NAME OF AUTHOR/*NOM DE L'AUTEUR* HENG-JOO NG

TITLE OF THESIS/*TITRE DE LA THÈSE* THE MEASUREMENT AND PREDICTION OF THE

EFFECT OF PRESSURE ON ENTHALPY

UNIVERSITY/*UNIVERSITÉ* UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED/
*GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE* Ph.D.

YEAR THIS DEGREE CONFERRED/*ANNÉE D'OBTENTION DE CE GRADE* 1975

NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* DR. A. E. MATHER

DATED/*DATÉ* 29/9/75 SIGNED/*SIGNÉ* Ng Heng Joo

PERMANENT ADDRESS/*RÉSIDENCE FIXE* @ 7, JALAN A. GHANI, LABIS, JOHORE,

MALAYSIA

THE UNIVERSITY OF ALBERTA

THE MEASUREMENT AND PREDICTION OF

THE EFFECT OF PRESSURE ON ENTHALPY

by

© HENG-JOO NG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA

SPRING, 1975

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "THE MEASUREMENT AND PREDICTION OF THE EFFECT OF PRESSURE ON ENTHALPY" submitted by HENG-JOO NG in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

.......................................
(Supervisor)

.......................................
(External Examiner)

.......................................

.......................................

.......................................

.......................................

Date ...21 April 1975...

TO MY FATHER

iv

## ABSTRACT

Accurate enthalpies of fluid mixtures over wide range of pressure and temperature are directly useful in design and provide an improved basis for the theories of fluids, improvement of methods of prediction, and for derivation of other thermodynamic properties. The purposes of this work are:

1) To construct a calorimeter for the existing recycle system to allow measurements on the isothermal effect of pressure on enthalpy.

2) To obtain accurate data on the effect of pressure on enthalpy for mixtures of methane with carbon dioxide, with carbon dioxide and nitrogen, with carbon dioxide and ethane, and with carbon dioxide, nitrogen and ethane.

3) To evaluate the available methods of prediction and to extend and improve the methods of prediction for the enthalpy of fluid mixtures.

An isothermal throttling calorimeter was chosen for measuring the effect of pressure on enthalpy. In common with several other throttling calorimeters, a capillary tube is used to cause the pressure drop. An insulated Nichrome wire which passes inside the capillary for its entire length serves to supply electrical energy. This arrangement makes the expansion essentially isothermal. The pressure drop across the calorimeter is measured by a differential pressure transducer and any temperature difference between the inlet and outlet is indicated by a calibrated thermopile.

Measurements were made with nitrogen as a test gas at four different temperatures from 273.15 to 374.15 K, and at pressures from 14 to 140 bar. The data are in good agreement with values from the literature. Measurements were made on the following six systems at pressures

from 14 to 140 bar: a) 14.5 mole percent of methane in carbon dioxide at temperatures of 0, 10, 20, 40, 60 and 90°C; b) 42.3 mole percent of methane in carbon dioxide at temperatures of 0, 40, 60 and 90°C, c) Equimolal mixture of methane, nitrogen and carbon dioxide at temperatures of -30, -10 and 10°C, d) Equimolal mixture of methane, carbon dioxide and ethane at temperatures of -10, 0, 20, 40, 60 and 90°C, e) methane rich mixture with carbon dioxide and ethane at temperatures of -10, 0, 20, 40, 60 and 90°C and, f) Equimolal mixture of methane, carbon dioxide, nitrogen, and ethane at temperatures of -30, -10, 10, 30 and 60°C.

Two enthalpy tables and diagrams for the two mixtures of methane and carbon dioxide were constructed which are based on this experimental work and that of B shnoi.

The availability of more accurate enthalpy data based on calorimetric determinations provides an improved basis for comparison of available methods of prediction and the testing of the mixing rules. Nine enthalpy correlations were evaluated and compared. Three of the correlations used equations of state and six of the correlations used the corresponding states method of Curl and Pitzer with six different mixing rules. The six different mixing rules are: 1) Method of Barner and Quinlan, 2) Proposed Method, 3) Modified Method of Gunn, 4) Method of Prausnitz and Gunn, 5) Method of Joffe-Stewart, Burkhardt and Voo, and 6) Method of Leland and Mueller. The three equations of state are Starling-BWR, Soave-Redlich-Kwong and Mark V correlation. It was found that the equation of state of Starling-BWR, Soave-Redlich-Kwong, Mark V and the corresponding states correlation with pseudocritical parameters estimated by method 2, are the most accurate of the nine enthalpy correlations tested.

# ACKNOWLEDGEMENTS

The author wishes to express his appreciation for the assistance of many people during the course of this research:

To Professor A.E. Mather for his advice and encouragement during the supervision of the work.

To Professor D.B. Robinson who was closely involved with this research, for his help, encouragement and serving on the doctoral committee.

To Professors F.D. Otto, G.S.H. Lock and S.E. Wanke for serving on the doctoral committee.

To J.I. Lee for many helpful discussions.

To members of the Workshop and Instrument shop, who made services whenever they were needed.

To Mrs. Kathie Therrien for typing the manuscript.

The author is also indebted to the following organizations:

To The Province of Alberta for a scholarship.

To The National Research Council of Canada for the scholarship and the financial support.

Finally, I would like to thank my parents for all they have given me.

# TABLE OF CONTENTS

# LIST OF FIGURES

x

# LIST OF TABLES

A knowledge of the enthalpies of fluid mixtures over a wide range of pressure and temperature is necessary for engineering designs and calculations of thermal processes. In the past, enthalpies used in process design were obtained principally from P-V-T data, either directly using thermodynamic relations or indirectly using equations of state. The process of generating enthalpies from compressibility data involves differentiation with attendant loss in accuracy of at least one order of magnitude. In a region where the derivatives are changing rapidly, such as the critical region, the error may be very large. In addition, accurate volumetric data for mixtures is still rather scarce, and the determination of enthalpy changes across the two-phase region involves the use of not only volumetric data and their derivatives, but also vapor-liquid equilibrium data and derivatives. For this reason it is desirable to have direct experimental determinations of the enthalpy behavior of fluid mixtures under pressure. These data are quite scarce in the literature.

The goal of this work was to construct a flow type calorimeter in a recycle system for the measurement of the isothermal effect of pressure on enthalpy. The isobaric effect of temperature on two binary mixtures of carbon dioxide and methane had been investigated by Bishnoi [9]. A specific purpose of the research has been to measure the isothermal effect of pressure on enthalpy of these two mixtures, so that it provides a thermodynamic consistency check and allows the construction of enthalpy tables for these two mixtures based on experimental data. In addition, experimental data of the isothermal effect of pressure on enthalpy were obtained for the following four systems: a) Equimolal carbon

dioxide-methane-nitrogen, (b) Equimolal carbon dioxide-methane-ethane, (c) methane-rich carbon dioxide-methane-ethane and (d) Equimolal carbon dioxide-methane-nitrogen-ethane.

There are many different methods of prediction which have been proposed for enthalpies of fluid mixtures. A comparative study has been made by Natural Gas Processors Association[79] on these numerous enthalpy correlations. The availability of more accurate enthalpy data based on calorimetric determinations provides an improved basis for comparison of available methods prediction and the testing of the mixing rules.

To reiterate, the specific goals of the present research were (1) to construct a calorimeter for obtaining the isothermal effect of pressure on enthalpy, (2) to make experimental enthalpy determinations on two carbon dioxide-methane mixtures, one carbon dioxide-methane-nitrogen mixture, two carbon dioxide-methane-ethane mixtures and one carbon dioxide-methane-nitrogen-ethane mixture, (3) to evaluate the available methods of prediction and (4) to extend and improve the method of prediction for the enthalpy of fluid mixtures.

*SECTION I*     *ELEMENTARY CONSIDERATIONS*

In this section, a discussion of flow calorimetry and the necessary equations for $\phi$ are applied, and a discussion of $\phi$ data in the literature are presented.

## *Flow Calorimeters*

Measurements of the enthalpy of fluids at elevated pressures have been made by a number of methods. A review of experimental methods was presented by Barieau [4]. Flow calorimeters have many advantages and have been used widely. The calorimeter may be designed to operate in a number of differing 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

$$[\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1}]_x = \frac{Q - \dot{W}}{F} \tag{1}$$

where $Q$ is the rate of the heat transfer, $\dot{W}$ the rate of electrical energy transfer, and $F$ is the mass flow rate. In the isobaric mode of operation, the pressure difference $P_2-P_1$ is made small and the fluid is heated to change its temperature. Equation (1) becomes:

$$[\underline{H}_{T_2} - \underline{H}_{T_1}]_{P_1, x} = -\frac{\dot{W}}{F} - \int_{P_1}^{P_2} (\frac{\partial \underline{H}}{\partial P})_T \, dP \Big|_{T_1} \tag{2}$$

where the integral term is a small correction for the fact that the pressure is not constant, and $Q$ is assumed to be negligible.

In the isenthalpic mode, no energy is added to the system and the heat leak is made negligible. For this case Equation (1) reduces to

$$[\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1}]_x = 0 \tag{3}$$

In the isothermal mode of operation, a pressure drop is imposed on the fluid, and energy is added so that the outlet temperature is equal to the inlet temperature. It is practical to utilize this scheme only when the Joule-Thomson coefficient is positive, i.e. when the fluid cools upon expansion. For an isothermal operation, Equation (1) becomes:

$$[H_{P_2} - H_{P_1}]_{T_1} x = -\frac{\dot{W}}{F} - \int_{T_1}^{T_2} C_P \, dT \Big|_{P_2} \tag{4}$$

where $\dot{Q}$ is assumed negligible and the integral corrects for any mismatch between the inlet and outlet temperatures. In this operation, a knowledge of the flow rate, the energy input and pressure drop are needed to determine the isothermal effect of pressure on enthalpy.

The enthalpy change on mixing can be determined in a flow calorimeter by mixing two pure gases in a chamber and adding electrical energy to equalize the inlet and outlet temperatures. The first law of thermodynamics for this calorimeter reduces to:

$$[H_{mix}]_{T_2,P_2} - [x_1 H_1 + x_2 H_2]_{T_1,P_1} = \frac{\dot{Q} - \dot{W}}{F} \tag{5}$$

Corrections can be made for the differences in pressure and temperature between the inlet and outlet. The excess enthalpy or heat of mixing can be determined by:

$$H^E = [H_{mix} - x_1 H_1 - x_2 H_2]_{P,T} \tag{6}$$

### Thermodynamic Relations

The relations presented above involve integral changes in enthalpy. These integral data in a single phase region may be interpreted to yield the derivative properties. Point values of the isothermal

throttling coefficient $\phi$ are estimated from the integral values by application of the following relation from Equation (4),

$$\phi \equiv \left(\frac{\partial H}{\partial P}\right)_{T,x} = \lim_{P_2 \to P_1} \left[\frac{H_{P_2} - H_{P_1}}{P_2 - P_1}\right]_{T,x} \tag{7}$$

The isothermal throttling coefficient can be estimated from known values of other thermodynamic properties. Thus, in making use of P-$\underline{V}$-T data the following identity applies:

$$\phi = \underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P \tag{8}$$

The identity involving $\mu$, the Joule-Thomson coefficient and $C_P$, the isobaric heat capacity, provides another method of calculating $\phi$. The functional relations between the enthalpy, the pressure and the temperature are:

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P$$

or

$$\phi = -\mu \, C_P \tag{9}$$

The virial equation of state is a power series in density:

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \ldots \tag{10}$$

The terms B, C, ... are known as the second, third, ... virial coefficients and they are related by the statistical theory of imperfect gases to the interactions of molecules in pairs, triplets, etc.

A similar power series is an expansion in pressure:

$$\frac{PV}{RT} = 1 + B'P + C'P^2 + \ldots \tag{11}$$

The coefficients of the two series are related by

$$B' = \frac{B}{RT}$$

$$C' = \frac{(C - B^2)}{(RT)^2} \tag{12}$$

Using Equation (8), (10), (11) and (12), $\phi$ can be expressed as:

$$\phi = -RT^2 \left[\frac{dB'}{dT} + P\frac{dC'}{dT} + \ldots\right]$$

or

$$\phi = \left(B - T\frac{dB}{dT}\right)\left(1 - \frac{2B}{RT}P + \frac{6B^2}{(RT)^2}P^2\right) + \frac{1}{RT}\left(2C - T\frac{dC}{dT}\right)P + \ldots \tag{13}$$

The zero-pressure value of the isothermal throttling coefficient is finite and depends only on B:

$$\phi^\circ = B - T\left(\frac{dB}{dT}\right) \tag{14}$$

Experimental values of $\phi^\circ$ can be used to derive changes in B upon integration of Equation (14):

$$B_{T_2} = T_2\left[\int_{\tau_1}^{\tau_2} \phi^\circ(\tau)d\tau + B_{T_1}\tau_1\right] \tag{15}$$

where $\tau = 1/T$. Experimental values of $\phi^\circ$ can be compared with values of $\phi^\circ$ calculated from virial coefficients obtained from other type of experiments. For mixtures, B is of the form:

$$B_{mix} = \sum_i \sum_j x_i x_j B_{ij} \tag{16}$$

where $B_{ii}$ and $B_{jj}$ are the pure component second virial coefficients and $B_{ij}$ is the interaction second virial coefficient. It follows that the derivative of $B_{mix}$ is:

$$\frac{dB_{mix}}{dT} = \sum_i \sum_j x_i x_j \left(\frac{dB_{ij}}{dT}\right) \tag{17}$$

*Previous Experimental Data for* $\phi$

All of the above methods have been used to obtain thermal data of fluids at elevated pressures. Most of the results have been for pure components. A recent review of available pure components and mixtures data at elevated pressures have been presented by Mather [57] and Yesavage [97]. Table I presents a listing of the experimental determinations of thermal properties under pressure by isothermal calorimeter, supplementing that of Mather [57]. Although an increased amount of enthalpy data are available, the need for more data to test methods of prediction and improve correlations remains.

TABLE I

Recent References to Isothermal Effect of

Pressure on Enthalpy of Fluid Under Pressure

| Year | System | Author | References |
|------|--------|--------|------------|
| 1967 | Nitrogen | | |
| | Propane-methane | Mather et al. | 57, 58, 59 |
| 1968 | Propane | | |
| | Propane-methane | Yesavage et al. | 97, 98, 99, 100 |
| 1968 | Methane-propane | Dillard et al. | 22 |
| 1969,70 | Carbon dioxide | Vukalovich et al. | 86, 87, 88 |
| 1970 | Methane-ethane | AlKasab | 2 |
| 1970 | Methane-ethane-propane | Furtado et al. | 26 |
| 1972 | Carbon dioxide-nitrogen | Vukalovich et al. | 89 |
| 1973 | Ethane | Miyazaki | 61a |
| 1974 | Methane-carbon dioxide | | |
| | Methane-carbon dioxide-ethane | | |
| | Carbon dioxide | Peterson & Wilson | 68 |

## SECTION II - THE CALORIMETER AND THE FLOW SYSTEM

A review of the previous work employing isothermal throttling calorimeters is presented here. The design of a new throttling calorimeter and the experimental equipment are discussed in this section.

### Background on Isothermal Throttling Calorimetry

All methods for measuring the isothermal effect of pressure on enthalpy involve some device to cause the pressure drop and a source of energy to compensate for the cooling effect resulting from the pressure drop. So, the methods are suitable only when $\phi$ is negative and no isothermal calorimeters have been designed to extract energy if the fluid warms on expansion.

A review of the development in isothermal throttling calorimetry had been presented by Mather [57]. In general, a porous media, a needle valve or a capillary tube is used to cause the pressure drop, and the electric heating coil is used as a source of energy.

The calorimeter designed by Mather [57] consists of a capillary coil to cause the pressure drop and the insulated heating wire is placed inside the capillary. Measurements were made on nitrogen and a mixture of propane and methane in the temperature range from -140°F to 200°F and in the pressure range from 100 to 2000 psia. Yesavage [97] used the same equipment to make measurements on propane and propane-methane mixtures.

Vukalovich et al. [86,87] reported the measurements on carbon dioxide by using adjustable needle valve with pressure drop up to 50 atm. Later on, Vukalovich et al. [88] designed a different type of calorimeter in which the throttling unit is pressure-relieved. Again the adjustable needle valve was used as the throttling unit.

Alkasab [1] designed an adjustable needle valve to study the isothermal throttling effect of methane-ethane mixtures.

Peterson and Wilson [68] constructed an integral isothermal throttling calorimeter by using throttling valve to cause the pressure drop. Measurements were made on pure carbon dioxide, and mixtures of equimolal methane-carbon dioxide, equimolal methane-ethane-carbon dioxide.

Eakin and DeVaney [25] designed a calorimeter which permits measurement of the Joule-Thomson coefficient, the isothermal enthalpy change on throttling and the isobaric enthalpy change. The idea of tubing packed with powder was used to cause the pressure drop. This idea was first used for Joule-Thomson experiments by Dawe and Snowdon [21].

## Design of Isothermal Throttling Calorimeter

The first requirement in the design of the calorimeter was that it should operate over a wide range of temperatures from -100°C to 200°C and at any pressure in this temperature range from 100 to 2000 psia. Stainless steel was selected as the material of construction because of anticipated subsequent experimental work with corrosive gases and its strength at low temperature.

Since the design was to allow for the possibility of measuring isothermal enthalpy changes across a two-phase region, the use of throttling valve was abandoned because the instability of two-phase flow through a valve caused by alternate slugs of liquid and vapor prevents accurate thermodynamic measurements.

A capillary was considered to be the best configuration for the throttle because the expansion is smooth and if energy is added to the fluid during expansion, the process will be almost isothermal. Since

enthalpy is a point function, it is not necessary for the expansion to isothermal. However, by making the path as nearly isothermal as possible, heat leakage from the surroundings to the system is minimized.

The disadvantage of capillary throttle is that it is not possible to vary flow rate and pressure drop independently. The disadvantage can be overcome by making the capillary removable so that various combinations of pressure drop and flow rate may be obtained.

The heater of the present calorimeter is an insulated Nichrome wire which passes inside the capillary for its entire length. Two copper power leads are connected to the heater wire at the ends of the capillary. In order to minimize the power losses through the leads the current must be kept low. The combination of heater size and capillary size allows different pressure drop and power input relations. With this arrangement, currents were kept below two amperes.

## Description of the Calorimeter

The isothermal throttling calorimeter of this work is shown in Figure 1. The fluid enters the vacuum jacket from the constant temperature bath. The pressure tap at the inlet portion of the calorimeter serves to measure the inlet pressure and a differential thermocouple is used to check the temperature between the inlet portion of the calorimeter and the bath. Then the fluid passes through the throttling portion. A removable capillary coil at the throttling portion causes the pressure drop. The outlet temperature of the fluid is brought back to the inlet temperature by applying power to the Nichrome wire, which is placed inside the capillary. In this work, three different capillary sizes are employed of 15 BWG, 16 BWG and 17 BWG hypodermic tubing, all about ten feet in

12
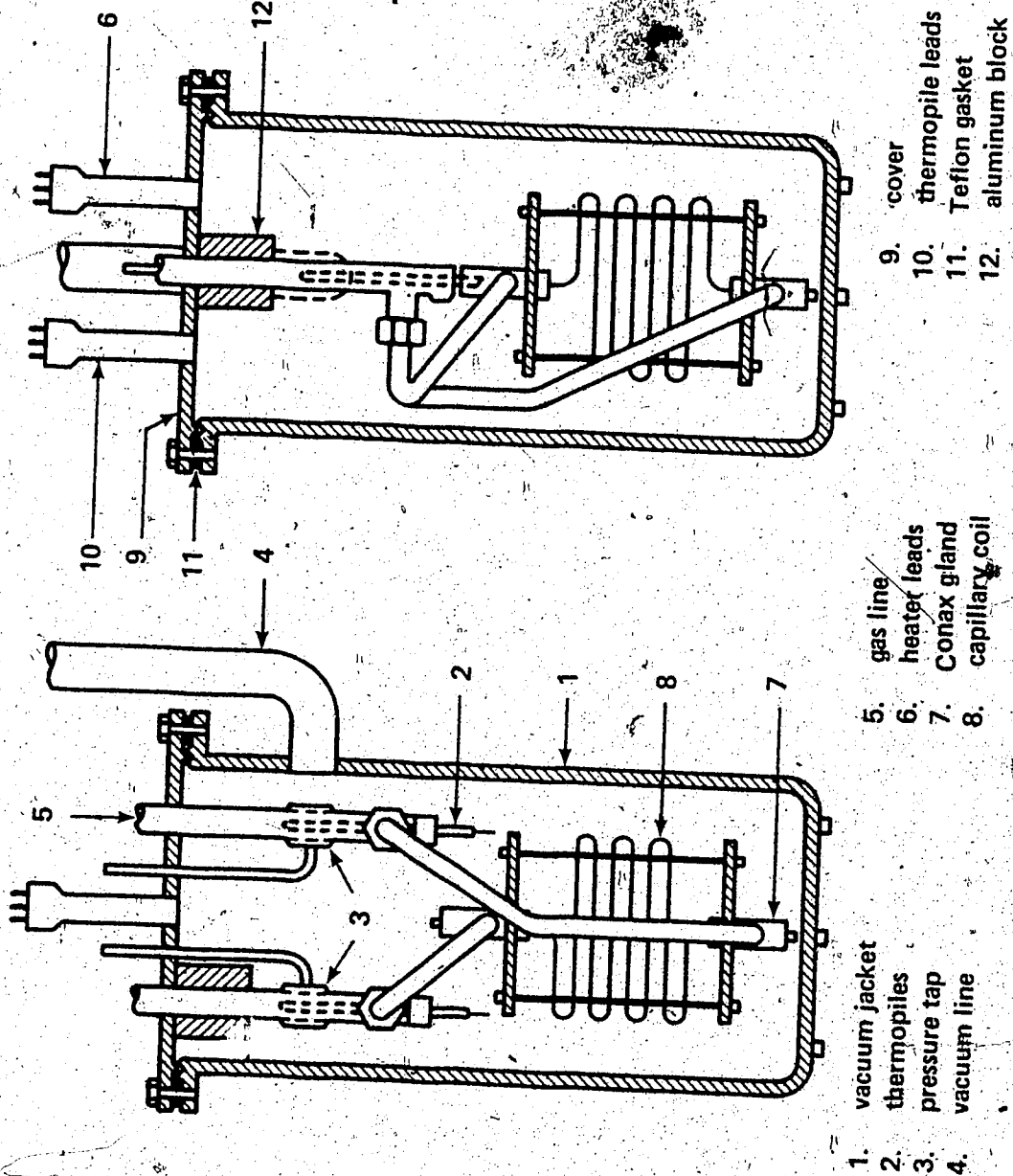


FIGURE 1. Assembly Drawing for Isothermal Throttling Calorimeter

1. vacuum jacket
2. thermopiles
3. pressure tap
4. vacuum line

5. gas line
6. heater leads
7. Conax gland
8. capillary coil

9. cover
10. thermopile leads
11. Teflon gasket
12. aluminum block

length. Two different sizes of Nichrome wire, 36 and 40 gauge, are used. A five junction differential thermopile is used to determine the equality of inlet and outlet temperature. The pressure drop is determined by the differential pressure transducer. As shown in Figure 1, all the pressure and temperature measurements are at the same elevation. The lead wires of the heater and the thermopile are wrapped around a massive aluminum thermal equalization block. The heater wire leads are brought from the vacuum jacket into both ends of the capillary by Conax connectors. The detail drawing of this portion is shown in Figure 2.

Other efforts were made to reduce heat transfer to the surroundings. A radiation shield completely enclosed the capillary coil. The power leads and thermopile leads are brought into contact with the vacuum jacket. The entire jacket is evacuated to less than five microns through the vacuum line.

## Experimental Equipment

The calorimeter is part of a recycle system, the evolution of which can be traced in the thesis of Bishnoi [9]. The recycle system serves to bring the fluid under investigation to the desired conditions of pressure and temperature for measurements. A schematic diagram of the flow system is shown in Figure 3. The fluid delivered by the compressor goes to the high pressure storage tanks, one of which is connected to the low pressure surge tank through the by-pass control valve BPCV. The fluid leaving the surge tanks goes to a hand valve and the high pressure control valve HPCV. The fluid passes through a long cooling coil before it enters the calorimeter. The cooling coil and the calorimeter are in the same bath. The pressure at the inlet of the calorimeter is governed
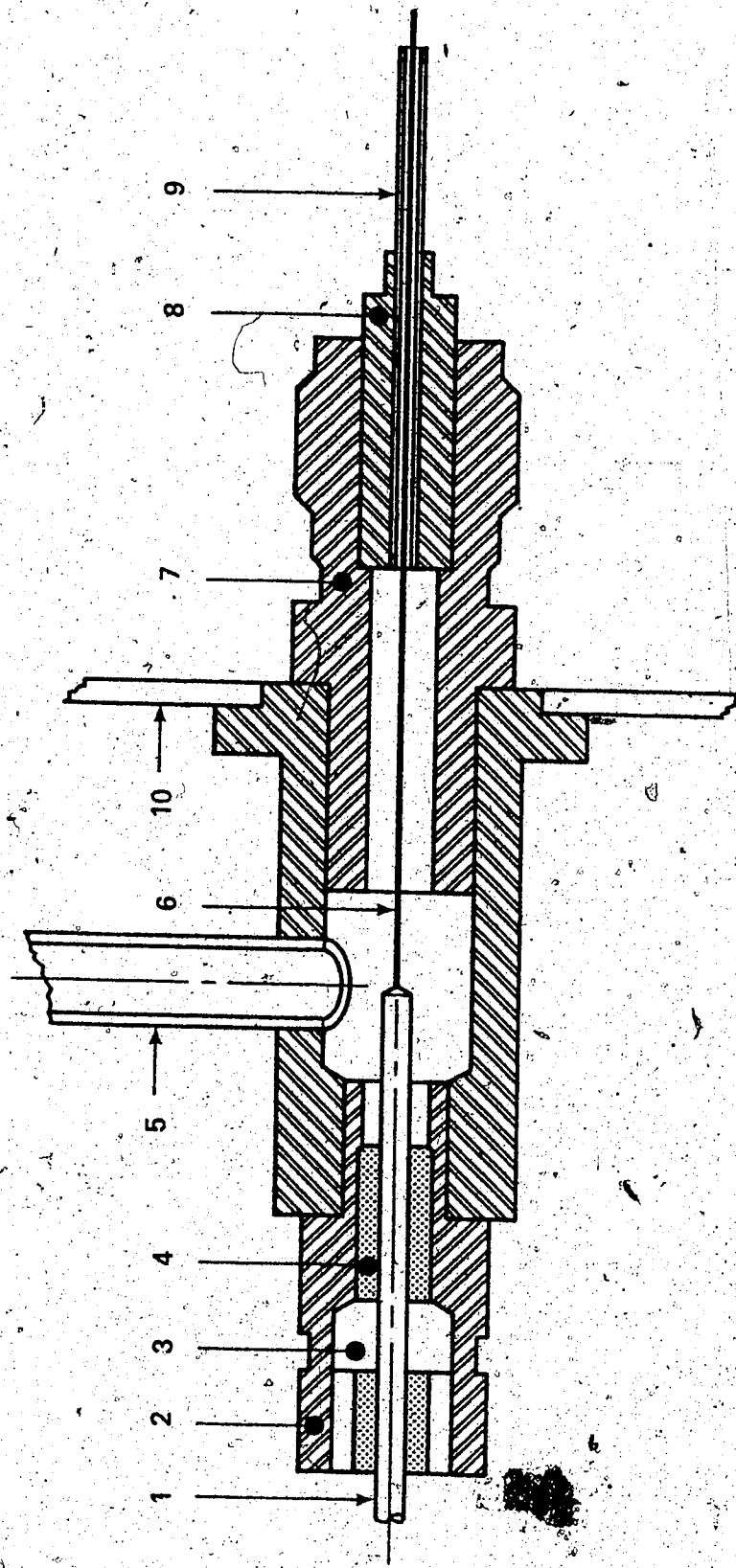
1. 16 gauge copper wire
2. Conax connector
3. Teflon sealant
4. ceramic insulators
5. ¼" O.D. S.S. tube

6. glass fabric insulated Nichrome wire
7. ¼" Swagelok connector
8. S.S. adapter
9. 17 gauge S.S. capillary tube
10. end plate

FIGURE 2. Detail Drawing for the Ends of the Capillary of the Calorimeter
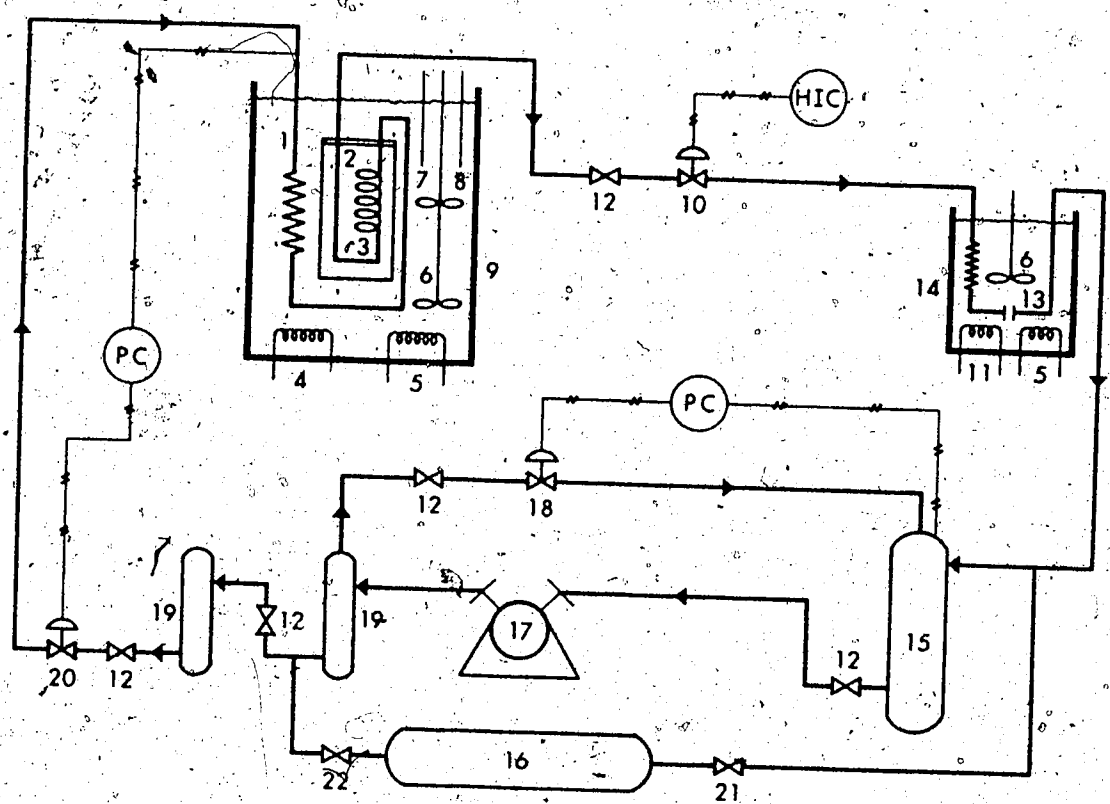
## LEGEND

1. Inlet tubing for the Calorimeter
2. Isothermal Calorimeter
3. Capillary Tubing
4. Liquid Nitrogen Cooling
5. Controlled Heat Input
6. Stirrer
7. Platinum Thermometer
8. Sensor for Heat Input Controller
9. Temperature Bath for the Calorimeter
10. Joule Thomson Control Valve
11. Water Cooling

12. Hand Valve
13. Orifice Meter
14. Temperature Bath for the Flow Meter
15. Low Pressure Tank
16. Storage Tank
17. Corblin Diaphragm Compressor
18. By-pass Control Valve
19. High Pressure Tank
20. High Pressure Control Valve
21. Feed Valve
22. Discharge Valve

FIGURE 3. Flow Diagram of the Apparatus

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, manipulated manually, gives the desired mass flow rate of the fluid through the calorimeter. The fluid is then passed through the flow meter. The constant inlet pressure of the flow meter is controlled by the BPCV valve which is governed by the set point of the controller. Then the fluid passes through a low pressure storage tank before returning to the intake of the compressor.

### *Auxiliary Equipment*

#### *1. Control Valves and Pressure Control*

It was necessary to control the pressure of fluid entering the calorimeter and the flow meter. 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 one to four standard cubic feet per minute for different gases such as methane, nitrogen, carbon dioxide, ethane or their mixtures.

Figure 3 gives 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 coefficient) calculations. The valves used are:

HPCV — Annin valve model 9460, trim size 0.02, air-to-close, can handle fluids from −400 to 750°F.

JTCV — Annin valve model 9460, trim size 0.003, air-to-open, can handle fluids from −400 to 750°F.

BPCV — Annin valve model 5061 "Wee-Willie", trim size "A" — $C_v$ range 0.0001 to 0.01, field reversible, can handle fluids from -200 to 465°F.

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

For both HPCV and BPCV, single feed back control loops having a controller with a proportional constant and an integral constant were used. Foxboro controllers with built-in power supplies were used for the high and low pressure controls. High and low pressures were measured, at the locations shown in Figure 3, by Foxboro pressure transmitters model 611 GH and 611 GM respectively. The current to pressure converters used in the pressure control loop are Fisher type 546 electro-pneumatic transducers.

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 to the valve positioner. Since the upstream pressure of JTCV and its resistance remained constant and the flow through the valve was sonic, this scheme gives constant mass flow rate through the calorimeter.

## 2. *Material Recirculating Device*

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

### 3. Gas Heaters

In order to maintain the steady-state operation, the control valves HPCV, BPCV and JTCV were maintained at constant opening. The pressure drop across the "HPCV" valve ranged from 50 to 400 psi and a strip heater was used to compensate the cooling effect due to the pressure drop. Since cooling effect is large because of pressure drop across the BPCV and JTCV ranged from 300 to 2000 psi, steam heaters were used to heat the fluid before it passed through the valves.

### 4. Temperature Controller

The calorimeter bath temperatures were controlled within ±0.01°C by a Hallikainen Thermotrol temperature controller, model 1053.

### Measuring Instruments

1. The temperature of the bath was determined by using a Leeds and Northrup platinum resistance thermometer, model number 8163 and it was calibrated for use in the range 90.188 K < T < 773.15 K on the International practical temperature scale of 1968 by National Research Council of Canada.

2. The inlet temperature of the fluid to the calorimeter was assumed to be equal to the bath temperature and a one-junction copper-constantan differential thermocouple was used to check the measurement. The temperature difference between inlet and outlet was measured by a five-junction copper-constantan differential thermopile. Both the one-junction thermocouple and the five-junction thermopile were calibrated for the zero reading at boiling and ice temperatures of water, and the melting temperature of dry ice. A d-c null voltmeter was used to read

the null point for the thermopile. The accuracy of the temperature measurement is about ±0.01°C.

3. The inlet pressure was measured by a Heise gauge and the pressure drop across the calorimeter was determined by a Validyne differential pressure transducer. Both Heise gauge and pressure transducer were calibrated by the Ruska dead weight tester. The accuracy of the gauge is 0.1 percent of full scale, and the accuracy of the pressure transducer is 0.5 percent of the full scale.

4. The electrical energy input to the calorimeter was supplied by Kepco DC power supply and was measured by a Hewlett-Packard model 3450 multifunction meter with the six-digit display.

5. In the early stage of this work a Nupro "F" inline filter was used as a flow meter. The mass flow rate for nitrogen and 42.3% methane in carbon dioxide mixture was determined from the inlet pressure and the pressure drop across the filter together with the constant temperature at the element. These data were used to solve the calibration equation:

$$\frac{P_1^2 - P_2^2}{Z\mu'F} = A + B[\frac{FM}{\mu'}] \tag{18}$$

for the mass flow rate F. The constants A and B were obtained from a least square fit of the calibration data obtained by the gasometer, where $P_1$ and $P_2$ are the inlet and outlet pressure of the flow meter which are given by pressure transducers. $\mu'$, Z and M are the viscosity, compressibility and molecular weight of the gas respectively.

During the data taking of the 42.3% methane in carbon dioxide mixture, it was found that the solid contamination in the flow meter element causes the changing of the calibration curve. The flow meter was recalibrated and after obtaining the experimental data of the mixture,

the flow meter was recalibrated again. It was found that the two calibration curves disagreed by 0.8 percent. So, the filter was abandoned as device for the flow measurement. The average mass flow rate calculated by the two calibration curves was used to reduce the experimental data of this mixture.

A square-edged orifice was then used for the flow measurement. 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 inlet pressure was maintained constant by the BPCV control valve, and was determined by a Validyne pressure transducer. The pressure drop across the orifice was measured by a Foxboro d/p cell transmitter type 613 M. The accuracy of the pressure transducer and d/p cell is 0.5 percent of the full scale. The orifice was calibrated using pure nitrogen, methane, ethane and carbon dioxide and argon by the gasometer. The orifice was calibrated at the completion of the experiments on every mixture using the gas mixture itself. The overall standard deviation of the flow rate is about 0.5 percent. The calibration of the orifice is given in Appendix A.

All the output signals of the presure transducers, d/p cell transmitter, platinum resistance thermometer, power to the calorimeter and thermopile were connected to a Hewlett-Packard model 3450 multi-function meter by a multi-junction selection switch.

Figure 4 shows the electric circuits of platinum resistance thermometer and the calorimeter heater.
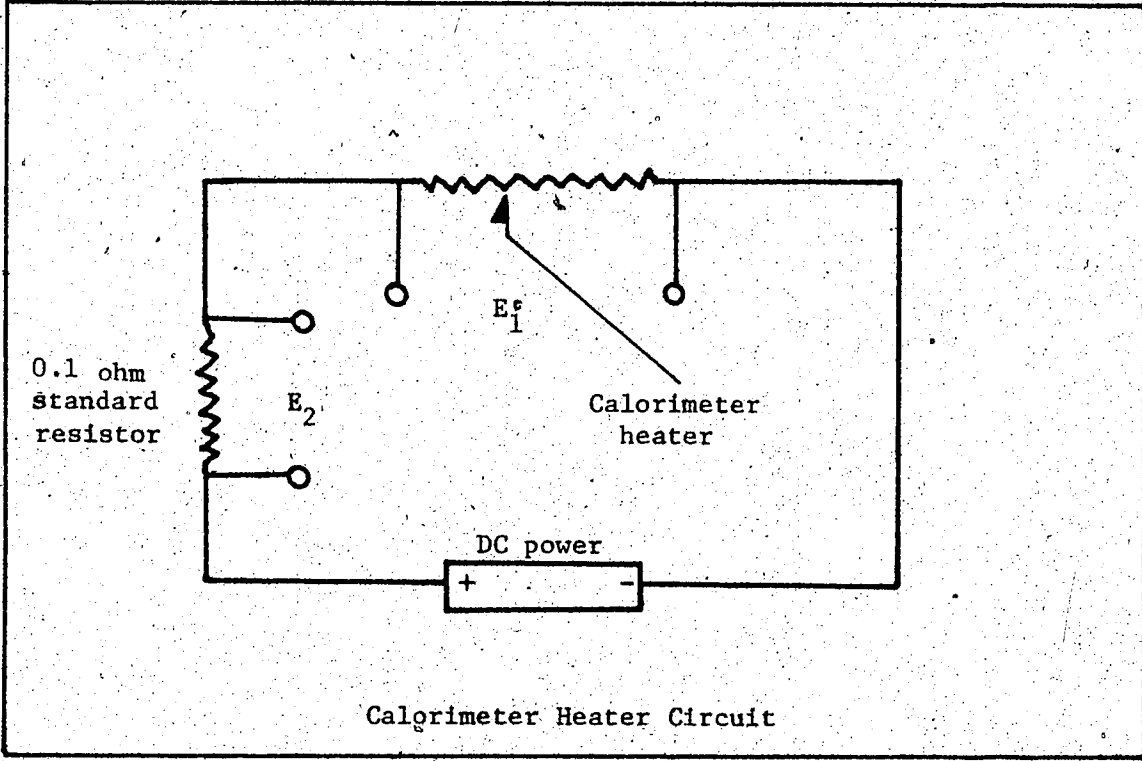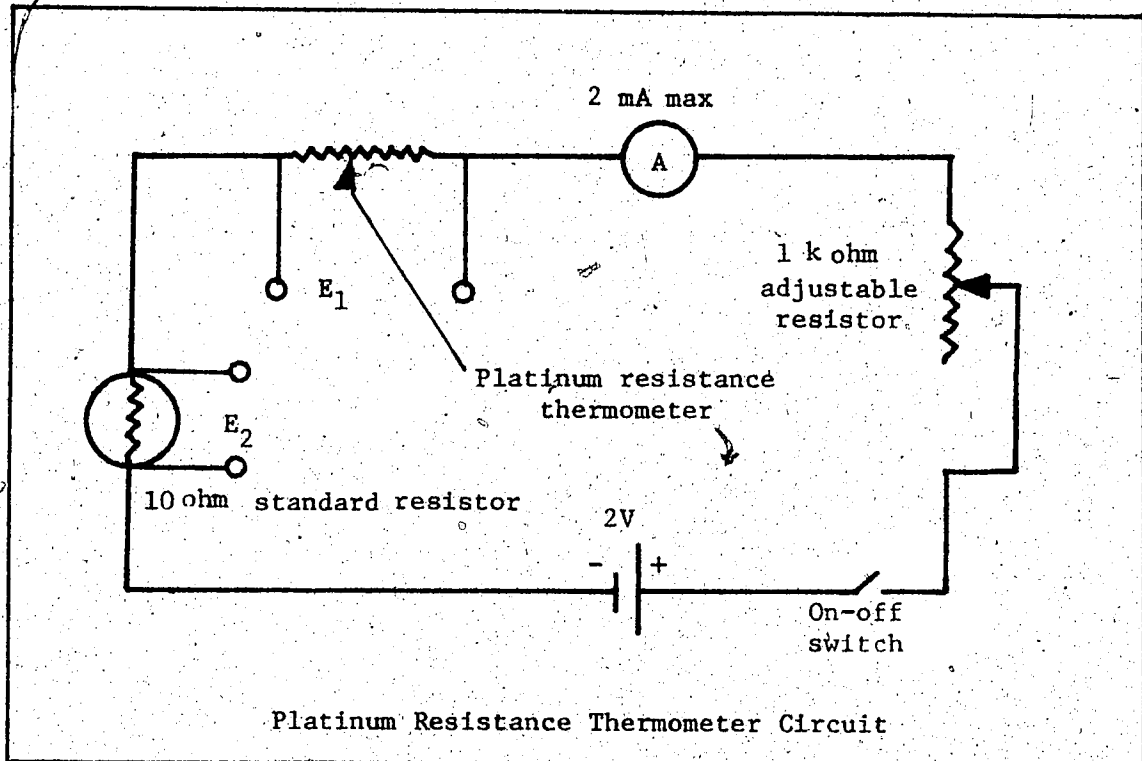
Figure 4: Wiring Diagram of Platinum Resistance Thermometer and
Calorimeter Heater Circuits

## SECTION III - EXPERIMENTAL RESULTS AND DISCUSSION

In this section, the experimental procedure, the materials used, and a summary of the techniques used in interpreting the experimental data obtained in this investigation are presented. The experimental results of $\phi$ of nitrogen, two mixtures of methane and carbon dioxide, two mixtures of methane, carbon dioxide and ethane, one mixture of methane, carbon dioxide and nitrogen, and a mixture of methane, carbon dioxide, nitrogen and ethane at various temperatures are also presented.

### Procedure of the Experimental Measurements

The fluid under study was brought to the desired state of pressure and temperature at the inlet to the calorimeter with the recycle system shown in Figure 3. A pressure drop of 60 to 250 psi was obtained by adjustment of the flow of fluid through the calorimeter section. The flow rate was adjusted by control valve JTCV, manipulated manually. The voltage supplied to the calorimeter heater wire was adjusted manually until the temperature difference between the inlet and outlet of the calorimeter, indicated by the differential thermopiles was less than two microvolts (0.01°C). When steady state was reached, as indicated by the constancy of the pressure drop and the zero temperature difference across the calorimeter, the values of the variables were recorded. The time of approach to steady state was of the order of half to one hour.

### Materials Used

The source and purity of the gases used in this work are given in Table II. The gases were used without further purification.

## TABLE II

### Materials

| Component | Supplier | Purity |
|---|---|---|
| Nitrogen | Consumer's Welding Co. | 99.993% |
| Methane | Matheson Gas Products | 99.97 % |
| Carbon dioxide | Canadian Liquid Air Co. Ltd. | 99.95 % |
| Ethane | Matheson Gas Products | 99.96 % |

## Composition Determination

The composition of the mixtures in this study was determined chromatographically. The calibrations for the gas chromatograph are presented in Appendix A. The precision of the composition determinations was approximately ±0.2 mole percent as was checked by making several runs for each isotherm.

## Interpretation of Data

The basic data were recorded in terms of quantities that can be readily measured, such as microvolts and height of a fluid. These quantities were converted to temperature, pressure, pressure drop, power input and flow rate. In the single phase region, the isothermal throttling coefficient $\phi$ which is shown in Equation (7) is obtained from the integral data by several techniques. Both graphical and computer reduction methods were used.

## Graphical Interpretation

One may consider determining $\phi$ at constant temperature as a function of pressure. The experimental data were reported as sets of T, $P_1$, $P_2$ and $(H_{P_2} - H_{P_1})$ over a wide range of temperature. For any one data point,

$$H_{P_2,T} - H_{P_1,T} = \int_{P_1}^{P_2} \phi \, dP \qquad (19)$$

or

$$\frac{H_{P_2,T} - H_{P_1,T}}{P_2 - P_1} = \phi_{T_m} = \frac{\int_{P_1}^{P_2} \phi \, dP}{P_2 - P_1} \qquad (20)$$

where $\phi_{T_m}$ is the mean isothermal throttling coefficient between $P_1$ and $P_2$. Values of $\phi_{T_m}$ were plotted as horizontal lines are shown in Figures 5 and 10. The smooth $\phi_{T_m}$ curve was obtained by satisfying Equation (19): the area under the horizontal line segments, $\phi_{T_m}*(P_2 - P_1)$, should equal the area under the smooth isothermal throttling coefficient curve.

## Computer Reduction

The above graphical procedures are extremely time consuming and in addition the equal area construction can easily lead to errors. Therefore, a computer program was developed for interpretation of integral data. The true isothermal throttling coefficient is given by,

$$\phi \equiv \lim_{\Delta P \to 0} \frac{q}{\Delta P} \equiv \left(\frac{\partial H}{\partial P}\right)_T$$

where $q = \frac{\dot{W}}{F}$ is the rate of electrical energy transfer per unit mass flow rate. The result of actual measurements is the mean $\phi$, $\phi_m = q/(P_2 - P_1)$, associated with the mean pressure of the interval, $P_m = (P_1 + P_2)/2$. Deviation from linearity of the $\phi$ versus $P$ curve will therefore require adjustment of the mean isothermal throttling coefficient by a curvature correction to yield the true isothermal throttling coefficient at $P_m$.

The curvature correction can be determined by considering the isothermal throttling coefficient to be represented by a cubic equation in pressure over a limited range

$$\phi = a_0 + a_1 P + a_2 P^2 + a_3 P^3 \tag{21}$$

then

$$q' = \int_{P_1}^{P_2} \phi \, dP$$

$$= a_0(P_2 - P_1) + \frac{a_1}{2}(P_2^2 - P_1^2) + \frac{a_2}{3}(P_2^3 - P_1^3) + \frac{a_3}{4}(P_2^4 - P_1^4) \quad (22)$$

and the mean $\phi$ is,

$$\phi_m = \frac{q}{P_2 - P_1}$$

$$= a_0 + \frac{a_1}{2}(P_2 + P_1) + \frac{a_2}{3}(P_2^2 + P_2 P_1 + P_1^2)$$

$$+ \frac{a_3}{4}(P_2^3 + P_2^2 P_1 + P_2 P_1^2 + P_1^3) \quad (23)$$

The difference between the true $\phi$ and the mean $\phi_m$ at $P_m$ is,

$$\phi - \phi_m = \frac{-(P_2 - P_1)^2}{24}[2a_2 + 3a_3(P_2 + P_1)] \quad (24)$$

Since at the mean pressure,

$$(\frac{\partial^2\phi}{\partial P^2}) = 2a_2 + 3a_3(P_1 + P_2) \quad (25)$$

the true isothermal throttling coefficient is,

$$\phi = \phi_m - \frac{(P_2 - P_1)^2}{24}(\frac{\partial^2\phi}{\partial P^2})_T \quad (26)$$

values of $(\frac{\partial^2\phi}{\partial P^2})_T$ were obtained by considering the mean isothermal to be sufficiently close to the true isothermal throttling coefficient and differentiating the smooth mean isothermal throttling coefficient.

The extended spline fit technique was used to obtain a smooth mean isothermal throttling coefficient and its second derivative with respect to P.

## The Extended Spline Fit Method

The spline fit technique has been discussed by Landis and Nilson [41]. This method puts a different cubic between every two

successive data points such that the curve passes exactly through each data point and that the first two derivatives of the curve on the right hand side of the data point are equal, respectively, to the first two derivatives of the curve on the left hand side of the data point, all derivatives evaluated at the data point.

If, instead of defining the interval boundaries to pass through every data point, interval boundaries are determined arbitrarily such that each interval may contain a number of data points, the method can be extended to provide smoothing of the data. The details of this method are discussed by Klaus and Van Ness.[39]

## Extension to Low Pressure

Since the lower limit in pressure of the recycle flow system is 200 psia, data from the literature are used in extending the enthalpy results to zero pressure. The experimental isothermal throttling coefficients obtained at elevated pressures should extrapolate to the zero pressure values derived from the experimental second virial coefficients using Equation (14). The resulting curve was integrated to determine the effect of pressure on enthalpy at low pressures.

## Experimental Results With Nitrogen

The experimental data were taken for nitrogen on the isothermal throttling calorimeter at four different temperatures from 273.15 to 374.15 K, and the pressure up to 2400 psia. Figure 5 shows the isothermal throttling coefficient, $\phi$ at 273.15 K plotted as a function of pressure. An equal area curve passing through the bars obtained point values of $\phi$. The agreement between this work and Mather[57] is less than 1.0%. Figure 6 and 7 show the comparison of two different temperatures with other experimental results. The experimental band indicates the precision of about ±1/2% for this experiment. The data of Ishkin and Kaganer[33] are believed to be high by as much as 5% (see Mather[58]).

The values of $\phi$ can be calculated from an equation of state using Equation (8). The Benedict-Webb-Rubin[6] equation is frequently used for calculation of thermodynamic properties. For nitrogen, two sets of constants for this equation are available, those of Stotler and Benedict[83] and those of Bloomer and Rao[12]. Isothermal throttling coefficients were also calculated from the equation of state for nitrogen from the U.S. Bureau of Mines[93]. The results of equation of state calculation were compared with the experimental data in Figure 8 and 9.

Table III presents the smoothed experimental measurements of $\phi$ by this work.

Enthalpy departures were calculated from the experimental data by integration of $\phi$ with respect to pressure. The results for the three isotherms of this work were compared with other experimental calorimetric results in Table IV. The present data were in very good agreement with the most recent experimental values in the literature.

## TABLE III

### ISOTHERMAL THROTTLING COEFFICIENTS FOR

### NITROGEN

$$-\phi \ (J \ mol^{-1} \ bar^{-1})$$

Temperature, °C

| PRESSURE (bar) | 0 | 30 | 70.3 | 101 |
|---|---|---|---|---|
| 0* | 7.48 | 5.93 | 4.58 | 3.62 |
| 10 | 7.33 | 5.83 | 4.44 | 3.51 |
| 20 | 7.17 | 5.69 | 4.30 | 3.40 |
| 30 | 7.03 | 5.54 | 4.16 | 3.29 |
| 40 | 6.86 | 5.39 | 4.01 | 3.17 |
| 50 | 6.66 | 5.21 | 3.87 | 3.04 |
| 60 | 6.46 | 5.04 | 3.72 | 2.92 |
| 70 | 6.26 | 4.89 | 3.58 | 2.81 |
| 80 | 6.06 | 4.73 | 3.43 | 2.71 |
| 90 | 5.85 | 4.55 | 3.31 | 2.60 |
| 100 | 5.63 | 4.37 | 3.18 | 2.48 |
| 110 | 5.39 | 4.20 | 3.05 | 2.37 |
| 120 | 5.14 | 4.01 | 2.91 | 2.26 |
| 130 | 4.88 | 3.83 | 2.79 | 2.14 |
| 140 | 4.75 | 3.65 | 2.67 | 2.04 |
| 150 | 4.34 | 3.46 | 2.55 | 1.93 |
| 160 | 4.07 | 3.27 | 2.42 | 1.82 |

$^{*} B - T\frac{dB}{dT}$
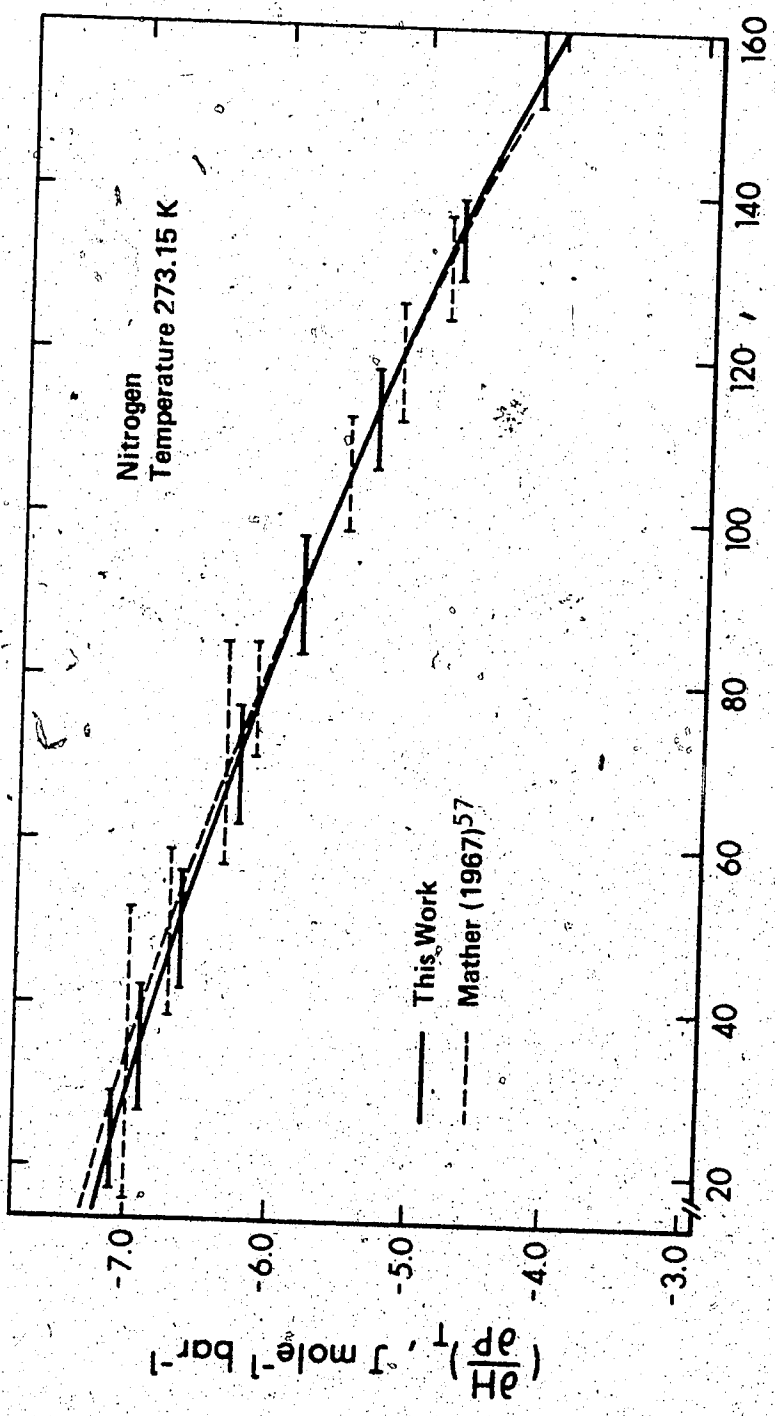
FIGURE 5. Isothermal Data on Nitrogen at 273.15 K
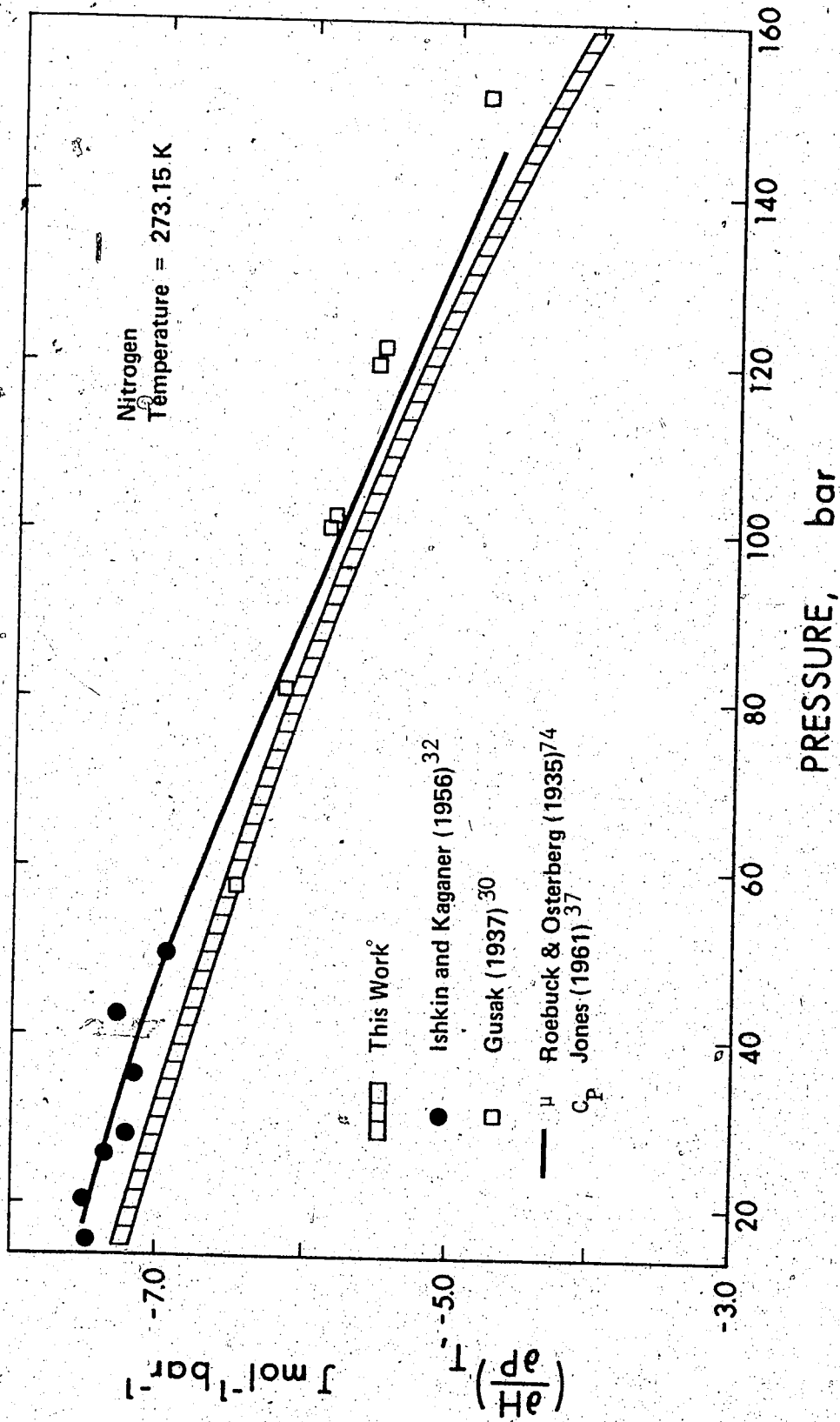
FIGURE 6. Comparison of Isothermal Data of Nitrogen With Other Experimental Data at 273.15 K
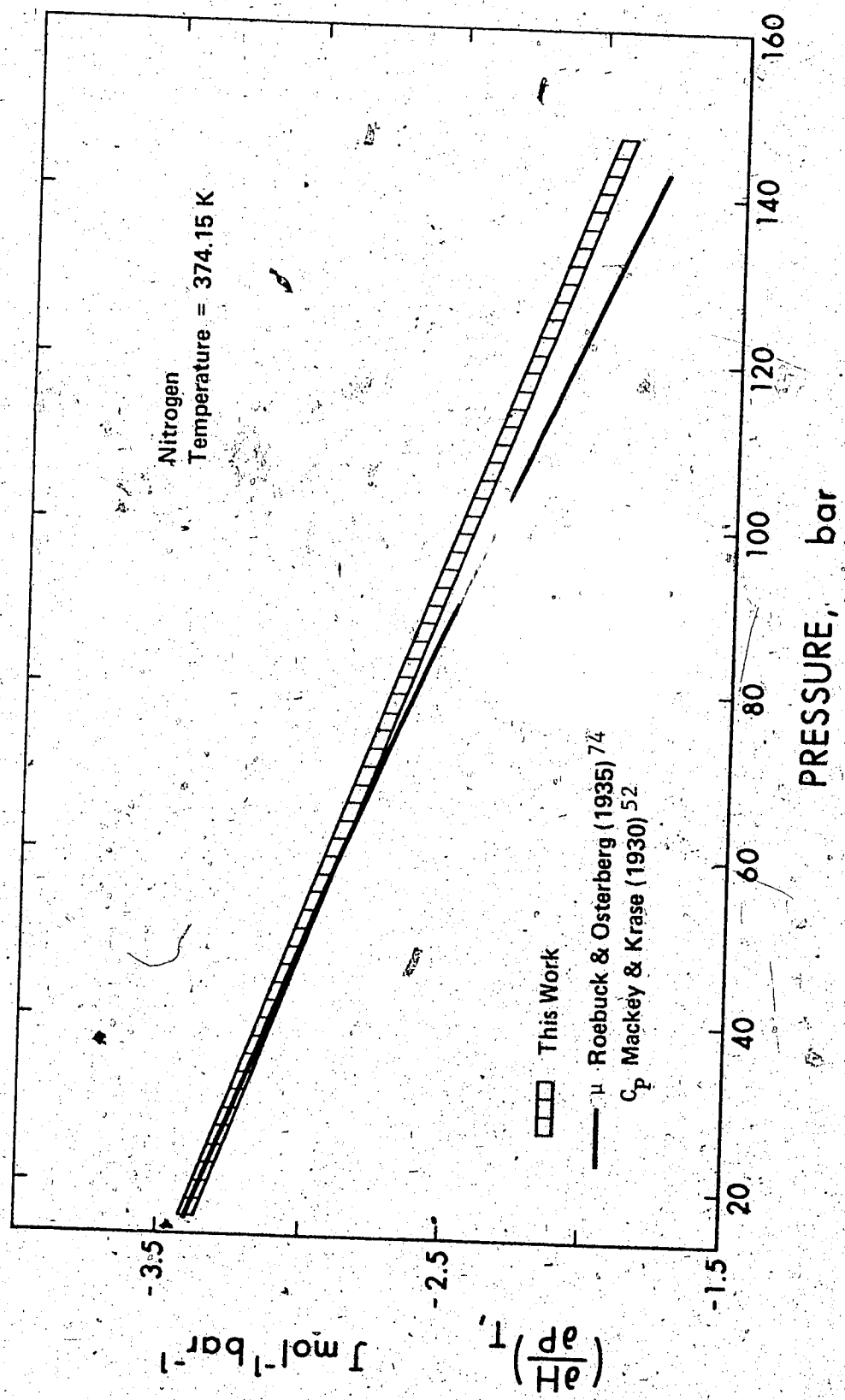
FIGURE 7. Comparison of $\phi$ of Nitrogen With Other Experimental Data at 374.15 K

Nitrogen
Temperature = 374.15 K

This Work
$\mu$ Roebuck & Osterberg (1935)[74]
$C_p$ Mackey & Krase (1930)[52]

PRESSURE, bar

$\left(\dfrac{\partial H}{\partial P}\right)_T$, J mol$^{-1}$ bar$^{-1}$
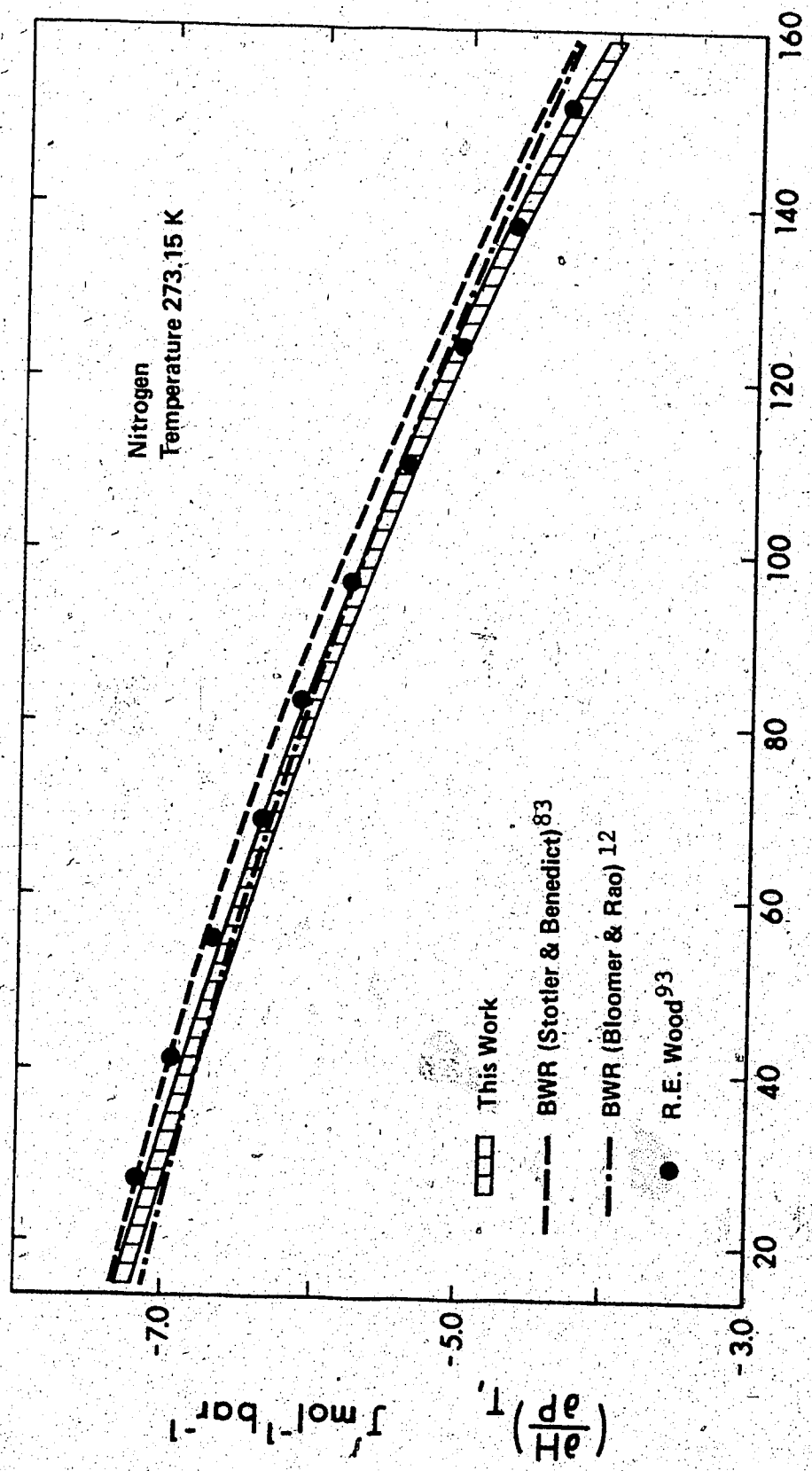
FIGURE 8. Comparison of Isothermal Data of Nitrogen with Values Predicted from Equations of State
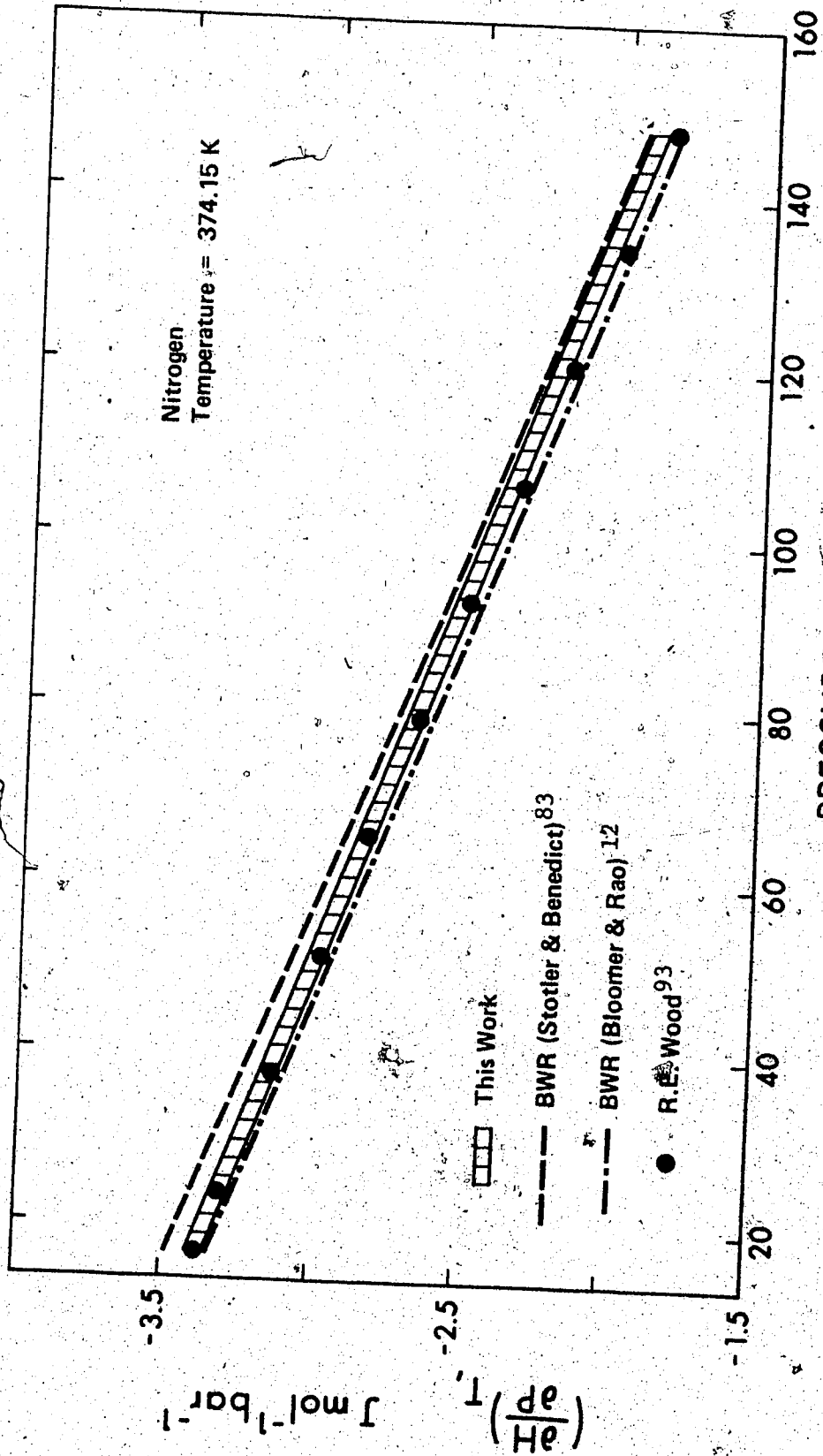
FIGURE 9.  Comparison of Isothermal Data of Nitrogen with Values Predicted from Equations of State

Nitrogen
Temperature = 374.15 K

□ This Work
— · — BWR (Stotler & Benedict)[83]
— · · — BWR (Bloomer & Rao)[12]
● R. E. Wood[93]

PRESSURE, bar

$\left(\dfrac{\partial H}{\partial P}\right)_T$, J mol$^{-1}$ bar$^{-1}$

34

## TABLE IV

## COMPARISON OF EXPERIMENTAL ENTHALPY DEPARTURES

## FOR NITROGEN WITH OTHER EXPERIMENTAL WORKS

| TEMPERATURE (K) | PRESSURE (bar) | $(H_o - H_p)_T$ , $J\ mol^{-1}$ | | |
|---|---|---|---|---|
| | | This Work | Mather[57] | Dawe & Snowdon[21] |
| 273.15 | 20 | 146.6 | 147 | 148 |
| | 40 | 287.0 | 290 | 291 |
| | 60 | 420.2 | 422 | 428 |
| | 80 | 545.4 | 543 | 558 |
| | 100 | 662.4 | 660 | 679 |
| 303.15 | 20 | 116.4 | – | 117 |
| | 40 | 227.2 | – | 230 |
| | 60 | 331.5 | – | 338 |
| | 80 | 429.2 | – | 439 |
| | 100 | 520.2 | – | 532 |
| 374.15 | 20 | 70.2 | – | 67 |
| | 40 | 136.0 | – | 132 |
| | 60 | 196.8 | – | 194 |
| | 80 | 253.1 | – | 252 |
| | 100 | 305.0 | – | 305 |

_Experimental Results With Methane - Carbon Dioxide Mixtures_

The measurements of the isothermal throttling coefficient were made on 42.3 mole percent of methane in carbon dioxide at four isotherms, 0, 40, 60 and 90°C. The pressure ranged from 400 to 2000 psia. Measurements were also made at six isotherms and the same pressure range for 14.5 mole percent of methane in carbon dioxide. The six isotherms were 0, 10, 20, 40, 60 and 90°C.

Typical isothermal data are presented in Figure 10. Average values of $\phi_m = (\Delta H/\Delta P)_T$ were plotted as horizontal lines and the computer reduction method was used to determine point values of $\phi = f(P)$ as illustrated by the solid curve. In extrapolating the results of the experimental investigation to zero pressure, it was necessary to use Equation (14) for $\phi°$ in terms of second virial coefficient. Values of $\phi°$ were calculated from the virial coefficients given by Dymond and Smith[24] and Ng[63]. The calculation of $\phi°$ is shown in Appendix C.

Tables of $\phi$ values of all of the experimental isotherms are presented in Table V and VI. Figure 11 and 12 present the plot of $\phi$ as a function of temperature at different isobars for the two mixtures.

_Comparison of Results_

Since the isothermal experimental data on the carbon dioxide-methane mixtures with same compositions are not available in the literature, comparison cannot be made. However, the isothermal throttling coefficients of two mixtures at each isotherm and at a pressure up to 2000 psia can be calculated by using BWR equation of state and Bishnoi and Robinson[11] mixing rules. The parameters of carbon dioxide and methane, reported by Bishnoi and Robinson[10] were utilized in the above calculations.

Mole Fraction $CO_2$  0.855
Mole Fraction $CH_4$  0.145
Temperature  40°C

▲  $\phi° = B - T\frac{dB}{dT}$

$\left(\frac{\partial H}{\partial P}\right)_T$,  $J\,mol^{-1}\,bar^{-1}$
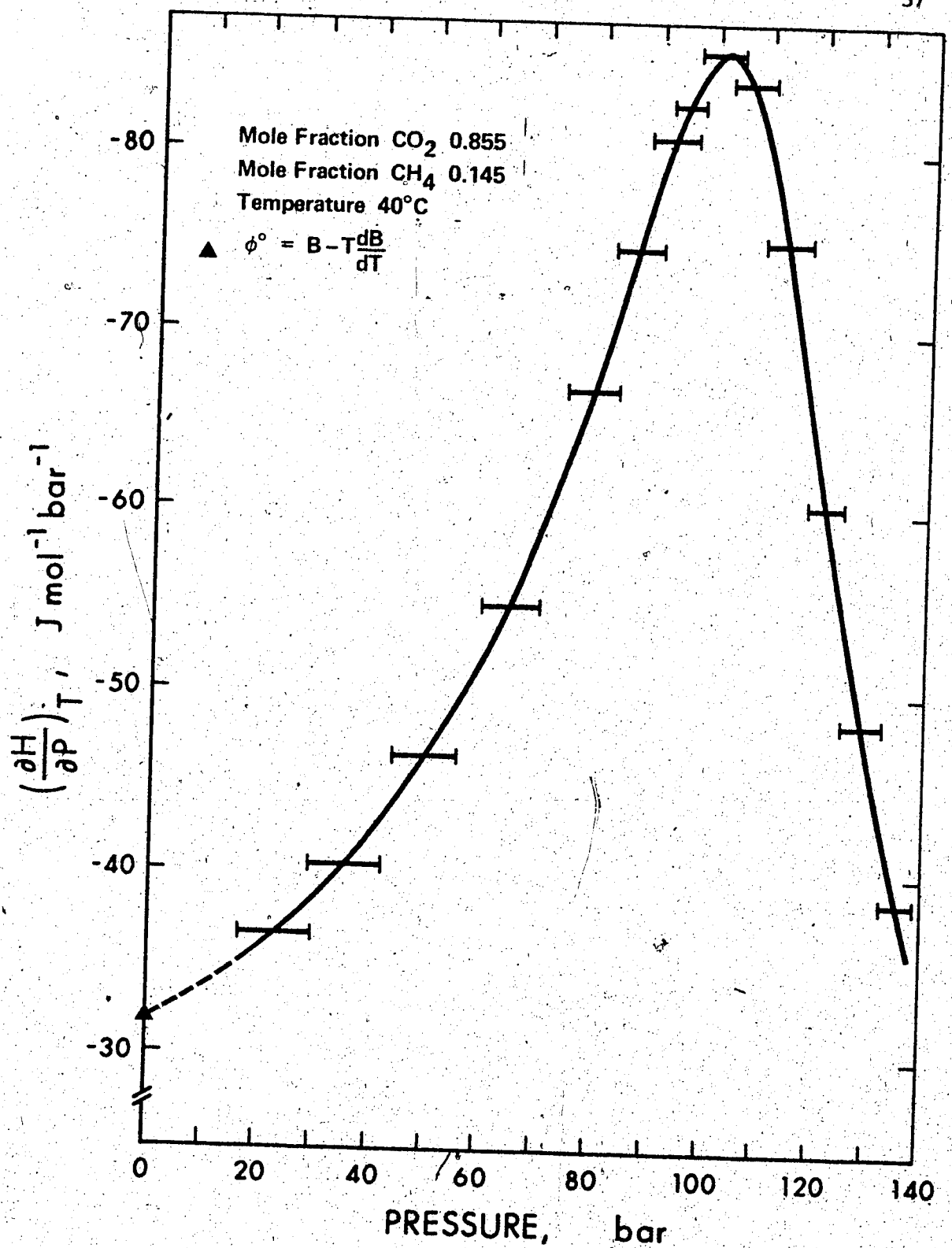
PRESSURE,  bar

FIGURE 10.  Isothermal Throttling Coefficient for the 14.5 percent $CH_4$ in $CO_2$ Mixture at 40°C

## TABLE V

## ISOTHERMAL THROTTLING COEFFICIENTS FOR

## THE 42.3 MOLE PERCENT METHANE IN CARBON DIOXIDE

$$-\phi \ (\text{J mol}^{-1} \ \text{bar}^{-1})$$

| PRESSURE (bar) | Temperature °C | | | |
|---|---|---|---|---|
| | 0 | 40 | 60 | 90 |
| 0* | 32.46 | 24.10 | 21.30 | 18.20 |
| 10 | 34.42 | 24.95 | 21.92 | 18.48 |
| 20 | 37.10 | 25.95 | 22.58 | 8.78 |
| 30 | 40.70 | 27.09 | 23.28 | 19.05 |
| 40 | 45.41 | 28.27 | 23.95 | 19.32 |
| 50 | 52.15 | 29.48 | 24.60 | 19.58 |
| 60 | 62.04 | 30.76 | 25.20 | 19.83 |
| 70 | 74.71 | 32.05 | 25.76 | 20.01 |
| 80 | 87.75 | 33.24 | 26.27 | 20.13 |
| 90 | 85.77 | 34.23 | 26.69 | 20.17 |
| 100 | 63.71 | 34.90 | 26.95 | 20.17 |
| 110 | 43.52 | 34.97 | 27.00 | 20.12 |
| 120 | 30.04 | 34.11 | 26.76 | 20.00 |
| 130 | 21.55 | 32.27 | 26.17 | 19.74 |
| 137 | 17.75 | 31.19 | 25.53 | 19.43 |

$$* \ B - T\frac{dB}{dT}$$

# TABLE VI

## ISOTHERMAL THROTTLING COEFFICIENTS FOR

### THE 14.5 MOLE PERCENT METHANE IN CARBON DIOXIDE

$-\phi$ (J mol$^{-1}$ bar$^{-1}$)

| PRESSURE (bar) | Temperature, °C | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 40 | 60 | 90 |
| 0* | 44.23 | 40.92 | 36.79 | 31.91 | 27.78 | 23.81 |
| 10 | 49.61 | 45.64 | 39.89 | 33.48 | 29.18 | 24.35 |
| 20 | 57.46 | 51.80 | 43.82 | 35.55 | 30.67 | 24.97 |
| 30 | 69.86 | 60.15 | 48.57 | 38.28 | 32.19 | 25.67 |
| 40 | - | 73.79 | 54.82 | 42.13 | 33.97 | 26.54 |
| 50 | - | 96.73 | 67.63 | 46.32 | 36.04 | 27.42 |
| 60 | - | - | 90.03 | 51.54 | 38.37 | 28.30 |
| 70 | - | - | 129.5 | 58.39 | 40.92 | 29.16 |
| 80 | 9.99 | - | 241.8 | 67.48 | 43.66 | 30.00 |
| 90 | 7.61 | 20.90 | 99.40 | 78.06 | 46.53 | 30.80 |
| 100 | 6.10 | 14.21 | 44.51 | 85.15 | 49.17 | 31.48 |
| 110 | 5.02 | 10.78 | 25.76 | 80.53 | 50.91 | 31.94 |
| 120 | 3.98 | 8.43 | 17.96 | 63.06 | 51.07 | 32.16 |
| 130 | - | 7.06 | 14.65 | 46.30 | 49.11 | 32.18 |
| 137 | - | 6.38 | 11.54 | 37.00 | 46.37 | 32.11 |

* $B - T\frac{dB}{dT}$
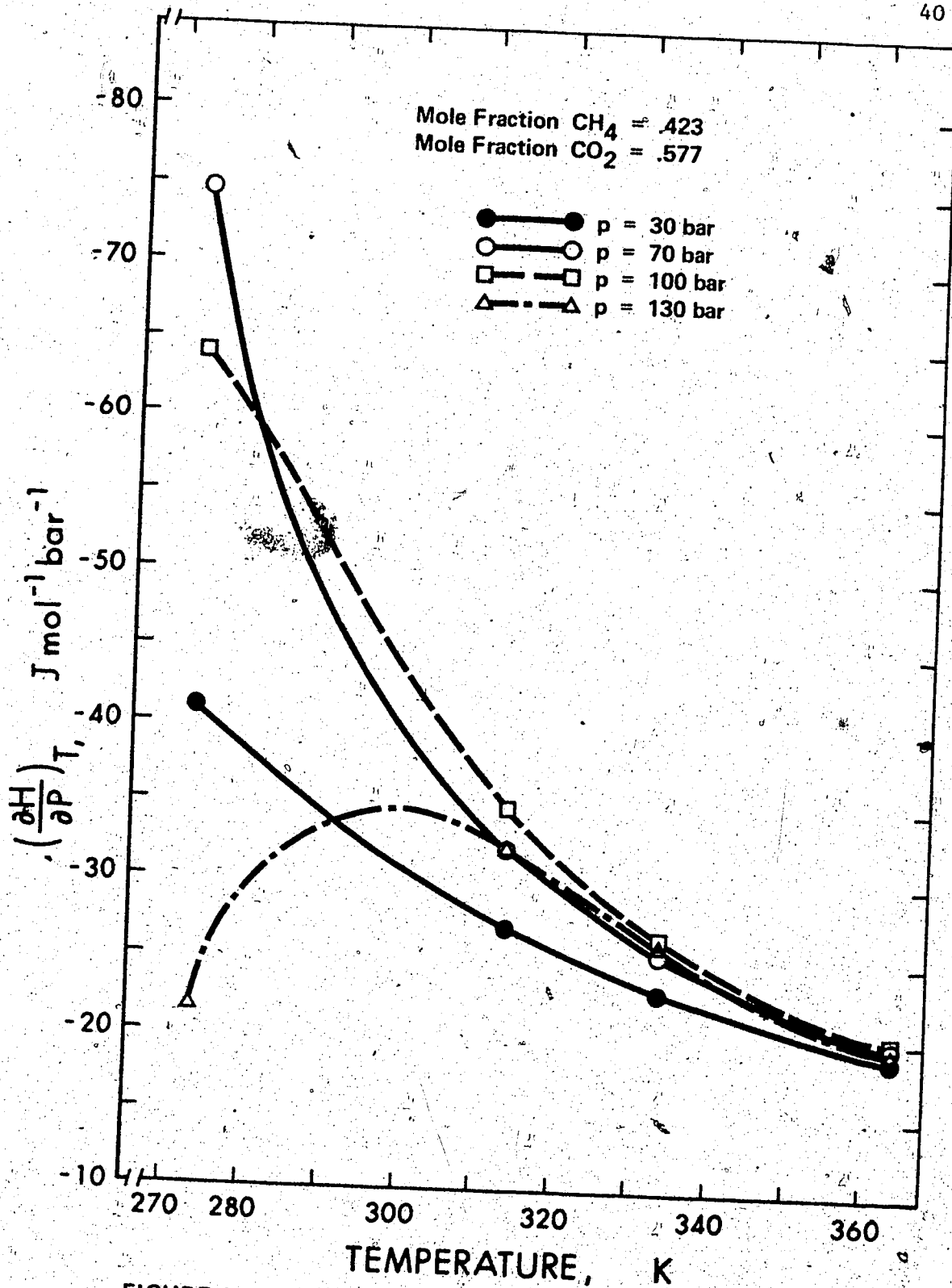
FIGURE 11. Isothermal Throttling Coefficient for the 42.3 percent CH$_4$ in CO$_2$ Mixture at Various Constant Pressures
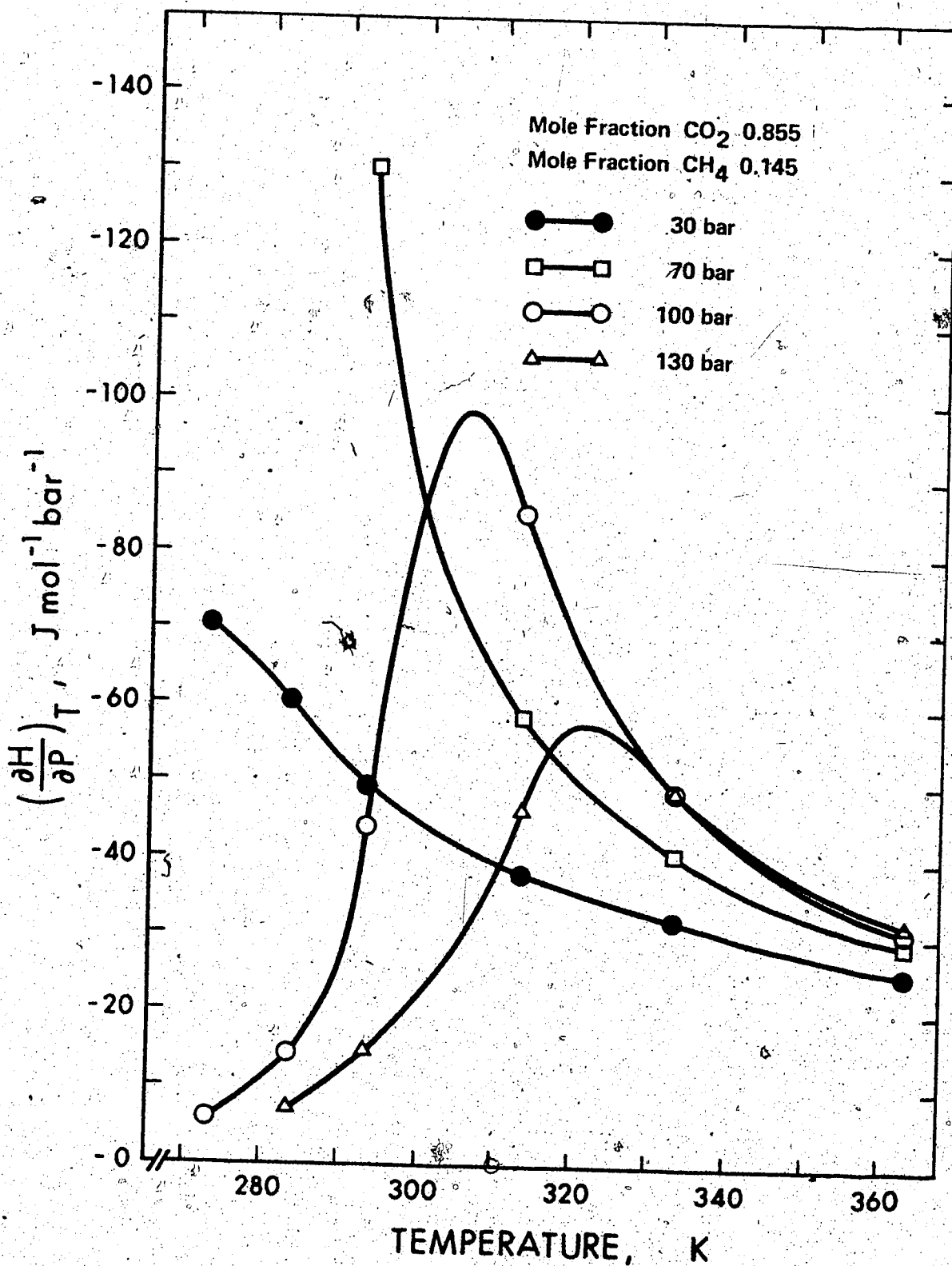
FIGURE 12. Isothermal Throttling Coefficient for the 14.5 percent $CH_4$ in $CO_2$ Mixture at Various Constant Pressures

In general, the deviations are larger at the lower pressures of the lower temperature. The comparison of the experimental data and the calculated values from BWR equation of state for 42.3 percent methane in carbon dioxide at 0°C and 14.5% mixture at 90°C are shown in Figure 13 and 14 respectively.

Peterson and Wilson[68] reported results of isothermal enthalpy departure from isothermal throttling experiments for equimolal methane-carbon dioxide mixture at pressure from 20 to 2000 psia and temperature from -50°F to 300°F. Isothermal enthalpy departures of the two mixtures of this work were calculated by integration with respect to pressure. The results were then interpolated to 100°F and 150°F at pressure of 800, 1200, 1600 and 2000 psia. The final results were plotted at constant pressure and temperature as a function of mole fraction. Enthalpy departure of pure methane and carbon dioxide were obtained from modified BWR equation proposed by Starling (BWRS)[50,78] with the parameters from Starling[80]. Figure 15 shows the comparison of the results between this work and that of Peterson and Wilson[68] at 100°F. The comparison at 150°F is also in good agreement.

## Enthalpy Tables and Diagrams

The experimental data on the effect of pressure on enthalpy by this work and the effect of temperature on enthalpy by Bishnoi[9] for the methane - carbon dioxide mixtures have been used to prepare skeleton enthalpy tables and diagrams. Tables and diagrams are presented for 14.5 42.3 mole percent methane in carbon dioxide mixtures. Comparisons were made with excess enthalpy data from the literature.
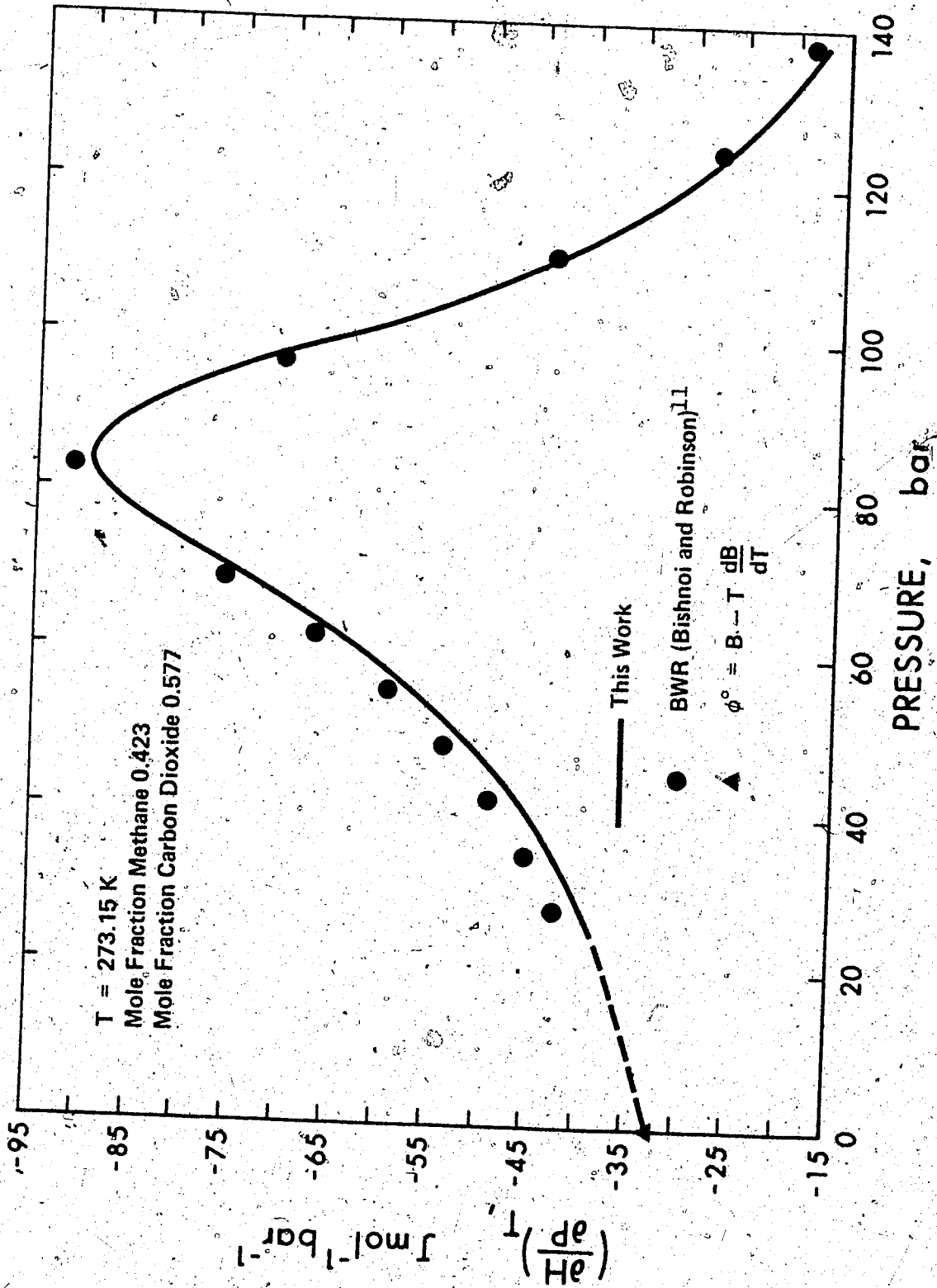
FIGURE 13. φ of 42.3 Mole Percent Mixture at 273.15 K
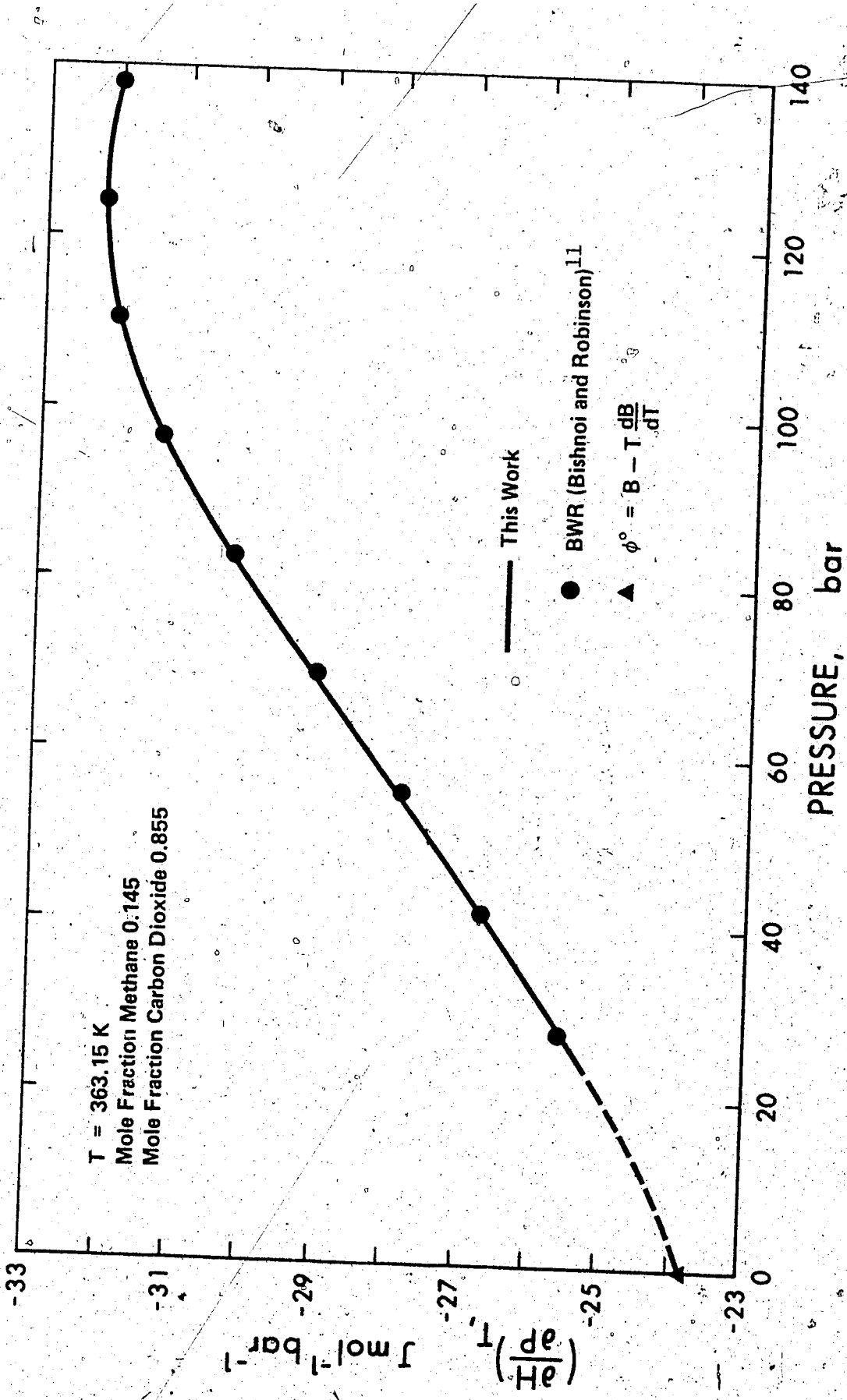
FIGURE 14. $\phi$ of 14.5 Mole Percent Mixture at 363.15 K

T = 363.15 K
Mole Fraction Methane 0.145
Mole Fraction Carbon Dioxide 0.855

This Work

BWR (Bishnoi and Robinson)[11]

$\phi^\circ = B - T\frac{dB}{dT}$

PRESSURE, bar

$\left(\frac{\partial e}{\partial He}\right)_T$, J mol$^{-1}$ bar$^{-1}$
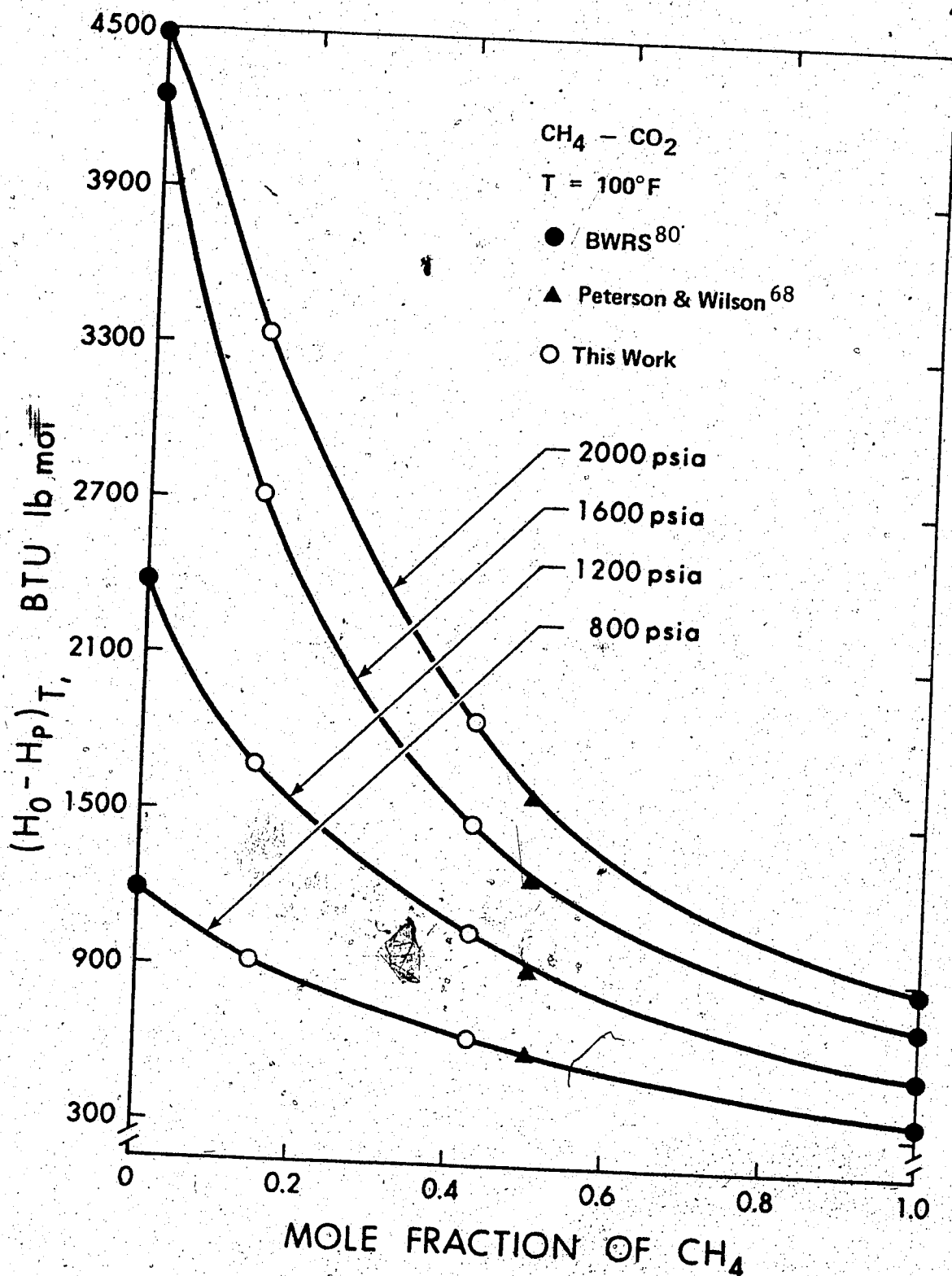
FIGURE 15. Enthalpy Departures for Mixtures of Methane and Carbon Dioxide

*Nominal 14.5 Percent Methane in Carbon Dioxide Mixture*

A skeleton enthalpy table and a pressure-enthalpy-temperature diagram for this mixture have been prepared which are based entirely on experimental calorimetric data. The following procedure was used in preparing the diagram and table:

1.      Reference state of 0 J/mole were taken to be the pure components as perfect crystals under zero pressure at absolute zero temperature.

2.      The enthalpy of pure methane as a gas at zero pressure and 0 K was calculated using the enthalpy of methane (saturated vapor) at 100 K reported by Din[23], the B-W-R equation of state with parameters from Bishnoi and Robinson[10] to correct from 0.344 atm to zero pressure, and value of the ideal gas enthalpies from McBride et al[61], the following results were obtained:

|  | kJ mol$^{-1}$ |
|---|---|
| Enthalpy of methane at 100 K and 0.344 atm | +12.4775 |
| Corrected to ideal gas (0.344 to 0 atm) | + 0.05535 |
| Ideal gas enthalpy change from 100 to 0 K | − 3.3126 |
|  | 9.22025 |

so, the enthalpy of pure methane from perfect crystal at 0 K to any temperature at zero pressure is,

$$H_T = 9.22025 + (H_T^\circ - H_0^\circ) \text{ kJ mol}^{-1}$$

where $(H_T^\circ - H_0^\circ)$ is the ideal gas enthalpy change reported by

3. The enthalpy of pure carbon dioxide as a gas at zero pressure and any temperature is reported by Vukalovich and Altunin[85] as follows:

$$H_T = 26.2235 + (H_T^\circ - H_o^\circ) \text{ kJ mol}^{-1}$$

where $(H_T^\circ - H_o^\circ)$ is the ideal gas enthalpy change reported by McBride et al.[61].

4. The enthalpy of methane-carbon dioxide mixture at zero pressure and any temperature T K was calculated assuming zero heat of mixing under these conditions.

$$H_{T,mix} = \sum_i x_i H_{T,i}$$

$$= 23.7580 + 0.145(H_T^\circ - H_o^\circ)_{CH_4} + 0.855(H_T^\circ - H_o^\circ)_{CO_2} \text{ kJ mol}^{-1}$$

5. The isothermal effect of pressure on enthalpy at 293.15, 313.15, 333.15 and 363.15 K was obtained from the integral $\phi$ data of this work from 0 to 138 bar. For temperatures at 283.15 and 273.15 K, the isothermal effect of pressure on enthalpy was obtained from 0 to 35 bar. The enthalpy departures for this mixture are presented as function of temperature in Figure 16 and comparison is made with values calculated from equations of state. BWR equation with Bishnoi and Robinson[11] mixing rules predicts higher departures, while Soave-Redlich-Kwong[76] equation with the interaction constant $k_{ij}$ from Peng[66] is seen to predict lower departures. BWRS equation with parameters of Hopke and Lin[32] gives better predictions.

6. The isobaric heat capacity data of Bishnoi[9], at 312.86, 333.71, 363.6 and 423.75 K was used to determine the isobaric effect of

temperature on enthalpy. Since enthalpy is a property, changes in enthalpy are independent of the path chosen and the consistency of the experimental data can be tested by making loop checks. A grid consisting of 8 loops which is shown in Figure 34 was constructed and the enthalpy change around each loop evaluated. The actual sum divided by the sum of the absolute values of the enthalpy differences in the loop,

$$\% \text{ deviation} \equiv \frac{\sum\limits_{i} \Delta H_i}{\sum\limits_{i} |\Delta H_i|} \times 100 \qquad (27)$$

provides a good measure of the consistency of the data[8]. The maximum percentage deviation of each loop is less than 0.37 percent and the percentage deviation of each loop is shown in Table XXVII.

Adjustments were made on individual values of $\Delta H_i$ as required to make $\sum\limits_{i} \Delta H_i = 0$ for all loops. These adjustments were made within the limits of precision of the basic data. The accuracy of the heat capacity data is within $\pm 0.5\%$[10]. Error analysis of this work is presented in Appendix A. The accuracy of the isothermal throttling coefficient is within $\pm 1.0\%$. The amount of the adjustments are presented in Figure 34.

7.     A smooth plot of the results was prepared and is shown in Figure 17. The values of enthalpy are given in Table VII.


## Nominal 42.3 Percent Methane in Carbon Dioxide Mixture

A skeleton enthalpy table and a pressure-enthalpy diagram for this mixture have been prepared.
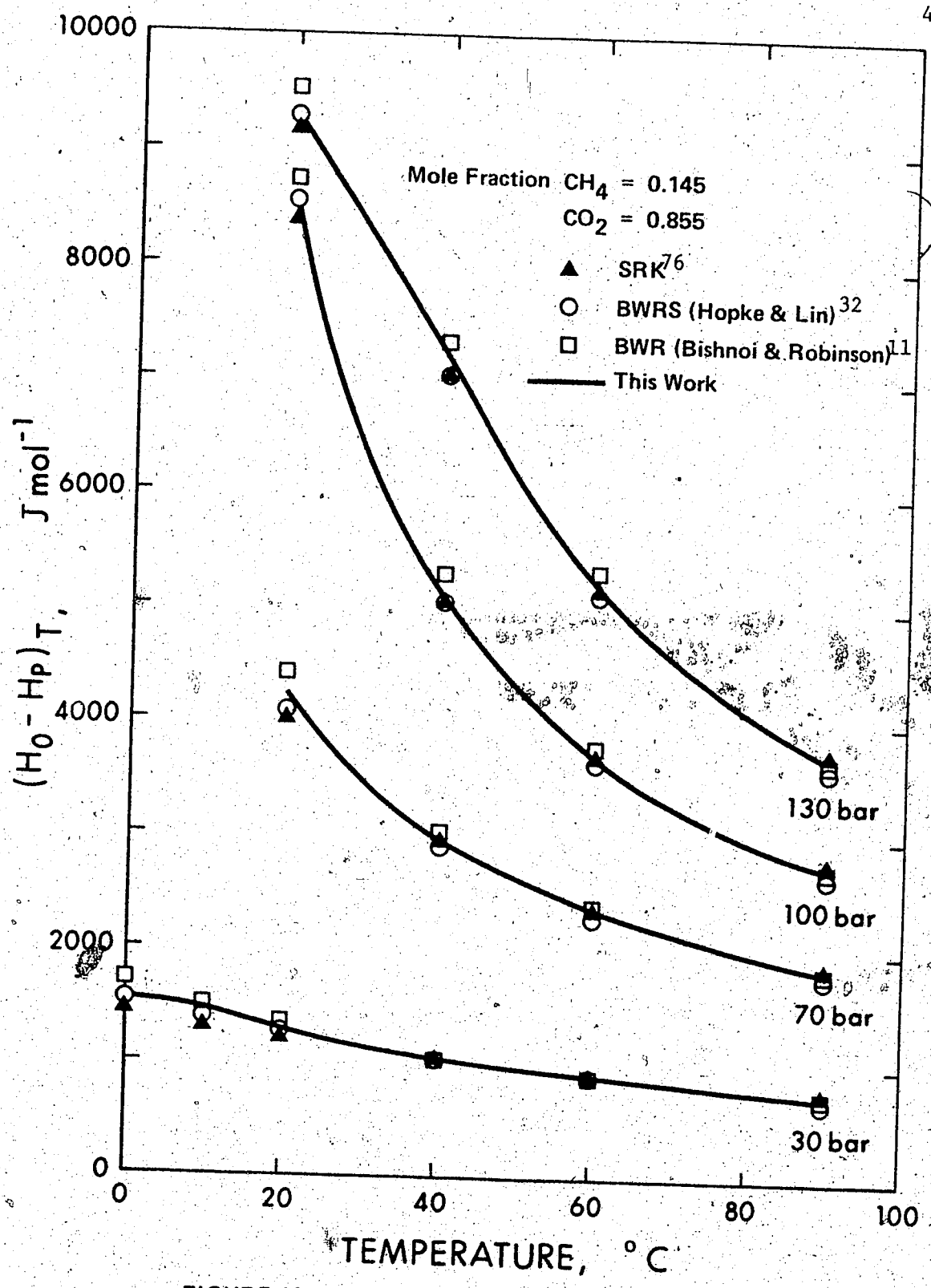
FIGURE 16.  Enthalpy Departures for the 14.5 Percent Mixture

## TABLE VII

### Tabulated Values of Enthalpy for the

### 14.5 Percent of Methane in Carbon Dioxide

Datum: Pure crystal of $CH_4$ + $CO_2$ at 0 K and zero pressure

$H_{P,T} - H_{o,o}^o$ (kJ mol$^{-1}$)

| P bar \ T K | 273.15 | 283.15 | 290 | 293.15 | 300 | 310 | 313.15 | 320 | 330 |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 32.313 | 32.673 | 32.920 | 33.038 | 33.290 | 33.660 | 33.781 | 34.035 | 34.415 |
| 10.00 | 31.865 | 32.245 | 32.505 | 32.645 | 32.915 | 33.320 | 33.435 | 33.725 | 34.120 |
| 20.00 | 31.315 | 31.735 | 32.060 | 32.225 | 32.525 | 32.965 | 33.100 | 33.390 | 33.815 |
| 30.00 | 30.690 | 31.175 | 32.585 | 31.770 | 32.095 | 32.580 | 32.725 | 33.040 | 33.495 |
| 40.00 | 29.800 | 30.545 | 31.060 | 31.255 | 31.625 | 32.170 | 32.325 | 32.675 | 33.155 |
| 50.00 | | 29.550 | 30.445 | 30.655 | 31.100 | 31.720 | 31.895 | 32.280 | 32.805 |
| 60.00 | | | 29.650 | 29.905 | 30.475 | 31.210 | 31.415 | 31.845 | 32.420 |
| 70.00 | | | 28.440 | 28.830 | 29.670 | 30.620 | 30.870 | 31.365 | 32.050 |
| 80.00 | | | 25.790 | 26.850 | 28.510 | 29.910 | 30.230 | 30.830 | 31.555 |
| 90.00 | | | 23.915 | 25.135 | 27.290 | 29.095 | 29.500 | 30.210 | 31.070 |
| 100.00 | | | 23.360 | 24.465 | 26.375 | 28.220 | 28.675 | 29.510 | 30.560 |
| 110.00 | | | | 24.130 | 25.560 | 27.355 | 27.830 | 28.825 | 30.045 |
| 120.00 | | | | 23.915 | 24.975 | 26.660 | 27.115 | 28.200 | 29.525 |
| 130.00 | | | | 23.750 | 24.615 | 26.130 | 26.585 | 27.650 | 29.000 |
| 137.89 | | | | 23.650 | 24.470 | 25.800 | 26.260 | 27.250 | 28.575 |

TABLE VII (continued)

$CH_4$ (14.5%) – $CO_2$

$H_{P,T} - H_{o,o}$ (kJ mol⁻¹)

| P bar \ T K | 333.15 | 340 | 350 | 360 | 363.15 | 370 | 380 | 390 |
|---|---|---|---|---|---|---|---|---|
| 0 | 34.542 | 34.810 | 35.200 | 35.590 | 35.715 | 35.990 | 36.400 | 36.805 |
| 10.00 | 34.260 | 34.530 | 34.945 | 35.355 | 35.480 | 35.770 | 36.190 | 36.620 |
| 20.00 | 33.960 | 34.245 | 34.680 | 35.110 | 35.230 | 35.540 | 35.970 | 36.410 |
| 30.00 | 33.645 | 33.950 | 34.400 | 34.850 | 34.985 | 35.300 | 35.750 | 36.095 |
| 40.00 | 33.310 | 33.645 | 34.110 | 34.580 | 34.725 | 35.050 | 35.515 | 35.970 |
| 50.00 | 32.960 | 33.320 | 33.815 | 34.300 | 34.460 | 34.795 | 35.275 | 35.740 |
| 60.00 | 32.595 | 32.970 | 33.505 | 34.020 | 34.190 | 34.530 | 35.030 | 35.510 |
| 70.00 | 32.205 | 32.605 | 33.180 | 33.725 | 33.895 | 34.265 | 34.780 | 35.280 |
| 80.00 | 31.780 | 32.215 | 32.835 | 33.415 | 33.595 | 33.985 | 34.525 | 35.055 |
| 90.00 | 31.330 | 31.820 | 32.485 | 33.095 | 33.300 | 33.705 | 34.270 | 34.830 |
| 100.00 | 30.850 | 31.410 | 32.120 | 32.770 | 32.980 | 33.415 | 34.015 | 34.610 |
| 110.00 | 30.365 | 30.995 | 31.755 | 32.450 | 32.665 | 33.130 | 33.755 | 34.375 |
| 120.00 | 29.865 | 30.550 | 31.370 | 32.120 | 32.345 | 32.830 | 33.495 | 34.140 |
| 130.00 | 29.360 | 30.090 | 30.975 | 31.780 | 32.025 | 32.530 | 33.230 | 33.900 |
| 137.89 | 28.950 | 29.710 | 30.650 | 31.510 | 31.770 | 32.300 | 33.020 | 33.700 |

TABLE VII (continued)

$$H_{P,T} - H_{o,o} \ (\text{kJ mol}^{-1})$$

| P bar \ T K | 400 | 410 | 420 | 423.15 | 430 |
|---|---|---|---|---|---|
| 0 | 37.220 | 37.620 | 38.030 | 38.173 | 38.440 |
| 10.00 | 37.040 | 37.460 | 37.860 | 38.000 | 38.285 |
| 20.00 | 36.850 | 37.285 | 37.685 | 37.830 | 38.125 |
| 30.00 | 36.655 | 37.095 | 37.515 | 37.660 | 38.125 |
| 40.00 | 36.445 | 36.900 | 37.345 | 37.660 | 37.970 |
| 50.00 | 36.230 | 36.710 | 37.170 | 37.490 | 37.800 |
| 60.00 | 36.020 | 36.510 | 36.995 | 37.320 | 37.625 |
| 70.00 | 35.805 | 36.315 | 36.815 | 37.145 | 37.450 |
| 80.00 | 35.595 | 36.120 | 36.630 | 36.975 | 37.290 |
| 90.00 | 35.390 | 35.930 | 36.450 | 36.800 | 37.115 |
| 100.00 | 35.190 | 35.735 | 36.270 | 36.620 | 36.950 |
| 110.00 | 34.975 | 35.540 | 36.090 | 36.445 | 36.780 |
| 120.00 | 34.755 | 35.335 | 35.910 | 36.270 | 36.610 |
| 130.00 | 34.530 | 35.135 | 35.720 | 36.085 | 36.440 |
| 137.89 | 34.345 | 34.965 | 35.560 | 35.900 | 36.270 |
|  |  |  |  | 35.747 | 36.130 |
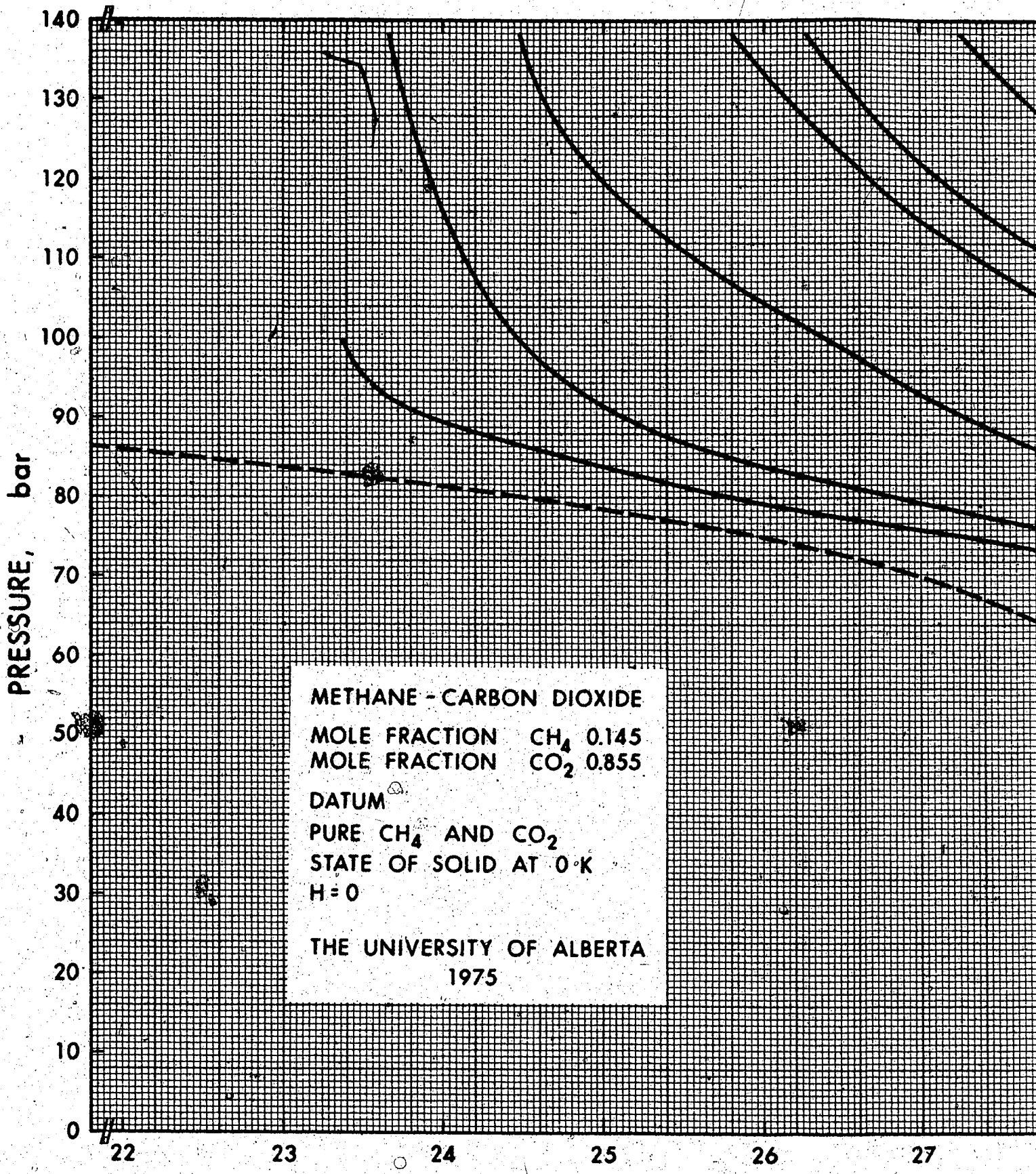
METHANE - CARBON DIOXIDE

MOLE FRACTION  $CH_4$  0.145
MOLE FRACTION  $CO_2$  0.855

DATUM
PURE $CH_4$ AND $CO_2$
STATE OF SOLID AT 0°K
H = 0

THE UNIVERSITY OF ALBERTA
1975
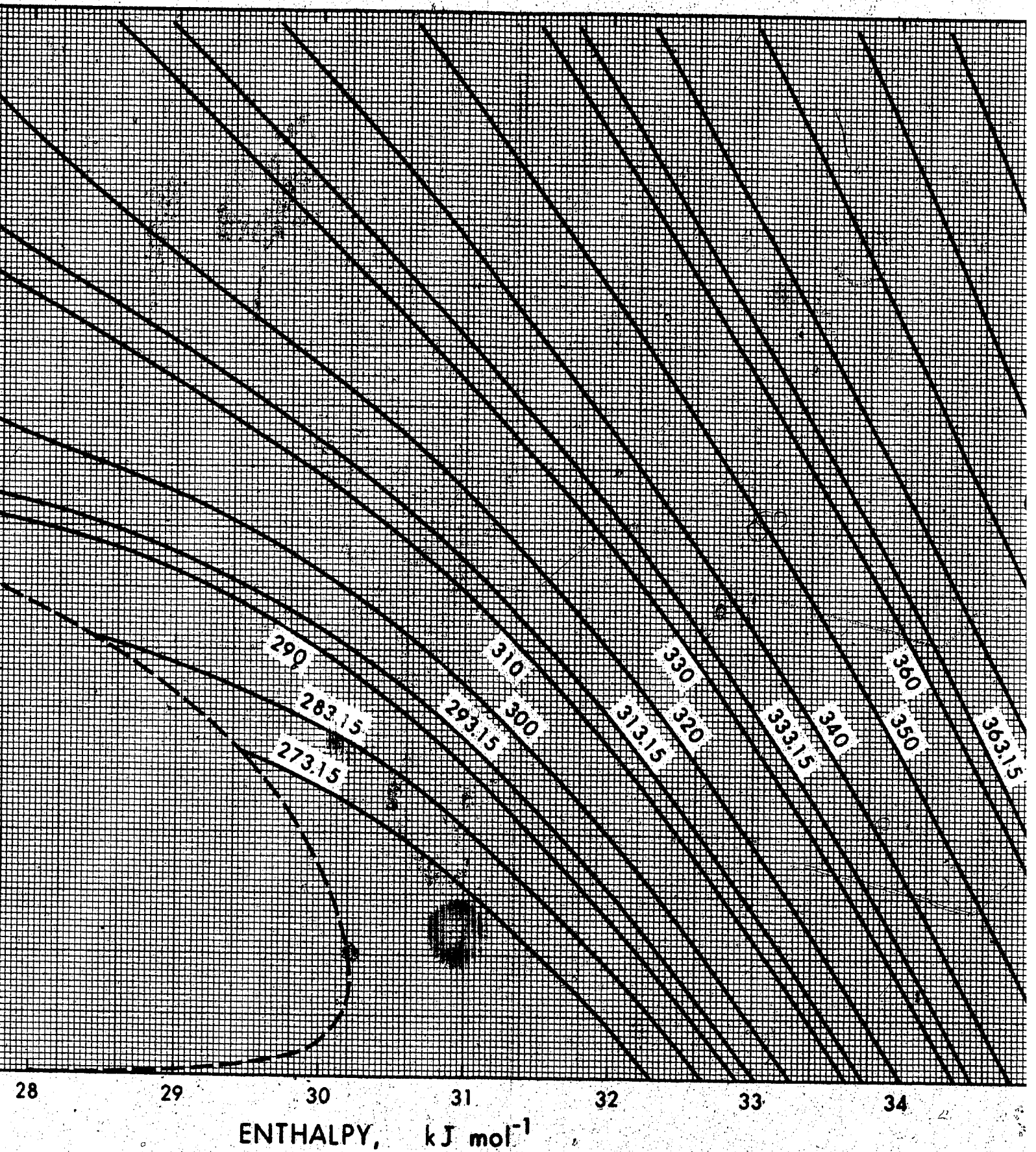
FIGURE 17. Pressure — Temperature — Enthalpy Diagram for 14.5 per cent of Methane in Carbon Dioxide

TEMPERATURE, K

333.15 340 350 360 363.15 370 380 390 400 410 420 423.15 430
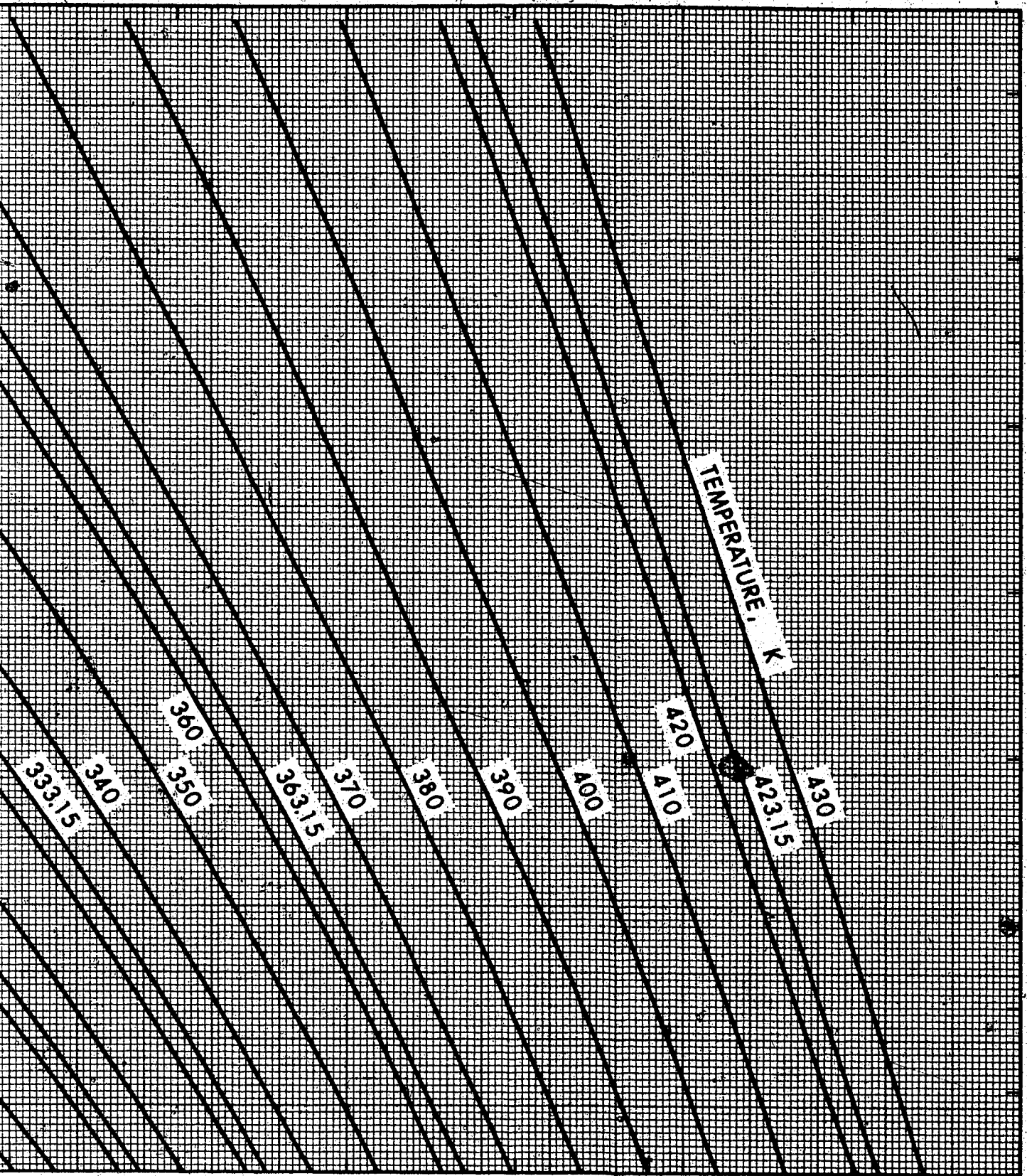
33    34    35    36    37    38    39

Dioxide

3 of 3

The isothermal effect of pressure on enthalpy at 273.15, 313.15 and 333.15K was obtained from the integrated $\phi$ data of this work from 0 to 138 bar.

The isobaric heat capacity data of Bishnoi[9] at 313.07, 33 and 363.45K was used to determine the isobaric effect of temperature on enthalpy.

A grid consisting of 8 loops was constructed and enthalpy change around each loop evaluated. Figure 35 shows the location and enthalpy changes of the loops. In all closure the percentage deviation is less than 0.3 percent and the percentage deviation of each loop is shown in Table XXVIII.

Adjustments were made to make $\Sigma \, \Delta H_i = 0$ for all loops and the amount of adjustment is presented in Figure 35.

A smooth plot of the results was prepared and is shown in Figure 18. The values of enthalpy are given in Table VIII.

## Comparison of Methane - Carbon Dioxide Mixtures Enthalpy Data

The heat of mixing or excess enthalpy for the two mixtures was calculated at various pressures from the data of Table VII and VIII together with the methane data of Din[23] and carbon dioxide data of Vukolovich et al.[85]. The results were compared with the excess enthalpy data of Lee and Mather[45] directly determined using a flow calorimeter. The comparison is shown in Figure 19 and 20. The agreement is generally good.

## TABLE VIII

### Tabulated Values of Enthalpy for the
### 42.3 Percent of Methane in Carbon Dioxide

Datum: Pure crystal of $CH_4$ + $CO_2$ at 0 K and zero pressure

$H_{P,T} - H_{0,0}$ (kJ mol$^{-1}$)

| P bar \ T K | 270 | 273.15 | 280 | 290 | 300 | 310 | 313.15 | 320 |
|---|---|---|---|---|---|---|---|---|
| 0 | 27.665 | 27.776 | 28.015 | 28.375 | 28.735 | 29.110 | 29.227 | 29.490 |
| 10.00 | 27.325 | 27.445 | 27.690 | 28.080 | 28.460 | 28.855 | 28.980 | 29.255 |
| 20.00 | 26.950 | 27.085 | 27.360 | 27.770 | 28.175 | 28.590 | 28.720 | 29.010 |
| 30.00 | 26.545 | 26.690 | 27.000 | 27.445 | 27.885 | 28.315 | 28.450 | 28.750 |
| 40.00 | 26.090 | 26.250 | 26.610 | 27.090 | 27.570 | 28.040 | 28.180 | 28.485 |
| 50.00 | 25.570 | 25.750 | 26.170 | 26.705 | 27.230 | 27.745 | 27.890 | 28.205 |
| 60.00 | 24.965 | 25.180 | 25.675 | 26.290 | 26.875 | 27.430 | 27.590 | 27.930 |
| 70.00 | 24.250 | 24.510 | 25.090 | 25.815 | 26.495 | 27.105 | 27.265 | 27.635 |
| 80.00 | 23.400 | 23.700 | 24.380 | 25.265 | 26.050 | 26.755 | 26.930 | 27.335 |
| 90.00 | 22.480 | 22.820 | 23.610 | 24.700 | 25.550 | 26.400 | 26.595 | 27.030 |
| 100.00 | 21.630 | 22.065 | 22.985 | 24.170 | 25.050 | 26.030 | 26.260 | 26.720 |
| 110.00 | 21.065 | 21.550 | 22.470 | 23.690 | 24.670 | 25.670 | 25.920 | 26.415 |
| 120.00 | 20.770 | 21.195 | 22.070 | 23.280 | 24.360 | 25.325 | 25.595 | 26.105 |
| 130.00 | 20.620 | 20.920 | 21.780 | 22.970 | 24.055 | 24.990 | 25.260 | 25.790 |
| 137.89 | 20.550 | 20.770 | 21.650 | 22.805 | 23.815 | 24.730 | 24.989 | 25.535 |

TABLE VIII(continued)

$CH_4$(42.3%) - $CO_2$

$H_{P,T} - H_{o,o}$ (kJ mol$^{-1}$)

| P bar \ T K | 330 | 333.15 | 340 | 350 | 360 | 363.15 | 370 |
|---|---|---|---|---|---|---|---|
| 0 | 29.875 | 29.980 | 30.255 | 30.645 | 31.025 | 31.142 | 31.405 |
| 10.00 | 29.645 | 29.770 | 30.030 | 30.440 | 30.830 | 30.955 | 31.230 |
| 20.00 | 29.410 | 29.550 | 29.815 | 30.235 | 30.640 | 30.770 | 31.050 |
| 30.00 | 29.175 | 29.320 | 29.600 | 30.025 | 30.445 | 30.580 | 30.880 |
| 40.00 | 28.930 | 29.080 | 29.380 | 29.810 | 30.250 | 30.390 | 30.695 |
| 50.00 | 28.680 | 28.830 | 29.150 | 29.605 | 30.060 | 30.195 | 30.510 |
| 60.00 | 28.420 | 28.575 | 28.910 | 29.395 | 29.870 | 30.005 | 30.330 |
| 70.00 | 28.150 | 28.320 | 28.670 | 29.180 | .565 | 29.805 | 30.145 |
| 80.00 | 27.880 | 28.055 | 28.415 | 28.945 | 29.450 | 29.605 | 29.965 |
| 90.00 | 27.610 | 27.790 | 28.160 | 28.710 | 29.245 | 29.405 | 29.780 |
| 100.00 | 27.345 | 27.530 | 27.915 | 28.485 | 29.040 | 29.210 | 29.590 |
| 110.00 | 27.070 | 27.260 | 27.670 | 28.265 | 28.840 | 29.015 | 29.405 |
| 120.00 | 26.795 | 26.995 | 27.425 | 28.050 | 28.650 | 28.830 | 29.230 |
| 130.00 | 26.515 | 26.730 | 27.180 | 27.830 | 28.450 | 28.640 | 29.050 |
| 137.89 | 26.290 | 26.521 | 26.995 | 27.665 | 28.305 | 28.440 | 28.915 |

METHANE - CARBON DIOXIDE

MOLE FRACTION CH₄ 0.423
MOLE FRACTION CO₂ 0.577

DATUM
PURE CH₄ AND CO₂
STATE OF SOLID AT 0 K
H = 0

THE UNIVERSITY OF ALBERTA
1975
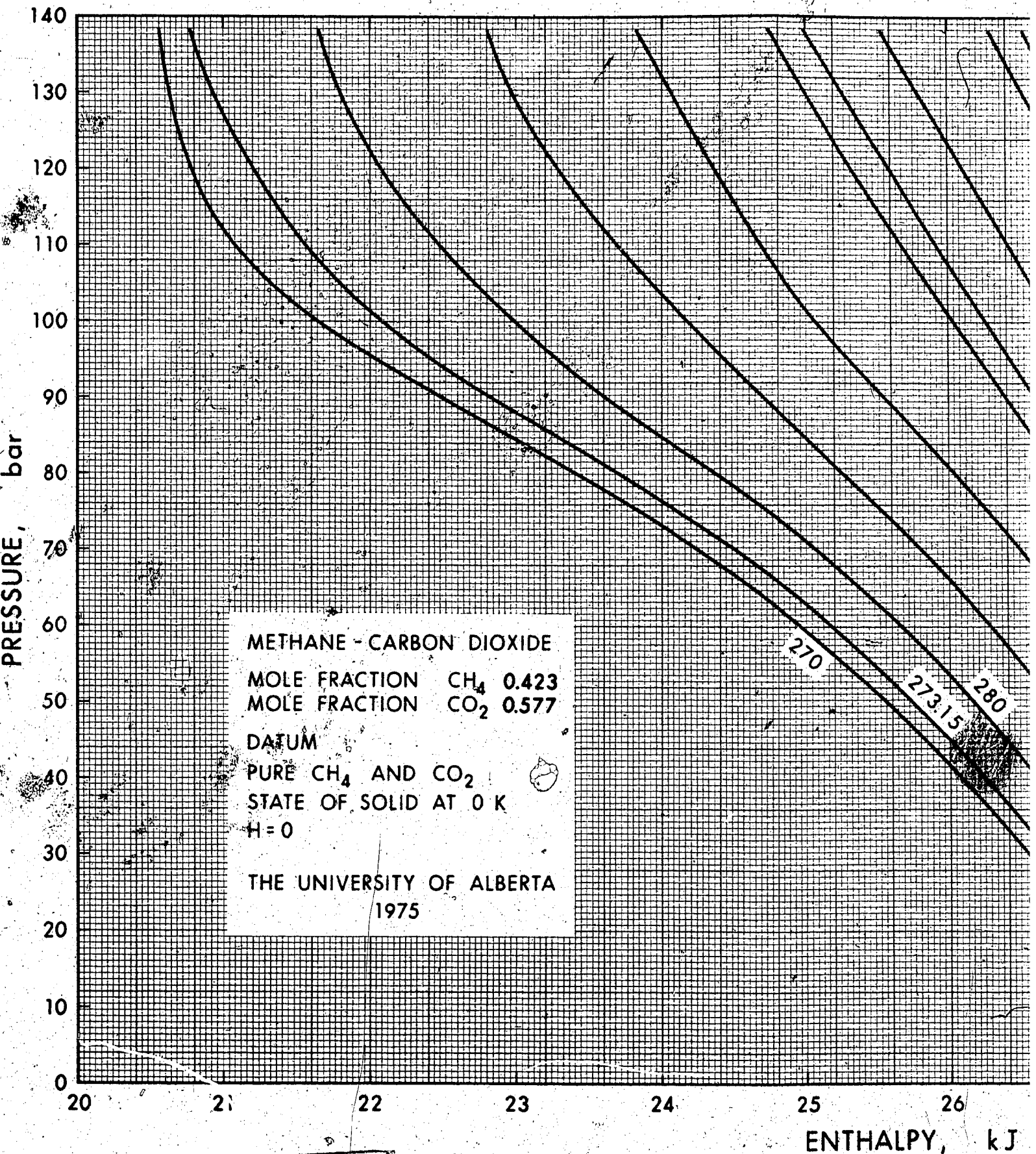
FIGURE 18. Pressure — Temperature — Enthalpy Diagram for 4

PRESSURE, bar

ENTHALPY, kJ

TEMPERATURE, K

280
290
300
310
313.15
320
330
333.15
340
350
360
363.15
370
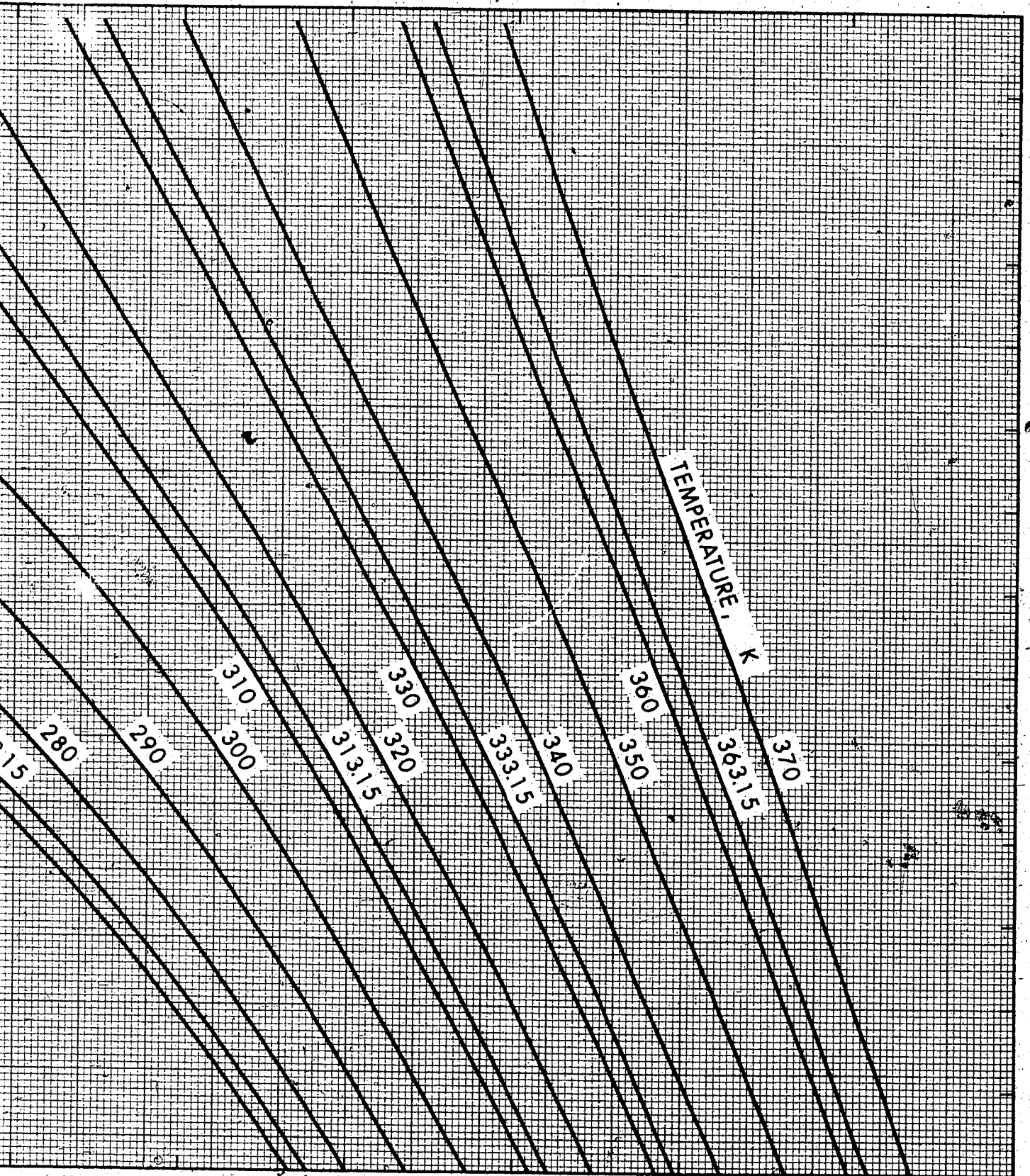
k J mol⁻¹

agram for 42.3 per cent of Methane in Carbon Dioxide
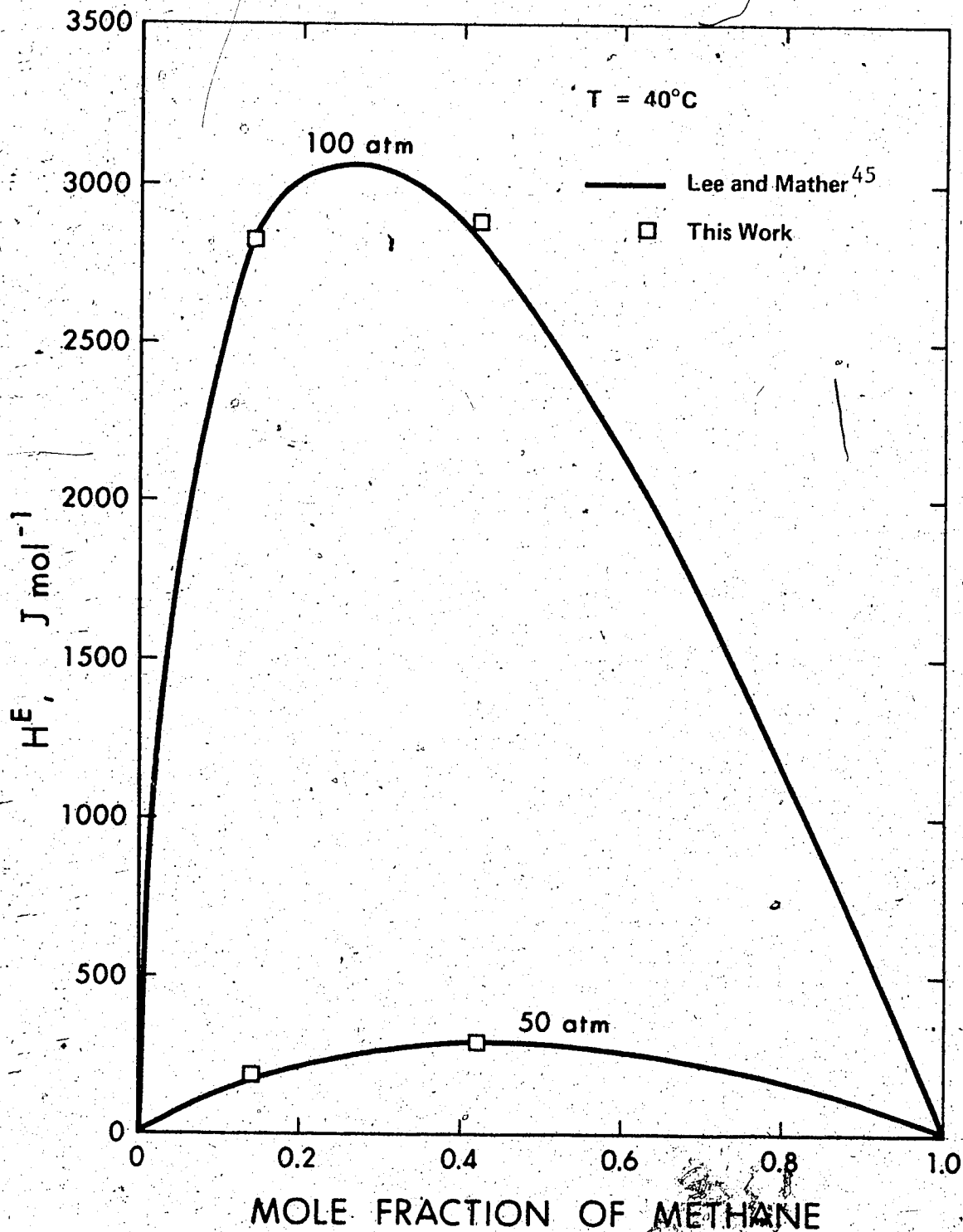
FIGURE 19. Comparison of Excess Enthalpy for Methane — Carbon Dioxide Mixtures
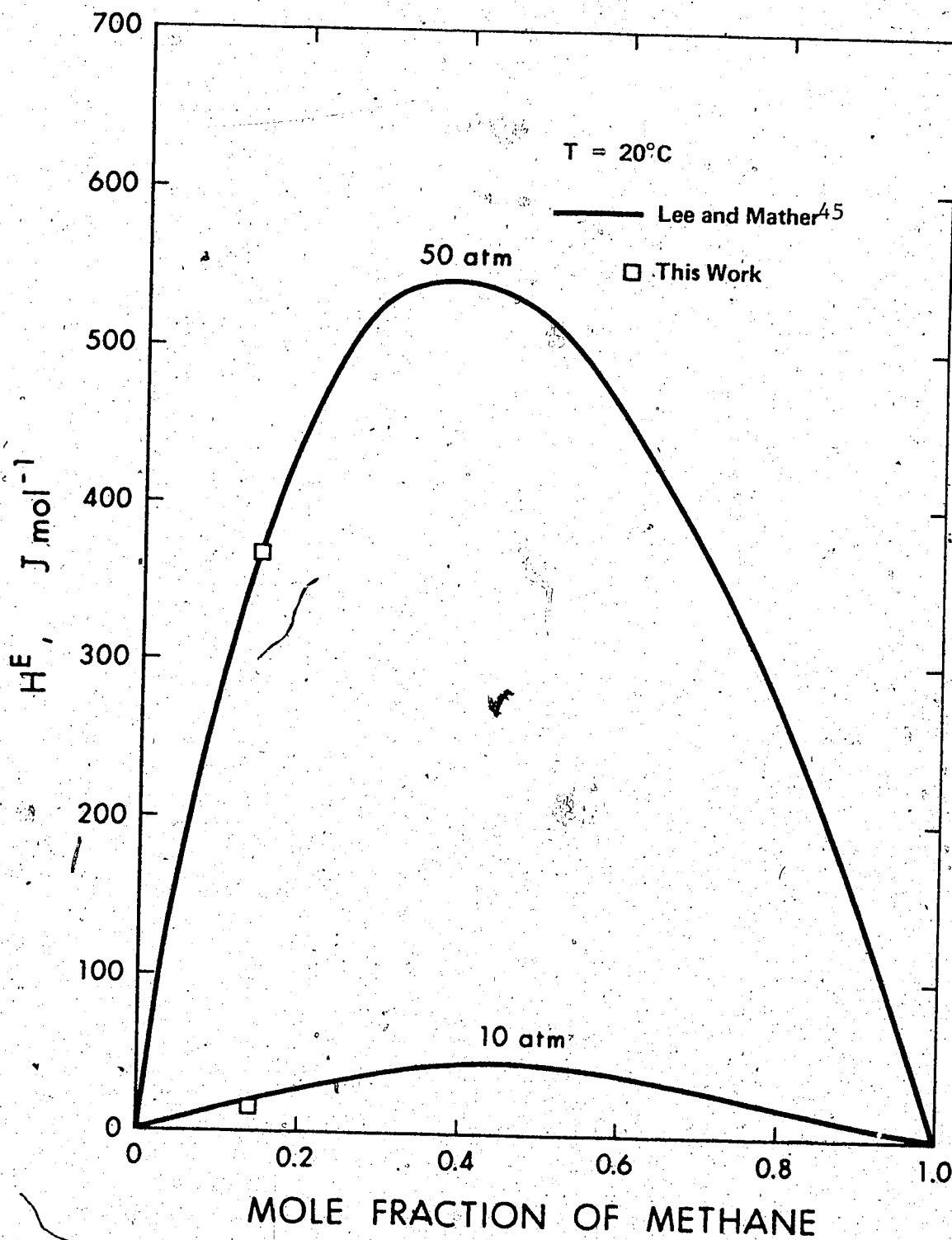
FIGURE 20. Comparison of Excess Enthalpy for Methane — Carbon Dioxide Mixture

## *Experimental Results With Equimolal Methane - Carbon Dioxide - Nitrogen Mixture*

The measurements of the isothermal throttling coefficient were made on an equimolal mixture of methane, carbon dioxide and nitrogen. The pressure range of the measurements was from 300 to 2000 psia and the three temperatures were 10, -10 and -30°C. The composition of the mixture was determined by the gas chromatograph and is given in Table IX.

The smoothed isothermal data is tabulated at Table X and is shown in Figure 21. Values of $\phi$ at zero pressure were calculated from the virial coefficients given by Dymond and Smith[24] and Ng[63]. The calculation of $\phi°$ is shown in Appendix C.

### TABLE IX

Composition of Equimolal Methane -

Carbon Dioxide - Nitrogen Mixture

| Composition | Mole Fraction |
|---|---|
| Methane | 0.333 |
| Nitrogen | 0.333 |
| Carbon dioxide | 0.334 |

## TABLE  X

### ISOTHERMAL THROTTLING COEFFICIENTS FOR
### THE EQUIMOLAL MIXTURE OF $CO_2$ - $CH_4$ - $N_2$

$-\phi$ ($J$ $mol^{-1}$ $bar^{-1}$)

Temperature, °C

| PRESSURE (bar) | 10 | -10 | -30 |
|---|---|---|---|
| 0* | 19.04 | 22.80 | 26.03 |
| 10 | 19.50 | 23.62 | 27.55 |
| 20 | 19.98 | 24.45 | 29.22 |
| 30 | 20.65 | 25.31 | 31.30 |
| 40 | 21.17 | 26.17 | 33.72 |
| 50 | 21.60 | 27.06 | 36.59 |
| 60 | 21.95 | 28.03 | 39.56 |
| 70 | 22.21 | 28.88 | 41.97 |
| 80 | 22.34 | 29.33 | 43.01 |
| 90 | 22.27 | 29.20 | 41.73 |
| 100 | 21.93 | 28.50 | 37.68 |
| 110 | 21.34 | 27.28 | 32.15 |
| 120 | 20.54 | 25.54 | 26.72 |
| 130 | 19.50 | 23.19 | 22.00 |
| 137 | 18.63 | 21.14 | 19.19 |

\* $B - T\frac{dB}{dT}$
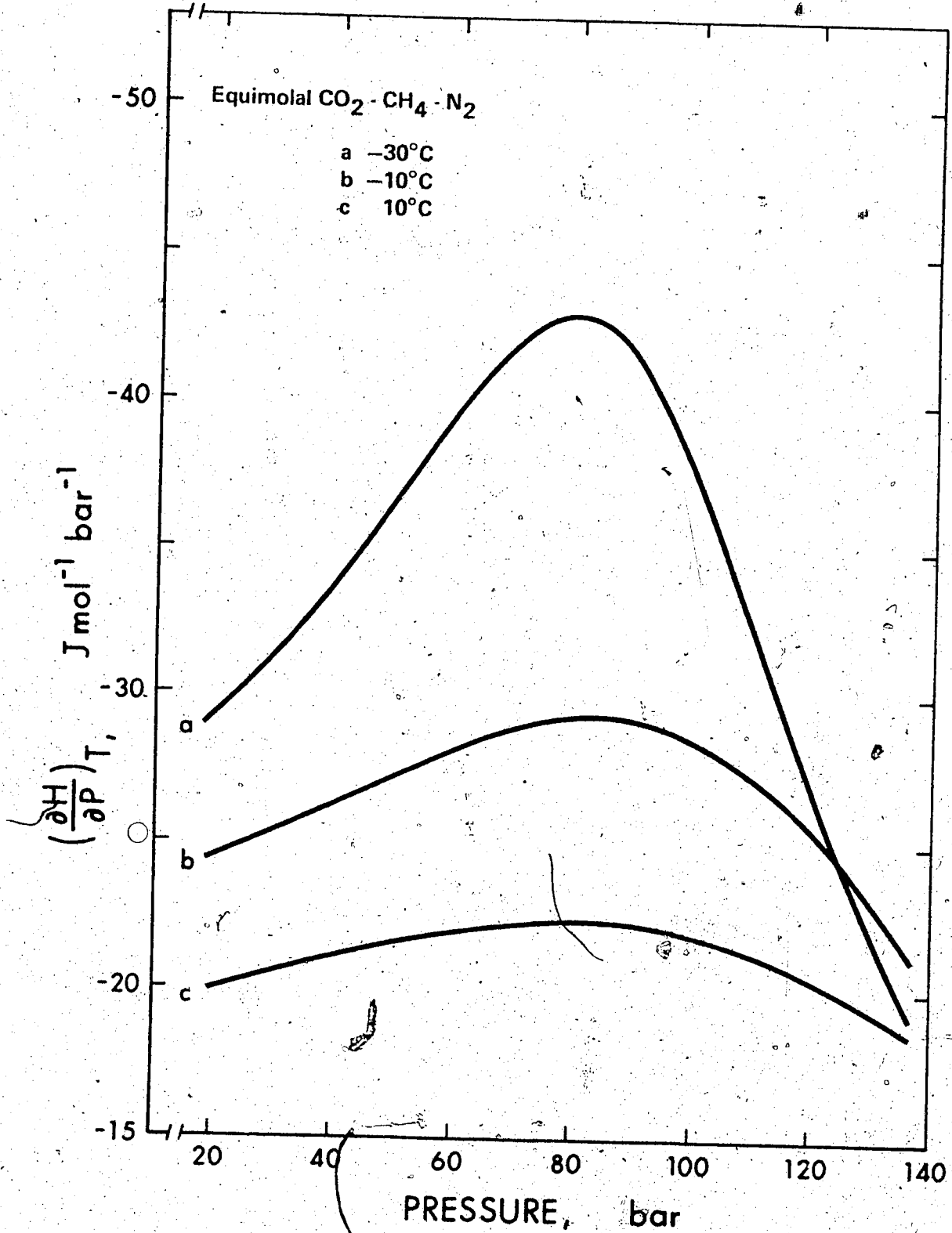
**FIGURE 21.** Isothermal Throttling Coefficient of the Equimolal Mixture of Methane, Carbon Dioxide and Nitrogen

## Comparison of Experimental Results

Isothermal enthalpy departures for the mixture were calculated by integration of isothermal throttling coefficients with respect to pressure. The results were used to study the possibility of predicting ternary or multicomponent mixtures by using the binary experimental data. The experimental binary excess enthalpy data are from Lee and Mather[44,45] for carbon dioxide-methane system and nitrogen-carbon dioxide system. The experimental excess enthalpy data of nitrogen-methane system are from Klein et al.[40] Pure component enthalpy data of nitrogen and methane are from Din[23] and carbon dioxide is from Vukalovich and Altunin[85].

Due to the limitation of the experimental excess enthalpy data available, the comparison is made only on isotherm of 10°C. The enthalpy departure of each equimolal binary system at 10°C and several different pressures was calculated from data of experimental excess enthalpy of the binary system and enthalpy of the pure component by the following relation,

$$\Delta H_{ij} = H_{ij}^E + \frac{1}{2}(H_i + H_j) - \frac{1}{2}(H_i^o + H_j^o) \tag{28}$$

where $\Delta H_{ij}$ is molal enthalpy departure of equimolal mixture of i and j

$H_{ij}^E$ is molal excess enthalpy of equimolal mixture of i and j

$H_i, H_j$ are molal enthalpy of i and j respectively

and $H_i^o, H_j^o$ are molal enthalpy at zero pressure of i and j respectively.

The molal enthalpy departure of the equimolal ternary mixture can be calculated as follows:

$$\Delta H_{m,T,P} = \frac{1}{3}(\Delta H_{12} + \Delta H_{23} + \Delta H_{13})_{T,P} \tag{29}$$

The molal enthalpy departure of the equimolal ternary mixture of methane, carbon dioxide and nitrogen was also calculated by using BWR equation of

state wit' ishnoi and Robinson mixing ules and parameters[11].

The comparison between experimental results of this work and values calculated from binary data is shown in Figure 22. The prediction by BWR uation of state is seen to in excellent agreement with these experimental re ilts. The lack of greement between this experimental data and the values calcul om binary data may be due to not taking account of ternary ii actions.

## Experimental Results With Equimolal Methane - Carbon Dioxide - Ethane Mixture

Data of isothermal throttling coefficients were obtained at six isotherms for the equimolal mixture. The composition of the mixture which was determined by gas chromatograph is given in Table XI. The pressure range was from 250 to 2000 psia and the six isotherms are -10, 0, 20, 40, 60 and 90°C.

TABLE XI

Composition of Equimolal Methane -
Carbon Dioxide - Ethane Mixture

| Composition | Mole Fraction |
|---|---|
| Methane | 0.340 |
| Ethane | 0.325 |
| Carbon dioxide | 0.335 |

The raw experimental data was treated by computer reduction method and the smooth isothermal throttling coefficients are tabulated in
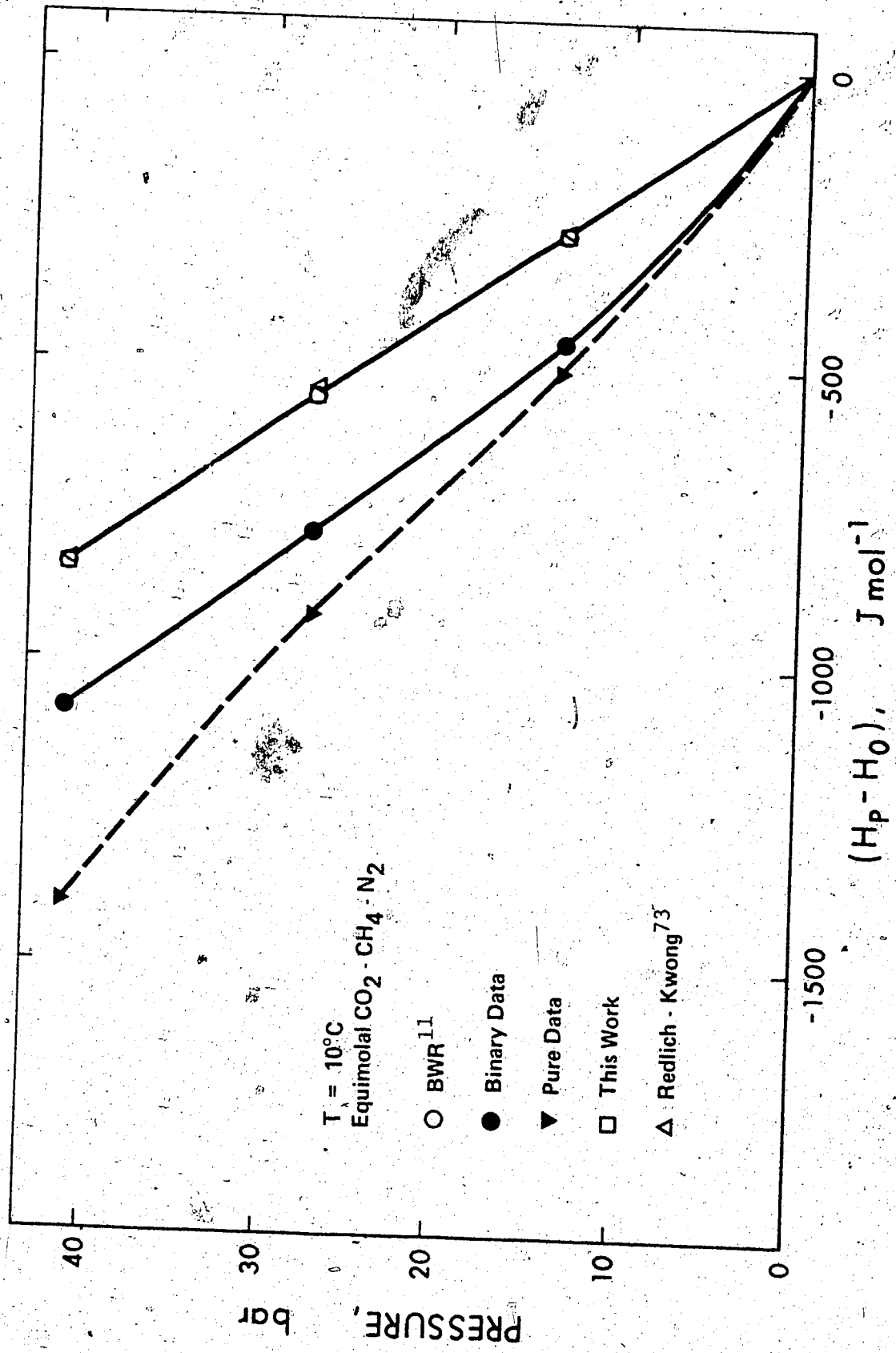
FIGURE 22. Enthalpy Departures for Equimolal Mixture of Methane, Carbon Dioxide and Nitrogen at 10°C

Table XII. The smooth isothermal throttling coefficient at constant temperature is plotted as function of pressure and it is shown in Figure 23. The zero pressure isothermal throttling coefficients were determined from second virial coefficient[20,24,27,31,63,101] by using Equation (14). The calculation of $\phi°$ is shown in Appendix C.

## Comparison of Results

Peterson and Wilson reported isothermal enthalpy departure from 20 to 2000 psia for this mixture at temperature from -50°F to 300°F. Enthalpy departures were calculated from the experimental isothermal throttling data which are listed in Table XII by integration with respect to pressure. The values obtained were plotted as function of temperature at constant pressure. Figure 24 shows the comparison between experimental data of Peterson and Wilson[68] and this work. The agreement is seen to be very good.

## Experimental Results with 50 Percent Methane in Carbon Dioxide and Ethane Mixture

Isothermal throttling coefficient determinations of this mixture were obtained in the gaseous region at temperatures from -10 to 90°C, at pressure from 250 to 2000 psia. The composition of this mixture was determined by gas chromatograph and the compositions are given in Table XIII.

## TABLE XII

### ISOTHERMAL THROTTLING COEFFICIENTS FOR THE

### EQUIMOLAL $CO_2$ - $CH_4$ - $C_2H_6$ MIXTURE

$-\phi$ (J mol$^{-1}$ bar$^{-1}$)

| PRESSURE (bar) | Temperature, °C | | | | | |
|---|---|---|---|---|---|---|
| | -10.0 | 0 | 20 | 40 | 60 | 90 |
| 0* | 41.80 | 40.20 | 34.60 | 30.40 | 26.80 | 22.60 |
| 10 | 46.83 | 42.87 | 36.39 | 31.39 | 27.55 | 22.92 |
| 20 | 52.83 | 47.40 | 38.99 | 32.96 | 28.46 | 23.41 |
| 30 | 63.32 | 54.16 | 42.18 | 34.74 | 29.55 | 23.93 |
| 38 | 77.29 | – | – | – | – | – |
| 40 | – | 64.55 | 46.22 | 36.66 | 30.67 | 24.42 |
| 50 | – | 80.96 | 51.50 | 39.01 | 31.82 | 24.86 |
| 60 | – | 114.5 | 58.09 | 41.64 | 32.97 | 25.25 |
| 70 | – | 142.2 | 65.04 | 44.16 | 34.06 | 25.59 |
| 80 | – | 99.01 | 70.61 | 46.13 | 34.91 | 25.83 |
| 90 | – | 48.30 | 70.55 | 47.17 | 35.34 | 25.90 |
| 100 | – | 29.57 | 60.75 | 46.76 | 35.19 | 25.77 |
| 110 | – | 19.19 | 46.50 | 44.34 | 34.46 | 25.43 |
| 120 | – | 14.30 | 34.92 | 39.75 | 33.29 | 24.89 |
| 130 | – | 10.94 | 26.25 | 34.36 | 31.38 | 24.15 |
| 137 | – | 8.86 | 21.67 | 30.83 | 29.31 | 23.52 |

* $B - T\frac{dB}{dT}$

**Equimolal $CO_2$ - $CH_4$ - $C_2H_6$**

a   0°C
b   20°C
c   40°C
d   60°C
e   90°C
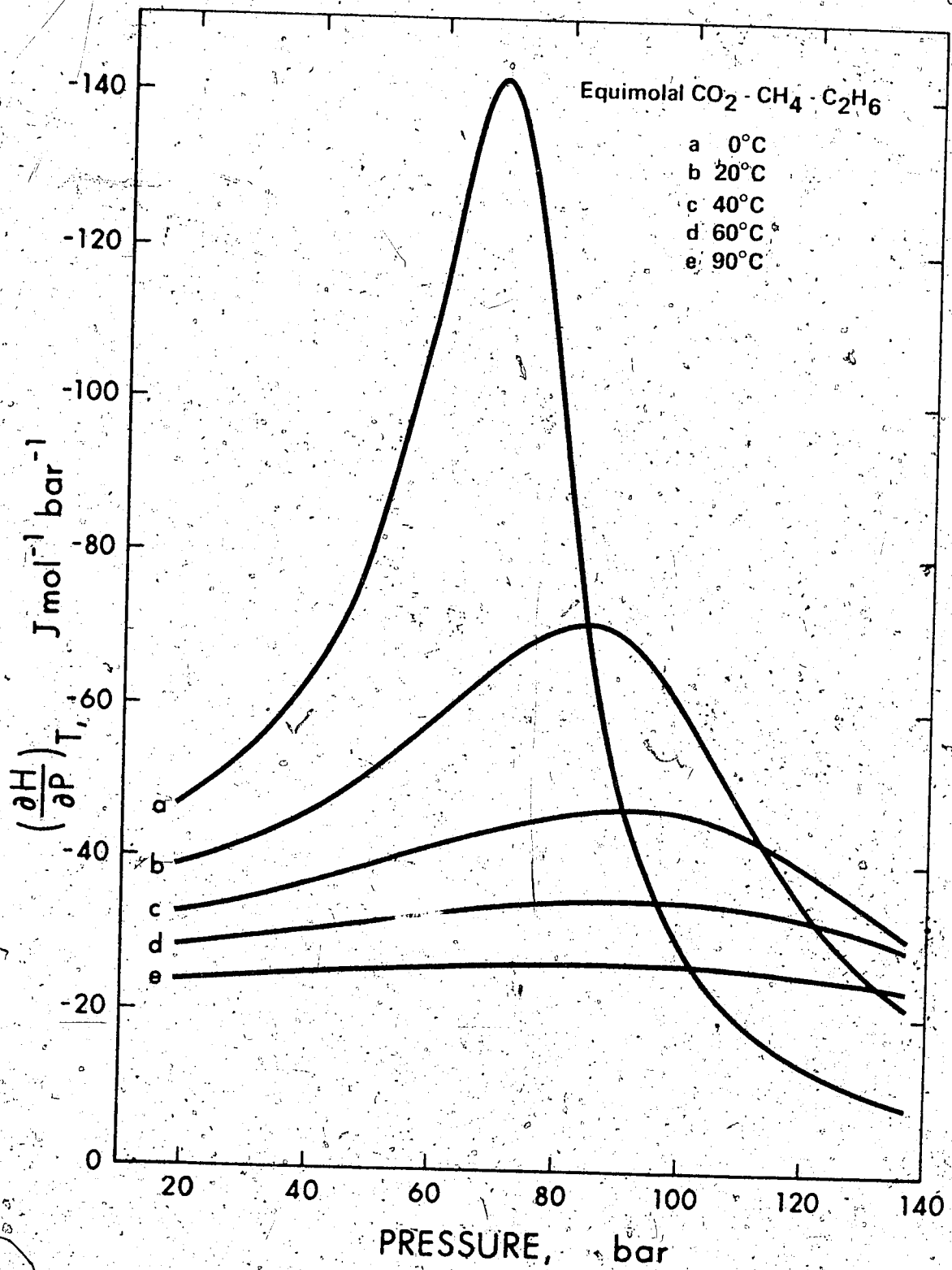
FIGURE 23.   Isothermal Throttling Coefficient for the Equimolal Mixture of Methane, Carbon Dioxide and Ethane
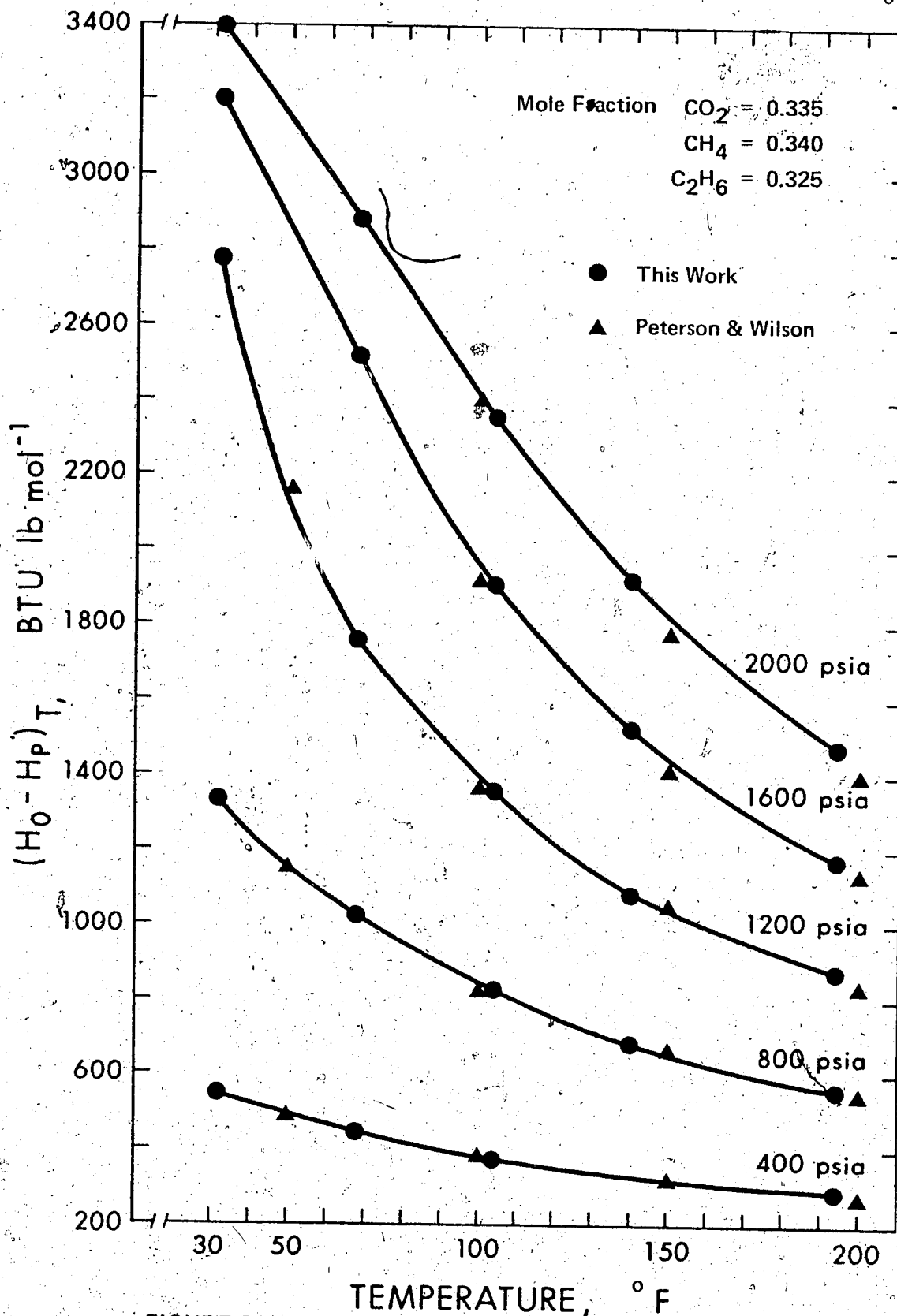
FIGURE 24. Enthalpy Departures for the Equimolal Mixture of Methane, Carbon Dioxide and Ethane

## TABLE XIII

Composition of 50 Percent Methane in Carbon

Dioxide and Ethane Mixture

| Composition | Mole Fraction |
|---|---|
| Methane | 0.514 |
| Ethane | 0.242 |
| Carbon Dioxide | 0.244 |

Isothermal throttling coefficients derived from the experimental data by computer reduction method are tabulated in Table XIV. A plot of the isothermal throttling coefficient at constant pressure as a function of temperature is shown in Figure 25.

### Experimental Results with Equimolal Methane – Carbon Dioxide – Nitrogen – Ethane Mixture

Isothermal throttling coefficient determinations of this mixture were obtained in the gaseous region at temperatures from -30 to 60°C, at pressure from 250 to 2000 psia. The composition of this mixture was determined by the gas chromatograph and the compositions are given in Table XV.

## TABLE XIV

## ISOTHERMAL THROTTLING COEFFICIENTS FOR THE

## 50 PERCENT $CH_4$ IN $CO_2$ - $C_2H_6$ MIXTURE

$-\phi$ ($J$ $mol^{-1}$ $bar^{-1}$)

| | Temperature, °C | | | | | |
|---|---|---|---|---|---|---|
| PRESSURE (bar) | -10 | 0 | 20 | 40 | 60 | 90 |
| 0* | 36.20 | 32.80 | 28.80 | 25.20 | 22.30 | 18.68 |
| 10 | 38.62 | 35.15 | 30.25 | 26.18 | 22.86 | 19.12 |
| 20 | 41.83 | 37.85 | 31.67 | 27.21 | 23.52 | 19.39 |
| 30 | 46.46 | 41.24 | 33.26 | 28.11 | 24.10 | 19.67 |
| 40 | 53.62 | 45.52 | 35.31 | 29.09 | 24.66 | 19.95 |
| 50 | 64.00 | 51.01 | 37.77 | 30.13 | 25.20 | 20.21 |
| 60 | 79.37 | 58.01 | 40.32 | 31.18 | 25.71 | 20.40 |
| 70 | 94.67 | 66.39 | 42.60 | 32.12 | 26.14 | 20.49 |
| 80 | 90.73 | 70.53 | 44.28 | 32.80 | 26.43 | 20.48 |
| 90 | 61.32 | 64.61 | 44.89 | 33.09 | 26.51 | 20.37 |
| 100 | 37.81 | 52.58 | 43.74 | 32.85 | 26.32 | 20.19 |
| 110 | 26.03 | 39.36 | 40.45 | 31.96 | 25.86 | 19.95 |
| 12 | 18.30 | 27.82 | 35.70 | 30.34 | 25.12 | 19.62 |
| 130 | 13.35 | 20.13 | 30.33 | 28.15 | 24.05 | 19.14 |
| 137 | 11.45 | 17.41 | 26.67 | 26.47 | 23.08 | 18.68 |

\* $B - T\dfrac{dB}{dT}$
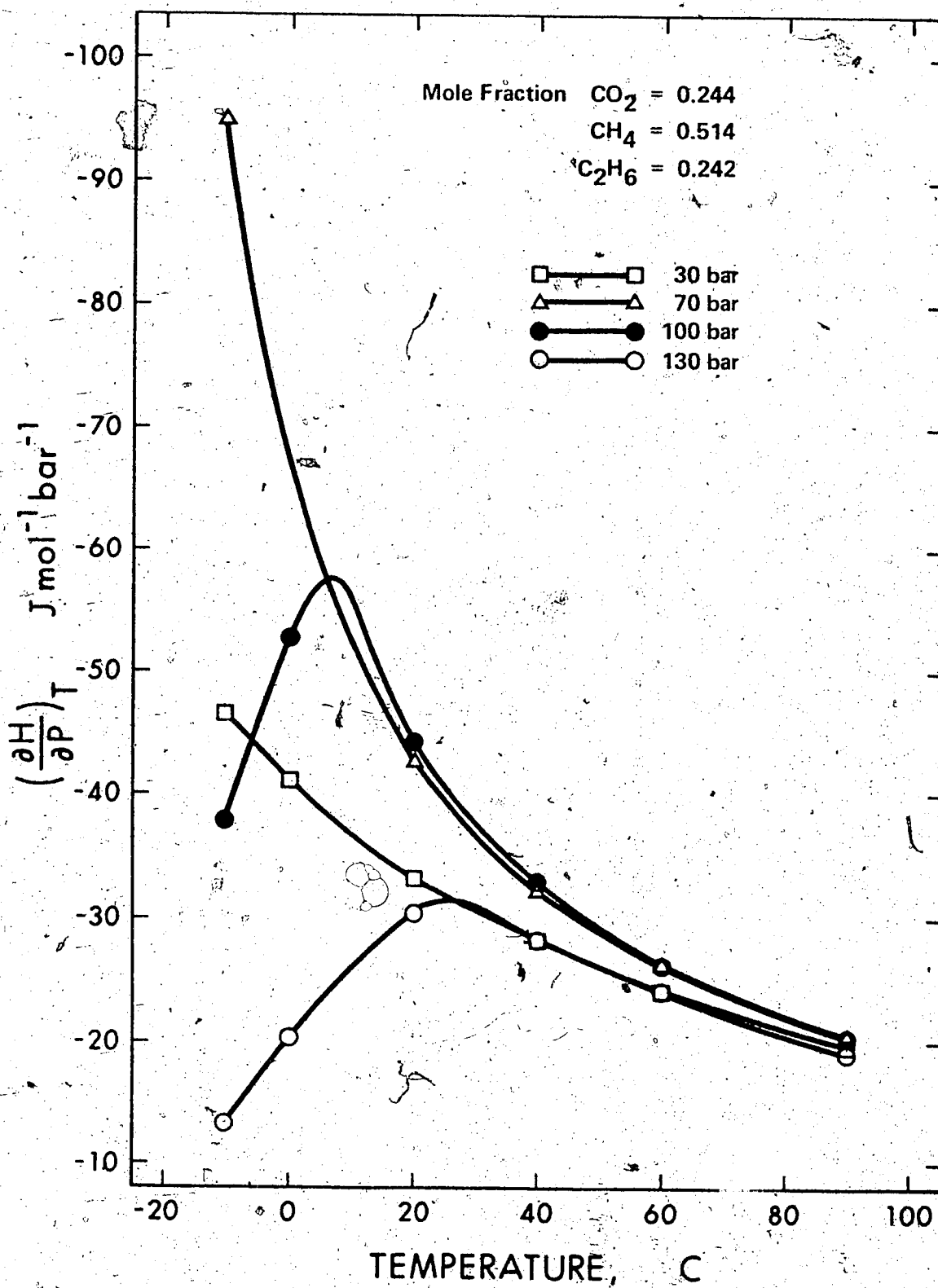
FIGURE 25. Isothermal Throttling Coefficient for the 50 Percent Mixture
of Methane in Carbon Dioxide and Ethane

## TABLE XV

### Composition of Equimolal Methane – Carbon

### Dioxide – Nitrogen – Ethane Mixture

| Composition | Mole Fraction |
|---|---|
| Methane | 0.2535 |
| Carbon Dioxide | 0.2555 |
| Ethane | 0.2365 |
| Nitrogen | 0.2545 |

Smooth isothermal throttling coefficient of this mixture by this experiment are tabulated at Table XVI. A plot of the isothermal throttling coefficients at constant temperature as function of pressure is shown in Figure 26. Zero pressure isothermal throttling coefficients were calculated from second virial coefficients [20,24,27,31,64,70,101] by Equation (14) and the calculation of $\phi^\circ$ is shown in Appendix C.

## TABLE XVI

### ISOTHERMAL THROTTLING COEFFICIENTS FOR THE

### EQUIMOLAL $CO_2 - CH_4 - N_2 - C_2H_6$ MIXTURE

$$-\phi \; (J \; mol^{-1} \; bar^{-1})$$

| PRESSURE (bar) | Temperature,°C | | | | |
|---|---|---|---|---|---|
| | -30 | -10 | 10 | 30 | 60 |
| 0* | 35.90 | 31.40 | 27.20 | 23.60 | 19.50 |
| 10 | 38.00 | 32.50 | 27.96 | 24.08 | 19.62 |
| 20 | 43.52 | 34.40 | 28.92 | 24.78 | 19.87 |
| 27 | 47.50 | | | | |
| 30 | – | 37.47 | 30.29 | 25.47 | 20.12 |
| 40 | – | 41.35 | 31.81 | 26.26 | 20.43 |
| 50 | – | 45.46 | 33.38 | 26.93 | 20.70 |
| 60 | – | 49.27 | 34.90 | 27.47 | 20.84 |
| 70 | – | 52.03 | 36.13 | 27.91 | 20.88 |
| 80 | – | 52.72 | 36.73 | 28.07 | 20.80 |
| 90 | – | 50.28 | 36.41 | 28.07 | 20.60 |
| 93 | 35.77 | – | – | – | – |
| 100 | 27.77 | 43.96 | 35.08 | 27.51 | 20.28 |
| 110 | 19.47 | 35.30 | 32.75 | 26.54 | 19.85 |
| 120 | 14.34 | 26.88 | 29.50 | 25.25 | 19.29 |
| 130 | 11.05 | 21.19 | 25.86 | 23.69 | 18.54 |
| 137 | 9.39 | 19.42 | 23.55 | 22.13 | 17.88 |

$$^* \quad B - T\frac{dB}{dT}$$
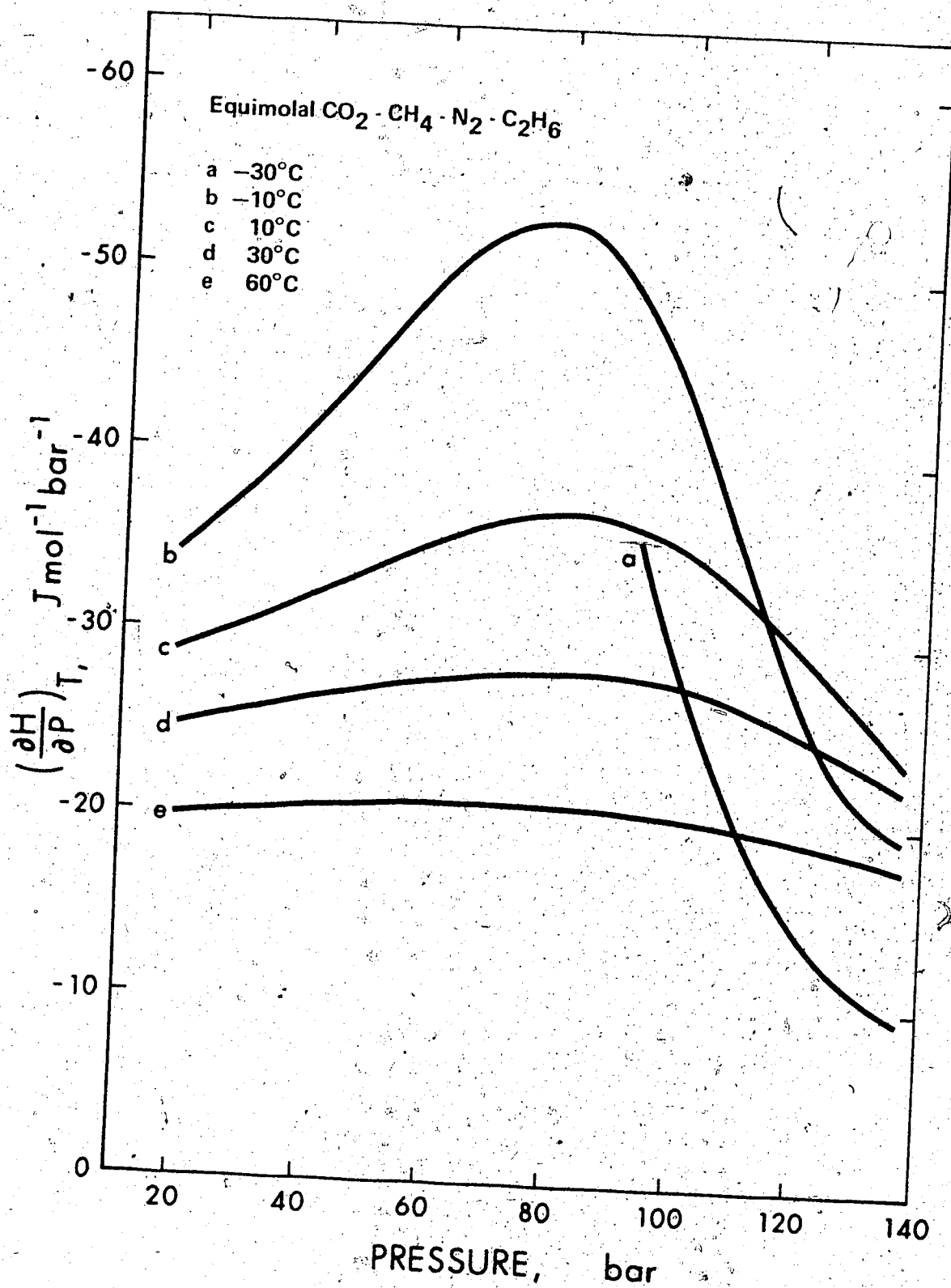
FIGURE 26. Isothermal Throttling Coefficient for the Equimolal Mixture of Methane, Carbon Dioxide, Nitrogen and Ethane

*SECTION IV - EVALUATION AND EXTENSION OF METHODS OF PREDICTION*

This section presents a review of the methods of prediction of thermodynamic properties and particularly enthalpy of mixtures. Two new methods are proposed for the enthalpy prediction.

To calculate the thermodynamic properties of a fluid or fluid mixture from a knowledge of molecular parameters by directly solving the equations of statistical mechanics, requires very detailed mathematical calculations as well as knowledge of the interactions between many particles. For this reason, no satisfactory solution has been achieved for all regions of enthalpy prediction. Statistical mechanics has been applied with some success in this endeavor especially with respect to the behavior of gases containing relatively simple molecules.

Although advances have been made in the area of predicting macroscopic properties, it appears that for some time to come less sophisticated methods of prediction must play an important role. To obtain quantitative representation of thermodynamic properties, assumptions are required which make use of experimental data and certain parameters or functional forms having no direct fundamental significance. These approaches and other methods developed from correlating thermodynamic data will be discussed.

## Method of Prediction Based on Thermodynamic Data

A recent review of the available methods of prediction of enthalpies of fluid mixture at elevated pressure was made by Nathan[62], Mather[57] and Yesavage[97]. The main groups into which the methods can be divided are:

1. Estimation of partial enthalpies

2. Equivalent pure component method

3. Application of PVT data

4. Application of equations of state

5. Generalized corresponding states correlations

1. _Estimation of Partial Enthalpies_

The enthalpy per mole of a mixture, $\underline{H}_m$, can be determined exactly from a knowledge of the partial molal enthalpies of the individual components $\overline{H}_i$, by application of the expression

$$\underline{H}_m = \sum_i x_i \overline{H}_i$$

(30)

The partial molal enthalpy of a component is generally a function of composition. For gases at zero pressure, the assumption that the enthalpy of a component in a mixture is the same as the enthalpy of the pure component is an accurate one. Therefore Equation (30) can be applied rigorously to establish the enthalpy of gaseous mixtures at zero pressure. In general, however, partial molal data are not abundant, and therefore, several methods of estimation have been suggested.

Very often the assumption is made that since hydrocarbons in a homologous series, are chemically similar, their solutions are ideal. Hence to compute a mixture properties, the sum of the property of each of the pure components (at the same temperature and total pressure) is taken in proportion to the quantity of the components present. This assumption may give good results at moderate pressures and relatively high temperatures. However, extreme care must be taken when applying this procedure since as Mather[57] has shown extreme values of the heat of mixing do exist, especially in critical regions. Charts for the pure

component enthalpies are given by Maxwell[60], Peters[67] and Scheibel and Jenny[75]. A difficulty arises in using these charts because it is not always possible to obtain the enthalpy data for the pure component for the conditions of temperature and pressure under which the mixture exists. Peters has derived auxiliary curves for estimation of partial enthalpies under those conditions and Maxwell used an extension of the vapor pressure curve for the partial enthalpy of a low-boiling component in a liquid mixture. In general, the plots presented by Peters were limited to a temperature range between -260 to +420°F at pressure up to 600 psia. Similarily, Maxwell's plots extend between -200 and +200°F at pressure below 150 atm.

A major drawback of this method is the fact that an enthalpy diagram must be available for every component present in a mixture.

## 2. *Equivalent Pure Component Method*

Several methods have been developed in which a new parameter is introduced to allow for the effect of composition. The data are usually presented as a series of enthalpy-temperature plots, there being a separate one for each pressure, with lines of this constant parameter. The forms that this parameter takes are most commonly the molal average boiling point, the average molecular weight or the mixture specific gravity.

Scheibel and Jenny[75] presented monographs based on the average molecular weight of a hydrocarbon mixture.

Papadopoulos et al.[65] showed that the molal average boiling point of a mixture defined as

$$M.A.B.P. = \sum_i x_i (B.P.)_i$$

(31)

where the $(B.P.)_i$ are the pure component boiling points, for lighter hydrocarbons served to correlate values of a partial molal enthalpies calculated from an equation of state. At the same time Canjar and Edmister[13] employed the same correlation using the fugacity coefficients, employing a numerical technique for differentiation, and derived partial molal enthalpies for lighter hydrocarbons. Canjar and Peterka[14] prepared plots of the isothermal enthalpy departure as a function of temperature at pressure for mixtures with different molal average boiling points. The plots of Canjar and Peterka are restricted to the temperature range -200 to 500°F at pressures below 1500 psia for mixtures with molal average boiling points from -270 to 190°F.

3. *Application of P-V-T Data*

Accurate P-V-T data can be used to calculate the effect of pressure on enthalpy of fluids and fluid mixtures. If the volumetric data are available, the enthalpy can be calculated by use of the relation,

$$\underline{H}(T,P) = \underline{H}(T,0) + \int_0^P [\underline{V} - T(\frac{\partial V}{\partial T})_P]dP_T \tag{32}$$

where $\underline{H}(T,0)$, the enthalpy at zero pressure, can be determined for most simple fluids. This is evaluated from ideal gas enthalpies of pure fluids either from statistical mechanics or from measured data. The ideal mixture enthalpy is determined by applying Equation (30).

The term in brackets of Equation (32) under the integral sign involves the difference between two terms, one of which includes a derivative. As a result, extremely accurate volumetric data are required to yield reliable estimates of the effect of pressure on enthalpy. A reduction of accuracy of one order of magnitude is to be expected.

Volumetric data for mixtures of the required accuracy are available but very rare.

### 4. *Application of Equation of State*

A large number of equations of state have been proposed but only a few have been used for extensive calculations of enthalpies. In general, most equations of state serve to relate pressure P as the dependent variable to temperature, T, and specific volume $\underline{V}$ as independent variables. As a result, it is convenient to transform Equation (32) to,

$$\underline{H}(T,\infty) - \underline{H}(T,\underline{V}) = RT - P\underline{V} + \int_{\infty}^{\underline{V}} [P - T(\frac{\partial P}{\partial T})_{\underline{V}}]d\underline{V}_T \qquad (33)$$

The virial equation of state has a sound theoretical foundation and is free of arbitrary assumptions. The relations between virial coefficients and intermolecular potential functions can be derived from statistical mechanics and the composition dependence of the coefficients is known exactly. This equation is restricted to vapors since the power series relation tends to diverge at densities approaching those of liquids.

Relatively simple equations like the Redlich-Kwong[73] equation of state have been used for enthalpy predictions. Several modifications had been attempted to improve the prediction, such as those by Wilson[91], Soave[76] and Chaudron, Asselineau and Renon[17]. More complex equations such as the Benedict-Webb-Rubin[6] and Martin-Hou[56] have also been used to predict thermodynamic properties, including enthalpy. New mixing rules which were proposed by Bishnoi and Robinson[11] for the BWR parameters are claimed to improve the accuracy of such predictions. The modification of BWR equation by Starling[32,50,77,78] is claimed to improve the prediction, especially at lower temperature regions. Other modifications of BWR type

of equations of state, such as that Bender[7] and McCarty[53] have also been proposed. Recently parameters for BWR[7,9,32,50,53,77] have been determined by multiproperties regressing on volumetric data, vapor pressure data, enthalpy and k-value data. This ensures thermodynamic consistency of all type of data.

Unfortunately neither accurate thermodynamic data nor parameters for equation of state such as BWR which need large amounts of experimental data are available for many components.

## 5. _Generalized Corresponding States Correlations_

Recently reviews of the application of the corresponding states principle have been presented by Stiel[81] and Leland and Chappelear[47]. These methods are based on the theory of corresponding states first put forward by van der Waals[62] in which he stated that all pure gases would have the same compressibility factor when measured at the same (reduced condition of) temperature and pressure. The law of corresponding states can be stated mathematically

$$\psi_i(T_{R_i}, P_{R_i}) = \psi_j(T_{R_j} = T_{R_i}, P_{R_j} = P_{R_i}) \tag{34}$$

where the symbols $\psi_i$, and $\psi_j$ represent corresponding dimensionless group properties of two fluids "i" and "j" given as function of their respective reduced temperature $T_{R_i} = T_i/T_{C_i}$ and reduced pressure $P_{R_i} = P_i/P_{C_i}$.

This statement of principle has become known as Two-Parameter Law of corresponding state because one must have knowledge of the two parameters ($T_C$ and $P_C$) in order to apply it and must assume that there are only two adjustable parameters in the intermolecular potential in order to derive it from statistical mechanics.

Lydersen, Greenkorn and Hougen (LGH)[51] correlated the
thermodynamic properties of pure compounds based on a modified correspond-
ing principle. This principle states that pure compound with the
same critical compressibility $Z_C$ values, the dimensionless groups of
properties of two pure compounds have the same numerical values at
corresponding reduced condition. The correlation of LGH has the form

$$\frac{\underline{H}(T,0) - \underline{H}(T,P)}{T_C} = [\frac{\underline{H}^0 - \underline{H}}{T_C}] + (Z_C - 0.27)[D] \tag{35}$$

where the bracketed terms are presented as generalized functions in
tabular form by the authors. The condition covered include $P_R \leq 30$ for
$0.5 \leq T_R \leq 15$. Yen and Alexander[95] and Yen and Garcia-Rangel[96] improved
the correlation of the isothermal effects on enthalpies for pure compounds
with the aid of reliable literature data.

Pitzer et al.[19] employed the acentric factor $\omega$, which is related
to the shape of the reduced vapor pressure curve as the third parameter.
The correlation of Curl and Pitzer[19] is given in the form,

$$\frac{\underline{H}(T,0) - \underline{H}(T,P)}{RT_C} = \left[\frac{\underline{H}^0 - \underline{H}}{RT_C}\right]^{(0)} + \omega\left[\frac{\underline{H}^0 - \underline{H}}{RT_C}\right]^{(1)} \tag{36}$$

where the bracketed terms are somewhat different generalized function
presented in tabular form by the authors. These tables cover the range
of pressure for $P_R \leq 9$ for $0.8 \leq T_R \leq 4$. Revision of the original
correlations which incorporated enthalpy data at elevated pressure in
addition to PVT data have been presented recently (Yarborough[94]). Chao
and Greenkorn[15] recently extended the Curl and Pitzer correlation tempera-

ture range down to $T_R = 0.35$. The extended enthalpy correlation was obtained upon differentiation of the generalized fugacity function pre....sly developed by Chao et al.[16] and upon combining with calorimetric data in the literature.

Leach and Leland[42,43] extended the two parameter law of corresponding states to include fluids which have structural dissimilarity. Molecular shape factors were introduced which modified the critical temperature and critical volume of fluids whose molecular structures were dissimilar to those of a fluid for which thermodynamic data were available.

Molecular shape factors ($\theta_{ij}$ and $\nu_{ij}$) of a fluid "i" relative to fluid "j" are defined mathematically by equations

$$Z_i = Z_j \tag{37}$$

$$\left(\frac{\Delta H}{RT_C}\right)_i = \left(\frac{\Delta H}{RT_C}\right)_j \tag{38}$$

at corresponding modified reduced conditions,

$$\frac{T_i}{\theta_{ij} T_{C_i}} = \frac{T_j}{T_{C_j}} \tag{39}$$

$$\frac{V_i}{\nu_{ij} V_{C_i}} = \frac{V_j}{V_{C_j}} \tag{40}$$

where Z is the compressibility factor of the two fluids.

In general, the molecular shape factors of a fluid are functions of its temperature, density and intermolecular parameters. Leach[43] correlated the shape factor for isomeric and paraffin hydrocarbon using

methane as a reference. Watson and Rowlinson[90] and Gunning and Rowlinson[29] used the same correlation for non-hydrocarbon systems. The molecular shape factor can be extended to predict thermodynamic properties of the mixtures. The mixing rules have been suggested by Leach[43].

## Application of Generalized Corresponding States Correlations to Mixtures

In applying the above correlation to mixtures, it is assumed that the reduced functions for a mixture behave in the same manner as those for a pure component. It is necessary to establish values of the three parameters for mixture. The concept of pseudocritical properties was first suggested by Kay[38]. The suggested linear form are:

$$T_{C_m} = \sum_i x_i T_{C_i} \tag{41}$$

$$P_{C_m} = \sum_i x_i P_{C_i} \tag{42}$$

and

$$\omega_m = \sum_i x_i \omega_i \tag{43}$$

There are several other mixing rules which have been proposed in the literature. The procedure and the original background of the derivation of the mixing rules is presented.

### i) Method of Pitzer and Hultgren[69]

Pitzer and Hultgren had extended the three parameter acentric factor corresponding state theory to binary gas mixtures, using the pseudocritical concept. By studying the experimental volumetric data,

it was found that simple quadratic formulas could be used to represent the composition dependence of the three pseudoproperties of each mixture. Applied to the multicomponent mixture, the equations of the mixing rule are:

$$T_{C_m} = \sum_i \sum_j x_i x_j T_{C_{ij}}$$  (44)

$$P_{C_m} = \sum_i \sum_j x_i x_j P_{C_{ij}}$$  (45)

$$\omega_m = \sum_i \sum_j x_i x_j \omega_{ij}$$  (46)

The constants $T_{C_{ij}}$, $P_{C_{ij}}$ and $\omega_{ij}$ $(i \neq j)$, must be evaluated from data on binary mixtures. These mixing rules reduces to Kay's rules when the constants $T_{C_{ij}}$, $P_{C_{ij}}$ and $\omega_{ij}$ are taken as arithmetric average of the pure constants.

ii) *Method of Joffe-Stewart, Burkhardt and Voo*[34, 35, 82]

The equations of the mixing rules are given as,

$$T_{C_m} = \frac{K^2}{J}$$  (47)

$$P_{C_m} = \frac{T_{C_m}^2}{J}$$  (48)

$$K^2 = \frac{T_{C_m}^2}{P_{C_m}} = \left[ \sum_i y_i \left( \frac{T_{C_i}}{P_{C_i}^{1/2}} \right) \right]^2$$  (49)

$$J = \frac{T_{C_m}}{P_{C_m}} = \frac{1}{8} \sum_i \sum_j y_i y_j \left[ \left( \frac{T_{C_i}}{P_{C_i}} \right)^{1/3} + \left( \frac{T_{C_i}}{P_{C_j}} \right)^{1/3} \right]^3$$  (50)

These rules were originally suggested by the mixing rules for the constants

in van der Waals equation. where,

$$a_m = \sum_i y_i a_i \tag{51}$$

$$b_m = \sum_i \sum_j y_i y_j b_{ij} \tag{52}$$

Since the van der Waals equation is a two parameter equation, the strict development is limited to mutually conformal substances. However, the rules can be applied to other mixtures by assuming a linear variation in the third parameter.

## iii) *Method of Leland and Mueller*[46]

The problem of defining pseudocritical values for a multicomponent phase is analogous to the problem of writing the virial coefficients for the pure components. The second virial coefficient for an m-component mixture is related to the pure component virials by:

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{53}$$

Leland and Mueller obtained the mixing rules by equating terms of a second virial coefficient expression for mixtures with those of a pure component and making appropriate simplifying assumptions. The pseudocritical constants are given as

$$T_{C_m} = \left[ \frac{\sum_i \sum_j y_i y_j \left(\frac{Z_C T_C^{\alpha+1}}{P_C}\right)_i^{1/\alpha} \left(\frac{Z_C T_C^{\alpha+1}}{P_C}\right)_j^{1/\alpha}}{\sum_i \sum_j y_i y_j \left[\frac{1}{2}\left(\frac{Z_C T_C}{P_C}\right)_i^{1/3} + \frac{1}{2}\left(\frac{Z_C T_C}{P_C}\right)_j^{1/3}\right]^3} \right]^{1/\alpha} \tag{54}$$

$$P_{C_m} = \cfrac{T_{C_m} \sum_i y_i Z_{C_i}}{\sum_i \sum_j y_i y_j \left[\frac{1}{2}\left(\frac{Z_C T_C}{P_C}\right)_i^{1/3} + \frac{1}{2}\left(\frac{Z_C T_C}{P_C}\right)_j^{1/3}\right]^3} \tag{55}$$

where $\alpha$ is a function of

$$\frac{T \sum_i y_i P_{C_i}}{P \sum_i y_i T_{C_i}}$$

and is tabulated by the authors. The pseudocritical constant obtained by this method is not only function of components of mixture but also function of temperature and pressure. Again the third parameter is assumed to be linear variation for the mixture.

### iv) *Method of Prausnitz and Gunn*[71]

The mixing rules of Prausnitz and Gunn are also suggested from relations for the second virial coefficient of conformal substances. These rules are given as:

$$T_{C_m} = \frac{\beta + \sqrt{\beta^2 + r V_{C_m} \gamma}}{2s V_{C_m}} \tag{56}$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \tag{57}$$

$$P_{C_m} = \frac{R T_{C_m}}{V_{C_m}} \sum_i y_i Z_{C_i} \tag{58}$$

$$\omega_m = \sum_i y_i \omega_i \tag{59}$$

where $Z_{C_i}$ can be obtained from

$$Z_{C_i} = 0.291 - 0.08 \, \omega_i \tag{60}$$

The quantities $\beta$ and $\gamma$ are computed,

$$\beta = \sum_i \sum_j y_i y_j \, (T_C V_C)_{ij} \tag{61}$$

$$\gamma = \sum_i \sum_j y_i y_j \, (V_C T_C^2)_{ij} \tag{62}$$

where

$$T_{C_{ij}} = (T_{C_i} T_{C_j})^{1/2} - \Delta T_{C_{ij}} \tag{63}$$

$$V_{C_{ij}} = \frac{1}{2}(V_{C_i} + V_{C_j}) - \Delta V_{C_{ij}} \tag{64}$$

where the $\Delta$ terms are small correction terms depending on the nature of the binary pairs. The quantities $r$ and $s$ are functions of $T_R$ and $\omega$ tabulated by the authors.

Prausnitz and Gunn also recommended the following simplified rules,

$$\omega_m = \sum_i y_i \omega_i \tag{59}$$

$$T_{C_m} = \sum_i y_i T_{C_i} \tag{41}$$

$$P_{C_m} = \frac{RT_{C_m}}{\sum\limits_{i} y_i V_{C_i}} \sum\limits_{i} y_i Z_{C_i} \tag{65}$$

where again $Z_{C_i}$ is given by Equation (60).

v) *Method of Barner and Quinlan*[5]

Barner and Quinlan suggested the mixing rules based on a modified form of Redlich-Kwong equation of state (Chueh and Prausnitz[18]). The mixing rules for the two constants of the equation of state is given by Joffe and Zudkevitch[36] as,

$$a_m = \sum\limits_{i} \sum\limits_{j} y_i y_j a_{ij} \tag{66}$$

$$b_m = \sum\limits_{i} \sum\limits_{j} y_i y_j b_{ij} \tag{52}$$

The suggested pseudocritical constant of the mixture is given by

$$T_{C_m} = \sum\limits_{i} \sum\limits_{j} y_i y_j T_{C_{ij}} \tag{44}$$

$$V_{C_m} = \sum\limits_{i} \sum\limits_{j} y_i y_j V_{C_{ij}} \tag{67}$$

$$\omega_m = \sum\limits_{i} y_i \omega_i \tag{59}$$

$$Z_C = 0.291 - 0.08\,\omega \tag{60}$$

$$P_{C_m} = \frac{RZ_{C_m} T_{C_m}}{V_{C_m}} \tag{68}$$

where

$$T_{C_{ij}} = (T_{C_i} + T_{C_j})(K_{ij}/2)$$

(69)

$$V_{C_{ij}} = [\ldots]^{/3}]^3$$

(70)

The interaction constants $K_{ij}$ are tabulated by the authors. $K_{ij}$ have been generalized as a function of $\ldots/V_{C_j}$ and are also given by the authors.

### vi) *Modified Method of Gunn*

Gunn[28] developed a corresponding states theory for fluid mixture. The pseudocritical temperature is obtained by using generalized equation for second virial coefficient of Curl and Pitzer[70] and the mixing rule for second virial coefficient.

$$B_m = \sum_i \sum_j y_i y_j B_{ij}$$

(53)

$$B_{R_m} = \frac{B_m}{V_{C_m}} = B_{R_m}^{(0)} + \omega_m B_{R_m}^{(1)}$$

(71)

The rigorous expression for the scaling temperature is obtained by equating Equation (53) and (71).

$$V_{C_m}[B_{R_m}^{(0)}(\frac{T}{T_{C_m}}) + \omega_m B_{R_m}^{(1)}(\frac{T}{T_{C_m}})] = \sum_i \sum_j [B_{R_{ij}}^{(0)}(\frac{T}{T_{C_{ij}}}) + \omega_{ij} B_{R_{ij}}^{(1)}(\frac{T}{T_{C_{ij}}})]V_{C_{ij}}$$

(72)

where

$$\omega_m = [\sum_i \sum_j y_i y_j V_{C_{ij}} \omega_{ij}] V_{C_m}^{-1}$$

(73)

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}}$$

(67)

A new correlation of second virial coefficient of both polar and non-polar system presented by Tsonopoulos[84] replaced that of Curl and Pitzer[70]. The new correlation for non-polar system is given by,

$$\frac{BP_C}{RT_C} = f^{(0)}\left(\frac{T}{T_C}\right) + \omega f^{(1)}\left(\frac{T}{T_C}\right) \tag{74}$$

where

$$f^{(0)}\left(\frac{T}{T_C}\right) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8} \tag{75}$$

$$f^{(1)}\left(\frac{T}{T_C}\right) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \tag{76}$$

Replace Equation (71) by (74),

$$B_m = \left(\frac{RT_{C_m}}{P_{C_m}}\right)\left[f^{(0)}\left(\frac{T}{T_{C_m}}\right) + \omega_m f^{(1)}\left(\frac{T}{T_{C_{ij}}}\right)\right]$$

$$= \sum_i \sum_j y_i y_j \left[\frac{RT_{C_{ij}}}{P_{C_{ij}}}\right]\left[f^{(0)}\left(\frac{T}{T_{C_{ij}}}\right) + \omega_{ij} f^{(1)}\left(\frac{T}{T_{C_{ij}}}\right)\right] \tag{77}$$

where

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \tag{78}$$

$$V_{C_{ij}} = \frac{1}{8}(V_{C_i}^{1/3} + \tag{70}$$

$$T_{C_{ij}} = (T_{C_i} T_{C_j})^{1/2}(1 - k_{ij}) \tag{79}$$

$$P_{C_{ij}} = \frac{T_{C_{ij}} \; [(\frac{P_C V_C}{T_C})_i + (\frac{P_C V_C}{T_C})_i]}{2V_{C_{ij}}} \qquad (80)$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \qquad (67)$$

$$Z_{C_m} = 0.291 - 0.08 \, \omega_m \qquad (60)$$

$$\omega_m = [\sum_i \sum_j y_i y_j V_{C_{ij}} \omega_{ij}]/V_{C_m} \qquad (73)$$

$$P_{C_m} = Z_{C_m} RT_{C_m}/V_{C_m} \qquad (68)$$

The interaction constant $k_{ij}$ is given by Prausnitz[72] or by fitting the experimental $B_{ij}$ with Equation (74). The pseudocritical constant $T_{C_m}$ and $P_{C_m}$ is obtained by solving Equation (77) and (68) simultaneously.

vii) _Proposed Method (Soave-Redlich-Kwong Equation of State)_

A modified Redlich-Kwong equation of state has been proposed by Soave[76]. The parameter a in the original equation is suggested to be temperature dependent. The modified equation is,

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)} \qquad (81)$$

where

$$a_i(T) = a_{C_i} \alpha_i(T) \qquad (82)$$

$$a_{C_i} = 0.42747 \frac{R^2 T_{C_i}^2}{P_{C_i}} \tag{83}$$

$$b_i = 0.08664 \frac{RT_{C_i}}{P_{C_i}} \tag{84}$$

$$\alpha_i(T) = 1 + m_i[1 - (\frac{T}{T_{C_i}})^{0.5}]^{0.5} \tag{85}$$

$$m_i = 0.480 + 1.574\,\omega_i - 0.176\,\omega_i^2 \tag{86}$$

Applying the equation of state to the mixture, the mixing rules for the two parameters are.

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \tag{66}$$

$$b_m = \sum_i y_i b_i \tag{87}$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \tag{88}$$

where $k_{ij}$ is an empirical correlation factor to be determined from the experimental vapor-liquid equilibrium data, for each binary component present in the mixture. Generalization of $k_{ij}$ has been attempted[66].

Starting by substituting Equation (82), (84) and (88) into Equation (66) and (87) respectively,

$$\alpha_m(\frac{T}{T_{C_m}})\frac{T_{C_m}^2}{P_{C_m}} = \sum_i \sum_j y_i y_j \left[ \frac{\alpha^{1/2}(\frac{T}{T_{C_i}})\alpha^{1/2}(\frac{T}{T_{C_j}})T_{C_i} T_{C_j}(1-k_{ij})}{P_{C_i}^{1/2} P_{C_j}^{1/2}} \right] \tag{89}$$

$$\frac{T_{C_m}}{P_{C_m}} = \sum_i y_i \frac{T_{C_i}}{P_{C_i}} \tag{90}$$

From Equation (90) to Equation (89),

$$\alpha_m T_{C_m} = \frac{\displaystyle\sum_i \sum_j y_i y_j \left[\frac{\alpha_i^{1/2} \alpha_j^{1/2} T_{C_i} T_{C_j} (1-k_{ij})}{P_{C_i}^{1/2} P_{C_j}^{1/2}}\right]}{\displaystyle\sum_i y_i \frac{T_{C_i}}{P_{C_i}}} \tag{91}$$

$$P_{C_m} = \frac{\dfrac{T_{C_m}}{\displaystyle\sum_i y_i \frac{T_{C_i}}{P_{C_i}}}}{} \tag{92}$$

$T_{C_m}$ and $P_{C_m}$ are obtained by solving Equation (91) and (92) simultaneously.
Here the linear variation for $\omega_m$ is assumed.

## Evaluation of Nine Enthalpy Correlations

The nine correlations evaluated and compared in this study are shown in Table XVII. Six of the correlations used corresponding states method of Curl and Pitzer[19] with six different mixing rules and three of the correlations used equations of state. The following six mixing rules for mixtures which have been discussed above to estimate the pseudo-critical parameters for the Curl and Pitzer generalized correlation are: 1) method of Barner and Quinlan, 2) proposed method (Soave-Redlich-Kwong equation of state), 3) modified method of Gunn, 4) method of Prausnitz and Gunn, 5) method of Joffe-Stewart, Burkhardt and Voo, and 6) method of Leland and Mueller. The equation of state correlations are Starling-BWR[32,77], Soave-Redlich-Kwong[76] equation and Mark V[92] correlation.

In this study, the Curl and Pitzer[19] generalized correlation tables for enthalpy departure and the extended correlation temperature range of Chao and Greenkorn[15] were used. The linear interpolation, performed by computer was utilized in the calculation of the enthalpy departure.

Presented in Table XVIII are the data sources, number of data point, and temperature and pressure regions of the data for the sixteen fluid compositions studied in this evaluation.

Presented in Table XIX for each correlation are the average absolute deviations between predicted enthalpy departures and experimental enthalpy departures for each of the sixteen fluid compositions used in this study. The overall average absolute deviation for the total data points is given for each correlation in Table XIX. It is to be noted that the BWRS yields the lowest average absolute deviations. Results

TABLE XVII

## CORRELATIONS EVALUATED IN THIS STUDY

| Correlation | Abbreviation | Developers | References |
|---|---|---|---|
| Starling-BWR | BWRS | Starling | 32, 77, 79 |
| Soave-Redlich-Kwong | SRK | Soave | 76 |
| Mark V | Mark V | Wilson | 92 |
| Corresponding State + | | Curl, Pitzer | 19 |
| Method of Barner & Quin | CPBQ | Barner, Quinlan | 5 |
| Proposed Method | CPNM | This work | — |
| Method of Prausnitz & Gunn | CPPG | Prausnitz, Gunn | 71 |
| Method of Joff-Stewart, Burkhardt & Voo | CPSV | Joffe, Stewart, Burkhardt, Voo | 34, 35, 82 |
| Method of Leland & Mueller | CPLM | Leland, Mueller | 46 |
| Modified Method of Gunn | CPMG | Gunn | 28 |

## TABLE XVIII

## DATA SOURCE OF SYSTEMS STUDIED

| System | References | No. Data Points | Lowest T °F | Highest T °F | Highest P psia |
|---|---|---|---|---|---|
| 42.3% $N_2$-56.6 $CH_4$ | 54,57 | 54 | -250 | 250 | 2000 |
| 100% $CH_4$ | 37,97 | 35 | -250 | 50 | 2000 |
| 94.8% $CH_4$-5.2% $C_3H_8$ | 55,57 | 47 | -250 | 250 | 2000 |
| 88.3% $CH_4$-11.7% $C_3H_8$ | 57 | 47 | -250 | 250 | 2000 |
| 72% $CH_4$-28% $C_3H_8$ | 57 | 45 | -250 | 250 | 2000 |
| 49.4% $CH_4$-50.6% $C_3H_8$ | 97 | 45 | -250 | 250 | 2000 |
| 23.4% $CH_4$-76.6% $C_3H_8$ | 97 | 50 | -250 | 250 | 2000 |
| 36.6% $CH_4$-31.1% $C_2H_6$-32.3% $C_3H_8$ | 26 | 31 | -240 | 240 | 2000 |
| 38.5% $C_5H_{12}$-61.5% $C_6H_{12}$ | 48 | 36 | 540 | 600 | 1400 |
| 59.7% $C_5H_{12}$-40.3% $C_8H_{18}$ | 49 | 66 | 75 | 600 | 1400 |
| 42.3% $CH_4$-57.7% $CO_2$ | This work | 20 | 32 | 194 | 2000 |
| 14.5% $CH_4$-85.5% $CO_2$ | This work | 22 | 50 | 194 | 2000 |
| Equimolal $CH_4$-$CO_2$-$N_2$ | This work | 15 | -22 | 50 | 2000 |
| Equimolal $CH_4$-$CO_2$-$C_2H_6$ | This work | 25 | 32 | 194 | 2000 |
| $CH_4 (\frac{1}{2})$-$CO_2 (\frac{1}{4})$-$C_2H_6 (\frac{1}{4})$ | This work | 30 | 14 | 194 | 2000 |
| Equimolal $CH_4$-$CO_2$-$C_2H_6$-$N_2$ | This work | 20 | 14 | 140 | 2000 |

TABLE XIX    SUMMARY OF RESULTS OF ENTHALPY CORRELATION EVALUATION

Average $|\Delta| = (\Delta H_{exp} - \Delta H_{cal})$, Btu lb$^{-1}$

| System / Rules | BWRS | CPBQ | CPNM | CPPG | CPSV | CPLM | CPMG | SRK | Mark V |
|---|---|---|---|---|---|---|---|---|---|
| Methane | 0.6* | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 2.5 | 3.2 |
| $C_1$ (0.95) $C_3$ (0.05) | 0.7* | 1.7 | 1.6 | 2.2 | 1.7 | 2.0 | 6.4 | 2.2 | 2.3 |
| $C_1$ (0.883) $C_3$ (0.117) | 0.7* | 1.9 | 1.7 | 2.4 | 2.5 | 2.1 | ** | 1.4 | 1.7 |
| $C_1$ (0.72) $C_3$ (0.28) | 0.9* | 2.4 | 2.0 | 2.6 | 4.1 | 2.8 | ** | 1.2 | 1.6 |
| $C_1$ (0.494) $C_3$ (0.506) | 1.3* | 3.2 | 3.0 | 3.9 | 5.6 | 2.5 | ** | 1.0 | 1.4 |
| $C_1$ (0.234) $C_3$ (0.766) | 0.9* | 1.6 | 1.7 | 4.4 | 3.2 | 1.6 | ** | 1.1 | 1.5 |
| $CO_2$ (0.577) $CH_4$ (0.423) | 0.4 | 1.8 | 1.1 | 0.6 | 0.7 | 1.8 | 1.1 | 0.8 | 1.4 |
| $CO_2$ (0.855) $CH_4$ (0.145) | 0.8 | 1.9 | 1.3 | 1.1 | 1.1 | 1.3 | 1.1 | 1.0 | 1.2 |
| $CO_2$ (1/3) – $N_2$ (1/3) – $CH_4$ (1/3) | 0.2 | 3.0 | 1.7 | 1.4 | 2.6 | 1.6 | 0.7 | 0.5 | 0.5 |
| $CO_2$ (1/3)–$CH_4$ (1/3)– $C_2H_6$ (1/3) | 0.7 | 1.5 | 0.9 | 1.1 | 3.3 | 5.5 | 0.9 | 0.8 | 1.9 |

TABLE XIX    SUMMARY OF RESULTS OF ENTHALPY CORRELATION EVALUATION

Average $|\Delta| = (\Delta H_{exp} - \Delta H_{cal})$, Btu lb$^{-1}$

(continued)

| Rules / System | BWRS | CPBQ | CPNM | CPPG | CPSV | CPLM | CPHG | SRK | Mark V |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2(1/4)-CH_4(1/2)-C_2H_6(1/3)$ | 0.4 | 2.1 | 1.4 | 0.7 | 1.4 | 3.5 | 0.7 | 0.8 | 1.5 |
| $CO_2(1/4)-CH_4(1/4)-N_2(1/4)-C_2H_6(1/4)$ | 0.7 | 1.3 | 0.9 | 0.7 | 0.9 | 4.0 | 0.7 | 0.4 | 0.4 |
| $CH_4$ (0.566) $-N_2$ (0.434) | 0.5* | 0.9 | 1.0 | -1.3 | 1.1 | 1.6 | ** | 0.8 | 1.0 |
| $CH_4-C_2H_6-C_3H_8$ 0.366-0.311-0.323 | 4.0* | 3.9 | 3.9 | 2.9 | 2.1 | 6.3 | ** | 0.9 | 1.3 |
| $n-C_5$ (0.385) $ECH_{12}$ (0.615) | 1.8* | 0.9 | 1.2 | 1.4 | 0.9 | 1.0 | ** | 1.3 | *** |
| $n-C_5-n-C_8$ (0.597-0.403) | 2.8* | 2.4 | 2.4 | 2.3 | 4.3 | 2.4 | ** | 4.0 | 3.0 |
| Overall Average | 0.9 | 2.0 | 1.70 | 1.91 | 2.32 | 2.6 |  | 1.21 | 1.60 |

\*     From Starling et al.[79]

\*\*    Poor prediction for liquid region

\*\*\*   Not available for cyclohexane

obtained using method two listed above, gives the lowest average absolute deviations among the six methods.

The pseudocritical parameters (temperature and pressure) which were obtained by the five different methods for the mixtures of 49.4 mole percent methane in propane plot as function of temperature are shown in Figure 27 and 28. Pseudocritical temperature and pressure obtained by modified method of Gunn shows very large deviation from others. Pseudocritical temperature and pressure obtained by method of Leland and Mueller are the function of temperature and pressure. They can not be shown in Figure 27 and 28.

## Conclusions

The conclusion of this study is the finding that the equations of state BWRS, Soave-RK, Mark V and the corresponding states with the proposed mixing rule which is derived from Soave-RK, are the most accurate of the nine enthalpy correlations tested. Conclusions relating to each correlation individually are given below.

## Starling-BWR

The average absolute deviation for this correlation is 0.9 Btu/ lb. This method is not a generalized correlation and therefore can be applied only when the parameters of this equation of state have been determined for each component in a mixture. Also binary data are needed to determine interaction constants.

## Soave-Redlich-Kwong Equation of State

The average absolute deviation for this correlation is 1.21
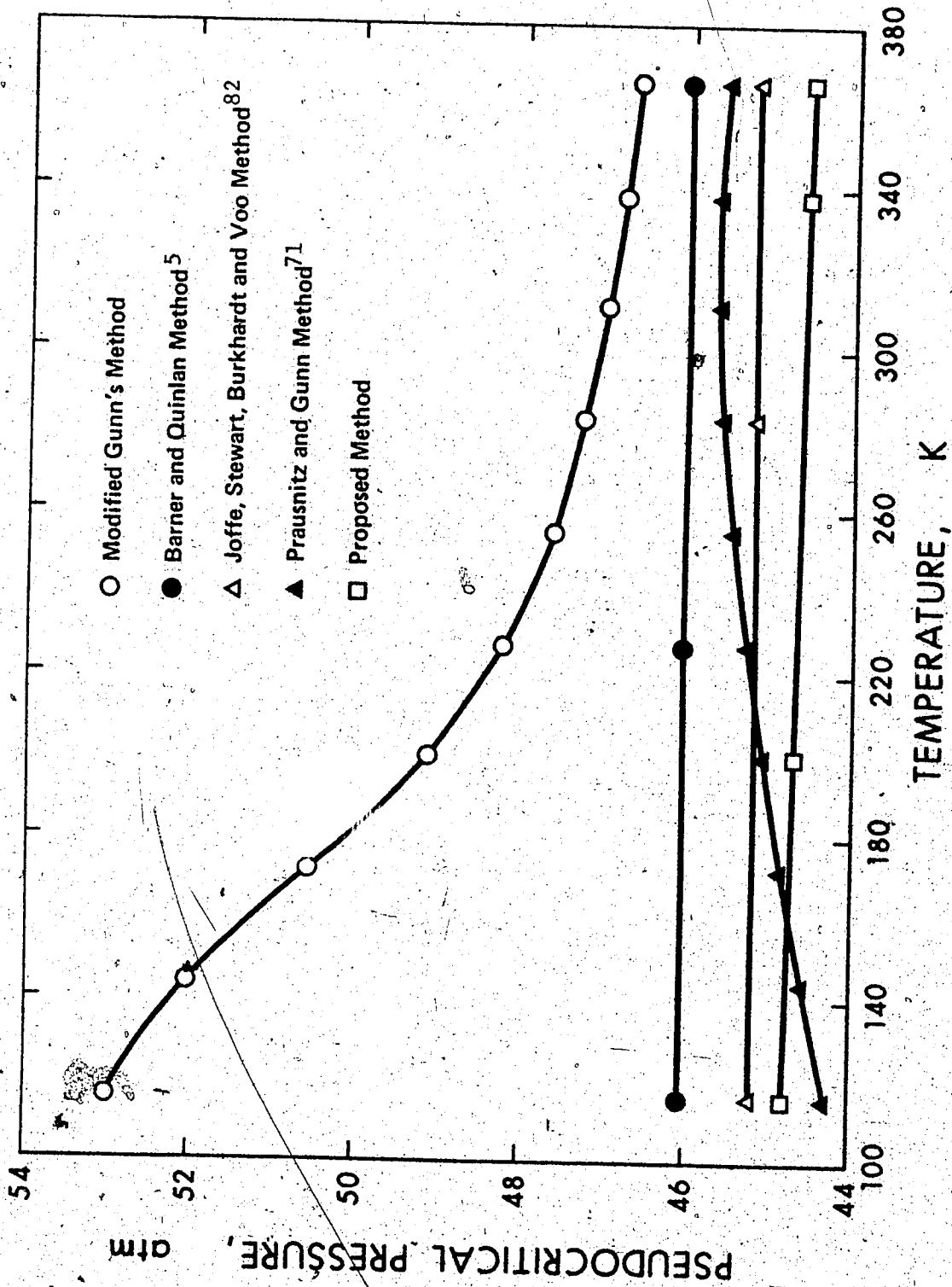
FIGURE 27. Pseudocritical Pressure at 49.4 percent Mixture of Methane in Propane

Legend:
- ○ Modified Gunn's Method
- ● Barner and Quinlan Method [5]
- △ Joffe, Stewart, Burkhardt and Voo Method [82]
- ▲ Prausnitz and Gunn Method [71]
- □ Proposed Method

TEMPERATURE, K

PSEUDOCRITICAL PRESSURE, atm
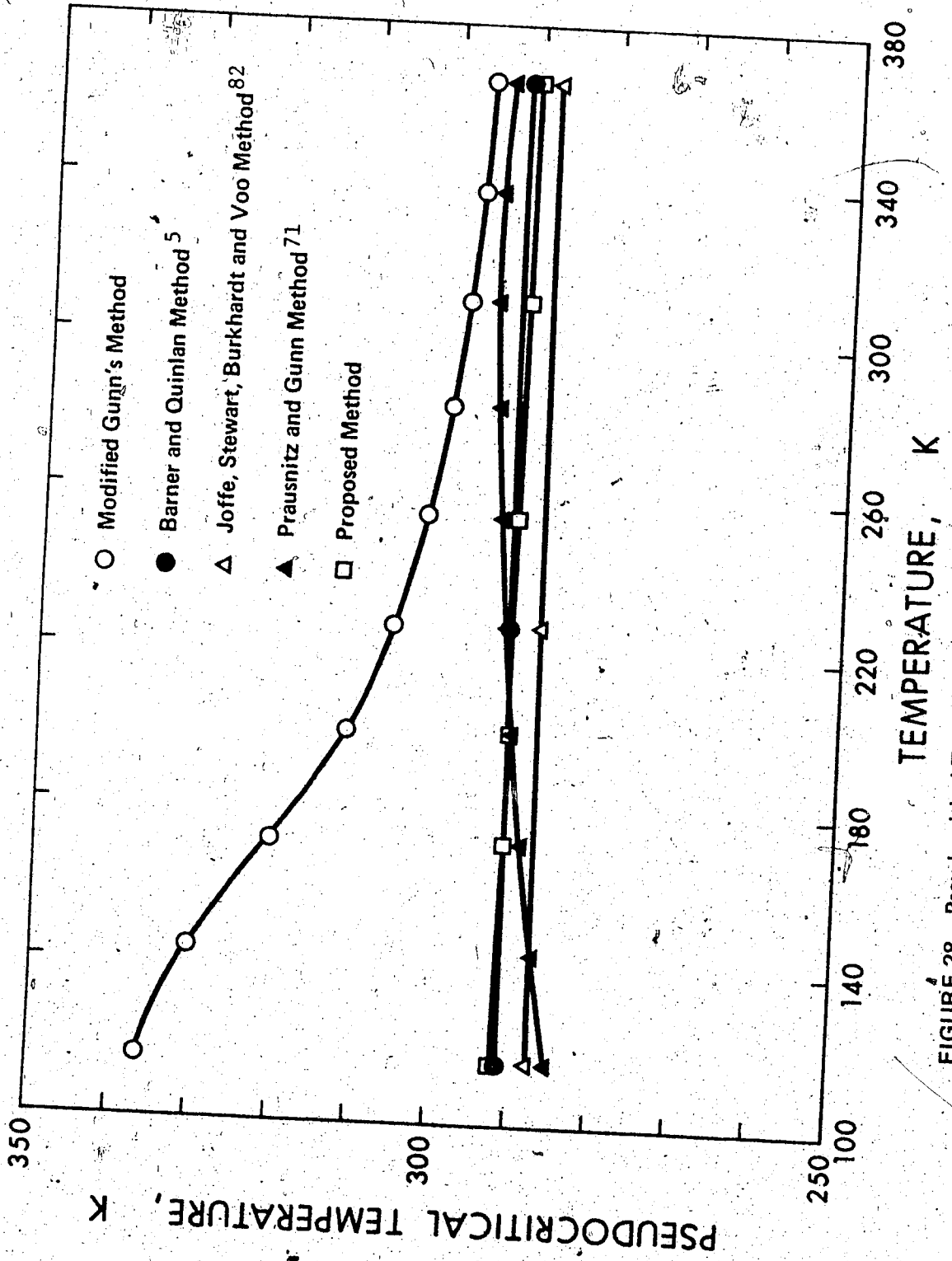
FIGURE 28. Pseudocritical Temperature of 49.4 percent Mixture of Methane in Propane

Legend:
- ○ Modified Gunn's Method
- ● Barner and Quinlan Method [5]
- △ Joffe, Stewart, Burkhardt and Voo Method [82]
- ▲ Prausnitz and Gunn Method [71]
- □ Proposed Method

X-axis: TEMPERATURE, K

Y-axis: PSEUDOCRITICAL TEMPERATURE, K

Btu/lb. This method can be considered as a generalized correlation because only critical properties and acentric factor of each component in mixture are required for the prediction. The only additional information is the interaction constant $k_{ij}$ which has to be determined from the binary vapor-liquid equilibrium data. Generalization of $k_{ij}$ for some system has been attempted[66]. This method requires very little computation time.

### Mark V Computer Program

The average absolute deviation for this correlation is 1.60 Btu/lb. This correlation always predicts too high at low pressure and predicts too low at high pressure.

### Corresponding State of Curl and Pitzer With Different Mixing Rules

#### Proposed Method

The average absolute deviation for this correlation is 1.70 Btu/lb. The interaction constant $k_{ij}$ for the Soave-Redlich-Kwong equation of state has to be determined from the binary vapor-liquid equilibrium data. The generalization of $k_{ij}$ has been attempted.

### Method of Barner and Quinlan

The average absolute deviation for this correlation is 2.0 Btu/lb. The mixing rules is derived from modified Redlich-Kwong equation of state (Chueh and Prausnitz[18]). Barner and Quinlan had generalized the binary interaction constant $K_{ij}$ for most of the system. The pseudocritical temperature and pressure of the mixture are independent of the temperature of the system.

## Method of Joffe, Stewart, Burkhardt and Voo

This correlation gives average absolute deviation of 2.32 Btu/lb. The mixing rules are derived based on van der Waals equation of state. No binary interaction constant is needed. It is not surprising that the prediction is less accurate than other methods which have one more adjustable parameter.

## Method of Leland and Mueller

The average absolute deviation for this correlation is 2.6 Btu/lb. The pseudocritical temperature and pressure obtained by this method are both functions of the temperature and pressure of the system. This correlation gives very good prediction for some systems but gives very poor prediction for some other systems.

## Modified Method of Gunn

This correlation gives very poor prediction in liquid region, but gives good prediction in gas region. The experimental data of this work are in gas region. It is shown in Table XIX that this correlation gives the lowest average absolute deviation among the corresponding states methods.

## Method of Prausnitz and Gunn

The average absolute deviation for this correlation is 1.91 Btu/lb. Equation of the form $B_m = \Sigma \Sigma x_i x_j B_{ij}$ forms the theoretical

basis on which the prediction of pseudocritical constants is based. The

two empirical constants $\Delta T_{C_{ij}}$ and $\Delta V_{C_{ij}}$ for each binary had been

generalized by the authors. Two more empirical constants s and

each mixture are needed to obtain the pseudocritical constants for the

mixture.

## *Summary and Conclusions*

1.   An isothermal throttling calorimeter for direct determination of the effect of pressure on enthalpy was designed, fabricated, and tested. The recycle flow facility, as described by Bishnoi, was used to recycle the material for this study.

2.   The effect of pressure on enthalpy was determined experimentally for nitrogen at temperatures from 0 to 100°C and pressures from 300 psia to 2000 psia. The data are in good agreement (within ± 1%) with other direct determinations in recent literature.

3.   Measurement of the effect of pressure on enthalpy were made on 14.5 mole percent and 42.3 mole percent of methane in carbon dioxide at gas region at pressure from 300 to 2000 psia.

4.   Skeleton enthalpy tables and enthalpy-pressure-temperature diagrams for those two mixtures were prepared, using isothermal enthalpy data of this work and isobaric heat capacity data of Bishnoi.

5.   Measurements of the effect of pressure on enthalpy were also made on equimolal mixture of methane, carbon dioxide and nitrogen, equimolal mixture of methane, carbon dioxide and ethane, methane rich mixture of methane, carbon dioxide and ethane, and equimolal mixture of methane, carbon dioxide, nitrogen and ethane. The measurements are in gas region and pressure up to 2000 psia.

6.   The data obtained in the course of this investigation plus data in the literature were used to compare several of the available methods of prediction. This comparative study indicates that corresponding states principle would be a most fruitful approach for extending methods of prediction.

7.   A new recipe for obtaining pseudocritical parameters for the

mixture of the three parameter corresponding states correlation of Curl and Pitzer was developed to predict the isothermal enthalpy departure of mixture. In comparison with sixteen fluid compositions of experimental data in the literature, this new method gives lowest average absolute deviation among other methods of obtaining pseudocritical parameters.

1.     The pressure transducer for measuring the pressure drop across the calorimeter should be replaced by a more accurate and wider range pressu  transducer.

2.     The new device of flow meter should be developed in order to obtain more accurate experimental data.

3.     The calorimeter should be modified in such a way that it would be easier to interchange the throttling coil.

4.     A higher pressure drop throttling coil should be constructed in order to study the effect of pressure on enthalpy in liquid region and region across the two phases.

5.     An oil and water removal unit should be installed at the outlet of the compressor in order to prevent the solid formation of oil or water which will plug the throttling unit of the calorimeter when operated at low temperature.

| | |
|---|---|
| $a_0, a_1, a_2, a_3$ | Constant in Equation (21) |
| $a, b, c, d$ | Constant in BWR or BWRS equation of state |
| $a, b$ | Constant in RK or SRK equation of state |
| $A_0, B_0, C_0, D_0, E_0$ | Constant in BWR or BWRS equation of state |
| $A, B$ | Calibration constants (flow meter) |
| $B$ | Second virial coefficient in volume expansion |
| $B'$ | Second virial coefficient in pressure expansion |
| $B_R$ | Reduced second virial coefficient |
| B.P. | Normal boiling point |
| $C$ | Third virial coefficient in volume expansion |
| $C'$ | Third virial coefficient in pressure expansion |
| $C_p$ | Isobaric heat capacity |
| $D$ | Correlation term of Lydersen, Greenkorn, Hougen correlation |
| $e$ | Base of natural logarithm |
| $F$ | Mass flow rate |
| $\underline{H}$ | Specific enthalpy |
| $\overline{H}$ | Partial molal enthalpy |
| $J, K$ | Expression in mixing rule of Joffe-Stewart, Burkhardt, Voo |
| $K$ | Interaction constant for Barner and Quinlan mixing rule |
| $k$ | Interaction constant |
| $M$ | Molecular weight |
| $m$ | Slope of $\alpha^{0.5}$ against $T_R^{0.5}$, Equation (85) |
| $P$ | Pressure |
| $P_C$ | Critical pressure |

$P_R$     Reduced pressure $P/P_C$

$\Delta P$     Pressure drop

$\dot{Q}$     Rate of heat transfer

$q$     Work per unit mass $\dot{W}/F$

$R$     Gas constant

$r,s$     Correction factor in mixing rule of Prausnitz and Gunn

$T$     Temperature

$T_C$     Critical temperature

$T_R$     Reduced temperature $T/T_C$

$V$     Specific volume

$\dot{W}$     Rate of transfer of work

$x$     Mole fraction

$y$     Mole fraction

$Z$     Compressibility factor

$\alpha$     Constant in mixing rule of Leland and Mueller

$\alpha, \gamma$     Constant in BWR or BWRS equation of state

$\beta, \gamma$     Expression in mixing rule of Prausnitz and Gunn

$\Delta$     Difference

$\mu$     Joule-Thomson coefficient

$\mu'$     Viscosity

$\rho$     Density

$\psi$     Dimensionless group of a thermodynamic property

$\theta; \nu$     Molecular shape factors

$\tau$     Reciprocal of temperature $1/T$

$\omega$     Acentric factor

$\Omega_a, \Omega_b$     Parameter in RK or SRK equation of state

$\phi$     Isothermal throttling coefficient

## Subscripts

| | |
|---|---|
| ad | Adiabatic condition |
| c | Critical point property |
| i,j | Component in a mixture |
| m | Mean value |
| m,mix | Mixture property |
| o | Zero pressure value |
| 0 | Reference substance property |
| 1 | Component 1 |
| 1 | Inlet condition |
| 11 | Component 1 |
| 12 | Interaction between component 1 and component 2 |
| 2,22 | Component 2 |
| 2 | Outlet condition |

## Superscripts

| | |
|---|---|
| o | Zero pressure value |
| E | Excess property |

*Bibliography*

1. Alkasab, K.A., Ph.D. Thesis, Illinois Institute of Technology (1970).

2. Alkasab, K.A., Shah, J.M., Laverman, R.J. and Budenhölzer, R.A., _Ind. Eng. Chem. Fundam._, 10 (2), 237 (1971).

3. Altunin, V.V., Kuznetsov, D.O. and Bondarenko, V.F., _Teploenergetika_, 20, (4), 61 (1973).

4. Barieau, R.E., U.S. Bur. Mines Information Circular 8245 (1965).

5. Barner, H.E. and Quinlan, C.W., _I. & EC., Proc. Des. and Devel._ 8, 407 (1969).

6. Benedict, M., Webb, G.B. and Rubin, L.C., _J. Chem. Phys._, 8, 334 (1940).

7. Bender, E., "Proc. of the 5th Symp. on Thermophysical Prop.", (ASME, NY, 1970) Page 227.

8. Bhird, V.L. and Powers, J.E. "Thermod. Prop. of a 5 mole percent Propane in Methane Mixture", Report to NGPA, 1969.

9. Bishnoi, P.R., Ph.D. Thesis, University of Alberta (1970).

10. Bishnoi, P.R. and Robinson, D.B., _Can. J. Chem. Eng._, 49, 642 (1971).

11. Bishnoi, P.R. and Robinson, D.B., _Can. J. Chem. Eng._, 50, 101 (1972).

12. Bloomer, O.T. and Rao, K.N., IGT Res. Bull., 18 (1952).

13. Canjar, L.N. and Edmister, W.C., _Chem. Eng. Prog. Symp. Ser._, 49 (7), 73 (1953).

14. Canjar, L.N. and Peterka, V.J., _AIChE J._, 2, 343 (1956).

15. Chao, K.C. and Greenkorn R.A., _Pro. 50th NGPA Ann. Conv._, 42 (1971).

16. Chao, K.C., Greenkorn, R.A., Olabisi, O. and Hensel, B.H., _AIChE J._ 17, 353 (1971).

17. Chaudron, J., Asselineau, L. and Renon, H., _Chem. Eng. Sci._, 28, 839 (1973).

18. Chueh, P.L. and Prausnitz, J.M., _Ind. Eng. Chem. Fundam._, 6, 492 (1967).

19. Curl, R.F. and Pitzer, K.S., _Ind. Eng. Chem._, 50, 265 (1958).

20. Dantzler, E.M., Knobler, C.M. and Windsor, M.L., _J. Phys. Chem._, 72, 676 (1968).

21. Dawe, R.A. and Snowdon, P.N., _J. Chem. Therm._, 6, 65 & 293 (1974).

22. Dillard, D.D., Edmister, W.C., Erbar, J.H. and Robinson, R.L. Jr., AIChE J., 14, 923 (1968).

23. Din, F. in Thermodynamic Functions of Gases, ed. F. Din, Vol. 3, 72 (1961).

24. Dymond, J.H. and Smith E.B., "The Virial Coefficient of Gases", Clarendon Press, Oxford (1969).

25. Eakin, B.E. and DeVaney, W.E., Proc 53rd Ann. Conv., NGPA Tech. Papers, 72 (1974).

26. Furtado, A.W., Katz, D.L. and Powers, J.E., Proc. 49th NGPA Ann. Conv., 1 (1970).

27. Gunn, R.D., M.Sc. Thesis, University of California, Berkeley (1958).

28. Gunn, R.D., AIChE J., 18, 183 (1972).

29. Gunning, A.J. and Rowlinson, J.S., Chem. Eng. Sci., 28, 521 (1973).

30. Gusak, I.M., Phys. Z. Sowjet., 11, 60 (1937).

31. Hoover, A., Nagata, I., Leland, T.W. Jr. and Kobayashi, R., J. Chem. Phys., 48, 2633 (1968).

32. Hopke, S.W. and Lin, C-J., Paper presented at 76th National AIChE Meeting, March 10-13, Tulsa, Oklahoma (1974).

33. Ishkin, I.P. and Kaganer, M.G., Zhur. Tekh. Fiz., 26, 2329 (1956).

34. Joffe, J., Ind. Eng. Chem., 39, 837 (1947).

35. Joffe, J., Ind. Eng. Chem., 40, 1738 (1948).

36. Joffe, J. and Zudkevitch, D., Chem. Eng. Prog. Symp. Ser., 63 (81), 43 (1967).

37. Jones, M.L., Ph.D. Thesis, University of Michigan (1961).

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

39. Klaus, R.L. and Van Ness, H.C., AIChE J., 13, 1132 (1967).

40. Klein, R.R., Bennett, C.O. and Dodge, B.F., AIChE J., 17, 958 (1971).

41. Landis, F. and Nilson, E.N., "Progress in International Research on Thermodynamic and Transport Properties", p. 218, Academic Press, New York (1962).

42. Leach, J.W., Chappelear, P.S., and Leland, T.W., AIChE J., 14, 568 (1968).

43. Leach, J.W., Ph.D. Thesis, Rice University (1967).

44. Lee, J.I. and Mather, A.E., J. Chem. Therm., 2, 881 (1970).

45. Lee, J.I. and Mather, A.E., Can. J. Chem. Eng., 50, 95 (1972).

46. Leland, T.W. and Mueller, W.H., Ind. Eng. Chem., 51, 597 (1959).

47. Leland, T.W. and Chappelear, P.S., Ind. Eng. Chem., 60 (7), 17 (1968).

48. Lenoir, J.M., Robinson, D.R. and Hipkin, H.G., Paper presented at 33rd Midyear Meeting of API Division of Refining, Philadelphia, May 1968.

49. Lenoir, J.M., Kuravila, G.K. and Hipkin, H.G., Paper presented at 34th Midyear Meeting of API Division of Refining, Philadelphia, May 1969.

50. Lin, C.J., Kwok, Y.C. and Starling, K.E., Can. J. Chem. Eng., 50, 644 (1972).

51. Lydersen, A.L. Greenkorn, R.A. and Hougen, O.A., University of Wisconsin Eng. Exp. Sta. Rept., 4 (1955).

52. Mackey, B.H. and Krase, N.W., Ind. Eng. Chem., 22, 1060 (1930).

53. McCarty, R.D., Cryogenics, 276 (1974).

54. Mage, D.T., Jones, M.L. Jr., Katz, D.L. and Roebuck, J.R., Chem. Eng. Prog. Symp. Ser. 59, (44), 61 (1963).

55. Manker, E.A., Ph.D. Thesis, University of Michigan (1964).

56. Martin, J.J. and Hou, Y.C., AIChE J., 1, 142 (1955).

57. Mather, A.E., Ph.D. Thesis, University of Michigan (1967).

58. Mather, A.E., Katz, D.L. and Powers, J.E., Trans. Faraday. Soc. 64, 2939 (1968).

59. Mather, A.E., Powers, J.E. and Katz, D.L., AIChE J., 15, 111 (1969).

60. Maxwell, J.B., "Data Book on Hydrocarbon", D. Van Nostrand, Princeton, N.J. (1950).

61. McBride, B.J., Heimel, S., Ehlers, J.G. and Gordon, S., "Thermodynamic Properties to 6000°K for 210 Substances Involving the First 18 Elements", NASA N63-23715, Washington, D.C. (1963).

61a. Miyazaki, T., Ph.D. Thesis, University of Michigan (1973).

62. Nathan, D.I., Brit. Chem. Eng., 12, 223 (1967).

63. Ng, H.J., M.Sc. Thesis, University of Alberta (1971).

64. Ng, H.J. and Mather, A.E., Unpublished Experimental Data (1971).

65. Papadopoulos, A., Pigford, R.L. and Friend, L., *Chem. Eng. Prog. Symp. Ser.*, 49 (7), 119 (1953).

66. Peng, D.Y., Personal Communication (1974).

67. Peters, H.F., *Petroleum Refiner*, 28 (15), 109 (1949).

68. Peterson, J.M. and Wilson, G.M., *Proc. 53rd NGPA Ann. Conv., Tech. Papers*, 57 (1974).

69. Pitzer, K.S. and Hultgren, G.O., *J. Am. Chem. Soc.*, 80, 4788 (1958).

70. Pitzer, K.S. and Curl, R.F. Jr., *J. Am. Chem. Soc.*, 79, 3869 (1957).

71. Prausnitz, J.M. and Gunn, R.D., *AIChE J.*, 4, 430 (1958).

72. Prausnitz, J.M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, p. 158 (1969).

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

74. Roebuck, J.R. and Ostenberg, H., *Phys. Rev.*, 48, 450 (1935).

75. Scheibel, E.G. and Jenny, F.J., *Ind. Eng. Chem.*, 37, 990 (1945).

76. Soave, G., *Chem. Eng. Sci.*, 27, 1197 (1972).

77. Starling, K.E., *Proc. NGPA Ann. Conv.*, 49, 9 (1970).

78. Starling, K.E. and Powers, J.E., *IEC Fundam.*, 9, 531 (1970).

79. Starling, K.E., Johnson, D.W. and Colver, C.P., *NGPA Research Report RR4* (1971).

80. Starling, K.E., "Fluid Thermodynamic Properties for Light Petroleum Systems", Gulf Publishing Co., Houston, 1973.

81. Steil, L.I., *Ind. Eng. Chem.*, 60 (5), 50 (1968).

82. Stewart, W.E., Burkhardt, S.F. and Voo, D., Paper presented at National AIChE Meeting, Kansas City, May 18, 1959.

83. Stotler, H.H. and Benedict, M., *Chem. Eng. Prog. Symp. Ser.*, 49 (6), 25 (1953).

84. Tsonopoulos, C., *AIChE J.*, 20, 263 (1974).

85. Vukalovich, M.P. and Altunin, V.V., "Thermophysical Properties of Carbon Dioxide", Collet's (Publishers) Ltd., London, 1968.

86. Vukalovich, M.P., Altunin, V.V., Bulle, Kh., Rasskazov, D.S. and Ertel, D., *Teploenergetika* 16, (11), 70 (1969).

87. *Idem*, *ibid.*, **17** (5), 60 (1970).

88. Vukalovich, M.P., Bulle, Kh., Rasskazov, D.S. and Ertel, D., *ibid.*, **17** (6), 63 (1970).

89. Vukalovich, M.P., Bulle, H., and Ertel, D., *Russ. J. Phys. Chem.*, **46** (10), 1475 (1972).

90. Watson, I.D. and Rowlinson, J.S., *Chem. Eng. Sci.*, **24** 1565 & 1575 (1969).

91. Wilson, G.M., Paper presented at 65th National AIChE Meeting, May 4-7, 1969.

92. Wilson, G.M. and DeVaney, W.E., "Mark V Computer Program", Available From P-V-T Inc. or the Gas Processors Assn.

93. Wood, R.E., U.S. Bureau of Mines, Rept. Inv., 7190 (1968).

94. Yarborough, L. in *Engineering Data Book*, NGPA, 8th Edition (1966), p. 203.

95. Yen, L.C. and Alexander, R.E., *AIChE J.*, **11**, 334 (1965).

96. Yen, L.C. and Garcia -Rangel, S., Paper presented at 159th Am. Chem. Soc. National Meeting. Symp. on Enthalpy of Mixtures, Houston, Texas, Feb. 1970.

97. Yesavage, V.F., Ph.D. Thesis, University of Michigan (1968).

98. Yesavage, V.F., Katz, D.L. and Powers, J.E., "4th Symposium on Thermophysical Properties", ASME, N.Y., **45** (1968).

99. Yesavage, V.F., Katz, D.L. and Powers, J.E., *J. of Chem. Eng. Data*, **14** (2), 137 (1969).

100. Yesavage, V.F., Katz, D.L. and Powers, J.E., *AIChE J.*, **16** (5), 867 (1970).

101. Zaalishvili, Sh.D., *Zhur. Fiz. Khim.*, **30**, 1891 (1956).

APPENDIX A

CALIBRATIONS AND ERROR ANALYSIS

## TABLE XX

### CALIBRATION DATA FOR 8163 MODEL PLATINUM RESISTANCE THERMOMETER

This thermometer was calibrated for use in the range $90.188 \text{ K} < T < 773.15 \text{ K}$ $(-182.962°C < t < 500.60°C)$ on the International practical temperature scale of 1968.

For $13.81 \text{ K} < T < 273.15 \text{ K}$

$$W = W_{cct} + dw$$

where $W = R/R(0°C)$ and $W_{cct}$ is a reference function, independent of any particular thermometer.

For $90.188 \text{ K} < T < 273.16 \text{ K}$

$$dw = A4 \, t + C4 \, (t - 100) \, t^3$$

For $0°C < t < 630.74°C$

$$t = t' + dt$$

where $t'$ is determined by

$$w = 1 + At' + B(t')^2$$

and

$$dt' = 0.45(t'/100)(\frac{t'}{100} - 1)(\frac{t'}{419.58} - 1)(\frac{t'}{630.74} - 1)$$

The coefficient in the above relations were found by fixed-point calibrations, i.e. triple point of water, the steam of tin point and the zinc point using continuous thermometer currents of 1 and 2 mA.

TABLE XX (continued)

|  | 0 mA | 2 mA |
|---|---|---|
| $A =$ | $3.985566 \times 10^{-3}$ | $3.985539 \times 10^{-3}$ |
| $B =$ | $-5.87663 \times 10^{-7}$ | $-5.87773 \times 10^{-7}$ |
| $A4 =$ | $8.3280 \times 10^{-7}$ | $7.9460 \times 10^{-7}$ |
| $C4 =$ | $2.2020 \times 10^{-14}$ | $2.4150 \times 10^{-14}$ |
| $R(0°C) =$ | $25.5145$ ohm | |

TABLE XXI

CALIBRATION OF HIGH PRESSURE GAUGE

Manufacturer: Heise

Serial No.: H39686

| Actual Pressure (psi) | Heise Gauge | |
|:---:|:---:|:---:|
| | up | down |
| 0 | 0 | 0 |
| 200 | 200 | 200 |
| 400 | 400 | 400 |
| 600 | 596 | 600 |
| 800 | 796 | 800 |
| 1000 | 996 | 1000 |
| 1200 | 1200 | 1200 |
| 1400 | 1400 | 1400 |
| 1600 | 1600 | 1600 |
| 1800 | 1800 | 1806 |
| 2000 | 2000 | 2005 |
| 2200 | 2200 | 2205 |
| 2400 | 2400 | 2405 |
| 2600 | 2600 | 2605 |
| 2800 | 2800 | 2804 |
| 3000 | 3000 | 3000 |

## TABLE XXII

## CALIBRATION OF 250 PSI DIFFERENTIAL PRESSURE TRANSDUCER

### Manufacturer: Validyne

| psi | Voltage up | down |
|-----|------------|------|
| 0 | 0.001 | 0.004 |
| 30 | 1.169 | 1.191 |
| 50 | 1.956 | 1.976 |
| 70 | 2.741 | 2.760 |
| 80 | 3.135 | 3.161 |
| 100 | 3.925 | 3.951 |
| 120 | 4.717 | 4.743 |
| 140 | 5.514 | 5.541 |
| 160 | 6.316 | 6.339 |
| 180 | 7.122 | 7.144 |
| 200 | 7.936 | 7.952 |
| 220 | 8.752 | 8.766 |
| 240 | 9.577 | 9.582 |
| 250 | 9.992 | 9.992 |

## TABLE XXIII

### CALIBRATION OF 75 PSI DIFFERENTIAL PRESSURE TRANSDUCER

#### Manufacturer: Validyne

| psi | Voltage (Volt) |
|-----|----------------|
| 0   | 0.001          |
| 10  | 0.654          |
| 20  | 1.311          |
| 30  | 1.971          |
| 40  | 2.635          |
| 50  | 3.303          |
| 60  | 3.976          |
| 70  | 4.656          |
| 75  | 4.999          |
| 70  | 4.657          |
| 60  | 3.980          |
| 50  | 3.310          |
| 40  | 2.642          |
| 30  | 1.979          |
| 20  | 1.318          |
| 10  | 0.658          |
| 0   | 0.001          |

TABLE XXIV

CALIBRATION OF 60 INS. OF WATER DIFFERENTIAL

PRESSURE TRANSDUCER

Manufacturer: Foxboro

| Inches of Water | Voltage (mV) |
|---|---|
| 0 | 0.983 |
| 4.293 | 1.275 |
| 8.945 | 1.597 |
| 12.541 | 1.841 |
| 17.752 | 2.184 |
| 20.209 | 2.352 |
| 25.041 | 2.676 |
| 30.70 | 3.059 |
| 35.70 | 3.399 |
| 40.37 | 3.713 |
| 45.45 | 4.057 |
| 50.05 | 4.363 |
| 60.27 | 5.055 |
| 54.60 | 4.671 |
| 48.55 | 4.263 |
| 31.39 | 3.105 |
| 22.043 | 2.477 |
| 18.354 | 2.225 |
| 14.150 | 1.194 |
| 11.310 | 1.747 |
| 7.313 | 1.476 |

## TABLE XXV

## FLOW METER CALIBRATION

### (Orifice)

EQUATION:
$$F = A + BY\sqrt{\frac{P \cdot \Delta P}{Z \cdot M}}$$

where

F:    $gm\text{-}mol\ min^{-1}$

A, B:    Calibration Constant

Y:
$$\sqrt{\gamma^{2/k}\left(\frac{k}{k-1}\right)\left(\frac{1-\gamma^{(k-1)/k}}{1-\gamma}\right)\left(\frac{1-\beta^4}{1-\beta^4\gamma^{2/k}}\right)}$$

k:    $C_p/C_v$

$\gamma$:    $1 - \Delta P/P$

$\beta$:    Ratio of orifice I.D. to tube I.D.

$\Delta P$:    Pressure drop across the orifice

P:    Inlet-pressure of the orifice

Z:    Compressibility factor of the gas (gas mixture)

TABLE XXV

| P<br>psia | ΔP<br>psi | $Y\sqrt{\dfrac{P \cdot \Delta P}{Z \cdot M}}$ | F | $F_{cal}$ | $F - F_{cal}$ |
|---|---|---|---|---|---|
| 44.0600 | 1.8476 | 1.3873 | 4.8095 | 4.8107 | -0.0012 |
| 44.1100 | 1.5086 | 1.2603 | 4.3566 | 4.3697 | -0.0131 |
| 44.1100 | 1.2735 | 1.1616 | 4.0145 | 4.0275 | -0.0130 |
| 44.1100 | 1.1880 | 1.1233 | 3.8783 | 3.8943 | -0.0160 |
| 44.0100 | 0.7536 | 0.8989 | 3.0989 | 3.1156 | -0.0167 |
| 44.1100 | 1.0314 | 1.0489 | 3.6234 | 3.6362 | -0.0128 |
| 44.0100 | 0.3266 | 0.5952 | 2.0726 | 2.0618 | 0.0107 |
| 44.1400 | 0.7712 | 0.9105 | 3.1324 | 3.1559 | -0.0235 |
| 44.1400 | 1.5615 | 1.2817 | 4.4199 | 4.4441 | -0.0242 |
| 44.1900 | 1.2612 | 1.1573 | 4.0049 | 4.0124 | -0.0075 |
| 44.1600 | 1.0469 | 1.0571 | 3.6544 | 3.6648 | -0.0104 |
| 44.1600 | 0.5788 | 0.7910 | 2.7370 | 2.7414 | -0.0044 |
| 44.1400 | 0.4266 | 0.6803 | 2.3446 | 2.3570 | -0.0124 |
| 44.0100 | 0.2342 | 0.5046 | 1.7528 | 1.7474 | 0.0053 |
| 43.8700 | 0.2860 | 0.6607 | 2.2939 | 2.2892 | 0.0046 |
| 43.8700 | 0.3779 | 0.7586 | 2.6288 | 2.6289 | -0.0001 |
| 43.8700 | 0.4917 | 0.8641 | 2.9967 | 2.9950 | 0.0016 |
| 43.8700 | 0.6184 | 0.9675 | 3.3570 | 3.3538 | 0.0031 |
| 43.8700 | 0.7413 | 1.0577 | 3.6774 | 3.6667 | 0.0106 |
| 43.8700 | 0.9240 | 1.1782 | 4.0825 | 4.0849 | -0.0024 |
| 43.8700 | 1.0988 | 1.2819 | 4.4605 | 4.4450 | 0.0154 |
| 43.9100 | 1.5861 | 1.5315 | 5.3041 | 5.3109 | -0.0068 |
| 43.9100 | 1.7790 | 1.6179 | 5.5864 | 5.5110 | -0.0246 |
| 43.9100 | 1.5407 | 1.5102 | 5.2467 | 5.2373 | 0.0093 |
| 43.9100 | 0.9288 | 1.1817 | 4.0697 | 4.0972 | -0.0275 |
| 43.9100 | 0.1239 | 0.8033 | 2.7951 | 2.7841 | 0.0109 |
| 43.9100 | 0.4426 | 0.8207 | 2.8506 | 2.8443 | 0.0062 |
| 43.9100 | 0.6237 | 0.9721 | 3.3938 | 3.3696 | -0.0241 |
| 43.9100 | 0.8364 | 1.1227 | 3.9297 | 3.8923 | 0.0373 |
| 43.9100 | 1.0149 | 1.2339 | 4.3044 | 4.2783 | 0.0260 |
| 43.9100 | 1.1971 | 1.3370 | 4.6666 | 4.6362 | 0.0303 |
| 43.9100 | 1.3558 | 1.4201 | 4.9209 | 4.9243 | -0.0034 |
| 43.9100 | 1.5428 | 1.5112 | 5.2716 | 5.2407 | 0.0308 |
| 43.9100 | 1.5834 | 1.5302 | 5.3535 | 5.3066 | 0.0468 |
| 43.9100 | 0.1011 | 0.3940 | 1.3637 | 1.3636 | 0.0000 |
| 43.9100 | 0.1343 | 0.4538 | 1.5852 | 1.5710 | 0.0141 |
| 43.9100 | 0.2459 | 0.6133 | 2.1479 | 2.1245 | 0.0233 |
| 43.9100 | 0.1909 | 0.5407 | 1.8980 | 1.8726 | 0.0253 |
| 43.9100 | 0.3389 | 0.719 | 2.5179 | 2.4917 | 0.0261 |
| 43.9100 | 0.2331 | 0.5972 | 2.0873 | 2.0686 | 0.0186 |
| 43.9100 | 0.2347 | 0.5992 | 2.0941 | 2.0757 | 0.0183 |
| 43.9100 | 0.2492 | 0.4957 | 1.7229 | 1.7166 | 0.0062 |
| 43.9100 | 0.3138 | 0.5559 | 1.9351 | 1.9252 | 0.0098 |
| 43.9100 | 0.4111 | 0.6353 | 2.2029 | 2.2011 | 0.0017 |
| 43.9700 | 2.2406 | 1.4474 | 5.0162 | 5.0191 | -0.0029 |

TABLE XXV (continued)

| P psia | $\Delta P$ psi | $Y\sqrt{\dfrac{P \cdot \Delta P}{Z \cdot M}}$ | F | $F_{cal}$ | $F-F_{cal}$ |
|---|---|---|---|---|---|
| 43.9700 | 2.2460 | 1.4490 | 5.0162 | 5.0247 | -0.0085 |
| 43.9700 | 2.0846 | 1.3991 | 4.8654 | 4.8517 | 0.0136 |
| 43.9700 | 1.8618 | 1.3264 | 4.5785 | 4.5993 | -0.0208 |
| 43.9700 | 1.6395 | 1.2486 | 4.3140 | 4.3291 | -0.0151 |
| 43.9700 | 1.4188 | 1.1851 | 4.0276 | 4.0393 | -0.0117 |
| 43.9700 | 1.2644 | 1.1022 | 3.8065 | 3.8211 | -0.0146 |
| 43.9700 | 1.0811 | 1.0217 | 3.5360 | 3.5420 | -0.0060 |
| 43.9700 | 0.9208 | 0.9450 | 3.2599 | 3.2758 | -0.0159 |
| 43.9700 | 0.7589 | 0.8598 | 2.9649 | 2.9801 | -0.0152 |
| 43.9700 | 0.6184 | 0.7776 | 2.6850 | 2.6948 | -0.0098 |
| 43.9700 | 0.5174 | 0.7123 | 2.4418 | 2.4681 | -0.0263 |
| 43.9700 | 0.4453 | 0.6614 | 2.2784 | 2.2915 | -0.0131 |
| 43.9100 | 0.4490 | 0.6637 | 2.3055 | 2.2994 | 0.0060 |
| 43.9100 | 0.6750 | 0.8113 | 2.7892 | 2.8116 | -0.0224 |
| 43.9100 | 0.8610 | 0.9139 | 3.1566 | 3.1677 | -0.0111 |
| 43.9100 | 1.0768 | 1.0190 | 3.5360 | 3.5327 | 0.0032 |
| 43.9100 | 1.2778 | 1.1070 | 3.8289 | 3.8378 | -0.0089 |
| 43.9100 | 1.6475 | 1.2506 | 4.3140 | 4.3361 | -0.0221 |
| 43.9100 | 1.9275 | 1.3474 | 4.6891 | 4.6721 | 0.0169 |
| 43.9100 | 2.1274 | 1.4115 | 4.9146 | 4.8947 | 0.0198 |
| 44.2400 | 0.3945 | 0.7602 | 2.6380 | 2.6345 | 0.0034 |
| 43.7800 | 1.7865 | 1.5696 | 5.4560 | 5.4433 | 0.0126 |
| 43.7800 | 1.3953 | 1.3950 | 4.8305 | 4.8373 | -0.0068 |
| 43.7800 | 0.8893 | 1.1217 | 3.8984 | 3.8889 | 0.0094 |
| 43.7800 | 0.5265 | 0.8675 | 2.9951 | 3.0067 | -0.0116 |
| 43.7800 | 0.3854 | 0.7437 | 2.5586 | 2.5771 | -0.0185 |
| 43.7800 | 0.2433 | 0.5920 | 2.0415 | 2.0508 | -0.0093 |
| 43.7800 | 0.1663 | 0.4901 | 1.6862 | 1.6970 | -0.0108 |

TOTAL SUM OF SQUARE = 0.97146E 03

SUM OF RESIDUAL = 0.28237E-05

SUM OF RESIDUAL SQUARE = 0.20049E-01

PERCENT STANDARD DEVIATION = 0.48473

STANDARD DEVIATION = 0.16804E-01

Y= A+ B*X

A= -0.00391

B= 3.47033
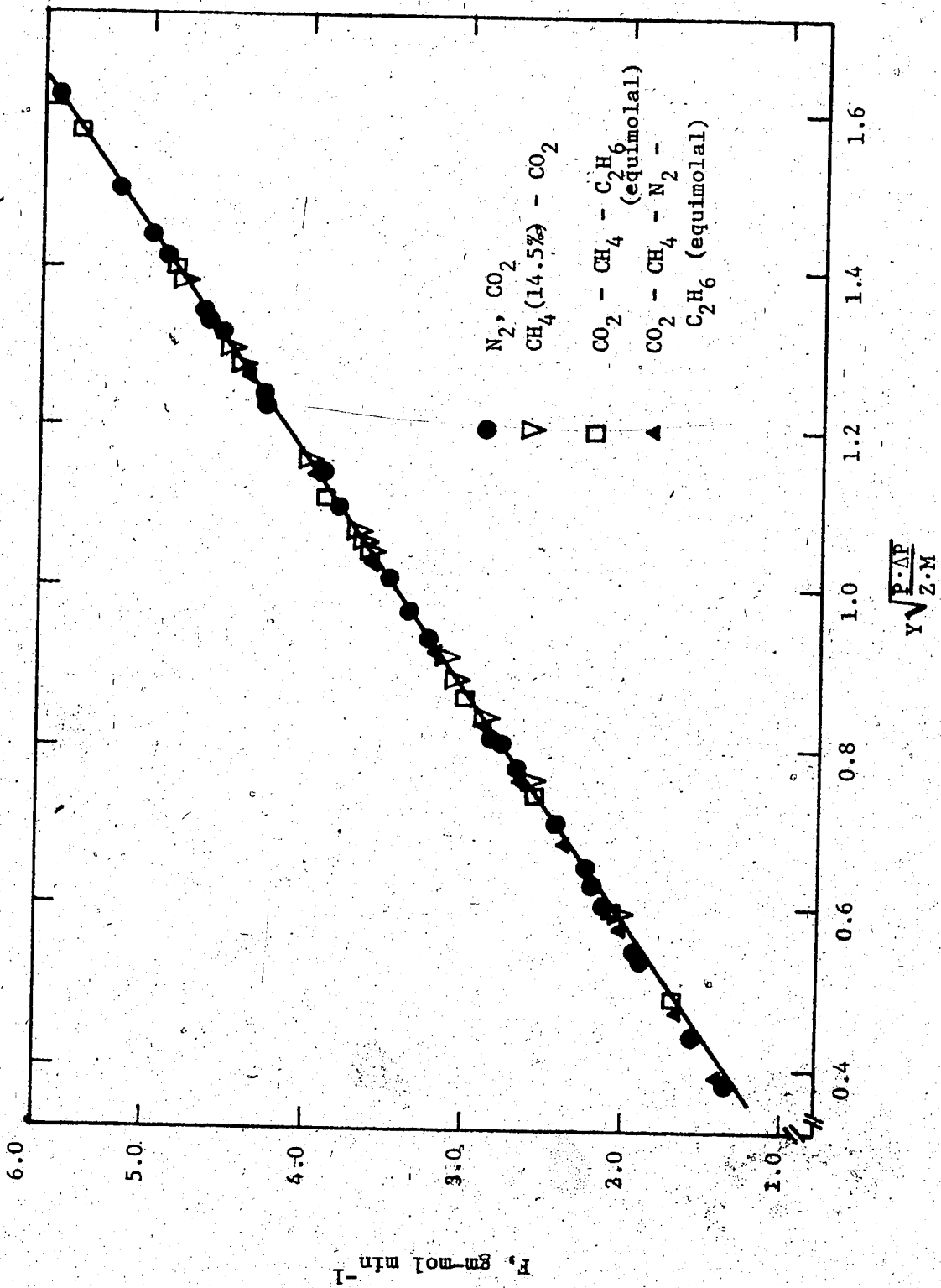
Figure 29: Calibration Curve of Orifice Meter

## Calibration of Gas Chromatograph

### 1) Methane - Carbon Dioxide Mixtures

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 and 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  -  50 ml/min

Column temperature  -  80°F

Detector Current  -  150 mA

Sample size  -  2 ml

Excellent separations, with sharp well-defined peaks were obtained and the area under a peak was determined by a disc integrator. Standard sample mixtures of carbon dioxide and mixture were prepared by weighing small sample bottles and the amounts of methane and carbon dioxide charged. The weights of the empty bottle and the mixtures sample charged were approximately 155 g. and 1.75 g. respectively. The weighings could be reproduced to within ± 0.1 mg. The error in a mixture composition thus prepared should 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 area under the carbon dioxide and methane peaks) was correlated to the known mole fraction of methane in the standards by the following functional relationship:

$$y = AX + BX^2$$

where A, B are constants

X = area fraction of methane

Y = mole fraction of methane

The constants, A and B, in the above relationship were determined by a least square fit and were found to be as follows:

A = 0.73451

B = 0.25721

The percent standard deviation of the fit was found to be ± 0.4%. A plot of Y versus X is shown in Figure 30.

## 2. *Methane, Carbon Dioxide and Ethane Mixture*

The mixtures were analysed on the same chromatograph using a one meter column of one-quarter inch diameter packed with porapak Type Q (80-100 mesh). The gas chromatograph was operated under the following conditions:

| | | |
|---|---|---|
| Carrier Gas | - | Helium |
| Carrier gas flowrate | - | 40 ml/min |
| Column temperature | - | 80°F |
| Detector current | - | 170 mA |
| Sample size | - | 2 ml |

Standard mixtures of methane - carbon dioxide - ethane were prepared in the same method as for binary mixtures. The standards were then analysed on the gas chromatograph and the area fraction of each component were plotted against its more fraction as shown in Figure 31. A straight line was drawn through each component. The response factors of each component were then determined from the calibration curve by
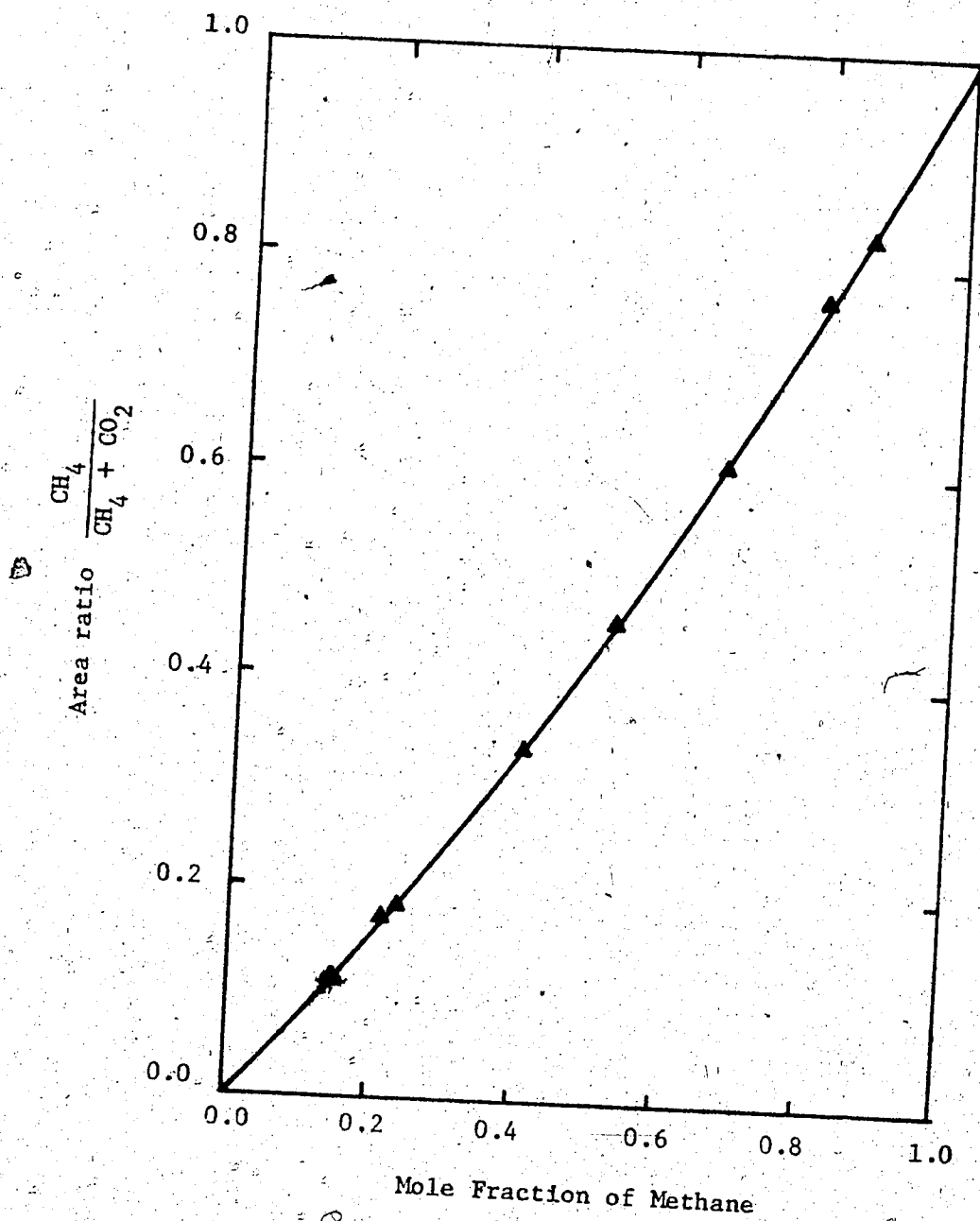
Figure 30: Gas Chromatograph Calibration for Methane-Carbon Dioxide Mixture

## TABLE XXVI

### RESPONSE FACTOR CALCULATED FROM CALIBRATION

Methane – Carbon Dioxide – Ethane System:

$$CH_4 \quad : \quad 36$$

$$CO_2 \quad : \quad 49$$

$$C_2H_6 \quad : \quad 53.5$$

Methane – Carbon Dioxide – Nitrogen System:

$$CH_4 \quad : \quad 36$$

$$N_2 \quad : \quad 41.8$$

$$CO_2 \quad : \quad 49$$

Methane – Carbon Dioxide – Nitrogen – Ethane System:

$$CH_4 \quad : \quad 36$$

$$N_2 \quad : \quad 41.7$$

$$CO_2 \quad : \quad 48.6$$

$$C_2H_6 \quad : \quad 54.5$$

assigning the response factor of methane equal 36. The calibrated response factors were listed in Table XXVI.

### 3. Methane - Carbon Dioxide - Nitrogen Mixture

The same gas chromatograph with same conditions and same procedure of the previous ternary system were used to calibrate mixture of this system. Figure 32 shows the area fractions of each component plotted as function of its mole fraction, and the calibrated response factors are listed in Table XXVI.

### 4. Methane - Carbon Dioxide - Nitrogen - Ethane Mixtures

The same gas chromatograph with same operating conditions and same procedure of the previous ternary system were used to calibrate mixture of methane - carbon dioxide - nitrogen - ethane. Figure 33 shows the calibration curve and the response factors are listed in Table XXVI
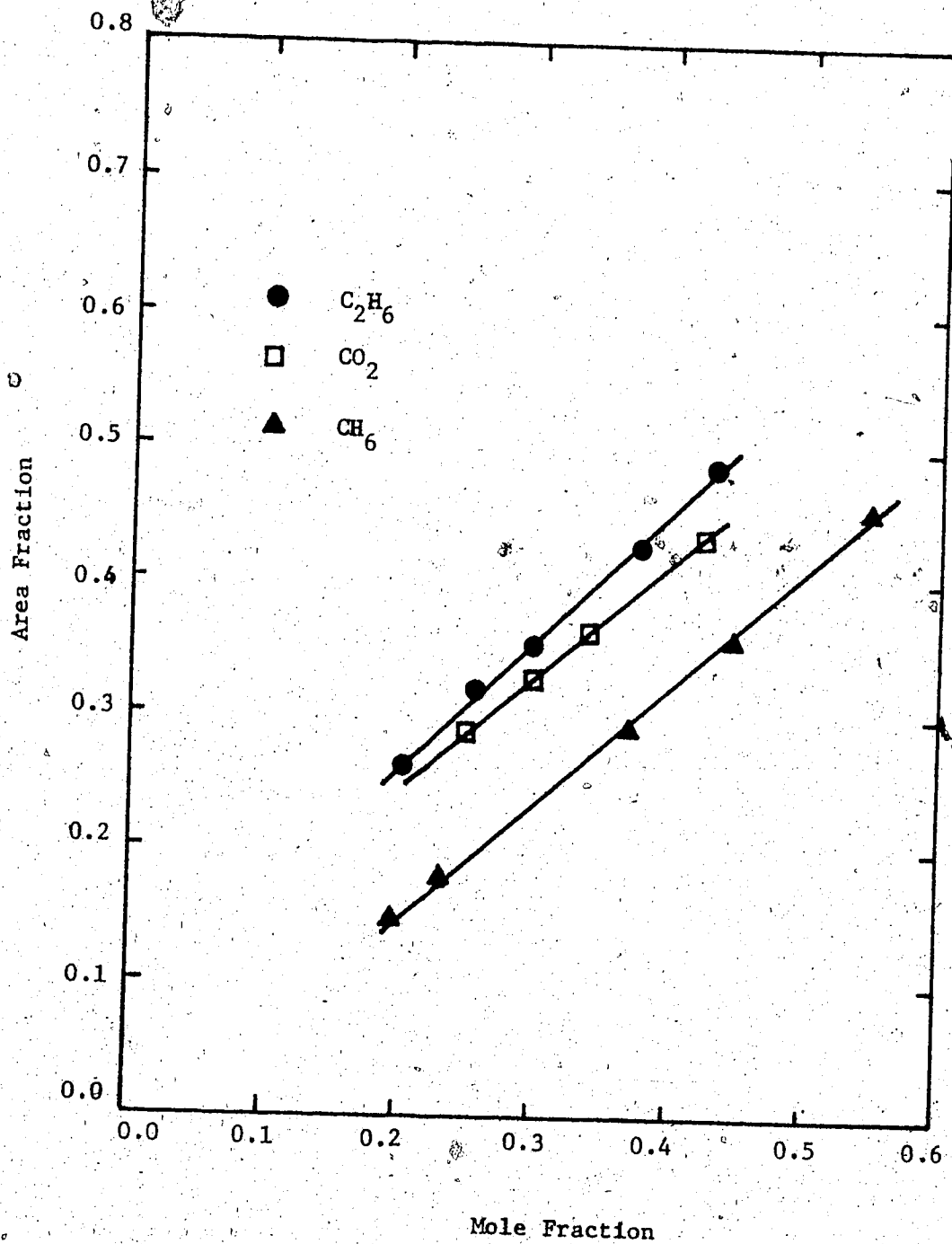
Figure 31: Gas Chromatograph Calibration for $CH_4$-$CO_2$-$C_2H_6$ Mixture
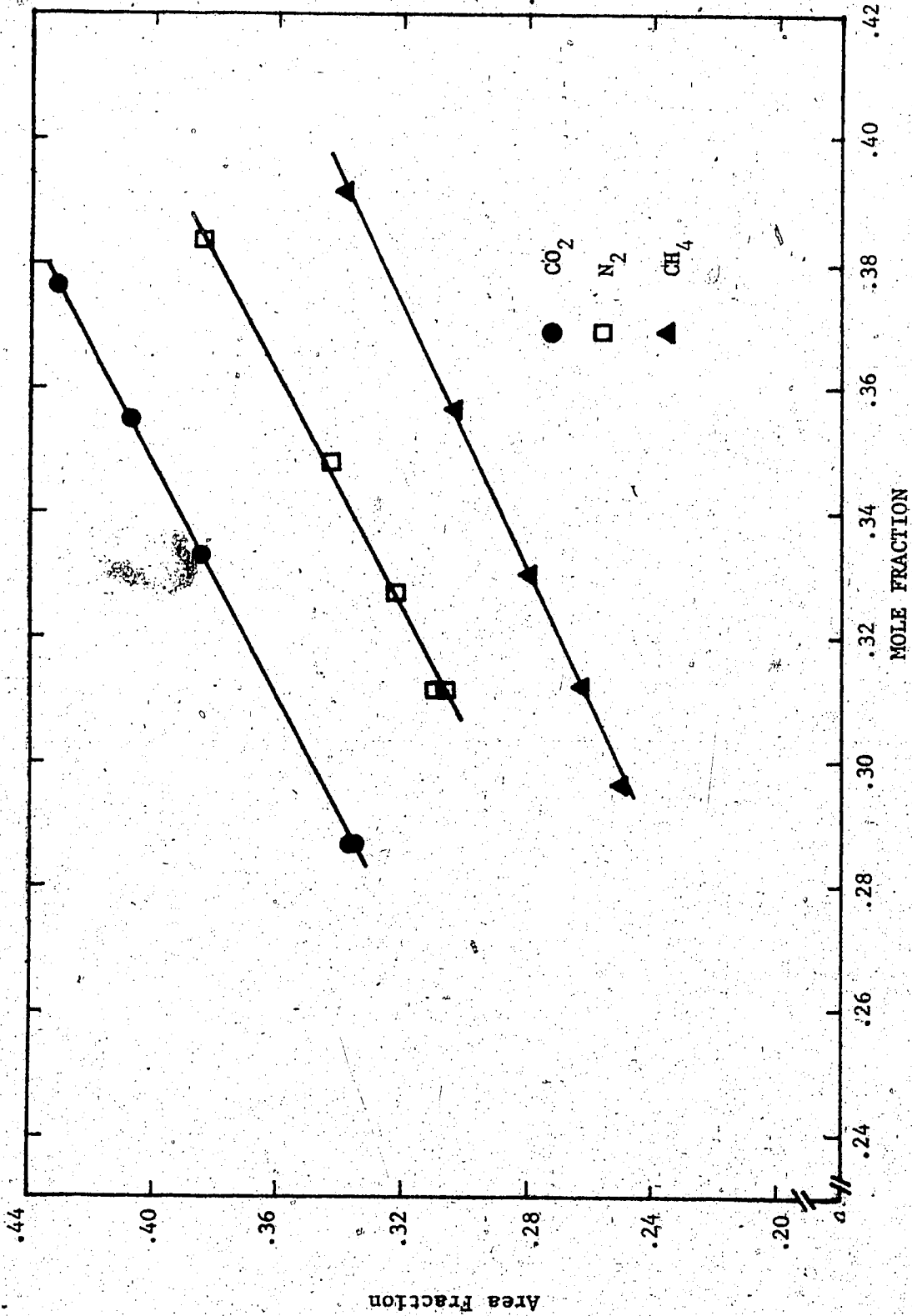
Figure 32: Gas Chromatograph Calibration for $CO_2$-$CH_4$-$N_2$ Mixture
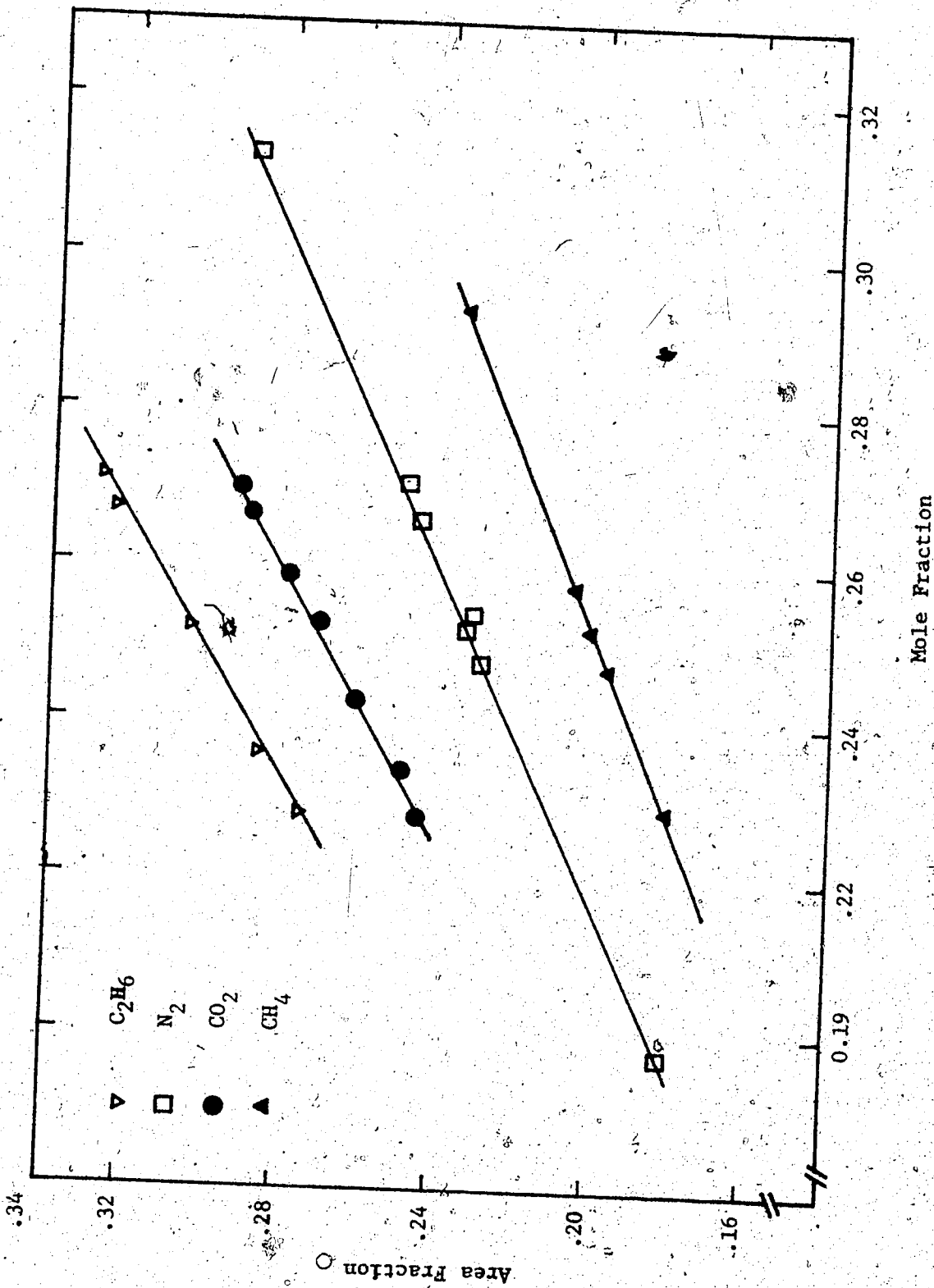
Figure 33: Gas Chromatograph Calibration for $CH_4-CO_2-N_2-C_2H_6$ Mixture

## *Error Analysis*

The desired values of the isothermal throttling coefficient is determined from the results of measurement:

$$\phi_m = \left(\frac{\Delta H}{\Delta P}\right)_T = -\frac{\dot{W}}{\Delta P \cdot F} \tag{A1}$$

where $\dot{W}$ = power supply

$F$ = mass flow rate

$\Delta P$ = pressure drop across the throttling unit

The maximum relative error of $\phi_m$ in the experiment is

$$\frac{\Delta \phi}{\phi} = \frac{\Delta \dot{W}}{\dot{W}} + \frac{\Delta(\Delta P)}{\Delta P} + \frac{\Delta F}{F} + \frac{1}{\phi}[\left(\frac{\partial \phi}{\partial P}\right)_{T,x} \Delta P_m$$

$$+ \left(\frac{\partial \phi}{\partial T}\right)_{P,x} \Delta T_m + \left(\frac{\partial \phi}{\partial x}\right)_{P,T} \Delta x] \tag{A2}$$

where $\Delta T_m$ = error in the measurement of inlet temperature of the gas in the calorimeter

$\Delta P_m$ = error in the measurement of the system pressure $P_m$

$\Delta x$ = error in the measurement of composition in the mixture

Clearly,

$$\frac{\Delta \dot{W}}{\dot{W}} = \frac{\Delta \dot{W}_H}{\dot{W}_H} + \left(\frac{\Delta \dot{W}}{\dot{W}}\right)_{rel} + \frac{\dot{W}_{loss}}{\dot{W}} \tag{A3}$$

where $\Delta \dot{W}_H / \dot{W}_H$ = calculated error of measurement of the compensating power of the calorimeter heater; $(\Delta \dot{W}/\dot{W})_{rel}$ = error in the value of the compensating power, due to the non-zero value of the temperature difference between the inlet and outlet; $\Delta \dot{W}_{loss}/\dot{W}$ = error connected with spurious heat transfer between the calorimeter and the thermostat.

In this experiment, a Hewlett-Packard Model 3450 multifunction meter is used for all electrical measurements. For $\dot{W} = IV$, the measurement of current I is by means of measuring the voltage drop across a standard resistor, the uncertainty of voltage is about $\pm 5$ microvolt. So the term $(\Delta\dot{W}/\dot{W})_H = \pm(0.005 - 0.002)$ %. The term $(\Delta\dot{W}/\dot{W})_{rel}$ can be replaced by the ratio $\Delta T_1/\Delta T_{ad}$, where $\Delta T_1$ = the degree of non-isothermal state of the inlet and outlet of the gas when the calorimeter is in operation; $\Delta T_{ad}$ = degree of non-isothermal state when no heat is added. The deviation of null meter which is used for the measurement of the output of the five junction thermopile is about $\pm 2\,\mu V$ which is equivalent to 0.01°C, then

$$\frac{\Delta T_1}{\Delta T_{ad}} = \frac{\pm 0.01}{\Delta T_{ad}} = \frac{\pm 1}{\Delta T_{ad}} \%$$

For nitrogen: $\qquad 0.1\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.35\%$

For $CH_4(43.3\%)-CO_2$: $\qquad 0.03\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.1\%$

For Equimolal $CO_2-CH_4-C_2H_6$: $0.03\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.1\%$

The term $(\dot{W}_{loss}/\dot{W})$ is minimized by using the radiation shield surrounding the throttling unit and the calorimeter is evacuated to about 5 microns. This term can be neglected. The error in determining $\Delta P$ and F are:

for $\qquad \dfrac{\Delta(\Delta P)}{\Delta P} = \pm 0.5\%$

and for $\quad (\Delta F/F)$:

$\qquad (\Delta F/F) \leq \pm 0.8\% \qquad$ for nitrogen

$\qquad\qquad\quad \leq \pm 1.0\% \qquad$ for 42.3% $CH_4$ in $CO_2$ mixture

$\qquad\qquad\quad \leq \pm 0.5\% \qquad$ for other mixtures

so, the maximum systematic error without the related error i.e. without allowing for the last term in Equation (A2) is

$\pm 0.5 \leq \epsilon \leq \pm 1.4$      for nitrogen

$\pm 0.5 \leq \epsilon \leq \pm 1.6$      for 42.3% methane in $CO_2$ mixture

$\pm 0.5 \leq \epsilon \leq \pm 1.1$      for other systems

The temperature of the gas in the calorimeter is measured with an error of less than $\pm 0.01°C$, i.e. $\Delta T_m = 0.01°C$. The test value $\phi$ are related to the pressure $P_m = P_1 - (\Delta P/2)$ and the inaccuracy of determining the pressure is taken as $\pm 1.0$ psi (the resolution of the Heise gauge). The term $\frac{1}{\phi} [(\frac{\partial \phi}{\partial P})_{T,x} \Delta P_m] = \epsilon_1$ will be,

$\pm 0.0003 \leq \epsilon_1 \leq 0.002\%$      for nitrogen-

and      $\pm 0.0005 \leq \epsilon_1 \leq 0.15\%$      for 42.3% $CH_4$ in $CO_2$ mixture. The term $\frac{1}{\phi} [(\frac{\partial \phi}{\partial T})_{P,x} \Delta T_m] = \epsilon_2$, will be less 0.1% for methane-carbon dioxide mixtures.

# APPENDIX B

## ENTHALPY FORMULAE AND LOOP CHECKS

*I. FORMULAE USED IN CALCULATION OF PROPERTIES FROM EQUATIONS OF STATE*

1. *Benedict-Webb-Rubin Equation*

a) *Enthalpy Departure*

$$(\underline{H}_P - \underline{H}_o)_T = (B_0RT - 2A_0 - \frac{4C_0}{T^2})\rho + (bRT - \frac{3a}{2})\rho^2 + \frac{6a\alpha\rho^5}{5}$$

$$+ \frac{c\rho^2}{T^2} [\frac{3(1 - e^{-\gamma\rho^2})}{\gamma\rho^2} - \frac{e^{-\gamma\rho^2}}{2} + \gamma\rho^2 e^{-\gamma\rho^2}]$$

b) *Isothermal Throttling Coefficient*

$$\phi = \sqrt{\frac{(B_0RT-2A_0-\frac{4C_0}{T^2}) + (2bRT-3a)\rho + 6a\alpha\rho^4 + \frac{e^{-\gamma\rho^2}}{T^2}[5\rho+5\gamma\rho^3-2\gamma^2\rho^5]}{RT + 2\rho(B_0RT-A_0-\frac{C_0}{T^2}) + 3\rho^2(bRT-a) + 6a\alpha\rho^5 + \frac{ce^{-\gamma\rho^2}}{T^2}[3\rho^2(1+\gamma\rho^2) - 2\gamma^2\rho^6]}}$$

2. *Soave-Redlich-Kwong Equation*

a) *Enthalpy Departure*

$$(\underline{H}_P - \underline{H}_o)_T = P\underline{V} - RT + \frac{T\frac{da}{dT} - a}{b} \ln \frac{\underline{V} + b}{\underline{V}}$$

b) *Isothermal Throttling Coefficient*

$$\phi = \underline{V} - T \frac{\left[\frac{R}{\underline{V} - b} - \frac{(\frac{da}{dT})}{\underline{V}(\underline{V} + b)}\right]}{\left[\frac{RT}{(\underline{V} - b)^2} - \frac{a(2\underline{V} + b)}{\underline{V}^2(\underline{V} + b)^2}\right]}$$

## 3. Starling Benedict-Webb-Rubin Equation

### a) Enthalpy Departure

$$(H_p - H_o)_T = (B_0RT - 2A_0 - \frac{4C_0}{T^2} - \frac{5D_0}{T^3} + \frac{6E_0}{T^4})\rho + \frac{1}{2}(2bRT - 3a - \frac{4d}{T})\rho^2 + \frac{1}{5}\alpha(6a + \frac{7d}{T})\rho^5 + \frac{c\rho^2}{\gamma T^2}[3 - (3 + \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4)\exp(-\gamma\rho^2)]$$

### b) Isothermal Throttling Coefficient

$$\phi = \frac{1}{\rho} - T\frac{\rho[R + (B_0R + \frac{2C_0}{T^3} - \frac{3D_0}{T^4} + \frac{4E_0}{T^5})\rho + (bR - \frac{d}{T^2})\rho^2 - \frac{\alpha d\rho^5}{T^2} - \frac{2c\rho^2}{T^3}(1+\gamma\rho^2)\,e^{-\gamma\rho^2}]}{\rho^2[R + \rho(2B_0R - \frac{2A_0}{T} - \frac{2C_0}{T^3} + \frac{2D_0}{T^4} - \frac{2E_0}{T^5}) + 3\rho^2(bR - \frac{a}{T} - \frac{d}{T^2}) + 6\alpha\rho^5(\frac{a}{T} + \frac{d}{T^2}) + \frac{(3c\rho^2 + 3c\gamma\rho^4 - 2c\gamma^2\rho^6)}{T^3}\,e^{-\gamma\rho^2}]}$$

## II. *THERMODYNAMIC CONSISTENCY CHECKS*

The isothermal data of two mixtures of methane and carbon dioxide of this work were used in conjunction with isobaric data of Bishnoi to test the consistency of the experimental data. The location of the loops is shown in Figure 34 and 35. The enthalpy change along different paths are given in Table XXVII and XXVIII. The maximum deviation was 0.37 percent.
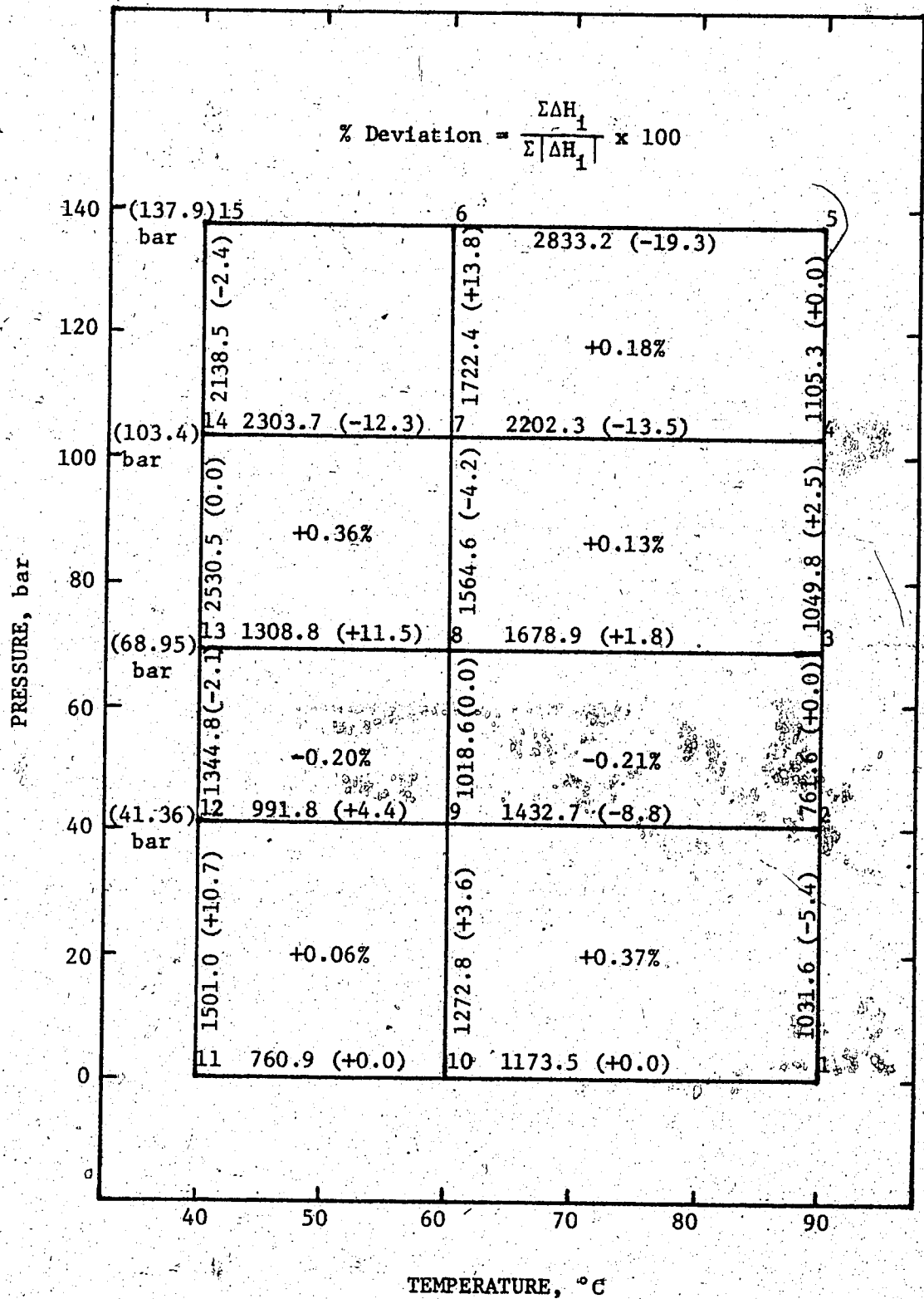
Figure 34:   Location of Experimental Loops for 14.5 Percent Methane
in Carbon Dioxide
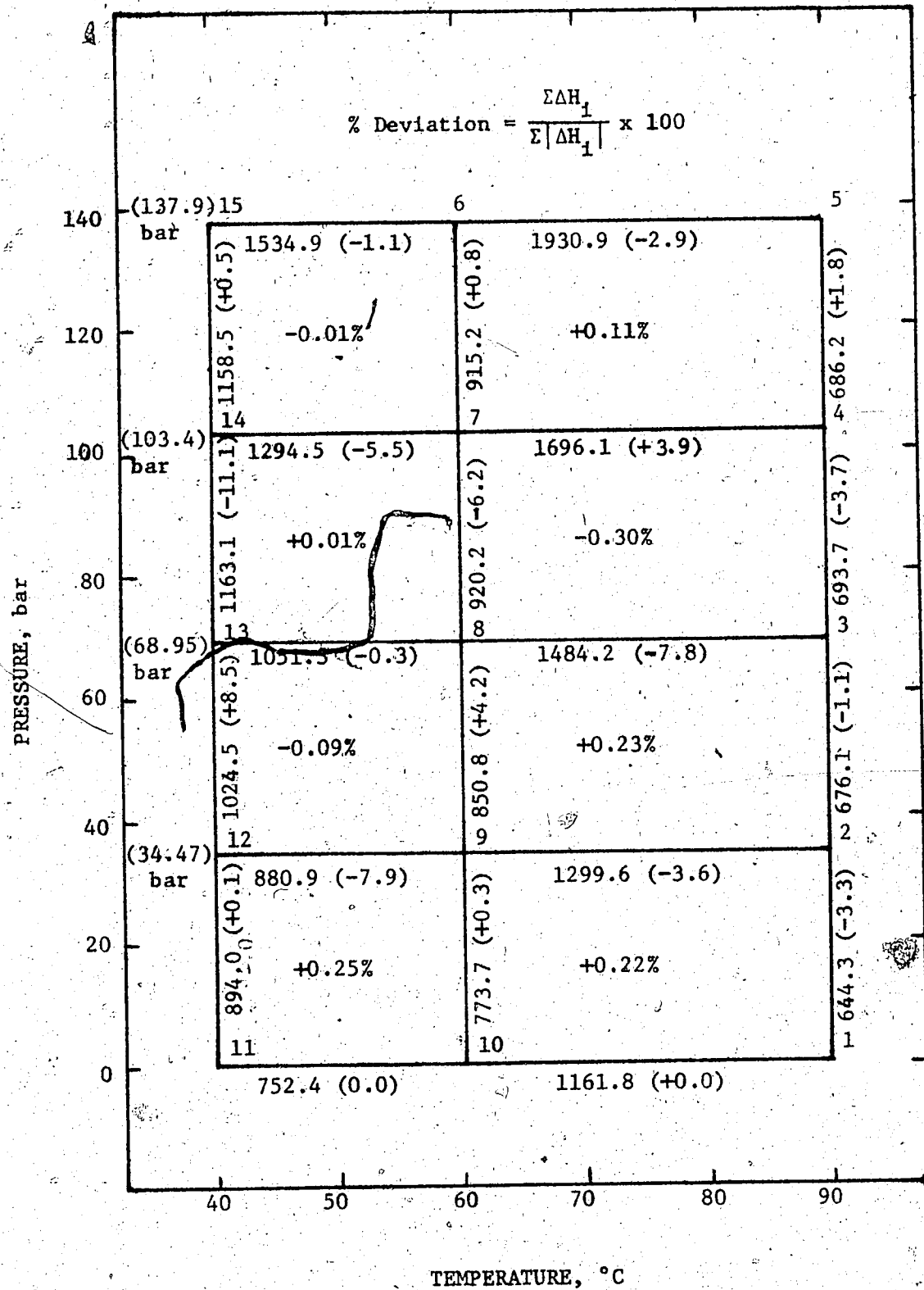
Figure 35: Location of Experimental Loops for 42.3 Percent Methane in Carbon Dioxide

TABLE XXVII

CONSISTENCY CHECKS ON THE MIXTURE OF 14.5

MOLE PERCENT METHANE IN CARBON DIOXIDE

| Loops | $\Delta H$ J mol$^{-1}$ | % Deviation |
|---|---|---|
| 1- 2- 9 | +2464.3 | |
| 1-10- 9 | -2446.3 | +0.37 |
| 2- 3- 8 | +2440.7 | |
| 2- 9- 8 | -2451.3 | -0.21 |
| 3- 4- 7 | +3252.1 | |
| 3- 8- 7 | -3243.5 | +0.13 |
| 4- 5- 6 | +3938.5 | |
| 4- 7- 6 | -3924.7 | +0.18 |
| 10- 9-12 | +2264.6 | |
| 10-11-12 | -2261.9 | +0.06 |
| 9- 8-13 | +2327.4 | |
| 9-12-13 | -2336.6 | -0.20 |
| 8- 7-14 | +3867.3 | |
| 8-13-14 | -3839.3 | +0.36 |

## TABLE XXVIII

## CONSISTENCY CHECKS ON THE MIXTURE OF 42.3
## MOLE PERCENT METHANE IN CARBON DIOXIDE

| Loops | $\Delta H$ J mol$^{-1}$ | % Deviation |
|-------|-------------------------|-------------|
| 1- 2- 9 | +1943.9 | |
| 1-10- 9 | -1935.5 | +0.22 |
| 2- 3- 8 | +2160.3 | |
| 2- 9- 8 | -2150.4 | +0.23 |
| 3- 4- 7 | +2389.8 | |
| 3- 8- 7 | -2404.4 | -0.30 |
| 4- 5- 6 | +2617.1 | |
| 4- 7- 6 | -2611.3 | +0.11 |
| 10- 9-12 | +1654.6 | |
| 10-11-12 | -1646.4 | +0.25 |
| 9- 8-13 | +1902.1 | |
| 9-12-13 | -1905.4 | -0.09 |
| 8- 7-14 | +2214.7 | |
| 8-13-14 | -2214.4 | +0.007 |
| 7- 6-15 | +2450.1 | |
| 7-14-15 | -2453.0 | -0.005 |

APPENDIX C


ISOTHERMAL THROTTLING COEFFICIENT

AT ZERO PRESSURE

TABLE XXIX

SECOND VIRIAL COEFFICIENT

| T (K) | B, cm³ mol⁻¹ | | | | B₁₂, cm³ mol⁻¹ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $CO_2$ | $CH_4$ | $N_2$ | $C_2H_6$ | $CO_2$-$CH_4$ | $CO_2$-$N_2$ | $CO_2$-$C_2H_6$ | $CH_4$-$N_2$ | $CH_4$-$C_2H_6$ | $N_2$-$C_2H_6$ |
| 233.15 | | -94.5 | -29.0 | - | -136.7 | -95.1 | - | -53.9 | - | |
| 253.15 | -150 | -65 | -15.5 | -254 | -97.6 | -68.9 | -175 | -33.4 | -136 | -80 |
| 273.15 | -127 | -54 | -10.5 | -220 | -81.2 | -57.3 | -155 | -26.7 | -113 | -66 |
| 293.15 | -110 | -45 | -5.8 | -192 | -67.3 | -45.7 | -133 | -19.6 | -97 | -54.8 |
| 313.15 | -95 | -37.5 | -2.0 | -166 | -57.3 | -37.3 | -113 | -15.1 | -84 | -45.2 |
| 333.15 | -83.5 | -31.5 | 1.0 | -145 | -48.5 | -30.5 | -96 | -10.6 | -73 | -37.0 |
| 353.15 | -73 | -26 | 3.8 | -127 | -43.1 | -25.1 | -83 | -7.14 | -64 | -29.9 |
| 373.15 | | -21 | 6.0 | -112 | -36.6 | -20.7 | -73 | -5.14 | -56 | -23.8 |

SOURCES:

Pure B are from Dymond and Smith[24]

B₁₂ for $CO_2$-$N_2$, $CO_2$-$CH_4$, and $CH_4$-$N_2$ are from Ng[63]

B₁₂ for $CO_2$-$C_2H_6$ is from Ng and Mather[64] and Zaalishvili[101]

B₁₂ for $CH_4$-$C_2H_6$ is from Hoover[31], Gunn[27] and Dantzler et al[20]

B₁₂ for $N_2$-$C_2H_6$ is from Pitzer and Curl Correlation[70]

## TABLE XXX

### $\phi°$ From Second Virial Coefficient

$$\phi° = B_m - T \frac{dB_m}{dT}$$

| T (K) | $B_m$ (cm³mol⁻¹) | $\frac{dB_m}{dT}$ (cm³mol⁻¹K⁻¹) | $\phi°$ (J mol⁻¹ bar⁻¹) | $B_m$ (cm³mol⁻¹) | $\frac{dB_m}{dT}$ (cm³mol⁻¹K⁻¹) | $\phi°$ (Jmol⁻¹bar⁻¹) |
|---|---|---|---|---|---|---|
| | **42.3% CH₄ in CO₂** | | | **14.5% CH₄ in CO₂** | | |
| 273.15 | −99.3 | 0.825 | −32.46 | −127.8 | 1.15 | −44.23 |
| 283.15 | − | − | − | −118.2 | 1.02 | −40.92 |
| 293.15 | − | − | − | −108.1 | 0.890 | −36.79 |
| 313.15 | −71.5 | 0.542 | −24.10 | −93.38 | 0.72 | −31.91 |
| 333.15 | −61. | 0.452 | −21.30 | −80.37 | 0.59 | −27.78 |
| 363.15 | −49.5 | 0.364 | −18.20 | −65.5 | 0.474 | −23.81 |
| | **Equimolal CH₄ − CO₂ − N₂** | | | **Equimolal CH₄ − CO₂ − N₂** | | |
| 243.15 | −80.91 | 0.738 | −26.03 | −115.5 | 1.00 | −35.90 |
| 263.15 | −66.96 | 0.609 | −22.8 | −97.0 | 0.825 | −31.40 |
| 283.15 | −54.88 | 0.514 | −19.04 | −84.0 | 0.67 | −27.20 |
| 303.15 | − | − | − | −69.5 | 0.55 | −23.60 |
| 333.15 | − | − | − | −53.5 | 0.425 | −19.87 |
| | **Equimolal CH₄ − CO₂ − C₂H₆** | | | **CO₂(0.25) − CH₄(0.5) − C₂H₆(0.25)** | | |
| 263.15 | −134.5 | 1.08 | −41.8 | −111.5 | 0.95 | −36.2 |
| 273.15 | −124.0 | 1.02 | −40.2 | −103.0 | 0.825 | −32.8 |
| 293.15 | −106.0 | 0.82 | −34.6 | −88.0 | 0.683 | −28.8 |
| 313.15 | −90.5 | 0.68 | −30.4 | −75.0 | 0.567 | −25.2 |
| 333.15 | −77.5 | 0.57 | −26.8 | −64.0 | 0.48 | −22.3 |
| 363.15 | −63.0 | 0.447 | −22.6 | −51.5 | 0.373 | −18.68 |

APPENDIX D

EXPERIMENTAL DATA

## TABLE XXXI

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
### TEMPERATURE (K) = 273.15

| PI | ΔP | POWER | FLOW | ΔH | −(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | IOL−BAR |
| 426.5 | 176.6 | 190.115 | 2.1936 | 86.666 | 7.117 |
| 607.5 | 201.4 | 282.256 | 2.9607 | 95.334 | 6.865 |
| 613.4 | 203.4 | 290.666 | 2.9842 | 97.400 | 6.945 |
| 813.4 | 205.0 | 339.198 | 3.6109 | 93.936 | 6.646 |
| 813.5 | 203.5 | 331.240 | 3.5841 | 92.419 | 6.586 |
| 1112.0 | 212.5 | 401.705 | 4.3842 | 91.625 | 6.253 |
| 1117.0 | 207.5 | 393.090 | 4.3947 | 89.445 | 6.252 |
| 1415.0 | 211.5 | 432.904 | 5.0767 | 85.272 | 5.847 |
| 1416.0 | 207.3 | 412.422 | 4.9977 | 82.520 | 5.773 |
| 1416.0 | 206.0 | 410.424 | 5.0208 | 81.743 | 5.755 |
| 1713.0 | 178.2 | 342.220 | 5.2161 | 65.607 | 5.339 |
| 1713.0 | 177.5 | 338.782 | 5.2024 | 65.119 | 5.321 |
| 1713.0 | 176.2 | 333.636 | 5.1748 | 64.473 | 5.307 |
| 2020.0 | 147.6 | 249.642 | 5.1748 | 8.241 | 4.740 |
| 2020.0 | 146.5 | 248.226 | 5.1470 | 48.227 | 4.774 |
| 2020.0 | 145.0 | 242.927 | 5.1190 | 47.455 | 4.746 |
| 2317.0 | 132.5 | 198.180 | 5.1748 | 38.297 | 4.192 |
| 431.5 | 173.0 | 189.505 | 2.1964 | 86.276 | 7.233 |
| 431.5 | 172.9 | 187.716 | 2.2049 | 85.133 | 7.141 |
| 431.5 | 172.7 | 188.537 | 2.1964 | 85.836 | 7.208 |
| 431.5 | 172.6 | 191.484 | 2.2106 | 86.620 | 7.278 |
| 431.5 | 172.6 | 186.866 | 2.2021 | 84.856 | 7.130 |
| 618.5 | 188.0 | 259.678 | 2.9374 | 88.403 | 6.820 |
| 618.5 | 187.0 | 255.522 | 2.9327 | 87.127 | 6.757 |
| 618.5 | 184.9 | 252.217 | 2.9163 | 86.483 | 6.783 |
| 813.5 | 186.5 | 293.902 | 3.4953 | 84.085 | 6.539 |
| 813.5 | 184.7 | 289.751 | 3.4748 | 83.385 | 6.547 |
| 1107.0 | 185.0 | 328.327 | 4.1731 | 78.675 | 6.168 |
| 1107.0 | 183.8 | 326.156 | 4.1731 | 78.155 | 6.167 |
| 1414.0 | 186.3 | 355.320 | 4.8055 | 73.938 | 5.756 |
| 1714.0 | 186.2 | 557.066 | 5.3453 | 104.214 | 8.117 |
| 1714.0 | 185.8 | 356.000 | 5.3453 | 66.599 | 5.198 |
| 1714.0 | 185.7 | 357.251 | 5.3453 | 66.833 | 5.219 |
| 1714.0 | 185.5 | 352.784 | 5.3320 | 66.163 | 5.173 |
| 2014.0 | 164.9 | 293.360 | 5.4640 | 53.689 | 4.722 |
| 2014.0 | 164.0 | 289.930 | 5.4588 | 53.112 | 4.697 |
| 2014.0 | 162.6 | 287.597 | 5.4301 | 52.963 | 4.724 |
| 2304.0 | 143.7 | 225.535 | 5.4562 | 41.335 | 4.172 |
| 2304.0 | 143.0 | 222.120 | 5.4379 | 40.846 | 4.142 |
| 2304.0 | 142.3 | 220.159 | 5.4248 | 40.583 | 4.136 |

## TABLE XXXI (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
#### TEMPERATURE (K) = 303.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 415.3 | 178.0 | 139.891 | 2.0399 | 68.576 | 5.587 |
| 425.3 | 182.0 | 149.643 | 2.0838 | 71.810 | 5.722 |
| 463.5 | 198.1 | 178.370 | 2.2331 | 79.874 | 5.845 |
| 463.5 | 197.0 | 175.081 | 2.2998 | 76.127 | 5.604 |
| 815.3 | 215.1 | 273.546 | 3.5260 | 77.578 | 5.229 |
| 615.3 | 208.0 | 225.506 | 2.8728 | 78.496 | 5.473 |
| 616.0 | 249.0 | 292.125 | 3.1245 | 93.493 | 5.445 |
| 619.5 | 211.5 | 230.857 | 2.9280 | 78.842 | 5.406 |
| 619.5 | 207.0 | 2 3.696 | 2.8093 | 79.626 | 5.579 |
| 619.5 | 206.9 | 2.568 | 2.8093 | 79.224 | 5.553 |
| 815.0 | 229.5 | 1.703 | 3.6452 | 82.766 | 5.230 |
| 817.0 | 232.2 | 305.814 | 3.6784 | 83.137 | 5.191 |
| 1115.0 | 204.8 | 287.775 | 4.1685 | 69.034 | 4.887 |
| 1117.3 | 212.5 | 304.097 | 4.2306 | 71.879 | 4.906 |
| 1412.0 | 223.5 | 348.631 | 4.9740 | 70.089 | 4.548 |
| 1415.3 | 206.4 | 308.324 | 4.7696 | 64.642 | 4.542 |
| 1715.3 | 198.7 | 299.385 | 5.2362 | 57.175 | 4.172 |
| 1719.4 | 183.5 | 264.414 | 5.0426 | 52.436 | 4.144 |
| 2018.4 | 149.2 | 192.258 | 4.9691 | 38.590 | 3.759 |
| 2021.3 | 152.3 | 197.369 | 4.9897 | 39.554 | 3.766 |
| 2353.3 | 122.7 | 135.247 | 4.8283 | 28.011 | 3.309 |
| 2413.4 | 107.7 | 108.010 | 4.5983 | 23.449 | 3.161 |

## TABLE XXXI (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
### TEMPERATURE (K) = 343.45

| PI PSIA | ΔP PSI | POWER J/MIN | FLOW MOL/MIN | ΔH J/MOL | -(ΔH/ΔP) J/MOL-BAR |
|---|---|---|---|---|---|
| 433.6 | 195.2 | 116.445 | 2.0103 | 57.923 | 4.302 |
| 437.7 | 194.2 | 115.902 | 2.0282 | 57.143 | 4.266 |
| 437.7 | 193.7 | 115.608 | 2.0282 | 56.998 | 4.266 |
| 437.8 | 197.2 | 119.322 | 2.0521 | 58.145 | 4.276 |
| 618.6 | 205.4 | 153.454 | 2.6657 | 57.564 | 4.064 |
| 618.8 | 213.5 | 163.650 | 2.7233 | 60.092 | 4.082 |
| 619.7 | 213.0 | 161.977 | 2.7095 | 59.780 | 4.070 |
| 619.7 | 212.5 | 160.043 | 2.7095 | 59.066 | 4.031 |
| 619.7 | 212.7 | 160.764 | 2.7095 | 59.332 | 4.045 |
| 619.7 | 212.7 | 161.977 | 2.7095 | 59.780 | 4.076 |
| 814.8 | 212.2 | 184.680 | 3.2676 | 56.517 | 3.862 |
| 821.7 | 215.2 | 189.234 | 3.3061 | 57.236 | 3.856 |
| 818.6 | 225.6 | 201.634 | 3.3716 | 59.803 | 3.843 |
| 821.7 | 214.7 | 187.693 | 3.2954 | 56.955 | 3.846 |
| 1117.6 | 219.0 | 215.542 | 4.0098 | 53.753 | 3.558 |
| 1419.6 | 190.3 | 185.521 | 4.2858 | 43.287 | 3.299 |
| 1723.5 | 216.2 | 230.575 | 5.0837 | 45.355 | 3.042 |
| 2015.5 | 170.0 | 157.410 | 4.9053 | 32.089 | 2.737 |
| 2330.5 | 154.0 | 133.733 | 5.0421 | 26.523 | 2.497 |
| 2410.5 | 116.8 | 85.158 | 4.4146 | 19.289 | 2.394 |

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
### TEMPERATURE (K) = 374.15

| PI PSIA | ΔP PSI | POWER J/MIN | FLOW MOL/MIN | ΔH J/MOL | -(ΔH/ΔP) J/MOL-BAR |
|---|---|---|---|---|---|
| 437.8 | 206.3 | 97.202 | 1.9710 | 49.315 | 3.467 |
| 438.8 | 200.0 | 91.735 | 1.9557 | 46.904 | 3.401 |
| 438.8 | 199.5 | 90.746 | 1.9557 | 46.398 | 3.373 |
| 438.8 | 199.5 | 89.227 | 1.9557 | 45.622 | 3.316 |
| 623.8 | 210.5 | 120.692 | 2.5715 | 46.933 | 3.233 |
| 819.8 | 210.0 | 136.690 | 3.0971 | 44.133 | 3.047 |
| 1117.8 | 198.8 | 140.176 | 3.6508 | 38.395 | 2.800 |
| 1427.8 | 204.1 | 153.367 | 4.2426 | 36.149 | 2.568 |
| 1717.8 | 210.8 | 163.650 | 4.7643 | 34.349 | 2.363 |
| 1717.8 | 199.3 | 161.677 | 4.7519 | 34.023 | 2.475 |
| 2013.8 | 194.5 | 141.971 | 5.0038 | 28.372 | 2.115 |
| 2243.8 | 162.1 | 104.853 | 4.8254 | 21.729 | 1.944 |

## TABLE XXXII

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 14.5 MOLE PERCENT OF CH4 IN CO2
### TEMPERATURE (K) =    363.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 463.6 | 194.5 | 599.291 | 1.7574 | 340.996 | |
| 515.6 | 203.2 | 670.778 | 1.8832 | 356.175 | 25.427 |
| 611.6 | 197.0 | 768.228 | 2.1577 | 356.024 | 25.416 |
| 611.6 | 196.2 | 762.697 | 2.1497 | 354.778 | 26.211 |
| 613.6 | 181.7 | 664.204 | 2.0273 | 327.616 | 26.219 |
| 809.6 | 175.6 | 825.870 | 2.4907 | 331.578 | 26.144 |
| 813.6 | 182.5 | 845.143 | 2.4602 | 343.519 | 27.386 |
| 1012.0 | 174.2 | 994.177 | 2.8914 | 343.837 | 27.300 |
| 1012.0 | 172.5 | 946.085 | 2.7823 | 340.035 | 28.619 |
| 1212.0 | 162.6 | 1057.043 | 3.1641 | 334.067 | 28.590 |
| 1216.0 | 157.5 | 979.680 | 3.0210 | 324.286 | 29.798 |
| 1412.0 | 158.2 | 1165.951 | 3.4688 | 336.118 | 29.862 |
| 1406.0 | 138.7 | 928.892 | 3.1363 | 296.173 | 30.815 |
| 1406.0 | 130.4 | 847.899 | 3.0333 | 279.527 | 30.959 |
| 1612.0 | 145.2 | 1158.108 | 3.6477 | 317.483 | 31.090 |
| 1612.0 | 141.0 | 1109.409 | 3.5917 | 308.880 | 31.712 |
| 1612.0 | 91.5 | 567.449 | 2.7933 | 203.146 | 31.772 |
| 1818.0 | 140.0 | 1211.007 | 3.9045 | 310.154 | 32.201 |
| 1994.0 | 118.0 | 1001.584 | 3.8234 | 261.961 | 32.131 |
| 2020.0 | 125.2 | 1098.551 | 3.9755 | 276.330 | 32.198 |
| | | | | | 31.998 |

TABLE XXXII (continued).

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) =      313.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 415.6 | 169.8 | 692.946 | 1.6171 | 428.501 | 36.601 |
| 605.6 | 184.5 | 1134.688 | 2.2090 | 513.666 | 40.380 |
| 605.6 | 184.0 | 1130.029 | 2.2066 | 512.100 | 40.366 |
| 813.6 | 163.5 | 1368.037 | 2.6132 | 523.509 | 46.439 |
| 1010.0 | 143.4 | 1578.056 | 2.9236 | 539.746 | 54.591 |
| 1010.0 | 142.5 | 1567.262 | 2.9155 | 537.552 | 54.712 |
| 1214.0 | 134.0 | 2047.897 | 3.3280 | 615.335 | 66.602 |
| 1214.0 | 133.2 | 2031.559 | 3.3210 | 611.727 | 66.584 |
| 1310.0 | 128.8 | 2295.553 | 3.5142 | 653.212 | 73.556 |
| 1412.0 | 127.3 | 2671.699 | 3.7815 | 706.508 | 80.495 |
| 1412.0 | 126.5 | 2647.914 | 3.7736 | 701.683 | 80.451 |
| 1415.0 | 83.0 | 1450.356 | 3.0791 | 471.026 | 82.309 |
| 1524.0 | 106.1 | 2314.756 | 3.7154 | 623.000 | 85.163 |
| 1524.0 | 104.9 | 2279.477 | 3.7003 | 616.013 | 85.171 |
| 1611.0 | 115.6 | 2776.365 | 4.1741 | 665.140 | 83.452 |
| 1701.0 | 109.2 | 2422.618 | 4.3113 | 561.915 | 74.632 |
| 1701.0 | 108.2 | 2378.256 | 4.2854 | 554.960 | 74.390 |
| 1814.0 | 96.0 | 1699.500 | 4.2540 | 399.502 | 60.357 |
| 1915.0 | 102.9 | 1577.787 | 4.5818 | 344.354 | 48.536 |
| 1915.0 | 102.5 | 1570.591 | 4.5735 | 343.410 | 48.592 |
| 1915.0 | 101.2 | 1536.208 | 4.5553 | 337.233 | 48.331 |
| 2013.0 | 86.0 | 981.341 | 4.2963 | 228.412 | 38.521 |

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) =    333.15

| PI | ΔP | POWER | FLOW | ΔH | −(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL−BAR |
| 513.6 | 215.5 | 931.854 | 1.9674 | 473.635 | 31.877 |
| 713.6 | 177.5 | 981.050 | 2.3166 | 423.471 | 34.602 |
| 915.6 | 157.4 | 1073.432 | 2.6157 | 410.375 | 37.814 |
| 915.6 | 156.5 | 1065.170 | 2.6118 | 407.829 | 37.796 |
| 1112.0 | 159.2 | 1376.845 | 3.0448 | 452.192 | 41.196 |
| 1112.0 | 158.9 | 1372.038 | 3.0414 | 451.107 | 41.175 |
| 1314.0 | 154.4 | 1639.549 | 3.4118 | 480.538 | 45.140 |
| 1314.0 | 154.0 | 1635.234 | 3.4099 | 479.550 | 45.164 |
| 1314.0 | 153.5 | 1626.892 | 3.4010 | 478.345 | 45.197 |
| 1512.0 | 136.5 | 1660.767 | 3.5912 | 462.452 | 49.137 |
| 1514.0 | 144.0 | 1798.145 | 3.7095 | 484.729 | 48.822 |
| 1514.0 | 142.4 | 1769.884 | 3.6826 | 480.600 | 48.950 |
| 1762.0 | 127.0 | 1770.634 | 3.9594 | 447.197 | 51.071 |
| 1762.0 | 128.0 | 1802.599 | 3.9817 | 452.714 | 51.297 |
| 1762.0 | 125.0 | 1730.858 | 3.9369 | 439.649 | 51.012 |
| 2012.0 | 102.8 | 1329.178 | 3.9817 | 333.816 | 47.097 |
| 2012.0 | 100.7 | 1290.213 | 3.9427 | 327.236 | 47.131 |

# TABLE XXXII (continued)

## TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 14.5 MOLE PERCENT OF CH4 IN CO2
### TEMPERATURE (K) = 293.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 418.5 | 156.8 | 830.148 | 1.7112 | 485.108 | 44.871 |
| 418.5 | 156.2 | 825.384 | 1.7067 | 483.607 | 44.904 |
| 419.5 | 159.0 | 823.012 | 1.6562 | 496.904 | 45.327 |
| 420.5 | 160.8 | 840.886 | 1.6770 | 501.398 | 45.224 |
| 517.5 | 157.5 | 1036.280 | 1.9754 | 524.579 | 48.307 |
| 517.5 | 156.1 | 1027.045 | 1.9631 | 523.157 | 48.608 |
| 555.5 | 142.5 | 1028.620 | 2.0659 | 497.883 | 50.675 |
| 609.5 | 140.0 | 1142.614 | 2.1992 | 519.543 | 53.823 |
| 613.5 | 145.5 | 1158.057 | 2.1467 | 539.437 | 53.772 |
| 708.5 | 142.5 | 1470.338 | 2.4938 | 589.575 | 60.007 |
| 807.5 | 142.5 | 1807.548 | 2.6698 | 677.030 | 68.908 |
| 957.6 | 168.5 | 1827.272 | 1.7617 | 1037.166 | 89.275 |
| 959.5 | 143.9 | 2817.071 | 3.0885 | 912.089 | 91.930 |
| 959.5 | 141.3 | 2779.054 | 3.1005 | 896.305 | 92.001 |
| 959.5 | 139.9 | 2753.518 | 3.1081 | 885.899 | 91.843 |
| 1009.6 | 165.0 | 2243.140 | 1.9000 | 1180.577 | 103.774 |
| 1014.0 | 102.2 | 2359.670 | 2.9580 | 797.721 | 113.209 |
| 1054.0 | 128.0 | 2302.114 | 2.0906 | 1101.130 | 124.770 |
| 1052.0 | 101.6 | 2267.335 | 2.4770 | 915.342 | 130.668 |
| 1054.0 | 102.2 | 2250.984 | 2.4568 | 916.193 | 130.022 |
| 1108.0 | 102.4 | 3348.740 | 2.8421 | 1178.242 | 166.884 |
| 1108.0 | 101.5 | 3375.931 | 2.8942 | 1166.423 | 166.675 |
| 1108.0 | 101.2 | 3362.466 | 2.8777 | 1168.420 | 167.455 |
| 1156.0 | 93.5 | 4276.152 | 3.0768 | 1389.764 | 215.581 |
| 1204.0 | 87.1 | 4685.280 | 3.2941 | 1422.285 | 236.837 |
| 1204.0 | 84.4 | 4551.967 | 3.2967 | 1380.748 | 237.276 |
| 1234.0 | 86.0 | 5017.247 | 3.8250 | 1311.665 | 221.210 |
| 1262.0 | 80.5 | 4043.094 | 3.8155 | 1059.625 | 190.914 |
| 1262.0 | 80.0 | 4009.822 | 3.8311 | 1046.641 | 189.753 |
| 1298.0 | 84.6 | 3654.539 | 4.1202 | 886.974 | 152.062 |
| 1318.0 | 82.5 | 3054.063 | 4.1635 | 733.520 | 128.955 |
| 1318.0 | 82.0 | 3013.848 | 4.1525 | 725.776 | 128.372 |
| 1318.0 | 81.7 | 3000.119 | 4.1399 | 724.667 | 128.646 |
| 1318.0 | 80.5 | 2933.559 | 4.1051 | 714.607 | 128.751 |
| 1362.0 | 84.6 | 2367.385 | 4.3587 | 543.137 | 93.115 |
| 1614.0 | 95.7 | 951.568 | 5.0363 | 188.941 | 28.634 |
| 1614.0 | 95.2 | 939.028 | 5.0300 | 186.682 | 28.441 |
| 1614.0 | 94.0 | 920.727 | 5.0000 | 184.144 | 28.412 |
| 1464.0 | 83.0 | 1298.474 | 4.5320 | 286.509 | 50.065 |
| 1813.0 | 92.5 | 566.047 | 5.0858 | 111.298 | 17.451 |
| 1813.0 | 92.5 | 566.047 | 5.0889 | 111.231 | 17.440 |
| 2008.0 | 79.0 | 311.398 | 4.7829 | 65.105 | 11.952 |
| 2009.0 | 75.4 | 293.467 | 4.6643 | 62.916 | 12.102 |

# TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) =  283.15

| PI<br>PSIA | ΔP<br>PSI | POWER<br>J/MIN | FLOW<br>MOL/MIN | ΔH<br>J/MOL | -(ΔH/ΔP)<br>J/MOL-BAR |
|---|---|---|---|---|---|
| 419.5 | 145.8 | 889.046 | 1.6090 | 552.526 | 54.963 |
| 419.5 | 145.6 | 887.201 | 1.6107 | 550.815 | 54.868 |
| 483.5 | 143.6 | 1036.845 | 1.7854 | 580.727 | 54.868 |
| 553.5 | 138.5 | 1191.556 | 1.9573 | 608.755 | 58.654 |
| 628.5 | 131.0 | 1366.217 | 2.1245 | 643.058 | 63.749 |
| 629.5 | 131.0 | 1367.535 | 2.1245 | 643.679 | 71.196 |
| 695.5 | 123.0 | 1529.424 | 2.2476 | 680.442 | 71.265 |
| 745.5 | 121.1 | 1772.513 | 2.3803 | 744.628 | 80.235 |
| 773.5 | 119.8 | 1955.877 | 2.4638 | 793.815 | 89.182 |
| 773.5 | 119.3 | 1944.557 | 2.4596 | 790.571 | 96.104 |
| 810.5 | 112.7 | 2129.922 | 2.5219 | 844.541 | 96.113 |
| 1246.5 | 100.5 | 1219.439 | 5.4257 | 224.750 | 108.687 |
| 1246.5 | 90.0 | 993.305 | 5.1261 | 193.771 | 32.435 |
| 1265.5 | 90.2 | 919.281 | 5.1564 | 178.276 | 31.226 |
| 1265.5 | 86.5 | 852.661 | 5.0463 | 168.967 | 28.666 |
| 1275.5 | 87.6 | 839.516 | 5.0833 | 165.149 | 28.331 |
| 1293.5 | 89.5 | 821.191 | 5.1534 | 159.347 | 27.343 |
| 1293.5 | 89.0 | 806.192 | 5.1504 | 156.528 | 25.822 |
| 1308.5 | 87.2 | 739.603 | 5.1017 | 144.969 | 25.508 |
| 1355.5 | 83.5 | 591.679 | 5.0245 | 117.758 | 24.112 |
| 1414.5 | 84.0 | 506.595 | 5.0864 | 99.597 | 20.454 |
| 1473.5 | 81.8 | 421.487 | 5.0419 | 83.596 | 17.196 |
| 1473.5 | 80.5 | 410.706 | 5.0026 | 82.098 | 14.822 |
| 1529.5 | 82.0 | 380.994 | 5.0864 | 74.903 | 14.791 |
| 1595.5 | 79.8 | 320.825 | 5.0431 | 63.615 | 13.248 |
| 1595.5 | 79.2 | 317.986 | 5.0214 | 63.326 | 11.562 |
| 1655.5 | 76.0 | 266.851 | 4.9362 | 54.060 | 11.596 |
| 1705.5 | 77.7 | 254.394 | 5.0182 | 50.693 | 10.316 |
| 1705.5 | 76.4 | 250.192 | 4.9806 | 50.233 | 9.462 |
| 1815.5 | 78.7 | 223.091 | 5.0956 | 43.780 | 9.536 |
| 1815.5 | 78.2 | 218.274 | 5.0772 | 42.991 | 8.068 |
| 1909.5 | 70.1 | 166.816 | 4.8295 | 34.541 | 7.973 |
| 2009.5 | 64.5 | 126.672 | 4.6552 | 27.210 | 7.146 |
| | | | | | 6.118 |

# TABLE XXXII (continued)

## TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 14.5 MOLE PERCENT OF CH4 IN CO2 TEMPERATURE (K) = 273.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 413.5 | 138.0 | 952.758 | 1.6319 | 583.803 | 61.357 |
| 413.5 | 137.5 | 941.973 | 1.6254 | 579.509 | 61.127 |
| 478.5 | 141.6 | 1214.074 | 1.8465 | 657.495 | 67.345 |
| 525.5 | 132.5 | 1312.969 | 1.9452 | 669.829 | 73.321 |
| 571.5 | 125.3 | 1424.137 | 2.0389 | 698.477 | 80.850 |
| 585.8 | 122.6 | 1464.387 | 2.0733 | 706.282 | 83.554 |
| 1051.0 | 89.5 | 1278.791 | 5.2261 | 244.688 | 39.652 |
| 1051.0 | 82.7 | 997.855 | 5.0250 | 198.575 | 34.825 |
| 1100.0 | 80.5 | 343.843 | 5.0062 | 68.682 | 12.374 |
| 1198.0 | 80.9 | 282.580 | 5.0623 | 55.819 | 10.007 |
| 1228.0 | 79.4 | 256.801 | 5.0125 | 51.231 | 9.358 |
| 1256.0 | 82.5 | 266.048 | 5.1299 | 51.862 | 9.117 |
| 1311.0 | 78.8 | 216.733 | 4.9365 | 43.903 | 8.080 |
| 1354.0 | 80.7 | 219.255 | 5.0932 | 43.048 | 7.736 |
| 1398.0 | 77.5 | 185.859 | 4.9999 | 37.172 | 6.956 |
| 1398.0 | 77.9 | 188.255 | 5.0125 | 37.556 | 6.992 |
| 1442.0 | 73.5 | 161.808 | 4.8786 | 33.166 | 6.544 |
| 1526.0 | 78.8 | 156.197 | 4.9873 | 31.318 | 5.764 |
| 1594.0 | 81.5 | 156.197 | 5.1771 | 30.170 | 5.369 |
| 1657.0 | 78.2 | 133.611 | 5.0809 | 26.296 | 4.877 |
| 1657.0 | 77.5 | 132.084 | 5.0561 | 26.123 | 4.888 |
| 1711.0 | 76.5 | 118.586 | 5.0281 | 23.584 | 4.471 |
| 1711.0 | 75.9 | 117.876 | 5.0094 | 23.530 | 4.496 |
| 1711.0 | 74.6 | 112.882 | 4.9684 | 22.719 | 4.417 |
| 1759.0 | 73.6 | 103.790 | 4.9410 | 21.005 | 4.139 |
| 1759.0 | 73.0 | 101.763 | 4.9173 | 20.694 | 4.111 |
| 1816.0 | 66.2 | 78.350 | 4.6995 | 16.671 | 3.652 |

## TABLE XXXIII

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 42.3 MOLE PERCENT OF CH4 IN CO2 TEMPERATURE (K) = 363.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 431.4 | 183.8 | 434.626 | 1.8047 | 240.829 | 19.004 |
| 431.4 | 183.2 | 431.792 | 1.7982 | 240.114 | 19.009 |
| 429.4 | 183.0 | 429.602 | 1.8017 | 238.442 | 18.897 |
| 619.4 | 195.0 | 616.525 | 2.3833 | 258.683 | 19.240 |
| 815.4 | 176.8 | 653.316 | 2.7407 | 238.370 | 19.554 |
| 815.4 | 176.2 | 649.560 | 2.7356 | 237.442 | 19.544 |
| 1017.0 | 167.5 | 709.719 | 3.0831 | 230.192 | 19.932 |
| 1017.0 | 166.8 | 705.380 | 3.0761 | 229.302 | 19.938 |
| 1217.0 | 168.2 | 812.023 | 3.4885 | 232.768 | 20.071 |
| 1217.0 | 167.5 | 806.890 | 3.4760 | 232.128 | 20.099 |
| 1217.0 | 167.0 | 801.588 | 3.4677 | 231.157 | 20.075 |
| 1415.0 | 161.4 | 842.537 | 3.7612 | 224.007 | 20.129 |
| 1613.0 | 164.5 | 939.909 | 4.1129 | 228.522 | 20.148 |
| 1613.0 | 164.0 | 936.676 | 4.1094 | 227.932 | 20.157 |
| 1811.0 | 148.8 | 859.777 | 4.2041 | 204.508 | 19.933 |
| 1811.0 | 148.0 | 857.203 | 4.1971 | 204.233 | 20.014 |
| 2017.0 | 126.9 | 707.543 | 4.1517 | 170.418 | 19.477 |
| 2017.0 | 121.8 | 668.143 | 4.0738 | 164.009 | 19.530 |
| 2017.0 | 119.6 | 649.549 | 4.0197 | 161.589 | 19.595 |

## TABLE XXXIII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOL PERCENT OF CH4 IN CO2
TEMPERATURE (K) =    333.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | /MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 426.5 | 173.2 | 506.400 | 1.8583 | 272.492 | 22.818 |
| 619.5 | 190.5 | 781.843 | 2.5147 | 310.903 | 23.670 |
| 820.5 | 184.2 | 936.376 | 2.9990 | 312.228 | 24.584 |
| 820.5 | 183.6 | 931.765 | 2.9956 | 311.035 | 24.570 |
| 1015.0 | | 1004.805 | 3.3490 | 300.031 | 25.477 |
| 1215.0 | | 1154.349 | 3.7777 | 305.565 | 26.115 |
| 1215.0 | 169.2 | 1150.465 | 3.7661 | 305.476 | 26.185 |
| 1215.0 | 168.3 | 1140.957 | 3.7622 | 303.264 | 26.134 |
| 1215.0 | 167.2 | 1129.555 | 3.7544 | 300.854 | 26.097 |
| 1415.0 | 167.0 | 1276.662 | 4.1448 | 308.008 | 26.750 |
| 1415.0 | 166.0 | 1265.803 | 4.1360 | 306.040 | 26.739 |
| 1613.0 | 150.2 | 1202.488 | 4.2988 | 279.724 | 27.011 |
| 1613.0 | 149.5 | 1190.880 | 4.2886 | 277.683 | 26.939 |
| 1813.0 | 152.3 | 1309.613 | 4.6685 | 280.517 | 26.714 |
| 1813.0 | 150.5 | 1288.312 | 4.6405 | 277.620 | 26.754 |
| 2015.0 | 128.0 | 1045.762 | 4.5934 | 227.663 | 25.796 |
| 2015.0 | 117.4 | 913.316 | 4.4027 | 207.443 | 25.627 |

# TABLE XXXIII (continued)

## TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
## THE 42.3 MOLE PERCENT OF CH4 IN CO2
## TEMPERATURE (K) =      313.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 427.4 | 166.5 | 583.498 | 1.9290 | 302.479 | 26.348 |
| 427.4 | 166.0 | 579.139 | 1.9224 | 301.248 | 26.320 |
| 427.4 | 165.8 | 577.903 | 1.9224 | 300.605 | 26.296 |
| 427.4 | 165.2 | 574.705 | 1.9158 | 299.971 | 26.336 |
| 615.4 | 183.0 | 906.149 | 2.5860 | 350.395 | 27.770 |
| 615.4 | 182.6 | 902.768 | 2.5807 | 349.807 | 27.784 |
| 615.4 | 182.5 | 899.968 | 2.5754 | 349.442 | 27.771 |
| 813.4 | 161.6 | 979.234 | 2.9702 | 329.680 | 29.589 |
| 813.4 | 161.4 | 978.313 | 2.9702 | 329.370 | 29.598 |
| 1017.0 | 148.0 | 1070.568 | 3.3488 | 319.677 | 31.327 |
| 1217.0 | 145.9 | 1253.064 | 3.7766 | 331.791 | 32.983 |
| 1417.0 | 144.3 | 1431.353 | 4.1623 | 343.884 | 34.564 |
| 1617.0 | 134.0 | 1435.355 | 4.4429 | 323.060 | 34.967 |
| 1617.0 | 132.2 | 1402.092 | 4.4023 | 318.488 | 34.941 |
| 1715.0 | 126.8 | 1367.427 | 4.5110 | 303.128 | 34.672 |
| 1715.0 | 126.0 | 1356.272 | 4.4917 | 301.949 | 34.757 |
| 1715.0 | 124.5 | 1330.150 | 4.4658 | 297.852 | 34.698 |
| 1815.0 | 127.4 | 1403.239 | 4.7025 | 298.399 | 33.971 |
| 1815.0 | 126.8 | 1392.201 | 4.6902 | 296.828 | 33.952 |
| 1815.0 | 126.4 | 1383.312 | 4.6871 | 295.126 | 33.864 |
| 1815.0 | 124.3 | 1352.728 | 4.6500 | 290.904 | 33.943 |
| 2021.0 | 103.7 | 1028.901 | 4.5874 | 224.285 | 31.369 |
| 2021.0 | 102.7 | 1010.614 | 4.5621 | 221.521 | 31.284 |
| 2021.0 | 102.0 | 1003.029 | 4.5440 | 220.733 | 31.387 |

TABLE XXXIII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) =     273.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 424.6 | 147.5 | 791.026 | 2.0285 | 389.938 | 38.342 |
| 424.6 | 147.3 | 789.374 | 2.0285 | 389.124 | 38.314 |
| 615.6 | 157.2 | 1307.205 | 2.7481 | 475.668 | 43.886 |
| 815.6 | 157.0 | 1960.814 | 3.4177 | 573.713 | 53.000 |
| 815.6 | 157.5 | 1968.975 | 3.4177 | 576.100 | 53.051 |
| 1016.0 | 148.5 | 2782.203 | 4.0433 | 688.090 | 67.204 |
| 1016.0 | 147.7 | 2772.157 | 4.0266 | 688.457 | 67.604 |
| 1016.0 | 147.5 | 2760.099 | 4.0229 | 686.083 | 67.463 |
| 1118.0 | 134.4 | 3026.130 | 4.1836 | 723.315 | 78.056 |
| 1118.0 | 133.3 | 2993.958 | 4.1766 | 716.826 | 77.994 |
| 1118.0 | 132.5 | 2971.018 | 4.1766 | 711.333 | 77.864 |
| 1214.0 | 126.5 | 3331.837 | 4.3918 | 758.640 | 86.981 |
| 1214.0 | 124.5 | 3266.655 | 4.3751 | 746.632 | 86.979 |
| 1214.0 | 125.4 | 3290.013 | 4.3751 | 751.971 | 86.973 |
| 1322.0 | 114.8 | 3158.507 | 4.5260 | 697.853 | 88.166 |
| 1322.0 | 113.5 | 3128.260 | 4.5356 | 689.700 | 88.134 |
| 1322.0 | 113.0 | 3111.921 | 4.5356 | 686.098 | 88.062 |
| 1416.0 | 110.0 | 2795.069 | 4.7454 | 588.997 | 77.660 |
| 1418.0 | 109.3 | 2777.665 | 4.7454 | 585.330 | 77.671 |
| 1418.0 | 108.7 | 2757.898 | 4.7485 | 580.791 | 77.494 |
| 1514.0 | 101.5 | 2117.643 | 4.8746 | 434.415 | 62.075 |
| 1514.0 | 101.2 | 2106.894 | 4.8717 | 432.473 | 61.981 |
| 1612.0 | 111.0 | 1998.708 | 5.3951 | 370.462 | 48.406 |
| 1612.0 | 110.3 | 1972.888 | 5.3714 | 367.289 | 48.296 |
| 1714.0 | 99.0 | 1325.974 | 5.3501 | 247.836 | 36.308 |
| 1812.0 | 92.6 | 973.487 | 5.3736 | 181.159 | 28.374 |
| 1812.0 | 92.1 | 959.989 | 5.3603 | 179.092 | 28.203 |
| 1812.0 | 90.4 | 930.153 | 5.2828 | 176.068 | 28.248 |
| 1914.0 | 85.8 | 696.325 | 5.2867 | 131.710 | 22.264 |
| 1914.0 | 80.0 | 617.927 | 5.0575 | 122.178 | 22.150 |
| 2016.0 | 76.6 | 477.233 | 5.0143 | 95.173 | 18.020 |

## TABLE XXXIV

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF CO2-CH4-N2
### TEMPERATURE (K) =      283.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 416.4 | 199.5 | 441.619 | 1.6133 | 273.720 | 19.899 |
| 419.4 | 200.0 | 450.868 | 1.6249 | 277.459 | 20.121 |
| 522.4 | 209.0 | 574.881 | 1.9451 | 295.553 | 20.510 |
| 607.4 | 212.5 | 667.732 | 2.1783 | 306.529 | 20.921 |
| 721.4 | 192.0 | 661.506 | 2.3471 | 281.835 | 21.290 |
| 806.4 | 182.5 | 672.763 | 2.4837 | 270.866 | 21.526 |
| 1009.4 | 172.7 | 740.144 | 2.8157 | 262.857 | 22.075 |
| 1009.4 | 171.5 | 731.693 | 2.8108 | 260.311 | 22.014 |
| 1208.4 | 170.4 | 826.584 | 3.1564 | 261.869 | 22.289 |
| 1410.4 | 163.5 | 858.777 | 3.4302 | 250.355 | 22.208 |
| 1410.4 | 163.2 | 855.692 | 3.4235 | 249.941 | 22.212 |
| 1410.4 | 162.5 | 849.331 | 3.4182 | 248.470 | 22.177 |
| 1558.4 | 163.2 | 897.053 | 3.6563 | 245.341 | 21.803 |
| 1558.4 | 162.2 | 890.252 | 3.6451 | 244.229 | 21.838 |
| 1715.4 | 165.5 | 943.792 | 3.9134 | 241.163 | 21.134 |
| 1715.4 | 165.0 | 938.749 | 3.9111 | 240.016 | 21.097 |
| 1858.4 | 164.0 | 938.985 | 4.1022 | 228.897 | 20.243 |
| 1858.4 | 163.2 | 935.717 | 4.0934 | 228.589 | 20.315 |
| 2029.4 | 146.1 | 777.128 | 4.0857 | 190.204 | 18.882 |

# TABLE XXXIV (continued)

## TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
## EQUIMOLAL MIXTURE OF CO2-CH4-N2
## TEMPERATURE (K) = 263.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 415.6 | 194.2 | 541.518 | 1.6735 | 323.575 | 24.166 |
| 563.6 | 216.0 | 799.529 | 2.1121 | 378.546 | 25.418 |
| 759.6 | 208.0 | 950.825 | 2.4959 | 380.944 | 26.563 |
| 759.6 | 206.0 | 945.096 | 2.4997 | 378.083 | 26.619 |
| 908.6 | 193.7 | 985.308 | 2.6657 | 369.619 | 27.676 |
| 908.6 | 191.4 | 975.728 | 2.6761 | 364.595 | 27.628 |
| 1017.6 | 176.6 | 1056.383 | 3.0580 | 345.445 | 28.370 |
| 1017.6 | 175.6 | 1051.193 | 3.0550 | 344.088 | 28.420 |
| 1059.6 | 194.8 | 1123.240 | 2.9281 | 383.604 | 28.561 |
| 1059.6 | 192.0 | 1107.195 | 2.9312 | 377.716 | 28.532 |
| 1205.6 | 195.5 | 1222.936 | 3.1178 | 392.231 | 29.098 |
| 1205.6 | 190.8 | 1194.714 | 3.1223 | 382.634 | 29.086 |
| 1309.6 | 170.0 | 1244.736 | 3.6045 | 345.319 | 29.461 |
| 1309.6 | 169.2 | 1229.464 | 3.5931 | 342.167 | 29.330 |
| 1363.6 | 183.0 | 1200.628 | 3.2596 | 368.331 | 29.192 |
| 1363.6 | 181.0 | 1183.325 | 3.2610 | 362.866 | 29.077 |
| 1506.6 | 152.5 | 1036.447 | 3.4354 | 301.693 | 28.693 |
| 1506.6 | 149.6 | 1108.530 | 3.7498 | 295.621 | 28.660 |
| 1506.6 | 146.3 | 1016.572 | 3.5172 | 289.028 | 28.653 |
| 1658.3 | 149.6 | 1128.871 | 4.0108 | 281.452 | 27.286 |
| 1658.3 | 148.8 | 1118.598 | 3.9995 | 279.679 | 27.260 |
| 1779.6 | 139.9 | 1009.040 | 4.0602 | 248.518 | 25.764 |
| 1909.6 | 132.5 | 918.665 | 4.1688 | 220.363 | 24.121 |
| 2013.6 | 136.3 | 896.962 | 4.3246 | 207.407 | 22.070 |
| 2013.6 | 135.1 | 882.717 | 4.3111 | 204.754 | 21.981 |

## TABLE XXXIV (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF $CO_2$-$CH_4$-$N_2$
### TEMPERATURE (K) = 243.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 418.3 | 185.5 | 665.239 | 1.7545 | 379.149 | 29.644 |
| 513.3 | 192.4 | 855.550 | 2.0720 | 412.899 | 31.125 |
| 604.3 | 174.5 | 881.086 | 2.2571 | 390.353 | 32.444 |
| 712.3 | 179.4 | 1103.229 | 2.5796 | 427.667 | 34.575 |
| 712.3 | 179.2 | 1103.721 | 2.5796 | 427.857 | 34.629 |
| 863.3 | 152.5 | 1103.743 | 2.7731 | 398.009 | 37.853 |
| 863.3 | 151.7 | 1094.312 | 2.7664 | 395.560 | 37.818 |
| 1004.3 | 156.0 | 1372.523 | 3.1506 | 435.632 | 40.502 |
| 1004.3 | 155.5 | 1365.143 | 3.1474 | 433.731 | 40.454 |
| 1109.3 | 158.1 | 1562.947 | 3.4032 | 459.249 | 42.130 |
| 1109.3 | 157.0 | 1552.092 | 3.4112 | 454.986 | 42.032 |
| 1109.3 | 156.3 | 1537.906 | 3.3898 | 453.682 | 42.099 |
| 1208.3 | 159.1 | 1689.764 | 3.5957 | 469.929 | 42.839 |
| 1208.3 | 156.7 | 1665.987 | 3.5970 | 463.154 | 42.868 |
| 1375.3 | 149.7 | 1642.378 | 3.8253 | 429.343 | 41.597 |
| 1559.3 | 142.3 | 1418.202 | 3.9931 | 355.160 | 36.199 |
| 1707.3 | 143.5 | 1282.090 | 4.2377 | 302.538 | 30.578 |
| 1707.3 | 142.5 | 1276.394 | 4.2377 | 301.194 | 30.655 |
| 1865.3 | 133.5 | 972.058 | 4.2619 | 228.077 | 24.778 |
| 1865.3 | 132.5 | 963.597 | 4.2755 | 225.373 | 24.669 |
| 2016.3 | 136.2 | 850.046 | 4.4720 | 190.079 | 20.241 |

TABLE XXXV

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) =     363.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 270.4 | 146.3 | 216.171 | 0.9227 | 234.268 | 23.224 |
| 372.4 | 196.5 | 417.219 | 1.3179 | 316.572 | 23.366 |
| 426.4 | 211.2 | 515.212 | 1.5023 | 342.932 | 23.550 |
| 520.4 | 219.0 | 635.649 | 1.7711 | 358.885 | 23.768 |
| 613.4 | 215.6 | 708.807 | 1.9757 | 358.758 | 24.134 |
| 713.4 | 218.2 | 812.725 | 2.2088 | 367.935 | 24.456 |
| 718.6 | 195.2 | 699.629 | 2.1125 | 331.184 | 24.607 |
| 903.6 | 214.0 | 948.509 | 2.5710 | 368.917 | 25.003 |
| 1107.6 | 215.8 | 1125.895 | 2.9639 | 379.858 | 25.530 |
| 1214.6 | 177.2 | 905.836 | 2.8686 | 315.767 | 25.845 |
| 1214.6 | 175.7 | 895.723 | 2.8591 | 313.285 | 25.861 |
| 1236.6 | 201.0 | 1101.612 | 3.0901 | 356.493 | 25.723 |
| 1253.6 | 191.0 | 1026.381 | 3.0397 | 337.653 | 25.640 |
| 1407.6 | 185.6 | 1071.682 | 3.2446 | 330.288 | 25.810 |
| 1413.6 | 191.0 | 1123.714 | 3.2943 | 341.105 | 25.902 |
| 1417.6 | 191.0 | 1122.845 | 3.3011 | 340.135 | 25.828 |
| 1413.6 | 172.7 | 968.771 | 3.1396 | 308.558 | 25.913 |
| 1458.6 | 165.5 | 925.215 | 3.1432 | 294.347 | 25.795 |
| 1611.6 | 164.6 | 968.889 | 3.3434 | 289.785 | 25.534 |
| 1618.6 | 172.2 | 1045.663 | 3.4323 | 304.645 | 25.659 |
| 1613.6 | 150.8 | 854.476 | 3.2039 | 266.698 | 25.650 |
| 1657.6 | 186.6 | 1182.802 | 3.6150 | 327.184 | 25.430 |
| 1814.6 | 129.4 | 708.324 | 3.2053 | 220.979 | 24.768 |
| 2031.6 | 111.6 | 577.409 | 3.1826 | 181.424 | 23.578 |

## TABLE XXXV (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
### EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
### TEMPERATURE (K) =    333.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 273.7 | 142.3 | 265.675 | 0.9754 | 272.357 | 27.759 |
| 322.7 | 164.6 | 375.110 | 1.1702 | 320.533 | 28.243 |
| 417.7 | 187.5 | 558.244 | 1.5061 | 370.651 | 28.671 |
| 515.7 | 189.8 | 677.809 | 1.7642 | 384.183 | 29.357 |
| 515.7 | 189.6 | 679.617 | 1.7616 | 385.785 | 29.511 |
| 715.7 | 196.0 | 942.049 | 2.2560 | 417.573 | 30.899 |
| 715.7 | 196.0 | 944.165 | 2.2566 | 418.396 | 30.960 |
| 912.7 | 199.1 | 1207.128 | 2.7070 | 445.912 | 32.483 |
| 912.7 | 197.3 | 1192.003 | 2.6935 | 442.548 | 32.532 |
| 1113.7 | 173.6 | 1193.501 | 2.9265 | 407.816 | 34.071 |
| 1319.7 | 164.6 | 1289.414 | 3.2200 | 400.431 | 35.284 |
| 1459.7 | 154.5 | 1263.842 | 3.3633 | 375.771 | 35.275 |
| 1459.7 | 153.2 | 1248.582 | 3.3525 | 372.428 | 35.258 |
| 1459.7 | 149.5 | 1202.081 | 3.3131 | 362.824 | 35.199 |
| 1459.7 | 142.8 | 1124.295 | 3.2355 | 347.483 | 35.292 |
| 1607.7 | 138.4 | 1131.518 | 3.4114 | 331.686 | 34.759 |
| 1607.7 | 139.5 | 1144.366 | 3.4285 | 333.770 | 34.702 |
| 1709.7 | 169.1 | 1573.905 | 3.9348 | 399.991 | 34.307 |
| 1709.7 | 164.2 | 1503.814 | 3.8719 | 388.389 | 34.306 |
| 1709.7 | 160.5 | 1447.880 | 3.8371 | 377.336 | 34.098 |
| 1815.7 | 142.8 | 1228.598 | 3.7628 | 326.506 | 33.162 |
| 2019.7 | 119.5 | 909.537 | 3.6942 | 246.202 | 29.881 |
| 2019.7 | 117.1 | 880.115 | 3.6551 | 240.788 | 29.823 |
| 2019.7 | 117.1 | 880.115 | 3.6526 | 240.950 | 29.843 |

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) =      313.15

| P I | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H / \Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 273.3 | 129.4 | 278.467 | 0.9723 | 286.385 | 32.099 |
| 319.3 | 149.9 | 390.678 | 1.1670 | 334.763 | 32.390 |
| 420.3 | 171.6 | 603.941 | 1.5211 | 397.033 | 33.557 |
| 521.3 | 195.5 | 873.902 | 1.8788 | 465.115 | 34.506 |
| 521.3 | 195.1 | 872.234 | 1.8788 | 464.227 | 34.510 |
| 713.3 | 193.0 | 1174.692 | 2.3573 | 498.316 | 37.448 |
| 918.3 | 194.0 | 1557.478 | 2.8598 | 544.593 | 40.714 |
| 1113.3 | 191.1 | 1904.919 | 3.2926 | 578.532 | 43.908 |
| 1215.3 | 180.2 | 1945.115 | 3.4353 | 566.204 | 45.572 |
| 1313.3 | 168.0 | 1910.388 | 3.5354 | 540.348 | 45.572 |
| 1313.3 | 167.0 | 1892.159 | 3.5253 | 536.729 | 46.649 |
| 1413.3 | 157.2 | 1859.563 | 3.6338 | 511.736 | 46.614 |
| 1413.3 | 155.5 | 1826.869 | 3.6153 | 505.305 | 47.214 |
| 1413.3 | 154.2 | 1803.783 | 3.6017 | 500.802 | 47.130 |
| 1414.3 | 146.5 | 1672.413 | 3.5075 | 476.803 | 47.104 |
| 1414.3 | 142.3 | 1607.940 | 3.4613 | 464.544 | 47.204 |
| 1511.3 | 143.0 | 1688.840 | 3.6558 | 461.957 | 47.348 |
| 1511.3 | 141.7 | 1668.011 | 3.6411 | 458.096 | 46.854 |
| 1511.3 | 141.4 | 1652.738 | 3.6356 | 454.589 | 46.888 |
| 1661.3 | 134.4 | 1559.186 | 3.8199 | 408.166 | 46.628 |
| 1661.3 | 133.1 | 1534.189 | 3.7954 | 404.212 | 44.047 |
| 1795.3 | 145.4 | 1696.760 | 4.1944 | 404.526 | 44.046 |
| 1915.3 | 139.3 | 1478.298 | 4.2869 | 344.835 | 40.351 |
| 1915.3 | 135.4 | 1412.976 | 4.2277 | 334.212 | 35.903 |
| 2028.3 | 126.3 | 1160.603 | 4.2225 | 274.865 | 35.800 |
|  |  |  |  |  | 31.563 |

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) =       293.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 269.5 | 131.6 | 344.346 | 1.0122 | 340.171 | 37.490 |
| 315.5 | 152.2 | 483.661 | 1.2128 | 398.765 | 38.000 |
| 365.5 | 175.6 | 676.531 | 1.4485 | 467.051 | 38.576 |
| 365.5 | 175.0 | 673.792 | 1.4437 | 466.712 | 38.680 |
| 419.5 | 179.3 | 799.318 | 1.6193 | 493.601 | 39.928 |
| 419.5 | 178.6 | 789.560 | 1.6164 | 488.439 | 39.665 |
| 613.5 | 181.6 | 1222.887 | 2.1853 | 559.593 | 44.692 |
| 613.5 | 181.0 | 1214.028 | 2.1810 | 556.614 | 44.602 |
| 815.5 | 184.5 | 1801.682 | 2.7519 | 654.700 | 51.466 |
| 1017.5 | 186.1 | 2589.961 | 3.3324 | 777.203 | 60.571 |
| 1017.5 | 185.2 | 2576.171 | 3.3310 | 773.379 | 60.566 |
| 1112.5 | 178.0 | 2790.391 | 3.4779 | 802.302 | 65.373 |
| 1112.5 | 176.5 | 2768.562 | 3.4870 | 793.962 | 65.243 |
| 1112.5 | 174.5 | 2741.524 | 3.4857 | 786.499 | 65.370 |
| 1215.5 | 152.7 | 2587.446 | 3.5088 | 737.400 | 70.040 |
| 1315.5 | 146.1 | 2657.803 | 3.6956 | 719.171 | 71.394 |
| 1415.5 | 127.6 | 2258.605 | 3.7911 | 595.754 | 67.717 |
| 1613.5 | 126.5 | 1870.031 | 4.2168 | 443.469 | 50.845 |
| 1613.5 | 126.3 | 1869.417 | 4.2157 | 443.433 | 50.922 |
| 1613.5 | 123.4 | 1796.158 | 4.1620 | 431.559 | 50.723 |
| 1817.5 | 119.4 | 1223.165 | 4.3916 | 278.520 | 33.832 |
| 1817.5 | 120.2 | 1232.599 | 4.4036 | 279.905 | 33.774 |
| 2021.5 | 117.8 | 839.696 | 4.5627 | 184.033 | 22.658 |
| 2021.5 | 110.4 | 761.704 | 4.4145 | 172.543 | 22.667 |

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) =      273.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 267.4 | 124.3 | 392.552 | 1.0333 | 379.889 | 44.326 |
| 275.6 | 129.0 | 422.358 | 1.0719 | 394.015 | 44.300 |
| 275.6 | 129.0 | 422.761 | 1.0719 | 394.391 | 44.342 |
| 314.4 | 144.3 | 565.733 | 1.2486 | 453.084 | 45.540 |
| 347.6 | 160.0 | 725.265 | 1.4099 | 514.380 | 46.627 |
| 368.4 | 166.0 | 805.086 | 1.4949 | 538.537 | 47.053 |
| 406.4 | 167.6 | 936.895 | 1.6590 | 564.712 | 48.869 |
| 406.4 | 167.1 | 929.545 | 1.6534 | 562.172 | 48.794 |
| 419.6 | 175.1 | 1006.886 | 1.6905 | 595.606 | 49.335 |
| 419.6 | 175.0 | 1011.034 | 1.6891 | 598.547 | 49.606 |
| 420.7 | 158.6 | 881.820 | 1.6309 | 540.666 | 49.443 |
| 614.6 | 179.0 | 1714.355 | 2.3176 | 739.700 | 59.935 |
| 614.6 | 178.1 | 1695.904 | 2.3076 | 734.900 | 59.847 |
| 613.4 | 165.5 | 1591.088 | 2.2501 | 707.108 | 61.968 |
| 715.4 | 160.1 | 1950.160 | 2.5297 | 770.889 | 69.836 |
| 718.6 | 163.9 | 2005.081 | 2.5502 | 786.221 | 69.574 |
| 718.6 | 163.5 | 2004.983 | 2.5502 | 786.182 | 69.740 |
| 814.6 | 148.4 | 2354.089 | 2.7393 | 859.354 | 83.988 |
| 814.6 | 147.7 | 2328.537 | 2.7276 | 853.682 | 83.829 |
| 819.4 | 144.6 | 2310.429 | 2.7375 | 843.988 | 84.654 |
| 853.6 | 144.5 | 2558.524 | 2.7980 | 914.387 | 91.779 |
| 853.6 | 143.5 | 2538.246 | 2.7939 | 908.468 | 91.820 |
| 856.4 | 129.6 | 2263.890 | 2.7090 | 835.663 | 93.520 |
| 987.4 | 175.5 | 5111.978 | 3.4635 | 1475.921 | 121.974 |
| 987.4 | 173.8 | 5081.935 | 3.4661 | 1466.150 | 122.351 |
| 987.4 | 172.8 | 5077.787 | 3.4778 | 1460.053 | 122.548 |
| 987.4 | 171.5 | 5047.374 | 3.4752 | 1452.386 | 122.828 |
| 987.4 | 159.0 | 4482.825 | 3.2918 | 1361.814 | 124.223 |
| 987.4 | 158.0 | 4444.522 | 3.2794 | 1355.261 | 124.407 |
| 987.4 | 138.5 | 3736.590 | 3.0717 | 1216.434 | 127.385 |
| 987.4 | 137.8 | 3729.116 | 3.0761 | 1212.257 | 127.593 |
| 1057.4 | 160.5 | 5491.198 | 3.5492 | 1547.132 | 139.808 |
| 1057.4 | 138.0 | 4528.551 | 3.3541 | 1350.136 | 141.899 |
| 1121.4 | 122.4 | 4020.247 | 3.5555 | 1130.686 | 133.980 |
| 1121.4 | 122.3 | 4006.903 | 3.5404 | 1131.756 | 134.217 |
| 1216.4 | 118.7 | 3271.451 | 4.0363 | 810.487 | 99.032 |
| 1216.4 | 116.4 | 3211.285 | 4.0560 | 791.722 | 98.651 |
| 1315.4 | 127.5 | 2581.864 | 4.5573 | 566.525 | 64.445 |
| 1315.4 | 127.3 | 2563.598 | 4.5516 | 563.226 | 64.170 |

## TABLE XXXV (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
### EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
### TEMPERATURE (K) =      273.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 1412.4 | 125.0 | 1674.845 | 4.7000 | 356.348 | 41.347 |
| 1412.4 | 124.8 | 1668.690 | 4.6935 | 355.527 | 41.318 |
| 1613.4 | 119.0 | 851.603 | 4.7993 | 177.442 | 21.626 |
| 1613.4 | 117.2 | 827.367 | 4.7622 | 173.734 | 21.500 |
| 1613.4 | 116.6 | 825.183 | 4.7486 | 173.773 | 21.615 |
| 1817.4 | 120.2 | 567.961 | 4.9660 | 114.369 | 13.800 |
| 1817.4 | 119.7 | 567.961 | 4.9312 | 115.175 | 13.955 |
| 2033.6 | 106.1 | 323.877 | 4.9231 | 65.786 | 8.992 |
| 2033.6 | 105.8 | 323.877 | 4.9055 | 66.022 | 9.050 |

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
### EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
### TEMPERATURE (K) =      263.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 269.6 | 122.5 | 442.983 | 1.0631 | 416.653 | 49.331 |
| 269.6 | 122.1 | 437.882 | 1.0587 | 413.566 | 49.125 |
| 348.6 | 154.2 | 789.237 | 1.4263 | 553.309 | 52.043 |
| 349.6 | 155.7 | 808.389 | 1.4426 | 560.359 | 52.198 |
| 420.6 | 185.0 | 1256.314 | 1.7814 | 705.210 | 55.287 |
| 420.6 | 184.7 | 1249.514 | 1.7801 | 701.906 | 55.118 |
| 420.6 | 137.8 | 859.040 | 1.5899 | 540.304 | 56.868 |
| 517.6 | 173.4 | 1574.284 | 2.0747 | 758.797 | 63.468 |
| 517.6 | 172.8 | 1561.740 | 2.0668 | 755.599 | 63.420 |
| 517.6 | 172.5 | 1551.990 | 2.0635 | 752.105 | 63.236 |
| 620.6 | 209.4 | 2750.847 | 2.6055 | 1055.779 | 73.127 |
| 620.6 | 209.4 | 2750.005 | 2.6055 | 1055.456 | 73.104 |
| 620.6 | 144.0 | 1719.275 | 2.2386 | 767.998 | 77.353 |

TABLE XXXVI

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF $CO_2(.25)-CH_4(.5)-C_2H_6(.25)$
TEMPERATURE (K) =     363.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 317.5 | 172.0 | 275.140 | 1.1996 | 229.342 | 19.339 |
| 317.5 | 171.0 | 271.279 | 1.1952 | 226.963 | 19.250 |
| 317.5 | 170.0 | 268.864 | 1.1907 | 225.784 | 19.263 |
| 422.5 | 185.1 | 378.732 | 1.5232 | 248.635 | 19.482 |
| 614.5 | 203.8 | 574.947 | 2.0673 | 278.103 | 19.791 |
| 614.5 | 203.2 | 572.480 | 2.0661 | 277.080 | 19.777 |
| 614.5 | 202.7 | 569.316 | 2.0571 | 276.746 | 19.802 |
| 817.5 | 204.3 | 708.245 | 2.4847 | 285.036 | 20.235 |
| 1009.5 | 196.0 | 771.254 | 2.7998 | 275.461 | 20.383 |
| 1215.5 | 196.3 | 875.964 | 3.1595 | 277.242 | 20.484 |
| 1215.5 | 196.0 | 874.591 | 3.1595 | 276.807 | 20.483 |
| 1215.5 | 195.5 | 869.678 | 3.1579 | 275.395 | 20.431 |
| 1415.5 | 184.1 | 871.225 | 3.3760 | 258.063 | 20.330 |
| 1415.5 | 182.5 | 861.078 | 3.3607 | 256.218 | 20.362 |
| 1617.5 | 187.8 | 966.356 | 3.3221 | 290.883 | 22.464 |
| 1617.5 | 187.5 | 960.948 | 3.7086 | 259.111 | 20.043 |
| 1815.5 | 165.7 | 842.595 | 3.7504 | 224.665 | 19.665 |
| 1815.5 | 164.5 | 829.216 | 3.7354 | 221.986 | 19.572 |
| 2049.5 | 155.5 | 783.325 | 3.8998 | 200.860 | 18.734 |
| 2049.5 | 154.9 | 778.882 | 3.8933 | 200.056 | 18.731 |
| 2049.5 | 147.2 | 720.927 | 3.7937 | 190.028 | 18.723 |

## TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) =     333.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 269.5 | 141.8 | 230.901 | 1.0221 | 225.904 | 23.106 |
| 320.5 | 166.8 | 333.096 | 1.2385 | 268.948 | 23.385 |
| 428.5 | 192.6 | 512.868 | 1.6301 | 314.617 | 23.692 |
| 608.5 | 193.9 | 689.526 | 2.1132 | 326.290 | 24.406 |
| 608.5 | 193.1 | 685.149 | 2.1094 | 324.793 | 24.395 |
| 608.5 | 193.0 | 682.959 | 2.1119 | 323.373 | 24.301 |
| 819.5 | 193.0 | 867.583 | 2.5889 | 335.108 | 25.183 |
| 819.5 | 192.4 | 863.495 | 2.5869 | 333.789 | 25.162 |
| 1009.5 | 187.9 | 988.240 | 2.9498 | 335.013 | 25.859 |
| 1009.5 | 187.7 | 986.245 | 2.9472 | 334.636 | 25.857 |
| 1009.5 | 187.7 | 984.511 | 2.9463 | 334.148 | 25.820 |
| 1212.5 | 185.3 | 1112.773 | 3.3127 | 335.905 | 26.291 |
| 1315.5 | 163.0 | 977.478 | 3.2866 | 297.407 | 26.463 |
| 1315.5 | 162.4 | 970.033 | 3.2827 | 295.495 | 26.390 |
| 1415.5 | 166.0 | 1057.050 | 3.4798 | 303.760 | 26.540 |
| 1415.5 | 165.5 | 1047.206 | 3.4754 | 301.314 | 26.406 |
| 1565.5 | 161.0 | 1070.825 | 3.6664 | 292.062 | 26.310 |
| 1565.5 | 160.0 | 1056.108 | 3.6538 | 289.040 | 26.201 |
| 1565.5 | 158.6 | 1044.875 | 3.6398 | 287.069 | 26.252 |
| 1715.5 | 159.5 | 1095.808 | 3.8893 | 281.746 | 25.620 |
| 1715.5 | 159.4 | 1091.680 | 3.8919 | 280.497 | 25.522 |
| 1871.5 | 149.5 | 1013.855 | 3.9836 | 254.504 | 24.690 |
| 1871.5 | 148.0 | 1004.240 | 3.9631 | 253.392 | 24.832 |
| 1871.5 | 146.5 | 982.897 | 3.9413 | 249.383 | 24.689 |
| 1871.5 | 140.0 | 916.900 | 3.8524 | 238.001 | 24.656 |
| 2037.5 | 132.5 | 836.259 | 3.9498 | 211.720 | 23.175 |
| 2037.5 | 132.4 | 837.429 | 3.9490 | 212.058 | 23.230 |
| 2037.5 | 131.8 | 832.146 | 3.9426 | 211.065 | 23.226 |
| 2037.5 | 131.0 | 823.312 | 3.9309 | 209.442 | 23.188 |

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) =      313.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 321.4 | 162.3 | 383.445 | 1.2766 | 300.342 | 26.839 |
| 415.4 | 184.7 | 568.778 | 1.6322 | 348.454 | 27.362 |
| 421.4 | 187.4 | 588.981 | 1.6579 | 355.252 | 27.494 |
| 421.4 | 187.0 | 586.830 | 1.6579 | 353.955 | 27.452 |
| 421.4 | 186.6 | 582.791 | 1.6547 | 352.195 | 27.374 |
| 616.4 | 190.7 | 831.712 | 2.2109 | 376.185 | 28.610 |
| 813.4 | 195.5 | 1103.845 | 2.7243 | 405.181 | 30.059 |
| 1007.4 | 190.8 | 1303.296 | 3.1434 | 414.606 | 31.516 |
| 1007.4 | 190.3 | 1296.973 | 3.1401 | 413.027 | 31.479 |
| 1007.4 | 190.0 | 1288.975 | 3.1335 | 411.344 | 31.400 |
| 1109.4 | 166.1 | 1162.725 | 3.1582 | 368.158 | 32.147 |
| 1109.4 | 165.6 | 1153.219 | 3.1524 | 365.812 | 32.039 |
| 1216.4 | 158.7 | 1178.006 | 3.2958 | 357.425 | 32.665 |
| 1316.4 | 159.0 | 1259.920 | 3.4855 | 361.469 | 32.972 |
| 1413.4 | 154.1 | 1270.359 | 3.6156 | 351.355 | 33.069 |
| 1563.4 | 160.1 | 1429.210 | 3.9560 | 361.272 | 32.728 |
| 1563.4 | 159.8 | 1421.867 | 3.9534 | 359.650 | 32.642 |
| 1717.4 | 145.8 | 1270.973 | 4.0355 | 314.947 | 31.330 |
| 1717.4 | 145.2 | 1267.520 | 4.0266 | 314.779 | 31.442 |
| 1867.4 | 136.0 | 1138.564 | 4.1200 | 276.346 | 29.471 |
| 1867.4 | 132.7 | 1100.317 | 4.0767 | 269.898 | 29.499 |
| 1867.4 | 129.4 | 1056.330 | 4.0254 | 262.414 | 29.412 |
| 2039.4 | 119.4 | 891.980 | 4.0829 | 218.462 | 26.537 |
| 2039.4 | 117.8 | 876.605 | 4.0593 | 215.948 | 26.588 |
| 2039.4 | 116.9 | 863.854 | 4.0342 | 214.130 | 26.567 |

## TABLE XXXVI (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25) TEMPERATURE (K) = 293.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|------|------|------|------|------|------|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 267.4 | 132.8 | 299.416 | 1.0623 | 281.839 | 30.781 |
| 327.4 | 159.0 | 456.306 | 1.3377 | 341.091 | 31.114 |
| 419.4 | 182.9 | 690.714 | 1.7116 | 403.527 | 31.999 |
| 419.4 | 182.7 | 719.774 | 1.7086 | 421.263 | 33.442 |
| 613.4 | 207.5 | 1184.079 | 2.4013 | 493.087 | 34.465 |
| 812.4 | 201.3 | 1526.031 | 2.9312 | 520.607 | 37.510 |
| 1010.4 | 185.0 | 1743.273 | 3.3389 | 522.105 | 40.932 |
| 1010.4 | 184.4 | 1734.217 | 3.3342 | 520.115 | 40.909 |
| 1212.4 | 174.7 | 1982.531 | 3.7502 | 528.633 | 43.887 |
| 1212.4 | 173.9 | 1971.079 | 3.7421 | 526.729 | 43.930 |
| 1312.4 | 161.0 | 1909.207 | 3.8391 | 497.302 | 44.799 |
| 1312.4 | 160.7 | 1900.309 | 3.8364 | 495.327 | 44.705 |
| 1413.2 | 156.8 | 1947.715 | 4.0255 | 483.834 | 44.754 |
| 1512.4 | 150.5 | 1892.049 | 4.1667 | 454.084 | 43.760 |
| 1512.4 | 150.0 | 1881.796 | 4.1582 | 452.548 | 43.757 |
| 1663.4 | 133.1 | 1556.252 | 4.2150 | 369.215 | 40.233 |
| 1663.4 | 132.7 | 1547.683 | 4.2066 | 367.915 | 40.212 |
| 1815.4 | 132.8 | 1450.446 | 4.4636 | 324.948 | 35.489 |
| 1815.4 | 131.3 | 1422.072 | 4.4433 | 320.048 | 35.353 |
| 1815.4 | 131.3 | 1420.996 | 4.4365 | 320.296 | 35.380 |
| 1815.4 | 127.8 | 1362.375 | 4.3851 | 310.677 | 35.258 |
| 2028.4 | 111.0 | 905.988 | 4.3598 | 207.803 | 27.152 |
| 2028.4 | 110.0 | 893.769 | 4.3413 | 205.875 | 27.145 |

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) =     273.15

| P | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 273.5 | 129.8 | 367.182 | 1.1326 | 324.177 | 36.223 |
| 337.5 | 157.2 | 579.779 | 1.4409 | 402.352 | 37.122 |
| 337.5 | 156.6 | 572.060 | 1.4336 | 399.031 | 36.957 |
| 420.5 | 190.6 | 922.269 | 1.8427 | 500.473 | 38.083 |
| 420.5 | 190.5 | 928.260 | 1.8456 | 502.944 | 38.291 |
| 613.5 | 179.8 | 1315.568 | 2.4195 | 543.721 | 43.859 |
| 811.5 | 185.9 | 2010.733 | 3.0739 | 654.110 | 51.033 |
| 811.5 | 185.2 | 1997.355 | 3.0672 | 651.189 | 50.997 |
| 1013.5 | 183.2 | 2857.021 | 3.6993 | 772.295 | 61.142 |
| 1013.5 | 182.7 | 2843.097 | 3.6938 | 769.685 | 61.102 |
| 1115.5 | 171.5 | 3063.815 | 3.9089 | 783.796 | 66.285 |
| 1115.5 | 170.8 | 3048.990 | 3.8984 | 782.094 | 66.412 |
| 1215.5 | 147.4 | 2805.575 | 3.9607 | 708.346 | 69.699 |
| 1215.5 | 147.0 | 2792.617 | 3.9562 | 705.877 | 69.645 |
| 1325.5 | 154.2 | 3179.131 | 4.3694 | 727.581 | 68.435 |
| 1411.5 | 151.3 | 3028.045 | 4.6403 | 652.546 | 62.553 |
| 1411.5 | 150.7 | 3011.289 | 4.6263 | 650.904 | 62.644 |
| 1508.5 | 142.2 | 2486.370 | 4.7646 | 521.840 | 53.225 |
| 1508.5 | 141.3 | 2462.425 | 4.7488 | 518.525 | 53.224 |
| 1659.5 | 143.9 | 1976.639 | 5.1159 | 386.369 | 38.942 |
| 1821.5 | 123.5 | 1140.630 | 4.9633 | 229.808 | 26.988 |
| 1821.5 | 122.5 | 1125.146 | 4.9448 | 227.537 | 26.940 |
| 1821.5 | 119.1 | 1071.676 | 4.8740 | 219.871 | 26.775 |
| 2030.5 | 117.1 | 720.952 | 5.0297 | 143.336 | 17.753 |
| 2030.5 | 116.5 | 717.082 | 5.0204 | 142.833 | 17.782 |
| 2030.5 | 116.0 | 713.062 | 4.9986 | 142.649 | 17.835 |

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) =   263.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 267.7 | 124.5 | 381.051 | 1.1260 | 338.381 | 39.420 |
| 324.7 | 148.0 | 580.372 | 1.4111 | 411.287 | 40.305 |
| 423.7 | 158.3 | 841.294 | 1.7772 | 473.361 | 43.370 |
| 423.7 | 158.1 | 841.294 | 1.7811 | 472.332 | 43.330 |
| 615.7 | 170.1 | 1477.360 | 2.4644 | 599.478 | 51.115 |
| 615.7 | 170.0 | 1476.989 | 2.4644 | 599.327 | 51.132 |
| 815.7 | 170.2 | 2375.540 | 3.1337 | 758.048 | 64.598 |
| 815.7 | 171.0 | 2387.989 | 3.1370 | 761.214 | 64.564 |
| 912.7 | 151.7 | 2602.301 | 3.3041 | 787.589 | 75.300 |
| 912.7 | 151.0 | 2590.558 | 3.3017 | 784.595 | 75.361 |
| 1009.7 | 161.0 | 3600.626 | 3.7550 | 958.881 | 86.381 |
| 1009.7 | 159.7 | 3563.855 | 3.7509 | 950.129 | 86.289 |
| 1009.7 | 159.5 | 3559.091 | 3.7419 | 951.122 | 86.488 |
| 1081.7 | 144.6 | 3578.233 | 3.8275 | 934.861 | 93.769 |
| 1139.7 | 151.6 | 4144.944 | 4.1463 | 999.665 | 95.639 |
| 1221.7 | 157.5 | 4489.967 | 4.5638 | 983.820 | 90.597 |
| 1221.7 | 156.7 | 4455.537 | 4.5505 | 979.126 | 90.625 |
| 1317.7 | 147.3 | 3653.621 | 4.8373 | 755.291 | 74.369 |
| 1413.7 | 140.0 | 2650.769 | 5.0314 | 526.837 | 54.579 |
| 1615.7 | 132.5 | 1401.536 | 5.2578 | 266.560 | 29.178 |
| 1818.7 | 125.3 | 815.006 | 5.3184 | 153.240 | 17.737 |
| 2021.7 | 112.2 | 468.467 | 5.1552 | 90.871 | 11.746 |
| 2024.7 | 111.0 | 458.927 | 5.1340 | 89.388 | 11.679 |
| 2024.7 | 110.0 | 454.335 | 5.1035 | 89.023 | 11.738 |

## TABLE XXXVII

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) =     333.15

| PI | ΔP | POWER | FLOW | ΔH | −(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL)MIN | J/MOL | J/MOL-BAR |
| 415.5 | 205.6 | 429.245 | 1.5222 | 281.983 | 19.892 |
| 415.5 | 204.1 | 425.893 | 1.5191 | 280.352 | 19.922 |
| 415.5 | 201.4 | 417.151 | 1.5191 | 274.597 | 19.775 |
| 415.5 | 197.7 | 406.962 | 1.5004 | 271.229 | 19.898 |
| 517.5 | 188.2 | 449.715 | 1.7275 | 260.319 | 20.061 |
| 617.5 | 195.8 | 543.574 | 1.9835 | 274.039 | 20.299 |
| 810.5 | 200.5 | 623.311 | 2.1822 | 285.631 | 20.662 |
| 810.5 | 200.4 | 622.585 | 2.1800 | 285.578 | 20.668 |
| 1015.6 | 196.8 | 705.873 | 2.4982 | 282.543 | 20.822 |
| 1215.6 | 193.1 | 765.084 | 2.7631 | 276.890 | 20.797 |
| 1414.6 | 188.9 | 798.078 | 2.9775 | 268.035 | 20.579 |
| 1414.6 | 187.2 | 789.815 | 2.9768 | 265.315 | 20.555 |
| 1414.6 | 186.5 | 780.994 | 2.9666 | 263.255 | 20.472 |
| 1614.6 | 179.2 | 784.009 | 3.1571 | 248.328 | 20.098 |
| 1614.6 | 177.6 | 777.186 | 3.1658 | 245.491 | 20.048 |
| 1614.6 | 177.2 | 770.474 | 3.1484 | 244.717 | 20.030 |
| 1813.6 | 155.7 | 693.393 | 3.3456 | 207.252 | 19.306 |
| 1813.6 | 147.2 | 680.825 | 3.4837 | 195.427 | 19.255 |
| 1813.6 | 146.4 | 659.660 | 3.3714 | 195.660 | 19.384 |
| 1813.6 | 146.3 | 673.077 | 3.4674 | 194.115 | 19.244 |
| 1813.6 | 145.0 | 664.880 | 3.4542 | 192.481 | 19.253 |
| 1813.6 | 143.7 | 648.452 | 3.4144 | 189.913 | 19.168 |
| 2023.6 | 139.9 | 632.434 | 3.6306 | 174.194 | 18.059 |
| 2023.6 | 138.5 | 623.708 | 3.6086 | 172.835 | 18.099 |
| 2023.6 | 133.1 | 587.434 | 3.5323 | 166.299 | 18.121 |

## TABLE XXXVII (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF $CO_2$-$CH_4$-$N_2$-$C_2H_6$
### TEMPERATURE (K) = 303.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| IA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 415.4 | 190.1 | 480.721 | 1.4711 | 326.776 | 24.931 |
| 416.4 | 190.3 | 482.089 | 1.4711 | 327.706 | 24.976 |
| 614.4 | 191.0 | 663.794 | 1.9433 | 341.578 | 25.938 |
| 614.4 | 190.1 | 660.030 | 1.9457 | 339.222 | 25.881 |
| 813.4 | 183.2 | 786.361 | 2.3147 | 339.711 | 26.894 |
| 813.4 | 182.2 | 780.798 | 2.3127 | 337.600 | 26.874 |
| 1013.4 | 189.5 | 986.420 | 2.7327 | 360.960 | 27.626 |
| 1211.4 | 190.1 | 1131.069 | 3.0777 | 367.501 | 28.038 |
| 1211.4 | 189.6 | 1127.485 | 3.0747 | 366.692 | 28.050 |
| 1211.4 | 189.1 | 1127.482 | 3.0747 | 366.691 | 28.124 |
| 1413.4 | 180.5 | 1158.717 | 3.3275 | 348.224 | 27.981 |
| 1413.4 | 180.2 | 1152.062 | 3.3187 | 347.140 | 27.940 |
| 1557.4 | 167.2 | 1070.390 | 3.3899 | 315.758 | 27.390 |
| 1557.4 | 166.2 | 1063.394 | 3.3925 | 313.445 | 27.353 |
| 1710.4 | 161.8 | 1020.516 | 3.4877 | 292.597 | 26.228 |
| 1710.4 | 160.3 | 1010.123 | 3.4877 | 289.617 | 26.204 |
| 1710.4 | 158.5 | 997.124 | 3   151 | 286.104 | 26.180 |
| 1867.4 | 146.8 | 868.417 | 3.4864 | 249.081 | 24.609 |
| 1867.4 | 145.5 | 858.415 | 3.4550 | 248.452 | 24.766 |
| 2027.4 | 143.7 | 787.175 | 3.5163 | 223.863 | 22.594 |
| 2027.4 | 141.0 | 769.763 | 3.4968 | 220.128 | 22.643 |
| 2027.4 | 140.8 | 769.763 | 3.5072 | 219.476 | 22.608 |
| 2027.4 | 139.5 | 757.690 | 3.4968 | 216.675 | 22.527 |
| 2027.4 | 136.7 | 738.706 | 3.4753 | 212.553 | 22.551 |

TABLE XXXVII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2
TEMPERATURE (K) =        283.15

| PI | ΔP | POWER | FLOW | ΔH | -(ΔH/ΔP) |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 223.4 | 111.6 | 174.517 | 0.8110 | 215.176 | 27.964 |
| 223.4 | 111.0 | 173.952 | 0.8052 | 216.024 | 28.226 |
| 273.4 | 133.0 | 264.477 | 1.0117 | 261.401 | 28.506 |
| 321.4 | 150.7 | 359.380 | 1.2139 | 296.033 | 28.481 |
| 425.4 | 188.2 | 606.380 | 1.5922 | 380.843 | 29.350 |
| 466.4 | 200.6 | 693.282 | 1.7002 | 407.761 | 29.482 |
| 562.4 | 192.7 | 804.377 | 1.9747 | 407.338 | 30.658 |
| 562.4 | 192.1 | 798.748 | 1.9699 | 405.459 | 30.612 |
| 713.4 | 195.9 | 1021.434 | 2.3521 | 434.260 | 32.151 |
| 859.4 | 181.2 | 1101.316 | 2.6018 | 423.289 | 33.881 |
| 1012.5 | 173.3 | 1210.317 | 2.8683 | 421.961 | 35.314 |
| 1163.5 | 163.1 | 1263.216 | 3.0843 | 409.551 | 36.419 |
| 1260.5 | 153.5 | 1231.207 | 3.1722 | 388.119 | 36.672 |
| 1413.5 | 161.0 | 1413.769 | 3.5158 | 402.114 | 36.224 |
| 1558.5 | 146.7 | 1252.298 | 3.5848 | 349.327 | 34.537 |
| 1711.5 | 147.5 | 1228.014 | 3.7993 | 323.220 | 31.782 |
| 1865.5 | 137.4 | 1010.529 | 3.7993 | 265.977 | 28.076 |
| 1865.5 | 134.6 | 988.668 | 3.7993 | 260.223 | 28.040 |
| 2011.5 | 140.9 | 945.761 | 3.9640 | 238.586 | 24.559 |

## TABLE XXXVII (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
### EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
### TEMPERATURE (K) = 263.15

| PI | ΔP | POWER | FLOW | ΔH | $-(\Delta H/\Delta P)_T$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 225.3 | 109.4 | 214.927 | 0.8664 | 248.052 | 32.885 |
| 269.3 | 128.0 | 312.493 | 1.0551 | 296.156 | 33.557 |
| 321.3 | 149.7 | 453.404 | 1.2808 | 353.989 | 34.296 |
| 323.3 | 150.6 | 458.225 | 1.2881 | 355.729 | 34.259 |
| 416.3 | 189.8 | 796.971 | 1.7158 | 464.481 | 35.493 |
| 420.4 | 196.0 | 798.788 | 1.6800 | 475.448 | 35.182 |
| 561.4 | 195.4 | 1072.526 | 2.1017 | 510.301 | 37.877 |
| 615.4 | 179.2 | 1064.553 | 2.1778 | 488.818 | 39.563 |
| 760.4 | 183.2 | 1410.298 | 2.5827 | 546.039 | 43.229 |
| 912.4 | 169.5 | 1615.325 | 2.8861 | 559.678 | 47.890 |
| 1005.4 | 134.9 | 1379.476 | 2.9538 | 467.014 | 50.211 |
| 1161.4 | 144.8 | 1833.884 | 3.4423 | 532.736 | 53.361 |
| 1261.4 | 157.2 | 2202.372 | 3.8259 | 575.647 | 53.111 |
| 1261.4 | 155.2 | 2162.717 | 3.8081 | 567.911 | 53.072 |
| 1261.4 | 150.5 | 2058.315 | 3.7364 | 550.873 | 53.088 |
| 1408.4 | 146.1 | 1966.599 | 4.0306 | 487.915 | 48.436 |
| 1565.4 | 145.3 | 1700.205 | 4.2212 | 402.774 | 40.204 |
| 1565.4 | 144.8 | 1694.263 | 4.2180 | 401.668 | 40.232 |
| 1706.4 | 142.0 | 1395.804 | 4.3458 | 321.179 | 32.805 |
| 1706.4 | 140.0 | 1373.656 | 4.3458 | 316.083 | 32.745 |
| 1856.4 | 132.2 | 1018.697 | 4.3264 | 235.460 | 25.832 |
| 1856.4 | 131.4 | 1006.008 | 4.3310 | 232.279 | 25.638 |
| 2015.4 | 118.8 | 681.711 | 4.1915 | 162.639 | 19.855 |
| 2016.4 | 119.2 | 686.333 | 4.2433 | 161.743 | 19.680 |
| 2016.4 | 118.7 | 684.337 | 4.2106 | 162.524 | 19.858 |

## TABLE XXXVII (continued)

### TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
### TEMPERATURE (K) = 243.15

| PI | $\Delta P$ | POWER | FLOW | $\Delta H$ | $-(\Delta H/\Delta P)$ |
|---|---|---|---|---|---|
| PSIA | PSI | J/MIN | MOL/MIN | J/MOL | J/MOL-BAR |
| 223.4 | 104.0 | 255.639 | 0.9013 | 283.622 | 39.553 |
| 269.4 | 122.0 | 377.421 | 1.1046 | 341.653 | 40.616 |
| 319.4 | 143.2 | 548.625 | 1.3351 | 410.917 | 41.619 |
| 365.4 | 161.0 | 751.365 | 1.5612 | 481.252 | 43.353 |
| 439.4 | 176.3 | 1037.230 | 1.8588 | 557.999 | 45.905 |
| 439.4 | 121.0 | 623.234 | 1.5938 | 391.021 | 46.870 |
| 1310.8 | 135.0 | 1159.172 | 3.2608 | 355.487 | 38.191 |
| 1310.8 | 133.3 | 1127.835 | 3.2622 | 345.727 | 37.617 |
| 1413.8 | 127.0 | 1000.310 | 3.2009 | 312.505 | 35.689 |
| 1413.8 | 124.2 | 976.829 | 3.1994 | 305.307 | 35.653 |
| 1563.8 | 131.7 | 756.385 | 3.3628 | 224.924 | 24.770 |
| 1714.8 | 127.0 | 522.315 | 3.4583 | 151.030 | 17.248 |
| 1863.8 | 145.0 | 483.065 | 3.7040 | 130.416 | 13.045 |
| 1863.8 | 143.0 | 480.100 | 3.7101 | 129.401 | 13.124 |
| 2015.8 | 133.0 | 321.090 | 3.5498 | 90.452 | 9.863 |
| 2015.8 | 131.8 | 317.981 | 3.5063 | 90.687 | 9.979 |

NAME:  Heng-Joo Ng

PLACE OF BIRTH:  Labis, Johore, Malaysia

YEAR OF BIRTH:  1946

POST SECONDARY EDUCATION AND DEGREES:

Nanyang University,
Singapore
1966-1969  B.Sc.

University of Alberta,
Edmonton, Alberta
1969-1971  M.Sc.

HONOURS AND AWARDS:

Lee Foundation Assistantship
Nanyang University
1967-1969

Gold Medal Award
Nanyang University
1969

Graduate Research Assistantship
University of Alberta
1969-1970

Graduate Teaching Assistantship
University of Alberta
1970-1971

Province of Alberta Graduate Studies Scholarship
University of Alberta
1971-1972

National Research Council (Post-graduate Scholarship)
University of Alberta
1972-1975

RELATED WORK EXPERIENCE:

Teaching Assistant
University of Alberta
1969-1974

Research Engineer
University of Alberta
Sept. 1974 -