Experimental Enthalpies for a Mixture of 80 Mole Percent Isobutane in Isopentane

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Prepared by
C. F. Braun and Company
Alhambra, California

ELECTRIC POWER RESEARCH INSTITUTE

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Prepared by

C. F. BRAUN AND COMPANY
1000 South Fremont Avenue
Alhambra, California 91802

Principal Investigators
C. R. Koppany
J. M. Lenoir

Prepared for

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 94304

EPRI Project Manager
V. W. Roberts
Fossil Fuel and Advanced Systems Division

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ABSTRACT

Seven enthalpy isobars were measured for a nominal mixture of 80% isobutane/20% isopentane. These data were used to construct a phase envelope for use in the design of a turbine expander and the heat exchangers for a geothermal power plant. The dew point values for the phase envelope are difficult to establish for a mixture, particularly in the region near the critical. It is recommended that more data points be measured to extend the isobars near the critical region to higher temperatures.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This final report for RP928-4 presents the results of test measurements that define the fluid properties of an 80% isobutane/20% isopentane mixture. Specifically, measurements of experimental enthalpies for the mixture were determined with the use of a calorimeter and proven data reduction techniques. This information will be compared with various equation-of-state correlations presently used by different organizations to predict thermodynamic properties of mixtures. The differences will be considered in defining the operating points of hydrocarbon turbines in geothermal power plant applications.

PROJECT OBJECTIVES

The objective of this project was to experimentally measure the enthalpy of this mixture as a function of temperature and pressure over the ranges 100-300°F and 50-700 psia. The specific values of interest were the values near the critical regions of turbine expansion and condenser operation.

PROJECT RESULTS

Before measurements were taken, the calorimeter and the associated instrumentation were checked against previously measured API values. The agreement between these values was good, with an average deviation of 2.0 Btu/lb and a trend of 0.5 Btu/lb. The results of 200 experimental data runs for the mixture were presented graphically as a phase envelope. Bubble and dew points were determined from the breaks or discontinuities between the single-phase and two-phase portions of the isobar. For the lower pressures, these breaks are rather sharp. As the critical point is approached, the breaks in the isobars become less definite.

In this study, the accuracy of the enthalpy data was estimated. Because of the individual estimated errors caused by various measurement uncertainties, an overall absolute uncertainty of 1.57 Btu/lb was estimated.

These experimental data will be beneficial in defining optimum expansion paths near the measured dew point phase boundary, and are critical for the proper design of hydrocarbon turbines. The proper design of such turbines is one of the prerequisites for the successful development of binary-cycle power plants.

Vasel W. Roberts, Project Manager
Fossil Fuel and Advanced Systems Division

CONTENTS

ILLUSTRATIONS

TABLES

SUMMARY

The Electric Power Research Institute contracted C. F. Braun and Company to undertake an experimental research program to measure enthalpies for a nominal mixture of 80 mole percent isobutane in isopentane. These data are needed to develop a phase envelope for use in the design of the turbine expander and the heat exchangers for a geothermal power plant.

The calorimeter employed was the same one used by C. F. Braun and Company, in an extensive API enthalpy measurement program. In order to establish confidence in the calorimeter, n-pentane and isobutane check runs were made. The results were compared against independent literature data and found to be satisfactory. The results of 200 experimental data runs (seven isobars) for the 80 mole percent isobutane/20 mole percent isopentane system are presented both graphically and in tables. The apparent bubble and dew points were determined from the discontinuities between the single-phase and two-phase portions of the isobars.

In the critical region, the dew point breaks in the isobars become less pronounced. The extrapolation technique of Ghormley and Lenoir (5-2) was used to establish that portion of the saturation locus in the critical region up to the cricondentherm. As a result of this extrapolation, the region of most uncertainty turns out to be the saturated vapor curve between about 240^{0}F and the cricondentherm. It is recommended that more data points be measured in order to extend each isobar to higher temperatures in the vapor superheat region. Emphasis should be placed on the area near the critical. These additional data will provide the following:

- More certainty in defining an optimum expansion path
- Better determination of the saturated vapor locus in the critical region

In this study, an attempt was made to estimate the accuracy of the basic enthalpy data reported. Due to the individual estimated errors caused by the various measurement uncertainties, an overall absolute uncertainty of 1.57 Btu/lb was estimated. This value is of the same order as the error quoted by Lenoir and Hipkin (1-1) in previous studies for the American Petroleum Institute.

Section 1

PROJECT SCOPE

OBJECTIVE

The Electric Power Research Institute (EPRI) has initiated a project with the broad objective of confirming the fluid properties of the hydrocarbon system to be used in the design of a low salinity moderate temperature, geothermal power plant.

The scope of work is to measure the enthalpy, of two hydrocarbon mixtures, as a function of temperature and pressure.

80 mole percent isobutane in isopentane

90 mole percent isobutane in propane

Of primary interest to EPRI at this time is calorimetric data for the 80 percent isobutane in isopentane mixture. EPRI plans to commission this mixture first in the geothermal power cycle.

REGIONS OF INTEREST

The specific regions of interest to EPRI are as follows.

Near the critical point where heating and turbine expansion will occur.

At lower pressures near the dew points and bubble points simulating condenser operation.

In these regions, EPRI has found that several equation-of-state correlations have predicted significantly different thermodynamic properties. Accurate definition of the dew point phase boundary is critical to the proper design of the hydrocarbon expander turbine.

The approximate pressure and temperature ranges to be covered are 50 to 700 psia and 100 to 300 degrees F. C F Braun & Co measured the hydrocarbon enthalpies using an isobaric flow calorimeter formerly used by Braun in an extensive API enthalpy measurement program. The complete description of this apparatus is given in an article by Lenoir, Robinson, and Hipkin (1-1).

PROJECT TASKS

The initial objective involved the measurement of experimental enthalpies for two mixtures. During the course of the project, the scope was modified to limit enthalpy measurements to the more critical 80 percent isobutane in isopentane mixture. The specific tasks required by Braun to implement the project were

> Modify the existing calorimeter where necessary and check it out by measuring the enthalpy of n-pentane and isobutane as standard fluids.
>
> Measure the enthalpy of the 80 mole percent isobutane in isopentane system over the ranges of pressure and temperature described above.
>
> Reduce the raw data and present it in graphical and tabular form relative to a datum of liquid at 75 degrees F and saturation pressure.
>
> Prepare a final report which documents facility description and checkout, experimental procedures, data reduction, presentation of experimental data, and uncertainty/accuracy analysis of the basic measurements.

This report provides all of the required documentation of the above defined tasks.

Section 2

EXPERIMENTAL PROCEDURE

APPARATUS

The calorimeter used in this study is a modification of the flow type described by Nelson and Holcomb (2-1) and Smith and co-workers (2-2, 2-3, 2-4, 2-5). This apparatus is well described in a 1970 publication by Lenoir and co-workers (1-1). The hydrocarbon (pure component or mixture) enters the calorimeter at a fixed pressure and a measured temperature and is cooled to the liquid state at 75 degrees F by evaporating Freon-11. By measuring the hydrocarbon and Freon-11 flowrates, the enthalpy difference over the specific temperature range is established.

For systems involving pentanes and heavier, the liquid hydrocarbon leaving the calorimeter is throttled down to ambient pressure at 75 degrees F for volumetric flow measurement. For mixtures lighter than pentane, the calorimeter effluent must be maintained at a pressure above atmospheric after throttling for the liquid flow measurement at 75 degrees F. The apparatus was modified accordingly in order to handle these operating conditions. The hydrocarbon receiver was made of thick glass to withstand pressures in excess of the vapor pressure of isobutane. A helium gas pad was provided in the hydrocarbon receiver so that the pressure could be adjusted and maintained.

PURITY OF FLUIDS

The n-pentane employed for check runs was prepared by distillation. It was of very high purity equivalent to research grade or better. The isobutane was a pure grade stock obtained from Phillips Petroleum Company. Its minimum purity is quoted as 99.0 mole percent. The 80-20 isobutane - isopentane mixture was prepared gravimetrically by Phillips Petroleum Company from pure grade hydrocarbons.

COMPOSITION ANALYSES

During the course of operating with the 80-20 mixture, the composition was monitored regularly. A Model 5750 Hewlett-Packard chromatograph with flame ionization detector was employed for the analyses. The separating column consisted of 10 feet of n-Octane/Porasil C packing and was maintained at ambient temperature. Helium was employed as the carrier gas with a flowrate of 35 ml/min. The air and hydrogen flowrates to the flame detector were 500 ml/min and 40 ml/min, respectively. Two to three replicate samples were periodically taken from the calorimeter hydrocarbon pump discharge.

PRESSURE AND TEMPERATURE

The hydrocarbon pressure measurements were made with two Heise Bourdon pressure gauges. One gauge covered the pressure range 0 to 400 psia, while the other covered a range of 0 to 1500 psia. Both gauges were checked and calibrated by Gauge Repair Service Engineering Company of Inglewood, California. All of the temperature measurements were made with chromel-constantan thermocouples connected to a standard potentiometer box.

Section 3

DATA REDUCTION PROCEDURE

FUNDAMENTAL EQUATIONS

The isobaric flow calorimeter is capable of measuring enthalpy differences between the fluid at an inlet temperature T and an outlet temperature of 75 degrees F. The outlet fluid must be totally in the liquid state. The inlet fluid can be gas, liquid, or a mixture of gas and liquid.

The fundamental equation for data reduction is

$$\Delta H = \frac{\rho_F \ \Delta H_F \ FM}{\rho \ H \ S} \tag{3-1}$$

The pertinent terms in this equation are defined in the nomenclature. Data for the Freon 11 density, ρ_F, and latent heat of vaporization, ΔH_F, were taken from two sources (3-1, 3-2). These data have been fitted to linear expressions as follows.

$$\rho_F = 92.38 - 0.0825 \ (T_2 - 74) \quad , \quad \text{lbm/cu ft} \tag{3-2}$$

$$\Delta H_F = 78.41 - 0.0875 \ (T_i - 74) \quad , \quad \text{Btu/lbm} \tag{3-3}$$

$$T_i = 1.7338 \ P_a + 22.793 \quad , \quad {}^\circ\text{F} \tag{3-4}$$

T_2 is the temperature of the Freon-11 in the glass receiver. P_a is the atmospheric pressure in inches of mercury absolute, and T_i is the temperature at which the Freon-11 boils.

Equation 3-1 gives the enthalpy difference, between a fixed hydrocarbon inlet temperature and the temperature of the liquid hydrocarbon in the glass receiver, for a fixed system pressure, P. This expression must be corrected to express ΔH relative to a hydrocarbon outlet condition of liquid at 75 degrees and bubble point pressure. The complete expression for data reduction is

$$\Delta H_C = \frac{\rho_F \ \Delta H_F \ FM}{\rho \ H \ S} - C_p \ (75 - T_1) + \left(\frac{\Delta H}{\Delta P}\right)_T (P - P_{BP}) \tag{3-5}$$

The second term in Equation 3-5 corrects for the fact that T_1, the measured hydrocarbon outlet temperature, may be slightly different than 75 degrees F. C_p is the liquid hydrocarbon isobaric heat capacity at 75 degrees F. Values for C_p are obtained from the Technical Data Book of the American Petroleum Institute (3-3). For C_4 and C_5 hydrocarbons at 75 degrees F, the heat capacity varies from about 0.5 to about 0.6 Btu/lbm-degrees F.

The last term in Equation 3-5 corrects ΔH to an outlet hydrocarbon condition of 75 degrees F and the bubble point pressure, P_{BP}. The rigorous thermodynamic expression for the effect of pressure on enthalpy at fixed temperature is given by Equation 3-6.

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{3-6}$$

Using liquid densities, this expression is well approximated by Equation 3-7.

$$\left(\frac{\Delta H}{\Delta P}\right)_T = 0.185\left[\frac{1}{\rho} - 535\left(\frac{\dfrac{1}{\rho_H} - \dfrac{1}{\rho_L}}{T_H - T_L}\right)\right], \quad \text{Btu/lbm-psi} \tag{3-7}$$

ρ is the hydrocarbon liquid density at T_1. ρ_H is the liquid density at a temperature T_H, higher than T_1. ρ_L is the density at a temperature T_L, lower than T_1. If T_L and T_H cover only a modest range, the density ρ is a linear function of temperature and can be expressed as

$$\rho = \left(\frac{T_H - T_1}{T_H - T_L}\right)(\rho_L - \rho_H) + \rho_H \tag{3-8}$$

The second and third terms of Equation 3-5 are always much smaller than the first term. The second term is usually less than 0.5 Btu/lb and the last term varies from 0.1 to 2 Btu/lb depending upon the system pressure.

Equations 3-1 through 3-8 were incorporated into a computer program which was used for reduction of the experimental data.

LIQUID DENSITY MEASUREMENT

The liquid densities for n-pentane, isobutane, and the 80-20 isobutane-isopentane mix have been measured in the C F Braun & Co Research Laboratory. Pycnometer type gravity determinations were made using two Aerosol Reaction Vessels. The graduations on these vessels were calibrated using water as a standard for the volume determinations. Tare and gross weighings of the vessels provided the mass of hydrocarbon which occupied a specific volume. For all fluids, specific gravities were measured at 60 and 80 degrees F. Table 3-1 lists the measured gravities for n-pentane, isobutane, and the 80-20 mixture. The estimated accuracy of the density measurements is ± 0.005 gms/ml. Also listed in Table 3-1 are pure component saturated liquid densities taken from the Technical Data Book of the API (3-3). The agreement between the measured and API densities is very good. The differences are well within our estimated accuracy of measurement.

Table 3-1

SATURATED LIQUID DENSITIES FOR HYDROCARBON SYSTEMS

System	Temperature Degrees F	Measured Density[a] gms/ml	Density From API Data Book (3-3) gms/ml
n-pentane	60	0.631	0.634
	80	0.620	0.622
Isobutane	60	0.565	0.565
	80	0.553	0.552
80-20 Isobutane-Isopentane	60	0.568	
	80	0.562	

[a] To convert to units of lbm/cu ft multiply by 62.43.

Section 4

EXPERIMENTAL RESULTS FOR CHECK RUNS

N-PENTANE

In order to establish certitude in the modified calorimeter, the enthalpy of n-pentane was measured and the results compared with values from API Project 44 (4-1). The results for 16 gas-phase measurements are summarized in Table 4-1. Pressure levels of 100, 200, 400, and 800 psia are covered. The base value for ΔH is the liquid phase at 75 degrees F and the pressure of measurement. This datum was chosen for the n-pentane data because it complied with the datum on which the API n-pentane data was based.

In general, the agreement between the measured and API values are good. Comparison of the n-pentane data with values from API Project 44 gave an overall absolute average deviation of 2.0 Btu/lb with a trend of -0.5 Btu/lb. This comparison is also shown graphically in Figure 4-1.

Table 4-1

ENTHALPY CHECK RUNS FOR N-PENTANE IN THE GAS PHASE

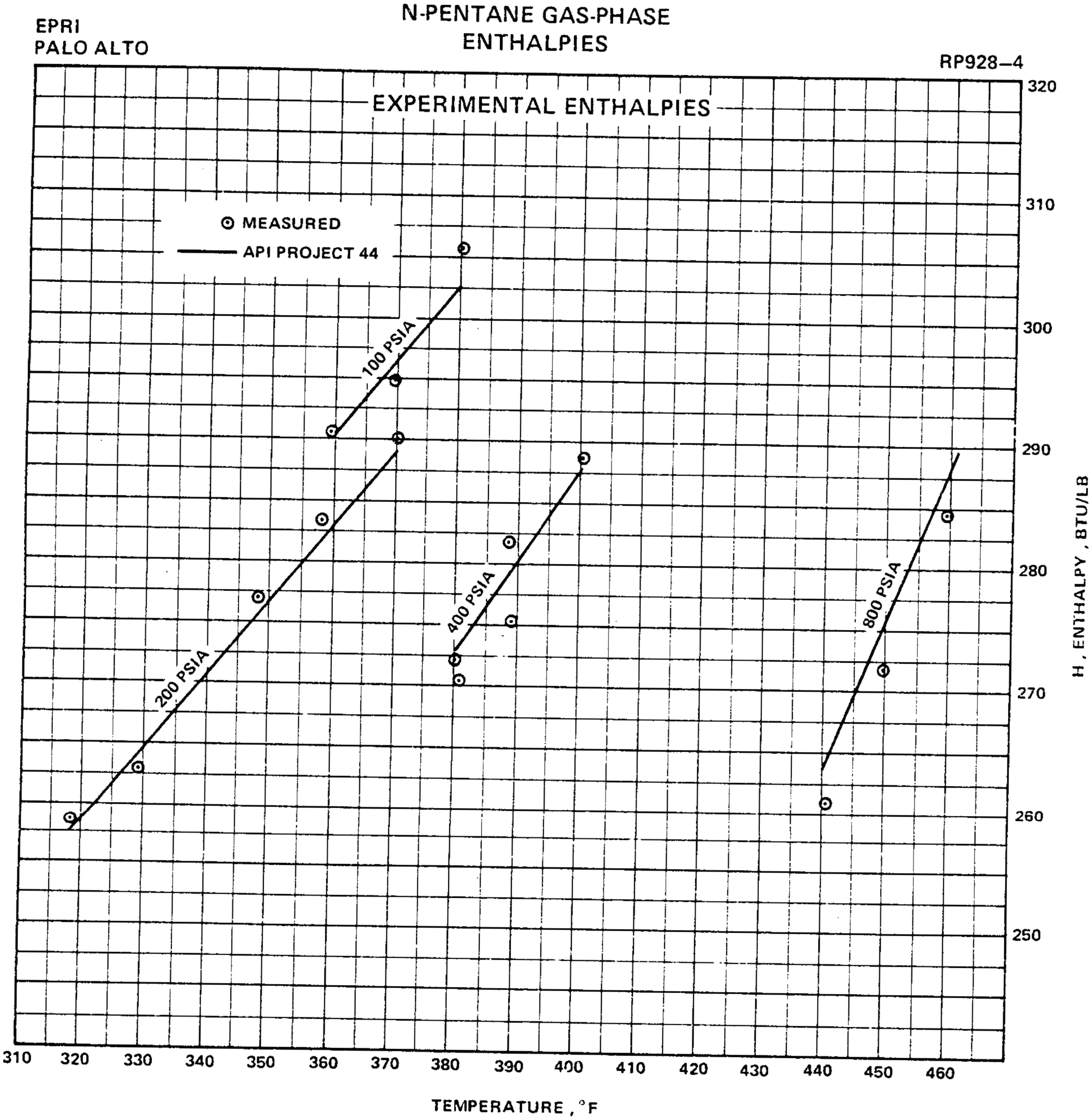
PRESSURE PSIA	TEMPERATURE DEGREES F	$\Delta H_{measured}^{(1)}$ BTU/LB	$\Delta H_{API44}^{(1)\,(2)}$ BTU/LB	DEV = $\Delta H_{measured} - \Delta H_{API44}$ BTU/LB
100	360.2	290.9	290.5	0.4
	369.5	294.9	296.1	-1.2
	380.1	305.7	302.7	3.0
200	318.5	258.5	257.5	1.0
	329.1	262.9	264.0	-1.1
	348.5	277.0	275.9	1.1
	358.6	283.5	282.0	1.5
	370.1	290.4	289.0	1.4
400	380.6	270.4	272.7	-2.3
	389.7	275.2	280.0	-4.8
	400.0	288.9	288.0	0.9
	380.0	271.9	272.4	-0.5
	388.8	281.6	279.4	2.2
800	440.4	260.9	263.8	-2.9
	449.5	271.8	275.4	-3.6
	459.4	284.4	287.7	-3.3

Absolute Average Deviation = 2.0
Trend = -0.5

NOTE (1) Base value for ΔH is the liquid phase at 75 degrees F and the pressure of measurement.

(2) ΔH_{API44} values are taken from API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Center, Texas A & M University, College Station, Texas, April 30, 1969.

FIGURE 4-1
COMPARISON OF N-PENTANE GAS-PHASE ENTHALPIES



ISOBUTANE

During a meeting with EPRI on September 13, 1977, Braun agreed to make a few enthalpy measurements with isobutane to gain experience with above-ambient pressure operation in the hydrocarbon flowmeter and surge sections. The operation of the modified calorimeter proved to be successful with the isobutane.

Forty-seven data runs were made at a single pressure of 250 psia. The results are listed in Table 4-2 and also presented graphically as a function of temperature in Figure 4-2. The liquid, two-phase, and vapor regions are covered. In Figure 4-2, the plotted experimental data points are compared against the best compilation of literature data (4-2, 4-3, 4-4).

In the liquid region, the measured values fall about 3 to 4 Btu/lb below the literature curve. In the vapor region, the measured points show some scatter near the dew point but fall nicely around the literature curve. In the two-phase region, agreement between the measured points and the literature curve is very good.

Table 4-2

EXPERIMENTAL ISOBARIC ENTHALPIES FOR ISOBUTANE

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	ΔH(1) MEASURED BTU/LB
1	250	169.7	56.3
2		170.5	58.4
3		170.3	59.4
4		169.9	58.6
5		179.3	64.7
6		179.0	63.2
7		178.6	64.6
8		178.1	63.6
9		191.1	73.1
10		191.7	72.0
11		192.4	72.9
12		195.4	77.3
13		195.4	77.3
14		195.8	78.3
15		198.8	163.6
16		199.0	156.3
17		198.5	157.5
18		197.8	134.4
19		197.7	129.0
20		197.6	110.6
21		197.5	112.6
22		197.4	107.3
23		197.4	108.9
24		197.4	113.6
25		197.5	113.9
26		196.7	83.3
27		196.8	83.9
28		197.1	93.0
29		197.3	100.7
30		197.4	101.2
31		197.5	113.5
32		197.9	116.4
33		197.7	117.2
34		197.8	120.7
35		197.9	130.0

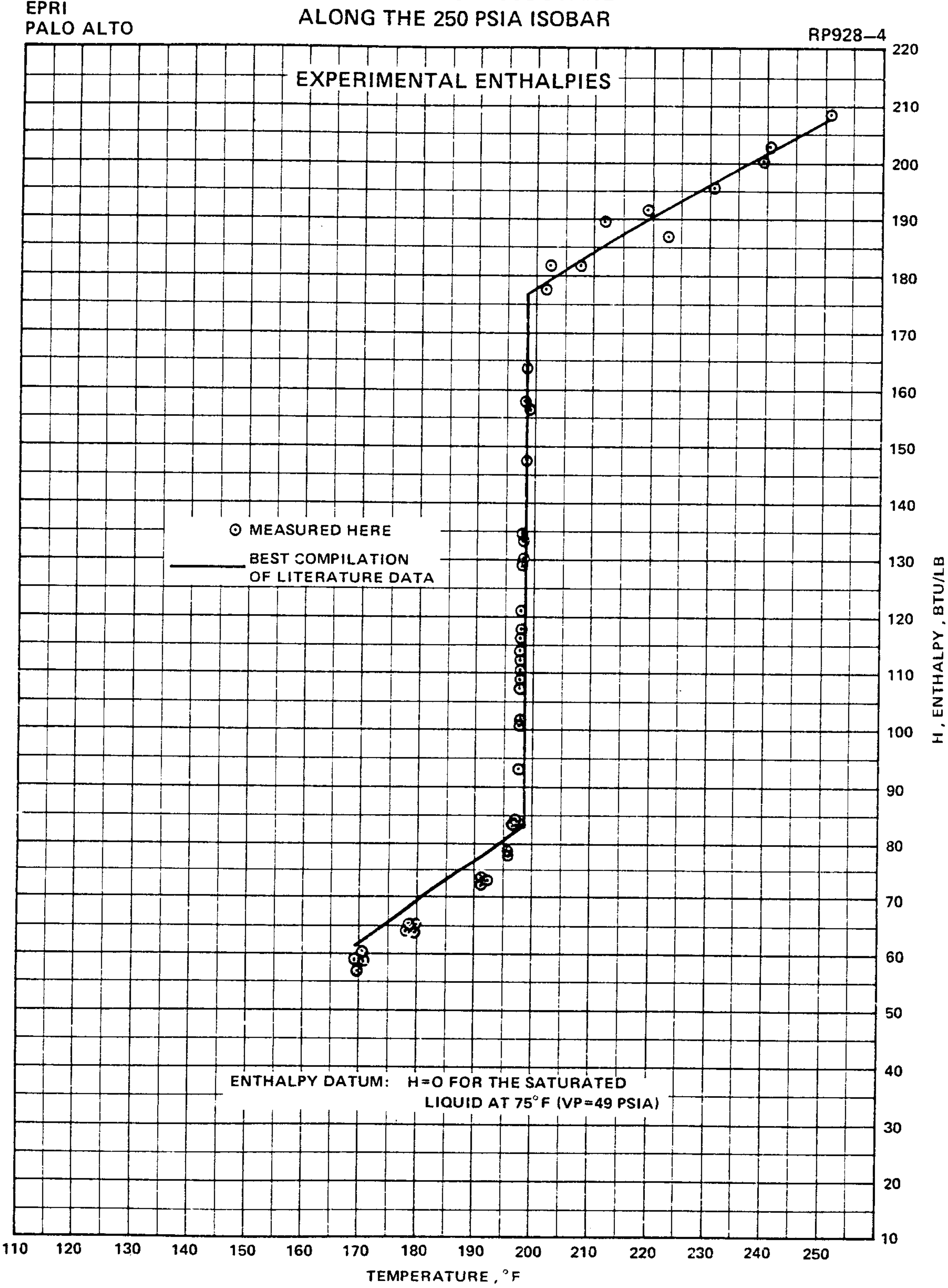
NOTE 1 Base value for ΔH is the saturated liquid at 75 degrees F.

Table 4-2 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	$\Delta H^{(1)}$ MEASURED BTU/LB
36	250	197.9	133.0
37		198.2	147.7
38		201.6	177.0
39		202.1	181.7
40		207.2	181.6
41		211.8	189.5
42		219.0	191.2
43		239.2	200.2
44		222.1	186.6
45		230.5	195.7
46		240.3	202.3
47		250.9	208.3

NOTE 1 Base value for ΔH is the saturated liquid at 75 degrees F.

FIGURE 4-2
ENTHALPIES FOR ISOBUTANE ALONG THE 250 PSIA ISOBAR



Section 5

EXPERIMENTAL RESULTS FOR THE MIXTURE

80-20 MIXTURE

The results of 200 experimental data runs for the 80 mole percent isobutane - 20 mole percent isopentane system are listed in Table 5-1 and presented graphically as a function of pressure and temperature in Figure 5-1. The solid curves shown in Figure 5-1 represent the best visual fit drawn through the data points using a french curve. The data cover seven isobars from 80 to 600 psia for a total temperature range of about 110 to 320 degrees F. The breaks or discontinuities between the single-phase and two-phase portions of the isobars determine the bubble and dew point loci. For the lower pressures, these breaks are rather sharp. As the critical point is approached, the breaks in the isobars become less definite.

MIXTURE COMPOSITION

During the course of measuring the 200 data points for the 80-20 mixture, liquid samples were taken periodically from the hydrocarbon pump discharge and analyzed with a flame ionization chromatograph. Twenty-one sets of these analyses were taken. They are reported in Table 5-1 along with the enthalpy measurements. The analyses showed that small concentrations of other hydrocarbon impurities were present. As expected, the major impurities were n-butane and n-pentane. In addition, traces of propane and butene-1 were also present.

Table 5-2 shows the analysis of the nominal 80-20 isobutane-isopentane mixture reported by Phillips Petroleum Company. A statistical analysis was made to determine the mean and standard deviation in the compositions of isobutane and isopentane reported in Table 5-1. A definition of the statistical parameters employed is given in Table 5-3. Table 5-4 presents the results for isobutane and isopentane. The values for the pertinent statistical parameters are summarized below.

Component	Mean Mole Percent $\bar{y}$	Standard Deviation S, Mol Percent	Relative Standard Deviation $S/\bar{Y}$ x 100, Percent
Isobutane	79.063	0.855	1.08
Isopentane	20.527	0.845	4.12

Figure 5-2 shows a plot of relative standard deviations for a host of chromatographic analyses taken from different sources. These data were compiled by S. H. Tan (5-1) of the Braun Research Department. The majority of these points are for proprietary mixtures analyzed in the Braun laboratories. The relative standard deviations for the isobutane and isopentane analyses of this study plot within the realm of uncertainty indicated by the previous analyses.

MIXTURE SATURATION LOCUS

In Figure 5-1, it was shown that the discontinuities between the single-phase and two-phase isobars were used to determine the saturated liquid and saturated vapor loci for the nominal 80-20 isobutane-isopentane mixture. This procedure was successfully used to determine the bubble point breaks for all the isobars and the dew point breaks for isobars of 200 psia and lower. Above 200 psia, the dew point breaks becomes much less definite. As a result, the dew point vapor region near the critical is not well-defined. In order to try to better define this area, an empirical technique developed by Ghormley and Lenoir (5-2) was used. Cailletet and Mathias (5-3) were the first investigators to show that the mean of the saturated vapor and liquid densities of a compound could be correlated with temperature. The mean density up to the critical point is very accurately represented by the quadratic equation

$$\frac{1}{2}(\rho_\ell + \rho_v) = A_o + B_o T + C_o T^2 \qquad (5\text{-}1)$$

By studying the behavior of the enthalpy of the saturated vapor and liquid of several hydrocarbon systems, Ghormley and Lenoir (5-2) showed that the mean enthalpy follows a similar relationship with temperature.

$$\frac{1}{2}(H_\ell + H_v) = A + BT + CT^2 \qquad (5\text{-}2)$$

The latent heat of vaporization can be related to temperature by the well-known Watson (5-4) relationship.

$$\lambda = H_v - H_\ell = \lambda_o (1 - T_R)^n \qquad (5\text{-}3)$$

In equation 5-2 and 5-3, the constants A, B, C, and λ_o are fitted from data. The constant n has a value of 0.38 for most hydrocarbons. For hydrocarbon mixtures, Ghormley and Lenoir recommend that the cricondentherm temperature be used in Equation 5-3. In that case, the reduced temperature is defined as

$$T_R = \frac{T}{T_{CT}} \qquad (5\text{-}4)$$

Several investigators (5-5, 5-2, 5-6, 5-7) have proposed correlations for predicting cricondentherm temperatures of aliphatic binary systems. Table 5-5 lists the temperatures predicted for the 80-20 mixture by five different correlations. Grieves and Thodos (5-6) predict a value much lower than the rest. Values predicted by the other investigators vary from 290 to 312 degrees F. The value of Silverman and Thodos (5-7) lies in between these values.

It also agrees quite nicely with the relative position of the isobars of Figure 5-1 in the critical region. For these reasons the cricondentherm temperature of Silverman and Thodos was chosen for use in Equation 5-3.

$$T_{CT} = 302.3°F = 762.0°R \qquad (5\text{-}5)$$

Equation 5-2 and 5-3 were fitted to the lower temperature portions of the saturated liquid and vapor curves of Figure 5-1. This region corresponds to temperatures below about 230 degrees F where the breaks in the isobars are relatively sharp and more easily determined. When the fitted constants are inserted into Equations 5-2 and 5-3 and these equations are combined, the following relationships for the saturated liquid and vapor enthalpies are obtained.

$$H_{\ell} = -293.30 + 0.7725T - 0.0001875T^{2} - 118.0 \left(1 - \frac{T}{762.0}\right)^{0.38} \qquad (5\text{-}6)$$

$$H_{v} = -293.30 + 0.7725T - 0.0001875T^{2} + 118.0 \left(1 - \frac{T}{762.0}\right)^{0.38} \qquad (5\text{-}7)$$

The temperature T is in degrees R and enthalpy is calculated in units of Btu/lb.

Equations 5-6 and 5-7 were subsequently used to generate the rest of the saturation locus up to the cricondentherm temperature. This portion of the saturation curve is shown dashed on Figure 5-1. The apparent dew point breaks indicated by the 300 and 400 psia isobars appear to occur at a higher value of enthalpy than the dashed curve would indicate. If the dew point curve did indeed follow these breaks, then it would tend to have more of a bulge in the critical region than is indicated by the Lenoir - Ghormley extrapolation technique. If this is the case, more care must be exercised in designing the power cycle expansion step in order to avoid entering the two-phase region.

Of the entire data set plotted in Figure 5-1, the saturated vapor region near the critical represents the area of maximum uncertainty. It is recommended that more data points be measured in the vapor region for all isobars, with emphasis on the critical region. These additional data will provide the following benefits.

> Better definition of both endpoints of the expansion step
>
> Better determination of the saturated vapor locus in the critical region.

TABLE 5-1

EXPERIMENTAL ISOBARIC ENTHALPIES FOR THE NOMINAL 80 MOLE PERCENT ISOBUTANE - 20 MOLE PERCENT ISOPENTANE SYSTEM

RUN	PRESSURE	TEMPERATURE	ΔH[1] MEASURED	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
NUMBER	PSIA	DEGREES F	BTU/LB	PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
1	80	119.0	26.6	0.01	81.44	0.19	0.002	18.27	0.08
2		119.1	27.8						
3		122.5	75.5						
4		122.6	77.5						
5A		123.2	81.6						
5B		124.0	86.7						
6		126.0	91.3						
7		126.8	92.6						
8		128.4	103.1						
9		128.4	127.9						
10		128.5	130.8						
11		131.9	144.8						
12		131.2	141.3						
13		132.3	159.6						
14		132.2	159.4						
15		136.0	166.7						
16		137.4	167.5						
17		142.3	167.8						
18		142.8	169.0						
19		153.1	172.3	0.015	79.353	0.213	0.003	20.312	0.103
20		170.1	183.5						
21		169.0	184.3						
22		160.1	180.7						
23		159.3	179.1						
24		179.4	186.2	0.015	79.067	0.330	0.013	20.445	0.129
25		180.4	189.3						

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	ΔH(1) MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
26	200	179.3	63.7						
27		178.2	63.7						
28		184.1	66.8						
29		183.8	68.0						
30		186.6	69.4						
31		186.8	69.1						
32		188.5	71.1						
33		188.3	70.3						
34		190.1	73.1	0.016	79.266	0.277	0.003	20.313	0.124
35		189.6	73.3						
36		193.1	82.6						
37		193.8	87.0						
38		198.0	134.8						
39		198.3	135.9						
40		201.1	160.2	0.017	79.233	0.227	0.004	20.401	0.119
41		201.4	159.8						
42		207.1	175.2						
43		205.6	171.4						
44		202.9	168.6						
46		200.5	156.1						
47		209.3	182.2						
48		209.2	182.9						
49		220.6	200.1(2)						
50		218.6	202.0(2)						
51		227.1	200.9						
52		227.1	200.8	0.016	78.677	0.275	0.003	20.901	0.128
53		236.2	206.5						
54		236.6	206.4						

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.
2 These points represent poor data and should not be used for testing correlations.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	ΔH[1] MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
55	500	246.4	112.7						
56		245.8	112.7						
57		256.2	120.5						
58		255.7	120.2						
59		273.0	136.3						
60		272.8	135.8						
61		281.8	146.1						
62		281.7	144.8						
63		284.7	151.1	0.016	78.304	0.269	0.004	21.278	0.130
64		284.3	148.5						
65		286.9	152.6						
66		286.6	153.3						
67		287.6	155.1						
68		288.0	157.5						
69		289.9	169.7	0.014	77.475	0.226	0.003	22.164	0.118
70		290.1	170.1						
71		291.3	183.2						
72		291.5	182.8						
73		293.6	196.5						
74		293.8	195.7						
75		296.2	203.5						
76		296.4	202.9						
77		297.5	206.6						
78		298.2	205.9						
79		299.9	210.3						
80		300.1	208.7	0.016	78.679	0.251	0.004	20.942	0.108

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	$\Delta H^{(1)}$ MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
81	600	260.6	124.3						
82		260.6	122.8						
83		269.0	131.3						
84		269.1	130.6						
85		278.5	139.7						
86		278.2	136.8						
87		284.2	145.0						
88		284.4	144.6						
89		284.3	142.9	0.017	80.576	0.303	0.003	18.954	0.147
90		289.3	149.4						
91		289.3	149.7						
92		291.3	150.8						
93		290.9	151.1						
94		292.2	151.9	0.016	78.369	0.259	0.003	21.204	0.150
95		293.0	151.1						
96		295.4	155.8						
97		295.3	156.7						
98		297.8	159.4						
99A		298.3	158.7						
99B		300.3	162.3						
100		300.5	163.0						
101		310.3	185.2	0.017	78.678	0.251	0.003	20.940	0.112
102		310.9	185.3						
103		318.6	207.7						
104		318.8	206.3						
105	200	215.9	194.2						
106		213.9	191.6						
107		213.9	192.6						
108		218.2	196.6						
109		217.8	195.2	0.017	79.369	0.267	0.003	20.215	0.129
110		221.8	195.2$^{(2)}$						
111		222.4	193.1$^{(2)}$						

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.

2 These points represent poor data and should not be used for testing correlations.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	ΔH(1) MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
112	125	137.9	33.8	0.013	78.602	0.232	0.004	21.018	0.131
113		140.7	38.2						
114		145.1	41.3						
115		149.2	45.3						
116		150.2	47.1						
117		152.8	53.9						
118		157.3	106.3						
119		157.3	110.3	0.014	79.576	0.210	0.003	20.092	0.105
120		157.6	113.5						
121		157.8	113.4						
122		160.1	127.5						
123		160.2	127.1						
124		163.2	146.0						
125		162.6	146.2						
126		160.9	145.1						
127		160.9	143.4						
128		165.5	157.0						
129		163.5	151.9						
130		166.4	164.1	0.016	78.336	0.238	0.004	21.289	0.118
131		166.6	163.1						
132		170.1	175.6						
133		170.3	174.9						
134		177.4	186.2(2)						
135		177.6	186.0(2)						
136		189.0	193.4(2)						
137		189.7	193.2(2)						
138		190.4	190.5						
139		190.2	191.1						
140		180.5	185.2						
141		180.3	186.4						
142		171.0	175.6						
143		170.9	173.9	0.018	79.788	0.212	0.004	19.873	0.105

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.
2 These points represent poor data and should not be used for testing correlations.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	ΔH(1) MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
144	300	218.3	94.2						
145		217.7	92.1						
146		224.9	99.5						
147		225.1	99.6						
148		226.7	100.6	0.018	78.450	0.187	0.003	21.235	0.106
149		227.3	100.2						
150		229.4	104.1						
151		229.7	104.0						
152		232.2	112.4						
153		232.7	112.3						
154		235.5	135.8						
155		235.3	137.7						
156		238.1	162.6						
157		238.5	167.8						
158		240.6	180.3						
159		241.4	182.2						
160		240.5	180.4						
161		242.2	185.0						
162		240.5	183.2						
163		246.2	197.9						
164		246.1	196.6						
165		248.1	204.4						
166		248.5	203.3						
167		262.5	215.2						
168		257.0	212.5						
169		258.3	215.3	0.018	79.348	0.189	0.004	20.334	0.107
170		268.5	219.3						
171		272.7	220.5						
172		272.2	221.6						

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.

TABLE 5-1 Continued

RUN NUMBER	PRESSURE PSIA	TEMPERATURE DEGREES F	$\Delta H^{(1)}$ MEASURED BTU/LB	MIXTURE COMPOSITION ANALYSIS, MOLE PERCENT					
				PROPANE	ISOBUTANE	N-BUTANE	BUTENE-1	ISOPENTANE	N-PENTANE
173	400	249.3	114.6						
174		250.0	115.6						
175		253.4	120.0						
176		253.2	120.7	0.017	78.448	0.503	0.003	20.845	0.183
177		255.4	121.9						
178		255.4	122.5						
179		257.1	125.9						
180		257.3	125.1						
181		259.8	128.0						
182		259.7	127.2						
183		261.8	129.4						
184		262.1	131.4						
185		263.5	134.6						
186		263.7	134.8						
187		265.6	150.2						
188		265.5	144.5						
189		267.7	171.5						
190		267.9	169.6						
191		269.6	182.7						
192		269.6	182.5						
193		274.3	197.3	0.018	79.289	0.498	0.003	20.040	0.152
194		272.6	197.5						
195		273.8	198.6						
196		276.3	211.2						
197		279.4	218.2						
198		279.0	215.5						
199		290.0	220.3						
200		289.8	220.8						

NOTE 1 Base value for ΔH is the saturated liquid phase at 75 degrees F.

FIGURE 5-1
ENTHALPY OF MIXTURE OF NOMINAL
80 MOLE PERCENT ISOBUTANE IN ISOPENTANE

EPRI
PALO ALTO

RP928–4

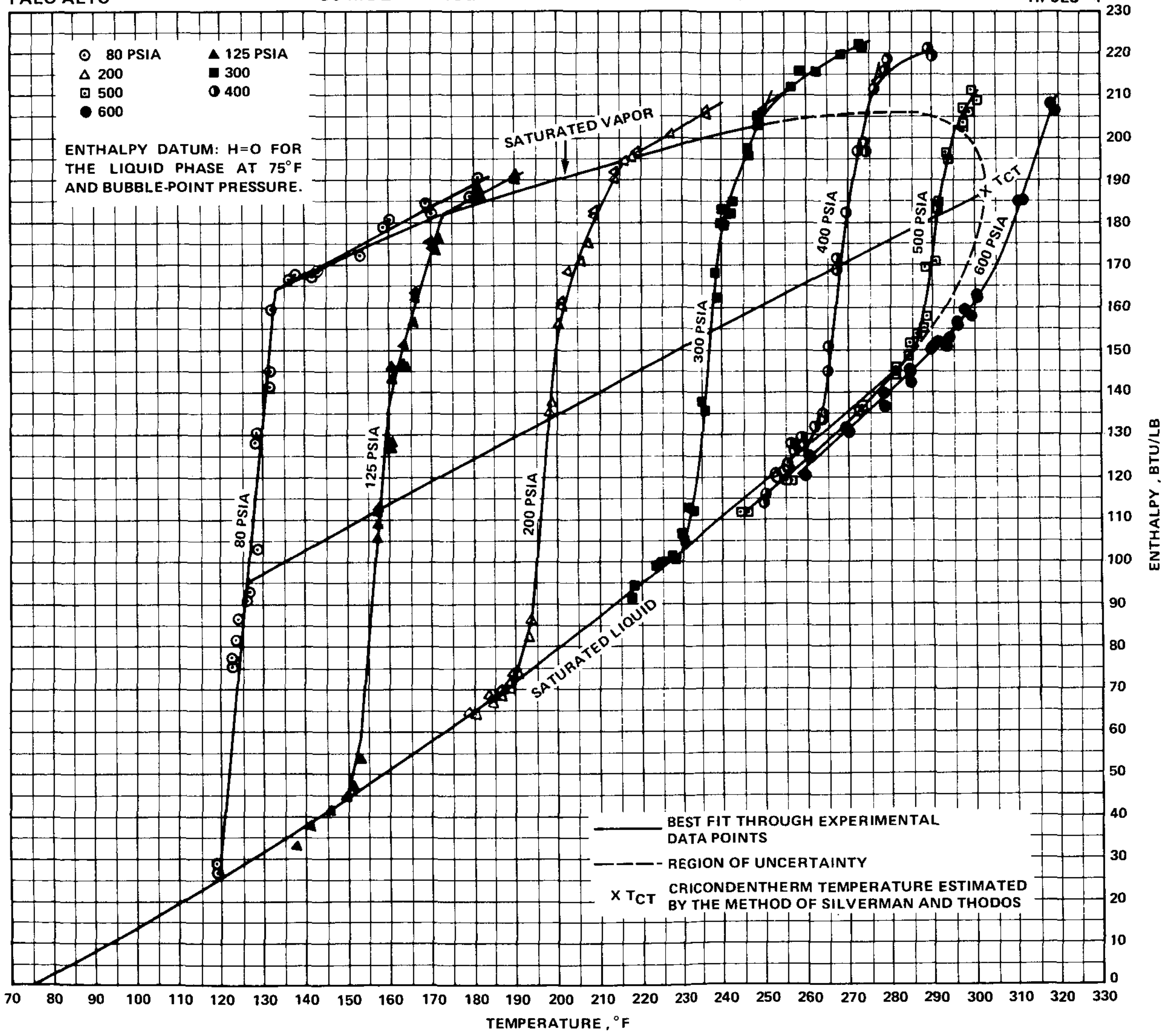


TABLE 5-2

ANALYSIS OF NOMINAL 80-20 ISOBUTANE-ISOPENTANE MIXTURE BY PHILLIPS PETROLEUM COMPANY

COMPONENTS	MOLE PERCENT
Isobutane	79.88
Isopentane	19.83
Propane	0.02
Pentene-1*	0.01
n-butane	0.13
n-pentane	0.13
	100.00

* Our analysis shows this component to be butene-1.

TABLE 5-3

DEFINITION OF STATISTICAL PARAMETERS

Definitions

Let y_i = individual measurement of component concentration, mole percent

$\bar{y}$ = sample mean, mole percent

= $\Sigma\, y_i/n$

n = number of analyses considered

Then

$$\text{Variance} = s^2 = \frac{\sum_{i=1}^{n} (y_i - \bar{y})^2}{n - 1}$$

$$\text{Standard Deviation} = s = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \bar{y})^2}{n - 1}}$$

95 percent confidence limit belt = $\pm\, 2s$

$$\text{Relative standard deviation} = \frac{s}{\bar{y}} \times 100$$

Table 5-4

VARIATION OF MIXTURE COMPOSITION ANALYSIS FOR THE NOMINAL 80-20 ISOBUTANE - ISOPENTANE SYSTEM

I Variation in Isobutane Concentration $n = 21$

y_i	$\bar{y}$	$y_i - \bar{y}$	$(y_i - \bar{y})^2$
81.439	79.063	2.376	5.6454
79.353		0.290	0.0841
79.067		0.004	0.00002
79.266		0.203	0.0412
79.233		0.170	0.0289
78.677		-0.386	0.1490
78.304		-0.759	0.5761
77.475		-1.588	2.5217
78.679		-0.384	0.1475
80.576		1.513	2.2892
78.369		-0.694	0.4816
78.678		-0.385	0.1482
79.369		0.306	0.0936
78.602		-0.461	0.2125
79.576		0.513	0.2632
78.336		-0.727	0.5285
79.788		0.725	0.5256
78.450		-0.613	0.3758
79.348		0.285	0.0812
78.448		-0.615	0.3782
79.289		0.226	0.0511
		$\Sigma =$	14.6226

$$S^2 = \frac{14.6226}{21-1} = 0.7311; \quad S = 0.855$$

$$95 \text{ percent Confidence Limit} = \bar{y} \pm 2S = \underline{79.063 \pm 1.710 \text{ Mol Percent}}$$

$$\text{Relative Standard Deviation} = \frac{S}{\bar{y}} \times 100 = \frac{0.855}{79.063} \times 100 = \underline{1.08 \text{ Percent}}$$

Table 5-4 Continued

II Variation in Isopentane Concentration n = 21

y_i	$\bar{y}$	$y_i - \bar{y}$	$(y_i - \bar{y})^2$
18.273	20.527	-2.254	5.0805
20.312		-0.215	0.0462
20.445		-0.082	0.0067
20.313		-0.214	0.0458
20.401		-0.126	0.0159
20.901		0.374	0.1399
21.278		0.751	0.5640
22.164		1.637	2.6798
20.942		0.415	0.1722
18.954		-1.573	2.4743
21.204		0.677	0.4583
20.940		0.413	0.1706
20.215		-0.312	0.0973
21.018		0.491	0.2411
20.092		-0.435	0.1892
21.289		0.762	0.5806
19.873		-0.654	0.4277
21.235		0.708	0.5013
20.334		-0.193	0.0372
20.845		0.318	0.1011
20.040		-0.487	0.2372
		$\Sigma =$	14.2669

$$S^2 = \frac{14.2669}{21-1} = 0.7133; \quad S = 0.845$$

95 percent Confidence Limit $= \bar{y} \pm 2S = \underline{20.527 \pm 1.690 \text{ Mol Percent}}$

Relative Standard Deviation $= \frac{S}{\bar{y}} \times 100 = \frac{0.845}{20.527} \times 100 = \underline{4.12 \text{ Percent}}$

FIGURE 5-2
RELATIVE STANDARD DEVIATIONS
OF GAS CHROMATOGRAPHIC ANALYSES

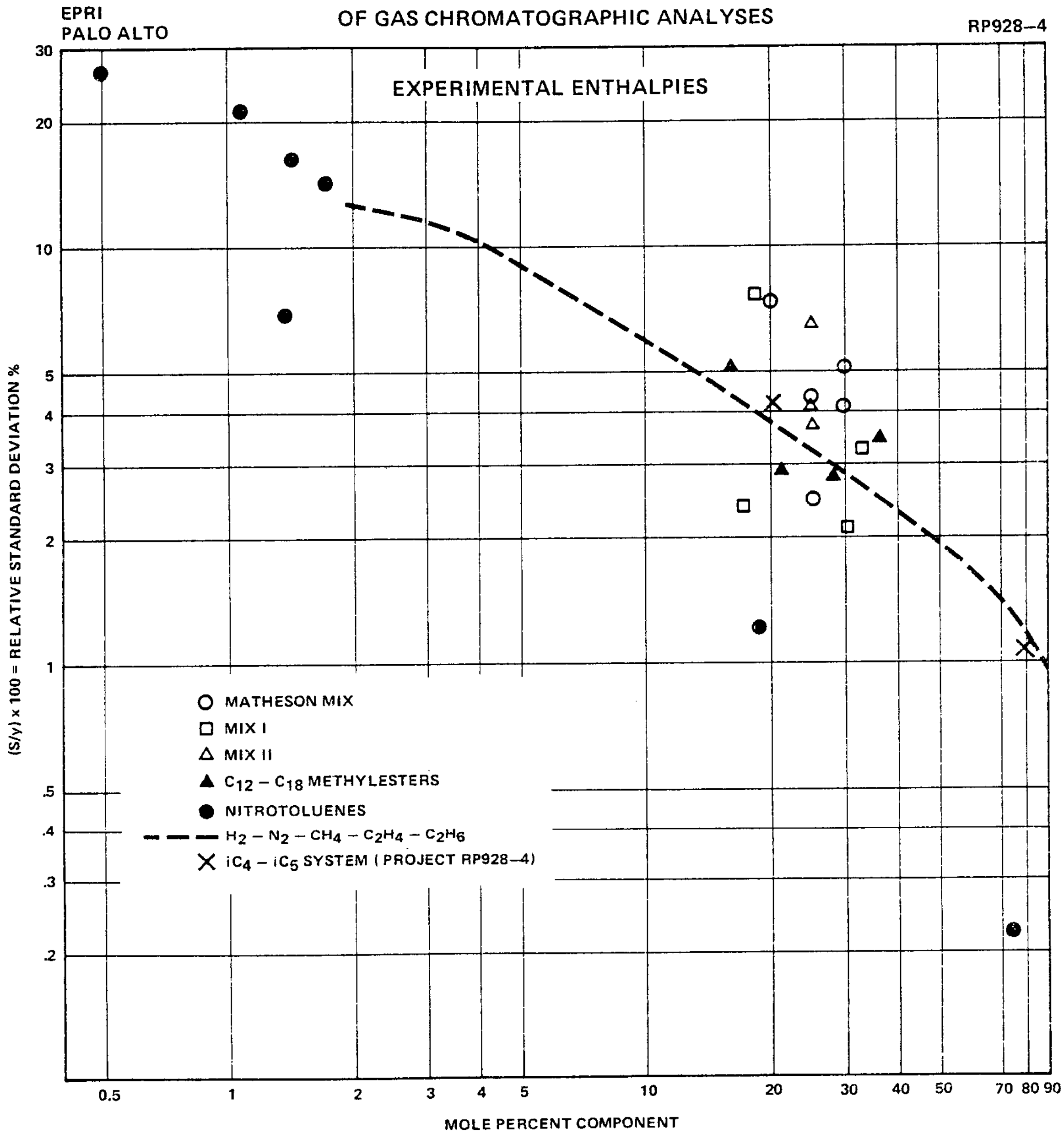


Table 5-5

80-20 MIXTURE CRICONDENTHERM TEMPERATURES PREDICTED BY VARIOUS CORRELATIONS

Prediction Correlation	T_{CT}, Degrees F
Ghormley-Lenoir	312.0
Silverman-Thodos (5-7)	302.3
Etter-Kay (5-5)	289.3
Grieves-Thodos (5-6)	258.0
Kay Pseudocritical[a]	293.8

[a] Simply computed as the molal average critical temperature

Section 6

EXPERIMENTAL ERROR ANALYSIS

PREVIOUS RESULTS

In a previous study, Lenoir and Hipkin (1-1) estimated the sources of error caused by the various measurement uncertainties, such as inlet calorimeter temperature, Freon-11 flowrate, hydrocarbon liquid flowrate, hydrocarbon liquid density, etc. They estimated an overall uncertainty of 1.1 Btu/lb.

By comparing their values for water and n-pentane with literature values (4-1, 6-1) Lenoir and Hipkin showed that the apparatus measures enthalpy differences with an average deviation of 1.5 Btu/lb.

In this study, an independent error analysis was made based on the measurements for the 80-20 mixture.

ERROR ANALYSIS

During the course of this experimental enthalpy study, it was determined that only the following measurement variables contributed significant sources of error to the overall measured ΔH.

Freon-11 volume in receiver, F

Timing the Freon-11 flow, S

Timing the hydrocarbon flow, M

Hydrocarbon density, ρ

Inlet hydrocarbon temperature, T

The formula for computing the total error in the measured ΔH is

$$\varepsilon_H = d(\Delta H) = \frac{\partial \Delta H}{\partial F} \Delta F + \frac{\partial \Delta H}{\partial S} \Delta S + \frac{\partial \Delta H}{\partial M} \Delta M + \frac{\partial \Delta H}{\partial \rho} \Delta \rho + \frac{\partial \Delta H}{\partial T} \Delta T \qquad (6\text{-}1)$$

ΔF, ΔS, ΔM, etc represent the corresponding measurement errors. The partial derivative terms represent the relative sensitivities of enthalpy to each measurement variable. In the analysis which follows they will be referred to as sensitivity coefficients.

The significant variables contributing to the uncertainty of the experimental enthalpy measurements are those in the first term of Equation 3-5. Table 6-1 lists the expressions defining the sensitivity coefficients for the significant variables. In addition to the four measured variables in the first term of Equation 3-5, Table 6-1 also defines the error in the measured inlet hydrocarbon temperature since it is directly related to the enthalpy change computed from Equation 3-5.

The top portion of Table 6-2 lists typical measurement values which were used in the error estimate analysis. The lower half of this table summarizes values for the sensitivity coefficients estimated, measurement errors, and the absolute error contribution for each measurement in Btu/lb. The Freon-11 volume in the receiver can be read to the nearest 0.1 ml. It is estimated that the operators can read the flowrate timers with an accuracy of at least 0.2 second. The hydrocarbon densities were measured in the Braun Research Laboratory. Their estimated measurement accuracy is 0.005 gms/ml. Finally, the effect of errors in the hydrocarbon inlet temperature measurements is reflected in the fluid isobaric heat capacity. For a single-phase vapor or liquid hydrocarbon, C_p should not exceed a value of about 0.7 Btu/lb-°F over the temperature ranges studied. The measurement error in the temperature itself is estimated to be 0.4 degree F (6-2) due to thermocouple inaccuracies and temperature reproducibility.

The bottom of Table 6-2 shows that an overall estimated absolute uncertainty of 1.57 Btu/lb is introduced into ΔH due to all of the significant measurement errors. The prime source of uncertainty is the hydrocarbon liquid density. This overall error is of the same order as the errors quoted by Lenoir and Hipkin (1-1) for the same calorimeter. This overall error quoted here is an absolute error. It represents the accumulation of all individual errors without regard to algebraic sign. It does not include the effect of variations in the composition analyses as shown in Table 5-1.

Table 6-1

ANALYTICAL EXPRESSIONS FOR SENSITIVITY COEFFICIENTS

Sensitivity Coefficient	Analytical Expression
$\frac{\partial \Delta H}{\partial F}$	$\frac{\rho_F \ \Delta H_F \ M}{\rho \ H \ S}$
$\frac{\partial \Delta H}{\partial S}$	$-\frac{\rho_F \ \Delta H_F \ FM}{\rho \ H \ S^2}$
$\frac{\partial \Delta H}{\partial M}$	$\frac{\rho_F \ \Delta H_F \ F}{\rho \ H \ S}$
$\frac{\partial \Delta H}{\partial \rho}$	$-\frac{\rho_F \ \Delta H_F \ FM}{\rho^2 \ H \ S}$
$\frac{\partial \Delta H}{\partial T}$	C_{Pavg}

Table 6-2

SUMMARY OF ERROR CONTRIBUTIONS TO ΔH

1. Typical Measurements Taken for the 80-20 Mixture

$F = 600.8$ ml	$\rho_F = 92.5$ lbm/cu ft
$S = 953.4$ sec	$\Delta H_F = 78.5$ Btu/lb
$H = 630.0$ ml (constant)	$\rho = 35.0$ lbm/cu ft
$M = 650.0$ sec	

2. Summary of Errors

Sensitivity Coefficient	Measurement Error	Error Contribution, Btu/lb
$\frac{\partial \Delta H}{\partial F} = 0.225$ Btu/lb-ml	$\Delta F = 0.1$ ml	$\frac{\partial \Delta H}{\partial F} \Delta F = 0.02$
$\frac{\partial \Delta H}{\partial S} = 0.141$ Btu/lb-sec	$\Delta S = 0.2$ sec	$\frac{\partial \Delta H}{\partial S} \Delta S = 0.03$
$\frac{\partial \Delta H}{\partial M} = 0.208$ Btu/lb-sec	$\Delta M = 0.2$ sec	$\frac{\partial \Delta H}{\partial M} \Delta M = 0.04$
$\frac{\partial \Delta H}{\partial \rho} = 3.85$ Btu-cu ft/lb^2	$\Delta \rho = 0.005$ gms/ml $= 0.312$ lb/cu ft	$\frac{\partial \Delta H}{\partial \rho} \Delta \rho = 1.20$
$\frac{\partial \Delta H}{\partial T} = C_p = 0.7$ Btu/lb-°F	$\Delta T = 0.4$°F	$\frac{\partial \Delta H}{\partial T} \Delta T = 0.28$
	Total Absolute Error, $\varepsilon_H{}^a = 1.57$ Btu/lb	

[a] This error is an absolute total error. It represents the accumulation of all individual errors without regard to the algebraic sign. This value is considered an upper bound.

Section 7

NOMENCLATURE

A_o, B_o, C_o	Constants in Equation 5-1
A, B, C	Constants in Equation 5-2
C_p	Isobaric heat capacity, Btu/lb-°F
F	Volume of Freon-11 measured in receiver, ml
H	Volume of hydrocarbon measured in receiver, ml
H_ℓ	Enthalpy of saturated liquid, Btu/lb
H_v	Enthalpy of saturated vapor, Btu/lb
ΔH	Enthalpy change of hydrocarbon between inlet and outlet of calorimeter, Btu/lb
ΔH_F	Heat of vaporization of Freon-11, Btu/lb
M	Time required to measure hydrocarbon volume H, sec
n	Constant in Equation 5-3
P	Hydrocarbon system pressure, psia
P_a	Atmospheric pressure, inches Hg absolute
P_{BP}	Bubble point pressure of hydrocarbon at 75 degrees F
S	Time required to measure Freon-11 volume F, sec
T	Hydrocarbon inlet temperature, degrees F or R
T_1	Hydrocarbon outlet temperature in the glass receiver, degrees F
T_2	Freon-11 glass receiver temperature, degrees F

NOMENCLATURE Continued

T_i	Boil-off temperature of Freon-11, degrees F
T_H	Temperature of liquid hydrocarbon somewhat higher than T_1, degrees F
T_L	Temperature of liquid hydrocarbon somewhat lower than T_1, degrees F
T_{CT}	Cricondentherm temperature, degrees R
T_R	Reduced temperature
V	Specific volume of hydrocarbon liquid, cu ft/lb

Greek Letters

ε_H	Total error in measured ΔH, Btu/lb
λ	Latent heat of vaporization of the hydrocarbon, Btu/lb
λ_o	Constant in Equation 5-3
ρ	Density of liquid hydrocarbon at T_1, lbm/cu ft
ρ_F	Density of liquid Freon-11 in glass receiver, lbm/cu ft
ρ_L	Density of liquid hydrocarbon at T_L, lbm/cu ft
ρ_H	Density of liquid hydrocarbon at T_H, lbm/cu ft
ρ_ℓ	Density of saturated liquid hydrocarbon, lbm/cu ft
ρ_v	Density of saturated vapor hydrocarbon, lbm/cu ft

Section 8

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