AN EXPERIMENTAL INVESTIGATION OF THE ISOTHERMAL EFFECT OF PRESSURE ON THE ENTHALPY OF THE METHANE-PROPANE SYSTEM

By

DONALD DWAYNE DILLARD

Bachelor of Science
University of Arkansas
Fayetteville, Arkansas
1965

Submitted to the faculty of the Graduate College of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
July, 1966

AN EXPERIMENTAL INVESTIGATION OF THE ISOTHERMAL EFFECT OF PRESSURE ON THE ENTHALPY OF THE METHANE-PROPANE SYSTEM

Thesis Approved:

Robert L. Robinson, Jr.
Thesis Adviser

K C Chao

Dean of the Graduate College

ACKNOWLEDGEMENT

The advice and guidance given by the members of the Chemical Engineering faculty during this study were gratefully received. Professor W.C. Edmister offered many suggestions while serving as thesis adviser during the early phases of the project. I am indebted to Dr. J.H. Erbar and Dr. R.L. Robinson, Jr. for serving as research advisers during the past year. I especially thank Dr. Robinson for his valuable assistance and the great amount of time he has given to this study.

I thank the Natural Gas Processors Association and the School of Chemical Engineering for the funds which made the construction of the experimental apparatus possible. The financial assistance of the National Defense Education Act fellowship was greatly appreciated.

I am particularly grateful to my wife, Donna, for her encouragement.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The effect of pressure on enthalpy becomes an important part of process calculations when large pressure changes are encountered. In most applications, the pressure dependence is estimated by employing empirical equations of state or generalized corresponding state correlations. These calculational procedures are not used with a high degree of confidence since experimental data needed to establish the reliability of the calculational methods are virtually nonexistent. This is particularly true for mixtures where mixing rules must be employed in the calculational procedure.

The purpose of this study is to provide experimental data to be used as a basis for comparing some of the commonly employed methods for estimating the effect of pressure on enthalpy. The specific objective is to experimentally determine the isothermal effect of pressure on the enthalpy of methane and on a mixture consisting of approximately 5 mole percent propane in methane. The study is to include temperatures of 90, 150, and 200°F and pressures of 500, 1000, 1500, and 2000 psia for each isotherm.

Modification and redesign of certain features of an existing isothermal flow calorimeter were necessary before the desired measurements could be made. The major modifications were in the method of charging the fluid to the calorimeter and the procedure for determining flow rates.

CHAPTER II

PREVIOUS INVESTIGATIONS

The thermodynamic theory supporting this investigation is given in many textbooks including that of Van Ness (29). The theory pertinent to this work is summarized below.

Enthalpy is a state property, and therefore is a function only of the variables necessary to define the state of the system. Thus, changes in enthalpy are determined solely by initial and final states. The independent variables normally selected are temperature, pressure, and composition, i.e., $H = f(T, P, C)$. In this work and similar investigations, the composition remains constant and the total differential of enthalpy can be expressed as

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad (1)$$

where H = enthalpy of the system, energy/unit mass

T = temperature

P = pressure

In isothermal calorimetry, the temperatures of the initial and final states are equal. With this stipulation, Equation 1 becomes

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (2)$$

The enthalpy change for a finite pressure change is given by integrating

Equation 2.

$$(H_2-H_1)_T = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (3)$$

Previous Experimental Work

Experimental methods have been designed to measure both differential and integral enthalpy changes. Most prior work has been directed toward the measurement of differential enthalpies. The experimental method consists of using an expansion device (capillary, valve, or porous plug) to attain a small pressure drop while adding a small quantity of energy to balance the temperature decrease caused by expansion. Thus, $(\Delta H/\Delta P)_T$ is measured and assumed to be equal to $(\partial H/\partial P)_T$. A complete enthalpy diagram can be constructed by combining measured values of $(\partial H/\partial P)_T$ at the pressures and temperatures of interest and a knowledge of heat capacities at all temperatures and one pressure. In the absence of heat capacity data at finite pressures, the values of $(\partial H/\partial P)_T$ can be obtained at low pressure and then extrapolated to zero pressure so that ideal gas state heat capacities can be employed. Two publications appeared in 1932 describing this experimental method. Collins and Keyes (21) used a capillary to attain a small pressure drop and for energy input. In a similar investigation, Eucken, et al. (14), used a valve for pressure drop and a wire heater for energy input. The former apparatus was modified by the original experimenters (6, 7), while modifications to the latter apparatus have been more recent (5, 19).

An apparatus designed to measure integral enthalpy changes for large pressure drops has been described by Gilliland and Lukes (15).

The relationship between this experimental method and the method described above is given by Equation 3. A long capillary was employed to throttle the fluid from a high inlet pressure. The capillary outlet exhausted into a relatively large volume maintained at atmospheric pressure. Energy was added by using the capillary as a resistance heater in an electrical circuit. This apparatus was recently modified and improved by Yarborough (31, 32).

CHAPTER III

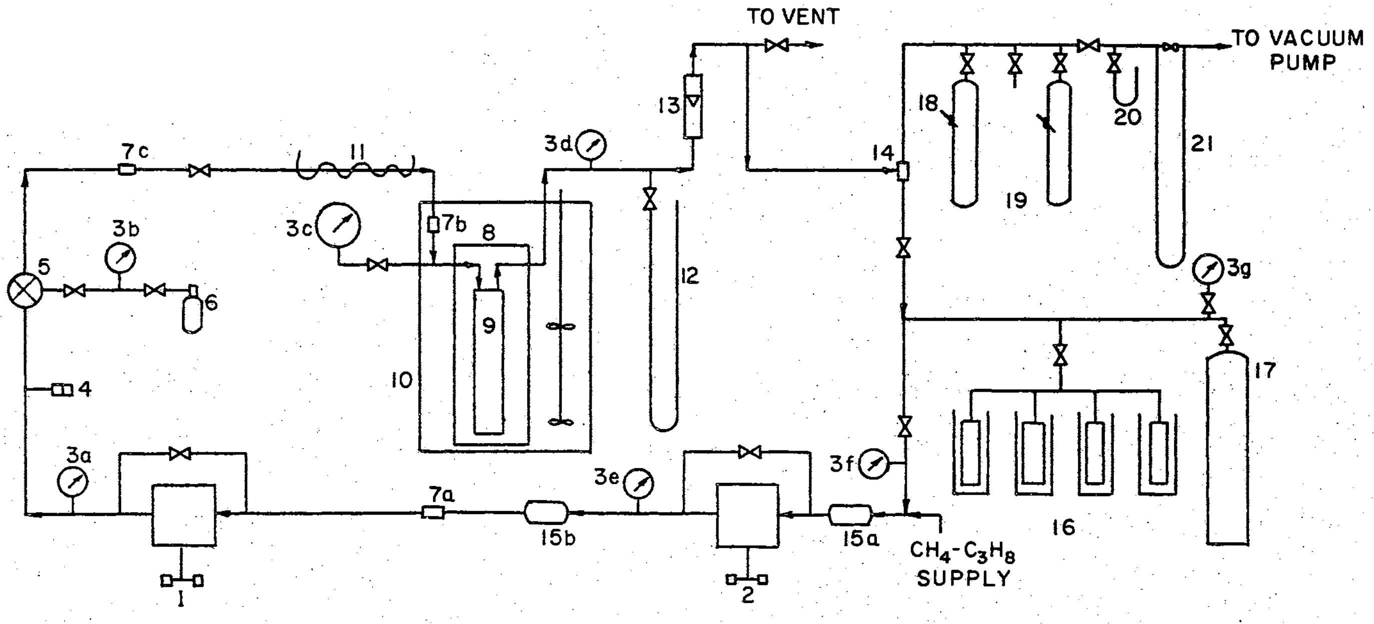
EXPERIMENTAL APPARATUS

A schematic diagram of the equipment used in this investigation is shown in Figure 1. The apparatus was designed for both once through and recycle operation. The essential elements of the apparatus are two stages of compression for gas circulation, a constant temperature bath, an isothermal flow calorimeter, and a glass collection system for flow rate determination.

The apparatus used in this study was originally designed, constructed, and operated by Yarborough (31, 32). The original investigation was concerned with the isothermal effect of pressure on the enthalpy of the propane-benzene system. This system was always charged to the calorimeter as a liquid. Thus, extensive modifications were necessary to adapt the apparatus for use with the gaseous methane-propane system.

The major modifications made were in the method of charging the fluids and the method of flow rate determination. Minor modifications were made to the calorimeter and constant temperature bath.

A detailed description of the apparatus is given below. Since some components of the apparatus were modified only slightly while others were unchanged, the description given here will be somewhat repetitious of that given by Yarborough (31). The calorimeter will be described first, followed by a description of flow and auxilary equipment. Finally, the electrical circuit will be described.



1 - AMINCO AIR-DRIVEN DIAPHRAGM GAS COMPRESSOR
2 - ELECTRICALLY-DRIVEN DIAPHRAGM GAS COMPRESSOR
3 - PRESSURE GAUGE
4 - RUPTURE DISK
5 - MITY-MITE PRESSURE REGULATOR
6 - NITROGEN SUPPLY CYLINDER
7 - MICRON FILTER
8 - STAGNANT AIR BATH
9 - CALORIMETER
10 - CONSTANT TEMPERATURE GLYCOL BATH
11 - PREHEATER
12 - MANOMETER
13 - ROTAMETER
14 - THREE-WAY SOLENOID VALVE
15 - SURGE TANK
16 - COLLECTION BOMBS IMMERSED IN LIQUID NITROGEN
17 - 12-GALLON STORAGE CYLINDER
18 - THERMOMETER
19 - GLASS COLLECTION BOMBS
20 - McLEOD GAUGE
21 - ABSOLUTE MANOMETER

Figure 1. Schematic Flow Diagram

Calorimeter

The design of the calorimeter was patterned after the one used by Gilliland and Lukes (15). The calorimeter was designed for an inlet pressure of 5000 psi. Originally, the effluent pressure was not to exceed approximately one atmosphere, but higher effluent pressures were required for the present investigation. The calorimeter was tested and it was observed that the calorimeter would withstand effluent pressures of approximately 50 psig.

The calorimeter is shown in Figure 2. The fluid enters the inlet stagnation chamber, 2, by way of 1/8-inch stainless steel tubing, 1a. A bare wire 24 gauge Conax thermocouple, 5, is sealed in the top of the inlet stagnation chamber and monitors the temperature of the inlet fluid. The fluid passes out of the inlet stagnation chamber through 1/8-inch stainless steel tubing, 16, and into 1/16-inch stainless steel tubing, 13. The 1/8-inch tubing is coupled to the 1/16-inch tubing by a High Pressure Equipment adapter, 10, which also serves to center the baffles around the capillary. The fluid passes to a stainless steel capillary, 18, which is silver soldered into the 1/16-inch tubing. The capillary used in this investigation was 0.0115 inch I.D. by 80 inches long and had a resistance of about 11 ohms at 25°C. The capillary was used as a resistance heater in the electrical circuit. One electrical lead, 23, was connected to the copper capillary anchor, 19, which was insulated from the calorimeter by Garlite washers, 21. The other electrical lead, 6, was connected to the calorimeter by a screw opposite set screw 12. Thus electrical continuity was made through the capillary via the 1/16-inch tubing, the tubing coupling, and brass ring 11. The capillary was

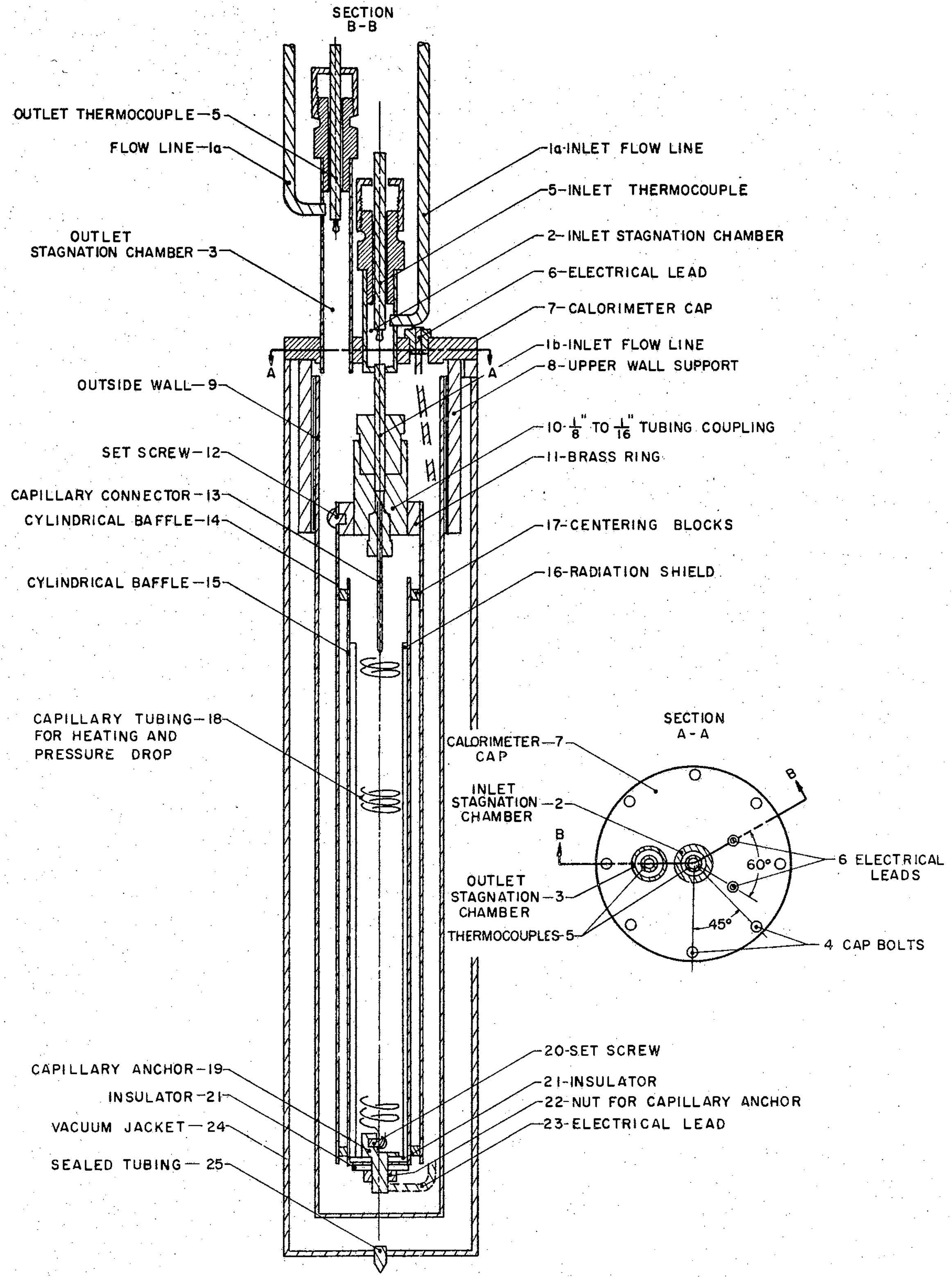


Figure 2. Calorimeter for Isothermal Pressure Effect on Enthalpy

kept from shorting by a silvered glass tube, 16, which also served as a radiation shield.

The fluid leaves the end of the capillary, held in place by set screw 20, and expands into the calorimeter volume. The fluid flows back over the outside of the capillary, where it is further heated, and then flows down between brass baffles 14 and 15 which are separated by copper centering blocks, 17. At the bottom of the calorimeter, the fluid turns up and flows between baffle 14 and the outside wall, 9. The fluid then enters the stainless steel outlet stagnation chamber, 3, where it contacts the outlet thermocouple, 5. The fluid then flows from the outlet stagnation chambers via 1/8-inch stainless steel tubing, 1a.

The electrical leads were teflon insulated 18 gage silverplated solid copper wire. The wires were sealed into the calorimeter with 3/32-inch Conax stainless steel compression fittings. The cap of the calorimeter was secured to the outside wall of the calorimeter by 8 steel screws. A teflon gasket was used between the surfaces, of which the lower surface had a raised knife-edge to insure deformation of the gasket and a leak-tight closure. All internal parts of the calorimeter were connected to the calorimeter cap. Thus by removing the cap these parts of the calorimeter were easily accessible.

To minimize the possibility of radiation heat leak, the exterior wall of the outer baffle, 14, the interior of the outside wall, 9, and the outside of the vacuum jacket, 24, were all polished. To minimize conduction heat loss, the vacuum jacket was evacuated to 5 microns of mercury through 1/8-inch stainless steel tubing which was then closed.

Calorimeter Constant Temperature Bath

The constant temperature bath used in this work is shown in Figures 3 and 4. The design of the bath was patterned after a bath used by the National Bureau of Standards (16).

The bath consisted of two similar tanks constructed from 20 gauge sheet steel. The tanks were constructed such that one tank could sit in the other with 1 1/2-inch of shredded asbestos insulation between them. The lid for the bath was constructed in two sections for ease in putting the calorimeter holder, heater, etc. in place. Both sections of the lid were double walled with 1 1/2-inch of glass wool insulation between the walls.

The calorimeter holder with the calorimeter in place is shown in Figure 3. The holder was constructed from 5 inch schedule 40 pipe with a plate welded to the bottom. The lid for the holder was secured by 8 capscrews. A rubber gasket was used to insure a leak-tight seal. The calorimeter was held in place by the 1/8-inch stainless steel tubes which served as flow lines to and from the calorimeter. The tubing connected to fittings which were welded into the wall of the holder. The electrical and thermocouple leads entered the holder via a 3/8-inch pipe which was connected to the holder with a tapped fitting. The interior of the holder was lined with aluminum foil to minimize heat loss by radiation. The holder was constructed such that the bath fluid could circulate below the holder as well as around it. Thus when the bath and calorimeter temperatures were equal, no heat loss from the calorimeter should occur.

The calorimeter holder was placed within the large part of the

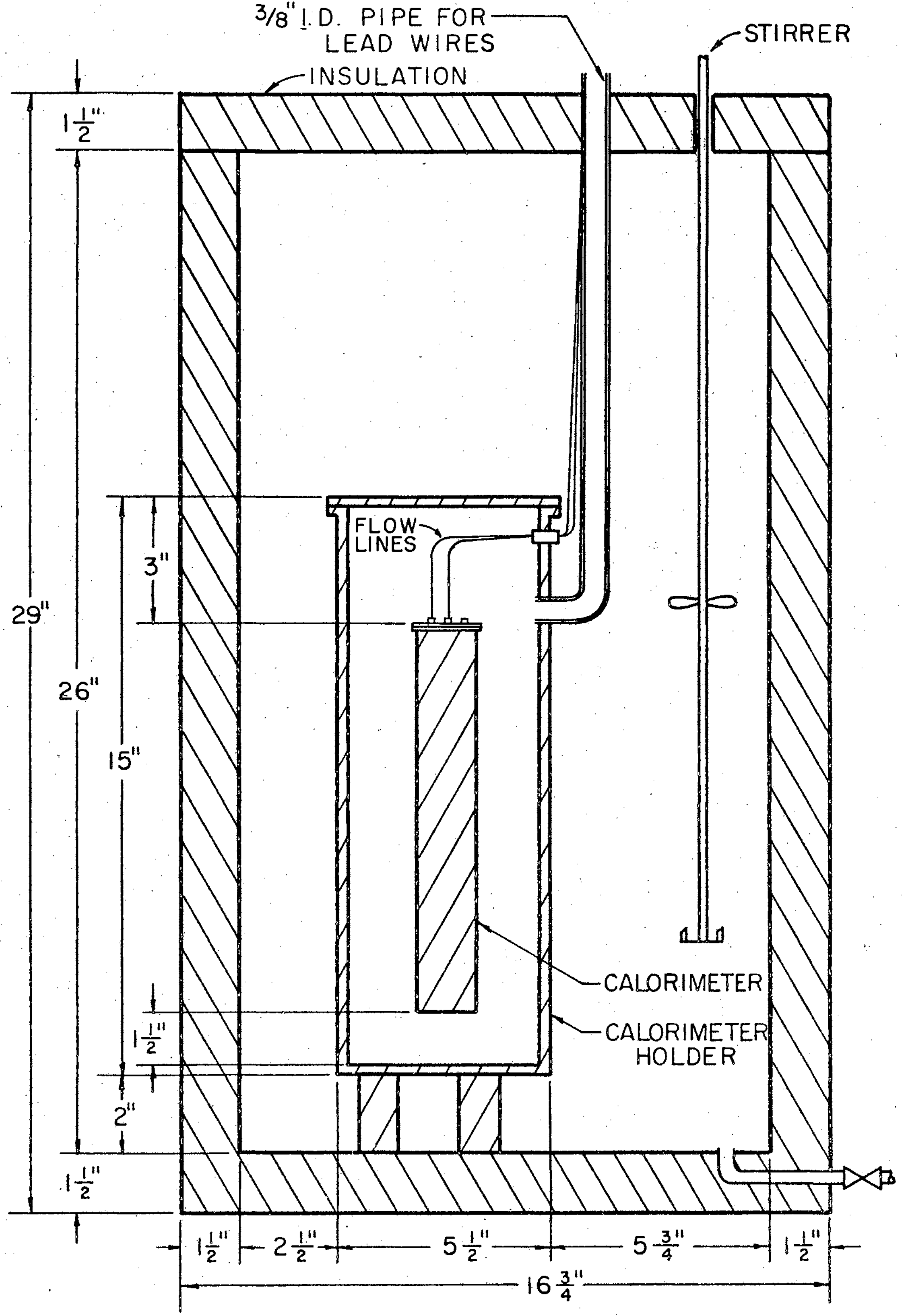


Figure 3. Side View of Temperature Bath

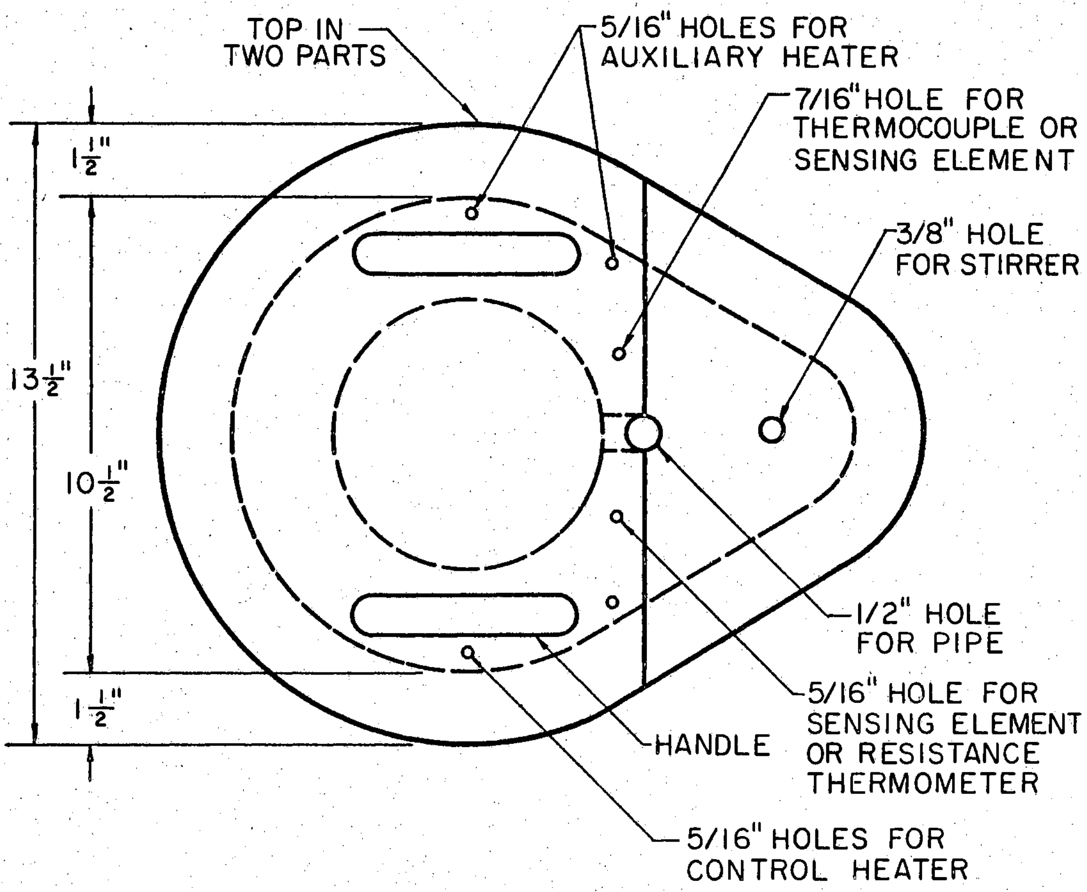


Figure 4. Top View of Temperature Bath

pear-shaped cross-section of the bath. In the small section of the bath, a Lightning Mixer Model F stirrer was installed. Two impellers were employed on the shaft of the mixer. Ths control heater for the bath was a 1000 watt flexible Precision Scientific immersion type heater. The heater was positioned between the bath wall and the calorimeter holder. An identical auxiliary heater was placed along the opposite wall of the bath. The temperature controller was a Hallikainen Thermotrol Model 1053A and the sensing element was a shielded platinum resistance thermometer, Hallikainen Model 1106. The Thermotrol could be operated as an on-off, proportional, or proportional with reset controller. The bath fluid used was Conoco ethylene-glycol base anti-freeze. The temperature of the bath could be controlled to within ±0.10°F if the heat load was held constant. When the heat load varied, the control was not as good and at times it was necessary to manually change the set point on the controller.

Description of Flow

A flow diagram of the apparatus is shown in Figure 1. The apparatus is operated with continuous recycle during the line out portion of the run. During continuous operation, the low pressure calorimeter effluent flows through a Matheson Model 604 rotameter, 13, through a two liter surge tank, 15a, to the suction of the first stage of compression, 2, a Pressure Products Inc. Model 1054 electrically driven diaphragm compressor. The calorimeter effluent pressure is monitored by either an open-ended mercury manometer, 12, or a 60 psi Ashcroft pressure gauge, 3d. The discharge pressure of the first stage compressor is indicated by a 2000 psi Ashcroft pressure gauge, 3c. The fluid then flows through a 1-liter surge tank, 15b, a 1/8-inch 10 to 15 micron Hoke sintered metal filter, 7a, to the suction of the second stage of compression, 1. The second stage compressor is an American Instrument Co. Model 46-1435 air-driven diaphragm compressor. The second stage discharge pressure is monitored by a 3000 psi Ashcroft pressure gauge, 3a. An Autoclave Engineers rupture union, 4, was installed in the discharge line of the second stage compressor. The disk was rated at 3100 psi at 72°F.

The discharge pressure of the second compressor was reduced to the desired run pressure by a Grove Model 94W Mity Mite diaphragm type pressure regulator. The dome of the regulator was gas loaded by means of a Grove loading cross No. 100-00801. High pressure nitrogen was used to load the dome. The nitrogen was stored in a Marison ICC3AA4000 cylinder, 6. The regulator dome pressure was indicated by a 3000 psi Ashcroft gauge, 3b. After passing through the Mity Mite regulator, the fluid passed through another Hoke micron filter, 7c, to the preheater, 11. The preheater was a 500 watt Briskeat flexible heating tape wound around 1/8-inch stainless steel tubing. The heating tape was wrapped with asbestos cloth to reduce heat leak. Power to the preheater was supplied and controlled with a Superior Electric Powerstat No. 117T.

After the preheater, the fluid flows to the constant temperature bath, 10, where it is brought to the bath temperature by an immersed tubing coil approximately 40 inches long, including an additional Hoke micron filter. The inlet pressure gauge, 3c, is connected into the system just prior to the point where the fluid enters the calorimeter holder. The gauge is a 16 inch 3000 psi calibrated Heise gauge, graduated in 2 psi increments. The calibration is given in Appendix B. After passing into the calorimeter holder, the fluid flows through the calorimeter and then back to the suction of the first stage compressor.

For batch-wise operation the calorimeter effluent is directed to 4 1-liter aluminum bombs which are immersed in Sulfrian Cryogenic dewars filled with liquid nitrogen. The aluminum bombs are MGM No. 61E/AL and had test pressures of 1000 psi. The dewars were constructed of stainless steel and were 4 1/2-inches I.D. x 18 inches inside depth. The calorimeter effluent pressure could be controlled by adjusting the valve directly above the collection bombs. Make-up gas is injected into the system at the suction of the first stage compressor. The pressure of the entering gas is indicated by a 30 psi Ashcroft gauge, 3f.

After a run, the gas condensed in the aluminum bombs was transferred to a 12 gallon high pressure storage cylinder, 17. The transfer was accomplished by allowing the gas held in the aluminum bombs to warm to room temperature. The pressure in the storage cylinder was indicated by a 3000 psi gauge, 3g. The gauge was supplied by U.S. Gauge Co.

For flow rate determination, the fluid is diverted to glass collection bombs, 19, by means of a three-way solenoid valve, 14, a Skinner No. B4DA9075 multi-purpose valve. The glass bombs had a total volumetric capacity of approximately 8 liters. The calibration for the volume of the collection system is shown in Appendix C. The evacuated pressure of the collection system was indicated by a McLeod gauge, 20. The pressure rise during a flow rate determination was indicated by an absolute mercury manometer, 21. A Gaertner Scientific Corp. No. 1584A cathetometer was used to determine the difference in the height of the two mercury legs. The flow times were monitored by two electric timers, a standard electric Time Co. No. SM60 with smallest divisions of .01 minute and a Model 8760 Millisecond Laboratory Stopclock with smallest divisions of .01 second. The timers were wired into the electrical circuit of the solenoid valve and could be actuated simultaneously with the valve.

Electrical Circuitry

Figure 5 is a schematic of the electrical potential measuring circuit. A Carling double-pole double-throw switch, 1, was used to switch from the energy circuit to the thermocouple circuit.

The thermocouple circuit consisted of a demineralized crushed ice and water cold junction in series with a shorting 6 position Centralab switch, 3. Four Conax copper-constantan thermocouples were connected to the switch. The thermocouples were numbered according to their respective position on the switch. Thermocouple 1 (TC1) indicated the temperature of the fluid entering the calorimeter, TC2 indicated the calorimeter outlet temperature, TC3 indicated the bath temperature, and TC4 monitored the fluid temperature just after preheating.

The energy circuit consisted of a Kepco Model SM75-SMX power supply and a parallel-series circuit. A 0.01 ohm resistor was installed in series with the parallel circuit. Measurement of the potential, E01, across the 0.01 ohm resistor allowed the total current through the circuit to be calculated. The 1 ohm resistor, E1, allowed the current in one leg of the parallel circuit to be measured. From these quantities and the known values of the standard resistors, the power input to the calorimeter heater was calculated. A Carling double-pole double-throw switch, 2, was used to switch betweem the standard resistors and the potentiometer.

The Kepco power supply had a load regulation of ±0.01 percent of the output voltage setting or 0.001 volt, whichever was greater. The ripple

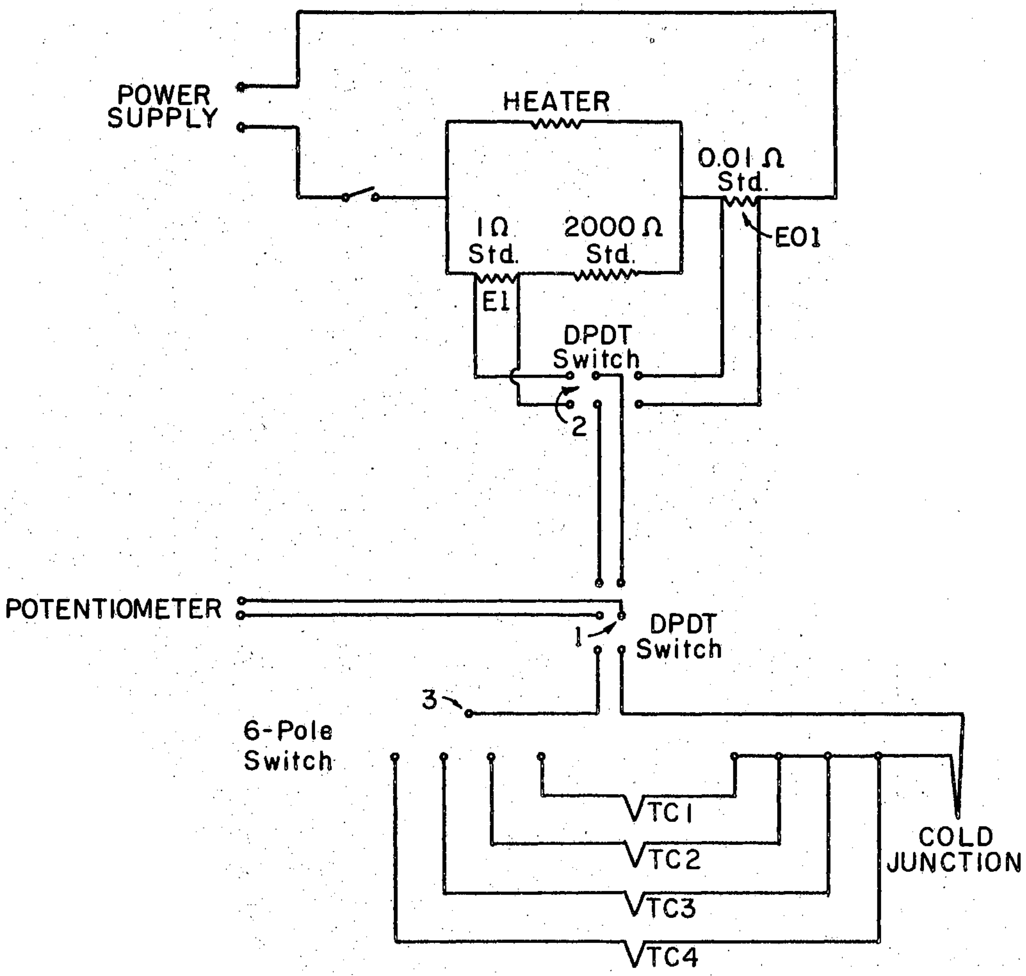


Figure 5. Schematic Diagram of Electrical Circuit

of the output voltage was 0.001 volt maximum. The standard resistors were supplied by Leeds and Northrup. The limits of error on the 1 and 2000 ohm resistors were ±0.01 percent for loads of 0.1 watt or less and ±0.04 percent for loads up to 1 watt. The limit of error for the 0.01 ohm watt was ±0.04 percent. The manufacturer's specifications for the resistors are given in Appendix D.

The potentiometer was a Tinsley Diesselhorst thermo-electric free potentiometer type 35892, Serial No. 158749. The potentiometer had two voltage ranges. The high scale had a range of 0.111110 to -0.011001 volt. The range of the low scale was 0.0111110 to -0.0011001 volt. The galvonometer used with the potentiometer was a Leeds and Northrup D-C Galvonometer No. 2430 with 495 ohms critical damping resistance and 24 ohms system resistance. The sensitivity was 0.0029 microamps/mm. The standard cell was a Guildline Instruments Type 4305 saturated standard cell, Serial No. 17816. The saturated cell was placed in an insulated box with a thermometer inserted near the standard cell.

Materials

The methane and methane-propane mixture used were supplied by Phillips Petroleum Co. The methane was Pure Grade, 99 mole percent minimum. The composition of the mixture was predetermined by Phillips Petroleum Co. Their analysis was accepted as correct and no attempt was made to further purify or analyze the sample. A listing of the mixture composition, as specified by Phillips Petroleum Co., is given in Appendix E.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental procedure will be described in the chronological order in which the various steps necessary in obtaining the experimental data were carried out. This will be followed by a description of the criteria for an acceptable run.

Preliminary Procedures

The cold junction for the thermocouple circuit was prepared from demineralized ice and water. While the cold junction was equilibrating, the valves in the flow loop were positioned for continuous recycle operation. The valves were checked individually to insure proper positioning. Next, the dome of the pressure regulator was loaded with nitrogen to a pressure of approximately 100 psi greater than the desired run pressure. The preheater Powerstat was set to a previously estimated value but not yet turned on.

Having allowed sufficient time for the cold junction to equilibrate, the calorimeter bath temperature was checked and minor adjustments in the Thermotrol set point were made if necessary. The bath was always at or near the desired temperatures since it was set and left controlling at the conclusion of the previous run. The power supply was left running continuously with the control dial positioned at zero when not in use. This eliminated waiting for the unit to line out and prolonged the life of the electrical components.

The final step in the preliminary procedures was to set a previously estimated value for the calorimeter power input into the power supply with the switch in the circuit open so that no current would flow through the calorimeter heater. The value for the power input was estimated from calculated values of the enthalpy change during the earlier runs. Experience proved that a better value could be obtained by plotting the current in the energy circuit as a function of the run pressure for previous runs and extrapolate the curve to the desired run pressure. For a given isotherm the resulting curve was essentially a straight line. The power input was ordinarily estimated to within 10 percent of the final run value.

Start-up

In starting the run, the main objective was to initiate flow through the apparatus at the desired calorimeter inlet pressure without undue upset of the initial thermal equilibrium between the calorimeter and calorimeter bath. The procedure described below was found to serve this purpose satisfactorily.

The by-pass around the second stage compressor was opened and the valve just upstream from the calorimeter closed. Gas was then injected to the suction of the first stage compressor at a regulated pressure. The pressure at which the gas was charged could be estimated from compressor performance curves and an estimated flow rate. The injection pressure was based on previous experience after data for the first isotherm had been obtained. Both compressors were then started, and the by-pass around the second compressor was adjusted until the discharge pressure reached 200 psi above the desired run pressure. The valve to the calorimeter was then opened and the calorimeter power turned on. Thus, flow through the calorimeter and power to the calorimeter heater were initiated simultaneously causing a minimum of upset to thermal equilibrium. The Heise pressure gauge valve was cracked and the flow through the apparatus was adjusted until the calorimeter inlet pressure reached approximately 20 to 50 psi above the desired run pressure. The dome pressure of the pressure regulator was then adjusted until the desired calorimeter inlet pressure was obtained as indicated by the Heise gauge. The injection of gas was terminated and the calorimeter effluent pressure minimized by slowly venting gas from the low pressure side of the flow loop and simultaneously closing the by-pass around the second compressor. This concluded the start-up and the apparatus was now running with continuous recycle.

Line Out

The objectives during the line out portion of the run were to maintain flow through the calorimeter at the desired inlet pressure and to equilibrate the calorimeter inlet, outlet, and bath temperatures. To achieve this, the run variables were monitored periodically and equipment set-points adjusted accordingly.

Adjustments in the power input to the calorimeter were dictated by the difference between the calorimeter inlet and outlet temperatures. The power input was increased when the outlet temperature decreased relative to the inlet temperature. When the outlet temperature increased relative to the inlet temperature, the power input was decreased. Due to small flow rates, the temperature response to a power change was slow.

For this reason, power changes were not made more often than once per hour. The magnitude of the change in power input was dictated by the rate of change between the inlet and outlet temperatures.

When both compressors were running smoothly, no adjustments were necessary to maintain flow through the calorimeter at the desired inlet pressure. However, the first stage compressor would occasionally lose its prime for a short duration, with consequent drop in flow rate. This caused an upset in the approach to thermal equilibrium, thus lengthening the time required to perform a run. Efforts of the writer, in addition to those of the manufacturer, to improve the operation of the compressor were unsuccessful.

The time required to line the apparatus out varied considerably. In the absence of compressor malfunctions, line out could be achieved in 8 to 12 hours, the primary variable being the initial estimate of the power input. Approximately one additional hour was required for each time the flow through the calorimeter was upset by a compressor malfunction.

Power and Temperature Measurements

After the equipment appeared to be operating at the desired temperatures in a steady-state manner, temperature and power measurements were made and recorded. The measurements were made at equal time intervals for a period of one hour. Usually the inlet and outlet calorimeter thermocouple readings were taken at 5 minute intervals. The calorimeter inlet and outlet pressures, standard resistor potentials, preheater temperature, and the bath temperature were taken at 15 minute intervals.

Flow Rate Determinations

After the temperature and energy measurements were completed, the flow rate through the calorimeter was determined. The procedure used for flow rate determination is described below.

The calorimeter effluent was diverted to the aluminum bombs immersed in liquid nitrogen and make-up gas was supplied in the same fashion as used in the start-up procedure. Using the valve directly above the aluminum bombs, the calorimeter effluent pressure was adjusted to approximately one atmosphere. The solenoid valve was then actuated, diverting the flow into the originally evacuated glass collection bombs. The two timers were started by the same electrical switch that actuated the solenoid valve. Flow into the glass collection bombs was continued until the calorimeter effluent pressure returned to the initial valve as indicated by the open-end manometer. The flow was then returned to the aluminum bombs. From the known pressure and temperature of the gas collected in the calibrated volume of the sample collection system, the mass of gas collected was calculated using a truncated virial equation of state. The mass and flow time serve to establish flow rate. Duplicate flow measurements indicate the precision of the method to be within ±0.5 percent.

The calorimeter effluent pressure and temperature during flow measurements differ slightly from the values for which the energy measurements were made. However, since the gas flow is in the critical regime, downstream pressure does not affect flow rate. Also, experimental data indicate that the temperature effects are entirely negligible.

Criteria for an Acceptable Run

A limiting factor in the precision of data taken by isothermal calorimetry is the degree to which the calorimeter inlet, outlet, and bath temperatures can be equilibrated. Ideally, these temperatures should be exactly identical and not vary with time so that no heat transfer between the calorimeter and bath would occur and steady state would be a certainty. In practice this can never be achieved. Even if a sufficient amount of time were available, small perturbations caused by transients in the components of the apparatus would surely occur. Thus, the investigator must compromise between the precision and the time required to perform a run.

For this investigation, the criteria for an acceptable run were that the inlet, outlet, and bath temperatures vary not more than 0.20°F during the one-hour period in which the temperature and energy measurements were made. Further, the inlet, outlet, and bath temperatures were to be within 0.5°F of the desired run temperature with no more than 0.5°F difference between any two of the three temperatures. Also, a run was not acceptable if any disruption of flow through the calorimeter occurred which caused the inlet calorimeter pressure to vary more than 2 psi.

CHAPTER V

RESULTS

Experimental data were obtained for the isothermal effect of pressure on the enthalpy of pure methane and a methane-propane mixture. The measurements were made at 150°F for methane and at 90, 150, and 200°F for the methane-propane mixture. At each temperature, data were taken for 500, 1000, 1500, and 2000 psia. The experimental results are shown in Table I. The raw data which were used in calculating the results are given in Appendix H.

Corrections to Experimental Data

Defining the system as the contents of the calorimeter, an enthalpy balance for the flow system existing in this investigation can be written as

$$h_T^o - h_T^p = Q \tag{4}$$

where h_T^o = enthalpy of outlet stream

h_T^p = enthalpy of inlet stream

Q = heat transferred from the surroundings to the system.

The above equation holds only when the assumptions listed below are valid.

1. Steady state operation
2. Kinetic energy effects are negligible

TABLE I

EXPERIMENTAL RESULTS

Run No.	Temp. °F	Pressure psia	Uncorrected $H_T^o - H_T^p$ Btu/lb	Temp. Correction Btu/lb	Pressure Correction Btu/lb	$H_T^* - H_T^p$ Btu/lb	$H_T^* - H_T^p$ Btu/lb-mol
METHANE							
1	150	500	11.258	0.026	0.112	11.40	182.8
4	150	1000	22.267	-0.076	0.533	22.72	364.5
5	150	1500	33.075	-0.178	0.809	33.71	540.7
2	150	2000	42.857	0.174	0.283	43.31	694.8
5.1 MOLE PERCENT PROPANE IN METHANE							
10	90	500	13.973	-0.026	0.472	14.42	254.1
11	90	1000	29.242	-0.099	0.793	29.94	527.5
12	90	1500	45.256	-0.049	1.051	46.26	815.1
13	90	2000	58.276	0.169	1.557	60.00	1057.2
6	150	500	12.189	-0.062	0.354	12.48	219.9
7	150	1000	23.733	-0.054	0.596	24.28	427.7
8	150	1500	35.191	-0.017	0.898	36.07	655.6
9	150	2000	43.135	0.052	1.151	44.34	781.2
14	200	500	13.709	-0.216	0.471	13.96	246.0
18	200	500	12.161	-0.072	0.496	12.59	221.8
22	200	500	9.021	-0.023	0.528	9.53	167.9
23	200	500	9.382	-0.066	0.528	9.85	173.5
24	200	500	9.830	-0.180	0.528	10.18	179.3
25	200	500	10.135	-0.185	0.528	10.48	184.6
15	200	1000	23.945	-0.088	0.491	24.35	429.0
19	200	1000	17.921	0.152	0.894	18.97	334.2
20	200	1000	18.726	-0.158	0.889	19.46	342.8
16	200	1500	28.219	-0.083	0.733	28.87	508.7
17	200	2000	34.912	-0.101	0.972	35.78	630.5
21	200	2000	34.785	-0.224	0.976	35.51	625.7

3. Potential energy effects are negligible

4. No shaft work

The third and fourth assumptions are valid by design and it is easily demonstrated that the second assumption is valid. For example, at the conditions where the kinetic energy effects are greatest, i.e., the highest flow rate and greatest volume change, the term $(U^2_{out} - U^2_{in})/2gc$ is less than 0.002 Btu/lb.

The validity of the first assumption is not as apparent as the latter assumptions. The requirements of steady state are: 1) constant mass flow rate, 2) the state variables, temperature, pressure, and composition, are constant at any point in the system, and 3) the rate of energy input to the system is constant with respect to time.

In this work, the requirement of constant composition was not questionable. At the conditions of the experiments, the samples were always gaseous. Thus no condensation, with consequent composition change, could have occurred. However, due to transients in the components of the apparatus and/or finite run times, the remaining requirements were never exactly satisfied. Therefore, the success of the experimental method depends on run acceptance criteria being sufficiently stringent to insure that errors due to nonsteady state are negligible. When the above assumptions are valid, Equation 4 expresses the total enthalpy change or the isothermal effect of pressure on enthalpy in terms of the heat input to the calorimeter.

The calorimeter outlet pressure varied from 1 to 4 atmospheres. For this reason, it was necessary to correct the experimental enthalpy values to zero pressure in order to obtain the difference between the real and ideal gas state enthalpy. The virial equation of state, truncated after the second term, was used to make this correction. Experimentally derived second virial coefficients (9, 18) were employed in the virial equation. The pressure correction was normally about 3 percent of the total enthalpy change and never exceeded 6 percent of the total reported value. The procedure and proper equations are given in Appendix J.

In addition to the pressure correction, the inlet and outlet enthalpy values were corrected to the desired run temperature. Ideal gas state heat capacities (1), combined with the effect of pressure on the heat capacity (22), were used in making these corrections. Since the temperatures were never more than 0.5°F from the desired run temperature, these corrections were always small compared to the total enthalpy change.

A sample calculation of the experimental data, complete with corrections, is given in Appendix F. The Fortran listing of the program written for these calculations is shown in Appendix G. The calculations were made on an IBM 7040 computer.

CHAPTER VI

DISCUSSION OF RESULTS

As reported in Chapter V, the isothermal effect of pressure on the enthalpy of methane and a mixture of approximately 5 mole percent propane in methane was experimentally determined. The study includes temperatures of 90, 150, and 200°F and pressures of 500, 1000, 1500, and 2000 psia for each isotherm. In this Chapter, these data are compared with enthalpies generated from experimental measurements of other workers and from commonly employed calculational procedures.

Although the main objective of this study, acquisition of data at the conditions mentioned above, was accomplished, the precision of the data was less than was desired by the writer. A precision of ±2 Btu/lb was desired; however, replicate runs, at selected conditions, showed that the enthalpy difference could not always be reproduced within this limit of uncertainty. Table II lists the results for duplicate runs. The maximum discrepancy is 4.5, 5.4, and 0.3 Btu/lb for runs at 500, 1000, and 2000 psia, respectively.

The most probable sources of error in the experimental results are: 1) errors in measurement, 2) insufficient approach to thermal equilibrium, and 3) heat transfer between the calorimeter and surroundings. The influence of each source of error is discussed below. These discussions are followed by data comparisons and comparisons with enthalpy values generated from calculational methods.

TABLE II

COMPARISON OF EXPERIMENTAL RESULTS FOR DUPLICATE METHANE-PROPANE RUNS

Run No.	Temp. °F	Press. psia	$H_T^* - H_T^p$ Btu/lb
14	200	500	14.0
18	200	500	12.6
22	200	500	9.5
23	200	500	9.9
24	200	500	10.2
25	200	500	10.5
15	200	1000	24.4
19	200	1000	19.0
20	200	1000	19.5
17	200	2000	35.8
21	200	2000	35.5

Errors in Measurement

The most meaningful evaluation of the experimental errors encountered would be a statistical evaluation. However, this would require many replicates at a given set of conditions in order to test the effect of the several run variables on the final results. Since the method of obtaining the experimental data is very time consuming, the possibility of a statistical study was ruled out. More convenient, but less meaningful methods of approximating the experimental errors are available.

When the fractional errors in the various experimental measurements are known or can be realistically estimated, the method of propagation of errors can be used to estimate the maximum error introduced by the uncertainties in the individual measurements (8). This method is quite simple and yields a reliable estimate of the maximum error.

The fractional limit of error in the experimentally measured quantities was estimated by considering the precision of the instruments used and the stability of the readings. Using these values, the maximum experimental error was calculated for runs at 500 and 2000 psia. The calculations indicate a maximum error of 0.8 and 0.3 Btu/lb for the 2000 and 500 psia runs, respectively. It is emphasized that this includes only the effect of uncertainties in the measurement of run variables. The details of this analysis are given in Appendix I.

Heat Transfer Between the Calorimeter and Surroundings

The usual method of testing for heat leaks in a calorimeter is to duplicate runs for a given set of state variables (P,T, and C) at different flow rates. The heat leak becomes small in comparison to the total heat input when the flow rate is sufficiently high. Thus, by comparing data taken at different flow rates, the magnitude of the heat leak can be estimated. In this investigation, it was not practical to vary the flow rate. Consequently, another method of testing for heat leaks was devised.

The heat leak was assumed to be a function only of the difference between the calorimeter and bath temperature. A series of eight consecutive runs were made with all run parameters except power input held constant. Extreme care was exercised to insure steady state conditions for each run. The apparatus was allowed to run for at least 8 hours at a particular power setting before the data were taken.

The heat leak was then estimated by writing an enthalpy balance around the calorimeter

$$Q_{HTR} + Q_{HL} = -\Delta h \qquad (5)$$

where Q_{HTR} = energy input to calorimeter heater, Btu/lb

Q_{HL} = heat leak, Btu/lb

Δh = isothermal effect of pressure on enthalpy, Btu/lb.

Since Δh is a constant for the series of runs and Q_{HTR} is measured directly, the heat leak, Q_{HL}, can be estimated for each of the runs. Run 22 was chosen as a standard from which Δh was numerically evaluated. The average calorimeter temperature, taken as (TC1 + TC2)/2, was almost identical to the bath temperature for this run. Thus, the heat leak was quite small for this run. Table III shows the results of this analysis.

The heat leak is plotted as a function of the difference between the average calorimeter temperature and bath temperature in Figure 5. As indicated on the plot, the maximum heat leak that could have occurred

TABLE III

RESULTS OF HEAT LEAK ANALYSIS

Run No.	Average Calorimeter Temp. mv	Bath Temp. mv	ΔT °F	Q_{HTR} Btu/lb	Δh Btu/lb	$-Q_{HL}$ Btu/lb	$-Q_{HL}$ Btu/hr
22	3.9832	3.9835	-0.014	9.527	9.527	0.000	0.000
23	3.9855	3.9846	0.033	9.845	9.527	0.318	0.067
24	3.9898	3.9852	0.177	10.178	9.527	0.651	0.138
25	3.9939	3.9882	0.221	10.478	9.527	0.951	0.201
26	3.9957	3.9866	0.357	10.649	9.527	1.122	0.237
27	4.0056	3.9937	0.462	11.170	9.527	1.643	0.347
28	4.0038	3.9883	0.602	11.289	9.527	1.762	0.363
29	4.0063	3.9859	0.793	11.461	9.527	1.934	0.408

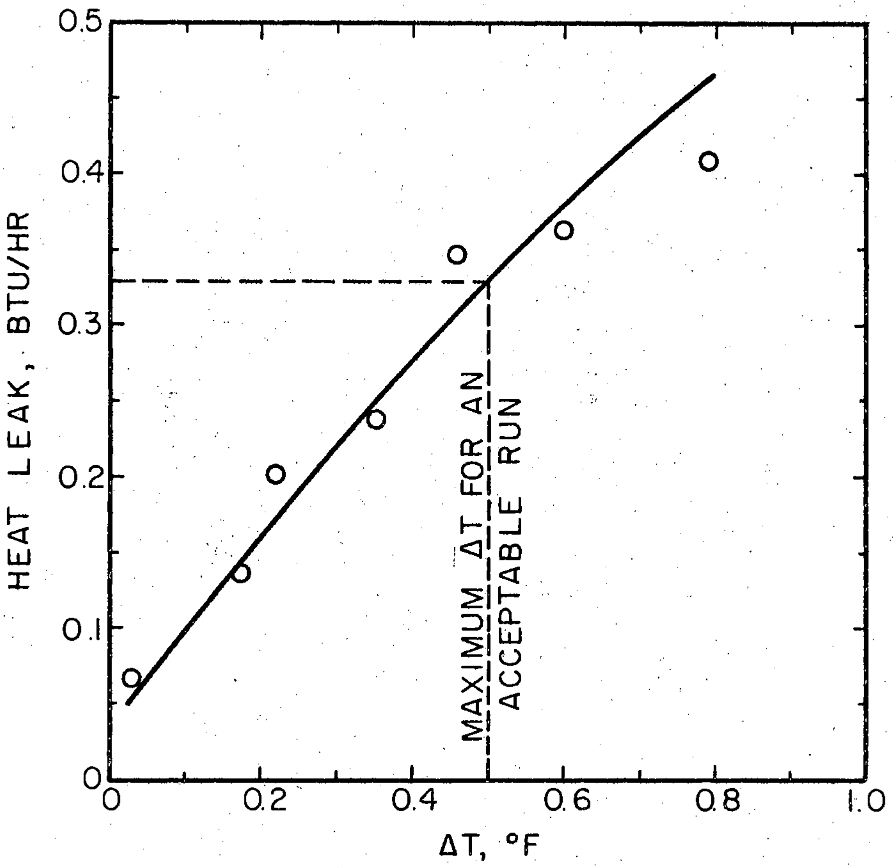


Figure 6. Results of Heat Leak Analysis

during an acceptable run is approximately 0.33 Btu/hr. This transfer rate converts to an estimated maximum error of 1.6, 1.2, 0.8, and 0.4 Btu/lb for runs at 500, 1000, 1500, and 2000 psia, respectively.

Insufficient Approach to Thermal Equilibrium

The difficulty in achieving steady state in an isothermal flow calorimeter is a function of the heat capacity of the calorimeter and the total power input to the calorimeter heater. Ideally, the heat capacity would be very small in comparison to the power input. For this case, upsets in the calorimeter temperature would line out quickly, and the sensible heat involved would be small compared to the total heat input.

Conditions were far from ideal in this work. The heat capacity of the calorimeter was estimated to be about 0.5 Btu/°F and the power input was typically as low as 2 Btu/hr for a 500 psia run. Thus, the sensible heat for a 1.0°F/hr change in the calorimeter temperature would amount to approximately 25 percent of the total energy input. Conditions were more favorable for runs made at higher pressures but the response of the system to adjustments in power input was always slow. Consequently, it was difficult to properly recognize steady state.

It is not possible to quantitatively predict the error introduced by nonsteady state conditions that could have existed during an acceptable run. However, in the writer's opinion, the discrepancy above ±1 Btu/lb in the experimental results for duplicate runs was probably caused by insufficient approach to steady state. The fact that runs 22 through 25, where special precautions were taken to insure steady state, agree within ±1 Btu/lb lends credence to this opinion. The outlet temperature for run 25 was a maximum for an acceptable run. Thus, the other sources of error were probably near the maximum encountered in any particular run.

Data Comparisons

There are no experimental data for the effect of pressure on enthalpy available for direct comparison with the results of this investigation. However, data are available from which enthalpies can be generated. Budenholzer, et al. (4), report partial enthalpies, generated from experimentally measured Joule-Thompson coefficients, for the methane-propane system. The study encompasses compositions ranging from zero to 0.6 weight fraction propane in methane, a temperature range of 70 to 310°F, and pressures to 1500 psia. Yarborough's treatment (30) of the PVTC data of Sage and Lacey (28) offers another source of enthalpy data in the P, T, and C ranges of interest in this work. The enthalpy tabulations of the above workers are for different temperature, pressure, and composition intervals than were used in this work. Thus, it was necessary to interpolate to compatible P, T, and C values before comparisons could be made.

Manker (23) reports a Mollier chart for a methane-propane binary of almost identical composition to the mixture studied in this investigation. However, this study was isobaric with the pressure dependence based largely on Budenholzer's data. Only one isotherm of the Mollier chart (90°F) overlaps the temperature range of this study and this isotherm represents a slight extrapolation of Manker's experimental data. Another Mollier chart, prepared by Edmister (10) from data from multiple sources, is available for comparison with the experimental methane data.

The data comparisons are shown in Table IV. Graphical comparisons

TABLE IV

ENTHALPY COMPARISONS FOR THE METHANE-PROPANE SYSTEM

Mole Fraction Methane	T, °F	P, psia	Smoothed Exp. Δh Btu/lb	Δh (A) Btu/lb	Δh (B) Btu/lb	Δh (C) Btu/lb	Δh (D) Btu/lb
1.00	150	500	11.4	11.2	11.0	--	11
1.00	150	1000	22.7	21.4	22.0	--	23
1.00	150	1500	33.8	31.5	32.5	--	34
1.00	150	2000	42.2	40.9	----	--	44
.95	90	500	15.0	14.1	15.0	15	--
.95	90	1000	30.3	30.0	31.7	31	--
.95	90	1500	45.9	46.6	48.6	48	--
.95	90	2000	60.5	63.3	----	67	--
.95	150	500	12.5	12.4	12.2	--	--
.95	150	1000	24.5	25.4	24.6	--	--
.95	150	1500	36.1	37.8	37.2	--	--
.95	150	2000	44.3	48.6	----	--	--
.95	200	500	10.0	10.7	10.1	--	--
.95	200	1000	19.8	21.4	20.8	--	--
.95	200	1500	29.1	31.7	30.7	--	--
.95	200	2000	35.8	40.7	----	--	--

(A) Yarborough's treatment of the PVTC data of Sage and Lacey
(B) Budenholzer's enthalpies from experimental Joule-Thompson coefficients
(C) Values from Manker's Mollier chart
(D) Values from Edmister's Mollier chart

are made in Figures 7 through 10. The experimental enthalpy differences reported for comparison with the generated values were taken from the best smooth curve that could be drawn for a plot of Δh versus P.

The data comparisons show the experimental enthalpies for methane to be in good agreement with the results of other workers. Figure 7 shows that the present measurements for methane are slightly higher than those reported by Budenholzer and Yarborough, but slightly lower than the values reported by Edmister.

The experimental mixture enthalpies agree well at low pressure. If differences of ±2 Btu/lb between data sources are considered within experimental accuracy, then the present data differs significantly from the data of other sources only at 2000 psia. However, the present work exhibits a general trend of smaller pressure dependence, particularly for pressures above 1000 psia. This trend is clearly illustrated in Figures 8 through 10.

The sources of error in the present investigation would tend to be random. Thus, the smaller pressure dependence at high pressure predicted by this work is not likely to be due to experimental errors. In fact, the reliability of the experimental data should be much better at high pressure than at low pressure where this work agrees well with the results reported by other workers.

Comparison with Calculation Methods

Enthalpies were generated from four different calculational procedures. These values were then compared with the experimental values to check the reliability of the calculational methods. The comparisons are shown in Table V.

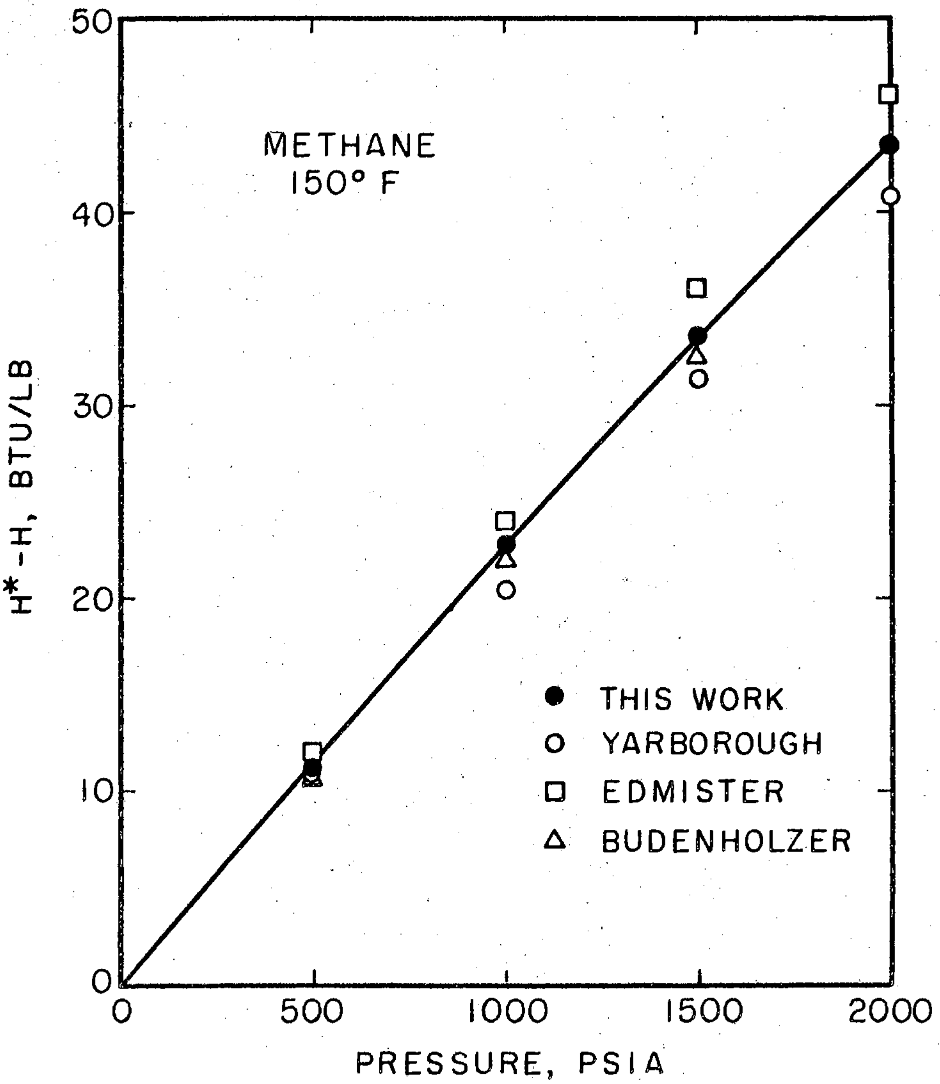


Figure 7. Enthalpy of Methane at 150°F

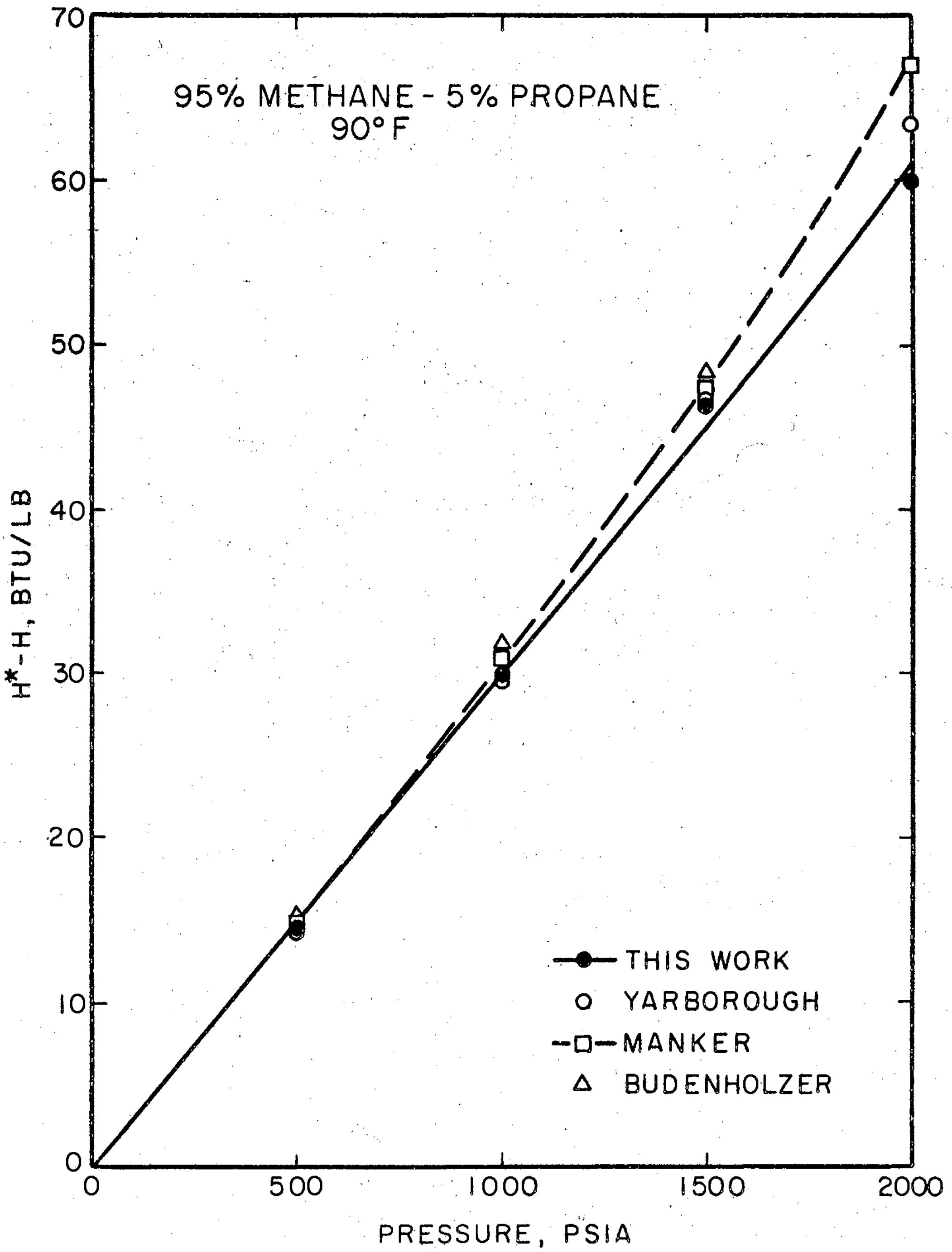


Figure 8. Enthalpy of Methane-Propane Mixture at 90°F

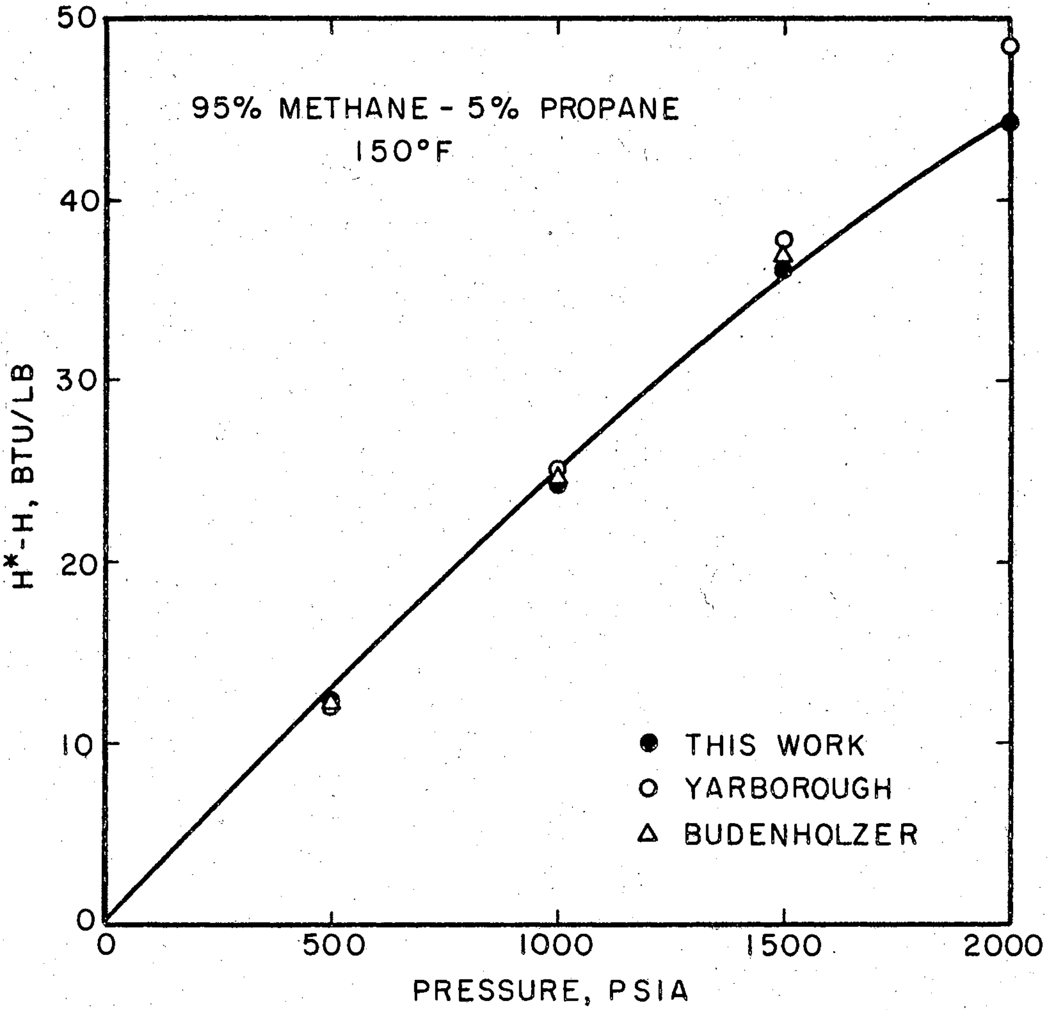


Figure 9. Enthalpy of Methane-Propane Mixture at 150°F

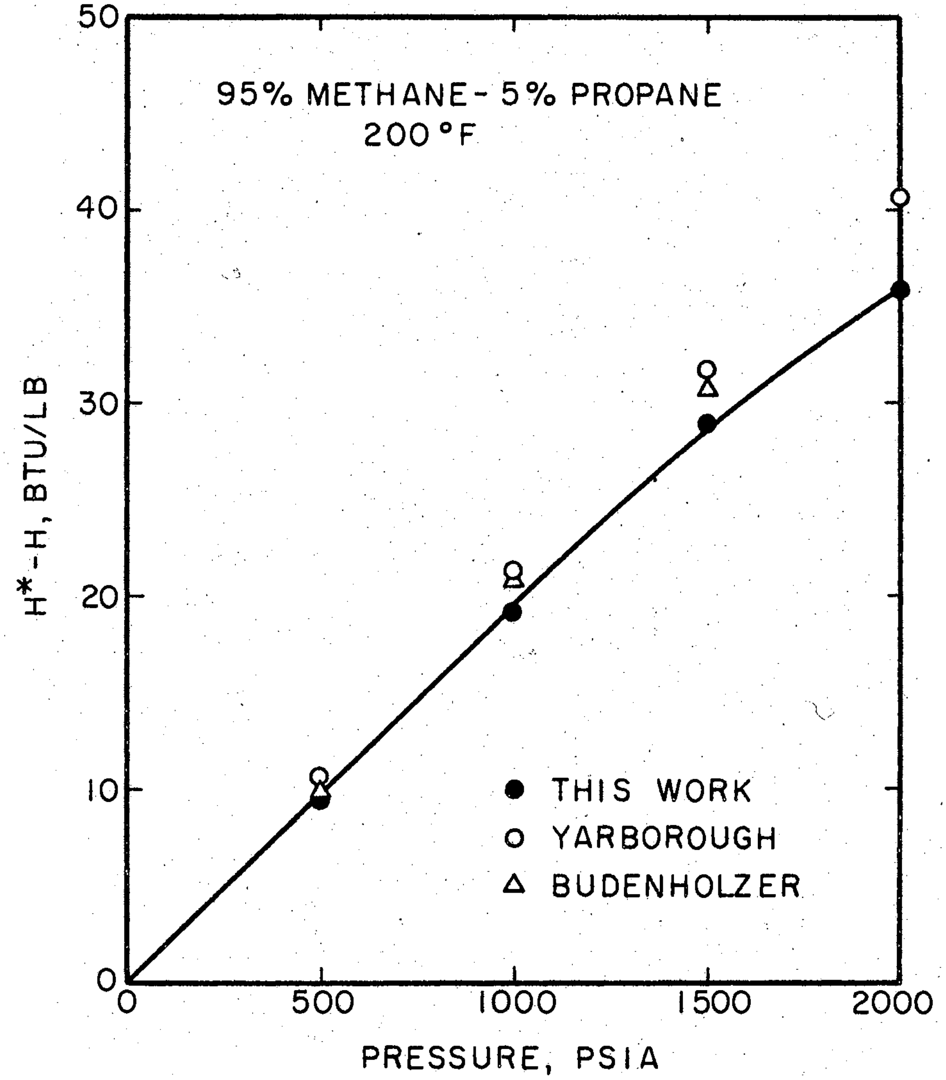


Figure 10. Enthalpy of Methane-Propane Mixture at 200°F

TABLE V

COMPARISON OF CALCULATIONAL METHODS

Mole Fraction Methane	T, °F	P, psia	Smoothed Exp. Δh Btu/lb	Δh (A) Btu/lb	Δh (B) Btu/lb	Δh (C) Btu/lb	Δh (D) Btu/lb
1.00	150	500	11.4	10.63	11.10	10.79	11.8
1.00	150	1000	22.7	20.97	22.17	22.56	22.4
1.00	150	1500	33.8	30.67	32.87	35.62	35.0
1.00	150	2000	42.2	39.38	42.78	50.55	43.6
.95	90	500	15.0	15.34	14.90	15.86	14.4
.95	90	1000	30.3	31.10	30.52	34.98	30.9
.95	90	1500	45.9	46.34	46.07	61.02	47.3
.95	90	2000	60.5	59.72	60.22	*	59.6
.95	150	500	12.5	12.48	12.01	12.37	12.3
.95	150	1000	24.5	24.79	24.14	26.24	25.1
.95	150	1500	36.1	36.46	35.92	42.32	37.0
.95	150	2000	44.3	46.89	46.79	62.23	47.3
.95	200	500	10.0	10.67	10.24	10.57	10.7
.95	200	1000	19.8	20.98	20.36	22.01	21.4
.95	200	1500	29.1	30.63	30.06	34.57	31.2
.95	200	2000	35.8	39.28	39.02	48.68	39.9

(A) Calculated via Redlich-Kwong equation of state
(B) Calculated via Benedict-Webb-Rubin euqation of state
(C) Calculated via truncated virial equation of state
(D) Calculated via Pitzer's generalized corresponding states correlations
* Equation calculated imaginary volume

Equations of State

Three different equations of state were used to generate enthalpies. The equations include a specific equation of state, a generalized equation of state and the virial equation of state. The equations and procedures are given in Appendix J.

The generalized equation employed was the empirical equation developed by Redlich and Kwong (27). This equation has received much attention in recent years. The equation requires only a knowledge of the critical temperature and pressure and is easily programmed for machine calculations. The equation has been employed previously to calculate mixture enthalpy and partial enthalpy differences for gases and vapors (11, 12, 13).

The enthalpies generated from the Redlich-Kwong equation compare reasonably well with the experimental data. The agreement is sufficient to justify the use of the equation for practical applications in the pressure, temperature, and composition range of this investigation. The calculated pressure effect on enthalpy was slightly lower than the experimental values for pure methane. This trend is consistent with the results of a previous investigation (31) of the pressure effect on the propane-benzene system. However, the calculated pressure dependence on the mixture enthalpies were slightly higher than the experimental values. This trend is in contrast with the results of the above investigation (31).

The specific equation of state used was the Benedict-Webb-Rubin (2) or BWR equation. The BWR is an eight constant equation which has been used extensively to predict thermodynamic properties. The eight constants can be adjusted to reproduce experimental data precisely. However, the equation is useful only when reliable PVT data are available for use in evaluating the constants. And, since the constants are fitted for a specific PVT range, the usefulness of the equation in predicting thermodynamic properties outside the range of the PVT data is questionable.

The constants for methane and propane recommended by Benedict, Webb, and Rubin (2) were used to generate the enthalpies for comparison with the experimental values. The calculated values were in excellent agreement with the experimental methane enthalpies. The mixture enthalpies agreed well, particularly at low pressure. The values for 2000 psia at 150 and 200°F were high. However, the BWR generally reproduced the experimental enthalpies more precisely than the other calculational methods checked.

The virial equation of state is the only equation, of the numerous equations (over 100) which have been proposed, that is based on theoretical considerations. The equation contains an infinite number of terms; the coefficients of the terms can be expressed in terms of intermolecular potential functions (17). However, for the comparisons reported here, the equation was truncated after the second term and experimentally derived second virial coefficients (9, 18) were employed. Truncating the equation and using experimentally derived coefficients effectively transforms the equation from general form to a one constant specific equation of state.

The enthalpy differences calculated via the virial equation, using only the second virial coefficient, compare well with the experimental data at 500 psia. The agreement was fair at 1000 psia. Above this pressure, the calculated values were significantly higher than the experimental values. The discrepancy becomes larger with decreasing temperature. The equation predicts an imaginary volume at 90°F and 2000 psia.

Corresponding States Theory

The generalized corresponding states correlation of Pitzer, et al. (25), was used to calculate both pure component and mixture enthalpy differences. The pseudocritical concept proposed by Kay (20) was employed for the calculation of mixture enthalpies. The calculated values were in the range where corrections for the deviation from a simple fluid were negligible. In view of this, the comparisons with the experimental data are probably not a severe test of the correlation.

The comparisons between the values predicted by the correlation and the experimental data are quite good. In most cases the values agree almost as well as those calculated from the BWR equation. The correlation predicts methane enthalpies more precisely than the Redlich-Kwong equation. The mixture enthalpies generally exhibit the same order of precision as obtained with the Redlich-Kwong equation.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Experimental

The isothermal effect of pressure on the enthalpy of methane and a mixture consisting of approximately 5.1 mole percent propane in methane was determined by means of isothermal flow calorimetry. The study included temperatures of 90, 150, and 200°F and pressures of 500, 1000, 1500, and 2000 psia for each isotherm.

Discrepancy in the experimental results for duplicate runs makes the reliability of the results somewhat questionable. However, only three out of a total of eleven duplicate runs were in disagreement by more than the anticipated precision of ±2 Btu/lb. Further, the average deviation from the average value of the enthalpy difference obtained for replicate runs never exceeded ±2.3 Btu/lb. In view of this, the precision of the smoothed experimental values, as reported in Tables IV and V, is probably within ±3 Btu/lb.

The present work generally agrees well with the enthalpy differences generated from experimental measurements of other workers, particularly for pressures below 1500 psia. However, the experimental mixture enthalpies exhibit a definite trend of smaller pressure dependence.

The most probable source of major error in this work was insufficient approach to steady state conditions. The difficulty in achieving steady state and/or proper recognition of steady state was due to slow response of the system to adjustments in the power input to the calorimeter heater. The slow response resulted from low flow rates with consequent power input being too small in relation to the heat capacity of the calorimeter. The flow rates varied from a minimum of 0.089 gr. mole/min to a maximum of 0.45 gr. mole/min for 500 and 2000 psi runs, respectively. The power input ranged from a minimum of 1.9 Btu/hr (0.56 watts) to a maximum of 61.0 Btu/hr (18 watts).

Based on the experience gained in this investigation, the following equipment changes are recommended as guidelines for future work:

1. The flow rate through the calorimeter should be increased by at least 10 fold for low pressure (500 psi) runs and at least doubled for the high pressure (2000 psi) runs. This could be accomplished by using higher capacity compressors and compatible capillary diameters. Only diaphragm type compressors should be considered so that composition change due to mass transfer between the sample and compressor lubricant will not be a problem.
2. The method of flow rate determination should be modified so that the measurements would be made at the same calorimeter effluent conditions existing during the temperature and power input measurements. This could be accomplished by installing a back-pressure regulator in the flow loop at a point just prior to the solenoid valve used to direct the flow to the glass sample collection system. Three distinct advantages would be gained from such a modification: 1) The flow determinations would not be contingent

on the flow being in the critical regime, 2) more than one flow determination per run could be made, and 3) the use of liquid nitrogen (a costly research item) could be eliminated.

3. The design of the calorimeter could be improved. Steady state could be reached faster if the calorimeter volume were smaller and lighter construction materials were used.

Calculational Methods

Four different calculational methods were investigated. The methods include the Redlich-Kwong, Benedict-Webb-Rubin, and virial equations of state and the generalized corresponding states correlation of Pitzer and co-workers. Based on comparisons of calculated enthalpy differences with the experimental data, the following recommendations and conclusions are made:

1. The generalized corresponding state correlations of Pitzer and co-workers can be used to make reliable estimates of the pressure dependence on the enthalpy of light hydrocarbon gases. The correlation appears to be adequate for both pure conponents and mixtures. The pseudocritical concept proposed by Kay can be used with confidence for the range of reduced properties included in this study.
2. The corresponding state correlation is recommended for practical engineering calculations in applications where the number of enthalpy values needed are not too numerous to be calculated by hand.
3. The virial equation of state utilizing only the second

virial coefficient should not be used for pressures above 1000 psia. For applications where the reduced temperature is less than that of this study ($\sim$1.5), the pressure limit should probably be lowered to 500 psia.

4. The Redlich-Kwong equation of state is adequate for most engineering purposes through the pressure, temperature, and composition range of this investigation.
5. The Redlich-Kwong equation is recommended for applications where enthalpy differences are desired for a wide range of state variables. However, the user should bear in mind the known (27, 31) limitations of the equation at reduced temperatures less than one.
6. The Benedict-Webb-Rubin equation agreed quite well with the experimental data. The BWR equation generally predicted enthalpy differences more precisely than the other calculational methods investigated.
7. The Benedict-Webb-Rubin equation is recommended for predicting enthalpy differences when reliable constants, evaluated from PVT data in the range of state variables of interest, are available.

A SELECTED BIBLIOGRAPHY

(1) API Research Project No. 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," A & M College of Texas, College Station, Texas (1953-date).

(2) Benedict, M., G.B. Webb and L.C. Rubin, Chem. Eng. Progr. 47, 419 (1951).

(3) Benedict, R.P. and H.F. Ashby, "Temperature, Its Measurement and Control in Science and Industry," Vol. III, Pt. 2, Ed. C.M. Hertfeld, Reinhold Publishing Corp., New York (1962), p. 51.

(4) Budenholzer, R.A., D.F. Botkin, B.H. Sage and W.N. Lacey, Ind. Eng. Chem. 34, 878 (1942).

(5) Charnley, A., G.L. Isles and J.R. Townley, Proc. Roy. Soc. (London) A128, 133 (1953).

(6) Collins, S.C. and F.G. Keyes, Proc. Am. Acad. Arts and Sci. (Daedalus) 72, 283 (1938).

(7) Collins, S.C. and F.G. Keys, J. Phy. Chem. 43, 5 (1939).

(8) Daniels, F., J.W. Williams, P. Bender, R.A. Alberty and C.D. Cornwell, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York (1962).

(9) Douslin, D.R., R.H. Harrison, R.T. Moore and J.P. McCullough, J. Chem. Eng. Data 9, 361 (1964).

(10) Edmister, W.C., "Applied Hydrocarbon Thermodynamics," Gulf Publishing Co., Houston, Texas (1961).

(11) Edmister, W.C., C.L. Persyn and J.H. Erbar, Paper Presented at 42nd Annual NGPA Convention, Houston, Texas, March, 1963.

(12) Edmister, W.C., R.E. Thompson and L. Yarborough, AIChE Journal 9, 240 (1963).

(13) Edmister, W.C. and L. Yarborough, AIChE Journal 9, 116 (1963).

(14) Eucken, A., K. Clusius and W. Berger, Ztchr. Techn. Phys. 13, No. 6, 247 (1932).

(15) Gilliland, E.R. and R.V. Lukes, *Ind. Eng. Chem. 32*, 957 (1940).

(16) Harrington, E.A., C.B. Green and E.H. Snyder, Research Performed at National Bureau of Standards Under "The Thermodynamic Properties of Petroleum Hydrocarbons," API Research Project No. 38.

(17) Hirschfelder, J.O., C.F. Curtiss and R.B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York (1954).

(18) Huff, J.A. and T.M. Reed, *J. Chem. Eng. Data 8*, 306 (1963).

(19) Iskin, I.P. and M.G. Kaganer, *Sov. Tech. Phys. 1*, 2255 (1956).

(20) Kay, W.B., *Ind. Eng. Chem. 28*, 1014 (1936).

(21) Keyes, F.G. and S.C. Collins, *Proc. Nat. Acad. Sci.* (Wash.) *18*, 328 (1932).

(22) Lyderson, A.C., R.A. Greenborn and O.A. Hougen, "Generalized Thermodynamic Properties of Pure Fluids," (Unpub. Manuscript, University of Wisconsin, 1955).

(23) Manker, E.A., "Thermodynamic Properties of Methane-Propane Mixture At Low Temperatures and High Pressures," (Ph.D. Thesis, University of Michigan, 1964).

(24) Lewis, G.N., and M. Randall, "Thermodynamics," Revised by K.S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill Book Co., New York (1961).

(25) Pitzer, K.S., and G.O. Hultgren, *J. Am. Chem. Soc. 80*, 4793 (1958).

(26) Prausnitz, J.M. and R.D. Gunn, *AIChE Journal 5*, 3 (1958).

(27) Redlich, O., and J.N.S. Kwong, *Chem. Rev. 44*, 233 (1949).

(28) Sage, B.H., and W.M. Lacey, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," API Research Project 37, API (1950).

(29) Van Ness, H.C. "Classical Thermodynamics of Non-Electrolytic Solutions," The MacMillan Company, New York (1964).

(30) Yarborough, L., "The Effect of Pressure and Composition on the Enthalpy of Methane Bianaries in the Vapor Phase," (M.S. Thesis, Oklahoma State University, 1962).

(31) Yarborough, L., "Calorimetric Determination of the Isothermal Effect of Pressure on the Enthalpy of the Propane-Benzene System," (Ph.D. Thesis, Oklahoma State University, 1964).

(32) Yarborough, L., and W.C. Edmister, *AIChE Journal 11*, 492 (1965).

APPENDIX A

CALIBRATION OF THERMOCOUPLES

Four copper-constantan thermocouples were used in this work. The thermocouples used to indicate the calorimeter inlet, outlet and bath temperatures were calibrated by a Leeds and Northrup platinum resistance thermometer, Model 8163, Serial No. 1576919. The thermometer had been calibrated by the National Bureau of Standards in August, 1961. The calibration data were furnished as constants for use in an equation and as a tabulation of temperature as a function of a resistance ratio R/R_o. R is the resistance at the unknown temperature and R_o is the resistance of the thermometer at the ice point. The tabulation was used to determine the temperature in this work.

The resistance of the thermometer was determined by a Leeds and Northrup Mueller bridge, Model 8069-B, Serial No. 1550042. The galvanometer used was a Leeds and Northrup Model 2284-D ballistic type with a sensitivity of 0.2 microvolts/mm. The reading scale was a Leeds and Northrup Model 2170. The galvanometer was placed on a pedestal that was sunk four feet into the earth and isolated from the building to remove vibrations.

A Hart constant temperature bath, No. 97-318 was used in conjunction with a Model 1253A Hallikainen Thermotrol unit for temperature control. The thermocouples were placed in the bath and positioned as near as possible to the resistance thermometer. The Thermotrol set point was adjusted to the desired temperature and allowed to equilibrate 24 hours before readings were made. The Thermotrol set point versus temperature was not known precisely but was always estimated within 2°F of the desired value.

Using the same thermocouple circuit described in Chapter III, from three to five readings were taken at a given temperature. In this manner, a calibration point was obtained for each of the thermocouples at a temperature very near the desired value. The calibration was then adjusted to the desired value by using the millivolts/°F as reported in the reference tables of Benedict and Ashby (3). The results of the thermocouple calibrations are shown in Table VI. The average value for all readings at a particular temperature is reported.

Too few readings were made to establish the precision of the calibrations by the usual method of statistics. However, the deviation between the readings taken for each thermocouple should be a fair indication of precision. The maximum deviation between any two readings for a particular thermocouple was 0.05°F.

TABLE VI

THERMOCOUPLE CALIBRATION

Temp, °F	Thermocouple Emf, mv Inlet TC1	Outlet TC2	Bath TC3
90	1.2875	1.2875	1.2882
150	2.7165	2.7165	2.7166
200	3.9867	3.9867	3.9873

APPENDIX B

CALIBRATION OF PRESSURE GAUGES

The calibration of the 3000 psi Heise gauge used to indicate the calorimeter inlet pressure is given in Table VII. The calibration was performed by L. Yarborough in September, 1963. The calibration of the 60 psi Ashcroft gauge used to indicate the pressure of the calorimeter effluent is given in Table VIII. The calibration was performed in November, 1965. The gauges were calibrated against a Budenburg dead-weight pressure tester Model No. 280L, Serial No. 2167. The Budenburg dead-weight pressure tester has a maximum pressure of 2000 psi and was specified on July 11, 1961, as being accurate to 0.05 percent of the pressure measured up to the maximum pressure.

TABLE VII

HEISE GAUGE CALIBRATION

Budenburg Pressure, psig	Heise Gauge Reading*, psig
100	101
200	200
300	300
400	400
500	500
600	600
700	700
750	750
800	800
900	900
1000	1000
1100	1100
1200	1200
1100	1100
1000	1000
900	900
800	800
750	750
700	700
600	600
500	500
400	400
300	300
200	200
100	101

* Heise gauge adjusted to zero at atmospheric pressure before starting calibration

TABLE VIII

ASHCROFT GAUGE CALIBRATION

Budenburg Pressure, psig	Ashcroft Gauge Reading, psig
10	11
20	21
30	31
40	41
50	51
60	61
50	51
40	41
30	31
20	21
10	12

APPENDIX C

CALIBRATION OF SAMPLE COLLECTION SYSTEM

The sample collection system consisted of two glass bombs and an interconnecting glass manifold. The bomb volumes were calibrated by weighing the amount of water required to fill the bombs. A precise 50 kilogram analytical balance was available for use in weighing the water. Duplicate determinations of the bomb volumes agreed to within 0.013 percent or 0.5 ml.

The volume of the interconnecting manifold was determined by expanding air at 1 atmosphere from the manifold into an initially evacuated bomb and measuring the change in the manifold pressure. Using the ideal gas law and the known volume of the bomb, the manifold volume could be calculated. An absolute manometer sealed directly into the manifold was used to measure the pressures. Since the manometer was an integral part of the manifold, corrections were necessary to offset volume changes due to changes in the mercury level. The corrections were made by calculating the volume change from the estimated inside diameter of the manometer and the measured change in mercury level. The equation used to calculate the manifold volume is easily derived from PV = nRT. The derived equation is:

$$V_m = \frac{\left(V_b - V_c\right)\left(\frac{P_{m+b}}{P_m}\right)}{1 - \left(\frac{P_{m+b}}{P_m}\right)} \qquad (6)$$

where V_m = volume of manifold

V_b = volume of bomb

V_c = correction due to change in manometer mercury level

P_m = manifold pressure before expansion

P_{m+b} = manifold pressure after expansion.

The above procedure was duplicated four times (twice for each of the two bombs). The average value obtained for the manifold volume was 129.2 ml; the maximum discrepancy between any two of the determinations was 1.7 ml.

The total volume of the sample collection system was obtained by adding the average value for the volume of each of the component parts of the system. The value obtained was 7.9367 $\pm$0.0016 liters. The limits of error reported above were calculated by simple addition of the absolute value of the deviation from the average value calculated for each of the parts of the collection system.

APPENDIX D

STANDARD RESISTOR INFORMATION

TABLE IX

STANDARD RESISTOR INFORMATION

Leeds and Northrup Catalog No.	Serial No.	Resistance, ohms	Date Specified
4035-B-S	1605213	2000.06	July, 1962
4020-B	1598852	1.00001	Feb., 1962
4361	1588504	0.0100	July, 1962

APPENDIX E

COMPOSITION OF METHANE-PROPANE MIXTURE

TABLE X

COMPOSITION OF METHANE-PROPANE MIXTURE

Component	Mole Fraction	Analytical Accuracy
Methane	0.9390	± 0.005
Ethane	0.0027	0.001
Propane	0.0509	0.004
Carbon Dioxide	0.0020	0.0005
Oxygen	0.0001	-----
Nitrogen	0.0053	0.001
Isobutane	Trace	-----
	1.0000	

APPENDIX F

SAMPLE CALCULATIONS

A sample calculation of the experimental data is shown for Run No. 13. The raw data used in the calculation are given in Appendix H. As mentioned previously, the data calculations for the reported enthalpy values were carried out on an IBM 7040 computer and a listing of the Fortran program used in the calculations is given in Appendix G. The sample calculations shown here will be made in the same general order as used in the machine calculations.

Flow Rate

For flow rate determinations, the calorimeter effluent is diverted to a glass collection system for a measured time interval. From a knowledge of the initial and final collection system pressure, system temperature, and the calibrated volume of the system, the mass of gas collected is calculated. The gas law (PV = NZRT) is used to calculate the initial and final mass contained in the collection system. The difference between the two values gives the amount collected during the measured time interval. The mass collected and the flow time establish the flow rate.

The compressibility factor is calculated from the virial equation of state, truncated after the second term and utilizing experimental second virial coefficients (9, 18). Since the initial pressure is always less than 0.5 mm Hg, the compressibility factor is taken to be one in the calculation of the initial mass contained in the collection system. The mechanics of the calculation are shown below.

P_i = 0.250 mm Hg = 0.00032890 atm

P_f = 537.58 mm Hg = 0.70721 atm

T = 26.0°C = 299.16°K

R = 82.0567 ml atm/g-mol °K

$\overline{V}$ = 7936.7 ml

B_m = -52.1 ml/g-mol

t = 30.44 sec

The compressibility factor at the final pressure is given by

$$Z = 0.5 + \left(\frac{1}{4} + \frac{\overline{B}_m P_f}{RT}\right)^{0.5}$$

Therefore,

$$Z = 0.5 + \left[\frac{1}{4} + \frac{(-52.1)(0.70721)}{(82.0567)(299.16)}\right]^{0.5} = 0.5 + 0.49855 = 0.99855$$

$$N_f \text{ (final mass)} = \frac{P_f\overline{V}}{ZRT} = \frac{(0.70721)\ (7936.7)}{(0.99855)(82.0567)(299.16)} = 0.22899 \text{ g-mol}$$

$$N_i \text{ (initial mass)} = \frac{P_i\overline{V}}{RT} = \frac{(0.000329)(7936.7)}{(82.0567)(299.16)} = 0.0001067 \text{ g-mol}$$

Mass Collected = $N_f - N_i$ = 0.22899 - 0.00011 = 0.22888 g-mol

Flow Rate = (0.22888)(60)/(30.44) = 0.45116 g-mol/min

or 0.059710 lb-mol/hr

Molecular Weight = 17.6

Flow Rate = 1.0509 lb/hr

Heat Input

The energy dissipated by the calorimeter heater is determined by measuring the potential across standard resistors in a parallel-series circuit (see Figure 5). The total current flowing through the circuit is calculated from the potential drop, E01, across a 0.01 ohm standard resistor. The current flowing through the standard resistor leg of the parallel circuit is obtained from the potential drop, E1, across a 1.0 ohm standard resistor. From these values the current flowing through the heater is calculated. The power of the heater is obtained by combining the heater current and the potential drop across the heater. The potential across the heater is given by the current-resistance product of the standard resistor leg of the parallel circuit. The power input is converted to a mass basis by combining the heater power and the flow rate through the calorimeter. The direct result is the uncorrected enthalpy difference.

E01 = 14.316 mv

E1 = 6.2957 mv

Total current = E01/0.01 = 1431.6 ma

Current through parallel leg = E1/1.0 = 6.2957 ma

Current through heater = 1431.6-6.30 = 1425.3 ma

$$\text{Potential across heater} = \frac{(2001.0)(6.2957)}{1000} = 12.598 \text{ volt}$$

$$\text{Heater power} = \frac{(12.598)(1425.3)}{1000} = 17.959 \text{ watt}$$

$$= (17.959)(3.4130) = 61.295 \text{ Btu/hr}$$

Flow Rate = 1.0509 lb/hr

$$H_T^o - H_T^p = 61.275/1.0509 = 58.322 \text{ Btu/lb}$$

Temperature Correction

The desired temperature of Run No. 13 was 90°F. From the calibration for the inlet and outlet thermocouples, the thermocouple e.m.f. corresponding to 90°F is 1.2875 mv. The values obtained during the run were 1.2883 and 1.2824 mv for the inlet and outlet thermocouple readings, respectively. Thus, the inlet temperature was slightly high and the outlet temperature was too low. At the conditions of the run, the heat capacity of the inlet stream was 15.90 Btu/lb-mol °F and the heat capacity of the outlet stream was 10.96 Btu/lb-mol °F. The inlet temperature correction is

$$\begin{aligned} H_T^p - H_{90}^p &= (1.2883 - 1.2875)(43.50\text{°F/mv})(15.80) = 0.5498 \text{ Btu/lb-mol} \\ &= 0.03124 \text{ Btu/lb} \end{aligned}$$

The outlet temperature correction is given by

$$\begin{aligned} H_{90}^o - H_T^o &= (1.2875 - 1.2824)(43.50\text{°Fmv})(10.96) = 2.432 \text{ Btu/lb-mol} \\ &= 0.1382 \text{ Btu/lb} \end{aligned}$$

Pressure Correction

The purpose of the pressure correction is to adjust the enthalpy of the outlet stream from the calorimeter outlet pressure to zero pressure (ideal gas state). Thus, the desired quantity is $(H_{90}^* - H_{90}^o)$. The enthalpy difference is generated from the virial equation of state, truncated after the second term. The proper equations are given in Appendix J. The second virial coefficient at 90°F is -49.1 ml/g-mol and the temperature derivative of the virial coefficient is 0.405 ml/g-mol °K.

Barometric pressure = 733.3 mm Hg = 0.9649 atm

Outlet pressure = 39.0 psig = 3.6185 atm

$$V = \frac{RT}{2P} + \left[\left(\frac{RT}{2P}\right)^2 + \frac{B_m RT}{P}\right]^{\frac{1}{2}}$$

$$\frac{RT}{2P} = 3{,}462.0$$

$$\left(\frac{RT}{2P}\right)^2 = 11{,}985{,}582$$

$$\frac{BRT}{P} = -339{,}976$$

$$V = 3{,}462.0 + (11{,}985{,}582 - 339{,}976)^{\frac{1}{2}}$$

$$V = 6{,}874.6 \text{ ml/g-mol}$$

$$\Delta H = \frac{-RT}{V}\left[B_m - T\,\frac{dB_m}{dT}\right]$$

$$(H^{*}-H^{o})_{90} = \left[\frac{-(1.987)(549.6°R)}{6{,}874.6}\right]\left[-49.1 - 305.33(0.405)\right]$$

$$= -(0.15592)(-172.76) = 27.442 \text{ Btu/lb-mol} = 1.5592 \text{ Btu/lb}$$

Corrected Enthalpy Difference

$$(H^{*}-H^{p})_{90} = (H^{o}_{T}-H^{p}_{T}) + (H^{p}_{T}-H^{p}_{90}) + (H^{*}_{90}-H^{o}_{T}) + (H^{*}-H^{o})_{90}$$

$$= 58.322 + 0.031 + 0.138 + 1.559 \doteqdot 60.05 \text{ Btu/lb}$$

APPENDIX G

FORTRAN LISTING FOR EXPERIMENTAL DATA CALCULATIONS

```
C       DON DILLARD   CH E
C      EXPERIMENTAL  ENTHALPIES
  101 FORMAT(6F12.6)
  102 FORMAT(1X,I2,4X,F8.1,2X,F8.1,2X,E12.5,2X,E12.5,2X,E12.5,2X,E12.5,
     12X,E12.5,2X,E12.5,2X,E12.5)
  103 FORMAT(1X,3HRUN,5X,6HTEMP,F,6X,4HPSIA,6X,7HMOL/MIN,4X,12HEXPERIMEN
     1TAL,4X,9HTEMP CORR,5X,10HPRESS CORR,5X,5HTOTAL,7X,8HTOTAL/LB,5X,
     26HPERCOR//)
  104 FORMAT(1H1)
  105 FORMAT(50X,20HENTHALPY   BTU/LBMOL)
  106 FORMAT(4X,I2)
C      FLOW RATE CALCULATIONS
      WRITE(6,104)
      WRITE(6,105)
      WRITE(6,103)
    1 READ(5,106)RNO
      READ(5,101)TRUN,PIN
      READ(5,101) PI,PF,TB,BM,WTMOL,TIM
      FPF=PF/760.0
      FPI=PI/760.0
      FTB=TB+273.16
      R=82.0567
      A=7936.7
      X=4.0*BM*FPF/(R*FTB)
      Z=0.5+((1.0+X)**0.5)/2.0
      AMOLI=FPI*A/(R*FTB)
      AMOLF=FPF*A/(R*FTB*Z)
      FRM=(AMOLF-AMOLI)*60.0/TIM
C      CALCULATION OF EXPERIMENTAL ENTHALPIES
      READ(5,101)TC1,TC2,R1,R2,CPO,CP1
      AIT=R1/0.01
      AIH=AIT-R2
      VH=R2*2.001
      PH=VH*AIH/1000.0
      PH=PH*0.05688
      EDHM=-PH*453.59/FRM
C      TEMPERATURE CORRECTIONS
      READ(5,101)CTC1,CTC2,DEGMV
      TDHO=(TC2-CTC2)*CPO*DEGMV
      TDH1=(CTC1-TC1)*CP1*DEGMV
      TDHTM=TDHO+TDH1
C      PRESSURE CORRECTION
      READ(5,101)P,T,BM,DBM,BARPR
      DBM=1.8*DBM
      TK=(T+459.6)/1.8
      PA=P/14.697+BARPR/760.0
      X=R*TK/PA
      U=X*BM
      XB=X/2.0
      IF((XB**2)+U)10,11,11
   10 DELHM=-0.0
      DELHL=-0.0
      GO TO 200
   11 VOL=XB+((XB**2)+U)**0.5
      PDHTM=1.98719*TK*(BM-TK*DBM)/(0.555919*VOL)
C      RESULTS
      DELHC=PDHTM+TDHTM
      DELHM=EDHM+DELHC
        PERER=(ABS(PDHTM)+ABS(TDHTM))/ABS(DELHM)
      PERER=PERER*100.0
      DELHL=DELHM/WTMOL
  200 WRITE(6,102)RNO,TRUN,PIN,FRM,EDHM,TDHTM,PDHTM,DELHM,DELHL,PERER
      GO TO 1
      END
```

Input Data Form

RNO = run number

TRUN = run temperature, °F

PIN = run pressure, psia

PI = initial sample collection system pressure, mm Hg

PF = final sample collection system pressure, mm Hg

TB = sample collection system temperature, °C

BM = second virial coefficient, ml/g-mol

PBM = temperature derivative of BM, ml/g-mol °R

WTMOL = molecular weight

TIM = time, sec

TC1 = inlet thermocouple emf, mv

TC2 = outlet thermocouple emf, mv

R1 = E01, potential drop across 0.01 ohm standard resistor, mv

R2 = E1, potential drop across 1.0 ohm standard resistor, mv

CPO = heat capacity at calorimeter outlet conditions, Btu/lb-mol °F

CPI = heat capacity at calorimeter inlet conditions, Btu/lb-mol °F

CTC1 = emf of inlet thermocouple corresponding to the desired run temperature, mv

CTC2 = emf of outlet thermocouple corresponding to the desired run temperature, mv

DEGMV = degrees per millivolt for copper-constantan thermocouple, °F/mv

T = run temperature, °F

P = calorimeter outlet pressure, psig

BARPR = barometric pressure, mm Hg

APPENDIX H

EXPERIMENTAL DATA USED IN CALCULATIONS

TABLE XI

EXPERIMENTAL DATA USED IN CALCULATIONS

					Calorimeter P		Glass Bomb P				
Run No.	Inlet Temp mv	Outlet Temp mv	E01 mv	E1 mv	Inlet psig	Outlet psig	Initial mm Hg	Final mm Hg	Flow Time sec	Glass Bomb Temp °C	Bar. Press. mm Hg
					METHANE						
1	2.7111	2.7099	2.8010	1.2764	486	-8.9	0.010	645.79	161.70	27.0	738.0
2	2.7153	2.7088	11.385	5.1888	1986	-0.7	0.015	519.92	30.14	25.5	739.0
4	2.7090	2.7105	5.6148	2.5577	986	11.2	0.500	599.80	74.13	26.0	744.0
5	2.7156	2.7219	8.4942	3.8716	1486	24.4	0.400	518.72	41.58	26.0	746.0
					5.1 MOLE PERCENT PROPANE IN METHANE						
6	2.7105	2.7125	2.9750	1.3554	486	0.9	0.120	616.00	163.21	26.0	743.0
7	2.7147	2.7165	5.9938	2.7315	986	11.2	0.225	590.91	75.06	26.0	746.0
8	2.7139	2.7140	9.0459	4.1234	1486	24.0	0.350	539.59	44.74	25.0	750.0
9	2.7132	2.7104	11.690	5.3265	1986	35.0	0.250	496.55	30.22	25.0	740.0
10	1.2805	1.2811	3.2976	1.4489	486	1.9	0.100	645.90	165.00	27.0	737.0
11	1.2839	1.2868	6.9378	3.0496	986	12.8	0.175	606.91	73.50	26.0	796.0
12	1.2871	1.2888	10.755	4.7297	1486	21.5	0.140	566.00	44.12	26.0	748.5
13	1.2883	1.2824	14.316	6.2957	1986	39.0	0.250	537.48	30.44	26.0	733.3
14	3.9832	3.9909	3.0005	1.4090	486	8.9	0.150	664.85	189.00	26.0	747.0
15	3.9846	3.9876	5.7137	2.6813	986	9.9	0.150	635.95	87.70	25.0	748.0
16	3.9921	3.9957	7.6850	3.6084	1486	22.0	0.160	586.50	52.31	26.0	739.3
17	3.9914	3.9957	9.9476	4.6726	1986	34.0	0.160	519.60	34.14	26.5	729.8
18	3.9905	3.9932	2.8446	1.3360	486	10.3	0.150	678.40	189.93	25.5	742.5
19	3.9791	3.9730	4.9646	2.3303	986	30.0	0.250	648.30	88.32	25.0	738.7
20	3.9838	3.9893	5.0742	2.3824	986	29.5	0.250	648.30	88.32	25.0	738.7
21	3.9785	3.9855	9.9748	4.6848	1986	34.0	0.300	535.95	34.93	26.0	741.0
22	3.9828	3.9835	2.4525	1.1515	486	12.0	0.200	650.57	182.78	25.0	734.2
23	3.9843	3.9866	2.5012	1.1743	486	11.5	0.200	650.57	182.78	25.0	734.2
24	3.9865	3.9930	2.5599	1.2021	486	12.5	0.200	650.57	182.78	25.0	734.2
25	3.9905	3.9973	2.5985	1.2210	486	13.0	0.200	650.57	182.78	25.0	734.2

APPENDIX I

ESTIMATED MAXIMUM EXPERIMENTAL ERRORS

The experimental enthalpy difference was obtained by combining the results of several independent measurements and the resistances of three standard resistors. The maximum influence of uncertainties in these values on the uncorrected enthalpy difference, h_a, was calculated from the equation

$$\Delta h_a = \left(\frac{\partial h_a}{\partial x_1}\right)\Delta x_1 + \left(\frac{\partial h_a}{\partial x_2}\right)\Delta x_2 + \ldots + \left(\frac{\partial h_a}{\partial x_n}\right)\Delta x_n \qquad (7)$$

where the x_1's are the various quantities from which the uncorrected enthalpy difference was calculated. The delta quantities correspond to the uncertainties in the data, which are known with respect to estimated magnitude but not with respect to sign. The estimated uncertainties in the data are listed in Table XII.

The inlet and outlet calorimeter temperature and pressure do not enter into the calculation of the uncorrected enthalpy difference. The limits of error in these quantities were directly converted to limits of error in terms of enthalpy. The results of the error analysis is shown in Table XIII for 500 and 2000 psia. It is emphasized that this analysis does not include the effects of systematic errors, approach to steady state, or heat leak.

TABLE XII

ESTIMATE OF MAXIMUM EXPERIMENTAL ERRORS

Quantity or Instrument	Error
Potentiometer	Negligible
Standard Resistors	
0.01	0.04%
1.0	0.01%
2000	0.01%
Inlet, Outlet, and Bath Temperatures	0.1°F
Collection Bomb Temperature	1.0°C
Time	0.1 sec.
Inlet Pressure	2 psi
Outlet Pressure	1 psi
Collection System Pressure	0.2 mm Hg

TABLE XIII

ESTIMATED MAXIMUM EXPERIMENTAL ERRORS IN ENTHALPY DIFFERENCES

Quantity	Error, Btu/lb-mol	
	500 psia	2000 psia
Flow Rate	$0.0038\ h_a$	$0.0090\ h_a$
Power Input	$0.0016\ h_a$	$0.0007\ h_a$
Inlet Pressure	1.06	1.06
Outlet Pressure	0.53	0.53
Inlet Temperature	1.3	1.5
Outlet Temperature	1.3	1.3
Total	$\pm(0.0054h_a+4.2)$	$\pm(0.0097h_a+4.2)$

APPENDIX J

EQUATIONS OF STATE

The virial equation of state is a series in reciprocal volume

$$Z = \frac{PV}{RT} = 1+\frac{\bar{B}}{V}+\frac{\bar{C}}{V^2}+\ldots \tag{8}$$

In this work the equation was truncated after the second term and solved for V

$$V = \frac{RT}{2P} + \left[\left(\frac{RT}{2P}\right)^2 + \frac{\bar{B}RT}{P}\right]^{\frac{1}{2}} \tag{9}$$

When Equation (9) is applied to a mixture, the second virial coefficient is given by

$$B_m = \sum_{ij} Y_i Y_i \bar{B}_{ij} \tag{10}$$

For a binary mixture, Equation (10) reduces to

$$B_m = Y_1{}^2\bar{B}_{11}+2Y_1Y_2\bar{B}_{12}+Y_2{}^2\bar{B}_{22} \tag{11}$$

The form of the virial equation used for calculating enthalpy differences is

$$\Delta H = \frac{RT}{V}\left[\bar{B}-T\frac{d\bar{B}}{dT}\right] \tag{12}$$

In this work the temperature derivative of the second virial coefficient was evaluated graphically.

The Redlich-Kwong (27) equation of state is a two constant equation of the form

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \tag{13}$$

which can be rearranged to yield

$$Z = \frac{1}{1-J} - \frac{A^2}{B}\left(\frac{J}{1+J}\right) \tag{14}$$

where $a = 0.4278\ R^2 T_c{}^{2.5}/P_c$

$b = 0.00867\ RT_c/P_c$

$A^2 = a/R^2T^{2.5}$

$B = B/RT$

$J = BP/Z$

The equation can be applied to mixtures by using the arbitrary combining rules

$$\begin{aligned} A_m &= \sum_i Y_i A_i \\ B_m &= \sum_i Y_i B_i \end{aligned} \tag{15}$$

The form of the Redlich-Kwong equation used for calculating enthalpy differences is

$$\Delta H = -RT\left[\frac{3}{2}\,\frac{A^2}{B}\ \ln(1+J)\right] +Z-1 \tag{16}$$

The Benedict-Webb-Rubin (2) equation of state is an eight constant equation of the form

$$P = \frac{RT}{V} + \left(BRT-A-\frac{C'}{T^2}\right)/T^2+(bRT-a)/V^3 + \frac{a\alpha}{V^6} + (cT^2V^3)(1+\ /V^2)\exp(-\gamma/V^2) \tag{17}$$

where A, B, C', a, b, c, α, and γ are specific constants. The BWR can be applied to mixtures by using arbitrary combining rules:

$$\begin{aligned} B &= \Sigma Y_i B_i & a &= (\Sigma Y_i a_i{}^{\frac{1}{2}})^2 \\ A &= (\Sigma Y_i A_i{}^{\frac{1}{2}})^2 & c &= (\Sigma Y_i c_i{}^{\frac{1}{3}})^3 \\ C &= (\Sigma Y_i C_i'{}^{\frac{1}{2}})^2 & &= (\Sigma Y_i \alpha_i{}^{\frac{1}{3}})^3 \\ b &= (\Sigma Y_i b_i{}^{\frac{1}{3}})^3 & &= (\Sigma Y_i \gamma_i{}^{\frac{1}{2}})^2 \end{aligned} \tag{18}$$

The form of the equation used for calculating enthalpy differences is

$$\Delta H = (BRT-2A-4C'/T^2)/V + (2bRT-3a)/2V^2 + 6a\alpha/5V^5 + (c/V^2T^2)\left\{3\left[1-\exp(-\;/V^2)\right]/(\gamma/V^2) - 0.5\exp(-\gamma/V^2) + \gamma\exp(-\gamma/V^2)/V^2\right\}$$

The calculations for the enthalpy differences generated by the above equations of state were carried out on an IBM 7040 computer.

NOMENCLATURE

a,A = constants in empirical equations of state

b,B = constants in empirical equations of state

$\overline{B}$ = second virial coefficient

c,C$'$ = constants in empirical equations of state

$\overline{C}$ = third virial coefficient

C = mixture composition

E1 = emf across 1 ohm standard resistor

E01 = emf across 0.01 ohm standard resistor

h,H = enthalpy/unit mass

Δh = isothermal effect of pressure on enthalpy or difference between ideal gas state enthalpy and enthalpy at a finite pressure, $H_T^* - H_T^P$.

J = BP/Z for Redlich-Kwong equation of state

n,N = number of moles

P = pressure

Q = heat input

Q_{HRT} = energy input to calorimeter heater

Q_{HL} = heat leak

R = universal gas constant

T = temperature

$U^2/2g_c$ = kinetic energy due to velocity U

V = volume/mole

W_S = shaft work

Z = compressibility factor, PV/RT

α = constant in Benedict-Webb-Rubin equation of state

γ = constant in Benedict-Webb-Rubin equation of state

Ω = ohms

Subscripts

a = uncorrected

c = critical

H_L = heat leak

HTR = heater

i,j = components

m = mixture

P = pressure

T = temperature

Superscripts

o = calorimeter outlet pressure

p = calorimeter inlet pressure

$*$ = ideal gas state

VITA

Donald Dwayne Dillard

Candidate for the Degree of

Master of Science

Thesis: AN EXPERIMENTAL INVESTIGATION OF THE ISOTHERMAL EFFECT OF PRESSURE ON THE ENTHALPY OF THE METHANE-PROPANE SYSTEM

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Plainview, Texas, September 10, 1940, the son of John Wesley and Elma M. Dillard. Married Donna Jo Bolin in Gentry, Arkansas, June, 1960.

Education: Attended elementary school in Silverton, Texas and Gentry, Arkansas; graduated in 1959 from Gentry High School; received the Bachelor of Science degree in Chemical Engineering from the University of Arkansas, Fayetteville, in January, 1965; completed the requirements for the Master of Science degree in July, 1966.

Membership in Scholarly or Professional Societies: Tau Beta Pi, Pi Mu Epsilon, Omega Chi Epsilon, American Institute of Chemical Engineers.

Professional Experience: Employed as a Process Engineer by Continental Oil Company, Ponca City, Oklahoma, during the summers of 1964 and 1965.