

6-30-1955

Isobaric heat capacity of propylene over a wide range of temperature and pressure

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**ISOBARIC HEAT CAPACITY OF PROPYLENE
OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE**

BY

JOSEPH P. TASSONEY

**SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE**

OF

**MASTER OF SCIENCE
IN CHEMICAL ENGINEERING**

IN THE

GRADUATE DIVISION

AT THE

NEWARK COLLEGE OF ENGINEERING

JUNE 1955

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

JUNE, 1955

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SUMMARY

This work was done to make possible more accurate design calculations for processes that require accurate data on the heat capacity of propylene at elevated temperatures and pressures.

The effect of pressure and temperature on the isobaric heat capacity and the heat capacity at constant volume for propylene relative to the ideal gas state is presented. The results cover pressures from 0 to 9,500 PSIA and temperatures from 350°F. to 2240°F.

An equation was derived from the Benedict-Webb-Rubin equation of state. This equation gives the deviation from the ideal gas state of the isobaric heat capacity of propylene for the wide range of pressures and temperatures covered. Graphs and tables relating the deviation of the isobaric heat capacity, the deviation of heat capacity at constant volume, pressure and temperature are included. The results indicate that deviation of the isobaric heat capacity from the ideal gas state caused by the effect of pressure is significantly large and must not be neglected. Small differences in P-V-T data appear to have a pronounced effect on the calculated heat capacity.

A comparison of the calculated data has been made and is included.

INTRODUCTION

Exact thermodynamic data are demanded in present-day industrial calculations in the fields of high temperatures and pressures. Industry is making a continued effort to obtain more accurate thermodynamic information in order to facilitate more accurate design calculations. There is a lack of basic thermodynamic data, particularly at elevated temperatures and pressures.

The thermodynamic property for which very little information is available is the heat capacity of gases and vapors at high pressures. Previous investigations of the heat capacity of propylene have been limited to low temperature and pressure for both the liquid and gaseous range. Amerbach, Sage and Lacey (19) gave the isobaric heat capacity values of propylene at the Bubble Point determined from 80°F. to 160°F. and at atmospheric pressure. Spencer (20) determined the empirical heat capacity equation for propylene in the ideal gaseous state from 291.1° to 1000°K. Kobe and Long (22) presented the heat capacity, mean heat capacity, enthalpy and heat capacity equation over a similar range to that covered by Spencer (20). Heat capacities for the ideal state of 29 hydrocarbon gases, including propylene, were calculated at atmospheric pressure from 250 to 1500°K by Stull (24). Heat capacity for the ideal gas over a similar range to that covered by Stull (24) is given by American Petroleum Institute Research Project 44 (1) from 459.69° to 2200°F. It is generally recognized that these are the most accurate data available to date but data are lacking when higher pressures are encountered. Calorimetric technique for obtaining

heat capacity data at high pressures is limited. Telfair (21) has done supersonic measurement of heat capacity of propylene from 273° to 490°K at low pressures.

Since there are limitations as well as difficulties in obtaining heat capacity data at the higher pressures, indirect methods such as the generalized correlations or equations of state are used to supply this information. An example is the generalized correlation of Minister (2), (4) which is very useful when no other data can be found.

It was the purpose of this work to obtain heat capacity values for propylene derived from an equation of state since the equation of state lends itself most readily to the evaluation of derived thermodynamic properties. Most of the equations presented are applicable to one fluid over a limited range of pressures and temperature. One of these equations is the van der Waals equation which has been used in the design of bottled gas cylinders (18). A very large number (over 100) of equations of state have come into common use. The two of the more valuable equations of state are the Beattie-Bridgeman and Benedict-Webb-Rubin.

Inasmuch as thermodynamic properties can be calculated from their derived relationship, the Beattie-Bridgeman equation and the Benedict-Webb-Rubin equation have been applied to a number of fluids and among them some hydrocarbons. The Beattie-Bridgeman equation of state has been applied to the calculation of specific heats of air, carbon monoxide, carbon dioxide, hydrogen, nitrogen, oxygen, methane and

ethylene for temperatures up to 4000°F. and pressures up to 10,000 pounds per square inch absolute (9). However, this equation was not designed to reproduce properties of the gas in the critical range or above the critical density as indicated by Sledjeski (6).

The Benedict-Webb-Rubin equation reproduces P-V-T data accurately up to approximately 1.8 times the critical density. Above this range, calculated values of pressure are too high. According to Benedict-Webb-Rubin (14) calculated and observed critical temperatures and pressures for propylene agree within 0.70°C. and 0.70 atmospheres. This equation is believed to be the most accurate in the field to date. The use of the Benedict-Webb-Rubin equation of state to predict isobaric heat capacities relative to the ideal gas state over a wide range of temperatures and pressures has been presented for methane by Sledjeski (6) (7), for propane by Seifarth (8) (9), for n-butane by Glueck (10), and for ethylene by Sibilia (11). Satisfactory agreement was established in all cases with published experimental data.

The present work is an extension of the above studies to another hydrocarbon, propylene. No experimental or calculated data on the heat capacities of propylene at high pressure can be found in the literature, so that up to the present time such heat capacities had to be estimated for propylene from generalized charts (2) (4) (23). The present study has aimed to remedy the situation by supplying calculated data on the heat capacities of propylene at elevated pressures.

In so far as the constants have been evaluated for propylene (13) (14), the Benedict-Webb-Rubin equation has been applied in the present work for the calculation of the isobaric and constant volume heat capacity of propylene. Values for the specific heat in the ideal gas state for propylene can be obtained from API Project 44 (1) for temperatures to 1500°K. No other published data have been found which cover the range given in this paper. The method of derivation from the Benedict-Webb-Rubin equation of the heat capacity relation follows.

DERIVATION OF THE EQUATION FOR $(C_p - C_p^*)$ FROM
THE BENEDICT-WEBB-HUBIN EQUATION OF STATE

The Benedict-Webb-Hubin Equation of State (5) is:

$$(1) \quad P = RTM \left[(B_0 RT - A_0 - C_0 T^{-2}) d^2 + (bRT - a) d^3 \right. \\ \left. + a d^6 + c d^3 (1 + \gamma d^2) T^{-2} - \gamma d^2 \right]$$

Expressing equation above in terms of volume rather than density,

$$(2) \quad P = RTV^{-1} \left[(B_0 RT - A_0 - C_0 T^{-2}) V^{-2} + (bRT - a) V^{-3} \right. \\ \left. + a V^{-6} + c V^{-3} (1 + \gamma V^{-2}) T^{-2} - \gamma V^{-2} \right]$$

Expanding terms for mathematical convenience,

$$(3) \quad P = RTV^{-1} + B_0 RTV^{-2} - A_0 V^{-2} - C_0 T^{-2} V^{-2} + bRTV^{-3} \\ - a V^{-3} + a V^{-6} + c V^{-3} T^{-2} - \gamma V^{-2} + c \gamma V^{-5} T^{-2} - \gamma V^{-2}$$

For an ideal gas:

$$(4) \quad C_p^* - C_v^* = R$$

For an actual gas we can write:

$$(5) \quad C_p - C_v - R = C_p - C_p^*$$

Adding and subtracting C_v on the left side of the equation and rearranging:

$$(6) \quad (C_p - C_v) + (C_v - C_v^*) - R = C_p - C_p^*$$

From Hougden and Watson (3) (pg. 461, Equation 90):

$$(7) \quad C_p - C_v = -T \left(\frac{\partial P}{\partial T} \right)_V^2 \left(\frac{\partial V}{\partial P} \right)_T \\ = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T$$

By rearranging:

$$(8) \quad C_p - C_v = -T \left(\frac{\partial P}{\partial T} \right)_V^2 \left/ \left(\frac{\partial P}{\partial V} \right)_T \right.$$

Differentiating equation (3) at constant volume with respect to temperature:

$$(9) \quad \left(\frac{\partial P}{\partial T} \right)_V = RV^{-1} + (B_0 R + 2C_0 T^{-3})V^{-2} + bRV^{-3} - 2cV^{-3}T^{-3} (1 + \gamma V^{-2})e^{-\gamma V^{-2}}$$

Differentiating equation (3) at constant temperature with respect to volume:

$$(10) \quad \left(\frac{\partial P}{\partial V} \right)_T = -RTV^{-2} - 2V^{-3} (B_0 RT - A_0 - C_0 T^{-2}) - 3V^{-4} (bRT - a) - 6a\gamma V^{-7} + cT^{-2} e^{-\gamma V^{-2}} (-3V^{-4} - 3\gamma V^{-6} + 2\gamma^2 V^{-8})$$

Substituting equations (9) and (10) in equation (8):

$$(11) \quad C_p - C_v = -T \frac{\left[RV^{-1} + (B_0 R + 2C_0 T^{-3})V^{-2} + bRV^{-3} - 2cV^{-3}T^{-3} (1 + \gamma V^{-2})e^{-\gamma V^{-2}} \right]^2}{\left[-RTV^{-2} - 2V^{-3} (B_0 RT - A_0 - C_0 T^{-2}) - 3V^{-4} (bRT - a) - 6a\gamma V^{-7} + cT^{-2} e^{-\gamma V^{-2}} (-3V^{-4} - 3\gamma V^{-6} + 2\gamma^2 V^{-8}) \right]}$$

From Heugen and Watson (3) (pg. 473, Equation 94) we have:

$$(12) \quad (\partial C_v / \partial V)_T = T (\partial^2 P / \partial T^2)_V$$

By rearranging:

$$(13) \quad \partial C_v = T (\partial^2 P / \partial T^2)_V \partial V$$

Or:

$$(14) \quad C_v - C_v^\infty = \int_{V=\infty}^V T (\partial^2 P / \partial T^2)_V \partial V$$

In order to evaluate the integral, which is the second derivative of the pressure at constant volume with respect to the temperature multiplied by the absolute temperature, Equation (9), the first derivative, must be differentiated again:

$$(15) \quad (\partial^2 P / \partial T^2)_V = 6T^{-4} (cV^{-3} e^{-\gamma V^{-2}} + c\gamma V^{-5} e^{-\gamma V^{-2}} - C_0 V^{-2})$$

Multiplying Equation (15) by T:

$$(16) \quad (\partial C_v / \partial V)_T = 6T^{-3} (cV^{-3} e^{-\gamma V^{-2}} + c\gamma V^{-5} e^{-\gamma V^{-2}} - C_0 V^{-2})$$

And:

$$(17) \quad C_v - C_v^* = 6cT^{-3} \int_{v=\infty}^v (v-3) e^{-\gamma v^{-2}} dv \\ + 6c\gamma T^{-3} \int_{v=\infty}^v (v-5) e^{-\gamma v^{-2}} dv - 6c_0 T^{-3} \int_{v=\infty}^v v^{-2} dv$$

Evaluating this series of integrals by performing the indicated integrations by parts, the following equation is obtained after collecting terms:

$$(18) \quad C_v - C_v^* = \frac{6c}{T^3} \left[\frac{e^{-\gamma v^{-2}}}{2v^2} + \frac{e^{-\gamma v^{-2}}}{\gamma} + \frac{C_0}{c v} \right]_{\infty}^v$$

Substituting Limits:

$$(19) \quad C_v - C_v^* = \frac{6c}{T^3} \left[\frac{e^{-\gamma v^{-2}}}{2v^2} + \frac{C_0}{c v} \right] - \frac{6c}{T^3} + \frac{6c}{T^3 \gamma} e^{-\gamma v^{-2}}$$

Substituting Equations (11) and (19) into Equation (6), the desired expression for $(C_p - C_p^*)$ in the terms of the Benedict-Webb-Rubin equation of state is derived. The complete equation (20) is shown in the following:

$$(20) \quad (C_p - C_p^*) = -T \left[\frac{R}{v} + \frac{(B_0 R + 2C_0/T^3)}{v^2} + \frac{bR}{v^3} - \frac{2c}{T^3 v^3} (1 + \gamma/v^2) e^{-\gamma v^{-2}} \right]^2 \\ + \frac{RT}{v^2} - \frac{2}{v^3} (B_0 RT - A_0 - C_0/T^2) - \frac{1}{v^4} (bRT - a) - \frac{6c}{v^4} \\ + \frac{c}{T^2} (-3/v^4 - 3\gamma/v^6 + 2\gamma^2/v^8) e^{-\gamma v^{-2}} \\ + \frac{6c}{T^3} \left[\frac{e^{-\gamma v^{-2}}}{\gamma} + \frac{e^{-\gamma v^{-2}}}{2v^2} + \frac{C_0}{c v} \right] - \frac{6c}{T^3} - R$$

METHOD OF CALCULATION

Values of heat capacity of propylene for the ideal gas state, C_p^* , are available from American Petroleum Institute Research Project 44 (1) and listed in Table IV. Since the values of heat capacity for the ideal gas state C_p^* and C_v^* are subject to constant revision, all of the calculations and graphs are presented in the form of the deviations from the ideal gas state ($C_p - C_p^*$) or ($C_v - C_v^*$) rather than calculate the absolute values. Equations 19 and 20 were used in calculating these deviations. The following method of calculation was used:

1. Values of molal volume ranging from 0.17 to 5.0 liters were assumed at proper intervals at a selected constant temperature and the corresponding pressure was calculated from Equation 2.
2. For the same values of pressure, volume and temperature, Equation 9 was used to calculate $(\partial P / \partial T)_V^2$ and Equation 10 was used to calculate $(\partial P / \partial V)_T$. These results are then substituted into Equation 11 to give values of $(C_p - C_v)$.
3. Taking values of $(C_v - C_v^*)$ which have been calculated by Equation 19 under the same conditions as above and substituting in Equation 20, the desired values of $(C_p - C_p^*)$ were obtained.

This procedure of calculation was repeated for fifteen isotherms from 350.31°F. to 2240.31°F. for pressures up to about 9,500 PSIA. The results of these calculations are given in Table I. Figure 1 is a plot of these data and covers a range of 350.31°F. to 2240.31°F. and pressures up to about 9,500 PSIA. A complete stepwise calculation is given in the Sample Calculation.

Using Figure 1, a cross-plot of the data was made showing the deviation in the heat capacity values as a function of temperature for isobars from 100 to 7,000 PSIA, as shown in Figure 2.

Likewise, values of $(C_v - C_v^*)$ versus pressure were plotted in Figure 6 and cross-plotted in Figure 7 to show the variation of $(C_v - C_v^*)$ with temperature for various isobars.

Marchman et al (13) also give constants for the Benedict-Webb-Rubin equation. A comparison of the data along two isotherms of 530.31°F. and 710.31°F. was made. The calculations were performed in the stepwise method as indicated above. Results are listed in Table II and comparison plot is shown in Figures 3, 4.

Thermodynamic data of Canjar, Goldman and Marchman (12) list enthalpy data of the superheated vapor in a pressure range from 0 - 200 atmospheres and temperature range from 120°F. to 480°F. These enthalpy data were converted into values of isobaric heat capacity $(C_p - C_p^*)$ by using the chord-area method of differentiation as described by Minister (17). The method is as follows:

1. At a selected pressure, tabulate $(H - \bar{H})$ for a series of temperatures.
2. Take increments of $\Delta(H - \bar{H})$ and (Δt) for each interval tabulated and values of $\Delta(H - \bar{H})/\Delta t$ for that interval.
3. Plot $\Delta(H - \bar{H})/\Delta t$ versus temperature by drawing a rectangle having the width (Δt) and the height of $\Delta(H - \bar{H})/\Delta t$.
4. Draw a smooth curve, cutting the horizontal lines in such a manner that the area under the curve equals the sum of the areas of the rectangles.
5. Read off the ordinate of the curve which represents $d(H - \bar{H})/dt$ and equals $(C_p - C_p^0)$ at any desired temperature.

An illustration using this method is presented in Figure 8 at 50 atmospheres. For comparison of present data with Canjar's data (12), pressures were selected at 35, 50, 100 and 200 atmospheres. Results are listed in Table III and a comparison plot is shown in Figure 5.

DISCUSSION OF RESULTS

In so far as no experimental heat capacity data are available in the literature for the range herein covered, it is difficult to estimate the accuracy of this work.

Since there were two sources of constants available, Marchman et al (13) and Benedict and co-workers (14), a comparison of results from the two sets of data was made to substantiate the accuracy of this work. The calculated data are listed in Tables I and II and results are compared in Figures 3 and 4.

Figure 3 shows the comparison with $(C_p - C_p^*)$ data for the 530.31°F. and 710.31°F. isotherms. An inspection of Figure 3 shows the values of Marchman's constants give greater deviation at the 530.31°F. isotherm from the ideal gas state than the values herein calculated. There is no deviation between the two sets of results at the 710.31°F. isotherm.

Figure 4 shows that the $(C_v - C_v^*)$ values using Marchman's constants give a greater deviation from the ideal gas state at 530.31°F. and at 710.31°F. than the values herein calculated. The difference between the two sets of data is more pronounced at the lower temperature. However, the absolute magnitude of the difference cannot be considered abnormally large.

Canjar, Goldman and Marchman et al (12) state that P-V-T data of Marchman et al (13) and Sage et al (15) agree rather well, but

deviate somewhat from those of Vaughan and Graves (16). However, the work of Vaughan and Graves (16) and Benedict (14) constants covers a greater temperature range (25 - 300°C.). Therefore it is felt that Benedict data used and presented in this paper are more applicable and preferable for the temperatures used.

In the thermodynamic tables of Canjar, Goldman and Marchman (12), enthalpy values are tabulated for the superheated region for a pressure range of 0 to 200 atmospheres and a temperature range of 120°F. to 480°F. Since the data of Canjar's (12) tabulate enthalpies, these enthalpy data had to be converted to heat capacities for purposes of comparison. The method of calculating the heat capacity data from enthalpy data is mentioned on pages 10, 11. The graphical comparison is presented in Figure 5.

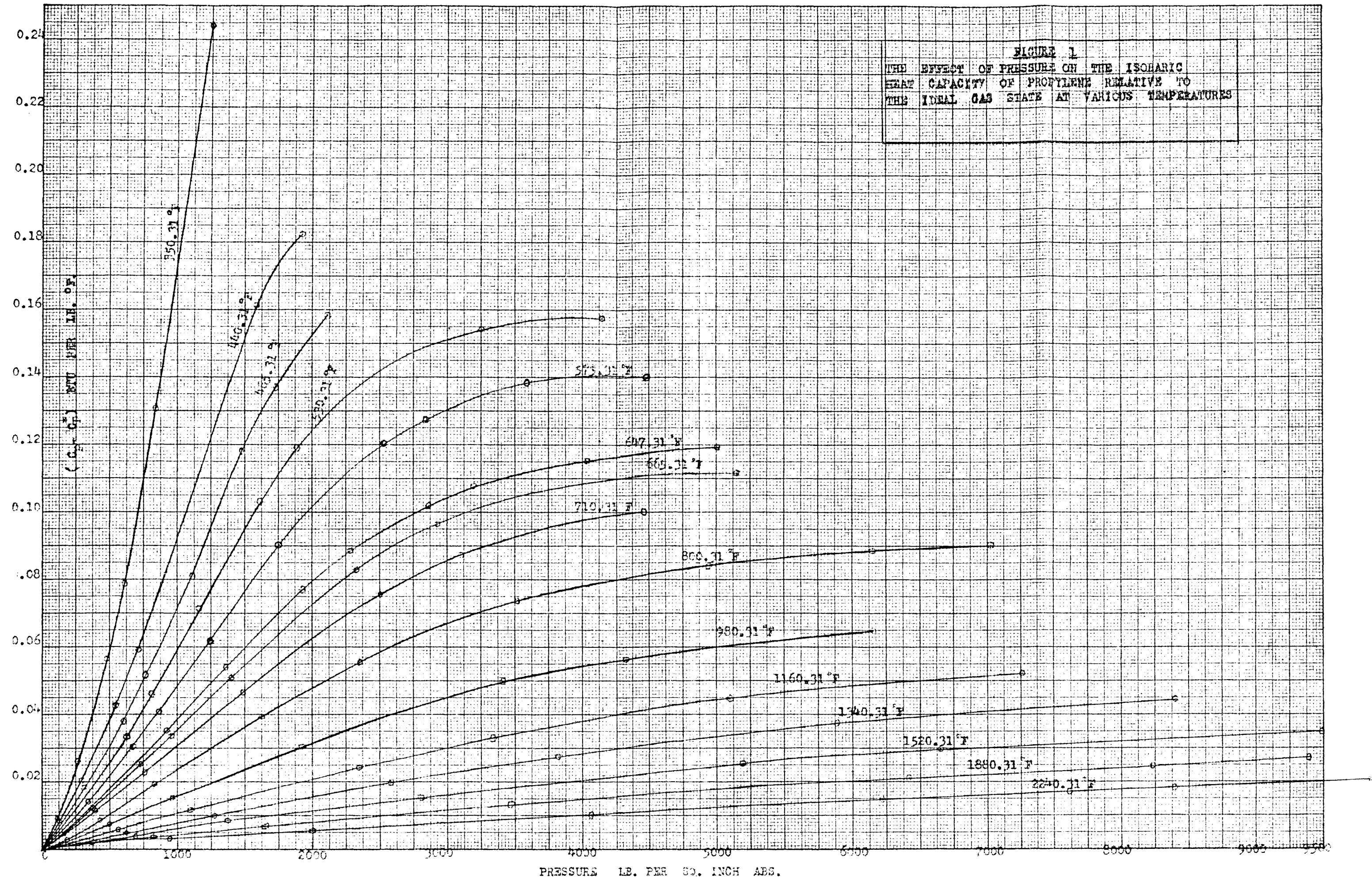
An inspection of Figure 5 shows substantial agreement between the present data and the $(C_p - C_p^*)$ values which have been calculated from Canjar's (12) tabulated enthalpy data. This is to be expected, since the present data and Canjar's tabulated enthalpy data are both based on the Benedict-Webb-Rubin equation. However, even though Canjar used residuals from the Benedict-Webb-Rubin equation so that $(C_p - C_p^*)$ values based on Canjar's data may be more accurate than the present data, Canjar's data cover only a small range of temperature and pressure. The discrepancy that occurs is a direct result of: (1) basing calculations on Canjar's enthalpy data which are tabulated to only four significant figures and enthalpy differences are therefore known to only 2 or 3 figures; (2) comparison of the data where slope of $C_p - C_p^*$

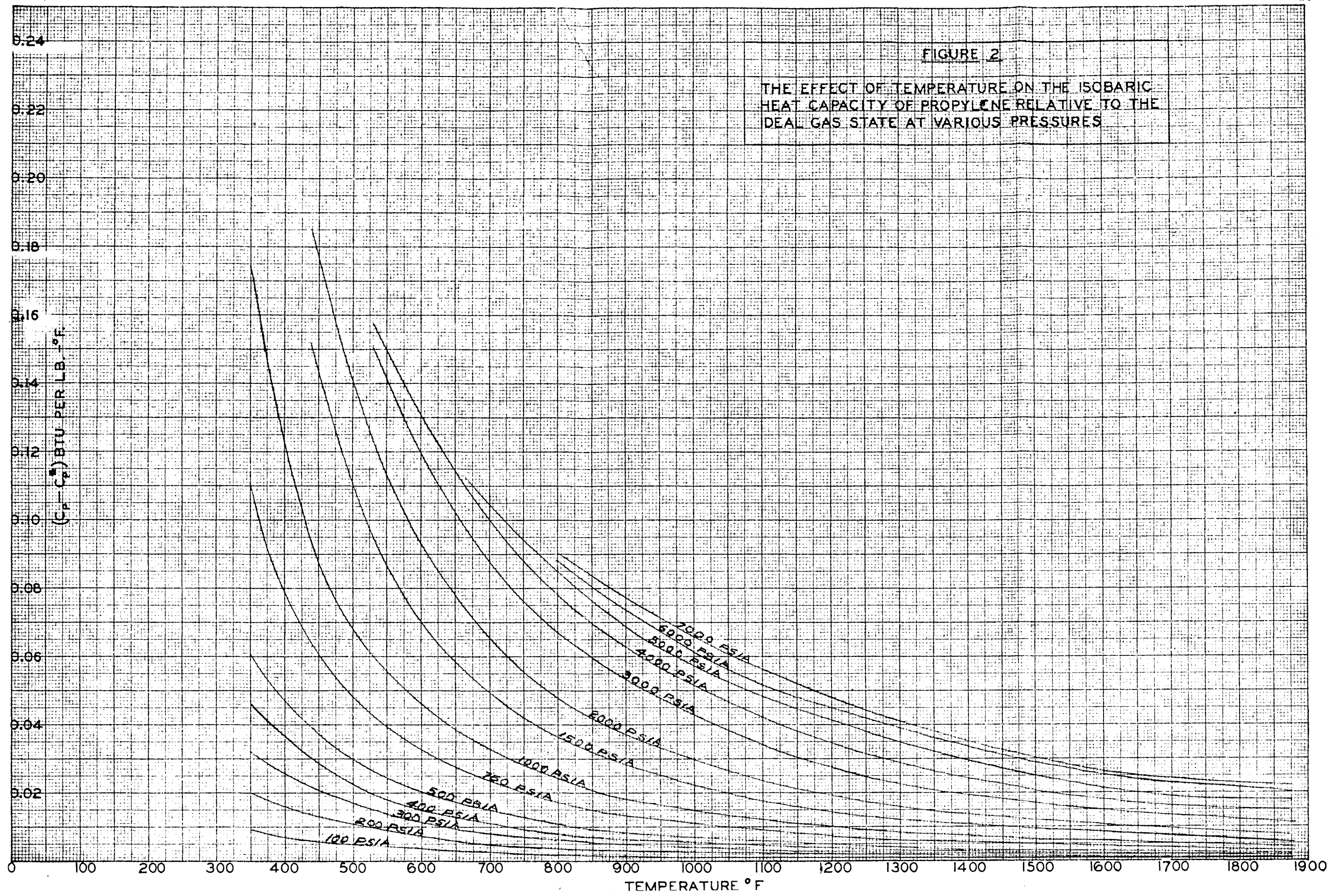
versus temperature is very steep so that graphical differentiation is not accurate; (3) minor graphical errors; (4) Canjar taking into account pressure residuals in deriving enthalpies with the E-W-R equation. The residuals correct for the deviation of E-W-R values from observed values of pressure. Hence, $C_p - C_p^*$ values based on Canjar's data may be more accurate than the present data.

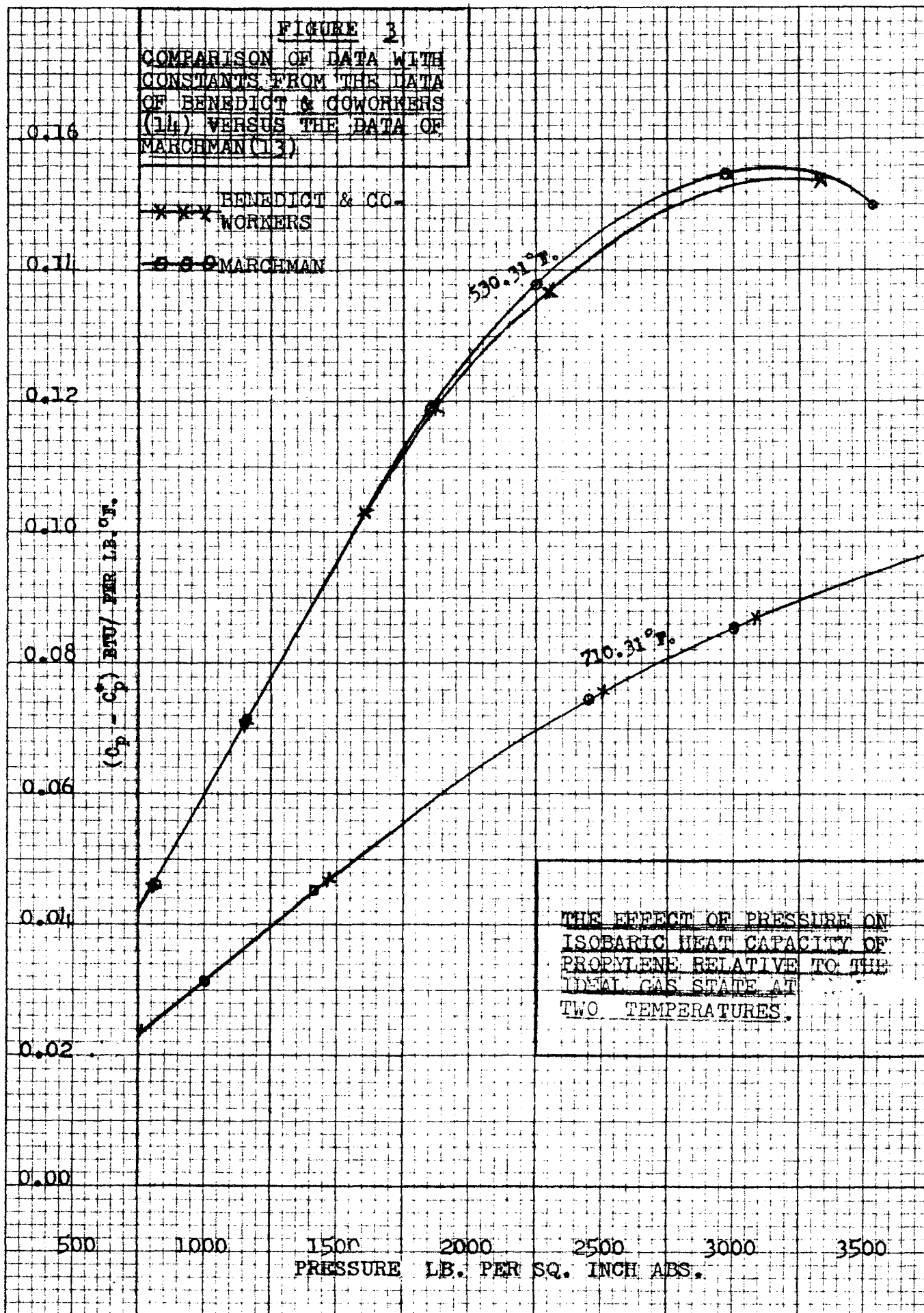
For the values of isobaric heat capacity and the specific heat at constant volume of propylene, results of the present study are recommended since no other values are to be found in the literature. Since small differences in p-V-T data appear to have a pronounced effect on $C_v - C_v^*$ values (Figure 4), the results presented in this paper for $C_v - C_v^*$ are believed to involve a larger percentage error than the results for $C_p - C_p^*$. However, $C_v - C_v^*$ represents a small correction to the heat capacity at constant volume and reliable values of C_v for propylene can be obtained with the aid of the chart for $C_v - C_v^*$ (Figure 7) developed in this paper. The correlation of $C_p - C_p^*$ (Figure 2) is likewise believed to be a reliable source for the calculation of C_p values of propylene over a wide range of temperatures and pressures.

The present work is the only systematic compilation of heat capacities of propylene at elevated pressures. It is recommended that these values should be used for accurate design calculations for processes that require accurate data on the heat capacity of propylene at elevated temperatures and pressures.

FIGURE 1
THE EFFECT OF PRESSURE ON THE ISOBARIC
HEAT CAPACITY OF PROPYLENE RELATIVE TO
THE IDEAL GAS STATE AT VARIOUS TEMPERATURES



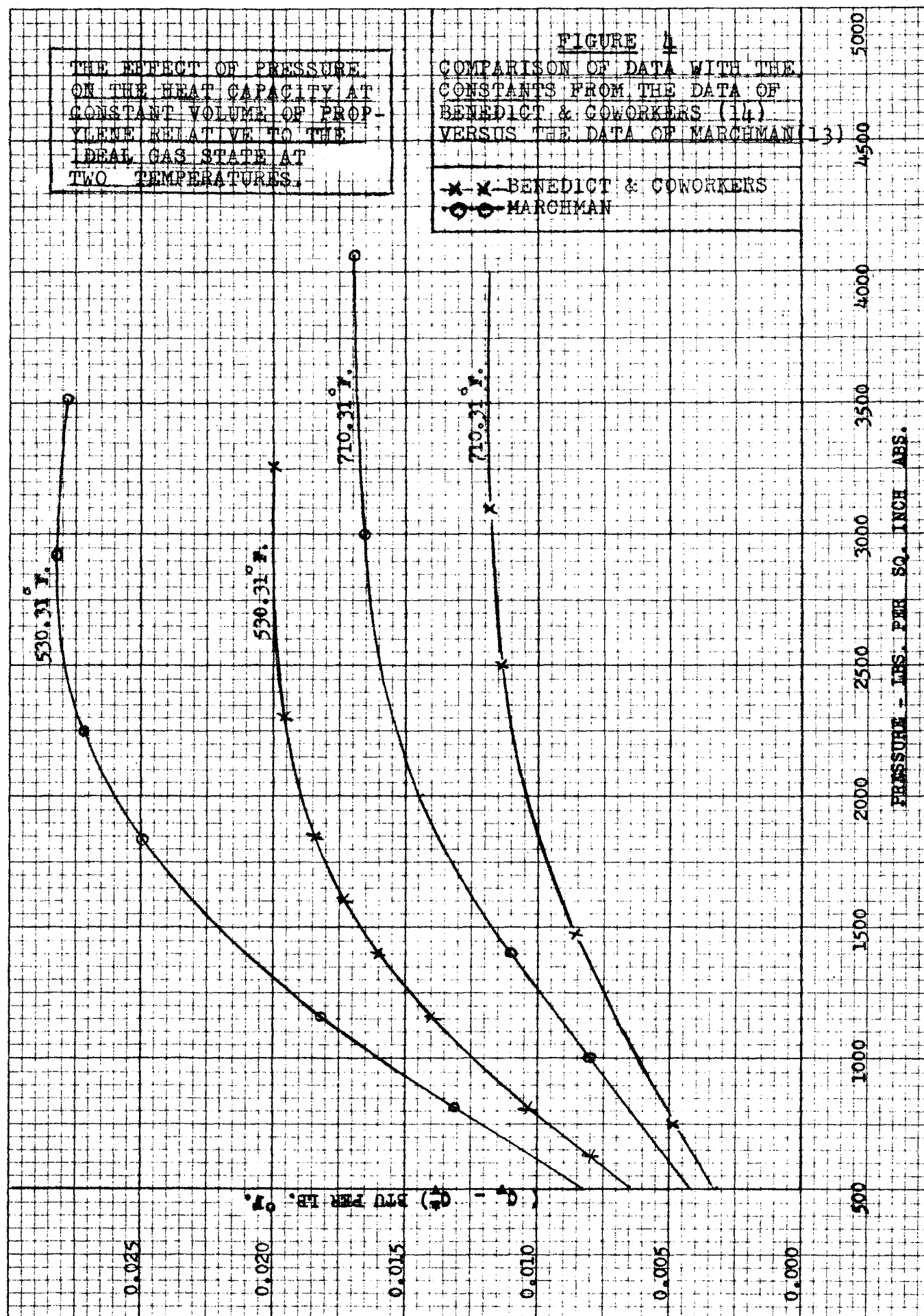


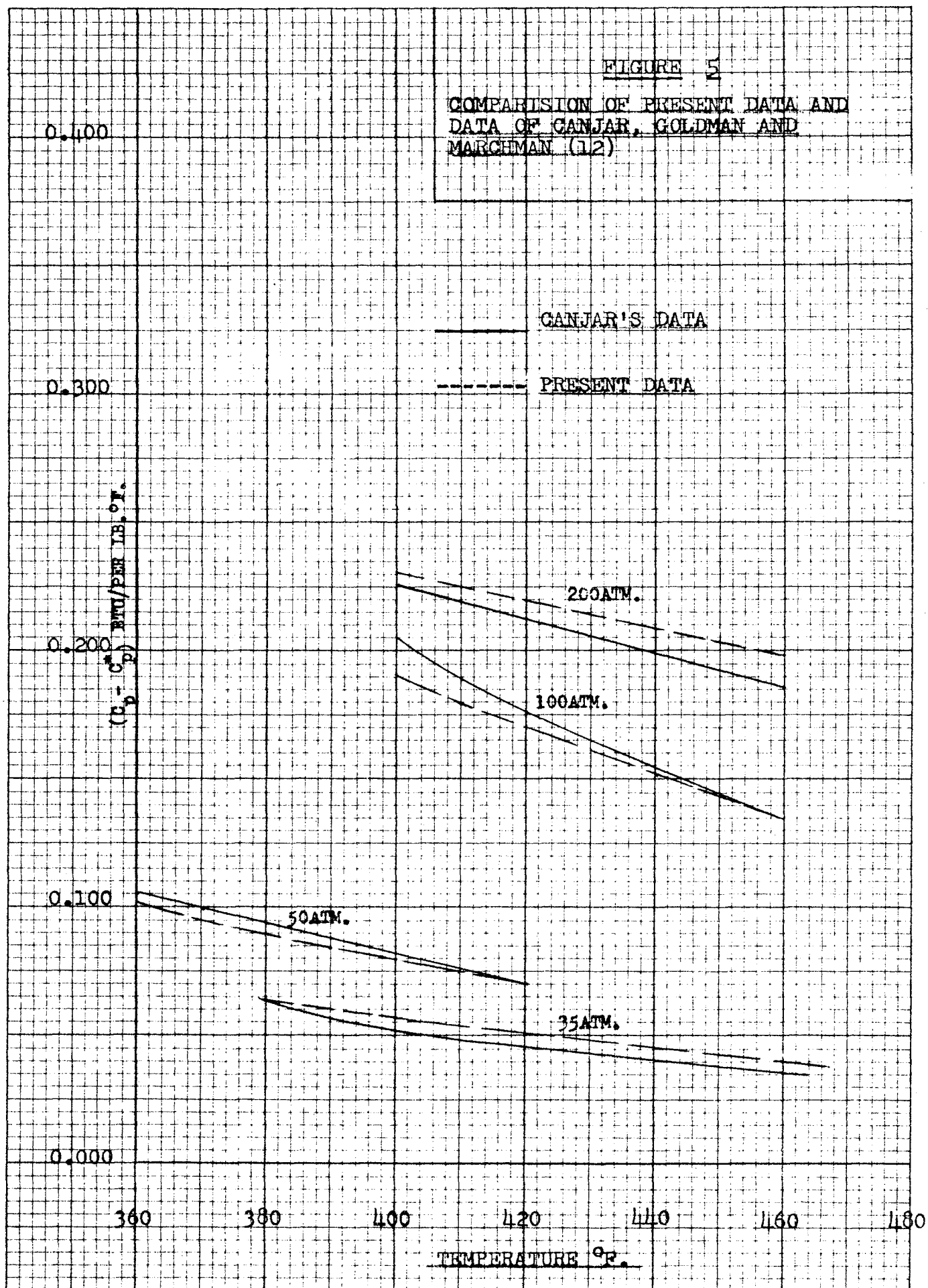


THE EFFECT OF PRESSURE
ON THE HEAT CAPACITY AT
CONSTANT VOLUME OF PROP-
YLENE RELATIVE TO THE
IDEAL GAS STATE AT
TWO TEMPERATURES.

FIGURE 4
COMPARISON OF DATA WITH THE
CONSTANTS FROM THE DATA OF
BENEDICT & COWORKERS (14)
VERSUS THE DATA OF MARCHMAN (13)

*-BENEDICT & COWORKERS
○-MARCHMAN





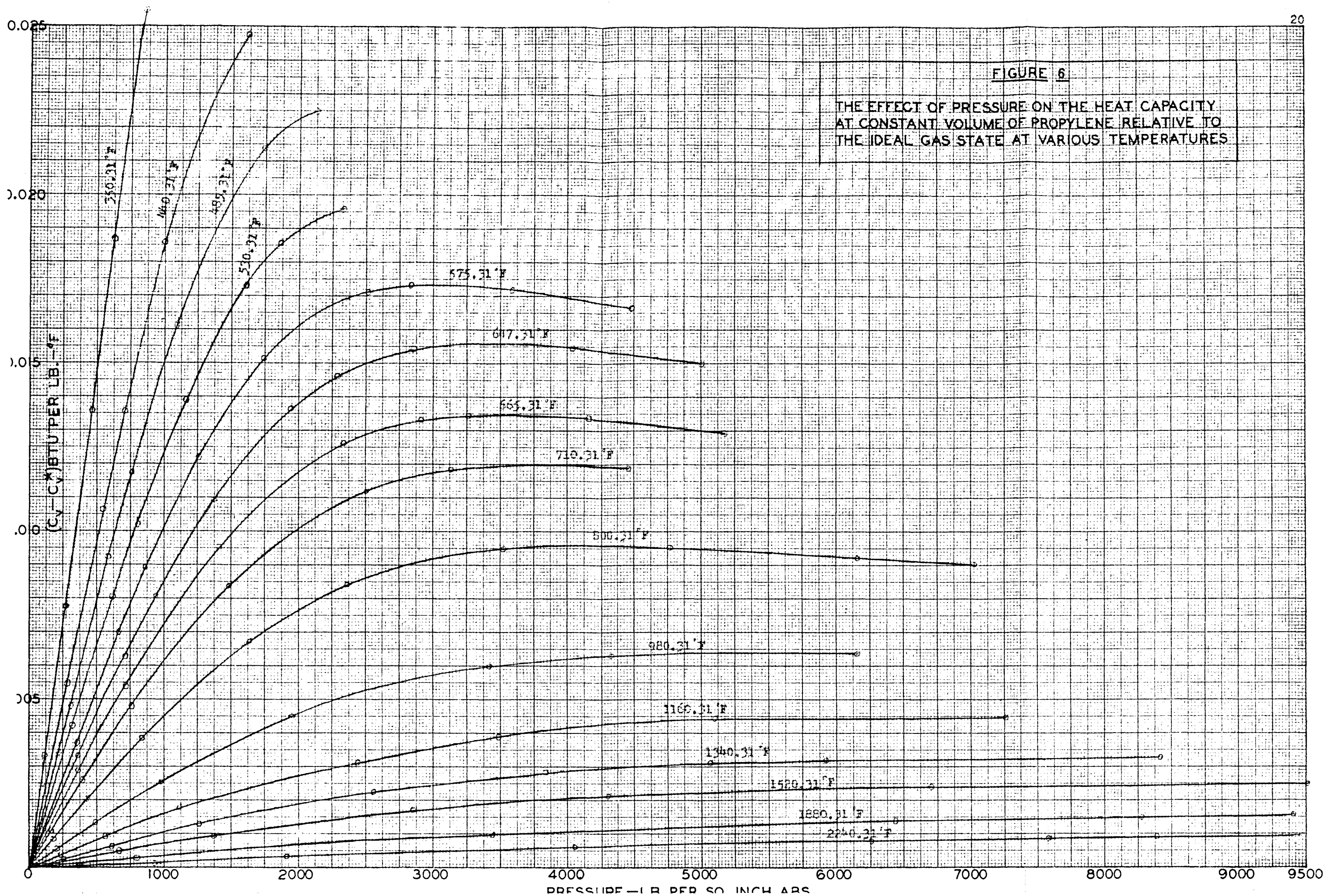


FIGURE 7

THE EFFECT OF TEMPERATURE ON THE HEAT CAPACITY
AT CONSTANT VOLUME OF PROPYLENE RELATIVE TO THE
IDEAL GAS STATE AT VARIOUS PRESSURES

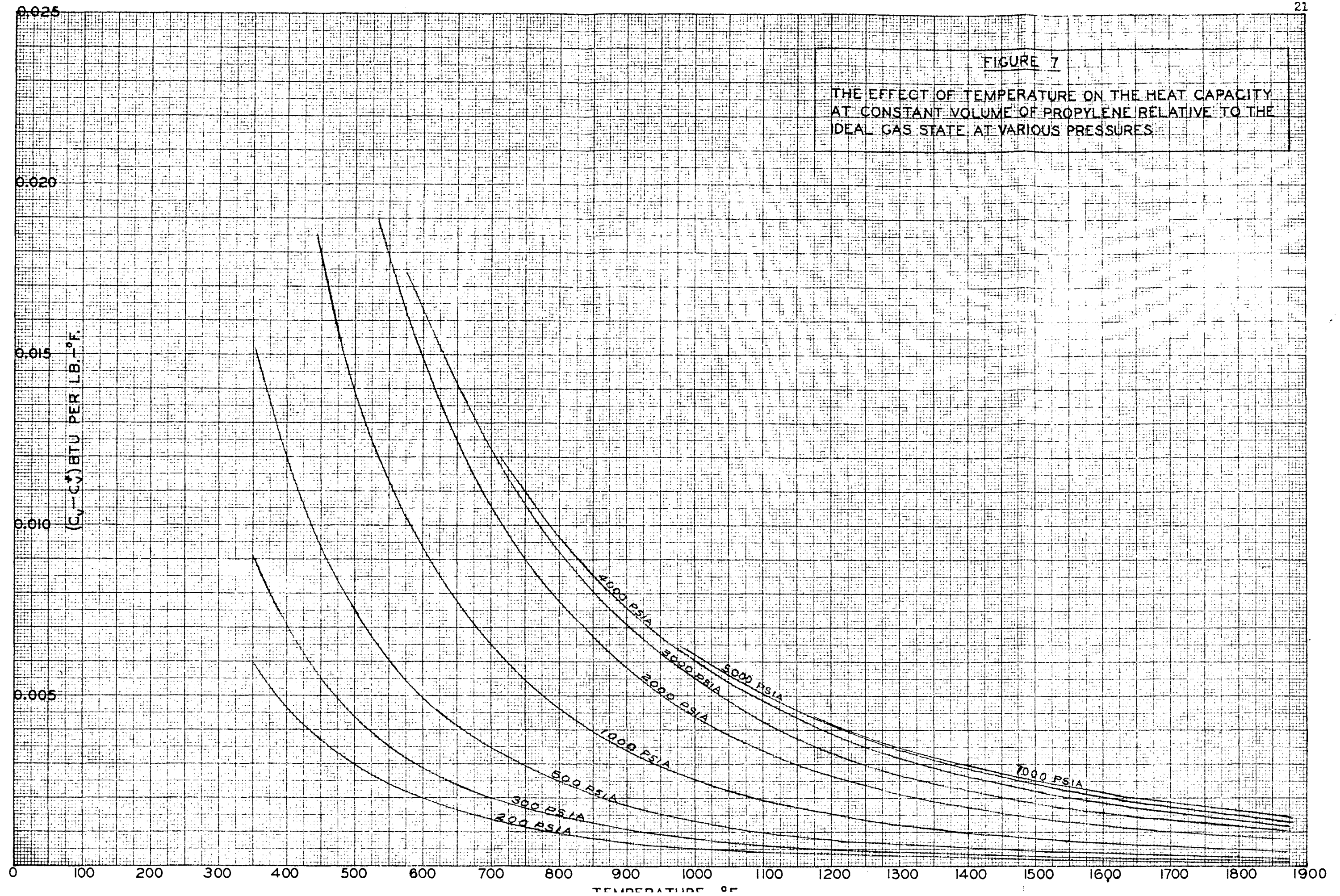
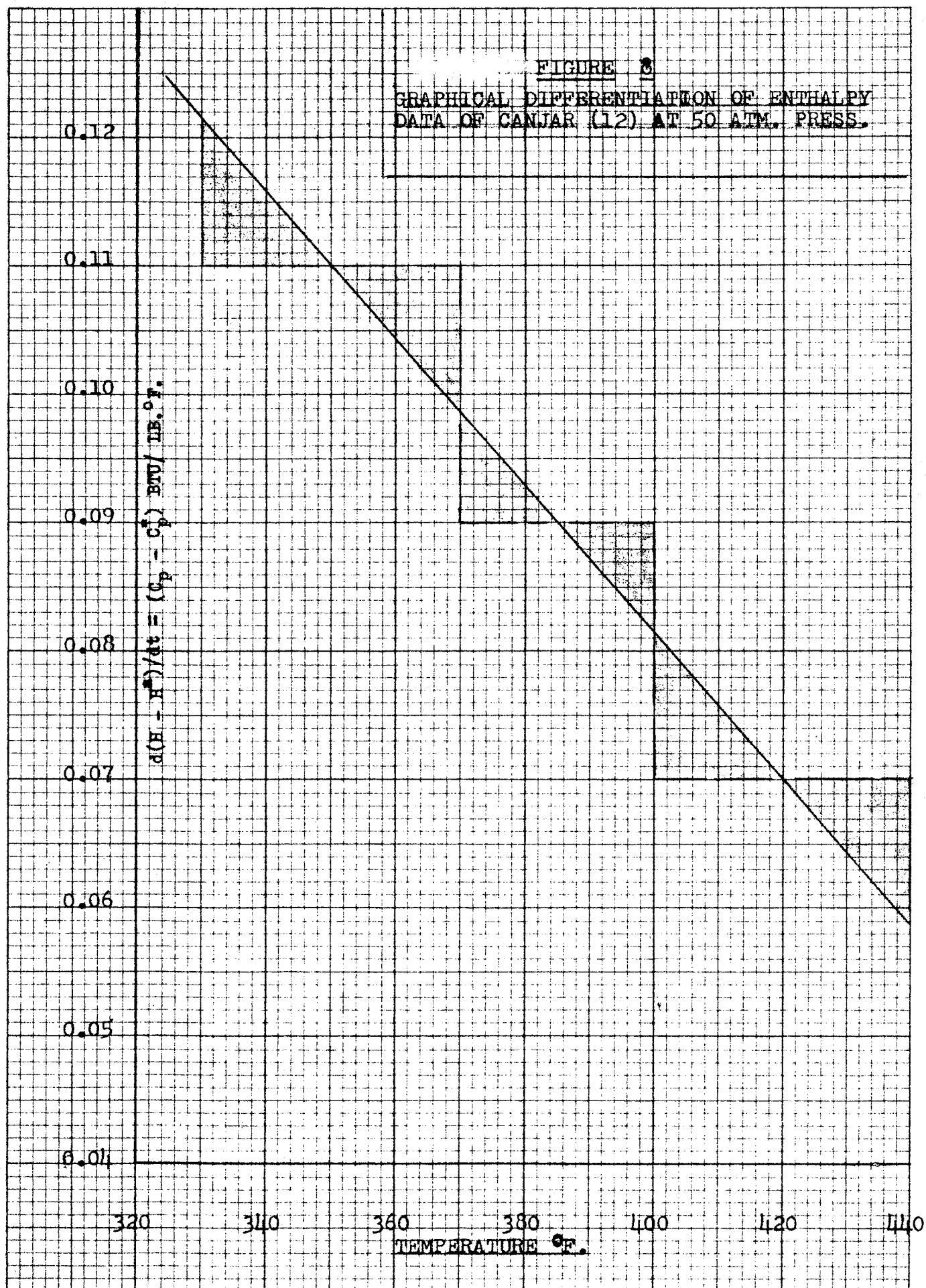


FIGURE 3
GRAPHICAL DIFFERENTIATION OF ENTHALPY
DATA OF CANJAR (12) AT 50 ATM. PRESS.



SAMPLE CALCULATION - EQUATION (2)

$$P = RT/V + (B_0RT - A_0 - C_0/T^2)1/V^2 + (bRT - a)1/V^3 + ad/V^6 + (c/V^3T^2) (1 + \gamma/V^2) (1/\phi \gamma/V^2)$$

T = Absolute temperature, °K
= 650.00°K

R = 0.08207 Liter Atmospheres
Gram-mol °K

V = Volume, Liters

P = Absolute Pressure,
Atmospheres

A₀ = 6.11220

B₀ = 0.0850647

C₀ = 439182.

b = 0.0187059

a = 0.774056

c = 102.611

d = 0.000455696

γ = 0.0182900

1 atm. = 14.696 lb./sq. in. abs.

1 Liter Atm. = 0.57567 BTU
Gram-mol °K Lb. Propylene °F

φ = 2.7183

V	RT/V	$\frac{(B_0RT - A_0 - C_0/T^2)}{V^2}$	$\frac{(bRT - a)}{V^3}$	$A_0 d/V^6$	$\frac{c(1 + \gamma/V^2)}{V^3 T^2 \phi \gamma/V^2}$	P - atm.	p - PSIA
0.10	296.363859	-80.674821	38.377625	81.891429	37.049442	373.007540	5481.718808
0.20	266.727500	-65.346600	27.977250	43.52047	28.00503	300.88365	4421.7861
0.25	231.936952	-49.411413	18.395490	18.815098	19.020471	238.75660	3508.76699
0.25	213.382000	-41.821824	14.324352	11.40863	14.99459	212.28775	3119.7808
0.30	177.818156	-29.042930	8.289554	3.820727	8.832594	169.71810	2494.1772
0.50	106.691000	-10.455456	1.790544	0.178260	1.938143	100.14248	1471.6939
1.00	53.345500	-2.613864	0.223818	0.002785	0.242821	51.20106	752.45078
2.00	26.672750	-0.653466	0.027977	0.000044	0.030357	26.07766	383.23729
5.00	10.669100	-0.104555	0.001791	0.0000002	0.001944	10.56827	155.31130

SAMPLE CALCULATION - EQUATION (9)

$$\left(\frac{\partial P}{\partial T}\right)^2_V = \left[\frac{R}{V} + \frac{B_0 R}{V^2} + \frac{2C_0}{V^2 T^3} + \frac{bR}{V^3} - \left(\frac{2c_0}{V^3 T^3}\right) \left(1 + \frac{\gamma}{V^2}\right) \left(\frac{1}{\phi} \frac{\gamma}{V^2}\right) \right]^2$$

V	R/V	$B_0 R/V^2$	$2C_0/V^2 T^3$	bR/V^3	$-(2c_0/V^3 T^3)(1 + \gamma/V^2)(1/\phi \gamma/V^2)$	$(\partial P/\partial T)_V$	$(\partial P/\partial T)^2_V$
0.18	0.455944	0.215471	0.098704	0.263236	-0.139676	0.893679	0.798662
0.20	0.410350	0.174532	0.079950	0.191899	-0.086172	0.770559	0.593761
0.23	0.356826	0.131971	0.060454	0.126177	-0.071707	0.603721	0.364479
0.25	0.328280	0.111700	0.051168	0.098252	-0.046138	0.543262	0.295134
0.30	0.273566	0.077570	0.035533	0.056859	-0.027178	0.416350	0.173347
0.50	0.164140	0.027925	0.012792	0.012282	-0.005964	0.211175	0.044595
1.0	0.08207	0.006981	0.003198	0.001535	-0.000747	0.093037	0.008656
2.0	0.041035	0.001745	0.000800	0.000192	-0.000094	0.043678	0.001908
5.0	0.016414	0.000279	0.000128	0.000012	-0.000006	0.016827	0.000283

SAMPLE CALCULATION - EQUATION (10)

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{(2/V^3)(B_0RT - A_0 - C_0/V^2) - (3/V^4)(bRT - a) - 6ad/V^7 + (c/V^2)(1/e^{1/V^2})}{(-3/V^4 - 3\delta/V^6 - 2\delta^2/V^8)}$$

V	$-RT/V^2$	$-\frac{2}{V^3} \left[B_0RT - A_0 - \frac{C_0}{V^2} \right]$	$-\frac{(3/V^4)(bRT - a) - 6ad/V^7}{(-3/V^4 - 3\delta/V^6 - 2\delta^2/V^8)}$	$\frac{c}{V^2} \left[\frac{-3}{V^4} - \frac{3\delta}{V^6} + \frac{2\delta^2}{V^8} \right]$	$\left(\frac{\partial P}{\partial V}\right)_T$
0.18	-1646.466181	896.388065	-639.626409	-345.670917	-2269.0195
0.20	-1333.637500	653.466000	-419.658750	-165.344531	-1645.0707
0.23	-1008.42146	429.664350	-239.941200	-62.159131	-1114.3150
0.25	-853.528000	334.574592	-171.892224	-34.675240	-897.50934
0.30	-592.727719	193.619519	-82.895495	-9.677221	-577.98578
0.50	-213.382000	41.821824	-10.743264	-0.270900	-194.16442
1.0	-53.345500	5.227728	-0.671454	-0.002116	-49.519642
2.0	-13.336375	0.653466	-0.041966	-0.000017	-12.770427
5.0	-2.133820	0.041822	-0.001074	-0.000000	-2.094238

SAMPLE CALCULATION - EQUATION (19)

$$(c_v - c_v^*) = \frac{6c}{T^3} \left[\frac{1}{\gamma_0 \gamma/V^2} + \frac{1}{2V^2_0 \gamma/V^2} + \frac{C_0}{cV} \right] - \frac{6c}{\gamma T^3}$$

V	$\frac{6c}{T^3} \left[\frac{1}{\gamma_0 \gamma/V^2} + \frac{1}{2V^2_0 \gamma/V^2} + \frac{C_0}{cV} \right]$	$-6c/\gamma T^3$	$(c_v - c_v^*)$
0.18	0.142684	-0.122572	0.020112
0.20	0.143308	-0.122572	0.020736
0.23	0.143511	-0.122572	0.020939
0.25	0.143241	-0.122572	0.020669
0.30	0.142179	-0.122572	0.019607
0.50	0.137292	-0.122572	0.014720
1.0	0.131044	-0.122572	0.008472
2.0	0.127087	-0.122572	0.004515
5.0	0.124502	-0.122572	0.001930

SAMPLE CALCULATION - EQUATION (20)

$$(c_p - c_p^*) = (c_p - c_v) + (c_v - c_v^*) - R$$

$$= -T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T} + (c_v - c_v^*) - R$$

V	$(\partial P / \partial T)_V^2$	$(\partial P / \partial V)_T$	$-T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T}$	$(c_v - c_v^*)$	-R	$(c_p - c_p^*)$ Liter-Atm. Gm-mol °K	$(c_p - c_p^*)$ BTU Lb. °F	P. PSIA
0.18	0.798662	-2269.0195	0.228791	0.020112	-0.08207	0.166833	0.096041	5481.7188
0.20	0.593761	-1645.0707	0.234607	0.020736	-0.08207	0.173273	0.099748	4421.7869
0.23	0.364479	-1114.3150	0.212607	0.020939	-0.08207	0.151476	0.087200	3508.7670
0.25	0.295134	-897.50934	0.213744	0.020669	-0.08207	0.152343	0.087699	3119.7808
0.30	0.173347	-577.98578	0.194945	0.019607	-0.08207	0.132482	0.076266	2494.1772
0.50	0.044595	-194.16442	0.149290	0.014720	-0.08207	0.081940	0.047171	1471.6939
1.0	0.008656	-49.51964	0.113620	0.008472	-0.08207	0.040022	0.023039	752.45078
2.0	0.001908	-12.77043	0.097115	0.004515	-0.08207	0.019560	0.011260	383.23729
5.0	0.000283	-2.09424	0.087836	0.001930	-0.08207	0.007696	0.004431	155.31144

TABLE I
CALCULATED DATA

V	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	-R	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>T = 350.31°F</u>							
0.30	1251.6147	0.447798	0.059088	-0.08207	0.424816	0.244554	0.034015
0.50	835.6373	0.264878	0.044361	-0.08207	0.227169	0.130774	0.025537
0.75	604.3582	0.187122	0.032551	-0.08207	0.137603	0.079214	0.018739
1.0	473.4797	0.154686	0.025531	-0.08207	0.098147	0.056500	0.014697
2.0	253.2690	0.114022	0.013604	-0.08207	0.045556	0.026225	0.007831
5.0	105.4896	0.093660	0.005815	-0.08207	0.017405	0.010020	0.003348
<u>T = 440.31°F</u>							
0.25	1928.8535	0.353783	0.045409	-0.08207	0.317122	0.182558	0.026141
0.30	1574.2751	0.319187	0.043075	-0.08207	0.280192	0.161298	0.024797
0.50	998.7233	0.211700	0.032339	-0.08207	0.161969	0.093241	0.018617
0.75	703.9719	0.160405	0.023730	-0.08207	0.102065	0.058756	0.013661
1.0	544.6837	0.137496	0.018612	-0.08207	0.074038	0.042621	0.010714
2.0	286.1818	0.107252	0.009917	-0.08207	0.035099	0.020205	0.005709
5.0	118.0840	0.091528	0.004239	-0.08207	0.013697	0.007885	0.002440

TABLE I
CALCULATED DATA (Cont.)

V	p (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	-R	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{lb. } ^\circ\text{F}}$
<u>T = 485.11° F</u>							
0.25	2118.2274	0.318241	0.039227	-0.08207	0.275398	0.158538	0.022582
0.30	1723.4118	0.283044	0.037211	-0.08207	0.238185	0.137116	0.021421
0.35	1483.9487	0.253053	0.034714	-0.08207	0.205697	0.118414	0.019984
0.50	1078.9258	0.194809	0.027936	-0.08207	0.140675	0.080982	0.016082
0.75	753.0106	0.151320	0.020499	-0.08207	0.089749	0.051666	0.011801
1.0	579.8048	0.131467	0.016079	-0.08207	0.065476	0.037693	0.009256
2.0	302.5000	0.104814	0.008567	-0.08207	0.031311	0.018025	0.004932
5.0	124.3133	0.090727	0.003662	-0.08207	0.012319	0.007092	0.002108
<u>T = 530.31° F</u>							
0.18	4137.1102	0.323103	0.032404	-0.08207	0.273439	0.157411	0.018654
0.20	3291.9947	0.315245	0.034227	-0.08207	0.267402	0.153935	0.019704
0.25	2319.2504	0.286036	0.034117	-0.08207	0.238083	0.137057	0.019640
0.30	1878.7474	0.256212	0.032363	-0.08207	0.206505	0.118679	0.018630
0.35	1609.9530	0.230979	0.030192	-0.08207	0.179101	0.103103	0.017381

TABLE I
CALCULATED DATA (Cont.)

T	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	$-R$	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atn.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atn.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>$T = 530.31^\circ\text{F}$ (Cont.)</u>							
0.50	1158.4454	0.181613	0.024297	-0.08207	0.123840	0.071291	0.013987
0.75	801.6577	0.144008	0.017829	-0.08207	0.079767	0.045919	0.010264
1.0	614.6806	0.126548	0.013984	-0.08207	0.058462	0.033655	0.008050
2.0	318.7473	0.102720	0.007451	-0.08207	0.028101	0.016177	0.004289
<u>$T = 575.31^\circ\text{F}$</u>							
0.18	4471.8278	0.295652	0.029052	-0.08207	0.242634	0.139677	0.016724
0.20	3573.8593	0.287821	0.029954	-0.08207	0.235705	0.138231	0.017244
0.23	2828.3722	0.272315	0.030248	-0.08207	0.220403	0.126931	0.017413
0.25	2519.8551	0.261474	0.029858	-0.08207	0.209262	0.120466	0.017188
0.35	1735.2221	0.213799	0.026423	-0.08207	0.158152	0.091043	0.015211
0.50	1237.3981	0.171067	0.021264	-0.08207	0.110261	0.063474	0.012241
0.75	849.9798	0.138026	0.015603	-0.08207	0.071559	0.041194	0.008982
1.0	649.3532	0.122474	0.012238	-0.08207	0.052642	0.030304	0.007045
2.0	334.9346	0.100968	0.006521	-0.08207	0.025419	0.014633	0.003754

TABLE I
CALCULATED DATA (Cont.)

V	p (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$ $\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ K}$	$-R$	$(c_p - c_p^*)$ $\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ K}$	$(c_p - c_p^*)$ $\frac{\text{BTU}}{\text{Lb. } ^\circ F}$	$(c_v - c_v^*)$ $\frac{\text{BTU}}{\text{Lb. } ^\circ F}$
<u>$T = 647.31^\circ K$</u>							
0.18	5009.5147	0.263119	0.026100	-0.08207	0.207149	0.119249	0.015025
0.20	4025.7120	0.255431	0.026911	-0.08207	0.200272	0.115291	0.015492
0.23	3191.3657	0.241673	0.027174	-0.08207	0.186777	0.107522	0.015643
0.25	2840.1185	0.232424	0.026824	-0.08207	0.177178	0.101996	0.015442
0.30	2279.6462	0.210908	0.025445	-0.08207	0.154283	0.088816	0.014648
0.35	1934.4145	0.193091	0.023738	-0.08207	0.134759	0.077577	0.013665
0.50	1362.7676	0.158019	0.019103	-0.08207	0.095052	0.054719	0.010997
0.75	926.7474	0.130443	0.014018	-0.08207	0.062391	0.035917	0.008070
1.0	704.4864	0.117247	0.010995	-0.08207	0.046172	0.026580	0.006330
2.0	360.7393	0.098710	0.005858	-0.08207	0.022498	0.012951	0.003372
5.0	146.6505	0.088509	0.002504	-0.08207	0.008943	0.005148	0.001442

TABLE I
CALCULATED DATA (Cont.)

V	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	-R	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>T - 665.31°R</u>							
0.18	5144.2831	0.256553	0.022622	-0.08207	0.197105	0.113467	0.013023
0.20	4138.8166	0.248910	0.023325	-0.08207	0.190165	0.109472	0.013428
0.23	3282.0705	0.235508	0.023553	-0.08207	0.176991	0.101888	0.013559
0.25	2920.0705	0.226573	0.023249	-0.08207	0.167752	0.096570	0.013384
0.30	2341.0220	0.205917	0.022055	-0.08207	0.145902	0.083991	0.012696
0.35	1984.0122	0.198470	0.020575	-0.08207	0.136975	0.078852	0.011844
0.50	1393.9551	0.155314	0.016558	-0.08207	0.089802	0.051696	0.009532
0.75	945.8506	0.128842	0.012150	-0.08207	0.058922	0.033920	0.006994
1.0	718.2141	0.116128	0.009530	-0.08207	0.043588	0.025092	0.005486
2.0	367.1740	0.098243	0.005078	-0.08207	0.021251	0.012234	0.002923
5.0	149.1262	0.088215	0.002170	-0.08207	0.008315	0.004787	0.001249

TABLE I
CALCULATED DATA (Cont.)

V	p (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$ $\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$-R$	$(c_p - c_p^*)$ $\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$(c_p - c_p^*)$ $\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$(c_v - c_v^*)$ $\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>$T = 710.31^\circ\text{F}$</u>							
0.20	4421.7869	0.234607	0.020736	-0.08207	0.173273	0.099748	0.011937
0.25	3119.7808	0.213744	0.020669	-0.08207	0.152343	0.087699	0.011898
0.30	2494.1772	0.194945	0.019607	-0.08207	0.132482	0.076266	0.011287
0.50	1471.6939	0.149290	0.014720	-0.08207	0.081940	0.047171	0.008474
1.0	752.4508	0.113620	0.008472	-0.08207	0.040022	0.023039	0.004877
2.0	363.2373	0.097115	0.004515	-0.08207	0.019560	0.011260	0.002599
5.0	155.3114	0.087836	0.001930	-0.08207	0.007696	0.004431	0.001111
<u>$T = 800.31^\circ\text{F}$</u>							
0.17	7025.971	0.222898	0.015717	-0.08207	0.156545	0.090118	0.009048
0.18	6158.426	0.219756	0.016102	-0.08207	0.153788	0.088531	0.009270
0.20	4988.477	0.212500	0.016602	-0.08207	0.147032	0.084642	0.009557
0.25	3518.587	0.193926	0.016548	-0.08207	0.128405	0.073919	0.009526
0.30	2913.345	0.177921	0.015698	-0.08207	0.111549	0.064216	0.009037
0.35	2354.021	0.165015	0.014645	-0.08207	0.097590	0.056180	0.008431

TABLE I
CALCULATED DATA (Cont.)

V	p (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$ <u>Liter-Atm.</u> <u>Gm-mol °K</u>	-R	$(c_p - c_p^*)$ <u>Liter-Atm.</u> <u>Gm-mol °K</u>	$(c_p - c_p^*)$ <u>BTU</u> <u>Lb. °F</u>	$(c_v - c_v^*)$ <u>BTU</u> <u>Lb. °F</u>
<u>T = 800.31°F (Cont.)</u>							
0.50	1626.340	0.139729	0.011785	-0.08207	0.069445	0.039977	0.006784
1.0	820.626	0.109536	0.006783	-0.08207	0.034248	0.019716	0.003905
2.0	415.663	0.092704	0.003614	-0.08207	0.014248	0.008202	0.002081
5.0	167.667	0.086787	0.001545	-0.08207	0.006262	0.003605	0.000890
<u>T = 980.31°F</u>							
0.20	6116.434	0.184039	0.011122	-0.08207	0.113091	0.065103	0.006403
0.25	4309.567	0.168470	0.011086	-0.08207	0.097486	0.056120	0.006382
0.30	3403.754	0.158064	0.010516	-0.08207	0.086511	0.049802	0.006054
0.50	1932.025	0.126981	0.007895	-0.08207	0.052816	0.030405	0.004545
1.0	955.814	0.103896	0.004544	-0.08207	0.026369	0.015180	0.002616
2.0	478.808	0.092883	0.002421	-0.08207	0.013234	0.007619	0.001394
5.0	192.323	0.086149	0.001035	-0.08207	0.005113	0.002944	0.000596

TABLE I
CALCULATED DATA (Cont.)

V	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	-R	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atn.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atn.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>T - 1160.31° F</u>							
0.20	7261.487	0.165757	0.007811	-0.08207	0.091498	0.052679	0.004497
0.25	5108.755	0.152186	0.007786	-0.08207	0.077902	0.044846	0.004482
0.35	3330.038	0.133821	0.006890	-0.08207	0.058641	0.033758	0.003967
0.50	2338.069	0.118571	0.005545	-0.08207	0.042046	0.024205	0.003192
1.0	1090.866	0.100055	0.003191	-0.08207	0.021177	0.012191	0.001837
2.0	542.731	0.090896	0.001701	-0.08207	0.010527	0.006060	0.000979
5.0	216.967	0.085548	0.000727	-0.08207	0.007741	0.004457	0.000419
<u>T - 1340.31° F</u>							
0.20	8400.099	0.153557	0.005695	-0.08207	0.077182	0.044431	0.003278
0.25	5902.123	0.141350	0.005676	-0.08207	0.064956	0.037393	0.003268
0.28	5049.660	0.135644	0.005515	-0.08207	0.059089	0.034016	0.003175
0.35	3815.542	0.125605	0.005024	-0.08207	0.048559	0.027954	0.002892
0.50	2541.616	0.112848	0.004043	-0.08207	0.034821	0.020045	0.002327
1.0	1225.153	0.097290	0.002327	-0.08207	0.017547	0.010101	0.001339
2.0	606.217	0.089132	0.001240	-0.08207	0.008302	0.004779	0.000714
5.0	241.804	0.085008	0.000530	-0.08207	0.003468	0.001200	0.000031

TABLE I
CALCULATED DATA (Cont.)

V	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$ Liter-Atn. Gm-mol $^{\circ}F$	$-R$	$(c_p - c_p^*)$ Liter-Atn. Gm-mol $^{\circ}F$	$(c_p - c_p^*)$ BTU Lb. $^{\circ}F$	$(c_v - c_v^*)$ BTU Lb. $^{\circ}F$
<u>$T = 1520.31^{\circ}F$</u>							
0.20	9514.144	0.139751	0.004278	-0.08207	0.061960	0.035668	0.002463
0.25	6680.375	0.129070	0.004265	-0.08207	0.051264	0.029511	0.002455
0.30	5206.197	0.121757	0.004540	-0.08207	0.044227	0.025460	0.002614
0.35	4289.207	0.116378	0.003774	-0.08207	0.038082	0.021923	0.002173
0.50	2837.002	0.106406	0.003037	-0.08207	0.027374	0.015758	0.001748
1.0	1355.476	0.095640	0.001748	-0.08207	0.015318	0.008818	0.001006
2.0	667.785	0.089549	0.000931	-0.08207	0.006548	0.003769	0.000536
<u>$T = 1880.31^{\circ}F$</u>							
0.23	9391.241	0.126441	0.002617	-0.08207	0.046988	0.027050	0.001507
0.25	8279.180	0.122998	0.002584	-0.08207	0.043512	0.025048	0.001487
0.30	6421.414	0.116349	0.002451	-0.08207	0.036730	0.021144	0.001411
0.50	3448.132	0.102926	0.001840	-0.08207	0.022696	0.013063	0.001059
1.0	1626.550	0.092622	0.001059	-0.08207	0.011611	0.006684	0.000610
2.0	796.247	0.088063	0.000564	-0.08207	0.006557	0.003775	0.000325

TABLE I
CALCULATED DATA (Cont.)

V	$p(\text{PSIA})$	$(c_p - c_v)$	$(c_v - c_v^*)$ <u>liter-atm.</u> <u>gm-mol °K</u>	$-R$	$(c_p - c_p^*)$ <u>liter-atm.</u> <u>gm-mol °K</u>	$(c_p - c_p^*)$ <u>BTU</u> <u>lb. °F</u>	$(c_v - c_v^*)$ <u>BTU</u> <u>lb. °F</u>
<u>$T = 2240.31^\circ\text{F}$</u>							
0.25	9862.200	0.116267	0.001682	-0.08207	0.035879	0.020654	0.000968
0.28	8377.055	0.112499	0.001634	-0.08207	0.032063	0.018498	0.000941
0.30	7623.120	0.110441	0.001595	-0.08207	0.029966	0.017251	0.000918
0.35	6230.331	0.106378	0.001488	-0.08207	0.025796	0.014850	0.000857
0.50	4050.806	0.099503	0.001198	-0.08207	0.018631	0.010725	0.000690
1.0	1893.530	0.090798	0.000689	-0.08207	0.009418	0.005421	0.000397
2.0	922.769	0.087091	0.000367	-0.08207	0.005389	0.003102	0.000212
5.0	364.464	0.085048	0.000157	-0.08207	0.003135	0.001805	0.000090

SAMPLE CALCULATION USING MARCHMAN CONSTANTS - EQUATION (2)

$$P = RT/V + (B_0 RT - A_0 - C_0/T^2)1/V^2 + (bRT - a)1/V^3 + a_d/V^6 + (c/V^3 T^2) (1 + \gamma/V^2) (1/e \gamma/V^2)$$

T = Absolute temperature, °K

T = 650.00°K

R = 0.0820544 Liter Atmospheres
Gram-mol °K

V = Volume, Liters

P = Absolute Pressure,
Atmospheres

A₀ = 4.01365

B₀ = 0.0467375

C₀ = 556093.

b = 0.0240732

a = 1.065493

c = 116.990

d = 0.000349627

γ = 0.016200

1 atm. = 14.696 lb./sq. in. abs.

1 Liter Atm. = 0.57567 BTU
Gram-mol °K lb. Propylene °F

e = 2.7183

V	RT/V	$\frac{(B_0 RT - A_0 - C_0/T^2)}{V^2}$	$\frac{(bRT - a)}{V^3}$	$\frac{A_d}{V^6}$	$\frac{c(1 + \gamma/V^2)}{V^3 T^2 \gamma/V^2}$	P - atm.	P - PSIA
0.18	296.30753	-87.564328	37.458865	41.25810	43.208120	330.66829	4859.5012
0.20	266.67680	-70.927100	27.307475	21.92625	32.435654	277.41908	4076.9508
0.25	213.34144	-45.393344	13.981427	5.74784	17.270334	204.94770	3011.9114
0.30	177.78452	-31.523152	8.0911022	1.92494	10.107522	166.38493	2445.1929
0.50	106.67072	-11.348336	1.747678	0.089810	2.210463	95.32238	1400.8577
0.75	71.11380	-5.043703	0.517831	0.007885	0.656080	67.25189	988.3338
1.0	53.33536	-2.837084	0.218460	0.001403	0.279518	50.99766	749.4616
2.0	26.66768	-0.709271	0.027308	0.000028	0.034612	26.02036	382.3952
5.0	10.66707	-0.113483	0.001748	0.000000	0.002216	10.55755	155.1538

SAMPLE CALCULATION USING MARCHMAN CONSTANTS - EQUATION (9)

$$(\Delta P/\Delta T)_V^2 = \left[R/V + B_0 R/V^2 + 2C_0/V^2 T^3 + bR/V^3 - (2c/V^3 T^3) (1 + \gamma/V^2) (1/e^{\gamma/V^2}) \right]^2$$

V	R/V	$B_0 R/V^2$	$2C_0/V^2 T^3$	bR/V^3	$-(2c/V^3 T^3) (1 + \gamma/V^2) (1/e^{\gamma/V^2})$	$(\Delta P/\Delta T)_V$	$(\Delta P/\Delta T)_V^2$
0.18	0.431865	0.118365	0.124998	0.889330	-0.132951	0.881377	0.776825
0.20	0.410272	0.095875	0.101249	0.753061	-0.099805	0.754405	0.569127
0.25	0.328218	0.061360	0.064799	0.515998	-0.053141	0.527656	0.278421
0.30	0.273515	0.042611	0.044999	0.389286	-0.031101	0.403184	0.162557
0.50	0.164109	0.015340	0.016200	0.195252	-0.006802	0.204650	0.041882
0.75	0.109406	0.006818	0.007200	0.120906	-0.002019	0.126087	0.015898
1.0	0.082054	0.003835	0.004050	0.087865	-0.000860	0.091055	0.008291
2.0	0.041027	0.000959	0.001012	0.042233	-0.000107	0.043138	0.001861
5.0	0.016411	0.000153	0.000162	0.016580	-0.000007	0.016735	0.000280

SAMPLE CALCULATION USING MARCHMAN CONSTANTS - EQUATION (10)

$$(P/V)_T = -RT/V^2 - (2/V^3)(B_0RT - A_0 - C_0/T^2) - (3/V^4)(bRT - a) - 6ac/V^7 + (c/T^2)(1/e)^{Y/V^2} \\ (-3/V^4 - 3\delta/V^6 - 2\delta^2/V^8)$$

V	$-RT/V^2$	$-\frac{2}{V^3} [B_0RT - A_0 - \frac{C_0}{T^2}]$	$-(3/V^4)(bRT - a)$	$-6ac/V^7$	$\frac{c}{T^2 e^{Y/V^2}} \left[-\frac{3}{V^4} - \frac{3Y}{V^6} + \frac{2Y^2}{V^8} \right]$	$(\partial P/\partial V)_T$
0.18	-1646.1532	972.2938	-624.3138	-365.064591	-640.1199	-2309.3577
0.20	-1333.3840	709.2710	-409.6121	-174.621094	-448.6680	-1657.0142
0.25	-853.3658	363.1467	-167.7771	-36.620675	-199.8723	-894.4892
0.30	-592.6151	210.1543	-80.9110	-10.220156	-99.22496	-572.81692
0.50	-213.34144	45.39334	-10.48607	-0.286099	-13.22791	-191.94818
0.75	-94.81838	13.44988	-2.07132	-0.016745	-2.62291	-86.07948
1.0	-53.33536	5.674168	-0.655379	-0.002235	-0.838409	-49.15722
2.0	-13.33384	0.709271	-0.040961	-0.000017	-0.053797	-12.719497
5.0	-2.13341	0.045393	-0.001049	-0.000000	-0.001337	-2.090407

SAMPLE CALCULATION USING MARCHMAN CONSTANTS - EQUATION (19)

$$(c_v - c_v^*) = \frac{6g}{T^3} \left[\frac{1}{\gamma \cdot \gamma/T^2} + \frac{1}{2V^2 \cdot \gamma/T^2} + \frac{C_0}{\sigma T} \right] - \frac{6g}{\gamma T^3}$$

T	$\frac{6g}{T^3} \left[\frac{1}{\gamma \cdot \gamma/T^2} + \frac{1}{2V^2 \cdot \gamma/T^2} + \frac{C_0}{\sigma T} \right]$	$-6g/\gamma T^3$	$(c_v - c_v^*)$
0.18	0.187203	-0.157778	0.029425
0.20	0.187340	-0.157778	0.029562
0.25	0.186571	-0.157778	0.028793
0.30	0.184170	-0.157778	0.026392
0.50	0.176968	-0.157778	0.019190
0.75	0.171716	-0.157778	0.013938
1.0	0.169696	-0.157778	0.011918
2.0	0.163537	-0.157778	0.005759
5.0	0.160204	-0.157778	0.002426

SAMPLE CALCULATION USING MARCHIANI CONSTANTS - EQUATION (20)

$$(c_p - c_p^*) = (c_p - c_v) + (c_v - c_v^*) - R'$$

$$= -T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T} + (c_v - c_v^*) - R'$$

V	$(\partial P / \partial T)_V^2$	$(\partial P / \partial V)_T$	$\frac{-T(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T}$	$(c_v - c_v^*)$	$-R'$	$(c_p - c_p^*)$ $\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$(c_p - c_p^*)$ $\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	P, PSIA
0.18	0.776825	-2303.3577	0.219218	0.029425	0.0820544	0.166589	0.095900	4859.5012
0.20	0.569127	-1657.0142	0.223252	0.029562	0.0820544	0.170760	0.098301	4076.9508
0.25	0.278421	-894.4892	0.202321	0.028793	0.0820544	0.149060	0.085809	3011.9140
0.30	0.162557	-572.81692	0.184460	0.026392	0.0820544	0.128798	0.074145	2445.1929
0.50	0.041882	-191.94818	0.141826	0.019190	0.0820544	0.078962	0.045456	1400.8577
0.75	0.015898	-86.07948	0.120048	0.013938	0.0820544	0.051932	0.029896	988.3338
1.0	0.008291	-49.15722	0.109631	0.011918	0.0820544	0.039495	0.022736	749.4616
2.0	0.001861	-12.719497	0.095102	0.005759	0.0820544	0.018807	0.010827	382.3952
5.0	0.000280	-2.090407	0.087064	0.002426	0.0820544	0.007436	0.004281	155.1538

TABLE II
CALCULATED DATA (Cont.)

V	p (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	$-R'$	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>T = 530.31°K</u>							
0.18	3532.935	0.295364	0.048570	-0.0820544	0.261848	0.150738	0.027960
0.20	2967.5161	0.303832	0.048796	-0.0820544	0.270542	0.155743	0.028090
0.25	2231.5129	0.274090	0.047526	-0.0820544	0.239530	0.137890	0.027359
0.30	1846.7661	0.245456	0.043564	-0.0820544	0.206934	0.119125	0.025079
0.50	1155.5989	0.174011	0.031676	-0.0820544	0.123601	0.071153	0.018235
0.75	800.8321	0.138888	0.023008	-0.0820544	0.079810	0.045944	0.013245
1.0	614.2919	0.122687	0.019673	-0.0820544	0.060193	0.034651	0.011325
2.0	318.2919	0.100865	0.009507	-0.0820544	0.028286	0.016283	0.005473
5.0	130.4937	0.094432	0.004005	-0.0820544	0.016351	0.009413	0.002306

TABLE II
CALCULATED DATA (Cont.)

V	P (PSIA)	$(c_p - c_v)$	$(c_v - c_v^*)$	$-R'$	$(c_p - c_p^*)$	$(c_p - c_p^*)$	$(c_v - c_v^*)$
			$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$		$\frac{\text{Liter-Atm.}}{\text{Gm-mol } ^\circ\text{K}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{Lb. } ^\circ\text{F}}$
<u>T = 710.31°K</u>							
0.18	4859.5012	0.219218	0.029425	-0.0820544	0.166589	0.095000	0.016939
0.20	4076.9508	0.223252	0.029562	-0.0820544	0.170760	0.098301	0.017018
0.25	3011.9140	0.202321	0.028793	-0.0820544	0.149060	0.085809	0.016575
0.30	2445.1929	0.184460	0.026392	-0.0820544	0.128798	0.074145	0.015193
0.50	1400.8577	0.141826	0.019190	-0.0820544	0.078962	0.045456	0.011047
0.75	988.3338	0.120048	0.013938	-0.0820544	0.051932	0.029896	0.008237
1.0	749.4616	0.109631	0.011918	-0.0820544	0.039495	0.022736	0.0068608
2.0	382.3952	0.095102	0.005759	-0.0820544	0.018807	0.010827	0.0033153
5.0	155.1538	0.087064	0.002426	-0.0820544	0.007436	0.004281	0.001397

TABLE III

CALCULATED DATA FROM THE ENTHALPY DATA OF CANJAR, GOLDMAN &
MARCHMAN (12) AS COMPARED WITH PRESENT DATA

T $^{\circ}F$	CANJAR, GOLDMAN & MARCHMAN DATA	PRESENT DATA
	$(C_p - C_p^*)$	$(C_p - C_p^*)$
	$\frac{BTU}{Lb. ^{\circ}F.}$	$\frac{BTU}{Lb. ^{\circ}F.}$
<u>P = 35 ATM.</u>		
380	0.063	0.0630
420	0.045	0.0515
460	0.035	0.0420
<u>P = 50 ATM.</u>		
350	0.110	0.1085
380	0.093	0.0873
420	0.070	0.0700
<u>P = 100 ATM.</u>		
400	0.208	0.190*
420	0.175	0.170*
460	0.133	0.1370
<u>P = 200 ATM.</u>		
400	0.225	0.228*
440	0.205	0.208*
460	0.185	0.197*

* extrapolated values

TABLE IV

VALUES OF THE ISOBARIC HEAT CAPACITY OF PROPYLENE
IN THE IDEAL GAS STATE AT VARIOUS TEMPERATURES (1)

Temperature	C_p°	Temperature	C_p°
$^\circ F$	BTU/Lb. $^\circ F$	$^\circ K$	Calories/Gram-Mol. $^\circ C$
0	0.3239	298.16	15.27
32	0.3400	300	15.34
60	0.3541	400	19.10
68	0.3581	500	22.62
77	0.3627	600	25.70
100	0.3742	700	28.37
200	0.4241	800	30.68
300	0.4727	900	32.70
400	0.5192	1000	34.46
500	0.5626	1100	35.99
600	0.6026	1200	37.32
700	0.6396	1300	38.49
800	0.6737	1400	39.51
900	0.7051	1500	40.39
1000	0.7342		
1100	0.7613		
1200	0.7863		
1300	0.8096		
1400	0.8310		
1500	0.8509		
1600	0.8693		
1700	0.8863		
1800	0.9022		
1900	0.9170		
2000	0.9306		
2100	0.9432		
2200	0.9549		

NOMENCLATURE

- c_p - Specific heat at constant pressure, Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- C_p - Specific heat at constant pressure, BTU/Lb. $^{\circ}\text{F}$
- c_p^* - Specific heat at constant pressure for a gas in the ideal state, Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- C_p^* - Specific heat at constant pressure for a gas in the ideal state, BTU/Lb. $^{\circ}\text{F}$
- c_v - Specific heat at constant volume, Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- C_v - Specific heat at constant volume, BTU/Lb. $^{\circ}\text{F}$
- c_v^* - Specific heat at constant volume for a gas in the ideal state, Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- C_v^* - Specific heat at constant volume for a gas in the ideal state, BTU/Lb. $^{\circ}\text{F}$
- T - Absolute temperature, $^{\circ}\text{K} = ^{\circ}\text{C} + 273.13^{\circ}$
- t - Temperature, $^{\circ}\text{F}$
- V - Volume, Liters
- P - Absolute pressure, Atmospheres
- p - Absolute pressure, Lbs. per Square Inch
- R - Gas constant, 0.08207 Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- R' - Gas constant, 0.0820544 Liter-Atm./Gm.-mol $^{\circ}\text{K}$
- $A_0, B_0, C_0, a, b, c, \dots$ - Constants in the Benedict-Webb-Rubin Equation of State
- e - Base of natural logarithms
- H - Enthalpy, BTU/lb.
- H^* - Enthalpy for gas in the ideal state, BTU/lb.
- Δ - Delta

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