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TITLE OF THESIS EXPERIMENTAL HEAT CAPACITIES OF CARBON DIOXIDE-METHANE MIXTURES AT ELEVATED PRESSURES, AND THE CORRELATION OF VOLUMETRIC AND THERMAL PROPERTIES

UNIVERSITY UNIVERSITY OF ALBERTA

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EXPERIMENTAL HEAT CAPACITIES OF CARBON DIOXIDE - METHANE MIXTURES AT ELEVATED PRESSURES AND THE CORRELATION OF VOLUMETRIC AND THERMAL PROPERTIES

BY

PRITHWI RAJ BISHNOI

A THESIS
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled EXPERIMENTAL HEAT CAPACITIES OF CARBON DIOXIDE-METHANE MIXTURES AT ELEVATED PRESSURES AND THE CORRELATION OF VOLUMETRIC AND THERMAL PROPERTIES submitted by PRITHWI RAJ BISHNOI in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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TO URMILA

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ABSTRACT

Accurate data on the thermal properties such as heat capacity and enthalpy are of great importance in process calculations and design. Such data are also useful in checking and improving the correlation procedures for the thermodynamic properties.

The various experimental methods for determining the thermal properties of gases were examined and the heat exchanger method of determining the heat capacity ratios was selected. Equipment was designed, fabricated, and assembled, in order to carry out the necessary experimental measurements.

The data on the ratios of heat capacity at a given pressure to the heat capacity at a low pressure (about 27 psia) were obtained for nitrogen at pressures up to 2250 psi and in a temperature range from 60° to 150°C. The results obtained agreed with the data available in the literature within the expected accuracies of about ± 0.5 percent for this work and the literature results. Data were also collected for two binary mixtures of carbon dioxide and methane containing 14.5 and 42.3 mole percent methane. The data were obtained in the temperature range from about 40° to 150°C and at pressures up to 2250 psi. The expected accuracies of the heat capacity ratios thus determined were better than ± 0.5 and ± 1 percent in the

regions removed from and close to the maxima respectively.

Various mathematical techniques for estimating the co-efficients of the Benedict-Webb-Rubin equation of state from only volumetric information were studied. These techniques were then extended for estimating the parameters by utilizing volumetric and heat capacity information, and the required computer programmes were developed.

An extensive evaluation of the various parameter sets obtained by different mathematical techniques was made, and their ability to predict the volumetric and heat capacity data of carbon dioxide, methane, and carbon dioxide-methane mixtures was compared. These comparisons were made in the region of pressures up to 5000 psi and temperatures between 40° and 200°C. The parameters estimated by the non-linear least squares method, choosing volume as a dependent variable, gave the best predictions of the compressibility factors and the heat capacities of the pure components. This was also true for the mixtures when the BWR combining rules were used. For correlating more than one property of a pure component, the non-linear least squares method of minimizing the sum of the weighted sum of relative error squares in volume and heat capacity was found to be superior to the use of the linear programming technique. For a given set of pure component coefficients, the P-V-T and heat capacities of mixtures were correlated better by using a mixing rule that provided an interaction term rather than the BWR mixing rules.

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I - INTRODUCTION

Thermodynamic data have long played an important role in process calculations and design. Until recently most of the information available for these calculations had been calculated from data obtained on the volumetric behavior of fluids. Such calculated values may have significant uncertainties because their determination normally requires evaluation of the density derivatives. In the past few years, however, a considerable effort has been made to develop sophisticated and more precise design procedures and methods for making process calculations. These methods, of course, are of limited importance if the data used in the calculations are not sufficiently reliable. The direct experimental determination of all the thermodynamic properties for every system, if not impossible, will surely be inconceivable from the point of view of required costs and human effort. Hence the development and improvement of methods for predicting these properties are highly desirable. The availability of accurate experimental thermodynamic data, at least on some systems, is essential for these efforts. A satisfactory representation of the thermodynamic properties of a system is one of the important steps of predictive methods. The representation by means of an equation of state has been found to be a very convenient and useful method. The information on various thermodynamic properties may be useful for the development of a suitable parameter estimation technique, so that more than one property could be represented satisfactorily by the same set of coefficients. Moreover the information on mixtures, if available, can be very useful in improving the methods of calculating mixture properties from the behavior of the pure components. As a result, in the past few years, an interest in the experimental determination of accurate thermodynamic data has been rejuvenated.

Thermal properties such as enthalpy and heat capacity belong to an important group of the thermodynamic properties. For a long time there has been considerable interest in experimental data on the thermal properties of fluids at elevated pressures and a relatively large number of data have been published for pure components. Reviews of the subject have been made by Partington and Shilling[1] and Masi,[2] and references to recent data are listed by Barieau,[3] Mage[4] and Yesavage et al.[5] and in the general thermodynamic reviews by Smith,[6] Smith et al.[7] and Caswell and Smith.[8]

With the possible exception of air, the amount of published experimental thermal data for mixtures is very meagre. Roebuck[9] was the first to publish data on the Joule-Thomson coefficients of the helium-air system. Some of the other earlier works include those of Sage and coworkers,[10,11,12,13] who determined Joule-Thomson coefficients of pure hydrocarbons and their mixtures. It is only recently that additional data on the thermal properties of fluid mixtures have been reported. A review of the more recent experimental work has been given by Yesavage et al.[5] Some of the more important determinations include the work carried out at the University of Michigan, Purdue University, the University of Oklahoma and Lehigh University. The programme at Purdue University concentrated on polar-nonpolar mixtures. The programme at the University of Michigan has dealt with mixtures involving fixed gases and saturated light hydrocarbons.[14] The benzene-propane system[15] has been studied at the University of Oklahoma and the nitrogen-trifluoromethane system has been investigated by Balaban[16] at Lehigh University.

Carbon dioxide is present in varying quantities in most natural gases and gas condensate well effluents, and there is a trend toward separation of these effluents into individual components. Vukalovich and Altunin have reported thermophysical properties of carbon dioxide.[17] Vukalovich and Gureev,[18] Vukalovich et al.,[19] Rivkin and Gukov,[20] and Altunin and Kuznetsov [21] have made extensive experimental determinations of the heat capacities of carbon dioxide over a wide range of temperatures and pressures. Thermal properties of methane have been studied by various workers.[22,23,24] Jones[25] has determined heat capacities of methane in the temperature range of -250°F to 50°F and pressures up to 2000 psi. Hujsak,[26] Colwell,[27] Sahgal et al.[28] and Wiener[29] have also reported experimental studies on the thermal properties of methane. Volumetric data of methane above room temperature are given by Douslin et al.[30] The volumetric behavior of carbon dioxide and its mixtures with methane have been studied by Reamer et al.[31] In addition, phase equilibria studies on the carbon dioxide-methane system in the liquid-vapour region have been reported by Donnelly and Katz[32] and others. However, the thermal properties of carbon dioxide-methane mixtures have not been reported in the literature.

With this background, work was undertaken to critically examine the various experimental methods of determining the thermal properties. The heat exchanger method of determining heat capacity ratios was selected because the measurements made in this method are simple and the data can be obtained, at least in principle, free of the usual calorimetry errors such as heat leak and Joule-Thomson effect. A suitable equipment facility was created for the experimental determinations by this method. The heat capacity ratio data on nitrogen were first collected and the performance of the equipment, developed in this work, was evaluated by comparing the results with those available in the literature. The data were then collected for the two binary mixtures of carbon dioxide and methane. The mixtures studied contained 14.49

and 42.30 mole percent methane and the data were obtained in the temperature range of about 40 to 150°C and at pressures up to 2250 psi.

The various mathematical techniques for estimating the coefficients of the Benedict-Webb-Rubin equation of state from only volumetric information were studied. These techniques were then extended for estimating the parameters by utilising the volumetric and heat capacity information, and the computer programmes required for parameter estimations were developed. An extensive comparison of the various parameter sets, obtained by different mathematical techniques, was also made for their ability to predict the volumetric and heat capacity data of carbon dioxide, methane, and carbon dioxide-methane mixtures.

II - DETERMINATION OF THERMAL PROPERTIES

The various experimental methods of determining thermal properties, such as enthalpy and heat capacity, have been reviewed by Partington and Shilling,[1] Masi,[2] Sturtevant,[33] Faulkner,[34] Barieau[3] and Yesavage et al.[5] In general, the experimental methods may be classified as indirect, direct or comparative. Indirect methods include the measurement of such phenomena as the velocity of sound,[35,36] resonance,[37,38] or self-sustained oscillation.[39] These methods were not considered further for this work because interpretation of the results requires additional data such as fluid densities. Direct and comparative methods have been widely used. Two basically different procedures are applied--constant volume calorimetry and flow calorimetry. In the former a known quantity of energy is added to a fixed amount of fluid, and the temperature rise is observed. In the latter a constant flow of fluid is passed through a calorimeter and the temperature and pressure changes are measured corresponding to different modes of operation involving energy transfer to or from the flowing fluid. Comparative methods are based on a knowledge of the heat capacity and/or the latent heat of a reference fluid. The fluid for which the properties are to be determined at an unknown set of conditions may itself be used as a reference fluid at the conditions where its properties are either known or can be estimated accurately.

Some of the direct and comparative methods used by various workers are discussed below.

A. Direct Methods

1. Constant Volume Calorimeters -

This type of calorimeter has frequently been used successfully for solids and liquids,[40] but rarely for fluids at elevated pressures. A major problem in constant volume calorimetry has been the determination of the heat capacity of the calorimeter itself since the energy input changes the temperature of the containing vessel as well as that of the fluid. Also, in obtaining the enthalpy values from constant volume heat capacity data volumetric data are also required.

2. Flow Calorimeters -

This type of calorimeter has been widely used for fluids at elevated pressures. At steady state, the heat capacity of the calorimeter does not affect the measurements of enthalpy changes, and the calorimeter may be designed to operate in a number of different modes, depending upon the type of enthalpy data desired.

The first law of thermodynamics, applied to a flow calorimeter with negligible potential and kinetic energy effects, is

$$(H_{T_2,P_2} - H_{T_1,P_1}) = \frac{\dot{Q} - \dot{W}}{F} \qquad \text{(II.1)}$$

where $\dot{Q}$ is the rate of heat transfer, $\dot{W}$ the rate of work input, and F the mass flow rate. Flow calorimeters are used to measure the isothermal change of enthalpy with pressure, the isenthalpic effect of pressure on temperature, the effect of composition on enthalpy at constant temperature and pressure and the isobaric effect of temperature on enthalpy.

a. The direct determination of the isothermal change of enthalpy with pressure.

The gas at a high pressure and temperature is passed through a suitable device so as to reduce its pressure and during this process energy is supplied to the gas to maintain the inlet temperature equal to the outlet temperature. The mass flow of the gas and the energy supplied are measured.

Collins and Keyes[41] obtained a very good approximation to an isothermal expansion by using the heater itself as the main obstruction in producing pressure drop.

Ishkin and Kaganer[42] used a valve to drop the pressure while measuring the isothermal Joule-Thomson coefficient for air and nitrogen.

Andersen[43] used an orifice in a flow calorimeter to induce the pressure drop in order to measure the isothermal enthalpy departures of air. Gilliland and Lukes[44] describe an apparatus for measuring the integral change of enthalpy with pressure at constant temperature. A capillary was used to produce the pressure drop and it also served as the electrical heater for maintaining constant temperature. Yarborough and Edmister[15] modified this type of calorimeter and obtained enthalpy data on mixtures.

Mather[45] recently developed a calorimeter which uses a capillary to induce the pressure drop, with an insulated heating wire coaxially inserted into the capillary. The input of electrical energy to the internal heater wire is adjusted to make the outlet temperature of the fluid equal to the inlet temperature and therefore the entire process is very nearly isothermal.

b. The direct determination of the Joule-Thomson Co-efficient, $(\partial T/\partial P)H$.

In 1853, Joule and Thomson[46] carried out experiments to study the free expansion of gases and to evaluate the co-efficient that bears their names. They used a porous plug to throttle the gas from a high pressure to a lower pressure in an adiabatic manner. Equation (II.1) becomes

$$H_{T2,P2} - H_{T1,P1} = 0$$

and the Joule-Thomson co-efficient, μ, may be determined by:

$$\mu \equiv (\partial T/\partial P)_H = \lim_{P_2 \to P_1} \left[\frac{T_2 - T_1}{P_2 - P_1} \right]_H \tag{II.2}$$

Since the original experiments, many workers have published results based on this method. Reamer et al[47] obtained Joule-Thomson co-efficients and isothermal enthalpy pressure derivatives of steam using radial flow in a porous alumina thimble. The authors emphasized that neither of the flow processes follows exactly an isenthalpic or isothermal path. Koeppe[48] used a valve to drop the pressure while measuring the integral Joule-Thomson effects. Johnston[49] designed a special valve for Joule-Thomson measurements. This design was later modified by Stockett and Wenzel[50] to make measurements for nitrogen-ethane mixtures.

In all the above mentioned experiments on the Joule-Thomson co-efficient, the only variables to be measured are the inlet and outlet temperatures and pressures. It has proven difficult to eliminate significant heat leaks because of the non-isothermal nature of the process. Kinetic energy effects may also be difficult to evaluate but they can be largely eliminated if the pressure drop is brought about through a porous plug.

c. Heat of mixing.

To measure the heat of mixing in a flow calorimeter, two pure fluids are mixed in a chamber, and energy is added or abstracted to equalize the outlet and inlet temperatures. The first law of thermodynamics applied to this type of calorimeter reduces to:

$$[H_M]_{T_2,P_2} - [X_A H_A - X_B H_B]_{T_1,P_1} = \frac{\dot{Q} - \dot{W}}{F} \qquad \text{(II.3)}$$

and the heat of mixing, H^E, is obtained after making corrections for the minor pressure and temperature differences between the inlet and outlet.

This type of flow calorimeter has been used in the past for measuring heats of mixing of liquids at essentially atmospheric pressure[51] but only recently for determining the enthalpy of gas mixtures at elevated pressures.[52,53]

d. Isobaric effect of temperature on enthalpy.

In this mode of operation the pressure drop is made as small as possible, and energy is added to the fluid to change its temperature. A small correction can be made for the small variation in pressure. For a calorimeter with electrical energy input, $\dot{W}$, and negligible heat leak, $\dot{Q}$, Equation (II.1) becomes

$$[H_{T_2} - H_{T_1}]_{P_1} = - \frac{\dot{W}}{F} - \int_{P_1}^{P_2} (\partial H/\partial P)_{T_2} dP \qquad \text{(II.4)}$$

Faulkner[34] designed a calorimeter which was capable of measuring heat capacity, C_p, of any gas mixture from -200 to 300°F and at pressures up to 2000 psia. Krase and Mackey[54] measured the heat capacity of nitrogen at pressures up to 800 atm in a calorimeter of a slightly different design.

In this calorimeter the fluid is passed through a coil in a heated liquid bath. The temperatures of the inlet and outlet gas together with the electrical energy added to the bath to maintain isothermal conditions allow the calculation of the heat capacity. Corrections are made for conduction along the flow lines and for energy added in stirring.

The measurements to be made in these experiments are mass flow rate, input energy rate, and the inlet and outlet temperatures and pressures.

B. Comparative Methods

1. Boil-off Method -

McCracken[55] describes a calorimeter in which enthalpy change is determined by passing the fluid through a coil which is submerged in liquid Freon. The amount of Freon evaporated and the rate of mass flow of the fluid are measured. Nelson and Holcomb[56] used this apparatus to determine enthalpies of a ternary mixture. Macriss[57] modified this type of calorimeter to obtain heat capacities of mono-methylamine at high temperatures and pressures.

2. Heat Exchanger Method -

The use of a heat exchanger for obtaining ratios of heat capacities was first proposed by Burnett,[58] in 1905, although he did not carry out any experiments. Callendar[59,60] and Romberg[61] used the proposed method to determine the specific heats of water. Workman,[62] in 1930, published a paper entitled "A New Method of Measuring the Variation of the Specific Heats (C_p) of Gases with Pressure". His final results[63] were published in 1931. He investigated gases such as oxygen, nitrogen and hydrogen over a temperature range from 26° to 60°C at pressures from 10 to 130 atmospheres and flow rates of 0.15 scfm (Standard Cubic Feet Per Minute). Balaban recently[16] used this method to take measurements on nitrogen in the temperature range from -20° to 60°C at pressures up to 2000 psi and on trifluoromethane from 22° to 60°C up to a pressure which gives a density 10 percent greater than the critical density. Measurements were also made on two mixtures of nitrogen and trifluoromethane. Jacobsen and Barieau[64] developed a double heat exchanger method to determine the heat capacity of a single-phase helium-nitrogen mixture in terms of the heat capacity of the pure components at the same conditions.

In Burnett's method, a heat exchanger (sometimes referred to as an interchanger) is used as the calorimeter. The high pressure gas at a given temperature is passed through the heat exchanger and the pressure of this stream is then dropped, outside the exchanger, to some lower value, at which the heat capacity of the gas is either known or can reliably be calculated. The temperature of this low pressure stream is adjusted to a suitable level by passing it through a heater. The low pressure gas is then passed through the calorimeter where it exchanges heat with the high pressure stream. The high and low pressure streams have the same mass flow rates. The first law of thermodynamics when applied to this calorimeter at steady state reduces to

$$H_1 - H_2 + H_3 - H_4 \pm \dot{Q}/F = 0 \qquad \text{(II.5)}$$

where H_i is the specific enthalpy of the fluid at the location i. Locations 1 and 3 refer to the inlet and locations 2 and 4 refer to the outlet of the high and low pressure streams respectively. $\dot{Q}$ is the rate of heat leak to or from the exchanger, and F is the mass flow rate of the fluid.

The only observations required when using this method are the inlet and outlet temperatures and pressures of the two streams. Quantities such as the mass flow rate or the energy transfer rate need not be measured accurately. Because of this simplicity of measurement, the heat exchanger method was examined further.

It is shown in Appendix D that if the pressure and temperature changes of the high and low pressure streams, passing through the exchanger are small enough so that μ, the Joule-Thomson co-efficient and C_p, the heat capacity, can be taken as constant, Equation (II.5) reduces to either (II.6) or (II.7) depending upon whether the high pressure gas is being cooled or heated.

$$\frac{C_p}{C_{p_o}} = \frac{|\Delta T_o|}{|\Delta T|} + \Phi(\mu, C_p, C_{p_o}, q) \qquad \text{(II.6)}$$

$$\frac{C_p}{C_{p_o}} = \frac{|\Delta T_o|}{|\Delta T|} - \Phi'(\mu, C_p, C_{p_o}, q) \qquad \text{(II.7)}$$

In these equations Φ and Φ' are functions of the properties shown within the parentheses and C_p and C_{p_o} are heat capacities of the high and low pressure streams. It is also shown in Appendix D that if the absolute temperature levels of the heat exchanger are not very much different for the two cases of heating and cooling the high pressure gas, the terms Φ and Φ' are of the same order of magnitude. This leads to the following interesting conclusions. If a series of experiments is conducted over a desired pressure range in order to obtain one set of data for heating the high pressure gas and another set for cooling it, two curves may be obtained by plotting $\Delta T_o/\Delta T$ versus pressure. The separation between these curves is related to Φ or Φ' both of which are dependent upon correction terms such as heat leak, Joule-Thomson effect of the gas due to pressure change in the exchanger, and the temperature measurement errors. The character as well as the position of the two curves can point out imperfections of the apparatus. For example, if the calorimeter is properly designed, the upper and the lower curves when extrapolated should pass symmetrically about unity at a pressure equal to that of the low pressure stream. A curve obtained by averaging the upper and the lower curves should give the dependence of C_p/C_{p_o} ratio on pressure at a constant temperature. The average curve when extrapolated to a pressure equal to that of the low pressure stream should pass through unity. Moreover, the C_p/C_{p_o} ratios thus obtained will be independent of the errors usually associated with calorimetry.

It can be seen from the above that the errors involved in determinations made by the heat exchanger method are not only evident from the nature and position of the two curves, but C_p/C_{p_o} ratios can be obtained which are independent of these errors. The validity of the data obtained may be immediately checked by extrapolating the average curve to a pressure equal to that of the low pressure stream. These features give the heat exchanger method a virtue which others seem to lack.

The absolute value of the heat capacity at a high pressure can be found if the heat capacity at the low pressure is known. The low pressure heat capacity can be calculated by applying a small correction to the zero pressure heat capacity. The zero pressure heat capacity for a simple molecule can be calculated from statistical thermodynamics with an accuracy equal to or better than the measured values.[2] The low pressure heat capacity can then be calculated from the zero pressure heat capacity by using a suitable equation of state for the fluid.

To construct enthalpy charts from the heat capacities obtained at elevated pressures, $(\partial H/\partial P)_T$ over the pressure range of interest for one isotherm has to be obtained by some other independent method. This is a limitation of heat capacity data for constructing enthalpy charts for any system.

In view of the above, it was decided to use the heat exchanger method to determine the heat capacity of nitrogen and methane-carbon dioxide mixtures at elevated pressures.

III - THE EXPERIMENTAL APPARATUS

A schematic representation of the apparatus designed and used for the heat capacity measurements is given in Figure (III.3). In general the equipment consisted of the following parts:

A. The calorimeter and its associated units and instruments

B. The auxiliary equipment such as heaters, control valves, flow measuring device, buffer tanks, and compressor.

This chapter deals with the important design considerations and specifications for the various components and the descriptions of the calorimeter and the total equipment used for the heat capacity determination.

A. Calorimeter Design Considerations

There are four broad aspects to the design of the calorimeter:

1. The measurement of pressures and temperatures
2. The provision of area for heat exchange between the two streams
3. The minimization of calorimetry errors
4. The simplicity of fabrication and operation of the calorimeter.

1. Measurements of Pressures and Temperatures -

a. Pressure measurement.

The pressure sensing elements for a stream can be located outside the calorimeter if the pressure drop between the points of pressure and temperature measurements is negligible. The pressures of the high and low pressure streams of the calorimeter were measured by two Heise gauges having the ranges from 0 to 3000 and from 0 to 100 psig respectively. The inlet and outlet pressures of each stream were measured by the same gauge using suitable valve arrangements. Both the gauges were calibrated against a Ruska dead weight gauge and had an accuracy at least equal to the resolution of each gauge. The resolutions on the low and high pressure gauges were 0.1 and 2 psi respectively.

b. Temperature measurement.

Perhaps the most important single consideration in designing the calorimeter was in the selection of the temperature measuring device. The temperatures of the gas streams in the calorimeter were measured by quartz crystal thermometers.

The operation of quartz thermometer is based on the temperature sensitivity of a Quartz Piezo-Electric resonator. The resonator is a precisely ground disc of quartz crystal approximately 0.18 mm thick by 6.3 mm in diameter. The resonator is sealed into a cold-welded copper case containing helium at a standard temperature and pressure. The sealed resonator assembly is normally enclosed in type 304 stainless steel to protect the copper case and leads from corrosion.

A small diameter, Teflon-insulated, coaxial cable is used to connect the sensor to an electronic solid state oscillator. The oscillator supplies a small amount of power to the resonator which acts as a highly selective filter that holds the frequency of oscillation very close to the natural frequency of the resonator. A special linear co-efficient angle of cut is used in the quartz thermometer sensor crystal. This exhibits a very linear, yet sensitive, correspondence between resonant frequency and temperature. The resonator frequency is 28208 kHz at 0°C and varies by 1000 Hz (nominal) per degree centigrade. Thus a quartz crystal sensor, unlike other thermometers, indicates temperature by a proportional change in frequency rather than a change in resistance, dimensions, or voltage generation. Two basic advantages are obtained by this method of sensing; (1) the temperature indication is almost completely immune to changes in connecting wire resistance, eliminating the need for a four wire lead system, and (2) the digital method of reading frequency eliminates the problems of calibration usually associated with analog instruments such as DC amplifiers and voltmeter. The quartz thermometers were supplied by the Hewlett-Packard (HP) Company.

The temperature range of quartz thermometers is from -80° to $+250^{\circ}C$. The HP - 2801A quartz thermometers together with the HP - 2850 temperature sensors are calibrated at the factory to within $0.02^{\circ}C$ absolute accuracy, using techniques directly traceable to the U.S. National Bureau of Standards. Since the sensitivity (temperature versus frequency slope) of the sensor crystal is a function of the angle of cut, it is not subject to change with time. Therefore, only a one-point field calibration is necessary and a conventional ice-bath is completely adequate for this purpose. The response of a quartz thermometer is considerably more linear than that of a platinum resistance thermometer, normally about ± 0.05 percent of the range compared with a typical figure of 0.55 percent. In addition the quartz thermometer offers very high sensitivity which is $0.0003^{\circ}C$ for absolute measurement, and $0.0001^{\circ}C$ for differential measurements.

The performance characteristics such as measurement repeatability, long-term stability, speed of response, self-heating, probe interchangeability, etc. of quartz thermometers are equal to or better than platinum resistance thermometers, thermistors or thermocouples. The excellent sensing characteristics of the quartz thermometers are supplemented by the advantages of direct digital readout, immunity to noise and cable resistance effects, no reference junction, and good interchangeability between sensing probes. There are, however, two practical problems which arise when using them for this work. The first and more serious is that the smallest available probe which could withstand 3000 psia pressure was about 3-1/4 in. long with a 1/4 in. pipe thread connection. It would be very difficult to design a housing for a probe having these dimensions so that the actual temperature of the gas flowing past the probe was the same as the indicated temperature. The second problem was associated with the coaxial cables used to connect the sensor to the thermometer. It would be very difficult to seal this type of cable into a vacuum or pressure chamber since the usual compression fittings could not be used.

The problem of probe housing was solved in the following manner. It was first considered in detail whether a long probe with plain ends (HP - 2850 D model) or a short probe with 1/4 in. pipe threat connection (HP - 2850 B model) should be used. The housings for the long probes were found to be very bulky and hence for small heat losses the short probes were selected. The frequent removal of the probes may damage the pipe threads. Hence the design of the probe housing had to be such that it would be possible to remove the probes without undoing the pipe threads. It was decided to put a 1 in. long and 3/4 in. o.d. sleeve on these threads and hold this sleeve inside a housing by means of a 'Swagelok' fitting. The chamber was made from a 3/4 in. tube male connector.

The inlet and outlet tubing to this chamber were so located that the gas always entered at the end closer to the sensor resonator of the probe. The details of this arrangement are shown in the calorimeter drawing given in Appendix A. The heat flow by conduction through the cables was minimized by cutting and removing the armoured cable which encloses the Teflon-insulated coaxial cable. The arrangement made for reducing the heat losses by radiation from the two inlet probe housings and the hexagonal probe ends are discussed later. In order to solve the problem of passing the coaxial cables through a vacuum chamber wall, the cables were cut and special bulk-head connectors were used.

2. Provision of Area for Heat Exchange Between the Two Streams -

An ideal calorimeter is one which has sufficient area for heat exchange, zero pressure drop of the flowing streams, zero surface exposed to the surroundings, zero mass and is perfectly adiabatic. All these requirements of an ideal calorimeter are interrelated and are only approached in practice at the expense of each other. Hence no calorimeter, designed and made in practice, can be ideal.

For a given heat load the area required depends upon the rate at which heat can be transferred from one fluid stream to the other. The rate of heat transfer depends upon the flow conditions and properties of the fluids involved, the properties of the material used in the provision of the area, and the temperature difference between the heat exchanging fluids. It was decided to make a calorimeter which could be used for hydrocarbons, inert gases and the corrosive gases like hydrogen sulphide. Hence all the parts of the exchanger which come in contact with the working fluid were made of type 316 stainless steel. Since in this method the mean heat capacity over a temperature range is measured, it was decided to limit the temperature change of each stream to about 5°C.

For any given geometry of the heat exchange area, the larger the mass flow rate, the higher is the pressure drop. Higher pressure drops cause undesirably large Joule-Thomson effects. If the flow rate is small the ratio of heat leak to the heat exchanged is large. A pressure drop of up to 2 psi for each stream was considered acceptable and a mass flow rate of about 2.5 scfm (Standard Cubic Feet Per Minute) was selected as a basis for design.

The exchanger can be designed to operate either co-currently or counter-currently. Counter-current exchange of heat is more efficient than co-current. However, if an exchanger is designed so that the temperature of the two outgoing streams are of the same order of magnitude, the calorimeter can be divided into three temperature zones namely two inlet temperatures and one average outlet temperature. Heat losses are easier to control with this kind of temperature arrangement because a surface can be defined which has an average temperature of the two outgoing streams. Under this temperature distribution the co-current exchanger is simpler to fabricate and easier to operate over a wide range of inlet temperatures. Hence, the co-current mode of heat exchange was selected to design the calorimeter.

Various schemes of physically providing the heat exchange area were considered. For simplicity of fabrication it was finally decided to use a 1/4 in. o.d. (outer diameter) high pressure tube inside a 1/2 in. o.d. low pressure tube. These concentric tubes were coiled to provide the required heat exchange area. For a rate of about 2.5 scfm both the high and low pressure streams would flow in the turbulent regime.

3. Heat Leak from the Calorimeter Body -

Heat can leak from the calorimeter to the surroundings by any or all of the following modes:

a. Heat loss by conduction

b. Heat loss by convection from the surface of the exchanger

c. Heat exchange by radiation between the surface of the calorimeter and the surroundings.

Heat leak by conduction is dependent upon the temperature gradient, (dT/dX), at the physical boundaries of the calorimeter, which connect it to the outside world, and the conduction area.

The main points of contact are the four temperature probe housings, the thermocouple wires leading out of the calorimeter and the four temperature probe cables. The reduction of heat loss by conduction through the probe cables is discussed elsewhere. The conduction through the gas carrying tubes was reduced by selecting tubes of a minimum possible wall thickness. The high pressure tube is 1/4 in. o.d. and has a wall thickness of 0.028 in. The low pressure tube is 1/2 in. o.d. and has a wall thickness of 0.022 in. The temperature gradient (dT/dX) at a probe housing was minimized by providing isothermal wall conditions over a considerable length of the connecting tubes upstream and downstream from the housings.

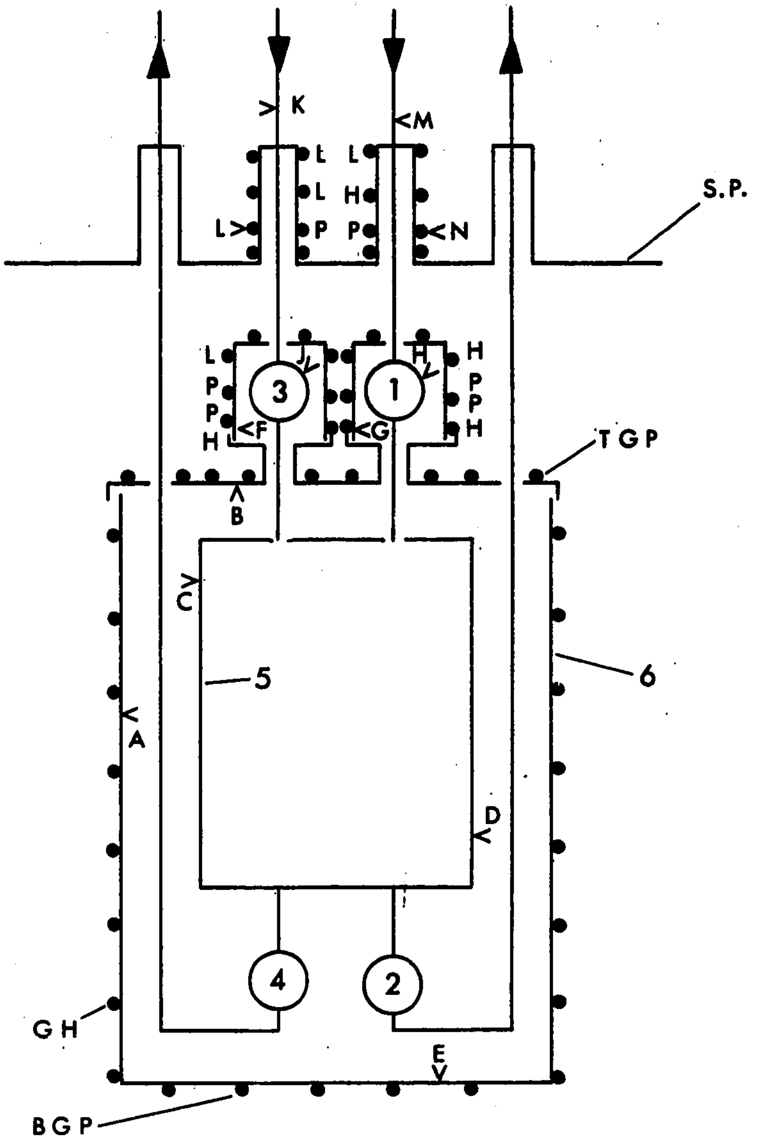
Convection losses were reduced by enclosing the calorimeter in a vacuum chamber. The heat exchange by radiation was minimized by enclosing the surface inside a copper 'guard' which was electrically heated and maintained at a temperature equal to that of the surface. Three such 'guards' were provided, one for each of the two inlet temperature probe housings and one for the main body of the calorimeter.

Description of the Calorimeter and Its Modifications

A schematic diagram of the calorimeter is given in

Figure (III.1) and a detailed drawing is attached in Appendix A. Each inlet line of the exchanger enters through a steel cylinder about 6 in. long and 1 in. in diameter welded to the supporting plate of the calorimeter and goes to the inlet temperature probe housing. The distance between the probe housing and the point where the tube is welded to the supporting cylinder is about 9 in. This distance is provided to take care of the conduction from the probe housing to the support point. The 1/2 in. and 1/4 in. tubes coming out of the probe housings are brought down for about 8 in., separated from each other. In order that these tubes do not exchange any heat with their surroundings, they are covered with several layers of aluminum foil shields. The 1/4 in. tube now enters the 1/2 in. tube. The concentric tubes are then coiled upwards in a coil of about 5 in. helical diameter and 9-1/2 turns. The last turn of this coil is brought out and the direction of coiling is reversed. The tubes are now coiled downwards in a coil of about 7 in. diameter and 2 turns. At the end of this coil the 1/4 in. tube is brought out of the 1/2 in. tube. These tubes then go to their respective outlet temperature probe housings located at the bottom part of the calorimeter. The outlet tubes of these housings are brought up from the bottom, through the cylinders welded at the supporting plate.

The outer coil of the calorimeter is covered with a



1,2,3,4	Probe Housings
5	Calorimeter Surface
6	Main Guard
S.P	Support Plate

Figure III . 1 . Schematic Representation of the Calorimeter.

0.031 in. thick copper sheet brazed on the coil. The surface of the calorimeter is defined by brazing a copper disc (thickness 0.031 in.) onto the 1/4 in. and 1/2 in. tubes just before they enter the outlet housings. The sides and top of the surface are made of a 0.022 in. thick copper hollow cylinder brazed onto the bottom disc. The surface thus defined does not physically touch any other part of the calorimeter but only the two points mentioned above.

In this arrangement, the high and low pressure streams do not exchange heat till they come to the inner coil. By the time the streams come out of the inner coil their temperatures are almost equal. Further exchange of heat might take place in the outer coil. The copper sheet brazed over the second coil works as a thermal radiation shield and it smooths out the temperature of the exterior of the exchanger. The temperatures of the two streams when they come out of the outer coil are almost equal. As a result the surface of the calorimeter as defined above reaches a temperature which is very close to that of the two outgoing streams and is most likely equal to their arithmetic average. Thus it is possible to divide the calorimeter into three temperature zones for controlling the radiation losses.

The heat flow by conduction through the outlet probe housings is negligible because the tube walls up and down these housings are almost at a uniform temperature, at least over some length, and moreover, they are enclosed in an environment which is maintained at their average temperature.

The calorimeter surface and the outlet probe housings are enclosed in a can made of 0.031 in. thick copper. The top plate of this can is not brazed but left loose so that it can be moved up and down the tubes. This can, including the top plate, is called hereafter the "main guard". The two inlet probe housings are enclosed in two separate chambers made of copper. These chambers rest on the bases provided over the top plate of the main guard. These chambers are named "probe housing guards".

Thermocouples are installed at various locations shown in Figure (III.1) so that the temperatures or the temperature differences can be read and maintained at desired levels by suitable controls as described below.

The differential temperatures indicated by the thermocouple junction pairs of K and L, M and N, F and J, G and H and B and C are maintained zero by manually adjusting the electrical power inputs to their respective heaters. The power inputs are regulated using "variacs". In practice these regulations are found to be quite easy since once a proper setting of the "variac" is found for any run further adjustments required are minor. The differential millivoltages of these pairs are read on a millivolt potentiometer through a selection switch. During a 'steady state reading' of an experiment the differential reading of the pair B and C is maintained within ± 0.005 mv and the other pairs are held within ± 0.02 mv from zero.

The differential temperature of the calorimeter surface (D) and the main guard (A) is controlled by a single feed back control loop. The differential millivolt reading is scaled by about 100,000 times in a Honeywell combination precision set point unit and deviation amplifier. The magnified signal is fed to a Foxboro controller, which drives a silicon crystal rectifier (SCR) laboratory made power regulator which adjusts the power input to the main guard resistance heaters GH and BGP. The difference signal under a controlled state is smaller than the resolution of the millivolt potentiometer mentioned above (i.e. about $0.1^{\circ}F$ or better).

The evolution of the calorimeter to the present final form used for the C_p measurements on the carbon dioxide-methane system took place as follows:

(1) The first trial run with nitrogen gas was made at $38.5^{\circ}C$. At this stage GH was the only heater that existed for preventing heat losses from the calorimeter to the outside world. The separation between the two curves (plot of $\Delta T_o/\Delta T$ vs. pressure for the two cases, one of heating and the other for cooling the high pressure gas), which can be taken

as an indication of the heat losses from the calorimeter, was approximately ± 4.5 percent. This was considered satisfactory when compared with the performance of similar calorimeters reported in the literature.

(2) Following these initial tests an attempt was made to obtain similar data at about 75°C. It was observed that the heat loss from the calorimeter was considerable. Hence the heaters LPPH and HPPH on the guards of the inlet temperature probe housings for the two streams were installed. The power input to these heaters could be adjusted so that the surface temperature of the probe housing was equal to its guard temperature. At this stage the only heaters in use were GH, LPPH, and HPPH. The heat losses of the calorimeter did reduce by approximately 2 percent but the performance was not considered satisfactory. It was then postulated that there might be heat loss due to conduction through the inlet tubes to the supporting plate of the calorimeter. To reduce this conduction loss the heaters LHP and LLP were installed. The power input to these heaters could be adjusted so that the surface temperature of the supporting cylinder was maintained equal to the surface temperature of the inlet tubes. There was a further reduction in the heat losses by about 1 percent when the experiment was carried out with the LHP, LLP, LPPH, HPPH and GH heaters in use.

(3) An experiment was then carried out at about 150°C.

The data obtained are shown in Figure (III.2). It can be seen that the separation between the two curves is about ± 18 percent, which indicates a heat loss of about 16.4 percent of the total heat exchanged in the calorimeter. This is a very high heat loss and the various possible methods of heat loss were analysed. It was postulated that the main loss of heat was due to the radiation from the calorimeter surface. The thermocouple reading on the top guard plate indicated that its temperature was about 10°F lower than the average calorimeter surface temperature. Hence the heater TGP was installed so that power input to this heater could be adjusted to maintain the top guard plate temperature, B, equal to the calorimeter surface temperature, C. A thermocouple E was installed at the bottom plate of the guard.

The experiment was repeated at about 150°C. The results of this experiment are also shown on Figure (III.2). The separation between these two curves was reduced to about ± 8 percent thereby indicating a heat loss of about 7.3 percent of the total heat exchanged.

During the above experiment it was observed that thermocouple E was reading about 10°F lower than the surface temperature of the calorimeter. It was therefore decided to extend the heater GH to the bottom of the guard by installing a heater BGP and coupling it with GH. The experiment at 150°C was again repeated. The results of this experiment are

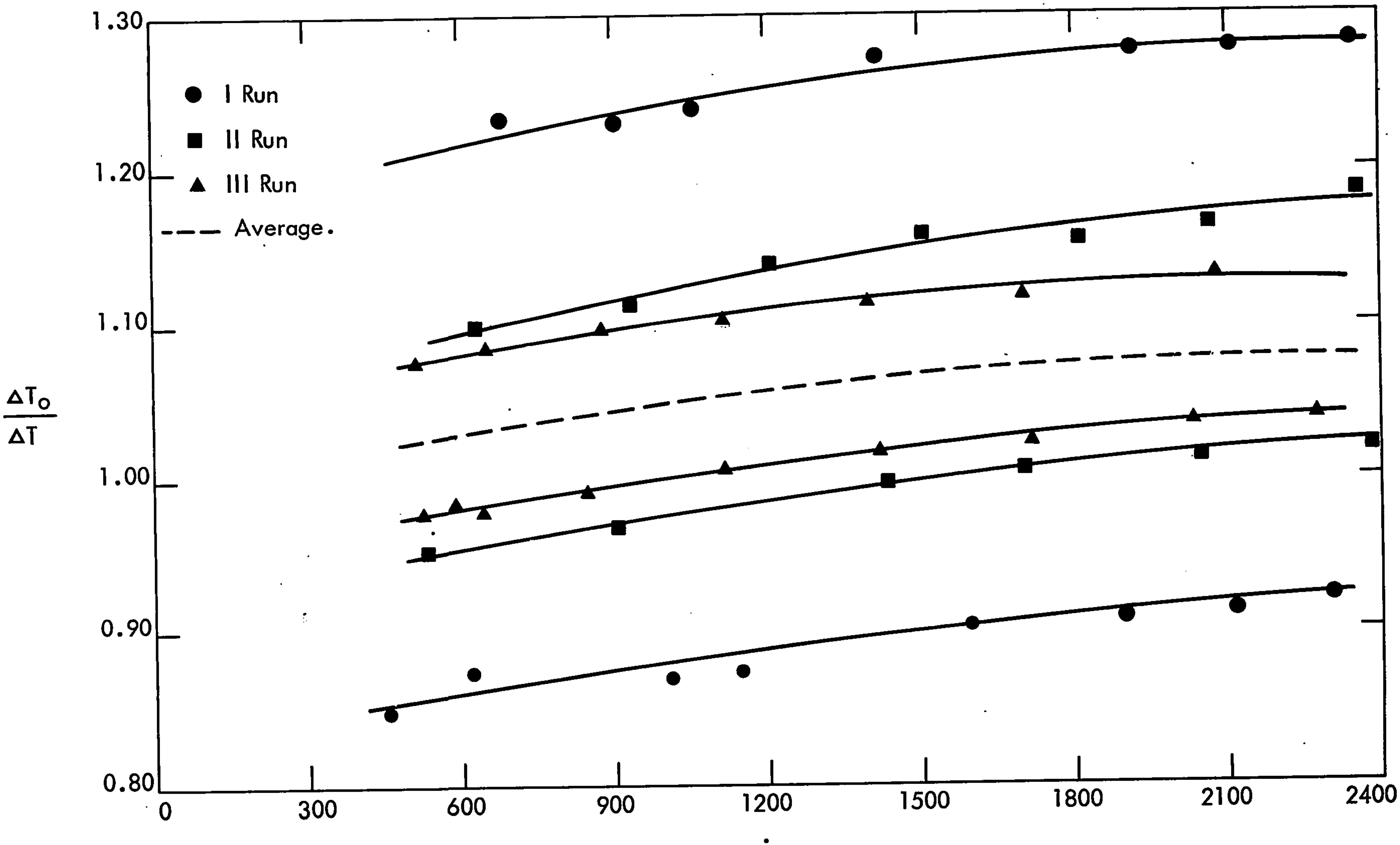


Figure III.2. Trial Runs with nitrogen at 150°C.

also shown on Figure (III.2). The temperature E during this experiment was about 2^{o}F lower than the surface temperature of the calorimeter. Under these conditions the temperatures B and C and A and D are maintained equal. It can be seen that the separation between the two curves is only about ± 5 percent indicating a heat loss of about about 4.65 percent of the total heat exchanged in the calorimeter. This heat leak compares with that at lower temperatures and was considered acceptable.

B. Auxiliary Equipment

1. Gas Heaters and Temperature Control -

It is desired to heat about 2.5 scfm of a flowing gas from a room temperature of about 21^{o}C to temperatures up to 200^{o}C and to achieve a stability of about ± 0.01^{o}C over a period of at least half an hour.

The high pressure gas heater was made from a 3/8 in. stainless steel type 316 tube with 1/4 in. inside diameter. A coil was made from this tube with an outside coil diameter of 4.25 in., a pitch of about 21/32 in. and with 16-1/2 turns. The coil was then forced inside a copper pipe of 4-1/2 in. o.d., 1/8 in. wall thickness, and approximately 11 in. long. Care was taken to make sure that all the turns of the coil were snugly fitted against the inside wall of the copper pipe. For better thermal contact a few turns from the bottom and top were brazed to the pipe wall.

Seven "Chromolox" strip heaters, each 10-1/2 in. long and having a resistance of about 151 ohms, were clamped, equally spaced, on the outer circumference of the copper pipe. The seven strips were connected in parallel to give an equivalent resistance of 21.6 ohms. The heater thus made was enclosed in a box insulated with asbestos. The low pressure gas heater was made exactly to the same specifications except that the coil was made of 1/2 in. tube (wall thickness 0.0355 in.) with a pitch of 13/16 in. and 13-1/2 turns.

The high and low pressure gas stream temperatures were controlled in an identical manner. The temperature control loop consisted of an iron-constantan thermocouple, a controller, a silicon crystal rectifier (SCR) power controller and the heater element. The controller had all the three modes of control--gain, reset-time, and derivative.

In the initial stages, during the trial runs, the thermocouple was located in the gas stream close to the inlet of the calorimeter. The temperature control was very poor. It appeared that the heater action and the thermocouple reading were completely out of phase. It was then decided to braze the thermocouple onto the inside surface of the copper pipe which housed the coiled tubes carrying the gas. The control capability was also improved by reducing the sensitivity of the SCR unit. Its input voltage was reduced from 208 volts to 110 volts A.C. A further improvement in the control capability was effected by replacing the integral time constant potentiometer in the controller circuit with a higher resistance potentiometer. This enabled the controller to work on gain plus the integral action.

With the above improvements it was possible to control the inlet gas temperatures to the calorimeter with a difference between the maximum and the minimum temperature of not more than 0.03°C over a period of about half an hour. The duration for which this control could be maintained depended sometimes on the stability of the flow conditions in the material circulation loop.

2. Control Valves and Pressure Control -

It was necessary to control the pressures of both streams entering the calorimeter. For flexibility, the low pressure control scheme should be such that it could maintain the pressure anywhere in the range of 10 to 50 psig. The high pressure control scheme was required to maintain any pressure up to about 3000 psig. Both the schemes should also be able to handle flow rates ranging from 1 to 3 scfm for different gases such as methane, nitrogen, carbon-dioxide or their mixtures. The pressure of the high pressure stream had to be reduced to about 10 psig. For any experiment, the flow rate through this pressure reducing mechanism remained constant, but for flexibility it should be possible to handle different flow rates in the range mentioned above.

Figure (III.3) gives the flow diagram of the equipment used and it shows the location of HPCV, the high pressure control valve JTCV, the pressure reducing control valve and BPCV, the by-pass control valve. These valves were sized by the standard method of C_v (valve flow co-efficient) calculations. The valves used are:

<u>HPCV</u> - Annin valve model 9460, trim size 0.02, air-to-close, can handle fluids from -400° to $750^\circ F$

<u>JTCV</u> - Annin valve model 9460, trim size 0.003, air-to-open, can handle fluids from -400° to $750^\circ F$

<u>BPCV</u> - Annin valve model 5061 "Wee-Willie", trim size "A"--C_v range 0.0001 to 0.01, field reversible, can handle fluids from -20° to $465^\circ F$.

The valves have pneumatic positioners and stainless steel type 316 bodies.

A single feed back control loop was considered to control the inlet high pressure of the calorimeter. The control capability of this scheme depends on the capacity (volume) and resistance of the system. The system can be considered to consist of the HPCV valve, the line from this valve to the JTCV valve through the calorimeter and the electric heater, and the JTCV valve. The flow through the

JTCV valve is always sonic. For the purpose of preliminary analysis, the system can be considered as a capacitance and a sonic flow restriction. The capacity can be taken equal to the volume enclosed in a 1/4 in. i.d. tube about 50 ft. long. This makes the 'controlled process' a first order system. The pressure measuring device and the control valve can be treated as first and second order systems respectively. This kind of analysis indicated that a controller with a proportional constant and integral constant should be able to give stable control.

Similar considerations for the low pressure control scheme also indicated that a single feed back control loop having a controller with a proportional constant and an integral constant should be satisfactory.

Foxboro controllers with built-in power supply were used for the high and low pressure controls. High and low pressures were measured, at the locations shown in the diagram, by Foxboro pressure transmitters model 611 GH and 611 GM respectively. The outputs from these transmitters were used for the respective control loops. A rough indication was given on a milliameter and a precise read-out was given on a digital voltmeter.

The current to pressure converters used in the pressure control loops are Fisher type 546 electro-pneumatic transducers.

In the initial stages of this work the inlet low pressure of the calorimeter was controlled by means of the valve JTCV. The control was achieved by the variations of mass flow rate across the valve caused by its control action. As a result, the mass flow rates on the high and low pressure sides of the calorimeter could be different at least for short periods. Since this violated the fundamental requirement of equal mass flow rates on the high and low pressure sides of the calorimeter, it was decided to control the low pressure by means of the by-pass valve BPCV as shown in Figure (III.3). The resistance of the valve JTCV was adjusted to give the desired flow rate by manually setting a potentiometer which supplied a current signal to the current-to-pressure converter, giving an air pressure signal to the valve positioner. Since the upstream pressure of JTCV and its resistance remained constant and the flow through the valve was sonic or super-sonic, this scheme guaranteed the same constant mass flow on the high and low pressure sides of the calorimeter. The pressure control by this scheme was such that if there were any pressure fluctuations, they would be so small that they could not be seen on the Heise gauge used for their measurement.

3. Flow Measurement -

A quadrant-edged orifice was used for metering the gas flow. The orifice had a diameter of 0.16 in. and it was located in a 1/2 in. tube with an inside diameter of 0.429 in. The pressure drop across the orifice was measured by a Foxboro d/p cell transmitter type 613 DM. The output signal of this transmitter was displayed on a milliammeter and on the digital voltmeter which was used for the high and low pressures of the calorimeter. The flow meter was calibrated using air in a wet gas meter at approximately atmospheric pressure. This was sufficiently accurate because the flow rates were not required for any of the calculations for C_p.

4. Buffer Tanks -

Two high pressure cylindrical vessels were used as dampers for the high pressure gas delivered by the compressor. A hand valve was also installed in the line connecting these tanks. The capacities of the tanks and the variable resistance of the valve stabilized the pressure of the fluid before it reached the high pressure control valve. Each tank was made from 3 feet of 4 in. seamless steel pipe (schedule 160) and standard welding caps. They were tested for a hydraulic pressure of 4500 psi. The volume of each tank was about 0.193 cubic feet.

Only one tank was used at the inlet of the compressor. The tank was made from 6 feet of 8 in. seamless steel pipe (schedule 40) and standard welding caps. The tank had an approximate capacity of 2.09 cubic feet and it was hydraulically tested for 1500 psi.

5. Material Recirculation Device -

A two stage diaphragm compressor was used to develop the necessary pressure and to circulate the gases. It was a Corblin A2CV250 which was rated for a discharge pressure of up to 3700 psi with a flow capacity of 3.5 scfm at a suction pressure of 14.7 psia. The inlet and delivery line of the compressor were connected to the surge tanks by means of flexible pipes.

Description of the Flow-sheet

A flow sheet of the experimental apparatus is given in Figure (III.3). The gas delivered by the compressor goes to the high pressure surge tanks, one of which is connected to the low pressure surge tank through the by-pass control valve BPCV. The gas leaving the surge tanks goes to the high pressure gas heater through a hand valve and the control valve HPCV. The temperature of the stream is adjusted in this heater to the desired level. A pressure drop of about 50 psi to 500 psi is required at the HPCV valve depending on the mass flow rate and the pressure level maintained in the calorimeter. The gas now passes through the calorimeter at an inlet pressure governed by the set point of the high pressure controller. The outlet stream of the calorimeter goes through a hand valve and the control valve JTCV. The opening of JTCV,

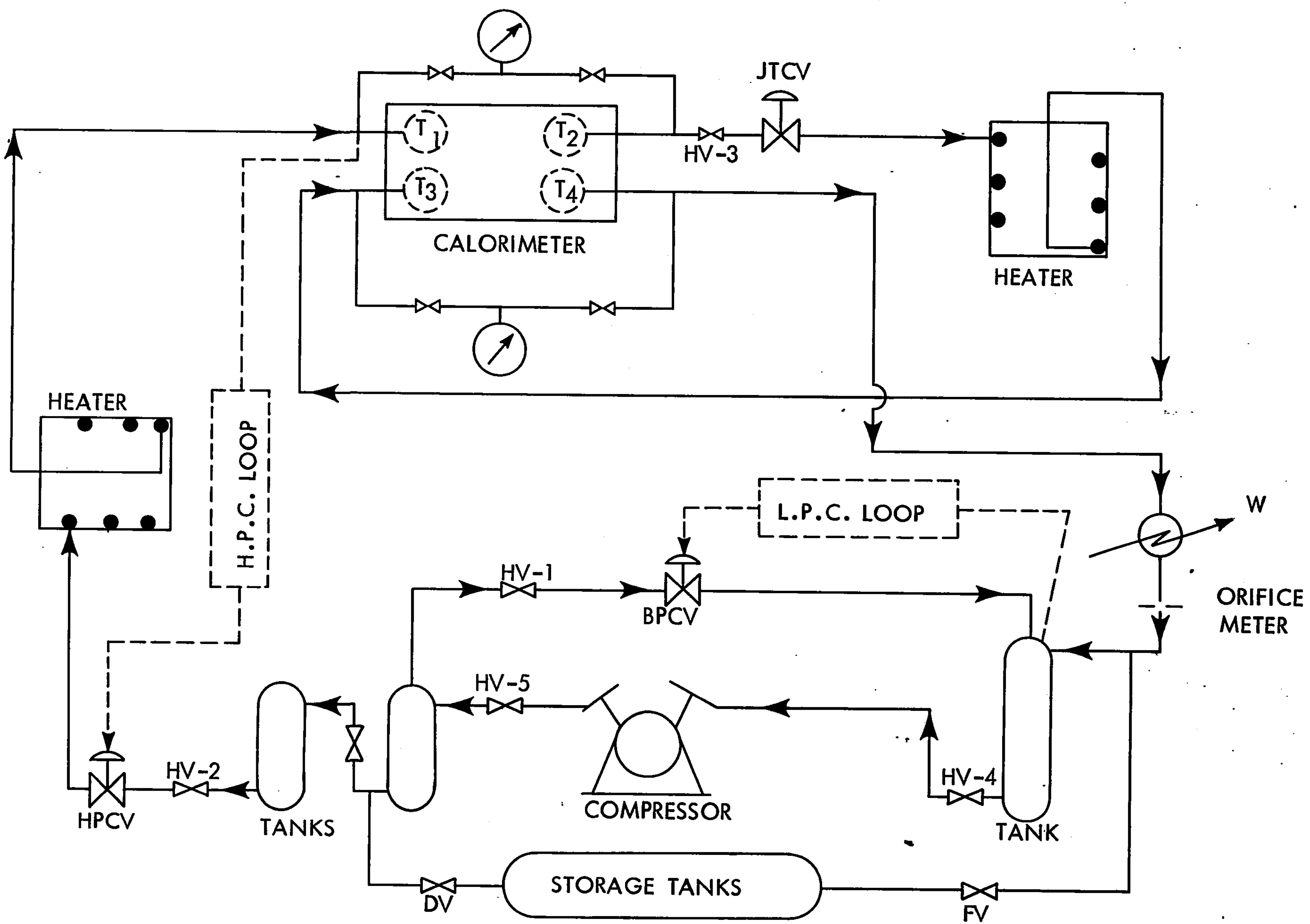


Figure III.3. Flow-Sheet.

manipulated manually, gives the desired mass flow rate of the gas through the calorimeter. The hand valve, when closed, isolates the high and low pressure sides of the calorimeter. The temperature of this throttled gas is raised to the desired value in the low pressure gas heater. The low pressure gas then passes through the calorimeter where it exchanges heat with the high pressure stream. The temperatures and the temperature changes of both the streams in the calorimeter are measured by the suitably located quartz thermometers. The inlet and outlet pressures of the two streams are measured by the Heise gauges as shown. The low pressure gas coming out of the calorimeter passes through an aftercooler and an orifice flow-meter before it is sent to the inlet low pressure surge tank. The low pressure control scheme controls the pressure of this surge tank by means of the valve BPCV. Thus, the inlet low pressure of the calorimeter is equal to the pressure of the surge tank plus a pressure drop of about 3 psi between these two locations.

The gas temperatures at the locations of the inlet of the two gas heaters, low pressure surge tank, the outlet of the compressor delivery cooler and the outlet of the after-cooler are indicated roughly on a Honeywell multipoint temperature indicator (not shown in the diagram).

The material is stored in three storage cylinders (only one shown), each of which is connected through hand valves to the low and high pressure sides of the compressor. It is possible to transfer material between the system and each storage cylinder separately or simultaneously by simple manipulation of the hand valves.

The different units of the equipment are connected by stainless steel type 316 tubes. The 3/8 in. (i.d. 1/4 in.) and 1/2 in. (i.d. 0.429 in.) tubes are used for the high and low pressures respectively. The sensing devices are connected if required to the equipment using 1/8 in. high pressure stainless steel tubes.

A pressure of about ten microns is maintained in the chamber housing the calorimeter by means of a vacuum pump.

When the working fluid was nitrogen the cooling effects associated with the pressure drops taking place in the valves HPCV, JTCV and BPCV were very small. However, when the carbon dioxide-methane mixtures were used the cooling effects were extremely large. In these circumstances, the valves were heated to avoid freezing or the formation of two phases. The valve BPCV was heated by 15 psig steam passing through a copper coil wrapped around the valve body. The water lines of the compressor delivery cooler were also modified so that the cooling of the high pressure gas coming out of the second head could be roughly controlled. The gas temperature at the outlet of this cooler was maintained at about 120°F. This also helped in avoiding excessive cooling at the valve BPCV. The bodies of the valves HPCV and JTCV were wrapped with electrical resistance heaters. The power input to these heaters was manually regulated so that the downstream gas was far above its condensation temperature. The hand valves which connect the storage cylinders to the system were also electrically heated while transferring the material.

The start-up, shut-down and data-taking procedures are given in Appendix B.

IV - EXPERIMENTAL RESULTS AND DISCUSSION

Experiments were first carried out to determine the heat capacity ratios, C_p/C_{p_o}, for nitrogen, at pressures up to 2250 psi and temperatures of about 60°, 75° and 150°C. The performance of the equipment was then evaluated by comparing the data obtained with those available in the literature. Following this, data were collected on two binary mixtures of carbon dioxide and methane containing 14.5 and 42.3 mole percent methane at temperatures of 40°, 60° and 90°C and pressures up to 2250 psia. Data on the former mixture were also obtained at about 150°C.

A. The Nitrogen Data

The measurements made on nitrogen are reported in Appendix C as Tables C-1 through C-3. The pressure and temperature are represented by P and T and the inlet locations for the high and low pressure streams are indicated by the subscripts 1 and 3 respectively. ΔT_o and ΔT represent the temperature changes for the low and high pressure streams. The difference between T_3 and T_1 was kept about 10°C and their average was approximately equal to the temperature at which the data were desired. For each isotherm two sets of experiments were carried out, the first for cooling and the second for heating the high pressure fluid. Since the temperature dependence of the heat capacity of nitrogen is approximately linear in the pressure and temperature range of interest, the two sets of data for each isotherm were obtained simply by interchanging the values of T_1 and T_3. The temperature reported for each isotherm was obtained by taking an average of all the values of T_1 and T_3.

The ratio $(\Delta T_o/\Delta T)$ was calculated from the observed temperature changes. These ratios were then adjusted for the ice-point and linearity corrections of the temperature probes, as illustrated in Appendix C. The corrected ratios, represented by $(\Delta T_o/\Delta T)_{corr.}$, were thus obtained for the two cases of heating and cooling the high pressure fluid for each isotherm and were smoothed separately by the method of linear least squares fit using the Forsythe polynomial.[65] The smoothed $(\Delta T_o/\Delta T)$ ratios for the two cases were generated at equal intervals of 50 psi and their averages were calculated. The average value calculated at a pressure is considered to be free of the calorimetry errors and is equal to the ratio of the heat capacity of the fluid at this pressure and the heat capacity of the fluid at the low pressure (about 27 psia). The smoothed values of the $(\Delta T_o/\Delta T)$ ratios for the two cases of heating and cooling the high pressure fluid and their averaged values (C_p/C_{p_o}), for the three isotherms, are reported in Tables IV.1 through IV.3. These values are represented by the curves shown in Figures IV.1 through IV.3. The experimental $(\Delta T_o/\Delta T)_{corr.}$ ratios of Tables C-1 through C-3 are

TABLE IV.1

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR NITROGEN

Isotherm Temperature	140.36°F	(60.20°C)
Low Pressure	27.2	psia
Low Pressure Heat Capacity	6.9774	Btu/(lb-mole,°R)

p psia	$\Delta T_o/\Delta T$ H.P. Fluid Heated	 H.P. Fluid Cooled	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
550.0	1.0604	1.0302	1.0453	7.2936
600.0	1.0649	1.0346	1.0498	7.3249
650.0	1.0693	1.0390	1.0542	7.3557
700.0	1.0737	1.0434	1.0585	7.3862
750.0	1.0780	1.0477	1.0629	7.4164
800.0	1.0823	1.0520	1.0671	7.4461
850.0	1.0865	1.0563	1.0714	7.4756
900.0	1.0906	1.0605	1.0755	7.5046
950.0	1.0946	1.0646	1.0796	7.5333
1000.0	1.0987	1.0687	1.0837	7.5617
1050.0	1.1026	1.0728	1.0877	7.5897
1100.0	1.1065	1.0769	1.0917	7.6173
1150.0	1.1103	1.0809	1.0956	7.6445
1200.0	1.1140	1.0848	1.0994	7.6715
1250.0	1.1177	1.0887	1.1032	7.6980
1300.0	1.1214	1.0926	1.1070	7.7242
1350.0	1.1249	1.0964	1.1107	7.7500
1400.0	1.1284	1.1002	1.1143	7.7755
1450.0	1.1319	1.1040	1.1179	7.8006
1500.0	1.1353	1.1077	1.1215	7.8253
1550.0	1.1386	1.1114	1.1250	7.8497
1600.0	1.1418	1.1150	1.1284	7.8738
1650.0	1.1450	1.1186	1.1318	7.8974
1700.0	1.1482	1.1221	1.1352	7.9208
1750.0	1.1513	1.1256	1.1384	7.9437
1800.0	1.1543	1.1291	1.1417	7.9663
1850.0	1.1572	1.1325	1.1449	7.9885
1900.0	1.1601	1.1350	1.1480	8.0104
1950.0	1.1629	1.1393	1.1511	8.0319
2000.0	1.1657	1.1426	1.1541	8.0531
2050.0	1.1684	1.1458	1.1571	8.0739
2100.0	1.1710	1.1491	1.1600	8.0943
2150.0	1.1736	1.1522	1.1629	8.1144
2200.0	1.1761	1.1554	1.1657	8.1341

TABLE IV.2

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR NITROGEN

Isotherm Temperature	168.26^{o}F	(75.7^{o}C)
Low Pressure	26.6	psia
Low Pressure Heat Capacity	6.9797	Btu/(lb-mole,^{o}R)

	$\Delta T_o/\Delta T$			
p psia	H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,^{o}R)
550.0	1.0004	1.0705	1.0355	7.2276
600.0	1.0038	1.0742	1.0390	7.2521
650.0	1.0071	1.0779	1.0425	7.2766
700.0	1.0104	1.0816	1.0460	7.3011
750.0	1.0137	1.0853	1.0495	7.3255
800.0	1.0170	1.0890	1.0530	7.3499
850.0	1.0204	1.0926	1.0565	7.3743
900.0	1.0237	1.0963	1.0600	7.3987
950.0	1.0270	1.0999	1.0635	7.4230
1000.0	1.0303	1.1036	1.0670	7.4473
1050.0	1.0336	1.1072	1.0704	7.4716
1100.0	1.0370	1.1109	1.0739	7.4958
1150.0	1.0403	1.1145	1.0774	7.5200
1200.0	1.0436	1.1181	1.0808	7.5442
1250.0	1.0469	1.1217	1.0843	7.5684
1300.0	1.0502	1.1253	1.0878	7.5926
1350.0	1.0535	1.1289	1.0912	7.6167
1400.0	1.0568	1.1325	1.0947	7.6408
1450.0	1.0601	1.1361	1.0981	7.6648
1500.0	1.0634	1.1397	1.1016	7.6889
1550.0	1.0667	1.1433	1.1050	7.7129
1600.0	1.0700	1.1469	1.1084	7.7369
1650.0	1.0733	1.1504	1.1119	7.7608
1700.0	1.0766	1.1540	1.1153	7.7847
1750.0	1.0799	1.1576	1.1187	7.8087
1800.0	1.0832	1.1611	1.1221	7.8325
1850.0	1.0865	1.1646	1.1256	7.8564
1900.0	1.0898	1.1682	1.1290	7.8802
1950.0	1.0931	1.1717	1.1324	7.9040
2000.0	1.0964	1.1752	1.1358	7.9278
2050.0	1.0996	1.1787	1.1392	7.9515
2100.0	1.1029	1.1823	1.1426	7.9753
2150.0	1.1062	1.1858	1.1460	7.9990
2200.0	1.1095	1.1893	1.1494	8.0226

TABLE IV.3

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR NITROGEN

Isotherm Temperature	302.72°F	(150.40°C)
Low Pressure	26.7	psia
Low Pressure Heat Capacity	7.0086	Btu/(lb-mole,°R)

p psia	$\Delta T_o/\Delta T$ H.P. Fluid Heated	 H.P. Fluid Cooled	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
550.0	1.0813	0.9798	1.0306	7.2231
600.0	1.0836	0.9821	1.0328	7.2390
650.0	1.0858	0.9843	1.0351	7.2546
700.0	1.0880	0.9865	1.0372	7.2699
750.0	1.0902	0.9886	1.0394	7.2850
800.0	1.0923	0.9907	1.0415	7.2997
850.0	1.0943	0.9928	1.0436	7.3142
900.0	1.0963	0.9948	1.0456	7.3283
950.0	1.0983	0.9969	1.0476	7.3422
1000.0	1.1002	0.9988	1.0495	7.3558
1050.0	1.1020	1.0008	1.0514	7.3691
1100.0	1.1038	1.0027	1.0533	7.3821
1150.0	1.1056	1.0046	1.0551	7.3948
1200.0	1.1073	1.0064	1.0568	7.4073
1250.0	1.1089	1.0082	1.0586	7.4194
1300.0	1.1105	1.0100	1.0603	7.4312
1350.0	1.1121	1.0117	1.0619	7.4428
1400.0	1.1136	1.0134	1.0635	7.4541
1450.0	1.1151	1.0151	1.0651	7.4651
1500.0	1.1165	1.0167	1.0666	7.4758
1550.0	1.1179	1.0183	1.0681	7.4862
1600.0	1.1192	1.0199	1.0695	7.4963
1650.0	1.1204	1.0214	1.0709	7.5061
1700.0	1.1217	1.0229	1.0723	7.5156
1750.0	1.1228	1.0244	1.0736	7.5249
1800.0	1.1240	1.0258	1.0749	7.5338
1850.0	1.1250	1.0272	1.0761	7.5425
1900.0	1.1261	1.0286	1.0773	7.5509
1950.0	1.1270	1.0299	1.0785	7.5590
2000.0	1.1280	1.0312	1.0796	7.5668
2050.0	1.1288	1.0325	1.0807	7.5743
2100.0	1.1297	1.0337	1.0817	7.5815
2150.0	1.1305	1.0349	1.0827	7.5884
2200.0	1.1312	1.0361	1.0836	7.5951

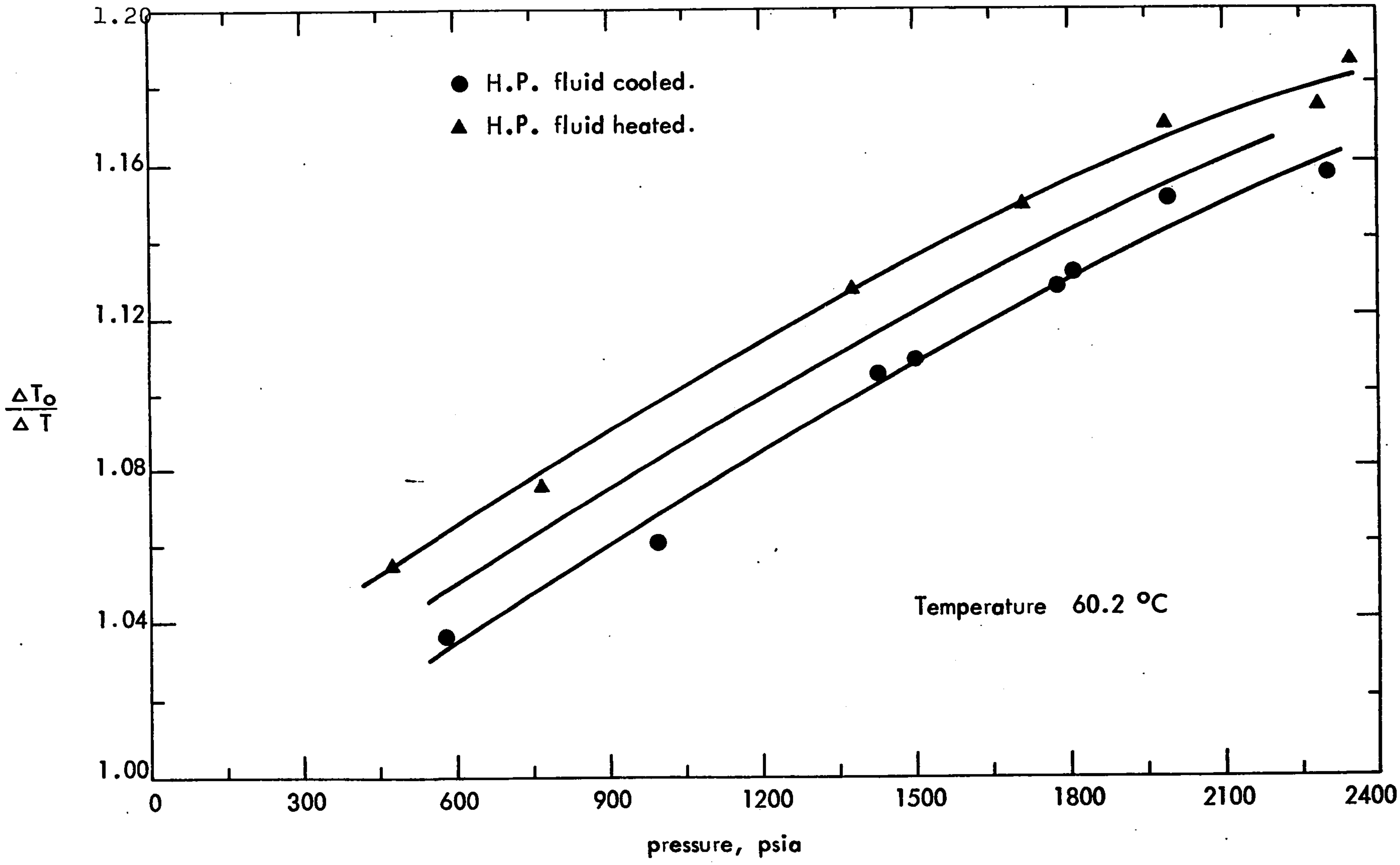


Figure IV. 1. Experimental C_p ratio for nitrogen.

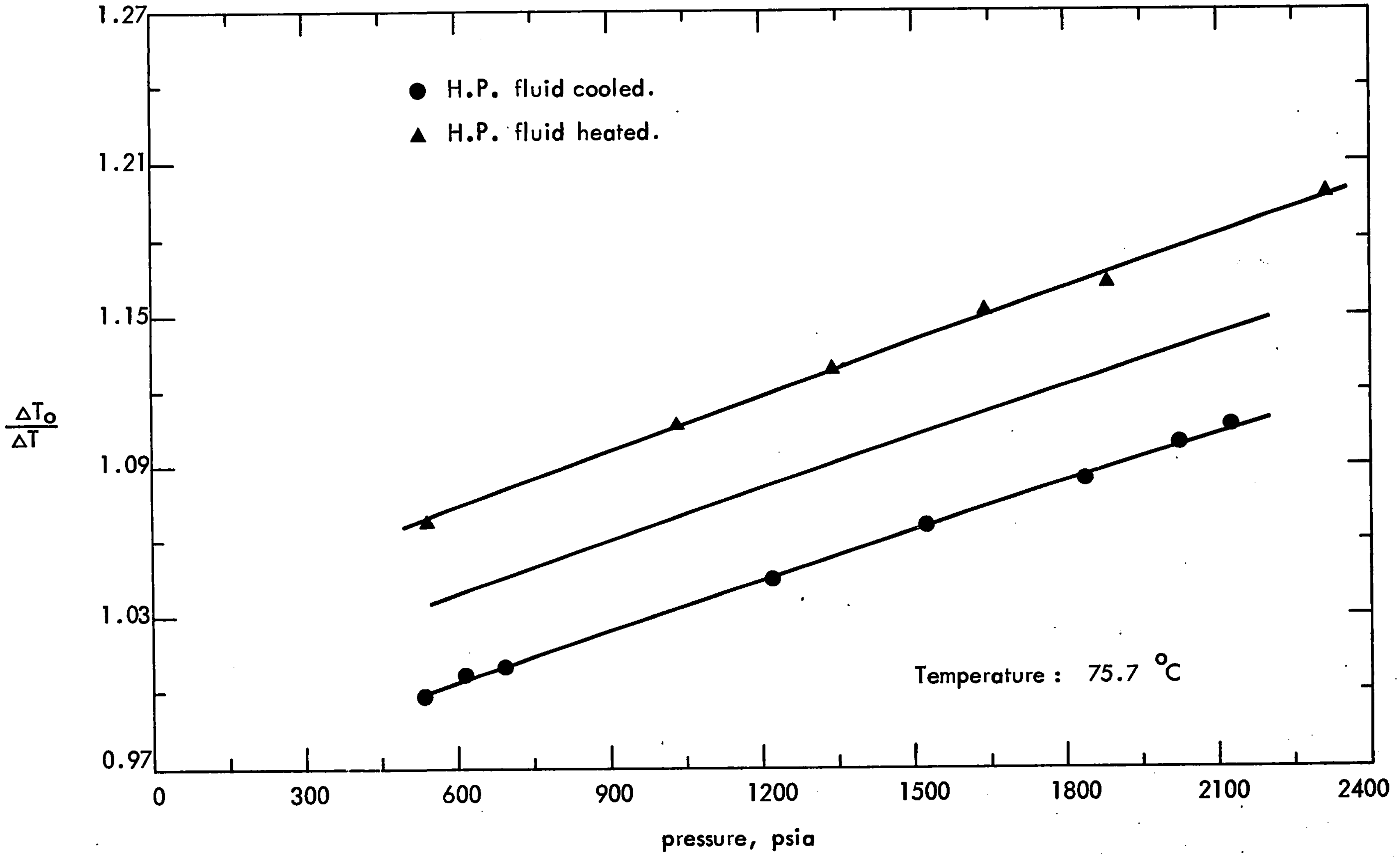


Figure IV. 2. Experimental Cp ratio for nitrogen

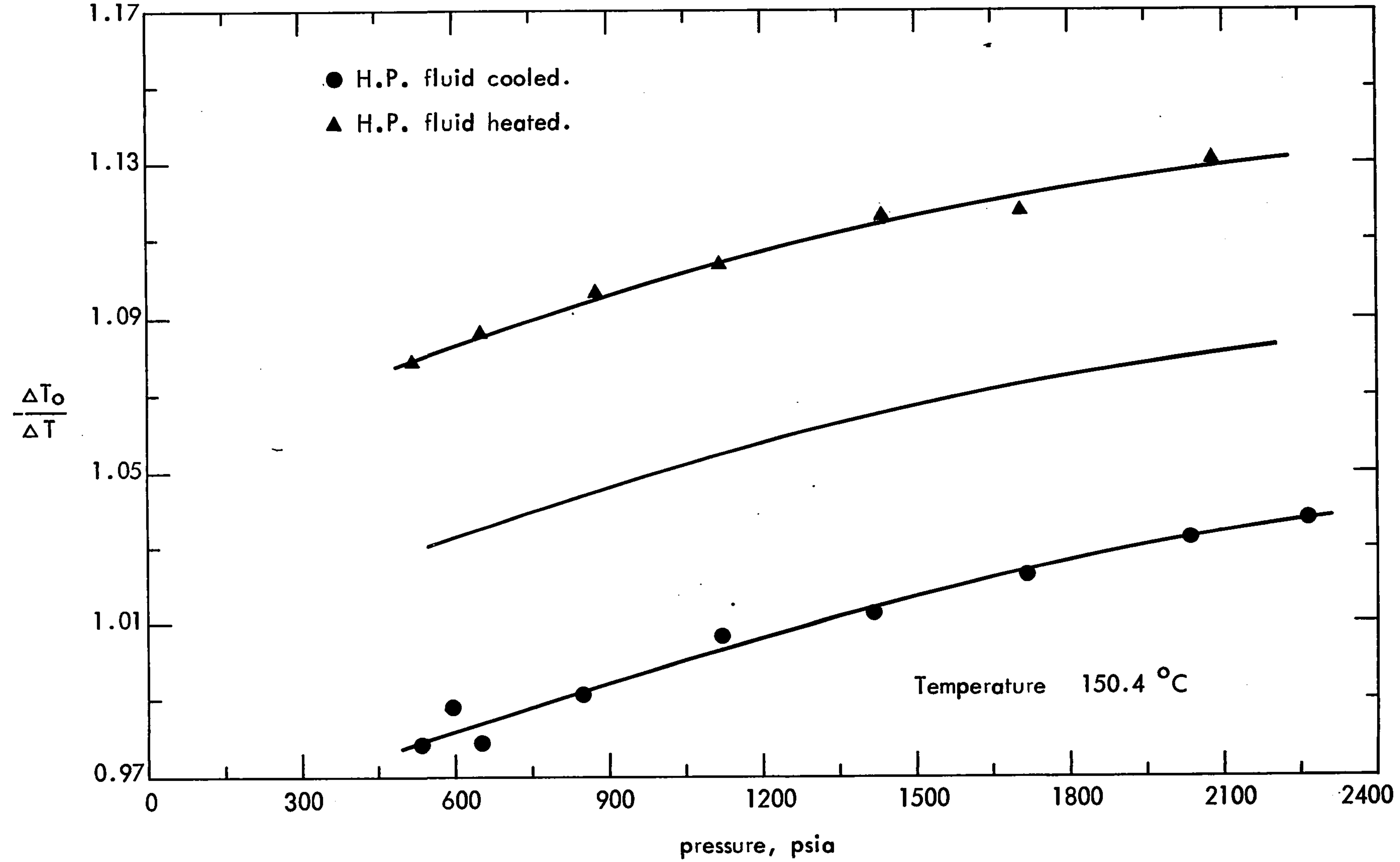


Figure IV. 3. Experimental C_p ratio for nitrogen.

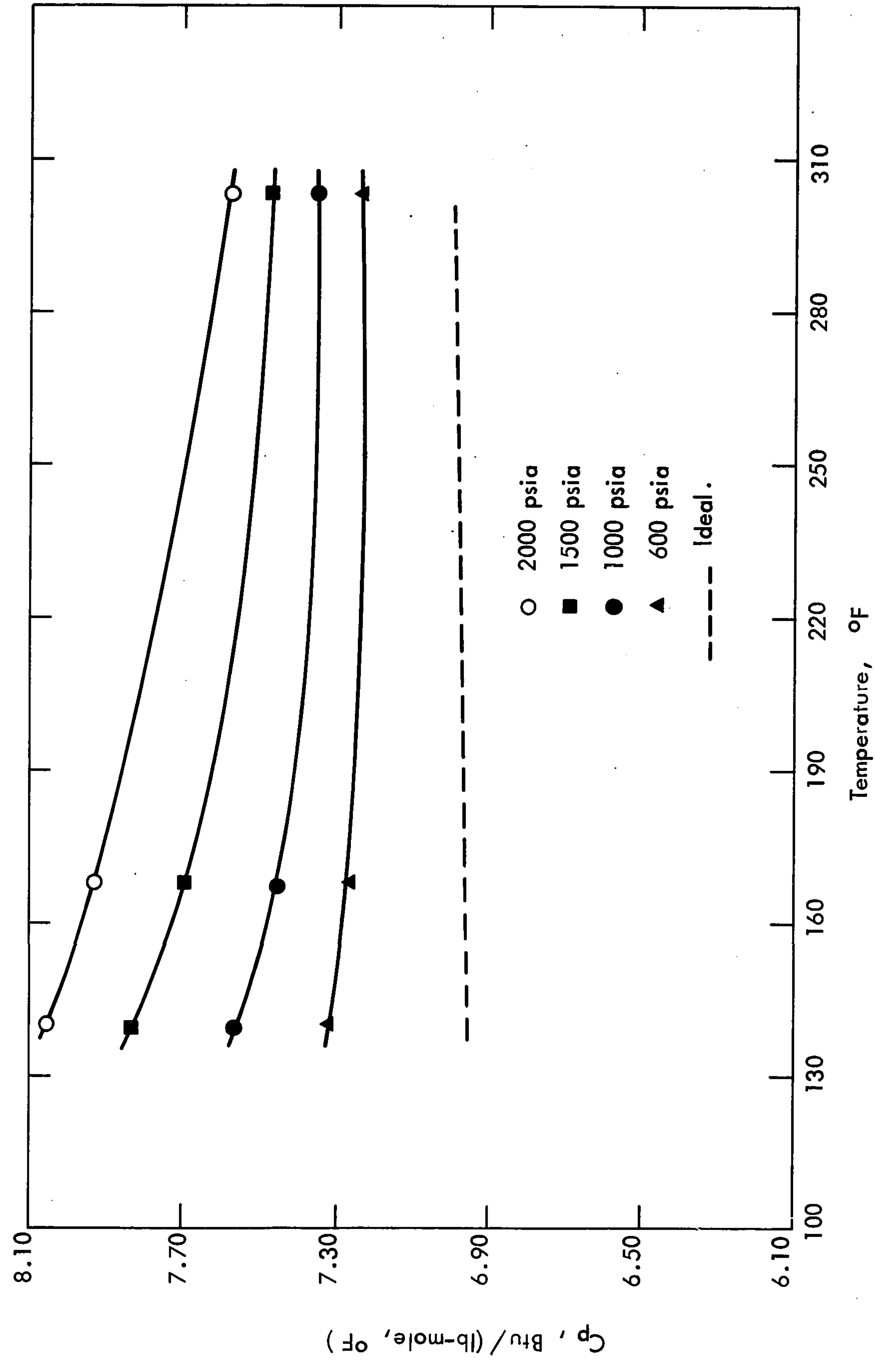


Figure IV. 4. C_p isobars for nitrogen.

also plotted in the respective figures. The C_p ratios thus obtained are at the isotherm temperature reported in the above tables.

The low pressure heat capacity of nitrogen, C_{p_o}, for each isotherm, was calculated by a computer programme developed by Wood[66] at the U.S. Bureau of Mines Helium Research Centre which utilizes a virial equation of state for the computation of thermodynamic properties. The value of the low pressure heat capacity is reported in the table for each isotherm. The heat capacities of nitrogen at elevated pressures were calculated from the low pressure heat capacity and the heat capacity ratios obtained in the present work and are reported in Tables IV.1 through IV.3. The isobaric curves of the C_p of nitrogen were then obtained from these tables and are shown in Figure IV.4. These plots showed that the heat capacity ratios of nitrogen, obtained in this work, are internally consistent.

B. The Carbon Dioxide-Methane Mixture Data

The measurements made on carbon dioxide-methane mixtures are reported in Appendix C as Tables C-4 through C-19. In these tables the temperature changes for the low and high pressure streams are represented by DT_o and DT respectively. The calculation of (DT_o/DT) ratios from the observed values of DT_o and DT over the duration of the steady state run and the application of ice-point and linearity temperature probe corrections to the observed DT_o and DT are illustrated in Appendix C through the Table C-4. The $(DT_o/DT)_{corr.}$ ratios were calculated from the probe corrected DT_o and DT values, and are also reported in the above tables.

The selection of T_1 and T_3 for the carbon dioxide-methane mixture experiments was done differently than that for the nitrogen experiments. Since the conditions at which the experimental data were collected were close to the critical points of the mixtures, the heat capacity is not linearly dependent on temperature. Hence the experiments for an isotherm were carried out in such a manner that the average high pressure gas temperature always remained at about the same level. Moreover since the heat capacity is a strong function of pressure, the DT_o values could be several times the DT values in some regions. Hence the temperatures T_1 and T_3 were adjusted for every point in the table for each isotherm. Two sets of experiments were carried out, one for cooling and then one for heating the high pressure fluid. The inlet temperature of the high pressure fluid in one set was approximately kept equal to the outlet temperature of this fluid in the other set. The inlet temperature of the low pressure fluid of course then had to be higher in one case and lower in the other than the corresponding inlet high pressure fluid temperature. Tables C-6 through C-11 also report the r.m.s. error of each point. This was calculated by finding the average of $(DT_o/DT)_{corr.}$ over the steady state period, and estimating the deviations of each observation over this period. The r.m.s. error thus corresponds to the standard error of observation of each point and is related to its repeatability.

The "isotherm temperature" was calculated by average high pressure gas temperatures for all the points in the data set for an isotherm. The $(DT_o/DT)_{corr.}$ values of each point of the isotherm were then further corrected for the deviation of average high and low pressure gas temperatures from the isotherm temperature. The method of applying these temperature corrections is explained in Appendix C through the Table C-12. The temperature corrected values are represented by $(DT_o/DT)^*$ and are reported in Table C-13 through C-19 corresponding to the isotherms for which the data were collected.

The $(DT_o/DT)^*$ values for the two cases of heating and cooling the high pressure fluid were then separately smoothed using the criterion of least squares. The data sets of isotherms 2 and 3, reported in Tables C-14 and C-15, were smoothed by the Spline fit technique, as outlined by Klaus and Van Ness,[67] using alternate points as the boundary points. The other data sets were smoothed by the Forsythe polynomial since the high degree polynomials were not required for the representation of these data sets. In the smoothing process for all the data sets of Tables C-14 through C-19, a weight inversely proportional to the square of r.m.s. error was assigned to each point. However, an equal weight of unity was assigned to all the points during the smoothing of the data set reported in Table C-13.

The smooth values of $(\Delta T_o/\Delta T)$ ratios for the two cases of heating and cooling the high pressure gas for each isotherm were generated at equal intervals of 50 psi and their average was calculated. The average values thus calculated are equal to the heat capacity ratios. The smooth values of temperature change and heat capacity ratios for all the isotherms are reported in Tables IV.4 through IV.10. These values are also represented graphically in Figures IV.5 through IV.11. Tables IV.4 through IV.7 and Figures IV.5 through IV.8 represent the data for the binary mixture containing 14.5 mole percent methane. The other tables and figures show the data for the binary mixture containing 42.3 mole percent methane. Figure (IV.8) shows curves of the smooth ΔT ratios for heating and cooling and also for the average. For the sake of clarity, however, the other figures only show the curve of the average value. The experimental $(DT_o/DT)^*$ values of Tables C-13 through C-19 are plotted in the corresponding figures. The low pressure heat capacity of the carbon dioxide-methane mixtures at

TABLE IV.4

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. CH_4	0.1449	
Isotherm Temperature	103.48°F	(39.71°C)
Low Pressure	30.3	psia
Low Pressure Heat Capacity	9.0624	Btu/(lb-mole,°R)

p	$\Delta T_o/\Delta T$			
psia	H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
555.0	1.2904	1.3396	1.3150	11.9170
600.0	1.3373	1.3800	1.3586	12.3122
650.0	1.3893	1.4265	1.4079	12.7589
700.0	1.4436	1.4771	1.4603	13.2338
750.0	1.5028	1.5337	1.5182	13.7585
800.0	1.5694	1.5985	1.5840	14.3548
850.0	1.6460	1.6739	1.6599	15.0427
900.0	1.7352	1.7618	1.7485	15.8456
950.0	1.8396	1.8646	1.8521	16.7844
1000.0	1.9616	1.9843	1.9729	17.8792
1050.0	2.1037	2.1229	2.1133	19.1515
1100.0	2.2667	2.2815	2.2741	20.6088
1150.0	2.4508	2.4611	2.4560	22.2572
1200.0	2.6563	2.6625	2.6594	24.1005
1250.0	2.8833	2.8867	2.8850	26.1450
1300.0	3.1321	3.1344	3.1332	28.3943
1350.0	3.4029	3.4067	3.4048	30.8556
1400.0	3.6956	3.7012	3.6984	33.5163
1450.0	3.9973	3.9982	3.9978	36.2296
1500.0	4.2805	4.2719	4.2762	38.7526
1550.0	4.5173	4.4964	4.5068	40.8424
1600.0	4.6793	4.6458	4.6625	42.2534
1650.0	4.7390	4.6981	4.7186	42.7618
1700.0	4.6939	4.6634	4.6787	42.4002
1750.0	4.5768	4.5668	4.5718	41.4314
1800.0	4.4228	4.4340	4.4284	40.1319
1850.0	4.2651	4.2898	4.2775	38.7644
1900.0	4.1154	4.1468	4.1311	37.4376
1950.0	3.9736	4.0065	3.9900	36.1589
2000.0	3.8395	3.8698	3.8547	34.9328
2050.0	3.7131	3.7377	3.7254	33.7610
2100.0	3.5942	3.6111	3.6027	32.6491
2150.0	3.4827	3.4911	3.4869	31.5996
2200.0	3.3784	3.3786	3.3785	30.6173

TABLE IV.5

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane	0.1449	
Isotherm Temperature	141.01°F	(60.56°C)
Low Pressure	30.3	psia
Low Pressure Heat Capacity	9.2657	Btu/(lb-mole,°R)

p psia	$\Delta T_o/\Delta T$ H.P. Fluid Cooled	$\Delta T_o/\Delta T$ H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
520.0	1.2051	1.2179	1.2115	11.2253
550.0	1.2234	1.2355	1.2295	11.3921
600.0	1.2532	1.2653	1.2592	11.6673
650.0	1.2826	1.2958	1.2892	11.9453
700.0	1.3123	1.3274	1.3198	12.2288
750.0	1.3430	1.3606	1.3518	12.5253
800.0	1.3753	1.3957	1.3855	12.8376
850.0	1.4101	1.4332	1.4216	13.1721
900.0	1.4479	1.4734	1.4607	13.5344
950.0	1.4895	1.5168	1.5032	13.9282
1000.0	1.5355	1.5638	1.5496	14.3581
1050.0	1.5867	1.6147	1.6007	14.8316
1100.0	1.6437	1.6699	1.6568	15.3514
1150.0	1.7071	1.7299	1.7185	15.9231
1200.0	1.7765	1.7945	1.7855	16.5439
1250.0	1.8512	1.8635	1.8573	17.2091
1300.0	1.9308	1.9364	1.9336	17.9161
1350.0	2.0145	2.0131	2.0138	18.6592
1400.0	2.1017	2.0930	2.0974	19.4338
1450.0	2.1918	2.1760	2.1839	20.2353
1500.0	2.2843	2.2617	2.2730	21.0609
1550.0	2.3784	2.3497	2.3640	21.9041
1600.0	2.4735	2.4396	2.4565	22.7611
1650.0	2.5680	2.5302	2.5491	23.6191
1700.0	2.6599	2.6195	2.6397	24.4586
1750.0	2.7472	2.7054	2.7263	25.2610
1800.0	2.8281	2.7861	2.8071	26.0097
1850.0	2.9004	2.8594	2.8799	26.6842
1900.0	2.9623	2.9234	2.9428	27.2671
1950.0	3.0117	2.9761	2.9939	27.7405
2000.0	3.0478	3.0163	3.0320	28.0936
2050.0	3.0720	3.0448	3.0584	28.3382
2100.0	3.0862	3.0631	3.0747	28.4892
2150.0	3.0924	3.0727	3.0825	28.5615
2200.0	3.0925	3.0747	3.0836	28.5717
2250.0	3.0884	3.0707	3.0796	28.5346

TABLE IV.6

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane	0.1449	
Isotherm Temperature	194.83°F	(90.46°C)
Low Pressure	30.4	psia
Low Pressure Heat Capacity	9.5524	Btu/(lb-mole, °R)

	$\Delta T_o/\Delta T$			
p psia	H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole, °R)
500.0	1.1103	1.1474	1.1289	10.7834
550.0	1.1289	1.1597	1.1443	10.9310
600.0	1.1476	1.1736	1.1606	11.0866
650.0	1.1665	1.1891	1.1778	11.2507
700.0	1.1857	1.2060	1.1959	11.4235
750.0	1.2054	1.2244	1.2149	11.6052
800.0	1.2257	1.2441	1.2349	11.7962
850.0	1.2466	1.2651	1.2559	11.9964
900.0	1.2682	1.2874	1.2778	12.2060
950.0	1.2907	1.3107	1.3007	12.4249
1000.0	1.3140	1.3352	1.3246	12.6530
1050.0	1.3382	1.3607	1.3494	12.8902
1100.0	1.3633	1.3871	1.3752	13.1364
1150.0	1.3893	1.4144	1.4019	13.3912
1200.0	1.4163	1.4425	1.4294	13.6542
1250.0	1.4441	1.4714	1.4578	13.9252
1300.0	1.4729	1.5009	1.4869	14.2036
1350.0	1.5025	1.5311	1.5168	14.4889
1400.0	1.5328	1.5618	1.5473	14.7805
1450.0	1.5639	1.5930	1.5784	15.0777
1500.0	1.5956	1.6245	1.6101	15.3799
1550.0	1.6278	1.6565	1.6421	15.6862
1600.0	1.6604	1.6887	1.6745	15.9958
1650.0	1.6933	1.7211	1.7072	16.3077
1700.0	1.7263	1.7536	1.7400	16.6210
1750.0	1.7594	1.7863	1.7728	16.9346
1800.0	1.7922	1.8189	1.8056	17.2474
1850.0	1.8248	1.8514	1.8381	17.5583
1900.0	1.8568	1.8839	1.8703	17.8660
1950.0	1.8880	1.9161	1.9021	18.1691
2000.0	1.9183	1.9481	1.9332	18.4664
2050.0	1.9473	1.9797	1.9635	18.7564
2100.0	1.9749	2.0110	1.9930	19.0375
2150.0	2.0009	2.0417	2.0213	19.3082
2200.0	2.0248	2.0720	2.0484	19.5669

TABLE IV.7

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane 0.1449
Isotherm Temperature 303.08°F (150.60°C)
Low Pressure 30.9 psia
Low Pressure Heat Capacity 10.1046 Btu/(lb-mole,°R)

p psia	$\Delta T_o/\Delta T$ H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
550.0	1.0393	1.1217	1.0805	10.9178
600.0	1.0480	1.1316	1.0898	11.0120
650.0	1.0568	1.1415	1.0991	11.1063
700.0	1.0656	1.1514	1.1085	11.2009
750.0	1.0744	1.1614	1.1179	11.2956
800.0	1.0832	1.1714	1.1273	11.3905
850.0	1.0920	1.1814	1.1367	11.4856
900.0	1.1008	1.1914	1.1461	11.5809
950.0	1.1097	1.2014	1.1556	11.6764
1000.0	1.1185	1.2115	1.1650	11.7720
1050.0	1.1274	1.2216	1.1745	11.8678
1100.0	1.1363	1.2317	1.1840	11.9639
1150.0	1.1452	1.2418	1.1935	12.0600
1200.0	1.1541	1.2520	1.2031	12.1564
1250.0	1.1631	1.2622	1.2126	12.2530
1300.0	1.1720	1.2724	1.2222	12.3497
1350.0	1.1810	1.2826	1.2318	12.4466
1400.0	1.1899	1.2928	1.2414	12.5438
1450.0	1.1989	1.3031	1.2510	12.6410
1500.0	1.2079	1.3134	1.2607	12.7385
1550.0	1.2169	1.3237	1.2703	12.8362
1600.0	1.2260	1.3340	1.2800	12.9340
1650.0	1.2350	1.3444	1.2897	13.0320
1700.0	1.2441	1.3548	1.2994	13.1302
1750.0	1.2532	1.3652	1.3092	13.2286
1800.0	1.2623	1.3756	1.3189	13.3272
1850.0	1.2714	1.3860	1.3287	13.4259
1900.0	1.2805	1.3965	1.3385	13.5248
1950.0	1.2896	1.4070	1.3483	13.6240
2000.0	1.2988	1.4175	1.3581	13.7232
2050.0	1.3079	1.4280	1.3680	13.8227
2100.0	1.3171	1.4386	1.3778	13.9224
2150.0	1.3263	1.4491	1.3877	14.0222
2200.0	1.3355	1.4597	1.3976	14.1222

TABLE IV.8

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane	0.4230	
Isotherm Temperature	103.86°F	(39.92°C)
Low Pressure	30.1	psia
Low Pressure Heat Capacity	8.9597	Btu/(lb-mole,°R)

p psia	$\Delta T_o/\Delta T$ H.P. Fluid Cooled	$\Delta T_o/\Delta T$ H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
500.0	1.1590	1.1851	1.1720	10.5012
550.0	1.1825	1.2077	1.1951	10.7080
600.0	1.2074	1.2315	1.2194	10.9257
650.0	1.2337	1.2565	1.2451	11.1557
700.0	1.2615	1.2831	1.2723	11.3993
750.0	1.2910	1.3112	1.3011	11.6575
800.0	1.3221	1.3411	1.3316	11.9309
850.0	1.3551	1.3727	1.3639	12.2201
900.0	1.3898	1.4061	1.3980	12.5254
950.0	1.4264	1.4413	1.4338	12.8468
1000.0	1.4647	1.4783	1.4715	13.1842
1050.0	1.5048	1.5170	1.5109	13.5371
1100.0	1.5464	1.5575	1.5520	13.9050
1150.0	1.5897	1.5995	1.5946	14.2870
1200.0	1.6343	1.6430	1.6387	14.6819
1250.0	1.6803	1.6878	1.6840	15.0885
1300.0	1.7273	1.7338	1.7305	15.5051
1350.0	1.7752	1.7807	1.7780	15.9301
1400.0	1.8238	1.8284	1.8261	16.3614
1450.0	1.8729	1.8766	1.8747	16.7968
1500.0	1.9220	1.9249	1.9235	17.2337
1550.0	1.9710	1.9732	1.9721	17.6695
1600.0	2.0195	2.0211	2.0203	18.1013
1650.0	2.0672	2.0681	2.0677	18.5258
1700.0	2.1137	2.1141	2.1139	18.9398
1750.0	2.1586	2.1584	2.1585	19.3395
1800.0	2.2014	2.2008	2.2011	19.7211
1850.0	2.2418	2.2407	2.2412	20.0806
1900.0	2.2792	2.2776	2.2784	20.4136
1950.0	2.3131	2.3111	2.3121	20.7156
2000.0	2.3430	2.3406	2.3418	20.9818
2050.0	2.3684	2.3655	2.3669	21.2071
2100.0	2.3887	2.3853	2.3870	21.3865
2150.0	2.4032	2.3993	2.4012	21.5143
2200.0	2.4114	2.4068	2.4091	21.5850
2250.0	2.4126	2.4073	2.4100	21.5925

TABLE IV.9

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane	0.4230	
Isotherm Temperature	140.86°F	(60.48°C)
Low Pressure	30.0	psia
Low Pressure Heat Capacity	9.1623	Btu/(lb-mole,°R)

p psia	ΔTo/ΔT H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	Cp Btu/(lb-mole,°R)
500.0	1.1318	1.1462	1.1390	10.4362
550.0	1.1457	1.1593	1.1525	10.5596
600.0	1.1608	1.1737	1.1673	10.6951
650.0	1.1772	1.1894	1.1833	10.8419
700.0	1.1948	1.2062	1.2005	10.9995
750.0	1.2135	1.2241	1.2188	11.1672
800.0	1.2333	1.2431	1.2382	11.3445
850.0	1.2540	1.2630	1.2585	11.5307
900.0	1.2756	1.2838	1.2797	11.7251
950.0	1.2980	1.3055	1.3018	11.9272
1000.0	1.3213	1.3279	1.3246	12.1363
1050.0	1.3452	1.3510	1.3481	12.3518
1100.0	1.3697	1.3748	1.3723	12.5730
1150.0	1.3948	1.3991	1.3970	12.7994
1200.0	1.4204	1.4239	1.4222	13.0304
1250.0	1.4464	1.4492	1.4478	13.2652
1300.0	1.4728	1.4748	1.4738	13.5032
1350.0	1.4995	1.5007	1.5001	13.7439
1400.0	1.5263	1.5268	1.5265	13.9867
1450.0	1.5533	1.5530	1.5532	14.2308
1500.0	1.5804	1.5794	1.5799	14.4756
1550.0	1.6076	1.6058	1.6067	14.7206
1600.0	1.6346	1.6321	1.6333	14.9651
1650.0	1.6615	1.6583	1.6599	15.2085
1700.0	1.6882	1.6843	1.6863	15.4502
1750.0	1.7147	1.7101	1.7124	15.6894
1800.0	1.7408	1.7355	1.7382	15.9257
1850.0	1.7666	1.7606	1.7636	16.1584
1900.0	1.7918	1.7852	1.7885	16.3868
1950.0	1.8165	1.8093	1.8129	16.6103
2000.0	1.8406	1.8328	1.8367	16.8283
2050.0	1.8641	1.8556	1.8598	17.0402
2100.0	1.8867	1.8777	1.8822	17.2454
2150.0	1.9086	1.8990	1.9038	17.4432
2200.0	1.9296	1.9194	1.9245	17.6330
2250.0	1.9496	1.9390	1.9443	17.8141

TABLE IV.10

SMOOTHED VALUES OF C_p/C_{p_o} AND C_p FOR THE CO_2-CH_4 SYSTEM

Mole Fr. Methane	0.4230	
Isotherm Temperature	194.54°F	(90.30°C)
Low Pressure	30.0	psia
Low Pressure Heat Capacity	9.4635	Btu/(lb-mole,°R)

p	$\Delta T_o/\Delta T$			
psia	H.P. Fluid Cooled	H.P. Fluid Heated	C_p/C_{p_o}	C_p Btu/(lb-mole,°R)
500.0	1.0776	1.1116	1.0946	10.3588
550.0	1.0893	1.1215	1.1054	10.4610
600.0	1.1013	1.1320	1.1166	10.5670
650.0	1.1135	1.1429	1.1282	10.6764
700.0	1.1259	1.1543	1.1401	10.7891
750.0	1.1386	1.1660	1.1523	10.9049
800.0	1.1515	1.1782	1.1649	11.0237
850.0	1.1646	1.1908	1.1777	11.1451
900.0	1.1779	1.2037	1.1908	11.2690
950.0	1.1914	1.2169	1.2041	11.3953
1000.0	1.2050	1.2304	1.2177	11.5236
1050.0	1.2188	1.2441	1.2315	11.6539
1100.0	1.2328	1.2581	1.2454	11.7859
1150.0	1.2468	1.2722	1.2595	11.9194
1200.0	1.2610	1.2865	1.2738	12.0543
1250.0	1.2753	1.3010	1.2881	12.1903
1300.0	1.2896	1.3156	1.3026	12.3272
1350.0	1.3041	1.3302	1.3172	12.4649
1400.0	1.3186	1.3449	1.3318	12.6031
1450.0	1.3331	1.3597	1.3464	12.7416
1500.0	1.3477	1.3744	1.3611	12.8803
1550.0	1.3623	1.3891	1.3757	13.0190
1600.0	1.3769	1.4037	1.3903	13.1574
1650.0	1.3915	1.4183	1.4049	13.2954
1700.0	1.4061	1.4328	1.4194	13.4327
1750.0	1.4206	1.4471	1.4338	13.5692
1800.0	1.4351	1.4612	1.4482	13.7047
1850.0	1.4496	1.4751	1.4624	13.8390
1900.0	1.4640	1.4888	1.4764	13.9718
1950.0	1.4782	1.5023	1.4903	14.1030
2000.0	1.4924	1.5154	1.5039	14.2324
2050.0	1.5065	1.5283	1.5174	14.3598
2100.0	1.5204	1.5408	1.5306	14.4850
2150.0	1.5342	1.5529	1.5436	14.6077
2200.0	1.5479	1.5647	1.5563	14.7279
2230.0	1.5560	1.5715	1.5638	14.7987

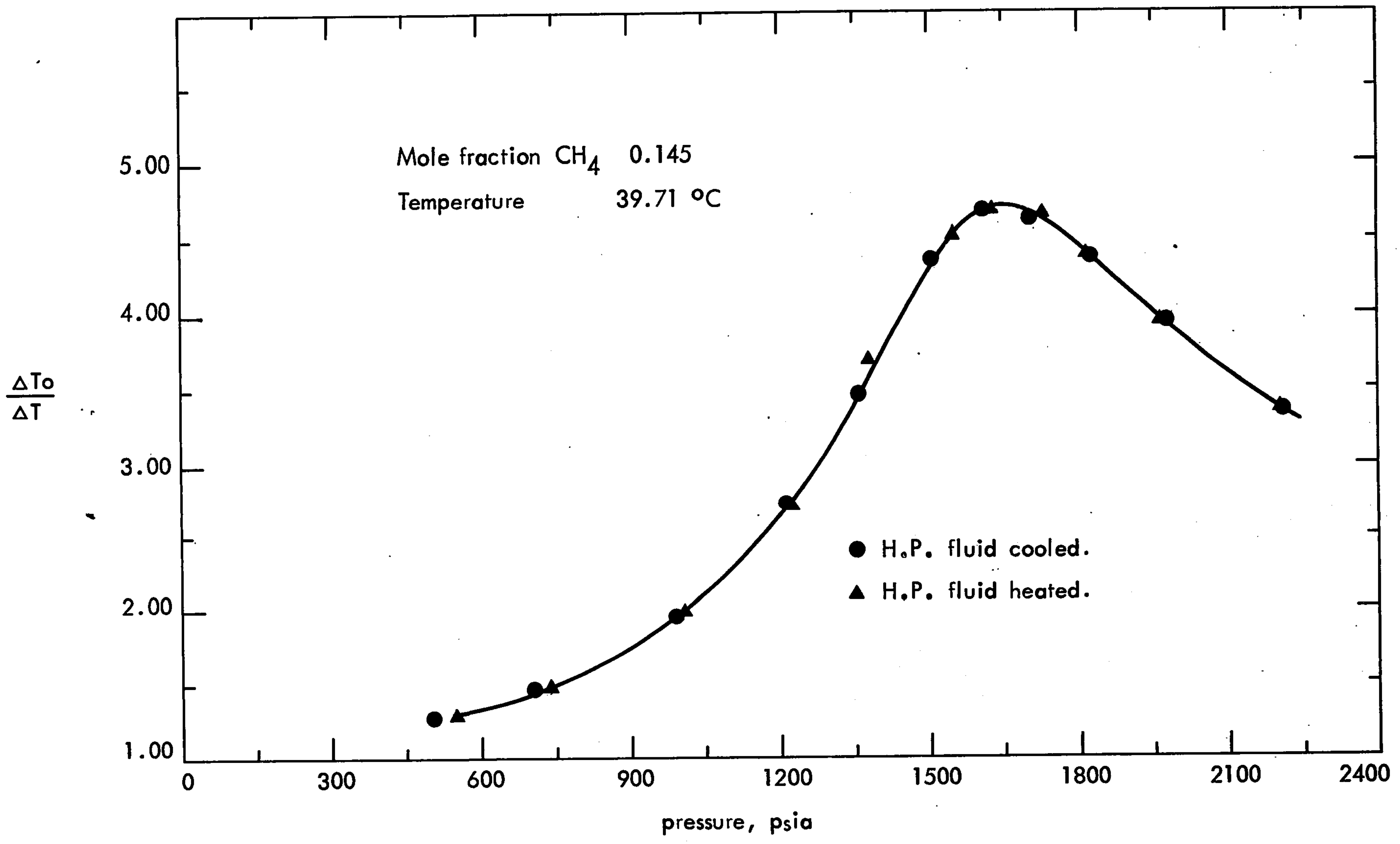


Figure IV. 5. Experimental Cp ratio for the CO_2 - CH_4 System.

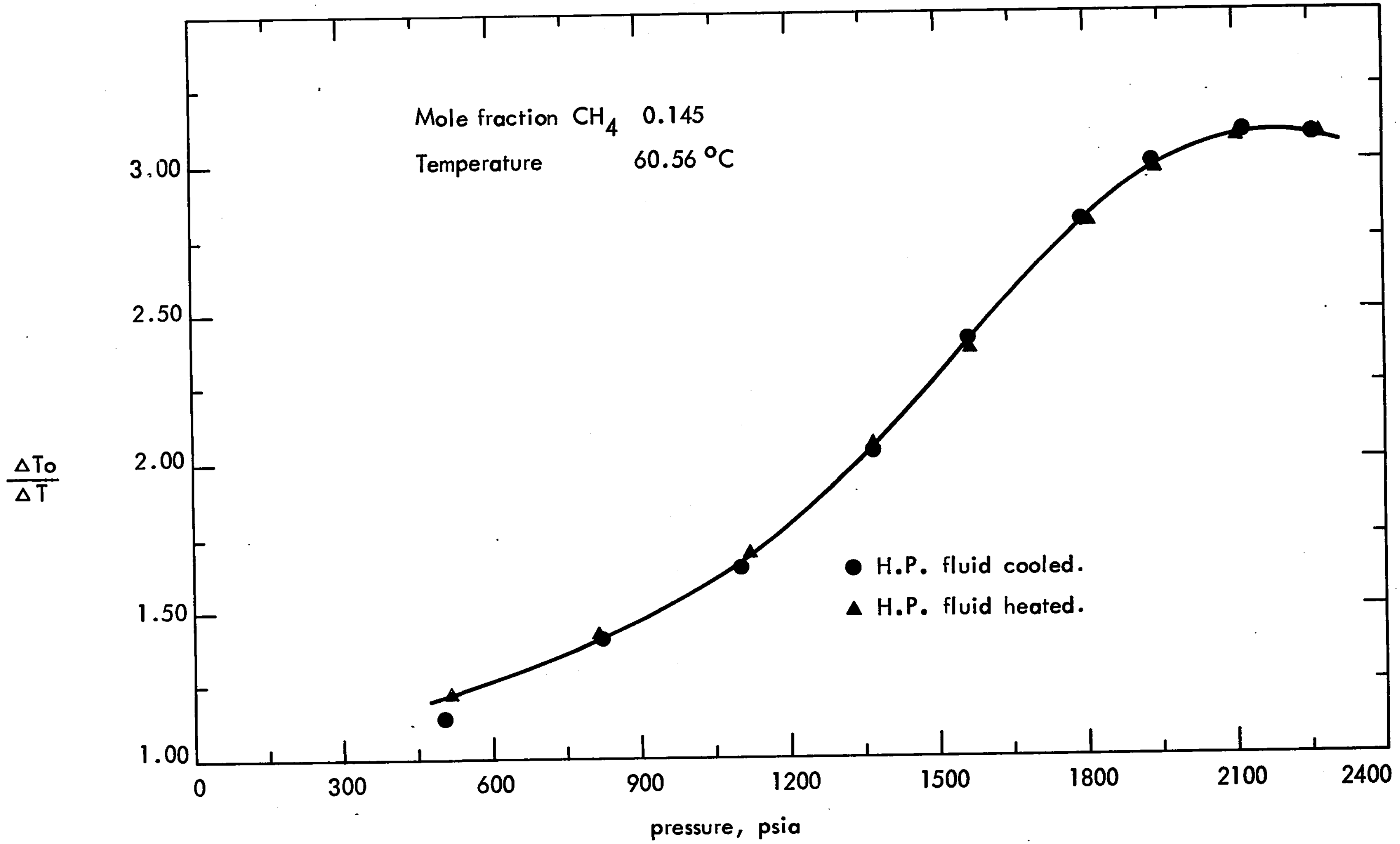


Figure IV. 6. Experimental C_p ratio for the CO_2 - CH_4 System.

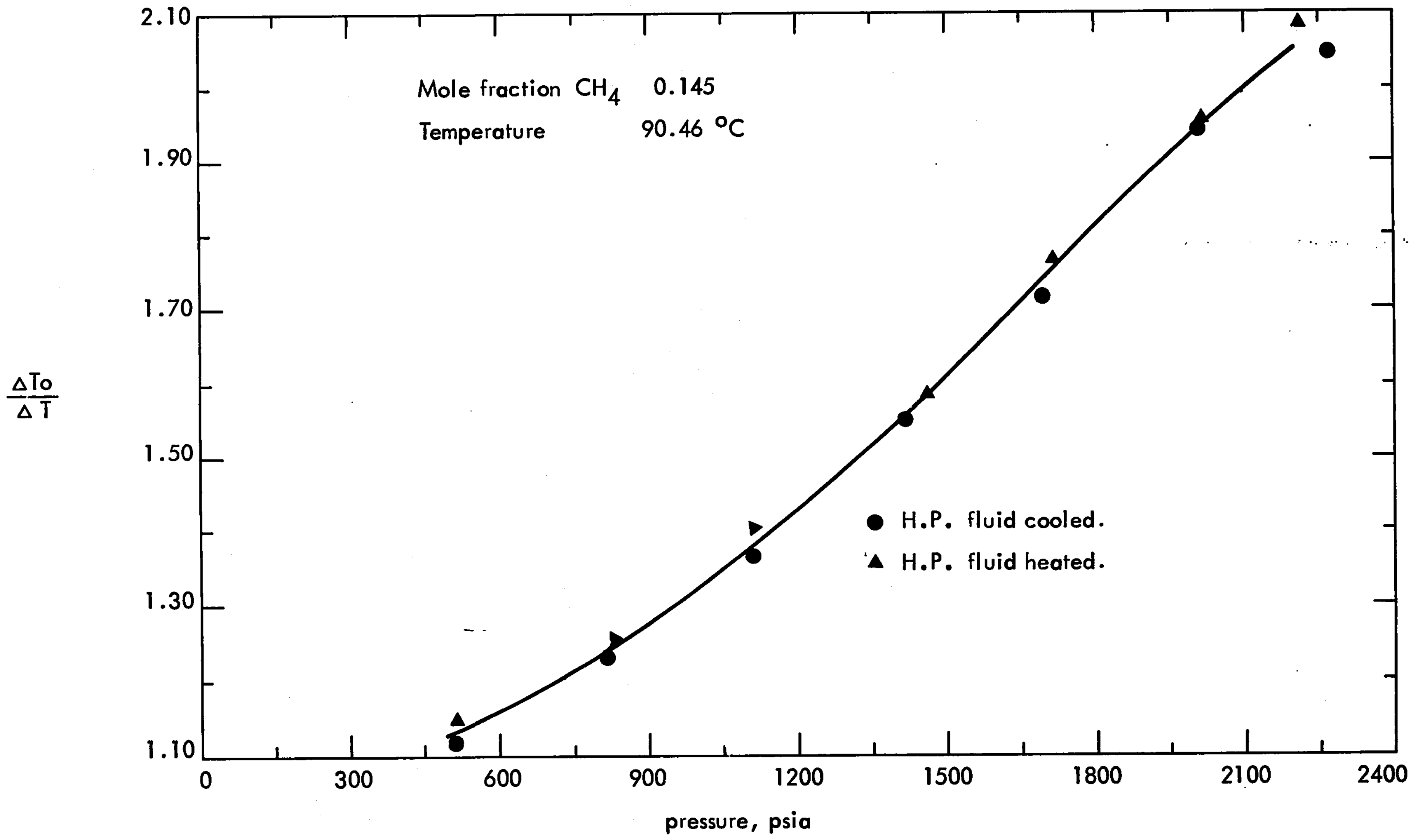


Figure IV. 7. Experimental Cp ratio for the CO_2 - CH_4 System.

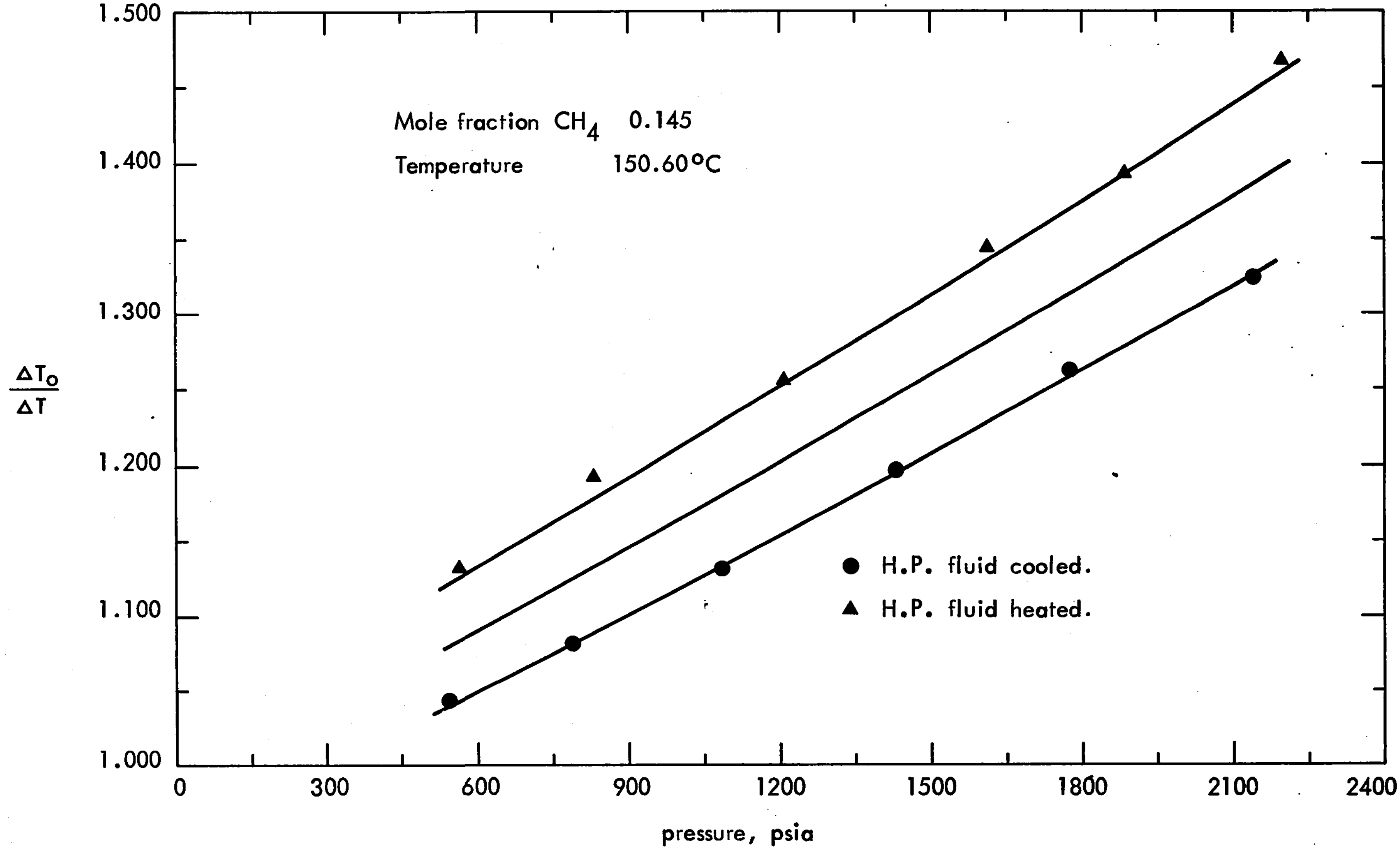


Figure IV . 8. Experimental Cp ratio for the CO_2 - CH_4 System.

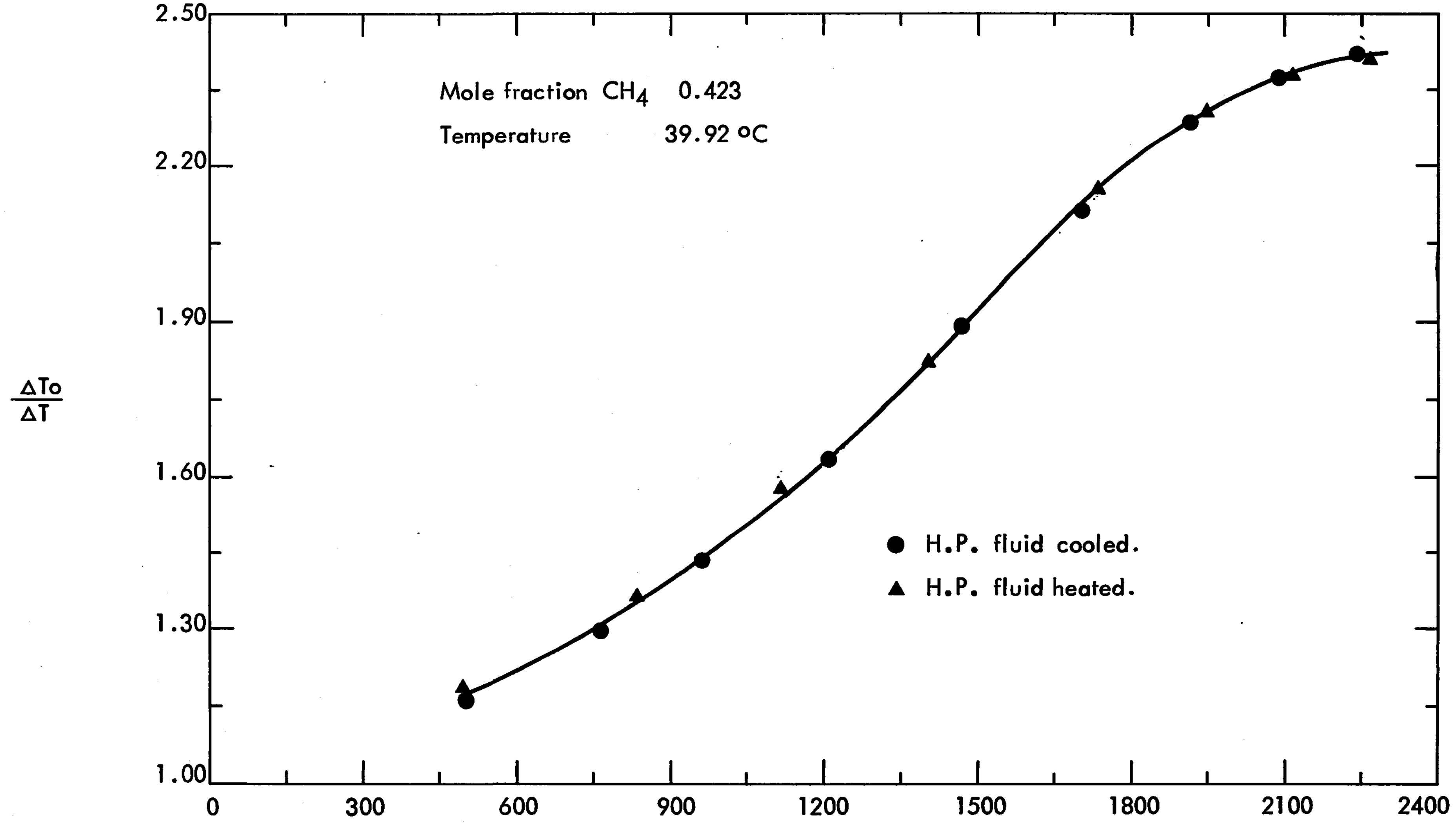


Figure IV . 9. Experimental Cp ratio for the CO_2 - CH_4 System

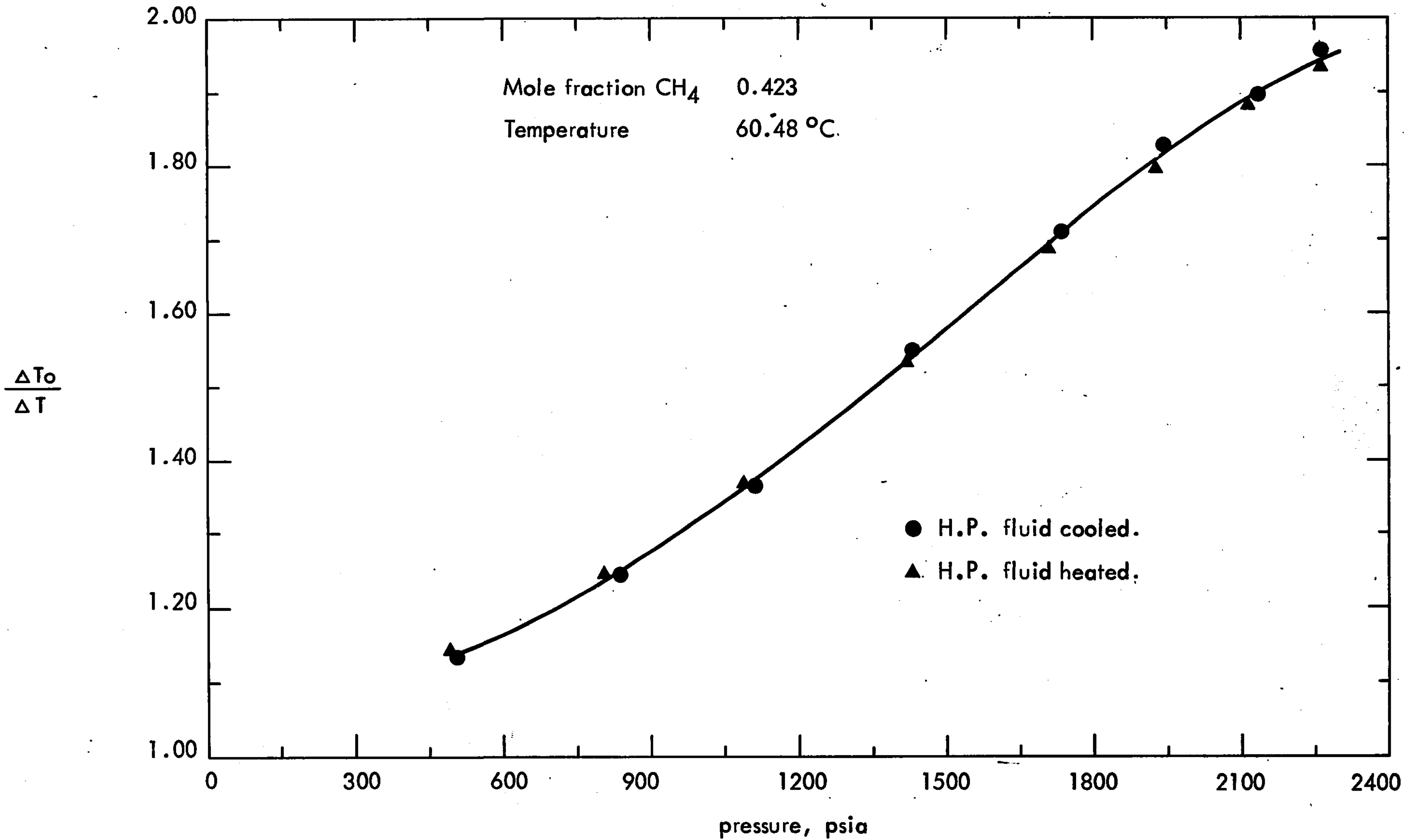


Figure IV. 10. Experimental Cp ratio for the CO_2 - CH_4 System.

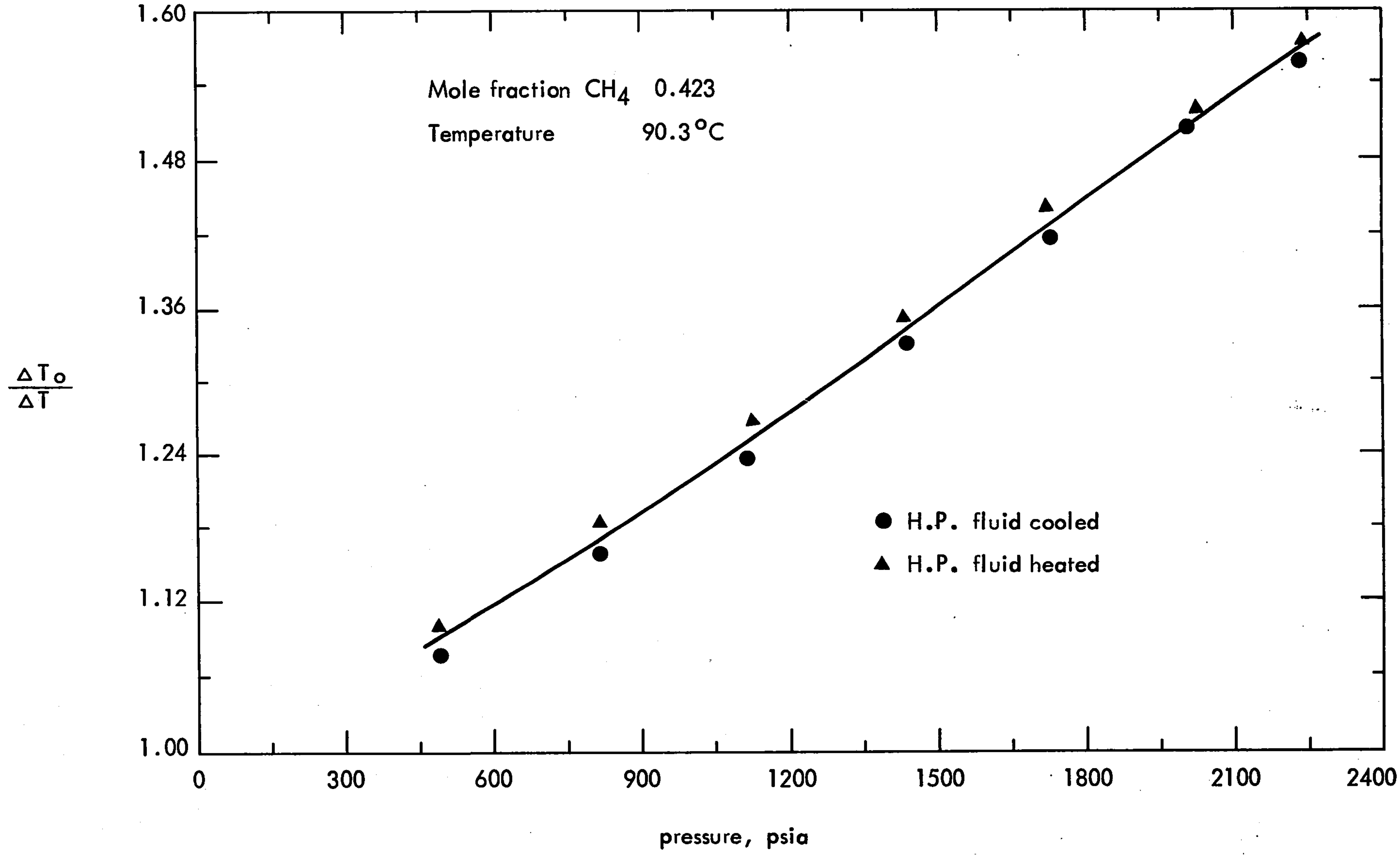


Figure IV . 11 . Experimental Cp ratio for the CO_2 - CH_4 System.

various "isotherm temperatures" were calculated from the BWR equation of state and the ideal gas heat capacity equations for carbon dioxide[68] and methane.[68] These equations approximate the ideal gas heat capacity data of carbon dioxide and methane reported by Woolley[69] and McBride et al.[68] respectively. The low pressure heat capacity, thus calculated, is also tabulated in each of the above tables and was used to calculate the heat capacities at elevated pressures from the heat capacity ratio data obtained in the present work. The heat capacities at pressures up to about 2250 psi at equal intervals of 50 psi are also reported in the above tables. The isobaric plots of C_p of the two binary mixtures were obtained from these tabulated values of the heat capacities and are shown in Figures IV.12 and 13.

C. Estimation of Accuracy

In order to estimate the overall accuracy of the experimental heat capacity ratios, the errors in the measurement of pressure, composition, temperature, and differential temperature are first considered separately.

1. Pressure Measurement -

During a steady state period the pressures of the high and low pressure streams were controlled such that the fluctuations were less than the precision of the pressure measurements. The absolute accuracy of pressure measurement by the Heise gauges was at least equal to the resolution of

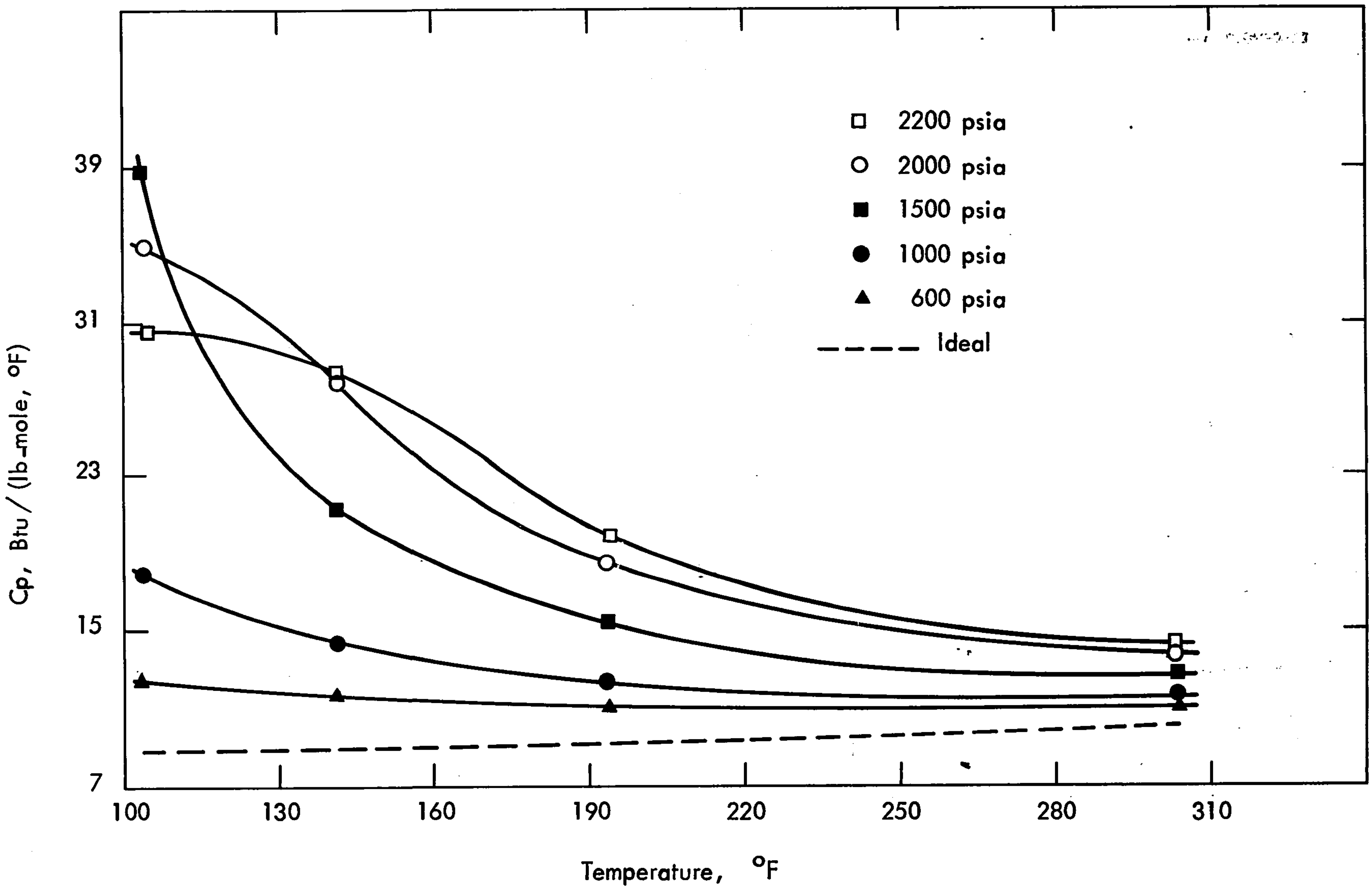


Figure IV . 12. Cp isobars of the CO_2 - CH_4 System — mole fraction CH_4 0.145.

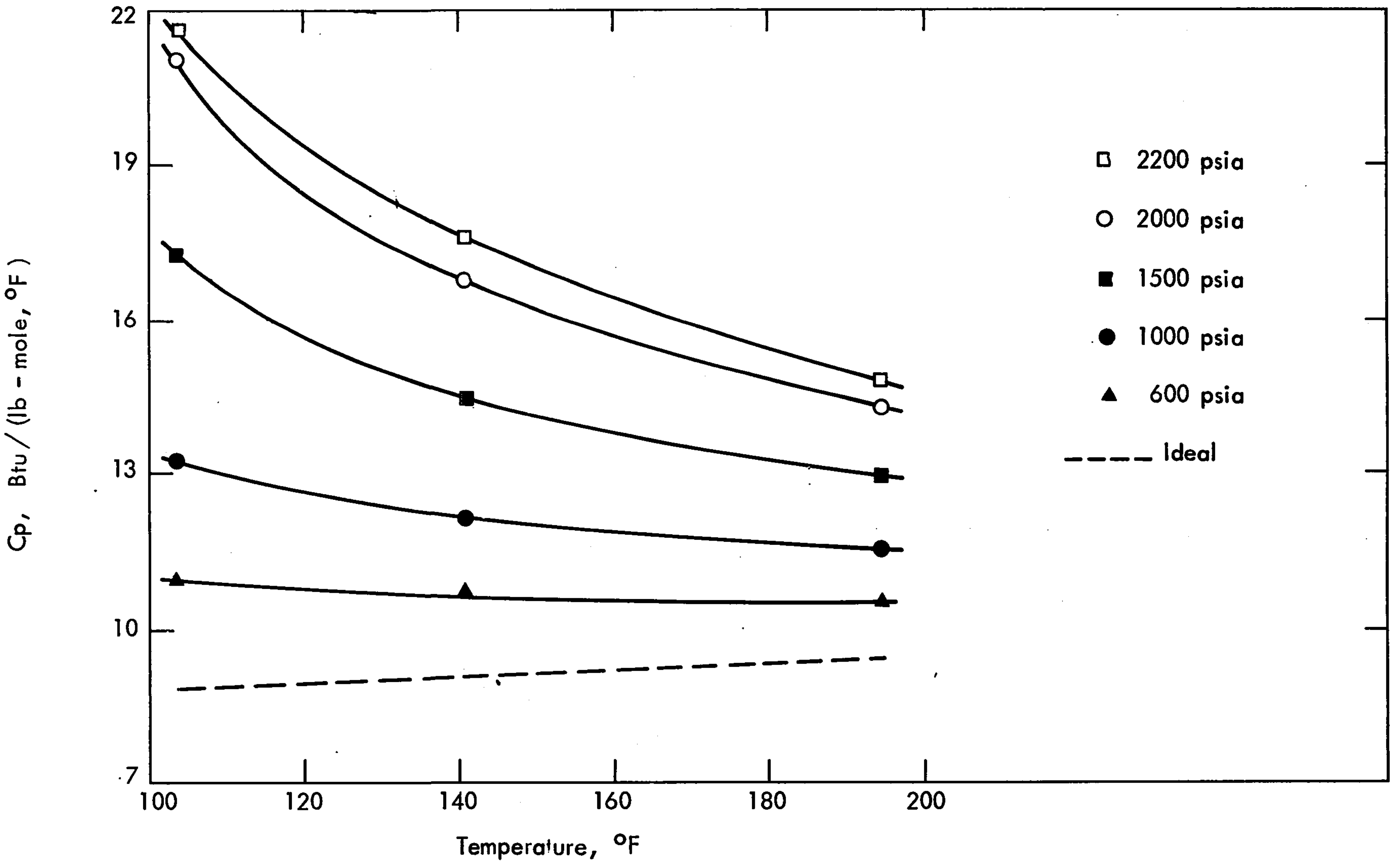


Figure IV .13. Cp isobars of the CO_2 - CH_4 System —

Mole fraction CH_4 0.423.

each gauge. The resolution of the high and low pressure gauges were 2 psi and 0.1 psi respectively. Thus the estimates of accuracy of pressure measurement is ± 1 psi for the high pressure fluid and ± 0.05 psi for the low pressure fluid.

2. Materials and Composition Determination -

a. Materials.

i. Nitrogen - The nitrogen supplied by a local supplier was used in the present work and according to the supplier's specifications had a minimum purity of 99.993 percent. The system was flushed several times with nitrogen by feeding fresh charge, circulating through the system and discharging to the atmosphere. The system was then charged with the required amount of gas and samples were drawn for mass spectrometer analysis. The analysis did not show any measurable impurities.

ii. Carbon dioxide - The carbon dioxide supplied by Canadian Liquid Air was stated to have the following chemical analysis:

CO_2	99.95 percent
S compounds	0 p.p.m.
CO	0 p.p.m.
oil	5 p.p.m.
balance	inerts

A mass spectrometer analysis of a carbon dioxide sample drawn from the cylinder did not show any measurable impurities.

iii. Methane - The methane used was supplied by Matheson and was of U.H.P. grade with the following chemical analysis according to the supplier:

CH_4	99.97 percent by volume
CO_2	$<$ 10 p.p.m.
O_2	9 p.p.m.
N_2	24 p.p.m.
C_2H_6	35 p.p.m.
C_3H_8	$<$ 5 p.p.m.

The mass spectroscopic analysis of the methane sample drawn from the cylinder did not show any measurable impurities.

The system was flushed several times with carbon dioxide and mixtures were prepared as explained in Appendix F.

b. Composition determination.

The composition of the carbon dioxide-methane mixtures was determined chromatographically. The procedure used and the experimental values are given in Appendix F. The precision of the composition determinations was approximately ± 0.2 mole percent.

3. Temperature Measurement -

The absolute accuracy of temperature measurement is equal to the sum of calibration, linearity and stability errors listed below:

a. The thermometer-probe combination is calibrated at the factory to within $\pm$ 0.02°C absolute, traceable to the U.S. National Bureau of Standards. To acheive this calibration accuracy, the ice-point correction was applied to each temperature reading. The ice-point calibration of the probes is given in Appendix E.

b. The linearity correction charts for each probe, giving corrections for the best straight line at

10°C increments, are furnished by the manufacturer and are reported in Appendix E.

c. <u>Stability</u>.

i. <u>Short term</u> - The expected reading to reading variation at constant probe temperature is less than 0.0001°C.

ii. <u>Long term</u> - Zero drift is less than ± 0.01°C at constant probe temperature for 30 days.

iii. <u>Hysteresis</u> - A hystersis of 0.001°C is typical over any 10°C span.

In summarizing then it could be said that the absolute accuracy of absolute temperature measurement is expected to be better than ± 0.~~04~~°C after applying the linearity and .02 ice-point corrections.

4. <u>Differential Temperature (ΔT and ΔT_e) Measurements</u> -

The maximum error on differential temperature measurement is equal to ± 0.025 percent of reading ± linearity correction ± 0.04°C. If we define

$$\Delta T_{corr.} = \Delta T \text{ obs.} \pm \text{ice-point correction} \pm \text{linearity correction}$$

the $\Delta T_{corr.}$ would have a maximum error of 0.025 percent of the reading ± 0.04°C. It must, however, be emphasized that the sign of the error in $\Delta T_{corr.}$ would be independent of the sign of the temperature change measured at any absolute temperature level.

Error in ΔT Ratios

For estimating the errors in the temperature change ratios ($\Delta T_o/\Delta T$), let us say that ΔT_o and ΔT are of the order of 5°C. Then the maximum error in ΔT or ΔT_o would be $\pm\ 0.04125^\circ$C.

If $\Delta T_o^{(t)}$ and $\Delta T^{(t)}$ represent the true values of ΔT_o and ΔT, corrected for the linearity and ice-point corrections, we may write:

$$\frac{\Delta T_o}{\Delta T} = \frac{\Delta T_o^{(t)}(1 \pm 0.04125/\Delta T_o^{(t)})}{\Delta T^{(t)}(1 \pm 0.04125/\Delta T^{(t)})}$$

$$\approx \frac{\Delta T_o^{(t)}}{\Delta T^{(t)}} \left[1 \pm \frac{0.04125}{\Delta T_o} \mp \frac{0.04125}{\Delta T}\right]$$

Therefore the largest fractional error in $\Delta T_o/\Delta T$ could be equal to $0.04125/\Delta T_o + 0.04125/\Delta T$. If ΔT_o and ΔT are of the same order of magnitude and the largest fractional error in $\Delta T_o/\Delta T$ ratio is represented by f_ℓ, we may say

$$f_\ell = \pm\, 0.0825/\Delta T$$

The most probable fractional error in ($\Delta T_o/\Delta T$) measurements may be approximated as:

$$f_p = \pm \sqrt{\left(\frac{0.04125}{\Delta T_o}\right)^2 + \left(\frac{0.04125}{\Delta T}\right)^2}$$

$$\approx \pm \frac{0.0585}{\Delta T} \text{ if } \Delta T_o = \Delta T$$

Therefore it may be concluded that the percent error in $\Delta T_o/\Delta T$ could be as high as 1.65 and most probable percent error in $\Delta T_o/\Delta T$ may be 1.17, assuming ΔT_o and ΔT are each equal to 5°C. For the carbon dioxide-methane mixtures these errors could be higher since the ΔT_o and ΔT are not equal and ΔT values are smaller than 5°C in certain regions.

Errors in the Heat Capacity Ratios

The following various types of errors are involved in the heat capacity ratio determinations:

1. The errors due to the differential temperature measurements
2. The errors due to the calorimeter inlet temperature fluctuations and deviations from a true steady state
3. The errors due to the difference of the calorimetery errors, such as heat leak and Joule-Thomson effects, in the two cases of heating and cooling the high pressure fluid
4. The uncertainties of temperature corrections and the errors introduced in assuming linear temperature dependence of heat capacities.

1. The Errors Due to the Differential Temperature Measurement -

The heat capacity ratios were calculated by averaging the $\Delta T_o/\Delta T$ ratios obtained for the two cases of heating and cooling the high pressure fluid. The heat capacity ratios thus obtained would be nearly independent of the absolute errors of measurement in ΔT, ΔT_o and $\Delta T_o/\Delta T$ ratios as illustrated below:

The errors in $(\Delta T_o/\Delta T)$ ratios are introduced by the measurement errors in ΔT and ΔT_o. It was pointed out earlier that at any temperature level the sign of the error in $\Delta T_{corr.}$ would be independent of the sign of the measured temperature change. For illustration, let us assume that the errors in the measurements of ΔT_o and ΔT are $+ \varepsilon_o$ and $- \varepsilon$ respectively (each would not be more than 0.025 percent of ΔT or ΔT_o plus 0.04^oC).

Case I: high pressure fluid cooled.

$$\Delta T = T_1 - T_2 = + \text{ve}$$
$$\Delta T_o = T_4 - T_3 = + \text{ve}$$
$$\Delta T_o/\Delta T = \frac{\Delta T_o^{(t)} + \varepsilon_o}{\Delta T^{(t)} - \varepsilon}$$
$$\approx \frac{\Delta T_o^{(t)}}{\Delta T^{(t)}}\left[1 + \frac{\varepsilon_o}{\Delta T_o^{(t)}} + \frac{\varepsilon}{\Delta T^{(t)}}\right]$$

where the superscript (t) indicates true value of the temperature changes and subscripts 1 and 3 represent the inlet and 2 and 4 represent the outlet locations of the calorimeter.

Case II: high pressure fluid heated.

$$DT = T_1 - T_2 = -\ \text{ve}$$

$$DT_o = T_4 - T_3 = -\ \text{ve}$$

$$\frac{-\ DT_o}{-\ DT} = \frac{-\ DT_o^{(t)} + \varepsilon_o}{-\ DT^{(t)} - \varepsilon}$$

$$\simeq \frac{DT_o^{(t)}}{DT^{(t)}} \left[1 - \frac{\varepsilon_o}{DT_o^{(t)}} - \frac{\varepsilon}{DT^{(t)}}\right]$$

Defining

$$E_1 = \Delta T_o/\Delta T \left[\varepsilon_o/\ \Delta T_o + \varepsilon/\Delta T\right]$$

and

$$E_2 = DT_o/DT \left[\varepsilon_o/DT_o + \varepsilon/DT\right]$$

we can write:

$$\Delta T_o^{(t)}/\Delta T^{(t)} \simeq \Delta T_o/\Delta T - E_1$$

$$DT_o^{(t)}/DT^{(t)} \simeq DT_o/DT + E_2$$

$$(C_p/C_{p_o})^{(t)} = 1/2 \left(\frac{\Delta T_o^{(t)}}{\Delta T^{(t)}} + \frac{DT_o^{(t)}}{DT^{(t)}}\right) + \frac{E_2 - E_1}{2}$$

Therefore

$$\frac{E_2 - E_1}{2} = 1/2 \left[\frac{DT_o}{DT} \left(\frac{\varepsilon_o}{DT_o} + \frac{\varepsilon}{DT}\right) - \frac{\Delta T_o}{\Delta T} \left(\frac{\varepsilon_o}{\Delta T_o} + \frac{\varepsilon}{\Delta T}\right)\right]$$

For the purpose of estimation let us say that temperature changes for the two streams are of the same order of magnitude in the two cases. Let us further assume that ε and ε_o

are each equal to $0.0413^{\circ}C$. The error in the C_p ratio could then be approximated by

$$\frac{E_2 - E_1}{2} \approx 1/2 \quad (\frac{\varepsilon_o}{\Delta T} + \frac{\varepsilon}{\Delta T})(\frac{DT_o}{DT} - \frac{\Delta T_o}{\Delta T})$$

$$= 0.0103(\frac{DT_o}{DT} - \frac{\Delta T_o}{\Delta T})$$

The largest difference between the temperature change ratios calculated for the two cases would occur at 150°C. Taking this difference as 0.10, an estimate of the C_p ratio error would be 0.001.

Summarizing the above discussion, it could be stated that although the maximum error in the $(\Delta T_o/\Delta T)$ ratios could be as high as 1.65 percent, the errors in the C_p ratios, introduced by the errors of differential temperature measurements, would not exceed 0.1 percent.

2. The Errors Due to the Calorimeter Inlet Temperature Fluctuations and the Deviations from a True Steady State -

During a "steady state period" the inlet temperatures of the high and low pressure streams were controlled such that the minimum and maximum temperatures of a stream were within $0.03^{\circ}C$. The difference between minimum and maximum values of the $(\Delta T_o/\Delta T)$ ratio for a data point could then be as high as 1.2 percent. This difference could be still higher for the carbon dioxide-methane mixtures at the points closer to the maxima of C_p versus pressure curve since the high pressure fluid temperature changes were smaller in this region. However, the standard deviation of a point from its mean value during the steady state period would of course be very much lower than 1.2 percent. In the data collected on the carbon dioxide-methane mixtures the root mean square percent error (percent standard deviation) of a point never exceeded 0.8 and for the majority of the points was less than 0.5. In general for any isotherm the percent r.m.s. error of a data point was higher at the higher pressures. This could be attributed to the relatively less stable flow conditions at the higher pressures.

A measured data point may have a very low r.m.s. error but may still deviate from its true value if the calorimeter did not reach a true steady state. To avoid any such possibility, the readings for a data point were taken at least 10 minutes longer than the time considered to be satisfactory for a steady state.

The deviation of a data point from its steady state value and its scatter about the mean value during the steady state period would be reflected by its deviation from the smooth curve obtained by the least squares fit. For almost all the data points collected on the carbon dioxide-methane mixtures, the deviation of a data point from the smoothed value did not exceed its r.m.s. error reported in the data tables of Appendix C. No statement to this effect could be made for the nitrogen data since the procedure followed for determining the $(\Delta T_o/\Delta T)$ ratios for these data was different than that followed from the carbon dioxide-methane mixtures. However, the standard deviations of fit for the 60°, 75° and 150°C isotherms of nitrogen were about 0.006, 0.002 and 0.004 respectively.

It may then be concluded from the above discussion that the expected repeatability of a data point for the $(\Delta T_o/\Delta T)$ ratio is about ± 0.5 percent. Since this is a random error the C_p ratios calculated from these data would also have an expected precision of about ± 0.5 percent. The expected precision about the maxima would be higher and could be about ± 1.0 percent. Since the errors of C_p ratios due to the differential temperature measurement errors are small compared to the repeatability errors due to inlet temperature fluctuations it could be stated that the absolute accuracy of the data would be within the repeatability errors stated above.

3. The Errors Due to the Difference of the Calorimetery Errors Such as Heat Leak and Joule-Thomson Effects, in the Two Cases of Heating and Cooling the High Pressure Fluid -

A direct quantitative estimation of errors of this type would be very difficult to make, however, some useful conclusions can be reached indirectly.

Any difference between the calorimetery errors in the two cases of heating and cooling the high pressure fluid should show as non-symmetry of the two ($\Delta T_o/\Delta T$) curves about their average. The data obtained showed a good symmetry of the two ($\Delta T_o/\Delta T$) curves for each isotherm about their mean curve. Furthermore when the mean curves for the nitrogen data at 60°, 75° and 150°C were extrapolated to a pressure equal to the low pressure, the value of C_p ratio calculated was found to be about 0.9955, 0.9986 and 1.0044 respectively. The deviation of the C_p ratio calculated at the low pressure was within the expected precision of the data and was random in behavior. It could be concluded that the terms Φ and Φ', derived in Appendix D for the two cases of heating and cooling the high pressure fluid, were almost of the same order of magnitude and the C_p ratios calculated were independent of the calorimetery errors.

In Figures IV.5, IV.6, IV.9 and IV.10 the two curves of cooling and heating the high pressure fluid either overlapped or crossed each other as they approached their maxima. In the region where the two curves either overlapped or crossed each other, the observed temperature changes of the high pressure fluid (ΔT) were small and hence a small error in either the ice-point or the linearity correction applied to the ΔT values could 'over-correct' the ($\Delta T_o/\Delta T$) ratios. Furthermore the difference between the two curves for these cases was within the r.m.s. errors of the data points. The errors in the ice-point and linearity correction could be looked upon as errors in the ΔT measurements, and hence, the errors in the calculated average values would be negligible as explained earlier.

In conclusion, then, it could safely be stated that the C_p ratios obtained in this work were free from calorimetery errors resulting from heat leak or Joule-Thomson effects due to pressure drops. If errors of this type existed at all, they were far smaller than the precision errors of the C_p ratios.

4. The Uncertainties of Temperature Corrections and the Errors Introduced in Assuming Linear Temperature Dependence of Heat Capacities -

The C_p isobars of nitrogen shown in Figure IV.4 indicate that the errors involved in assuming linear dependence of heat capacities upon temperature and calculating heat capacity ratios at an average temperature would be very small and could easily be neglected compared to the precision errors of the data obtained. Figures IV.12 and IV.13 contain the C_p isobars showing temperature dependence of the heat capacities for the binary mixtures of carbon dioxide and methane containing 14.5 and 42.3 mole percent methane respectively. These plots indicated that the uncertainties in temperature corrections and the errors of calculating the heat capacity ratios at an average temperature would be larger for the values of the mixture containing 14.5 mole percent methane. These errors would be the largest for the C_p ratios obtained at 39.7°C in the pressure range of 1300 and 2000 psi for this mixture. The largest difference between the experimental C_p values and those predicted by the BWR equation that was used in applying temperature corrections was found to be about 22 percent. The largest temperature correction applied to the ΔT ratios was about 0.1 at a value of about 3.8. This resulted in an uncertainty in temperature correction of about 0.5 percent in the worst possible case. It could further be seen from Figure IV.12 that the largest deviation from linear temperature dependence of C_p occurs in the vicinity of the inflection in the curves and would not be more than 0.5 percent over a temperature change of about 15°F. Thus, calculating the C_p ratio at an average temperature could introduce a maximum possible error of about 0.5 percent in the mean C_p values. The combined effect of reporting the C_p values at an average temperature and the application of temperature correction could then, at worst, be as high as one percent in the region of a maximum. It must be emphasized that the C_p ratios reported in this work were the ratios of the mean heat capacities over a temperature change that took place in the calorimeter.

In summarizing, the following limits of errors for the heat capacity ratio determinations would be considered realistic:

	Maximum Error
a. Nitrogen data	
i. Pressure	± 1 psi
ii. Temperature	± 0.04°C ?
iii. Temperature difference	± 0.0413°C
iv. Temperature difference ratios	± 1.65 percent
v. Heat capacity ratios	± 0.5 percent
b. Carbon dioxide-methane mixture data	
i. The errors of pressure, temperature, temperature difference and temperature difference ratios would be the same as those in the nitrogen data.	
ii. Heat capacity ratios	± 0.5 percent (in the region removed from the maxima) ± 1.0 percent (close to the maxima)
iii. Composition	± 0.2 mole percent

The heat capacity values reported in the Tables IV.1 through IV.10 would have additional errors due to the polynomial approximations of the ideal gas heat capacities and the calculations of the low pressure heat capacities from the ideal gas values.

D. Comparison With Literature Values

A comparison at some points of the heat capacity ratios of nitrogen obtained in this work with the experimentally determined values of Balaban,[16] Workman,[63] and Mackey and Krase[54] is given in Table IV.11. The original data of Balaban and Workman report the ratios of heat capacity at various pressures to that at one atmosphere. The values reported in the above table were calculated from these data and the ratio of heat capacity at one atmosphere to the heat capacity at 27 psi. Mackey and Krase report the heat capacities of nitrogen from which the ratios of heat capacity at a pressure to the heat capacity at one atmosphere were calculated and then these values were converted to the values reported in the table by the method followed for the data of Balaban and Workman.

Table IV.12 gives a comparison of the experimental heat capacity ratios of nitrogen determined in this work with the ratios obtained from the calculated heat capacity results of Lunbeck et al.[70] and Wood.[66] The values of Lunbeck et al. and Wood, reported in the table were calculated by the method used for the data of Mackey and Krase as explained above.

The comparison with the literature experimental values at 60°C showed that the values obtained in this work were higher by about 0.003 at the lower pressures and by about 0.007 at the higher pressures. However, at 150°C the values in this work were higher at the lower pressures but they agreed at the higher pressures.

The calculated values of Lunbeck et al. at 60°C

TABLE IV.11

COMPARISON OF EXPERIMENTAL HEAT CAPACITY RATIOS OF NITROGEN

Temp. °C (approx.)	Pressure psia	*Balaban[16]	*Workman[63]	*Mackey and Krase[54]	This Work
60	711	1.056	1.054	-	1.059
60	996	1.075	1.077	-	1.083
60	1280	1.098	1.098	-	1.105
60	1565	1.117	1.118	-	1.126
60	1849	1.137	1.138	-	1.144
150	735	-	-	1.032	1.038
150	1469	-	-	1.056	1.065
150	1800	-	-	1.072	1.075
150	2200	-	-	1.084	1.084

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*See text for the explanation of how these ratios are calculated from the original data.

TABLE IV.12

COMPARISON OF EXPERIMENTAL AND CALCULATED HEAT CAPACITY RATIOS OF NITROGEN

Temp. °C (approx.)	Pressure psia	*Lunbeck et al.[70]	*Wood[66]	This Work
60	735	†1.058	-	1.061
60	1469	†1.113	-	1.119
60	700	-	1.054	1.058
60	1500	-	1.112	1.122
60	2200	-	1.154	1.165
75	735	1.051	-	1.048
75	1469	1.100	-	1.099
75	1800	†1.123	1.117	1.122
75	2100	†1.138	-	1.143
75	700	-	1.048	1.046
75	1500	-	1.100	1.102
75	2000	-	1.127	1.136
150	735	1.028	-	1.038
150	1469	1.057	-	1.065
150	1800	†1.069	1.072	1.075
150	2000	-	1.079	1.080
150	2100	†1.079	-	1.082
150	2200	†1.083	1.085	1.084

---

*See text for the explanation of how these ratios are calculated from the original data

†Interpolated values

were obtained by interpolating their reported values at 50° and 75°C. The results of Workman and Balaban seemed to agree with the calculated values of Lunbeck et al. at this temperature. Hence it could be expected that the values of Lunbeck et al. at 75°C would be very close to the experimental values. A comparison of the C_p ratios obtained in this work at about 75°C with those of Lunbeck et al. showed that the values of this work were lower by about 0.003 at the lower pressures, had a good agreement at medium pressures and were higher by about 0.005 at the higher pressures. A comparison with the calculated values of Wood showed similar trend at this temperature.

A comparison of the calculated values of Wood and Lunbeck et al. at 150°C with the results of this work showed a behavior similar to that observed in the comparison with the values of Mackey and Krase.

All the literature experimental and calculated values of the heat capacity ratios of nitrogen that were compared in the above tables agreed with the results obtained in this work within the expected accuracies of about ± 0.5 percent for this work and the literature results.

Since the experimental data on the carbon dioxide-methane mixtures were not available in the literature, comparisons could not be made. However, the heat capacities of carbon dioxide-methane mixtures were calculated at the temperatures and compositions corresponding to the data obtained in this work, and at pressures up to 2250 psi with an interval of 200 psi. The calculations were performed with the help of the BWR equation of state and the BWR mixing rules.[71] The parameters of carbon dioxide and methane, reported by Cullen and Kobe[72,73] and Douslin et al.[30] respectively, were utilized in the above calculations. The deviations of the calculated values from the heat capacities reported in Tables IV.4 through IV.10 were estimated and the r.m.s. and largest percent deviations were evaluated. The results are summarized as follows:

mole percent methane	r.m.s. percent deviation in C_p	largest percent deviation in C_p	no. of points
14.49	23.50	51.33	41
42.30	6.96	16.26	30

In general, the deviations were larger for the 14.49 mole percent methane mixture and were largest at 563.15°R (39.71°C) for this composition. The experimental and calculated heat capacities at this isotherm are plotted in Figure IV.14 for illustration. The large deviations as shown above emphasize the importance of determining experimentally the heat capacities of the carbon dioxide-methane system.

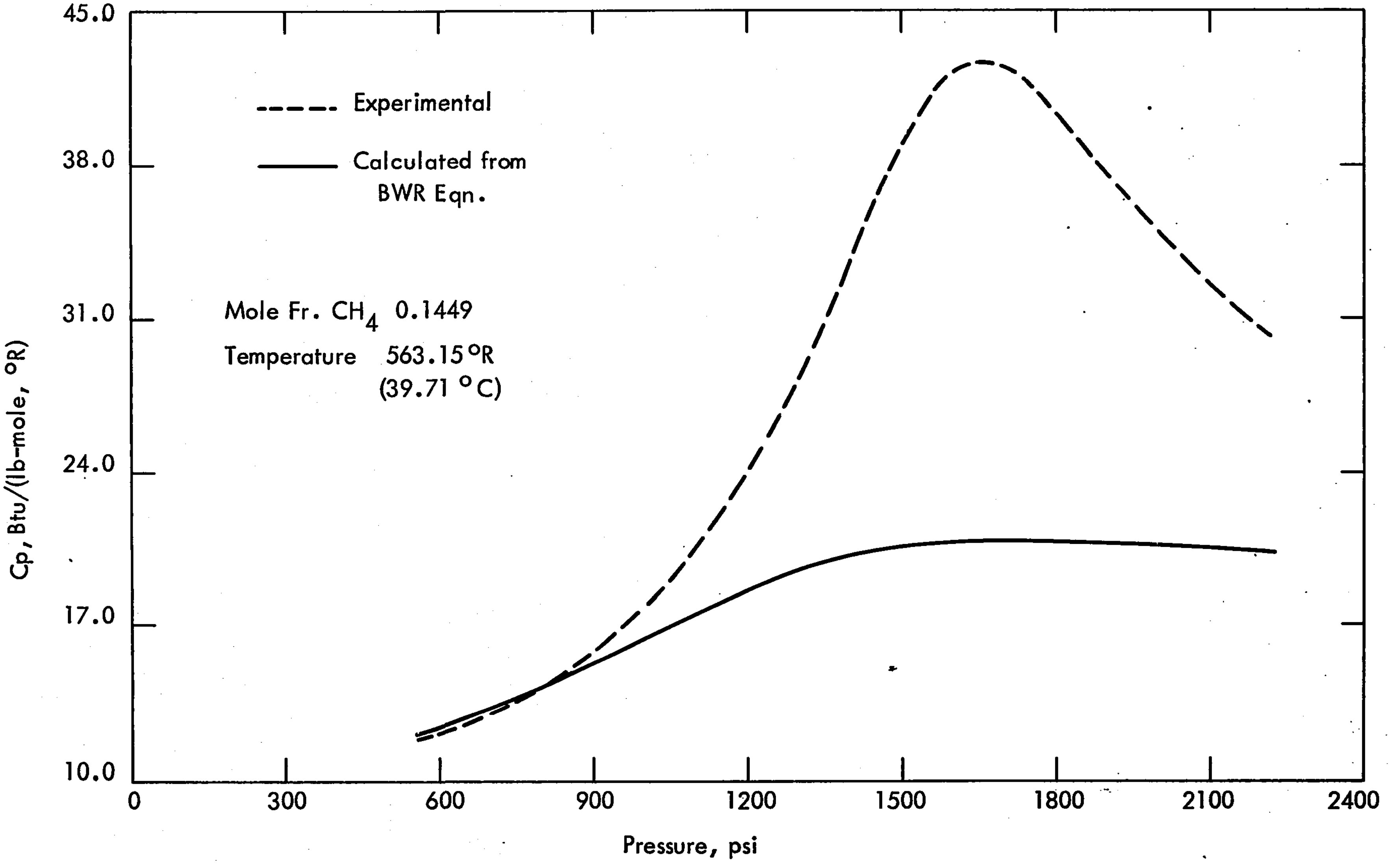

Figure IV . 14. Experimental and Calculated (from literature BWR Parameters) C_p of the CO_2 - CH_4 system.

V - PROCEDURES FOR CORRELATING THERMODYNAMIC PROPERTIES

The importance of knowing the thermodynamic properties of a fluid for studying various processes cannot be overemphasized. The relationship of these properties to their independent state variables can be represented graphically, tabulated, or given by an equation. A relationship in the form of an equation is called an equation of state of the fluid and it contains a number of parameters together with the independent state variables. These parameters are sometimes also known as the equation of state constants or simply the constants of the fluid. The property volume has been studied very extensively and hence for subsequent discussions a functional relationship between the pressure, temperature and volume will be referred to as an equation of state.

If a satisfactory equation of state and the ideal gas heat capacities are known, it is possible, at least in theory, to calculate all the thermodynamic properties of a system. An equation of state may be called satisfactory if it can meet the following two requirements:

1. The equation must be able to represent accurately the volumetric behaviour of the system at least over a certain range of pressure and temperature.
2. The equation must permit the calculation of the

thermodynamic properties of a system within a reasonable degree of accuracy.

The object of all efforts to develop a satisfactory equation of state is to find a relationship which is suitable in form for all materials but which allows for the differences between materials in the assignment of values to the constants appearing in the equation. It has been found in practice that a single set of constants for any equation is unable to predict with good accuracy the volumetric behaviour of a fluid over the complete range of conditions. However, a given equation of state may correlate the volumetric behavior of a system over a limited range with satisfactory accuracy but it may completely fail to make even reasonable estimations of the thermodynamic properties such as enthalpy and heat capacity, which require the determination of derivatives from this equation. The uncertainty of predictions builds up with successive differentiation of the equation.

An equation of state may have a thermodynamic or a kinetic basis for its derivation. The forms of almost all the important equations of state have been derived on the basis of certain kinetic considerations and their parameters have been evaluated from the experimental knowledge of the volumetric data by considering these equations empirical. In the past few years a considerable amount of experimental data on the thermodynamic properties such as enthalpy departure, heat capacity and Joule-Thomson effect has been made available in the literature. This information should be utilized to improve the existing forms and evaluate the parameters of a model describing the thermodynamic state so that a simultaneous prediction of volumetric behaviour as well as the properties can be made satisfactorily. Some attempts have been made recently[74,75] in this direction but complete success still remains elusive.

As mentioned earlier, the main aim of this work was to develop a suitable facility and to obtain experimental data on heat capacities. It was not the primary purpose of this work to develop a new form of an equation or to find new methods of evaluating the parameters. However, some of the methods of evaluating the parameters of an equation from volumetric data alone and from volumetric and thermal data were examined. The methods, which were considered attractive, were extended to utilize the volumetric and heat capacity information for evaluating the parameters of an equation of state. The methods of correlating the mixture properties and their possible improvements were also examined.

A. Selection of Models

As mentioned earlier, a large number of equations of state have been proposed in the literature. In the past few years the Benedict, Webb and Rubin (BWR) equation[76] has been widely used for correlating the thermodynamic behaviour of hydrocarbons. Hence for the subsequent considerations of the thermodynamic correlation methods the BWR equation is used as a model for the volumetric behaviour. However, it should be emphasized that the methods are general and can be adapted for any model that one might choose.

It would be convenient to express the behaviour of mixtures in terms of the known behaviour of the pure components and the composition. Experimental investigations and theoretical considerations indicate that the equations of state used for pure gases can be applied to gas mixtures. Thus, if an equation of state can be used to represent the thermodynamic behaviour of each component in the mixture, the simplest way to describe the behaviour of the mixture would be by means of some combination of constants of the equation for the components. The methods of combining these constants are generally known as mixing or combining rules. Many mixing rules have been proposed in the literature but again none of these are entirely satisfactory. For the BWR equation, Benedict et al.[71] have recommended combining rules to calculate the mixture coefficients.

When the experimental data on a given mixture are available, the constants can be easily determined in the same manner as for a pure substance. In the case of a binary mixture it has frequently been assumed on the basis of kinetic theory that a mixture constant, k_m, is related to the constants for the pure components, k_{ii} and k_{jj} by the equation

$$k_m = \sum_i \sum_j k_{ij} x_i x_j$$

$$= k_{ii} x_i^2 + 2 k_{ij} x_i x_j + k_{jj} x_j^2 \qquad (V.1)$$

where k_{ij} is the interaction constant and x_i and x_j the mole fractions for components i and j respectively.

Tiwari[77] has suggested that the mixing rule (V.1) be incorporated in the data correlation scheme and that the constants be determined directly. In this case, twenty-four constants are determined for the BWR model from mixture and pure component volumetric data.

The mixture data have a source of error in composition determination which the pure component data do not have. Hence more weight may be given to the co-efficients of the pure components determined from pure component data. This may be achieved by first evaluating the pure component coefficients, substituting these values into equation (V.1) and then determining only the interaction constants from the mixture data. This method will have the added advantage that the interaction constants thus determined may be correlated to the pure component co-efficients and the composition. If different types of mixtures are treated in this way and the interaction co-efficients determined for a variety of combination of different molecules, some generalized mixing models may be formulated. This work does not concern itself with mixing model formulation but the suggested method of determining interaction constants was used for the carbon dioxide-methane mixtures just to demonstrate that this kind of approach is feasible.

B. Mathematical Techniques

The equation of state may be used as an approximating function for the actual behaviour of a gas. The parameters estimated are not unique but depend upon the closed limits of the experimental data used and the criterion of best fit chosen for their evaluation. Generally speaking any of the following three criteria of fit may be used:

1. Minimizing the sum of absolute deviations
2. Minimizing the maximum absolute error (the Chebyshev criterion)
3. Minimizing the sum of squares of deviations (the least squares criterion).

1. Sum of Absolute Deviations -

The problem formulation and its solution by linear programming procedures using the criterion of minimizing the sum of absolute deviation is given by Wagner.[78] However, this criterion has not been commonly used to correlate the thermodynamic properties and hence in the present work it was not considered further.

2. Chebyshev Criterion -

Wagner[78] and Leung[79] utilized this criterion to formulate the problem of data correlation and suggested its solution using a linear programming technique. Leung developed a computer programme to evaluate the BWR parameters from the volumetric data of methane. Clare[74] used this program for the Martin-Hou equation and extended it to handle the additional constraints of enthalpy departures.

A detailed explanation of data correlation by linear programming is given by Wagner[78] and Leung[79], however only the concept of problem formulation is summarized here.

Consider the approximating function,

$$y_i = \sum_{j=1}^{n} \alpha_j \, g_j \, (x_i) \tag{V.2}$$

where y_i and x_i are the dependent and independent variables for the data point i, α_j are the parameters associated with the specified functions $g_j \, (x_i)$ and n is the number of parameters. Employing the Chebyshev criterion of best fit, we seek α_j such that

$$\underset{\alpha_j}{\text{minimize}} \ \{\underset{i}{\text{maximum}} \left| \sum_j \alpha_j \, g_j \, (x_i) - y_i \right| \} \tag{V.3}$$

We can now transform (V.3) to the linear programming model as follows:

$$\text{minimize } \lambda \text{(non-negative)} \tag{V.4a}$$

Subject to the constaints:

$$- \lambda \leqq \sum_{j=1}^{n} \alpha_j \; g_j \; (x_i) - y_i \leqq \lambda \tag{V.4b}$$

$$i = 1, 2, \ldots m$$

or

$$\text{minimize:} \quad Z = \lambda \tag{V.5}$$

Subject to the constraints

$$- \sum_{j=1}^{n} \alpha_j \; g_j \; (x_i) + \lambda \geqq - y_i \tag{V.5a}$$

$$\sum_{j=1}^{n} \alpha_j \; g_j \; (x_i) + \lambda \geqq y_i \tag{V.5b}$$

$$i = 1, 2, \ldots m$$

In these equations, m is the number of data points.

With the introduction of slack and artificial variables the problem becomes:

$$\text{minimize} \quad z = \lambda + M \sum_{i=1}^{m} u_i \tag{V.6}$$

where M is a penalty co-efficient, subject to:

$$\lambda + \sum_{j=1}^{n} (\beta_{1_j} - \beta_{2_j}) \; g_j \; (x_i)$$

$$- V_{1_j} + u_i = y_i \tag{V.7a}$$

$$\lambda - \sum_{j=1}^{n} (\beta_{1_j} - \beta_{2_j})\ g_j\ (x_i) + V_{2_i} = - y_i \qquad \text{(V.7b)}$$

$$i = 1, 2, \ldots m$$

where V_{1_i}, V_{2_i} are the slack variables and u_i are the artificial variables. The parameters α_j are not restricted in sign so the substitution

$$\alpha_j = \beta 1_j - \beta 2_j$$

was made. Thus all the variables λ, $\beta 1_j$, $\beta 2_j$, V_{1_i}, V_{2_i}, and u_i are non-negative.

The problem formulated by (V.6), (V.7a), and (V.7b) can be solved by the Simplex algorithm[80] to obtain an optimum solution for α_j. However, if the number of data points, m, is very large the problem becomes too large to handle. An elegant way to get around this difficulty is to formulate a dual* of the primal problem stated by (V.5), (V.5a) and (V.5b). The dual formation is

$$\text{maximize } B = \sum_{i=1}^{m} y_i\ d_{2_i} - \sum_{i=1}^{m} y_i\ d_{1_i} \qquad \text{(V.8)}$$

Subject to the constraints

$$- \sum_{i=1}^{m} g_j\ (x_i)\ d_{1_i} + \sum_{i=1}^{m} g_j\ (x_i)\ d_{2_i} = 0 \qquad \text{(V.9a)}$$

$$j = 1, 2, \ldots n$$

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*A comprehensive discussion on Duality Theorem in linear programming is given by G. Hadley in his book Linear Programming, Chapter 8; Addison-Wesley Publishing Company, Inc., 1963.

and

$$\sum_{i=1}^{m} d1_i + \sum_{i=1}^{m} d2_i \leqq 1 \qquad \text{(V.9b)}$$

$d1_i$, $d2_i$ non-negative.

The model defined by (V.8), (V.9a) and (V.9b) is a regular linear programming problem in n + 1 relations and may be solved by the standard Simplex alogrithm.[80]

Now to convert (V.9b) into an equation, a slack variable has to be introduced. However, if we assume that we are dealing with a non-trivial case, in which $\lambda > 0$, this slack variable will not enter the optimal solution at a positive level--in other words this slack variable cannot be in the final basis and must therefore take a value of zero.[79] Thus the constraint (V.9b) may be written as

$$\sum_{i=1}^{m} d_{1_i} + \sum_{i=1}^{m} d2_i = 1 \qquad \text{(V.9c)}$$

When the optimal solution is reached

$$(Z)_{opt} = (\lambda)_{opt} = (B)_{opt}$$

it can be seen that the optimal basic vector of the dual system will correspond to those constraints in the primal that gives the optimum λ. After solving these constraints in the primal in the form of equalities the various coefficients α_j and λ will be determined.

The advantage of this approach is that the number of constraints in the dual is equal to the number of coefficients plus one for λ; thus it is independent of the number of data points. Furthermore, if an extra co-efficient in the primal system is required, it is equivalent to an additional constraint in the dual.

A thermodynamic property can be expressed explicitly in terms of the equation of state parameters and the state variables. Such a relationship can be easily derived from the laws of thermodynamics and the equation of state. Suppose the property q and the equation of state are expressed by

$$P_i = f(V_i, T_i, \alpha_j) \qquad \text{(V.10)}$$

$$q_i = G(V_i, T_i, \alpha_j) \qquad \text{(V.11)}$$

where α_j are the parameters and P_i, V_i, T_i are pressure, volume and temperature for the data point i. The experimental information on q can be used as additional constraints in the formulation of the linear programming problem as follows:

minimize the maximum absolute deviation λ and β

subject to

$$|P_i - f(V_i, T_i, \alpha_j)| \leqq \lambda \qquad \text{(V.12a)}$$

$$|q_i - G(V_i, T_i, \alpha_j)| \leqq \beta \qquad \text{(V.12b)}$$

This problem cannot be solved directly, as linear programming allows the optimization of only one objective function. The formulated problem contains two objective functions, λ and β. Clare[74] has suggested two means of overcoming this difficulty.

1. Let $\beta = \omega\lambda$, where ω is arbitrary known weighting factor. This may be based on the relative accuracy of the two kinds of data.
2. Let $\beta = K$, where K is some predecided arbitrary constant.

Caution must be exercised when using method (2). If the constant K specified is too small, there may not be a solution to the linear programming problem.

Instead of minimizing the maximum absolute deviation, the maximum absolute relative deviation may be minimized. The formulation then can be stated as:

$$\text{minimize } Z = \lambda \tag{V.13a}$$

Subject to

$$\left| \frac{P_i - f(V_i, T_i, \alpha_j)}{P_i} \right| \leqq \lambda \tag{V.13b}$$

$$\left| \frac{q_i - G(V_i, T_i, \alpha_j)}{q_i} \right| \leqq \beta \tag{V.13c}$$

The problem stated by (V.12) or (V.13) can be solved by dual transformation as discussed earlier.

The linear programming technique of data fitting has the following characteristics.[74]

1. The approximating function has to be linear in parameters. It can be any linear combination of the specified functions.
2. No specific data point spacing is required.
3. The data to be fitted must be well smoothed and free of large random errors for the results to be meaningful. However, large random errors can be detected by careful examination of the data points which control the fit. Several controlling data points occurring within a small range of the variables indicates a questionable data point. Data points in such a region should be graphically plotted in order to pinpoint a possible error.
4. There are no computational difficulties encountered in solving for the equation co-efficients, even for high order equations. The method does not suffer from the ill-conditioning problems usually encountered in the least squares method.
5. Various constraints on the function fit such as derivatives of the function can readily be incorporated into the fitting procedures.
6. If an extra co-efficient in the primal system is required, it is equivalent to an additional constraint in the dual. For fitting this additional

constraint the calculation need not be repeated from the beginning.

Heat capacity data and the linear programming technique. The BWR equation and the derived relationships for enthalpy and heat capacity departures are given in Appendix G. The BWR and the enthalpy departure equations are linear functional relationships between the equation of state parameters for a known value of the co-efficient γ which appears in the exponential term. Thus these approximating functions can be handled by the linear programming technique for an assumed value of γ. If different assumed values of γ are tried, the value of the objective function obtained in the optimum solution can be plotted against γ and the quantity γ corresponding to the minimum can be located.

The functional relationship of heat capacity departure is non-linear and cannot be easily linearized. Thus if the information of experimentally determined heat capacities for any system are to be utilized directly, linear programming does not appear to be a suitable technique for evaluating the parameters of the BWR equation. However the heat capacity data can be used to calculate the isobaric enthalpy changes. The isobaric enthalpy change can be related to the enthalpy departure equation in the following manner:

$$dH = (\partial H/\partial T)_p dT + (\partial H/\partial P)_T dP$$

Integration between state 1 of P_1, T_1 and state 2 of P_2, T_2 can be done along two alternate paths:

$$H_2 - H_1 = \int_{T_1}^{T_2} (\partial H/\partial T)_{P_1} dT + \int_{P_1}^{P_2} (\partial H/\partial P)_{T_2} dP$$

(V.14)

or alternatively,

$$H_2 - H_1 = \int_{T_1}^{T_2} (\partial H/\partial T)_{P_2} dT + \int_{P_1}^{P_2} (\partial H/\partial P)_{T_1} dP$$

(V.15)

If $P_1 \rightarrow 0$, $(\partial H/\partial T)_{P_1} = C_p o$ = ideal gas heat capacity. Since enthalpy is a state property, (V.14) and (V.15) can be equated:

$$\int_{T_1}^{T_2} C_{p}o dT + \int_{0}^{P_2} (\partial H/\partial P)_{T_2} dP = \int_{T_1}^{T_2} C_p dT + \int_{0}^{P_2} (\partial H/\partial P)_{T_1} dP$$

(V.16)

or

$$\int_{0}^{P_2} (\partial H/\partial P)_{T_2} dP - \int_{0}^{P_2} (\partial H/\partial P)_{T_1} dP = \int_{T_1}^{T_2} C_{p2} dT - \int_{T_1}^{T_2} C_{p}o dT$$

(V.17)

where C_p is the heat capacity along the isobar P_2. The terms

$\int_{0}^{P_2} (\partial H/\partial P)_{T_2} dP$ and $\int_{0}^{P_2} (\partial H/\partial P)_{T_1} dP$ are the enthalpy departures along the isotherms T_2 and T_1 respectively. Each of these terms can be expressed in terms of the equation parameters by the relation given in Appendix G. For brevity assume that the functional relationships can be epxressed as:

$$\int_0^{P_2} (\partial H/\partial P)_{T_2} dP = D_{P_2,T_2}(\alpha_j) \quad \text{and} \quad \int_0^{P_2} (\partial H/\partial P)_{T_2} dP = D_{P_2,T_2}(\alpha_j) \tag{V.18}$$

Substituting (V.18) into (V.17):

$$D_{P_2,T_2}(\alpha_j) - D_{P_2,T_1}(\alpha_j) = \int_{T_1}^{T_2} C_{p2} dT - \int_{T_1}^{T_2} C_{po} dT \tag{V.19}$$

The first term on the right hand side of (V.19) can be calculated by integrating the experimental heat capacity data along the isobar P_2 between the temperatures T_1 and T_2. The second term can be calculated from the ideal gas heat capacity data. The left hand side is a functional relationship of enthalpy departure difference along the two isotherms T_2 and T_1. Thus the information of isobaric enthalpy changes, calculated from the experimental heat capacity data, can be used as additional constraints in the formulation of the linear programming problem defined by (V.12) or (V.13) and substituting

$$q = \int_{T_1}^{T_2} C_p dT - \int_{T_1}^{T_2} C_{po} dT \tag{V.20}$$

and

$$G(V_i,\ T_i,\ \alpha_j) = D_{P_2T_2}(\alpha_j) - D_{P_2T_1}(\alpha_j)$$

(V.21)

The computer programme of Clare[74] was modified so as to handle the enthalpy departure difference constraints. The modified programme is more general and is capable of trying different values of γ and/or calculating co-efficients for one given value of γ with or without enthalpy departure difference constraints. By the choice of a suitable 'flag' the maximum absolute deviation or relative deviation can be minimized. The listing of this modified programme and the explanation for its use are given in Appendix H.

A computer programme was also developed to calculate the interaction constants in the mixing rule (V.1) from the mixture data and the pure component co-efficients. The listing and the explanation for use of this programme are also given in Appendix H.

3. Least Squares Criterion -

The Gaussian "law" of errors states that measurements of a given quantity which are subject to accidental errors are distributed normally about the mean of the observations. This may be stated in a functional form as:

$$f(y|x) = \frac{1}{\sigma(y)\sqrt{2\pi}} \cdot \exp\{-(y - \bar{y})^2/2\sigma(y)^2\}$$

(V.22)

where $f(y|x)$ is the probability density function of y for a given value of x, and $\sigma(y)$ and $\bar{y}$ are the standard deviation and mean of the observations of y. The parameters $\bar{y}$ and $\sigma(y)$ characterize this normal distribution. Though the Gaussian error 'law' or the normal error 'law' is by no means universally true, it has been widely assumed to hold for experimental observations in the scientific field.

Suppose we have M experimental data points y_i, x_{1i}, x_{2i}, . . . x_{pi} for the variables Y_i, X_{1i}, X_{2i}, . . . X_{pi} ($i = 1, 2, . . . M$). Let us also assume Y to be the dependent variable and the X's to be the independent variables. Furthermore, let the mean or the expected value of Y for any ith observation of X's be given by

$$E(Y|X) = f(X_{1i}, X_{2i}, . . . X_{pi}, \alpha_1, \alpha_2, . . . \alpha_N) \tag{V.23}$$

where α_j are the co-efficients or the parameters (no distinction is made here between the term co-efficients and parameters though the latter is normally used when the co-efficients are estimated from an infinite number of data points) and p is the number of independent variables. If the normal "error" law holds for Y, the probability density function of Y_i for given values of X_i's can be written as:

$$f(Y_i|X) = \frac{1}{\sigma(Y_i)\sqrt{2\pi}} \exp\left[-\frac{1}{2}.\{ \frac{y_i - E(Y_i|X)}{\sigma(Y_i)} \}^2 \right] \tag{V.24}$$

where y_i is the experimentally observed value of the variable Y for the ith observation. If each of M observations can be considered as an independent event, the joint probability density function for the set can be written as:[81]

$$\prod_{i=1}^{M} f(Y_i|X) = \prod_{i=1}^{M} \frac{1}{\sigma(Y_i)\sqrt{2\pi}} \exp\left[-\frac{1}{2}\cdot\left\{\frac{y_i - E(Y_i|X)}{\sigma(Y_i)}\right\}^2\right]$$

$$= \left(\prod_{i=1}^{M} \frac{1}{\sigma(Y_i)\sqrt{2\pi}}\right)\cdot \exp\left[-\frac{1}{2}\cdot\sum_{i=1}^{M}\left\{\frac{y_i - E(Y_i|X)}{\sigma(Y_i)}\right\}^2\right] \qquad \text{(V. 25)}$$

where exp (u) = e^u.

The aim now is to get an estimate of those values of the parameters, α_j, which maximizes the joint probability density function given by (V.25). Maximizing this function reduces the problem to minimizing with respect to the parameters, α_j, the sum of deviation squares given by (V.26).

$$S = \sum_{i=1}^{M}\left\{\frac{y_i - E(Y_i|X)}{\sigma(Y_i)}\right\}^2 \qquad \text{(V.26)}$$

In physical terms this would mean that we are looking for those α_j, which would bring the expected values of the dependent variable as close to the observed values as possible.

If an equation of state is assumed to be an approximating function for the volumetric behaviour, an estimate of the property calculated from this equation can be considered as its expected value. Suppose y_c represents the calculated property from this equation.

$$y_{ci} = h_i(x_{1i}, x_{2i}, \ldots x_{pi}, \alpha_j) \qquad (V.27)$$

$$j = 1, 2, \ldots N$$

Defining $\omega_i = 1/\sigma(Y_i)^2$, we can get from (V.26):

$$S = \sum_{i=1}^{M} f_i^2 = \sum_{i=1}^{M} \omega_i \{y_i - y_{ci}\}^2 \qquad (V.28)$$

where f_i is the residual at the ith data point.

In (V.28) ω_i may be viewed as the weight assigned to the data point i. It may be calculated from a priori variance knowledge of the ith experimental data point for the property y. If such information is not available, it is a normal practice to allocate equal weights of unity to all the data points.

a. Linear least squares method.

If the relation (V.27) is linear in the equation parameters, α_j, we can write:

$$\begin{aligned} y_{ci} &= \sum_{j=1}^{N} \alpha_j \, g_j \, (x_i) \\ &= \sum_{j=1}^{N} \alpha_j \, g_{ji} \, (x) \qquad (V.29) \end{aligned}$$

where $g_{ji}(x)$ is the function associated with the parameter

α_j and calculated for the data point i.

Substituting (V.29) in (V.28),

$$S = \sum_{i=1}^{M} f_i^{2} = \sum_{i=1}^{M} \omega_i \{y_i - \sum_{j=1}^{N} \alpha_j \; g_{ji} \; (x)\}^2 \tag{V.30}$$

To minimize S with respect to α_j ($j = 1, 2, \ldots N$), we form N partial derivative equations

$$(\partial S/\partial \alpha_k)_{j \neq k} = 0. \tag{V.31}$$

$$(k = 1, 2, \ldots N)$$

Substitution of (V.30) into (V.31) results in

$$(\partial S/\partial \alpha_k)_{j \neq k} = 2 \sum_{i=1}^{M} \omega_i \{y_i - \sum_{j=1}^{N} \alpha_j \; g_{ji} \; (x)\} \; \{- g_{ki}(x)\}$$

$$= 0$$

or

$$\sum_{i=1}^{M} \omega_i \{ \sum_{j=1}^{N} \alpha_j \; g_{ji}(x)\} \; \{g_{ki}(x)\} = \sum_{i=1}^{M} \omega_i \; y_i \; g_{ki}(x)$$

$$k = 1, 2, \ldots N \tag{V.32}$$

Equation (V.32) represents N simultaneous linear algebraic equations, commonly known as the normal equations. These equations can be written in matrix notation as

$$\underset{\rightarrow}{A}\vec{\alpha} = \vec{b} \tag{V.33}$$

where an arrow over and under a variable represents a vector and a matrix respectively. The elements of $\vec{b}$ are given by

$$b_k = \sum_{i=1}^{M} \omega_i \; y_i \; g_{ki}(x) \tag{V.34}$$

The elements of $\underset{\rightarrow}{A}$ are given by

$$A_{kj} = \sum_{i=1}^{M} \omega_i \; g_{ji}(x) \cdot g_{ki}(x) \tag{V.35}$$

$$k = 1, 2, \ldots N$$

$$j = 1, 2, \ldots N$$

Equation (V.33) can be solved by inverting the matrix A utilizing any standard technique.[65]

$$\vec{\alpha} = \underset{\rightarrow}{A}^{-1} \vec{b} \tag{V.36}$$

This parameter estimation technique for a linear equation of the type (V.29) is known as the Linear Least Squares Method.

The pressure or the compressibility factor may be expressed in the form of (V.29) for a known value of the co-efficient γ for the BWR equation. Different values of γ may be tried and the co-efficients corresponding to the minimum S, defined by (V.30), can be estimated. The co-efficients thus obtained will be the optimum set for the data treated and the dependent variable chosen.

Up to now the choice of the dependent or the independent variable has been left arbitrary. In the development of the least squares method, it was implicitly assumed that the independent variables X are known exactly, that is they are free from the random or the accidental errors of experimentation, and only the dependent variable is subject to random errors. Statistically then, if we have to come close to this implication, the dependent variable chosen should be such that its random error is by far the largest compared to the random errors in the other variables. This of course will depend upon the type of equipment used for determining the volumetric behavior. However, in general it can be said that pressures and temperatures can be measured with relatively more accuracy than the specific volumes of a fluid. It seems, therefore, that from the point of view of the theory of errors, the dependent variable chosen should be volume and not the pressure or the compressibility factor. Since the BWR equation is a polynomial in volume it can not be expressed explicitly. Hence the linear least squares method can not be employed for estimating the parameters. However, the problem can be handled by the Non-Linear Least Squares Method described later. It must, however, be emphasized here that the conclusion for a choice of dependent variable can be reached only by separately correlating the given data choosing pressure, compressibility factor or volume as dependent variable and then seeing which choice brings the expected values closest to the observed values.

b. Non-linear Least Squares Method.

Suppose Equation (V.27) is non-linear and represents an approximating function for the chosen dependent variable. The observed and the calculated values for this variable at the ith data point are given by y_i and y_{ci} respectively. Let us represent a residual at the ith point by f_i. The objective function for minimization given by (V.28) can be written as:

$$S = \sum_{i=1}^{M} f_i = \sum_{i=1}^{M} \omega_i \{y_i - y_{ci}\}^2$$

$$= \sum_{i=1}^{M} \omega_i \{y_i - h(x_{1i}, x_{2i}, \ldots x_{pi}, \alpha_j)\}^2 \qquad \text{(V.37)}$$

where

$$f_i = \sqrt{\omega_i}\ \{y_i - h(x_{1i}, x_{2i}, \ldots x_{pi}, \alpha_j)\}$$

$$j = 1, 2, \ldots N \qquad \text{(V.38)}$$

Since (V.38) is a non-linear equation we choose an initial solution, $p_o = (\alpha_1^{(o)}, \alpha_2^{(o)}, \ldots \alpha_N^{(o)})$ at which it is assumed that S does not have a stationary value, and take first-order Taylor expansions of f_i about p_o. This gives a set of linear approximations to the residuals

$$f_i(\alpha_j) \approx F_i(\alpha_j) = f_i(p_o) + (\partial f_i/\partial\alpha_1)d\alpha_1 + (\partial f_i/\partial\alpha_2)d\alpha_2$$

$$+ \ldots (\partial f_i/\partial\alpha_N)d\alpha_N$$

$$\simeq f_i(p_o) + (\partial f_i/\partial \alpha_1)\Delta\alpha_1 + (\partial f_i/\partial \alpha_2)\Delta\alpha_2$$

$$+ \ . \ . \ . \ (\partial f_i/\partial \alpha_N)\Delta\alpha_N$$

$$= f_i(p_o) + \sum_{k=1}^{N} (\partial f_i/\partial \alpha_k)_{j\neq k} \cdot \Delta\alpha_k \qquad (V.39)$$

where $\Delta\alpha_k = \alpha_k - \alpha_k^{(o)}$ and all the partial derivatives are evaluated at the initial solution p_o. Now, the Gauss-Newton or the standard method consists of minimizing

$$S \simeq s = \sum_{i=1}^{M} F_i^2 \qquad (V.40)$$

by setting the partial derivatives of s with respect to the parameters α_k $(k = 1, 2, . . . N)$ equal to zero and getting the normal equations:

$$(\partial s/\partial \alpha_k)_{j\neq k} = 2 \ . \sum_{i=1}^{M} F_i(\partial F_i/\partial \alpha_k)_{j\neq k} = 0.$$

or

$$1/2 \ (\partial s/\partial \alpha_k)_{j\neq k} = \sum_{i=1}^{M}\Big[\{f_i(p_o) + (\partial f_i/\partial \alpha_1)\Delta\alpha_1$$

$$+ (\partial f_i/\partial \alpha_2)\Delta\alpha_2 + \ . \ . \ . \ (\partial f_i/\partial \alpha_N)\Delta\alpha_N\}$$

$$\{\partial f_i/\partial \alpha_k\}\Big] = 0$$

$$k = 1, 2, . . . N \qquad (V.41)$$

(V.41) are N standard normal equations.

Substituting

$$f_i^{(o)} = \sqrt{\omega_i}\ \{y_i - h_i^{(o)}\ (x_{1i}, x_{2i}, . . . \alpha_j)\}$$

and

$$\partial f_i/\partial \alpha_k = - \sqrt{\omega_i}\ \partial h_i/\partial \alpha_k$$

in (V.41) we have:

$$1/2\ (\partial s/\partial \alpha_k) = \sum_{i=1}^{M} \Big[\{\sqrt{\omega_i}\ (y_i - h_i^{(o)}(x_{1i}, x_{2i}, \ldots x_{pi}, \alpha_j)) - \sqrt{\omega_i}\ \frac{\partial h_i}{\partial \alpha_1}\Delta\alpha_1 - \sqrt{\omega_i}\ \frac{\partial h_i}{\partial \alpha_2}\Delta\alpha_2 \ldots \sqrt{\omega_i}\ \frac{\partial h_i}{\partial \alpha_N}\Delta\alpha_N\}\{\sqrt{\omega_i}\ \frac{\partial h_i}{\partial \alpha_k}\}\Big]$$

$$= 0 \qquad (V.42)$$

$$k = 1, 2, \ldots N$$

where superscript (o) emphasizes the fact that the quantities are estimated at the initial solution $p_o = (\alpha_1^{(o)}, \alpha_2^{(o)}, \ldots \alpha_N^{(o)})$, h_i is written for $h_i(x_{1i}, x_{2i}, \ldots x_{pi}, \alpha_j)$ for brevity.

Rearranging (V.42) we get

$$\sum_{i=1}^{M} \omega_i \Big[\{\sum_{j=1}^{N} (\partial h_i/\partial \alpha_j)\Delta\alpha_j\}\{\partial h_i/\partial \alpha_k\}\Big] = \sum_{i=1}^{M} \omega_i \Big[\{y_i - h_i^{(o)}\}\{\partial h_i/\partial \alpha_k\}\Big]$$

$$k = 1, 2, 3, \ldots N \qquad (V.43)$$

(V.43) represents N simultaneous linear algebriac equations and may be called as the standard or the Gauss-Newton normal equations. These can be written in the matrix notation as

$$\underset{\sim}{A}\vec{\delta} = \vec{b} \qquad (V.44)$$

The elements of the vector $\vec{b}$ are given by

$$b_k = \sum_{i=1}^{M} \omega_i \left[\{y_i - h_i^{(o)}\}\{(\partial h_i/\partial\alpha_k)_{(o)}\}\right] \qquad (V.45)$$

The elements of the matrix $\underset{\sim}{A}$ are given by

$$A_{kj} = \sum_{i=1}^{M} \omega_i (\partial h_i/\partial\alpha_j)_{(o)} (\partial h_i/\partial\alpha_k)_{(o)} \qquad (V.46)$$

The subscript (o) has been used to remind us that the derivatives are evaluated at the initial solution $p_o = (\alpha_1^{(o)}, \alpha_2^{(o)}, \ldots \alpha_N^{(o)})$. The elements of vector $\vec{\delta}$ are

$$\delta_j = \Delta\alpha_j \qquad (V.47)$$

The elements of the right hand side vector b and the standard normal matrix A can be calculated analytically for an initial guess of the parameters $p_o = (\alpha_1^{(o)}, \alpha_2^{(o)} \ldots \alpha_N^{(o)})$. Equation (V.44) can then be solved for local minima and $\vec{\delta}$ estimated. The improved values of the parameter vector can be calculated and these may be used as the initial guess for the second trial. The procedure is repeated till the universal minima is located. However, in this scheme there is no assurance that successive trials will drive the objective function towards its universal minima. In fact it has been found in many cases that even if the first estimate of the parameters is nearly correct, the successive estimates may diverge. The probability of successful convergence can be improved as indicated by Levenberg[82] and Marquardt[83] by forming what might be called the 'damped' least squares normal matrix. Levenberg and Marquardt, by independent and somewhat different reasonings, came to the conclusion that a non-negative damping factor, $W \gtreqless 0$, may be added to the principal diagonal elements of the standard normal matrix $\underset{\to}{A}$ defined by (V.46) before (V.44) is solved for $\vec{\delta}$. Levenberg suggested that W for every trial may be calculated from

$$W = \sum_{j=1}^{N} b_j / 0.5\ S(p_o) \qquad (V.48)$$

Where b_j are calculated from (V.45), $S(p_o)$ is the sum of residual squares calculated from (V.37), and $p_o = (\alpha_1^{(o)}, \alpha_2^{(o)}, \ldots \alpha_N^{(o)})$. The p_o is the set of parameters at the previous trial which becomes the initial guess for the present trial. However, Marquardt suggests that for the first trial W may be taken as 0.01 and for every subsequent trial W may be increased or decreased by a factor of 10 depending upon whether the sum of residual squares, S, calculated with the new estimate of α_j is diverging from or converging towards the universal minima. Marquardt argues that by increasing W the norm $||\delta||$ is decreased and hence a W can always be found so that the new value of S is lower than the S calculated in the previous trial. Also, when we approach the correct solution, W can be taken towards zero so that the method becomes the standard least squares method. Thus Marquardt claims that in his scheme the probability of convergence is greatly increased. The trials can be terminated when

$$\frac{|\delta_j{}^{(r)}|}{\tau + |\alpha_j{}^{(r)}|} \leqq 10^{-5} \text{ for all } j;$$

where $\tau = 10^{-3}$, $\alpha_j{}^{(r)}$ is the jth element of the parameter vector at the rth trial and $\delta_j{}^{(r)}$ is the increment in the jth parameter vector element calculated at the rth trial.

In the present work, experience with the Marquardt scheme indicated that if the initial guess is too close to the correct solution, a false convergence is reached because the starting value of W(= 0.01) is too large. Moreover if the initial guess is far removed from the correct solution, the starting value of W (= 0.01) is too small and a few trials are required in the beginning before the solution starts moving towards the minima.

Experience with the Levenberg scheme showed that if the initial guess is far removed from the true solution, the method moves rapidly towards the minima. Furthermore if the initial guess is too close to the true solution, the starting value of W calculated is nearer to the required one which moves the solution towards its convergence. However, as the true solution is approached it may start oscillating.

In view of the experience gained with both the methods it was decided to adopt a scheme which is a combination of the two. The starting value of W is calculated by (V.48) and for every subsequent trial W is increased or decreased by a factor of 10 depending upon whether the solution is moving away or towards the minima. This scheme may be called the "Levenberg-Marquardt combination convergence scheme".

A computer programme was developed for the BWR equation utilizing the Levenberg-Marquardt combination scheme. The steps involved in this scheme and the developed computer program are given in Appendix H. The programme is written so that the compressability factor, Z, or the specific volume, V, may be chosen as dependent variable. When V is chosen as the dependent variable only the sum of relative deviation squares is minimized. However, in case of Z the sum of deviation squares or the relative deviation squares can be minimized. Equal weights of unity are assigned to all the data points treated.

When Z is chosen as the dependent variable and expressed by (V.27), the derivatives involved in (V.45) and (V.46) can be estimated very readily by direct differentiation. The expressions used for calculating these derivatives are given in Appendix G.

In the BWR equation, the property V cannot be expressed explicitly. Immediately we face a problem of calculating a residual $(y_i - h_i^{(o)})$ in the equation (V.45). It may be recalled that $h_i^{(o)}$ is the calculated property (volume) from the equation of state with the knowledge of the parameters assumed as the initial guess. Since the BWR equation is a polynomial in V, a trial and error or some suitable iterative scheme will be required to calculate volume and hence the residual $(y_i - h_i^{(o)})$. The Newton-Raphson iterative scheme is used in the programme developed.

In using equations (V.45) and (V.46), it is necessary to calculate the derivatives $(\partial h_i/\partial \alpha_k)$ i.e. $(\partial V_{k_i}/\partial \alpha_k)$ (where V_{k_i} is the calculated volume at the ith data point). Again, because volume is not expressed explicitly, such calculations present a problem. The difficulty was overcome by expressing Z in terms of P, V, T and α_j and performing an implicit differentiation. The required expressions for these derivatives are also given in Appendix G.

c. Evaluation of parameters by the least squares criterion when the information on more than one property is available.

When the P-V-T data are available for a system and information on other properties like heat capacity and enthalpy departures is known for a few points, the method of least squares with constraints as suggested by Hust and McCarty[84] may be used. The method becomes unmanageable, however, if the properties are known at a large number of points and it is desired to use all the available information to evaluate the parameters. To overcome this difficulty, it was postulated that an objective function defined by (V.49) may be minimized.

$$S = S_V + S_C + S_H \qquad \text{(V.49)}$$

where S_V, S_C and S_H are the sum of relative deviation squares for the dependent variables volume, heat capacity, and enthalpy departure respectively. Recently Bono[75] also reached a similar conclusion by extending equation (V.25) to a multiproperty set of ℓ different properties with M_ℓ data point sets of defining independent variables. The joint probability density function for the multiproperties can be obtained from (V.25), assuming the probabilities of each property are independent and that each of the i data sets represents an independent event.

$$\prod_{\ell=1}^{\eta_p}\prod_{i=1}^{M_\ell} f(Y_{\ell i}|X) = \prod_{\ell=1}^{\eta_p}\prod_{i=1}^{M_\ell} \frac{1}{\sigma(Y_{\ell i})\sqrt{2\pi}} \cdot$$

$$\exp\left[-\frac{1}{2}\left\{\frac{y_{\ell i} - E(Y_{\ell i}|X)}{\sigma(Y_{\ell i})}\right\}^2\right] = \left[\prod_{\ell=1}^{\eta_p}\prod_{i=1}^{M_\ell}\frac{1}{\sigma(Y_{\ell i})\sqrt{2\pi}}\right] \cdot$$

$$\exp\left[-\frac{1}{2}\cdot\sum_{\ell=1}^{\eta_p}\sum_{i=1}^{M_\ell}\left\{\frac{y_{\ell i} - E(Y_{\ell i}|X)}{\sigma(Y_{\ell i})}\right\}^2\right] \qquad \text{(V.50)}$$

where η_p = the total number of different properties

M_ℓ = the number of data points for the ℓth property

$Y_{\ell i}$ = the ith dependent variable defining ℓth property

$y_{\ell i}$ = the experimentally observed value of $Y_{\ell i}$

X = the independent variable vector

$E(Y_{\ell i}|X)$ = the expected value of Y_ℓ at the ith observation point, calculated from the approximating function for the ℓth property

$\sigma(Y_{\ell i})$ = the standard deviation of the dependent variable Y_ℓ for the ith data point.

The maximization of (V.50) is equivalent to the minimization of

$$S = \sum_{\ell=1}^{\eta_p} \sum_{i=1}^{M_\ell} \left\{\frac{y_{\ell i} - E(Y_{\ell i}|X)}{\sigma(Y_{\ell i})}\right\}^2 \qquad (V.51)$$

If the approximating function for the ℓth property is written as

$$y_{c\ell i} = h_{\ell i}(X_{1i}, X_{2i}, \ldots X_{pi}, \alpha_j)$$

the Equation (V.51) may be written as

$$S = \sum_{\ell=1}^{\eta_p} \sum_{i=1}^{M_\ell} \left\{\frac{y_{\ell i} - y_{c\ell i}}{\sigma(Y_{\ell i})}\right\}^2 \qquad (V.52)$$

where $y_{c\ell i}$ represents the calculated value of the ℓth property at the ith data point.

As Equation (V.28) $\sigma^2(Y_{\ell i})$ may be considered as the weight assigned to the ith point for the ℓth property. If a priori information on these standard deviations is not available, equal weights may be assigned to all the data points for each property. Since the magnitudes of these properties may be different, an elegant way would be to take these weights proportional to the observed values, that is

$$\sigma(Y_{\ell i}) = m_\ell \, y_{\ell i} \qquad (V.53)$$

The constant of proportionality m_ℓ may be considered related to the over-all accuracy of the data set of the ℓth property.

Substituting (V.53) in (V.52) we get:

$$\begin{aligned} S &= \sum_{\ell=1}^{n_p} \sum_{i=1}^{M_\ell} \{\frac{y_{\ell i} - y_{c\ell i}}{m_\ell \, y_{\ell i}}\}^2 \\ &= \sum_{\ell=1}^{n_p} \frac{1}{m_\ell^2} \sum_{i=1}^{M_\ell} \{\frac{y_{\ell i} - y_{c\ell i}}{y_{\ell i}}\}^2 \qquad (V.54) \end{aligned}$$

Defining $\omega_\ell = 1/m_\ell^2$ and substituting in (V.54) we obtain:

$$\begin{aligned} S &= \sum_{\ell=1}^{n_p} \omega_\ell \sum_{i=1}^{M_\ell} \{\frac{y_{\ell i} - y_{c\ell i}}{y_{\ell i}}\}^2 \\ &= \sum_{\ell=1}^{n_p} \omega_\ell \, S_\ell \qquad (V.55) \end{aligned}$$

where S_ℓ is the sum of relative deviation squares for the ℓth property.

If the accuracies of the treated data sets for different properties are of the same order of magnitude the weights, ω_ℓ, can be taken equal. Under these assumptions Equation (V.55) is equivalent to (V.49).

A computer programme was developed for evaluating the BWR parameters, using the non-linear least squares technique, from volumetric and/or heat capacity departure data for a pure component. The volumetric data handling capability of this programme is discussed elsewhere. When volumetric and heat capacity departure data are treated together, unit weight is assigned to the former and a predecided weight to the latter.

The heat capacity departure and the derivatives required in Equations (V.45) and (V.46) are evaluated from the volume calculated by the Newton-Raphson iterative scheme. The parameters which are considered to be the best at any stage of the trials are used for these calculations. The expressions required for calculating the derivatives are given in Appendix G. The use of this computer programme is explained in Appendix H.

VI - THE APPLICATION OF CORRELATING PROCEDURES TO VOLUMETRIC AND THERMAL PROPERTIES AND THEIR COMPARISONS

The various techniques of data correlation developed in Chapter V were utilized to evaluate the BWR parameters for the systems CO_2, CH_4 and CO_2-CH_4 mixtures. The volumetric and heat capacity data, used for the determination of the BWR parameters, were obtained from the following sources:

1.	Volumetric data	
a.	Carbon dioxide	Reamer et al.[31]
b.	Methane	Douslin et al.[30]
c.	Carbon dioxide-methane mixtures	Reamer et al.[31]
2.	Heat capacity data of Carbon dioxide	Rivkin and Gukov[20].

The P-V-T data from the above sources were chosen in a common range of pressures up to 5000 psi and temperatures between 100°F and 400°F. The carbon dioxide heat capacity data were selected for pressures up to about 4000 psi and temperatures between 100°F and 400°F.

The usefulness of various mathematical techniques is examined in the following pages by selecting a common ground of comparison for the abilities of the different parameter sets obtained. For easy identification, the parameter sets obtained by various techniques and types of information are assigned I.D. numbers as summarized in Table VI.1. In this table, data represents the property information used for evaluating a parameter set and P, Z, V, C_p, and ΔH_p denote pressure, compressibility factor, molal volume, heat capacity, and isobaric enthalpy change respectively. S_V, S_Z, and S_C represent the sum of relative error squares in volume, compressibility factor and heat capacity respectively. L.P. and NLRLSTQ are abbreviations for linear programming and non-linear least squares techniques. The values of the co-efficients corresponding to the I.D. numbers of the parameter sets are reported in Table VI.2. The units of co-efficients are psia, cu. ft. per lb-mole, and degrees Rankine.

Comparison of Correlation Ability of the Various Methods

A. Compressibility Factor

1. Pure Components -

a. Carbon dioxide.

The parameter sets C.1, C.2, and C.3 were obtained for carbon dioxide from the information on only volumetric behavior. The P-V-T data used were obtained from the literature source mentioned elsewhere. The set C.1 was evaluated by the linear programming technique choosing pressure as the dependent variable and minimizing the maximum absolute percent deviation in pressure. The maximum percent error in P was about 1.57, and the average deviation in P

TABLE VI.1

IDENTIFICATION OF BWR PARAMETER SETS

I.D. No.	System	Data	Technique	Dependent Variable	Criterion of Minimization	Computer Programme Used for Evaluation
C.1	CO_2	P-V-T	L.P.	P	Max. % P Dev.	PGM-1
C.2	CO_2	P-V-T	NLRLSTQ	Z	S_z	PGM-3
C.3	CO_2	P-V-T	NLRLSTQ	V	S_v	PGM-3
C.4	CO_2	P-V-T + ΔH_p	L.P.	P	Max. % P Dev. and $\Delta H_p \leq 12\%$	PGM-1
C.5	CO_2	P-V-T + C_p	NLRLSTQ	V and C_p	$S_v + \omega S_c$	PGM-3
M.1	CH_4	P-V-T	L.P.	P	Max. % P Dev.	PGM-1
M.2	CH_4	P-V-T	NLRLSTQ	Z	S_z	PGM-3
M.3	CH_4	P-V-T	NLRLSTQ	V	S_v	PGM-3
CM.1	CO_2-CH_4	P-V-T Mixture	L.P.	P	Max. % P Dev.	PGM-2

TABLE VI.2

VALUES OF THE BWR PARAMETER* SETS

I.D. No.	B_o	A_o x 10^{-4}	C_o x 10^{-9}	b	a x 10^{-3}	a.α x 10^{-3}	c x 10^{-9}	γ
C.1	1.3034859	1.7404422	0.36260634	0.63239557	0.58162671	1.2625315	1.3054636	1.93
C.2	0.79234560	1.0738380	1.4470909	0.98170677	6.4061324	1.9838514	2.2649382	1.2526619
C.3	0.52965326	0.73614334	2.0824774	1.6945616	15.260541	2.9553593	3.8342846	1.1139757
C.4	-0.26861787	0.084287402	2.4145485	3.7358294	34.176516	3.5566714	5.5111557	0.853
C.5	0.52883072	0.73570897	2.0814854	1.6909084	15.264813	2.9424985	3.8329741	1.1201692
M.1	0.69329554	0.65652070	0.41703706	0.67490953	2.3703381	2.5849048	0.64238208	2.32
M.2	0.69225947	0.66088972	0.39445193	0.66614267	2.1688664	2.3796615	0.56980814	2.1630098
M.3	0.70858101	0.67758187	0.37113321	0.64459244	1.9595127	2.3803570	0.54036127	2.2242751
CM.1	0.70280749	0.64135977	1.1336586	0.093484819	-2.5209067	1.2828691	0.42382618	1.90

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*Units: psi, cu. ft., lb-mole, °R

was 0.914 percent. In the evaluation of this parameter set, the experimental values of V and T were assumed to be exact. The computer programme PGM-1, developed in this work was first used to find the objective functions for different assumed values of the co-efficient γ. The values of the objective function thus obtained were plotted against γ, and the value of γ corresponding to a minimum objective function was estimated. With this known value of γ, PGM-1 was used again, with a choice of proper "flags", as explained in Appendix H, and the parameter set C.1 was estimated.

Parameter sets C.2 and C.3 were evaluated from the non-linear least squares technique using the computer programme PGM-3 which was developed in this work. For determining these parameters an initial solution of unit vector and proper "flags" were chosen as explained in Appendix H. Set C.2 was found by choosing Z as the dependent variable and assuming that the experimental information of V and T is exact. Set C.3 was determined by choosing V as the dependent variable and assuming that experimental P and T are error-free.

For any practical situation we normally confront the problem of estimating compressibility factor for a given P and T. Thus it would be desirable to compare the compressibility factors calculated by the sets C.1, C.2 and C.3 at the conditions where Z are experimentally known and then comparing which parameter set brings the expected values closest to the experimental values. A computer programme PGM-4 was written for this purpose. PGM-4 calculates Z factors and their deviations at the experimental P and T, and evaluates r.m.s. percent error. The r.m.s. percent error and the largest percent deviation for the 75 experimental data points were obtained as follows:

I.D. no.	r.m.s. percent deviation in Z	Largest percent deviation in Z
C.1	2.06	14.35
C.2	1.43	10.94
C.3	0.388	0.98

In general the deviations calculated by the three sets were larger at the conditions where Z versus P curves at constant temperatures approached minima and were the largest when a minimum had a steep approach. Compressibility factors calculated by the set C.3 had by far the least deviations from the experimental values. This of course also is illustrated by the r.m.s. and largest percent deviations reported above. It can then be concluded that for the case of carbon dioxide the best correlation of compressibility factors is given by the parameter set C.3 which was obtained from the non-linear least squares technique choosing volume as the dependent variable.

b. Methane.

The parameter sets M.1, M.2 and M.3 were obtained for methane from the information of only the volumetric behaviour. The P-V-T data used were obtained from the literature source mentioned elsewhere. The set M.1 was evaluated from the linear programming technique choosing pressure as the dependent variable. The maximum and average percent error in P were about 0.1224 and 0.061 respectively. In the evaluation of this parameter set the experimental values of V and T were assumed to be error-free. The computer programme PGM-1 was used for the evaluation of the parameter set M.1 by following a method similar to that used for the carbon dioxide.

Parameter sets M.2 and M.3 were evaluated from the non-linear least squares technique using the PGM-3 in the same manner as that for the carbon dioxide. Sets M.2 and M.3 were determined by choosing Z and V as the dependent variables respectively.

Compressibility factors were calculated from the sets M.1, M.2 and M.3 by the computer programme PGM-4 and deviations from the experimental values were evaluated. The r.m.s. and largest percent deviation for the 170 experimental data points were obtained as follows:

I.D. no.	r.m.s. percent deviation in Z	Largest percent deviation in Z
M.1	0.0699	0.143
M.2	0.0549	0.155
M.3	0.0536	0.208

The compressibility factor deviations, calculated with the parameter sets M.1, M.2 and M.3, were found to be of the same order of magnitude. This is also illustrated by the r.m.s. and largest percent errors tabulated above. Since the temperature and pressure range of the methane volumetric data, used in the evaluation of the parameter sets, were removed from the critical, the curves of Z versus P at constant temperatures did not pass through sharp minima. This is probably one of the reasons that parameter sets calculated from all the three techniques were generally satisfactory for calculating the compressibility factors.

2. Carbon Dioxide-Methane Mixtures -

The mixture data correlation has an added uncertainty of mixing model. The prediction of mixture compressibility factors was examined first by comparing the calculated values from different parameter sets of the pure components for a given mixing model. Then the values calculated from different mixing models for the given pure component parameter sets were compared with the experimental compressibility factors of Reamer et al.[31] These comparisons were done by using the computer programme PGM-4.

a. Comparison of parameter sets for a given mixing model.

Compressibility factors of carbon dioxide-methane mixtures at various compositions were calculated from the parameter pairs of C.1 and M.1, C.2 and M.2, and C.3 and M.3, and from the BWR mixing rules.[71]

Deviations from the experimental values were estimated for the 75 data points at each composition and the r.m.s. and largest percent deviations were calculated. The results are summarized as follows:

I.D. no.	Mole percent methane	r.m.s. percent deviation in Z	Largest percent deviation in Z
C.1-M.1	20.35	2.46	8.11
C.2-M.2	20.35	2.35	8.28
C.3-M.3	20.35	0.691	1.57
C.1-M.1	40.55	2.29	5.90
C.2-M.2	40.55	2.42	6.28
C.3-M.3	40.55	0.663	1.38
C.1-M.1	60.50	1.69	4.32
C.2-M.2	60.50	1.91	4.68

I.D. no.	Mole percent methane	r.m.s. percent deviation in Z	Largest percent deviation in Z
C.3-M.3	60.50	0.570	1.36
C.1-M.1	84.69	0.947	2.46
C.2-M.2	84.69	0.662	1.82
C.3-M.3	84.69	0.339	0.692

In general for all the three pairs, the deviations were larger at the lower compositions and were largest at the lower temperatures. Furthermore, the estimates from the three sets came closer to each other as the compositions moved towards the pure methane. These trends are also indicated by the r.m.s. and largest percent deviations given above. Thus even for the mixture compressibility factors, the results calculated by the co-efficients C.3 and M.3 are by far the best compared to those calculated from the other parameter sets.

b. Comparison of mixing model for a given parameter set.

The interaction parameters k_{ij} of equation (V.1) were evaluated for the BWR co-efficients by the linear programming technique. The computer programme, PGM-2, developed in this work, was utilized for the estimation of the interaction parameters. P-V-T data on the carbon dioxide-methane mixture and the pre-estimated co-efficient sets

C.1 and M.1 were used as input information for the programme PGM-2. As reported in Table VI.1 the interaction constants are identified by their I.D. number CM.1 and their values are given in Table VI.2.

Compressibility factors of carbon dioxide-methane mixtures were calculated from the parameter sets C.1, M.1 and CM.1 and the mixing model V.1. Compressibility factors were also calculated by the parameter sets C.1 and M.1 using the BWR mixing rules. Deviations from the experimental values were then estimated and the r.m.s. and largest percent errors were calculated for the 75 data points at each composition. The calculation results are summarized as follows:

I.D. no.	Mixing model	Mole percent methane	r.m.s. percent deviation in Z	Largest percent deviation in Z
C.1-M.1	BWR rules	20.35	2.46	8.11
C.1-M.1-CM.1	V.1	20.35	0.561	1.18
C.1-M.1	BWR rules	40.55	2.29	5.90
C.1-M.1-CM.1	V.1	40.55	0.327	0.748
C.1-M.1	BWR rules	60.50	1.69	4.32
C.1-M.1-CM.1	V.1	60.50	0.450	0.945
C.1-M.1	BWR rules	84.69	0.947	2.46
C.1-M.1-CM.1	V.1	84.69	0.420	0.819

In general the deviations of the compressibility factors calculated by the mixing model V.1 were smaller than those calculated by the BWR mixing rules. This is also indicated by the r.m.s. and largest percent deviations reported above. Hence it could be concluded that for a given set of BWR co-efficients of the pure components the correlation of mixture compressibility factors by means of the interaction constants and equation (V.1) is superior to the correlation by means of the BWR mixing rules. This points out the need for calculating interaction constants for a wide variety of systems and attempting to find some better mixing rules.

The above discussion on the compressibility factor correlation could be summarized as follows:

1. For a pure component the parameters estimated by choosing volume as the dependent variable give the best correlation of the volumetric data. Superiority of the co-efficients, thus determined, is vividly illustrated in the regions closer to the critical.
2. If the BWR mixing rules are used, the volumetric behavior of mixtures is best correlated by the pure component co-efficients which are estimated by choosing volume as the dependent variable.
3. For a given set of pure component co-efficients,

the volumetric behavior of mixtures is best correlated by the interaction constants and the Equation (V.1).

B. Heat Capacities and Multiproperties

1. Pure Components -

a. Co-efficients obtained from P-V-T data alone.

Heat capacities of carbon dioxide were calculated, at the pressures and temperatures for which the experimental values were available in the literature, using the parameter sets C.1, C.2 and C.3. The deviations of the calculated values from the experimental data were estimated and the r.m.s. and the largest percent deviations were calculated for 145 data points, using the computer programme PGM-4. The results are summarized below:

I.D. no.	r.m.s. percent deviation in C_p	Largest percent deviation in C_p
C.1	14.42	49.20
C.2	5.46	32.40
C.3	6.69	20.97

In general the deviations were larger at about 100°F for all pressures and were largest at about 100°F and 1280 psi. In this range the C_p isobar of carbon dioxide passed through a sharp maximum. The C_p values calculated from the parameter set C.1 had extremely large errors and did not even give a maximum but only dropped monotonically with an increase in temperature at 1280 psi. The values calculated from the co-efficients C.2 and C.3 did pass through a maximum and had relatively smaller errors. The errors in the calculated values of the set C.3 were distributed and as indicated in the above table the largest error was smaller than that calculated by the set C.2. Thus the values calculated by the parameter set C.3 could be considered more satisfactory than the results of other parameter sets.

b. Co-efficients obtained from multiproperty information.

The heat capacity data of carbon dioxide were integrated numerically using the method of assigned sample points at unequal intervals where the function values were available.[85] Ideal gas enthalpy changes were calculated by analytical integration of the ideal gas heat capacity equation of carbon dioxide.[68] The results are tabulated below:

p psi	T_1 °R	T_2 °R	ΔH_p Btu/(lb-mole,°R)	ΔH^o Btu/(lb-mole,°R)
1280.1	727.8	560.2	4108.31	1588.34
1429.5	574.9	560.7	1098.02	128.66
1429.5	708.0	574.9	3175.72	1260.41
1706.8	588.6	560.9	1292.22	251.57
1706.8	722.7	588.6	3253.12	1279.53
2145.3	603.2	564.6	1029.92	353.02
2145.3	724.4	603.2	3312.39	1162.22
2857.0	636.9	559.5	2045.26	714.36
2857.0	723.7	636.9	2056.43	839.52
3555.8	726.0	576.3	3439.10	1424.51

In the above table, $\Delta H_p = \int_{T_1}^{T_2} C_p \, dT$

and $$\Delta H^o = \int_{T_1}^{T_2} C_{po} \, dT$$

and correspond to the values required in the equations (V.19) and (V.20). Isobaric enthalpy changes were used as additional constraints by choosing β of equation (V.13c) as 0.12, and the parameter set C.4 was evaluated with the linear programming technique as outlined in Chapter V. Volumes at temperatures T_1 and T_2 were first calculated with the parameter set C.1 and then the computer programme PGM-1 was used for estimating the parameter set C.4.

Parameter set C.5 was determined from the non-linear least squares technique by minimizing a sum of the weighted sums of deviation squares in volume and heat capacities, as defined by the equation (V.55). The weights of unity and 0.517 (= 75/145, i.e. ratio of the numbers of P-V-T and C_p data points) were assigned to the sums of relative deviation squares in volume and heat capacity respectively.

Parameter sets C.4 and C.5 were used to calculate the heat capacities of carbon dioxide and their deviations from the experimental values were estimated. The r.m.s. and largest percent deviations, evaluated for 145 data points, are reported as follows:

I.D. no.	r.m.s. percent deviation in C_p	Largest percent deviation in C_p
C.4	14.07	28.79
C.5	4.46	10.59

In general the values of heat capacities calculated by the parameter set C.4 had very large deviations from the experimental values. A comparison of the values calculated by C.1 and C.4 showed that the largest percent deviation (49.20) was reduced (to 28.79) by distributing the errors to other points and hence the r.m.s. percent deviations remained just about the same in the two cases.

A comparison of the results calculated by the parameter sets C.3 and C.5 showed that the latter gave overall improved values. The deviations in some regions were somewhat increased but the large deviations were considerably reduced.

It could then be concluded that the linear programming is a poor technique as compared to the non-linear least squares method of estimating the parameters for correlating more than one property of a system. In linear programming technique the constraints of isobaric enthalpy changes are satisfied at the cost of the objective function (max. absolute percent P deviation). Thus at any data point the deviation in the calculated P with the experimental information of V and T most likely becomes larger.

When volume is calculated for the given P and T from this parameter set (obtained by satisfying isobaric enthalpy change constraints) the deviation from experimental volume may become large enough to cause intolerable errors in the calculated heat capacities. Whereas, in the non-linear least squares technique, since the deviations in C_p and V are minimized simultaneously, the calculated volumes are kept within the minimization criterion. It is probably due to this reason that the parameters estimated by the non-linear least squares method correlate more than one property more satisfactorily than the parameters obtained by the linear programming method.

2. Carbon Dioxide-Methane Mixtures -

a. Co-efficients obtained from P-V-T data alone.

i. Comparison of parameters for the given BWR mixing rules.

The parameter set pairs C.1 and M.1, C.2 and M.2 and C.3 and M.3 were used, along with the BWR mixing rules, to calculate the heat capacities of carbon dioxide-methane mixtures at 200 psi pressure intervals and the temperatures at which the experimental data are reported in Chapter IV. The deviations of calculated and experimental values were estimated and the r.m.s. and largest percent error were evaluated. The results are shown as follows:

I.D. no.	Mole percent CH_4	r.m.s. percent deviation in C_p	Largest percent deviation in C_p
C.1-M.1	14.49	13.88	29.16
C.2-M.2	14.49	5.37	16.71

I.D. no.	Mole percent CH_4	r.m.s. percent deviation in C_p	Largest percent deviation in C_p
C.3-M.3	14.49	4.25	11.61
		No. of data points 41	
C.1-M.1	42.30	9.69	17.90
C.2-M.2	42.30	6.83	11.86
C.3-M.3	42.30	4.38	5.93
		No. of data points 30.	

Some interesting features of the deviations were noticed. For the 14.49 mole percent methane mixture the values calculated by C.2-M.2 and C.3-M.3 were lower at some points and higher at other points. Whereas the values calculated by C.1-M.1 were always lower than the experimental results and had very large errors. The largest deviations for all the three pairs occurred at 563.12°R (39.71°C) isotherm. The calculated results and the experimental values at this isotherm are shown in Figure VI.1 for illustration.

For the 42.30 mole percent methane mixture the values calculated by C.2-M.2 and C.3-M.3 were always higher, whereas the values calculated by C.1-M.1 were always lower than the experimental results. In general, the deviations were higher at lower temperatures and the values calculated by C.1-M.1 were greatly in error.

Once again it could be concluded that if the BWR mixing rules are used the co-efficients obtained by linear programming are poor compared to those calculated by the non-linear least squares method. Furthermore, the results calculated from the co-efficients, obtained by choosing volume as the dependent variable, had the least deviations from the experimental values.

ii. Comparison of the mixing models for the given parameter sets

The pure component parameter sets C.1 and M.1 were used to calculate the heat capacities of carbon dioxide-methane mixtures with the help of BWR mixing rules in one case and the interaction constants CM.1 and mixing model V.1 in the other case. Deviations of the calculated values from the experimental results were calculated in the two cases and the r.m.s. and largest percent deviations were evaluated. The results are summarized as follows:

I.D. no.	Mixing model	Mole percent methane	r.m.s. percent deviation in C_p	Largest percent deviation in C_p
C.1-M.1	BWR rules	14.49	13.8	29.16
C.1-M.1 CM.1	V.1	14.49	7.65	15.44
			No. of data points 41	
C.1-M.1	BWR rules	42.30	9.69	17.90
C.1-M.1 CM.1	V.1	42.30	1.98	4.56
			No. of data points 30.	

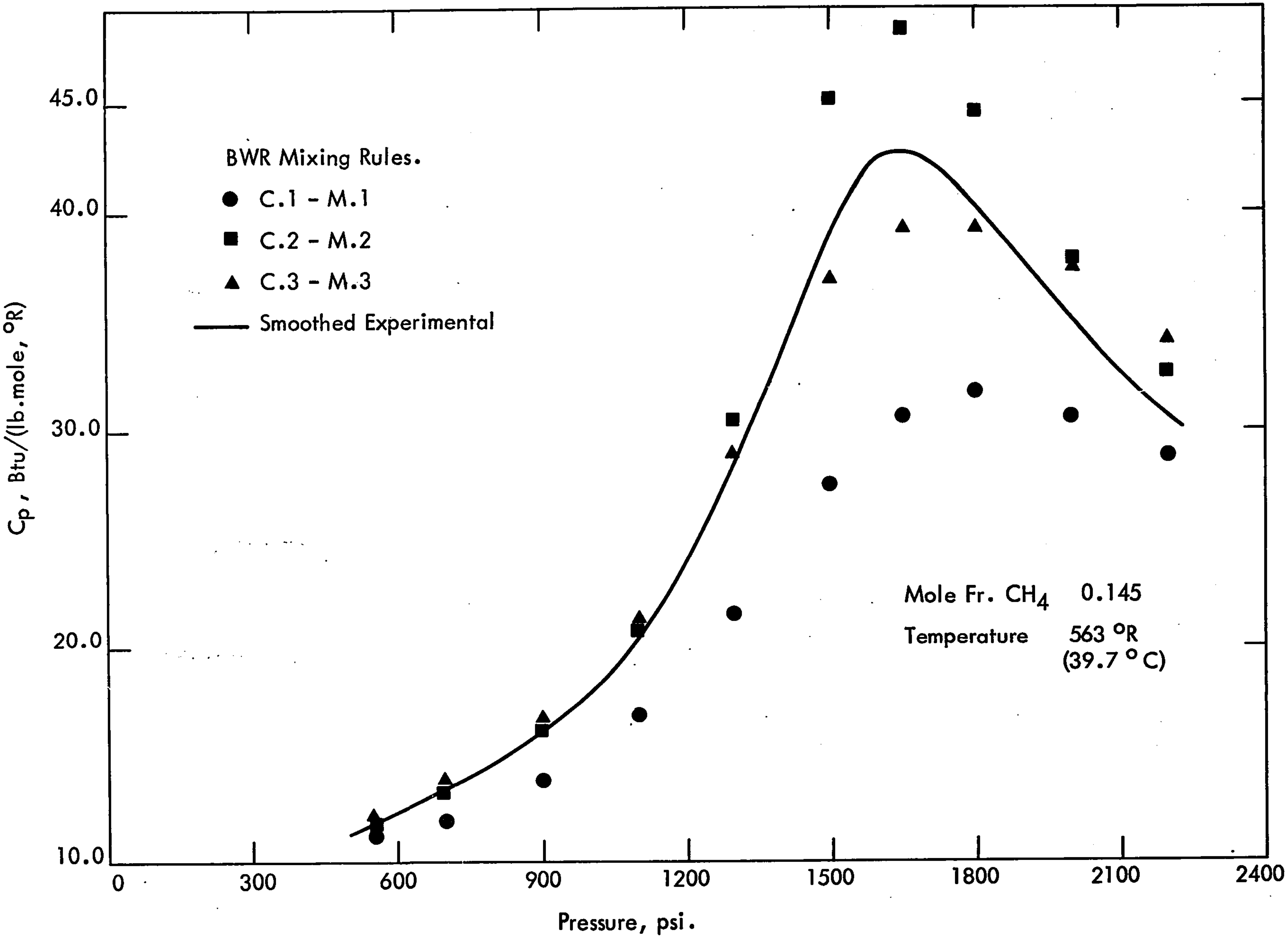

Figure VI.1. Comparison of Calculated and Experimental C_p for the CO_2 - CH_4 System.

For the 42.30 mole percent methane mixture the values calculated by BWR mixing rules were always lower whereas the results calculated by model V.1 were always higher. In general for both the mixtures the mixing model V.1 gave far better results than the BWR mixing rules. As a matter of fact, for the 42.30 mole percent methane mixture the heat capacities calculated with the help of interaction constants were slightly better than even those determined by the parameter sets C.3 and M.3 and the BWR mixing rules.

A comparison of the values calculated by the parameter sets C.1-M.1 and C.3-M.3 with the help of the BWR mixing rules and the results estimated by C.1-M.1-CM.1 and model V.1 is shown in Figure VI.2. The results shown in the figure are for the 42.30 mole percent methane mixture at 563.53°R (39.92°C). The above comparison once again points out the superiority of interaction constants over the BWR mixing rules.

b. Co-efficients obtained from multiproperty information.

The parameter sets C.4 and C.5 were obtained from the knowledge of the volumetric and thermal behaviour of carbon dioxide using the linear programming and non-linear least squares techniques respectively. Such multiproperty parameters could not be obtained for methane as the heat capacity data in the temperature range of interest were not available. However, the heat capacities of carbon dioxide-methane mixtures were calculated from the parameter sets

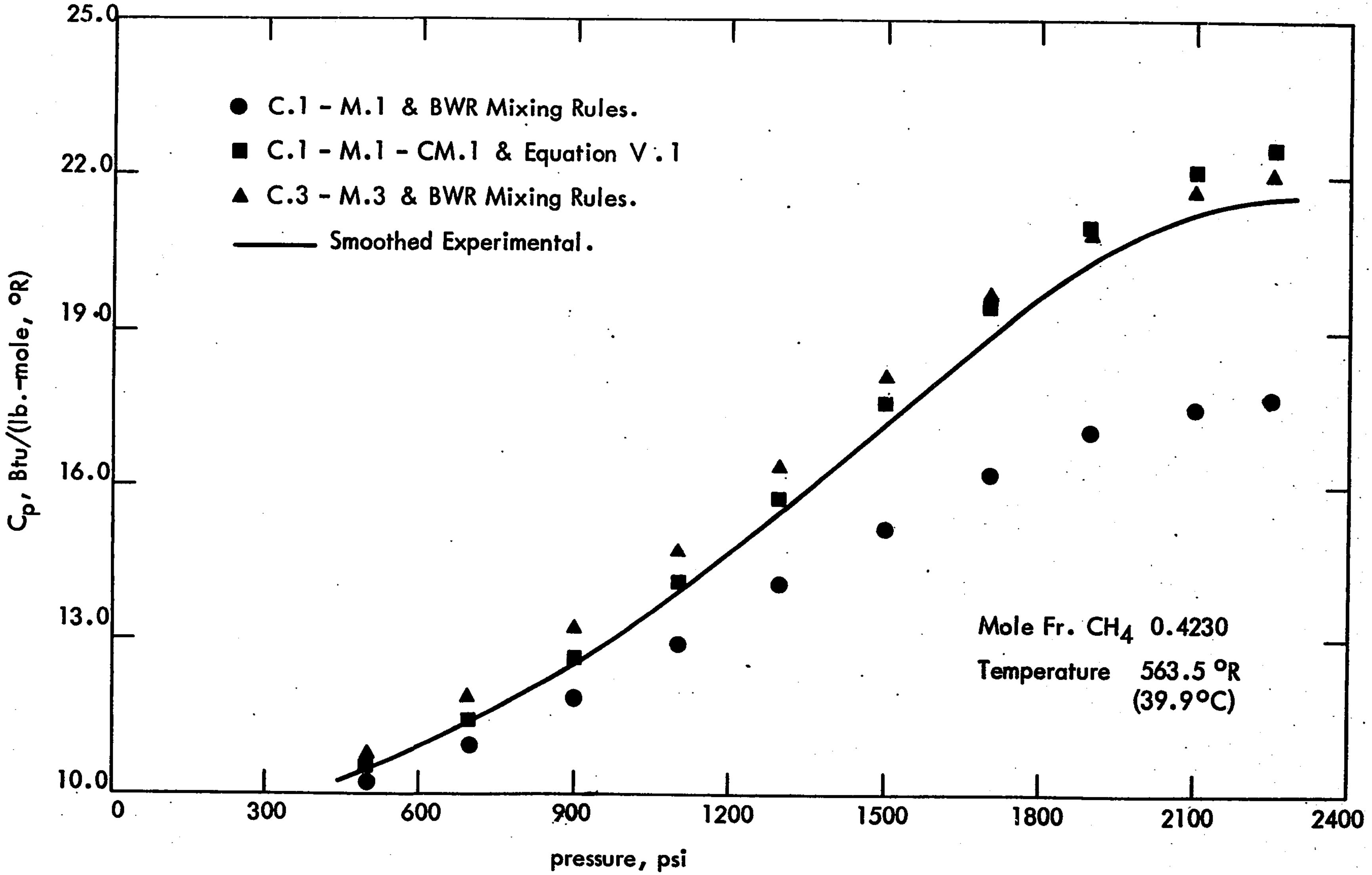

Figure VI.2. Comparison of calculated and Experimental C_p for the CO_2 - CH_4 system.

C.4-M.1 and C.5-M.3 with the help of BWR mixing rules. The deviations of the calculated values from the experimental data, reported in Chapter IV, were calculated and the r.m.s. and largest percent errors were evaluated. The results are shown as below:

I.D. no.	Mole percent methane	r.m.s. percent deviation of C_p	Largest percent deviation of C_p
C.4-M.1	14.49	20.18	45.03
C.5-M.3	14.49	4.50	14.08
		No. of data points	41
C.4-M.1	42.30	13.44	27.37
C.5-M.3	42.30	4.44	5.96
		No. of data points	30

In general the deviations were larger for the 14.49 mole percent methane mixture and were largest at the lowest temperature of 563°R (39.71°C). The values calculated by the set C.5-M.3 were far better than those estimated by the set C.4-M.1. Moreover the values calculated by C.4-M.1 were worse than even the results of C.1-M.1. In other words, the application of enthalpy constraints for evaluating the set C.4 made the calculated heat capacities of mixtures worse than those calculated with the co-efficients obtained from only the volumetric information.

A comparison of the results calculated by C.3-M.3 and C.5-M.3 showed that there was no significant improvement in the values obtained from using the parameter set C.5. At least, the use of C_p information of carbon dioxide in evaluating C.5 set did not have any deteriorating effect on the mixture heat capacity calculations.

It could then definitely be concluded that linear programming is not a suitable technique for evaluating the pure component parameters from multiproperty information, so that the evaluated parameters could be used for calculating the mixture properties.

Summary of the Discussion on Heat Capacities and Multiproperties

1. For a pure component, the parameters estimated from only the volumetric behavior by choosing volume as the dependent variable, give the best calculated values of the heat capacities.
2. For correlating more than one property of a pure component, the non-linear least squares method of minimizing the sum of the weighted sum of relative error squares in volume and heat capacity is far superior to the use of linear programming technique.
3. For calculating mixture heat capacities from only the volumetric information of pure components and the BWR mixing rules, the pure component parameters estimated by choosing volume as the dependent

variable give far better results than any other parameter sets.

4. For calculating the binary mixture heat capacities from the volumetric information of pure components and the binary mixtures, the procedure which uses interaction constants, defined in V.1, is superior to the method of using BWR mixing rules.
5. For calculating the mixture heat capacities from information on the volumetric and thermal properties of pure components and the BWR mixing rules, the pure component parameter sets obtained from the non-linear least squares method by choosing volume and heat capacity as the dependent variables are better than those obtained from the linear programming technique.

This work of comparing different calculation schemes points out that a computer programme should be developed for evaluating interaction parameters with the help of the non-linear least squares technique which chooses volume as a dependent variable. If such interaction parameters were available, the parameter sets M.3 and C.3 or C.5 along with the interaction parameters should correlate the volumetric as well as the thermal properties of carbon dioxide-methane mixtures very satisfactorily.

VII - CONCLUSIONS

A. Experimental

1. A facility for experimentally determining the ratio of heat capacity at a given pressure to heat capacity at a low pressure by the heat exchanger method has been designed, fabricated, and tested. The equipment is capable of operating with single phase fluid systems at pressures up to 3000 psi in the temperature interval from ambient to about 200°C with an expected accuracy of ±0.5 percent.
2. Experimental measurements were made on heat capacity ratios for nitrogen at pressures up to 2250 psi in a temperature range of 60° to 150°C. The results agreed to within ±0.5 percent of the previously published data.
3. Heat capacity ratios for two binary mixtures of methane and carbon dioxide containing 14.49 and 42.30 mole percent methane were determined in a temperature interval from about 40° to 150°C at pressures up to 2250 psi. The data had an expected accuracy within ±0.5 percent except in the vicinity of pressure maxima where the accuracy may only be within ±1.0 percent.
4. The Benedict-Webb-Rubin equation of state using the parameters reported in the literature for pure methane and carbon dioxide together with the Benedict mixing rules does not give a good representation of the specific heat of the mixtures. This is particularly

true for the richer carbon dioxide mixture where deviations in the order of 50 percent occurred at pressures between 1500 and 1800 psi.

B. Correlating Procedures Using the BWR Equation of State

1. Mathematical Techniques

a. Linear programming or non-linear least squares techniques may be used to evaluate the parameters in an equation of state correlating the volumetric behavior of a fluid, but the non-linear least squares method has the advantage in that volume as well as compressibility factor (or pressure) may be chosen as the dependent variable in a pressure explicit equation.

b. Schemes were formulated for estimating the parameters of an equation of state utilizing volumetric and heat capacity data on a system by means of linear programming and non-linear least squares techniques. It was found that a combination of Levenberg and Marquardt algorithms provided a good convergence scheme in the non-linear least squares method.

2. Compressibility Factor Correlation

a. The non-linear least squares method of parameter estimation choosing volume as the dependent variable gave the best correlation of the P-V-T data for carbon dioxide. The improvement over the linear programming method using pressure as the dependent variable was about 5 fold in the r.m.s. error and 15 fold in the maximum error which occurred in the vicinity of the critical.

b. The linear programming and non-linear least squares methods correlated the methane P-V-T data, where the reduced temperatures were above about 2, to comparable accuracy.

c. When BWR mixing rules were used, the volumetric behavior was best correlated by the pure component coefficients which were estimated by choosing volume as the dependent variable.

d. For a given set of pure component coefficients, the volumetric behavior of mixtures was best correlated by the interaction constants estimated from the mixture P-V-T data by incorporating the general binary mixing rule directly into the equation of state (BWR).

3. <u>Heat Capacity and Multi-property Correlation</u>

a. When using P-V-T data only, the best calculated values of the heat capacities for a pure component were obtained when volume was chosen as the dependent variable for estimating the equation of state parameters.

b. The non-linear least squares method of minimizing the sum of the weighted sums of relative error squares in volume and heat capacity was far superior to the use of the linear programming technique for correlating more than one property of a pure component.

c. When using P-V-T data on the pure components and the BWR mixing rules, the best calculated values of the heat capacities for mixtures were obtained when volume was chosen as the dependent variable for estimating the parameters.

d. The procedure which used a quadratic mixing rule and binary interaction constants was superior to the BWR mixing rules for calculating binary mixture heat capacities.

e. For calculating mixture heat capacities from the information on volumetric and thermal properties of pure components and the BWR mixing rules, the pure component parameter sets obtained from the nonlinear least squares method by choosing volume and heat capacity as the dependent variables were better than those obtained from the linear programming technique.

C. Recommendations for Future Work

1. The by-pass control valve BPCV was sometimes unable to cope with the sudden variations that occurred in the compressor capacity. The sudden variations in the compressor capacity also affected the temperature control capability of the equipment. These problems could possibly be overcome by the following modifications in the equipment.

a. One additional control valve may be installed in parallel with the BPCV valve. The valve could be of smaller trim size so that it could be used at the higher delivery pressures and the present BPCV valve could be used at lower delivery pressures. Thus by installing hand valves at suitable locations, the two control valves could be operated with the same controller driving only one of them at any stage.

b. The length of the gas carrying tube of each of the two heaters may be increased preferably by installing two heaters in series. The gas could be preheated by constant power input in one of the heaters and the other could then be put under automatic control. Alternatively large oil baths housing longer gas carrying tubes may be used. In this arrangement even if the flow conditions changed due to any sudden disturbances the long paths would ensure constant temperatures at the inlet of the calorimeter.

2. A computer programme should be developed for evaluating interaction parameters with the help of the non-linear least squares technique which chooses volume as the dependent variable. The volumetric as well as the thermal properties of carbon dioxide-methane mixtures could be correlated more satisfactorily with the parameter sets M.3 and C.3 or C.5 along with the interaction parameters evaluated by this programme.

NOMENCLATURE

A_o, B_o, C_o, a, b, c, α, γ	Co-efficients of the BWR equation of state
A	Specified function, matrix
B	Objective function
C	Heat capacity, specific heat capacity, flow co-efficient, centigrade
D	Departure function, small increment or change
E	Energy, expectation function, expected value, error term
F	Approximated function, Fahrenheit, flow-rate
G	Specified function
H	Enthalpy, specific enthalpy
J	Conversion factor
K	Kelvin, constant
M	Penalty co-efficient, no. of data points
N	No. of parameters, number
P	Pressure
Q	Heat, heat transfer rate
R	Universal gas constant, Rankine
S	Sum of error squares
T	Temperature
U	Energy
V	Slack variable, volume, specific volume
W	Damping factor, work function, work input rate

X	Parameter vector, variable vector, variable, independent variable vector
Y	Dependent variable
Z	Compressibility factor, objective function
a	Co-efficient, constant
b	Vector, constant
c	Co-efficient
d	Dual co-efficients, differential operator
e	Natural logarithmic base
f	Function, residual, probability density function, fractional error
g	Specified function
h	Approximating function
i	Location, matrix row, matrix column, vector element location
j	Location, matrix row, matrix column, vector element location
k	Location, matrix row, matrix column, vector element location
l	Location, matrix row, matrix column, vector element location, property description
m	Mass
n	Number of parameters, number
p	Pressure, parameter vector
q	Thermodynamic property, rate of flow of heat per unit mass flow rate of gas
s	Sum of error squares

u	Artificial variable, variable
w	Weight factor
x	Variable vector, variable, experimental value of X
y	Variable vector, property, variable, experimental value of Y

Greek Letters

α	Co-efficient
β	Co-efficient, objective function
δ	Increment vector
Δ	Small increment or difference
π	Constant Pi
Π	Multiplication over a variable
Σ	Summation over a variable
γ	Co-efficient
ε	Measurement error, small quantity
σ	Standard error
σ^2	Variance
μ	Joule-Thomson co-efficient
η	No. of different properties
ℓ	Property identification
ω	Weighting factor
Φ	Calorimetry error term, function
λ	Objective function
∂	Partial differential operator

$\int$	Integration operator
τ	A constant

Subscripts

c	Calculated value of a property or a variable
i	Location, state, row of a matrix
j	Location, state, column of a matrix
k	Location, state, row of a matrix, column of a matrix, calculated value of a property
o	Property at low pressure, property or function evaluated at initial guess
p	Property or function at constant pressure, probable value of a quantity
z	Property or function value for compressibility factor
ij	Interaction term, matrix element at ith row and jth column
H	Property or function value at constant enthalpy, property or function value for enthalpy
V	Property or function value at constant volume, property or function value for volume
C	Property or function value for heat capacity
P	Property or function value at constant pressure
T	Property or function value at constant temperature
N	Location

M	Mixture property
ℓ	Variable corresponding to ℓth property, row or column of a matrix, location
→	Under a variable represents matrix

Superscripts

-1	Inverse of a matrix
o	Value of a property at the ideal gas state, value of the variable or parameter vector at the initial guess
→	Over a variable represents vector
—	Over a variable or a quantity represents average value. Over a parameter or variable represents a vector
.	Over a quantity represents rate
E	Excess property
t	True value of a property or a variable
r	Iteration or trial number

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APPENDIX A

CALORIMETER

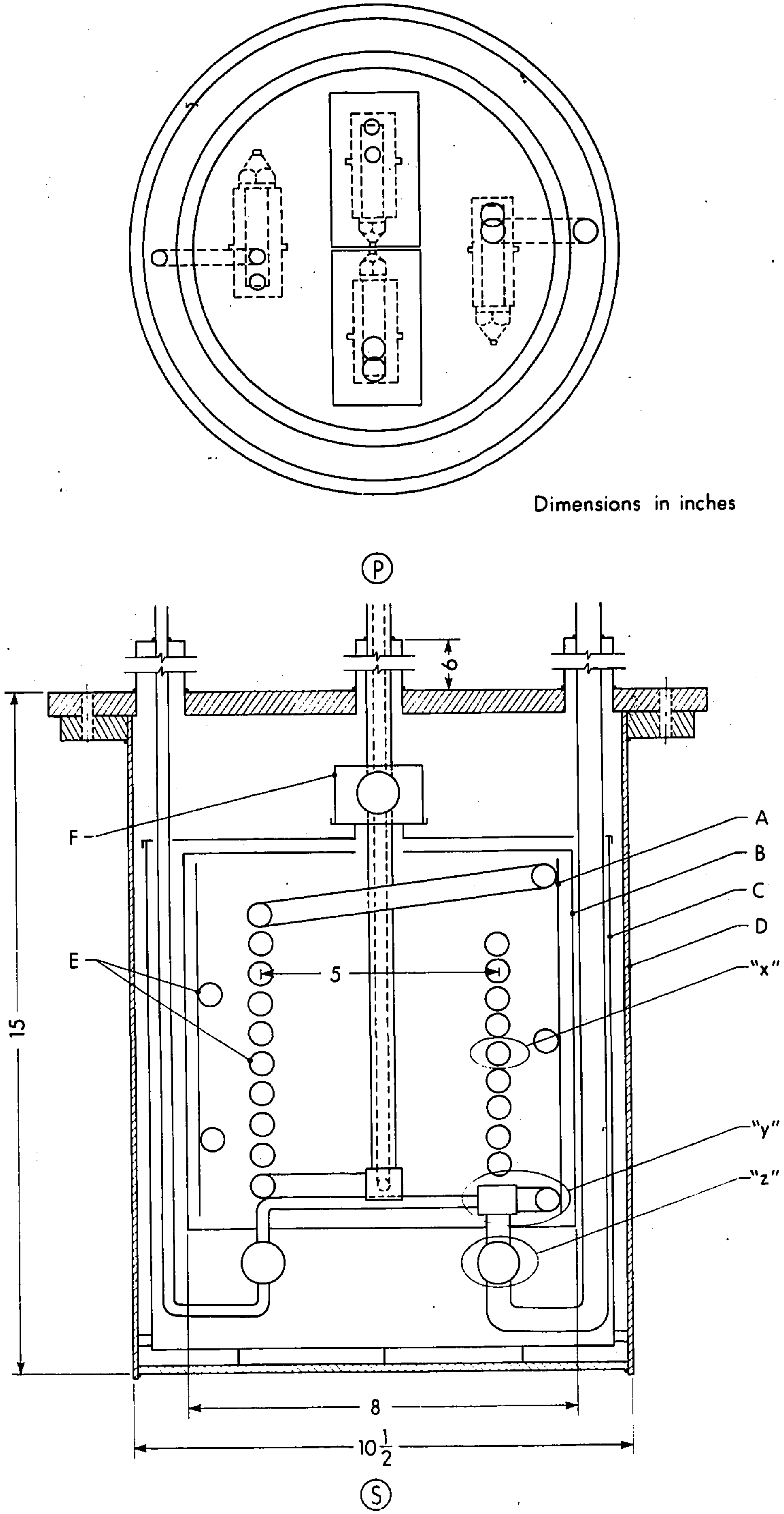
This appendix includes the drawings of the calorimeter assembly and other pertinent details.

Figure A-1 gives Calorimeter Assembly. In Plan P, flange of the enclosing vessel and top covering plate are not shown. In elevation S, the description of various items shown is as follows:

A. Copper shield
B. Calorimeter surface (copper)
C. Main 'guard' (copper)
D. Enclosing vessel (stainless steel)
E. Concentric helical coils
F. Probe housing 'guards' (copper)

The details "X", "Y" and "Z" of the elevation S are shown in Figure A-2.

The combined weight of the four probe housings, the coils, the copper shield A, and the calorimeter surface B was approximately 9.5 lbs.

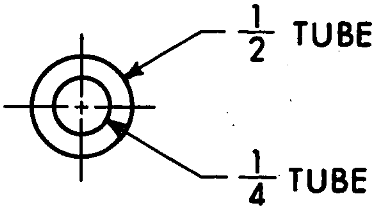


Dimensions in inches

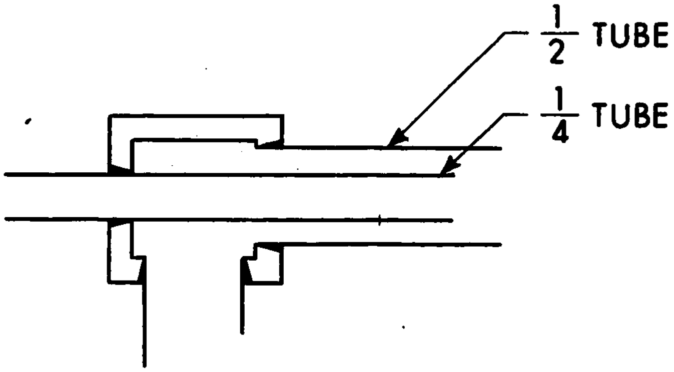
Fig. A1 CALORIMETER ASSEMBLY

DIMENSIONS IN INCHES

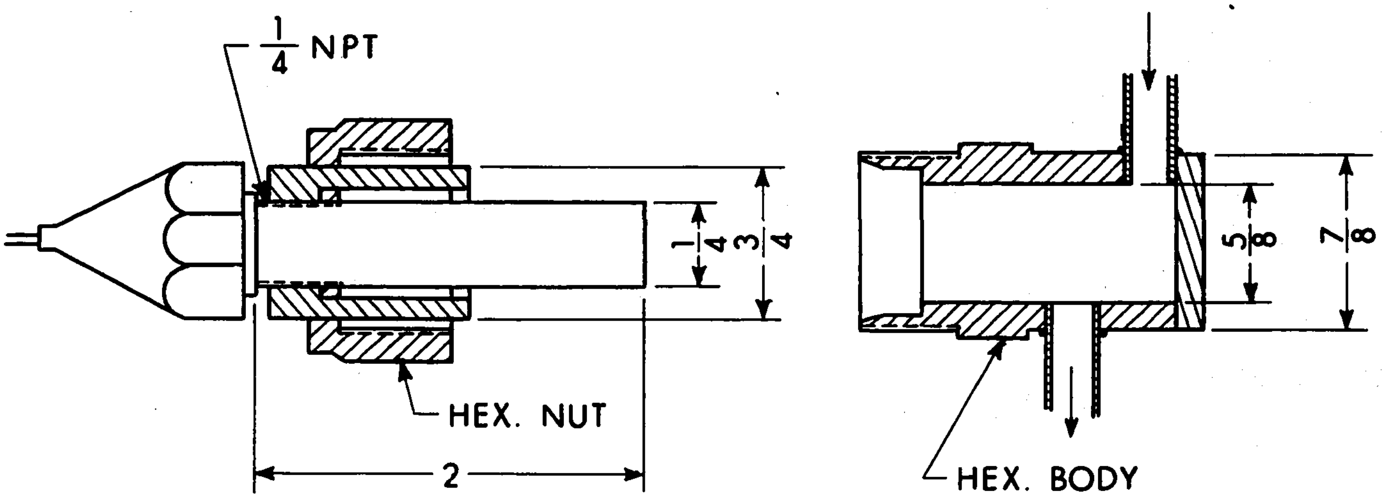
FULL SCALE



DETAIL "X"

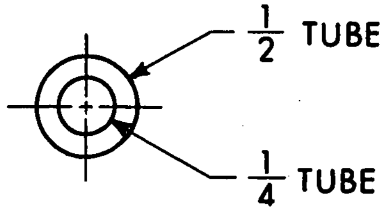


DETAIL "Y"



DETAIL "Z"

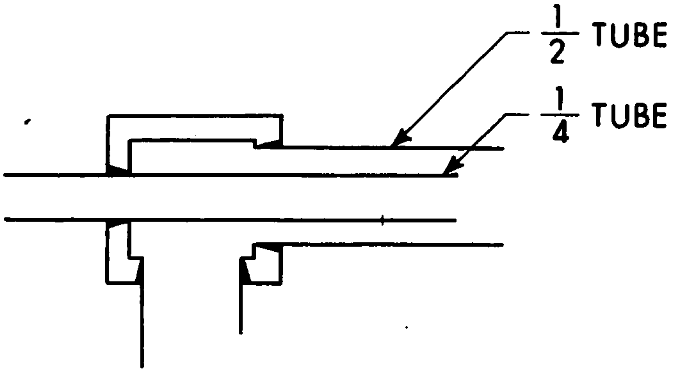
FIGURE A2: DETAILS "X", "Y", "Z"



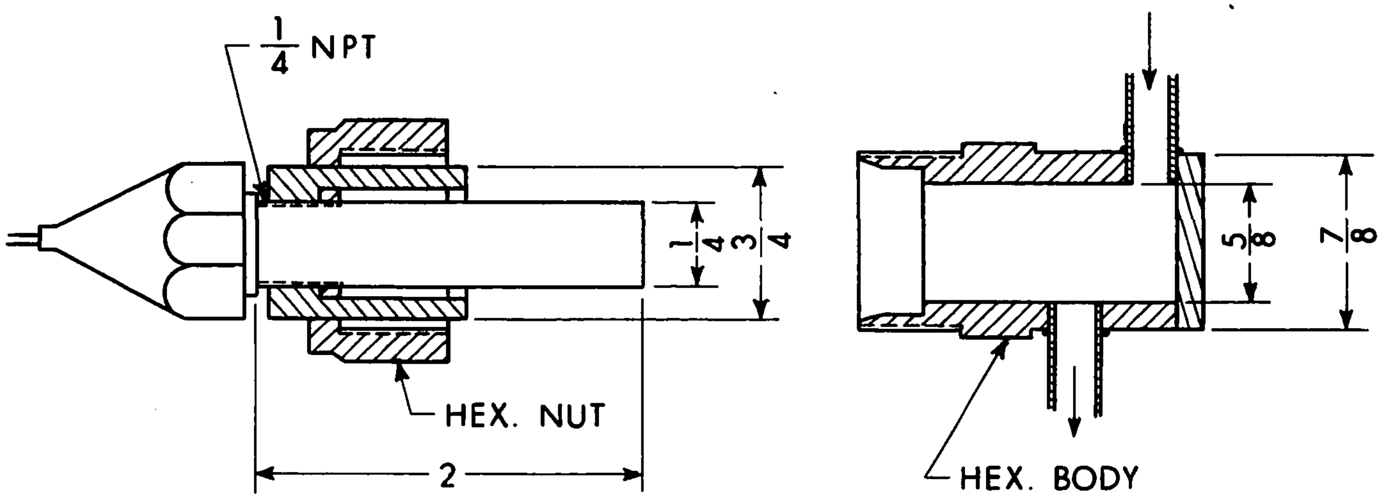
DIMENSIONS IN INCHES

DETAIL "X"

FULL SCALE



DETAIL "Y"



DETAIL "Z"

FIGURE A2: DETAILS "X", "Y", "Z"

The start-up, shut-down and data-taking procedures are discussed here with reference to Figures (III.1) and (III.3) in the main body of the thesis.

1. Start-up -

Activate the two gas heaters and put them under automatic control. The relationship of the set point dial reading and the temperature controlled is supplied by the manufacturer. However, the temperature controlled is that of the copper pipe, which houses the coil carrying the gas. Thus some experience with the equipment is required to estimate the set point dial reading in order to get a desired gas temperature at the inlet of the calorimeter.

If carbon dioxide-methane mixtures are being handled, supply power at a very low voltage to the heaters of the feed valves 'FV' (only one shown in the diagram) and the valves 'JTCV' and 'HPCV'. After pouring liquid nitrogen into the cold trap, start the vacuum pump. Put the differential temperature (between A and D of the calorimeter) under automatic control. Close the hand valves 'HV2' and 'HV3'. Feed material from the storage tanks into the low pressure surge tank till it reaches a pressure of about 25 psig. Put the low pressure surge tank under automatic pressure control. If carbon dioxide-methane mixtures are being handled, open the steam valve for the 'BPCV' valve body heater. Start water for the after cooler.

Check to see if the hand valve 'HV5' is closed. This valve should be closed if the high pressure surge tank contains some gas. Open the hand valves 'HV1' and 'HV4' and the water supply to the compressor. Start the compressor and allow its delivery pressure to rise. During this pressure build-up, feed material to the system, if needed, so that the inlet compressor pressure never drops below 15 psig. When the compressor delivery pressure exceeds the high pressure surge tank pressure, open the hand valve 'HV5'. Feed material from the storage cylinders keeping the inlet surge tank pressure between 15 and 20 psig. During this feeding, increase the power input to the feed valve heaters. If necessary alternate feeding from different cylinders so that their feed valves do not freeze.

When the pressure in the high pressure surge tanks reaches about 1,000 psi put on the high pressure control loop with zero set point. Open hand valves 'HV2' and 'HV3'. Slow the feeding rate and increase the set point of the high pressure controller to about 450 psi. Regulate manually the opening of 'JTCV' so as to get the desired flow rate. If carbon dioxide-methane mixtures are being used increase the power input to the heaters of the valve bodies of 'JTCV' and 'HPCV'. The power input is adjusted so that the temperature of the gas downstream from these valves does not go below the condensation temperature. When the desired flow is achieved in the calorimeter, stop feeding material and shut off the feed valve heaters. Adjust the set points of the pressure controllers to get the desired pressures at the inlet of the calorimeter.

Put on the heaters LLP, LHP, LPPH, HPPH and TGP and adjust their power input manually so as to get zero differential millivoltage generation. This is achieved over the next one and one-half hours or so.

The equipment is now running but it takes about two hours to achieve proper thermal distribution. The set points of the gas heaters might need some adjustment so that the desired inlet temperatures are reached.

The equipment requires very little attention during the time it is running. A periodic check of inlet compressor pressure has to be made. It has been found by experience that the interstage pressure of the compressor has a great bearing on its capacity. If, due to some unknown factors, the interstage pressure suddenly drops or increases by 20-30 psi, the control valve 'BPCV' may not be able to keep pace with the changed capacity of the compressor. The only other thing to be checked periodically during this period of waiting for thermal equilibrium is the differential millivolt readings of the various points in the calorimeter which need manual power adjustment.

The data-taking and characterization of a 'steady state reading' of the calorimeter are discussed elsewhere.

If it is desired to go to a higher pressure level in the calorimeter, more material may be required in the system. The material is fed by reducing the flow through the calorimeter and opening the feed valves. During this feeding, the excessive cooling of gas at any point in the system is avoided by properly adjusting the power inputs to the various heaters mentioned above.

2. Shut-down-

Shut off all the heaters on the calorimeter. Put the power on for the feed valves 'FV' and the discharge valves 'DV'. Discharge material from the system into the storage cylinders by means of the valves 'DV'. If carbon dioxide-methane mixtures are used the discharge rate has to be very low because of the cooling effect at the valves 'DV'. Intermittently stop discharging and let these valves warm up. During the discharge period, keep a close watch on the inlet pressure of the compressor. If necessary, increase the opening of the valve 'JTCV' and if this is not sufficient feed material from the storage cylinder so that inlet compressor pressure always remains between 15-25 psig. When the material cannot be discharged any more from the system to the storage tanks, shut off the compressor. Immediately close the valves 'HV3', 'HV5', 'HV1' and 'HV2'. Shut off the power to all the heaters and the steam supply to the 'BPCV' valve body heater. Close the water to the compressor and the after cooler. Check to make sure that no power is left on to any of the heaters.

For emergency shut-down close the valves 'HV3', 'HV2' and 'HV1' and shut off the compressor. Shut off the power to all the heaters and gradually discharge the material from the system to the storage tanks.

3. Data-taking -

The procedure followed in obtaining an "experimental steady state point" is given below.

Allow the pressure distribution and the flow rate to stabilize in the equipment. For the experimental data reported in this work a flow rate corresponding to between 40 and 50 ma reading of the d/p cell transmitter was maintained. The absolute pressures at the orifice meter for the work reported on nitrogen gas and carbon dioxide-methane mixtures was about 27 and 30 psia respectively. The flow rate corresponding to the reading of 40-50 ma for nitrogen and carbon dioxide-methane mixtures is about 3 SCFM.

When the inlet temperatures of the calorimeter have stabilized and the differential temperatures indicated by the thermocouple junction pairs of K and L, M and N, F and J, G and H and B and C have been adjusted close to zero, start recording the inlet temperatures T_1 (high pressure) and T_3 (low pressure) every five minutes. During this period keep adjusting the power input to the respective heaters of the 'pairs' mentioned above. When the temperatures T_1 and T_3 hold within ± 0.01 of their stable values for at least ten minutes start recording the temperatures T_1 and T_3 and the temperature changes ΔT (high pressure stream) and ΔT_o (low pressure stream) every minute. For at least the next 20 minutes if each of the T_1, T_3, ΔT, and ΔT_o have remained stable within $0.03^\circ C$, it is considered that an 'experimental steady state point' has been obtained. During this interval check the flow rate and the pressure readings for any fluctuations. Actually, any fluctuations in these quantities are immediately reflected on the temperatures of the calorimeter. Also during this period, maintain the pair B and C within ± 0.005 mv and the other 'pairs' within ± 0.02 mv from zero.

At the end of the steady state reading record the calorimeter surface temperature (D), the main guard temperatures (A) and (E), the flow rate, the inlet pressures P_1 (high pressure) and P_3 (low pressure) and the outlet temperatures and pressures T_2, T_4, P_2 and P_4.

APPENDIX C

RAW DATA AND CORRECTIONS

This appendix includes the data obtained in this work and illustrates the application of various corrections.

1. Nitrogen -

The data obtained on nitrogen are given in Tables C-1 through C-3. For every point reported the low and high pressure temperature changes are represented by ΔT_o and ΔT, and were observed every three minutes over the duration of a steady state period. The $\Delta T_o/\Delta T$ ratios were calculated for every observation and an average was found. The average thus calculated is reported in the tables as $(\Delta T_o/\Delta T)$. A value of ΔT corresponding to a ratio close to the average was chosen and ΔT_o calculated. These values of ΔT_o and ΔT are reported in the tables along with the average $(\Delta T_o/\Delta T)$ ratio for an experimental point. The total probe correction (sum of the linearity and ice-point corrections) was then applied to the ΔT_o and ΔT values. For example for the point 1 of Table C-1, the probe corrected ΔT_o and ΔT would be:

$$\begin{aligned}\Delta T_o &= -5.3043 + (-0.024)\\ &= -5.3283\\ \Delta T &= -4.9247 + (-0.122)\\ &= -5.0467\end{aligned}$$

$(\Delta T_o/\Delta T)_{corr.}$ would then be equal to 5.3283/5.0467 i.e. 1.0557. This value was then reported for $(\Delta T_o/\Delta T)_{corr.}$ in Table C-1. Similar calculations were done for all the points in a table.

TABLE C-1

EXPERIMENTAL DATA FOR NITROGEN

Average Temperature	60.2°C
Low Pressure	27.2 psia

Zero Correction for L.P. Temperature Change	-0.034
Linearity Correction for L.P. Temperature Change	0.01
Zero Correction for H.P. Temperature Change	-0.082
Linearity Correction for H.P. Temperature Change	-0.04

Point No.	P_1 psia	P_3 psia	T_1 °C	T_3 °C	ΔT_o	ΔT	$\frac{\Delta T_o}{\Delta T}$	$(\frac{\Delta T_o}{\Delta T})_{corr.}$
1	469.5	26.9	55.421	65.626	-5.3043	-4.9247	1.0771	1.0557
2	764.5	27.0	55.143	65.406	-5.3481	-4.8739	1.0973	1.0753
3	1379.5	27.1	55.850	65.095	-4.9649	-4.3031	1.1538	1.1274
4	1710.5	27.0	55.606	65.731	-5.4675	-4.660	1.1733	1.1483
5	1985.5	27.0	54.802	64.273	-5.1708	-4.3180	1.1975	1.1700
6	2284.5	27.1	55.203	65.572	-5.6597	-4.720	1.1991	1.1738
7	2349.5	26.9	55.241	65.665	-5.7189	-4.719	1.2119	1.1863
8	581.5	27.3	65.651	55.260	5.2182	5.129	1.0174	1.0373
9	996.5	27.4	65.024	55.793	4.7079	4.540	1.0370	1.0601
10	1500.5	27.3	65.293	54.579	5.5205	5.082	1.0863	1.1081
11	1434.5	27.2	65.571	54.722	5.6402	5.208	1.0830	1.1042
12	1784.5	27.0	65.279	54.470	5.6611	5.133	1.1029	1.1249
13	1804.5	27.1	65.318	54.440	5.701	5.141	1.1089	1.1311
14	1988.5	27.3	65.292	54.968	5.4137	4.802	1.1274	1.1516
15	2306.5	27.2	65.208	54.562	5.6159	4.958	1.1327	1.1563

TABLE C-2

EXPERIMENTAL DATA FOR NITROGEN

Average Temperature 75.7°C
Low Pressure 26.6 psia

Zero Correction for L.P. Temperature Change	-0.034
Linearity Correction for L.P. Temperature Change	0.010
Zero Correction for H.P. Temperature Change	-0.082
Linearity Correction for H.P. Temperature Change	-0.040

Point No.	P_1 psia	P_3 psia	T_1 °C	T_3 °C	ΔT_o	ΔT	$\Delta T_o/\Delta T$	$(\frac{\Delta T_o}{\Delta T})$corr.
1	539.5	25.9	80.930	70.917	4.932	5.038	0.9789	0.9983
2	614.5	26.3	81.103	71.014	4.9916	5.056	0.9872	1.0068
3	695.5	32.8	81.756	71.601	5.087	5.132	0.9912	1.0100
4	1225.5	27.2	81.267	71.150	5.106	4.987	1.0238	1.0440
5	1520.5	27.5	81.952	71.879	5.123	4.905	1.0444	1.0660
6	1803.5	27.3	80.634	71.053	4.901	4.620	1.0608	1.0840
7	2024.5	25.8	80.870	71.440	4.851	4.526	1.0718	1.0960
8	2127.5	25.8	81.037	71.402	4.936	4.563	1.0817	1.1060
9	539.5	26.2	70.434	80.611	-5.318	-4.868	1.0924	1.0700
10	1035.5	26.3	70.507	80.452	-5.286	-4.683	1.1287	1.1050
11	1337.5	26.2	70.242	79.938	-5.199	-4.503	1.1545	1.1290
12	1639.5	26.0	70.048	80.716	-5.670	-4.820	1.1763	1.1520
13	1879.5	26.3	70.690	80.950	-5.584	-4.695	1.1893	1.1640
14	2315.5	25.6	70.294	80.987	-5.904	-4.823	1.2241	1.1980

TABLE C-3

EXPERIMENTAL DATA FOR NITROGEN

Average Temperature 150.4°C
Low Pressure 26.4 psia

Zero Correction for L.P. Temperature Change	-0.0256
Linearity Correction for L.P. Temperature Change	0.02
Zero Correction for H.P. Temperature Change	-0.0873
Linearity Correction for H.P. Temperature Change	0.00

Point No.	P_1 psia	P_3 psia	T_1 °C	T_3 °C	ΔT_o	ΔT	$\Delta T_o/\Delta T$	$(\frac{\Delta T_o}{\Delta T})_{corr.}$
1	535.4	26.3	155.978	145.606	5.0408	5.234	0.9631	0.9783
2	597.4	26.5	155.870	145.559	5.0483	5.190	0.9727	0.9882
3	653.4	26.5	155.598	145.679	4.8226	5.010	0.9626	0.9785
4	853.4	26.4	155.668	145.612	4.9316	5.055	0.9756	0.9916
5	1113.4	26.4	155.645	145.475	5.0238	5.070	0.9909	1.0071
6	1413.4	26.5	156.255	145.509	5.3285	5.344	0.9971	1.0125
7	1723.4	26.5	155.949	145.409	5.248	5.212	1.0069	1.0229
8	2030.4	26.2	155.449	145.280	5.0851	5.007	1.0156	1.0324
9	2269.4	26.2	155.388	145.187	5.1437	5.038	1.0210	1.0378
10	520.4	26.2	145.800	155.215	-4.9533	-4.510	1.0983	1.0786
11	646.4	26.3	146.142	155.235	-4.8025	-4.338	1.1071	1.0865
12	873.4	26.3	145.495	155.484	-5.2932	-4.746	1.1153	1.0963
13	1117.4	26.3	145.528	155.412	-5.265	-4.686	1.1235	1.1041
14	1403.4	26.5	145.981	155.455	-5.0675	-4.455	1.1375	1.1168
15	1698.4	26.2	144.717	154.737	-5.3415	-4.700	1.1365	1.1169
16	2083.4	26.0	144.763	154.554	-5.2651	-4.572	1.1516	1.1312

The average temperature reported in each table were obtained by averaging T_1 and T_3 given in that table. Similarly the average P_3 was obtained by averaging all the P_3 values in each table.

2. Carbon Dioxide-Methane Mixtures -

The data collected on carbon dioxide-methane mixtures are reported in Tables C-5 through C-11 and are identified by their 'isotherm number'. In these tables P_1, P_3, T_1, T_3, DT_o and DT represent inlet high pressure, inlet low pressure, inlet high pressure gas temperature, inlet low pressure gas temperature, low pressure temperature change and high pressure temperature change respectively. (DT_o/DT) represents the ratio of observed temperature changes and the values reported are the average over a steady state period for each point. $(DT_o/DT)_{corr.}$ is the ratio of probe corrected temperature changes of the high and low pressure fluids.

For the isotherm no. 1, the values of (DT_o/DT) and $(DT_o/DT)_{corr.}$ for each point were obtained by the method that was followed for the nitrogen data. However, for the isotherms 2 through 7, DT_o and DT were observed every minute over the duration of a steady state period of each point and the respective linearity and zero corrections were added to every observation. The probe corrected DT_o and DT were then used to calculate the $(DT_o/DT)_{corr.}$ ratio for each observation and their average was determined over the steady state period of each point. The values of (DT_o/DT) and $(DT_o/DT)_{corr.}$ reported in the tables are the averages over the steady state period. The r.m.s. error was then calculated by summing up the square of the deviations of every observation from the average value, dividing by the number of observations and then finding its square root. For the purpose of illustration, observations and calculations for point no. 3 of isotherm n 3 are reported in Table C-4.

Temperature correction was applied to the $(DT_o/DT)_{corr.}$ values reported in Tables C-5 through C-11. The temperature corrected values are represented by $(DT_o/DT)^*$ and are given in Tables C-13 through C-19. The method followed for applying this correction is illustrated below for point no. 3 of isotherm no. 3.

First of all an average of the average high pressure gas temperatures (AVG.H.P.TEMPT.) is calculated, and is called as isotherm temperature.

a. <u>Correction due to the average L.P. (low pressure) gas temperature being different from the isotherm temperature.</u>

Isotherm temperature = 60.560°C (standard or reference temp.)

From a heat balance of the calorimeter,

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = (DT_o/DT)_{corr.} \pm \phi \qquad (C.1)$$

where

$$(DT_o/DT)_{corr.} = 1.6574$$

Φ = calorimetery errors

$\overline{C}_p$ = H.P. heat capacity at the H.P. average temperature for the point no. 3, i.e. at 60.752°C

$\overline{C}_{p_o}$ = L.P. heat capacity at the L.P. average temperature of the point no. 3, i.e. at 55.940°C.

Define

$$(EPS{+}{+}) = \overline{C}^{(s)}_{p_o} - \overline{C}_{p_o} \qquad (C.2)$$

where

$\overline{C}^{(s)}_{p_o}$ = L.P. heat capacity at 60.560°C and 30.3 psi

$\overline{C}_{p_o}$ = L.P. heat capacity at 55.940°C and 30.7 psi.

The above heat capacities are calculated from the BWR equation of state and (EPS++) is estimated from the above relation.

(EPS++) = 0.0438 (Table C-12).

Substituting (C.2) in (C.1) and approximating by the Binomial expansion, we can get

$$\frac{\overline{C}_p}{\overline{C}^{(s)}_{p_o}} = \left[\left(\frac{DT_o}{DT}\right)_{corr.} - \frac{\overline{C}_p}{(\overline{C}^{(s)}_{p_o})^2} \cdot (EPS{+}{+})\right] \pm \Phi \qquad (C.3)$$

Define

$$(E{+}{+}) = \frac{\overline{C}_p}{(\overline{C}^{(s)}_{p_o})^2} \cdot (EPS{+}{+})$$

Equation (C.3) then can be written as

$$\frac{C_p}{\overline{C}_{p_o}^{(s)}} = \left[\left(\frac{DT_o}{DT}\right)_{corr.} - (E{+}{+})\right] \pm \phi$$

$$= \left[\left(\frac{DT_o}{DT}\right)_{++}\right] \pm \phi \qquad (C.4)$$

where

$$\left[\left(\frac{DT_o}{DT}\right)_{++}\right] = \left[\left(\frac{DT_o}{DT}\right)_{corr.} - (E{+}{+})\right]$$

The calculated values are:

$(E{+}{+}) = 0.0073$ (Table C-12)

and

$\left[\left(\frac{DT_o}{DT}\right)_{++}\right] = 1.6500$ (Table C-12)

b. Correction due to the average H.P. temperature being different from the isotherm temperature (standard temperature)

define $$(EPS^*) = \overline{C}_p - \overline{C}_p^{(s)} \qquad (C.5)$$

Substituting (C.5) in (C.4) and rearranging we get:

$$\frac{\overline{C}_p^{(s)}}{\overline{C}_{p_o}^{(s)}} = \left[\left(\frac{DT_o}{DT}\right)_{++}\right] - \frac{1}{\overline{C}_{p_o}^{(s)}} \cdot (EPS^*) \pm \Phi$$

$$= \left[\left(\frac{DT_o}{DT}\right)^*\right] \pm \phi \qquad (C.6)$$

where

$$\left(\frac{DT_o}{DT}\right)^* = \left[\left(\frac{DT_o}{DT}\right) ++\right] - \frac{1}{\overline{C}^{(s)}_{p_o}} (EPS^*)$$

$\overline{C}^{(s)}_{p}$ = H.P. heat capacity at the isotherm (standard) temperature.

The calculated values are:

$$(EPS^*) = -0.0186 \text{ (Table C-12)}$$

$$(E^*) = \frac{1}{\overline{C}^{(s)}_{p_o}} (EPS^*) = -0.0020 \text{ (Table C-12)}$$

$$\left[\left(\frac{DT_o}{DT}\right)^*\right] = 1.6500 - (-0.0020) = 1.6520$$

The calculated $\left(\frac{DT_o}{DT}\right)^*$ values at various isotherms are given in Tables C-13 through C-19.

TABLE C-4 $CO_2 + CH_4$ SYSTEM

OBSERVATIONS FOR POINT NO. 3

MOLE FRACTION CH4 = 0.1449

EXPERIMENTAL DATA FOR ISOTHERM NO. 3

POINT NO. 3

CORRECTION FOR L.P. TEMPERATURE CHANGE = -0.0155
CORRECTION FOR H.P. TEMPERATURE CHANGE = -0.1273
AVERAGE TEMPT. FOR H.P. GAS = 60.752 AVERAGE TEMPT. FOR L.P. GAS = 55.940

OBS. NO.	DTO	DT	DTO/DT UNCORR.	DTO CORRECTED	DT CORRECTED	DTO/DT CORRECTED	DEVIATION	PERCENTAGE DEVIATION
1	5.8970	3.6750	1.6046	5.8814	3.5477	1.6578	0.0003	0.0238
2	5.8870	3.6840	1.5979	5.8714	3.5567	1.6508	-0.0066	-0.3989
3	5.8780	3.6780	1.5981	5.8624	3.5507	1.6510	-0.0063	-0.3835
4	5.8870	3.6700	1.6040	5.8714	3.5427	1.6573	-0.0000	-0.0053
5	5.8870	3.6690	1.6045	5.8714	3.5416	1.6577	0.0003	0.0229
6	5.8820	3.6740	1.6009	5.8664	3.5467	1.6540	-0.0033	-0.2031
7	5.8810	3.6750	1.6002	5.8654	3.5477	1.6532	-0.0041	-0.2482
8	5.8720	3.6620	1.6034	5.8564	3.5347	1.6568	-0.0005	-0.0350
9	5.8700	3.6610	1.6033	5.8544	3.5337	1.6567	-0.0006	-0.0408
10	5.8710	3.6640	1.6023	5.8554	3.5366	1.6556	-0.0018	-0.1086
11	5.8700	3.6710	1.5990	5.8544	3.5437	1.6520	-0.0053	-0.3229
12	5.8710	3.6660	1.6014	5.8554	3.5387	1.6546	-0.0027	-0.1650
13	5.8710	3.6600	1.6040	5.8554	3.5327	1.6574	0.0000	0.0044
14	5.8750	3.6500	1.6095	5.8594	3.5227	1.6633	0.0059	0.3568
15	5.8700	3.6500	1.6082	5.8544	3.5227	1.6619	0.0044	0.2712
16	5.8640	3.6560	1.6039	5.8484	3.5286	1.6573	-0.0000	-0.0018
17	5.8600	3.6650	1.5989	5.8444	3.5377	1.6520	-0.0053	-0.3244
18	5.8610	3.6620	1.6004	5.8454	3.5347	1.6537	-0.0036	-0.2228
19	5.8640	3.6550	1.6043	5.8484	3.5277	1.6578	0.0004	0.0264
20	5.8680	3.6460	1.6094	5.8524	3.5187	1.6632	0.0058	0.3509
21	5.8720	3.6430	1.6118	5.8564	3.5156	1.6657	0.0083	0.5052
22	5.8680	3.6420	1.6112	5.8524	3.5147	1.6651	0.0077	0.4651
23	5.8630	3.6400	1.6107	5.8474	3.5127	1.6646	0.0072	0.4364

AVERAGE DTO/DT = 1.6040
AVERAGE CORRECTED DTO/DT = 1.6574
STANDARD DEVIATION I.E. ROOT MEAN SQUARE DEVIATION = + OR - 0.0045
ROOT MEAN SQUARE PERCENT DEVIATION = + OR - 0.2717

TABLE C- 5 CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 1

MOLE FR. CH4 0.1449

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0200
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	0.0000

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.
1	546.6	32.2	152.866	142.953	150.387	145.447	1.0271	1.0448
2	787.6	32.0	152.500	143.270	150.285	145.628	1.0648	1.0849
3	1083.6	32.3	152.154	142.530	149.896	145.049	1.1158	1.1365
4	1436.6	30.9	152.891	143.074	150.660	145.707	1.1806	1.2029
5	1782.6	30.3	154.357	143.298	151.920	146.325	1.2423	1.2637
6	2141.6	30.2	153.018	142.937	150.832	145.767	1.3031	1.3285
7	569.6	30.8	148.458	158.164	150.727	155.558	1.1480	1.1275
8	826.6	31.7	147.761	157.493	150.001	154.842	1.1832	1.1618
9	1202.6	29.6	149.703	158.389	151.628	155.935	1.2741	1.2473
10	1615.6	30.2	148.688	157.755	150.616	155.118	1.3674	1.3386
11	1883.6	30.1	148.402	157.233	150.235	154.631	1.4195	1.3880
12	2229.6	30.2	147.978	158.020	149.979	155.034	1.4918	1.4614

TABLE C- 6 CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 2

MOLE FR. CH4 0.1449

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0000
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	-0.0300

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	551.5	31.1	42.049	31.911	39.818	34.731	1.2642	1.2924	0.0018
2	741.5	31.1	42.241	31.644	40.102	34.779	1.4617	1.4967	0.0010
3	1007.5	30.5	42.034	32.057	40.335	35.316	1.9173	1.9779	0.0034
4	1217.5	30.2	40.672	31.396	39.407	34.735	2.6323	2.7492	0.0095
5	1377.5	30.0	39.883	31.452	38.957	34.712	3.5786	3.8098	0.0350
6	1531.5	30.0	40.373	31.230	39.499	34.883	4.2445	4.5374	0.0324
7	1631.5	30.3	40.186	31.080	39.362	34.769	4.3904	4.7022	0.0346
8	1724.5	29.7	40.946	31.553	40.068	35.332	4.3354	4.6331	0.0260
9	1813.5	30.1	40.817	30.515	39.831	34.637	4.1511	4.3984	0.0292
10	1965.5	30.0	40.065	30.311	39.039	34.125	3.7515	3.9678	0.0124
11	2203.5	29.7	40.538	30.887	39.399	34.541	3.2182	3.3826	0.0117
12	503.5	30.8	38.729	48.066	40.744	45.417	1.3147	1.2837	0.0009
13	711.5	30.5	38.632	48.888	40.673	45.806	1.5111	1.4750	0.0063
14	999.5	30.8	37.910	48.772	39.699	45.143	2.0312	1.9736	0.0059
15	1220.5	30.4	37.625	48.335	38.999	44.376	2.8695	2.7612	0.0120
16	1355.5	30.1	37.745	48.668	38.903	44.388	3.7015	3.5334	0.0169
17	1513.5	30.4	37.387	48.442	38.317	43.878	4.8516	4.5799	0.0101
18	1611.5	30.2	39.045	48.746	39.856	44.728	4.8678	4.5625	0.0252
19	1705.5	30.2	39.020	48.673	39.836	44.690	4.8715	4.5598	0.0279
20	1823.5	30.3	39.314	48.948	40.172	45.011	4.5787	4.3003	0.0203
21	1971.5	30.2	39.490	48.960	40.411	45.164	4.1393	3.9041	0.0195
22	2203.5	30.1	39.287	49.026	40.360	45.250	3.5399	3.3670	0.0148

TABLE C- 7   CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 3

MOLE FR. CH4 0.1449

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0100
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	-0.0400

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	508.6	30.6	62.439	52.667	60.187	55.288	1.1576	1.1877	0.0055
2	821.6	30.9	62.365	51.764	60.133	54.816	1.3764	1.4134	0.0024
3	1103.6	30.7	62.575	53.004	60.752	55.940	1.6040	1.6574	0.0045
4	1371.6	30.6	62.315	52.880	60.731	55.988	1.9673	2.0447	0.0065
5	1561.5	29.9	62.843	52.836	61.327	56.303	2.2957	2.3914	0.0056
6	1791.5	30.1	62.662	51.426	61.142	55.490	2.6820	2.7944	0.0122
7	1941.5	31.3	62.484	51.604	61.104	55.633	2.8547	2.9842	0.0178
8	2119.5	30.0	62.045	51.071	60.675	55.146	2.9649	3.1031	0.0133
9	2261.5	29.9	62.578	51.036	61.124	55.305	2.9489	3.0796	0.0161
10	516.5	30.8	58.567	68.117	60.692	65.472	1.2421	1.2096	0.0022
11	815.5	30.4	58.691	68.024	60.598	65.269	1.4431	1.4005	0.0026
12	1116.5	30.8	57.999	68.913	59.976	65.447	1.7374	1.6872	0.0047
13	1367.5	30.5	58.456	69.168	60.168	65.537	2.1116	2.0404	0.0061
14	1569.5	30.2	58.600	69.062	60.091	65.340	2.4865	2.3900	0.0106
15	1804.5	30.2	58.371	69.024	59.721	65.075	2.9407	2.8134	0.0179
16	1945.5	30.0	58.889	68.508	60.049	64.873	3.1492	2.9912	0.0151
17	2113.5	30.1	59.393	69.150	60.548	65.440	3.2120	3.0502	0.0170
18	2269.5	29.9	59.834	70.124	61.062	66.219	3.1842	3.0322	0.0155

TABLE C- 8   CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 4

MOLE FR. CH4   0.1449

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0200
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	-0.0300

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	511.6	30.5	92.673	82.781	90.315	85.356	1.0937	1.1204	0.0018
2	815.6	30.6	92.720	82.081	90.320	84.981	1.2094	1.2386	0.0028
3	1109.6	30.6	92.275	82.173	90.123	85.048	1.3391	1.3754	0.0056
4	1414.6	30.5	91.164	81.475	89.245	84.378	1.5216	1.5682	0.0060
5	1693.6	30.4	92.741	81.507	90.656	85.012	1.6703	1.7170	0.0061
6	2010.6	30.3	91.712	81.915	90.021	85.095	1.8934	1.9590	0.0099
7	2266.6	30.0	92.892	82.269	91.133	85.775	1.9815	2.0478	0.0085
8	511.6	30.6	88.393	97.454	90.472	95.004	1.1767	1.1458	0.0031
9	832.6	30.9	88.398	97.353	90.349	94.831	1.2869	1.2507	0.0024
10	1110.6	30.7	88.407	98.887	90.562	95.801	1.4393	1.4023	0.0063
11	1459.6	30.7	88.438	98.528	90.350	95.402	1.6229	1.5763	0.0075
12	1715.6	30.1	89.401	98.291	90.982	95.426	1.8187	1.7552	0.0064
13	2013.6	30.2	88.882	98.368	90.437	95.188	2.0156	1.9445	0.0098
14	2218.6	29.8	90.053	99.018	91.487	95.971	2.1408	2.0582	0.0091

TABLE C- 9 CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 5

MOLE FR. CH4 0.4230

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0000
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	-0.0300

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	497.6	30.4	42.379	32.967	40.180	35.464	1.1376	1.1629	0.0040
2	763.6	30.4	42.416	30.981	39.919	34.187	1.2818	1.3074	0.0003
3	961.6	30.2	41.609	32.055	39.633	34.841	1.4089	1.4453	0.0012
4	1209.6	30.2	41.650	31.645	39.741	34.722	1.6095	1.6536	0.0013
5	1467.6	30.5	41.483	31.509	39.736	34.730	1.8517	1.9086	0.0031
6	1699.6	30.0	41.893	31.195	40.154	34.775	2.0559	2.1200	0.0027
7	1915.6	30.0	41.822	31.140	40.174	34.804	2.2221	2.2959	0.0020
8	2093.6	29.8	41.910	32.134	40.429	35.518	2.2868	2.3720	0.0038
9	2247.6	29.7	41.974	32.432	40.541	35.746	2.3183	2.4080	0.0032
10	503.5	29.7	37.673	48.273	40.072	45.377	1.2032	1.1797	0.0020
12	831.5	30.3	37.450	48.544	39.777	45.329	1.3820	1.3535	0.0010
13	1123.5	30.3	37.821	48.056	39.777	44.900	1.6108	1.5704	0.0019
14	1405.5	30.5	38.268	46.616	39.708	43.892	1.8861	1.8209	0.0056
15	1733.5	29.9	38.036	49.197	39.770	45.361	2.2089	2.1437	0.0052
16	1943.5	30.0	38.161	48.575	39.702	44.918	2.3811	2.3017	0.0035
17	2111.5	29.8	38.199	48.441	39.673	44.801	2.4547	2.3694	0.0085
18	2261.5	29.6	38.173	48.990	39.724	45.142	2.4886	2.4056	0.0084

TABLE C-10 CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 6

MOLE FR. CH4 0.4230

ZERO CORRECTION FOR L.P. TEMPT. CHANGE	-0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE	0.0100
ZERO CORRECTION FOR H.P. TEMPT. CHANGE	-0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE	-0.0400

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	503.5	30.5	62.320	52.380	59.966	54.988	1.1115	1.1391	0.0012
2	827.5	30.5	62.546	51.559	60.083	54.574	1.2272	1.2565	0.0014
3	1105.5	30.5	62.803	52.116	60.527	55.164	1.3386	1.3735	0.0020
4	1427.5	29.8	62.592	52.211	60.536	55.327	1.5115	1.5557	0.0042
5	1729.5	30.1	62.694	52.147	60.725	55.432	1.6636	1.7149	0.0052
6	1937.5	29.7	62.732	52.378	60.864	55.664	1.7676	1.8259	0.0076
7	2124.5	29.8	62.797	52.187	60.934	55.602	1.8368	1.8975	0.0038
8	2261.5	29.8	62.823	52.219	60.996	55.666	1.8907	1.9549	0.0071
9	493.5	30.1	58.303	68.387	60.629	65.673	1.1656	1.1379	0.0009
10	797.5	30.1	58.668	67.867	60.690	65.291	1.2727	1.2376	0.0017
11	1093.5	30.1	58.077	68.674	60.284	65.588	1.3980	1.3622	0.0022
12	1417.5	30.1	58.544	68.396	60.456	65.386	1.5722	1.5255	0.0026
13	1703.5	29.9	58.580	68.468	60.380	65.333	1.7355	1.6806	0.0029
14	1922.5	29.9	58.466	68.156	60.154	65.005	1.8577	1.7948	0.0048
15	2107.5	29.7	58.523	68.481	60.209	65.195	1.9454	1.8793	0.0046
16	2253.5	29.5	58.473	68.990	60.227	65.492	1.9966	1.9309	0.0038

TABLE C-11 CO2 + CH4 SYSTEM.

EXPERIMENTAL DATA FOR ISOTHERM NO. 7

MOLE FR. CH4 0.4230

ZERO CORRECTION FOR L.P. TEMPT. CHANGE -0.0256
LINEARITY CORRECTION FOR L.P. TEMPT. CHANGE 0.0200
ZERO CORRECTION FOR H.P. TEMPT. CHANGE -0.0873
LINEARITY CORRECTION FOR H.P. TEMPT. CHANGE -0.0300

PT. NO.	P1 PSIA	P3 PSIA	T1 DEG.C	T3 DEG.C	AVG.H.P. TEMPT.	AVG.L.P. TEMPT.	DTO/DT	DTO/DT CORR.	R.M.S. ERROR
1	493.5	30.1	92.647	81.727	90.003	84.528	1.0598	1.0827	0.0009
2	815.5	30.3	93.147	81.486	90.431	84.584	1.1408	1.1650	0.0015
3	1116.5	30.2	93.051	81.443	90.439	84.616	1.2159	1.2427	0.0014
4	1431.5	30.3	92.370	81.832	90.088	84.800	1.3044	1.3377	0.0028
5	1725.5	29.9	92.485	81.778	90.250	84.876	1.3875	1.4236	0.0037
6	2001.5	29.8	92.083	81.783	90.012	84.844	1.4762	1.5175	0.0079
7	2233.5	29.5	92.822	81.924	90.673	85.199	1.5176	1.5588	0.0051
8	494.4	30.2	87.350	98.292	89.920	95.392	1.1283	1.1042	0.0019
9	814.4	30.1	88.373	98.223	90.607	95.530	1.2057	1.1761	0.0025
10	1121.4	30.1	88.391	98.247	90.542	95.468	1.2910	1.2580	0.0034
11	1430.4	30.1	88.940	97.905	90.822	95.302	1.3807	1.3405	0.0028
12	1720.4	30.2	88.285	98.845	90.422	95.701	1.4713	1.4333	0.0029
13	2017.4	29.9	87.964	98.972	90.120	95.626	1.5516	1.5117	0.0044
14	2237.4	30.1	87.787	98.531	89.837	95.212	1.6107	1.5673	0.0044

TABLE C-12 $CO_2 + CH_4$ SYSTEM

ILLUSTRATION OF TEMPERATURE CORRECTION

MOLE FR. METHANE =0.1449

EXPERIMENTAL DATA FOR ISOTHERM NO. 3

HEAT CAPACITY AT P= 30.3 AND T= 60.560 IS 9.2657 B.T.U./(LB.MOLE.DEG R)

STANDARD TEMPT. = 60.560

POINT NO.	P1 PSIA	P3 PSIA	DTO/DT CORR.	CPO AT AVG TEMP	EPS++	E++	(DTO/DT)++	CP AT AVG TEMP	CP AT STD TEMP	EPS*	E*	(DTO/DT)*
1	508.6	30.6	1.1877	9.2152	0.0505	0.0063	1.1813	10.7315	10.7286	0.0028	0.0003	1.1810
2	821.6	30.9	1.4134	9.2114	0.0543	0.0077	1.4056	12.3006	12.2845	0.0160	0.0017	1.4038
3	1103.6	30.7	1.6574	9.2218	0.0438	0.0073	1.6500	14.4057	14.4243	-0.0186	-0.0020	1.6520
4	1371.6	30.6	2.0447	9.2220	0.0437	0.0088	2.0358	17.3590	17.3948	-0.0358	-0.0038	2.0397
5	1561.5	29.9	2.3914	9.2234	0.0423	0.0097	2.3816	19.7581	19.9981	-0.2399	-0.0259	2.4075
6	1791.5	30.1	2.7944	9.2160	0.0496	0.0132	2.7811	22.8428	23.0870	-0.2442	-0.0263	2.8075
7	1941.5	31.3	2.9842	9.2203	0.0454	0.0128	2.9713	24.3928	24.6331	-0.2402	-0.0259	2.9972
8	2119.5	30.0	3.1031	9.2124	0.0533	0.0159	3.0871	25.7250	25.7734	-0.0484	-0.0052	3.0923
9	2261.5	29.9	3.0796	9.2137	0.0520	0.0157	3.0638	25.9549	26.1628	-0.2079	-0.0224	3.0863
10	516.5	30.8	1.2096	9.3143	-0.0485	-0.0060	1.2156	10.7593	10.7604	-0.0011	-0.0001	1.2158
11	815.5	30.4	1.4005	9.3115	-0.0457	-0.0065	1.4070	12.2459	12.2473	-0.0013	-0.0001	1.4071
12	1116.5	30.8	1.6872	9.3141	-0.0483	-0.0082	1.6954	14.6049	14.5448	0.0600	0.0064	1.6889
13	1367.5	30.5	2.0404	9.3143	-0.0485	-0.0098	2.0502	17.4246	17.3421	0.0825	0.0089	2.0413
14	1569.5	30.2	2.3900	9.3117	-0.0459	-0.0108	2.4008	20.2659	20.1116	0.1543	0.0166	2.3842
15	1804.5	30.2	2.8134	9.3092	-0.0434	-0.0119	2.8253	23.6090	23.2403	0.3686	0.0397	2.7855
16	1945.5	30.0	2.9912	9.3069	-0.0410	-0.0119	3.0031	24.8982	24.6671	0.2310	0.0249	2.9781
17	2113.5	30.1	3.0502	9.3125	-0.0468	-0.0140	3.0642	25.7523	25.7472	0.0051	0.0005	3.0636
18	2269.5	29.9	3.0322	9.3195	-0.0538	-0.0162	3.0484	25.9889	26.1723	-0.1833	-0.0197	3.0682

THE HEAT CAPACITY VALUES REPORTED HERE ARE CALCULATED FROM THE B.W.R. EQN. OF STATE.
THESE VALUES ARE USED FOR APPLYING CORRECTION TO THE DTO/DT RATIOS TO REDUCE THEM TO THE SAME TEMPT. LEVEL.

TABLE C-13 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 1

MOLE FR. METHANE 0.1449

ISOTHERM TEMPT.	150.602	DEG. C
LOW PRESSURE	30.9	PSIA
LOW PRESSURE HEAT CAPACITY	10.1046	BTU/(LB MOLE.DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	546.6	1.0448	1.0401
2	787.6	1.0849	1.0802
3	1083.6	1.1365	1.1307
4	1436.6	1.2029	1.1977
5	1782.6	1.2637	1.2614
6	2141.6	1.3285	1.3233
7	569.6	1.1275	1.1321
8	826.6	1.1618	1.1660
9	1202.6	1.2473	1.2533
10	1615.6	1.3386	1.3435
11	1883.6	1.3880	1.3916
12	2229.6	1.4614	1.4646

TABLE C-14 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 2

MOLE FR. METHANE 0.1449

ISOTHERM TEMPT.	39.711	DEG. C
LOW PRESSURE	30.3	PSIA
LOW PRESSURE HEAT CAPACITY	9.0624	BTU/(LB MOLE.DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	551.5	1.2924	1.2867
2	741.5	1.4967	1.4920
3	1007.5	1.9779	1.9827
4	1217.5	2.7492	2.7182
5	1377.5	3.8098	3.7021
6	1531.5	4.5374	4.4802
7	1631.5	4.7022	4.6179
8	1724.5	4.6331	4.6632
9	1813.5	4.3984	4.3860
10	1965.5	3.9678	3.9308
11	2203.5	3.3826	3.3714
12	503.5	1.2837	1.2931
13	711.5	1.4750	1.4892
14	999.5	1.9736	1.9838
15	1220.5	2.7612	2.7298
16	1355.5	3.5334	3.4588
17	1513.5	4.5799	4.3510
18	1611.5	4.5625	4.6083
19	1705.5	4.5598	4.6008
20	1823.5	4.3003	4.3689
21	1971.5	3.9041	3.9452
22	2203.5	3.3670	3.3718

TABLE C-15 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 3

MOLE FR. METHANE 0.1449

ISOTHERM TEMPT.	60.560	DEG. C
LOW PRESSURE	30.3	PSIA
LOW PRESSURE HEAT CAPACITY	9.2657	BTU/(LB MOLE.DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	508.6	1.1877	1.1810
2	821.6	1.4134	1.4038
3	1103.6	1.6574	1.6520
4	1371.6	2.0447	2.0397
5	1561.5	2.3914	2.4075
6	1791.5	2.7944	2.8075
7	1941.5	2.9842	2.9972
8	2119.5	3.1031	3.0923
9	2261.5	3.0796	3.0863
10	516.5	1.2096	1.2158
11	815.5	1.4005	1.4071
12	1116.5	1.6872	1.6889
13	1367.5	2.0404	2.0413
14	1569.5	2.3900	2.3842
15	1804.5	2.8134	2.7855
16	1945.5	2.9912	2.9781
17	2113.5	3.0502	3.0636
18	2269.5	3.0322	3.0682

TABLE C-16 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 4

MOLE FR. METHANE 0.1449

ISOTHERM TEMPT. 90.460 DEG. C
LOW PRESSURE 30.4 PSIA
LOW PRESSURE HEAT CAPACITY 9.5524 BTU/(LB MOLE,DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	511.6	1.1204	1.1147
2	815.6	1.2386	1.2318
3	1109.6	1.3754	1.3671
4	1414.6	1.5682	1.5506
5	1693.6	1.7170	1.7102
6	2010.6	1.9590	1.9427
7	2266.6	2.0478	2.0495
8	511.6	1.1458	1.1508
9	832.6	1.2507	1.2559
10	1110.6	1.4023	1.4097
11	1459.6	1.5763	1.5829
12	1715.6	1.7552	1.7689
13	2013.6	1.9445	1.9526
14	2218.6	2.0582	2.0846

TABLE C-17 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 5

MOLE FR. METHANE 0.4230

ISOTHERM TEMPT.	39.924	DEG. C
LOW PRESSURE	30.1	PSIA
LOW PRESSURE HEAT CAPACITY	8.9597	BTU/(LB MOLE.DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	497.6	1.1629	1.1576
2	763.6	1.3074	1.2993
3	961.6	1.4454	1.4352
4	1209.6	1.6536	1.6416
5	1467.6	1.9086	1.8936
6	1699.6	2.1200	2.1148
7	1915.6	2.2959	2.2913
8	2093.6	2.3720	2.3770
9	2247.6	2.4080	2.4156
10	503.5	1.1797	1.1867
11	831.5	1.3535	1.3608
12	1123.5	1.5704	1.5774
13	1405.5	1.8209	1.8247
14	1733.5	2.1437	2.1518
15	1943.5	2.3017	2.3069
16	2111.5	2.3694	2.3739
17	2261.5	2.4056	2.4133

TABLE C-18 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 6

MOLE FR. METHANE 0.4230

ISOTHERM TEMPT.	60.478	DEG. C
LOW PRESSURE	30.0	PSIA
LOW PRESSURE HEAT CAPACITY	9.1623	BTU/(LB MOLE.DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	503.5	1.1391	1.1322
2	827.5	1.2565	1.2475
3	1105.5	1.3735	1.3659
4	1427.5	1.5557	1.5474
5	1729.5	1.7149	1.7087
6	1937.5	1.8259	1.8221
7	2124.5	1.8975	1.8948
8	2261.5	1.9549	1.9533
9	493.5	1.1379	1.1444
10	797.5	1.2376	1.2446
11	1093.5	1.3622	1.3689
12	1417.5	1.5255	1.5337
13	1703.5	1.6806	1.6884
14	1922.5	1.7948	1.7988
15	2107.5	1.8793	1.8845
16	2253.5	1.9309	1.9372

TABLE C-19 CO2 + CH4 SYSTEM.

TEMPT. CORRECTED EXPT. DATA FOR ISOTHERM NO. 7

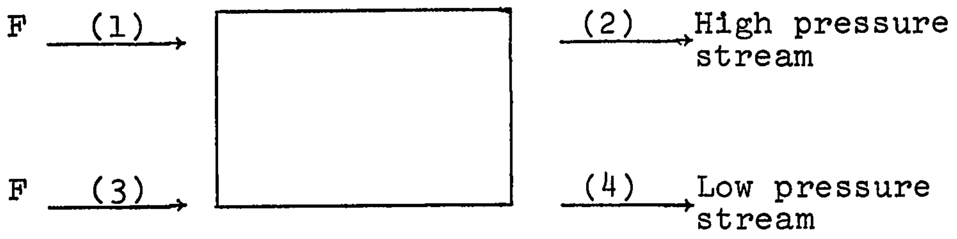
MOLE FR. METHANE 0.4230

ISOTHERM TEMPT.	90.297	DEG. C
LOW PRESSURE	30.0	PSIA
LOW PRESSURE HEAT CAPACITY	9.4635	BTU/(LB MOLE,DEG R)

POINT NO.	P1 PSIA	DTO/DT CORR.	(DTO/DT)*
1	493.5	1.0827	1.0759
2	815.5	1.1650	1.1579
3	1116.5	1.2427	1.2353
4	1431.5	1.3377	1.3290
5	1725.5	1.4236	1.4149
6	2001.5	1.5175	1.5067
7	2233.5	1.5588	1.5527
8	494.4	1.1042	1.1102
9	814.4	1.1761	1.1829
10	1121.4	1.2580	1.2654
11	1430.4	1.3405	1.3495
12	1720.4	1.4333	1.4423
13	2017.4	1.5117	1.5192
14	2237.4	1.5673	1.5723

APPENDIX D

THE CALORIMETRY ERRORS OF THE HEAT EXCHANGER METHOD



Define

F = Mass flow rate of the fluid

P_i = Pressure of the fluid at location i

T_i = Temperature of the fluid at location i

H_i = Specific enthalpy of the fluid at location i

ΔT = Outlet temperature-inlet temperature

ΔP = Inlet pressure-outlet pressure

$\dot{Q}$ = The rate of heat leak to or from the exchanger.

The quantities written with the subscript o are for the low pressure stream and those without this subscript are for the high pressure stream. The first law of thermodynamics when applied to this calorimeter at steady state gives

$$H_1 - H_2 + H_3 - H_4 \pm \dot{Q}/F = 0 \qquad \text{(D.1)}$$

$$dH = (\partial H/\partial T)_p dT + (\partial H/\partial P)_T dP$$

Integrating

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} (\partial H/\partial T)_{p_1} dT + \int_{p_1}^{p_2} (\partial H/\partial P)_{T_2} dP$$

$$= \int_{T_1}^{T_2} C_p \, dT + \int_{p_1}^{p_2} (- \mu C_p)_{T_2} dP$$

$$= \int_{T_1}^{T_2} C_p \, dT + \int_{p_2}^{p_1} \mu C_p \, dP$$

$$= \overline{C}_p \, \Delta T + (\overline{\mu C}_p) \, \Delta P$$

where

$\overline{C}_p = \int_{T_1}^{T_2} C_p \, dT \, / \, (T_2 - T_1)$ = mean heat capacity at the pressure P_1 over the temperature range of T_1 and T_2.

Similarly

$$\Delta H_o = H_4 - H_3 = \overline{C}_{p_o} \Delta T_o + (\overline{\mu}_o \overline{C}_{p_o}) \, \Delta P_o$$

where

$$\overline{C}_{p_o} = \int_{T_3}^{T_4} C_p \, dT \, / \, (T_4 - T_3)$$

If the pressure and temperature changes of the two streams as they pass through the exchanger are small, the $\overline{C}_p$ and $\overline{\mu}$ for the streams can be taken as constant over this range of conditions.

$$\text{Therefore } \Delta H = \overline{C}_p \Delta T + \overline{\mu C}_p \Delta P$$

$$\Delta H_o = \overline{C}_{p_o} \, T_o + \overline{\mu}_o \overline{C}_{p_o} \Delta P_o$$

Equation (D.1) becomes

$$-\Delta H - \Delta H_o \pm \dot{Q}/F = 0$$

or

$$\Delta H + \Delta H_o \mp q = 0$$

where $q = \dot{Q}/F$ = quantity of heat leak per unit mass of the fluid flowing or

$$\overline{C}_p\Delta T + \overline{\mu}\overline{C}_p\ \Delta P + \overline{C}_{p_o}\Delta T_o + \overline{\mu}_o\overline{C}_{p_o}\Delta P_o \mp q = 0$$

or

$$\overline{C}_p(\Delta T + \overline{\mu}\Delta P) = -\ \overline{C}_{p_o}(\Delta T_o + \overline{\mu}_o\Delta P_o) \mp q = 0$$

or

$$\frac{\overline{C}_p}{\overline{C}_{p_o}}(\Delta T + \overline{\mu}\Delta P) = -\ (\Delta T_o + \overline{\mu}_o\Delta P_o) \mp q/C_{p_o}$$

or

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = -\ \frac{(\Delta T_o + \overline{\mu}_o\Delta P_o \pm q/\overline{C}_{p_o})}{\Delta T + \overline{\mu}\Delta P}$$

$$= -\ \frac{\Delta T_o}{\Delta T}\left(1 + \frac{\overline{\mu}_o\Delta P_o}{\Delta T_o} \pm \frac{q}{\Delta T_o\overline{C}_{p_o}}\right)\left(1 + \frac{\overline{\mu}\Delta P}{\Delta T}\right)^{-1}$$

Expanding by the Binomial theorem this may be written

$$\left(1 + \frac{\overline{\mu}\Delta P}{\Delta T}\right)^{-1} = \left\{1 - \frac{\overline{\mu}\Delta P}{\Delta T} + \left(\frac{\overline{\mu}\Delta P}{\Delta T}\right)^2 - .\ .\ .\right\}$$

Therefore

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = -\ \frac{\Delta T_o}{\Delta T}\left(1 + \mu_o\frac{\Delta P_o}{\Delta T_o} \pm \frac{q}{\Delta T_o C_{p_o}}\right).$$

$$\left[1 - \frac{\overline{\mu}\Delta P}{\Delta T} + \left(\frac{\overline{\mu}\Delta P}{\Delta T}\right)^2 - .\ .\ .\right]$$

$$= -\ \frac{\Delta T_o}{\Delta T}\left[1 + \overline{\mu}_o\frac{\Delta P_o}{\Delta T_o} \pm \frac{q}{\Delta T_o\overline{C}_{p_o}} - \frac{\overline{\mu}\Delta P}{\Delta T} - \frac{\overline{\mu}\overline{\mu}_o\Delta P\Delta P_o}{\Delta T\Delta T_o}\right.$$

$$\mp \frac{q}{\Delta T_o C_{p_o}} \cdot \frac{\bar{\mu}\Delta P}{\Delta T} + \left(\frac{\bar{\mu}\Delta P}{\Delta T}\right)^2 + \frac{\bar{\mu}_o \Delta P_o}{\Delta T_o} \left(\frac{\bar{\mu}\Delta P}{\Delta T}\right)^2 \mp \frac{q}{\Delta T_o C_{p_o}} \cdot$$

$$\left(\frac{\bar{\mu}\Delta P}{\Delta T}\right)^2 - \cdot \cdot \cdot \Big]$$

$$= - \frac{\Delta T_o}{\Delta T} - \Big[\bar{\mu}_o \frac{\Delta P_o}{\Delta T} \mp \frac{q}{\bar{C}_{p_o} \Delta T} - \frac{\bar{\mu} \Delta P \Delta T_o}{(\Delta T)^2} - \frac{\bar{\mu}\bar{\mu}_o \Delta P \Delta P_o}{(\Delta T)^2}$$

$$\mp \frac{q}{(\Delta T)^2 C_{p_o}} \cdot \bar{\mu}\Delta P + \frac{(\bar{\mu}\Delta P)^2}{(\Delta T)^3} \cdot \Delta T_o + \frac{\bar{\mu}_o \Delta P_o (\bar{\mu}\Delta P)^2}{(\Delta T)^3}$$

$$\pm \frac{q}{C_{p_o}} \frac{(\bar{\mu}\Delta P)^2}{(\Delta T)^3} - \cdot \cdot \cdot \Big]$$

The terms $\frac{\bar{\mu}_o \Delta P_o (\bar{\mu}\Delta P)^2}{(\Delta T)^3}$ and $q/C_{p_o} \cdot \frac{(\bar{\mu}\Delta P)^2}{(\Delta T)^3}$ can be neglected. Thus

$$\frac{\bar{C}_p}{\bar{C}_{p_o}} = - \frac{\Delta T_o}{\Delta T} - \Big[\{\bar{\mu}_o \frac{\Delta P_o}{\Delta T} \pm \frac{q/C_{p_o}}{\Delta T} - \frac{\bar{\mu}\Delta P \Delta T_o}{(\Delta T)^2}\}$$

$$- \frac{\bar{\mu}\bar{\mu}_o \Delta P \Delta P_o}{(\Delta T)^2} \mp q/C_{p_o} \cdot \frac{\bar{\mu}\Delta P}{(\Delta T)^2} + \frac{\Delta T_o}{(\Delta T)^3} (\bar{\mu}\Delta P)^2 \Big]$$

$$+ \cdot \cdot \cdot \cdot$$

$$\frac{\bar{C}_p}{\bar{C}_{p_o}} = - \frac{\Delta T_o}{\Delta T} - \Big[\frac{1}{\Delta T}\{\bar{\mu}_o \Delta P_o \pm q/C_{p_o} - \bar{\mu}\Delta P \frac{\Delta T_o}{\Delta T}\} - \frac{\bar{\mu}\Delta P}{(\Delta T)^2} \{\bar{\mu}_o \Delta P_o$$

$$\pm q/C_{p_o} - \frac{\bar{\mu}\Delta P}{\Delta T} \cdot \Delta T_o\}\Big]$$

or

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = -\frac{\Delta T_o}{\Delta T} - \{\overline{\mu}_o \Delta P_o \pm \frac{q}{C_{p_o}} - \overline{\mu}\Delta P\,\frac{\Delta T_o}{\Delta T}\}\{\frac{1}{\Delta T} - \frac{\overline{\mu}\Delta P}{(\Delta T)^2}\}$$

Case I. When the high pressure gas is cooled

$$\Delta T = T_2 - T_1 = -\text{ ve}$$

$$\Delta T_o = T_4 - T_3 = +\text{ ve}$$

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = \frac{|\Delta T_o|}{|\Delta T|} + \left[\{\overline{\mu}_o \Delta P_o \pm q/C_{p_o} + \overline{\mu}\Delta P\frac{|\Delta T_o|}{|\Delta T|}\}\{\frac{1}{|\Delta T|} + \frac{\overline{\mu}\Delta P}{(\Delta T)^2}\}\right]$$

$$= \frac{|\Delta T_o|}{|\Delta T|} + \Phi$$

where the quantities written between the two vertical lines are their absolute values; and

$$\Phi = \{\overline{\mu}_o \Delta P_o \pm q/C_{p_o} + \overline{\mu}\Delta P\,\frac{|\Delta T_o|}{|\Delta T|}\}\{\frac{1}{|\Delta T|} + \frac{\overline{\mu}\Delta P}{(\Delta T)^2}\}$$

Case II. When the high pressure gas is heated

$$\Delta T = T_2 - T_1 = +\text{ ve}$$

$$\Delta T_o = T_4 - T_3 = -\text{ ve}$$

$$\frac{\overline{C}_p}{\overline{C}_{p_o}} = \frac{|\Delta T_o|}{|\Delta T|} - \left[\{\overline{\mu}_o \Delta P_o \pm q/\overline{C}_{p_o} + \overline{\mu}\Delta P\,\frac{|\Delta T_o|}{|\Delta T|}\}\{\frac{1}{|\Delta T|} - \frac{\overline{\mu}\Delta P}{(\Delta T)^2}\}\right]$$

$$= \frac{|\Delta T_o|}{|\Delta T|} - \Phi'$$

where

$$\Phi' = \{\bar{\mu}_o \Delta P_o \pm q/C_{p_o} + \bar{\mu}\Delta P \frac{|\Delta T_o|}{|\Delta T|}\}\{\frac{1}{|\Delta T|} - \frac{\bar{\mu}\Delta P}{(\Delta T)^2}\}$$

The terms $\bar{\mu}\Delta P$ and $\bar{\mu}_o \Delta P_o$ do not differ greatly from each other and they both are small in comparison to $|\Delta T|$ and $|\Delta T_o|$. The quantity q is small in comparison to the amount of heat exchanged in the calorimeter per unit mass of the fluid and is also approximately the same for both the cases if the temperature level of the exchanger does not differ appreciably. Therefore

$$\Phi - \Phi' \simeq \{\bar{\mu}_o \Delta P_o \pm q/C_{p_o} + \bar{\mu}\Delta P \frac{|\Delta T_o|}{|\Delta T|}\}\{\frac{\bar{\mu}\Delta P}{(\Delta T)^2} + \frac{\bar{\mu}\Delta P}{(\Delta T)^2}\}$$

$$= \{\bar{\mu}_o \Delta P_o \pm q/C_{p_o} + \bar{\mu}\Delta P \frac{|\Delta T_o|}{|\Delta T|}\} \cdot 2 \frac{\bar{\mu}\Delta P}{(\Delta T)^2}$$

$\simeq$ a product of two very small quantities

= negligible.

APPENDIX E

CALIBRATIONS

This appendix includes linearity and ice-point calibrations for the temperature probes.

1. Linearity Calibration Charts for the Temperature Probes -

The linearity correction charts for the quartz thermometer probes were supplied by the manufacturer and are reported in Table E-1 for the temperature range of interest. Linearity corrections (L.C.) for ΔT_o and ΔT were calculated by the following relations:

$$\text{L.C. for } \Delta T_o = \text{L.C. for } T_4 - \text{L.C. for } T_3$$

$$\text{L.C. for } \Delta T = \text{L.C. for } T_1 - \text{L.C. for } T_2.$$

The subscripts 1 and 3 are for the inlet and 2 and 4 are for the outlet. The temperature differences read by the thermometers were in the manner represented by the above relations.

2. Ice-point Calibration for the Temperature Probes -

A 0°C reference was established by using an ice bath, consisting of an intimate mixture of crushed ice and water. A Dewar flask was first filled with crushed clear ice, and enough water was added to fill all the spaces between the pieces of ice, but not enough to float the ice. The sensor probe was inserted through a hole in the split cork of the flask. The tips of the probes were kept about

TABLE E-1

LINEARITY CORRECTION TO INDICATED TEMPERATURE

All Data Degrees Centigrade

Temp.	T_1	T_2	T_3	T_4
	Add to Indicated			
30	-0.03	0.00	-0.03	-0.03
40	-0.04	-0.01	-0.03	-0.03
50	-0.04	-0.01	-0.04	-0.04
60	-0.05	-0.01	-0.05	-0.04
70	-0.05	-0.01	-0.05	-0.04
80	-0.04	0.00	-0.05	-0.04
90	-0.03	0.00	-0.05	-0.03
100	-0.02	0.01	-0.04	-0.03
110	-0.01	0.02	-0.03	-0.01
120	0.01	0.03	-0.02	0.00
130	0.02	0.04	-0.01	0.01
140	0.03	0.05	0.00	0.02
150	0.05	0.05	0.01	0.03

four inches below the surface of the slush, and the probes were about one-half inch away from the side of the flask.

Two such ice-baths were prepared and the inlet and outlet probes were inserted in the baths. Enough time was given for the probes to reach equilibrium. The readings were taken for the two sets of the probes and the temperatures and temperature differences indicated were as follows:

T_1 = Inlet high pressure gas temperature
= $0.0385^{\circ}C$

T_2 = Outlet high pressure gas temperature
= $-0.0505^{\circ}C$

$\Delta T = (T_1 - T_2)$ = high pressure temperature change = $+ 0.0873^{\circ}C$

T_3 = Inlet low pressure gas temperature
= $-0.1242^{\circ}C$

T_4 = Outlet low pressure gas temperature
= $-0.0897^{\circ}C$

$\Delta T_o = (T_4 - T_3)$ = low pressure temperature change = + 0.0256

The ice-point corrections to be added to the indicated readings would then be:

Corrections (add), $^{\circ}C$

T_1 -0.0385	T_2 +0.0505	ΔT -0.0873
T_3 +0.1242	T_4 +0.0897	ΔT_o -0.0256

APPENDIX F

MIXTURE PREPARATION AND ANALYSIS

This appendix includes the mixture preparation and its chemical analysis.

1. Mixture Preparation -

The equipment was flushed several times with carbon dioxide by feeding a fresh charge of carbon dioxide, circulating the material in the system and discharging to the atmosphere. With the knowledge of an approximate volume of the system the required weights of carbon dioxide and methane were calculated for a desired 15 mole percent methane mixture at a system pressure of about 3000 psi. The required weight of carbon dioxide was charged into the storage tanks by weighing the carbon dioxide cylinder at the beginning and end of the charging process. The methane cylinder was then connected to the storage tanks and connections were made so that its pressure could be read accurately on the high pressure Heise gauge. Knowing approximate volume and accurate pressure of the methane cylinder, the calculations were made, with the help of the BWR equation, for a pressure that cylinder would have after withdrawing the desired weight of methane. Methane was then charged into the storage tanks till the methane cylinder reached the final calculated pressure. The cylinder was then left for about four hours and allowed to reach room temperature. The cylinder pressure was checked and, if needed, more gas was withdrawn so that final cylinder pressure was equal to the calculated pressure. The equipment was started and the gas was then allowed to mix by circulating through the system for about a total of 40 hours. At the end of the mixing process the material was stored in the storage tanks and samples were drawn from the system and the storage tanks for mass spectroscopic and chromatographic analysis. The mass spectroscopy was done to check if any air was drawn in during the feeding process. The analysis did not reveal any observable quantities of nitrogen, oxygen or water. The samples drawn from the different storage tanks were analysed chromatographically for the methane-carbon dioxide ratio and if their analysis differed by more than 0.3 mole percent the gases were mixed again.

The 42.3 mole percent methane mixture was prepared by calculating the extra amount of methane required, charging it into the system and mixing the gases by the procedure that was followed for the preparation of 14.5 mole percent methane mixture.

2. Mixture Analysis -

The binary mixtures of carbon dioxide and methane were analysed on a Burrell K-2 Kromo-tog chromatograph using a three foot column of one-quarter inch diameter packed with silica gel (40-100 mesh). A thermal conductivity detector was employed and helium was used as a carrier gas. Other variables were maintained at the following conditions:

Carrier gas flow rate - 77 ml./min.

Column temperature - 82°F

Detector current - 176 mA.

Sample size - 2 ml.

Excellent separation, with sharp well-defined peaks, was obtained and the area under a peak was determined by a disc integrator. Eight standard mixtures of carbon dioxide and methane were prepared by weighing small sample bottles and the amounts of methane and carbon dioxide charged. The weights of the empty bottle and the mixture sample charged were approximately 155 g and 1.75 g respectively. The weighings could be reproduced to within ± 0.15 mg. The error in a mixture composition thus prepared would not exceed ± 0.2 percent. The standards were then analysed on the chromatograph and the area fraction of methane (area under a methane peak divided by the sum of the areas under the carbon dioxide and methane peaks) was correlated to the known mole fraction of methane in the standards by the following functional relationship:

$$Y = A(X - X^2) + X^2$$

where

A = a constant

X = area fraction of methane

Y = mole fraction of methane

The constant A in the above relationship was determined by a least squares fit and was found to be equal to 1.342042. Compositions of the samples determined gravimetrically and from the above functional relationship are listed below along with the area fractions of methane and the deviations.

Area Fr. CH_4	Mole Fr. CH_4 by weighing	Mole Fr. CH_4 calc. from eqn.	Deviation
0.0827	0.1078	0.1086	-0.0008
0.0935	0.1207	0.1224	-0.0017
0.1367	0.1795	0.1770	0.0024
0.1512	0.2010	0.1950	0.0059
0.1837	0.2351	0.2349	0.0001
0.2536	0.3111	0.3183	-0.0072
0.3325	0.4083	0.4084	-0.0001
0.3921	0.4758	0.4736	0.0021

The standard error of fit was found to be $\pm\ 0.3578 \times 10^{-2}$.

The mixtures of carbon dioxide and methane, for which the heat capacity ratio data were collected, were analysed before and after collecting the data and the agreement in the two analysis sets were found to be within 0.3 mole percent.

APPENDIX G

MATHEMATICAL EXPRESSIONS

This appendix includes statements of the mathematical expressions required in the computer programmes developed for estimating BWR parameters by the various correlation techniques outlined in Chapter V.

Benedict-Webb-Rubin Equation of State -

$$P = RT\rho + (B_oRT - A_o - C_o/T^2)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3(1 + \gamma\rho^2)(e^{-\gamma\rho^2})}{T^2} \tag{G.1}$$

$$Z = \frac{P}{RT\rho} = 1 + (B_o - A_o/RT - C_o/RT^3)\rho + (b - a/RT)\rho^2 + \frac{a\alpha}{RT}\rho^5 + c/RT^3 \,.\, \rho^2\,(1 + \gamma\rho^2)\,.\, e^{-\gamma\rho^2} \tag{G.2}$$

Isothermal Enthalpy Departure -

$$\frac{1}{J}(H_p - H^o)_T = (B_oRT - 2A_o - 4C_o/T^2)\rho + (bRT - \tfrac{3}{2}a)\rho^2 + \frac{6a\alpha}{5}\rho^5 + \frac{c\cdot\rho^2}{T^2}\left[\frac{3(1 - e^{-\gamma\rho^2})}{\gamma\rho^2} - \frac{e}{2}^{-\gamma\rho^2} + \gamma\rho^2\, e^{-\gamma\rho^2}\right] \tag{G.3}$$

Isobaric Heat Capacity Departure -

$$\frac{C_p}{J} = \frac{C_p{}^o}{J} - R + \frac{6C_o}{T^3}\rho - \frac{6c}{\gamma T^3} + \left(\frac{6c}{\gamma T^3} + \frac{3c}{T^3}\rho^2\right) e^{-\gamma\rho^2} + \frac{\left[R + B_oR\rho + bR\rho^2 + 2C_o\rho/T3 - (2c\rho^2/T3)(1 + \gamma\rho^2)e^{-\gamma\rho^2}\right]^2}{R + \rho(2B_oR - 2A_o/T - 2C_o/T^3) + \rho^2(3bR - 3a/T) + 6a\alpha\rho^5 + \left(\frac{3c\rho^2 + 3c\gamma\rho^4 - 2c\gamma^2\rho^6}{T^3}\right)e^{-\gamma\rho^2}} \tag{G.4}$$

In the above equations:

P = pressure

ρ = molal density

T = temperature

Z = compressibility factor

R = universal gas constant

= 10.73147 (in psi, cu. ft., lb-mole, ^{o}R units)

= 0.0820544 (in atm., litres, g-mole, ^{o}K units)

J = conversion factor

= 144/777.9 (in psi, cu. ft., lb-mole, ^{o}R Btu units)

= 100./4.130 (in atm., litres, g-mole, ^{o}K calorie units).

1. Linear Programming -

The BWR co-efficients were defined as follows:

$X_2 = B_o \qquad X_3 = A_o \qquad X_4 = C_o \qquad X_5 = b \qquad X_6 = a$

$X_7 = a.\alpha \qquad X_8 = c \qquad GAM = \gamma$

For a known value of γ Equation (G.1) was written as:

$$P = RT\rho + \sum_{j=2}^{8} X_j A_j \qquad \text{(G.5)}$$

where

$A_2 = RT\rho^2 \qquad A_3 = -\rho^2 \qquad A_4 = -\frac{\rho^2}{T^2} \qquad A_5 = RT\rho^3 \qquad A_6 = -\rho^3$

$A_7 = \rho^6 \qquad A_8 = \frac{\rho^3}{T^2}(1 + \gamma\rho^2)e^{-\gamma\rho^2}$

The functions A for every data point were calculated from the known information of P, T, ρ and γ and Equation (G.5) was substituted in Equation (V.13b).

When additional constraints of isobaric enthalpy changes were applied the departure difference $D_{P_2,T_2}(X_j) - D_{P_2,T_1}(X_j)$ of Equation (V.21) was expressed as follows:

$$
\begin{aligned}
D_{P_2,T_2}(\alpha_j) - D_{P_2,T_1}(\alpha_j) = J \,.\, \Big[& (B_oRT_2 - 2A_o - 4C_o/T_2^2)\rho_2 \\
& + (bRT_2 - \tfrac{3}{2}a)\rho_2^2 + \frac{6a\alpha}{5}\rho_2^5 + \frac{c\rho_2^2}{T_2^2}\Big\{\frac{3(1 - e^{-\gamma\rho_2^2})}{\gamma\rho_2^2} \\
& - \frac{e^{-\gamma\rho_2^2}}{2} + \gamma\rho_2^2 e^{-\gamma\rho_2^2}\Big\} - (B_oRT_1 - 2A_o - \frac{4C_o}{T_1^2})\rho_1 \\
& + (bRT_1 - \tfrac{3}{2}a)\rho_1^2 + \frac{6a\alpha}{5}\rho_1^5 + \frac{c\rho_1^2}{T_1^2}\Big\{\frac{3(1 - e^{-\gamma\rho_1^2})}{\gamma\rho_1^2} \\
& - \frac{e^{-\gamma\rho_1^2}}{2} + \gamma\rho_1^2 e^{-\gamma\rho_1^2}\Big\}\Big] \qquad \text{(G.6)}
\end{aligned}
$$

The molal densities ρ_2 and ρ_1 were evaluated at P_2, T_2 and P_2, T_1 respectively.

2. Non-linear Least Squares -

The BWR co-efficients were defined as follows:

$X_1 = B_o$ $X_2 = A_o$ $X_3 = C_o$ $X_4 = b$ $X_5 = a$

$X_6 = a.\alpha$ $X_7 = c$ $X_8 = \gamma$

a. Choosing Z as dependent variable.

Z was expressed as follows:

$$Z = PV/RT = 1 + \sum_{j=1}^{6} X_j \, g_j + X_7(\rho^2/RT^3)(1 + X_8\rho^2)e^{-X_8\rho^2} \qquad (G.7)$$

$$(\partial Z/\partial X_1) = g_1 = \rho$$

$$(\partial Z/\partial X_2) = g_2 = - \rho/RT$$

$$(\partial Z/\partial X_3) = g_3 = - \rho/RT^3$$

$$(\partial Z/\partial X_4) = g_4 = \rho^2$$

$$(\partial Z/\partial X_5) = g_5 = - \rho^2/RT$$

$$(\partial Z/\partial X_6) = g_6 = \rho^5/RT$$

$$(\partial Z/\partial X_7) = g_7 = (\rho^2/RT^3)(1 + X_8\rho^2)e^{-X_8\rho^2}$$

$$(\partial Z/\partial X_8) = - X_7X_8(\rho^6/RT^3) \cdot e^{-X_8\rho^2}$$

The above relations were used for the formulation of normal equations defined by Equation (V.43).

b. Choosing V as the dependent variable.

Z was expressed by Equation (G.7) and implicit differentiation was performed for obtaining the required derivatives of volume.

Defining $G_j = dg_j/d\rho$ (g_j are defined in section 2a)

$j = 1, 2, . . . 7$

and $V = 1/\rho$

we have:

$G_1 = 1. = g_1/\rho$

$G_2 = g_2/\rho$

$G_3 = g_3/\rho$

$G_4 = 2.\ g_4/\rho$

$G_5 = 2.\ g_5/\rho$

$G_6 = 5.\ g_6/\rho$

$G_7 = (1/RT^3)\left[2\rho e^{-X_8\rho^2}(1 + X_8\rho^2 - X_8^2\rho^4)\right]$

The derivatives of volume with respect to the parameters would then be:

$$(\partial V/\partial X_j)_{\substack{X\ell \\ \ell\neq j}} = g_j/S$$

$$j = 1, 2, \ldots 7$$

where

$$S = P/RT + \rho^2 \sum_{i=1}^{7} X_i\ G_i$$

and

$$(\partial V/dX_8)_{\substack{X\ell \\ \ell\neq 8}} = \frac{-X_7\ X_8\ \rho^6\ e^{-X_8\rho^2}}{RT^3\ .\ S}$$

The above relations were used for the formulation of normal equations defined by Equation (V.43). The volume required in the estimation of the above derivatives was calculated from the BWR equation at the initial guess of the parameters.

c. Normal equations for C_p departure.

For brevity Equation (G.4) was expressed as

$$CPD = A + (Nr)^2/(Dr) = h(\overline{X}, V) \tag{G.8}$$

where

$$A = -R + 6X_3\ \rho/T^3 - 6X_7/X_8T^3 + (6X_7/X_8T^3 + 3X_7\rho^2/T^3)\ e^{-X_8\rho^2}$$

$$Nr = R + X_1R\rho + X_4R\rho^2 + 2X_3\rho/T^3 - 2X_7\rho^2/T^3\ (1 + X_8\rho^2)e^{-X_8\rho^2}$$

$$Dr = R + \rho(2X_1R - 2X_2/T - 2X_3/T^3) + \rho^2(3X_4R - 3X_5/T)$$
$$+ 6X_6\rho^5/T + \frac{(3X_7\rho^2 + 3X_7X_8\rho^4 - 2X_7X_8{}^2\rho^6)}{T^3}\ e^{-X_8\rho^2}$$

The derivatives of C_p departure required in Equation V.43 were determined from the following steps:

$$(\partial h_i/\partial X_j)_{\substack{X\ell \\ \ell\neq j}} = (\partial h_i/\partial V_i)_{\overline{X}}(\partial V_i/\partial X_j)_{\substack{X\ell \\ \ell\neq j}} + (\partial h_i/\partial X_j)_{\substack{X\ell, V \\ \ell\neq j}}$$

$$j = 1, 2, 3, \ . \ . \ . \ 8 \tag{G.9}$$

$$(\partial h/\partial V)_{\overline{X}} = -(1/V^2)(\partial h/\partial \rho)_{\overline{X}} \tag{G.10}$$

$$(\partial h/\partial \rho)_{\overline{X}} = 6X_3/T^3 - 6X_7\rho e^{-X_8\rho^2}\{1 + X_8\rho^2\}\ /T^3$$
$$- (Nr/Dr)^2(\partial\, Dr/\partial \rho)_{\overline{X}} + 2(Nr/Dr)(\partial\, Nr/\partial \rho)_{\overline{X}} \tag{G.11}$$

$$(\partial\ Dr/\partial \rho)_{\overline{X}} = 2(X_1R - X_2/T - X_3/T^3) + 6\rho(X_4.R - X_5/T)$$
$$+ 30.X_6\rho^4/T + (e^{-X_8\rho^2}/T^3).\ X_7\rho\{6 + 12X_8\rho^2$$
$$- 12X_8{}^2\rho^4 - 2X_8\rho^2(3 + 3X_8\rho^2 - 2X_8{}^2\rho^4)\} \tag{G.12}$$

$$(\partial Nr/\partial \rho)_{\overline{X}} = X_1R + 2X_4R\rho + 2X_3/T^3 + (4X_7\rho e^{-X_8\rho^2}/T^3)(X_8{}^2\rho^4 - 1 - X_8\rho^2) \qquad (G.13)$$

$(\partial h_i/\partial V)_{\overline{X}}$ were calculated by combining Equations (G.10) through (G.13). The terms $(\partial V_i/\partial X_j)_{X_\ell \atop \ell \neq j}$ were evaluated by the equations given in section 2.b.

The derivatives $(\partial h_i/\partial X_j)_{X_\ell, V \atop \ell \neq j}$ were evaluated by the following relations:

From Equation (G.8), we write

$$(\partial h_i/\partial X_j)_{X_\ell, V \atop \ell \neq j} = (\partial A/\partial X_j)_{X_\ell, V \atop \ell \neq j} + 2(Nr/Dr)(\partial Nr/\partial X_j)_{X_\ell, V \atop \ell \neq j} - (Nr/Dr)^2(\partial Dr/\partial X_j)_{X_\ell, V \atop \ell \neq j} \qquad (G.14)$$

$$(\partial h/\partial X_1)_{X_\ell, V \atop \ell \neq 1} = 2R\rho(1 - Nr/Dr)(Nr/Dr) \qquad (G.15)$$

$$(\partial h/\partial X_2)_{X_\ell, V \atop \ell \neq 2} = 2\rho/T(Nr/Dr)^2 \qquad (G.16)$$

$$(\partial h/\partial X_3)_{X_\ell, V \atop \ell \neq 3} = (2\rho/T^3)\{3 + 2(Nr/Dr) + (Nr/Dr)\} \qquad (G.17)$$

$$(\partial h/\partial X_4)_{X_\ell, V \atop \ell \neq 4} = R\rho^2(Nr/Dr)\ \{2 - 3(Nr/Dr)\} \qquad (G.18)$$

$$(\partial h/\partial X_5)_{X_\ell, V \atop \ell \neq 5} = (Nr/Dr)^2(3\rho^2/T) \qquad (G.19)$$

$$(\partial h/\partial X_6)_{\substack{X_\ell, V\\ \ell\neq 6}} = -\ (Nr/Dr)^2(6\rho^5/T) \qquad (G.20)$$

$$\begin{aligned}(\partial h/\partial X_7)_{\substack{X_\ell, V\\ \ell\neq 7}} = {} & e^{-X_8\rho^2}(6/X_8T^3 + 3\rho^2/T^3) - 2(Nr/Dr)\{ \\ & (2\rho^2/T^3)(1+ X_8\rho^2)\ e^{-X_8\rho^2}\} - \\ & (Nr/Dr)^2\ e^{-X_8\rho^2}\ \{\frac{3\rho^2 + 3X_8\rho^4 - 2X_8{}^2\rho^6}{T^3}\} \\ & - 6/X_8T^3\end{aligned} \qquad (G.21)$$

$$\begin{aligned}(\partial h/\partial X_8)_{\substack{X_\ell, V\\ \ell\neq 8}} = {} & e^{-X_8\rho^2}.(X_7/T^3)\{- 6/X_8{}^2 - 6\rho^2/X_8 - 3\rho^4 \\ & + 4(Nr/Dr)\ X_8\rho^6 - (Nr/Dr)^2\ \rho^6X_8\ (2X_8\rho^2 - 7)\} \\ & + 6X_7/T^3X_8{}^2\end{aligned} \qquad (G.22)$$

$(\partial h_i/\partial X_j)_{\substack{X_\ell, V\\ \ell\neq j}}$, $(\partial h_i/\partial V_i)_{\overline{X}}$ and $(\partial V_i/\partial X_j)_{\substack{X_\ell\\ \ell\neq j}}$ were evaluated from the above relations and substituted in Equation (G.9) in order to get $(\partial h_i/\partial X_j)_{\substack{X_\ell\\ \ell\neq j}}$ for all j. The terms $(\partial h_i/\partial X_j)_{\substack{X_\ell\\ \ell\neq j}}$ were then used in Equation (V.43) to formulate the normal equations.

APPENDIX H

COMPUTER PROGRAMMES

Four computer programmes are included in this appendix. The programmes are identified as follows:

1. PGM-1 - Estimates BWR parameters for pure components by the linear programming technique
2. PGM-2 - Estimates interaction constants of a binary mixture defined by Equation (V.1) for the BWR parameters
3. PGM-3 - Estimates BWR parameters for a pure component by the nonlinear least squares technique
4. PGM-4 - Calculates the compressibility factors or the heat capacities of a pure component or binary mixtures and estimates the deviations between the calculated and the experimental values.

1. PGM-1 -

This programme evaluates the BWR parameters for a pure component by the linear programming technique. The parameters may be estimated either from the P-V-T data only or from the P-V-T data and the isobaric and ideal gas enthalpy changes. This is achieved by choosing an appropriate value of the variable NCASE, as explained in the listing. The objective function may be chosen as percent deviation or absolute deviation by assigning a proper value to the variable NREL. The predecided arbitrary constant β of Equation (V.12b) may be taken as equal to either $\omega\lambda$ or K. When it is chosen as K and percent error is being minimized, the value of CONST to be read is a fraction. That is, if the isobaric enthalpy change constraint had to be less than or equal to 12 percent, the value of CONST to be read is 0.12. If the enthalpy constraint is coupled with the objective function of P, the value of CONST is equal to the chosen ω. The programme is capable of handling various units as indicated in the listing.

The input information has to be in the following sequence:

a. N, NCASE, M1, NGAMA, NUNIT, NREL, NOPT
   N = No. of co-efficients to be evaluated
   M1 = No. of P-V-T data points.
   The values of NCASE, NGAMA, NUNIT, NREL, and NOPT are chosen according to the explanation given in the listing.

b. GAMA (I), the values of γ to be tried, one card for each value. If the optimum value of γ is known, only one value is read.

c. WT, molecular weight of the gas

d. P, T, V

Pressure, temperature and volume data are read in according to Format (1Hb,3F15.8). Total no. of cards equals M1.

If the isobaric enthalpy changes are used as additional constraints the following input information is required in addition to the above:

e. NT(I), the no. of $\int_{Tref}^{T} C_p dT$ points at each temperature T. One card for each NT(I)

f. CONST, the value for β as explained previously

g. $\int_{Tref}^{T} C_p dT$, T, V, Tref., Vref

where V is the volume at temperature T and pressure of the isobar, Vref is the volume at temperature Tref. and pressure of the isobar. Total no. of cards = $\sum_{I=1}^{NCASE} NT(I)$

h. CPODT(I), the $\int_{Tref}^{T} C_p^o dT$ at all the temperatures for which $\int_{Tref}^{T} C_p dT$ data were read. Total no. of cards equals NCASE.

The output of the programme will be self explanatory and hence it is not included here. When only one value of γ is used the final solution vector for the parameters is printed. The first element of this vector is the value of the objective function λ, and other elements are the values of the parameters X_2 to X_8.

```
    C      MAIN

C      MAIN

C     ****************************************************
C     *
C      COMPUTER PROGRAMME NO.  PGM-1
C
C      THIS PROGRAMME EVALUATES BWR PARAMETERS BY THE LINEAR
C      PROGRAMMING TECHNIQUE FOR A PURE COMPONENT.
C
C      NUNIT IS ZERO WHEN INPUT DATA ARE IN PSIA
C      ,CU.FT./LB.MOLE,DEGREE R AND BTU/LB.MOLE
C      NUNIT IS ONE WHEN INPUT DATA ARE IN ATMOSPHERES,
C      LITRES/G.MOLE, D KELVIN AND CALORIES/G.MOLE
C      NUNIT IS TWO WHEN INPUT DATA ARE IN PSIA,
C      CU.FT./LB.MOLE, DEGREE RANKIN AND BTU/LB.
C
C      NREL IS ONE WHEN PERCENT P AND PERCENT CPDT
C      DEVIATIONS ARE TO BE MINIMISED
C      NREL IS ZERO WHEN ABSOLUTE P AND ABSOLUTE CPDT
C      DEVIATIONS ARE TO BE MINIMISED.
C
C
C      NOPT IS ONE WHEN ERROR IN INTEGRAL CPDT IS COUPLED
C      WITH THE ERROR IN P
C
C
C      NGAMA IS THE NO. OF TIMES DIFFERENT VALUES OF GAMMA
C      ARE TO BE TRIED.
C      NGAMA IS ONE WHEN ONLY ONE GAMMA IS TRIED
C
C      MT IS TOTAL NO. OF POINTS INCLUDING REFERENCE
C      TEMPERATURES.
C      M1 IS NO. OF P-V-T POINTS.
C      M2 IS TOTAL NO. OF POINTS FOR WHICH INTEGRAL CPDT
C      DATA ARE FED.
C      NT(I) ARE NO. OF INTEGRAL CPDT POINTS AT TEMPT. T(I).
C      NCASE ARE NO. OF TEMPERATURES AT WHICH INTEGRAL CPDT
C      ARE CALCULATED.
C      NCASE IS ZERO IF ONLY P-V-T DATA ARE TO BE PROCESSED
C      TREF(I) IS THE REFERENCE TEMP. FOR T(I)
C      N IS THE NO. OF COEFFICIENTS TO BE EVALUATED IN THE
C      EQUATION OF STATE
C     *
C     ****************************************************

      COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRGAM
      COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
      COMMON /COE1/TC,WT,CON,X,R,GAM
      COMMON /COE2/SPG,SHG,TCONT,VCONT,HCONT,VRCON,TRCON
     *,PPCON,VPCON,TPC
```

```
      C       MAIN                 ...(CONT'D)
     1ON,NH,N1,CPCON
      COMMON /PVT/TT,VV,PCAL
      COMMON /DP/VVREF,TTREF,DPDIFK
      DIMENSION A(16,550),B(16),C(550),F(550),K(16),RX(16)
     *,PP(250),VV(25
     10),CPDT(50),TTREF(50),VVREF(50),FF(250),TT(250)
      DIMENSION SHG(16),SPG(16),TCONT(16),VCONT(16)
     *,PCONT(16),VRCON(16),
     1TRCON(16),HCONT(16),PPCON(16),VPCON(16),TPCON(16)
     *,X(16),CPCON(16)
      DIMENSION PCAL(250),DPDIFK(50),CPDTK(50)
      DIMENSION GAMA(10),AA(16,550)
      DIMENSION NT(20),CPODT(20),NTREF(20)
      READ(5,1)N,NCASE,M1,NGAMA,NUNIT,NREL,NOPT
    1 FORMAT(7I4)
      IF(NCASE.EQ.0)WRITE(6,5)
    5 FORMAT(10X,'ONLY THE P-V-T DATA ARE BEING PROCESSED')
      IF(NCASE.GT.0) WRITE(6,6)
    6 FORMAT(10X,'THE P-V-T DATA WITH INTEGRAL CPDT
     * CONSTRAINTS ARE BEIN
     1G PROCESSED')
      IF(NREL.EQ.0) WRITE(6,7)
    7 FORMAT(10X,'THE MAXIMUM ABSOLUTE DEVIATION IS BEING
     * MINIMIZED.')
      IF(NREL.EQ.1) WRITE(6,8)
    8 FORMAT(10X,'THE MAXIMUM PERCENT DEVI/TION IS BEING
     * MINIMIZED.')
      IF(NCASE.GT.0.AND.NOPT.EQ.0) WRITE(6,9)
    9 FORMAT(10X,'THE MAXIMUM DEVIATION IN INTEGRAL CPDT IS
     * EQUAL TO AN
     1 ARBITRARY CONSTANT.')
      IF(NOPT.EQ.1) WRITE(6,10)
   10 FORMAT(10X,'THE MAXIMUM DEVIATION IN INTEGRAL CPDT IS
     * EQUAL TO AN
     1ARBITRARY CONSTANT TIMES THE MAXIMUM DEVIATION IN
     * PRESSURE.')
      READ(5,502)(GAMA(I),I=1,NGAMA)
  604 M2=0
      CONST=0.
      TC=0.
      M=M1
      READ(5,300)WT
 300   FORMAT(1H ,2F15.8)
      IF(NUNIT.EQ.0.OR.NUNIT.EQ.2) R=10.73147
      IF(NUNIT.EQ.1) R=0.0820544
      IF(NUNIT.EQ.0) CON=144.0/777.9
      IF(NUNIT.EQ.1) CON=100.0/4.130
      IF(NUNIT.EQ.2) CON=144.0/(WT*777.900)
      NA=N+1
      M11=M1+1
```

```
C       MAIN                    ...(CONT'D)
      MM=M+M
      ITRGAM=1
      IF(NGAMA.EQ.1) GAM=GAMA(1)
       DO 102 I=1,M1
      READ(5,101)PP(I),TT(I),VV(I)
      P=PP(I)
      V=VV(I)
      DE=1.0/VV(I)
      T=TT(I)
101    FORMAT(1H ,3F15.8)
       WRITE(6,400) I,P,T,V
400    FORMAT(1H ,I3,3F15.8)
      DD=DE**2
      F(I)=P-R*T*DE
      IF(NREL.EQ.1) F(I)=F(I)/P
      FF(I)=F(I)
      A(2,I)=R*T*DD
      A(3,I)=-DD
      A(4,I)=-DD/(T**2)
      A(5,I)=R*T*DD*DE
      A(6,I)=-DD*DE
      A(7,I)=DE**6
      IF(NGAMA.GT.1) GO TO 102
      EA=GAM*DD
      A(8,I)=(1.0+EA)*DE**3/(T*T*EXP(EA))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/P
  102 CONTINUE
      DO 703 I=1,M1
      P=PP(I)
      DO 703 J=2,N
      IF(NREL.EQ.1) A(J,I)=A(J,I)/P
  703 AA(J,I)=A(J,I)
      IF(NCASE.EQ.0) GO TO 605
      DO 600 I=1,NCASE
      READ(5,601)NT(I)
      NTREF(I)=NT(I)
  600 CONTINUE
  601 FORMAT(I2)
      M2=0
      DO 602 I=1,NCASE
      M2=M2+NT(I)
      M2REF=M2
  602 CONTINUE
      MT=M2+M1+M2REF
      M=M2+M1
      MM=M+M
      IF(NCASE.NE.0) READ(5,2)CONST
  2    FORMAT(1H ,F10.4)
      DO 210 I=M11,M
      J=I-M1
```

```
        C      MAIN                 ...(CONT'D)
    READ(5,103)CPDT(J),TT(I),VV(I),TTREF(J),VVREF(J)
210 CONTINUE
    DO 401 I=M11,M
    J=I-M1
    H=CPDT(J)
    T=TT(I)
    V=VV(I)
    DE=1./V
    TREF=TTREF(J)
    VREF=VVREF(J)
    DEREF=1./VREF
    WRITE(6,104)I,H,T,V,TREF,VREF
103 FORMAT(5F15.8)
104 FORMAT(I4,5F15.8)
    DD=DE**2
    DDREF=DEREF**2
    F(I)=H
    A(2,I)=R*(T*DE-TREF*DEREF)*CON
    A(3,I)=-2.*CON*(DE-DEREF)
    A(4,I)=-4.*CON*(DE/T**2-DEREF/TREF**2)
    A(5,I)=R*CON*(T*DD-TREF*DDREF)
    A(6,I)=-1.5*CON*(DD-DDREF)
    A(7,I)=6.*CON*(DE**5-DEREF**5)/5.
    IF(NGAMA.GT.1) GO TO 401
    EA=GAM*DD
    EAREF=GAM*DDREF
    EX=EXP(-EA)
    EXREF=EXP(-EAREF)
    A(8,I)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
   *-(DDREF/TREF**2)*
   1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
    IF(NREL.EQ.1) A(8,I)=A(8,I)/CPDT(J)
401 CONTINUE
    DO 701 I=M11,M
    II=I-M1
    DO 701 J=2,N
    IF(NREL.EQ.1) A(J,I)=A(J,I)/CPDT(II)
701 AA(J,I)=A(J,I)
    DO 503 I=1,NCASE
    READ(5,502)CPODT(I)
503 CONTINUE
    NM=0
    NC=1
505 MI=NT(NC)
    DO 504 I=1,MI
    NM=NM+1
    II=M1+NM
    F(II)=F(II)-CPODT(NC)
    IF(NREL.EQ.1) F(II)=F(II)/CPDT(NM)
    FF(II)=F(II)
```

```
  509 FORMAT(I4,F15.8)
      WRITE(6,509)II,F(II)
  504 CONTINUE
      IF(NC.EQ.NCASE) GO TO 506
      NC=NC+1
      GO TO 505
  506 CONTINUE
  502 FORMAT(F20.5)
      IF(NOPT.NE.1) WRITE(6,3)M1,M2,CONST
 3    FORMAT (1H0, 5X, I4, 23H POINTS LESS THAN LAMDA,/6X,
     * I4, 17H POINT
     1S LESS THAN , E15.6)
      IF(NOPT.EQ.1)WRITE(6,4)M1,M2,CONST
    4 FORMAT(6X,I4,'POINTS LESS THAN LAMDA',/6X,I4,'POINTS
     * LESS THAN',E1
     15.6,'TIMES LAMDA')
  605 CONTINUE
      IF(NGAMA.EQ.1) GO TO 700
      ITRGAM=1
  705 GAM=GAMA(ITRGAM)
      DO 702 I=1,M1
      V=VV(I)
      P=PP(I)
      T=TT(I)
      DE=1./V
      DD=DE**2
      EA=GAM*DD
      A(8,I)=(1.0+EA)*DE**3/(T*T*EXP(EA))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/P
  702 CONTINUE
      IF(NCASE.EQ.0) GO TO 700
      DO 704 I=M11,M
      J=I-M1
      V=VV(I)
      T=TT(I)
      VREF=VVREF(J)
      TREF=TTREF(J)
      DE=1./V
      DEREF=1./VREF
      DD=DE**2
      DDREF=DEREF**2
      EA=GAM*DD
      EAREF=GAM*DDREF
      EX=EXP(-EA)
      EXREF=EXP(-EAREF)
      A(8,I)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
     *-(DDREF/TREF**2)*
     1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/CPDT(J)
  704 CONTINUE
```

```
      C       MAIN                 ...(CONT'D)

  700 CONTINUE
      CALL DUAL
       CALL SIMPEX
      IF(NGAMA.EQ.1) GO TO 706
      IF(ITRGAM.EQ.NGAMA) GO TO 67
      ITRGAM=ITRGAM+1
      DO 707 I=1,M
      F(I)=FF(I)
      DO 707 J=2,N
  707 A(J,I)=AA(J,I)
      GO TO 705
  706 NH=0
       N1=0
      DO 200 I=1,NA
      IF(K(I).GT.M) GO TO 201
       IF(NCASE.EQ.0) GO TO 607
      IF(K(I).GT.M1) GO TO 203
  607 KM=K(I)
      N1=N1+1
      PPCON(N1)=PP(KM)
      VPCON(N1)=VV(KM)
      TPCON(N1)=TT(KM)
        SPG(N1)=1.0
      GO TO 200
  203 KM=K(I)
      NH=NH+1
      HCONT(NH)=FF(KM)
      VCONT(NH)=VV(KM)
      TCONT(NH)=TT(KM)
      KMM=KM-M1
      VRCON(NH)=VVREF(KMM)
      TRCON(NH)=TTREF(KMM)
      CPCON(NH)=CPDT(KMM)
      SHG(NH)=1.0
       GO TO 200
  201 KM=K(I)-M
      IF(M.EQ.M1) GO TO 606
      IF(KM.GT.M1) GO TO 202
  606  N1=N1+1
      PPCON(N1)=PP(KM)
      VPCON(N1)=VV(KM)
      TPCON(N1)=TT(KM)
        SPG(N1)=-1.0
      GO TO 200
  202 NH=NH+1
      HCONT(NH)=FF(KM)
      VCONT(NH)=VV(KM)
      TCONT(NH)=TT(KM)
      KMM=KM-M1
      VRCON(NH)=VVREF(KMM)
```

```
          C       MAIN                 ...(CONT'D)
      TRCON(NH)=TTREF(KMM)
      CPCON(NH)=CPDT(KMM)
      SHG(NH)=-1.0
  200 CONTINUE
      DO 205 I=1,N1
      WRITE(6,400)I,PPCON(I),TPCON(I),VPCON(I)
  205 CONTINUE
      IF(NCASE.EQ.0) GO TO 608
      DO 206 I=1,NH
      WRITE(6,104)I,HCONT(I),TCONT(I),VCONT(I),TRCON(I)
     *,VRCON(I)
  206 CONTINUE
  608 CONTINUE
      CALL COEFFI

C
C     CHECK OF SOLUTIONS.
C
C

      AM=FLOAT(M1)
      AMAN=AM-FLOAT(N)
      CALL PCALCU
       WRITE(6,213)
 213   FORMAT(1H1,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),9X
     *,6HP.EXP.,8X,
     1 7HP.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.)
       SR=0.0
       SP=0.0
      SUM=0.
      DO 609 I=1,M1
      PK=PCAL(I)
      P=PP(I)
      V=VV(I)
      T=TT(I)
       DEV=ABS(P-PK)
       PERC=DEV*100.0/P
       WRITE(6,61) V,T,P,PK,DEV,PERC
  61   FORMAT(1H ,F15.4,F15.2,4F15.4)
       SR=SR+DEV
       SP=SP+PERC
      SUM=SUM+PERC**2
  609 CONTINUE
       SRA=SR/AM
       SPE=SP/AM
      STDPER=SQRT(SUM/AMAN)
       WRITE(6,212) SRA,SPE,STDPER
 212   FORMAT(1H ,9HAVE.DEV.=,F10.6,13HAVE.PER.DEV.=,F10.6
     *,1X,'RMS OF PE
     1R DEV = ',F10.6)
```

```
        C       MAIN                ...(CONT'D)
      IF(NCASE.EQ.0) GO TO 67
      MMM1=M-M1
      A1=FLOAT(MMM1)
       WRITE(6,214)
 214   FORMAT(1H ,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),9X
     *,6HH.EXP.,8X,
     1 7HH.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.)
      CALL DDIFCL
      NM=0
      NC=1
  805 MI=NT(NC)
      DO 804 I=1,MI
      NM=NM+1
      CPDTK(NM)=DPDIFK(NM)+CPODT(NC)
  804 CONTINUE
      IF(NC.EQ.NCASE) GO TO 806
      NC=NC+1
      GO TO 805
  806 CONTINUE
       SR=0.0
       SP=0.0
      SUM=0.
      DO 807 I=M11,M
      J=I-M1
      H=CPDT(J)
      V=VV(I)
      T=TT(I)
      HK=CPDTK(J)
       DEV=ABS(H-HK)
       PERC=DEV*100.0/ABS(H)
       WRITE(6,61) V,T,H,HK,DEV,PERC
       SR=SR+DEV
       SP=SP+PERC
      SUM=SUM+PERC**2
  807 CONTINUE
       SRA=SR/A1
       SPE=SP/A1
      STDPER=SQRT(SUM/A1)
       WRITE(6,212) SRA,SPE,STDPER
  67   CONTINUE
       STOP
      END
```

SUBROUTINE DUAL

```
      SUBROUTINE DUAL
      COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRG/M
      COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
      DIMENSION A(16,550),B(16),C(550),F(550),K(16),RX(16)
     *,GAMA(10)
      M11=M1+1
      DO 5 J=1,M1
      JM=J+M
      F(JM)=-F(J)
       A(1,J)=1.00
      IF(NREL.EQ.1) A(1,J)=0.01*A(1,J)
       A(1,JM)=1.00
      IF(NREL.EQ.1) A(1,JM)=0.01*A(1,JM)
      DO 5 I=2,NA
5     A(I,JM)=-A(I,J)
      IF(NCASE.EQ.0) GO TO 100
      DO 6 J=M11,M
      JM=J+M
      IF(NOPT.EQ.1) GO TO 150
       F(JM)=-F(J)-CONST
       F(J)=F(J)-CONST
      A(1,J)=0.00
      A(1,JM)=0.00
      GO TO 151
  150 F(JM)=-F(J)
      A(1,J)=CONST
      IF(NREL.EQ.1)A(1,J)=0.01*A(1,J)
      A(1,JM)=A(1,J)
  151 DO 6 I=2,NA
6     A(I,JM)=-A(I,J)
  100 BB=0.00
      K(1)=1
      B(1)=1.
      DO 7 I=2,NA
      XX=A(I,1)
      B(I)=-XX
      A(I,1)=0.00
      DO 7 J=2,MM
7     A(I,J)=A(I,J)-XX*A(1,J)
      DO 8 I=2,NA
      IF (B(I).GE.0.0) GO TO 8
      B(I)=-B(I)
      DO 9 J=1,MM
9     A(I,J)=-A(I,J)
8     CONTINUE
      DO 10 L=2,NA
      XX=A(L,1)
      JA=1
      DO 11 J=2,MM
      IF (A(L,J).LE.XX) GO TO 11
```

SUBROUTINE DUAL ...(CONT'D)

```
      XX=A(L,J)
      JA=J
11    CONTINUE
      K(L)=JA
      B(L)=B(L)/XX
      DO 12 J=1,MM
12    A(L,J)=A(L,J)/XX
      DO 13 I=1,NA
      IF (I.EQ.L) GO TO 13
      YY=A(I,JA)
      B(I)=B(I)-B(L)*YY
      DO 14 J=1,MM
14    A(I,J)=A(I,J)-A(L,J)*YY
13    CONTINUE
10    CONTINUE
40    DO 30 I=1,NA
      IF (B(I).GE.0.0) GO TO 30
      IA=I
      GO TO 50
30    CONTINUE
      GO TO 31
50    B(IA)=-B(IA)
      DO 51 J=1,MM
51    A(IA,J)=-A(IA,J)
      XX=0.00
      JA=0
      DO 52 J=1,MM
      DO 53 I=1,NA
      IF (J.EQ.K(I)) GO TO 52
53    CONTINUE
      IF (A(IA,J).LE.XX) GO TO 52
      XX=A(IA,J)
      JA=J
52    CONTINUE
      K(IA)=JA
      B(IA)=B(IA)/XX
      DO 54 J=1,MM
54    A(IA,J)=A(IA,J)/XX
      DO 55 I=1,NA
      IF (I.EQ.IA) GO TO 55
      YY=A(I,JA)
      B(I)=B(I)-B(IA)*YY
      DO 56 J=1,MM
56    A(I,J)=A(I,J)-A(IA,J)*YY
55    CONTINUE
      GO TO 40
31    DO 20 I=1,NA
      IA=K(I)
20    BB=BB+F(IA)*B(I)
      DO 21 J=1,MM
```

SUBROUTINE DUAL ...(CONT'D)

```
      C(J)=0.00
      DO 22 I=1,NA
      IA=K(I)
22    C(J)=C(J)+F(IA)*A(I,J)
21    C(J)=C(J)-F(J)
      WRITE (6,25)
25    FORMAT (1H1, 15X, 22H FOR INITIAL TABLEAU - )
      WRITE(6,28)ITRGAM,GAMA(ITRGAM)
   28 FORMAT(1H0,37X,'TRIAL  NO.',I6,5X,'GAMMA =  ',F15.8)
      WRITE (6,26) BB
26    FORMAT (1H0, 16X, 21HOBJECTIVE FUNCTION = , E15.8)
      WRITE (6,27) (K(L), B(L), L=1,NA)
27    FORMAT (1H , 18X, 16HINDEP. VECTOR = , I4, 5X, E15.6)
      RETURN
      END
```

SUBROUTINE SIMPE

```
      SUBROUTINE SIMPEX
      COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRGAM
      COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
      DIMENSION A(16,550),B(16),C(550),F(550),K(16),RX(16)
     *,GAMA(10)
  399 QX=C(1)
      JA=1
      DO 300 J=2,MM
      IF (C(J).GE.QX) GO TO 300
      JA=J
      QX=C(J)
  300 CONTINUE
      IF (QX.GE.0.0) GO TO 330
      DO 301 I=1,NA
      IF (A(I,JA).LE.0.0) GO TO 302
      RX(I)=B(I)/A(I,JA)
      GO TO 301
  302 RX(I)=-1.00
  301 CONTINUE
      DO 303 I=1,NA
      IF (RX(I).LT.0.0) GO TO 303
      QA=RX(I)
      II=I
      GO TO 304
  303 CONTINUE
      WRITE (6,307)
  307 FORMAT (1H0, 15X, 20H UNBOUNDED SOLUTION. )
      GO TO 398
  304 IF (II.GE.NA) GO TO 310
      IC=II+1
      DO 305 I=IC,NA
      IF (RX(I).LT.0.0.OR.RX(I).GT.QA) GO TO 305
      IF (RX(I).EQ.QA) GO TO 306
      QA=RX(I)
      II=I
      GO TO 305
  306 IF (K(II).GE.K(I)) GO TO 305
      QA=RX(I)
      II=I
  305 CONTINUE
  310 DX=A(II,JA)
      B(II)=B(II)/DX
      DO 311 J=1,MM
  311 A(II,J)=A(II,J)/DX
      DO 312 I=1,NA
      IF (I.EQ.II) GO TO 312
      DXX=A(I,JA)
      B(I)=B(I)-DXX*B(II)
      DO 313 J=1,MM
      IF (J.EQ.JA) GO TO 314
```

SUBROUTINE SIMPEX ...(CONT'D)

```
      A(I,J)=A(I,J)-DXX*A(II,J)
      GO TO 313
314   A(I,J)=0.00
313   CONTINUE
312   CONTINUE
      BB=BB-C(JA)*B(II)
      DO 315 J=1,MM
      IF (J.EQ.JA) GO TO 315
      C(J)=C(J)-C(JA)*A(II,J)
315   CONTINUE
      C(JA)=0.00
      K(II)=JA
      GO TO 399
330   WRITE (6,331)
331   FORMAT (1H1, 30H THIS IS THE OPTIMUM SOLUTION.   )
      WRITE(6,28)ITRGAM,GAMA(ITRGAM)
  28  FORMAT(1H0,37X,'TRIAL  NO.',I6,5X,'GAMMA =  ',F15.8)
      WRITE (6,321) BB
321   FORMAT (1H , 20X, 22H OBJECTIVE FUNCTION = , E15.8)
      WRITE (6,322)
322   FORMAT (1H0, 25X, 48HBASIC VARIABLES   AND   VALUES
     * ARE AS FOLLO
     1WS    )
      WRITE (6,323) (K(I), B(I), I=1,NA)
323   FORMAT (1H , 29X, I4, 12X, E15.8)
398   CONTINUE
      RETURN
      END
```

SUBROUTINE COEFF

```
   SUBROUTINE COEFFI
   COMMON /INT2/CONST,NA,NCASE,NREL,NOPT
   COMMON /COE1/TC,WT,CON,X,R,GAM
   COMMON /COE2/SPG,SHG,TCONT,VCONT,HCONT,VRCON,TRCON
  *,PPCON,VPCON,TPC
  1ON,NH,N1,CPCON
    DOUBLE PRECISION G(16,17),S,D,B,SIG,DIV(16),Y(16),Q
  *,AST
   DIMENSION X(16),SPG(16),SHG(16),TCONT(16),VCONT(16)
  *,HCONT(16),VRCO
  1N(16),TRCON(16),PPCON(16),VPCON(16),TPCON(16)
  *,CPCON(16)
 4  FORMAT(1H ,8HSINGULAR)
 5  FORMAT(1H ,5HERROR)
   N=NA
   NN=N+1
    DO 52 I=1,N1
   SG=SPG(I)
   P=PPCON(I)
   V=VPCON(I)
   T=TPCON(I)
   DE=1./V
   DD=DE**2
   G(I,1)=1.
   IF(NREL.EQ.1) G(I,1)=0.01*G(I,1)
   G(I,2)=R*T*DD
   G(I,3)=-DD
   G(I,4)=-DD/(T**2)
   G(I,5)=R*T*DD*DE
   G(I,6)=-DD*DE
   G(I,7)=DE**6
   EA=GAM*DD
   G(I,8)=(1.0+EA)*DE**3/(T*T*EXP(EA))
   G(I,9)=P-R*T*DE
   DO 53 J=2,NN
   IF(NREL.EQ.1) G(I,J)=G(I,J)/P
   G(I,J)=G(I,J)*SG
53 CONTINUE
52 CONTINUE
   IF(NCASE.EQ.0) GO TO 100
   IF(NH.EQ.0) GO TO 100
   DO 300 K=1,NH
   I=K+N1
   H=HCONT(K)
    V=VCONT(K)
   T=TCONT(K)
   VREF=VRCON(K)
   TREF=TRCON(K)
   SG=SHG(K)
   DE=1./V
```

SUBROUTINE COEFFI ...(CONT'D)

```
      DEREF=1./VREF
      DD=DE**2
      DDREF=DEREF**2
      EA=GAM*DD
      EAREF=GAM*DDREF
      EX=EXP(-EA)
      EXREF=EXP(-EAREF)
      G(I,1)=0.0
      IF(NOPT.EQ.1) G(I,1)=CONST
      IF(NOPT.EQ.1.AND.NREL.EQ.1)G(I,1)=0.01*G(I,1)
      G(I,2)=R*(T*DE-TREF*DEREF)*CON
      G(I,3)=-2.*CON*(DE-DEREF)
      G(I,4)=-4.*CON*(DE/T**2-DEREF/TREF**2)
      G(I,5)=R*CON*(T*DD-TREF*DDREF)
      G(I,6)=-1.5*CON*(DD-DDREF)
      G(I,7)=6.*CON*(DE**5-DEREF**5)/5.
      G(I,8)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
     *-(DDREF/TREF**2)*
     1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
      DO 301 J=2,N
      IF(NREL.EQ.1) G(I,J)=G(I,J)/CPCON(K)
      G(I,J)=G(I,J)*SG
  301 CONTINUE
      IF(NOPT.EQ.1) G(I,9)=H*SG
      IF(NOPT.EQ.1) GO TO 300
      G(I,9)=H*SG-CONST
  300 CONTINUE
  100  NN=N+1
       DO 70 J=1,N
   70  DIV(J)=DABS(G(1,J))
       DO 71 J=1,N
       DO 71 I=1,N
   71  G(I,J)=G(I,J)/DIV(J)
       K=N
   60  MAX=1
       Q=DABS(G(1,K))
      DO 65 I=2,K
      IF(DABS(G(I,K)).LT.Q) GO TO 65
       MAX=I
      Q=DABS(G(MAX,K))
   65  CONTINUE
       DO 62 J=1,NN
       AST=G(MAX,J)
       G(MAX,J)=G(K,J)
   62  G(K,J)=AST
       K=K-1
       IF(K.GE.2) GO TO 60
    9  K=N
   11 IF(G(K,K).NE.0.0)GO TO 14
   16  M=K-1
```

SUBROUTINE COEFFI ...(CONT'D)

```
  22 IF(G(M,K).EQ.0.0)GO TO 20
  18  DO 19 J=1,K
     S=G(M,J)
      G(M,J)=G(K,J)
  19  G(K,J)=S
      S=G(M,NN)
      G(M,NN)=G(K,NN)
      G(K,NN)=S
      GO TO 14
  20  M=M-1
      IF(M.LT.0) GO TO 99
      IF(M.GT.0) GO TO 22
  23  WRITE(6,4)
      GO TO 401
  14  D=G(K,K)
      DO 26 J=1,K
  26 G(K,J)=G(K,J)/D
      G(K,NN)=G(K,NN)/D
      I=K-1
  30  IF(G(I,K).EQ.0.0) GO TO 28
  27  B=G(I,K)
      DO 29 J=1,K
  29  G(I,J)=G(I,J)-B*G(K,J)
      G(I,NN)=G(I,NN)-B*G(K,NN)
  28  I=I-1
      IF(I.LT.0) GO TO 99
      IF(I.GT.0) GO TO 30
  32  K=K-1
      IF(K.LT.1) GO TO 99
      IF(K.GT.1) GO TO 11
  34  IF(G(1,1).NE.0.0) GO TO 36
  35  WRITE(6,4)
      GO TO 401
  36  G(1,NN)=G(1,NN)/G(1,1)
      DO 40 I=2,N
      SIG=0.0
      NI=I-1
      DO 38 J=1,NI
  38  SIG=SIG+G(I,J)*G(J,NN)
  40  G(I,NN)=G(I,NN)-SIG
      DO 400 I=1,N
400   Y(I)=G(I,NN)
      DO 63 I=1,N
 63   X(I)=Y(I)/DIV(I)
     WRITE (6,55)
55   FORMAT (1H0, 10X, 16HFINAL SOLUTIONS. )
     WRITE(6,200) GAM
 200 FORMAT(1H0,15X,'GAMMA =  ',F15.8)
      WRITE(6,56) (X(I),I=1,N)
 56   FORMAT(1H ,E15.8)
```

SUBROUTINE COEFFI ...(CONT'D)

```
      GO TO 401
  99  WRITE(6,5)
401   CONTINUE
     RETURN
     END
```

SUBROUTINE PCALC

```
      SUBROUTINE PCALCU
      COMMON /INT1/M,MM,N,M1
      COMMON /COE1/TC,WT,CON,X,R,GAM
      COMMON /PVT/TT,VV,PCAL
      DIMENSION TT(250),VV(250),PCAL(250),X(16)
      DO 1 I=1,M1
      T=TT(I)
      V=VV(I)
      DE=1./VV(I)
      DD=DE**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      PK=RT*DE+X(2)*RT*DD-X(3)*DD-X(4)*DD/(T**2)+X(5)*RT*DD
     **DE-X(6)*DD*D
     1E+X(7)*(DE**6)+X(8)*DD*DE*(1.+EA)*EX/(T**2)
      PCAL(I)=PK
    1 CONTINUE
      RETURN
      END
```

SUBROUTINE DDIFC

```
      SUBROUTINE DDIFCL
      COMMON /INT1/M,MM,N,M1
      COMMON /COE1/TC,WT,CON,X,R,GAM
      COMMON /PVT/TT,VV,PCAL
      COMMON /DP/VVREF,TTREF,DPDIFK
      DIMENSION TT(250),VV(250),PCAL(250),VVREF(50)
     *,TTREF(50),DPDIFK(50)
     1,X(16)
      M11=M1+1
       DO 301 J=M11,M
      V=VV(J)
      DE=1./V
      T=TT(J)
      DD=DE**2
      TS=T**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      HK=(X(2)*RT-2.*X(3)-4.*X(4)/TS)*DE+X(5)*RT*DD-1.5*X(6)
     **DD+6.*X(7)*
     1DE**5/5.+X(8)*DD*(3.*(1.-EX)/EA-EX/2.+EA*EX)/TS
      I=J-M1
       V=VVREF(I)
      T=TTREF(I)
      DE=1./V
      DD=DE**2
      TS=T**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      HR=(X(2)*RT-2.*X(3)-4.*X(4)/TS)*DE+X(5)*RT*DD-1.5*X(6)
     **DD+6.*X(7)*
     1DE**5/5.+X(8)*DD*(3.*(1.-EX)/EA-EX/2.+EA*EX)/TS
      HR=CON*HR
      HK=HK*CON
      DPDIFK(I)=HK-HR
  301 CONTINUE
      RETURN
      END
```

2. PGM-2 -

This programme evaluates the interaction constants of a binary mixture defined by Equation (V.1) for the BWR parameters. The parameters may be estimated either from the mixture P-V-T data only or from the mixture P-V-T data and the isobaric and ideal gas mixture enthalpy changes. The choice of various 'flags' is similar to that of PGM-1.

The input information has to be in the following sequence:

a. N, NCASE, NCOMP, NGAMA, NUNIT, NREL, NOPT.
   The explanation of these variables is given in the listing

b. GAMA (I)
   The values of γ interaction, which have to be tried, are read from the cards, each of which contains only one value. The no. of cards equals NGAMA

c. XMETH (I)
   The BWR parameters for methane are read from eight cards, each of which contain one parameter.

d. XCO2 (I)
   The BWR parameters for carbon dioxide are read from eight cards.

e. The P-V-T and composition information is read by a DO-loop in the following manner:
   i. Read XMFR, NP

where NP is the no. of P-V-T data points at XMFR mole fraction methane

ii. Read P, T, V, XFR

NP cards contain the P-T-V and mole fraction information for NP points. XFR equals XMFR. Steps (i) and (ii) are repeated NCOMP times.

If isobaric enthalpy changes for the mixtures are used as additional constraints, the following input information is required in addition to the above:

f. Read XHMFR, NT

NT are the number of $\int C_p dT$ points at the mole fraction XHMFR

g. Read CPDT, T, V, Tref., Vref., CPODT

These variables are read NT times for each XHMFR. Total no. of cards equals NT

h. Steps (f) and (g) are repeated NCASE times. NCASE is the number of compositions at which $\int C_p dT$ information is available

i. CONST

The values of CONST are chosen in a manner similar to that for the PGM-1.

The output of the programme will be self explanatory and hence it is not included here. When only one value of γ is used, the final solution vector for the parameters is printed in a manner similar to that of the programme PGM-1.

```
    C      MAIN

C      MAIN

C     ****************************************************
C     *
C     *
C      COMPUTER PROGRAMME NO.  PGM-2
C
C      THIS PROGRAM FINDS THE INTERACTION CONSTANTS FOR A
C      BINARY MIXTURE USING THE LINEAR PROGRAMMING
C      TECHNIQUE.
C
C      CHEBYSHEV CRITERION OF MINIMISING THE MAXIMUM
C      DEVIATION IS USED.
C
C
C      NCOMP IS THE NO. OF COMPOSITIONS FOR WHICH P-V-T DATA
C      ARE PROCESSED.
C      NP(IC) IS THE NO. P-V-T POINTS AT THE COMPOSITION
C      XMFR(IC), MOL FR. CH4.
C      X(I) IS THE INTERACTION CONSTANT FOR THE ITH
C      COEFFICIENT.
C      GAMMA(I) IS THE INTERACTION CONSTANT FOR THE GAMMAS
C      OF THE TWO PURE COMPONENTS.
C
C      NUNIT IS ZERO WHEN INPUT DATA ARE IN PSIA
C      ,CU.FT./LB.MOLE,DEGREE RANKIN AND BTU/LB.MOLE.
C      NUNIT IS ONE WHEN INPUT DATA ARE IN ATMOSPHERES,
C      LITRES/G.MOLE, DEGREES KELVIN AND CALORIES/G.MOLE.
C
C      NREL IS ONE WHEN PERCENT P AND PERCENT CPDT
C      DEVIATIONS ARE TO BE MINIMISED
C      NREL IS ZERO WHEN ABSOLUTE P AND ABSOLUTE CPDT
C      DEVIATIONS ARE TO BE MINIMISED.
C
C
C      NOPT IS ONE WHEN ERROR IN INTEGRAL CPDT IS COUPLED
C      WITH THE ERROR IN PRESSURE. NOPT CAN BE ONE ONLY WHEN
C      NREL IS ALSO ONE.
C
C
C      NGAMA IS THE NO. OF TIMES DIFFERENT VALUES OF GAMMA
C      ARE TO BE TRIED.
C      NGAMA IS ONE WHEN ONLY ONE GAMMA IS TRIED.
C
C
C      M1 IS NO. OF P-V-T POINTS.
C      M2 IS TOTAL NO. OF POINTS FOR WHICH INTEGRAL CPDT
C      DATA ARE FED.
C      NCASE IS ZERO IF ONLY P-V-T DATA ARE TO BE PROCESSED
C      OTERWISE IT IS EQUAL TO THE NO. OF COMPOSITIONS AT
```

```
C        WHICH INTEGRAL CPDT DATA ARE PROCESSED.
C
C        TREF(I) IS THE REFERENCE TEMP. FOR T(I)
C
C
C        N IS THE NO. OF INTERACTION COEFFICIENTS TO BE
C        EVALUATED IN THE BWR EQUATION OF STATE.
C
C       *
C       *
C       ***************************************************************

        COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRGAM
        COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
        COMMON/COE1/CON,X,R,GAM
        COMMON /COE2/SPG,SHG,TCONT,VCONT,HCONT,VRCON,TRCON
       *,PPCON,VPCON,TPC
       1ON,NH,N1,CPCON,FFCON,GAMCON,XFRCON,XHCON,GMHCON
        COMMON /PVT/TT,VV,PCAL
        COMMON /DP/VVREF,TTREF,DPDIFK
        COMMON/PVT1/XMETH,XCO2,XMFRM,XMFRC,IK,NP,NT
        DIMENSION A(10,740),B(10),C(740),F(740),K(10),RX(10)
       *,PP(370),VV(37
       10),CPDT(70),TTREF(70),VVREF(70),FF(370),TT(370)
       *,XFR(370),GAMCON(10
       2),XFRCON(10)
        DIMENSION SHG(10),SPG(10),TCONT(10),VCONT(10)
       *,PCONT(10),VRCON(10),
       1TRCON(10),HCONT(10),PPCON(10),VPCON(10),TPCON(10)
       *,X(10),CPCON(10)
        DIMENSION PCAL(370),DPDIFK(70)
        DIMENSION GAMA(10),AA(10,740)
        DIMENSION NT(5),CPODT(70),XHMFR(5),XHCON(10)
       *,GMHCON(10)
        DIMENSION XMETH(10),XCO2(10),XMFR(5),NP(5),FFCON(10)
        READ(5,1)N,NCASE,NCOMP,NGAMA,NUNIT,NREL,NOPT
      1 FORMAT(7I4)
        IF(NCASE.EQ.0)WRITE(6,5)
      5 FORMAT(10X,'ONLY THE P-V-T DATA ARE BEING PROCESSED')
        IF(NCASE.GT.0) WRITE(6,6)
      6 FORMAT(10X,'THE P-V-T DATA WITH INTEGRAL CPDT
       * CONSTRAINTS ARE BEIN
       1G PROCESSED')
        IF(NREL.EQ.0) WRITE(6,7)
      7 FORMAT(10X,'THE MAXIMUM ABSOLUTE DEVIATION IS BEING
       * MINIMIZED.')
        IF(NREL.EQ.1) WRITE(6,8)
      8 FORMAT(10X,'THE MAXIMUM PERCENT DEVIATION IS BEING
       * MINIMIZED.')
        IF(NCASE.GT.0.AND.NOPT.EQ.0) WRITE(6,9)
```

```
          C       MAIN                    ...(CONT'D)

    9 FORMAT(10X,'THE MAXIMUM DEVIATION IN INTEGRAL CPDT IS
     * EQUAL AN ARB
     1ITRARY CONSTANT.')
      IF(NOPT.EQ.1) WRITE(6,10)
   10 FORMAT(10X,'THE MAXIMUM DEVIATION IN INTEGRAL CPDT IS
     * EQUAL TO AN
     1ARBITRARY CONSTANT TIMES THE MAXIMUM DEVIATION IN
     * PRESSURE.')
      READ(5,502)(GAMA(I),I=1,NGAMA)
  502 FORMAT(F20.8)
  604 M2=0
      M1=0
      CONST=0.
      NA=N+1
      READ(5,905)(XMETH(I),I=1,NA)
      READ(5,905)(XCO2(I),I=1,NA)
  905 FORMAT(E15.8)
      WRITE(6,905)(XMETH(I),I=1,NA)
      WRITE(6,905)(XCO2(I),I=1,NA)

C       XMETH(I) AND XCO2(I) ARE COEFFICIENTS FOR CH4 AND
C       CO2.
C       XMETH(1) AND XCO2(1) ARE GAMMA VALUES FOR CH4 AND
C       CO2.
C

  300  FORMAT(1H ,2F15.8)
      IF(NUNIT.EQ.0.OR.NUNIT.EQ.2) R=10.73147
      IF(NUNIT.EQ.1) R=0.0820544
      IF(NUNIT.EQ.0) CON=144.0/777.9
      IF(NUNIT.EQ.1) CON=100.0/4.130
      ITRGAM=1
      I=0
  900 FORMAT(F15.8,I5)
      DO 102 IC=1,NCOMP
      READ(5,900) XMFR(IC),NP(IC)
      NNP=NP(IC)
      XMFRM=XMFR(IC)
      XMFRC=1.-XMFRM
      IF(NGAMA.GT.1) GO TO 903
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     ***GAMA(1)
  903 DO 901 IP=1,NNP
      I=I+1
      M1=M1+1
      READ(5,101)PP(I),TT(I),VV(I),XFR(I)
      P=PP(I)
      V=VV(I)
      DE=1.0/VV(I)
      T=TT(I)
```

```
      C       MAIN                    ....(CONT'D)
  101  FORMAT(1H ,4F15.8)
      WRITE(6,400)I,P,T,V,XMFRM
   400 FORMAT(10X,I3,4F15.8)
      DD=DE**2
      F(I)=P-R*T*DE
      IF(NREL.EQ.1) F(I)=F(I)/P
      FF(I)=F(I)
      A(2,I)=R*T*DD
      A(3,I)=-DD
      A(4,I)=-DD/(T**2)
      A(5,I)=R*T*DD*DE
      A(6,I)=-DD*DE
      A(7,I)=DE**6
      SUM=0.
      DO 703 J=2,N
      IF(NREL.EQ.1) A(J,I)=A(J,I)/P
        SUM=SUM+A(J,I)*(XMETH(J)*XMFRM**2+XCO2(J)*XMFRC**2)
      A(J,I)=2.*XMFRM*XMFRC*A(J,I)
  703 AA(J,I)=A(J,I)
      F(I)=F(I)-SUM
      FF(I)=F(I)
      IF(NGAMA.GT.1) GO TO 901
      EA=GAM*DD
      A(8,I)=(1.0+EA)*DE**3/(T*T*EXP(EA))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/P
      F(I)=F(I)-A(8,I)*(XMETH(8)*XMFRM**2+XCO2(8)*XMFRC**2)
      FF(I)=F(I)
      A(8,I)=2.*XMFRM*XMFRC*A(8,I)
  901 CONTINUE
  102 CONTINUE
      M=M1
      M11=M1+1
      MM=M+M
      IF(NCASE.EQ.0) GO TO 605
      M2=0
      I=M1
      DO 600 IC=1,NCASE
      READ(5,900) XHMFR(IC),NT(IC)

C       NT(I) ARE THE NO. OF INTEGRAL CPDT POINTS AT THE
C       XHMFR(I) MOLE FRACTION OF METHANE.
C
C       NCASE IS THE NO. OF COMPOSITIONS AT WHICH INTEGRAL
C       CPDT POINTS ARE PROCESSED.

      NNT=NT(IC)
      XMFRM=XHMFR(IC)
      XMFRC=1.-XMFRM
      IF(NGAMA.GT.1) GO TO 601
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
```

```
     **GAMA(1)
 601  DO 602 IP=1,NNT
      M2=M2+1
      I=I+1
      J=I-M1
      READ(5,103)CPDT(J),TT(I),VV(I),TTREF(J),VVREF(J)
     *,CPODT(J)
 103  FORMAT(6F12.6)
      XFR(I)=XMFRM
      HO=CPODT(J)
      H=CPDT(J)
      T=TT(I)
      V=VV(I)
      DE=1./V
      TREF=TTREF(J)
      VREF=VVREF(J)
      DEREF=1./VREF
      WRITE(6,104)I,H,T,V,TREF,VREF,HO,XMFRM
 104  FORMAT(I4,7F15.8)
      F(I)=H-HO
      IF(NREL.EQ.1) F(I)=F(I)/H
      DD=DE**2
      DDREF=DEREF**2
      A(2,I)=R*(T*DE-TREF*DEREF)*CON
      A(3,I)=-2.*CON*(DE-DEREF)
      A(4,I)=-4.*CON*(DE/T**2-DEREF/TREF**2)
      A(5,I)=R*CON*(T*DD-TREF*DDREF)
      A(6,I)=-1.5*CON*(DD-DDREF)
      A(7,I)=6.*CON*(DE**5-DEREF**5)/5.
      SUM=0.
      DO 210 L=2,N
      IF(NREL.EQ.1) A(L,I)=A(L,I)/H
        SUM=SUM+A(L,I)*(XMETH(L)*XMFRM**2+XCO2(L)*XMFRC**2)
      A(L,I)=2.*XMFRM*XMFRC*A(L,I)
 210  AA(L,I)=A(L,I)
      F(I)=F(I)-SUM
      FF(I)=F(I)
      IF(NGAMA.GT.1) GO TO 602
      EA=GAM*DD
      EAREF=GAM*DDREF
      EX=EXP(-EA)
      EXREF=EXP(-EAREF)
      A(8,I)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
     *-(DDREF/TREF**2)*
     1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/H
      F(I)=F(I)-A(8,I)*(XMETH(8)*XMFRM**2+XCO2(8)*XMFRC**2)
      FF(I)=F(I)
      A(8,I)=2.*XMFRM*XMFRC*A(8,I)
 602  CONTINUE
```

```
C      MAIN                   ...(CONT'D)
  600 CONTINUE
      M=M2+M1
      MM=M+M
      READ(5,2) CONST
 2     FORMAT(1H ,F10.4)
      IF(NOPT.NE.1) WRITE(6,3)M1,M2,CONST
3     FORMAT (1H0, 5X, I4, 23H POINTS LESS THAN LAMDA,/6X,
     * I4, 17H POINT
     1S LESS THAN , E15.6)
       IF(NOPT.EQ.1)WRITE(6,4)M1,M2,CONST
    4 FORMAT(6X,I4,'POINTS LESS THAN LAMDA',/6X,I4,'POINTS
     * LESS THAN',E1
     15.6,'TIMES LAMDA')
  605 CONTINUE
      IF(NGAMA.EQ.1) GO TO 700
      ITRGAM=1
  705 I=0
      DO 702 IC=1,NCOMP
      NNP=NP(IC)
      XMFRM=XMFR(IC)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(ITRGAM)
      DO 902 IP=1,NNP
      I=I+1
      V=VV(I)
      P=PP(I)
      T=TT(I)
      DE=1./V
      DD=DE**2
      EA=GAM*DD
      A(8,I)=(1.0+EA)*DE**3/(T*T*EXP(EA))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/P
      F(I)=F(I)-A(8,I)*(XMETH(8)*XMFRM**2+XCO2(8)*XMFRC**2)
      A(8,I)=2.*XMFRM*XMFRC*A(8,I)
  902 CONTINUE
  702 CONTINUE
      IF(NCASE.EQ.0) GO TO 700
      I=M1
      DO 704 IC=1,NCASE
      NNT=NT(IC)
      XMFRM=XHMFR(IC)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(ITRGAM)
      DO 410 IP=1,NNT
      I=I+1
      J=I-M1
      V=VV(I)
      T=TT(I)
```

```
C       MAIN                      ...(CONT'D)
      VREF=VVREF(J)
      TREF=TTREF(J)
      DE=1./V
      DEREF=1./VREF
      DD=DE**2
      DDREF=DEREF**2
      EA=GAM*DD
      EAREF=GAM*DDREF
      EX=EXP(-EA)
      EXREF=EXP(-EAREF)
      A(8,I)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
     *-(DDREF/TREF**2)*
     1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
      IF(NREL.EQ.1) A(8,I)=A(8,I)/CPDT(J)
      F(I)=F(I)-A(8,I)*(XMETH(8)*XMFRM**2+XCO2(8)*XMFRC**2)
      A(8,I)=2.*XMFRM*XMFRC*A(8,I)
  410 CONTINUE
  704 CONTINUE
  700 CONTINUE
      CALL DUAL
       CALL SIMPEX
      IF(NGAMA.EQ.1) GO TO 706
      IF(ITRGAM.EQ.NGAMA) GO TO 67
      ITRGAM=ITRGAM+1
      DO 707 I=1,M
      F(I)=FF(I)
      DO 707 J=2,N
  707 A(J,I)=AA(J,I)
      GO TO 705
  706 NH=0
       N1=0
      DO 200 I=1,NA
      IF(K(I).GT.M) GO TO 201
       IF(NCASE.EQ.0) GO TO 607
      IF(K(I).GT.M1) GO TO 203
  607 KM=K(I)
      N1=N1+1
      XFRCON(N1)=XFR(KM)
      XMFRM=XFR(KM)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      GAMCON(N1)=GAM
      FFCON(N1)=FF(KM)
      PPCON(N1)=PP(KM)
      VPCON(N1)=VV(KM)
      TPCON(N1)=TT(KM)
        SPG(N1)=1.0
      GO TO 200
  203 KM=K(I)
```

```
C        MAIN                          ...(CONT'D)
      NH=NH+1
      XHCON(NH)=XFR(KM)
      XMFRM=XFR(KM)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      GMHCON(NH)=GAM
      HCONT(NH)=FF(KM)
      VCONT(NH)=VV(KM)
      TCONT(NH)=TT(KM)
      KMM=KM-M1
      VRCON(NH)=VVREF(KMM)
      TRCON(NH)=TTREF(KMM)
      CPCON(NH)=CPDT(KMM)
      SHG(NH)=1.Q
       GO TO 200
  201 KM=K(I)-M
      IF(M.EQ.M1) GO TO 606
      IF(KM.GT.M1) GO TO 202
  606  N1=N1+1
      XFRCON(N1)=XFR(KM)
      XMFRM=XFR(KM)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      GAMCON(N1)=GAM
      FFCON(N1)=FF(KM)
      PPCON(N1)=PP(KM)
      VPCON(N1)=VV(KM)
      TPCON(N1)=TT(KM)
        SPG(N1)=-1.0
      GO TO 200
  202 NH=NH+1
      XHCON(NH)=XFR(KM)
      XMFRM=XFR(KM)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      GMHCON(NH)=GAM
      HCONT(NH)=FF(KM)
      VCONT(NH)=VV(KM)
      TCONT(NH)=TT(KM)
      KMM=KM-M1
      VRCON(NH)=VVREF(KMM)
      TRCON(NH)=TTREF(KMM)
      CPCON(NH)=CPDT(KMM)
      SHG(NH)=-1.0
  200 CONTINUE
      DO 205 I=1,N1
      WRITE(6,400)I,PPCON(I),TPCON(I),VPCON(I)
```

```
  205 CONTINUE
      IF(NCASE.EQ.0) GO TO 608
      DO 206 I=1,NH
      WRITE(6,104)I,HCONT(I),TCONT(I),VCONT(I),TRCON(I)
     *,VRCON(I)
  206 CONTINUE
  608 CONTINUE
      CALL COEFFI

C
C     CHECK OF SOLUTIONS.
C
C

      AM=FLOAT(M1)
       WRITE(6,213)
 213   FORMAT(1H1,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),9X
     *,6HP.EXP.,8X,
     1 7HP.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.,5X,'MOLE
     * FR.CH4')
       SR=0.0
       SP=0.0
      I=0
      DO 609 IC=1,NCOMP
      IK=IC
      NNP=NP(IC)
      XMFRM=XMFR(IC)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      CALL PCALCU
      DO 609 J=1,NNP
      I=I+1
      P=PP(I)
      V=VV(I)
      T=TT(I)
      PK=PCAL(I)
       DEV=ABS(P-PK)
       PERC=DEV*100.0/P
      WRITE(6,61)V,T,P,PK,DEV,PERC,XMFRM
   61 FORMAT(1H ,F15.4,F15.2,5F15.4)
       SP=SR+DEV
       SP=SP+PERC
  609 CONTINUE
       SRA=SR/AM
       SPE=SP/AM
       WRITE(6,212) SRA,SPE
 212   FORMAT(1H ,9HAVE.DEV.=,F10.6,13HAVE.PER.DEV.=,F10.6)
      IF(NCASE.EQ.0) GO TO 67
      MMM1=M-M1
```

```
        C       MAIN                    ...(CONT'D)
      A1=FLOAT(MMM1)
       WRITE(6,214)
214    FORMAT(1H ,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),9X
     *,6HH.EXP.,8X,
     1 7HH.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.,5X,'MOL. FR.
     * CH4')
       SR=0.0
       SP=0.0
      I=M1
      DO 807 IC=1,NCASE
      IK=IC
      NNT=NT(IC)
      XMFRM=XHMFR(IC)
      XMFRC=1.-XMFRM
      GAM=XMETH(1)*XMFRM**2+XCO2(1)*XMFRC**2+2.*XMFRM*XMFRC
     **GAMA(1)
      CALL DDIFCL
      DO 804 IP=1,NNT
      I=I+1
      J=I-M1
      H=CPDT(J)
      V=VV(I)
      T=TT(I)
      HK=DPDIFK(J)+CPODT(J)
       DEV=ABS(H-HK)
       PERC=DEV*100.0/ABS(H)
      WRITE(6,61)V,T,H,HK,DEV,PERC,XMFRM
       SR=SR+DEV
       SP=SP+PERC
804   CONTINUE
807   CONTINUE
       SRA=SR/A1
       SPE=SP/A1
       WRITE(6,212) SRA,SPE
67     CONTINUE
       STOP
      END
```

SUBROUTINE DUAL

```
      SUBROUTINE DUAL
      COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRGAM
      COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
      DIMENSION A(10,740),B(10),C(740),F(740),K(10),RX(10)
     *,GAMA(10)
      M11=M1+1
      DO 5 J=1,M1
      JM=J+M
      F(JM)=-F(J)
       A(1,J)=1.00
      IF(NREL.EQ.1) A(1,J)=0.01*A(1,J)
       A(1,JM)=1.00
      IF(NREL.EQ.1) A(1,JM)=0.01*A(1,JM)
      DO 5 I=2,NA
5     A(I,JM)=-A(I,J)
      IF(NCASE.EQ.0) GO TO 100
      DO 6 J=M11,M
      JM=J+M
      IF(NOPT.EQ.1) GO TO 150
       F(JM)=-F(J)-CONST
       F(J)=F(J)-CONST
      A(1,J)=0.00
      A(1,JM)=0.00
      GO TO 151
  150 F(JM)=-F(J)
      A(1,J)=CONST
      IF(NREL.EQ.1)A(1,J)=0.01*A(1,J)
      A(1,JM)=A(1,J)
  151 DO 6 I=2,NA
6     A(I,JM)=-A(I,J)
  100 BB=0.00
      K(1)=1
      B(1)=1.
      DO 7 I=2,NA
      XX=A(I,1)
      B(I)=-XX
      A(I,1)=0.00
      DO 7 J=2,MM
7     A(I,J)=A(I,J)-XX*A(1,J)
      DO 8 I=2,NA
      IF (B(I).GE.0.0) GO TO 8
      B(I)=-B(I)
      DO 9 J=1,MM
9     A(I,J)=-A(I,J)
8     CONTINUE
      DO 10 L=2,NA
      XX=A(L,1)
      JA=1
      DO 11 J=2,MM
      IF (A(L,J).LE.XX) GO TO 11
```

SUBROUTINE DUAL ...(CONT'D)

```
      XX=A(L,J)
      JA=J
11    CONTINUE
      K(L)=JA
      B(L)=B(L)/XX
      DO 12 J=1,MM
12    A(L,J)=A(L,J)/XX
      DO 13 I=1,NA
      IF (I.EQ.L) GO TO 13
      YY=A(I,JA)
      B(I)=B(I)-B(L)*YY
      DO 14 J=1,MM
14    A(I,J)=A(I,J)-A(L,J)*YY
13    CONTINUE
10    CONTINUE
40    DO 30 I=1,NA
      IF (B(I).GE.0.0) GO TO 30
      IA=I
      GO TO 50
30    CONTINUE
      GO TO 31
50    B(IA)=-B(IA)
      DO 51 J=1,MM
51    A(IA,J)=-A(IA,J)
      XX=0.00
      JA=0
      DO 52 J=1,MM
      DO 53 I=1,NA
      IF (J.EQ.K(I)) GO TO 52
53    CONTINUE
      IF (A(IA,J).LE.XX) GO TO 52
      XX=A(IA,J)
      JA=J
52    CONTINUE
      K(IA)=JA
      B(IA)=B(IA)/XX
      DO 54 J=1,MM
54    A(IA,J)=A(IA,J)/XX
      DO 55 I=1,NA
      IF (I.EQ.IA) GO TO 55
      YY=A(I,JA)
      B(I)=B(I)-B(IA)*YY
      DO 56 J=1,MM
56    A(I,J)=A(I,J)-A(IA,J)*YY
55    CONTINUE
      GO TO 40
31    DO 20 I=1,NA
      IA=K(I)
20    BB=BB+F(IA)*B(I)
      DO 21 J=1,MM
```

SUBROUTINE DUAL ...(CONT'D)

```
      C(J)=0.00
      DO 22 I=1,NA
      IA=K(I)
22    C(J)=C(J)+F(IA)*A(I,J)
21    C(J)=C(J)-F(J)
      WRITE (6,25)
25    FORMAT (1H1, 15X, 22H FOR INITIAL TABLEAU - )
      WRITE(6,28)ITRGAM,GAMA(ITRGAM)
   28 FORMAT(1H0,37X,'TRIAL  NO.',I6,5X,'GAMMA =  ',F15.8)
      WRITE (6,26) BB
26    FORMAT (1H0, 16X, 21HOBJECTIVE FUNCTION = , E15.8)
      WRITE (6,27) (K(L), B(L), L=1,NA)
27    FORMAT (1H , 18X, 16HINDEP. VECTOR = , I4, 5X, E15.6)
      RETURN
      END
```

SUBROUTINE SIMPE

```
      SUBROUTINE SIMPEX
      COMMON /DU/A,B,C,F,RX,BB,K,GAMA,ITRGAM
      COMMON /INT1/M,MM,N,M1/INT2/CONST,NA,NCASE,NREL,NOPT
      DIMENSION A(10,740),B(10),C(740),F(740),K(10),RX(10)
     *,GAMA(10)
 399  QX=C(1)
      JA=1
      DO 300 J=2,MM
      IF (C(J).GE.QX) GO TO 300
      JA=J
      QX=C(J)
 300  CONTINUE
      IF (QX.GE.0.0) GO TO 330
      DO 301 I=1,NA
      IF (A(I,JA).LE.0.0) GO TO 302
      RX(I)=B(I)/A(I,JA)
      GO TO 301
 302  RX(I)=-1.00
 301  CONTINUE
      DO 303 I=1,NA
      IF (RX(I).LT.0.0) GO TO 303
      QA=RX(I)
      II=I
      GO TO 304
 303  CONTINUE
      WRITE (6,307)
 307  FORMAT (1H0, 15X, 20H UNBOUNDED SOLUTION. )
      GO TO 398
 304  IF (II.GE.NA) GO TO 310
      IC=II+1
      DO 305 I=IC,NA
      IF (RX(I).LT.0.0.OR.RX(I).GT.QA) GO TO 305
      IF (RX(I).EQ.QA) GO TO 306
      QA=RX(I)
      II=I
      GO TO 305
 306  IF (K(II).GE.K(I)) GO TO 305
      QA=RX(I)
      II=I
 305  CONTINUE
 310  DX=A(II,JA)
      B(II)=B(II)/DX
      DO 311 J=1,MM
 311  A(II,J)=A(II,J)/DX
      DO 312 I=1,NA
      IF (I.EQ.II) GO TO 312
      DXX=A(I,JA)
      B(I)=B(I)-DXX*B(II)
      DO 313 J=1,MM
      IF (J.EQ.JA) GO TO 314
```

SUBROUTINE SIMPEX ...(CONT'D)

```
      A(I,J)=A(I,J)-DXX*A(II,J)
      GO TO 313
  314 A(I,J)=0.00
  313 CONTINUE
  312 CONTINUE
      BB=BB-C(JA)*B(II)
      DO 315 J=1,MM
      IF (J.EQ.JA) GO TO 315
      C(J)=C(J)-C(JA)*A(II,J)
  315 CONTINUE
      C(JA)=0.00
      K(II)=JA
      GO TO 399
  330 WRITE (6,331)
  331 FORMAT (1H1, 30H THIS IS THE OPTIMUM SOLUTION.   )
      WRITE(6,28)ITRGAM,GAMA(ITRGAM)
   28 FORMAT(1H0,37X,'TRIAL  NO.',I6,5X,'GAMMA =  ',F15.8)
      WRITE (6,321) BB
  321 FORMAT (1H , 20X, 22H OBJECTIVE FUNCTION = , E15.8)
      WRITE (6,322)
  322 FORMAT (1H0, 25X, 48HBASIC VARIABLES   AND   VALUES
     * ARE AS FOLLO
     1WS   )
      WRITE (6,323) (K(I), B(I), I=1,NA)
  323 FORMAT (1H , 29X, I4, 12X, E15.8)
  398 CONTINUE
      RETURN
      END
```

SUBROUTINE COEFF

```
      SUBROUTINE COEFFI
      COMMON /INT2/CONST,NA,NCASE,NREL,NOPT
      COMMON/COE1/CON,X,R,GAM
      COMMON /COE2/SPG,SHG,TCONT,VCONT,HCONT,VRCON,TRCON
     *,PPCON,VPCON,TPC
     1ON,NH,N1,CPCON,FFCON,GAMCON,XFRCON,XHCON,GMHCON
       DOUBLE PRECISION G(10,11),S,D,B,SIG,DIV(10),Y(10),Q
     *,AST
      DIMENSION X(10),SPG(10),SHG(10),TCONT(10),VCONT(10)
     *,HCONT(10),VRCO
     1N(10),TRCON(10),PPCON(10),VPCON(10),TPCON(10)
     *,CPCON(10),FFCON(10)
      DIMENSION GAMCON(10),XFRCON(10),XHCON(10),GMHCON(10)
    4  FORMAT(1H ,8HSINGULAR)
    5  FORMAT(1H ,5HERROR)
      N=NA
      NN=N+1
       DO 52 I=1,N1
      XMFRM=XFRCON(I)
      XMFRC=1.-XMFRM
      SG=SPG(I)
      P=PPCON(I)
      V=VPCON(I)
      T=TPCON(I)
      GAM=GAMCON(I)
      DE=1./V
      DD=DE**2
      G(I,1)=1.
      IF(NREL.EQ.1) G(I,1)=0.01*G(I,1)
      G(I,2)=R*T*DD
      G(I,3)=-DD
      G(I,4)=-DD/(T**2)
      G(I,5)=R*T*DD*DE
      G(I,6)=-DD*DE
      G(I,7)=DE**6
      EA=GAM*DD
      G(I,8)=(1.0+EA)*DE**3/(T*T*EXP(EA))
      G(I,9)=FFCON(I)*SG
      DO 53 J=2,N
      IF(NREL.EQ.1) G(I,J)=G(I,J)/P
      G(I,J)=G(I,J)*SG*2.*XMFRM*XMFRC
   53 CONTINUE
   52 CONTINUE
      IF(NCASE.EQ.0) GO TO 100
      IF(NH.EQ.0) GO TO 100
      DO 300 K=1,NH
      I=K+N1
      XMFRM=XHCON(K)
      XMFRC=1.-XMFRM
      GAM=GMHCON(K)
```

SUBROUTINE COEFFI ...(CONT'D)

```
      H=HCONT(K)
       V=VCONT(K)
      T=TCONT(K)
      VREF=VRCON(K)
      TREF=TRCON(K)
      SG=SHG(K)
      DE=1./V
      DEREF=1./VREF
      DD=DE**2
      DDREF=DEREF**2
      EA=GAM*DD
      EAREF=GAM*DDREF
      EX=EXP(-EA)
      EXREF=EXP(-EAREF)
      G(I,1)=0.0
      IF(NOPT.EQ.1) G(I,1)=CONST
      IF(NOPT.EQ.1.AND.NREL.EQ.1)G(I,1)=0.01*G(I,1)
      G(I,2)=R*(T*DE-TREF*DEREF)*CON
      G(I,3)=-2.*CON*(DE-DEREF)
      G(I,4)=-4.*CON*(DE/T**2-DEREF/TREF**2)
      G(I,5)=R*CON*(T*DD-TREF*DDREF)
      G(I,6)=-1.5*CON*(DD-DDREF)
      G(I,7)=6.*CON*(DE**5-DEREF**5)/5.
      G(I,8)=CON*((DD/T**2)*(3.*(1.-EX)/EA-EX/2.+EA*EX)
     *-(DDREF/TREF**2)*
     1(3.*(1.-EXREF)/EAREF-EXREF/2.+EAREF*EXREF))
      DO 301 J=2,N
      IF(NREL.EQ.1) G(I,J)=G(I,J)/CPCON(K)
      G(I,J)=G(I,J)*SG*2.*XMFRM*XMFRC
301   CONTINUE
      IF(NOPT.EQ.1) G(I,9)=H*SG
      IF(NOPT.EQ.1) GO TO 300
      G(I,9)=H*SG-CONST
300   CONTINUE
100    NN=N+1
       DO 70 J=1,N
70     DIV(J)=DABS(G(1,J))
       DO 71 J=1,N
       DO 71 I=1,N
71     G(I,J)=G(I,J)/DIV(J)
       K=N
60     MAX=1
       Q=DABS(G(1,K))
       DO 65 I=2,K
      IF(DABS(G(I,K)).LT.Q) GO TO 65
       MAX=I
      Q=DABS(G(MAX,K))
65     CONTINUE
       DO 62 J=1,NN
       AST=G(MAX,J)
```

```
      G(MAX,J)=G(K,J)
 62   G(K,J)=AST
      K=K-1
      IF(K.GE.2) GO TO 60
  9   K=N
 11   IF(G(K,K).NE.0.0) GO TO 14
 16   M=K-1
 22   IF(G(M,K).EQ.0.0) GO TO 20
 18   DO 19 J=1,K
      S=G(M,J)
      G(M,J)=G(K,J)
 19   G(K,J)=S
      S=G(M,NN)
      G(M,NN)=G(K,NN)
      G(K,NN)=S
      GO TO 14
 20   M=M-1
      IF(M.LT.0) GO TO 99
      IF(M.GT.0) GO TO 22
 23   WRITE(6,4)
      GO TO 401
 14   D=G(K,K)
      DO 26 J=1,K
 26   G(K,J)=G(K,J)/D
      G(K,NN)=G(K,NN)/D
      I=K-1
 30   IF(G(I,K).EQ.0.0) GO TO 28
 27   B=G(I,K)
      DO 29 J=1,K
 29   G(I,J)=G(I,J)-B*G(K,J)
      G(I,NN)=G(I,NN)-B*G(K,NN)
 28   I=I-1
      IF(I.LT.0) GO TO 99
      IF(I.GT.0) GO TO 30
 32   K=K-1
      IF(K.LT.1) GO TO 99
      IF(K.GT.1) GO TO 11
 34   IF(G(1,1).NE.0.0) GO TO 36
 35   WRITE(6,4)
      GO TO 401
 36   G(1,NN)=G(1,NN)/G(1,1)
      DO 40 I=2,N
      SIG=0.0
      NI=I-1
      DO 38 J=1,NI
 38   SIG=SIG+G(I,J)*G(J,NN)
 40   G(I,NN)=G(I,NN)-SIG
      DO 400 I=1,N
400   Y(I)=G(I,NN)
      DO 63 I=1,N
```

SUBROUTINE COEFFI ...(CONT'D)

```
 63   X(I)=Y(I)/DIV(I)
     WRITE (6,55)
55   FORMAT (1HO, 10X, 16HFINAL SOLUTIONS. )
      WRITE(6,56) (X(I),I=1,N)
 56   FORMAT(1H ,E15.8)
      GO TO 401
  99  WRITE(6,5)
401   CONTINUE
     RETURN
     END
```

SUBROUTINE PCALC

```
      SUBROUTINE PCALCU
      COMMON /INT1/M,MM,N,M1
      COMMON/COE1/CON,X,R,GAM
      COMMON /PVT/TT,VV,PCAL
      COMMON/PVT1/XMETH,XCO2,XMFRM,XMFRC,IK,NP,NT
      DIMENSION TT(370),VV(370),PCAL(370),X(10)
      DIMENSION NP(5),XMETH(10),XCO2(10),Y(10),NT(5)
      IC=IK
      NNP=NP(IC)
      NA=N+1
      DO 2 I=2,NA
      Y(I)=XMETH(I)*XMFRM**2+X(I)*2.0*XMFRM*XMFRC+XCO2(I)
     **XMFRC**2
    2 CONTINUE
      NS=0
      IF(IC.EQ.1) GO TO 4
      DO 3 I=2,IC
    3 NS=NS+NP(I-1)
    4 DO 1 J=1,NNP
      I=J+NS
      T=TT(I)
      V=VV(I)
      DE=1./VV(I)
      DD=DE**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      PK=RT*DE+Y(2)*RT*DD-Y(3)*DD-Y(4)*DD/(T**2)+Y(5)*RT*DD
     **DE-Y(6)*DD*D
     1E+Y(7)*(DE**6)+Y(8)*DD*DE*(1.+EA)*EX/(T**2)
      PCAL(I)=PK
    1 CONTINUE
      RETURN
      END
```

SUBROUTINE DDIFC

```
      SUBROUTINE DDIFCL
      COMMON /INT1/M,MM,N,M1
      COMMON/COE1/CON,X,R,GAM
      COMMON /PVT/TT,VV,PCAL
      COMMON /DP/VVREF,TTREF,DPDIFK
      COMMON/PVT1/XMETH,XCO2,XMFRM,XMFRC,IK,NP,NT
      DIMENSION TT(370),VV(370),PCAL(370),VVREF(70)
     *,TTREF(70),DPDIFK(70)
     1,X(10),XMETH(10),XCO2(10),NP(5),NT(5),Y(10)
      IC=IK
      NNT=NT(IC)
      NA=N+1
      DO 2 I=2,NA
      Y(I)=XMETH(I)*XMFRM**2+X(I)*2.0*XMFRM*XMFRC+XCO2(I)
     **XMFRC**2
    2 CONTINUE
      NS=0
      IF(IC.EQ.1) GO TO 4
      DO 3 I=2,IC
    3 NS=NS+NT(I-1)
    4 DO 301 K=1,NNT
      J=K+NS+M1
      V=VV(J)
      DE=1./V
      T=TT(J)
      DD=DE**2
      TS=T**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      HK=(Y(2)*RT-2.*Y(3)-4.*Y(4)/TS)*DE+Y(5)*RT*DD-1.5*Y(6)
     **DD+6.*Y(7)*
     1DE**5/5.+Y(8)*DD*(3.*(1.-EX)/EA-EX/2.+EA*EX)/TS
      I=J-M1
       V=VVREF(I)
      T=TTREF(I)
      DE=1./V
      DD=DE**2
      TS=T**2
      RT=R*T
      EA=GAM*DD
      EX=EXP(-EA)
      HR=(Y(2)*RT-2.*Y(3)-4.*Y(4)/TS)*DE+Y(5)*RT*DD-1.5*Y(6)
     **DD+6.*Y(7)*
     1DE**5/5.+Y(8)*DD*(3.*(1.-EX)/EA-EX/2.+EA*EX)/TS
      HR=CON*HR
      HK=HK*CON
  301 DPDIFK(I)=HK-HR
      RETURN
      END
```

3. PGM-3 -

This programme evaluates the BWR parameters for a pure component by the non-linear least squares technique. The parameters may be estimated from the P-V-T data only, the P-V-T and heat capacity data or the C_p data only. When only the P-V-T data are used, either Z or V could be chosen as the dependent variable. When Z is chosen as a dependent variable either the deviations or the relative deviations could be minimized. When P-V-T and heat capacity data are used V and C_p are chosen as the dependent variables.

The input information has to be in the following sequence:

a. N, M1, NCASE, NTIME, NREL, NOUT, NV, NCHOIS
   These variables are read by the Format (8I4) and their values are chosen according to the explanation given in the listing. This information is contained on one card
b. X (I)
   The initial guess of the BWR parameters is read from eight cards, each containing one parameter value. An initial guess of unit vector may be chosen, in which case there will be eight cards, each containing 1.0 E 00 according to the Format (D 15.8)
c. SCALE (I)
   These factors are used to scale the BWR parameters

so as to avoid ill-conditioning of the least squares matrix. Values of these scale factors may be chosen equal to the figures shown in the 'DATA' card of the main programme. The scale factors are read by the Format (D 15.8) and eight cards are required for reading eight scale factors

d. PP (I), TT (I), VV (I)

P-T-V data are read by the Format (1Hb,3F 15.8). The no. of cards required would be equal to the no. of P-T-V data points i.e. M1.

If heat capacities are also used, the following additional information is required:

e. M2

M2 is the number of C_p data points and is read by the Format (I4)

f. WC

WC is the weight assigned to the sum of relative error squares in C_p departures

g A2 (J)

These are the co-efficients of the power polynomial which describes the temperature dependence of the ideal gas heat capacity, and are read by the Format (5E 15.7)

h. PPC (I), TTC (I), CP (I)

The pressure, temperature and heat capacity data are read by the Format (1Hb,3(F 15.8,3X)). The no. of cards required would be equal to the no. of data points i.e. M2.

If the parameters are estimated from the C_p data only, the information included in (a) through (c) and (e) through (h) are read in.

When the parameters are estimated from either the C_p data only or from P-V-T and C_p data the initial guess of the parameters may be taken as equal to the final solution obtained by treating the P-V-T data only. When only the P-V-T data are processed the initial guess may be taken as the unit vector.

The "Levenberg-Marquardt combination convergence scheme" is utilized in the programme. The steps involved in this scheme are as follows:

i. Calculate objective function from the initial guess of the parameter vector X

ii. Calculate non-damped least squares matrix A and normalize it

iii. If it is the first trial, calculate W by Equation (V.48), otherwise skip this step

iv. Formulate damped matrix A by adding W in the diagonal elements of the un-damped matrix

v. Calculate δ

vi. Calculate parameter vector $X^{(r + 1)}$

vii. Calculate new objective function using the parameter vector $X^{(r + 1)}$

viii. Compare old and new objective functions. If the new value is less than the old value, make $X^{(r + 1)}$ as the initial guess. Calculate new W by W = W/10, and go to step (i)

ix. If the new objective function is greater than the old value, keep $X^{(r)}$ as the initial guess. Calculate new value of W by W = 10.W. Make diagonal elements of matrix A equal to (1. + W) and keep the other elements the same as those previously calculated with the parameter vector $X^{(r)}$. Go to step (v).

These steps are followed in the programme by generating a flag "IFLAG". IFLAG is generated zero when the objective function calculated at (r + 1)th iteration is less than that calculated for the rth trial. Otherwise it is greater than zero. IFLAG is generated in the main programme and the value of W is increased or decreased in the Subroutine NLRLST depending upon whether IFLAG is greater than or equal to zero. The trials are terminated when the convergence criterion described in Chapter V is satisfied.

The volumes are calculated by the Subroutine VOLUM which utilizes the Newton-Raphson method of finding roots of a polynomial. The matrix A is inverted by partitioning it into its lower and upper diagonal matrices. The partitioning and inversion are effected by the Subroutines PARTN and INVER respectively.

For every trial which decreases the objective function, the output of the programme prints the parameter vector, sum of error squares (or relative error squares) and standard error (or relative error) of fit in the dependent variable. When the convergence is achieved a message 'THE PROGRAMME CONVERGED. THE ABOVE PARAMETERS ARE OPTIMUM' is printed. This is followed by a tabular listing of the input data of P, T, and V, or C_p, and estimated dependent variable and relative error for each point. The values of the BWR parameters are obtained from the printed optimum solution by multiplying them with their respective scale factors.

```
    C      MAIN
C     MAIN
C     **************************************************
C
C     COMPUTER PROGRAMME NO.    PGM-3
C
C     EVALUATION OF THE B.W.R. PARAMETERS USING NON-LINEAR
C     LEAST SQUARE TECHNIQUE. REF. LEVENBERG,K.QUART. APPL.
C     MATH. VOL.2,NO.2, 164-68 AND MARQUARDT,D.W.,
C     J.SOC.INDUST.APPL. MATH. VOL.11,NO.2,JUNE,1963
C     P.431-441.
C
C     PROGRAMMED BY P.R.BISHNOI.
C
C
C     N IS NO. OF B.W.R. PARAMETERS I.E. 8
C     M1 IS NO. OF P-V-T DATA POINTS.
C     NCASE IS ZERO IF ONLY PVT DATA ARE TO BE TREATED.
C
C
C     NREL IS ONE IF SUM OF RELATIVE ERROR SQUARES IN
C     MINIMIZED.
C     NV IS ONE IF ALL THE EXPERIMENTAL ERRORS ARE
C     CONSIDERED TO BE IN VOLUME AND P AND T ARE ERROR
C     FREE.
C
C     NOUT IS ZERO IF INVERSE OF THE NORMAL EQUATIONS
C     MATRIX IS TO BE CHECKED AND INDENTITY MATRIX IS TO BE
C     PRINTED. NOUT IS ONE IF THIS CHECK AND PRINTING ARE
C     TO BE SUPRESSED.
C
C     NTIME ARE THE MAXIMUM NO. OF TRIALS TO BE TAKEN FOR
C     THE NLRLSTQ.
C
C     NCHOIS IS ZERO IF PROGRAMME IS TO BE RUN WITH
C     DECREASING VALUE OF LAMDA(I.E. W) WITHOUT CONSIDERING
C     WHETHER SUM OF ERROR SQUARES IS DECREASING OR NOT.
C     NCHOIS IS ONE IF LAMDA VALUES ARE TO BE CHOSEN BY THE
C     PROGRAMME LOGIC SO AS TO DECREASE THE SUM OF ERROR
C     SQUARES FOR EVERY SUBSEQUENT ITERATION.
C
C
C     SCALE(I) ARE THE FACTORS TO BE USED TO SCALE THE
C     B.W.R. PARAMETER
C     X(I) ARE THE B.W.R. PARAMETERS.
C
C     M2 ARE NO. OF CP DATA POINTS.
C
C     WC IS THE WEIGHTING FACTOR FOR SUM OF ERROR SQUARES
C     IN CP DEPARTURES. WC IS 1. IF ONLY THE SUM OF CP
```

```
C      DEPARTURES ERRORS IS TO BE MINIMIZED.
C
C      A2(I) ARE COEFFICIENTS OF THE IDEAL GAS HEAT CAPACITY
C      EQUATION .
C
C      IFLAG IS THE FLAG GENERATED. IT IS ZERO IF THE
C      OBJECTIVE FUNCTION CALCULATED FOR THE (R+1)TH
C      ITERATION IS LESS THAN THAT CALCULATED FOR THE RTH
C      ITERATION. OTHERWISE IT IS GREATER THAN 0.
C
C     ******************************************************

      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      COMMON/LSQ/G,F,PP,TT,VV,ZZ,DX,SERS,VVK
      COMMON/VOL/X,SCALE,R,T,P,V,Z
      COMMON/INT1/N,KOUNT
      COMMON/INT2/M1,NCASE,NREL,NOUT,IFLAG,NV,NCHOIS,M2
      COMMON/CP/PPC,TTC,RN,DR,CPD,FC,VVC,WC,CON
      DOUBLE PRECISION X(10),DX(10),Y(10),SCALE(10)
      DOUBLE PRECISION TAU,EPS,CONCRI
      DIMENSION G(8,400),F(400),PP(400),TT(400),VV(400)
     *,ZZ(400),VVK(400)
      DIMENSION PPC(200),TTC(200),RN(200),DR(200),CPD(200)
     *,FC(200),VVC(2
     100)
      DIMENSION CPDK(200),CP(200),A2(5)
      DIMENSION TITLE(2,8)
      DATA TITLE/'X1*E',' 00 ','X2*E','-04 ','X3*E','-09 '
     *,'X4*E',' 00 '
     1,'X5*E','-03 ','X6*E','-03 ','X7*E','-09 ','GAM*','E
     * 00'/
      EPS=1.0D-05
      TAU=1.0D-03
      ICONV=0
      IFLAG=0
      KOUNT=0
      R=10.7335
      CON=144.0/777.9
      READ(5,1)N,M1,NCASE,NTIME,NREL,NOUT,NV,NCHOIS
    1 FORMAT(8I4)
      READ(5,502)(X(I),I=1,N)
  502 FORMAT(D15.8)
      READ(5,502)(SCALE(I),I=1,N)
      NA=N-1
      AN=FLOAT(N)
      AM=FLOAT(M1)
      AMAN=AM-AN
      ZERS=0.
      IF(M1.EQ.0)GO TO 123
      DO 108 I=1,M1
```

```
C       MAIN                       ...(CONT'D)
      READ(5,101)PP(I),TT(I),VV(I)
      P=PP(I)
      T=TT(I)
      RT=R*T
      ZZ(I)=P*VV(I)/RT
  108 CONTINUE
  101 FORMAT(1H ,3F15.8)
  109 IF(KOUNT.GE.NTIME) GO TO 67
      IF(M1.EQ.0)GO TO 123
      DO 102 I=1,M1
      P=PP(I)
      T=TT(I)
      RT=T*R
      Z=ZZ(I)
      IF(NV.NE.1)V=VV(I)
      IF(NV.EQ.1)CALL VOLUM
      IF(NV.EQ.1)VVK(I)=V
      DE=1./V
      G(1,I)=DE*SCALE(1)
       G(2,I)=-DE/RT*SCALE(2)
      RTT=RT*T**2
      DD=DE**2
      G(3,I)=-DE/RTT*SCALE(3)
      G(4,I)=DD*SCALE(4)
      G(5,I)=-DD/RT*SCALE(5)
      G(6,I)=DD*DD*DE/RT*SCALE(6)
  102 CONTINUE
  500 IF(KOUNT.GE.NTIME)GO TO 67
      GAM=X(8)*SCALE(8)
      ZERS=0.
      DO 103 I=1,M1
      T=TT(I)
      IF(NV.NE.1)V=VV(I)
      IF(NV.EQ.1)V=VVK(I)
      P=PP(I)
      DE=1./V
      DD=DE**2
      EA=GAM*DD
      EX=DEXP(-EA)
      RTT=R*T**3
      G(7,I)=DD*(1.+EA)*EX/RTT*SCALE(7)
      IF(NV.EQ.1)GO TO 110
      ZK=1.0
      DO 104 J=1,NA
      ZK=ZK+G(J,I)*X(J)
  104 CONTINUE
      Z=ZZ(I)
      F(I)=Z-ZK
      IF(NREL.EQ.1)F(I)=F(I)/Z
      GO TO 111
```

```
      C       MAIN                  ...(CONT'D)
110 F(I)=1.-VVK(I)/VV(I)
111 ZERS=ZERS+F(I)**2
103 CONTINUE
    SERS=ZERS
115 FORMAT(1H ,3(F15.8,3X))
    IF(NCASE.EQ.0) GO TO 112
123 IF(KOUNT.GT.0) GO TO 117
    READ(5,113)M2
113 FORMAT(I4)
    AM2=FLOAT(M2)
    READ(5,503)WC
503 FORMAT(F15.8)
    READ(5,122)(A2(J),J=1,5)
122 FORMAT(5E15.7)
    DO 114 I=1,M2
    READ(5,115)PPC(I),TTC(I),CP(I)
    T=TTC(I)/1.8
    CPO=0.
    DO 121 J=1,5
    CPO=CPO+A2(J)*T**(J-1)
121 CONTINUE
    CPO=CPO*1.9871
    CPD(I)=CP(I)-CPO
114 CONTINUE
117 CPER=0.
    X1=X(1)*SCALE(1)
    X2=X(2)*SCALE(2)
    X3=X(3)*SCALE(3)
    X4=X(4)*SCALE(4)
    X5=X(5)*SCALE(5)
    X6=X(6)*SCALE(6)
    X7=X(7)*SCALE(7)
    X8=X(8)*SCALE(8)
    DO 116 I=1,M2
    P=PPC(I)
    T=TTC(I)
    CALL VOLUM
    VVC(I)=V
    DE=1./V
    DD=DE**2
    EA=X8*DD
    EX=DEXP(-EA)
    TTT=T**3
      CPDK(I)=6.*X3*DE/TTT-6.*X7/(X8*TTT)+(6./X8+3.*DD)*X7
   **EX/TTT-R
    RN(I)=R+X1*R*DE+X4*R*DD+2.*X3*DE/TTT-(1.+EA)*EX*2.*X7
   **DD/TTT
    DR(I)=R+DE*2.*(X1*R-X2/T-X3/TTT)+3.*DD*(X4*R-X5/T)+6.
   **X6*DD*DD*DE/
   1T+X7*DD*(3.+3.*EA-2.*EA**2)*EX/TTT
```

```
C       MAIN                  ...(CONT'D)
      CPDK(I)=(CPDK(I)+RN(I)**2/DR(I))*CON
      FC(I)=1.-CPDK(I)/CPD(I)
      CPER=CPER+FC(I)**2
  116 CONTINUE
      VARCP=CPER/AM2
      STERCP=DSQRT(VARCP)
      SERS=ZERS+WC*CPER
  112 CONTINUE
      IF(NCHOIS.EQ.0) GO TO 125
      IF(KOUNT.EQ.0)GO TO 106
      IF(SERS.LE.SZER)GO TO 125
      IFLAG=IFLAG+1
      DO 107 I=1,N
      X(I)=Y(I)
  107 CONTINUE
      GO TO 118
  125 IFLAG=0
  106 VAR=ZERS/AMAN
      STDERZ=DSQRT(VAR)
      WRITE(6,200)KOUNT
      WRITE(6,202)((TITLE(J,I),J=1,2),X(I),I=1,N)
      IF(M1.EQ.0)GO TO 124
      IF(NV.NE.1)WRITE(6,201)ZERS,VAR,STDERZ
      IF(NV.EQ.1)WRITE(6,203)ZERS,VAR,STDERZ
  200 FORMAT(1H-,10X,'AFTER TRIAL NO. ',I3,1X,'THE REFINED
     * APPROXIMATION
     1OF THE B.W.R. PARAMETERS IS --',/)
  201 FORMAT(1H-,10X,'SUM OF ERROR SQUARES IN Z = ',E15.8
     *,'VARIANCE = ',
     1E15.8,'STANDARD ERROR = ',E15.8)
  202 FORMAT(15X,2A4,5X,D15.8)
  203 FORMAT(1H-,10X,'SUM OF ERROR SQUARES IN V = ',E15.8,'
     * VARIANCE =
     1',E15.8,'  STANDARD ERROR = ',E15.8)
      IF(NCASE.EQ.0)GO TO 118
  124 WRITE(6,119)CPER,VARCP,STERCP
      WRITE(6,120)SERS
  119 FORMAT(1H-,10X,'SUM OF ERROR SQUARES IN CP DEPARTURES
     * = ',E15.8,'
     1 VARIANCE= ',E15.8,'  STANDARD ERROR = ',E15.8)
  120 FORMAT(1H-,10X,'THE COMBINED WEIGHTED SUM OF ERROR
     * SQUARES = ',E15
     1.8)
  118 IF(IFLAG.EQ.0.AND.ICONV.EQ.1) GO TO 67
      CALL NLRLST
      KOUNT=KOUNT+1
      DO 105 I=1,N
      Y(I)=X(I)
      X(I)=X(I)+DX(I)
  105 CONTINUE
```

```
C       MAIN                    ...(CONT'D)
      DO 126 I=1,N
      CONCRI=DABS(DX(I))/(TAU+DABS(Y(I)))
      IF(CONCRI.LT.EPS)GO TO 127
      ICONV=0
      GO TO 128
  127 ICONV=1
  126 CONTINUE
  128 CONTINUE
      IF(IFLAG.EQ.0)SZER=SERS+1.0E-08
      IF(NV.EQ.1)GO TO 109
      GO TO 500
   67 CONTINUE
      IF(ICONV.EQ.0)GO TO 1167
      WRITE(6,129)
  129 FORMAT(1H-,20X,'THE PROGRAMME CONVERGED. THE ABOVE
     * PARAMETERS ARE
     1OPTIMUM.')
      IF(M1.EQ.0)GO TO 130
      WRITE(6,131)
      WRITE(6,132)
      WRITE(6,133)
  131 FORMAT(1H1,20X,'P',16X,'T',16X,'V',16X,'Z',11X
     *,'ESTIMATED',10X,'RE
     1LATIVE')
  132 FORMAT(18X,'PSIA',26X,'CU.FT/MOLE',27X,'DEPENDENT',9X
     *,'ERROR')
  133 FORMAT(84X,'VARIABLE',//)
      DO 134 I=1,M1
      P=PP(I)
      T=TT(I)
      V=VV(I)
      Z=ZZ(I)
      IF(NV.EQ.1)GO TO 135
      ZK=1.
      DO 136 J=1,NA
      ZK=ZK+G(J,I)*X(J)
  136 CONTINUE
      DEPVAR=ZK
      GO TO 137
  135 DEPVAR=VVK(I)
  137 WRITE(6,138)P,T,V,Z,DEPVAR,F(I)
  134 CONTINUE
  138 FORMAT(12X,2(F15.2,2X),4(F15.8,2X))
  130 CONTINUE
      IF(NCASE.EQ.0)GO TO 1167
      WRITE(6,139)
      WRITE(6,140)
      WRITE(6,141)
  139 FORMAT(1H1,20X,'P',16X,'T',16X,'V',15X,'CP',12X,'CP
     * DEP.',11X,'EST
```

```
      C       MAIN                  ...(CONT'D)
     1IMATED',7X,'RELATIVE')
 140 FORMAT(20X,'PSIA',27X,'CU FT/MOLE',8X,'BTU/MOLE',9X
     *,'EXPTL.',9X,'C
     1P DEP.',13X,'ERROR')
 141 FORMAT(52X,'CAL.',11X,'DEG. R',//)
     DO 142 I=1,M2
     P=PPC(I)
     T=TTC(I)
     V=VVC(I)
     CPEX=CP(I)
     CPDEX=CPD(I)
     CPDCAL=CPDK(I)
     WRITE(6,143)P,T,V,CPEX,CPDEX,CPDCAL,FC(I)
 142 CONTINUE
 143 FORMAT(12X,2(F15.2,2X),5(F15.8,2X))
1167 CONTINUE
     STOP
     END
```

SUBROUTINE VOLUM

```
      SUBROUTINE VOLUM
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      COMMON/VOL/X,SCALE,R,T,P,V,Z
      DOUBLE PRECISION Y(10),X(10),SCALE(10)

C      NEWTON RAPHSON METHOD IS USED TO FIND THE ROOTS OF
C      B.W.R. EQUATION.
C      ONLY THE GAS PHASE VOLUME WILL BE DETERMINED.
C

      DO 110 I=1,8
  110 Y(I)=X(I)*SCALE(I)
      GAM=Y(8)
      RT=R*T
      TS=T**2
      V=RT/P
      DO 200 I=1,91
      DE=1./V
      DD=DE**2
      EA=GAM*DD
      EX=DEXP(-EA)
      PK=RT*DE+Y(1)*RT*DD-Y(2)*DD-Y(3)*DD/(T**2)+Y(4)*RT*DD
     **DE-Y(5)*DD*D
     1E+Y(6)*(DE**6)+Y(7)*DD*DE*(1.+EA)*EX/(T**2)
      FDE=(PK-P)/DE
      DFDE=P/DD+Y(1)*RT-Y(2)-Y(3)/TS+2.*Y(4)*RT*DE-2.*Y(5)
     **DE+5.*Y(6)*DD
     1**2+Y(7)*2.*DE*EX*(1.+EA-EA**2)/TS
      DFV=-DD*DFDE
      VVK=V-FDE/DFV
      ZK=P*VVK/RT
      ERROR=DABS(V-VVK)
      IF(ERROR-0.1E-05)100,100,101
  101 IF(I-90)102,103,103
  102 V=VVK
  200 CONTINUE
  100 V=VVK
      GO TO 104
  103 V=VVK
      WRITE(6,105)P,T,ERROR
  105 FORMAT(1X,'NEWTON-RAPHSON DID NOT CONVERGE FOR P = '
     *,F10.4,'AND FO
     1R T = ',F10.4,'ERROR AT THE LAST ITERATION = ',E10.4)
  104 RETURN
      END
```

SUBROUTINE NLRLS

```
      SUBROUTINE NLRLST
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      COMMON/LSQ/G,F,PP,TT,VV,ZZ,DX,ZERS,VVK
      COMMON/VOL/X,SCALE,R,T,P,V,Z
      COMMON/INT1/N,KOUNT
      COMMON/INT2/M1,NCASE,NREL,NOUT,IFLAG,NV,NCHOIS,M2
      COMMON/CP/PPC,TTC,RN,DR,CPD,FC,VVC,WC,CON
      COMMON/INV/S,Q
      COMMON/PAR/A,D,U
      DOUBLE PRECISION XTX,XTB,BTB,CGAM,ANGLE,CCGAM,ANGCRI
     *,FKR,BB
      DOUBLE PRECISION DAS(10),WS,SCALE(10)
      DOUBLE PRECISION A(10,10),B(10),X(10),D(10,10),U(10
     *,10),S(10,10),Q
     1(10,10),DX(10),W,FAC,WW,WWW,BMAX
      DIMENSION G(8,400),F(400),PP(400),TT(400),VV(400)
     *,ZZ(400),VVK(400)
      DIMENSION DH(10),DG(10)
      DIMENSION PPC(200),TTC(200),RN(200),DR(200),CPD(200)
     *,FC(200),VVC(2
     100)

C       THE SUBROUTINE EVALUATES THE INCREMENTS OF THE B.W.R.
C       PARAMETERS BY THE NON-LINEAR LEAST SQUARES TECHNIQUE.
C

      NA=N-1
      FAC=1.0D 06
      ANGCRI=45.
      IF(KOUNT.EQ.0)FKR=1.
      IF(IFLAG.GT.0.AND.IANG.GT.0) GO TO 116
      IF(IFLAG.GT.0)GO TO 98
      DO 25 I=1,N
      B(I)=0.
      DX(I)=0.
      DAS(I)=0.
      DO 26 J=1,N
      A(I,J)=0.
      D(I,J)=0.
      U(I,J)=0.
      S(I,J)=0.
      Q(I,J)=0.
   26 CONTINUE
   25 CONTINUE
      IF(M1.EQ.0)GO TO 92
      DO 40 I=1,M1
      IF(NV.EQ.1)GO TO 75
      DO 41 J=1,NA
      DH(J)=G(J,I)
      IF(NREL.EQ.1)DH(J)=DH(J)/ZZ(I)
```

SUBROUTINE NLRLST ...(CONT'D)

```
   41 CONTINUE
C      DH ARE DERIVATIVES OF THE APPROXIMATING FUNCTION FOR
C      Z WITH RESPECT TO THE B.W.R. PARAMETERS.
C

      V=VV(I)
      DE=1./V
      DD=DE**2
      EA=X(8)*DD*SCALE(8)
      EX=DEXP(-EA)
      T=TT(I)
      RTT=R*T**3
      DH(8)=-X(7)*X(8)*EX*DD**3/RTT*SCALE(7)*SCALE(8)
      IF(NREL.EQ.1)DH(8)=DH(8)/ZZ(I)
      GO TO 76
   75 CONTINUE
      P=PP(I)
      V=VV(I)
      T=TT(I)
      RT=R*T
      VK=VVK(I)
      DK=1./VK
      DD=DK**2
      DG(1)=G(1,I)/DK
      DG(2)=G(2,I)/DK
      DG(3)=G(3,I)/DK
      DG(4)=2.*DK*SCALE(4)
      DG(5)=2.*G(5,I)/DK
      DG(6)=5.*G(6,I)/DK
      RTT=RT*T**2
      EA=X(8)*DD*SCALE(8)
      EX=DEXP(-EA)
      DG(7)=2.*DK*EX*(1.+EA-EA**2)/RTT*SCALE(7)
C      DG ARE DERIVATIVES OF THE G TERMS OF B.W.R. EQUATION
C      WITH RESPECT TO THE DENSITY.
C

      SUM=0.
      DO 77 J=1,NA
      SUM=SUM+X(J)*DG(J)
   77 CONTINUE
      SUM=P/RT+SUM*DD
      DO 78 J=1,NA
      DH(J)=G(J,I)/SUM
   78 CONTINUE
      EXTRA=-X(7)*X(8)*EX*DD**3/RTT*SCALE(7)*SCALE(8)
      DH(8)=EXTRA/SUM
      DO 79 J=1,N
```

```
      DH(J)=DH(J)/VV(I)
   79 CONTINUE
   76 CONTINUE
      DO 42 J=1,N
      B(J)=B(J)+F(I)*DH(J)
   42 CONTINUE
      DO 43 K=1,N
      DO 44 L=1,N
      A(K,L)=A(K,L)+DH(K)*DH(L)
   44 CONTINUE
   43 CONTINUE
   40 CONTINUE
      IF(NCASE.EQ.0)GO TO 104
   92 X1=X(1)*SCALE(1)
      X2=X(2)*SCALE(2)
      X3=X(3)*SCALE(3)
      X4=X(4)*SCALE(4)
      X5=X(5)*SCALE(5)
      X6=X(6)*SCALE(6)
      X7=X(7)*SCALE(7)
      X8=X(8)*SCALE(8)
      DO 80 I=1,M2
      P=PPC(I)
      T=TTC(I)
      TTT=T**3
      V=VVC(I)
      DE=1./V
      DD=DE**2
      EA=X8*DD
      EX=DEXP(-EA)
      RATIO=RN(I)/DR(I)

C       DERIVATIVES OF V W.R. TO B.W.R. PARAMETERS IS
C       CALCULATED BELOW.
C

      RT=R*T
      RTT=RT*T**2
      G(1,I)=DE*SCALE(1)
       G(2,I)=-DE/RT*SCALE(2)
      G(3,I)=-DE/RTT*SCALE(3)
      G(4,I)=DD*SCALE(4)
      G(5,I)=-DD/RT*SCALE(5)
      G(6,I)=DD*DD*DE/RT*SCALE(6)
      G(7,I)=DD*(1.+EA)*EX/RTT*SCALE(7)
      DK=1./V
      DH(1)=G(1,I)/DK
      DH(2)=G(2,I)/DK
      DH(3)=G(3,I)/DK
      DH(4)=2.*DK*SCALE(4)
```

```
      DH(5)=2.*G(5,I)/DK
      DH(6)=5.*G(6,I)/DK
      DH(7)=2.*DK*EX*(1.+EA-EA**2)/RTT*SCALE(7)
      SUM=0.
      DO 105 J=1,NA
      SUM=SUM+X(J)*DH(J)
  105 CONTINUE
      SUM=P/RT+SUM*DD
      DO 106 J=1,NA
      DH(J)=G(J,I)/SUM
  106 CONTINUE
      EXTRA=-X(7)*X(8)*EX*DD**3/RTT*SCALE(7)*SCALE(8)
      DH(8)=EXTRA/SUM

C      DH(J) ARE DERIVATIVES OF VOLUME W.R. TO B.W.R.
C      PARAMETERS.
C

      DDR=2.*(X1*R-X2/T-X3/TTT)+6.*DE*(X4*R-X5/T)+30.*X6*DD
     **DD/T
      DDRR=6.+12.*X8*DD-12.*EA**2-2.*EA*(3.+3.*EA-2.*EA**2)
      DDR=DDR+EX*X7*DE*DDRR/TTT
      DNR=EA**2-1.-EA
      DNR=DNR*4.*X7*DE*EX/TTT
      DNR=DNR+X1*R+2.*X4*R*DE+2.*X3/TTT
      DHDE=6.*X3/TTT-6.*X7*DE*EX*(1.+EA)/TTT
      DHDE=DHDE-DDR*RATIO**2+2.*RATIO*DNR
      DHDE=-DD*DHDE

C       DHDE NOW IS DERIVATIVE OF THE APPROXIMATING FUNCTION
C       FOR CP DEPARTURE W.R. TO VOLUME.
C

      DG(1)=2.*R*DE*(1.-RATIO)*RATIO
      DG(2)=2.*DE*RATIO**2/T
      DG(3)=2.*DE*(3.+2.*RATIO+RATIO**2)/TTT
      DG(4)=R*DD*RATIO*(2.-RATIO*3.)
      DG(5)=3.*DD*RATIO**2/T
      DG(6)=-6.*DD*DD*DE*RATIO**2/T
      DG(7)=6./(X8*TTT)+3.*DD/TTT
      DG(7)=DG(7)-4.*RATIO*DD*(1.+EA)/TTT
      DG(7)=DG(7)-DD*RATIO**2*(3.+3.*EA-2.*EA**2)/TTT
      DG(7)=EX*DG(7)-6./(X8*TTT)
      DG(8)=-6./(X8**2)-6.*DD/X8-3.*DD*DD
      DG(8)=DG(8)+4.*RATIO*DD*DD*EA
      DG(8)=DG(8)-RATIO**2*DD*DD*EA*(2.*EA-7.)
      DG(8)=DG(8)*X7*EX/TTT+6.*X7/(TTT*X8**2)
      DO 81 J=1,N
      DG(J)=DG(J)+DHDE*DH(J)
      DG(J)=CON*DG(J)/CPD(I)
```

SUBROUTINE NLRLST ...(CONT'D)

```
   81 CONTINUE
      DO 82 J=1,N
      B(J)=B(J)+FC(I)*DG(J)*WC
   82 CONTINUE
      DO 83 K=1,N
      DO 84 L=1,N
      A(K,L)=A(K,L)+DG(K)*DG(L)*WC
   84 CONTINUE
   83 CONTINUE
   80 CONTINUE
  104 CONTINUE
C       MATRIX A WILL NOW BE NORMALISED.
C
      DO 85 I=1,N
      DAS(I)=DSQRT(A(I,I))
   85 CONTINUE
      DO 86 I=1,N
      DO 87 J=1,N
      WS=DAS(I)*DAS(J)
      IF(WS.GT.0.)GO TO 88
      A(I,J)=0.
      GO TO 87
   88 A(I,J)=A(I,J)/WS
   87 CONTINUE
      IF(DAS(I).GT.0.)GO TO 89
      B(I)=0.
      GO TO 86
   89 B(I)=B(I)/DAS(I)
   86 CONTINUE
   98 DO 93 I=1,N
      A(I,I)=1.
   93 CONTINUE
C       MATRIX A WILL NOW BE DAMPED.
C
      SUM=0.
      IF(KOUNT.EQ.0)GO TO 48
      IF(IFLAG.EQ.0)W=W/10.
      IF(IFLAG.GT.0)W=10.*W
      IF(W.LT.1.0D-52)W=1.0D-52
      GO TO 47
   48 DO 45 I=1,N
      SUM=SUM+B(I)**2
   45 CONTINUE
      W=SUM/(0.5*ZERS)
   47 WRITE(6,103)W
  103 FORMAT(1H ,40X,'THE VALUE OF W IS ',D15.8,/)
```

SUBROUTINE NLRLST ...(CONT'D)

```
      DO 46 I=1,N
      A(I,I)=A(I,I)+W
   46 CONTINUE
      WW=W
C       MATRIX A WILL NOW BE SCALED TO AVOID UNDERFLOWS.
C
      DO 2 I=1,N
      DO 1 J=1,N
      A(I,J)=A(I,J)*FAC
    1 CONTINUE
    2 CONTINUE
C       MATRIX A WILL NOW BE PARTITIONED.
C
      CALL PARTN
C       INVERSE OF THE LOWER AND UPPER DIAGONAL MATRICES WILL
C       BE DONE NOW
C
      CALL INVER
C       Q IS INVERSE OF THE LOWER DIAGONAL MATRIX
C       S IS INVERSE OF THE UPPER DIAGONAL MATRIX.
C
  100 FORMAT(1X,4(D15.8,4X))
      DO 70 I=1,N
      DO 69 J=1,N
      D(I,J)=0.
      DO 68 K=1,N
      D(I,J)=D(I,J)+S(I,K)*Q(K,J)*FAC
   68 CONTINUE
   69 CONTINUE
   70 CONTINUE
C       D IS INVERSE OF THE MATRIX A
C
C       CHECK OF THE INVERSION IS DONE AS FOLLOWS.
C
      IF(NOUT.EQ.1) GO TO 49
      DO 73 I=1,N
      DO 72 J=1,N
      U(I,J)=0.
      DO 71 K=1,N
      U(I,J)=U(I,J)+A(I,K)*D(K,J)/FAC
```

SUBROUTINE NLRLST ...(CONT'D)

```
   71 CONTINUE
   72 CONTINUE
   73 CONTINUE
      WRITE(6,102)KOUNT
  102 FORMAT(1H1,20X,'TRIAL NO. ',I3,//)
      WRITE(6,101)
  101 FORMAT(5X,'IDENTITY MATRIX IS',/)
      WRITE(6,100)((U(I,J),J=1,N),I=1,N)
      WRITE(6,504)
  504 FORMAT(1H-,10X,'INVERSE OF THE  DAMPED NORMAL
     * EQUATIONS MATRIX IS-
     1--',/)
      WRITE(6,100)((D(I,J),J=1,N),I=1,N)
C       NOW THE SOLUTION VECTOR IS CALCULATED.
C

   49 DO 91 I=1,N
      DX(I)=0.
      DO 90 J=1,N
      DX(I)=DX(I)+D(I,J)*B(J)
   90 CONTINUE
      DX(I)=DX(I)/DAS(I)
   91 CONTINUE
      DO 107 I=1,N
      DO 108 J=1,N
      A(I,J)=A(I,J)/FAC
  108 CONTINUE
  107 CONTINUE
      XTX=0.
      XTB=0.
      BTB=0.
      DO 109 I=1,N
      BB=DAS(I)*B(I)
      XTB=XTB+DX(I)*BB
      BTB=BTB+BB**2
      XTX=XTX+DX(I)**2
  109 CONTINUE
      CGAM=XTB/DSQRT(XTX*BTB)
      CCGAM=CGAM
      JGAM=1
      IF(CGAM.GT.0.) GO TO 110
      JGAM=2
      CGAM=DABS(CGAM)
  110 ANGLE=57.2957795*(1.5707288+CGAM*(-0.2121144+CGAM
     **(0.074261-CGAM*.
     *0187293)))*DSQRT(1.-CGAM)
      WRITE(6,111)CCGAM,ANGLE
  111 FORMAT(1H-,20X,'COSINE OF ANGLE GAMMA = ',D15.8,'  AND
     * ANGLE =',D1
```

SUBROUTINE NLRLST ...(CONT'D)

```
     15.8)
      GO TO (112,113),JGAM
  113 ANGLE=180.-ANGLE
  112 IF(ANGLE.GE.ANGCRI) GO TO 114
  116 IF(IFLAG.EQ.0)GO TO 114
      FKR=FKR/2.
      IANG=1
      GO TO 115
  114 IANG=0
      FKR=1.
C
C       IANG IS THE FLAG GENERATED. IANG IS ZERO IF ANGLE
C       GAMMA IS GREATE OR EQUAL TO THE CRITERION ANGLE. IANG
C       IS ONE IF THIS ANGLE IS LES THAN THE CRITERION ANGLE.
C
  115 DO 117 I=1,N
      DX(I)=DX(I)*FKR
  117 CONTINUE
      RETURN
      END
```

SUBROUTINE PARTN

```
      SUBROUTINE PARTN
      COMMON/INT1/N,KOUNT
      COMMON/PAR/A,D,U
      DOUBLE PRECISION A(10,10), D(10,10), U(10,10)
C     DETERMINATION OF L$U MATRICES
C

      INTEGER N
      DO 31 I=1,N
      DO 30 J=1,N
      D(I,J)=0.0
      U(I,J)=0.0
   30 CONTINUE
   31 CONTINUE
      D(1,1)=1.0
      U(1,1)=A(1,1)
      DO 32 J=2,N
      U(1,J)=A(1,J)
      D(J,1)=A(J,1)/U(1,1)
   32 CONTINUE
      DO 34 K=2,N
      KA=K-1
      KB=K+1
      DO 37 J=K,N
      U(K,J)=A(K,J)
      DO 36 I=1,KA
      U(K,J)=U(K,J)-D(K,I)*U(I,J)
   36 CONTINUE
   37 CONTINUE
      D(K,K)=1.0
      IF(KB-N)41,41,34
   41 DO 38 I=KB,N
      D(I,K)=A(I,K)
      DO 40 J=1,KA
      D(I,K)=D(I,K)-U(J,K)*D(I,J)
   40 CONTINUE
      D(I,K)=D(I,K)/U(K,K)
   38 CONTINUE
   34 CONTINUE
      RETURN
      END
```

SUBROUTINE INVER

```
      SUBROUTINE INVER
      COMMON/INT1/N,KOUNT
      COMMON/PAR/A,D,U
      COMMON/INV/P,Q
      DOUBLE PRECISION D(10,10), U(10,10), P(10,10), Q(10
     *,10),A(10,10)
      INTEGER N
C     INVERSION OF L-U MATRICES
C
      DO 46 I=1,N
      DO 45 J=1,N
      P(I,J)=0.0
      Q(I,J)=0.0
   45 CONTINUE
   46 CONTINUE
      DO 50 I=1,N
      P(I,I)=1.0/U(I,I)
   50 CONTINUE
      DO 52 J=2,N
      JA=J-1
      DO 54 K=1,JA
      I=J-K
      IA=I+1
      DO 56 IR=IA,J
      P(I,J)=P(I,J)+U(I,IR)*P(IR,J)
   56 CONTINUE
      P(I,J)=-P(I,J)/U(I,I)
   54 CONTINUE
   52 CONTINUE
      DO 60 I=1,N
      Q(I,I)=1.0/D(I,I)
   60 CONTINUE
      DO 66 I=2,N
      IA=I-1
      DO 64 K=1,IA
      J=I-K
      DO 62 IR=J,IA
      Q(I,J)=Q(I,J)+D(I,IR)*Q(IR,J)
   62 CONTINUE
      Q(I,J)=-Q(I,J)/D(I,I)
   64 CONTINUE
   66 CONTINUE
      RETURN
      END
```

4. PGM-4 -

This programme calculates the compressibility factors or the heat capacities of a pure component or binary mixtures and estimates the deviations of the calculated values from the experimental values. The r.m.s. (root mean square) percent deviation for a data set are also calculated. For the calculation of the mixture properties either the inter-action constants or the BWR mixing rules may be used.

The input information required by the programme is easily understood from the listing.

```
          C
C
C      COMPUTER PROGRAMME NO.      PGM-4
C
C      THIS PROGRAMME CALCULATES Z OR CP FOR A PURE
C      COMPONENT OR BINARY MIXTURES USING BWR EQUATION OF
C      STATE AND EITHER BWR MIXING RULES OR THE INTERACTION
C      CONSTANTS, AND EVALUATES DEVIATIONS BETWEEN THE
C      CALCULATED AND EXPERIMENTAL VALUES.
C
C      THE UNITS OF BWR COEFFICIENTS    PSI,CU.-FT.,LB-MOLE
C      ,DEG.R.
C
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER (I-N)
      COMMON/VOL/Y,R,T,P
      DIMENSION Y(10)
      DIMENSION A(5),A1(5),A2(5),Y1(8),Y2(8),X(8)
      N=8
      R=10.7335
      CON=144.0/777.9
      NA=5
      KOUNT=0
      SUMT=0.
      MS=0
      READ(5,101)MIX,MIXRUL,IPRPTY
  101 FORMAT(10I2)
C
C       MIX = 1 IF PURE, MIX=2 IF BINARY.
C       MIXRUL = 1 IF INTERACTION CONSTANTS USED.
C       MIXRUL = 2 IF BWR RULES OF MIXING USED.
C      IPRPTY =0 IF Z COMPARED.
C      IPRPTY = 1 IF CP COMPARED.
C       N IS NO. OF COEFFICIENTS IN B.W.R. EQN. = 8
C      M IS NO. OF DATA POINTS.
C      Y ARE NO. OF COEFFICIENTS OF BWR EQN.., Y(8)=GAMMA.
C
      IF(MIX.EQ.2)GO TO 204
      IF(IPRPTY.EQ.1)READ(5,103)(A(I),I=1,5)
      READ(5,100)(Y(I),I=1,8)
      IF(IPRPTY.EQ.1)WRITE(6,103)(A(I),I=1,5)
      WRITE(6,100)(Y(I),I=1,8)
  100 FORMAT(E15.8)
      GO TO 201
  204 CONTINUE
  103 FORMAT(5E15.7)
      IF(IPRPTY.EQ.1)READ(5,103)(A1(I),I=1,5)
      IF(IPRPTY.EQ.1)READ(5,103)(A2(I),I=1,5)
      READ(5,100)(Y1(I),I=1,8)
```

```
           C                                   ...(CONT'D)
      READ(5,100)(Y2(I),I=1,8)
      IF(IPRPTY.EQ.1)WRITE(6,103)(A1(I),I=1,5)
      IF(IPRPTY.EQ.1)WRITE(6,103)(A2(I),I=1,5)
      WRITE(6,103)(Y1(I),I=1,8)
      WRITE(6,103)(Y2(I),I=1,8)
      READ(5,101)NMIXTR
  501 READ(5,102)XFR
C
C       XFR IS MOLE FR. CH4
C

      KOUNT=KOUNT+1
      XXFR=1.-XFR
      WRITE(6,104)XFR
  104 FORMAT(1H1,20X,'MOLE FR. CH4 =',F10.4)
      IF(IPRPTY.EQ.0)GO TO 208
      DO 301 I=1,NA
      A(I)=XFR*A1(I)+XXFR*A2(I)
  301 CONTINUE
  208 CONTINUE
      IF(MIXRUL.EQ.2)GO TO 205
      IF(KOUNT.EQ.1)READ(5,100)(X(I),I=1,8)
      IF(KOUNT.EQ.1)WRITE(6,103)(X(I),I=1,8)
C
C        X ARE INTERACTION CONSTANTS.
C

      DO 300 I=1,N
      Y(I)=Y1(I)*XFR**2+2.*XFR*XXFR*X(I)+Y2(I)*XXFR**2
  300 CONTINUE
      GO TO 201
  205 CONTINUE
      DO 302 I=1,N
      Y(I)=0.
  302 CONTINUE
      Y(1)=Y1(1)*XFR+Y2(1)*XXFR
      Y(2)=(DSQRT(Y1(2))*XFR+DSQRT(Y2(2))*XXFR)**2
      Y(3)=(DSQRT(Y1(3))*XFR+DSQRT(Y2(3))*XXFR)**2
      Y(8)=(DSQRT(Y1(8))*XFR+DSQRT(Y2(8))*XXFR)**2
      Q=1./3.
      Y(4)=(XFR*Y1(4)**Q+XXFR*Y2(4)**Q)**3
      Y(5)=(XFR*Y1(5)**Q+XXFR*Y2(5)**Q)**3
      Y(7)=(XFR*Y1(7)**Q+XXFR*Y2(7)**Q)**3
      ALPH1=Y1(6)/Y1(2)
      ALPH2=Y2(6)/Y2(2)
      ALPH=(XFR*ALPH1**Q+XXFR*ALPH2**Q)**3
      Y(6)=Y(2)*ALPH
  201 CONTINUE
      SUM=0.
      M=0
```

```
      C                                   ...(CONT'D)
 500  IF(IPRPTY.EQ.0)READ(5,102)P,T,V
      IF(IPRPTY.GT.0)READ(5,105)P,T,CPEX
 102  FORMAT(1H ,3F15.8)
      IF(P-0.)67,67,68
  68  RT=R*T
      M=M+1
      IF(IPRPTY.GT.0)GO TO 206
      Z=P*V/RT
      CALL VOLUM(VK)
      ZK=P*VK/RT
      RDEVZ=(Z-ZK)/Z
      SUM=SUM+RDEVZ**2
      WRITE(6,200)P,T,Z,ZK,RDEVZ
 200  FORMAT(5X,2(F15.2,5X),3(F15.8,5X))
      GO TO 500
 206  CONTINUE
      T=T/1.8
      CPO=0.
      DO 303 J=1,5
      CPO=CPO+A(J)*T**(J-1)
 303  CONTINUE
      CPO=CPO*1.9871
      T=T*1.8
      X1=Y(1)
      X2=Y(2)
      X3=Y(3)
      X4=Y(4)
      X5=Y(5)
      X6=Y(6)
      X7=Y(7)
      X8=Y(8)
      CALL VOLUM(V)
      DE=1./V
      DD=DE**2
      EA=X8*DD
      EX=DEXP(-EA)
      TTT=T**3
 105  FORMAT(3F15.8)
           CPDK=6.*X3*DE/TTT-6.*X7/(X8*TTT)+(6./X8+3.*DD)*X7
     **EX/TTT-R
      RNNNN=R+X1*R*DE+X4*R*DD+2.*X3*DE/TTT-(1.+EA)*EX*2.*X7
     **DD/TTT
      DRRRR=R+DE*2.*(X1*R-X2/T-X3/TTT)+3.*DD*(X4*R-X5/T)+6.
     **X6*DD*DD*DE/
     1T+X7*DD*(3.+3.*EA-2.*EA**2)*EX/TTT
         CPDK=(CPDK    +RNNNN**2/DRRRR)*CON
      CPK=CPDK+CPO
      RDEVCP=1.-CPK/CPEX
      SUM=SUM+RDEVCP**2
      WRITE(6,200)P,T,CPEX,CPK,RDEVCP
```

```
      C                                ...(CONT'D)
      GO TO 500
   67 CONTINUE
      AN=FLOAT(N)
      AM=FLOAT(M)
      VAR=SUM/(AM-AN)
      RMSPE=DSQRT(VAR)*100.
      WRITE(6,202)RMSPE
  202 FORMAT(1H-,20X,'RMS PERC ERROR =',E15.8)
      MS=MS+M
      SUMT=SUMT+SUM
      IF(MIX.EQ.1)GO TO 69
      IF(KOUNT.EQ.NMIXTR)GO TO 69
      GO TO 501
   69 CONTINUE
      AMS=FLOAT(MS)
      VAR=SUMT/AMS
      RMSPE=DSQRT(VAR)*100.
      WRITE(6,202)RMSPE
      STOP
      END
```

SUBROUTINE VOLUM

```
      SUBROUTINE VOLUM(V)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      COMMON/VOL/Y,R,T,P
      DIMENSION Y(10)
C       NEWTON RAPHSON METHOD IS USED TO FIND THE ROOTS OF
C       B.W.R. EQUATION
C       ONLY THE GAS PHASE VOLUME WILL BE DETERMINED.
C

      GAM=Y(8)
      RT=R*T
      TS=T**2
      V=RT/P
      DO 200 I=1,91
      DE=1./V
      DD=DE**2
      EA=GAM*DD
      EX=DEXP(-EA)
      PK=RT*DE+Y(1)*RT*DD-Y(2)*DD-Y(3)*DD/(T**2)+Y(4)*RT*DD
     **DE-Y(5)*DD*D
     1E+Y(6)*(DE**6)+Y(7)*DD*DE*(1.+EA)*EX/(T**2)
      FDE=(PK-P)/DE
      DFDE=P/DD+Y(1)*RT-Y(2)-Y(3)/TS+2.*Y(4)*RT*DE-2.*Y(5)
     **DE+5.*Y(6)*DD
     1**2+Y(7)*2.*DE*EX*(1.+EA-EA**2)/TS
      DFV=-DD*DFDE
      VVK=V-FDE/DFV
      ZK=P*VVK/RT
      ERROR=DABS(V-VVK)
      IF(ERROR-0.1E-05)100,100,101
  101 IF(I-90)102,103,103
  102 V=VVK
  200 CONTINUE
  100 V=VVK
      GO TO 104
  103 V=VVK
      WRITE(6,105)P,T,ERROR
  105 FORMAT(1X,'NEWTON-RAPHSON DID NOT CONVERGE FOR P = '
     *,F10.4,'AND FO
     1R T = ',F10.4,'ERROR AT THE LAST ITERATION = ',E10.4)
  104 RETURN
      END
```