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ISOBARIC HEAT CAPACITY OF NITRIC OXIDE
OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE

By

Leonard M. Salzarulo

Submitted in Partial Fulfilment
of the Requirements for the
Degree of MASTER OF SCIENCE
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at the
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SUMMARY

The effect of pressure and temperature on the isobaric heat capacity and the heat capacity at constant volume for nitric oxide relative to the ideal gas state is presented. Results are reported for pressures ranging from 0 to 6000 PSIA and for temperatures ranging from 300 to 1800°R.

Based on the Benedict-Webb-Rubin equation of state, an equation was derived for the deviation of isobaric heat capacity from the ideal gas state. Graphs and tables relating the isobaric heat capacity and the deviation of heat capacity at constant volume to pressure and temperature for nitric oxide are included.

The results show that the effect of pressure on the isobaric heat capacity must be considered in thermal calculations, since a considerable error is introduced if the pressure effect is neglected. If the effect of pressure is neglected, the greatest error would occur near the critical point.

Also included is a comparison of the calculated data with those of Opfell, Schlinger and Sage.

INTRODUCTION

The lack of basic knowledge at elevated temperatures and pressures has become more apparent in recent years with the development of new processes and with the advancement of engineering. As a result, the petroleum industry is making a continued effort to accumulate more accurate thermodynamic data over an increasing range of temperatures and pressures. The American Petroleum Institute Research Project 44 (1) lists accurate thermodynamic properties over the temperature and pressure range normally encountered, and at elevated temperatures. However, the effect of pressure on the heat capacity of gases and vapors is, in general, neglected. The absence of these data is due primarily to the difficulty encountered in making calorimetric measurements at high pressure.

There are two methods available which may be used to gather the desired information. The first method involves the use of a generalized correlation, of which the correlations presented by: Edminster (2), Watson and Smith (3), and Hougen and Watson (4) are excellent examples. The second method requires the use of an equation of state which is exemplified by the equations of van der Waals, Berthelot (5), Dieterici (5), Onnes (5), Wohl (6), Keyes (7), Beattie and Bridgeman (8), and Benedict, Webb and Rubin (9).

If generalized correlations are used to determine the effect of pressure and temperature on heat capacity, a full knowledge of the limitations of the correlation must be had. On the other hand, in order to apply one of the equations of state for this purpose, it is necessary to obtain the empirical constants for the specific fluid being considered.

Of the eight equations of state mentioned above, and the several hundred other equations available (most of the equations are applicable to one fluid over a limited range of temperatures and pressures), the Beattie-Bridgeman and the Benedict, Webb and Rubin equations are the two most useful for the interpolation and extrapolation of experimental data when a high degree of precision is desired.

The Beattie-Bridgeman equation is one of the most widely used equations of state. It employs five empirical constants and has been found to agree within a fraction of one per cent with experimental data for a number of gases over a wide range of conditions. An extensive tabulation of the constants for the Beattie-Bridgeman equation and a list of the range of conditions for which they apply, is given in Dodge (10). The equation was not designed to reproduce properties of gases in the critical range or below the critical volume. Ellenwood, Kulik, and Gay (11) used the Beattie-Bridgeman equation of state as a basis in computing the specific heats of air, CO, CO₂, H₂, N₂, O₂, CH₄ and C₂H₆ for the temperature range of 460°R to 4500°R and a pressure range of 0 to 10,000 PSIA.

Developed specifically for the lighter hydrocarbons (from the experimental data for methane, ethane, propane and n-butane) the Benedict-Webb-Rubin equation contains eight empirical constants. The equation is similar to the van der Waals equation, in that it assumes the continuity of the liquid and gaseous states. The same equation may be used to reproduce P-V-T data accurately for both the liquid and gaseous states of a fluid, up to approximately 1.8 times the critical density. According to Hougen and Watson the Benedict-Webb-Rubin equation holds within 0.34 per cent, even at gas densities which are double the critical density for methane, ethane, propane and n-butane.

Employing the Benedict-Webb-Rubin equation of state isobaric heat capacities relative to the ideal gas state have been computed over a wide range of pressures and temperatures: for methane by Sledjeski (12, 13), for propane by Seifarth (14, 15), for n-butane by Glueck (16), and for ethylene by Sibilia (17). Glueck and Sibilia also report the variation of the heat capacity at constant volume relative to the ideal gas state over a wide temperature and pressure range for n-butane and ethylene respectively.

In the present work the isobaric heat capacity at constant pressure of nitric oxide, relative to the ideal gas state from 0 to 6000 PSIA and from 300 to 1800°R is computed using the Benedict-Webb-Rubin equation. Also presented, is the variation of the heat capacity at constant volume relative to the ideal gas state for nitric oxide over the same pressure and temperature range.

The Benedict-Webb-Rubin constants were evaluated by Opfell, Schlinger and Sage (18) who report a standard deviation of 0.00458 in the compressibility factor form ~ 100°F to 220°F and for pressures up to 3000 PSIA. Opfell, Schlinger and Sage report that these constants do not adequately describe the properties of nitric oxide in the critical or heterogeneous regions. They state that at temperatures of 100°R and 200°R marked disagreement occurred between the estimated behavior and the behavior predicted by the Benedict-Webb-Rubin equation using these constants. Therefore, no attempt was made to predict the properties of nitric oxide below 300°R. However, this work does include calculations which represent an extrapolation of the available data used by Opfell, Schlinger and Sage from 680° to 1800°R and from 3000 to 6000 PSIA.

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

The Benedict-Webb-Rubin Equation of State (9) is:

$$(E-1) \quad p = RTd + (B_0RT - A_0 - C_0T^{-2})d^2 + (bRT - a)d^3 + ad^6 + cd^3(1 + \gamma d^2)T^{-2}e^{-\gamma d^2}$$

Substituting molal volume for density in equation (E-1):

$$(E-2) \quad p = RTV^{-1} + (B_0RT - A_0 - C_0T^{-2})V^{-2} + (bRT - a)V^{-3} - av^{-3} + cv^{-3}(1 + \delta v^{-2})T^{-2}e^{-\gamma v^{-2}}$$

Expanding equation (E-2):

$$(E-3) \quad p = RTV^{-1} + B_0RTV^{-2} - A_0V^{-2} - C_0T^{-2}V^{-2} + bRTV^{-3} - av^{-3} + adV^{-6} + cv^{-3}T^{-2}Q - \delta V^{-2} + c\delta V^{-5}T^{-2}Q - \gamma V^{-2}$$

For an ideal gas:

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

Rearranging (E-4):

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

Adding C_p , the actual heat capacity, at constant pressure to each side of equation (E-4):

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

Adding and subtracting C_v to the left side of (E-6):

$$(E-7) \quad (C_p - C_v) + (C_v - C_v^*) = R \equiv C_p - C_p^*$$

Equation 90 on page 461 of Hougen and Watson (4) is as follows:

$$(E-8) \quad (C_p - C_v) \equiv -T \left(\frac{\delta V}{\delta T} \right)_P^2 \left(\frac{\delta P}{\delta V} \right)_T$$

Equation 89 on the same page of Hogen and Watson (4) is :

$$(E-9) \quad \left(\frac{\delta V}{\delta T}\right)_P = \frac{\left(\frac{\delta p}{\delta T}\right)_V}{\left(\frac{\delta p}{\delta V}\right)_T}$$

Substituting (E-9) into (E-8) :

$$(E-10) \quad C_p - C_v = \frac{-T \left(\frac{\delta p}{\delta T}\right)_V^2}{\left(\frac{\delta p}{\delta V}\right)_T}$$

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

$$(E-11) \quad \left(\frac{\delta p}{\delta T}\right)_V = RV^{-1} + B_0 RV^{-2} + 2C_0 V^{-2} T^{-3} + bRV^{-3} \\ -2cV^{-3} e^{-\gamma V^{-2}} T^{-3} -2c \gamma V^{-5} e^{-\gamma V^{-2}} T^{-3}$$

$$\text{or } \left(\frac{\delta p}{\delta T}\right)_V = RV^{-1} + (B_0 R + 2C_0 T^{-3})V^{-2} + bRV^{-3} \\ -2cV^{-3} T^{-3} e^{-\gamma V^{-2}} (1 + \gamma V^{-2})$$

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

$$(E-12) \quad \left(\frac{\delta p}{\delta V}\right)_T = -RTV^{-2} -2B_0 RTV^{-3} + 2A_0 V^{-3} + 2C_0 T^{-2} V^{-3} -3bRTV^{-4} \\ + 3aV^{-4} -6a \alpha V^{-7} + 2 \gamma CV^{-6} T^{-2} e^{-\gamma V^{-2}} -3CV^{-4} T^{-2} e^{-\gamma V^{-2}} \\ + 2c \gamma 2V^{-8} T^{-2} e^{-\gamma V^{-2}} -5c \gamma V^{-6} T^{-2} e^{-\gamma V^{-2}}$$

$$\text{or } \left(\frac{\delta p}{\delta V}\right)_T = -RTV^{-2} -2V^{-3}(B_0 RT - A_0 - C_0 T^{-2}) -3V^{-4}(bRT - a) \\ -6a \alpha V^{-7} + cT^{-2} e^{-\gamma V^{-2}} (-3V^{-4} -3 \gamma V^{-6} + 2 \gamma^2 V^{-8})$$

Substituting (E-11) and (E-12) into equation (E-10) :

(E-13)

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

From Hogen and Watson (4) (equation 94, page 473) :

$$(E-14) \quad \left(\frac{\delta C_V}{\delta V}\right)_T = T \left(\frac{\delta^2 p}{\delta T^2}\right)$$

Rearranging (E-14):

$$(E-15) \quad dC_V = T \left(\frac{\delta^2 p}{\delta T^2} \right)_V dV$$

Integrating (E-15):

$$(E-16) \quad C_V - C_V^* = \int_{\infty}^{V_T} \left(\frac{\delta^2 p}{\delta T^2} \right)_V dV$$

Differentiating equation (E-11) with respect to temperature at constant volume:

$$(E-17) \quad \left(\frac{\delta p}{\delta T} \right)_V = -6c_0 V^{-2} T^{-4} + 6c V^{-3} e^{-\gamma V^{-2}} T^{-4} \\ + 6c \gamma V^{-5} e^{-\gamma V^{-2}} T^{-4}$$

$$\text{or } \left(\frac{\delta p}{\delta T} \right)_V = 6T^{-4} (c V^{-3} e^{-\gamma V^{-2}} + c \gamma V^{-5} e^{-\gamma V^{-2}} - c_0 V^{-2})$$

Substituting (E-17) into (E-16):

$$(E-18) \quad C_V - C_V^* = 6 T^{-3} \int_{\infty}^V (c V^{-3} e^{-\gamma V^{-2}} + c \gamma V^{-5} e^{-\gamma V^{-2}} - c_0 V^{-2}) dV$$

$$\text{or } C_V - C_V^* = 6c T^{-3} \int_{\infty}^V (V^{-3} e^{-\gamma V^{-2}}) dV + 6c \gamma T^{-3} \int_{\infty}^V (V^{-5} e^{-\gamma V^{-2}}) dV - 6c_0 T^{-3} \int_{\infty}^V V^{-2} dV$$

Evaluation of (E-18) yields:

$$(E-19) \quad C_V - C_V^* = 6c T^{-3} \left[\frac{e^{-\gamma V^{-2}}}{2V^2} + \frac{e^{-\gamma V^{-2}}}{\gamma} + \frac{c_0}{cV} \right]_{\infty}^V$$

Substituting limits:

$$(E-20) \quad C_V - C_V^* = 6c T^{-3} \left[\frac{e^{-\gamma V^{-2}}}{2V^2} + \frac{e^{-\gamma V^{-2}}}{\gamma} + \frac{c_0}{cV} \right] - \frac{6c T^{-3}}{\gamma}$$

Substituting equations (E-13) and (E-20) into equation (E-7) results in the desired expression for $(C_p - C_p^*)$ in terms of the Benedict-Webb-Rubin equation of state:

$$(E-21) \quad (C_p - C_p^*) = -T \frac{\left[RV^{-1} + (B_o R + 2C_o T^{-3}) V^{-2} + bRV^{-3} - 2cV^{-3}(1 + \gamma V^{-2}) e^{-\gamma V^{-2}} T^{-2} \right]}{\left[-RTV^{-2} - 2V^{-3}(B_o RT - A_o - C_o T^{-2}) - 3V^{-4}(bRT - a) \right.} \\ \left. - 6a\gamma V^{-7} + cT^{-2}(-3V^{-4} - 3\gamma V^{-6} + 2\gamma^2 V^{-8}) e^{-\gamma V^{-2}} \right] \\ + 6cT^{-3} \left[\frac{e^{-\gamma V^{-2}}}{2V^2} + \frac{e^{-\gamma V^{-2}}}{\gamma} + \frac{C_o}{cV} \right] - \frac{6cT^{-3}}{\gamma} - R$$

METHOD OF CALCULATION

Since the values of C_p^* and C_v^* are subject to constant revision as methods and techniques are improved, all calculations and graphs present the deviation of C_p and C_v from the ideal gas state. That is, all calculations and graphs are presented in the form ($C_p - C_p^*$) and ($C_v - C_v^*$). Table II lists the values of C_p^* for nitric oxide from -450.69°F to 2200°F given by API Project 44(1). C_p^* values presented by Witmer (19) are listed in Table III for temperatures which range from 1°K to 500°K .

Equation (E-2) is explicit in pressure and implicit in molal volume and temperature. Therefore, the solution of equation (E-2) is accomplished, most conveniently, by substituting assumed values of temperature and molal volume into (E-2), and solving for the pressure. Substituting the same assumed values into equation (E-21) yields the desired value of ($C_p - C_p^*$) at the assumed temperature and the calculated pressure. Stepwise, the calculations were carried out as follows:

1. Assuming a temperature such as 300°R , molal volumes ranging from 1 to $20 \text{ ft}^3/\text{lb. mole}$ were substituted into equation (E-2), and the equation was solved for the corresponding pressure.
2. Equation (E-11) was then used to calculate the corresponding value of $(\delta P / \delta T)_V$ for the assumed molal volumes at 300°R .
3. $(\delta P / \delta T)_V^2$ was obtained by squaring each of the values obtained in step 2.
4. Values of $(\delta P / \delta V)_T$ were then calculated using equation (E-12).
5. Substituting the values of $(\delta P / \delta T)_V^2$ and $(\delta P / \delta V)_T$ obtained in step 3 and 4 into equation (E-13) resulted in the evaluation of ($C_p - C_v$).

6. Using equation (E-20) values of $(C_v - C_v^*)$ were computed for the 300°R isotherm.
7. The substitution of the values obtained from equations (E-13) and (E-20) into equation (E-21) provided the desired values of $(C_p - C_p^*)$.
8. The procedure outlined in steps 1 through 7 was repeated for the following temperatures: 400°R , 500°R , 600°R , 700°R , 1000°R , 1800°R , and 2500°R .

A complete stepwise calculation is given in the Sample Calculation.

The data obtained by these calculations was tabulated in Table I and plotted in Figure 1. A cross-plot was made of Figure 1 which shows the deviation of heat capacity as a function of temperature for the following isobars: 100 PSIA, 200 PSIA, 500 PSIA, 1000PSIA, 2000 PSIA, 3000 PSIA, 4000 PSIA, 5000 PSIA, and 6000 PSIA. This is shown in Figure 2.

In a similar manner values of $(C_v - C_v^*)$ versus pressure were plotted in Figure 3 and cross plotted in figure 4 to show the variation of $(C_v - C_v^*)$ as a function of temperature for nine isobars.

DISCUSSION OF RESULTS

The accuracy of the present work can not be determined, since experimental data are not available in the literature for the range covered by this work. The values presented herein, represent an extrapolation of the data of Opfell, Schlinger, and Sage (18) who report the isobaric heat capacity of nitric oxide at pressures up to 2000 PSIA in the temperature range from -100 to 220°F. The data of Opfell, Schlinger, and Sage (18) are compared to the present work in Figures 5 and 6. In order to obtain the data in the proper form C_p^* values, given by API project 44 (1), were subtracted from the C_p values reported by Opfell, Schlinger, and Sage and these data were plotted in Figure 5. In Figure 6 C_p^* values presented by Witmer (19) were used in place of the values given by API project 44.

Figures 5 and 6 show close agreement between the data thus obtained and the data presented by Salzarulo. This was expected, since the present work is based on the Benedict, Webb, and Rubin constants evaluated by Opfell, Schlinger, and Sage.

The above named authors state that the Benedict-Webb-Rubin constants were established by the methods of Brough and Selleck and therefore do not necessarily give a satisfactory description of the volumetric behavior of nitric oxide beyond the ranges of temperature and pressure for which the coefficients were established (from -100 to

12

220°F and for pressures up to 3000 PSI). However, for most engineering applications, the extrapolated values for the isobaric heat capacity and the heat capacity at constant volume presented herein are sufficiently accurate. If a greater degree of accuracy is warrented, the required data must be obtained experimentally.

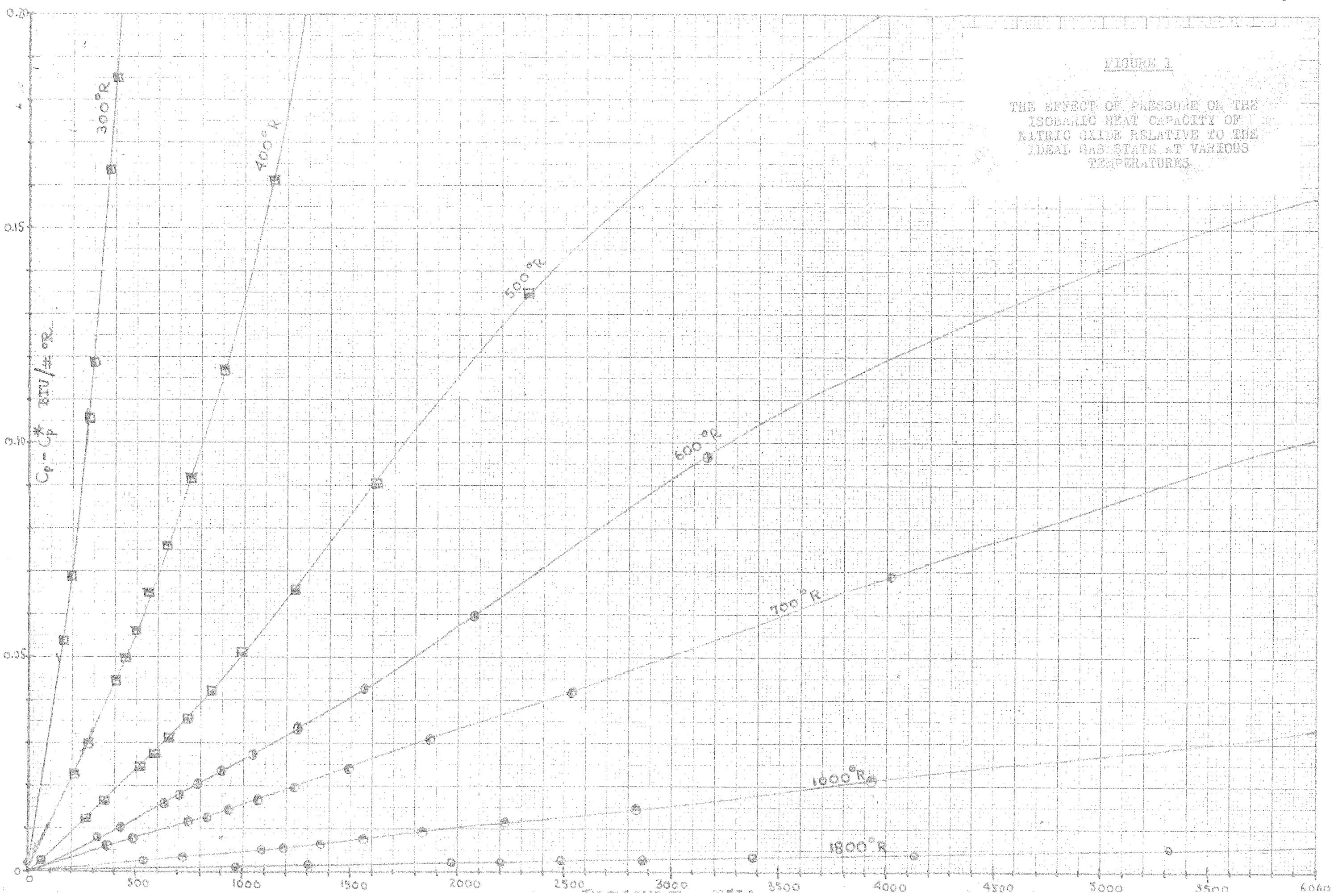


FIGURE 1

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

FIGURE 2

THE EFFECT OF TEMPERATURE ON THE ISOPARIC HEAT CAPACITY OF NITRO OXIDE RELATIVE TO THE IDEAL GAS STATE AT VARIOUS PRESSURES

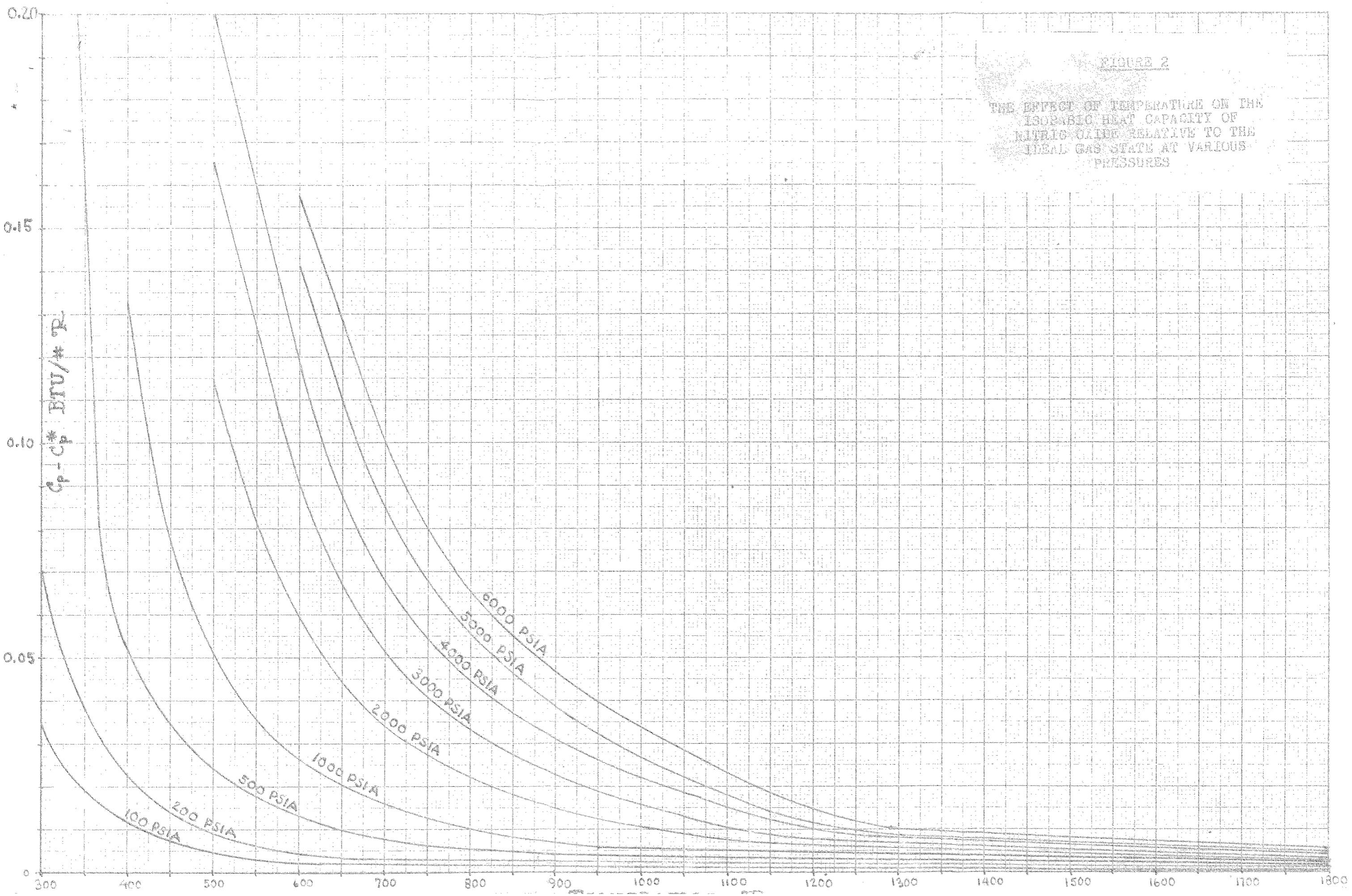


FIGURE 3

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

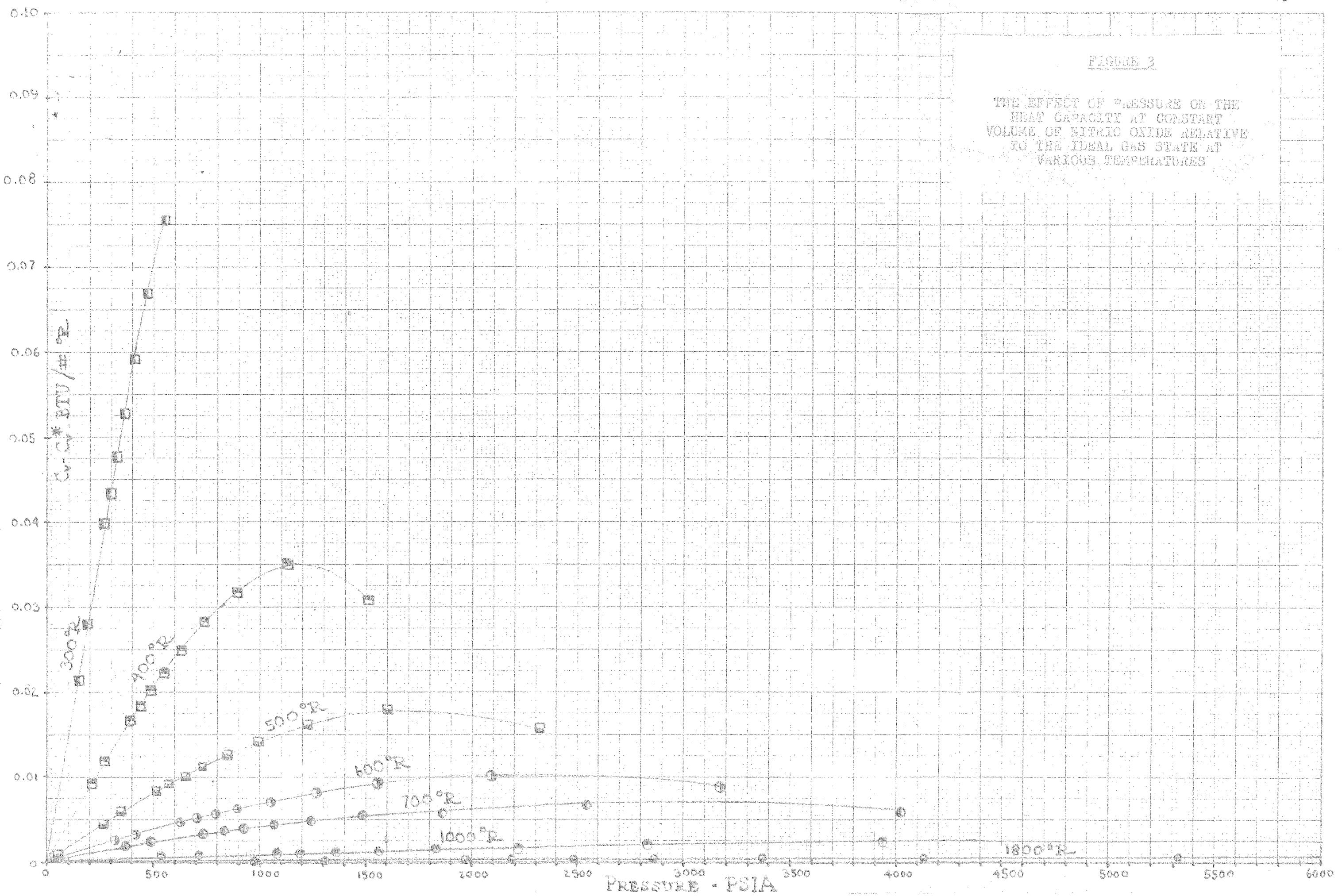
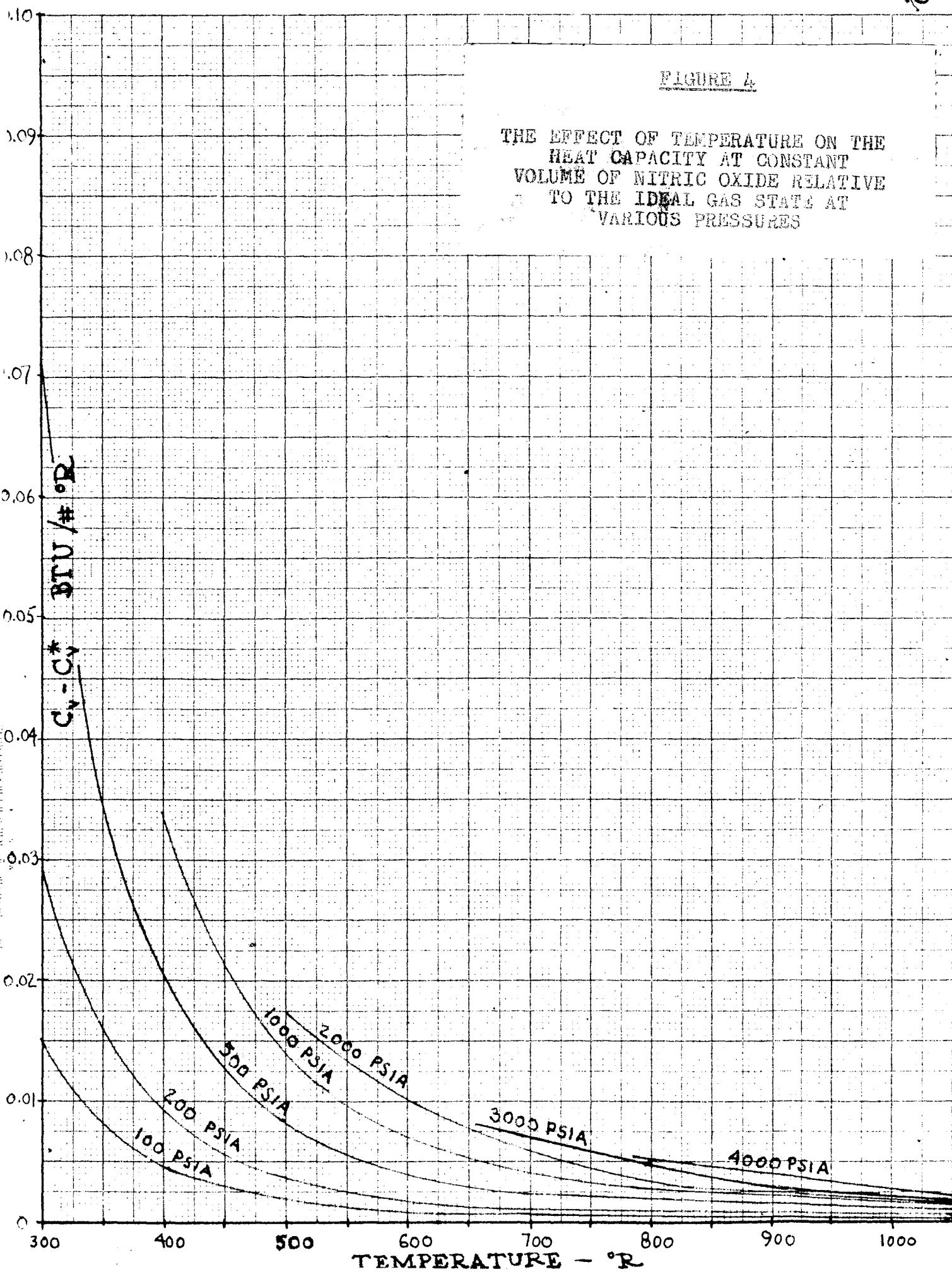
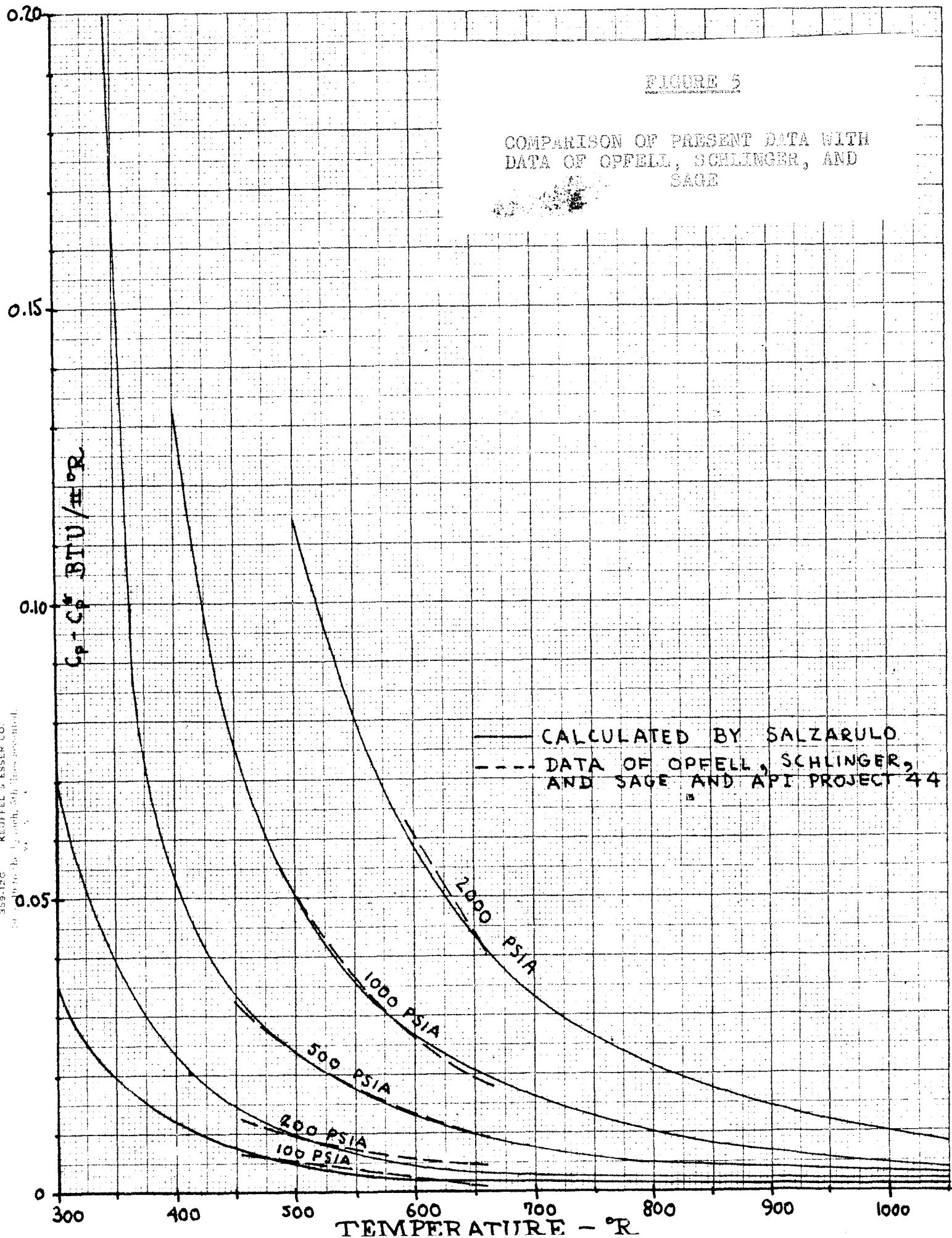


FIGURE 4

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





0.20

FIGURE 6

COMPARISON OF PRESENT DATA WITH
DATA OF OPPELL, SCHLINGER AND
SAGE

0.15

0.10

0.05

0.00

* BTU / # °R

CALCULATED BY SALZARULO

--- DATA OF OPPELL, SCHLINGER,
AND SAGE AND WITMER

300

400

500

600

700

800

900

1000

TEMPERATURE - °R

100

200

300

400

500

600

700

800

900

1000

1100

1200

1300

1400

1500

1600

1700

1800

1900

2000

2100

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SAMPLE CALCULATION → EQUATION E-2

$$P = RT/V + \left(B_0 RT - A_0 - \frac{C_0/T^2}{V^2} \right) \frac{1}{V^2} + \left(bRT - a \right) \frac{1}{V^3} + \left(\alpha \right) \frac{1}{V^6} + \left(\frac{c}{V^3 T^2} \right) \left(1 + \frac{\gamma}{V^2} \right) \left(e^{-\frac{\delta}{V^2}} \right)$$

P = Absolute Pressure, psia
 V = Molal Volume, $\text{ft}^3/\#\text{mole}$
 T = Absolute Temperature, $^{\circ}\text{R}$
 $= ^{\circ}\text{F} + 459.63$
 e = 2.71828
 R = 10.73147, $\text{ft}^3(\text{psi})/\#\text{mole}^{\circ}\text{R}$
 $(\text{ft}^3)(\text{psi}) = 0.0061683 \text{ Btu}$
 $(\#\text{mole})(^{\circ}\text{R}) = \text{Lb. Nitric Oxide } ^{\circ}\text{F}$

$A_0 = 1630.78 (\text{psi})(\text{ft}^3)^2/(\#\text{mole})^2$
 $B_0 = 0.0156389 (\text{ft}^3)/(\#\text{mole})^2$
 $C_0 = 335.286 \times 10^6 (\text{psi})(\text{ft}^3)^4(^{\circ}\text{R})^2/(\#\text{mole})^2$
 $a = 14188.61 (\text{psi})(\text{ft}^3)^3/(\#\text{mole})^3$
 $b = 2.21283 (\text{ft}^3)^2/(\#\text{mole})^2$
 $c = 915.645 \times 10^6 (\text{psi})(\text{ft}^3)^3(^{\circ}\text{R})^2/(\#\text{mole})^3$
 $\alpha = 0.0512202 (\text{ft}^3)^3/(\#\text{mole})^3$
 $\gamma = 0.5000000 (\text{ft}^3)^2/(\#\text{mole})^2$

$$T = 500^{\circ}\text{R}$$

V	RT/V	$\frac{(B_0 RT - A_0 - C_0/T^2)}{V^2}$	$\frac{bRT - a}{V^3}$	$\frac{\alpha \alpha}{V^6}$	$\frac{c(1 + \gamma/V^2)}{V^3 T^2 e^{\delta/V^2}}$	P-psia
1	5365.735	-2132.782	-2315.150	726.7434	3332.202	4976.749
2	2682.868	-533.196	-289.394	11.3554	454.530	2326.164
3	1788.578	-236.976	-85.746	0.9969	135.448	1602.301
4	1341.434	-133.299	-36.174	0.1774	57.200	1229.339

SAMPLE CALCULATION - EQUATION E-2 (CONTINUED).

500° R

V	RT/V	$\frac{B_0 RT - A_0 - C_0/T^2}{V^2}$	$\frac{bRT - a}{V^3}$	$\frac{a\alpha}{V^6}$	$\frac{c(1 + \gamma/V^2)}{V^3 T^2 \bar{Q}^{8/r^2}}$	P - psia
5	1073.147	- 85.311	- 18.521	0.0465	29.294	998.657
6	894.289	- 59.244	- 10.718	0.0155	16.955	841.297
7	766.534	- 43.526	- 6.750	0.0062	10.678	726.941
8	670.717	- 33.325	- 4.522	0.0028	7.153	640.627
9	596.193	- 26.331	- 3.176	0.0014	5.024	571.712
10	536.574	- 21.328	- 2.315	0.0007	3.663	516.594
15	357.716	- 9.479	- 0.686	0.0001	1.085	348.636
20	268.287	- 5.332	- 0.289	0.0000	0.458	263.123
100	53.657	- 0.213	- 0.002	0.0000	0.004	53.445
1000	5.366	- 0.002	- 0.000	0.0000	0.000	5.364

SAMPLE CALCULATION → EQUATION E-II

$$(\frac{\delta P}{\delta T})_V = [R/V + B_0 R/V^2 + 2 C_0/V^2 T^3 + bR/V^3 - (2c/V^3 T^3)(1+\frac{b}{V^2})(e^{-\frac{b}{V^2}})]^2$$

V	R/V	B ₀ R/V ²	2C ₀ /V ² T ³	bR/V ³	- (2c/V ³ T ³)(1+ $\frac{b}{V^2}$)(e ^{-$\frac{b}{V^2}$})	($\frac{\delta P}{\delta T}$) _V	($\frac{\delta P}{\delta T}$) _V ²
1	10.73147	1.678284	5.364576	23.746920	-13.328840	28.192441	794.81372
2	5.36574	0.419570	1.341144	2.968365	-1.818122	8.276693	68.50364
3	3.57716	0.186476	0.596064	0.879516	-0.541797	4.697415	22.06571
4	2.68287	0.104893	0.335286	0.371046	-0.228802	3.265290	10.66212
5	2.14629	0.067131	0.214583	0.189975	-0.117179	2.500804	6.25402
6	1.78858	0.046619	0.149016	0.109939	-0.067819	2.026334	4.10603
7	1.53307	0.034251	0.109481	0.069233	-0.042710	1.703322	2.90131
8	1.34143	0.026223	0.083822	0.046381	-0.028613	1.469246	2.15868
9	1.19239	0.020720	0.066229	0.032575	-0.020096	1.291813	1.66878
10	1.07315	0.016783	0.053646	0.023747	-0.014650	1.152672	1.32865
15	0.71543	0.007459	0.023843	0.007036	-0.004341	0.749428	0.56164
20	0.53657	0.004196	0.013411	0.002968	-0.000183	0.556966	0.31021
100	0.10731	0.000168	0.000536	0.000024	-0.000015	0.108028	0.01167
1000	0.01073	0.000002	0.000005	0.000000	-0.000000	0.010739	0.00012

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SAMPLE CALCULATION - EQUATION E-12

$$\left(\frac{\delta P}{\delta V}\right)_T = -\frac{RT}{V^2} - \left(\frac{2}{V^3}\right)\left(B_0 RT - A_0 - \frac{C_0}{T^2}\right) - \left(\frac{3}{V^4}\right)(bRT - a) - \frac{6ad}{V^7} + \left(\frac{C}{T^2}\right)\left(e^{-\frac{C}{V^2}}\right)\left(-\frac{3}{V^4} - \frac{38}{V^6} + \frac{28^2}{V^8}\right)$$

V	$-\frac{RT}{V^2}$	$\cdot \frac{2}{V^3} \left[B_0 RT - A_0 - \frac{C_0}{T^2} \right]$	$-\frac{3}{V^4} [bRT - a]$	$-\frac{6ad}{V^7}$	$\frac{C}{T^2} \left(e^{-\frac{C}{V^2}} \right) \left[\frac{3}{V^4} - \frac{38}{V^6} + \frac{28^2}{V^8} \right]$	$\left(\frac{\delta P}{\delta V}\right)_T$
1	-5365.735	4265.564	6945.450	-4360.460	-8885.873	-7401.055
2	-1341.434	533.196	434.091	-34.066	-737.712	-1145.926
3	-596.193	157.984	85.746	-1.994	-135.185	-489.642
4	-335.358	66.649	27.131	-0.266	-42.873	-284.718
5	-214.629	34.125	11.113	-0.056	-17.572	-187.020
6	-149.048	19.750	5.359	-0.016	-8.476	-132.433
7	-109.505	12.436	2.893	-0.005	-4.576	-98.757
8	-83.840	8.331	1.696	-0.002	-2.683	-76.497
9	-66.244	5.851	1.059	-0.001	-1.675	-61.009
10	-53.657	4.266	0.695	-0.000	-1.099	-49.796
15	-23.848	1.264	0.137	-0.000	-0.217	-22.664
20	-13.414	0.533	0.043	-0.000	-0.069	-12.906
100	-0.537	0.004	0.000	-0.000	0.000	-0.532
1000	-0.005	0.000	0.000	-0.000	0.000	-0.005

SAMPLE CALCULATION-EQUATION E-20

$$(C_v - C_v^*) = \frac{6c}{T^3} \left[\frac{e^{-\frac{\gamma}{V^2}}}{\gamma} + \frac{e^{-\frac{\gamma}{V^2}}}{2V^2} + \frac{C_0}{cV} \right] - \frac{6c}{8T^3}$$

V	$\frac{6c}{T^3} \left[\frac{e^{-\frac{\gamma}{V^2}}}{\gamma} + \frac{e^{-\frac{\gamma}{V^2}}}{2V^2} + \frac{C_0}{cV} \right]$	$-\frac{6c}{8T^3}$	$C_v - C_v^*$
1	82.737779	-87.90192	-5.164141
2	90.468362	-87.90192	2.566442
3	90.825955	-87.90192	2.924035
4	90.552084	-87.90192	2.650164
5	90.241733	-87.90192	2.339813
6	89.973786	-87.90192	2.071876
7	89.752572	-87.90192	1.850652
8	89.570276	-87.90192	1.668356
9	89.418799	-87.90192	1.516879
10	89.291588	-87.90192	1.389668
15	88.877143	-87.90192	0.975223
20	88.651684	-87.90192	0.749764
100	88.060658	-87.90192	0.158738
1000	87.918037	-87.90192	0.016117

SAMPLE CALCULATION - EQUATION E-21.

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

V	$(\delta P/\delta T)_V^2$	$(\delta P/\delta V)_T$	$-T \frac{(\delta P/\delta T)_V^2}{(\delta P/\delta V)_T}$	$(c_v - c_v^*)$	-R	$\frac{(c_p - c_p^*)}{\text{ft}^3 - \text{psi}}$ # mole °R	$\frac{(c_p - c_p^*)}{\text{Btu}}$ # °F	P psia
1	794.81372	-7401.055	53.69598	-5.164141	-10.73147	37.800364	0.233164	4976.749
2	68.50364	-1145.926	29.89007	2.566442	-10.73147	21.725047	0.134007	2326.164
3	22.06571	-489.642	22.53250	2.924035	-10.73147	14.725069	0.090828	1602.301
4	10.66212	-284.718	18.72402	2.650164	-10.73147	10.642716	0.065647	1229.339
5	6.25402	-187.020	16.72017	2.339813	-10.73147	8.328512	0.051373	998.657
6	4.10603	-132.433	15.50229	2.071876	-10.73147	6.842695	0.042208	841.297
7	2.90131	-98.757	14.68906	1.850652	-10.73147	5.808242	0.035827	726.941
8	2.15868	-76.497	14.10953	1.668356	-10.73147	5.046415	0.031128	640.027
9	1.66878	-61.009	13.67644	1.516879	-10.73147	4.461844	0.027522	571.712
10	1.32865	-49.796	13.34086	1.389668	-10.73147	3.999054	0.024657	516.594
15	0.56164	-22.664	12.39079	0.975223	-10.73147	2.634544	0.016251	348.636
20	0.31021	-12.906	12.01769	0.749764	-10.73147	2.035987	0.012559	263.123
100	0.01167	-0.532	10.96093	0.158738	-10.73147	0.388199	0.002395	53.445
1000	0.00012	-0.005	10.75415	0.016117	-10.73147	0.038798	0.000239	5.364

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TABLE I
CALCULATED DATA - T=300°R

V ft ³ /#mole	P psia	$C_p - C_v$ ft ³ -psi #mole°R	$C_v - C_v^*$ ft ³ -psi #mole°R	-R ft ³ -psi #mole°R	$C_p - C_p^*$ ft ³ -psi #mole°R	$C_p - C_p^*$ Btu # °F	$C_v - C_v^*$ Btu # °F
1	1285.08	0.112378	-23.90806	-10.73147	-34.527152	-0.21297	-0.147470
2	787.43	36.684813	11.88168	-10.73147	37.835023	0.23338	0.073290
3	649.55	62.975280	13.53720	-10.73147	65.781010	0.40576	0.083502
4	550.25	46.444161	12.26928	-10.73147	47.981971	0.29597	0.075681
5	474.66	36.981231	10.83247	-10.73147	37.082231	0.22873	0.066818
6	416.18	31.258083	9.59197	-10.73147	30.118583	0.18578	0.059166
7	369.96	27.500762	8.56783	-10.73147	26.337122	0.16246	0.052849
8	332.68	24.869703	7.72387	-10.73147	21.862103	0.13485	0.047643
9	302.07	22.933931	7.02259	-10.73147	19.225051	0.11859	0.043317
10	276.53	21.453840	6.43365	-10.73147	17.156020	0.10582	0.039685
15	193.98	17.372846	4.51492	-10.73147	11.156296	0.06882	0.027849
20	149.23	15.927404	3.47113	-10.73147	8.667064	0.05346	0.021411

TABLE. I
CALCULATED DATA - T = 400° R

V ft ³ /#mole	P psia	$C_p - C_v$ ft ³ -psi #mole°R	$C_v - C_v^*$ ft ³ -psi #mole°R	-R ft ³ -psi #mole°R	$C_p - C_p^*$ ft ³ -psi #mole°R	$C_p - C_p^*$ Btu #OF	$C_v - C_v^*$ Btu #OF
1	2481.06	72.006124	-10.08622	-10.73147	51.188434	0.31575	-0.062215
2	1517.87	39.679283	5.01258	-10.73147	33.960390	0.20948	0.030919
3	1130.36	31.089988	5.71100	-10.73147	26.069518	0.16080	0.035227
4	898.48	24.492308	5.17610	-10.73147	18.936938	0.11681	0.031928
5	744.62	21.050611	4.56994	-10.73147	14.889081	0.09184	0.028189
6	635.37	18.962653	4.04661	-10.73147	12.277793	0.07573	0.024961
7	553.90	17.568347	3.61455	-10.73147	10.451427	0.06447	0.022296
8	490.86	16.573991	3.25851	-10.73147	9.101031	0.05614	0.020099
9	440.66	15.830124	2.96265	-10.73147	8.061304	0.04973	0.018275
10	399.74	15.253227	2.71419	-10.73147	7.235945	0.04463	0.016742
15	272.90	13.615256	1.90473	-10.73147	4.788516	0.02954	0.011749
20	207.12	12.993322	1.46438	-10.73147	3.726232	0.02299	0.009033

TABLE I
CALCULATED DATA T=600° R

V ft ³ /#mole	P psia	$C_p - C_v$ $\frac{ft^3 - psi}{\# mole ^\circ R}$	$C_v - C_v^*$ $\frac{ft^3 - psi}{\# mole ^\circ R}$	$-R$ $\frac{ft^3 - psi}{\# mole ^\circ R}$	$C_p - C_p^*$ $\frac{ft^3 - psi}{\# mole ^\circ R}$	$C_p - C_p^*$ $\frac{Btu}{\# ^\circ F}$	$C_v - C_v^*$ $\frac{Btu}{\# ^\circ F}$
1	7984.04	42.537361	-2988507	-10.73147	28.817384	0.177750	-0.0184343
2	3165.10	24.822341	1.485210	-10.73147	15.576081	0.096078	0.0091612
3	2070.76	18.775080	1.692150	-10.73147	9.735760	0.060053	0.0104384
4	1553.35	16.180990	1.533660	-10.73147	6.983180	0.043074	0.0094601
5	1246.44	14.804333	1.354059	-10.73147	5.426922	0.033475	0.0083522
6	1042.01	13.965795	1.198997	-10.73147	4.433322	0.027346	0.0073958
7	895.70	13.406249	1.070980	-10.73147	3.745759	0.023105	0.0066061
8	785.65	13.009135	0.965484	-10.73147	3.243149	0.020005	0.0059554
9	699.80	12.711425	0.877824	-10.73147	2.857779	0.017628	0.0054147
10	630.94	12.481991	0.804206	-10.73147	2.554727	0.015758	0.0049606
15	423.12	11.836189	0.564365	-10.73147	1.669084	0.010295	0.0034812
20	318.38	11.576930	0.433892	-10.73147	1.279352	0.007891	0.0026764

TABLE I
CALCULATED DATA T = 700 °R

V $\frac{ft^3}{\# \text{mole}}$	P psia	$C_p - C_V$ $\frac{ft^3 - \text{psi}}{\# \text{mole} \text{ °R}}$	$C_V - C_V^*$ $\frac{ft^3 - \text{psi}}{\# \text{mole} \text{ °R}}$	-R $\frac{ft^3 - \text{psi}}{\# \text{mole} \text{ °R}}$	$C_p - C_p^*$ $\frac{ft^3 - \text{psi}}{\# \text{mole} \text{ °R}}$	$C_p - C_p^*$ $\frac{\text{Btu}}{\# \text{ °F}}$	$C_V - C_V^*$ $\frac{\text{Btu}}{\# \text{ °F}}$
1	11232.86	36.124714	-1.881975	-10.73147	23.511269	0.145023	-0.0116093
2	4018.49	20.948570	0.935293	-10.73147	11.152393	0.068791	0.0057692
3	2537.58	16.700868	1.065611	-10.73147	7.035009	0.043394	0.0065730
4	1874.14	14.771469	0.965804	-10.73147	5.005803	0.030877	0.0059574
5	1494.26	13.744358	0.852702	-10.73147	3.865590	0.023244	0.0052597
6	1240.27	13.118146	0.755054	-10.73147	3.141730	0.019379	0.0046574
7	1062.43	12.700491	0.674437	-10.73147	2.643458	0.016306	0.0041601
8	929.60	12.403759	0.608002	-10.73147	2.280291	0.014066	0.0037503
9	826.50	12.182869	0.552794	-10.73147	2.004198	0.012362	0.0034098
10	744.11	12.012390	0.506440	-10.73147	1.787360	0.01025	0.0031239
15	497.01	11.534660	0.355403	-10.73147	1.158593	0.007147	0.0021922
20	373.29	11.339621	0.273238	-10.73147	0.881389	0.005437	0.0016854

TABLE I
CALCULATED DATA $T=1000^{\circ}\text{R}$

V $\text{ft}^3/\#\text{mole}$	P psia	$c_p - c_v$ $\frac{\text{ft}^3 - \text{psi}}{\#\text{mole}^{\circ}\text{R}}$	$c_v - c_v^*$ $\frac{\text{ft}^3 - \text{psi}}{\#\text{mole}^{\circ}\text{R}}$	$-R$ $\frac{\text{ft}^3 - \text{psi}}{\#\text{mole}^{\circ}\text{R}}$	$c_p - c_p^*$ $\frac{\text{ft}^3 - \text{psi}}{\#\text{mole}^{\circ}\text{R}}$	$c_p - c_p^*$ $\frac{\text{Btu}}{\#\text{F}}$	$c_v - c_v^*$ $\frac{\text{Btu}}{\#\text{F}}$
1	21561.79	27.223753	-0.645518	-10.73147	15.846765	0.097748	-0.0039817
2	6613.57	16.355039	0.320805	-10.73147	5.944374	0.036667	0.0019788
3	3934.05	13.795751	0.365504	-10.73147	3.429785	0.021156	0.0022545
4	2828.71	12.822830	0.331271	-10.73147	2.422631	0.014944	0.0020434
5	2218.62	12.284673	0.292477	-10.73147	1.845680	0.011385	0.0018041
6	1829.09	11.958840	0.258483	-10.73147	1.486353	0.009168	0.0015975
7	1557.74	11.742221	0.231332	-10.73147	1.242083	0.007662	0.0014269
8	1357.40	11.588619	0.208545	-10.73147	1.065694	0.006574	0.0012864
9	1190.10	11.474428	0.189610	-10.73147	0.932568	0.005752	0.0011696
10	1080.74	11.386384	0.173709	-10.73147	0.828623	0.005111	0.0010715
15	717.26	11.140331	0.121903	-10.73147	0.530764	0.003274	0.0007519
20	537.16	11.035881	0.093721	-10.73147	0.398132	0.002456	0.0005781

b2

TABLE I
CALCULATED DATA T=1800°R

V ft ³ /#mole	P psia	$c_p - c_v$ ft ³ ·psi #mole°R	$c_v - c_v^*$ ft ³ ·psi #mole°R	-R ft ³ ·psi #mole°R	$c_p - c_p^*$ ft ³ ·psi #mole°R	$c_p - c_p^*$ Btu # °F	$c_v - c_v^*$ Btu # °F
1	47827.85	22.061545	-0.110686	-10.73147	11.219389	0.0692056	-0.00068274
2	13306.50	13.541319	0.055008	-10.73147	2.864857	0.0176711	0.00033930
3	7565.17	12.035484	0.062672	-10.73147	1.366686	0.0084301	0.00038658
4	5324.18	11.540280	0.056802	-10.73147	0.865612	0.0053394	0.00035037
5	4127.03	11.313554	0.050150	-10.73147	0.632234	0.0038998	0.00030934
6	3377.99	11.186432	0.044407	-10.73147	0.499369	0.0030803	0.00027392
7	2863.11	11.105453	0.039666	-10.73147	0.413649	0.0025515	0.00024467
8	2486.49	11.049296	0.035759	-10.73147	0.353585	0.0021810	0.00022057
9	2198.56	11.008025	0.032512	-10.73147	0.309067	0.0019064	0.00020054
10	1971.06	10.976342	0.029785	-10.73147	0.274657	0.0016942	0.00018373
15	1301.36	10.887477	0.020902	-10.73147	0.176909	0.0010912	0.00012893
20	972.36	10.847483	0.016070	-10.73147	0.132083	0.0008147	0.00009913

TABLE I
CALCULATED DATA T=2500°R

V ft ³ /#Mole	P psia	$C_p - C_v$ ft ³ -psi #mole °R	$C_v - C_v^*$ ft ³ -psi #mole °R	$-R$ ft ³ -psi #mole °R	$C_p - C_p^*$ ft ³ -psi #mole °R	$C_p \cdot C_p^*$ Btu # °F	$C_v - C_v^*$ Btu # °F
1	75378.68	18.923265	-0.041313	-10.73147	8.150482	0.0502754	-0.00025483
2	19719.04	12.060807	0.020531	-10.73147	1.349869	0.0083264	0.00012664
3	10,901.62	11.009693	0.023392	-10.73147	0.301615	0.0018605	0.00014429
4	7572.51	10.914734	0.021201	-10.73147	0.204465	0.0012612	0.00013078
5	5828.84	10.857107	0.018719	-10.73147	0.144356	0.0008904	0.00011546
6	4751.06	10.836852	0.016575	-10.73147	0.121957	0.0007523	0.00010224
7	4016.07	10.827512	0.014805	-10.73147	0.110847	0.0006837	0.00009132
8	3481.35	10.821742	0.013347	-10.73147	0.103619	0.0006391	0.00008233
9	3074.14	10.817256	0.012135	-10.73147	0.097921	0.0006040	0.00007485
10	2753.31	10.813345	0.011117	-10.73147	0.092992	0.0005736	0.00006858
15	1813.17	10.797517	0.007802	-10.73147	0.073849	0.0004555	0.00004812
20	1353.38	10.786592	0.005998	-10.73147	0.061120	0.0003770	0.00003700

TABLE II

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

Temperature <u>°F</u>	<u>C*</u> BTU/LB. °F
-459.69	0
0	0.2386
32	0.2381
60	0.2378
88	0.2377
77	0.2377
100	0.2375
200	0.2378
300	0.2392
400	0.2416
500	0.2446
600	0.2480
700	0.2515
800	0.2550
900	0.2583
1000	0.2615
1100	0.2644
1200	0.2671
1300	0.2697
1400	0.2720
1500	0.2741
1600	0.2760
1700	0.2778
1800	0.2794
1900	0.2809
2000	0.2822
2100	0.2835
2200	0.2846

TABLE III

VALUES OF THE ISOBARIC HEAT CAPACITY OF NITRIC OXIDE
IN THE IDEAL GAS STATE AT VARIOUS TEMPERATURES (19)

Temperature °K	C_p^* Cal./g.mole °K
1	5.1191
2	6.2642
3	6.7552
4	6.8707
5	6.9079
10	6.9442
20	6.9723
30	7.137
40	7.396
50	7.6176
60	7.743
70	7.801
80	7.798
90	7.762
100	7.7112
110	7.653
120	7.596
130	7.540
140	7.489
150	7.442
160	7.400
170	7.362
180	7.329
190	7.299
200	7.272
220	7.226
240	7.188
300	7.133
400	7.158
500	7.295

NOMENCLATURE

- c_p - Specific heat at constant pressure, $\text{Ft}^3\text{-PSI/Lb mol } {}^\circ\text{R}$
- c_p - Specific heat at constant pressure, $\text{BTU/Lb. } {}^\circ\text{R}$
- c_p^* - Specific heat at constant pressure for a gas in the ideal gas state, $\text{Ft}^3\text{-PSI/Lb mol } {}^\circ\text{R}$
- c_p^* - Specific heat at constant pressure for a gas in the ideal gas state, $\text{BTU/Lb. } {}^\circ\text{R}$
- c_v - Specific heat at constant volume, $\text{Ft}^3\text{-PSI/Lb mol } {}^\circ\text{R}$
- c_v - Specific heat at constant volume, $\text{BTU/Lb. } {}^\circ\text{R}$
- c_v^* - Specific heat at constant volume for a gas in the ideal gas state, $\text{Ft}^3\text{-PSI/Lb mol } {}^\circ\text{R}$
- c_v^* - Specific heat at constant volume for a gas in the ideal gas state, $\text{BTU/Lb. } {}^\circ\text{R}$
- T - Absolute temperature, ${}^\circ\text{R} = \text{OF} + 459.69$
- V - Molal volume, $\text{Ft}^3/\text{Lb. mol.}$
- P - Absolute pressure, Atmospheres
- p - Absolute pressure, Lbs. per Square Inch
- R - Gas constant, $10.73147 \text{ Ft}^3\text{-PSI/Lb. mol. } {}^\circ\text{R}$
- $A_0, B_0, C_0, a, b, c, \alpha, \gamma$ - Constants in the Benedict-
webb-Rubin Equation of State
- e - Base of the natural logarithms

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