^*}{2T}\right)^{3/2}\\+2\omega_4\left(\frac{T^*}{2T}\right)^2\end{array}\right](Y+1) \tag{2.30}$$

REQUIRED PURE FLUID PROPERTIES

Both the PR and PGR EOSs require pure component properties as input variables for the enthalpy departure model. Both equations use the critical temperature, T_c, critical pressure, p_c, and acentric factor, ω. Molecular weights of the substances are necessary to report enthalpy departures on a unit mass basis. The PGR also required the characteristic temperature, T*, and volume, v*, and the degrees of freedom parameters, c.

The pure fluid values of T_c, p_c, and ω used are those given by Daubert (2). However, the pure fluid properties for cis-2-pentene, ethylcyclohexane, cis-decalin, trans-decalin, tetralin, and hexadecane were taken from Reid et al. (5). These values are listed in Table 1. The values of T*, v* and c were obtained from Row (14), and are listed in Table 2.

Table 1.

Pure Fluid Critical Properties Used in Evaluations

No.	Compound	Formula	Molecular Weight	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	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	Pentane	C_5H_{12}	72.150	488.6	385.8	0.2514
8	Heptane	C_7H_{16}	100.204	396.8	512.7	0.3494
9	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	Hexadecane	$C_{16}H_{34}$	226.448	205.7	830.93	0.7420
12	Cyclohexane	C_6H_{12}	84.161	590.8	536.60	0.2096
13	Methylcyclohexane	C_7H_{14}	98.188	503.5	570.27	0.2358
14	Ethylcyclohexane	C_8H_{16}	112.216	439.4	636.50	0.2430
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	0.2400
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	834.50	0.3030
21	cis-Decalin	$C_{10}H_{18}$	138.254	455.6	804.30	0.2300
22	trans-Decalin	$C_{10}H_{18}$	138.254	455.6	782.30	0.2700
23	Carbon monoxide	CO	28.010	507.5	-220.43	0.0484
24	Carbon dioxide	CO_2	44.010	1071.0	87.91	0.2667
25	Hydrogen Sulfide	H_2S	34.080	1300.0	212.45	0.0948
26	Sulfur dioxide	SO_2	64.060	1143.0	315.80	0.2548
27	Carbonyl Sulfide	COS	60.070	852.37	215.33	0.0990
28	Hydrogen	H_2	2.0159	188.1	-399.90	-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	0.0000

Table 2.

Pure Fluid Parameters for the Park-Gasem-Robinson Equation of State

No.	Compound	T* (K)	v* (cm^3/mol)	c
1	Methane	81.217	20.413	1.0000
2	Ethane	116.67	27.809	1.3459
3	Propane	137.74	37.752	1.4821
9	Octane	180.89	79.449	2.5204
12	Cyclohexane	189.76	50.448	1.9383
17	Benzene	196.03	44.800	1.8007
18	Toluene	203.28	55.991	1.9281
22	trans-Decalin	207.06	123.79	2.4176

EQUATION OF STATE SOFTWARE

The enthalpy departure models for the PR EOS was incorporated into the 'GEOS' program by Rastogi (4). GEOS is thermodynamic software package for calculating volumetric, phase equilibrium and calorimetric properties (22). The software has the capability to handle multiple systems simultaneously. To validate the enthalpy departures generated by GEOS, Rastogi compared his results with similar predictions by the ASPEN PLUS™ simulator. Good agreement was found between the enthalpy values reported by GEOS and ASPEN PLUS™. Some minor changes were made to the input and output of GEOS software. Many test cases were run to confirm the integrity of the software.

The PGR EOS was also incorporated into GEOS for enthalpy departure data. Comparing the results for methane produced by Row (14) validated these data.

The program inputs needed to perform the enthalpy departure predictions and to make 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. In the enthalpy departure predictions, the "raw ability" of the PR EOS was employed, in that, the mixing rules with no interaction parameters were used ($C_{ij} = 0$).

CHAPTER III

METHODOLOGY OF ENTHALPY DATA SCREENING

This chapter is contains an outline of the tools needed to interpret the results of the evaluation completed on the Gas Processors Association (GPA) databank. Two example cases are also presented. The utilized tools are as follows:

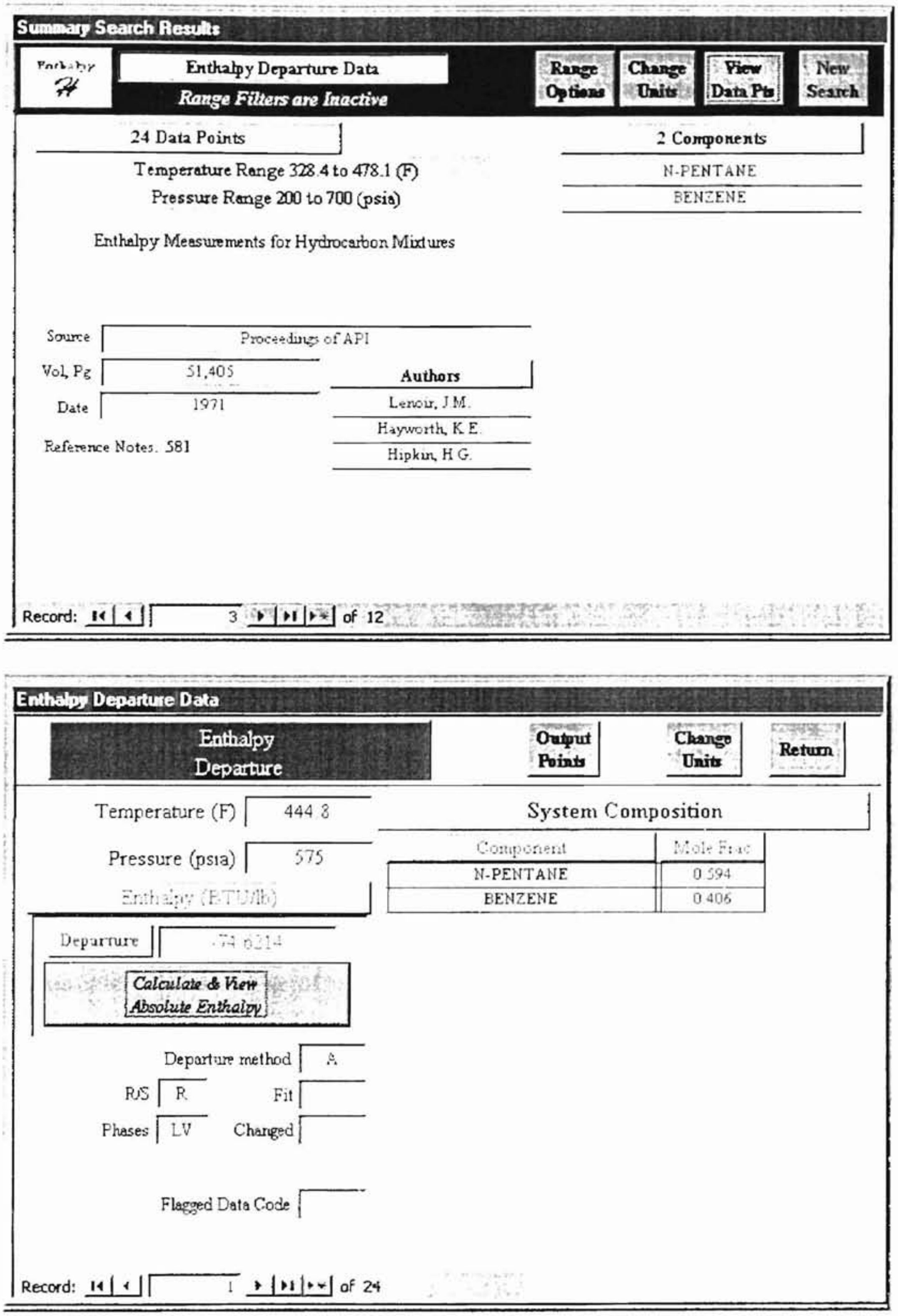
- Direct checks of the correctness of the GPA enthalpy database. Typical checks are titles of references, reference numbers, names of components and weight fractions, although this list is not totally inclusive of all search criteria.
- Necessary screening criteria for the equation of state evaluation of the database.
- Graphical methods to aid in the equation-of-state criteria.

The example cases are as follows:

- Liquid cyclohexane, and
- Vapor benzene (0.406) + pentane (0.597).

DIRECT EVALUATION OF ENTHALPY DEPARTURE DATA

Many items were verified against the original references for every enthalpy data set in the GPA database. Figure 1 shows an example of the enthalpy data screens in the GPA database. The screen at the top of the page contains information on the data set. It includes the composition of the data, the reference for the data set, temperature and



Enthalpy Departure Data

Range Filters are Inactive

24 Data Points

Temperature Range 328.4 to 478.1 (F)

Pressure Range 200 to 700 (psia)

Enthalpy Measurements for Hydrocarbon Mixtures

2 Components

N-PENTANE

BENZENE

Source: Proceedings of API

Vol, Pg: 51,405

Date: 1971

Reference Notes: 581

Authors

Lenoir, J.M.

Hayworth, K.E.

Hipkin, H.G.

Enthalpy Departure

Temperature (F): 444.8

Pressure (psia): 575

Enthalpy (BTU/lb)

Departure: -74.6214

Departure method: A

R/S: R

Fit:

Phases: LV

Changed:

Flagged Data Code:

System Composition

Component	Mole Frac
N-PENTANE	0.594
BENZENE	0.406

Figure 1. Example Enthalpy Departure Data Screens from the GPA Database

pressure range of the data and the number of points. All this information can be compared to the original source. The screen at the bottom of the page contains the specific information for each individual point. All information can be checked against the original reference, except for the enthalpy departure value.

Several errors were located during this process. Most errors were likely typographical. Tables 3, 4 and 5 outline the errors found during the initial direct check of the databank to the original references. All errors listed in the following tables, which were possible to resolve, have been corrected in the database.

DATA SCREENING USING EQUATIONS OF STATE

The GPA converted all the enthalpy data one of two reference states in order to eliminate variation in the reported data. In 1974, Cochran and Lenoir (23) devised techniques for data conversion to two reference states (23): the ideal gas state at 0 K, and the elemental states at 25°C. This helps make the data consistent; however, it makes direct point-by-point checks of the enthalpy values with the original references almost impossible. An equation of state had to be employed in order to do a point-by-point check. All references used in the GPA enthalpy departure database are listed in Appendix A.

The Peng-Robinson enthalpy model was chosen for the evaluation. Reasons for choosing this model were discussed in Chapter II. Approximately fifteen thousand single phase data points were screened. In order to screen the data, a list of criteria had to be

Table 3.

Errors Located During Direct Evaluation of Enthalpy Data for Pure Fluids

No.	Error
1.	The following reference numbers were found to have no citation associated citation: 368 375
2.	For the n-heptane system: Reference 556 is not correct, change to 666.
3.	For the iso-Pentane system: This system is actually n-Pentane
4.	For the Methylcyclohexane system: Reference 675 is incorrect.. The correct reference could not be located. Since this reference only contains two data points, the suggested action is to remove this system from the database. Reference 375 has no citation. The citation could not be located. Since this reference only contains one data point, the suggested action is to remove this system from the database.
5.	For reference 667: Add the following boldface word to the title GPA Experimental **Enthalpy** Values ..
6.	For reference 684: Change the page number from pg. 461 to 476. Correct the title from **Enthalpies** to **Enthalpy**.
7.	For reference 686: Add the following boldface words to the title: Thermodynamic Properties of Pure Hydrogen **Sulfide and Mixtures Containing Hydrogen Sulfide** with Methane, ...
8.	For references 579, 580, 581, 584 and 663: Change the source from "Proceedings of API" to "Proceedings - Division of Refining", this is the title of the journal and the American Petroleum Institute (API) is the publisher

Table 4.

Errors Located During Direct Evaluation of Enthalpy Data for Binary Mixtures

No.	Error
1.	Reference 368 has no associated citation in the database.
2.	For the Methane + Propane system: Reference 666 and 680 need to be changed to 667 Reference 368 has no citation. This system contains only one data point, the suggested action is to remove it from the database.
3.	In the following systems, iso-Pentane should be changed to n-Pentane iso-Pentane + Cyclohexane iso-Pentane + trans-Decalin iso-Pentane + 1,2,3,4-Tetrahydronaphthalene iso-Pentane + Benzene iso-Pentane + n-Hexadecane iso-Pentane + n-Octane iso-Pentane + cis-2-Pentene
4.	For the iso-Pentane + Cyclohexane system: Reference 673 is not correct, change to 677
5.	For the Propane + n-Pentane system Change n-Pentane to iso-Pentane
6.	For the Methane + iso-Butene system: Reference 670 is incorrect. The correct reference was not located. Since the system contains only two data points, the suggested action is to remove it from the database
7.	The following references could not be checked: For the Methane + Propane system: 370 For the Ethane + Propane system: 671

Table 5.

Errors Located During Direct Evaluation of Enthalpy Data for Multicomponent Mixtures

No.	Error
1.	For the iso-Pentane + Cyclohexane + Benzene system: Change iso-Pentane to n-Pentane Reference 684 is incorrect, change to 683
2.	The following references have not been verified: For the Methane + Ethane + Propane system: 574 671 For the iso-Pentane + Cyclohexane + Benzene system: 665 - Private Communication

developed. The criteria had to identify data points whose differences between reported and predicted deviation were larger than expected within a data set. Table 6 shows the criteria developed by Rastogi (4) and used in this evaluation.

When using an equation of state to predict enthalpy, the researcher needs to be aware of some potential pitfalls. Special attention needed to be paid at the critical point, near the phase envelope and at areas in high temperature and high pressure. This work typically saw large deviations in those areas. Without reliable predictions, the data could only be flagged. No determination could be made whether this data were outliers or good data. The data distribution is important to help better identify these areas where the equation of state has potential problems.

GRAPHICAL EVALUATION OF ENTHALPY DEPARTURE DATA

The graphical method of evaluating the deviation of the enthalpy data complements the equation of state screening. By presenting the data on graphs, trends where the equation of state may be failing were easier to identify. Data near the phase envelope became clear, as well as data near the critical point. All the problem areas where pitfalls may exist became clear, thus helping in interpretation of the equation-of-state predictions. Development of the three-dimensional enthalpy deviation graph is discussed in detail in Chapter IV.

After applying all three tools, a good interpretation of the accuracy of the data can be accomplished. However, the analysis is still an interpretation. This requires placing suspect data into two categories: flagged data and outliers.

Table 6.

Criteria Used for the Equation of State Data Screening

No.	Criteria
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.

The flagged data are points initially identified by the four criteria listed in Table 6. If the data happens to be in a region identified as a pitfall for the equation of state, then whether the data is correct or not may not be able to be determined. Also groups of data identified by the criteria which show a progressive trend in deviation also will need to remain flagged.

Outliers are data identified by the four criteria that clearly exhibit a break from the norm for the system. Any points with over three times the root-mean-square-error are candidates for outliers. Also, singular data points showing a large, abrupt change in deviation sign within an isotherm or isobar are also good candidates for outliers. Examples of the methodology described above are covered in the next section.

EXAMPLES OF ENTHALPY DATA SCREENING METHODOLOGY

Two cases were selected for examples: 1) liquid cyclohexane and 2) vapor benzene + pentane with mole fractions of 0.406 and 0.594, respectively. These two systems were selected because they show distinctly most of the pitfalls encountered when using an equation-of-state evaluation.

Liquid Cyclohexane

The first step in screening the data is to perform a direct comparison of the system with the original reference. No errors were found when the liquid cyclohexane system was checked against the original references for the items on the two data screens shown in Figure 1.

The second step is to perform the equation-of-state evaluation. The output from this evaluation is shown in Table 7. To facilitate an evaluation, the data are sorted by reference, then pressure and lastly by temperature. The data record column corresponds to the data label number given each record in the GPA database.

In order to evaluate the data set, some benchmarks are needed. The root-mean-square-error (RMSE) for the liquid cyclohexane system is 3.0 BTU/lb. Any data point exceeding two times the RMSE will be flagged for further inspection.

The bolded points in Table 7 were marked as flagged data or outliers. Data record 56 at 181°F and 15.40 psia for reference 584 shows a deviation of -4.7 BTU/lb. This is within 2×RMSE, but shows an abrupt change in deviation sign from all the other points at the 15.4 psia isobar. Its deviation is 6 BTU/lb from the nearest point in the isobar, clearly showing this point is a potential outlier. A few data points show deviation of greater than 2×RMSE. These data records include 54, 150, 148 and 78 for reference 584 and data records 6, 20, 27, 134 and 150 for reference 677. Of these, only record 78 at 512.1°F and 1000.0 psia exceeds 3×RMSE with a deviation of 10.7 BTU/lb, making it a potential outlier

The third stage of the evaluation is to plot the deviations of the data records as functions of to temperature and pressure. Figure 2 shows this deviation plot. The development of this figure is discussed in detail in Chapter IV.

The figure reveals the true situations of the data in question. Point 56 at 181°F and 15.40 psia is represented as the blue data point on Figure 2. Not only does no other data point in the 15.4 psia isobar show negative deviation, no point below 240°F at all

Table 7.

Output for Peng-Robinson Equation of State for Enthalpy Data of Liquid Cyclohexane

```
DATA  TEMP      PRESS      H(L)        H CALC       DEV        %DEV    L/N   REF
(F)   (PSIA)  (BTU/LB)  (BTU/LB)     (BTU/LB)

 53   117.00   15.40   -161.7000   -158.9465    2.7535     -1.70   1.000 584
 52   130.10   15.40   -160.6000   -157.5543    3.0457     -1.90   1.000 584
 51   138.80   15.40   -158.5000   -156.6216    1.8784     -1.19   1.000 584
 50   145.20   15.40   -157.4000   -155.6057    1.7943     -1.14   1.000 584
 49   158.00   15.40   -156.8000   -154.5370    2.2630     -1.44   1.000 584
 45   169.10   15.40   -156.0000   -153.3135    2.6865     -1.72   1.000 584
 35   172.40   15.40   -155.7000   -152.9468    2.7532     -1.77   1.000 584
 46   177.70   15.40   -155.0000   -152.3552    2.6448     -1.71   1.000 584
 56   181.80   15.40   -147.2000   -151.8949   -4.6949      3.19   1.000 584
 67   150.60  100.00   -158.6000   -155.1608    3.4392     -2.17   1.000 584
 57   199.70  100.00   -151.8000   -149.7067    2.0933     -1.38   1.000 584
 65   248.90  100.00   -145.5000   -143.8720    1.6280     -1.12   1.000 584
 75   296.20  100.00   -137.1000   -137.7287    -.6287       .46   1.000 584
 63   307.20  100.00   -136.2000   -136.1985     .0015       .00   1.000 584
 62   319.80  100.00   -133.9000   -134.3928    -.4928       .37   1.000 584
 11   150.60  200.00   -158.6000   -154.9414    3.6586     -2.31   1.000 584
  2   201.30  200.00   -151.0000   -149.3435    1.6565     -1.10   1.000 584
 10   248.70  200.00   -144.5000   -143.7723     .7277      -.50   1.000 584
 18   300.20  200.00   -137.1000   -137.1638    -.0638       .05   1.000 584
  9   349.30  200.00   -129.5000   -129.9901    -.4901       .38   1.000 584
  8   357.50  200.00   -128.6000   -128.6817    -.0817       .06   1.000 584
102   368.40  200.00   -125.8000   -126.8607   -1.0607       .84   1.000 584
  6   378.40  200.00   -125.3000   -125.1113     .1887      -.15   1.000 584
 55   382.90  200.00   -124.9000   -124.2960     .6040      -.48   1.000 584
  4   389.90  200.00   -124.3000   -122.9885    1.3115     -1.06   1.000 584
 13   151.00  400.00   -157.0000   -154.4546    2.5454     -1.62   1.000 584
 27   199.20  400.00   -151.5000   -149.2083    2.2917     -1.51   1.000 584
 37   251.40  400.00   -143.0000   -143.1840    -.1840       .13   1.000 584
 25   299.10  400.00   -136.6000   -137.2218    -.6218       .46   1.000 584
 24   349.00  400.00   -129.3000   -130.2633    -.9633       .74   1.000 584
 21   399.10  400.00   -121.8000   -122.0722    -.2722       .22   1.000 584
 20   447.80  400.00   -113.2000   -111.8204    1.3796     -1.22   1.000 584
 54   471.20  400.00   -113.6000   -105.0793    8.5207     -7.50   1.000 584
 19   151.00  588.00   -157.2000   -154.0312    3.1688     -2.02   1.000 584
118   198.30  588.00   -150.6000   -148.9456    1.6544     -1.10   1.000 584
125   248.50  588.00   -144.1000   -143.2616     .8384      -.58   1.000 584
141   298.30  588.00   -137.7000   -137.2021     .4979      -.36   1.000 584
153   347.70  588.00   -130.6000   -130.5832     .0168      -.01   1.000 584
155   393.30  588.00   -123.8000   -122.8101     .9899      -.80   1.000 584
156   447.30  588.00   -115.0000   -113.6394    1.3606     -1.18   1.000 584
152   496.50  588.00   -105.3000   -100.7420    4.5580     -4.33   1.000 584
150   519.00  588.00    -98.3000    -91.1615    7.1385     -7.26   1.000 584
148   531.10  588.00    -91.3000    -81.7299    9.5701    -10.48   1.000 584
151   479.50  700.00   -106.8000   -107.3832    -.5832       .55   1.000 584
117   499.00  700.00   -107.5000   -102.2533    5.2467     -4.88   1.000 584
 77   520.00  700.00   -100.6000    -95.4051    5.1949     -5.16   1.000 584
 92   299.70  800.00   -136.3000   -136.8527    -.5527       .41   1.000 584
 91   349.90  800.00   -129.2000   -130.3383   -1.1383       .88   1.000 584
 90   395.20  800.00   -122.1000   -123.1606   -1.0606       .87   1.000 584
```

Table 7. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Liquid Cyclohexane

DATA	TEMP	PRESS	H(L)	H CALC	DEV	%DEV	L/N	REF
(F)	(PSIA)	(BTU/LB)	(BTU/LB)	(BTU/LB)				
89	448.70	800.00	-114.0000	-114.7034	-.7034	.62	1.000	584
88	473.50	800.00	-108.1000	-109.7349	-1.6349	1.51	1.000	584
87	497.90	800.00	-106.0000	-104.0937	1.9063	-1.80	1.000	584
86	524.50	800.00	-99.5000	-96.5943	2.9057	-2.92	1.000	584
82	300.00	1000.00	-135.5000	-136.6233	-1.1233	.83	1.000	584
81	349.40	1000.00	-128.4000	-130.4079	-2.0079	1.56	1.000	584
80	398.30	1000.00	-121.7000	-123.6157	-1.9157	1.57	1.000	584
79	447.30	1000.00	-114.1000	-115.8718	-1.7718	1.55	1.000	584
78	512.10	1000.00	-113.9000	-103.1962	10.7038	-9.40	1.000	584
114	487.90	1200.00	-107.9000	-109.6791	-1.7791	1.65	1.000	584
113	508.30	1200.00	-107.2000	-105.8647	1.3353	-1.25	1.000	584
112	528.80	1200.00	-103.8000	-101.7277	2.0723	-2.00	1.000	584
109	151.70	1400.00	-155.5000	-152.0701	3.4299	-2.21	1.000	584
108	201.10	1400.00	-149.3000	-146.9851	2.3149	-1.55	1.000	584
107	250.80	1400.00	-142.3000	-141.6767	.6233	-.44	1.000	584
96	300.00	1400.00	-135.8000	-136.1596	-.3596	.26	1.000	584
105	350.00	1400.00	-128.9000	-130.1927	-1.2927	1.00	1.000	584
116	399.10	1400.00	-122.5000	-123.8605	-1.3605	1.11	1.000	584
103	448.60	1400.00	-114.3000	-116.8385	-2.5385	2.22	1.000	584
97	499.50	1400.00	-107.1000	-108.7088	-1.6088	1.50	1.000	584
57	300.00	100.00	-136.1000	-137.2052	-1.1052	.81	1.000	677
58	320.00	100.00	-133.4000	-134.3634	-.9634	.72	1.000	677
49	300.00	200.00	-136.0000	-137.1909	-1.1909	.88	1.000	677
48	320.00	200.00	-133.3000	-134.3920	-1.0920	.82	1.000	677
47	340.00	200.00	-130.6000	-131.4342	-.8342	.64	1.000	677
46	360.00	200.00	-127.8000	-128.2712	-.4712	.37	1.000	677
45	380.00	200.00	-124.9000	-124.8236	.0764	.06	1.000	677
98	400.00	300.00	-121.6000	-121.5005	.0995	-.08	1.000	677
99	420.00	300.00	-118.7000	-117.4241	1.2759	-1.07	1.000	677
100	440.00	300.00	-114.8000	-112.6882	2.1118	-1.84	1.000	677
83	300.00	400.00	-135.8000	-137.1039	-1.3039	.96	1.000	677
84	320.00	400.00	-133.1000	-134.4200	-1.3200	.99	1.000	677
85	340.00	400.00	-130.4000	-131.5879	-1.1879	.91	1.000	677
76	360.00	400.00	-127.5000	-128.5929	-1.0929	.86	1.000	677
21	380.00	400.00	-124.7000	-125.3865	-.6865	.55	1.000	677
18	400.00	400.00	-121.5000	-121.9087	-.4087	.34	1.000	677
17	420.00	400.00	-118.7000	-118.0683	.6317	-.53	1.000	677
14	440.00	400.00	-114.8000	-113.7187	1.0813	-.94	1.000	677
13	460.00	400.00	-111.3000	-108.5493	2.7507	-2.47	1.000	677
2	480.00	400.00	-106.5000	-101.8532	4.6468	-4.36	1.000	677
6	500.00	500.00	-103.2000	-96.6305	6.5695	-6.37	1.000	677
30	500.00	588.00	-103.9000	-99.5151	4.3849	-4.22	1.000	677
20	520.00	588.00	-98.1000	-90.5893	7.5107	-7.66	1.000	677
27	530.00	588.00	-92.3000	-82.9771	9.3229	-10.10	1.000	677
149	520.00	700.00	-100.4000	-95.4051	4.9949	-4.98	1.000	677
134	530.00	700.00	-97.7000	-91.3166	6.3834	-6.53	1.000	677
150	540.00	700.00	-95.0000	-86.2663	8.7337	-9.19	1.000	677
139	300.00	800.00	-135.4000	-136.8156	-1.4156	1.05	1.000	677
138	320.00	800.00	-132.7000	-134.2956	-1.5956	1.20	1.000	677

Table 7. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Liquid Cyclohexane

```
DATA  TEMP     PRESS      H(L)        H CALC       DEV         %DEV    L/N    REF
(F)   (PSIA)   (BTU/LB) (BTU/LB)     (BTU/LB)

137  340.00   800.00  -129.9000   -131.6765   -1.7765       1.37  1.000 677
136  360.00   800.00  -127.0000   -128.9415   -1.9415       1.53  1.000 677
138  380.00   800.00  -124.5000   -126.0699   -1.5699       1.26  1.000 677
140  400.00   800.00  -121.3000   -123.0358   -1.7358       1.43  1.000 677
154  420.00   800.00  -118.6000   -119.7922   -1.1922       1.01  1.000 677
165  440.00   800.00  -115.0000   -116.3103   -1.3103       1.14  1.000 677
164  460.00   800.00  -111.9000   -112.5174    -.6174        .55  1.000 677
163  480.00   800.00  -108.1000   -108.3177    -.2177        .20  1.000 677
162  500.00   800.00  -104.6000   -103.5620    1.0380       -.99  1.000 677
161  520.00   800.00  -100.9000    -97.9986    2.9014      -2.88  1.000 677
160  530.00   800.00   -99.0000    -94.7812    4.2188      -4.26  1.000 677
159  540.00   800.00   -96.6000    -91.1554    5.4446      -5.64  1.000 677
119  500.00 1000.00  -106.0000   -105.8584     .1416       -.13  1.000 677
121  520.00 1000.00  -101.7000   -101.3609     .3391       -.33  1.000 677
148  530.00 1000.00  -100.6000    -98.9122    1.6878      -1.68  1.000 677
115  540.00 1000.00   -99.1000    -96.3048    2.7952      -2.82  1.000 677
109  300.00 1400.00  -134.8000   -136.1596   -1.3596       1.01  1.000 677
108  320.00 1400.00  -132.1000   -133.8225   -1.7225       1.30  1.000 677
107  340.00 1400.00  -129.4000   -131.4205   -2.0205       1.56  1.000 677
106  360.00 1400.00  -126.3000   -128.9464   -2.6464       2.10  1.000 677
105  380.00 1400.00  -124.1000   -126.3886   -2.2886       1.84  1.000 677
103  400.00 1400.00  -121.1000   -123.7391   -2.6391       2.18  1.000 677
116  420.00 1400.00  -118.6000   -120.9853   -2.3853       2.01  1.000 677
125  440.00 1400.00  -115.1000   -118.1135   -3.0135       2.62  1.000 677
132  460.00 1400.00  -112.7000   -115.1081   -2.4081       2.14  1.000 677
131  480.00 1400.00  -110.4000   -111.9515   -1.5515       1.41  1.000 677
130  500.00 1400.00  -108.0000   -108.6234    -.6234        .58  1.000 677
129  520.00 1400.00  -105.2000   -105.1016     .0984       -.09  1.000 677
128  530.00 1400.00  -103.7000   -103.2608     .4392       -.42  1.000 677
127  540.00 1400.00  -102.2000   -101.3629     .8371       -.82  1.000 677

   C(1,2), D(1,2) =  .00000E+00   .00000E+00
   E(1)......E(N) =  .00000E+00   .00000E+00   .00000E+00  .00000E+00
                     .00000E+00   .00000E+00

   HENRY(BAR =       .0000              VIPM(CC/MOLE,=    .0000

   RMSE =     3.0055 BTU/lb  AAD =    2.1452            %AAD =     1.86
   BIAS =      .9159                                    NPTS =   128
```

pressures for the data show negative deviation. Clearly, data record 56 for reference 584 is an outlier

Next, look at the data records exceeding 2×RMSE, excluding data record 78 for now. These data points are in green on Figure 2. Even though these data exceed 2×RMSE, a definite trend in deviation can be seen as the data goes to high temperature and low pressure for this data set. This rise in deviation is probably caused from limitations in the equation of state, which gives poor predictions in the critical region ($T_c \approx 540°F$, $p_c \approx 590$ psia for cyclohexane). Unfortunately, they also may be caused by a systematic error in the experimental data. No conclusions for these data are made and the data remain flagged.

Finally, look at point 78 at 512.1°F and 1000.0 psia. This point shows deviation exceeding 3×RMSE. No other data point along the 1000.0 psia isobar shows deviations exceeding 2×RMSE. Even though some data in the same temperature range exceeds 2×RMSE, the pressure must drop 300 psia before these points are reached. This data point can be quickly identified as an outlier

Vapor Benzene(0.406) + Pentane(0.594)

Again, the evaluation begins with a direct comparison of the system to the original reference. The system was originally found to be incorrect. As listed in Table 4, the system was originally identified as isopentane. When the reference was checked, it was found this data was actually for benzene + pentane. No other errors were found

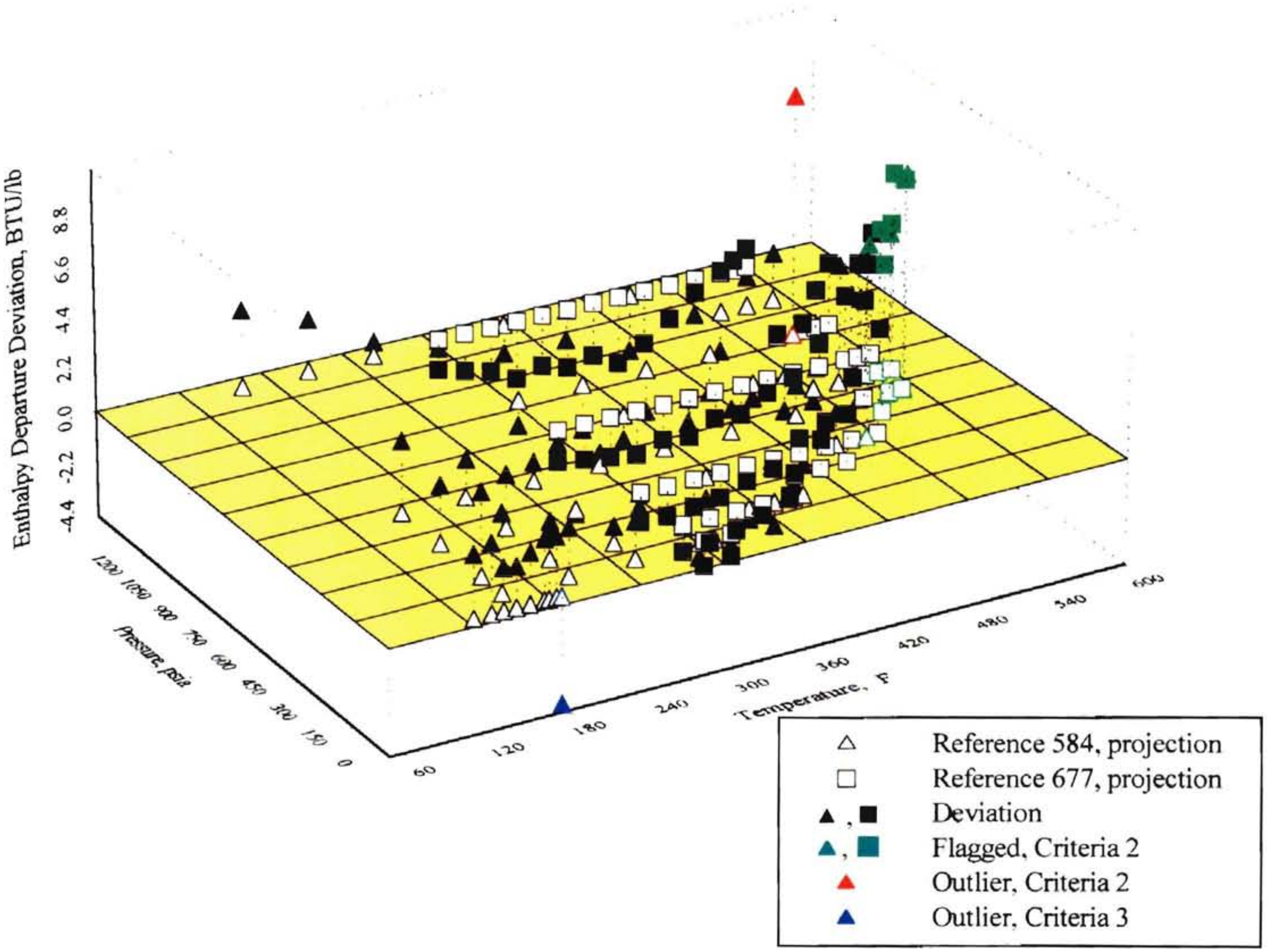


Figure 2. Enthalpy Departure Deviations for Liquid Cyclohexane, Generated by the Peng-Robinson Equation of State

Next the equation-of-state evaluation is performed. The output from this evaluation is shown in Table 8. The data are sorted by reference, then pressure and lastly by temperature as for liquid cyclohexane. The data record column corresponds to the data label number given each record in the GPA database.

In order to evaluate the data set, some benchmarks are needed. The root-mean-square-error (RMSE) for the liquid cyclohexane system is 7.0 BTU/lb. Any data point exceeding two times the RMSE will be flagged.

The bolded points in Table 8 were marked as flagged data or outliers. Data records 129 for reference 584, along with data records 97, 69, 70, 71, 72, 173 and 174 for reference 681 all show deviations over 2×RMSE. Data records 73, 74, 85, 86, 168 and 177 for reference 681 all show deviations exceeding 3×RMSE. All these data records are flagged and need to be checked graphically to see if any should be considered outliers. Figure 3 shows this deviation plot.

The figure reveals all the data points in question reside in the same area of temperature and pressure. These data points are shown in green on Figure 3. A deviation trend can be easily seen on this plot. Looking at the entire data set, the lower bound of the data seems to be following along a phase envelope. The equation of state may be predicting the phase change from vapor to two-phase a little early. Or, the samples may have been flashing during data collection. Vapor-liquid-equilibrium data would help clarify the phase envelope location. With the data being at what may be the top of the

Table 8.

Output for Peng-Robinson Equation of State for Enthalpy Data of Vapor Benzene(0.406) + Pentane(0.594)

DATA (F)	TEMP (PSIA)	PRESS (BTU/LB)	H(L) (BTU/LB)	H CALC (BTU/LB)	DEV	%DEV	L/N	REF
22	459.80	700.00	-88.6062	-78.2250	10.3812	-11.72	.000	581
21	464.30	700.00	-85.1900	-76.3253	8.8647	-10.41	.000	581
23	469.60	700.00	-79.6091	-73.6321	5.9770	-7.51	.000	581
24	478.10	700.00	-67.9546	-65.4016	2.5530	-3.76	.000	581
70	205.50	25.00	-3.7409	-2.0613	1.6796	-44.90	.000	584
69	249.30	25.00	-5.9142	-1.8650	4.0492	-68.47	.000	584
68	301.40	25.00	-7.7920	-1.6676	6.1244	-78.60	.000	584
67	349.50	25.00	-6.4958	-1.5126	4.9832	-76.71	.000	584
66	398.50	25.00	-7.8899	-1.3760	6.5139	-82.56	.000	584
64	448.00	25.00	-4.9954	-1.2557	3.7397	-74.86	.000	584
63	499.90	25.00	-7.4490	-1.1452	6.3038	-84.63	.000	584
57	548.60	25.00	-7.0012	-1.0536	5.9476	-84.95	.000	584
62	598.20	25.00	-7.7283	-.9705	6.7578	-87.44	.000	584
71	648.00	25.00	-6.1316	-.8958	5.2358	-85.39	.000	584
61	692.90	25.00	-4.3230	-.8348	3.4882	-80.69	.000	584
10	366.30	200.00	-20.1367	-13.6716	6.4651	-32.11	.000	584
16	386.50	200.00	-20.1914	-12.9138	7.2776	-36.04	.000	584
25	402.40	200.00	-21.4534	-12.3755	9.0779	-42.31	.000	584
14	449.40	200.00	-19.8291	-11.0221	8.8070	-44.41	.000	584
13	500.70	200.00	-19.3855	-9.8303	9.5552	-49.29	.000	584
31	547.20	200.00	-16.6099	-8.9324	7.6775	-46.22	.000	584
11	596.90	200.00	-17.5684	-8.1144	9.4540	-53.81	.000	584
36	401.00	300.00	-27.3479	-20.7402	6.6077	-24.16	.000	584
35	403.80	300.00	-26.1597	-20.5305	5.6292	-21.52	.000	584
34	408.00	300.00	-26.4839	-20.2306	6.2533	-23.61	.000	584
15	449.20	300.00	-23.4243	-17.7677	5.6566	-24.15	.000	584
32	501.00	300.00	-23.8494	-15.4785	8.3709	-35.10	.000	584
49	550.20	300.00	-23.4060	-13.7990	9.6070	-41.05	.000	584
53	424.60	400.00	-33.1541	-29.0119	4.1422	-12.49	.000	584
52	450.30	400.00	-31.9014	-25.9398	5.9616	-18.69	.000	584
51	500.50	400.00	-27.2764	-21.9043	5.3721	-19.69	.000	584
42	548.50	400.00	-26.6445	-19.2123	7.4322	-27.89	.000	584
50	597.30	400.00	-25.7019	-17.1043	8.5976	-33.45	.000	584
5	446.60	500.00	-43.7625	-38.5038	5.2587	-12.02	.000	584
4	452.00	500.00	-44.6941	-37.0826	7.6115	-17.03	.000	584
2	478.00	500.00	-40.1006	-32.2471	7.8535	-19.58	.000	584
41	497.80	500.00	-33.6040	-29.6966	3.9074	-11.63	.000	584
93	474.10	600.00	-45.8118	-45.9073	-.0955	.21	.000	584
94	479.50	600.00	-42.9058	-43.9475	-1.0417	2.43	.000	584
87	498.40	600.00	-38.1311	-39.0397	-.9086	2.38	.000	584
88	548.40	600.00	-30.4878	-31.6205	-1.1327	3.72	.000	584
74	595.90	600.00	-27.9844	-27.2979	.6865	-2.45	.000	584
86	649.60	600.00	-25.8987	-23.7808	2.1179	-8.18	.000	584
95	692.20	600.00	-25.0889	-21.5913	3.4976	-13.94	.000	584
89	482.10	660.00	-52.0037	-47.4902	4.5135	-8.68	.000	584
119	491.50	660.00	-47.6809	-48.5501	-.8692	1.82	.000	584
90	502.70	660.00	-43.5779	-44.7955	-1.2176	2.79	.000	584
96	550.40	660.00	-36.1189	-35.6162	.5027	-1.39	.000	584
129	481.20	800.00	-84.5193	-67.4228	17.0965	-20.23	.000	584
128	491.80	800.00	-74.6433	-64.4507	10.1926	-13.66	.000	584

Table 8. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Vapor Benzene(0.406) + Pentane(0.594)

```
DATA  TEMP     PRESS      H(L)       H CALC        DEV        %DEV    L/N   REF
 (F)  (PSIA)  (BTU/LB)  (BTU/LB)    (BTU/LB)

 127  500.30  800.00    -67.3672   -62.0164    5.3508     -7.94    .000 584
 126  519.80  800.00    -56.5867   -55.6102     .9765     -1.73    .000 584
 125  550.00  800.00    -47.4927   -46.5520     .9407     -1.98    .000 584
 122  596.70  800.00    -39.6206   -38.2438    1.3768     -3.47    .000 584
  98  480.30 1000.00    -90.5359   -78.7705   11.7654    -13.00    .000 584
  99  548.60 1000.00    -62.8013   -62.9621    -.1608       .26    .000 584
 100  598.70 1000.00    -49.9204   -49.8872     .0332      -.07    .000 584
 101  648.80 1000.00    -44.0149   -41.9533    2.0616     -4.68    .000 584
 112  692.20 1000.00    -39.6890   -37.1061    2.5829     -6.51    .000 584
 109  501.20 1400.00    -92.3584   -87.3442    5.0142     -5.43    .000 584
 110  549.40 1400.00    -80.0532   -79.8032     .2500      -.31    .000 584
 111  598.40 1400.00    -69.3452   -68.4698     .8754     -1.26    .000 584
 116  649.20 1400.00    -59.2566   -57.9871    1.2695     -2.14    .000 584
 113  693.90 1400.00    -53.9438   -50.9319    3.0119     -5.58    .000 584
  44  340.00  200.00    -16.3000   -14.8173    1.4827     -9.10    .000 681
  43  360.00  200.00    -15.5000   -13.9279    1.5721    -10.14    .000 681
  42  380.00  200.00    -14.5000   -13.1478    1.3522     -9.33    .000 681
  34  400.00  200.00    -13.1000   -12.4539     .6461     -4.93    .000 681
  40  410.00  200.00    -12.9000   -12.1367     .7633     -5.92    .000 681
  49  420.00  200.00    -12.6000   -11.8336     .7664     -6.08    .000 681
  38  430.00  200.00    -12.0000   -11.5450     .4550     -3.79    .000 681
  37  440.00  200.00    -11.5000   -11.2697     .2303     -2.00    .000 681
  36  450.00  200.00    -11.2000   -11.0067     .1933     -1.73    .000 681
  56  460.00  200.00    -10.7000   -10.7549    -.0549       .51    .000 681
  20  470.00  200.00    -10.2000   -10.5135    -.3135      3.07    .000 681
  39  480.00  200.00     -9.9000   -10.2818    -.3818      3.86    .000 681
  35  490.00  200.00     -9.5000   -10.0592    -.5592      5.89    .000 681
  41  500.00  200.00     -9.4000    -9.8450    -.4450      4.73    .000 681
  65  520.00  200.00     -7.9000    -9.4396   -1.5396     19.49    .000 681
  64  540.00  200.00     -7.5000    -9.0621   -1.5621     20.83    .000 681
  63  560.00  200.00     -6.7000    -8.7092   -2.0092     29.99    .000 681
  62  580.00  200.00     -6.0000    -8.3784   -2.3784     39.64    .000 681
  61  600.00  200.00     -5.5000    -8.0674   -2.5674     46.68    .000 681
  60  620.00  200.00     -5.2000    -7.7743   -2.5743     49.51    .000 681
  59  640.00  200.00     -5.2000    -7.4974   -2.2974     44.18    .000 681
  50  660.00  200.00     -4.9000    -7.2353   -2.3353     47.66    .000 681
  57  680.00  200.00     -4.3000    -6.9868   -2.6868     62.48    .000 681
  66  700.00  200.00     -4.0000    -6.7508   -2.7508     68.77    .000 681
  52  380.00  300.00    -23.3000   -22.5019     .7981     -3.43    .000 681
  51  400.00  300.00    -21.3000   -20.8156     .4844     -2.27    .000 681
  58  410.00  300.00    -20.9000   -20.0917     .8083     -3.87    .000 681
  21  420.00  300.00    -20.3000   -19.4311     .8689     -4.28    .000 681
  15  430.00  300.00    -19.4000   -18.8213     .5787     -2.98    .000 681
  14  440.00  300.00    -18.6000   -18.2552     .3448     -1.85    .000 681
  13  450.00  300.00    -18.0000   -17.7264     .2736     -1.52    .000 681
  11  460.00  300.00    -17.2000   -17.2325    -.0325       .19    .000 681
  16  470.00  300.00    -16.5000   -16.7671    -.2671      1.62    .000 681
  10  480.00  300.00    -15.9000   -16.3279    -.4279      2.69    .000 681
   9  490.00  300.00    -15.0000   -15.9119    -.9119      6.08    .000 681
   8  500.00  300.00    -14.4000   -15.5169   -1.1169      7.76    .000 681
```

Table 8. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Vapor Benzene(0.406) + Pentane(0.594)

DATA (F)	TEMP (PSIA)	PRESS (BTU/LB)	H(L) (BTU/LB)	H CALC (BTU/LB)	DEV	%DEV	L/N	REF
7	520.00	300.00	-12.7000	-14.7858	-2.0858	16.42	.000	681
2	540.00	300.00	-12.1000	-14.1179	-2.0179	16.68	.000	681
3	560.00	300.00	-11.0000	-13.5049	-2.5049	22.77	.000	681
4	580.00	300.00	-10.0000	-12.9390	-2.9390	29.39	.000	681
1	600.00	300.00	-8.5000	-12.4140	-3.9140	46.05	.000	681
32	410.00	400.00	-31.9000	-31.4279	.4721	-1.48	.000	681
31	420.00	400.00	-31.0000	-29.6977	1.3023	-4.20	.000	681
30	430.00	400.00	-29.2000	-28.2712	.9288	-3.18	.000	681
29	440.00	400.00	-27.7000	-27.0462	.6538	-2.36	.000	681
28	450.00	400.00	-26.4000	-25.9701	.4299	-1.63	.000	681
23	460.00	400.00	-24.9000	-25.0090	-.1090	.44	.000	681
27	470.00	400.00	-23.4000	-24.1397	-.7397	3.16	.000	681
12	480.00	400.00	-22.1000	-23.3443	-1.2443	5.63	.000	681
26	490.00	400.00	-20.7000	-22.6142	-1.9142	9.25	.000	681
17	500.00	400.00	-19.5000	-21.9369	-2.4369	12.50	.000	681
24	520.00	400.00	-17.8000	-20.7145	-2.9145	16.37	.000	681
33	540.00	400.00	-16.8000	-19.6354	-2.8354	16.88	.000	681
22	560.00	400.00	-15.4000	-18.6692	-3.2692	21.23	.000	681
19	580.00	400.00	-14.0000	-17.7946	-3.7946	27.10	.000	681
18	600.00	400.00	-12.4000	-17.0009	-4.6009	37.10	.000	681
48	620.00	400.00	-11.6000	-16.2704	-4.6704	40.26	.000	681
132	640.00	400.00	-10.6000	-15.5961	-4.9961	47.13	.000	681
147	660.00	400.00	-9.9000	-14.9704	-5.0704	51.22	.000	681
148	680.00	400.00	-9.0000	-14.3875	-5.3875	59.86	.000	681
149	700.00	400.00	-8.7000	-13.8424	-5.1424	59.11	.000	681
154	440.00	500.00	-41.4000	-40.6388	.7612	-1.84	.000	681
155	450.00	500.00	-38.3000	-37.5827	.7173	-1.87	.000	681
156	460.00	500.00	-35.3000	-35.3184	-.0184	.05	.000	681
157	470.00	500.00	-32.9000	-33.4924	-.5924	1.80	.000	681
158	480.00	500.00	-30.8000	-31.9585	-1.1585	3.76	.000	681
159	490.00	500.00	-28.8000	-30.6270	-1.8270	6.34	.000	681
160	500.00	500.00	-27.1000	-29.4486	-2.3486	8.67	.000	681
153	520.00	500.00	-25.2000	-27.4297	-2.2297	8.85	.000	681
137	540.00	500.00	-23.6000	-25.7361	-2.1361	9.05	.000	681
131	560.00	500.00	-21.3000	-24.2776	-2.9776	13.98	.000	681
151	580.00	500.00	-19.5000	-22.9957	-3.4957	17.93	.000	681
133	600.00	500.00	-17.7000	-21.8531	-4.1531	23.46	.000	681
134	620.00	500.00	-16.3000	-20.8225	-4.5225	27.75	.000	681
130	450.00	560.00	-52.1000	-50.3332	1.7668	-3.39	.000	681
138	460.00	560.00	-45.1000	-44.4686	.6314	-1.40	.000	681
139	470.00	560.00	-40.3000	-41.0096	-.7096	1.76	.000	681
140	480.00	560.00	-37.1000	-38.4695	-1.3695	3.69	.000	681
141	490.00	560.00	-34.2000	-36.4367	-2.2367	6.54	.000	681
142	500.00	560.00	-32.4000	-34.7308	-2.3308	7.19	.000	681
144	450.00	575.00	-55.8000	-52.8139	2.9861	-5.35	.000	681
135	460.00	575.00	-47.1000	-47.5988	-.4988	1.06	.000	681
167	450.00	600.00	-82.7000	-69.1167	13.5833	-16.42	.000	681
179	460.00	600.00	-57.0000	-54.5877	2.4123	-4.23	.000	681
180	470.00	600.00	-47.8000	-47.7105	.0895	-.19	.000	681
181	480.00	600.00	-43.0000	-43.7837	-.7837	1.82	.000	681

Table 8. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Vapor Benzene(0.406) + Pentane(0.594)

DATA (F)	TEMP (PSIA)	PRESS (BTU/LB)	H(L) (BTU/LB)	H CALC (BTU/LB)	DEV	%DEV	L/N	REF
182	490.00	600.00	-39.1000	-40.9516	-1.8516	4.74	.000	681
193	500.00	600.00	-36.5000	-38.7103	-2.2103	6.06	.000	681
184	520.00	600.00	-32.6000	-35.2426	-2.6426	8.11	.000	681
178	540.00	600.00	-29.6000	-32.5807	-2.9807	10.07	.000	681
186	560.00	600.00	-27.0000	-30.4110	-3.4110	12.63	.000	681
187	580.00	600.00	-25.1000	-28.5768	-3.4768	13.85	.000	681
188	600.00	600.00	-22.9000	-26.9892	-4.0892	17.86	.000	681
189	620.00	600.00	-21.2000	-25.5865	-4.3865	20.69	.000	681
190	640.00	600.00	-19.7000	-24.3373	-4.6373	23.54	.000	681
191	660.00	600.00	-17.9000	-23.2062	-5.3062	29.64	.000	681
192	680.00	600.00	-16.2000	-22.1744	-5.9744	36.88	.000	681
185	700.00	600.00	-15.0000	-21.2321	-6.2321	41.55	.000	681
177	450.00	660.00	-90.8000	-55.1947	35.6053	-39.21	.000	681
168	460.00	660.00	-80.8000	-52.4030	28.3970	-35.14	.000	681
162	470.00	660.00	-62.2000	-49.9066	12.2934	-19.76	.000	681
170	480.00	660.00	-52.8000	-47.7518	5.0482	-9.56	.000	681
171	490.00	660.00	-47.8000	-49.1586	-1.3586	2.84	.000	681
172	500.00	660.00	-44.5000	-45.5973	-1.0973	2.47	.000	681
173	450.00	700.00	-95.5000	-76.5177	18.9823	-19.88	.000	681
174	460.00	700.00	-88.8000	-73.4005	15.3995	-17.34	.000	681
175	470.00	700.00	-79.2000	-69.0917	10.1083	-12.76	.000	681
176	480.00	700.00	-65.2000	-63.4973	1.7027	-2.61	.000	681
103	490.00	700.00	-55.4000	-55.8733	-.4733	.85	.000	681
83	500.00	700.00	-51.3000	-50.9397	.3603	-.70	.000	681
68	520.00	700.00	-43.3000	-44.5819	-1.2819	2.96	.000	681
47	540.00	700.00	-38.0000	-40.3361	-2.3361	6.15	.000	681
143	560.00	700.00	-33.7000	-37.1374	-3.4374	10.20	.000	681
84	580.00	700.00	-30.2000	-34.5636	-4.3636	14.45	.000	681
85	460.00	800.00	-94.5000	-71.2961	23.2039	-24.55	.000	681
86	470.00	800.00	-90.4000	-69.1105	21.2895	-23.55	.000	681
97	480.00	800.00	-85.0000	-66.6432	18.3568	-21.60	.000	681
88	490.00	800.00	-76.0000	-63.9614	12.0386	-15.84	.000	681
82	500.00	800.00	-66.1000	-61.2184	4.8816	-7.39	.000	681
90	520.00	800.00	-53.8000	-55.5303	-1.7303	3.22	.000	681
91	540.00	800.00	-46.3000	-49.0219	-2.7219	5.88	.000	681
92	560.00	800.00	-40.4000	-44.4321	-4.0321	9.98	.000	681
93	580.00	800.00	-36.0000	-40.9177	-4.9177	13.66	.000	681
94	600.00	800.00	-32.6000	-38.0747	-5.4747	16.79	.000	681
95	620.00	800.00	-29.8000	-35.6873	-5.8873	19.76	.000	681
96	640.00	800.00	-27.2000	-33.6407	-6.4407	23.68	.000	681
67	660.00	800.00	-25.0000	-31.8447	-6.8447	27.38	.000	681
81	680.00	800.00	-23.0000	-30.2434	-7.2434	31.49	.000	681
87	700.00	800.00	-21.7000	-28.8113	-7.1113	32.77	.000	681
74	450.00	1000.00	-99.9000	-76.9127	22.9873	-23.01	.000	681
73	460.00	1000.00	-97.0000	-75.5070	21.4930	-22.16	.000	681
72	470.00	1000.00	-94.0000	-74.0321	19.9679	-21.24	.000	681
71	480.00	1000.00	-90.8000	-72.4826	18.3174	-20.17	.000	681
70	490.00	1000.00	-86.9000	-70.8564	16.0436	-18.46	.000	681
69	500.00	1000.00	-83.4000	-69.1580	14.2420	-17.08	.000	681

Table 8. (Continued)

Output for Peng-Robinson Equation of State for Enthalpy Data of Vapor Benzene(0.406) + Pentane(0.594)

```
DATA  TEMP     PRESS       H(L)        H CALC       DEV         %DEV    L/N    REF
 (F)  (PSIA)  (BTU/LB)  (BTU/LB)     (BTU/LB)

 103  520.00 1000.00    -72.5000    -65.6000    6.9000       -9.52    .000 681
  80  540.00 1000.00    -62.6000    -61.9839     .6161        -.98    .000 681
  89  560.00 1000.00    -54.2000    -58.5276   -4.3276        7.98    .000 681
 115  580.00 1000.00    -47.8000    -53.9343   -6.1343       12.83    .000 681
 116  600.00 1000.00    -43.1000    -49.6337   -6.5337       15.16    .000 681
 117  620.00 1000.00    -40.0000    -46.1007   -6.1007       15.25    .000 681
 118  640.00 1000.00    -37.2000    -43.1273   -5.9273       15.93    .000 681
 129  660.00 1000.00    -34.2000    -40.5706   -6.3706       18.63    .000 681
 120  680.00 1000.00    -32.0000    -38.3395   -6.3395       19.81    .000 681
 114  700.00 1000.00    -30.0000    -36.3571   -6.3571       21.19    .000 681
 121  450.00 1400.00   -103.8000    -94.0997    9.7003       -9.35    .000 681
 105  460.00 1400.00   -101.9000    -92.7342    9.1658       -8.99    .000 681
  99  470.00 1400.00    -99.7000    -91.3467    8.3533       -8.38    .000 681
 119  480.00 1400.00    -97.7000    -89.9349    7.7651       -7.95    .000 681
 101  490.00 1400.00    -95.1000    -88.4968    6.6032       -6.94    .000 681
 102  500.00 1400.00    -92.7000    -87.0304    5.6696       -6.12    .000 681
 113  520.00 1400.00    -87.9000    -84.0115    3.8885       -4.42    .000 681
 104  540.00 1400.00    -83.9000    -80.8839    3.0161       -3.59    .000 681
  98  560.00 1400.00    -79.0000    -77.6731    1.3269       -1.68    .000 681
 106  580.00 1400.00    -73.3000    -72.9554     .3446        -.47    .000 681
 107  600.00 1400.00    -66.9000    -68.0959   -1.1959        1.79    .000 681
 108  620.00 1400.00    -61.1000    -63.6606   -2.5606        4.19    .000 681
 109  640.00 1400.00    -56.2000    -59.6747   -3.4747        6.18    .000 681
 110  660.00 1400.00    -52.1000    -56.1161   -4.0161        7.71    .000 681
 111  680.00 1400.00    -48.2000    -52.9401   -4.7401        9.83    .000 681
 112  700.00 1400.00    -44.7000    -50.0971   -5.3971       12.07    .000 681

   C(1,2), D(1,2) =  .00000E+00  .00000E+00
   E(1)......E(N) =  .00000E+00  .00000E+00  .00000E+00  .00000E+00
                     .00000E+00  .00000E+00

   HENRY(BAR)=      .0000               VIPM(CC/MOLE)=   .0000

   RMSE =  6.9920  BTU/lb  AAD =    4.6567         %AAD =    17.75
   BIAS =  1.8830                                  NPTS =   225
```

phase envelope, the mixture may be near its critical point. Also, equations of state show potential problems in the critical area. Nevertheless, the data points in question cannot be verified or rejected, and must remain flagged.

These two examples clearly show the importance of using all three tools: 1) direct comparison to original data sets, 2) equation-of-state evaluation and 3) graphical evaluation. The data plots made the separation between flagged and outliers easier to determine. Unfortunately, without being able to check enthalpy data directly with to the original references, the evaluation is subject to interpretation.

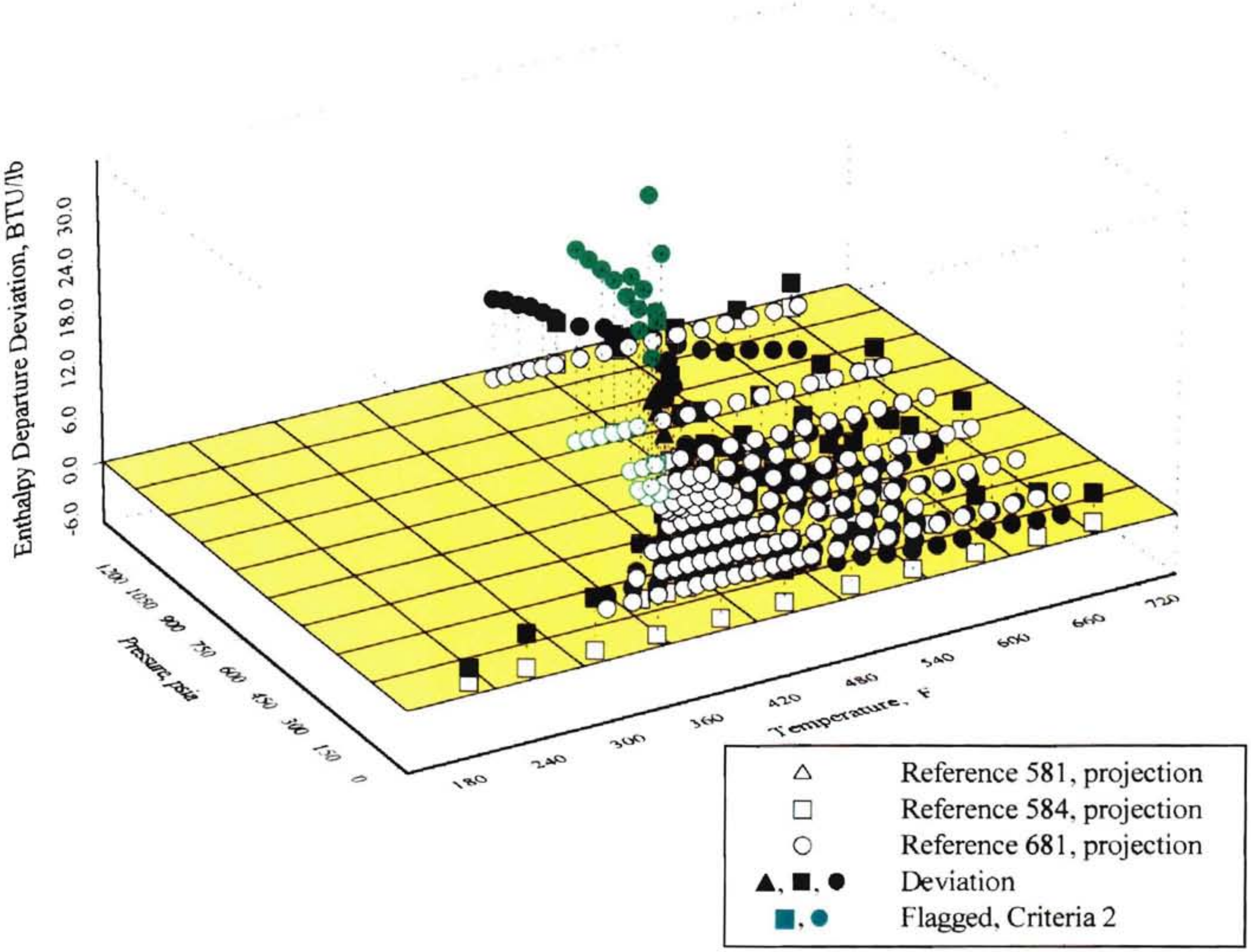


Figure 3. Enthalpy Departure Deviations for Vapor Benzene(0.406) + n-Pentane(0.594), Generated by the Peng-Robinson Equation of State

CHAPTER IV

DEVELOPMENT OF THREE DIMENSIONAL ENTHALPY DEVIATION GRAPH

The purpose of this chapter is to give some background on the development of a novel method for deviation plotting. The necessity for this plot is described, then the different types of plots are discussed. The chapter is broken into four sections:

- Reasons for graphical representation of data. Included is also what information needs to be included on the data plot.
- Overview of a previous graphical method using two-dimensional data plots.
- Discussion of the three-dimensional surface plots.
- Discussion of the three-dimensional data plots.

Advantages and disadvantages of each type of plot are listed in the corresponding section.

NEED FOR GRAPHICAL EVALUATION OF ENTHALPY DATA

The four main criteria for evaluating enthalpy data discussed in Table 6 can sometimes be difficult to interpret. In Chapter III, Figure 3 showed how trends in deviation are very clear in a plot. The points exceeding 3×RMSE may have been determined to be outliers if such a plot was not developed. The graph aids in the interpretation of the output from the enthalpy prediction model. Greater accuracy resulting from a clear view of the data under evaluation is the goal of the enthalpy plots.

The graph should conform to several constraints. It should be easy to understand and read. The plot should distinguish between different references for the same system and give the reader a clear picture of the temperature and pressure range of the enthalpy data. The deviation of the enthalpy data should be clearly represented to allow for easy sighting of trends, and points where deviations abruptly change

This graphical representation should also be displayed for the user of the database. This will empower users to make their own judgment calls on data points without needing the actual evaluation results tables.

PREVIOUS GRAPHICAL METHOD

As a starting point for development of the new graphical method, the old graphical method needed to be evaluated. The main criterion, which needed to be seen clearly on a graph, was twice the root-mean-squared-error (2×RMSE). A simple plot of enthalpy deviation as a function of either temperature or pressure with the zero deviation line and the 2×RMSE lines, positive and negative, clearly labeled was sufficient. Figure 4 shows the deviation for liquid cyclohexane plotted as a function of pressure, while Figure 5 is plotted as a function of temperature. The points exceeding 2×RMSE clearly show up on both graphs. The point showing an abrupt change in deviation sign also shows up clearly. In addition, the temperature and pressure ranges of the data are evident. On Figure 5, trends in temperature clearly show up. The deviation begins positive, turns toward negative then shoots to high positive values, with the deviation

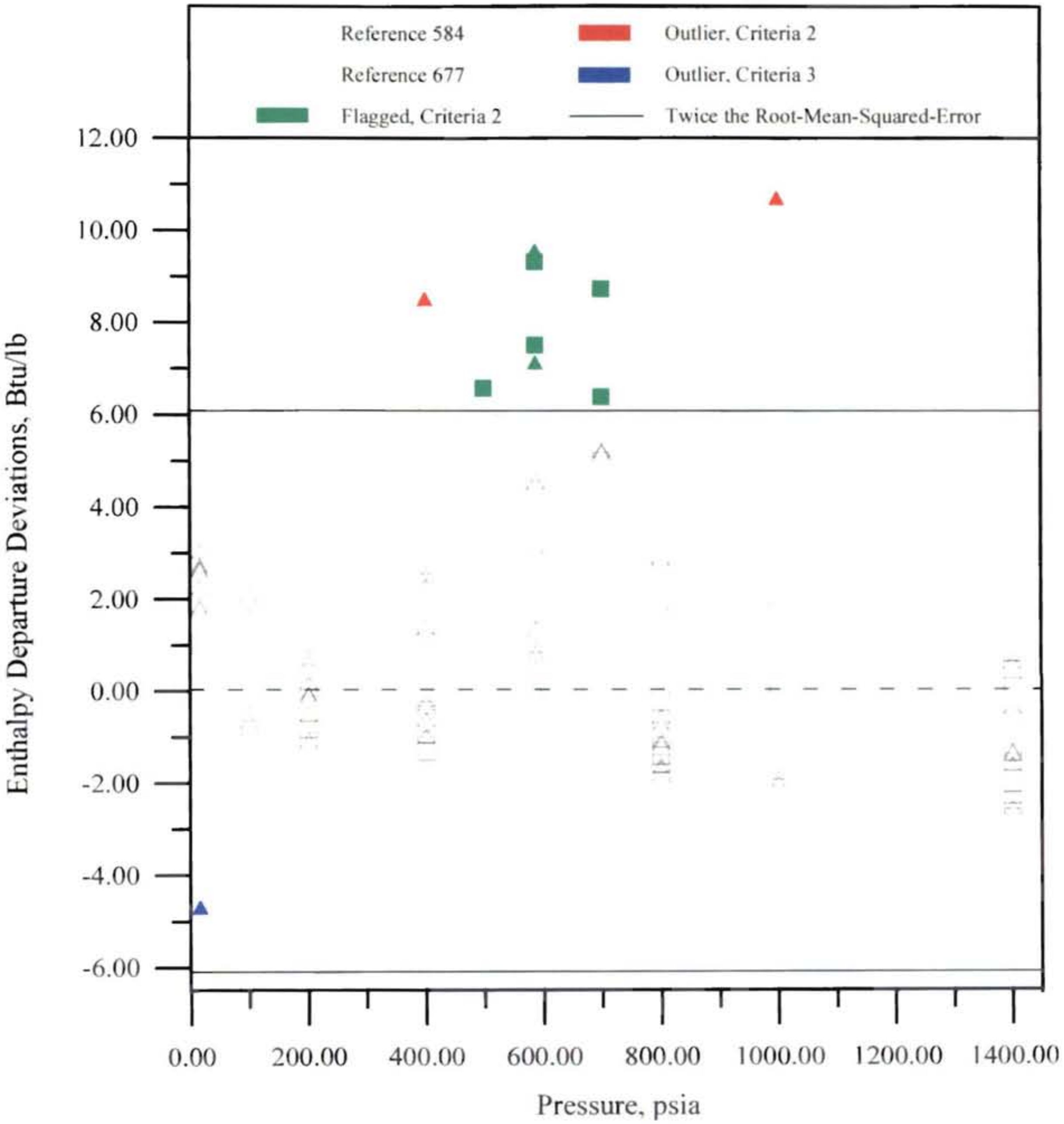


Figure 4. Peng-Robinson Equation of State Enthalpy Departure Deviations for Liquid Cyclohexane as a Function of Pressure

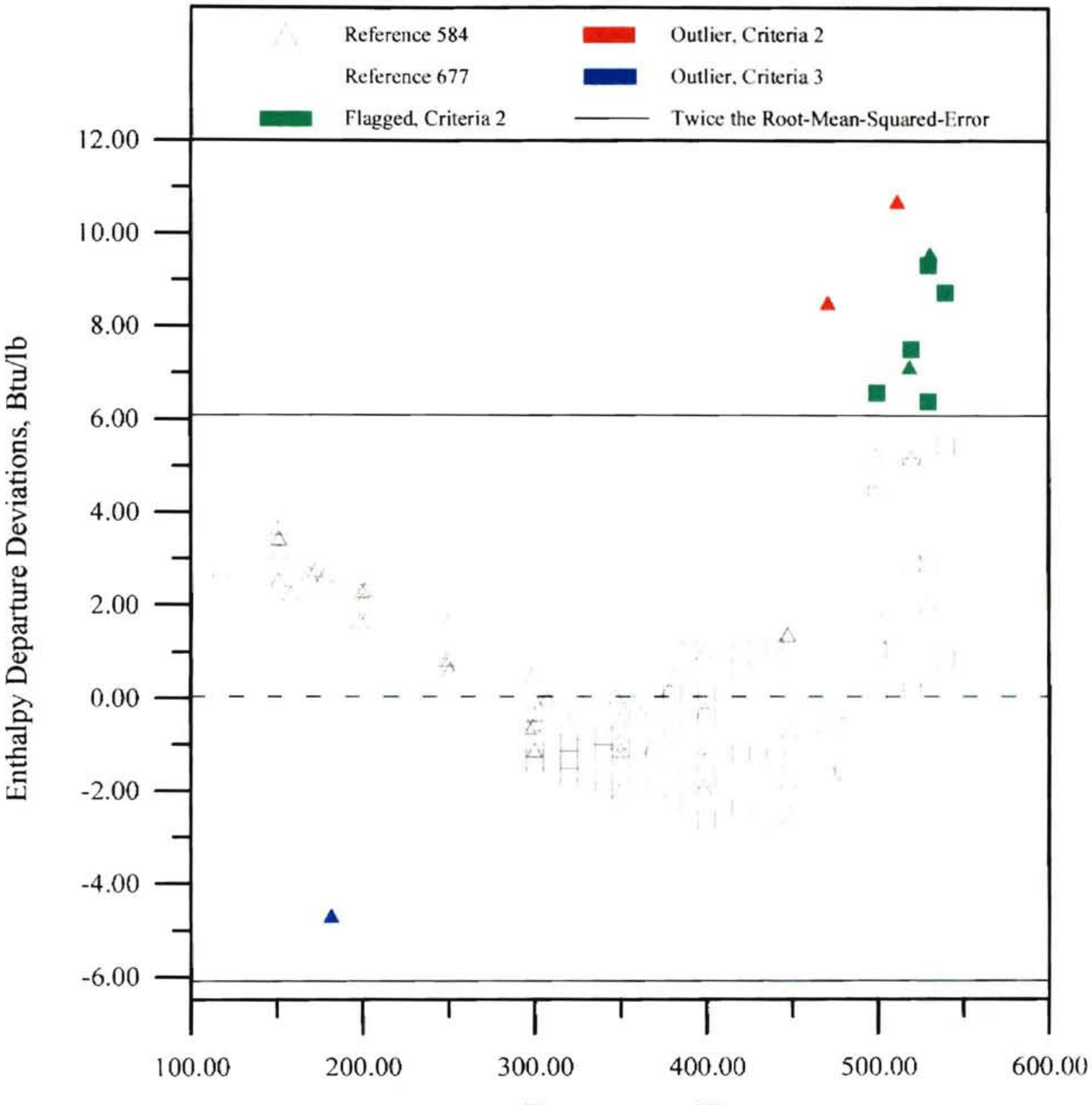


Figure 5. Peng-Robinson Equation of State Enthalpy Departure Deviations for Liquid Cyclohexane as a Function of Temperature

exceeding 2×RMSE around 450°F. However, the trends in deviation on the pressure graph are not so clear. The deviation changes positive to negative along the same isobar, yielding no useful trend information. The temperature range along any isobar or the pressure range along any isotherm cannot be seen at all. This makes the determination between outliers and data following the natural trend in deviation from the equation of state difficult, and a user cannot quickly determine whether sufficient data exist in the needed range of temperature and pressure.

While trends are difficult to determine, two graphs are needed for one data evaluation. A third graph of temperature versus pressure just to show the scope of the data would be even more inconvenient. For a user to pull up two or three figures from within the database would not be convenient. Also it would be three times the labor to incorporate three figures into the database itself. In order to see the trends of both temperature and pressure together along with the scope of the data, a three dimensional graph is needed.

THREE DIMENSIONAL SURFACE PLOT

The first attempt to see the trends and the scope of the data was with a three-dimensional surface plot. Figure 6 shows a plot of the liquid cyclohexane data with temperature and pressure on the x-y plane. Deviation is plotted along the z-axis. Figure 6 tries to represent what happens to the enthalpy departure deviation as a function of temperature and pressure. This figure shows the deviation starting out a little positive on the low temperature range, moving toward zero in the middle, then deviation increasing dramatically at higher temperatures, with spikes along the pressure range at

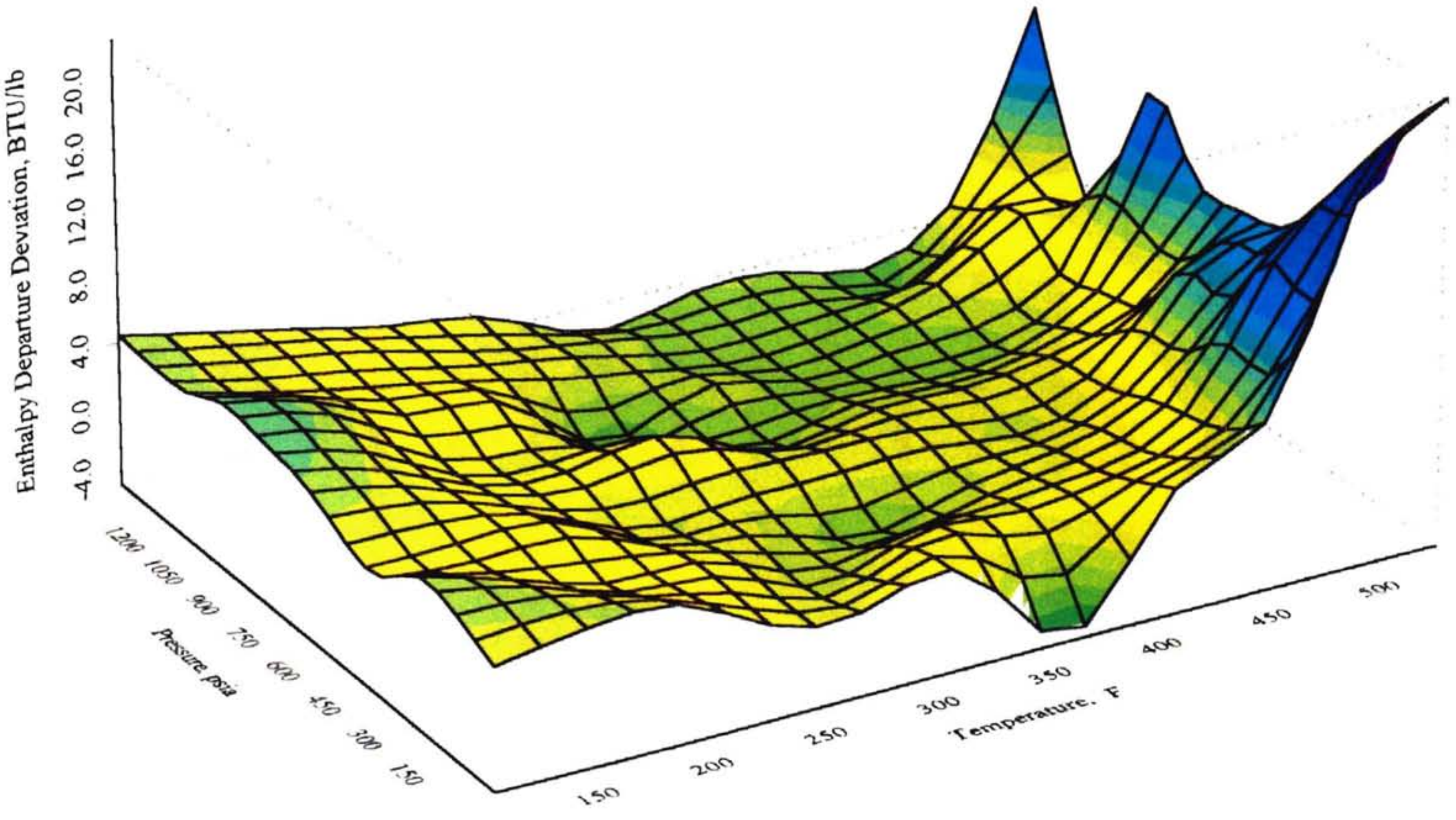


Figure 6. 3-D Surface Plot of Enthalpy Departure Deviations for Liquid Cyclohexane, Generated by the Peng-Robinson Equation of State

higher temperatures. The greatest deviation from the experimental data occurs at the high temperature, low pressure area. This is due to the liquid is nearing the two-phase region.

This general surface representation of the cyclohexane enthalpy departure data seems useful, but is easy to misinterpret. It can easily lead to false conclusions. Figure 7 shows the same surface plot with the data for the enthalpy departure deviations overlaid. There are three main areas of interest on this figure. First, the area of high temperature, moderate pressure shows a huge spike in deviation. This spike is caused by one point, while all the surrounding points show relatively smaller deviations. The spike is not representative of the data set, instead it represents one point which has been identified as an outlier compared to the surrounding points. The second area of interest is high pressure and temperature. This area shows a large deviation spike when none of the data is shown to be increasing significantly compared to the surrounding points. The third area occurs at low temperature and moderate pressure. This area contains no data, but the surface shows an increase in deviation compared to the surrounding area. This increase in deviation may or may not be correct, since no data are recorded in this area for this system. Along with these phenomena, the surface extrapolates errors more than double the maximum error of the data.

The smoothing function of the surface plot creates the phenomena detailed above. Figure 7 uses 3D cubic spline smoothing (interpolation) to create the surface plot.

A surface plot initially seems to be a good choice for analyzing deviations. Unfortunately, without well-behaved data blanketing the entire range of the data set, too

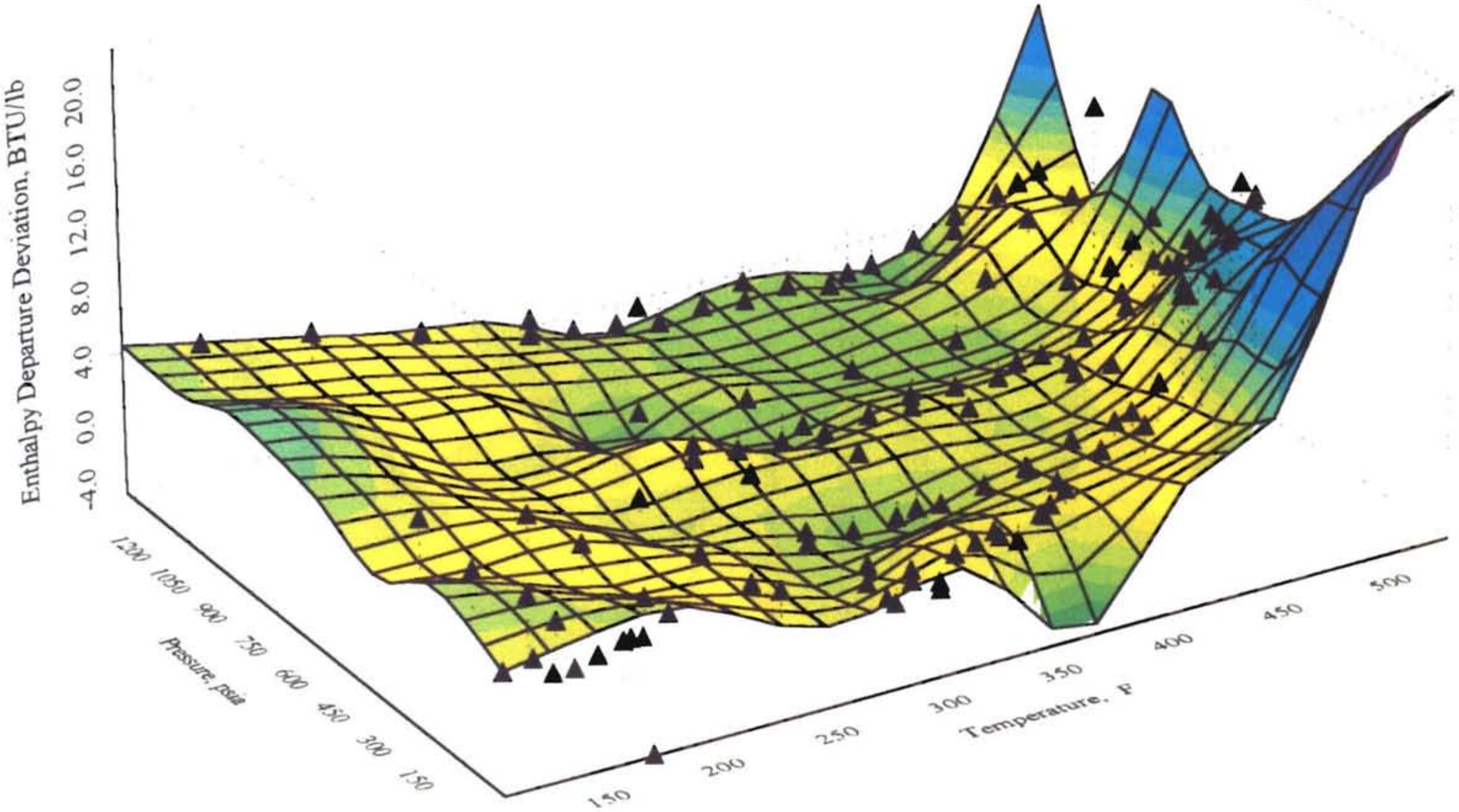


Figure 7. 3-D Surface Plot with Data of Enthalpy Departure Deviations Shown for Liquid Cyclohexane, Generated by the Peng-Robinson Equation of State

much interpolation and extrapolation occur by the graphing software. The advantage of pressure on one figure is beneficial, so the three dimensional attribute should be retained in the final version of the enthalpy plot.

THREE DIMENSIONAL DATA PLOT

While the surface plot has its shortcomings, the ability to see the temperature and pressure ranges together is important. The question remained on how to combine the simplicity of a two-dimensional plot with the power of seeing the temperature and pressure range simultaneously. In order to complete this task, a three-dimensional plot was developed with a two-dimensional plot overlaid on the zero-deviation plane. A flat grid at zero deviation was inserted on the deviation plot. This grid is the temperature-pressure plot. The data were plotted so any user could quickly scan the graph and determine the temperature and pressure ranges with ease. Since the plot is two-dimensional, easy determination of the coordinates of the point is not complicated by adding three-dimensional space on a sheet of paper.

In order to see trends in deviation along the temperature and pressure ranges simultaneously, a three-dimensional plot is needed. To do this, the deviations were plotted on the same graph, with deviation plotted on the z-axis. Dotted drop-down lines were then used to connect the deviation point to the corresponding point on the temperature-pressure plot. The drop-down lines help the user quickly identify the corresponding projection of the deviation plot onto the temperature-pressure plane. Now the figure has each point represented twice, once in a two-dimensional temperature-pressure plot, then again with a corresponding point showing the enthalpy departure deviation. The length of the drop line represents the amount of deviation. This helps eliminate the problem of a three-dimensional graph on a sheet of paper. Finally, color facilitates quick reading of the figure. Black represents data considered to be what is typically expected, or normal, for the system. Other colors represent points of interest which fall under one of the four criteria discussed in Chapter III.

Figure 2 in Chapter III is the final version of the new method of plotting for liquid cyclohexane. The data point showing an abrupt change in deviation shows up clearly. Also, one point in the high temperature, moderate pressure range shows significant deviation from any of the surrounding points, and is outside the 2×RMSE. This point is also identified as an outlier. The cluster of data points in the high temperature and low pressure range also show deviation over 2×RMSE, but this data are following a trend. The temperature is increasing along a narrow band of pressure, and the deviation is steadily increasing, unlike the data point around the same temperature and at higher pressure. These data follow a trend and are flagged. On the two-dimensional plots, the point at 400 psia was called an outlier: it is now seen to be part of a trend

Other useful information crops up from this graph. In the mid-range temperatures covering the entire pressure range, the Peng-Robinson equation of state agrees well with the experimental data. Several isobars are seen easily, which agree with Figure 4. The data concentrates in the higher temperature region, but covers a wider pressure range at lower temperatures. The change from positive to negative and back to positive deviations is clearly seen on this figure, which corresponds with Figure 5.

Figure 2 has the advantages of Figures 3 and 4, and adds in the new advantage of the temperature-pressure plot It also has the advantage of a surface plot where trends can be easily identified, and outliers stand out. At the same time, the three-dimensional representation remains easy to understand using colors and drop lines. This type of plot proved to be crucial throughout the data evaluation

CHAPTER V

RESULTS OF THE GPA DATA EVALUATION

The purpose of this chapter is to present the results of the Peng-Robinson and Park-Gasem-Robinson data evaluations. Comparisons between the two models are detailed. Complete listings of the suspect data points, are given in Appendix B for Peng-Robinson and Appendix C for Park-Gasem-Robinson.

RESULTS OF THE PENG-ROBINSON ENTHALPY EVALUATION

Table 9 shows the overall RMSE for each phase studied for the pure, binary and multicomponent systems. The overall deviation for all the data sets is about 6.0 BTU/lb. There were ten systems of requiring closer analysis, showing RMSE for the data set over 3×RMSE. Table 10 presents these data Below lists the findings of the analysis of each of these data sets.

The phase listings in Table 9 have some nomenclature used in the GPA database. For clarification, liquid-liquid-vapor data is near the bubble point, and liquid-vapor-vapor data is near the dew point.

Table 9.

Overall RMSE for the GPA Enthalpy Database Using the Peng-Robinson Equation of State

No.	Group	Phase	RMSE (BTU/lb)
1.	Pure	Liquid	4.22
2.	Pure	Vapor	5.04
3.	Pure	Liquid-Liquid-Vapor	8.24
4.	Pure	Liquid-Vapor-Vapor	6.48
5.	Binary	Liquid	5.76
6.	Binary	Vapor	6.73
7.	Binary	Liquid-Liquid-Vapor	7.65
8.	Binary	Liquid-Vapor-Vapor	5.61
9.	Multicomponent	Liquid	5.37
10.	Multicomponent	Vapor	7.36
11.	Multicomponent	Liquid-Liquid-Vapor	4.01
12.	Multicomponent	Liquid-Vapor-Vapor	1.28

Table 10.

Systems With Over Three Times the Total RMSE for Enthalpy Data Using the Peng-Robinson Equation of State

No.	Component	Mole Fraction	Phase	RMSE (BTU/lb)	No. Pts.
1.	Benzene	1.000	Liquid-Liquid-Vapor	36.32	10
2.	Ethane Propane	0.724 0.276	Liquid	22.38	26
3.	Methane Toluene	0.500 0.500	Liquid	37.39	40
4	Carbon Monoxide Hydrogen	0.250 0.750	Vapor	18.29	58
5.	Carbon Monoxide Hydrogen	0.500 0.500	Vapor	24.64	57
6.	Pentane 1,2,3,4-Tetrahydronaphthalene	0.197 0.803	Vapor	44.33	56
7.	Benzene Pentane	0.406 0.594	Liquid-Liquid-Vapor	38.79	14
8.	Methane Carbon Dioxide	0.4761 0.5239	Liquid-Vapor-Vapor	25.10	4
9	Toluene Hydrogen Sulfide Methane Methylcyclohexane	0.1031 0.3037 0.4946 0.0986	Vapor	40.31	61
10.	Toluene Hydrogen Sulfide Methane Methylcyclohexane	0.1031 0.3037 0.4946 0.0986	Liquid-Liquid-Vapor	113.38	5

- Four of these data sets of concern have less than fifteen data points in the data set. No conclusive statements are made for these data sets, since there is not enough data to concretely represent any certain region.
- The liquid ethane + propane data set with mole fractions of 0.724 and 0.276, respectively has one data point causing the entire data set to show a tremendous amount of error (deviation of 104 BTU/lb). With the exclusion of this data point, the RMSE drops to 9.3 BTU/lb.
- The liquid methane (0.500) + toluene (0.500) system shows a consistently high deviation among most of the data points. This system was also run on ASPEN PLUS™ to confirm the predicted enthalpy values. ASPEN PLUS™ was in good agreement with GEOS. The results on this data set are inconclusive.
- The two carbon monoxide + hydrogen systems show high deviations at extremely low temperatures, but the majority of the points are within expected deviation.
- The vapor pentane + 1,2,3,4-tetrahydronaphthalene system has several data points which should be considered suspect. Figure 8 shows the results of this data set. There seems to be a curved line where the deviation greatly increases. This may be the result of the equation of state predicting the phase envelope poorly, or data points taken within the two-phase region. No vapor-liquid-equilibrium data was available in the database for the system, therefore, his data is suspect until vapor-liquid-equilibrium data is compared to the results to find the phase envelope.

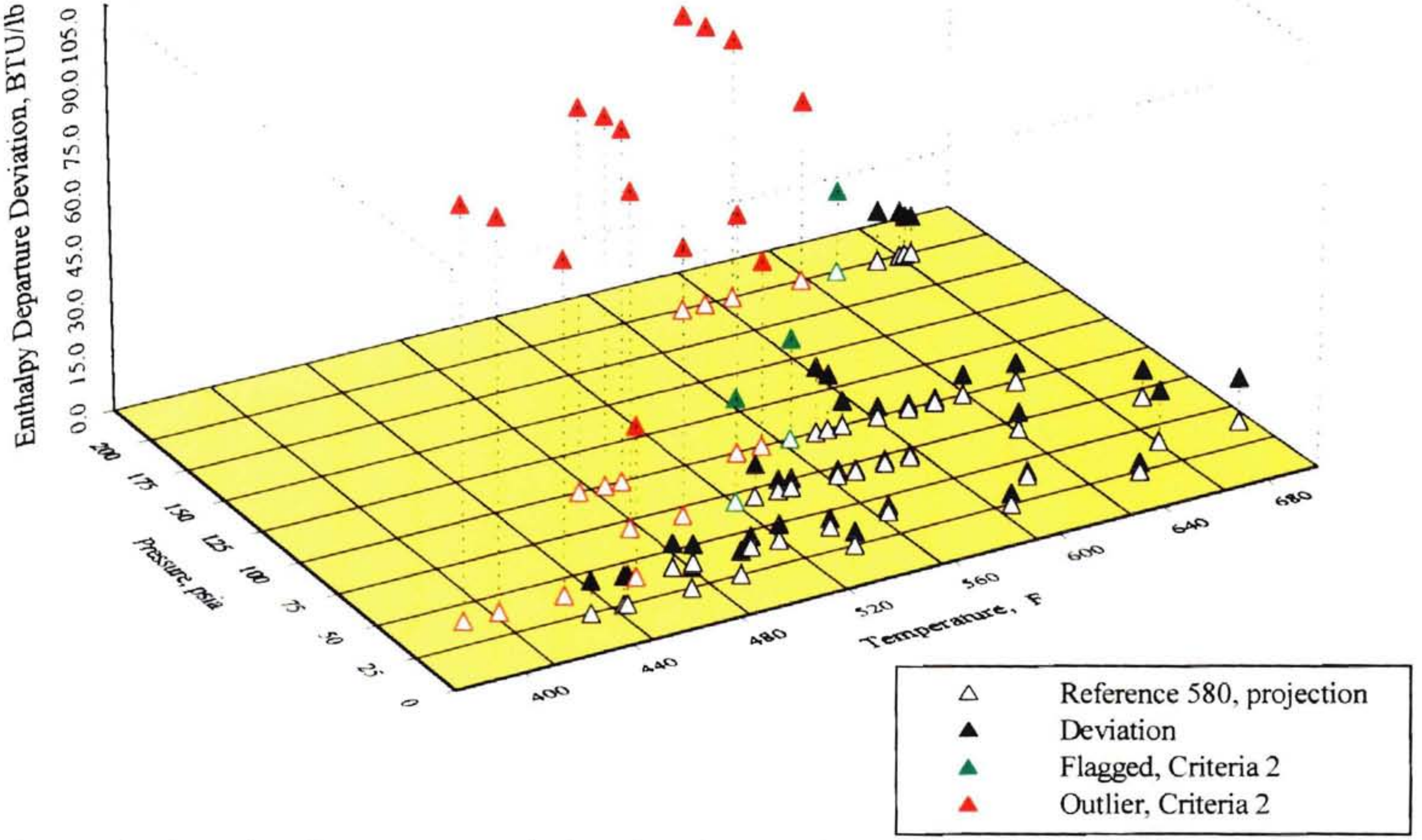


Figure 8. Enthalpy Departure Deviations for Vapor n-Pentane(0.197) + 1,2,3,4-Tetrahydronaphthalene(0.803), Generated by the Peng-Robinson Equation of State

- The vapor multicomponent system listed in Table 10 shows a steady increase in deviation as the pressure and temperature increases. This is likely to be a shortcoming of the PR EOS as the system became increasingly non-ideal.

Overall, the PR EOS performed well for the studied enthalpy data. Results of all flagged and outlier data points are located in Appendix B.

RESULTS OF THE PARK-GASEM-ROBINSON ENTHALPY EVALUATION

The purpose of this section is to compare the ability of the PGR enthalpy model to the PR. Table 11 shows the results of the twenty pure component systems studied using the PGR compared to the PR. The PR performs consistently better than the PGR in the liquid region. On the other hand, the PGR performs better in the vapor region. Both equations seem to have similar problems close to the phase envelope. The overall RMSE from the absolute difference in point-by-point deviation (Deviation_{PR} - Deviation_{PGR}) is 5.8 BTU/lb. In general, the PR equation predicts enthalpies greater in value at low temperatures than the PGR equation. However, at higher temperatures, the PGR EOS predicts enthalpies greater in value. Figure 9 shows a typical comparison between the predictive capabilities of the two equations. A complete listing of all flagged points recognized by the Park-Gasem-Robinson EOS is located in Appendix C

EXAMPLE CASE COMPARING THE PR EOS TO THE PGR EOS FOR ENTHALPY PREDICTIONS

This purpose of this section is to evaluate the differences between the predictive capabilities of the two equations of state. Liquid cyclohexane has been used as an

Table 11.

Results of the Park-Gasem-Robinson EOS Compared to the Peng-Robinson EOS for the GPA Enthalpy Data

No.	Component	Phase	PR RMSE (BTU/lb)	PGR RMSE (BTU/lb)	PR-PGR RMSE (BTU/lb)
1.	Benzene	Liquid	4.76	7.19	3.47
2.	Benzene	Vapor	7.33	7.46	8.03
3.	Benzene	Liquid-Liquid-Vapor	36.31	35.25	2.16
4.	Benzene	Liquid-Vapor-Vapor	3.92	10.22	8.93
5.	Cyclohexane	Liquid	3.01	7.70	7.39
6.	Ethane	Liquid	2.56	3.95	3.13
7.	Ethane	Vapor	8.39	5.45	6.43
8.	Methane	Liquid	1.82	1.90	2.03
9.	Methane	Vapor	3.44	3.40	10.31
10.	Octane	Liquid	2.34	4.60	3.55
11.	Octane	Vapor	6.97	6.97	6.18
12.	Octane	Liquid-Liquid-Vapor	4.10	6.49	2.47
13.	Propane	Liquid	5.71	11.20	6.50
14.	Propane	Vapor	7.60	6.92	5.19
15.	Toluene	Liquid	3.35	4.18	2.89
16	Toluene	Vapor	2.49	2.92	2.47
17.	trans-Decalin	Liquid	4.11	19.22	19.40
18.	trans-Decalin	Vapor	4.46	7.64	3.61
19.	trans-Decalin	Liquid-Liquid-Vapor	6.93	3.92	6.29
20	trans-Decalin	Liquid-Vapor-Vapor	10.72	15.94	5.48

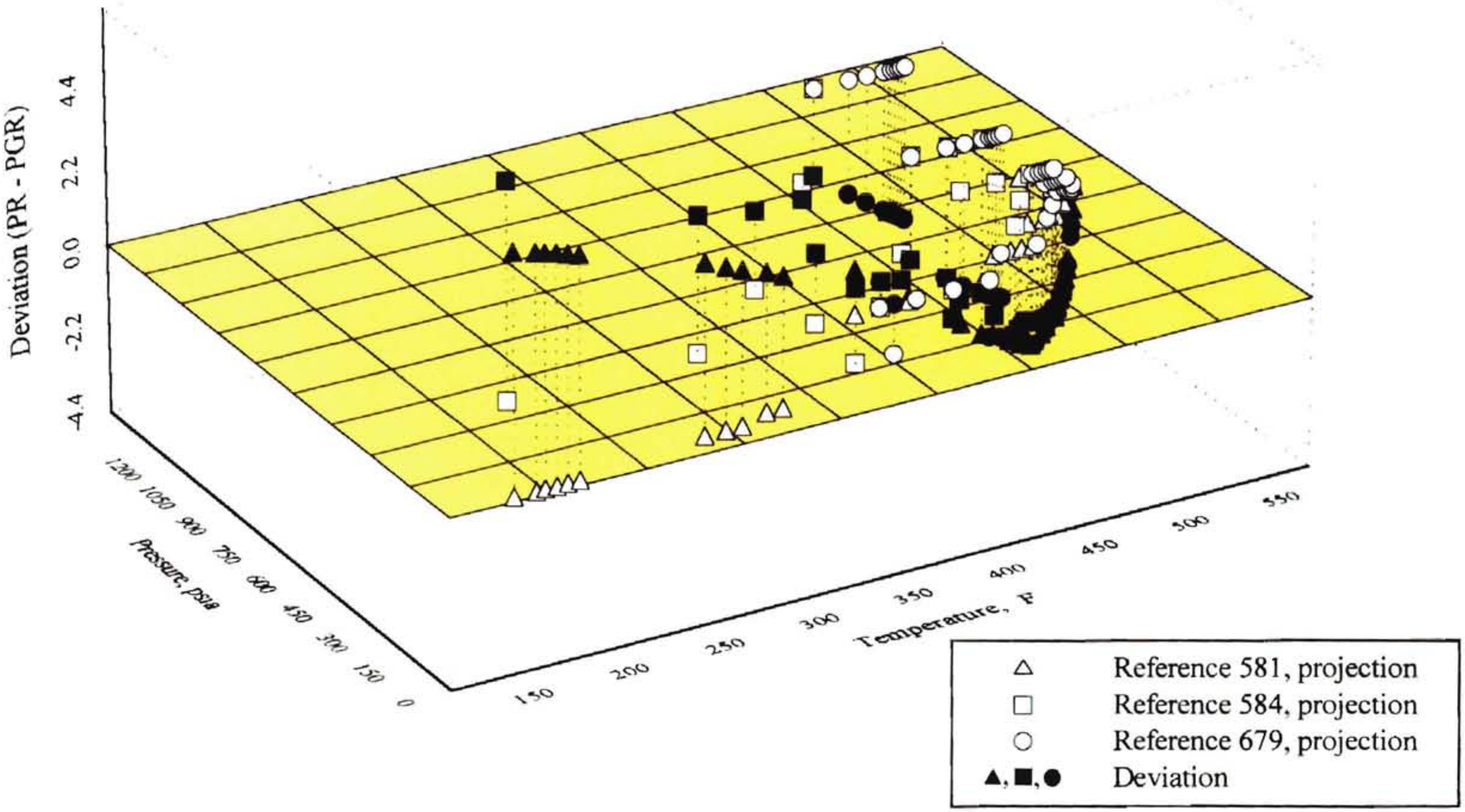


Figure 9. Comparison of the Peng-Robinson and Park-Gasem-Robinson Equations of State for the Prediction of Enthalpy Departure Data for Liquid Benzene

Table 12.

Possible Outliers for Liquid Cyclohexane from the PR and PGR Equations of State

Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria*	Ref.
		Peng-Robinson Equation of State			
56	181.8	15.4	-4.6949	O3	584
54	471.2	400.0	8.5207	F2	584
150	519.0	588.0	7.1385	F2	584
148	531.1	588.0	9.5701	F2	584
78	512.1	1000.0	10.7038	O2	584
6	500.0	500.0	6.5695	F2	677
20	520.0	588.0	7.5107	F2	677
27	530.0	588.0	9.3229	F2	677
134	530.0	700.0	6.3834	F2	677
150	540.0	700.0	8.7337	F2	677
		Park-Gasem-Robinson Equation of State			
56	181.8	15.4	-17.2237	F2	584

example case throughout this work and will serve as a suitable example here. Table 12 lists the flagged and outlier data identified by both equations for liquid cyclohexane.

Using the PR EOS eight data points are flagged and two points are considered outliers. Data point 78 was determined to be an outlier because it exceeds 3×RMSE, while outlier data point 56 showed an abrupt change in deviation sign. All other flagged data exceeded the 2×RMSE mark, but is concentrated within a trend. These data are plotted on Figure 2.

On the other hand, the PGR EOS only shows one flagged data point. Point 56, considered to show an abrupt change in deviation sign according to the PR EOS, the PGR EOS only flags this data point for exceeding 2×RMSE. The deviation plotted for the PGR EOS is shown in Figure 10.

The overall deviation difference plays a major role in the number of flagged data points for the data set. The PR EOS reports less than one-third the deviation of the PGR at low temperatures for liquid cyclohexane. The greater deviation of the PGR causes the overall RMSE to increase. Since the PGR EOS improves in prediction capabilities at higher temperature, the higher RMSE masks the flagged data from the PR EOS. The outlier now falls below the 2×RMSE threshold.

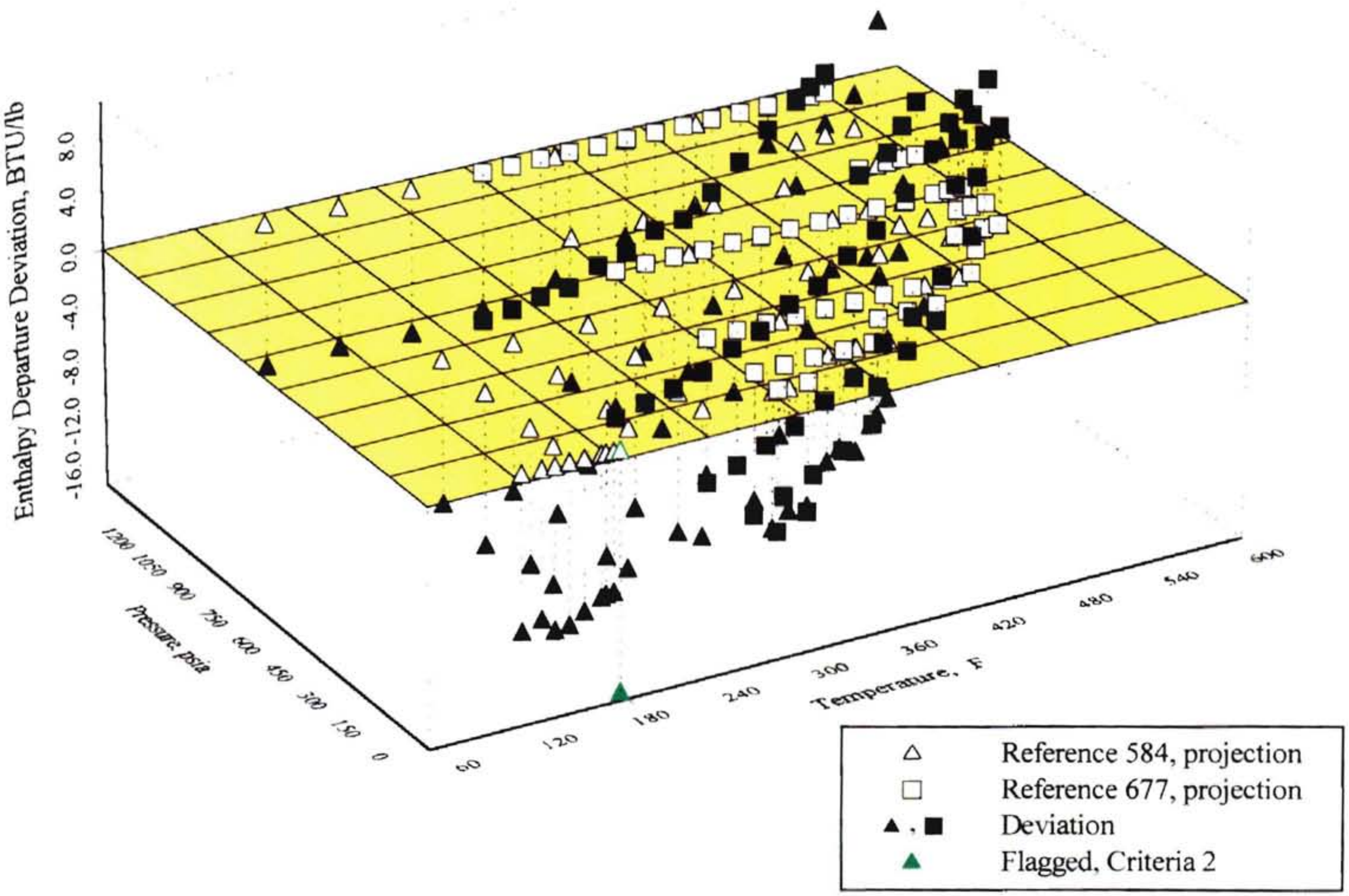


Figure 10. Enthalpy Departure Deviations for Liquid Cyclohexane, Generated by the Park-Gasem-Robinson Equation of State

CHAPTER VI.

SUMMARY

The enthalpy data contained within the Gas Processors Association Database were evaluated for reliability. Enthalpy departure deviations from the Peng-Robinson equation of state were used to compare to experimental values. Also, the modified Park-Gasem-Robinson equation of state proposed by Row (14) was evaluated for twenty systems. Lastly, this work developed a new graphical method to assist enthalpy evaluations

PENG-ROBINSON AND PARK-GASEM-ROBINSON EQUATIONS OF STATE

The PR EOS showed an average deviation of 2 to 5 Btu/lb for the entire databank. It gave slightly better predictions for alkanes than for cyclic compounds. Also, the PR model was effective in handling the multicomponent natural gas systems contained within the database. This work tagged less than one percent of the total data as flagged data, of which only a small percentage was outliers.

The PGR EOS showed comparable accuracy to the PR EOS. The PR predicted larger enthalpy values in the low temperature regions of the studied data sets. At higher temperatures, the PR model typically predicted lower values of enthalpy departure than the PGR model. Since the PR EOS was able to predict enthalpy values closer to the experimental values on average, more data points were flagged for exceeding 2×RMSE.

An expanded study of the PGR EOS should be completed for the GPA enthalpy departure database. Preliminary evaluation shows the equation has merit, and may to be a useful addition to the literature for enthalpy departure prediction.

GRAPHICAL EVALUATION OF ENTHALPY DEPARTURE DATA

Equations of state evaluations of enthalpy data alone are not sufficient for accurate analysis of a database. Direct comparison of the experimental references is required. Only a small number of data sets were found to contain errors using this method. However, errors in the composition of a system have a major impact on the utility of the data. Direct comparison of as much information within a database should be completed before beginning an equation-of-state evaluation.

Three-dimensional plotting of enthalpy data proved to be critical in obtaining an accurate evaluation, when used in conjunction with direct comparisons and equations of state. Major shortcomings of the equations of state clearly show up on the graphs. Trends in excessive deviation commonly appear near the phase envelope, around the critical region and as the system exceeded the critical point into non-ideal regions of high temperature and pressure. The two-dimensional temperature-pressure plot contained on the deviation plots give a quick reference tool to determine whether any system contains sufficient data in the region of the users' interest. The deviation plots also proved useful when comparing two models against each other. The plots quickly revealed the temperature trend mentioned above.

The deviation plots along with the tables contained in Appendixes B and C should be included in the GPA databank. These two tools would enable the end user to evaluate quickly the credibility of any data system. Another useful feature to add to the deviation plots would be the location of the critical point when applicable.

Several data sets within the GPA enthalpy database provided a limited amount of data over a wide range of temperature and pressure. Such data sets could easily be identified using the deviation plots and should be targeted for addition of new data within the temperature and pressure already outlined by these data sets. In addition, any new data collected by the Gas Processors Association should be included, when applicable, to the scope of the database.

BIBLIOGRAPHY

1. Albright M. A., "An Overview of Cooperative Research/GPA, API, and DIPPR," *Fluid Phase Equilibria*, 14, 393-400 (1983).

2. Daubert T. E., "GPA Data Bank of Selected Enthalpy and Equilibria Values, Pennsylvania State University, University Park, Pennsylvania." Projects 806/822-91, GPA Research Report *RR-64C* (1993).

3. Park, J. K., "Binary Vapor-Liquid Equilibrium Measurements for Selected Asymmetric Mixtures and Equation of State Development," Ph.D. Dissertation, Oklahoma State University, Stillwater, Oklahoma (1994).

4. Rastogi, Abhishek, "Evaluation and Maintenance of an Enthalpy Database," M.S Thesis, Oklahoma State University (1996).

5. Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, "*The Properties of Gases and Liquids*," Second Edition, McGraw-Hill Book Company, New York (1977).

6. Passut, C. A., and R. P. Danner, "Correlation of Ideal Gas Enthalpy, Heat Capacity, and Entropy," *Ind. Eng. Chem. Process Des. Develop.*, 11(4), 543-546 (1972).

7. Thinh, T. P., J. L. Duran, R. S. Ramalho, and S. Kaliaguine, "Equations Improve C_p^* Predictions," *Hydrocarbon Processing*, 98-104, January (1971).

8. Aly F. A., and L. L. Lee, "Self-Consistent Equations for Calculating the Ideal Gas Heat Capacity, Enthalpy, and Entropy," *Fluid Phase Equilibria*, 6, 169-179 (1981).

9. Yuan, S. C., and Y. Mok, "New Look at Heat Capacity Prediction," *Hydrocarbon Processing*, 47 (3): 133 (1968).

10. Duran, J. L., T. P. Thinh, R. S. Ramalho, and S. Kaliaguine, "Predict Heat Capacity more Accurately," *Hydrocarbon Processing*, 55 (8): 153 (1976).

11. Mayer, J. E., and M. G. Mayer, "*Statistical Mechanics*," Wiley, New York (1940).

12. Godnev, I. N., "Calculation of thermodynamic functions from molecular data, AEC-tr-385," Office of Technical Services, Department of Commerce, Washington D. C. (1959).

13. Hill, T. L., "*An Introduction to Statistical Thermodynamics*," Addison-Wesley, Reading, Massachusetts (1960).

14. Row, K. Y., "Evaluation of the Modification of the PGR Equation of State for Selected Pure Components," Ph. D. Dissertation, Oklahoma State University (1998)

15. Adachi, Y., H. Sugie and C.Y.L. Benjamin, "Taking Advantage of Available Cubic Equations of State," *Can. J. of Chem. Eng.*, 68, 639 (1990).

16. Schmidt, G., and H. Wenzel, "A Modified Van der Waals Equation of State," *Chem. Eng. Sci.*, 35, 1503-1512 (1980)

17. Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, 27, 1197-1203 (1972).

18. Harmens, A., and H. Knapp, "Three Parameter Cubic Equation of State for Normal Substances," *Ind. Eng. Chem. Process Des. Dev.*, 14, 209 (1975).

19. Kumar, K. H., and K. E. Starling, "The most General Density-Cubic Equation of State: Application to Pure Nonpolar Fluids," *Ind. Eng. Chem. Fundam.*, 21, 255-262 (1982).

20. Adachi, Y., H. Sugie, and B.C.-Y. Lu, "Evaluation of Cubic Equation of State," *J Chem. Eng. Jpn.*, 17, 624-631 (1984).

21. Peng, D. Y., and Robinson, D. B., "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, 15, 59-64 (1976).

22. Gasem, K. A. M., K. Keerthukumar, and R. L. Robinson, Jr. "GEOS for Calculating Volumetric and Phase Equilibrium Properties," AIChE 1991 Annual Meeting, Los Angeles, California

23. Cochran, G. A., and J. M. Lenoir, "GPA Experimental Values Referred to Two Base Levels," GPA Research Report *RR-11* (1974)

APPENDIX A

LITERATURE REFERENCES IN THE GPA ENTHALPY DATABASE

This appendix provides a listing of the literature reference numbers along with their corresponding literature sources for all the enthalpy data in the GPA Enthalpy Database

358. Pitzer, K. S., "The Thermodynamics of n-Heptane and 2,2,4-Trimethylpentane, Including Heat Capacities, Heats of Fusion and Vaporization, and Entropies," J. Am. Chem. Soc. 62, 1224 (1940).

458. Storvic, T. S. and J. M. Smith, "Thermodynamic Properties of Polar Substances: Enthalpy of Hydrocarbon-Alcohol Systems," J. Chem. Eng. Data 5, 133 (1960).

564. Yarborough, L. and W. C. Edmister, "Calorimetric Determination of the Isothermal Pressure Effect on the Enthalpy of the Propane-Benzene System," AIChE Journal 11, 492 (1965).

570. Bhirud, V. L. and J. E. Powers, "Thermodynamic Properties of a 5 Mole Percent Propane in Methane Mixture," Report to the NGPA, August 1969.

573. Dillard, D. D., W. C. Edmister, J. H. Erbar and R. L. Robinson, "Calorimetric Determination of the Isothermal Effect of Pressure on the Enthalpy of Methane and Two Methane Propane Mixtures," AIChE Journal, 14, 923 (1968).

574. Furtado, A. W., D. L. Katz and J. E. Powers, Paper presented at 159th National ACS meeting, Houston, Texas, February (1970).

578. Jones, M. L., D. T. Mage, R. C. Faulkner and D. L. Katz, "Measurement of the Thermodynamic Properties of Gases at Low Temperature and High Pressure-Methane," Chem. Eng. Prog. Sym. Series, 59 (44), 52-60 (1963).

579. Lenoir, J. M., "A Program of Experimental Measurement of Enthalpies of Binary Hydrocarbon Mixtures Above 100 deg. F and in the Critical Region." Proceedings of API 47,640-52 (1967).

580. Lenoir J. M., K. E. Hayworth and H. G. Hipkin, "Some Measurements and Predictions of Enthalpy of Hydrocarbon Mixtures." Proceedings of API 50, 212 (1970).

581. Lenoir, J. M., K. E. Hayworth and H. G. Hipkin, "Enthalpy Measurements for Hydrocarbon Mixtures," Proceedings of API 51, 405 (1971).

582. Lenoir, J. M., K. E. Hayworth and H. G. Hipkin, "Enthalpies of Decalin and trans-Decalin and n-Pentane Mixtures." J. Chem. Eng. Data 16, 129 (1971).

583. Lenoir, J. M. and H. G. Hipkin, "Enthalpies of Mixtures of n-Hexadecane and n-Pentane," J. Chem. Eng. Data 15, 368 (1970).

584. Lenoir, J. M., G. K. Kuravila and H. G. Hipkin, "Measured Enthalpies of Binary Mixtures of Hydrocarbons with Pentane," Proceedings of API 49, 89 (1969).

585. Lenoir, J. M., D. R. Robinson, and H. G. Hipkin, "Flow Calorimeter and Measurement of the Enthalpy of n-Pentane," J. Chem. Eng. Data 15, 23 (1970).

586. Lenoir, J. M., D. R. Robinson and H. G. Hipkin, "Enthalpies of Mixtures of n-Octane and n-Pentane," J. Chem. Eng. Data 15, 26 (1970).

587. Mage, D. T., M. L. Jones Jr., D. L. Katz and J. R. Roebuck, "Experimental Enthalpies for Nitrogen." Chem. Eng. Prog. Sym. Series 59 (44), 61 (1963).

588. Mather, A. E., "The Direct Determination of the Enthalpy of Fluids Under Pressure," Ph.D. Thesis, University of Michigan (1967).

590. Yesavage, V. F., "The Measurement and Prediction of the Enthalpy of Fluid Mixtures Under Pressure," Ph.D. Thesis, University of Michigan (1968).

591. Starling, K. E., D. W. Johnson and C. P. Colver, "Evaluation of Eight Enthalpy Correlations," NGPA Research Report RR-4 (1971).

592. Starling, K. E., "1971-1972 Enthalpy Correlation Evaluation Study," NGPA Research Report RR-8 (1972).

661. Bhirud, V. L. and J. E. Powers, "Thermodynamic Properties of a 5 Mole Percent Propane in Methane Mixture," Report to the NGPA, Tulsa, Oklahoma, August 1969, and Manker, E. E., Ph.D. Thesis, University of Michigan (1964).

663. Lenoir, J. M., D. R. Robinson and H. G. Hipkin, "Measurement of the Enthalpy of Pentane, Octane, and Pentane-Octane Mixtures," Proceedings of API 48, 346-96 (1968).

664. Powers, J. E., University of Michigan, Ann Arbor, Michigan, Private Communication (1972).

665 Lenoir, J. M., University of Southern California, Los Angeles, California, Private Communication (1972).

666. Eakin, B. E., G. M. Wilson and W. E. DeVaney, "Enthalpies of Methane-Seven Carbon Systems," NGPA Research Report RR-6 (1972).

667. Cochran, G. A. and J. M. Lenoir, "GPA Experimental Values Referred to Two Base Levels," GPA Research Report RR-11 (1974).

670. Eakin, B. E. and W. E. DeVaney, "Enthalpies of Hydrogen Sulfide-Methane-Ethane Systems," NGPA Research Report RR-9 (1973).

671. Furtado, A. W., "The Measurement and Prediction of Thermal Properties of Selected Mixtures of Methane, Ethane, and Propane,' Technical Report, Project 345330, Division of Research Development and Administration, Ann Arbor, Michigan, January (1974).

672. Peterson, J. M. and G. M. Wilson, "Enthalpy and Phase Boundary Measurements on Carbon Dioxide and Mixtures of Carbon Dioxide with Methane, Ethane, and Hydrogen Sulfide," NGPA Project 731, Paper presented at Annual NGPA Meeting, Denver, Colorado, March (1974).

673. Berryman, J. M., W. E. DeVaney, B. E. Eakin and N. L. Bailey, "Enthalpy Measurements on Synthetic Gas Systems: Hydrogen-Methane, Hydrogen-Carbon Monoxide," GPA Research Report RR-37, (1979).

674. Scheloske, J. J., K. R. Hall, P. T. Eubank and J. C. Holste, "Experimental Densities and Enthalpies for Water- Natural Gas Systems," GPA Research Report RR-53 (1981).

675. Lenoir, J. M., K. E. Hayworth and H. G. Hipkin, "Enthalpies of Tetralin and Mixtures of Tetralin and n-Pentane," J. Chem. Eng. Data, 15, 474(1970).

676. Cediel, L. E., P. T. Eubank, J. C. Ho and K. R. Hall, "Experimental Enthalpies for Pure Toluene and Pure Methylcyclohexane," GPA Research Report RR-63 (1982).

677. Lenoir, J. M., G. K. Kuravila and H. G. Hipkin, "Enthalpies of Cyclohexane and Mixtures of n-Pentane and Cyclohexane," J. Chem. Eng. Data 16, 271 (1971).

678. Lenoir, J. M., C. J. Rebert and H. G. Hipkin, "Enthalpies of Cis-2-Pentene and a Mixture with n-Pentane," J. Chem. Eng. Data 16, 401 (1971).

679. Lenoir, J. M., K. E. Hayworth and H. G. Hipkin, "Enthalpies of Benzene with n-Octane," J. Chem. Eng. Data 16, 280 (1971).

680. Lenoir, J. M., K. E. Hayworth and H. G. Hipkin, "Enthalpies of Mixtures of Benzene and Cyclohexane," J. Chem. Eng. Data 16, 285 (1971).

681. Lenoir, J. M. and H. G. Hipkin, "Measured Enthalpies for Mixtures of Benzene with n-Pentane," J. Chem. Eng. Data 17, 319 (1972).

682. Hayworth, K. E., J. M. Lenoir and H. G. Hipkin, "Enthalpies of Mixtures of Benzene and Hexadecane," J. Chem. Eng. Data 16, 276 (1971).

683. Lenoir, J. M. M. Bal and H. G. Hipkin, "Enthalpies of Ternary System Pentane-Cyclohexane-Benzene," J. Chem. Eng. Data 17, 461 (1972).

684. Lenoir, J. M. and H. G. Hipkin, "Enthalpies of Two Ternary Mixtures of Benzene-Octane-Tetralin," J. Chem. Eng. Data 17, 461 (1972).

685. Cunningham, J. R, "Enthalpy and Phase Boundary Measurements -- Equal Molar Mixtures of n-Pentane with Carbon Dioxide and Hydrogen Sulfide," GPA Research Report RR-103 (1986).

686. Bailey, D. M., "Thermodynamic Properties of Pure Hydrogen Sulfide with Methane, Carbon Dioxide, Methyl-Cyclohexane, and Toluene," GPA Research Report RR-107 (1987).

687. Eubank, P. T., K. R. Hall, J. C. Holste and M. G. Johnson, "Experimental Enthalpies of Pentanes-plus Fractions," GPA Research Report RR-121 (1989).

688. Bailey, D. M., "Properties of Carbon Dioxide Mixtures with Nitrogen and Methane," GPA Research Report RR-122 (1989).

689. Christensen, S. P., J. J. Christensen and R. M. Izatt, "Enthalpies of Solution CO_2 in Aqueous Diglycolamine Solutions," GPA RR-85 (1985).

690. Merkeley, K. E., J. J. Christensen and R. M. Izatt, "Enthalpies of Solution CO_2 in Aqueous Methyldiethanolamine Solutions," GPA RR-102 (1986).

691. Helton, R., J. J. Christensen and R. M. Izatt, "Enthalpies of Solution CO_2 in Aqueous Diethanolamine Solutions," GPA RR-108 (1987).

692. Van Dam, R., J. J. Christensen, J. J., R. M. Izatt and J. L. Oscarson, "Enthalpies of H_2S in Aqueous Diethanolamine Solutions," GPA RR-114 (1988).

693. Oscarson, J. L. and R. M. Izatt, "Enthalpies of Solution of H_2S in Aqueous Methyldiethanolamine Solutions," GPA RR-127 (1990).

APPENDIX B

SUMMARY OF POSSIBLE OUTLIERS FOR THE GPA ENTHALPY DATABASE USING THE PR EOS

The following tables contain a summary of all suspect enthalpy data in the GPA database. These suspect data were identified using direct comparisons, Peng-Robinson equation-of-state evaluations and graphical deviation plots. See Table 5 in Chapter III for the four criteria listed in the outlier/flagged column of the tables. Each phase for the pure, binary and multicomponent groups are contained within a separate table.

Table B.1.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
1	Benzene	4.7617	4.0226	108						
2	cis-2-Pentene	3.3380	2.6805	49	61	390.3	540.0	7.4815	F2	581
					43	370.0	450.0	7.3576	F2	581
					77	380.0	480.0	7.0114	F2	581
3	cis-Decalin	8.1152	7.2935	34						
4	Cyclohexane	3.0055	2.1452	128	56	181.8	15.4	-4.6949	O3	584
					54	471.2	400.0	8.5207	F2	584
					150	519.0	588.0	7.1385	F2	584
					148	531.1	588.0	9.5701	F2	584
					78	512.1	1000.0	10.7038	O2	584
					6	500.0	500.0	6.5695	F2	677
					20	520.0	588.0	7.5107	F2	677
					27	530.0	588.0	9.3229	F2	677
					134	530.0	700.0	6.3834	F2	677
					150	540.0	700.0	8.7337	F2	677

Table B.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
5	Ethane	2.5562	1.8404	41	65	-240.0	1500.0	5.3212	F2	592
					34	-240.0	2000.0	5.5985	F2	592
6	Ethylbenzene	2.1109	1.5194	33	21	170.4	290.0	4.5357	F2	687
					43	170.4	725.0	4.3206	F2	687
					29	170.4	1450.0	4.4673	F2	687
					3	170.4	2900.0	5.1767	F2	687
7	Ethylcyclohexane	9.1946	8.0854	21	7	548.4	290.0	19.8262	F2	687
8	iso-Octane	1.7564	1.5839	18	1	476.4	290.0	4.0395	F2	687
9	Methane	1.8186	1.3763	14	22	-150.0	500.0	4.4193	F2	578
10	Methylcyclohexane	7.3090	6.4363	122						
11	Heptane	7.5828	7.0643	105						
12	Hexadecane	3.9531	2.2656	81	17	599.9	25.0	21.2493	O2	584
					40	199.5	200.0	9.7797	F2	584
					34	202.7	1400.0	9.4079	F2	584

Table B.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
					33	249.7	1400.0	8.4517	F2	584
					39	297.0	1400.0	8.2749	F2	584
					29	354.7	1400.0	10.6417	F2	584
13	Nitrogen	0.9883	0.8480	7						
14	Octane	2.3351	1.6989	154	14	539.8	360.0	7.9783	F2	663
					15	540.0	360.0	8.2909	F2	663
					24	533.6	400.0	5.0967	F2	663
					26	544.5	400.0	6.0677	F2	663
					94	521.5	500.0	5.0531	F2	663
					95	540.8	500.0	4.8597	F2	663
15	Pentane	3.3816	2.3630	141	43	350.0	400.0	10.0095	F2	458
					27	350.0	500.0	8.7998	F2	458
					113	348.0	400.0	8.2837	F2	663
					43	348.3	400.0	8.2346	F2	663
					20	353.7	400.0	7.9636	F2	663
					21	353.8	400.0	9.2209	F2	663
					33	358.5	489.0	6.8891	F2	663

Table B.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
					62	403.6	600.0	10.4127	F2	663
					54	403.7	600.0	8.8214	F2	663
16	Propane	5.7067	4.3146	40	14	-250.0	2000.0	12.4343	F2	590
17	1,2,3,4-Tetrahydronaphthalene	4.7569	3.1320	70	114	121.4	100.0	12.6825	F2	580
					113	151.0	100.0	11.1114	F2	580
					69	119.4	400.0	13.1545	F2	580
					68	150.6	400.0	11.6557	F2	580
					53	102.1	1400.0	15.3424	F2	580
					52	198.1	1400.0	11.5906	F2	580
18	Toluene	3.3522	2.8967	107						
19	trans-Decalin	4.1090	3.2197	120	42	120.9	31.0	8.4926	F2	580
					50	120.1	1400.0	8.7842	F2	580
					17	600.0	150.0	-8.9445	F2	582
					33	580.0	1000.0	-8.5542	F2	582
					34	600.0	1000.0	-9.7345	F2	582
					35	620.0	1000.0	-12.3563	F2	582

Table B.2.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
1	Benzene	7.3328	3.3219	239	13	553.6	750.0	20.8375	F2	581
					18	559.1	1000.0	29.3631	F2	584
					19	581.1	1000.0	24.4511	F2	584
					1	600.7	1000.0	15.4910	F2	584
					26	554.0	750.0	19.8556	F2	679
					13	556.0	750.0	16.5718	F2	679
					17	554.0	800.0	25.2648	F2	679
					12	556.0	800.0	24.3117	F2	679
					15	558.0	800.0	23.5570	F2	679
					16	560.0	800.0	22.1110	F2	679
					20	565.0	800.0	18.9975	F2	679
					41	570.0	800.0	14.7080	F2	679
					69	554.0	1000.0	30.3679	F2	679
					61	556.0	1000.0	30.2878	F2	679
					43	558.0	1000.0	29.7148	F2	679
					36	560.0	1000.0	29.0492	F2	679
					59	565.0	1000.0	28.1194	F2	679
					38	570.0	1000.0	27.3411	F2	679
					39	600.0	1000.0	15.8191	F2	679

Table B.2. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
2	cis-2-Pentene	7.3182	4.1317	193	20	399.3	570.0	20.6786	F2	581
					43	402.7	570.0	16.3074	F2	581
					55	397.1	600.0	19.1010	F2	581
					175	405.0	650.0	14.9364	F2	581
					170	401.8	700.0	14.8750	F2	581
					111	395.0	519.0	57.6186	O2	678
					78	400.0	570.0	21.6098	F2	678
					98	400.0	600.0	22.8936	F2	678
					89	400.0	650.0	18.7753	F2	678
					96	400.0	700.0	17.7088	F2	678
					15	440.0	700.0	-4.0056	F3	678
					9	400.0	800.0	14.9310	F2	678
3	cis-Decalin	3.8231	3.2303	30	18	580.0	100.0	7.7811	F2	582
					19	600.0	100.0	8.7590	F2	582
4	Cyclohexane	5.1420	3.2080	176	69	671.9	15.4	-12.3765	F2	584
					93	561.2	700.0	23.6151	F2	584
					104	547.6	1000.0	17.5430	F2	584
					83	597.6	1000.0	11.0438	F2	584
					147	560.0	700.0	24.8114	F2	677

Table B.2. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
					158	560.0	800.0	23.1992	F2	677
					157	580.0	800.0	12.4698	F2	677
					117	560.0	1000.0	16.4378	F2	677
					114	580.0	1000.0	14.0838	F2	677
					113	600.0	1000.0	11.5697	F2	677
5	Ethane	8.3893	3.8567	28	63	120.0	1000.0	32.2626	F2	592
					22	120.0	1500.0	25.9186	F2	592
6	Ethylbenzene	0.8803	0.8380	12						
7	Hydrogen Sulfide	4.8922	2.2326	59	3	260.3	1885.5	15.0377	F2	686
					17	260.3	2030.6	18.9828	F2	686
					20	260.3	2175.6	19.8789	F2	686
					23	260.3	2900.8	16.2360	F2	686
8	Methane	3.4403	2.7445	25	29	-100.0	1000.0	46.2843	F2	578
					1	-100.0	1500.0	29.1146	F2	578
					2	-100.0	2000.0	10.5423	F2	578

Table B.2. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
9	Methylcyclohexane	7.2707	6.0449	46	26	600.0	600.0	17.4771	F2	592
					29	600.0	800.0	18.9053	F2	592
					15	600.0	1000.0	16.6455	F2	592
10	Heptane	4.6910	3.4127	52	20	550.0	600.0	15.0070	F2	556
					8	550.0	800.0	14.1671	F2	556
					50	550.0	1000.0	10.6736	F2	556
11	Hexadecane	4.5638	4.3312	20						
12	Nitrogen	2.9495	1.7421	48	54	-210.0	800.0	10.4796	F2	587
					49	-210.0	1000.0	12.3342	F2	587
					12	-210.0	1500.0	8.7725	F2	587
13	Octane	6.9678	5.3806	81	1	570.0	400.0	18.3817	F2	586
					28	568.9	400.0	19.7051	F2	663
					96	570.3	500.0	15.4536	F2	663
					97	570.8	500.0	14.7698	F2	663
					98	579.6	500.0	14.0383	F2	663
					115	579.9	500.0	15.6976	F2	663

Table B.2. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
14	Pentane	6.8273	3.3127	249	14	400.0	700.0	29.4751	F2	458
					12	400.0	800.0	21.2468	F2	458
					189	390.0	500.0	20.4747	F2	585
					181	390.0	600.0	36.7474	F2	585
					58	400.0	600.0	32.7295	F2	585
					26	420.0	600.0	15.4658	F2	585
					3	390.0	800.0	32.1633	F2	585
					4	400.0	800.0	30.2798	F2	585
					5	420.0	800.0	26.9701	F2	585
					6	440.0	800.0	18.8211	F2	585
					80	390.0	1000.0	23.9496	F2	585
					81	400.0	1000.0	23.0371	F2	585
					96	420.0	1000.0	19.3407	F2	585
					59	390.0	1400.0	14.8191	F2	585
					145	402.5	1400.0	14.5475	F2	663
15	Propane	7.5998	4.5539	21	6	200.0	500.0	17.9754	F2	364
					47	250.0	1000.0	21.5360	F2	590
					12	250.0	1500.0	16.6295	F2	590

Table B.2. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
16	1,2,3,4-Tetrahydronaphthalene	1.6075	1.3453	34	77	499.2	40.0	-2.9592	O3	580
					1	650.0	150.0	3.3228	F2	675
17	Toluene	2.4930	2.1473	38						
18	trans-Decalin	4.4592	3.8927	33	46	597.3	31.0	10.1636	F2	580

Table B.3.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Liquid-Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Benzene	36.3162	23.9860	10						
2	cis-2-Pentene	4.1128	3.7479	19						
3	cis-Decalin	1.2361	0.9066	10						
4	Cyclohexane	6.4900	4.9966	5						
5	Hexadecane	1.6455	1.6455	1						
6	Octane	4.0969	3.7988	3						
7	Pentane	8.6163	8.6163	1						
8	1,2,3,4-Tetrahydronaphthalene	4.7253	4.2663	20						
9	trans-Decalin	6.9317	6.6483	4						

Table B.4.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Vapor-Vapor Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Benzene	3.9245	3.2698	4						
2	cis-2-Pentene	5.1448	3.7043	17						
3	cis-Decalin	6.7289	6.5163	2						
4	Cyclohexane	4.5686	4.0437	5						
5	Hydrogen Sulfide	4.0542	3.4692	2						
6	Hexadecane	14.0233	14.0233	1						
7	Pentane	2.7851	2.6121	4						
8	1,2,3,4-Tetrahydronaphthalene	6.3465	5.7292	2						
9	trans-Decalin	10.7236	10.3206	17						

Table B.5.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Benzene	0.419	9.0025	7.7841	60						
	Hexadecane	0.581									
2	Benzene	0.670	12.3542	10.8984	66	1	440.0	200.0	-18.1091	O3	682
	Hexadecane	0.330				41	440.0	1400.0	-18.9464	O3	682
3	Benzene	0.814	11.2995	10.0184	64						
	Hexadecane	0.186									
4	Benzene	0.920	9.5417	8.5897	65	48	600.0	800.0	15.8467	F2	682
	Hexadecane	0.080									
5	Benzene	0.963	6.8484	6.1184	83	165	565.7	800.0	17.8940	F2	580
	Hexadecane	0.037									
6	Benzene	0.271	3.4420	2.4856	96	73	532.7	400.0	9.0514	F2	581
	Octane	0.729				74	538.7	400.0	10.9949	F2	581
						59	546.6	500.0	7.0132	F2	581
						49	551.7	500.0	7.4742	F2	581
						44	556.9	500.0	9.6673	F2	581
						58	555.9	600.0	6.9570	F2	581

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
						48	565.7	600.0	7.9688	F2	581
						7	540.0	400.0	8.6678	F2	679
7	Benzene	0.446	4.9921	4.0208	132	88	527.0	450.0	10.9677	F2	581
	Octane	0.554				49	535.7	500.0	11.0514	F2	581
						81	541.5	500.0	12.8398	F2	581
						51	546.9	500.0	14.3607	F2	581
						55	538.7	600.0	10.4577	F2	581
						71	547.8	600.0	10.8921	F2	581
						63	549.9	700.0	10.0196	F2	581
8	Benzene	0.676	5.7567	4.9141	103	94	206.3	20.0	-3.4856	O3	581
	Octane	0.324				122	533.1	568.0	11.8848	F2	581
						121	538.6	568.0	13.0611	F2	581
						120	543.2	568.0	14.2898	F2	581
						111	547.2	600.0	11.6297	F2	581
9	Benzene	0.771	5.5339	4.4942	56	32	552.9	700.0	11.3824	F2	581
	Octane	0.229									

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
10	Benzene	0.857	5.9343	4.9023	97	157	523.7	600.0	11.1710	F2	581
	Octane	0.143				156	527.7	600.0	10.9240	F2	581
						149	529.3	600.0	11.6356	F2	581
						101	541.3	640.0	14.0701	F2	581
						100	545.0	545.0	640.0	F2	581
						99	546.8	546.8	640.0	F2	581
						90	537.1	700.0	10.9103	F2	581
						89	547.6	700.0	10.4061	F2	581
						115	552.0	700.0	11.1039	F2	581
						87	558.6	700.0	13.5528	F2	581
11	Benzene	0.930	4.9960	4.2044	71	29	513.8	600.0	10.7138	F2	581
	Octane	0.070				18	525.2	600.0	10.1114	F2	581
						105	542.3	675.0	10.4517	F2	581
12	Benzene	0.199	2.7292	2.1570	54	51	416.8	600.0	5.4947	F2	584
	Pentane	0.801				13	408.1	528.0	6.2884	F2	681
13	Benzene	0.406	3.5187	2.8853	61	29	382.6	400.0	7.4756	F2	584
	Pentane	0.594				8	429.9	600.0	8.3824	F2	584
						7	434.6	600.0	8.2749	F2	584

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
14	Benzene	0.600	2.5492	2.0655	93	121	360.0	1400.0	-5.5572	F2	681
	Pentane	0.400				116	400.5	1000.0	-8.5984	F2	584
15	Benzene	0.814	3.4937	2.3903	64	17	152.0	15.2	-17.6115	O2	584
	Pentane	0.186				14	420.0	400.0	-8.4105	F2	681
16	Benzene	0.203	6.0463	4.6618	3						
	Propane	0.797									
17	Benzene	0.502	3.3851	2.8227	7						
	Propane	0.498									
18	Benzene	0.748	4.4894	4.0002	9						
	Propane	0.252									
19	Ethane	0.500	6.4482	5.1015	25						
	Hydrogen Sulfide	0.500									
20	Ethane	0.237	10.7390	8.6757	60	22	117.0	716.0	-22.7331	F2	671
	Propane	0.763				72	144.0	1000.0	-22.7853	F2	671
						84	147.0	1000.0	-25.4662	F2	671

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
21	Ethane	0.502	4.6070	3.3233	48	32	130.0	760.0	9.8391	F2	671
	Propane	0.498				33	140.0	760.0	9.9696	F2	671
						1	-280.0	2000.0	10.6005	F2	671
						4	-260.0	2000.0	9.5516	F2	671
22	Ethane	0.724	22.3801	8.6756	26	9	120.0	500.0	104.1695	O2	592
	Propane	0.276				14	160.0	1000.0	36.2076	F2	592
						30	140.0	1000.0	22.1932	F2	671
23	Ethylbenzene	0.271	2.2238	2.2130	4						
	Octane	0.729									
24	iso-Pentane	0.197	2.4693	2.2404	36						
	1,2,3,4-Tetrahydronaphthalene	0.803									
25	iso-Pentane	0.399	3.5446	3.3399	12						
	1,2,3,4-Tetrahydronaphthalene	0.601									

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
26	iso-Pentane	0.893	7.6431	7.4268	32						
	1,2,3,4-Tetrahydronaphthalene	0.107									
27	Methane	0.500	7.4381	7.2006	6						
	Hydrogen Sulfide	0.500									
28	Methane	0.883	6.8794	6.8794	1						
	iso-Butene	0.117									
29	Methane	0.500	8.419	8.0292	68	44	-100.0	50.0	-19.4904	F2	667
	Methylcyclohexane	0.500				35	-50.0	50.0	-18.0836	F2	667
						1	250.0	200.0	-88.4200	O2	667
30	Methane	0.249	5.0601	3.7231	90	68	200.0	50.0	16.3300	O2	667
	Heptane	0.751				39	250.0	100.0	15.2600	O2	667
						55	300.0	200.0	10.3200	F2	667
						15	-100.0	600.0	17.7415	O2	667
31	Methane	0.491	6.0916	5.3929	15						
	Heptane	0.509									

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
32	Methane	0.951	8.0142	7.4368	6						
	Heptane	0.049									
33	Methane	0.566	2.2431	2.1730	7						
	Nitrogen	0.434									
34	Methane	0.234	4.5218	3.3081	322	26	-280.0	250.0	9.7905	F2	370
	Propane	0.766				34	-270.0	250.0	9.5702	F2	370
						42	-260.0	250.0	9.1157	F2	370
						27	-280.0	500.0	9.8454	F2	370
						49	-270.0	500.0	9.5043	F2	370
						43	-260.0	500.0	9.1419	F2	370
						28	-280.0	750.0	9.8005	F2	370
						36	-270.0	750.0	9.3571	F2	370
						29	-280.0	1000.0	9.6558	F2	370
						25	-270.0	1000.0	9.3102	F2	370
						30	-280.0	1250.0	9.5870	F2	370
						38	-270.0	1250.0	9.4356	F2	370
						31	-280.0	1500.0	9.8341	F2	370
						39	-270.0	1500.0	9.6787	F2	370
						47	-260.0	1500.0	9.3009	F2	370

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
						32	-280.0	1750.0	9.7818	F2	370
						40	-270.0	1750.0	9.7225	F2	370
						48	-260.0	1750.0	9.3404	F2	370
						33	-280.0	2000.0	9.6301	F2	370
						41	-270.0	2000.0	9.3670	F2	370
35	Methane	0.494	4.3430	3.6054	252	57	-280.0	2000.0	8.8332	F2	370
	Propane	0.506									
36	Methane	0.720	2.5970	2.0572	210	83	-260.0	250.0	5.5291	F2	370
	Propane	0.280				80	-280.0	500.0	5.0847	F2	370
						88	-270.0	500.0	5.6449	F2	370
						75	-260.0	500.0	5.3117	F2	370
						81	-280.0	750.0	5.3867	F2	370
						89	-270.0	750.0	5.4453	F2	370
						82	-280.0	1000.0	5.5128	F2	370
						90	-270.0	1000.0	5.3484	F2	370
						93	-280.0	1250.0	5.6299	F2	370
						84	-280.0	1500.0	5.9490	F2	370
						78	-280.0	1750.0	5.6699	F2	370
						86	-280.0	2000.0	5.4926	F2	370

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
37	Methane	0.883	1.9598	1.5848	190	58	-50.0	1250.0	4.4227	F2	370
	Propane	0.117				210	-40.0	1250.0	4.7474	F2	370
						300	-30.0	1250.0	3.9423	F2	370
						27	-250.0	250.0	4.1829	F2	370
38	Methane	0.948	1.5146	1.2560	166	222	-110.0	800.0	3.1463	F2	370
	Propane	0.052				231	-100.0	800.0	4.2946	F2	370
						232	-100.0	1000.0	3.3292	F2	370
						97	-90.0	1000.0	4.0987	F2	370
						108	-80.0	1100.0	4.0887	F2	370
						71	-70.0	1100.0	3.1982	F2	370
39	Methane	0.500	37.3908	39.3038	40	3	300.0	200.0	85.3299	F2	667
	Toluene	0.500				4	300.0	400.0	90.1368	F2	667
						77	350.0	400.0	74.2453	F2	667
						100	300.0	600.0	70.7833	F2	667
						75	350.0	600.0	70.1652	F2	667
40	Pentane	0.500	13.3086	13.0253	25						
	Carbon Dioxide	0.500									

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
41	Pentane	0.502	4.3619	3.5494	43						
	cis-2-Pentene	0.498									
42	Pentane	0.197	3.3100	2.7902	97	81	521.4	800.0	9.5078	F2	584
	Cyclohexane	0.803				31	500.0	600.0	8.3977	F2	677
43	Pentane	0.385	1.9899	1.6129	96	7	376.3	300.0	6.1328	O2	580
	Cyclohexane	0.615									
44	Pentane	0.612	3.0603	2.5734	89	33	127.4	200.0	-4.5480	O3	584
	Cyclohexane	0.388				87	161.5	600.0	3.2793	F3	584
						91	208.9	600.0	-3.1527	F3	584
						92	258.1	600.0	-4.0608	F3	584
						93	258.9	600.0	2.7432	F3	584
						94	318.4	600.0	-5.0834	F3	584
						95	318.5	600.0	3.0863	F3	584
						96	368.1	600.0	-1.1665	F3	584
						110	368.4	600.0	4.3663	F3	584
						89	418.4	600.0	6.5083	F2	584
						83	420.0	500.0	8.9178	F2	677
						82	440.0	600.0	6.4925	F2	677

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
45	Pentane	0.793	3.2797	2.6473	82	107	368.8	500.0	6.9856	F2	584
	Cyclohexane	0.207				61	389.5	500.0	8.5051	F2	584
						22	400.0	500.0	9.0807	F2	677
46	Pentane	0.167	3.9076	3.3426	28						
	Hexadecane	0.833									
47	Pentane	0.386	3.4869	2.9034	39	5	620.0	200.0	-7.5401	F2	583
	Hexadecane	0.614				40	178.5	40.0	7.6949	F2	584
						41	220.2	40.0	7.8274	F2	584
48	Pentane	0.587	3.3075	2.8916	41	68	600.0	400.0	-4000.352	O1	583
	Hexadecane	0.413									
49	Pentane	0.794	2.9333	2.6371	60	52	625.1	1400.0	7.4416	O2	584
	Hexadecane	0.206									
50	Pentane	0.218	2.5240	1.9750	66	108	502.0	400.0	6.0104	F2	663
	Octane	0.782				121	509.9	400.0	5.7659	F2	663
						46	539.9	500.0	5.6875	F2	663
						26	540.0	500.0	6.2427	F2	663

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
						76	539.1	600.0	5.5874	F2	663
51	Pentane Octane	0.392 0.608	3.0892	2.5567	52	25	499.1	540.0	6.7245	F2	663
52	Pentane Octane	0.597 0.403	3.4675	2.8768	51	104	500.1	800.0	7.4262	F2	663
53	Pentane Octane	0.809 0.191	1.2042	0.9414	10	99	75.0	1400.0	2.6657	F2	663
54	Pentane 1,2,3,4-Tetrahydronaphthalene	0.197 0.803	7.2344	5.9318	45						
55	Pentane 1,2,3,4-Tetrahydronaphthalene	0.399 0.601	6.0644	5.3643	27						

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
56	Pentane	0.588	6.1539	5.8397	38						
	1,2,3,4-Tetrahydronaphthalene	0.412									
57	Pentane	0.795	4.3861	4.1817	49						
	1,2,3,4-Tetrahydronaphthalene	0.205									
58	Pentane	0.893	3.1929	2.9630	46	108	134.4	25.0	-4.5366	O3	580
	1,2,3,4-Tetrahydronaphthalene	0.107				129	234.8	100.0	-1.3470	F3	580
						75	377.8	400.0	-2.4592	O3	580
59	Pentane	0.322	4.7420	4.3499	84	17	596.8	1400.0	9.7562	F2	580
	trans-Decalin	0.678									
60	Pentane	0.561	4.3132	3.5938	63	145	598.2	1000.0	9.1438	F2	580
	trans-Decalin	0.439				73	460.0	800.0	7.8402	O3	580
61	Pentane	0.725	3.5367	2.7934	60	85	118.9	30.0	11.7739	O2	580
	trans-Decalin	0.275				84	138.5	30.0	14.1595	O2	580

Table B.5 (Continued).

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
62	Pentane trans-Decalin	0.884 0.116	2.6076	2.2446	76	123	120.4	20.0	-3.1423	O3	580
63	Propane iso-Pentane	0.430 0.570	5.2487	4.3173	14						

Table B.6.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
1	Benzene	0.419	6.4553	6.2928	7						
	Hexadecane	0.581									
2	Benzene	0.670	10.3470	10.2069	9						
	Hexadecane	0.330									
3	Benzene	0.814	9.8159	9.1052	20						
	Hexadecane	0.186									
4	Benzene	0.920	7.8353	6.8727	69	102	384.0	20.0	16.8225	F2	580
	Hexadecane	0.080				45	572.4	400.0	17.9448	F2	580
						46	580.0	100.0	-4.9069	F3	682
5	Benzene	0.963	6.9639	5.5269	124	11	311.8	20.0	17.4593	F2	580
	Hexadecane	0.037				19	331.5	20.0	15.5096	F2	580
						30	350.1	40.0	16.2383	F2	580
						29	366.1	40.0	15.5182	F2	580
						87	397.1	70.0	15.1439	F2	580
						78	536.6	70.0	-1.4286	F3	580
						147	499.0	300.0	14.5658	F2	580

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
6	Benzene	0.271	8.3335	5.8686	90	53	572.6	500.0	19.7462	F2	581
	Octane	0.729				84	570.6	600.0	22.8416	F2	581
						54	576.2	600.0	20.3430	F2	581
						97	580.3	600.0	21.1865	F2	581
						98	586.4	600.0	20.1504	F2	581
						99	593.1	600.0	19.5248	F2	581
						96	576.2	700.0	18.8294	F2	581
						2	560.0	500.0	23.6328	F2	679
7	Benzene	0.446	7.4203	5.5928	89	58	566.6	600.0	21.4392	F2	581
	Octane	0.554				65	577.1	700.0	16.4085	F2	581
						68	567.5	800.0	15.0689	F2	581
						67	540.0	600.0	22.3777	F2	679
						19	560.0	600.0	21.8107	F2	679
						60	560.0	700.0	17.1914	F2	679
8	Benzene	.0676	5.8652	4.1627	89	136	556.9	800.0	22.4246	F2	581
	Octane	0.324				162	577.8	800.0	19.8916	F2	581
						142	566.9	1000.0	13.3193	F2	581
						141	586.1	1000.0	13.0448	F2	581
						59	560.0	800.0	16.0305	F2	679

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
9	Benzene	0.771	6.5131	3.7826	76	26	557.7	800.0	22.5062	F2	581
	Octane	0.229				25	567.0	800.0	20.7565	F2	581
						24	578.4	800.0	18.6791	F2	581
						18	566.7	1000.0	18.3162	F2	581
						56	587.5	1000.0	15.3782	F2	581
						90	595.3	1000.0	13.4632	F2	581
						61	560.0	700.0	22.1023	F2	679
10	Benzene	0.857	4.9381	3.5247	103	118	566.6	1000.0	11.5771	F2	581
	Octane	0.143				69	560.0	700.0	22.0591	F2	679
						61	560.0	800.0	17.5138	F2	679
						38	560.0	1000.0	14.3897	F2	679
						39	580.0	1000.0	10.8267	F2	679
11	Benzene	0.930	4.9592	2.9789	88	77	568.0	800.0	12.1667	F2	581
	Octane	0.070				72	576.8	1000.0	10.0337	F2	581
						17	380.0	200.0	120.6413	O1	679
						70	560.0	800.0	22.6437	F2	679
						64	560.0	1000.0	19.4280	F2	679
						63	580.0	1000.0	15.5781	F2	679
						15	560.0	1400.0	10.6980	F2	679

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
12	Benzene	0.199	7.2138	4.4157	224	136	430.4	700.0	32.9606	F2	584
	Pentane	0.801				125	440.8	700.0	27.5678	F2	584
						123	440.7	800.0	16.4852	F2	584
						103	420.0	600.0	2.5315	F2	681
						135	430.0	600.0	14.7904	F2	681
						149	420.0	700.0	34.3302	F2	681
						134	430.0	700.0	32.1435	F2	681
						133	440.0	700.0	26.5837	F2	681
						126	420.0	800.0	17.3625	F2	681
						137	430.0	800.0	15.4619	F2	681
						60	420.0	1000.0	21.2618	F2	681
						59	430.0	1000.0	19.9664	F2	681
						58	440.0	1000.0	18.2320	F2	681
						57	460.0	1000.0	14.7463	F2	681
13	Benzene	0.406	6.9920	4.6567	225	129	481.2	800.0	17.0965	F2	584
	Pentane	0.594				177	450.0	660.0	35.6053	F2	681
						168	460.0	660.0	28.3970	F2	681
						173	450.0	700.0	18.9823	F2	681
						174	460.0	700.0	15.3995	F2	681
						85	460.0	800.0	23.2039	F2	681

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
						86	470.0	800.0	21.2895	F2	681
						97	480.0	800.0	18.3568	F2	681
						74	450.0	1000.0	22.9873	F2	681
						73	460.0	1000.0	21.4930	F2	681
						72	470.0	1000.0	19.9679	F2	681
						71	480.0	1000.0	18.3174	F2	681
						70	490.0	1000.0	16.0436	F2	681
						69	500.0	1000.0	14.2420	F2	681
14	Benzene	0.600	6.0818	4.0295	248	73	510.9	1000.0	12.9883	F2	581
	Pentane	0.400				78	492.7	700.0	21.9570	F2	584
						109	490.8	800.0	17.5330	F2	584
						101	501.2	800.0	13.2759	F2	584
						113	530.8	800.0	-19.4964	F2	584
						141	490.0	700.0	17.4483	F2	681
						58	490.0	800.0	26.8658	F2	681
						77	500.0	800.0	22.5541	F2	681
						54	510.0	800.0	16.3338	F2	681
						108	490.0	1000.0	22.4490	F2	681
						109	500.0	1000.0	21.0729	F2	681
						110	510.0	1000.0	20.0957	F2	681

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
						111	520.0	1000.0	18.6126	F2	681
15	Benzene	0.814	6.5033	3.6848	202	61	540.6	800.0	21.7377	F2	584
	Pentane	0.186				49	540.2	1000.0	13.7885	F2	584
						52	520.0	700.0	33.1095	F2	681
						84	520.0	800.0	29.9698	F2	681
						59	530.0	800.0	26.5900	F2	681
						57	540.0	800.0	18.5289	F2	681
						111	520.0	1000.0	26.5014	F2	681
						104	530.0	1000.0	24.6479	F2	681
						105	540.0	1000.0	22.9302	F2	681
						106	550.0	1000.0	19.8576	F2	681
						107	560.0	1000.0	16.0234	F2	681
						61	540.6	800.0	21.7377	F2	584
						49	540.2	1000.0	13.7885	F2	584
16	Benzene	0.203	2.8726	2.2757	5						
	Propane	0.797									
17	Benzene	0.502	1.1474	0.9343	2						
	Propane	0.498									

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
18	Benzene	0.748	4.7723	3.7268	2						
	Propane	0.252									
19	Carbon Dioxide	0.0816	6.7709	4.4606	94	110	305.3	2175.6	18.3872	F2	686
	Hydrogen Sulfide	0.9148				30	395.3	5801.6	13.7971	F2	686
						3	440.3	5801.6	13.4921	F2	686
						4	350.3	6526.8	14.7315	F2	686
						5	395.3	6526.8	15.0100	F2	686
						15	350.3	7252.0	17.4761	F2	686
						7	395.3	7252.0	15.9996	F2	686
						1	350.3	7977.2	19.6888	F2	686
						9	395.3	7977.2	16.7931	F2	686
						10	395.3	8702.4	17.3821	F2	686
						11	395.3	9427.6	17.8027	F2	686
20	Carbon Dioxide	0.5141	6.6018	5.0960	79	13	170.3	1740.5	15.8727	F2	686
	Hydrogen Sulfide	0.4859				9	170.3	1885.5	15.3081	F2	686
						5	170.3	2030.6	14.0380	F2	686
						26	260.3	5801.6	-13.7564	F2	686
						19	350.3	8702.4	-13.2220	F2	686

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
21	Carbon Monoxide	0.250	18.2899	12.5012	58	64	-250.0	1000.0	-42.1434	F2	673
	Hydrogen	0.750				66	-225.0	1000.0	-36.8538	F2	673
						21	-200.0	1500.0	-43.7386	F2	673
						16	-200.0	2000.0	-51.8797	F2	673
						61	-200.0	2000.0	-57.9352	F2	673
22	Carbon Monoxide	0.500	24.6411	15.9396	57	16	-200.0	1000.0	-51.9830	F2	673
	Hydrogen	0.500				46	-200.0	1500.0	-59.8539	F2	673
						51	-200.0	2000.0	-67.4290	F2	673
						66	-200.0	2500.0	-74.2768	F2	673
						65	0.0	2500.0	-49.7183	F2	673
23	Ethane	0.500	1.7641	1.2193	18	15	150.0	500.0	-3.5010	F2	670
	Hydrogen Sulfide	0.500				21	200.0	500.0	-4.8333	F2	670
24	Ethylbenzene	0.271	10.2396	7.0751	10						
	Octane	0.729									
25	Ethane	0.237	16.6717	12.7484	37	25	105.0	500.0	88.86	F2	671
	Propane	0.763				45	110.0	500.0	100.85	F2	671
						37	115.0	500.0	114.04	F2	671

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
26	Ethane	0.502	4.9555	2.5893	28	28	200.0	1000.0	10.5442	F2	592
	Propane	0.498				41	200.0	760.0	-13.1207	F2	671
						42	210.0	760.0	-18.5681	F2	671
27	Ethane	0.724	16.7203	14.1490	23	15	200.0	1000.0	45.7437	F2	592
	Propane	0.276				28	220.0	1000.0	33.9209	F2	671
28	iso-Pentane	0.197	3.1339	2.6762	21	68	500.0	70.0	69.9749	O2	675
	1,2,3,4-Tetrahydronaphthalene	0.803				59	520.0	70.0	26.6748	O2	675
29	iso-Pentane	0.399	3.0906	2.5735	7						
	1,2,3,4-Tetrahydronaphthalene	0.601									
30	iso-Pentane	0.588	2.9660	2.3823	23	2	460.0	70.0	5.9841	F2	675
	1,2,3,4-Tetrahydronaphthalene	0.412				47	580.0	200.0	6.0897	F2	675

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
31	iso-Pentane	0.795	1.9650	1.4078	29	8	480.0	200.0	5.4535	F2	675
	1,2,3,4-Tetrahydronaphthalene	0.205				52	520.0	300.0	4.2171	F2	675
						53	540.0	300.0	3.9536	F2	675
32	iso-Pentane	0.893	3.6015	2.8247	72	81	340.0	70.0	9.5419	F2	675
	1,2,3,4-Tetrahydronaphthalene	0.107				87	360.0	100.0	10.6021	F2	675
						57	400.0	200.0	10.2997	F2	675
						119	440.0	300.0	7.8901	F2	675
						136	460.0	400.0	7.2135	F2	675
33	Methane	0.4761	7.8789	5.9310	183	103	8.3	2175.6	-15.8687	F2	688
	Carbon Dioxide	0.5239				108	8.3	2900.8	-16.3090	F2	688
						85	8.3	3626.0	-17.1341	F2	688
						81	32.0	4351.2	-16.6682	F2	688
						77	32.0	5076.4	-17.7080	F2	688
						86	60.0	5076.4	-15.8467	F2	688
						89	60.0	5801.6	-16.9586	F2	688
						92	80.3	6526.8	-16.6942	F2	688
						93	80.3	7252.0	-17.7613	F2	688

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
34	Methane	0.500	5.3380	4.5249	40	10	50.0	1200.0	-10.7678	F2	667
	Carbon Dioxide	0.500				45	100.0	2000.0	-12.0484	F2	667
35	Methane	0.500	4.0430	2.8740	77	72	0.0	2000.0	-8.2351	F2	673
	Hydrogen	0.500				67	200.0	2000.0	-9.2654	F2	673
						63	0.0	2500.0	-9.2618	F2	673
						62	200.0	2500.0	-10.7013	F2	673
						61	400.0	2500.0	-8.9783	F2	673
36	Methane	0.4927	12.8426	10.8569	81	31	170.3	2900.8	-29.3930	F2	686
	Hydrogen Sulfide	0.5073									
37	Methane	0.500	5.8130	2.8208	25	24	150.0	2000.0	-23.2406	O2	670
	Hydrogen Sulfide	0.500				26	200.0	2000.0	-14.2757	O2	670
38	Methane	0.500	4.1469	3.5675	36						
	Methylcyclohexane	0.500									
39	Methane	0.249	4.1525	3.7645	35						
	Heptane	0.751									

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
40	Methane	0.491	4.9671	3.2705	44	23	300.0	50.0	10.2989	F2	592
	Heptane	0.509				12	250.0	50.0	18.2577	F2	667
						3	300.0	100.0	14.1548	F2	667
41	Methane	0.951	1.6185	1.1018	79	27	150.0	200.0	7.4840	F2	592
	Heptane	0.049				3	200.0	400.0	6.2458	F2	592
						51	600.0	600.0	-3.3976	F2	592
42	Methane	0.566	4.1497	2.6359	369	19	-150.0	1000.0	24.0333	F2	591
	Nitrogen	0.434				11	-250.0	1500.0	26.9957	F2	591
						5	-150.0	1500.0	18.4824	F2	591
						7	-250.0	2000.0	11.7263	F2	591
						1	-150.0	2000.0	10.8611	F2	591
						119	-150.0	750.0	10.0372	F2	667
						85	-140.0	1000.0	16.8770	F2	667
						108	-130.0	1000.0	9.5389	F2	667
						97	-150.0	1250.0	23.4412	F2	667
						91	-140.0	1250.0	19.0271	F2	667
						115	-130.0	1250.0	13.2612	F2	667
						100	-140.0	1500.0	15.8450	F2	667
						114	-130.0	1500.0	12.5042	F2	667

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
						40	-120.0	1500.0	9.3762	F2	667
						96	-150.0	1750.0	14.9130	F2	667
						89	-140.0	1750.0	12.6519	F2	667
						113	-130.0	1750.0	10.8235	F2	667
						116	-120.0	1750.0	8.5074	F2	667
						88	-140.0	2000.0	9.9528	F2	667
43	Methane	0.234	1.8313	1.3097	102	295	200.0	1250.0	8.5762	O2	370
	Propane	0.766				313	210.0	1250.0	5.1975	F2	370
						33	200.0	1000.0	8.0312	O2	590
44	Methane	0.494	1.0658	0.085	136	314	260.0	1250.0	-2.3500	F2	370
	Propane	0.506				23	150.0	1500.0	3.5145	F2	590
45	Methane	0.720	2.4802	2.0834	175	367	300.0	1750.0	-5.0563	F2	370
	Propane	0.280				318	300.0	2000.0	-5.0922	F2	370
46	Methane	0.874	3.9862	3.8102	12						
	Propane	0.126									

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
47	Methane	0.883	3.1668	2.9494	213						
	Propane	0.117									
48	Methane	0.948	2.8634	2.3640	250						
	Propane	0.052									
49	Methane	0.949	5.2858	4.8040	12						
	Propane	0.051									
50	Methane	0.500	1.1436	0.8603	33	21	600.0	1500.0	3.1716	F2	592
	Toluene	0.500				18	600.0	2500.0	2.5665	F2	592
51	Methylcyclohexane	0.1067	12.5378	10.4360	63	74	305.3	2900.8	-26.6759	F2	686
	Hydrogen Sulfide	0.8933				71	305.3	3626.0	-26.0562	F2	686
						68	305.3	4351.2	-25.1101	F2	686
52	Pentane	0.500	6.9056	3.7893	28	10	150.0	100.0	30.5308	O2	685
	Carbon Dioxide	0.500									
53	Pentane	0.502	7.2343	3.8834	116	71	391.1	600.0	30.6105	O2	581
	cis-2-Pentene	0.498				73	393.1	600.0	28.5189	O2	581

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
						69	400.0	600.0	28.2908	O2	581
						75	407.3	600.0	18.5252	F2	581
						68	393.5	800.0	14.9393	F2	581
						80	400.0	600.0	24.8325	O2	678
						23	400.0	700.0	14.8335	F2	678
54	Pentane	0.197	5.3783	3.5378	170	57	547.8	1000.0	17.9818	O2	584
	Cyclohexane	0.803				4	520.0	700.0	25.8455	O2	677
						59	520.0	800.0	22.0425	O2	677
						60	540.0	800.0	14.7556	F2	677
						69	520.0	1000.0	14.5049	F2	677
						70	540.0	1000.0	12.6079	F2	677
55	Pentane	0.385	4.4467	2.8629	167	52	528.6	1000.0	10.4595	F2	584
	Cyclohexane	0.615				49	500.0	700.0	23.3782	O2	677
						58	520.0	700.0	10.6465	F2	677
						42	500.0	800.0	22.1910	O2	677
						43	520.0	800.0	14.4332	O2	677
						146	500.0	1000.0	15.9501	O2	677
						133	520.0	1000.0	11.9588	F2	677
						137	680.0	1000.0	-14.9748	O2	677

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
56	Pentane	0.612	5.1316	2.7591	190	73	477.0	1000.0	23.3875	O2	584
	Cyclohexane	0.388				74	529.3	1000.0	12.3131	F2	584
						81	460.0	600.0	29.1611	O2	677
						80	640.0	600.0	-14.4014	F2	677
						69	460.0	700.0	29.3265	O2	677
						87	480.0	700.0	11.3131	F2	677
						158	460.0	800.0	23.8209	O2	677
						159	48.0	800.0	17.2091	O2	677
						170	500.0	1000.0	14.5865	O2	677
57	Pentane	0.793	5.7857	3.0371	233	89	448.5	1000.0	21.1097	O2	584
	Cyclohexane	0.207				88	498.9	1000.0	12.1637	O2	584
						143	420.0	600.0	41.4525	O2	677
						142	440.0	600.0	36.4077	O2	677
						162	420.0	800.0	24.7883	O2	677
						110	440.0	800.0	19.7940	O2	677
						98	460.0	800.0	14.6066	F2	677
						89	420.0	1000.0	21.9098	O2	677
						99	440.0	1000.0	17.2049	F2	677
						112	460.0	1000.0	16.6120	F2	677
						97	480.0	1000.0	13.1406	F2	677

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
58	Pentane	0.167	2.8947	2.8839	2						
	Hexadecane	0.833									
59	Pentane	0.386	3.2903	2.9569	16	38	616.9	25.0	7.1377	F2	584
	Hexadecane	0.614									
60	Pentane	0.587	1.8288	1.5734	16						
	Hexadecane	0.413									
61	Pentane	0.794	7.8628	2.2849	31	76	400.0	40.0	43.1891	O2	583
	Hexadecane	0.206				20	480.4	25.0	4.0880	F2	584
62	Pentane	0.218	5.9870	4.1038	80	33	530.0	400.0	33.9237	O2	663
	Octane	0.782				32	540.0	400.0	16.4755	F2	663
						25	550.0	500.0	13.0082	F2	663
63	Pentane	0.392	7.6429	5.7898	61	75	520.0	500.0	23.3317	O2	663
	Octane	0.608				78	540.0	500.0	10.6075	F2	663
						82	500.0	600.0	21.8134	F2	663
						83	520.0	600.0	19.3372	F2	663

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
64	Pentane	0.597	7.4886	5.5356	69	94	480.0	600.0	25.2826	F2	663
	Octane	0.403				93	490.0	600.0	23.5731	F2	663
						92	500.0	600.0	21.0826	F2	663
						87	480.0	800.0	16.2600	F2	663
						86	490.0	800.0	15.8911	F2	663
65	Pentane	0.809	8.5868	4.5915	74	112	75.0	600.0	57.7779	O2	663
	Octane	0.191				136	460.0	800.0	20.1051	O2	663
66	Pentane	0.197	44.3324	27.3293	56	71	401.0	40.0	111.5244	O1	580
	1,2,3,4-Tetrahydronaphthalene	0.803				70	413.9	40.0	106.1801	O1	580
						69	438.0	40.0	90.5941	O1	580
						68	464.7	40.0	41.1105	O1	580
						41	480.4	70.0	91.7755	O1	580
						40	500.7	70.0	73.2579	O1	580
						39	520.5	70.0	28.7392	F2	580
						145	479.0	100.0	104.9167	O1	580
						144	488.7	100.0	100.9410	O1	580
						143	495.1	100.0	96.5067	O1	580
						142	539.3	100.0	65.8289	O1	580
						141	548.9	100.0	51.2948	O1	580

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
						14	560.0	100.0	27.9915	F2	580
						103	578.7	200.0	82.6918	O1	580
						102	587.4	200.0	78.1315	O1	580
						101	598.5	200.0	72.7567	O1	580
						95	625.6	200.0	50.8696	O1	580
						99	639.8	200.0	22.8380	F2	580
67	Pentane	0.399	6.0894	5.1337	39	80	676.3	25.0	12.6095	F2	580
	1,2,3,4-Tetrahydronaphthalene	0.601				93	676.9	100.0	13.4365	F2	580
68	Pentane	0.588	7.3355	7.0582	36						
	1,2,3,4-Tetrahydronaphthalene	0.412									
69	Pentane	0.795	5.3193	5.0269	75	75	357.6	40.0	11.2003	F2	580
	1,2,3,4-Tetrahydronaphthalene	0.205				64	367.9	40.0	-3.4202	F3	580

Table B.6. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
70	Pentane	0.893	8.6393	5.7521	86	89	200.2	40.0	39.3928	F3	580
	1,2,3,4-Tetrahydronaphthalene	0.107				72	375.6	385.0	41.7570	F3	580
71	Pentane	0.322	5.6897	4.8316	45						
	trans-Decalin	0.678									
72	Pentane	0.561	5.7050	4.5577	41						
	trans-Decalin	0.439									
73	Pentane	0.725	3.7981	3.2381	78	136	549.1	700.0	10.6160	F2	580
	trans-Decalin	0.275									
74	Pentane	0.884	2.4423	1.8227	88	191	349.4	100.0	5.7986	F2	580
	trans-Decalin	0.116				178	356.1	100.0	6.7533	F2	580
75	Propane	0.430	9.4602	8.0236	21						
	iso-Pentane	0.570									

Table B.7.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Liquid-Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Benzene	0.963	3.3990	3.3990	1						
	Hexadecane	0.037									
2	Benzene	0.199	5.7067	5.3109	6						
	Pentane	0.801									
3	Benzene	0.406	38.7932	20.7128	14						
	Pentane	0.594									
4	Benzene	0.600	1.5459	1.4110	5						
	Pentane	0.400									
5	Benzene	0.814	4.5775	3.9474	4						
	Pentane	0.186									
6	Pentane	0.500	10.6590	10.6141	3						
	Carbon Dioxide	0.500									
7	Pentane	0.197	6.3749	4.9600	5						
	Cyclohexane	0.803									

Table B.7. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Liquid-Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
8	Pentane Cyclohexane	0.385 0.615	5.2716	4.4067	6						
9	Pentane Cyclohexane	0.612 0.388	6.1035	5.2791	3						
10	Pentane Cyclohexane	0.793 0.207	7.0507	6.7887	3						
11	Pentane Octane	0.218 0.782	2.3220	2.3220	1						
12	Pentane Octane	0.392 0.608	2.5014	2.5014	1						
13	Pentane Octane	0.597 0.403	7.9990	7.9709	2						
14	Pentane Octane	0.809 0.191	4.6240	4.4860	2						

Table B.8.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Vapor-Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Benzene Octane	0.771 0.229	1.3090	1.2655	2						
2	Benzene Pentane	0.199 0.801	1.9428	1.5838	10						
3	Benzene Pentane	0.406 0.594	4.3075	3.1411	3						
4	Benzene Pentane	0.600 0.400	1.2771	0.9144	9						
5	Benzene Pentane	0.814 0.186	1.8602	1.5740	8						
6	Carbon Dioxide Hydrogen Sulfide	0.0816 0.9148	2.6793	2.6633	2						
7	Methane Carbon Dioxide	0.4761 0.5239	25.0999	13.2976	4						

Table B.8. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Vapor-Vapor Binary Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
8	Methylcyclohexane Hydrogen Sulfide	0.1067 0.8933	14.1756	13.4501	3						
9	Pentane Cyclohexane	0.197 0.803	8.0385	7.8403	7						
10	Pentane Cyclohexane	0.385 0.615	3.0636	2.7526	9						
11	Pentane Cyclohexane	0.612 0.388	2.8217	2.2961	7						
12	Pentane Cyclohexane	0.793 0.207	4.7804	3.9636	11						
13	Pentane Octane	0.218 0.782	2.8594	2.8594	1						
14	Pentane Octane	0.392 0.608	8.8448	8.1943	3						

Table B.8. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Vapor-Vapor Binary Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
15	Pentane Octane	0.597 0.403	4.9672	4.5076	6						
16	Pentane Octane	0.809 0.191	1.7294	1.6016	7						

Table B.9.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Multicomponent Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Carbon Dioxide	0.333	13.4593	13.2917	5						
	Methane	0.333									
	Ethane	0.334									
2	Hydrogen Sulfide	0.333	9.4629	9.3952	12						
	Ethane	0.333									
	Methane	0.334									
3	Methane	0.366	6.3621	5.2984	19						
	Propane	0.323									
	Ethane	0.311									
4	Methane	0.3702	3.3564	2.2764	140	35	-80.0	250.0	-18.2753	O2.3	671
	Propane	0.3243				172	60.0	750.0	-9.4692	O2,3	671
	Ethane	0.3055				71	-280.0	1000.0	6.7189	F2	671
						69	-280.0	1500.0	6.7760	F2	671
						67	-280.0	2000.0	6.7368	F2	671
5	Pentane	0.200	3.5976	2.8378	59	95	352.1	1400.0	-7.5581	F2	665
	Cyclohexane	0.202				106	399.3	1400.0	-8.8752	F2	665
	Benzene	0.598				93	445.3	1400.0	-9.1773	F2	665
						92	497.1	1400.0	-7.4831	F2	665

Table B.9. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid Multicomponent Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
5	Pentane	0.200	3.5976	2.8378	59	95	352.1	1400.0	-7.5581	F2	665
	Cyclohexane	0.202				106	399.3	1400.0	-8.8752	F2	665
	Benzene	0.598				93	445.3	1400.0	-9.1773	F2	665
						92	497.1	1400.0	-7.4831	F2	665
6	Pentane	0.333	2.2433	1.9002	76	5	460.0	1400.0	-4.8423	F2	683
	Cyclohexane	0.334									
	Benzene	0.333									
7	Pentane	0.601	2.5603	2.1061	91	63	341.3	1000.0	-7.7947	F2	665
	Cyclohexane	0.199				35	420.0	500.0	5.4881	F2	683
	Benzene	0.200				71	340.0	1000.0	-6.7272	F2	683
						62	360.0	1000.0	-5.1425	F2	683
8	1,2,3,4-Tetrahydronaphthalene	0.333	3.0888	2.6920	87	39	580.0	400.0	6.6683	F2	684
						40	600.0	500.0	6.3785	F2	684
	Benzene	0.333									
	Octane	0.334									
9	1,2,3,4-Tetrahydronaphthalene	0.100	4.2162	3.5116	84	83	500.1	1400.0	-9.1516	F2	581
	Benzene	0.450									
	Octane	0.450									

Table B.10.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Multicomponent Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
1	Carbon Dioxide	0.333	6.4148	5.5543	38	13	50.0	1600.0	12.7802	O3	672
	Methane	0.333									
	Ethane	0.334									
2	Hydrogen Sulfide	0.333	3.7754	2.0008	27	17	150.0	2000.0	-11.6274	O2	670
	Ethane	0.333				2	200.0	2000.0	-11.9523	O2	670
	Methane	0.334									
3	Methane	0.366	1.9192	1.6910	12						
	Propane	0.323									
	Ethane	0.311									
4	Methane	0.3702	1.3421	1.1888	24						
	Propane	0.3243									
	Ethane	0.3055									
5	Pentane	0.200	4.9514	3.3676	132	68	559.3	700.0	-15.7143	F2	665
	Cyclohexane	0.202				105	518.5	800.0	17.5785	F2	665
	Benzene	0.598				104	528.3	800.0	14.8038	F2	665
						101	566.5	800.0	-13.2652	F2	665
						99	521.7	1000.0	13.4729	F2	665
						123	541.2	1000.0	10.6107	F2	665

Table B.10. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Multicomponent Systems

System Results						Data Point Results					
No.	Components	Mole Fraction	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
6	Pentane	0.333	3.7314	2.8625	139	62	501.0	660.0	9.9841	F2	581
	Cyclohexane	0.334				69	511.6	800.0	13.8868	F2	581
	Benzene	0.333				43	521.9	800.0	9.3465	F2	581
7	Pentane	0.601	6.4195	2.4141	152	75	462.5	800.0	15.8469	O2	665
	Cyclohexane	0.199				64	472.8	800.0	12.9912	O2	665
	Benzene	0.200				72	484.1	800.0	7.5515	F2	665
						85	463.0	1000.0	14.8433	O2	665
	Methane	0.0104				93	478.1	1000.0	11.3218	O2	665
	Methylcyclohexane	0.2358				63	500.0	800.0	8.1679	F2	683
8	1,2,3,4-	0.100	4.4500	3.0763	47	40	598.5	400.0	-10.1331	F2	581
	Tetrahydronaphthalene					64	593.9	450.0	-9.3305	F2	581
	Benzene	0.450									
	Octane	0.450									
9	1,2,3,4-	0.3030	3.9173	2.6664	25	26	560.0	200.0	12.5436	O3	684
	Tetrahydronaphthalene										
	Benzene	0.2093									
	Octane	0.3977									

Table B.10. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Vapor Multicomponent Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
12	Propane	0.0190	3.9385	3.2018	8						
	Carbon Dioxide	0.0029									
	Ethane	0.0284									
	Helium	0.0013									
	Hydrogen	0.0001									
	iso-Butane	0.0092									
	Methane	0.8579									
	Butane	0.0092									
	Pentane	0.0030									
	Nitrogen	0.0159									
	Propene	0.0001									
	Water	0.0500									
	iso-Pentane	0.0029									

Table B.11.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Liquid-Vapor Multicomponent Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Pentane	0.601	5.7236	5.7236	1						
	Cyclohexane	0.199									
	Benzene	0.200									
2	Pentane	0.200	2.2847	1.6700	11						
	Cyclohexane	0.202									
	Benzene	0.598									

Table B.12.

Summary of Possible Outliers in Enthalpy Data Using the Peng-Robinson Equation of State for Liquid-Vapor-Vapor Multicomponent Systems

System Results						Data Point Results					
No.	**Components**	**Mole Fraction**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
1	Toluene	0.1031	113.380	111.620	5						
	Hydrogen Sulfide	0.3037									
	Methane	0.4946									
	Methylcyclohexane	0.0986									
2	Pentane	0.200	0.3104	0.2937	3						
	Cyclohexane	0.202									
	Benzene	0.598									
3	Pentane	0.601	0.9257	0.9095	2						
	Cyclohexane	0.199									
	Benzene	0.200									
4	1,2,3,4-Tetrahydronaphthalene	0.100	2.5999	2.5999	1						
	Benzene	0.450									
	Octane	0.450									

APPENDIX C

SUMMARY OF POSSIBLE OUTLIERS FOR THE GPA ENTHALPY DATABASE USING THE PGR EOS

The following table contains a summary of all suspect enthalpy data located by the Park-Gasem-Robinson equation of state in conjunction with deviation plots. See Table 5 in Chapter III for the four criteria listed in the outlier/flagged column of the tables. Each phase for the pure components are separated within the table.

Table C.1.

Summary of Possible Outliers in Enthalpy Data Using the Park-Gasem-Robinson Equation of State for Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
				Liquid Data						
1	Benzene	7.1856	6.2547	108						
2	Cyclohexane	7.6989	6.9118	128	56	181.8	15.4	-17.2237	F2	584
3	Ethane	3.9497	3.3075	41	34	-240.0	2000.0	8.1000	F2	592
4	Methane	1.9014	1.6459	14						
5	Octane	4.6001	3.6509	154	10	540.0	400.0	9.7429	F2	586
					24	550.0	400.0	9.5340	F2	586
					14	539.8	360.0	11.8900	F2	663
					15	540.0	360.0	12.1898	F2	663
					24	533.6	400.0	9.5303	F2	663
					26	544.5	400.0	10.1648	F2	663
6	Propane	11.2019	6.4177	40	26	-250.0	500.0	30.6352	F2	590
					27	-200.0	500.0	13.6084	F2	590
					37	-250.0	1000.0	30.6003	F2	590

Table C.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Park-Gasem-Robinson Equation of State for Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
					38	-200.0	1000.0	13.5243	F2	590
					1	-250.0	1500.0	30.6667	F2	590
					9	-200.0	1500.0	13.6439	F2	590
					14	-250.0	2000.0	31.8344	F2	590
					23	-200.0	2000.0	14.5669	F2	590
7	Toluene	4.1802	3.6845	107						
8	trans-Decalin	19.2158	8.4317	120	78	637.5	200.0	98.3615	O2	580
					86	639.0	300.0	95.3819	O2	580
					88	644.2	300.0	95.8066	O2	580
					96	637.3	450.0	97.9138	O2	580
					Vapor Data					
9	Benzene	7.4641	6.4227	239	57	549.4	700.0	16.1210	F2	581
					16	558.7	750.0	-4.0027	F3	581
					63	535.9	600.0	15.7083	F2	584
					54	551.1	700.0	15.2924	F2	584
					3	554.1	714.0	19.4547	F2	584

Table C.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Park-Gasem-Robinson Equation of State for Pure Systems

System Results					Data Point Results					
No.	Components	RMSE (BTU/lb)	AAD	NPTS	Data Point	Temperature (°F)	Pressure (psia)	Deviation (BTU/lb)	Outlier(O)/ Flagged(F) Criteria	Ref.
					14	555.5	714.0	17.2194	F2	584
					137	540.0	650.0	15.6443	F2	679
					158	550.0	700.0	16.3068	F2	679
					23	554.0	714.0	17.8696	F2	679
					24	556.0	714.0	15.3543	F2	679
10	Ethane	5.4477	4.3212	28	63	120.0	1000.0	12.5158	F2	592
11	Methane	3.3978	2.6375	25	29	-100.0	1000.0	7.3999	F2	578
12	Octane	6.9721	6.4811	81	45	570.0	360.0	-13.1032	F3	586
					17	565.0	360.0	-12.8563	F3	663
					33	571.2	360.0	-12.6370	F3	663
13	Propane	6.9200	4.4088	21	6	200.0	500.0	24.6160	O2	364
14	Toluene	2.9248	2.3843	37	43	650.0	600.0	6.0333	F2	592
					9	650.0	800.0	-6.2173	O2,3	592
15	trans-Decalin	7.6420	6.7731	33	22	620.0	150.0	15.5572	F2	582

Table C.1. (Continued)

Summary of Possible Outliers in Enthalpy Data Using the Park-Gasem-Robinson Equation of State for Pure Systems

System Results					Data Point Results					
No.	**Components**	**RMSE (BTU/lb)**	**AAD**	**NPTS**	**Data Point**	**Temperature (°F)**	**Pressure (psia)**	**Deviation (BTU/lb)**	**Outlier(O)/ Flagged(F) Criteria**	**Ref.**
				Liquid-Liquid-Vapor Data						
16	Benzene	35.2466	24.5361	10	79	502.0	500.0	-69.8164	F2	581
					70	506.4	500.0	-69.2538	F2	581
					15	529.7	600.0	-47.4698	F2	581
17	Octane	6.4910	6.2615	3						
18	trans-Decalin	3.9207	3.4175	4						
				Liquid-Vapor-Vapor Data						
19	Benzene	10.2239	9.3220	4						
20	trans-Decalin	15.9376	15.2699	17						

VITA

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