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HEAT CAPACITIES OF ETHANE
OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE

BY

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SUMMARY

The effects of pressure and temperature on the isobaric heat capacity, the constant volume heat capacity, and the ratio of heat capacities of ethane are presented. The range of conditions covered are pressures from 0 to 10,000 psia and temperatures from 150 to 1400^o F. The calculation of these effects is based on equations derived from the Benedict-Webb-Rubin equation of state. The derived equations express the deviations of the heat capacities from ideal gas behavior.

The results show that ignoring the effect of pressure on the heat capacities of ethane may lead to large errors in engineering calculations. Graphs and tables are presented to permit an evaluation of the heat capacities over the range investigated. Comparisons are made with data of previous investigators, and relative accuracies are discussed.

INTRODUCTION

Light hydrocarbons are coming into increasing commercial use, especially in the petrochemical industry. For example, raw materials are being obtained for alcohol and polymer production from the pyrolysis of petroleum gases to produce light unsaturated hydrocarbons. Typical operating conditions in this process include 1200° F and 50 psig in the furnaces and 150° F and 350 psig at the compressor discharge prior to cooling and fractionating (1). Thus it can be seen that such processes are extending the ranges of temperatures and pressures where accurate thermodynamic properties should be known. The purpose of this paper is to help fill one of the gaps in the available thermodynamic properties by extending the heat capacity data on ethane into the high temperature and pressure range.

Similar investigations of the effect of pressure on the heat capacity of light hydrocarbons have been made in the past. For example, Sledjeski (2) has determined the effect of pressure on the isobaric heat capacity of methane in the temperature range from 75° F to 1400° F. Seifarth and Jaffe (3) also reported on the isobaric heat capacity of propane over a range of temperature of 200° F to 1350° F and a pressure range of 100 to 10,000 psia. The present paper helps complete such data on light hydrocarbons by adding ethane to the list of compounds investigated.

Generally, previous investigations into the heat capacity of ethane have been limited to the liquid and low temperature or low pressure gaseous range. For example, Dailey and Felsing (4) determined, by means of an adiabatic flow calorimeter, the isobaric heat capacity of ethane from 75-330°C at low pressure. Eucken and Weigert (5) report values of the isobaric heat capacity at one atmosphere from 70°F to 220°F. Wiebe, Hubbard, and Brevoort (6) determined with a standard calorimeter the heat capacity of saturated liquid ethane from the boiling point to the critical temperature (90°F). Numerous studies have been made on the ideal gas isobaric heat capacity by spectroscopic and statistical methods as part of the investigations of molecular structure and bond energies. Pitzer (7) has done work in this latter field.

The American Petroleum Institute's Research Project 44 (8) involved taking all the above data and similar data from other sources and determining the most accurate values for the thermodynamic properties. Included among the data reported, is the ideal gas state isobaric heat capacity from 0°F to 2200°F. These values are under constant revision to obtain the highest accuracy possible. Therefore, this present paper has included expressions of the deviations of heat capacities from the ideal gas state. In the future, the heat capacity at actual conditions can be found accurately by adding the deviations reported here to the latest ideal gas values.

The primary source of experimental data that gives the effect of pressure on the isobaric heat capacity of ethane in any part of the range of temperatures covered in this work has been reported by Sage, Webster, and Lacey (9). These authors report the heat capacity from 50°F to 250°F and from 14.7 to 1500 psia in graphical form. The tabulated form was used to present the same data in an article by Sage, Budenholzer, and Lacey (10). The isobaric heat capacity data were based in part on measurements of the Joule-Thomson coefficients at pressures from atmospheric to 600 pounds per square inch for five temperatures between 70° and 220°F. The additional basis for the Sage et. al. data was graphical differentiation of the isobaric lines on a temperature-heat content curve. The data from the two sources, Joule-Thomson and graphical, are compared and seem to agree, at least for the 600 psia isobar shown. The Joule-Thomson isobaric heat capacity was only slightly lower than the graphical data at temperatures from 175 to 250°F indicating that possibly the graphical values are high. No data was reported above 250°F.

Edmister has developed a generalized correlation for obtaining thermodynamics properties of hydrocarbons (11,12,13,14). The generalized method of determining properties was based on a new correlation of available P-V-T data using a graphical reduced equation of state. This type of correlation is valuable, especially when large

amounts of data are used in its development. It is useful for determining values of properties when no other data are available, but must be used with caution and should be checked when data do become available. The properties that may be determined by the Edmister generalized correlation include: the effect of pressure on the isobaric heat capacity, $c_p - c_p^*$ (11,12,13); the difference between the actual isobaric heat capacity and the constant volume heat capacity, $c_p - c_v$ (12); and the ratio of actual specific heats, c_p/c_v (12,14). From the above data plus values of the ideal gas isobaric heat capacity from Reference 8, it is also possible to evaluate the actual constant volume heat capacity.

To extend the work of previous investigators, several methods were considered. The generalized correlation of Edmister might be extrapolated, but without corroborating data it was felt that this might give inaccurate results. Direct extrapolation of experimental data is possible. This was ruled out because of the extreme lack of data and wide range of temperatures and pressures to be covered. The other method, that of evaluation of thermodynamic properties from an equation of state, was selected.

Several of the many equations of state were considered. The Van der Waals equation, while being one of

the simplest and well known equations, would not give accurate enough values. The Berthelot equation, which is an improvement on the Van der Waals, and has been used to correct atmospheric c_p data to ideal gas state (4), also would not give the desired accuracy. The Beattie-Bridgeman equation might be accurate enough for application in this work. However, the Beattie-Bridgeman equation was not developed to reproduce P-V-T data of gases in the critical region. Thus, the equation selected for this work was the Benedict-Webb-Rubin equation of state (15).

The Benedict-Webb-Rubin equation was developed primarily for hydrocarbons. In the same manner as the Van der Waals equation, it assumes that one equation can represent both the liquid and gas phases. The authors have stated that the equation can be regarded as a modified form of the Beattie-Bridgeman equation with more constants for increased accuracy. It is applicable up to gas densities equal to 1.8 times the critical density. The average error in calculated pressure up to this density is only 0.34 per cent. Beyond this range the calculated values are high. Further improvements in accuracy would have required several more parameters or constants. It is believed that the Benedict-Webb-Rubin equation is the most accurate equation applicable to the calculation of heat capacities available to date. The constants for use in the equation were reported in Reference 15. The Benedict-Webb-Rubin equation is readily applied since it may be

differentiated and integrated with respect to density or volume and temperature.

Barkeley, Valentine, and Hurd (16) in 1947 used the Benedict-Webb-Rubin equation to construct a pressure-enthalpy curve in the range of 0 to 500^oF and 10 to 1500 psia. In doing this work, the authors determined a new set of constants to represent more accurately the volumetric data by including data made available since the original constants were determined in 1940. The new constants reproduce the data between 100^oF and 460^oF and up to 1500 psia. As indicated later in this paper, these new constants have been considered in the calculation of the heat capacities. Barkeley, Valentine, and Hurd (16) reported that a comparison of their temperature-enthalpy curves with the graph of Sage, Webster, Lacey (9) reveals that the actual vapor enthalpy minus the enthalpy at zero pressure differed by as much as 6 Btu per pound at high pressures. Sage et. al. values were on the low side. Edmister (11) also noted that the Sage et. al. pressure correction to the enthalpy was lower than his method would predict at high pressure. Barkeley et al. believed that this discrepancy resulted from differences in volumetric data used as a basis. The authors pointed out that enthalpies based on the saturated volumes would be questionable due to the difficulties in obtaining accurate data.

The method of application of the Benedict-Webb-Rubin equation of state to the determination of heat capacity on ethane follows.

DERIVATION OF EQUATIONS USED IN CALCULATIONS

The equation of state presented by Benedict, Webb, Rubin (15) is as follows:

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + \frac{a\alpha d^6 + c d^3(1 + \gamma d^2)e^{-\sigma d^2}}{T^2} \quad (1)$$

in terms of density, d , moles/unit volume.

Rewritten in terms volume, V , the equation is

$$P = \frac{RT}{V} + (B_0RT - A_0 - C_0/T^2) \frac{1}{V^2} + (bRT - a) \frac{1}{V^3} + \frac{a\alpha/V^6 + c(1 + \gamma/V^2)e^{-\sigma/V^2}}{V^3 T^2} \quad (2)$$

The above equations are explicit in pressure; therefore, to simplify subsequent calculations, the derived equations will be explicit in pressure also.

For an ideal gas it has been established that

$$C_p^* - C_v^* = R \quad (3)$$

or

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

Subtracting (4) from both sides of $C_p = C_p^*$, the following is obtained:

$$C_p - C_p^* = C_p - C_v^* - R \quad \text{for an actual gas.} \quad (5)$$

Adding and subtracting C_v on the right-hand side of (5)

$$C_p - C_p^* = C_p - C_v^* - R + C_v - C_v$$

or

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

is obtained.

The terms $(C_p - C_v)$ and $(C_v - C_v^*)$ are now evaluated from thermodynamic relationships.

The following relationships have been derived in texts on thermodynamics (17, p. 473 Equation 90):

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

Since by definition,

$$\left(\frac{\partial V}{\partial P} \right)_T = 1 / \left(\frac{\partial P}{\partial V} \right)_T \quad , \quad (7) \text{ above may } (8)$$

be written

$$(C_p - C_v) = \frac{-T \left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T} \quad (9)$$

The expression $\left(\frac{\partial P}{\partial T} \right)_V$ is obtained by differentiating equation 2 with respect to temperature at constant volume. The result is

$$\begin{aligned} \left(\frac{\partial P}{\partial T} \right)_V &= R V^{-1} + B_0 R V^{-2} + 2 C_0 V^{-2} T^{-3} + b R V^{-3} \\ &\quad - 2 c V^{-3} T^{-3} (1 + \delta V^{-2}) e^{-\delta V^{-2}} \end{aligned} \quad (10)$$

The expression $\left(\frac{\partial P}{\partial V} \right)_T$ is obtained by differentiating equation 2 with respect to volume at constant temperature. The result is

$$\begin{aligned} \left(\frac{\partial P}{\partial V} \right)_T &= -R T V^{-2} - 2 V^{-3} (B_0 R T - A_0 - C_0 T^{-2}) - 3 V^{-4} (b R T - a) \\ &\quad - 6 a \alpha V^{-7} - 3 c V^{-4} T^{-2} e^{-\delta V^{-2}} - 3 \delta c V^{-6} T^{-2} e^{-\delta V^{-2}} \\ &\quad + 2 \delta^2 c V^{-8} T^{-2} e^{-\delta V^{-2}} \end{aligned} \quad (11)$$

Equation 9 is now expressed by substituting from equations 10 and 11. The resulting expression after collecting

terms is:

$$C_p - C_v = \frac{-T \left[RV^{-1} + B_0 RV^{-2} + 2C_0 V^{-2} T^{-3} + b RV^{-3} \right]^2}{\left[-RTV^{-2} - 2V^{-3}(B_0 RT - A_0 - C_0 T^{-2}) - 3V^{-4}(bRT - a) \right.} \quad (12)$$

$$\left. - 6a\alpha V^{-7} + e^{-\gamma V^{-2}}(-3\kappa V^{-4} T^{-2} - 3\kappa\gamma V^{-6} T^{-2} + 2\kappa\gamma^2 T^{-2} V^{-8}) \right]}$$

Thus the first term on the right-hand side of equation 6 has been expressed in terms of T and V with the Benedict-Webb-Rubin constants and the Universal Gas Constant.

The next term $C_v - C_v^*$ is evaluated in the same terms. From Reference 17 p. 473, Equation 94, the following is obtained:

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \quad (13)$$

or in another form

$$C_v - C_v^* = \int_{\infty}^V T \left(\frac{\partial^2 P}{\partial T^2} \right)_V dV \quad (14)$$

The second derivative of P with respect to T at constant V is obtained by differentiating equation 10, with respect to T at constant V.

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_V = -6C_0 V^{-2} T^{-4} + 6\kappa V^{-3} T^{-4} (1 + \gamma V^{-2}) e^{-\gamma V^{-2}} \quad (15)$$

or

Equation 15 substituted into equation 14 and rearranging terms gives

$$C_V - C_V^* = \int_{\infty}^V 6T^{-3} (cV^{-3}e^{-\gamma V^{-2}} + \gamma cV^{-5}e^{-\gamma V^{-2}} - c_0V^{-2}) dV \quad (16)$$

Separating equation 16 into individual integrals gives

$$C_V - C_V^* = 6cT^{-3} \int_{\infty}^V (V^{-3}e^{-\gamma V^{-2}}) dV + 6cT^{-3} \gamma \int_{\infty}^V (e^{-\gamma V^{-2}} V^{-5}) dV - 6c_0T^{-3} \int_{\infty}^V V^{-2} dV \quad (17)$$

The series of integrals in equation 17 are evaluated and the terms are collected to give

$$C_V - C_V^* = 6cT^{-3} \left[\gamma^{-1} e^{-\gamma V^{-2}} + V^{-2} e^{-\gamma V^{-2}} / 2 + c_0 c^{-1} V^{-1} \right]_{\infty}^V \quad (18)$$

Substituting limits gives

$$C_V - C_V^* = 6cT^{-3} \left[\gamma^{-1} e^{-\gamma V^{-2}} + V^{-2} e^{-\gamma V^{-2}} / 2 + c_0 c^{-1} V^{-1} \right] - 6c\gamma^{-1} T^{-3} \quad (19)$$

Equations 19 and 12 are substituted into equation 6 to give

$$C_P - C_P^* = -T \left[\frac{[RV^{-1} + B_0RV^{-2} + 2C_0V^{-2}T^{-3} + bRV^{-3} - 2cV^{-3}T^{-3}(1 + \gamma V^{-2})e^{-\gamma V^{-2}}]}{-RTV^{-2} - 2V^{-3}(B_0RT - A_0 - C_0T^{-2}) - 3V^{-4}(bRT - a) - 6a\alpha V^{-7} + e^{-\gamma V^{-2}}(3cV^{-4}T^{-2} - 3c\gamma V^{-6}T^{-2} + 2c\gamma^2 T^{-2}V^{-8})} \right] + \left[6cT^{-3}(\gamma^{-1}e^{-\gamma V^{-2}} + V^{-2}e^{-\gamma V^{-2}}/2 + c_0c^{-1}V^{-1}) - 6c\gamma^{-1}T^{-3} \right] - R \quad (20)$$

Dividing out V and changing signs in the first term and rearranging the second term gives

$$C_P - C_P^* = \left[\frac{T[R + B_0RV^{-1} + 2C_0V^{-1}T^{-3} + 6RV^{-2} - 2cV^{-2}T^{-3}(1 + \gamma V^{-2})e^{-\gamma V^{-2}}]}{RT + 2V^{-1}(B_0RT - A_0 - C_0T^{-2}) + 3V^{-2}(bRT - a) + 6a\alpha V^{-5} + e^{-\gamma V^{-2}}cV^{-2}T^{-2}(3 + 3\gamma V^{-2} - 2\gamma^2 V^{-4})} \right] + 6C_0T^{-3}V^{-1} + 6\gamma^{-1}cT^{-3}(e^{-\gamma V^{-2}} - 1) + 3cT^{-3}V^{-2}e^{-\gamma V^{-2}} - R \quad (21)$$

For ease of expression and calculation the following equations were used.

$$C_p - C_p^* = T \left[\frac{\phi^2}{\Theta} \right] + \Psi - R \quad (22)$$

$$\begin{aligned} \phi = R + B_0 R V^{-1} + 2C_0 V^{-1} T^{-3} + 6 R V^{-2} \\ - 2 \epsilon V^{-2} T^{-3} (1 + \gamma V^{-2}) e^{-\delta V^{-2}} \end{aligned} \quad (23)$$

$$\begin{aligned} \Theta = RT + 2V^{-1} (B_0 RT - A_0 - C_0 T^{-2}) + 3V^{-2} (6RT - a) \\ + 6a \alpha V^{-5} + e^{-\delta V^{-2}} \epsilon V^{-2} T^{-2} (3 + 3V^{-2} \gamma - 2\delta V^{-4}) \end{aligned} \quad (24)$$

$$C_p - C_v = T \left[\frac{\phi^2}{\Theta} \right] \quad (25)$$

$$\Psi = 6C_0 T^{-3} V^{-1} + 6\epsilon \delta^{-1} T^{-3} (e^{-\delta V^{-2}} - 1) + 3\epsilon T^{-3} V^{-2} e^{-\delta V^{-2}} \quad (26)$$

$$\Psi = C_v - C_v^* \quad (27)$$

METHOD OF CALCULATION

Since both equations 2 and 21 are explicit in pressure, they were solved by assuming values for volume at the various temperatures and calculating the pressure, then calculating $c_v - c_v^*$, and $c_p - c_p^*$ corresponding to the assumed temperature and the calculated pressure. These calculations were carried out as follows:

- 1) The values of volume varying from 1.35 ft³/#-mole to 50 ft³/#-mole were assumed and pressures were calculated by equation 2 using the Benedict et. al. constants shown in Table 2. The lower limits of volumes were based on not exceeding 1/(1.8x critical density). The critical density used was 0.442#/mole/CF. This represents the author's recommended limit to the Benedict-Webb-Rubin equation of state. In addition the lower limits of volumes assumed for calculating the isotherms were set by not obtaining pressures much above 10,000 psia or $c_p - c_p^*$ values much greater than 0.24 Btu/#, °F. The upper limits of assumed values for volume were set so that $c_p - c_p^*$ values of not more than about 0.020 Btu/#, °F for the lower temperatures or 0.010 for higher temperatures were obtained.
- 2) For the same values of pressure and volume used in step 1) above the values of $c_p - c_v$, $c_v - c_v^*$, and $c_p - c_p^*$ were calculated. Equations 22 through 27 were used

for these calculations. Since the calculations involved a small difference between large numbers, all calculations were made to six significant figures. Seven-place logarithms were used in the calculations (18). The isotherms selected for calculation were 150°F, 250°F, 400°F, 500°F, 600°F, 800°F, 1000°F and 1400°F. Sample calculations for the 500°F isotherm are shown in Table 1. The calculated data are shown in Table 3.

3) Since alternate values of constants for use in the Benedict-Webb-Rubin equation of state have been presented in the literature (16), it was necessary to repeat the calculations as indicated in 1) and 2) above. Barkelew et. al. stated that the alternate constants were calculated to reproduce P-V-T data including those made available since the original constants were determined. These alternate constants are applicable to ethane in the range of 100-460°F and up to 1500 lbs/sq.in.abs. only (see Table 2). Therefore the following isotherms were calculated: 150°F, 250°F, 300°F and 400°F. These calculated data are shown in Table 4.

4) The values of $c_p - c_p^*$ were plotted versus pressure with parameters of temperatures. An enlarged section (low pressure) was plotted to increase accuracy. These plots are shown on figures 1 and 2. Both the

values resulting from the Benedict et. al. constants and the Barkelew et. al. constants were plotted for comparison purposes. The curves through the Barkelew data points were used within their range of application in subsequent cross plots.

5) A crossplot of Figures 1 and 2 was made on Figure 3. Here $c_p - c_p^*$ is plotted versus temperatures from 150 to 1400°F with parameters of pressure from 100 to 10,000 psia.

6) For purposes of comparison, the generalized correlation of Edmister was used to calculate $c_p - c_p^*$. The table in Reference 11 was used for $\frac{\Delta C_p}{k_2}$, where k_2 is a constant applicable for ethane. The original value suggested for k_2 for ethane was 1.457 in Reference 11. Later Edmister suggested that k_2 should be 1.438 in Reference 12. This latter value was used in the present calculations. The resulting $c_p - c_p^*$ data were plotted on Figure 4 with isobars from 5) above also plotted for comparison. The calculated data from the Edmister generalized correlation are shown in Table 5. The values of critical pressure and temperature used were: 708.3 psia, 549.77°R.

7) The values of $c_p - c_p^*$ obtained from experimental data given by Sage et. al. in Reference 9 and 10 were plotted on Figure 5. Here again isobars from Figure 3

are also plotted for comparison.

8) Using the values of c_p^* from Reference 8 and the calculated data from steps 1), 2), and 3) c_p was obtained and plotted versus pressure with temperature as parameters (See Figure 6). A crossplot was again made to obtain c_p versus temperature with parameters of pressure; this plot is shown on Figure 7. Values of c_p similarly obtained from $c_p - c_p^*$ values using the Edmister generalized correlation were plotted on Figure 8. The Sage et. al. experimental data was also included on Figure 8 for comparison purposes.

9) The values of $c_v - c_v^*$ obtained in steps 2) and 3) were plotted as in step 4). A crossplot was again made to obtain a graph of $c_v - c_v^*$ versus temperature with parameters of pressure. These plots are shown on Figures 9 and 10.

10) Using equation 3 and values of c_p^* from Reference 8 values of c_v^* were obtained. With these values of c_v^* and values of $c_v - c_v^*$ from steps 2) and 3), c_v data were obtained and plotted on Figure 11 to show effect on total c_v of the deviation from ideal gas state.

11) From the calculated c_p data from step 8) and the calculated c_v data from step 10) values of c_p/c_v were determined. These are plotted on Figure 12. A cross

plot was made to show c_p/c_v versus temperature with parameters of pressures as shown in Figure 13. The values of c_p/c_v are shown in Tables 3 and 4.

12) Edmister has presented a generalized correlation for determining c_p/c_v (14). The values of c_p/c_v for ethane were determined from this correlation and were plotted on Figure 14. Two isobars from Figure 13 were also plotted for comparison purposes. The calculated values of c_p/c_v are shown on Table 5.

DISCUSSION OF RESULTS

General

It should be noted before proceeding that any comparisons to determine the accuracy of the heat capacity data presented herein will be sharply limited by the lack of available data. Thus the comparisons will be confined to the one set of available experimental data, that presented by Sage et. al. (9 and 10), and the Edmister generalized correlation (11,12,13,14). The following discussion and comparisons have been divided into four sections: discussion of isobaric heat capacity; constant volume heat capacity; ratio of heat capacities; and general conclusions.

Isobaric Heat Capacity, $c_p - c_p^*$ and c_p

As indicated on Figures 1, 2, and 6 the values of $c_p - c_p^*$ and c_p calculated from the Benedict-Webb-Rubin equation using the original constants (15) agree very well with those obtained from the use of the newer constants of Barkelew et. al. (16). Values of $c_p - c_p^*$ and c_p were calculated for the 150, 250, and 400^oF isotherms using both sets of constants. From this agreement in values it was concluded that accurate determinations could be made using the Barkelew et. al. constants within their range of application (150 to 450^oF and 0 to 1500 psia) and the original Benedict et. al. constants in the remainder of the range

investigated.

Figures 3 and 7 indicate that large errors may be encountered in engineering calculations if the deviation of isobaric heat capacity from the ideal gas values were neglected. The large increase in the deviation from ideality at the lower temperatures would be expected since both $c_p - c_p^*$ and c_p become infinite at the critical point (approx. 90°F and 709 psia). The dashed lines on the higher pressure isobars on Figures 3 and 7 have been plotted to show that at higher pressures (theoretically, those above the critical pressure) the deviation from ideality is reduced as pressure is increased within certain temperature ranges. For ethane, the 4000, 5000, 8000 and 10,000 psia isobars show such a trend towards ideality at temperatures below 700°F . This same phenomenon may be seen on the common compressibility factor versus reduced pressure plots. For these latter plots it has been explained that the phenomenon results from the actual volume of the molecules becoming an increasing factor while the forces of attraction between molecules become less of a factor in determining the deviation from ideality.

On Figure 4 it can be seen that the values of $c_p - c_p^*$ determined from the Edmister generalized correlation agree with those calculated from the Benedict-Webb-Rubin equation.

The differences between values does seem to increase with increasing pressures. However, the 2500 psia isobar shown is about the upper limit of values that may be obtained from the Edmister correlation in its present form. It should be pointed out that Edmister has himself indicated that the value of k_2 used in the $c_p - c_p^*$ calculation is subject to revision to increase the correlation's accuracy. Figure 8 also shows agreement between c_p values obtained from the Edmister correlation and from the Benedict-Webb-Rubin equation.

A comparison of the Sage et. al. (9,10) data with those of the present study are shown on Figures 5 and 8. It was felt that though isotherms in the range of 175 to 225°F would show good agreement, the true comparison would require the wide range of temperatures shown. These figures indicated that below about 200°F this investigator's calculated values are higher than the Sage et. al. values, while at temperatures above 200°F, they are lower. The slope of the isobars at 250°F indicate that the Sage et. al. would be higher over a large range of higher temperature. The values of c_p , and hence $c_p - c_p^*$, for pressures 600 psia and below were obtained from measurements of the Joule-Thomson coefficient of ethane. As indicated on Figures 5 and 8 the values obtained by this investigator do not deviate widely from the Sage et. al. data at 500 psia and below. Above

600 psia Sage et. al. obtained their c_p data by graphical differentiation of the temperature-heat content plot which in turn was based on saturated gas volume data. As indicated in the introduction to the present paper, Barkelew et. al. (16) have pointed out that values obtained from such volumetric data are questionable due to the difficulties in obtaining accurate saturated volumetric data. Barkelew et. al. indicated that the pressure correction to the heat content they obtained were higher than those obtained by Sage et. al. at temperatures above 200^oF. Edmister (11) noted the same discrepancy between his data and the Sage et. al. data. Since these pressure corrections to the heat content are subtracted from the ideal gas heat content, a plot of heat content versus temperature with parameters of pressure would reveal that the Sage et. al. data have a higher slope (hence isobaric heat capacity) than either the Barkelew et. al. or Edmister data would show. Thus the values of heat capacity of ethane by Sage et. al. at pressures above 600 psia may be on the high side.

On the basis of the comparisons made above, the following recommendations are made:

- 1) Below 250^oF the Sage et. al. data for $c_p - c_p^*$ and c_p should be used, keeping in mind that the values at pressures above 600 psia may very well be on the high side.
- 2) Above 250^oF the $c_p - c_p^*$ and c_p of the present invest-

igator should be used with some consideration being given to the fact that the values may be on the low side.

Constant Volume Heat Capacity $c_v - c_v^*$ and c_v

Figure 9 indicates a seemingly wider discrepancy in the calculated values obtained from the original Benedict et. al. constants and the Barkelew et. al. constants, than with the $c_p - c_p^*$ values. This is due in part to the fact that relatively smaller deviations are exhibited by the constant volume heat capacity than the isobaric heat capacity (0.0 to 0.04 versus 0.0 to 0.30). Figure 11 indicates that the discrepancy has a very small effect on the total heat capacity, c_v . Therefore, it was concluded that the results obtained by the Barkelew et. al. constants can be used within their range of conditions and that the values from the Benedict et. al. constants can be used over the remainder of the range.

Figures 10 and 11 indicate that pressure has relatively less effect on the constant volume heat capacity than on the isobaric heat capacity. For example, at temperatures above 400°F a maximum error of only 5% would result from using the ideal gas value.

The phenomenon of a return to ideality with increasing pressure was exhibited with the constant volume heat capacity. Since this trend was described in the previous section on isobaric heat capacity, it will not be further

dealt with here except to note that the break in the isobars towards ideality occurs at higher temperatures for the same pressures.

It should be noted that Edmister (12) has developed a method for obtaining c_v from his generalized correlation. This involves obtaining from a graph the value of $c_p - c_v$ as a function of reduced temperature and pressure only. Thus it would be possible to compare c_v values from Edmister's data with those calculated herein.

It is recommended that where a correction for the effect of pressure on the constant volume heat capacity of ethane is necessary in engineering calculations, the data on Figure 10 be used.

Ratio of Heat Capacities c_p/c_v

The values of c_p/c_v calculated from the Benedict et.al. and the Barkelew et.al. constants are practically equal as shown on Figure 12.

Figure 13 shows that large deviations of the c_p/c_v ratio from ideality may be encountered and must be recognized in engineering calculations.

It has been pointed out by Edmister (14) that the use of more accurate c_p/c_v ratios greatly improves the accuracy of the horsepower obtained from the equation for single

stage adiabatic compression even though it was derived for ideal gases.

$$H.P. = \frac{144 P.V.}{33,000} \left(\frac{c_p/c_v}{c_p/c_v - 1} \right) \left[\left(\frac{P_2}{P_1} \right)^{\frac{c_p/c_v - 1}{c_p/c_v}} - 1 \right]$$

The deviation from ideality of the c_p/c_v ratio has a larger effect on the answers obtained from the equation than the deviation of pressure, volume, and temperature relationship from ideality. Here again as the critical point is approached, the deviation from ideality of the ratio of c_p/c_v approaches infinity. On Figures 12 and 13 the trend towards ideality with increase in pressure is again indicated.

The values of c_p/c_v obtained from the Edmister (12 and 14) generalized correlation have been plotted on Figure 14. Two isobars from the values calculated from the Benedict-Webb-Rubin equation are also shown for comparison purposes. The data from the two sources are in agreement at temperatures above 250°F. Below this temperature the Edmister values are lower. In making this comparison it should be remembered that the values of c_p/c_v from the generalized correlation are read from a graph and some of the discrepancy may very well result from this. Edmister compared values from his correlation with c_p/c_v values at atmospheric pressures and found a deviation of only 4%.

Based on the comparison on Figure 14 it is recommended that above 250°F and below 750 psia either the Edmister or the present investigator's c_p/c_v values can be used. Outside this range of temperature and pressure the values obtained from the Benedict-Webb-Rubin equation (Figure 13) should be used.

Conclusions

For values of isobaric heat capacity, c_p , and its deviation from ideality, $c_p - c_p^*$, the values of Sage et.al. (9,10) are recommended for temperatures below 250°F. It should be remembered, however, that the values at pressures above 600 psia may be on the high side. At temperatures above 250°F the values obtained by this investigator are recommended.

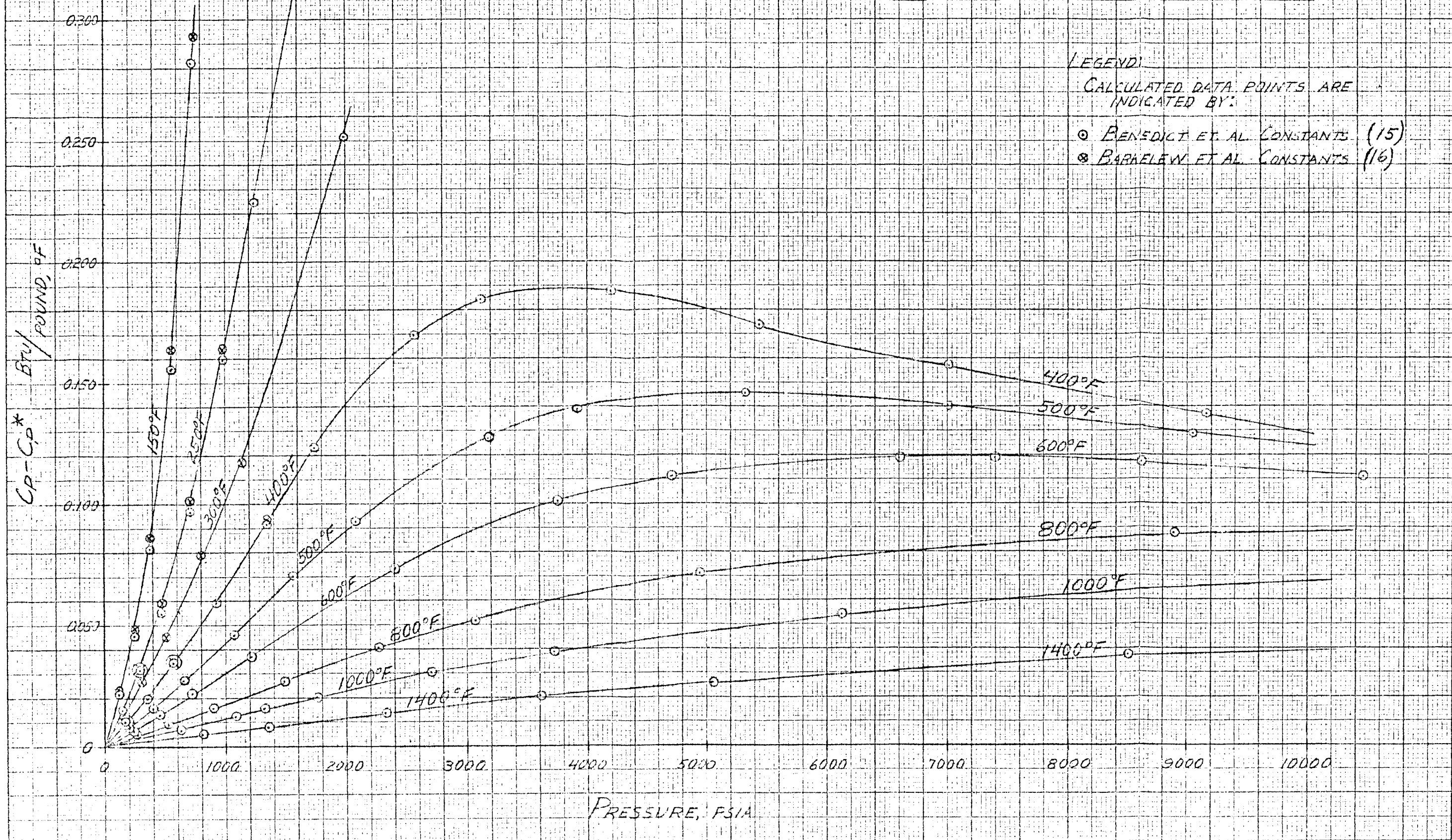
For values of constant volume heat capacity, c_v , and its deviation from ideality, $c_v - c_v^*$, the data of this investigator are recommended.

For values of the ratio of heat capacities, c_p/c_v , at temperatures above 250°F and pressures below 750 psia either the Edmister generalized correlation or this investigator's data may be used. Outside this range of temperature and pressure, the values obtained by this investigator should be used.

Since the accuracy of any thermodynamic properties derived from the Benedict-Webb-Rubin equation is directly dependent on the accuracy of the original constants, more accurate constants might require a revision of the values of heat capacities presented in this paper. Selleck, Opfell, and Sage (19) by utilizing computing machines and statistical methods were able to determine the most accurate values of constants for the Benedict-Webb-Rubin equation for propane. If such a study were made for ethane, the recalculation of the heat capacities would yield more accurate results than presented herein. Of course, comparison with experimental data as it becomes available will also aid in determining and improving the heat capacity values of ethane.

FIGURE 1

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



LEGEND:
 CALCULATED DATA POINTS ARE INDICATED BY:
 ○ BENEDICT ET AL. CONSTANTS (15)
 ⊗ BARRELEW ET AL. CONSTANTS (16)

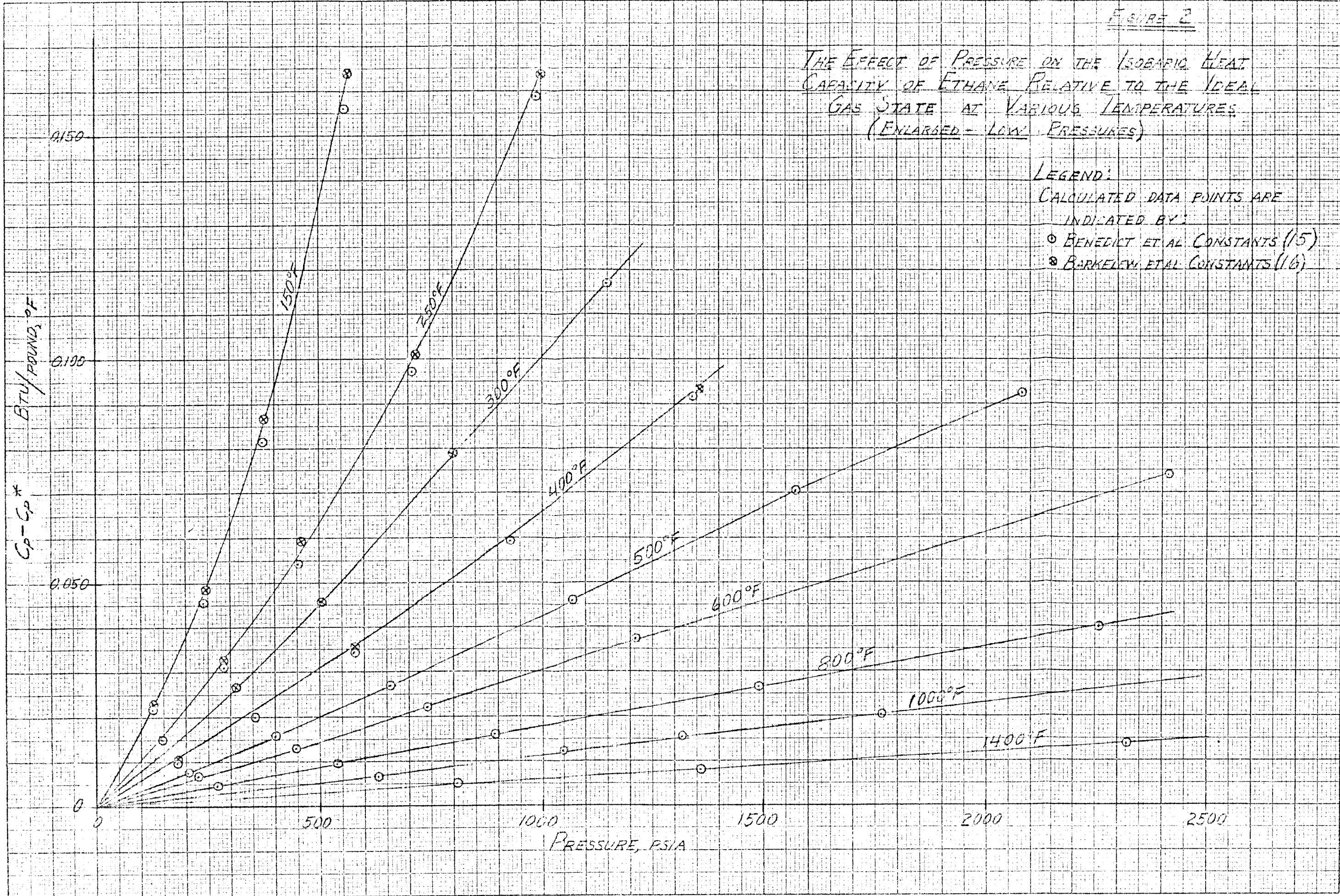
SCALE 10 X TO THE 1/4 INCH
 FEDERAL RESERVE CO.

FIGURE 2

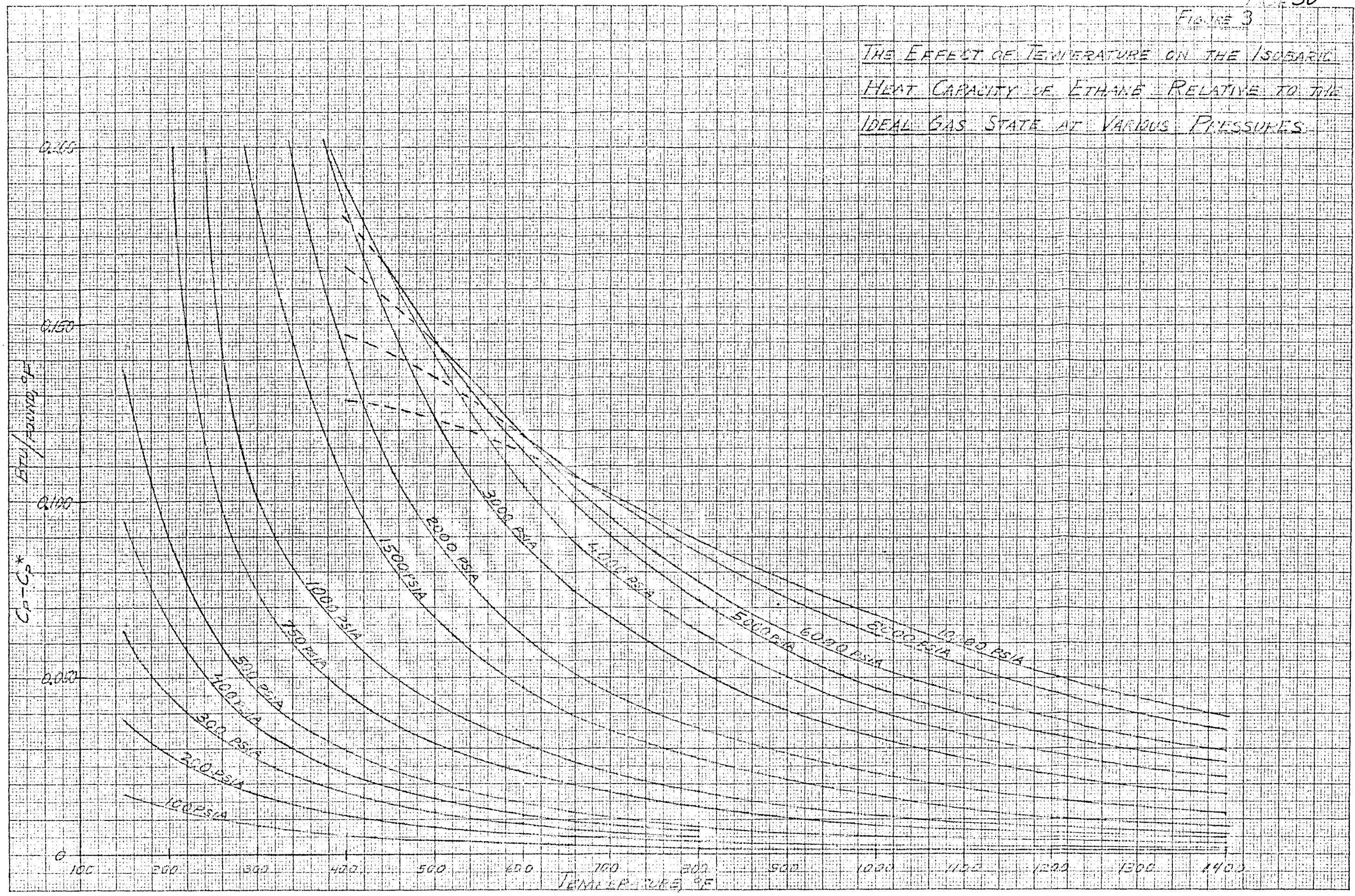
THE EFFECT OF PRESSURE ON THE ISOBARIC HEAT CAPACITY OF ETHANE RELATIVE TO THE IDEAL GAS STATE AT VARIOUS TEMPERATURES (ENLARGED - LOW PRESSURES)

LEGEND:

- CALCULATED DATA POINTS ARE INDICATED BY:
- BENEDICT ET AL. CONSTANTS (15)
- ⊗ BERKELEY ET AL. CONSTANTS (16)

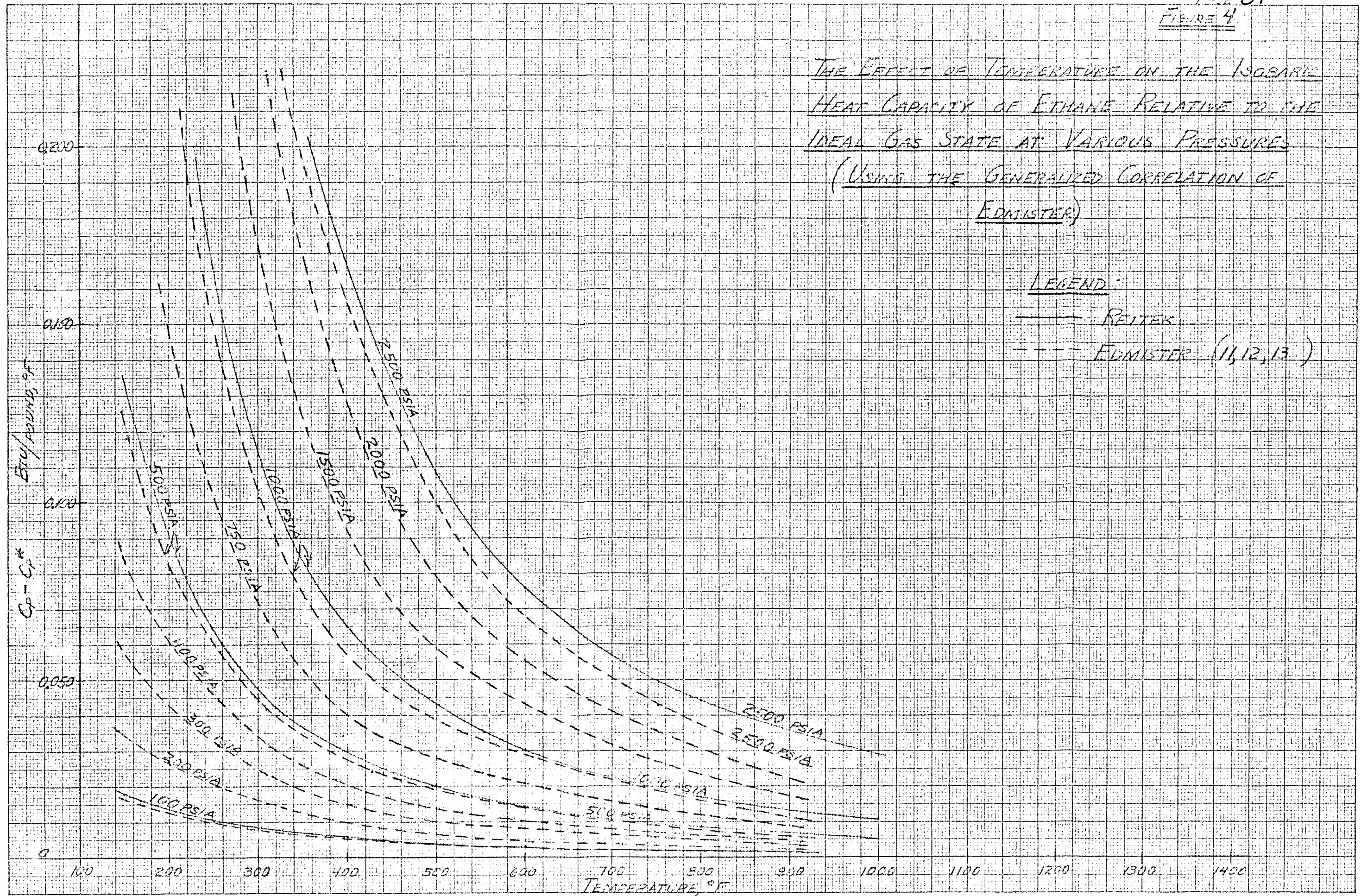


THE EFFECT OF TEMPERATURE ON THE ISOBARIC
HEAT CAPACITY OF ETHANE RELATIVE TO THE
IDEAL GAS STATE AT VARIOUS PRESSURES.



KEUFEL & ESSER CO., N. Y. NO. 330 14L
Millimeters, 5 mm. lines spaced, cm. line heavy.
MADE IN U. S. A.

THE EFFECT OF TEMPERATURE ON THE ISOBARIC
HEAT CAPACITY OF ETHANE RELATIVE TO THE
IDEAL GAS STATE AT VARIOUS PRESSURES
(USING THE GENERALIZED CORRELATION OF
EDMISTER)



LEGEND:
 ——— REITER
 - - - EDMISTER (11, 12, 13)

Millimeter, 5 mm. lines, accuracy, cm. lines heavy.
 MADE IN U. S. A.

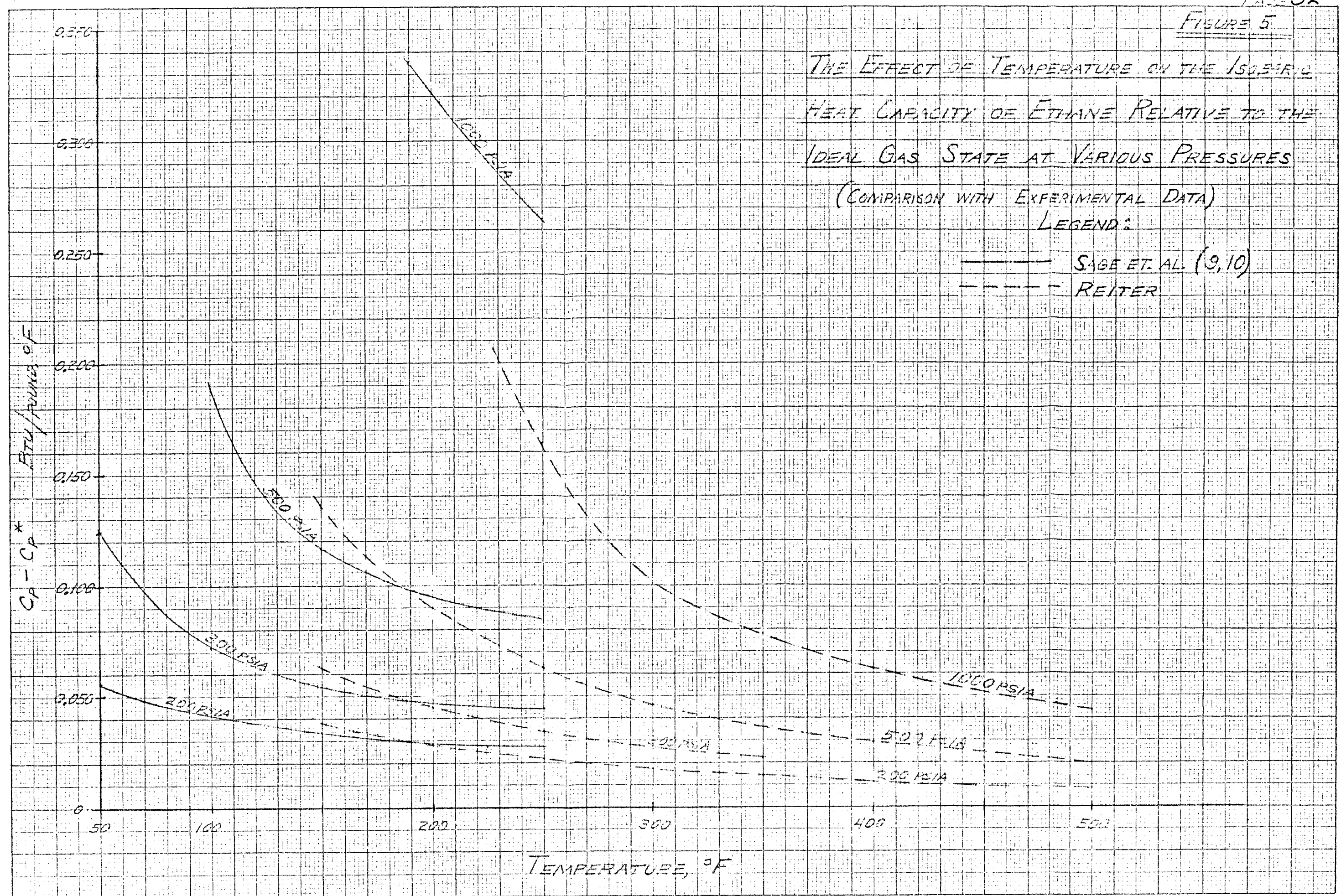
FIGURE 5

THE EFFECT OF TEMPERATURE ON THE SPECIFIC HEAT CAPACITY OF ETHANE RELATIVE TO THE IDEAL GAS STATE AT VARIOUS PRESSURES

(COMPARISON WITH EXPERIMENTAL DATA)

LEGEND:

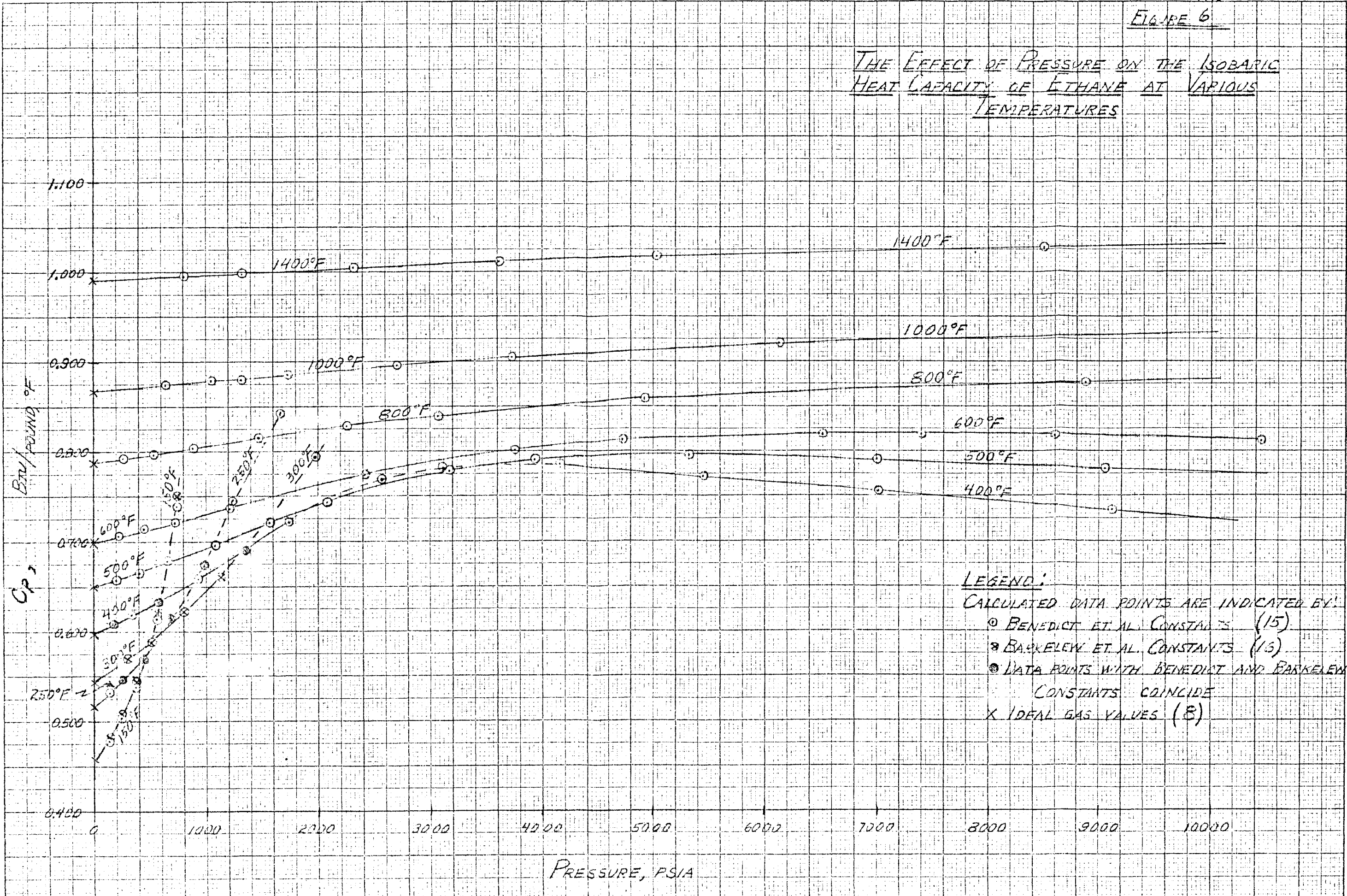
- SAGE ET AL. (9,10)
- - - - REITER



10 X 10 TO THE 1/4 INCH
KUPFFEL & ESSER CO.
NEW YORK

FIGURE 6

THE EFFECT OF PRESSURE ON THE ISOBARIC HEAT CAPACITY OF ETHANE AT VARIOUS TEMPERATURES

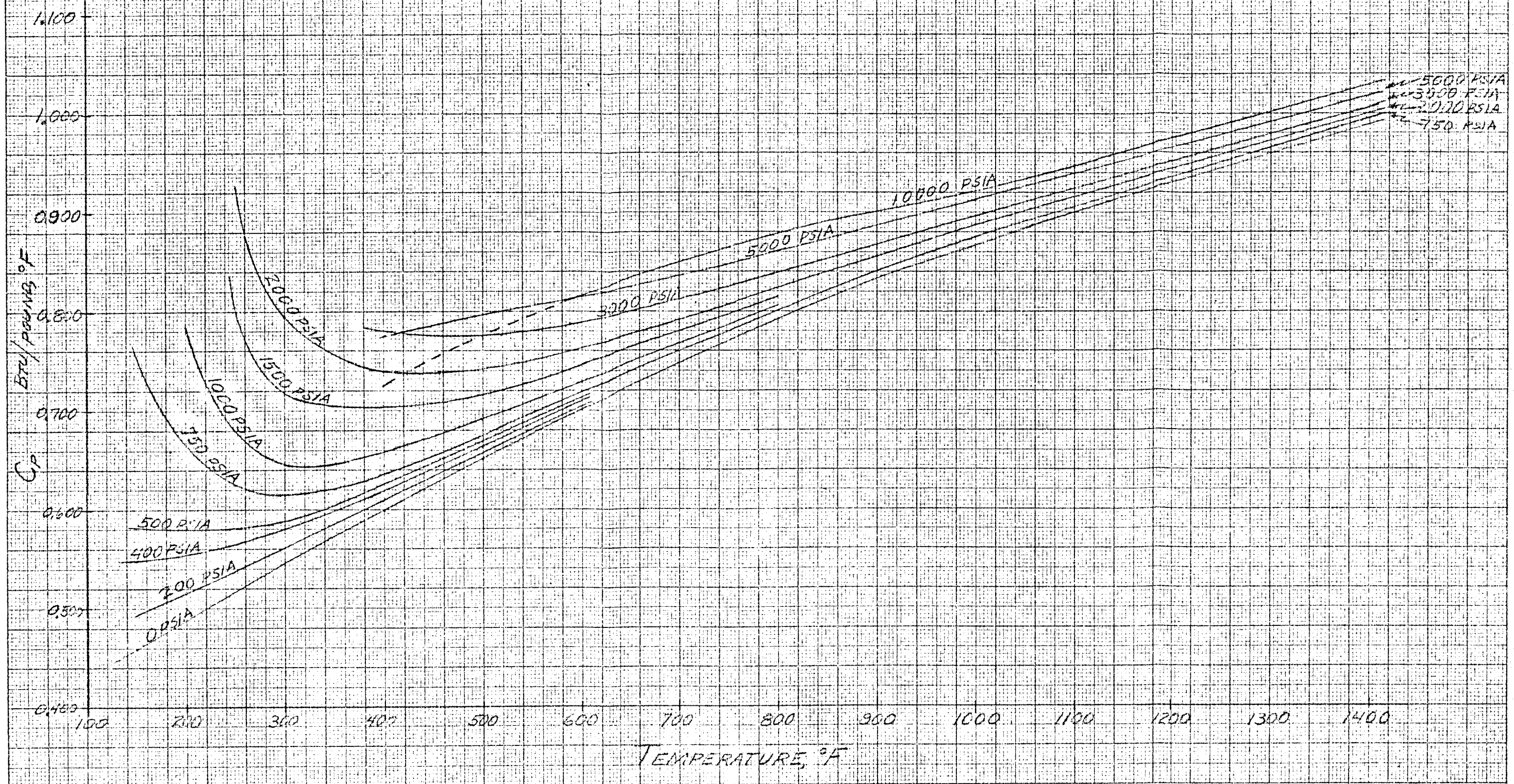


LEGEND:
 CALCULATED DATA POINTS ARE INDICATED BY:
 ○ BENEDICT ET AL. CONSTANTS (15)
 □ BARKELEW ET AL. CONSTANTS (15)
 ● DATA POINTS WITH BENEDICT AND BARKELEW
 CONSTANTS COINCIDE
 X IDEAL GAS VALUES (8)

K. H. FISHER CO.

FIGURE 7

THE EFFECT OF TEMPERATURE ON THE ISOBARIC
HEAT CAPACITY OF ETHANE AT VARIOUS
PRESSURES

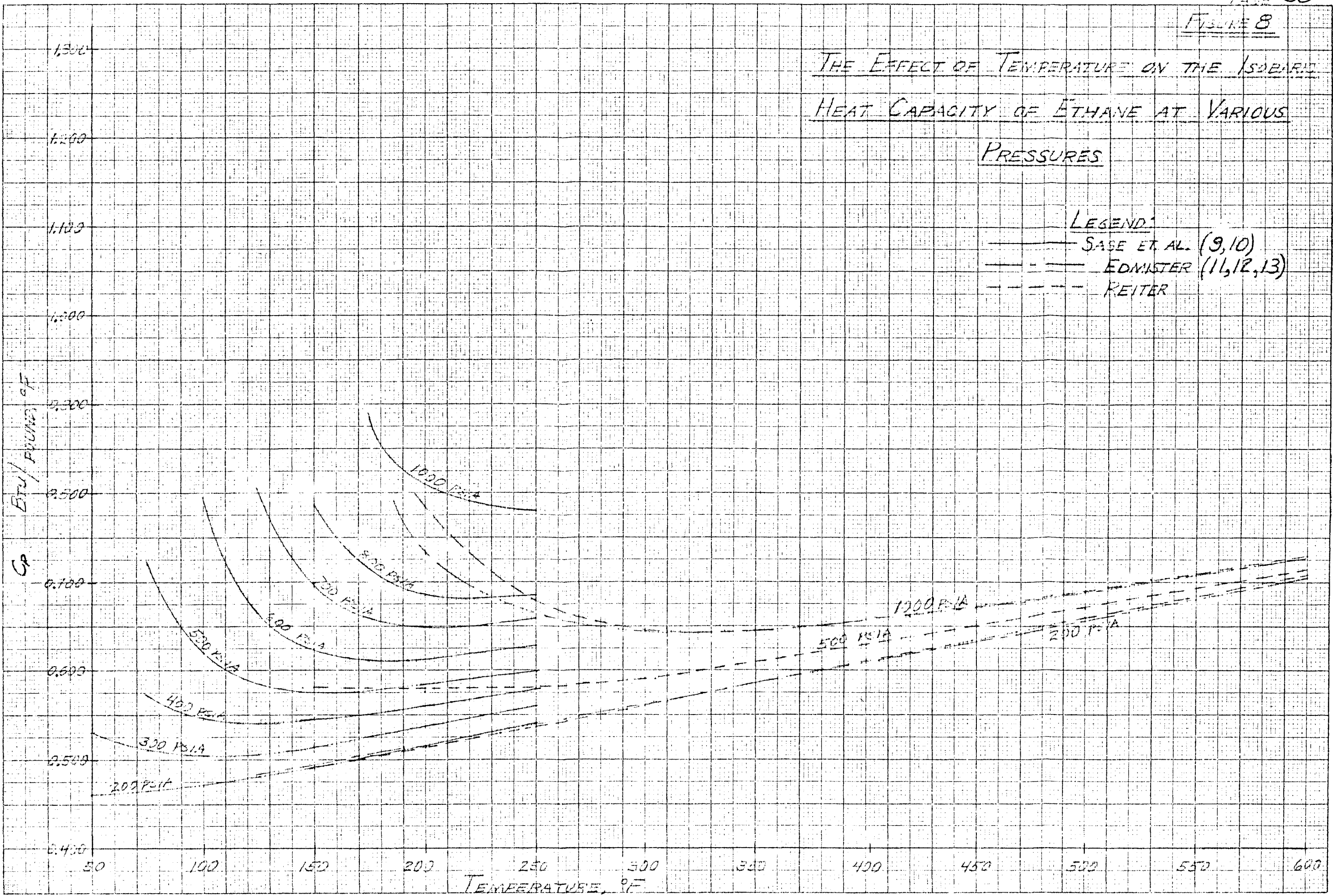


KEUFFEL & ESSER CO., N. Y. NO. 3-1141
Millimeters, 3 mm. line weight, 6 mm. blue heavy.
MADE IN U. S. A.

FIGURE 8

THE EFFECT OF TEMPERATURE ON THE ISOBARIC
HEAT CAPACITY OF ETHANE AT VARIOUS
PRESSURES

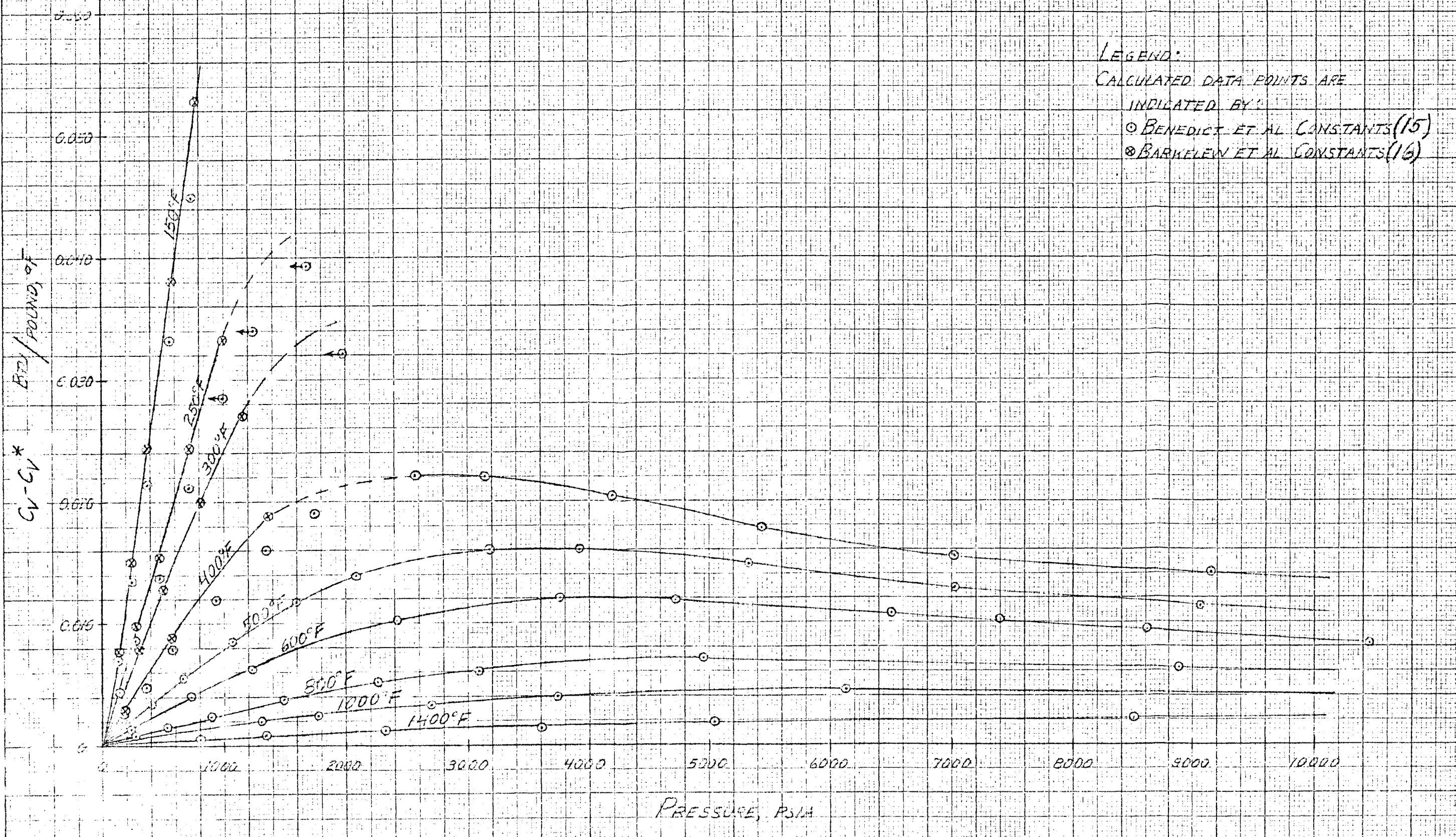
LEGEND:
—— SASE ET AL. (9,10)
- - - EDWINSTER (11,12,13)
- - - REITER



10 X 10 TO THE 1/4 INCH
359-11L
KAPTEL & ASSOCIATES

FIGURE 9

THE EFFECT OF PRESSURE ON THE CONSTANT VOLUME HEAT CAPACITY OF ETHANE RELATIVE TO IDEAL GAS STATE AT VARIOUS TEMPERATURES

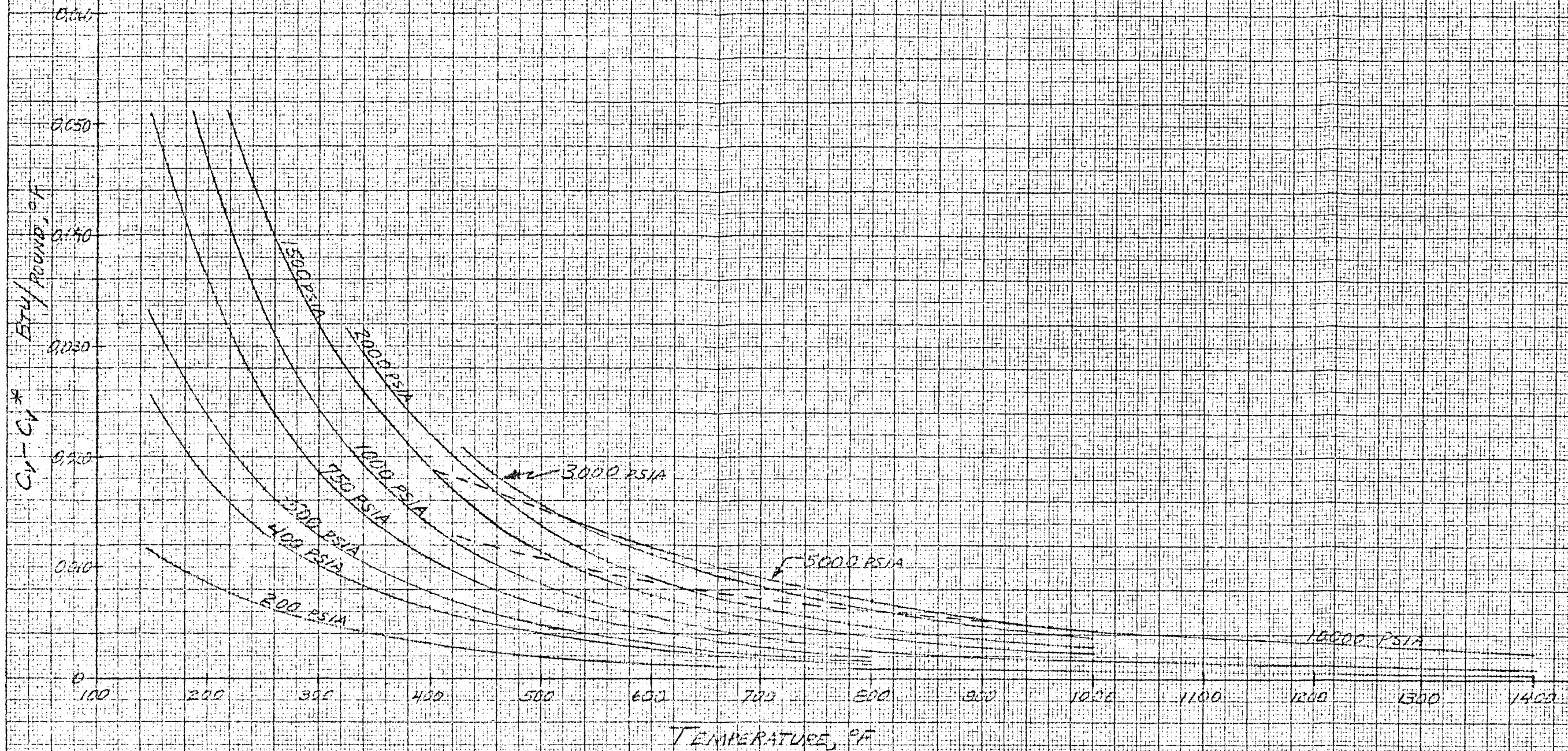


LEGEND:
 CALCULATED DATA POINTS ARE INDICATED BY:
 ○ BENEDICT ET AL. CONSTANTS (15)
 ⊗ BARROW ET AL. CONSTANTS (16)

SHEET 10 X 10 IN THE INCH 359-111
 1957
 CHEMICAL ENGINEERING

FIGURE 10

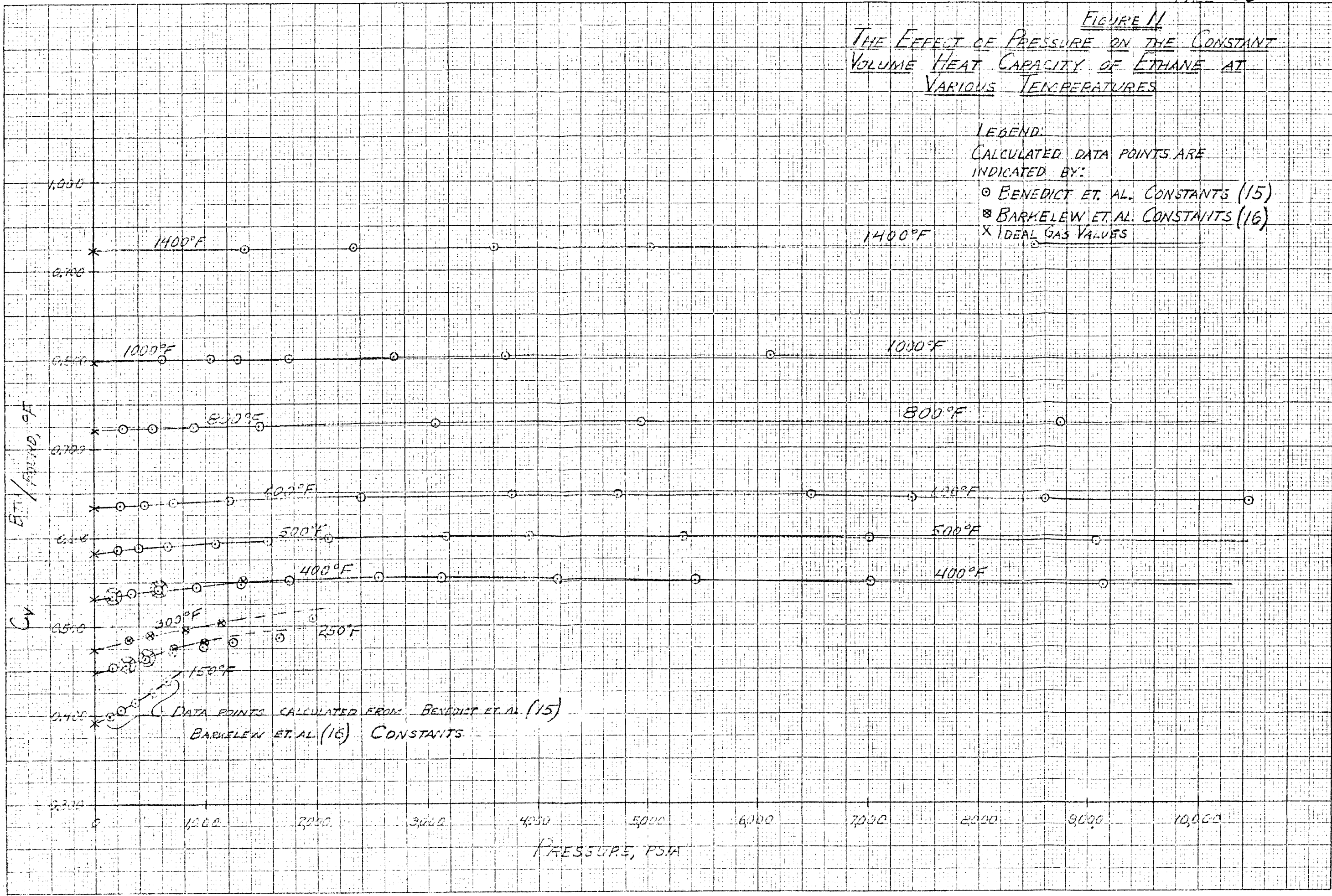
THE EFFECT OF TEMPERATURE ON THE CONSTANT VOLUME HEAT CAPACITY OF ETHANE RELATIVE TO THE IDEAL GAS STATE AT VARIOUS PRESSURES



KEUPELL A. CHEMICAL CO., N. Y. NO. 35-1141
Manufactured by the American Graphical and Paper Co.,
MADE IN U. S. A.

FIGURE II
THE EFFECT OF PRESSURE ON THE CONSTANT
VOLUME HEAT CAPACITY OF ETHANE AT
VARIOUS TEMPERATURES

LEGEND:
CALCULATED DATA POINTS ARE
INDICATED BY:
○ BENEDICT ET. AL. CONSTANTS (15)
⊗ BARKELEW ET. AL. CONSTANTS (16)
x IDEAL GAS VALUES



DATA POINTS CALCULATED FROM BENEDICT ET. AL. (15)
BARKELEW ET. AL. (16) CONSTANTS

10 X 10 TO THE 1/2 INCH 359-11L
MILWAUKEE A. SINGER CO.

FIGURE 12
THE EFFECT OF PRESSURE ON THE RATIO OF HEAT CAPACITIES OF ETHANE AT VARIOUS TEMPERATURES

LEGEND:
CALCULATED DATA POINTS ARE INDICATED BY:
○ BENEDICT ET AL. CONSTANTS (15)
⊗ BARRELETT ET AL. CONSTANTS (16)
* IDEAL GAS VALUES (8)

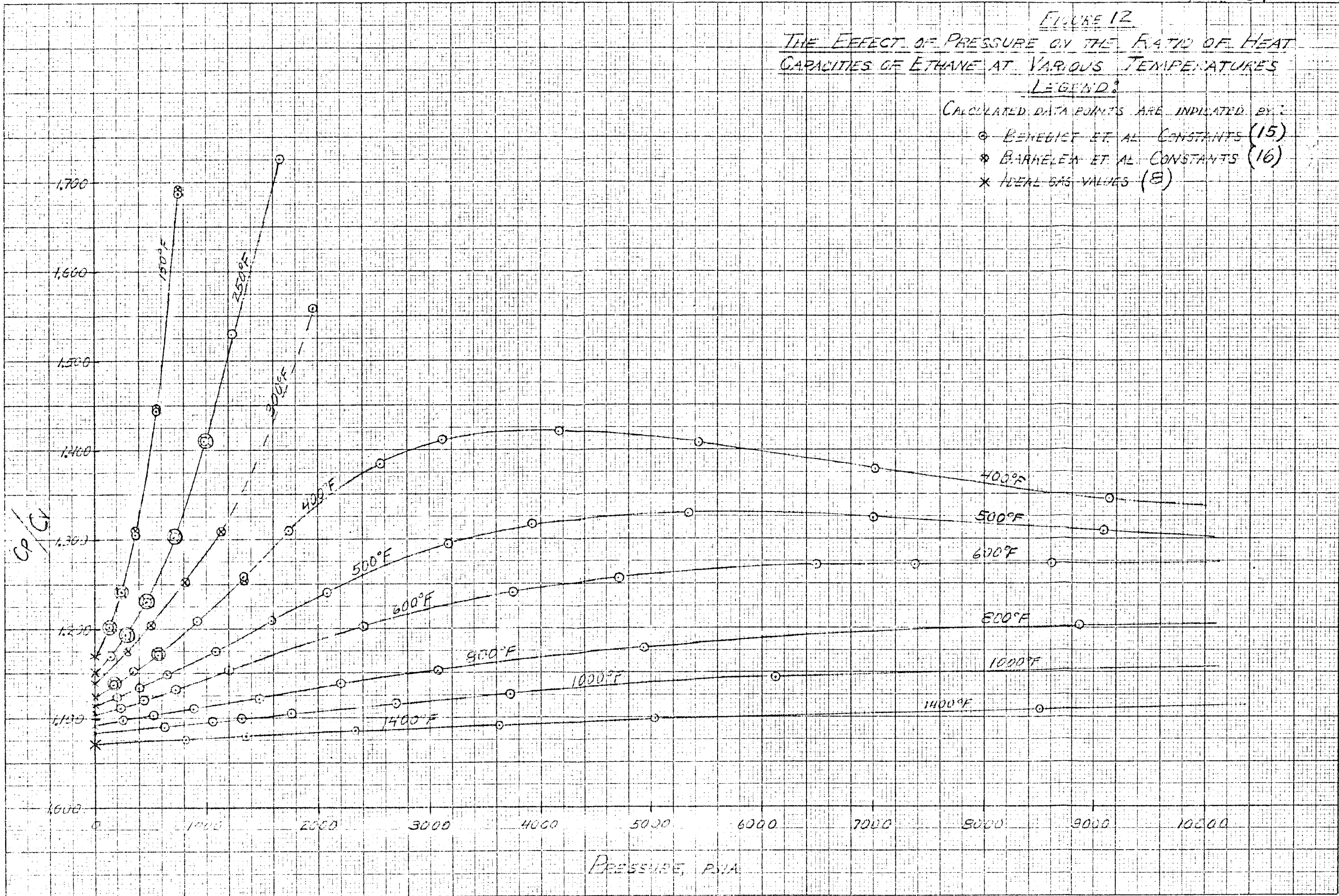
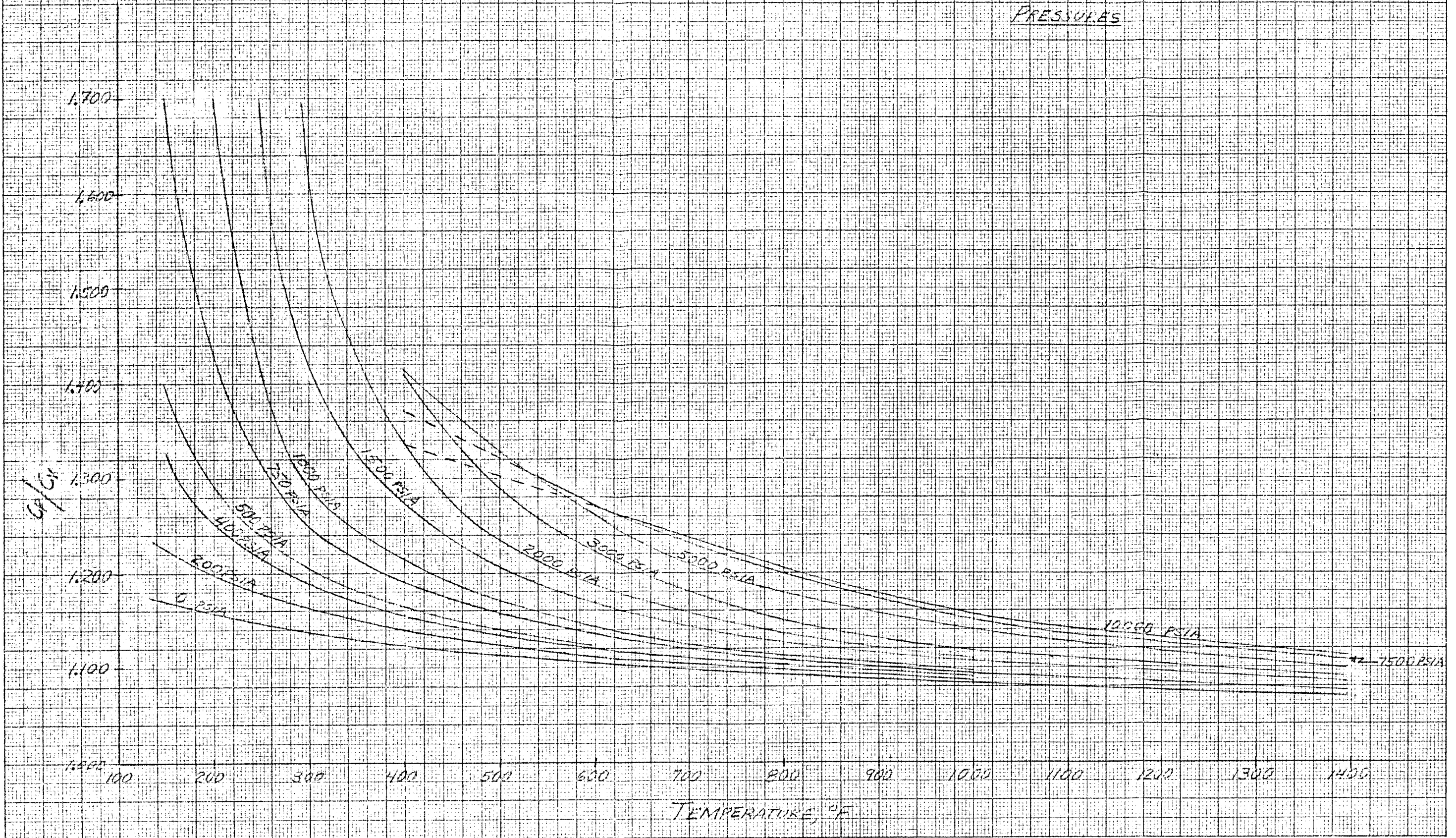


FIGURE 13

THE EFFECT OF TEMPERATURE ON THE RATIO
OF HEAT CAPACITIES OF ETHANE AT VARIOUS
PRESSURES



ESBER CO., N. Y. NO. 175-114
Millimeter, 9 mm. line is correct, cm. line heavy.
MADE IN U.S.A.

THE EFFECT OF TEMPERATURE ON THE
RATIO OF HEAT CAPACITIES OF ETHANE
AT VARIOUS PRESSURES

(USING GENERALIZED
CORRELATION OF EDMISTER)

LEGEND:
—— EDMISTER (11,12,13)
---- REITER

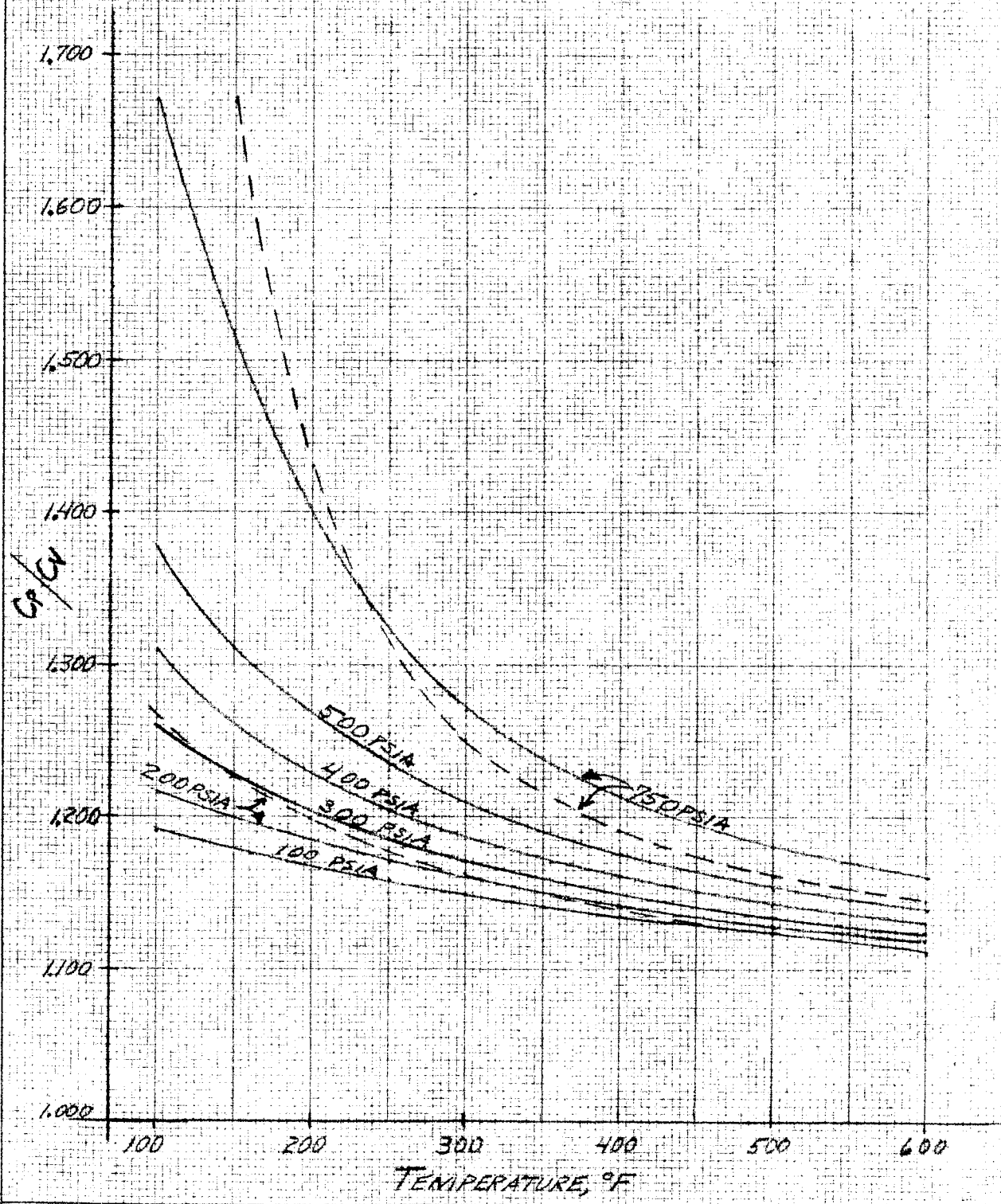


TABLE 1

Sample Calculations

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

$$T = ^\circ F + 459.63$$

$$A_0 = 15670.7$$

$$T = 500 + 459.63 = 959.63 \text{ } ^\circ R$$

$$B_0 = 1.00554$$

$$R = 10.7335$$

$$C_0 = 2.19427 \times 10^9$$

$$V = \text{cubic feet/\#-mole}$$

$$a = 20850.2$$

$$P = \text{psia}$$

$$b = 2.85393$$

$$e = 2.71828$$

$$c = 6.41314 \times 10^9$$

$$1 \text{ Btu} = 778.16 \text{ ft-}\#$$

$$\gamma = 3.02790$$

$$\text{Molecular Weight} = 30.047$$

$$\alpha = 1.00044$$

V	RT/V	$(B_0RT - A_0 - C_0/T^2) 1/V^2$	$(bRT - a) 1/V^3$
1.35	7629.769	-4222.890	3473.383
1.50	6866.792	-3420.541	2532.096
1.70	6058.935	-2663.052	1739.432
2.00	5150.094	-1924.055	1068.228
2.50	4120.075	-1231.395	546.9330
3.00	3433.396	- 855.1355	316.5121
4.50	2288.931	- 380.0602	93.7814
6.00	1716.698	- 213.7838	32.1332
9.00	1144.466	- 95.0150	11.7227
15.00	686.6792	- 34.2054	2.47446
25.00	412.0076	- 12.3140	0.546933
50.00	206.0038	- 3.07849	0.068367

TABLE 1 (Continued)

Sample Calculations

V	$a\alpha/V^6$	$c(1/\delta V^2) e^{-\delta/V^2} / V^3 T^2$	P
1.35	3445.868	1430.329	11756.46
1.50	1831.275	1260.155	9069.78
1.70	864.1876	1018.050	7017.55
2.00	325.9278	717.4450	5337.31
2.50	85.44004	407.5800	3928.63
3.00	28.61370	246.2251	3169.61
4.50	2.5120393	75.64953	2080.81
6.00	0.4470887	32.13320	1575.06
9.00	0.0392506	9.546396	1070.76
15.00	0.0018313	2.016339	656.97
25.00	0.0000854	0.445695	400.69
50.00	0.0000013	0.055715	203.05

From Equation

$$C_p - C_p^* = T \frac{\phi^2}{\Theta} + \Psi - R \dots \text{in } \# \text{ft}^3 / \text{in}^2, \# \text{mole}, ^\circ \text{R}$$

$$\phi = R + B_0 R / V + 2C_0 / VT^3 + bR / V^2 - 2c(1 + \delta / V^2) e^{-\delta / V^2} / V^2 T^3$$

$$\Theta = RT + 2(B_0 RT - A_0 - C_0 / T^2) / V + 3(bRT - a) / V^2 + 6a / V^5 + e^{-\delta / V^2} c(3 + 3\delta / V^2 - 2\delta^2 / V^4) / V^2 T^2$$

$$\Psi = 6C_0 / T^3 V + 6c(e^{-\delta / V^2} - 1) T^3 + 3ce^{-\delta / V^2} / V^2 T^3$$

$$\Psi = C_v - C_v^* \dots \text{in } \# \text{ft}^3 / \text{in}^2, \# \text{mole}, ^\circ \text{R}$$

$$T \frac{\phi^2}{\Theta} = C_p - C_v \dots \text{in } \# \text{ft}^3 / \text{in}^2, \# \text{mole}, ^\circ \text{R}$$

TABLE 1 (Continued)

Sample Calculations

V	$B_0 R/V$	$2C_0/VT^3$	bR/V^2
1.35	7.994789	3.678535	16.80805
1.50	7.195310	3.310682	13.61452
1.70	6.348804	2.921190	10.59954
2.00	5.396483	2.483011	7.658167
2.50	4.317186	1.986409	4.901227
3.00	3.597655	1.655341	3.403630
4.50	2.398437	1.103561	1.512724
6.00	1.798828	0.8276704	0.8509074
9.00	1.199219	0.5517803	0.3781810
15.00	0.719531	0.3310682	0.1361452
25.00	0.431719	0.1986409	0.0490123
50.00	0.215859	0.0993205	0.0122537

V	$2c(1 + \delta/V^2)e^{-\gamma V^2}/V^2 T^3$	ϕ
1.35	4.024352	35.19052
1.50	3.939502	30.91451
1.70	3.606984	26.99605
2.00	2.990507	23.28065
2.50	2.123631	19.81469
3.00	1.539501	17.85063
4.50	0.7094878	15.03873
6.00	0.4018200	13.76409
9.00	0.1790639	12.68362
15.00	0.0643548	11.85589
25.00	0.0232225	11.38965
50.00	0.0058059	11.05513

TABLE 1 (Continued)

Sample Calculations

V	RT	$2(B_0RT - A_0 - C_0/T^2)/V$	$3(bRT - a)/V^2$
1.35	10300.19	-11401.81	14067.20
1.50	10300.19	-10261.62	11394.44
1.70	10300.19	- 9054.375	8871.102
2.00	10300.19	- 7696.219	6409.371
2.50	10300.19	- 6156.975	4101.997
3.00	10300.19	- 5130.812	2848.609
4.50	10300.19	- 3420.542	1266.049
6.00	10300.19	- 2565.406	712.1521
9.00	10300.19	- 1710.271	316.5122
15.00	10300.19	- 1026.162	113.9444
25.00	10300.19	- 615.6975	41.01997
50.00	10300.19	- 307.8487	10.25500

V	$6ad/V^5$	$e^{-b/V^2} c(3/38/V^2 - 2b^2/V^4)/V^2T^2$	θ
1.35	27911.53	1787.509	42664.63
1.50	16481.48	2752.030	30666.51
1.70	8814.714	3336.535	22268.17
2.00	3911.134	3368.735	16293.21
2.50	1281.601	2734.642	12261.45
3.00	515.046	2090.919	10623.95
4.50	67.82506	1008.026	9221.55
6.00	16.09520	575.8817	9038.91
9.00	2.11954	257.5213	9166.07
15.00	0.164814	92.83487	9480.97
25.00	0.012816	33.42662	9758.95
50.00	0.000401	8.354873	10010.95

TABLE 1 (Continued)

Sample Calculations

v	$6C_0/T^3v$	$6c(e^{-v/v^2}-1)T^3$	$3ce^{-v/v^2}/v^2T^3$
1.35	11.03561	-11.64990	2.268179
1.50	9.932045	-10.63643	2.519150
1.70	8.763572	- 9.336604	2.642200
2.00	7.449035	- 7.634761	2.553117
2.50	5.959228	- 5.521654	2.145857
3.00	4.966023	- 4.108264	1.727934
4.50	3.310682	- 1.997195	0.9258004
6.00	2.483011	- 1.160037	0.5559685
9.00	1.655341	- 0.527638	0.2589173
15.00	0.9932045	- 0.192223	0.0954671
25.00	0.5959228	- 0.069500	0.0346654
50.00	0.2979614	- 0.017406	0.0087084

TABLE 1 (Continued)

V	Ψ	$T \frac{d^2}{S}$	Sample Calculations		
			$C_p - C_p^*$ #ft ³ /in ² , #mole, °R	$c_p - c_p^*$ Btu/#, °F	$c_v - c_v^*$ Btu/#, °F
1.35	1.653890	27.85398	18.77437	0.115627	0.010186
1.50	1.814762	29.90642	20.98768	0.129258	0.011177
1.70	2.069167	31.40652	22.74219	0.140063	0.012740
2.00	2.367390	31.99540	23.62929	0.145527	0.014580
2.50	2.583430	30.72815	22.57808	0.139053	0.015911
3.00	2.585693	28.78223	20.63442	0.127082	0.015925
4.50	2.239288	23.53545	15.04124	0.092635	0.013790
6.00	1.878943	20.11318	11.25862	0.069339	0.011572
9.00	1.386621	16.84251	7.495627	0.046164	0.008540
15.00	0.8964482	14.22720	4.390148	0.027038	0.005521
25.00	0.5610880	12.75620	2.583790	0.015913	0.003456
50.00	0.2892639	11.71536	1.271128	0.007829	0.001782

TABLE 1 (Continued)

Sample Calculations

$$c_p^* - c_v^* = 0.0661 \dots \text{Btu/\#, } ^\circ\text{R}$$

$$c_p^* @ 500^\circ\text{F} = 0.6510$$

$$c_v^* = 0.6510 - 0.0661 = 0.5849$$

V	c_v	c_p	c_p/c_v
1.35	0.5951	0.7666	1.2882
1.50	0.5961	0.7803	1.3090
1.70	0.5976	0.7911	1.3238
2.00	0.5995	0.7965	1.3286
2.50	0.6008	0.7910	1.3166
3.00	0.6008	0.7781	1.2951
4.50	0.5987	0.7436	1.2420
6.00	0.5965	0.7211	1.2089
9.00	0.5934	0.6972	1.1749
15.00	0.5904	0.6780	1.1484
25.00	0.5884	0.6669	1.1334
50.00	0.5867	0.6588	1.1229

TABLE 1 (Continued)

Sample Calculations

V	$c_p - c_v$ (from $T \frac{\phi^2}{e}$)
1.35	0.171546
1.50	0.184186
1.70	0.193425
2.00	0.197052
2.50	0.189247
3.00	0.177263
4.50	0.144949
6.00	0.124684
9.00	0.103729
15.00	0.087627
25.00	0.078562
50.00	0.072152

TABLE 2Constants for Use in Benedict-Webb-Rubin Equation of State

<u>Constants</u>	<u>Benedict et.al. Reference</u>	<u>Barkelaw et.al. Reference</u>
A ₀	15,670.7	14,646.3
B ₀	1.00554	---
B ₀ R	---	10.5601
C ₀	2.19427 x 10 ⁹	2.46787 x 10 ⁹
a	20850.2	18,532.1
b	2.85393	---
bR	---	27.3328
c	6.41314 x 10 ⁹	6.40322 x 10 ⁹
α	1.00044	1.07021
γ	3.02790	3.26000
T in °R	°F / 459.63	°F / 459.69
R	10.7335	10.7315
Molecular Weight	30.047	30.068

Units

P	#/sq. in. absolute
T	°R
V	cubic feet/#-mole

TABLE 3

Calculated Data

V ft ³ /#-mole	P psia	Using Benedict et.al. Constants (15)					
		$c_p - c_v$ Btu/#, °F	$c_v - c_v^*$ Btu/#, °F	$c_p - c_p^*$ Btu/#, °F	c_p Btu/#, °F	c_v Btu/#, °F	c_p/c_v
<u>T = 150°F</u>							
6.00	744.042	0.302756	0.045135	0.281780	0.7399	0.4371	1.6927
9.00	556.522	0.188783	0.033309	0.155987	0.6141	0.4253	1.4439
15.00	373.954	0.126192	0.021534	0.081621	0.5397	0.4135	1.3052
25.00	238.712	0.098139	0.013478	0.045512	0.5036	0.4055	1.2419
50.00	124.992	0.080791	0.006948	0.021639	0.4797	0.3989	1.2026
	0	0.0661	0	0	0.4581	0.3920	1.1686
<u>T = 250°F</u>							
3.00	1676.34	0.354380	0.039381	0.327656	0.8429	0.4886	1.7251
4.50	1232.40	0.256171	0.034105	0.224171	0.7394	0.4833	1.5299
6.00	989.200	0.196430	0.028617	0.158942	0.6741	0.4778	1.4108
9.00	712.322	0.142234	0.021119	0.097248	0.6124	0.4703	1.3021
15.00	456.760	0.106623	0.013650	0.054171	0.5694	0.4629	1.2301
25.00	285.754	0.088599	0.008525	0.031019	0.5462	0.4577	1.1934
50.00	147.498	0.076702	0.004405	0.015002	0.5302	0.4536	1.1689
	0	0.0661	0	0	0.5152	0.4492	1.1469

TABLE 3 (Continued)

Calculated Data

T = 300°F

3.00	1976.25	0.285241	0.032105	0.251241	0.7946	0.5094	1.5599
	0	0.0661	0	0	0.5434	0.4773	1.1385

T = 400°F

1.35	9154.40	0.188464	0.014170	0.136529	0.7351	0.5467	1.3446
1.50	7016.41	0.207785	0.015548	0.157228	0.7558	0.5480	1.3792
1.70	5436.86	0.224103	0.017728	0.175727	0.7743	0.5502	1.4073
2.00	4178.21	0.233388	0.020283	0.187567	0.7861	0.5528	1.4220
2.50	3137.04	0.228233	0.022135	0.184262	0.7829	0.5546	1.4116
3.00	2573.89	0.213717	0.022154	0.169766	0.7684	0.5547	1.3853
4.50	1745.03	0.169677	0.019024	0.122878	0.7215	0.5515	1.3083
6.00	1343.62	0.141716	0.016098	0.091709	0.6903	0.5486	1.2583
9.00	929.079	0.113575	0.011880	0.059350	0.6580	0.5444	1.2087
15.00	577.615	0.092721	0.007681	0.034297	0.6329	0.5402	1.1716
25.00	355.001	0.081337	0.004807	0.020039	0.6186	0.5373	1.1513
50.00	180.905	0.073436	0.002478	0.009809	0.6084	0.5330	1.1372
	0	0.0661	0	0	0.5986	0.5325	1.1241

V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p/c_v
ft ³ /#-mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	

TABLE 3 (Continued)

Calculated Data

V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p / c_v
ft ³ /#mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	
<u>T = 500°F</u>							
1.35	11756.5	0.171546	0.010186	0.115627	0.7666	0.5951	1.2882
1.50	9069.78	0.184186	0.011177	0.129258	0.7803	0.5961	1.3090
1.70	7017.55	0.193425	0.012740	0.140063	0.7911	0.5976	1.3238
2.00	5337.31	0.197052	0.014580	0.145527	0.7965	0.5995	1.3286
2.50	3928.63	0.189247	0.015911	0.139053	0.7910	0.6008	1.3166
3.00	3169.61	0.177263	0.015925	0.127082	0.7781	0.6008	1.2951
4.50	2080.81	0.144949	0.013790	0.092635	0.7436	0.5987	1.2420
6.00	1575.06	0.124684	0.011572	0.070150	0.7211	0.5965	1.2089
9.00	1070.76	0.103729	0.008540	0.046164	0.6972	0.5934	1.1749
15.00	656.966	0.087627	0.005521	0.027038	0.6780	0.5904	1.1484
25.00	400.686	0.078562	0.003456	0.015913	0.6669	0.5884	1.1334
50.00	203.049	0.072152	0.001782	0.007829	0.6588	0.5867	1.1229
	0	0.0661	0	0	0.6510	0.5849	1.1130

TABLE 3 (Continued)

Calculated Data

T = 600°F

1.50	10447.2	0.163724	0.008302	0.110920	0.8109	0.6422	1.2627
1.70	8611.09	0.173982	0.009465	0.117343	0.8173	0.6434	1.2703
1.85	7395.43	0.174768	0.010224	0.118887	0.8189	0.6441	1.2714
2.00	6505.14	0.173920	0.010830	0.118918	0.8189	0.6447	1.2702
2.50	4721.97	0.165686	0.011818	0.111399	0.8114	0.6457	1.2566
3.00	3764.10	0.155275	0.011828	0.100998	0.8010	0.6457	1.2405
4.50	2413.81	0.129575	0.010244	0.073714	0.7737	0.6441	1.2012
9.00	1211.12	0.097170	0.006343	0.037409	0.7374	0.6402	1.1518
15.00	735.749	0.084114	0.004100	0.022110	0.7221	0.6380	1.1318
25.00	446.149	0.076620	0.002567	0.013082	0.7131	0.6365	1.1203
50.00	225.134	0.071241	0.001323	0.006460	0.7065	0.6352	1.1122
	0	0.0661	0	0	0.7000	0.6339	1.1043
V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p / c_v
ft ³ /#-mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	

TABLE 3 (Continued)

Calculated Data

T = 800°F

1.70	11,821.4	0.150598	0.005635	0.090128	0.8783	0.7277	1.2069
2.00	8,854.78	0.147371	0.006447	0.087713	0.8759	0.7285	1.2023
3.00	4,950.86	0.130156	0.007041	0.071092	0.8593	0.7291	1.1786
4.50	3,074.76	0.111612	0.006098	0.051605	0.8398	0.7282	1.1533
6.00	2,258.51	0.101041	0.005117	0.040054	0.8283	0.7272	1.1390
9.00	1,489.46	0.089248	0.003776	0.026714	0.8149	0.7259	1.1226
15.00	892.286	0.079645	0.002441	0.015981	0.8042	0.7245	1.1100
25.00	536.670	0.074104	0.001528	0.009527	0.7977	0.7236	1.1024
50.00	269.196	0.070073	0.000788	0.004756	0.7930	0.7229	1.0970
	0	0.0661	0	0	0.7882	0.7221	1.0915
V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p/c_v
ft ³ /#-mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	

TABLE 3 (Continued)

Calculated Data

T = 1000°F

2.00	11211.3	0.132305	0.004143	0.070344	0.9359	0.8036	1.1646
3.00	6135.93	0.116267	0.004525	0.054687	0.9203	0.8040	1.1447
4.50	3731.86	0.101507	0.003919	0.039327	0.9049	0.8034	1.1264
6.00	2709.66	0.093120	0.003288	0.030304	0.8959	0.8028	1.1160
9.00	1765.98	0.084099	0.002427	0.020421	0.8860	0.8019	1.1049
12.00	1319.39	0.079680	0.001908	0.015484	0.8811	0.8014	1.0995
15.00	1048.31	0.076935	0.001569	0.012399	0.8780	0.8011	1.0960
25.00	626.883	0.071797	0.000982	0.006675	0.8723	0.8005	1.0897
	0	0.0661	0	0	0.8656	0.7995	1.0827

T = 1400°F

2.00	14261.5	0.133982	0.002003	0.069880	1.0613	0.9273	1.1445
3.00	8503.99	0.101420	0.002188	0.037503	1.0289	0.9275	1.1093
4.50	5040.77	0.090571	0.001895	0.026361	1.0178	0.9272	1.0977
6.00	3607.97	0.084827	0.001590	0.020312	1.0117	0.9269	1.0915
9.00	2322.83	0.078821	0.001173	0.013889	1.0053	0.9265	1.0851
15.00	1358.73	0.073442	0.000759	0.008096	0.9995	0.9261	1.0793
25.00	806.896	0.070755	0.000475	0.005125	0.9965	0.9258	1.0764
	0	0.0661	0	0	0.9914	0.9253	1.0714

V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p/c_v
ft ³ /#-mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	

TABLE 4

Calculated Data		Using Barkelew et.al. Constants (16)					
V	P	$c_p - c_v$	$c_v - c_v^*$	$c_p - c_p^*$	c_p	c_v	c_p/c_v
ft ³ /#-mole	psia	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	Btu/#, °F	
<u>T = 150°F</u>							
6.00	749.287	0.307196	0.525546	0.293634	0.7517	0.4445	1.6912
9.00	564.779	0.191906	0.038239	0.164099	0.6222	0.4302	1.4462
15.00	374.655	0.128084	0.024488	0.086530	0.5446	0.4165	1.3078
25.00	245.040	0.099171	0.015249	0.048374	0.5065	0.4072	1.2436
50.00	125.042	0.081240	0.007833	0.023027	0.4811	0.3998	1.2034
<u>T = 250°F</u>							
6.00	997.632	0.196287	0.033316	0.163557	0.6788	0.4825	1.4070
9.00	716.090	0.142713	0.024246	0.100912	0.6161	0.4734	1.3014
15.00	461.844	0.109966	0.015527	0.059446	0.5746	0.4647	1.2367
25.00	286.228	0.088900	0.009669	0.032523	0.5477	0.4589	1.1935
<u>T = 300°F</u>							
6.00	1143.94	0.155798	0.027161	0.116913	0.6604	0.5045	1.3090
9.00	801.152	0.125342	0.019767	0.079062	0.6225	0.4971	1.2523
15.00	503.088	0.099022	0.012658	0.045634	0.5891	0.4900	1.2022
25.00	311.017	0.084811	0.007883	0.026648	0.5701	0.4852	1.1750
<u>T = 400°F</u>							
6.00	1353.58	0.140437	0.018743	0.093134	0.6917	0.5512	1.2549
15.00	579.412	0.092461	0.008735	0.035149	0.6337	0.5412	1.1711
50.00	181.062	0.073343	0.002794	0.010090	0.6087	0.5353	1.1371

TABLE 5
Calculated Values of $c_p - c_p^*$, c_p , and c_p/c_v for Ethane
from Edmister Generalized Correlations (11,12,13,14)

<u>$c_p - c_p^*$, Btu/#, °F</u>	Temperature, °F							
	145	200	255	310	420	530	750	915
100	0.0169	0.0126	0.0097	0.0074	0.0046	0.0030	0.0017	0.0011
200	0.0359	0.0265	0.0200	0.0151	0.0090	0.0060	0.0033	0.0022
300	0.0593	0.0426	0.0316	0.0233	0.0136	0.0095	0.0054	0.0032
400	0.0880	0.0602	0.0444	0.0320	0.0183	0.0127	0.0072	0.0043
500	0.126	0.0814	0.0582	0.0415	0.0235	0.0171	0.0091	0.0054
750	0.316	0.148	0.0980	0.0668	0.0370	0.0261	0.0141	0.0081
1000	---	0.246	0.144	0.0957	0.0515	0.0350	0.0188	0.0107
1500	---	0.472	0.249	0.161	0.0830	0.0532	0.0279	0.0161
2000	---	---	0.306	0.221	0.115	0.0705	0.0359	0.0211
2500	---	---	---	0.239	0.142	0.0868	0.0427	0.0259

TABLE 5 (Continued)

c_p , Btu/#, °F

Pressure psia	Temperature, °F							
	145	200	255	310	420	540	700	915
0	0.4554	0.4865	0.5180	0.5490	0.6091	0.6657	0.7700	0.8338
100	0.4723	0.4991	0.5277	0.5564	0.6137	0.6687	0.7717	0.8349
200	0.4913	0.5130	0.5380	0.5641	0.6181	0.6717	0.7733	0.8360
300	0.5147	0.5291	0.5496	0.5723	0.6227	0.6752	0.7754	0.8370
400	0.5434	0.5467	0.5624	0.5810	0.6274	0.6784	0.7772	0.8381
500	0.5814	0.5679	0.5762	0.5905	0.6326	0.6828	0.7791	0.8392
750	0.7714	0.6345	0.6160	0.6158	0.6461	0.6918	0.7841	0.8419
1000	---	0.7325	0.6620	0.6447	0.6606	0.7007	0.7838	0.8445
1500	---	0.9585	0.7670	0.7100	0.6921	0.7189	0.7979	0.8499
2000	---	---	0.8240	0.7700	0.7241	0.7362	0.8059	0.8549
2500	---	---	---	0.7880	0.7511	0.7525	0.8127	0.8597

c_p/c_v (Values approximate since read from graph)

Pressure psia	Temperature, °F					
	100	250	300	400	500	600
100	1.190	1.158	1.148	1.135	1.125	1.105
200	1.215	1.170	1.160	1.140	1.127	1.118
300	1.258	1.185	1.175	1.145	1.135	1.125
400	1.308	1.204	1.182	1.163	1.142	1.130
500	1.377	1.240	1.200	1.175	1.152	1.138
750	1.670	1.365	1.270	1.215	1.175	1.158

TABLE 6

Values of c_p and $c_p - c_p^*$ of Ethane from Experimental Data (9.10)

I Sage, Webster, Lacey Ind. Eng. Chem. 29, No. 6,658 June 1937
(Graphical Data)

c_p , Btu/#, F (Values are approximate since read from graph)

Pressure, psia	Temperature, °F								
	50	75	100	125	150	175	200	225	250
200	0.460	0.465	0.472	0.481	0.492	0.505	0.515	0.528	0.542
300	0.528	0.510	0.503	0.505	0.515	0.525	0.535	0.545	0.560
400	---	0.572	0.545	0.540	0.545	0.550	0.560	0.567	0.578
500	---	0.720	0.620	0.585	0.575	0.577	0.585	0.590	0.592
600	---	---	0.795	0.666	0.623	0.610	0.613	0.620	0.628
700	---	---	---	0.800	0.697	0.658	0.648	0.650	0.660
800	---	---	---	---	0.785	0.715	0.685	0.682	0.685
1000	---	---	---	---	---	0.883	0.810	0.787	0.780
0	0.4038	0.4175	0.4312	0.4447	0.4581	0.4722	0.4865	0.5009	0.5152

TABLE 6 (Continued)

<u>$c_p - c_p^*$, Btu/#, °F</u>									
	<u>Pressure,</u>								
<u>psia</u>	<u>Temperature, °F</u>								
	<u>50</u>	<u>75</u>	<u>100</u>	<u>125</u>	<u>150</u>	<u>175</u>	<u>200</u>	<u>225</u>	<u>250</u>
200	0.056	0.047	0.041	0.036	0.034	0.033	0.028	0.027	0.027
300	0.124	0.092	0.072	0.060	0.057	0.053	0.048	0.044	0.045
400	---	0.154	0.114	0.095	0.087	0.078	0.073	0.066	0.063
500	---	0.302	0.189	0.140	0.117	0.105	0.098	0.089	0.077
600	---	---	0.364	0.221	0.165	0.138	0.126	0.119	0.113
700	---	---	---	0.355	0.239	0.186	0.161	0.149	0.145
800	---	---	---	---	0.327	0.243	0.198	0.181	0.170
1000	---	---	---	---	---	0.411	0.323	0.286	0.265

TABLE 6 (Continued)

II Sage, Budenholzer, Lacey, Inc. Eng. Chem. 31, 1288
(Tabulated Data) (1939)

c_p , Btu/#, °F

Pressure, psia	Temperature, °F					
	70	100	130	160	190	220
0	0.417	0.433	0.445	0.465	0.482	0.498
250	0.484	0.489	0.497	0.506	0.519	0.534
500	0.765	0.620	0.585	0.575	0.579	0.588
750	---	---	0.869	0.706	0.671	0.665
1000	---	---	---	0.993	0.817	0.795
1250	---	---	---	1.358	1.108	0.933
1500	---	---	---	1.178	1.118	1.070

$c_p - c_p^*$, Btu/#, °F

Pressure, psia	Temperature, °F					
	70	100	130	160	190	220
250	0.067	0.056	0.052	0.041	0.037	0.036
500	0.348	0.187	0.140	0.110	0.097	0.090
750	---	---	0.424	0.241	0.189	0.167
1000	---	---	---	0.528	0.335	0.297
1250	---	---	---	0.893	0.626	0.435
1500	---	---	---	0.713	0.636	0.572

TABLE 7

Values of Isobaric Heat Capacity of Ethane in the
Ideal Gas State for Various Temperatures

Rossini et.al. "Selected Values of Physical & Thermodynamic Properties of hydrocarbons and Related Compounds", (1953)
Carnegie Press (Continuation of work on American Petroleum Institute Research Project 44 at National Bureau of Standards, Washington, D. C.) (8)

Temperature, °F	c_p^* Btu/#, °F
-459.69	0.0000
0	0.3769
32	0.3940
60	0.4092
100	0.4312
150	0.4581
200	0.4865
250	0.5152
300	0.5434
350	0.5712
400	0.5986
500	0.6510
600	0.7000
700	0.7457
800	0.7882
900	0.8282
1000	0.8656
1100	0.9005
1200	0.9329
1300	0.9632
1400	0.9914
1500	1.018

NOTATION

The symbols used are:

C_p	Heat capacity at constant pressure, molal basis, Btu/#, $^{\circ}F$
c_p	Heat capacity at constant pressure in Btu/#, $^{\circ}F$
C_p^*	Heat capacity at constant pressure of the gas when exhibiting ideal gas behavior, molal basis, Btu/#-mole, $^{\circ}F$ or #, ft ³ /in ² , mole, $^{\circ}R$
c_p^*	Heat capacity at constant pressure of the gas when exhibiting ideal gas behavior, Btu/#, $^{\circ}F$
C_v	Heat capacity at constant volume, molal basis, Btu/#-mole, $^{\circ}F$ or #, ft ³ /in ² , mole, $^{\circ}R$
c_v	Heat capacity at constant volume, Btu/#, $^{\circ}F$
C_v^*	Heat capacity at constant volume of the gas when exhibiting ideal gas behavior, molal basis, Btu/#-mole, $^{\circ}F$
c_v^*	Heat capacity at constant volume of the gas when exhibiting ideal gas behavior, Btu/#, $^{\circ}F$
P	Absolute pressure, #/square inch, psia
R	Universal Gas Constant (See Table of Constants)
T	Absolute temperature, $^{\circ}R$, (See Table of Constants for conversion from $^{\circ}F$ to $^{\circ}R$)
V	Molal Volume, cubic feet/#-mole
$A_0, B_0, C_0,$ a, b, c, r, α	Constants for Benedict-Webb-Rubin equation of state (See Table of Constants)
ΔC_p	$= C_p - C_p^*$ (Used in calculations by Edmister methods)

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