AUTOMATIC GENERATION OF THERMODYNAMIC NETWORKS

by

Gerald Gruber

B.Ch.E., City College of New York
(1959)

S.M., Massachusetts Institute of Technology
(1961)

Submitted in Partial Fulfillment

of the Requirements for the

Degree of Doctor of Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 1964

Signature of Author . . . .
                            Department of Chemical Engineering

Certified by. . . . .
                            Thesis Supervisor, Robert C. Reid

        . . . .
                            Thesis Supervisor, Charles M. Mohr

Accepted by . . . .
                Chairman,
                Departmental Committee on Graduate Theses

AUTOMATIC GENERATION OF THERMODYNAMIC NETWORKS

by

Gerald Gruber

Submitted to the Department of Chemical Engineering
on September 21, 1964, in partial fulfillment of the require-
ments for the degree of Doctor of Science in Chemical Engi-
neering.

ABSTRACT

An attempt has been made to generate, automatically,
a thermodynamic network, from the measuring of the required
data to the final calculation of thermodynamic properties.
Based on a study of available instrumentation, an experimen-
tal system is proposed that will measure volumetric data, to
an accuracy of about 1.0 per cent, for a gas, by means of a
mass and volumetric flowmeter. A computor program was written
that will calculate a thermodynamic network from the data
measured in the proposed experiment. It is also possible to
use the computor program to calculate a thermodynamic net-
work from volumetric data already in the literature.

In order to check the accuracy of the computor pro-
gram in treating experimental data, the thermodynamic proper-
ties of nitrogen were calculated, and compared with the
thermodynamic properties of nitrogen existing in the litera-
ture. It was found that good agreement was achieved when
volumetric data of 0.1 to 0.01 per cent accuracy were used
as input to the computor program. The results calculated
in this work were compared with three other sets of results.
When comparisons are made with each set of results, there
are no significant differences. Some of the thermodynamic
properties that were calculated and compared were the
enthalpy, entropy, constant pressure heat capacity, fuga-
city coefficient and Joule-Thomson coefficient.

The thermodynamic properties of nitrogen were also
calculated from volumetric data that had a random error of
1.0 per cent, and from volumetric data that were rounded to
only two significant figures. In each instance, the result-
ing thermodynamic properties of enthalpy, entropy and heat
capacity were compared with the corresponding properties cal-
culated from volumetric data with no purposely introduced

error. In both cases the agreement was good. The differences found in the comparisons were of the same order of magnitude as the differences found between the various sets of thermodynamic properties found in the literature. This would indicate that errors of about 1.0 per cent in the volumetric data do not have a significant influence on the calculated thermodynamic network.

By combining the proposed experiment with the computor program that was developed, it is possible to generate a thermodynamic network in an automatic manner. Volumetric data could be measured with an accuracy of about 1.0 per cent, and the calculated thermodynamic network would be of sufficient accuracy for most engineering purposes. This could be done much quicker, and with less expense, then has previously been the case.

Thesis Supervisors: Robert C. Reid,
Associate Professor
of Chemical Engineering

Charles M. Mohr,
Assistant Professor
of Chemical Engineering

ACKNOWLEDGEMENTS

CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. SUMMARY

A. Objective

Thermodynamic Networks, i.e., tabulations or plots of enthalpy, entropy, and other properties as functions of temperature and pressure, are not readily available for most organic and inorganic materials. They are, however, of great value to engineers. The reason for the dearth of such networks seems to be due principally to two causes: (a) necessary data required in the calculations are either unavailable or unreliable or (b) the effort required to transform raw data into final, convenient networks cannot be justified.

Considering the enormous number of chemical compounds presently being manufactured, or which will be in the future, it is inconceivable that any more than a minute fraction will ever be studied experimentally to the extent that the physical or thermodynamic properties will be established. Recognizing this limitation, progress has been directed in two paths. The physical chemist has chosen a few selective compounds and has measured their properties with considerable accuracy, correlated the data, and sometimes even established reliable values of the derived properties such as entropy, enthalpy, fugacity, etc. The other path has been chosen by the engineer; he has taken the results of the physical chemist, generalized them, for example with the law of

corresponding states, and applied the resulting generaliza-
tions to all materials. The engineer recognizes that this
expediency requires a sacrifice in accuracy and, in many
cases, he has to apply generalized correlations even to
situations where he knows the accuracy is poor. There exists
a middle-of-the-road course between these extremes and this
concept is developed in this thesis.

It is proposed to design simple experiments, requir-
ing a minimum of sophisticated instrumentation, to product
sufficient data of the kind that may be used to calculate
thermodynamic networks. Some sacrifice is made in the
accuracy of basic measurements to achieve generality, reli-
ability, and ease of data generation. The experimental data
are recorded from electrical or pneumatic signals directly
onto punched tape or cards. These stored data may then be
used as input to a computor program, written to calculate
all desired properties. The accuracy of the data will be
such that the experimental phase will be kept simple and
rapid. The final results probably would not suit a chemical
physicist interested in determining force constants of the
molecules, but would be well suited to a process design
engineer charged with making equilibrium calculations, heat
and material balances, heat transfer estimates and the like.
In such cases, accuracies of 5 per cent would not be rejected
as this is often much better than he can now obtain from
generalized correlations.

In this thesis, an accuracy of 1 or 2 per cent is used as a target. An experimental and calculational scheme is proposed to determine thermodynamic networks to this degree of accuracy. The experimental phase has only been planned but the calculational phase has been studied in some detail. These areas are discussed below.

Finally, to present a picture of the overall project, it is visualized that a simple "black box" experimental apparatus may be built and operated by some central research facility. Gas, liquid, pure or mixture samples could be sent to this facility and connected to this "box". The customer specifies the temperature and pressure range of interest and the desired list of thermodynamic properties. The experiments are carried out automatically, data fed to a computor, and the calculated results printed out, all in a manner of minutes. Although only gas phase thermodynamic properties and vapor pressure were studied in this thesis, such an idea is amenable to liquid properties, vapor-liquid equilibrium, transport properties, etc.

B. <u>Methods</u> <u>Now</u> <u>Being</u> <u>Used</u> <u>to</u> <u>Determine</u> <u>Thermodynamic</u> <u>Networks</u>

Accurate volumetric data are first measured over the temperature, pressure and composition range of interest. These data are smoothed either graphically or analytically and used as input to some method to generate the network. Ordinarily several differentiations and integrations are

necessary. Such operations may be performed graphically
(with a sacrifice in accuracy) or analytically (19-23, 26,
81, 91) with a great deal of tedious computation. Some of
this work has been done on computors and several such pro-
grams have been described (9, 15, 38, 75). These programs,
however, have not been general. They have either been written
for one gas, or have been very restricted in the type of
input data required. In this work, a computor program has
been written that will calculate a thermodynamic network for
any gas, and that has a good deal of flexibility in the
allowable format of the input data.

C. Proposed Method

1. Computor Program

A computor program has been written that will cal-
culate a thermodynamic network from volumetric data taken
from the literature, or from volumetric data generated auto-
matically in a proposed experiment to be described later.
As the only restriction to the program input, the data should
be in the form of volumetric isobars. The isobars do not
have to be evenly spaced, or at any particular rounded values
of pressure. Also, the temperatures, corresponding to the
measured specific volumes, do not have to be evenly spaced
or rounded. In addition to the volumetric data, the constant
pressure heat capacity, as a function of temperature, is
required at one pressure. Also, vapor pressure data are

required, if the thermodynamic network is to be extended to the saturation curve, and may be measured, automatically, by the method of Spauschus (79). When vapor pressure data are not measured, or otherwise available, Riedel's generalized correlation is used (69).

The calculated output of the computor program consists of all of the common thermodynamic properties, tabulated at evenly spaced values of the pressure and temperature. The properties of the vapor on the saturation curve are also tabulated. At each temperature and pressure on the thermo-dynamic network, the following properties are tabulated; specific volume, enthalpy, entropy, heat capacity at constant pressure, fugacity coefficient, compressibility factor, residual volume, Joule-Thomson coefficient, heat capacity at constant volume, $C_p - C_v$, C_p/C_v and sonic velocity.

In the computor program, the properties are calculated along an isotherm, after a reference line has been estab-lished. Values for the enthalpy and entropy are selected at a reference pressure and temperature. At the reference pressure, the enthalpy and entropy are calculated as a func-tion of temperature from the heat capacity data. Then, at the first temperature on the thermodynamic network, each of the thermodynamic properties are calculated as a function of pressure. Below the critical temperature, the calculation is carried out to the vapor pressure. At temperatures above the critical temperature, the calculation is carried out to

some pre-selected pressure, which would be the highest pressure for the particular isotherm. After the calculation is completed at the last pressure on the isotherm, the process is repeated, starting at the lowest pressure on the next highest isotherm.

Some of the equations used in the calculation are as follows:

$$H_P = H_o + \int_{P_o}^{P} \left[V - T(\partial V/\partial T)_P \right] dP \qquad (V.46)$$

$$S_P = S_o - \int_{P_o}^{P} (\partial V/\partial T)_P dP \qquad (V.13)$$

$$RT \ln (f/P) = - \int_{o}^{P} (RT/P - V) dP \qquad (V.48)$$

$$C_p = C_{po} - T \int_{P_o}^{P} (\partial^2 V/\partial T^2)_P dP \qquad (V.23)$$

$$C_v = C_p + \left\{ T(\partial V/\partial T)_P^2 \right\} \Big/ (\partial V/\partial P)_T \qquad (V.31)$$

$$\mu = \frac{T(\partial V/\partial T)_P - V}{C_p} \qquad (V.25)$$

$$a^2 = \frac{-C_p V}{T(\partial V/\partial T)_P^2 + C_p (\partial V/\partial P)_T} \qquad (V.43)$$

In order to apply these equations, various numerical techniques are used. A fifth degree least squares polynomial was found to give a good representation of volumetric data as a function of temperature, over wide pressure and temperature ranges. In the computor program the fifth degree polynomial was used to represent the input volumetric data as a function of temperature at constant pressure. The derivatives, $(\partial V/\partial T)_P$ and $(\partial^2 V/\partial T^2)_P$, were then easily calculated by differentiation. In order to calculate the specific volume and its derivatives at pressures other than for which data were measured, a five point Lagrangian interpolation polynomial was used. The least square polynomial was used first to calculate the volume and its derivatives at the desired temperature, at the measured pressures. Then the Lagrangian interpolation polynomial was used to interpolate to the desired pressure. The derivative, $(\partial V/\partial P)_T$, was also calculated by using the five point Lagrangian interpolation polynomial, which was differentiated with respect to pressure (32). When a numerical integration was required, it was done by using a three point Legendre-Gauss integration formula, which gives exact results for any function that can be represented by a fifth degree polynomial (32).

An accurate thermodynamic network can be calculated using these numerical techniques. The use of the computor does away with the drudgery of numerical and graphical smoothing of data and differentiation. Furthermore, it eliminates

the subjective judgement involved in graphical smoothing and differentiation.

2. Proposed Experiment

In order to make the best utilization of the computor program, the proper type of data should be available. Most of the required data are volumetric isobars. In order to measure the specific volume as a function of temperature, at constant pressure, a mass flowmeter may be used in series with a volumetric flowmeter. The gas under investigation passes through each meter in series, and the specific volume can be found by dividing the volumetric flow rate by the mass flow rate.

A flowsheet for the proposed experiment can be seen in Figure IV.1. The gas circulates in a closed loop, or may be vented after passing once through the system. The system consists of a gas supply, a volumetric flowmeter, a mass flowmeter and various heat exchangers, pumps and reducing valves as required to maintain the desired pressure and temperature. It is supposed that the gas will pass through the mass flowmeter at some convenient temperature and pressure. Since the mass flow rate is independent of the pressure and temperature, the specific volume is measured at the pressure and temperature at which the gas passes through the volumetric flowmeter. At each pressure, the specific volume is measured at a series of convenient temperatures. During the

series of measurements, the pressure must be held constant at some convenient value. The constant pressure heat capacity can also be measured in a flow calorimeter, using the same mass flowmeter to measure the mass flow rate.

The crucial instruments, so far as accuracy is concerned, are the mass flowmeter and the volumetric flowmeter. Suitable instruments are available commercially which are of high accuracy, and of small enough size to be suitable for experimental work. The recommended mass flowmeter is the Pottermeter model SP-157PHP, manufactured by the Potter Aeronautical Corporation (63). For measuring the volumetric flow rate, a suitable instrument is the Cox turbine flowmeter, model number Il (16). It is estimated that the specific volume of any gas may be measured to an accuracy of at least 1.0 per cent, over a wide range of temperatures and pressures. An accuracy of 1.0 per cent in the volumetric data will be sufficient for generating a thermodynamic network which will be accurate enough for most engineering purposes.

D. Calculated Thermodynamic Properties of Nitrogen

In order to test the accuracy of the numerical techniques and approximations used in the computor program, a thermodynamic network for nitrogen was calculated and the results compared with other thermodynamic networks for nitrogen found in the literature. Din's work (23) was selected

as a standard of comparison since it was the most complete
and thorough. Other works used for comparison of results
were the thermodynamic networks of Woolley (90) and of Miller
and Sullivan (57). As a source of volumetric data, for input
to the computor program, Din's tabulated specific volumes
were used. Thus, a comparison between Din's results and the
results calculated in this work would be based on exactly the
same data, and any differences would be due solely to varia-
tions in the different calculational techniques used.

The works of Woolley and Miller and Sullivan are based
on the same experimental volumetric data as Din's work (3,
33, 53, 54, 60). However, the tabulated specific volumes
in each work do not agree exactly with one another. This is
due to the different procedures used by each investigator to
smooth and round the experimental data. There are also dif-
ferences in the tabulated thermodynamic properties of each
investigator, due to the different calculational procedures
used in arriving at a final thermodynamic network. Thus,
the various thermodynamic networks, all based on the same
data, are in slight disagreement with each other. As will
be seen, the thermodynamic network, calculated in this work,
will also not agree exactly with any of the other thermo-
dynamic networks, but will be in fairly good agreement with
all of them.

Some of the results of this work, compared with the
results of the other works are shown graphically in Figures
VIII.2, VIII.4 and IX.2. In Figure VIII.2, the entropy

calculated in this work is compared with entropy values cal-
culated by Din (23), Woolley (90) and Miller and Sullivan (57).
All of the entropy values are for the 300°K isotherm, and are
plotted as a function of pressure. Din's results are used
as a reference for comparison purposes, and are shown by a
solid line. The other values, including the ones of this
work, are indicated by points on the graph. The entropy
scale is greatly enlarged so that small differences between
the various results can be seen.

In Figure VIII.4, the same type of graph is shown for
the enthalpy at 240°K. The additional points are the enthal-
pies calculated by the generalized correlation method of
Lyderson, Greenkorn and Hougen (49), and are used to compare
the differences between the generalized correlation method
and a rigorous calculation. It is seen that this generalized
correlation gives good results for nitrogen. The parallel,
dot-dash lines on the graph represent Din's estimate of the
error bounds in his calculated enthalpy values. These error
bounds represent the combined effects of errors in the exper-
imental data, and errors introduced in the numerical calcula-
tions. The enthalpy is shown on a greatly enlarged scale so
that small differences in the values of the different inves-
tigators may be seen.

The isotherms shown in Figures VIII.2 and VIII.4
represent only a portion of the thermodynamic network cal-
culated in this work. The entire network for nitrogen

covered isotherms from the saturation curve up to 700°K. A more complete comparison was made between the results of this work, and the results tabulated by Woolley and Miller and Sullivan, with Din's results, covering the complete range, where possible. In the superheated gas region, the average deviation in enthalpy between this work and Din's work was 29 joules/gmol. When Miller and Sullivan's results are compared with Din's, the average deviation is 26 joules/gmol, and when Woolley's results are compared the average deviation is 44 joules/gmol. The error estimated by Din is much larger, being about 100-250 joules/gmol in the temperature range 200°K-400°K, up to 100 atmospheres, and being much larger outside of this temperature range. The average deviations for the entropy values, in joules/gmol-°K, when compared with Din's values, are 1.09 for Miller and Sullivan, 1.16 for Woolley and 0.62 for the present work. Din's estimate of the error varies from 0.65 to 2.5 in the pressure and temperature range for which the comparisons were made.

In general, the differences found among the different thermodynamic networks, including the one calculated in this work, were not significant.

In Figure IX.2, the region in the vicinty of the saturation curve is shown on temperature entropy diagram for nitrogen. Woolley's work did not extend to the saturation region, so comparisons are made only among Din's results, Miller and Sullivan's results and the results of this work. Good agreement exists among the three saturation curves at

the lower pressures. At higher pressures along the saturation curve, especially as the critical point is approached (126.2°K and 33.5 atmospheres) the differences in the saturation curves become large. This may be expected, since the calculation of thermodynamic properties in the critical region is uncertain, regardless of the numerical method used. For example, in Din's work, the value of the entropy at the critical point had to be arbitrarily reduced by 3.2 joules/gmol-°K in order to prevent the 145°K isotherm from passing through the two phase boundary when plotted on a volume-entropy diagram.

By comparing the results obtained by different investigations, including this work, it is seen that each set of results, for entropy and enthalpy, differ by about the same amount from each other set of results. Since the results of each investigation are based on the same volumetric data, the small differences among the various sets of results are attributed to the different procedures used in smoothing and rounding the initial data, and in the different numerical methods used in calculating thermodynamic properties from the volumetric data. Thus, the different methods used for calculating the thermodynamic networks discussed here are equally satisfactory.

E. Effect of Errors in Volumetric Data on Calculated Thermo-
    dynamic Properties of Nitrogen

Din's volumetric data for nitrogen, which was used as

input to the computor program described above, has an accuracy of from 0.10 to 0.01 per cent throughout most of the superheated gas region. The accuracy of the data is much less near the critical region. In the superheated gas region, there was excellent agreement between the thermodynamic networks calculated in this work and by Din. This might be expected since the same high accuracy data were used in both instances.

If an attempt was made to calculate a thermodynamic network based on the volumetric data generated by a mass flowmeter and volumetric flowmeter, the results would be expected to be less accurate, reflecting the influence of the less accurate data. Using a mass flowmeter and volumetric flowmeter to measure specific volumes, it is expected that an accuracy of 1.0 per cent can be obtained, compared to the 0.1 to 0.01 per cent accuracy of Din's nitrogen data.

In order to see how well a thermodynamic network could be calculated from volumetric data that have errors as large as 1.0 per cent, an error of 1.0 per cent was purposely introduced into Din's volumetric data, and the calculation of the thermodynamic network for nitrogen was repeated. Two types of 1.0 per cent errors were introduced into the volumetric data. In one instance a biased error of 1.0 per cent was introduced. This consisted of putting errors of plus and minus 1.0 per cent into alternate data points. These errors would have a tendency to cancel out when the volumetric data are curve fit. The other type of error introduced

was a random error of 1.0 per cent. The criterion used was the least significant figure of each volumetric data point. If the least significant figure was an odd number, a positive error of 1.0 per cent was introduced. If the least significant figure was even, a negative error of 1.0 per cent was introduced. Thus, a random error is introduced into the data which is more realistic than the alternate 1.0 per cent error previously discussed. However, even the random error of 1.0 per cent purposely introduced into the data is not representative of an error of 1.0 per cent in experimental volumetric data.

An error of 1.0 per cent in experimental data usually means that there is some sort of error distribution, with the errors being less than 1.0 per cent at the 95 per cent confidence level. The actual error of any experimentally measured point would usually be less than the 1.0 per cent, and would take on all values, with equal probability, between minus 1.0 per cent and plus 1.0 per cent. The present case, using an error which always attains the maximum magnitude of 1.0 per cent, represents a situation which is less favorable than if actual experimental data of "1.0 per cent accuracy" were used.

A thermodynamic network for nitrogen was calculated using volumetric data containing a random error, and an alternate error of 1.0 per cent. Each of these two thermodynamic networks were compared to the thermodynamic network calculated when the "full precision" volumetric data were

used. Some of the results are shown in Figure X.3, for entropy, and in Figure X.7 for enthalpy.

In each of the figures the solid lines represent the values calculated using the method developed in this work, and using Din's full precision volumetric data for nitrogen. These results have already been compared with Din's results and were seen to be in excellent agreement. In each of the graphs, the ordinate scale is enlarged so that the small differences between the sets of results will show up more readily. In general, the results calculated from data having errors of 1.0 per cent are in excellent agreement with the results calculated from the full precision volumetric data. Only a few of these isotherms are shown, but the results are typical of those obtained for the other isotherms. It should be noted that the isotherms shown in Figures X.3 and X.7 cover the range from critical region to ideal gas region.

Since a thermodynamic network calculated from data having errors of 1.0 per cent shows no significant differences when compared with a thermodynamic network calculated from data of 0.10 to 0.01 per cent accuracy, it may be inferred that a thermodynamic network of sufficient accuracy for engineering use may be calculated from volumetric data having errors as large as 1.0 per cent.

F. Thermodynamic Properties of Ethane

In order to confirm some of the results obtained with

nitrogen, a thermodynamic network for ethane was also cal-
culated, using the computor program developed in this work.
This calculation also emphasizes the fact that the computor
program is general, and may be used for any gas for which
data is available.

The volumetric, and other data, required as input for
the computor program was taken from Tester's compilation of
the thermodynamic properties of ethane. The calculated
results are also compared with Tester's results (81) and
with Rossinis' results for ethane (73).

A pressure-enthalpy diagram is represented in Figure
XIV.C.1. For greater clarity, some of the isotherms have
been omitted, although the saturation curve is included.
The complete thermodynamic network actually obtained extends
from the saturation curve up to $500^{\circ}K$, with properties being
tabulated every ten degrees. In the superheated region,
comparisons are made among the results of Tester (81),
Rossini (73) and the present work. On the saturation curve,
comparison is made between the calculated results of the
present work and Tester's results. There is excellent agree-
ment, even on the saturation curve, between the various sets
of results. Even with the relatively large scale used for
enthalpy in Figure XIV.C.2, the difference in enthalpy
values are scarcely noticeable. These results are typical
of the more complete comparisons made throughout the entire
thermodynamic network, and for the other thermodynamic pro-
perties as well.

G.   Discussion

It has been shown that a thermodynamic network can be calculated automatically on a computor that is in good agreement with a thermodynamic network, based on the same data and calculated by conventional methods. The results for ethane are in better agreement with each other on, and near, the saturation curve, especially at the higher pressures, than the results for nitrogen. This may best be seen by examining the results plotted in Figures IX.2 and XIV.C.1. This is due to the fact that the thermodynamic network for ethane, as calculated in this work, covered a temperature range of about $300^{\circ}K$, whereas the network for nitrogen covered a range of almost $600^{\circ}K$. In the case of ethane, the volumetric data are better represented by the least squares polynomial since the polynomial covers a smaller temperature range. Comparable accuracy can be obtained for nitrogen by carrying through the calculation in two stages, so that the 600 degree temperature interval is divided into halves.

In any event, when the full precision data is used for the calculation, the results for nitrogen are in good agreement with Din's results, and the results for ethane are in good agreement with Tester's results. This indicates that the numerical techniques used in the computor program are satisfactory.

When a thermodynamic network is calculated using data of only 1.0 per cent accuracy, the final results are still

of sufficient accuracy for engineering purposes. When the
network for nitrogen calculated by Din's full precision data,
is compared with the results of Din, Woolley and Miller and
Sullivan, the differences in the thermodynamic properties
are not significant. When the network for nitrogen, calcu-
lated with Din's full precision data, is compared with the
thermodynamic network calculated from data having random
errors of 1.0 per cent, the differences between the two are
also very small. Thus, if a thermodynamic network was cal-
culated from experimental data of 1.0 per cent accuracy,
the results should be of at least sufficient accuracy for
engineering purposes.

Since it is anticipated that specific volumes of a
gas may be measured in a simple, automatic manner, by using
a mass flowmeter and volumetric flowmeter in series, to an
accuracy of about 1.0 per cent it is only necessary to use
these data as input to the computor program. Thus, a com-
plete thermodynamic network may be generated, quickly and
conveniently, for any gas. The computor program, which was
written in the fortran language for the IBM 7094 computor at
the M.I.T. Computation Center, can calculate a complete
thermodynamic network, for about 20 temperatures and pres-
sures, in less than one minute of running time.

The computor program can also be of great utility in
treating existing volumetric data in the literature. The only
restriction on the volumetric data is that it be in the form
of isobars. The pressures and temperatures at which the data
are available do not have to be evenly spaced or rounded.

II. INTRODUCTION

A. Object

The object of this thesis is to devise a semi-automatic system that would be used to generate a thermodynamic network for any gas, i.e., a relationship between pressure, temperature, entropy, enthalpy, fugacity coefficient, and heat capacity. The system is to meet the following requirements:

1. Experimental data must be obtained conveniently with simple equipment over wide ranges of pressure and temperature, and in a continuous manner.

2. The measured data should be capable of being used directly as input to a computor program which will perform the necessary calculations to produce the desired results.

3. The overall accuracy of the entire system should be such that the results obtained for any gas studied be better than any of the generalized correlations now available, i.e., about one per cent.

4. The use of commercially available equipment and instruments is desirable but not essential.

5. The analytical treatment of the data should be at least as good as any of the graphical or numerical methods previously used.

B. **Previous Work**

1. Typical Methods

In general, the thermodynamic properties of most
interest to the engineer are the enthalpy, entropy, specific
volume, and fugacity. These are all interrelated, and usually
the specific volume is measured and the other properties are
calculated from it. In most previous calculations of thermo-
dynamic networks a base value of H and S are chosen and var-
iations from this base are obtained by making use of the
fact that H and S are point functions, i.e.,

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (II.1)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad (II.2)$$

or

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{dT}\right)_P\right] dP \qquad (II.3)$$

$$dS = \frac{C_P dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad (II.4)$$

In each equation the coefficient of dT requires a knowledge
of the heat capacity, or equivalent property, over the pres-
sure and temperature range of interest, while the second
term requires volumetric data or the equivalent which will
allow calculations of isothermal changes in enthalpy and

entropy. At constant temperature, the equations become;

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad\qquad (II.5)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad\qquad (II.6)$$

In addition the isothermal change in fugacity can also be calculated,

$$RT \ln\left(\frac{f}{P}\right) = \int_0^P \left(V - \frac{RT}{P}\right) dP \qquad\qquad (II.7)$$

Equations (II.5 - II.7) allows one to calculate isothermal changes in the thermodynamic properties. In addition, one would measure the heat capacity in order to calculate iso- baric changes.

Considering isothermal changes, the main problem has been in the measurement of specific volumes and in treating the data so as to retain its precision, which usually involves laborious calculations and graphical operations. (19-23, 26, 81, 91). Although a common procedure is to carry out the calculations on the original data by a com- bination of numerical and graphical techniques, it is also possible to fit the measured data to an equation of state and use an analytical expression for further calculations (2, 5, 7, 39, 47, 70). However, one must still calculate the constants of the equation of state, usually by numerical

and graphical methods (4, 20, 42, 75). Also in calculating

thermodynamic properties, use can be made of a combination of

an equation of state and of graphical methods (85).

As a typical example one may choose H,S = 0 at some

reference temperature and pressure. The heat capacity data

are often spectroscopic in nature and apply to the ideal gas

state of zero pressure. Thus, H and S, at the reference

pressure would be calculated as a function of temperature by

the use of the heat capacity data. The pressure range is

then covered by using the volumetric data in Equation (II.5)

and (II.6).

2. Alternate Techniques

While it is not intended to give a complete review

of the literature on the data required for calculating

thermodynamic networks, mention will be made of some alter-

nate techniques. For example, there are measurements other

than specific volume and heat capacity which can be used in

calculating a thermodynamic network. In order to circumvent

the difficulty of measuring specific volume, the Joule-

Thomson coefficient can be measured and has been used in

calculating thermodynamic networks (10, 14, 70, 74). Also,

the sonic velocity has been used, with other data, in cal-

culating thermodynamic properties (44, 59, 68).

3. Some New Techniques

Although a wide variety of methods have been used previously they all have some common disadvantages. Data is collected point by point and compilations are accompanied by a large amount of tedious calculation (23). It was not until recently that some progress was made in gathering large amounts of data in a single, simple experiment, that would be convenient for calculating a thermodynamic network. Edwards (25), devised a method by which measurements could be made automatically and continuously. His system was a high pressure tank filled with gas which was to be discharged while simaltaneous and continuous measurements of pressure, temperature, and mass were being made. From the measured data, a thermodynamic network was to be generated on an analogue computor. However, heat exchange between the system and surroundings could only be roughly estimated, seriously decreasing the precision of the results. In addition, it was not possible to make mass measurements accurately by weighing the entire tank with strain gauge techniques.

Another system was devised by Chalfant (12) which required measurements of sonic velocity, Joule-Thomson coefficient and $(\partial V/\partial P)_H$. This data would have been sufficient, however it was not clear how the last parameter was to be measured. Manganero (51) devised an automatic system that used a mass flowmeter. With an accurate mass flowmeter specific volume data can readily be obtained as a function

of P and T, and a thermodynamic network calculated. This system and the mass flowmeter will be more fully discussed.

4. Automatic Computation

In addition to the experimental aspects, some work has been done on the machine computation of thermodynamic networks. Much of it has been oriented towards a single substance and a completely general program for calculating the thermodynamic properties of any substance is not in the literature. Kang and McKetta (38) calculated a thermodynamic network for sulfer dioxide on a digital computor, using data from various sources. The network was calculated directly from the data, without using an equation of state. Cornell (15) has written a computor program to calculate enthalpy and entropy in the superheated region for any gas. However, the input is rather restricted as the program calls for a compressibility table at evenly spaced pressures and temperatures. Other work in machine computation has also been done, especially in finding the constants of equations of state and using the equations to calculate the thermodynamic properties (9, 75).

C. Instruments and Measurements

Since one of the aims of this thesis is to devise an experiment which will generate the required data automatically and continuously, a flow system is to be given serious

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts
September 21, 1964

Professor Philip Franklin
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Professor Franklin:

In accordance with the regulations of the Faculty,
I herewith submit a thesis, entitled "Automatic Generation
of Thermodynamic Networks," in partial fulfillment of the
requirements for the degree of Doctor of Science in Chemi-
cal Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Gerald Gruber

Gerald Gruber

consideration. In order to decide exactly how the experiment is to be carried out and what measurements are to be made, an investigation of the basic measurements is required. Factors of interest include the accuracy and precision of measurements, the convenience of making the measurements, and the convenience of the output of the instruments for calculating thermodynamic properties. A brief review of instruments is desirable to indicate what is readily available commercially or what has been previously done experimentally. Of particular interest are instruments or measuring systems that have been proved accurate and are well tested. The detailed construction of these instruments will not be discussed, but an indication of what is available for use will be made. With the information of how well each parameter of interest can be measured, it will be possible to get at least a qualitative estimate of the accuracy of any proposed system to measure data for the generation of a thermodynamic network.

1. Pressure and Pressure Differential

Pressure measurements can be made with very high accuracy. A Bourdon Gage, for example, is capable of 0.1 per cent accuracy up to 500 psi. (87). Other commercial instruments are available (28, 58, 88) that are accurate to 0.05 per cent up to 2500 psi. A dead weight piston gage has been described that is accurate to 0.01 per cent and has a sensitivity of 0.002 per cent (36).

For differential pressure instruments, the situation is similar. Instruments are commercially available that are accurate to 0.05 per cent (29), and an instrument has been described that is capable of measuring differential pressures as low as 1 μHg (48).

Measurements of pressure and pressure differential can be made to accuracies of 0.1 per cent or better, and will present no difficulties for the intended application.

2. Temperature and Temperature Differential

The measurement of temperature and temperature difference can also be made with a high degree of accuracy. A thermocouple has been described (18) which can measure temperature differences to within 0.0002°C, and can also be used to measure and control any temperature to within the same amount by comparison with a standard temperature source by means of a suppressed voltage. A copper-constantan thermocouple was used that had a sensitivity of 4 volts/°C in conjunction with am amplification system of 0.01 μ volt sensitivity.

Resistance thermometers have also been described (43, 80) with accuracies of the same order of magnitude, which can be used over a wide range of pressures and temperatures, and have extremely fast response times.

Absolute temperatures can be measured to the same precision that the thermodynamic temperature scale is known to, and differential temperatures can be readily measured

to a thousandth of a degree Centigrade, both with small time lags.

3. Sonic Velocity

The sonic velocity is of interest since it is a thermodynamic property. It can be related to the usual thermodynamic properties, i.e.

$$a^2 = \left(\frac{\partial P}{\partial \rho}\right)_S \tag{II.8}$$

This is also a property that can be measured to a high degree of accuracy. Many methods have been described in the literature for measuring the sonic velocity of gases and liquids with accuracies ranging from 0.01 per cent to 0.1 per cent (44, 59, 68, 78, 83, 89). A typical experiment is reported by Wilson (89), which was carried for pressures up to 14,000 psi and was accurate to 0.1 meter/sec. The sonic velocity can be easily and conveniently measured to at least 0.1 per cent, which will be of sufficient accuracy for calculating other thermodynamic properties.

4. Joule-Thomson Coefficient

The Joule-Thomson coefficient is not measured directly, but is calculated from measurements of pressure and temperature. Although pressure and temperature can be measured to a high accuracy, the calculated Joule-Thomson coefficient

will be of lesser accuracy due to heat leaks during the experiment, and due to the error involved in calculating the Joule-Thomson coefficient from the measured, integral Joule-Thomson effect. Many of the older results as well as some more recent ones, show an accuracy of about one per cent in the Joule-Thomson coefficient, although the pressure and temperature measurements were of much higher accuracy (14, 37, 64, 71, 72). Recently, Reamer described an apparatus that would be capable of measuring the Joule-Thomson coefficient to an accuracy of about 0.2 per cent (66). This is extremely good accuracy, but in order to achieve it the apparatus and experiment have to be made considerably more complex than for previous Joule-Thomson experiments.

Thus, the Joule-Thomson coefficient could be obtained from measurements to an accuracy of from 0.2 per cent to 1.0 per cent, although some difficulty would be encountered in attaining the highest accuracy.

5. Isentropic Coefficient

Like the Joule-Thomson coefficient the isentropic coefficient, $(\partial T/\partial P)_S$, is not measured directly, although it can be approximated by a measurement of the integral pressure and temperature change caused by the adiabatic expansion of a gas confined in a container (8, 27, 62).

However, this type of experiment was carried out with good accuracy, and may be useful for calculating $(\partial T/\partial P)_S$,

or in measuring the relationship between temperature and pressure along an isentrope. The accuracy would be comparable to the Joule-Thomson coefficient, or to the integral Joule-Thomson effect.

6. Heat Capacity

The heat capacity of a flowing fluid can be determined by measuring the mass flow rate of the fluid, the heat input to the fluid and the temperature change of the fluid caused by the heat input. The major sources of error would be in determining the mass flow rate, and in correcting for the extraneous heat exchange. For this type of experiment, it is necessary to measure the mass flow rate. An apparatus has been described (31), that is capable of measuring heat capacities in a continuous flow system by means of a reference method, that does not require measuring the mass flow rate. The ratio of the heat capacity at any temperature and pressure is found by using two flow calorimeters in series. In one, the pressure and temperature are fixed in some convenient reference state where the heat capacity is known. In the other, the temperature and pressure are adjusted to the state at which the unknown heat capacity is to be determined. Since the unknown mass flow rate is the same in both calorimeters, the ratio of the heat capacities in the two states is found as a ratio of temperature differentials and heat inputs. The apparatus is so arranged that the heat

input ratio in the two calorimeters is equal to the ratio of the resistances of two resistors which are kept at constant temperature, outside of the apparatus. Corrections for heat loss are necessary, and are described in this paper. The accuracy would be about one per cent or better depending on the complexity of the instrumentation.

7. Volumetric Flow Rate

Since a very simple method of determining densities would be to measure mass and volumetric flow rates in series, volumetric flow meters will be of interest. Also, a combination of volumetric flow meters may be used to measure the ratio of volumes in two different states. Thus, if the density of the fluid is known in one state, it can be determined over a wide range of pressures and temperatures. This method would also be applicable if the reference state was selected to be in the liquid region.

For high accuracy measurements of the volumetric flow rate of a fluid, there are many different types of meters available. That fact that the physical properties of the fluid will be unknown rules out many types of meters. For example, with an orifice meter, the density and viscosity of the fluid should be known. In particular, the discussion will be limited to a consideration of turbine meters and positive displacement meters, as these are most convenient for measuring volumetric flow rates independently of the properties of the fluid.

Turbine meters for gases have not been as well developed as turbine meters for liquids, but they are capable of accuracies of about 0.1 per cent (56). Meters are commercially available which do attain these accuracies. For measuring gas flows as low as 1 cfm, a linearity of 0.5 per cent and a repeatability of 0.1 per cent or better can be attained. For larger flow rates, accuracies can be improved to 0.05 per cent (16).

Positive displacement meters, such as the piston or diaphragm type, are also capable of high accuracy. A commercially available diaphragm pump has recently been described (13) which has a reproducible accuracy of 0.5 per cent over a twenty-fold flow range. Inaccuracies are due, in part, to variations in pump speed. A method has been described (65) whereby the stroke rate of a piston pump could be measured and controlled to within 0.01 per cent by means of an electronic counter. An overall accuracy of 0.1 per cent in displacement can be obtained over a 6000 fold flow range. Accuracies greater than 0.1 per cent can be achieved by special maching of parts. Thus, measurements of volumetric flow rate could be made to an accuracy of about 0.1 per cent.

8. Mass Flow Rate

True mass flow meters are a recent development, some of the earliest having been described by Li and Lee (46), and by Orlando and Jennings (61). A more recent survey of

various types of mass flow meters has been given by Miesse
(55). Most of the commercially available mass flow meters
are of limited accuracy and are designed for high flow rates.
The most promising instrument for the intended application
is the "Pottermeter", manufactured by Potter Aeronautical
(63). This instrument consists of a rotor having two sets
of turbine blades with different blade angles on each,
coupled by a spring and capable of relative angular motion
with respect to each other. As a result of the blade angle
difference, the two sets of blades tend to rotate at dif-
ferent speeds, but cannot because of the spring coupling.
Thus, they take on an angular displacement with respect to
each other, the magnitude of which is directly proportional
to the flow momentum.

$$\sigma = k_o M = k_1 \rho V^2 \qquad\qquad (II.9)$$

Where M is the momentum, ρ the density and V the velocity of
the fluid, σ the angular displacement and k_o and k_1 are con-
stants. However, the rotor assembly, considered as a unit,
functions as a volumetric flow meter, rotating at a speed
proportional to the fluid velocity.

$$S = k_2 V \qquad\qquad (II.10)$$

where S is the angular velocity of the rotor assembly, and
k_2 a constant. Thus, by measuring the time interval required

for the phase angle displacement to traverse a reference point, the mass flow rate can be measured.

$$t = \sigma/S = k_0 M/S = k_1 \rho V^2/k_2 V = k_3 \rho V \qquad \text{(II.11)}$$

where $k_3 \rho V$ is directly proportional to the mass flow rate.

The smallest size meter available is for gas flows of about 10 CFM, and is capable of an accuracy of 0.5 per cent or better (6). Since this apparatus functions as a mass flow meter and a volumetric flowmeter, the single instrument can be used to measure the density of the flowing gas. The output of the meter consists of pulses, the time interval between pulses being equal to the time it takes for the phase angle difference to pass a reference point. A timer is provided to record the pulses. In addition, the frequency of rotation of the rotor assembly is measured, which is proportional to the volumetric flow rate. These quantities are printed out on paper in parallel columns at an adjustable printing rate. The rotation frequency divided by the time between pulses is directly proportional to the specific volume. For automatic input to a computer, the output can be on punched tape.

This setup is limited in range since the mass flow rate, volumetric flow rate and specific volume are not all independent. In order to achieve better accuracy and a wider range, two separate instruments should be used. A mass flow meter is used with gas passing through it at some convenient

pressure and temperature. At another point, a volumetric
flow meter is used, with the gas passing through it at the
pressure and temperature of the density determination. The
accuracy for density determination would be between 0.1 and
1.0 per cent. For mass flow rate determinations, the accuracy
would be in the same range.

D. Possible Systems

    1. Mass and Volumetric Flow Rate and Heat Capacity

    One of the most direct experiments for determining
the necessary data for the generation of a thermodynamic net-
work, is the measurement of volumetric and mass flow rates
of the same stream to determine density. The heat capacity
can also be determined in a flow calorimeter if the mass flow
is known. This experiment would consist of a mass flow meter,
volumetric flow meter and calorimeter in series in a pipe
line. The fluid is passed through the mass flow meter at
some convenient temperature and pressure, then the tempera-
ture and pressure of the flowing gas are adjusted to the
desired values for determining density and heat capacity.
The gas then passes through the calorimeter and volumetric
flowmeter, and the specific volume and heat capacity are
obtained as a function of pressure and temperature.

    In practice, there are many ways of collecting the
data. For example, the density may be measured as a func-
tion of pressure and temperature, and the heat capacity as a

function of temperature at one pressure. Then the entire thermodynamic network can be calculated using Equations (II.5-II.7). Or, the heat capacity can be measured as a function of pressure and temperature, and the density measured in a small temperature region as a function of pressure. This leads to more complicated calculations, but may be preferable overall. Then, since

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T \qquad (II.12)$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,(T=T)} = \left(\frac{\partial V}{\partial T}\right)_{P,(T=T_0)} - \int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_{T,(P=P)} dT \qquad (II.13)$$

$$V_{T,P} = V_{T_0,P} + \int_{T_0}^{T}\left(\frac{\partial V}{\partial T}\right)_{P,(T=T_0)} dT$$

$$- \int_{T_0}^{T}\int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_{T,(P=P)} dT\, dT \qquad (II.14)$$

and since $(\partial V/\partial T)_P$ at T_0 is not a function of temperature

$$V_{T,P} = V_{T_0,P} + (T-T_0)\left(\frac{\partial V}{\partial T}\right)_{P,T_0} - \int_{T_0}^{T}\int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_{T,(P=P)} dT\, dT$$

$$(II.15)$$

Equation (II.15) is integrated at various constant pressures to give the specific volume as a function of pressure and temperature. For each pressure, the specific volume and $(\partial V/\partial T)_P$ must be known at the one temperature corresponding to T_O. Thus, the density must be measured at some convenient temperature, T_O, as a function of pressure, and at some temperatures in the neighborhood of T_O so that $(\partial V/\partial T)_P$ may be calculated at T_O. Furthermore, $(\partial C_P/\partial P)_T$ must be known as a function of pressure and temperature, and can be calculated from C_P, which is measured as a function of pressure and temperature throughout the entire region. Thus, the data may be measured in different ways, even in this relatively simple system.

While the above system assumes the use of a mass flowmeter, it is possible to obtain the same information by other methods, and use the same calculational procedure. For example, if the heat capacity is known at one temperature and pressure, the mass flow rate can be determined by measuring the heat input to the gas at the temperature and pressure at which the heat capacity is known. Similarly, if the density is known at one temperature and pressure, the mass flow rate can be determined by measuring the volumetric flow rate at the pressure and temperature corresponding to the known density. These methods of measuring mass flow rate can be applied to liquids, as well as gases.

2. Joule-Thomson Coefficient and Heat Capacity

The Joule-Thomson coefficient can be measured accurately, although complicated apparatus and elaborate precautions are necessary to achieve the highest accuracy (66). In the present study, simplicity of experimental apparatus is desired, where possible. However, the Joule-Thomson experiment may be useful.

Roebuck and coworkers (71, 72), have made extensive measurements on a variety of gases. They measured the integral pressure and temperature difference, in an isenthalpic expansion, and used these data instead of the derivative $(\partial T/\partial P)_H$. Their procedure was to start at a given pressure and temperature and allow the gas to undergo a series of pressure drops of increasing magnitude, so that pressure and temperature could be measured along an isenthalp corresponding to the original pressure and temperature. This procedure is repeated for a series of different initial temperatures and pressures so that a family of isenthalps are obtained. At this point, the difference in enthalpy between any of the isenthalps is unknown. In order to assign numerical values to the isenthalps, the heat capacity must be known at one pressure as a function of temperature. If this is done, then the result would be a graph of pressure and temperature at various constant enthalpies. In order to calculate volumes over the range, the equation

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \qquad \text{(II.5)}$$

is integrated, where $(\partial H/\partial P)_T$ can be calculated from the data. Then from equation (II.5)

$$V = TV_o/T_o - T \int_{T_o}^{T} (\partial H/\partial P)_T (1/T^2) dT \qquad (II.16)$$

where the integration is carried out at constant pressure. In order to cover the entire pressure range, one isotherm must be known in order to supply V_o at each pressure of integration. Therefore, in addition to the measurements of the integral Joule-Thomson effect, the supplementary data required are heat capacity and specific volume at one pressure as a function of temperature.

Another method which requires the same supplementary data, and which uses the Joule-Thomson coefficient, consists of integrating the equation (10):

$$-(\partial C_P/\partial P)_T = \mu(\partial C_P/\partial T)_P + C_P(\partial \mu/\partial T)_P \qquad (II.17)$$

In order to carry out the integration, the heat capacity must be known as a function of temperature at one pressure. Then the resulting first-order, linear, partial differential equation is integrated numerically to give values of the heat capacity as a function of temperature and pressure. Volumes are calculated from Equation (II.15) with the aid of some supplementary volumetric data.

3. Joule-Thomson Coefficient and Isentropic Coefficient

If the isentropic coefficient $(\partial T/\partial P)_S$ could be measured, a thermodynamic network could be calculated using it and the Joule-Thomson coefficient. This would be a desirable method since only measurements of temperature and pressure would be required. The equations used may be derived as follows:

$$\mu = (\partial T/\partial P)_H = -\frac{1}{C_P}\left[V - T(\partial V/\partial T)_P\right] \qquad (II.18)$$

or

$$\mu = -(V/C_P) + (T/C_P)(\partial V/\partial T)_P \qquad (II.19)$$

$$\alpha = (\partial T/\partial P)_S = (T/C_P)(\partial V/\partial T)_P \qquad (II.20)$$

or

$$\mu = \alpha - V/C_P \qquad (II.21)$$

Combining Equations (II.20) and II.21),

$$\mu = \alpha - \alpha V/T(\partial V/\partial T)_P \qquad (II.22)$$

Equation (II.22) is rearranged and integrated to give,

$$\ln(V) = \ln(V_o) + \int_{T_o}^{T} \left[\alpha/(\alpha-\mu)\right]\, d\ln T \qquad (II.23)$$

where V_o is the specific volume at T_o and the pressure of integration. In order to cover the complete pressure range,

one isotherm of volume versus pressure must be known. On the other hand, if C_p is known as a function of pressure (from some other source, perhaps) then, from Equation (II.21)

$$V_o = (\alpha_o - \mu_o) C_{P_O} \qquad (II.24)$$

But, in either case, some supplementary information is required.

This experiment suffers from two main disadvantages. In order to obtain Joule-Thomson data of high accuracy, elaborate apparatus is required, and the measurement of the isentropic coefficient also presents difficulties. In both cases, the differential coefficients must be calculated from finite difference measurements, which introduces an error.

If a gas could be expanded adiabatically and reversably, a possibility exists for measuring the isentropic coefficient. An isentropic flow is approximated in large nozzles, but in a small nozzle, suitable for experimental work, irreversibilities would be expected to be large due to the relatively high wall friction and heat transfer. One might estimate pressure losses due to friction, and thus estimate what the pressure should be for a truly isentropic flow. This, however, requires a knowledge of the properties of the fluid, which are as yet unmeasured. However, it might be possible to estimate a true isentropic coefficient from a measured coefficient with approximate fluid properties, and use the

corrected isentropic coefficient to calculate a better approximation to the fluid properties. This suggests an iterative procedure which may lead to useful results.

However, the actual measurement of an isentropic coefficient, even approximately, might not be possible to carry out in a flow system. In a Joule-Thomson experiment, under isenthalpic flow conditions, the temperature drop is caused by an irreversible pressure drop. In an isentropic flow, the temperature drop is caused by a reversible pressure drop due to a change in flow area, which converts thermal energy to velocity (kinetic energy). If the free-stream gas temperature, and not the recovery temperature could be measured, this system might be feasible. It may be possible to obtain the desired data in a different type of experiment, one in which the gas does mechanical work as it expands adiabatically. One example would be a high pressure piston in which the gas is allowed to expand. This type of experiment no longer has the desirable feature of continuous flow, although this type of work has been carried out with results of good accuracy (<u>8</u>, <u>27</u>, <u>62</u>).

4. Sonic Velocity and Pressure-Temperature Along an Isentrope

Taken by itself, the sonic velocity is not too useful, although it is an easily made, direct measure of a thermodynamic property. Too many unknown parameters are involved, i.e.,

$$a^2 = (\partial P/\partial \rho)_S = -V^2(\partial P/\partial V)_S \qquad (II.25)$$

Combined with the isentropic coefficient, the result would be:

$$\left(\frac{V}{a}\right)^2 = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial T}{\partial P}\right)_S - \left(\frac{\partial T}{\partial P}\right)_V\right] \qquad (II.26)$$

which is still not very convenient for calculating volume-tric behavior. Adding additional measured quantities, such as the Joule-Thomson coefficient, still does not help very much, i.e.,

$$\mu T\left(\frac{\partial V}{\partial T}\right)_P = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\left[\left(\frac{\partial T}{\partial P}\right)_V + \frac{V^2}{a^2(\partial V/\partial T)_P}\right] \qquad (II.27)$$

However, using the sonic velocity, and the relationship between pressure and temperature along an isentrope, a thermodynamic network can be calculated in a rather roundabout way, although no supplementary data will be required. Let

$$\sigma = (\partial P/\partial \rho)_S \qquad (II.28)$$

which is obtained by measuring the sonic velocity over a complete range of pressures and temperatures. Thus, from direct measurements,

$$\sigma = f_1(P,T) \qquad \text{or} \qquad P = f_2(\sigma,T) \qquad (II.29)$$

Now the results of an experiment that measures pressure and temperature along an isentrope must be available. This may

be measured in an expansion type process as was proposed for $(\partial T/\partial P)_S$. Thus, it will be assumed that values of f_3 and f_4 are known, where

$$P = f_3(T) \qquad \text{at constant entropy} \qquad (II.30)$$

or

$$T = f_4(P) \qquad \text{at constant entropy} \qquad (II.31)$$

Then, if Equation (II.31) is substituted into Equation (II.29)

$$\sigma = f_1(P, f_4(P)) = f_5(P) \qquad \text{at constant entropy} \qquad (II.32)$$

Now, from the measurements, the functional relationship between σ and pressure has been deduced along an isentrope. This is known for a number of different entropies, covering the entire range, but at present numerical values cannot be assigned to the isentropes. However, for each isentrope, a pressure corresponding to any given temperature is known. If an integration is carried out along each isentrope, the result is given by

$$\rho = \int_{P_o}^{P} (1/f_5(P))\,dP + \rho_o \qquad \text{at constant entropy} \qquad (II.33)$$

where ρ_o is the density at P_o at the entropy of integration. But from Equation (II.31), the temperature on the isentrope, corresponding to P_o, is known. Therefore, ρ_o is the density at P_o and T_o, where T_o is given by

$$T_0 = f_4(P_0) \qquad \text{at constant entropy} \qquad \text{(II.31)}$$

Assuming that a value can be assigned to ρ_0, the density can be determined as a function of pressure at constant entropy by carrying out the integration indicated by Equation (II.33). Thus, the following relationships may be obtained:

$$V = f_6(P) \qquad \text{at constant entropy} \qquad \text{II.34)}$$

$$V = f_6(f_3(T)) = f_7(T) \quad \text{at constant entropy} \quad \text{(II.35)}$$

The specific volume as a function of pressure and temperature has now been established. In order to assign numerical values to the isentropes, the thermodynamic relation

$$(\partial V/\partial T)_S = -(\partial S/\partial P)_V \qquad \qquad \text{(II.36)}$$

is integrated at constant volume, to give the entropy as a function of pressure. Then the entropy can be expressed as a function of pressure and temperature, and enough data is now available to calculate all of the other properties of interest.

The constant of integration, ρ_0, in Equation (II.33) has to be evaluated. It might be thought that by carrying the integration down to a low pressure, the ideal gas region may be reached and ρ_0 could be taken as the ideal value. However, on closer examination, this is seen to be untrue,

since the integration is carried out at constant entropy, and in reducing the pressure, the temperature must also be reduced. In the high entropy region, reducing the pressure may lead to an ideal gas region, so that ρ_0 may be taken as the ideal value. In the low entropy region, however, the ideal gas region may not be reached by reducing the pressure, at constant entropy, because condensation may occur. Therefore, some supplementary data must be obtained so that ρ_0 can be evaluated in the low entropy region.

This method does not have the disadvantage of requiring heat capacity data, or of requiring measurements of the Joule-Thomson coefficient. It does suffer from the requirement that the pressure must be measured as a function of temperature along an isentrope.

5. Vapor Pressure

Up to this point the discussion has been confined to the superheated gas region, although some of the procedures are applicable to the homogeneous liquid, as well. For completeness, a thermodynamic network should include a vapor pressure curve, which serves as a boundary between gas and liquid. Regardless of the method used for generating a thermodynamic network in the homogeneous region, a determination of the vapor pressure will serve as a useful addition, especially if it can be done automatically, simply and accurately. Fortunately, such a procedure already exists.

The method was described by Spauschus (79) and fits in remarkably well with the rest of this thesis, as it is a completely automatic system for measuring vapor pressure data. The apparatus consists of a high pressure cell, connected to a gas handling system from which condensable gases are introduced. The cell is confined in a temperature controlled cabinet where it can be heated or cooled. During the experiment the contents of the cell are magnetically stirred to ensure vapor-liquid equilibrium, and the pressure and temperature are recorded at discrete intervals. The pressure measurements were made with a Consolidated Electrodynamics Engineering Corporation electromanometer, model 37-103, which has a range of 0-35 atm., and is linear to 0.05 per cent. Temperature measurements were made by a Leeds and Northrup model 816B platinum resistance thermometer, accurate to $0.01^{\circ}C$. The thermometer is placed in a well in the pressure cell, below the liquid-gas interface. The cell is heated continuously at a rate of about $0.3^{\circ}C/min.$, which is slow enough to maintain equilibrium. The resistance of the thermometer is measured by a bridge circuit, with the bridge set to a predetermined resistance. A galvanometer follows the unbalance in the bridge circuit, and when the unbalance in the circuit becomes zero at the pre-set resistance, a reading of pressure and temperature is taken simultaneously. After the reading, the resistance is automatically advanced, creating a new unbalance. In this way, readings can be taken automatically at preselected temperatures.

The data are taken on punched paper tape, and are fed directly to a computor which calculates the constants in a vapor pressure equation.

To test the apparatus, the vapor pressure of dichloro-difluoro-methane (CCl_2F_2) was measured. The results compared extremely well with other values found in the literature (30, 41, 52) and the method appears to give as accurate data as any of the other procedures, and has the advantage of being completely automatic.

Thus, with a simple auxiliary experiment, accurate vapor pressures may be included with the thermodynamic network.

6. Other Systems

Using the basic component measurements such as mass flow rate, volumetric flow rate, sonic velocity, etc., it is possible to imagine other combinations to form a system capable of measuring the necessary data to generate a thermodynamic network. However, other possible systems will not be discussed, or even listed, but it is merely pointed out that other combinations do exist.

E. Selection of System

In order to select a system for further detailed study, it will be helpful to review the desired character-istics of the system. The proposed experiment should be

convenient and simple to carry out. The instrumentation
should be available, and all the necessary techniques estab-
lished. While not essential, the instruments, or measuring
systems, should be available commercially. Within these
limitations, the accuracy of the measurements and overall
results should be as high as possible, and the proposed
experiment should be standardized so that the same type of
data is generated each time. Also, the proposed system
should be capable of generating the large amount of data
required automatically and continuously. The data generated
must be amenable to treatment on a high-speed digital computor
with little or no loss in accuracy.

With these requirements, an excellent system would
consist of only measurements of pressure and temperature,
and possibly sonic velocity, since it is these variables
that can be measured easily and to high accuracy. While a
system of this type might lead to complex and roundabout
calculations, it may be preferable to a more straight for-
ward system, since any loss in precision in carrying out
complex calculations on a computor would be compensated for
by a higher initial accuracy of data, and, thus a higher
overall accuracy of the final results. One possibility is
the combination of Joule-Thomson coefficient and isentropic
coefficient data. However, this system also requires some
additional data, and even though pressures and temperatures
can be measured to a high precision, the Joule-Thomson

coefficient cannot be measured too accurately, except with
the most elaborate apparatus. Also, the measurement of the
isentropic coefficient cannot be carried out conveniently in
a flow experiment. In addition, in both of these measure-
ments, the true conditions only approximate the ideal condi-
tions, which are isenthalpic in one case and isentropic in
the other. Therefore, various corrections would have to be
applied to the measurements, which would make it inconven-
ient for automatic computation. Although this is an inter-
esting system, it is beset with experimental difficulties
and better possibilities exist.

Another possible system would be the one which com-
bines the sonic velocity and the measurement of the pressure-
temperature relationship along an isentrope. Many of the
disadvantages of the Joule-Thomson, isentropic coefficient
method are by-passed. A new variable, the sonic velocity
has to be measured, but this can be done simply and accurate-
ly. Measuring the pressure-temperature relationship along
an isentrope has also been carried out to a fair accuracy,
although this experiment also requires corrections to data.
Additionally, the experiment is not done in a flow system
and is not easily automated. Another disadvantage of this
method is the complex calculation required to arrive at a
thermodynamic network. The complexity of the calculation is
not significant because of the time required to carry out a
calculation, but due to the fact that in repeated numerical
operations, small errors, present initially, tend to propagate

and accumulate. Although this system is feasible, it is not too promising for use as an automatic method.

If the Joule-Thomson experiment is removed from consideration as a component of possible systems, the remaining possibilities require the measurement of density, combined with heat capacity or equivalent data. For density, the use of a mass flowmeter and volumetric flowmeter is preferred, since they can be operated continuously and automatically. Although the heat capacity can be measured in a flow calorimeter, heat loss corrections are required for precise results, which makes the experiment inconvenient, although feasible. The use of a mass flowmeter and volumetric flowmeter to measure density is straight forward and convenient, and its utility is limited only by the accuracy which may be obtained. The data generated can be treated in a relatively simple and direct calculation to give the desired results, and extremely high accuracy in the initial data is not as important as in some of the other systems. Indeed, a system which makes use of a mass flowmeter appears to be the most promising, in spite of the relatively low accuracy of the mass flowmeter and the overall simplicity of the system.

Thus, the selected system will consist of mass and volumetric flowmeters to measure densities. Instead of measuring heat capacities directly, it is proposed that they may be calculated from a combination of the sonic velocity and P-V-T data.

$$C_P = \frac{-T(\partial V/\partial T)_P{}^2}{(\partial V/\partial P)_T + (V^2/a^2)} \qquad\qquad \text{(II.37)}$$

Since the sonic velocity can be measured more accurately then the heat capacity, it is anticipated that the calculated heat capacity will be at least as accurate as it would have been if it were measured, provided that sufficiently accurate volumetric data are available. In fact, the choice of measuring heat capacity or sonic velocity will not change the computor program greatly, as it can easily be set up to take care of either possibility.

Thus, the system selected for detailed study will consist of a mass flowmeter and volumetric flowmeter to measure densities, and the sonic velocity will be included to calculate heat capacities and complete the thermodynamic network. This system has the advantage that no assumptions are required as to the state of the system. For example, in the Joule-Thomson experiment it is assumed that the flow is isenthalpic, which will not be true in general. Similarly, it is impossible to achieve a perfect isentropic system, as may be required in some experiments, and likewise, in measuring heat capacities, extraneous heat leaks are unavoidable. In the present system, none of these factors are relevant, which is a decided advantage in carrying out the calculations in a standardized and automatic manner. Finally, to round out the system, an independent measurement of the vapor pressure is necessary. This is an experiment that is carried out independently.

III. PRELIMINARY CALCULATIONS

In carrying out the proposed experiment as described in Section (II.E), a large amount of data will be measured. The bulk of this data will consist of volumetric isobars. Some preliminary calculations were carried out in order to evaluate, quantitatively, various methods of converting these data into a thermodynamic network.

A part of the calculation will consist of the following: given a set of specific volumes at temperatures, T_i, and pressures, P_i, calculate   a set of specific volumes at temperatures, T_j, and pressures, P_j. This type of calculation will comprise a large portion of the computor program, and there is more than one way in which it can be carried out.

Other preliminary calculations that were made were the calculations of heat capacities from sonic velocity and volumetric data, the effect of error propagation and some examination of the results that would be achieved if the gas were ideal. Some of the preliminary calculations were carried out to insure that reasonable results could be achieved before embarking on a full scale program.

Volumetric isobars, and other data used in the preliminary calculations were taken from published values for nitrogen (23) and water vapor (40).

A. Treatment of Measured Data

1. Selection of Method

Some technique is required to convert the isobars of specific volume, heat capacity, or sonic velocity into some convenient analytical form for further calculations. The discussion will be confined to the treatment of the specific volume isobars, since the method used for the others will be the same.

One possibility would be to store all of the experimental volumes at the measured pressure and temperature, using interpolation techniques to find volumes at other pressures and temperatures, and for calculating derivatives as well. The simplest interpolation process is linear, which consists in finding the desired value from two surrounding points. This is equivalent to passing a straight line through the points and calculating intermediate points on the line. This process can be improved by fitting a parabola to three neighboring points, and calculating intermediate points as if they were on the same parabola. This process is also known as the three point interpolation. Similarly, the process can be extended to four or more points.

If the data were exactly linear then two point interpolation would yield exact results. If the data followed a second degree curve exactly (parabola), then three point interpolation would be exact. In general, n-point

interpolation would be exact if the data could be represented exactly by a polynomial of degree (n-1). The actual interpolation may be done by a number of different numerical procedures, depending on the data and the type of calculation.

Using interpolation procedures to handle the initial data, however, is inconvenient. For one thing it means that all of the measured data must be stored during the operation of the program. This is inconvenient, but it can be stored on tapes and does not have to be in the core of the program. The major disadvantage, however, is that the raw experimental data should be smoothed. This is especially true when subsequent operations require a differentiation of the data by numerical methods.

To circumvent these difficulties it was decided to use a least-squares curve fit to represent the initial data. For each measured isobar, the coefficients are calculated for an expression of the type

$$V = \sum_i a_i T^{i-1} \qquad (III.1)$$

Thus, for each measured isobar, it is only necessary to store the coefficients a_i. In addition to giving the best representation of the measured data the least-squares curve fit also smoothes the data.

2. Least-Squares Curve Fitting

As a preliminary calculation it was decided to fit

the various volumetric isobars by the method of the least-squares in order to answer the following questions:

1. What would be the best degree of polynomial to use in the curve fit.

2. How well could the data be fitted to polynomials of various degrees.

3. How is the accuracy of the approximation related to the number of experimental points used and to the spacing of the points.

4. How well could the derivative be calculated.

5. How well could errors be estimated in the final results of the curve fit.

Implicit in these questions is the assumption that the data for various gases, under a wide range of conditions, could also be adequately represented by the same type of polynomial. This assumption is reasonable, as all gases do show the same general type of behavior, i.e., the law of corresponding states. Furthermore, if a good representation can be achieved in the critical region, then it is assumed that a good representation can also be achieved in an ideal region, or in other regions, using the same type of polynomial.

The answers to these questions would aid in planning the structure of the computor program for generating a thermodynamic network. Also, the resulting program for these perliminary calculations could also be incorporated into the

final program. Thus, it was decided to program a routine for carrying out the least-squares curve fit. The data input to this program would be sets of specific volumes and temperatures at various constant pressures. The constants for least square polynomial would be calculated for polynomials of different degrees. From the data points that are input, the program could selectively operate on only some of them. For example, it could select every other point, or every third point to curve fit. Also, the program could select points at the low, middle, or high range of the data, and it could also select as many total points as desired. In this manner, the effect of spacing, range and thermodynamic region of fit could be varied. In addition to varying these parameters, the program could also make estimates of the error associated with the curve fit. The output of the program would be the coefficients of the curve-fitting polynomial, the calculated volume at each point that was input, as well as the input volume, and the root mean square error.

3. Curve Fitting Analysis

The following procedure has been adapted, with some changes, from Hildebrand (32).

Suppose that the true function $f(x)$ is to be represented by an approximation $y(x)$ in a certain region. The criterion of how good the approximation is can be expressed quantitatively by requiring that the sum of the squares of

the differences between the true function and the approxima-
tion be a minimum over the range. If the approximation is
expressed in the form

$$y(x) = \sum_{k=0}^{n} a_k x^k \qquad (III.2)$$

then the difference between the true function and the appro-
ximation, at some point x is expressed as

$$R(x) = f(x) - \sum_{k=0}^{n} a_k x^k = f(x) - y(x) \qquad (III.3)$$

The best approximation in the least squares sense, would be
the one that makes the sum (or integral, for a continuous
distribution) of $R^2(x)$ over the region, a minimum. Since
the present discussion will be limited to a region of dis-
crete points the requirement is that the sum of $R^2(x)$ be a
minimum. Or

$$\sum_{i=0}^{N} \left\{ f(x_i) - \sum_{k=0}^{n} a_k x_i^k \right\}^2 = \text{minimum} \qquad (III.4)$$

Thus, the constants in the polynomial must be calculated so
that Equation (III.4) is satisfied. This condition will be
satisfied if, for each of the a_k (k = o, 1, 2, 3, ..., n)

$$\frac{\partial}{\partial a_r} \left(\sum_{i=0}^{N} \left\{ f(x_i) - \sum_{k=0}^{n} a_k x_i^k \right\}^2 \right) = 0, \qquad (III.5)$$

$$(r = 0, 1, 2, ..., n)$$

Carrying out the indicated differentiation, the result is

$$\sum_{i=0}^{N} \sum_{k=0}^{n} (a_k x_i^{r+k}) = \sum_{i=0}^{N} x_i^r f(x_i) \quad, \qquad (III.6)$$

$$(r = 0, 1, 2, \ldots n)$$

which leads to $n+1$ linear equations in the $n+1$ unknowns $a_0, a_1, \ldots a_n$. Thus, the constants for the polynomial can be evaluated by solving the set of linear equations (III.6), or normal equations, as they are sometimes called. If the function, $f(x)$, is known exactly, then

$$\overline{E}_{RMS} = \left[\sum_{i=0}^{N} \frac{f(x_i) - y(x_i)}{N + 1}^2 \right]^{1/2} \qquad (III.7)$$

is defined as the root mean square error of the approximation. Frequently, as in the present case, the true function, $f(x)$, is not known, but only a measured approximation to it, $\overline{f}(x)$. If it is assumed that the true function can be exactly represented by the least square polynomial, but due to random errors in the measurements this exact fit is not achieved, then some additional information may be derived.

If $f(x_i)$ is replaced by $\overline{f}(x_i)$ in Equation (III.6) so that the coefficients are calculated to correspond to the measured $\overline{f}(x_i)$, then

$$\overline{f}(x_i) = \sum_{k=0}^{n} \overline{a}_k x_i^k \qquad (III.8)$$

whereas the proper equations are given by

$$f(x_i) = \sum_{k=0}^{n} a_k x_i^{\,k} = \overline{f}(x_i) + e(x_i) \qquad\qquad \text{(III.9)}$$

where $e(x_i)$ is the error associated with the observed value $\overline{f}(x_i)$. The normal equations (III.6) can then be written by replacing a by $\overline{a}$.

$$\sum_{i=0}^{N} \sum_{k=0}^{n} \overline{a}_k x_i^{\,r+k} = \sum_{i=0}^{N} x_i^{\,r}\, \overline{f}(x_i) \quad , \qquad\qquad \text{(III.10)}$$

$$(r = 0,\ 1,\ \ldots,\ n)$$

The corresponding approximation to the function at x_i can be represented by $\overline{y}(x_i) = \sum \overline{a}_k x_i^{\,k}$, and the residual is given by

$$\overline{R}(x_i) = \overline{f}(x_i) - \overline{y}(x_i) \qquad\qquad \text{(III.11)}$$

The normal equations may be represented by writting the coefficient array for the set of linear equations. The array will be the same for Equations (III.10) and (III.6). For example, if A_{rk} is the element of the row r and column k, then

$$A_{rk} = \sum_{i=0}^{N} x_i^{\,r+k} \qquad\qquad \text{(III.12)}$$

If B_{rk} is the cofactor of A_{rk} in the coefficient array

$$
\begin{array}{cccc}
A_{00} & A_{01} & \cdots\cdots & A_{0n} \\
A_{10} & A_{11} & \cdots\cdots & A_{1n} \\
\multicolumn{4}{c}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \\
A_{n0} & A_{n1} & \cdots\cdots & A_{nn}
\end{array}
\qquad\text{(III.13)}
$$

and C_{rk} is the reduced cofactor, $C_{rk} = B_{rk}/D$, where D is the determinant of the array, and noticing that $C_{rk} = C_{kr}$ since the array is symmetrical, then the solution of the set (III.10) is

$$
\bar{a}_r = \sum_{i=0}^{N} \left\{ \sum_{k=0}^{n} C_{rk} x_i^{\,k} \right\} \bar{f}(x_i) \qquad\text{(III.14)}
$$

Similarly, a_r is given by

$$
a_r = \sum_{i=0}^{N} \left\{ \sum_{k=0}^{n} C_{rk} x_i^{\,k} \right\} f(x_i) \qquad\text{(III.15)}
$$

Subtracting Equation (III.14) from Equation (III.15) the result is

$$
(a_r - \bar{a}_r) = \sum_{i=0}^{N} \left\{ \left(\sum_{k=0}^{n} C_{rk} x_i^{\,k} \right) \left(f(x_i) - \bar{f}(x_i) \right) \right\} \qquad\text{(III.16)}
$$

or using the definition of $e(x_i)$ from Equation (III.9)

$$
(a_r - \bar{a}_r) = \sum_{i=0}^{N} \left\{ \left(\sum_{k=0}^{n} C_{rk} x_i^{\,k} \right) e(x_i) \right\} \qquad\text{(III.17)}
$$

This relationship gives the difference between the coefficients actually obtained and those which would have been obtained if no round-off error was present. It is based on the assumption that the data could be fit exactly to a polynomial if there were no errors in the data. Since the error, $e(x_1)$, of a measurement, can only be estimated, only an estimate can be made of the absolute magnitude of the error in the calculation coefficient, $\bar{a}_r$. For the overall measure of the fit, there are two other root mean square errors of interest. It can be shown (32) that

$$\bar{e}_{RMS} = \left[\frac{\sum_{1=0}^{N} (\bar{R}(x_1))^2}{N + 1} \right]^{1/2}$$
(III.18)

measures the root mean square deviation between the observed function and its calculated approximation over the N + 1 points involved. In the case where it is assumed that the true function can be exactly represented by a polynomial,

$$E_{RMS} = \left(\sum_{1=0}^{N} (\bar{R}(x_1))^2 / N - n \right)^{1/2}$$
(III.19)

represents the root mean square deviation between the true function and the observed function. In Equation (III.19), N - n is the number of points used less the degree of the polynomial.

In the present work, none of the equations apply exactly. The measurements are inexact and the representation

of the data by a given polynomial is only an approximation.
However, the results may be useful in getting reasonable
estimates of errors.

4. Results of Curve Fitting Experiments

A small computor program was set up to solve Equations (III.6) and carry out some other calculations which
will be explained. The fortran listing of the curve-fitting
program will be found in Appnedix A.

In order to invert the coefficient matrix of Equations (III.6), a modification of the Crout reduction (17)
was used. The coefficients were then adjusted by an iterative calculation in order to reduce round-off errors. At
first, the inverse of the coefficient matrix was calculated
in order to estimate $(a_r - \bar{a}_r)$ from Equation (III.17).
Since the elements of the inverse matrix can be identified
with the corresponding reduced cofactors, C_{rk}, Equation
(III.17) can be used if $e(x_1)$ were known. However, $e(x_1)$
is the error in an observation, which can only be estimated.
It was hoped that by assigning a maximum bound to $e(x_1)$,
then a maximum bound for each $(a_r - \bar{a}_r)$ could be estimated.
Then, if an upper bound for the error in each coefficient or
the least squares polynomial were known, an upper bound could
be estimated for the error in the derivative. For example,
if the specific volume is curve-fit as a polynomial in
temperature as

$$V = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5 \qquad \text{(III.20)}$$

Then

$$\frac{dV}{dT} = a_1 + 2a_2T + 3a_3T^2 + 4a_4T^3 + 5a_5T^4 \qquad \text{(III.21)}$$

Then if an upper bound for the error in each a_r is known the upper bound for the error in dV/dT could be estimated. Similarly, the upper bounds for errors in any other property that is subsequently calculated from V and/or dV/dT could be estimated. This way, an upper bound for errors could be a priori predicted for any property which is calculated. If the upper bounds are small enough to be negligible, then a good deal of confidence could be placed in the calculation. If the upper bounds are so large as to be unreasonable, it does not mean that the procedure is unrealistic, but that the error estimates are too conservative, and some other means is required for assessing the value of the calculation. Unfortunately, it turned out that the error estimates were too conservative to be useful.

For example, a third degree polynomial was fit to 13 volume-temperature points for water vapor at 3300 psia. The volumes ranged from 0.16 to 0.26 cubic feet per pound, and temperatures ranged from 1280 to 1610 degrees Rankine. An estimate of $e(V_i)$ of 0.0002 was made for all V_i which was realistic. The calculated $\bar{e}_{RMS}$ from Equation (III.18) was 0.000188, and the calculated E_{RMS} from Equation (III.19)

was 0.000226. These values indicate that the true function can be adequately represented by a third degree polynomial. The four calculated errors, $a_r - \bar{a}_r$, varied from six to eight per cent of the calculated a_r. The upper bound for the error in the derivative was calculated, and it is about 300 per cent of the value. The reason for this is that the derivative is relatively small and is calculated as the sum of two large positive terms and two large negative terms. The upper error bound of the derivative is calculated as the root mean square value of the terms, so the plus and minus terms do not cancel out. Also, in calculating the error in the coefficient, it is assumed that the estimated error in the data, $e(V_i)$, always attains the maximum value of 0.0002, and always has the most unfavorable sign, plus or minus, While this is unrealistic, it was hoped that the error estimates would still be small enough to be useful. A more reasonable estimate could have been obtained by assuming a distribution of $e(V_i)$, so that it varies from -0.0002 to +0.0002, and thus carrying through a statistical analysis and calculating the anticipated errors at each step in the calculation. This would involve calculating the errors in the entropy and enthalpy from the errors in the specific volumes. However, this becomes rather complicated, and as will be seen later, a better method is available for assessing the accuracy of the calculation.

Consequently, the portion of the program that carried out the error calculation was deleted, and the program was

further modified since it was no longer necessary to find the inverse of the coefficient matrix.

5. Selection of Polynomial

A computor program for fitting data to a least-squares polynomial was set up. Published results for steam (40) and nitrogen (23) were used as the source of data, and as a comparison for the calculations. Volumes and temperatures on an isobar were taken as input in groups ranging from 8 to 29 points and various constant pressures. Also, the spacing between the points was varied. The output of the preliminary computor program were the coefficients of a polynomial which related volume to temperature, the calculated volume corresponding to each input point, the derivative of volume with respect to temperature at each input point and the root mean square error between the calculated and input volumes, $\bar{e}_{rms}$, and the root mean square error between the calculated results and the "true" function, E_{rms}. For a given set of conditions the program was run to curve fit the data to various degree polynomials from two to seven. Then each root mean square error was plotted against the degree of the polynomial. This was done over a wide range of conditions as mentioned above. The behavior of all the curves followed the same pattern. The root mean square deviation, $\bar{e}_{rms}$, at first decreased sharply as the degree of the polynomial was increased, and then leveled off, usually quite sharply. Thus, the fit is
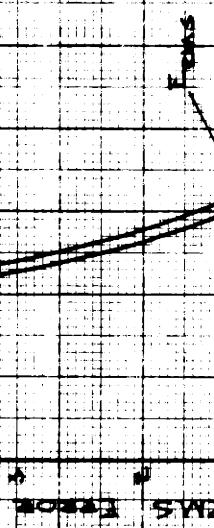
continuously improved up to a point, and thereafter little, or no, improvement is effected by increasing the degree of the curve fitting polynomial. The reason for this is that when the leveling off begins the data are essentially fitted to the correct degree of polynomial. By increasing the degree of polynomial only small perturbations in the data are fitted which do not reflect any serious departure from a smooth curve.

In all of the cases examined, the leveling off occurred when the degree of the curve fitting polynomial was 4 or 5. For this reason, a curve fitting polynomial of the fifth degree was selected to represent all of the isobars. By eliminating this parameter (the degree of the polynomial) the final program is greatly simplified. Some of these results are shown in Figures III.1 to III.4, where $\bar{e}_{rms}$ and E_{rms} are plotted against the degree of curve fitting polynomial for various situations. Selecting a fifth degree polynomial in this manner insures that the calculated volumes agree with the measured volumes. However, one of the purposes of the least squares curve fit is to calculate the derivative $(\partial V/\partial T)_P$. The data can always be represented by using a high enough degree of polynomial. However, if the data are followed so closely that every random variation is followed, then the calculation of the derivative will be in error.

To insure that the calculated derivative was a good approximation, the calculated derivative was plotted versus
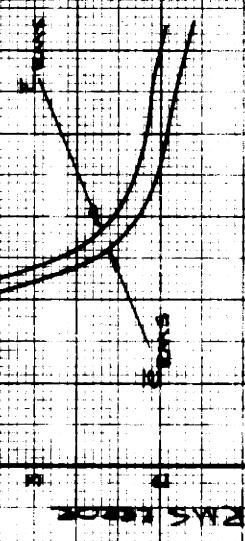
68

Figure III.1

Figure III.2

69

FIGURE III A

H_2O 3300 psia
15 Points
1150°R — 1610°R

RMS ERROR × 10³

DEGREE OF POLYNOMIAL

ROOT MEAN SQUARE ERROR FOR
LEAST SQUARES POLYNOMIAL

FIGURE III B

H_2O 3500 psia
24 Points
1150°R — 1610°R

RMS ERROR × 10³

DEGREE OF POLYNOMIAL

ROOT MEAN SQUARE ERROR FOR
LEAST SQUARES POLYNOMIAL
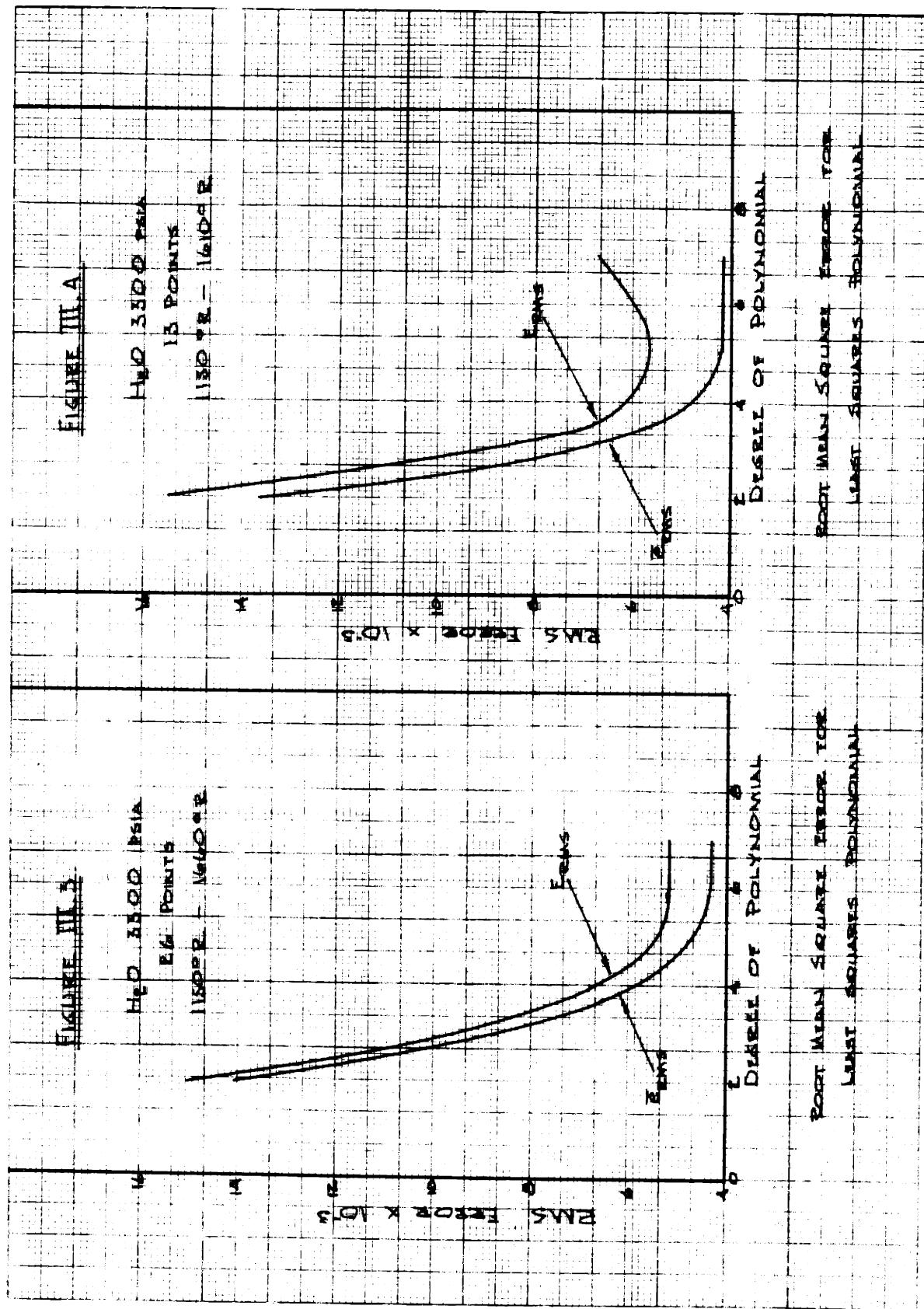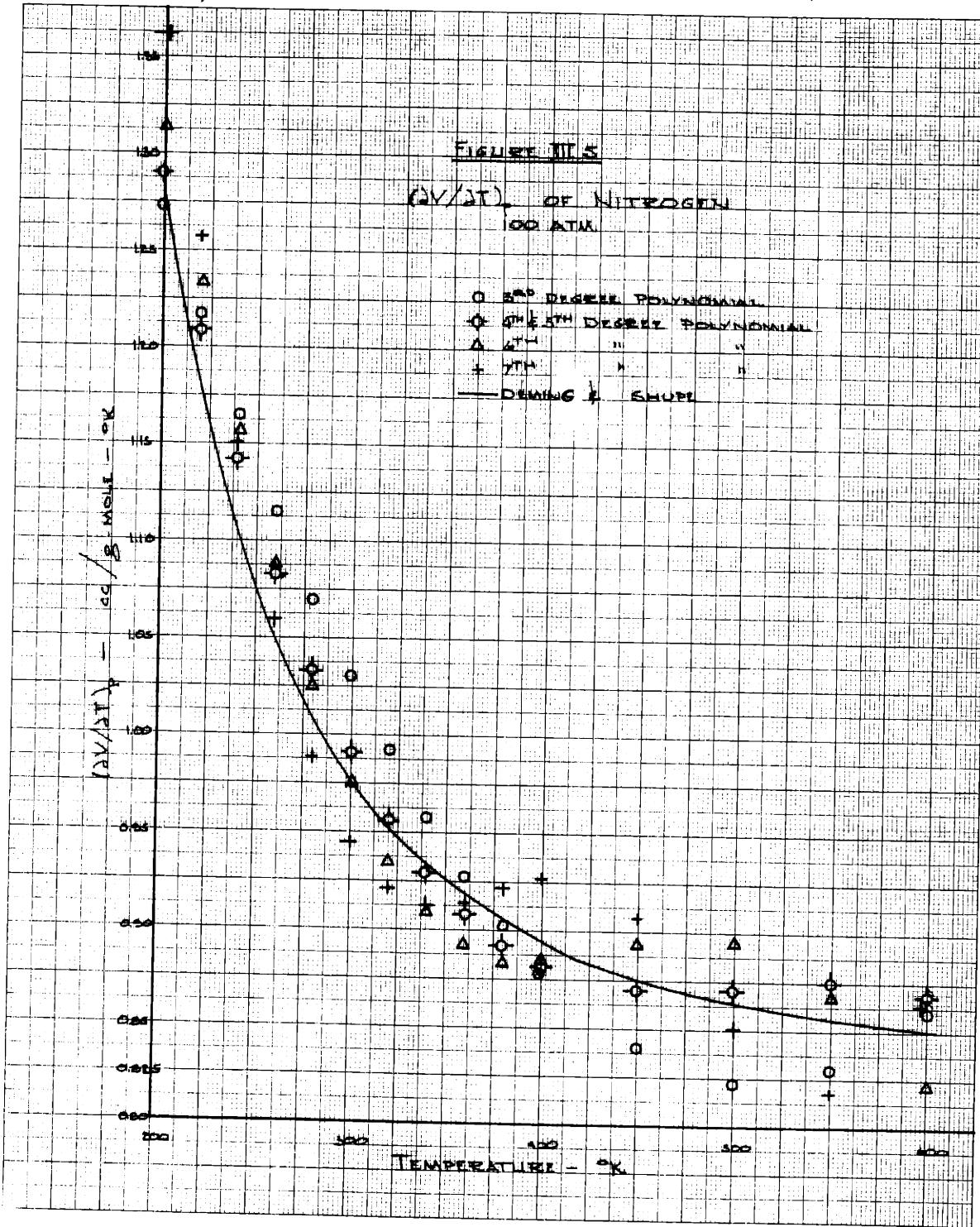
temperature for various degrees of polynomial. When the data are being overfitted, i.e., the degree of polynomial is too high, the calculated derivatives begin to show wide variations. A number of these graphs were constructed for nitrogen and water vapor at various constant pressures, using various spacings and numbers of data points. In addition, an independent approximation to the true derivative was made by the method of Deming and Shupe ([21]), which has been proven reliable for estimating $(\partial V/\partial T)_P$. If the residual volume, α, is defined as

$$\alpha = V - \frac{RT}{P} \qquad \qquad \text{(III.22)}$$

then

$$(\partial V/\partial T)_P = R/P + (\partial \alpha/\partial T)_P \qquad \qquad \text{(III.23)}$$
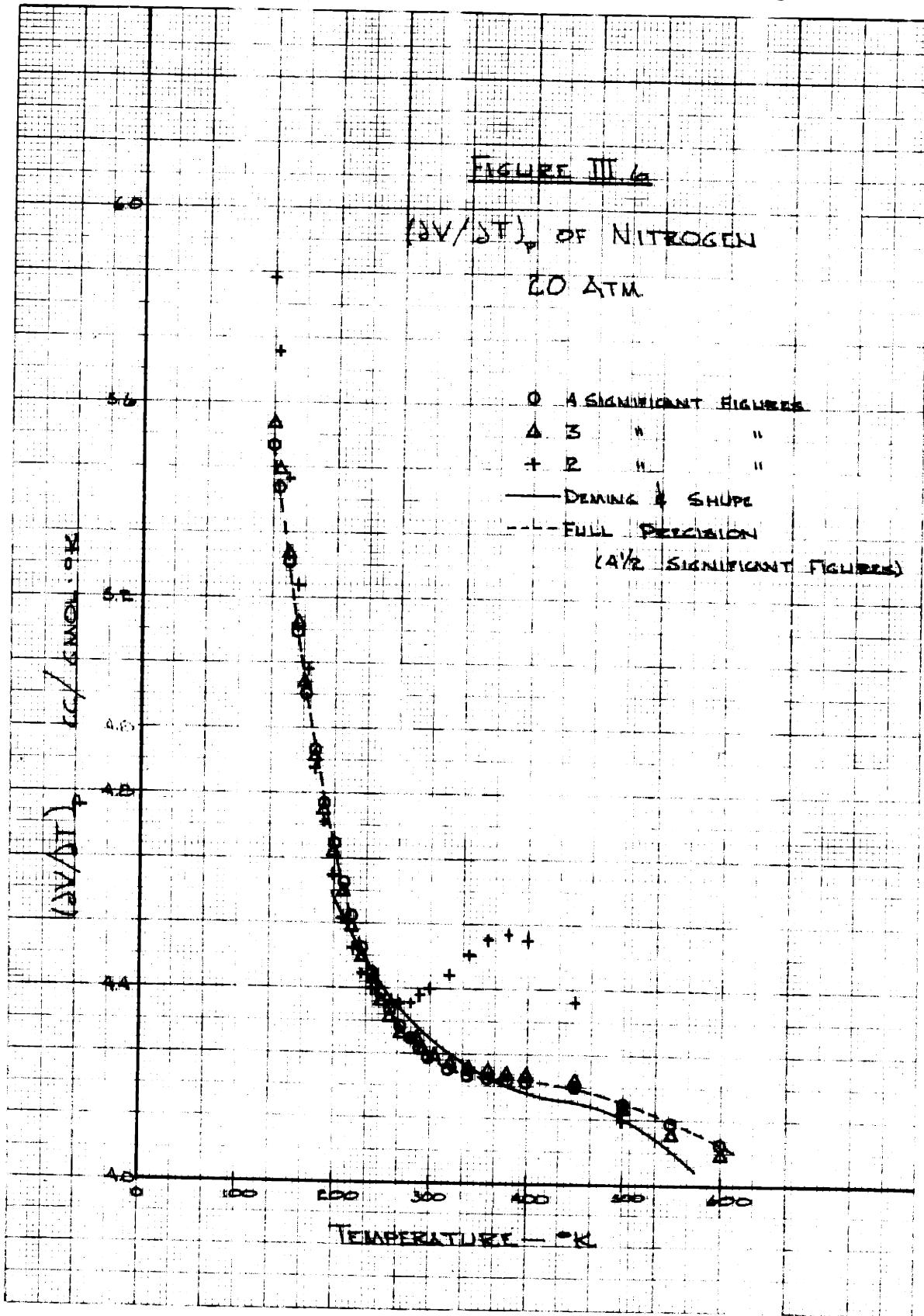
A plot of residual volume versus temperature is prepared, the slope of the curve can be estimated with a straightedge. While this procedure is inaccurate, $(\partial \alpha/\partial T)_P$ is much smaller than R/P, so that the total error in $(\partial V/\partial T)_P$ is small. Derivatives calculated in this manner were used as a comparison, with the derivatives calculated from the least squares polynomial, and were all plotted on the same graph. A typical plot for nitrogen is shown in Figure II.5. The graph indicates that the derivatives can be well approximated by a fifth degree polynomial.

Figure III-5

$(\partial V / \partial T)_P$ OF NITROGEN 100 ATM

B. Effect of Accuracy of Initial Data on Calculated Derivative

Volumetric data for nitrogen at a pressure of twenty atmospheres were fitted to a least squares polynomial, and the derivative, $(\partial V/\partial T)_P$, was calculated as a function of temperature. The range of the data was from 453.1 cubic centimeters per gram-mole at $135^{\circ}K$ to 2896.0 cubic centimeters per gram-mole at $700^{\circ}K$. As given, the volumes contained between four and five significant figures, corresponding to an accuracy of about 0.01 per cent. In order to estimate the effect of accuracy of the initial volumetric data , the specific volumes were rounded off to four significant figures, three significant figures, and two significant figures. Each of these sets of volumetric data were curve fit, and were used in calculating $(\partial V/\partial T)_P$ as a function of temperature. When the data is rounded to four significant figures, the precision varies from 0.01 per cent to 0.1 per cent. Similarly, for three significant figures retained, the precision is between 0.1 per cent and 1.0 per cent, and for two significant figures it is between 1.0 per cent and 10.0 per cent.

The results of these calculations are shown in Figure III.6, with the additional curve of $(\partial V/\partial T)_P$ calculated graphically by the method of Deming and Shupe (21). It is seen that the derivative can be fairly well represented until the precision of the data falls as low as two significant figures, or between one and ten per cent.

Figure III 4

$(\partial V/\partial T)_p$ of Nitrogen
20 Atm.

C. Curve Fitting of Ideal Gas Data

Having selected a polynomial of the fifth degree to represent the volumetric data, and to calculate $(\partial V/\partial T)_P$, it was desired to examine this approximation when the data were truly linear. To this end, volumes were calculated to six significant figures for a hypothetical ideal gas with a molecular weight of ten. The specific volumes were curve fit, and the derivatives calculated, for various constant pressures, as a function of temperature. The results for all pressures were encouraging, and a brief summary will be given for the results at 8 psia.

At each temperature, from $490^{\circ}R$ to $710^{\circ}R$, corresponding to an input volume, a volume was calculated from the least squares polynomial. There were eight of these points and agreement was exact, i.e., to six significant figures. At each of the eight points the derivative, $(\partial V/\partial T)_P$, was calculated. For an ideal gas, $(\partial V/\partial T)_P = R/P$. For a pressure of eight psia, the derivative should be 10.73/8 or 1.34125 cubic feet/lb.-R, which is independent of temperature. The range of the calculated derivative was from 1.34124 to 1.34131 with a mean of 1.34126 and a standard deviation of about 2 digits in the least decimal place.

These results indicated that the fifth degree polynomial could adequately represent even linear data, and could also adequately represent the first derivative, if the initial data was of high enough accuracy.

D. Calculation of Heat Capacity from Sonic Velocity

The heat capacity can be calculated from the sonic velocity and volumetric data as explained in Section I.E from Equation (II.37).

$$c_P = \frac{-T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T + (V/a)^2}$$

(II.37)

The derivative $(\partial V/\partial T)_P$ is calculated from the least squares polynomial. The derivative, $(\partial V/\partial P)_T$, is calculated from a Lagrangian interpolation polynomial using five points (32). Calculations were made using sonic velocity data from the literature (24, 34, 76, 82, 84) for nitrogen, using calculated sonic velocities from Woolley's compilation of thermodynamic properties of nitrogen (90), and for a hypothetical ideal gas.

1. Using Measured Data

Most of the measured data for the sonic velocity of nitrogen comes from Shilling and Partington (76) and from Dixon, Parker, and Campbell (24). Each gives results for one atmosphere as a function of pressure. They are in good agreement. Hubbard and Hodge give data as a function of pressure at 300°K (34). All of the experimental data were plotted, smoothed and interpolated so that values of the
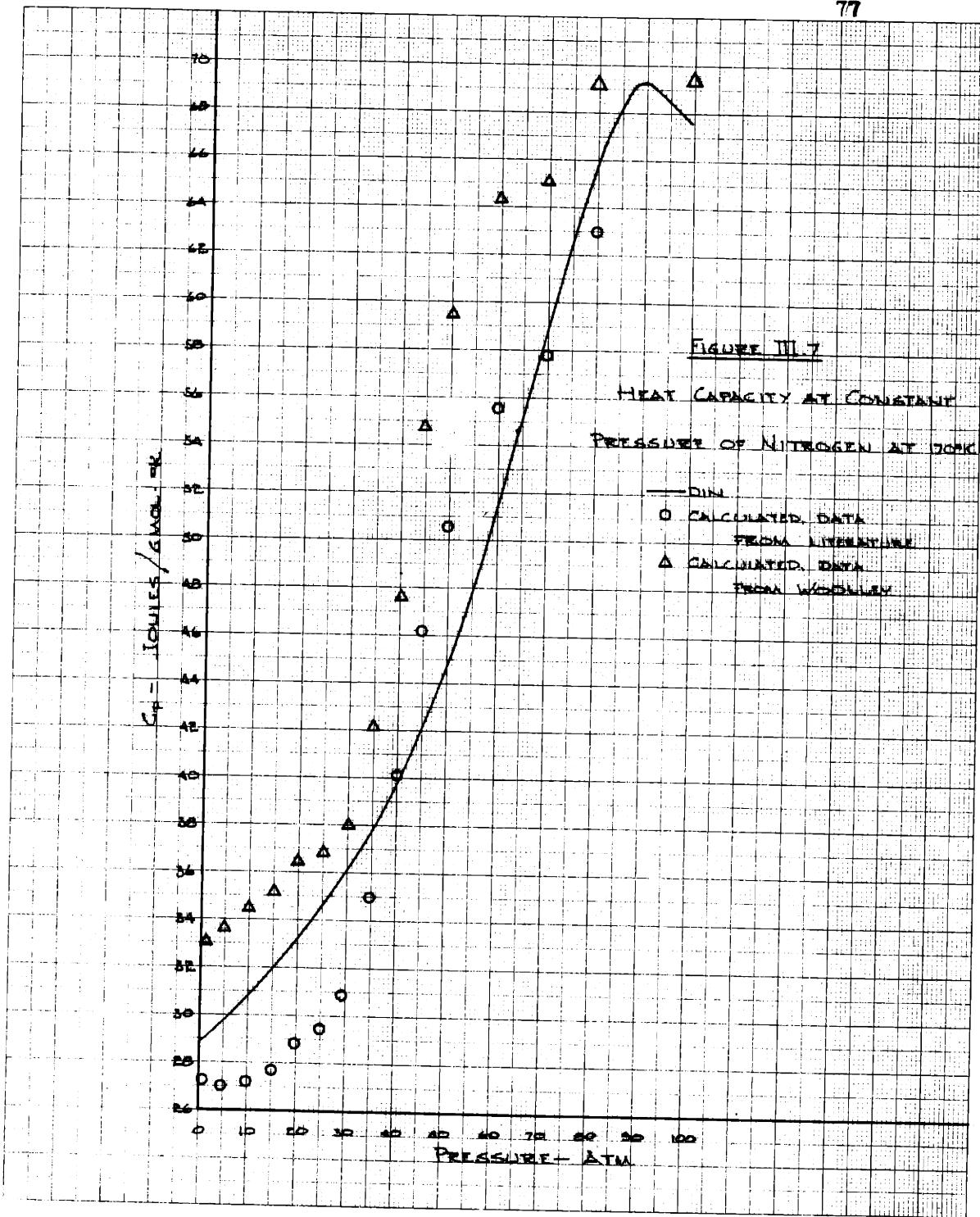
sonic velocity could be obtained at any desired pressure and temperature. The derivatives $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ and the specific volume was also calculated at the same pressure and temperature. From these data, the heat capacity at constant pressure is calculated from Equation (II.37). The results are compared with those of Din (23) in Figures III.7 and III.8. It is seen that the agreement is poor, deviations of up to ten per cent being common. This in itself would not be too bad, since the heat capacities at high pressure tabulated by Din are calculated using the relationship
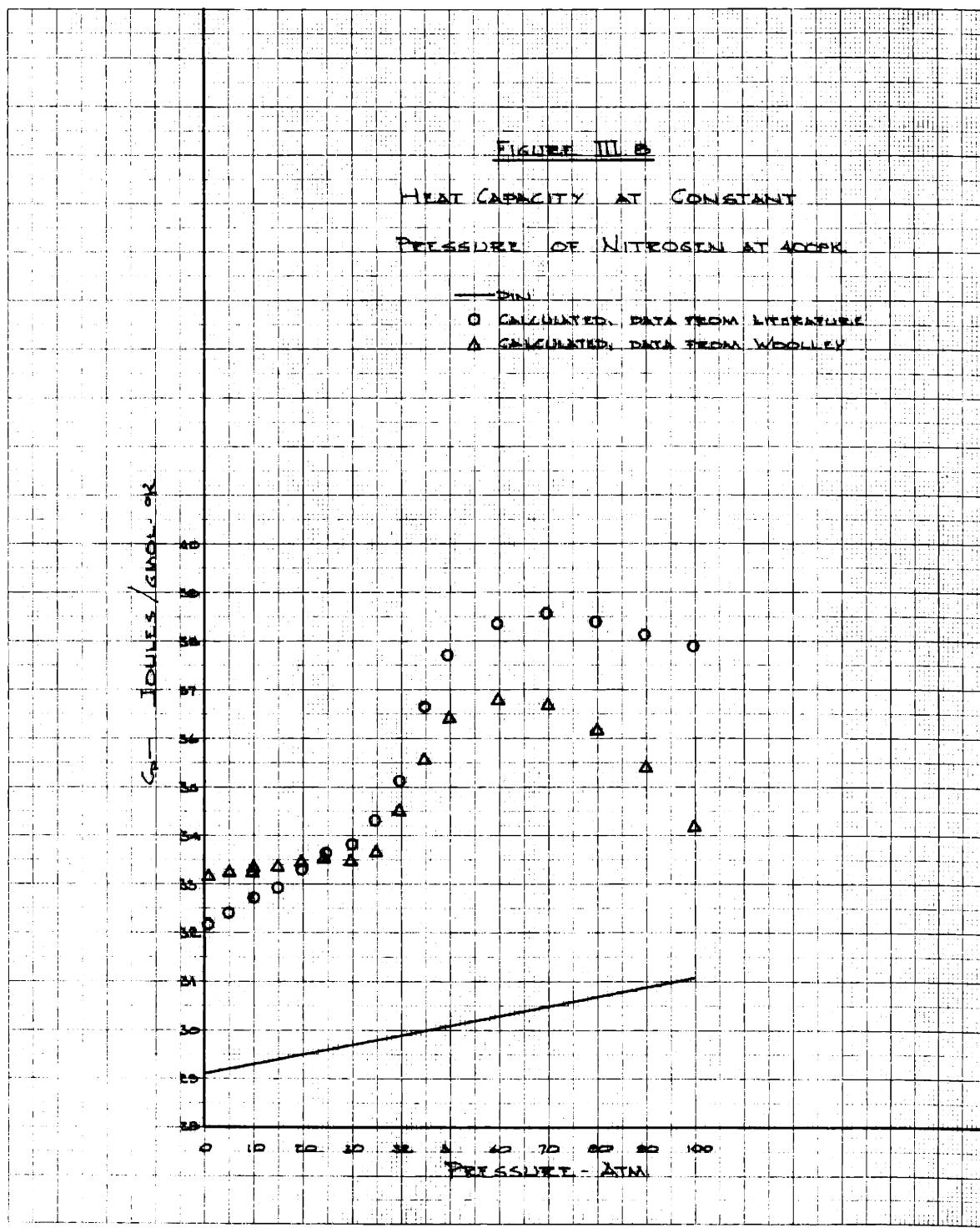
$$(\partial c_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \qquad (III.24)$$

and may be in error due to the difficulty in estimating the second derivative. However, Din's heat capacities do agree well with other compilations (54, 90), and with measured results (54).

2. Using Calculated Data

Woolley (90), in his compilation, uses volumetric data and heat capacities to calculate sonic velocities. These calculated values did not agree with the measured values found in the literature, and Woolley concluded that the literature values of Shilling and Partington (76) and of Dixon, Parker and Campbell were in error.

FIGURE III-7

HEAT CAPACITY AT CONSTANT

PRESSURE OF NITROGEN AT 70°K

——— DIN

○ CALCULATED DATA
FROM LITERATURE

△ CALCULATED DATA
FROM WOOLLEY

FIGURE III B

HEAT CAPACITY AT CONSTANT

PRESSURE OF NITROGEN AT 400°K

—— DIN
O CALCULATED, DATA FROM LITERATURE
△ CALCULATED, DATA FROM WOOLLEY

The calculation described in the preceeding section were repeated using Woolley's values for sonic velocity, and are also shown in Figures III.7 and III.8. The results are still not very satisfactory.

The poor calculation is due mainly to errors in estimating the derivatives, $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ but part of the discrepancy may be due to poor values of the sonic velocity.

3. Ideal Gas

In order to determine how well heat capacities could be calculated using exact values for sonic velocity, the calculations were carried out using data for a hypothetical ideal gas.

If a heat capacity ratio, C_p/C_v, of 1.4 is assumed, the heat capacity of ideal gas can be calculated since $C_p-C_v = R$. Thus, a value for C_p of 6.95 BTU/16-mole-R should result, when 1.4 is selected as the heat capacity ratio. Now the sonic velocity is calculated as

$$a = (\frac{C_p}{C_v} RT)^{1/2} \tag{III.25}$$

and a value of the heat capacity at constant pressure could be calculated from Equation (II.37). This was done for a number of temperatures and pressures, and the calculated heat capacities were generally within a half per cent of the true value, 6.95.

4. Summary of Heat Capacity Calculations

While heat capacities can be calculated from sonic velocities, this is probably not the best procedure. Since the calculation of C_p is very sensitive to fluctuations in the volumetric derivatives only a very rough result could be achieved. In Figures III.7 and III.8, it is noted that the calculated heat capacity curve fluctuates irregularly, which should not happen. The sonic velocity input, in all cases, did not fluctuate, but was a smooth function of pressure and temperature. While the accuracy of the sonic velocity data may be questionable, the precision was high, and the resulting heat capacity should be a smooth function of pressure. The fact that it did not indicates that the fluctuations are caused by variations in the derivatives.

In order to see this more clearly, the denominator of Equation (II.37) can be examined.

$$C_p = \frac{-T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T + (V/a)^2} \qquad (II.37)$$

The two terms, $(\partial V/\partial P)_T$ and V^2/a^2, are both the same order of magnitude. Since $(\partial V/\partial P)_T$ is negative, when the two terms are combined, some precision is lost and the percentage error is magnified. The important term is $(\partial V/\partial P)_T$, since it is the least accurate.

Generally it is not necessary to know the heat capacity at high pressures very accurately, especially if they

are not to be used in further calculations, but are an end
result. Thus, calculating heat capacities from sonic velocity
data can be roughly approximated, but calculations of C_p change
with pressure would be meaningless. On the other hand, the
heat capacity must be known accurately at one pressure in
order to generate a thermodynamic network. Frequently such
data is available for the ideal gas state.

In order to insure that heat capacity data is avail-
able at one pressure at least, it will be assumed that it
will be measured directly at one pressure.

Thus, the final computor program will be set up so
that either heat capacities or sonic velocities can be used
as input data.

IV. PROPOSED SYSTEM

As a result of the preliminary investigations, enough information was obtained so that a system could be selected for detailed study. The system is a hypothetical experiment, from which the necessary data can be obtained for calculating a thermodynamic network.

A. Parameters to be Measured
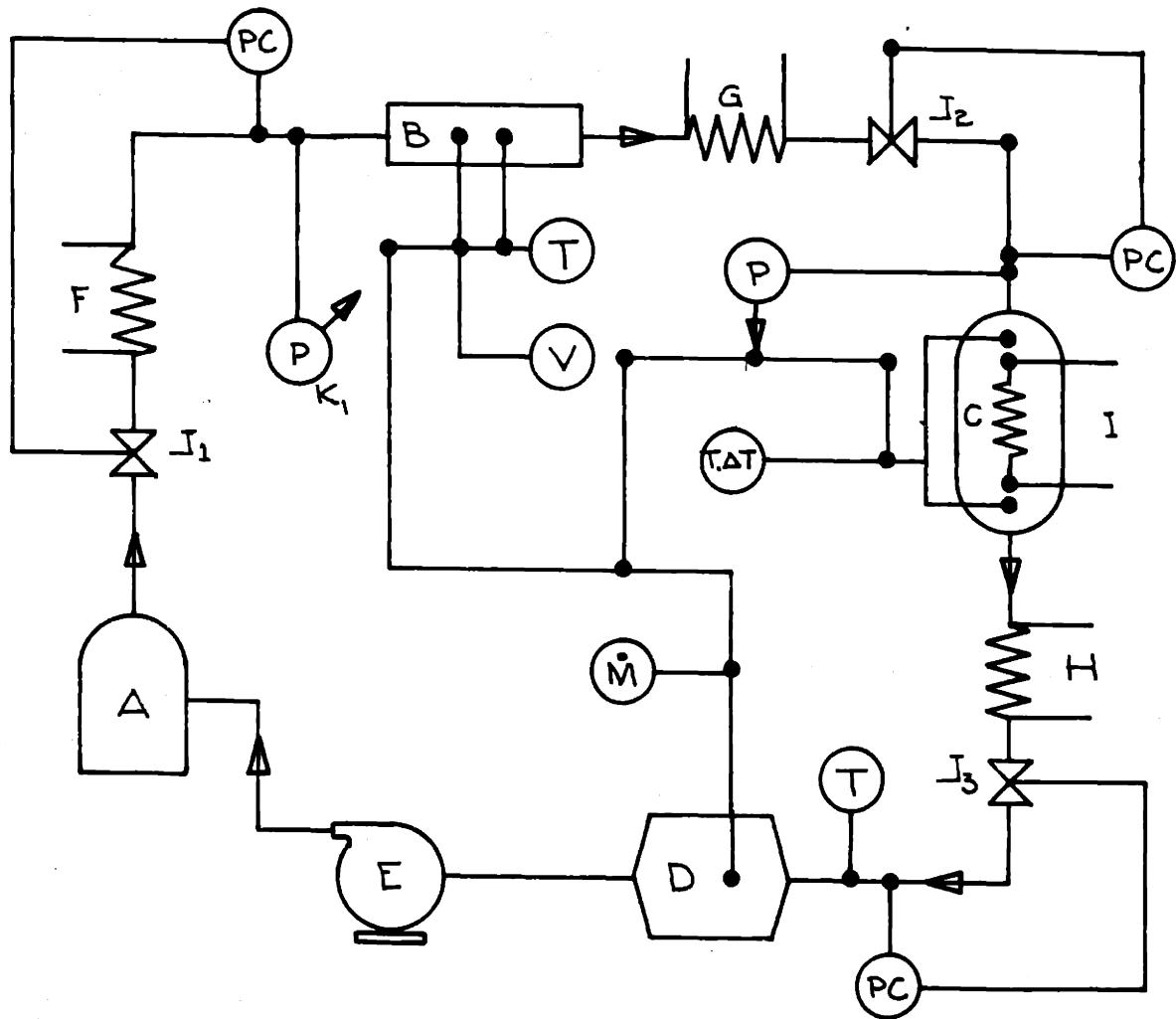
The system selected for detailed analysis has already been discussed in Section II.E, and will consist of measurements of the specific volume as a function of pressure and temperature. Specific volumes will be measured by combining measurements of volumetric flow rate and mass flow rate. In addition, the heat capacity at constant pressure will be measured at one pressure as a function of temperature. An experiment to measure vapor pressure is included as described in Section II.D.5.

Thus, the volumetric data will consist of specific volume isobars for a number of different pressures, and the experiment will be carried out so that the volumes are measured at constant pressure at a function of temperature.

B. Experimental Setup

A schematic diagram of the experimental setup is shown in Figure IV.1. The gas is released from a high pressure

FIGURE IV.1
SCHEMATIC OF PROPOSED EXPERIMENTAL SETUP

A – STORAGE TANK
B – VOLUMETRIC FLOWMETER
C – CALORIMETER
D – MASS FLOWMETER

E – COMPRESSOR
F,G,H – HEAT EXCHANGERS
I – RESISTANCE HEATER
J – PRESSURE CONTROLLER

K – PRESSURE TRANSDUCER

storage tank (A) and is heated by a heat exchanger(F) to the desired temperature for a measurement. The pressure of the gas is controlled by the pressure controller (J_1). The gas passes through the volumetric flowmeter (B) at the desired pressure and temperature. The signal from a pressure transducer (K_1) is compared with a reference pressure. When the pressure in the line is the same as the reference pressure, a reading is taken of temperature, volumetric flow rate and mass flow rate. This is done to insure that measurements are taken at the same pressure along an isobar. The gas then passes through a heat exchanger (G) before entering the calorimeter section (C). The nominal pressure of the gas entering the calorimeter is controlled by the pressure controller (J_2). A measured quantity of heat is added to the gas passing through the calorimeter tube by an electrical resistance heater (I). Again, the output of a pressure transducer (K_2) is compared with the signal of a preset reference pressure and measurements are recorded when the outputs of the two pressure signals are the same. The measurements taken are of pressure, temperature, mass flow rate, rate of heat input and the temperature rise of the gas as it passes through the calorimeter. The gas is then cooled by heat exchanger (H) and its pressure is reduced and/or controlled by pressure controller (J_3) before it enters the mass flowmeter (D). The temperature and pressure of the gas entering the mass flowmeter have to be controlled only to nominal values. Since the mass flow rate is independent of

pressure and temperature, the measurement of mass flow rate can be made at any convenient temperature and pressure.

By simultaneously measuring the mass flow rate and volumetric flow rate, the density is determined at the pressure and temperature at which the volumetric flow rate was measured. Similarly, the heat capacity measurement is made at the pressure and temperature of the gas as it passes through the flow calorimeter.

After the gas leaves the mass flowmeter, it is compressed by the compressor (E) and is returned to the storage tank (A).

C. Instrumentation

1. Temperature

Temperature measurements have been discussed in Section I.C.2. For measurements of high accuracy, with fast response times, resistance thermometers are recommended. Specifically, a platinum resistance thermometer should be used. In general, platinum resistance thermometers have a useful range of from $25^{\circ}R$ to $2000^{\circ}R$ and can be used for pressures up to 12,000 psia. Accuracies of $0.01^{\circ}F$ can be achieved, and even higher accuracies are possible for temperature difference measurements, depending on the read-out equipment. There are many suitable commercial instruments available, such as the Leeds and Northrop model 816B or the Rosemount Engineering Co. model 110F.

2. Pressure
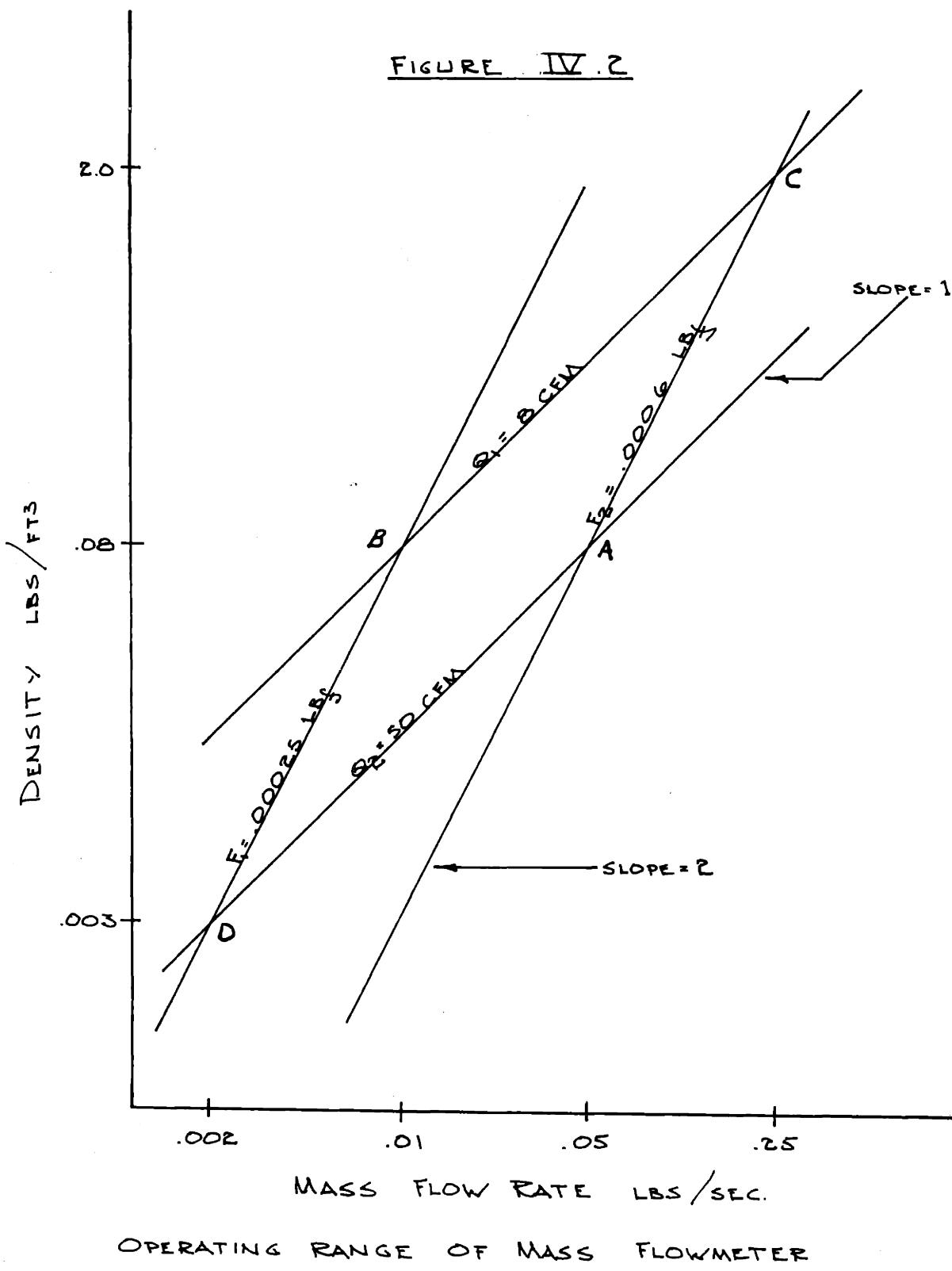
a. Measurement

Pressure instruments were discussed in Section I.C.1. Depending on the pressure and temperature ranges to be encountered, a wide variety of instruments are available for selected ranges. For narrow ranges, extremely high accuracies can be achieved. However, it is possible to cover wide ranges with a single instrument and still achieve good accuracy. For example, the Norwood strain guage pressure transducer, models 111 and 112, manufactured by Advanced Technology Laboratories, comes in ranges up to 0-15,000 psia, and is equipped with a water cooled housing so that it may be used for temperatures as high as 2000°F. The linearity is at least 0.25 per cent and it is repeatable to at least 0.1 per cent. An instrument with those specifications would be sufficient to cover most areas of interest.

b. Control

When measurements are made of volumetric flow rate, simultaneous measurements of pressure, temperature and mass flow rate are also made. Since it is proposed that the volumetric data be measured at constant pressure, the pressure must be controlled, as well as measured. This can be done by a combination of two methods. Referring to Figure IV.2, it is seen that the pressure of the gas stream is controlled at three different points. While a constant pressure

FIGURE IV.2

OPERATING RANGE OF MASS FLOWMETER

could be maintained to a close tolerance at any one point in the system, attempting to control it at three points simultaneously may lead to an unstable system. This would especially be true if very narrow tolerances on pressure were required.

Since the stability of the system can only be established experimentally, an alternate procedure is suggested, which could be used if required.

For example, consider the volumetric flowmeter. Instead of controlling the pressure to an extremely narrow tolerance, it is only controlled to a nominal value. When the system is in operation the pressure of the gas will fluctuate about the nominal value. Since measurements of pressure, temperature, volumetric flow rate and mass flow rate are taken at discrete intervals in time, the data can be measured only at the time when the fluctuating pressure agrees exactly (or within a prescribed tolerance) of some pre-selected pressure. For example, suppose that it was desired to determine the density of the gas at 100.0 psia as a function of temperature by measuring the pressure, temperature and mass and volumetric flow rates. The gas is circulating in the system, and the pressure of the gas as it enters the volumetric flowmeter, is set to be controlled to a nominal pressure of 100 psia. However, the pressure of the gas fluctuates between 90 psia and 110 psia. At the instant when the fluctuating pressure is exactly 100.0 psia, the temperature and mass and volumetric flow rates are

recorded. Then the temperature is allowed to change and the procedure is repeated for the next point on the isobar. This insures that points on the same isobar are really measured at the same pressure.

This operation can be carried out automatically be comparing the output signal of a pressure transducer, that monitors the fluctuating pressure, to a reference signal which corresponds to the exact pressure of the isobar. At the instant that the two signals are equal, the data can be recorded.

3. Heat Capacity

A specific system for measuring the heat capacity at constant pressure will not be recommended, since these systems are not commercially available. A system for measuring heat capacity in a flow system will consist of four main parts; the calorimeter itself, a system for measuring mass flow rate, a system for measuring heat input and a system for measuring the temperature rise in the flowing gas. Temperature measurements have been discussed in Section IV.C.1. The heating is usually done electrically and the measurement of the heat input is accomplished by measuring electrical quantities, i.e., current and resistance. Electrical measurements will not be discussed since they can be carried out to sufficiently high accuracy so that they do not limit the accuracy of the resulting heat capacities. The measurement

of mass flow rate is important, since it will be the least
accurate measurement, and thus will limit the accuracy of
the results. The measurement of mass flow rate will be
discussed in Section IV.C.5.

In addition to the measurements of mass flow rate,
temperature rise, and heat input, the calorimeter itself is
important since its design will determine extraneous heat
losses. The calorimeter should be constructed so that heat
losses can be minimized, and accounted for.

4. Volumetric Flow Rate

Volumetric flow meters for gases are commercially
available in sizes well suited for experimental work. Tur-
bine type flowmeters have the best accuracies of commer-
cially available instruments and are well suited for the
intended application. An example of a turbine flowmeter
with an extremely high accuracy is the Cox model number I1
(16). This instrument is available in a one inch size and
is suitable for gas flows of from five to fifty standard
cubic feet per minute. It has a repeatability of 0.05 per
cent and is linear to 0.5 per cent of the reading. The
standard pressure rating is 2500 psia, but higher pressures
can be used by changing the flanges. The temperature range
is from $5^{\circ}R$ to $1200^{\circ}R$. The meter has a very fast response
time and other sizes are available, with similar character-
istics, to accommodate lower or higher flow rates.

5. Mass Flow Rate

As has been mentioned in Section I.C.8, the instrument to be used for measuring mass flow rate is the Potter-meter model SP-157PHP mass flow meter, manufactured by the Potter Aeronautical Corporation. This instrument consists of two turbines with different blade angles, which would tend to rotate at different speeds due to the fluid velocity. The turbines are connected by a spring which causes the two turbines to take on an angular displacement with respect to each other. The angular displacement is proportional to the flow momentum. The two turbines, considered as a unit, rotate at a speed proportional to the fluid velocity. Thus, by measuring the momentum and velocity, the mass flow rate can be determined.

While this meter can be used over a range of pressure and temperature, in the experiment it will be operated at near ambient conditions. The extreme range for mass flow rate is from 0.002 to 0.20 pounds per second, but this range depends on the density and volumetric flow rate. For example, in Figure IV.2, the logarithm of the gas density, ρ, is plotted against the logarithm of the gas mass flow meter rate, $\dot{M}$, for constant volumetric flow rate, Q, and also for constant flow momentum force F. From the continuity equation

$$\rho = \frac{\dot{M}}{Q}$$

(IV.1)

or

$$\log \rho = \log \dot{M} - \log Q \qquad \text{(IV.2)}$$

Thus, if $\log \rho$ is plotted against $\log \dot{M}$ at constant Q, the resulting curve is a straight line with a slope of one. Also, since

$$F = \rho A V^2 \qquad \text{(IV.3)}$$

$$F = \frac{\rho^2 A^2 V^2}{\rho A} \qquad \text{(IV.4)}$$

or

$$\rho = \frac{\rho^2 A^2 V^2}{AF} = \frac{\dot{M}^2}{AF} \qquad \text{(IV.5)}$$

and

$$\log \rho = 2 \log \dot{M} - \log AF \qquad \text{(IV.6)}$$

So, if $\log \rho$ is plotted against $\log \dot{M}$, for a given sized meter, at constant F, the result is a straight line with a slope of two.

In Figure IV.2 the limits of momentum force and volumetric flow rate (or velocity for a meter of given size) are drawn for the one inch size meter. The quadrilateral, ABCD, defines the range of possible combinations of mass flow rate and density. The whole area may be shifted by changing the internal design of the meter, i.e., blade angles or spring stiffness. The values on the graph are for a typical design and are approximate. Line AC represents the angular limit of the spring coupling, since the angle is

proportional to the flow momentum force. Similarly, line BD represents the minimum fluid momentum required to maintain a good resolution angle between the two rotating turbines. Line DA represents the highest fluid velocity which can be used due to the limit of rotational speed of the rotor and line CB represents the minimum velocity for which the meter can maintain good resolution. While this instrument can be used as a volumetric flowmeter, as well as a mass flowmeter, doing so will seriously limit its range, since the mass flow rate is not independent of the volumetric flow rate. Thus, the instrument will be used only to measure flow rate at some convenient pressure and temperature, so that it will operate within the area ABCD in Figure IV.2.

D. Summary

Based on the preceeding sections, it is anticipated that measurements could be made with the following accuracy.

Pressure . . . . 0.1 $^o/o$

Temperature. . . . . 0.1 $^o/o$

Specific Volume. . . 0.1 - 1.0 $^o/o$

Heat Capacity. . . . 0.1 - 1.0 $^o/o$

Sonic Velocity . . . 0.1 $^o/o$

V. CALCULATION OF THERMODYNAMIC NETWORKS

A. Method of Calculation

1. Treatment of Measured Data

The data measured in the experiments described in Section IV will be used in a standard manner. For each isobar, the data will consist of a set of measured specific volumes and temperatures. These will be represented by a least squares fifth degree polynomial. The coefficients of the polynomial will be stored in the computor program.

The other measured data, such as isobaric heat capacity, vapor pressure, and sonic velocity will also be represented by least squares polynomials in temperature. In order to calculate a thermodynamic network, a reference temperature and pressure are selected and a matrix of regularly spaced temperatures and pressures is set up. Each property will be calculated as a function of temperature and pressure and will be tabulated at the pre-selected temperature and pressure points.

2. Thermodynamic Relationships

This section will contain the derivations of the various thermodynamic relationships, upon which the calculations are based. As a starting point, a statement of the combined first and second laws of thermodynamics and some definitions will be used.

$$dE = TdS - PdV \qquad (V.1)$$

$$H = E + PV \qquad (V.2)$$

$$F = H - TS \qquad (V.3)$$

From Equation (V.2)

$$dH = dE + PdV + VdP \qquad (V.4)$$

and substituting dE from Equation (V.1)

$$dH = TdS + VdP \qquad (V.5)$$

Similarly, by differentiating Equation (V.3) and substituting dH from Equation (V.5) one obtains

$$dF = -SdT + VdP \qquad (V.6)$$

Since dF is an exact differential,

$$dF = (\partial F/\partial P)_T dP + (\partial F/\partial T)_P dT \qquad (V.7)$$

Equating the coefficients of Equation (V.6) and Equation (V.7), it is seen that

$$S = -(\partial F/\partial T)_P \qquad (V.8)$$

and

$$V = (\partial F/\partial P)_T \qquad (V.9)$$

In addition, from Equation (V.8)

$$(\partial S/\partial P)_T = -(\partial^2 F/\partial P \partial T) \qquad (V.10)$$

and from Equation (V.9)

$$(\partial V/\partial T)_P = \partial^2 F/\partial T \partial P \qquad (V.11)$$

and since

$$\frac{\partial^2 F}{\partial T \partial P} = \frac{\partial^2 F}{\partial P \partial T} \qquad (V.12)$$

it is seen that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (V.13)$$

which relates the isothermal change in entropy to the volumetric behavior.

Before continuing, the heat capacity at constant pressure and the heat capacity at constant volume will be defined.

$$C_P = (\partial H/\partial T)_P \qquad (V.14)$$

$$C_V = (\partial E/\partial T)_V \qquad (V.15)$$

Now since the entropy is a state function

$$dS = (\partial S/\partial P)_T dP + (\partial S/\partial T)_P dT \qquad (V.16)$$

If Equation (V.16) is substituted into Equation (V.5), the result is

$$dH = T(\partial S/\partial T)_P dT + \left[V + (\partial S/\partial P)_T T\right] dP \qquad (V.17)$$

From Equation (V.5) and the definition of the heat capacity at constant pressure, it is seen that

$$(\partial S/\partial T)_P = \frac{1}{T}(\partial H/\partial T)_P = C_p/T \qquad (V.18)$$

Substituting Equations (V.18) and (V.13) into Equation (V.17), the result is

$$dH = C_p dT + \left[V - T(\partial V/\partial T)_P\right] dP \qquad (V.19)$$

Therefore, the isothermal change in enthalpy, is related to the volumetric behavior by

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \qquad (V.20)$$

From Equation (V.20), the isothermal change in the heat capacity at constant pressure may easily be deduced. Recalling the definition of the heat capacity at constant pressure;

$$C_p = (\partial H/\partial T)_P \qquad (V.14)$$

and since the order of the differentiation is immaterial

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial(\frac{\partial H}{\partial T})_P}{\partial P}\right)_T = \left(\frac{\partial(\frac{\partial H}{\partial P})_T}{\partial T}\right)_P \qquad (V.21)$$

Substituting Equation (V.20) into Equation (V.21), and carrying out the indicated differentiation,

$$\left(\frac{\partial c_p}{\partial P}\right)_T = \left(\frac{\partial \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$- \left(\frac{\partial V}{\partial T}\right)_P \qquad (V.22)$$

or

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (V.23)$$

which is the desired result.

The Joule-Thomson coefficient is defined as

$$\mu = (\partial T/\partial P)_H \qquad (V.24)$$

Since, $dH = 0$ at constant enthalpy, it follows immediately from Equation (V.19) that

$$(\partial T/\partial P)_H = \frac{T(\partial V/\partial T)_P - V}{C_p} \qquad (V.25)$$

From the definitions of the heat capacities at constant volume and constant pressure, Equations (V.14) and (V.15),

$$C_p - C_v = (\partial H/\partial T)_p - (\partial E/\partial T)_v \qquad (V.26)$$

Rearranging Equation (V.2),

$$E = H - PV \qquad\qquad (V.27)$$

and substituting Equation (V.27) into Equation (V.26) and carrying out the differenitation,

$$C_p - C_v = (\partial H/\partial T)_p - (\partial H/\partial T)_v + V(\partial P/\partial T)_v \qquad (V.28)$$

From Equation (V.19)

$$dH = V - T(\partial V/\partial T)_p dP + (\partial H/\partial T)_P dT \qquad (V.29)$$

or

$$(\partial H/\partial T)_v = \left[V - T(\partial V/\partial T)_p \right] (\partial P/\partial T)_v + (\partial H/\partial T)_p$$

$$(V.30)$$

Combining Equations (V.28) and (V.30) and simplifying the result is

$$C_p - C_v = T(\partial V/\partial T)_p (\partial P/\partial T)_v \qquad (V.31)$$

This can be put into a more convenient form since

$$dV = (\partial V/\partial P)_T dP + (\partial V/\partial T)_P dT \qquad (V.32)$$

or, at constant volume, since dV = 0,

$$(\partial P/\partial T)_V = - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \qquad (V.33)$$

Thus, by substitution of Equation (V.33), Equation (V.31) becomes

$$C_p - C_v = - \frac{T(\partial V/\partial T)_P^{\,2}}{(\partial V/\partial P)_T} \qquad (V.34)$$

The sonic velocity is defined as

$$a^2 = (\partial P/\partial \rho)_S \qquad (V.35)$$

Since $\rho = 1/V$,

$$a^2 = -V^2(\partial P/\partial V)_S \qquad (V.36)$$

but since the entropy is a state function

$$dS = (\partial S/\partial P)_V dP + (\partial S/\partial V)_P dV \qquad (V.37)$$

or

$$(\partial P/\partial V)_S = - \frac{(\partial S/\partial V)_P}{(\partial S/\partial P)_V} \qquad (V.38)$$

From Equations (IV.13), (IV.16) and (IV.18),

$$dS = -(\partial V/\partial T)_P dP + \frac{C_p}{T} dT \qquad (V.39)$$

So it follows that

$$(\partial S/\partial V)_P = \frac{C_p}{T}(\partial T/\partial V)_P \qquad (V.40)$$

and

$$(\partial S/\partial P)_V = -(\partial V/\partial T)_P + \frac{C_p}{T}(\partial T/\partial P)_V \qquad (V.41)$$

Combining Equations (V.36), (V.38), (V.40) and (V.41), the result is

$$a^2 = \frac{V^2 C_p (\partial T/\partial V)_P}{C_p T(\partial T/\partial P)_V - T(\partial V/\partial T)_P} \qquad (V.42)$$

This result can be put into a more convenient form, using Equation (V.33),

$$a^2 = \frac{-C_p V^2}{C_p (\partial V/\partial P)_T + T(\partial V/\partial T)_P^2} \qquad (V.43)$$

This completes the derivation of the thermodynamic relationships which will be used in the following sections.

3. Properties Calculated

At each point in the pressure-temperature matrix, the following thermodynamic properties will be calculated and tabulated: specific volume, heat capacity at constant pressure, heat capacity at constant volume, ratio of heat capacities, difference of heat capacities at constant pressure and constant volume, enthalpy, entropy, fugacity coefficient, compressibility factor, residual volume, sonic velocity and Joule-Thomson coefficient.

a. Specific Volume

The specific volume is measured at a set of temperatures T_i, and pressures P_i, but usually must be calculated at another set of temperatures T_j, and pressures P_j. This is done by using a least squares polynomial at each of the measured pressures P_i, to relate specific volume to temperature. At each measured pressure, P_i, the volume can be calculated at T_j, the desired temperature for the tabulation. At each T_j, the volume is calculated at P_j by interpolation from a set of surrounding pressures, P_i.

b. Heat Capacity

The heat capacity at constant pressure is measured at some reference pressure, P_o, and is represented by a least squares polynomial. Usually this will be at one atmosphere, or in the ideal gaseous state, but it may be measured at any pressure. The heat capacity is calculated at other pressures by the thermodynamic relationship

$$(\partial c_p/\partial P)_T = - T(\partial^2 V/\partial T^2)_P \qquad (V.23)$$

which is integrated numerically at constant temperature. The second derivative of volume with respect to temperature is found by differentiating the least squares polynomial twice.

An alternative method is to calculate the heat capacity at constant pressure from sonic velocity and volumetric

data. By rearranging Equation (V.43),

$$C_p = \frac{- T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T + (V/a)^2} \qquad \text{(V.44)}$$

As discussed in Section III.D, due to errors in the derivative $(\partial V/\partial P)_T$ this method is inaccurate and will not be used. It is presented here since an improvement in the calculation of $(\partial V/\partial P)_T$ may make this method feasible.

c. Enthalpy

A reference value for the enthalpy is selected at some convenient reference pressure and temperature. At the reference pressure, the enthalpy is calculated as a function of temperature. From Equation (V.19), it follows that

$$H_{T,P_0} = H_{T_0,P_0} + \int_{T_0}^{T} C_{P_0} dT \qquad \text{(V.45)}$$

This integration is carried out analytically since the heat capacity has already been expressed as a function of temperature by the least-squares polynomial.

At each temperature for the tabulation, the enthalpy is calculated as a function of pressure using the relationship

$$dH = (V - T(\partial V/\partial T)_P) dP \qquad \text{(V.46)}$$

which also follows from Equation (V.19). Equation (V.46) is integrated numerically, and the enthalpy is calculated at each pressure desired for the tabulation.

d. Entropy

The calculation of the entropy is similar to the calculation of the enthalpy. At the reference pressure and temperature, a reference value for the entropy is selected. At the reference pressure, the entropy is calculated as a function of temperature, from Equation (V.18).

$$S_{T,P_O} = S_{T_O,P_O} + \int_{T_O}^{T} \frac{C_{P_O}}{T} dT \qquad (V.47)$$

To calculate the entropy as a function of pressure, at constant temperature, the relationship

$$dS = - (\partial V/\partial T)_P dP \qquad (V.13)$$

is numerically integrated for each constant temperature.

e. Fugacity Coefficient

The fugacity coefficient, f/P, is defined as

$$RT \ln (f/P) = - \int_{O}^{P} (\frac{RT}{P} - V) dP \qquad (V.48)$$

at constant temperature. It is assumed that the gas is in

an ideal state at the reference pressure P_o, from which it follows that

$$\int_0^{P_o} (RT/P - V)dP = 0 \qquad\qquad (V.49)$$

Thus, the fugacity coefficient is calculated, for each constant temperature, by the relationship

$$RT \ln f/P = - \int_{P_o}^P (RT/P - V)dP \qquad\qquad (V.50)$$

If Equation (V.49) does not hold for the reference pressure selected then the calculated fugacity coefficient must be multiplied by the true fugacity coefficient at the reference pressure. Since

$$(f/P)_{True} = e^{-1/RT \cdot \int_0^P (RT/P - V)dP} \qquad\qquad (V.51)$$

$$(f/P)_{True} = e^{-1/RT \cdot \left[\int_{P_o}^P (RT/P - V)dP \right.}$$

$$\left. + \int_{P_o}^P (RT/P - V)dP\right] \qquad\qquad (V.52)$$

$$(f/P)_{True} = (f/P)_{Calc} \left\{ e^{-1/RT \cdot \int_0^{P_o} (\frac{RT}{P} - V)dP} \right\} \qquad (V.53)$$

$$(f/P)_{True} = (f/P)_{Calc} \times (f/P)_{P_o} \qquad (V.54)$$

The calculated fugacity coefficient is only equal to the true fugacity coefficient when the reference pressure is selected to be in the ideal gas region. If not, then the calculated fugacity coefficient must be multiplied by the fugacity coefficient at the reference pressure.

Equation (V.50) is integrated numerically, and the result is interpreted according to whether or not the reference pressure is in the ideal gas region.

f. Heat Capacity at Constant Volume

The heat capacity at constant volume is calculated from the heat capacity at constant pressure and the volumetic behavior of the gas, from Equation (V.31)

$$C_v = C_p + \frac{T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} \qquad (V.31)$$

The derivative, $(\partial V/\partial T)_P$ is calculated from the least squares polynomial, and the derivative, $(\partial V/\partial P)_T$, is estimated from an interpolating polynomial. The heat capacity at constant volume is calculated for each point in the pressure-temperature matrix. The ratio of the heat capacities, C_p/C_v, and the difference of the heat capacities, C_p-C_v, are also calculated for each point in the pressure-temperature matrix.

g. Sonic Velocity

If the sonic velocity was measured, it would be treated in the same way as the specific volume. The data would be least-squares curve fit at the measured pressures and the values on the pressure matrix would be found by inter-polation. The only difference would be that the square of the sonic velocity would be curve fit since a better approxi-mation could be obtained.

Since it is anticipated that the heat capacity at constant pressure will be measured, the sonic velocity may be calculated from it and the volumetric derivatives by Equation (V.43).

$$a^2 = \frac{- c_p V^2}{T(\partial V/\partial T)_P^2 + c_p(\partial V/\partial P)_T} \qquad (V.43)$$

The heat capacity and specific volume are calculated at the desired pressure and temperature, $(\partial V/\partial T)_P$ is calculated from the least squares polynomial and $(\partial V/\partial P)_T$ is calculated from an interpolating polynomial.

h. Joule-Thomson Coefficient

The Joule-Thomson coefficient is defined as

$$\mu = (\partial T/\partial P)_H \qquad (V.24)$$

For each point in the pressure-temperature matrix, it is calculated from the equation

$$\mu = \frac{T(\partial V/\partial T)_P - V}{C_p} \tag{V.25}$$

where each item on the right hand side of Equation (V.25) is determined by methods previously described.

i. Compressibility Factor and Residual Volume

The compressibility factor and residual volume are both calculated, from their definitions, at each point on the pressure-temperature matrix.

$$Z = \frac{PV}{RT} \tag{V.55}$$

$$\alpha = \frac{RT}{P} - V \tag{V.56}$$

B. Numerical Techniques

Having considered the thermodynamic relationships to be used in calculating a thermodynamic network, it is now appropriate that an examination be made of the actual method of carrying out the calculation. The numerical techniques used may be conveniently placed under the following headings: curve-fitting, interpolation, integration and differentiation.

1. Curve-Fitting

A discussion of curve-fitting techniques has already been presented in Section III.A. In order to curve fit the

volumetric data, a fifth degree least squares polynomial was
selected. For an ideal gas, the specific volume is propor-
tional to the temperature. Thus, by analogy, the square of
the sonic velocity will also be fit to a fifth degree least
squares polynomial, if this calculation is required.

For convenience, the heat capacity at constant pres-
sure is also fit to a fifth degree polynomial as a function
of temperature. The vapor pressure is fit to an equation of
the form

$$\text{Log } P = \frac{A}{T} + B + CT + DT^2 + ET^3 + FT^4 \qquad (V.57)$$

This is rearranged to

$$T \text{ Log } P = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \qquad (V.58)$$

so that the quantity (T Log P) is also curve fit to a fifth
degree polynomial. Thus, all curve fitting is done with a
fifth degree polynomial. This consistency provides a slight
simplification of the computor program.

2. Interpolation

By using a least squares curve fit, the data is not
only represented by the "best" equation along an isobar, but
is also smoothed. Since measurements will be made at a
finite number of pressures, a method is required by which

values can be calculated at pressures other than the measured
ones. If this was done by curve-fitting (volumes, for example)
at constant temperature and getting a least-squares polyno-
mial in pressure, the calculated results would be inconsis-
tent. For example, the volume calculated at P_1 and T_1 using
a temperature polynomial would necessarily agree with the
volume calculated at P_1 and T_1 using a pressure polynomial.

Since the data have been smoothed, calculations at
various pressures may be made by interpolation. Because for
an ideal gas, the specific volume is inversely proportional
to pressure, the interpolation is not carried out on the
specific volume, but on the product of the pressure and the
specific volume. In curve-fitting, a fifth degree polynomial
was used to represent the volume and fourth degree polynomial
will be used to represent (PV) when interpolating.

The interpolating polynomial is given by (32),

$$y(x) = \sum_{k=0}^{4} L_k(x) \, y(x_k) \tag{V.59}$$

where $L_k(x)$ is given by

$$L_k(x) = \frac{(x-x_0)\ldots(x-x_{k-1})(x-x_{k+1})\ldots(x-x_4)}{(x-x_0)\ldots(x_k-x_{k-1})(x_k-x_{k+1})-(x_k-x_4)} \tag{V.59a}$$

Equation (V.59) is the result of fitting a fourth degree
polynomial to the five points x_0, x_1, x_2, x_3, x_4. The value
of the dependent variable y, is found at any point x, by

substitution of the value of x into Equations (V.59a) and
(V.59). $y(x_k)$, for k = o, 1, 2, 3, 4, are the values of the
dependent variable at each of the five known points. In the
present application, PV is equivalent to y, and P is equiva-
lent to x. For example, if the specific volume were known
at five pressures, P_0, P_1, P_2, P_3, P_4, and it was desired to
find the specific volume at some other pressure, P, the inter-
polating equation would be

$$PV = \frac{(P - P_1)(P - P_2)(P - P_3)(P - P_4)}{(P_0 - P_1)(P_0 - P_2)(P_0 - P_3)(P_0 - P_4)} P_0 V_0 \quad +$$

$$\frac{(P - P_0)(P - P_2)(P - P_3)(P - P_4)}{(P_1 - P_0)(P_1 - P_2)(P_1 - P_3)(P_1 - P_4)} P_1 V_1 \quad +$$

$$\frac{(P - P_0)(P - P_1)(P - P_3)(P - P_4)}{(P_2 - P_0)(P_2 - P_1)(P_2 - P_3)(P_2 - P_4)} P_2 V_2 \quad +$$

$$\frac{(P - P_0)(P - P_1)(P - P_2)(P - P_4)}{(P_3 - P_0)(P_3 - P_1)(P_3 - P_2)(P_3 - P_4)} P_3 V_3 \quad +$$

$$\frac{(P - P_0)(P - P_1)(P - P_2)(P - P_3)}{(P_4 - P_0)(P_4 - P_1)(P_4 - P_2)(P_4 - P_3)} P_4 V_4 \quad (V.60)$$

Equation (V.60) is seen to be a fourth degree polynomial in
P. The desired result, V, is obtained by dividing the result

of Equation (V.60) by the known pressure, P. The interpolation polynomial defined by Equations (V.59a) and (V.59) is known as the Lagrangian interpolation polynomial. It is unique in that it expresses the interpolant, $y(x)$, as a linear function of the ordinates, $y(x_k)$, instead of in differences.

3. Differentiation

It is required to numerically differentiate the data in order to find $(\partial V/\partial T)_P$, and $(\partial V/\partial P)_T$. In order to find $(\partial V/\partial T)_P$, the fifth degree least squares polynomial is differentiated to give

$$(\partial V/\partial T)_P = B + 2CT + 3DT^2 + 4DT^3 + 5ET^4 \qquad (V.61)$$

In order to calculate $(\partial V/\partial P)_T$, Equation (V.59) is differentiated with respect to pressure

$$\left(\frac{\partial PV}{\partial P}\right)_T = \sum_{k=0}^{4} \frac{\partial L_k}{\partial P} P_k V_k \qquad (V.62)$$

where the derivatives $(\partial L_k/\partial P)$ will not be written out as they can be readily obtained from Equation (V.59a), or Equation (V.60). Then $(\partial V/\partial P)_T$ is obtained from $(\partial PV/\partial P)_T$ by

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P} \left(\frac{\partial PV}{\partial P}\right)_T - \frac{V}{P} \qquad (V.63)$$

Equations (V.62) and (V.63) are used to find the derivative

at the pressures, $P_{k'}$, where the volumes are known, as well as
at the pressure, P, where the volumes are unknown.

4. Integration

When carrying out numerical integrations, the usual
procedure is to fit a polynomial to the known points and inte-
grating the polynomial. For example, the trapezoidal rule
consists in fitting a straight line to two points and inte-
grating the resulting analytical expression. Similarly, the
parabolic formula (or Simpson's rule) consists in fitting a
parabola to three points and integrating the resulting analy-
tical expression. In general, an n-point integration consists
of fitting a polynomial of degree (n-1) to n points .
The error caused by the approximation will be proportional to
the n-th, or (n+1) derivative of the function. For example,
an approximation to an integral using two points (trapezoidal
rule) is given by

$$\int_{x_0}^{x_1} f(x)dx = \frac{x_1 - x_0}{2} \left[f(x_0) + f(x_1) \right] + E \qquad (V.64)$$

where the error in the approximation, E, is given by

$$E = \frac{(x_0 - x_1)^3}{12} \frac{d^2 f(x)}{dx^2} \qquad (V.65)$$

where the derivative is evaluated at some point between x_0

and x_1. If the function were truly linear then the error would be zero, since the second derivative is zero everywhere.

Since the least-squares curve fit is done with a fifth degree polynomial, and interpolation with a fourth degree polynomial, the results would be exact if the functions were exactly expressible by fourth or fifth degree polynomials. Using a five point integration, a typical formula would be (_32_)

$$\int_{-1}^{1} f(x)dx = \frac{1}{45} \left[7f(-1) + 32f(-\tfrac{1}{2}) + 12f(0) + \right.$$

$$\left. 32f(\tfrac{1}{2}) + 7f(1) \right] \tag{V.66}$$

with an error given by

$$E = \frac{1}{15120} \frac{d^6 f(x)}{dx^6} \tag{V.67}$$

Equation (V.66) would give exact results for a function which could be expressed exactly by a fifth degree polynomial. The range of integration has been normalized to (-1, 1), and it is seen that the five ordinates used are equally spaced within the range (-1, 1).

If, instead of evaluating the function at evenly ordinates, the ordinates are evaluated at some special points, it is possible to achieve a greater order of accuracy, with the same number of points, or the same order of accuracy

with a smaller number of points. By order of accuracy is
meant the degree of polynomial for which the approximation
will give exact results. For example, the Legendre-Gauss
three point formula (32),

$$\int_{-1}^{1} f(x)dx = \frac{1}{9}\left[5f(-\frac{\sqrt{15}}{5}) + 8f(0) + 5f(\frac{\sqrt{15}}{5})\right]$$

$$(V.68)$$

with an error given by

$$E = \frac{1}{15750}\frac{d^6 f(x)}{dx^6} \qquad\qquad (V.69)$$

contains only three ordinates but is about as accurate as
Equation (V.66), which contains five ordinates. The objec-
tion to Equation (V.68) is that the ordinates have to be
evaluated at inconvenient points, i.e., $(\sqrt{15}/5)$, but when
carrying out the calculations on a computor, it is no more
difficult to evaluate the ordinates at irrational values of
the abscissas then it is for integer values.

Both of the Equations (V.66) and (V.68) are exact
for functions which can be represented exactly by a fifth
degree polynomial. Since Equation (V.68) requires the eval-
uation of three ordinates, compared to five ordinated for
Equation (V.66), it will be used for carrying out the numeri-
cal integrations.

In carrying out the numerical integrations, the range will be (P_1, P_2), instead of $(-1, 1)$. For example, if the integral

$$\int_{P_1}^{P_2} X dP$$

is to be evaluated, Equation (V.68) is transformed to

$$\int_{P_1}^{P_2} X dP = \frac{P_2 - P_1}{18} (5X_a + 8X_b + 5X_c) \qquad (V.70)$$

where X_a is evaluated at the pressure

$$P_a = 0.1127015 \, P_2 + 0.8872985 \, P_1 \qquad (V.71)$$

X_b is evaluated at

$$P_b = 0.5 \, P_2 + 0.5 \, P_1 \qquad (V.72)$$

and X_c is evaluated at

$$P_c = 0.1127015 \, P_1 + 0.8872985 \, P_2 \qquad (V.73)$$

Thus, the Legendre-Gauss formula will be used for carrying out the numerical integrations.

VI. COMPUTOR PROGRAM FOR CALCULATING THERMODYNAMIC NETWORKS

A. General Description

A computor program was written in the FORTRAN language (35) to carry out the calculation of thermodynamic networks. The program is general in the sense that it is applicable for any gas for which the necessary data are available. The type of data which are used as input is restricted to certain standardized formats, but a reasonable amount of flexibility is provided.

The FORTRAN statements for the programs, together with a detailed explanation will be found in Appendix B. A detailed explanation of the input and output will also be found in Appendix B and in Appendix C.

B. Standard Input

The standard input to the program will consist of the following data:

1. Vapor pressure
2. Heat capacity as a function of temperature at the reference pressure
3. Specific volume as a function of temperature at various constant pressures

The pressures covered by the volumetric isobars will determine the pressure limits of the thermodynamic network, and the temperature range of the heat capacity data will determine the temperature range of the network.

C. Order of Calculation

The program is divided into subroutines, each of which performs a different operation. The calculation starts in the main program for some preliminary calculations, after which control is transferred to the subroutine SETUP. In SETUP, the pressure-temperature matrix of the thermodynamic network is defined. The matrix consists of the evenly spaced pressures and temperatures for which the final results will be calculated. Then, the actual calculation begins. The first set of specific volumes and temperatures at some pressure, P_1, are read into the program. Control is transferred to the subroutine CURFT, which calculates the constants for the least squares polynomial which represents the set of specific volumes and temperatures at P_1. The coefficients of the polynomial are stored and control is transferred back to SETUP. The second set of specific volumes and temperatures, at P_2, are read into the program and the same procedure is followed. Thus, control is transferred back and forth between SETUP and CURFT until all the volumetric data has been read and curve fit. When the curve fitting of the volumetric data is completed, at a set of pressures

P_1, P_2, ..., the same procedure of curve fitting is used for the heat capacity and vapor pressure data.

All of the data having been read into the program and curve fit, control transfers to the subroutine HSTARK. In HSTARK, the enthalpy and entropy are calculated as a function of temperature at the reference pressure, by using the least squares polynomial which gives the heat capacity as a function of temperature. The enthalpy and entropy are calculated at each temperature on the temperature-pressure matrix.

The calculation of the isothermal changes in enthalpy, entropy, and heat capacity are carried out in the subroutine PRNT. This is accomplished by integrating Equations (V.13), (V.23), and (V.46)

$$dS = -(\partial V/\partial T)_P dP \tag{V.13}$$

$$dC_P = -T(\partial^2 V/\partial T^2)_P dP \tag{V.23}$$

$$dH = \left[V - T(\partial V/\partial T)_P\right] dP \tag{V.46}$$

The integrations are carried out using the Legendre-Gauss three point formula. The enthalpy, entropy and heat capacity are calculated and tabulated at each pressure on the pressure-temperature matrix. This process is repeated for each constant temperature, and in this manner the entire thermodynamic network is constructed.

In addition to the calculations of enthalpy, entropy and heat capacity, the specific volumes are calculated at each point on the network by interpolation. The other properties, such as heat capacity at constant volume, Joule-Thomson coefficient, fugacity coefficient and compressibility factor are also calculated.

D. Standard Output

The standard output will consist of a tabulation, at constant temperature, of specific volume, enthalpy, entropy, and constant pressure heat capacity, all as a function of pressure.

The first line identifies the substance and the second line gives the temperature, together with its units. The next two lines have the column headings and corresponding units. Then, the remaining lines contain the tabulation, which may extend as far as necessary to cover the entire pressure range. The entire table is repeated for the other temperatures on the network.

In addition, the coefficients of the vapor pressure equation are printed and vapor pressures are tabulated at even temperatures, and at even pressures.

E. Input and Output Options

1. Output

In addition to the standard output of specific

volume, enthalpy, entropy and heat capacity, additional output may be tabulated, if desired. The optional tabulated output consists of the compressibility factor, residual volume, fugacity coefficient, Joule-Thomson coefficient, heat capacity at constant volume, difference of heat capacities, ratio of heat capacities, and sonic velocity.

2. Input

a. Heat Capacity Coefficients

It frequently happens that heat capacity data are available in the form of a temperature polynomial in the literature. In this case, the coefficients are read directly into the program, and the curve-fitting of the heat capacity data may be eliminated. When heat capacity data are curve-fit in the program, the result is a fifth degree polynomial in temperature. When the coefficients of a polynomial are read into the program, the corresponding polynomial may be as high as the fifth degree, but may also be of a lower degree.

b. Sonic Velocity

The calculation of heat capacities from sonic velocity data was described in Section II.D. If it is desired to go through this calculation, an option to read sonic velocity data into the program is available. If this is done, all heat capacities at constant pressure are calculated from the sonic velocity data.

c.   Vapor Pressure Correlation

When the vapor pressure is measured, or when data
are available in the literature, the program calculates the
constants of a vapor pressure equation from actual measured
data. When measured data are not available, it is still
possible to estimate the vapor pressure using a generalized
correlation. The method used in this program is Riedels'
correlation (69) as presented by Reid and Sherwood (67).
Using only the critical pressure and temperature and one
other vapor pressure point, it is possible to calculate the
entire vapor pressure curve. The additional vapor pressure
point would usually be the normal boiling point. When it is
desired to carry out this calculation, an input option is
provided so that the necessary data may be read into the
program.

F.   Using the Computor Program

1.   Running Time

The calculation of a thermodynamic network, using
the computor program written for the IBM 7094 digital com-
putor, requires very little time. For example, one of the
calculations of a thermodynamic network of nitrogen took
0.89 minutes. The thermodynamic network was calculated for
21 temperatures covering the range from $135^{\circ}K$ to $700^{\circ}K$, and
18 pressures, covering the range from 1 atmosphere to 100
atmospheres. Thus, a total of 378 points were calculated on

the thermodynamic network. At each of these points the following properties were calculated and tabulated:

1. Specific volume

2. Enthalpy

3. Entropy

4. Constant pressure heat capacity, C_p.

5. Compressibility factor

6. Residual volume

7. Fugacity coefficient

8. Joule-Thomson coefficient

9. Heat capacity at constant volume, C_v.

10. C_p/C_v

11. $C_p - C_v$

12. Sonic velocity

The calculation also included fitting vapor pressure data to a least squares polynomial, and calculating vapor pressures at evenly spaced pressures and at evenly spaced temperatures. Thus, a complete thermodynamic network can be calculated in about one minute.

The output is printed out, and also punched out on cards. From the information punched on the cards, additional print-outs may be obtained. In addition, the cards may be rearranged so that data may be selectively printed out without altering the computor program.

2. Size of Network

Presently, the computor program will calculate a

thermodynamic network with a maximum of 75 printed pressures and 75 printed temperatures. There is sufficient storage space available to calculate a network using a few thousand pressures and temperatures. This may be done by a slight modification of the program, i.e., increasing the fortran dimension statement. It is also possible to calculate larger thermodynamic networks without modifying the program. This can be done by running the program a number of times. For example, if it was desired to have the thermodynamic properties tabulated at 150 temperatures, then two runs are sufficient with 75 temperatures per run.

3. Reference Points for Thermodynamic Network

The computor program is set up so that the reference pressure and temperature for entropy and enthalpy are automatically selected as the lowest pressure, P_0, and temperature, T_0, on the thermodynamic network. Usually a reference value of entropy and of enthalpy will be selected that will correspond to the reference pressure and temperature as described above. It may happen, however, that it is desired to fix the values of the entropy and enthalpy at some other pressure, P_1, and temperature, T_1. If the values of the entropy and enthalpy are known at P_0 and T_0 that will give the desired values of entropy and enthalpy at P_1 and T_1, then the reference point may be shifted. Generally, these values will not be known, but may be calculated by starting

the program at P_1 and T_1, and working backwards to P_0 and T_0 in order to calculate the entropy and enthalpy. Then the calculation is repeated by feeding in the entropy and enthalpy, at P_0 and T_0, which will give the desired values at P_1 and T_1. Thus, if a preliminary calculation is made with the program, then there is no restriction on the reference pressure and temperature.

The fact that the reference point is not restricted to the lowest pressure and temperature is important. One use is when it is desired to make a comparison with another thermodynamic network. Another use is when it is desired to avoid certain pressures and temperatures as the reference points. For example, it may be desired to extend the network to a very low temperature, which would normally be the reference temperature. However, at the low temperature the input data may not be as reliable as the data in some other region. Thus, the reference point may be selected at a point where the data are well established.

4. Method of Running Problems

The input and output have been described above in this section. A more detailed explanation with a sample calculation for ethane will be found in Appendix C.

In Section III, the results of the least squares curve fitting were presented. It was seen that the constant pressure volumetric data could be represented as a fifth

degree polynomial in temperature. While a single polynomial could be used to represent data from the saturation curve to high temperature in the ideal gas region, it might be preferable to use more than a single polynomial. This would be desirable if there are a large number of data points which cover a large temperature range.

When there are more than 75 data points per isobar two or more polynomials must be used. In order to do this, the program must be run two or more times. For example, the first run through would cover the range of the first 75 data points, say from T_o to T_1. The next run through would use the next 75 data points to calculate the remaining portion of the thermodynamic network, say from T_1 to T_2. Additional runs may be used as required.

Successive jobs may be run without interruption by stacking the necessary sets of data cards. When a job is completed, the program will automatically proceed to the next set of data cards. When there are no more data cards the calculation is terminated.

VII. IDEAL GAS MODEL

A. Description of Method Used

Having developed a computor program it was necessary to verify that the results obtained with the program were reliable. A simple way to make such a check was to assume an ideal gas, so that the results of the calculation were known in advance. Not only was it important to check out the program, but also to check the accuracy of the approximation techniques used.

By feeding in ideal gas data that was exact (about six significant figures) the efficiency of the approximation techniques used can be determined by comparing the calculated results with the theoretical results for an ideal gas.

Toward this end, volumetric data were calculated for a hypothetical ideal gas which had a molecular weight of 10, and a heat capacity ratio of 1.400.

In one case heat capacities at constant pressure were used as input (constant at 0.69513 BTU/lb-^{o}R), and in another case, sonic velocity data were used. The heat capacity, sonic velocity and heat capacity ratio used are all consistent for a gas with a molecular weight of 10. The output is expressed on a per pound basis, and quantities per mole are easily obtained (if desired) by shifting the decimal point one place to the right.

The fact that the calculations are carried out for an ideal gas does not have any effect on the accuracy of the results, since the numerical techniques are the same. Data is read in, curve fit, interpolated, differentiated and integrated by the same equations as would be used in the general case. The steps in the calculation are in no way simplified because the gas is ideal. By carrying through the calculations in this matter, the accuracy of the numerical methods may be determined since it is known that the input data are exact.

B. Results of Calculation

The results are presented in Table VII.1 for the case when heat capacity data were used as input, and in Table VII.2 when sonic velocity data were used as input. In each case the full output is tabulated, consisting of specific volume, enthalpy, entropy, heat capacity at constant pressure, compressibility factor, residual volume, fugacity coefficient, Joule-Thomson coefficient, heat capacity at constant volume, C_p/C_v, $C_p - C_v$ and sonic velocity. For each case the results are tabulated at $650^\circ R$ only. The results for other temperatures are not presented as they will provide no additional useful information.

1. Volume, Entropy, Enthalpy and Heat Capacity at Constant Pressure

Examining Table VII.1, one may verify that the

TABLE VII.1

THERMODYNAMIC PROPERTIES OF HYPOTHETICAL IDEAL GAS
CALCULATED FROM HEAT CAPACITY DATA

TEMPERATURE   650.0 DEG R

PRESSURE PSIA	VOLUME CU FT/LB	ENTHALPY BTU/LB	ENTROPY BTU/LB-R	HEAT CAP BTU/LB-R
10.000	.69745E 02	.10427E 03	.18238E 00	.69513
20.000	.34872E 02	.10427E 03	.44717E-01	.69510
30.000	.23248E 02	.10427E 03	-.35812E-01	.69511
40.000	.17436E 02	.10427E 03	-.92948E-01	.69512
50.000	.13949E 02	.10427E 03	-.13727E 00	.69509

PRESSURE PSIA	COMP. FACTOR	RESIDUAL VOLUME CU FT/LB	FUGACITY COEF.	J-T COEF. DEG R/PSIA
10.000	1.00000	.381470E-04	1.00000	-.00005
20.000	1.00000	.152588E-04	1.00000	.00008
30.000	1.00000	-.500670E-05	1.00000	-.00002
40.000	1.00000	.119209E-05	1.00000	-.00005
50.000	1.00000	.301600E-04	1.00000	.00005

PRESSURE PSIA	CV BTU/LB-R	CP-CV BTU/LB-R	CP/CV	SONIC VELOCITY FT/SEC
10.000	.496524	.198608	1.40000	2126.9315
20.000	.496490	.198613	1.40003	2126.9617
30.000	.496498	.198611	1.40002	2126.9546
40.000	.496516	.198604	1.40000	2126.9274
50.000	.496480	.198611	1.40004	2126.9441

TABLE VII.2

THERMODYNAMIC PROPERTIES OF HYPOTHETICAL IDEAL GAS
CALCULATED FROM SONIC VELOCITY DATA

TEMPERATURE   650.0 DEG R

PRESSURE PSIA	VOLUME CU FT/LB	ENTHALPY BTU/LB	ENTROPY BTU/LB-R	HEAT CAP BTU/LB-R
10.000	.69745E 02	.10427E 03	.18238E 00	.69514
20.000	.34872E 02	.10427E 03	.44722E-01	.69516
30.000	.23248E 02	.10427E 03	-.35808E-01	.69516
40.000	.17436E 02	.10427E 03	-.92944E-01	.69513
50.000	.13949E 02	.10427E 03	-.13726E 00	.69512

PRESSURE PSIA	COMP. FACTOR	RESIDUAL VOLUME CU FT/LB	FUGACITY COEF.	J-T COEF. DEG R/PSIA
10.000	1.00000	.381470E-04	1.00000	-.00005
20.000	1.00000	.152588E-04	1.00000	.00008
30.000	1.00000	-.500679E-05	1.00000	.00002
40.000	1.00000	.119209E-05	1.00000	-.00005
50.000	1.00000	.301600E-04	1.00000	.00005

PRESSURE PSIA	CV BTU/LB-R	CP-CV BTU/LB-R	CP/CV	SONIC VELOCITY FT/SEC
10.000	.496536	.198608	1.39999	2126.9243
20.000	.496551	.198613	1.39998	2126.9243
30.000	.496548	.198611	1.39998	2126.9243
40.000	.496521	.198604	1.39999	2126.9243
50.000	.496512	.198611	1.40001	2126.9243

volumes, enthalpies, and entropies correspond to the theore-
tical value from the ideal gas law. For entropy and enthalpy,
the reference state is $500°R$ and 10 psia, where $S = 0$ and
$H = 0$. It is seen at a glance that the calculated enthalpy
is not a function of pressure, as, of course, is predicted
by the ideal gas law. A heat capacity of 0.69513 is input
at 10 psia and heat capacities at higher pressures are cal-
culated by integrating

$$(\partial c_p/\partial P)_T = -T(\partial^2 v/\partial T^2)_P \qquad (V.23)$$

Equation (V.23) requires the evaluation of the second deriv-
ative at a number of different pressures in order to carry
out the numerical integration. In spite of the relative
loss of accuracy in the differentiation, the resulting heat
capacities, as a function of pressure, are almost constant,
as required for an ideal gas. The largest discrepancy is
four digits in the least significant figure, or a maximum
error of about 0.006 per cent.

2. Compressibility Factor, Residual Volume, Fugacity
   Coefficient, and Joule-Thomson Coefficient

It is seen from Table VII.1, as well as from Table
VII.2, all compressibility factors and fugacity coefficients
are unity to at least six significant figures. The tabulated
residual volumes should be zero, and would round off to zero
when compared with the specific volumes. The small discrepencies

are due to round-off errors and are of no significance. For example, at 10 psia the residual volume is given as 0.000038 ft^3/lb, which is clearly insignificant when compared to a specific volume of 69.754 ft^3/lb. The same may be said of the tabulated Joule-Thomson coefficients, i.e., the maximum value calculated is only 8 x 10^{-5} °R/psia, whereas they should be zero for an ideal gas.

3. Heat Capacity at Constant Volume, Difference of Heat Capacities, Ratio of Heat Capacities, Sonic Velocity

The heat capacity at constant volume is calculated accurately to four significant figures, i.e., 0.4965 BTU/lb-°R, with a maximum error of about 0.005 per cent. This result is quite good considering that C_v is calculated from Equation (V.31)

$$C_v = C_p + T \frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} \qquad (V.31)$$

Since the calculated C_p requires the second derivative $(\partial^2 V/\partial T^2)_P$, there are many places where inaccurate derivatives could lead to poor values of C_v in Equation (V.31). Nevertheless, C_v is calculated with high accuracy.

In the calculation $C_p - C_v$, the same comments apply. For an ideal gas, the result should be equal to the universal gas constant, R. This turns out to be the case, to five significant figures. For the ratio of heat capacities,

the exact answer should be 1.400. The maximum error is 0.00004 or about 0.003 per cent. It is also seen that the sonic velocity is constant and calculated correctly to five significant figures in Table VII.1.

In Table VII.2, the sonic velocity data are input, and the heat capacities are calculated from Equation (V.44)

$$C_p = \frac{-T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T + (V/a)^2} \tag{V.44}$$

In this case, the heat capacities are calculated to about the same accuracy as when Equation (V.23) is used. The same comment applies to the other quantities which are subsequently calculated from the constant pressure heat capacity.

C. Discussion of Results

It is seen that, given sufficiently accurate data, it is possible to calculate the thermodynamic properties of an ideal gas with excellent accuracy, using the numerical methods discussed previously. These results are important, not for calculating the properties of an ideal gas, but to prove that the proposed method is adequate for at least this simple case. If the results of the calculations gave poor agreement for an ideal gas, then the numerical methods certainly would not have been adequate for treating real gas data. However, by proving that the techniques are satisfactory for an ideal

gas, by no means proves that they will be as satisfactory for a real gas.

From examining the results of the ideal gas calculations, a good deal of information can be obtained concerning the calculation of the thermodynamic networks of real gases. For example, none of the numerical techniques used make special use of the fact that the gas is ideal. Discrete data is curve fit, interpolated, differentiated and integrated without any regard to the fact that it may, or may not, be exactly represented by some analytical function. As it turns out, the numerical techniques are exact for data which can be analytically represented by polynomials of the fourth or fifth degree. Thus, exact results (except for round-off error) would be expected for an ideal gas, as well as for any real gas whose equation of state could be exactly represented by a set of fourth or fifth degree polynomials.

In general, the analytical behavior of a real gas is not known, although complex algebraic equations of state have been used to represent the behavior of many real gases to within experimental accuracy. The experimental data on many gases can be represented by fifth degree polynomials. For example, a set of polynomials relating volume to temperature at various constant pressures, or a set of polynomials relating volume to pressure at various constant temperature. For gases whose equation of state cannot be represented by such simple polynomials, the calculated results will be in error, in addition to any round-off error introduced by the

calculation. Thus, the thermodynamic properties of any real gas could be calculated to good accuracy, given sufficiently accurate data, and if the actual volumetric data of the gas can be expressed by fourth or fifth degree polynomials without too much error.

VIII. COMPARISON OF CALCULATED AND LITERATURE THERMODYNAMIC PROPERTIES OF NITROGEN

A. Method of Comparison

The best way of determining the accuracy of the calculated thermodynamic network is to make a comparison with a reliable thermodynamic network based on the same data. Nitrogen was chosen since it is a substance which has been well investigated and a number of excellent compilations of its properties exist. For comparison purposes, the compilations of Din (23), Woolley (90) and Miller and Sullivan (57) were selected. These compilations have the further advantage in that they are all based, in general, on the same volumetric data (1, 3, 33, 53, 54, 60), so that a comparison of the final results will be meaningful. In addition, these compilations represent examples of different techniques.

For the thermodynamic network generated in this work, volumetric data, as well as heat capacity data, were taken from Din, to be used as input to the computor program. These data do not correspond exactly to the measured data since they have been rounded off and interpolated by Din. Also, these data do not agree exactly with that presented by the other compilations due to different rounding procedures. However, there are only small discrepencies, which are usually less than the experimental error, and which should not affect any calculated thermodynamic properties.

B. Other Compilations Found in the Literature

A brief discussion is given below to indicate the various methods used by previous investigators to calculate the thermodynamic network of nitrogen.

1. Din's Compilation (23)

Din's compilation is the most comprehensive, covering pressures up to 10,000 psia and temperatures to 700°K. The calculational procedure used was a combination of numerical and graphical techniques. The volumetric data was plotted, smoothed, cross-plotted and smoothed a number of times. Eventually the derivatives, $(\partial V/\partial T)_P$ and $(\partial^2 V/\partial T^2)_P$, were calculated by taking first and second central differences respectively, as a function of pressure and temperature at a set of evenly spaced temperatures and pressures. From the second derivative, combined with heat capacity data at one atmosphere, the constant pressure heat capacity was calculated as a function of pressure, for various constant temperatures. Selecting a reference temperature for the entropy and enthalphy, the entropy and enthalpy are then calculated as a function of pressure at the reference pressure. Then, the enthalpy and entropy are calculated as a function of temperature at each pressure for which the high pressure heat capacities have been calculated. The final results are tabulated at evenly spaced pressures and temperatures.

2. Woolley's Compilation (90)

Woolley fitted experimental P-V-T data to a virial equation of state based on a Lennard-Jones 6-12 potential function. Thus, the thermodynamic functions can be calculated analytically once the constants of the equation of state are determined. The problem here is that an exact representation of the data cannot be achieved, especially at low temperatures. Consequently, Woolley's network is incomplete near the critical region and around the saturation curve.

3. Miller and Sullivan's Compilation (57)

The compilation of Miller and Sullivan has been reworked by Burnett (11) to include additional data. However, the original Miller and Sullivan network is more convenient for the intended purpose as it includes a tabulation.

Their method was similar to the one used in the present work as the steps in the calculation followed the same path. They first calculate the enthalpy and entropy as a function of temperature at one atmosphere, and then calculate the isothermal variations in enthalpy and entropy by using the first derivative, $(\partial V/\partial T)_P$, which was found graphically. The essential difference between their work and the present work, is that they used a combination of graphical and numerical techniques, whereas in the present work, all calculations are carried out on a computor.

4. Other Works

The results will also be compared with the generalized correlation of Lyderson, Greenkorn and Hougen (49) and with some calculated values of fugacity coefficient and Joule-Thomson coefficient for nitrogen reported by Deming and Shupe (21).

C. Results

1. Method of Presentation

The thermodynamic network for nitrogen calculated in the present work covers the temperature range from the saturation curve up to $700^{\circ}K$, and for pressures up to 100 atm. The reference enthalpy and entropy were selected to agree with Din's values for the vapor at $135^{\circ}K$ at 1 atm. At this point H = 10801 joules/gmol and S = 168.20 joules/gmol-$^{\circ}K$. When comparing results with the other compilations, the necessary adjustments were made so that agreement was obtained at $135^{\circ}K$ and 1 atm. The unit used for energy is the joule, rather than the calorie or BTU. This was done to be consistent with Din, whose compilation was the most complete. For the convenience of the reader the following conversions are given for nitrogen:

$$R = 8.31439 \text{ joules/mole-}^{\circ}K$$

$$1 \text{ calorie} = 4.185 \text{ joules}$$

$$1 \text{ BTU} = 1054.8 \text{ joules}$$

$$1 \text{ joule} = 9.480 \times 10^{-4} \text{ BTU}$$

1 joule = 0.2392 calories

1 joule/gm-mole = 0.00853 calories/gm

1 joule/gm-mole - .01532 BTU/lb

1 BTU/lb = 65.2 joules/gm-mole
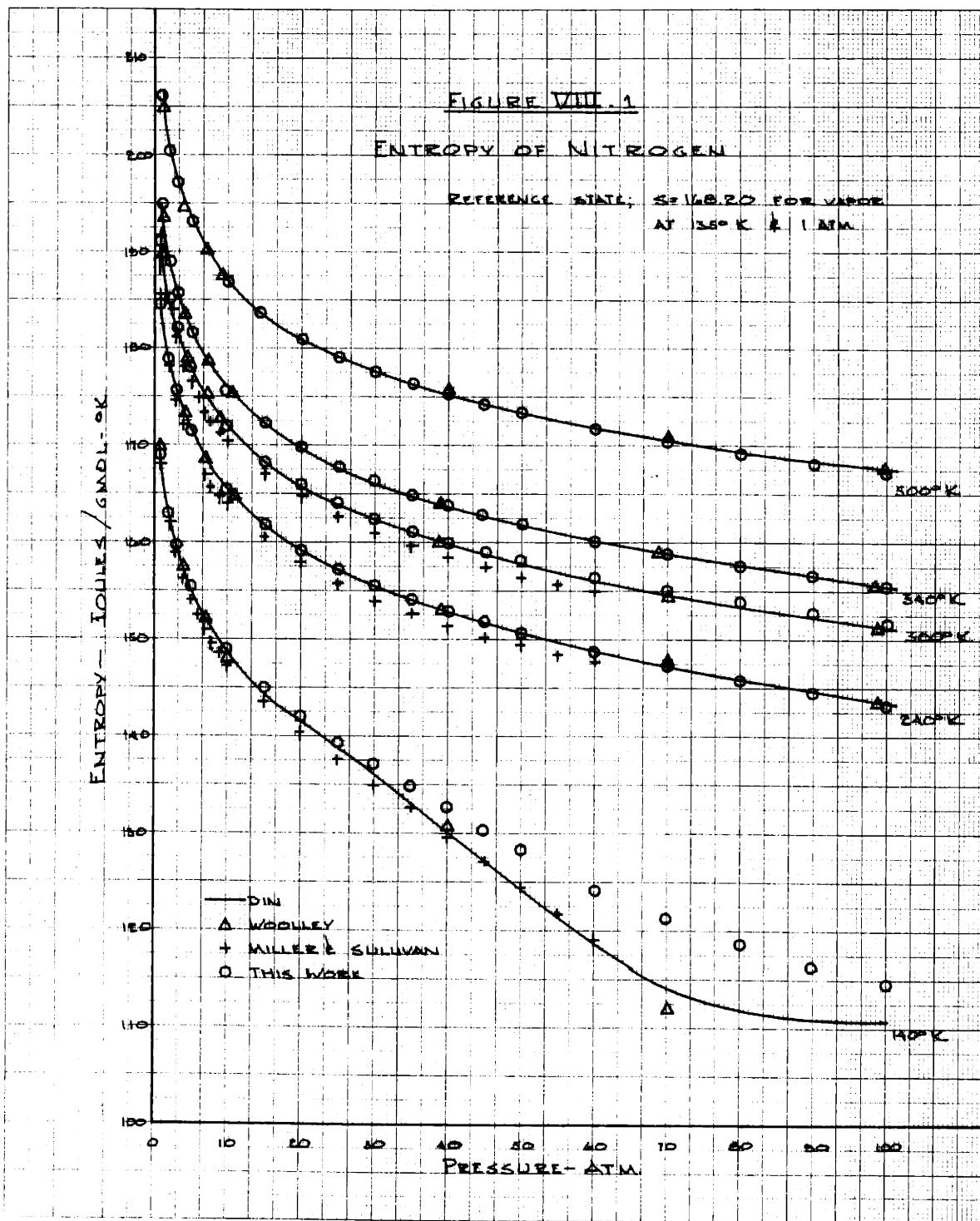
1 cal/gm = 117.1 joules/gm-mole
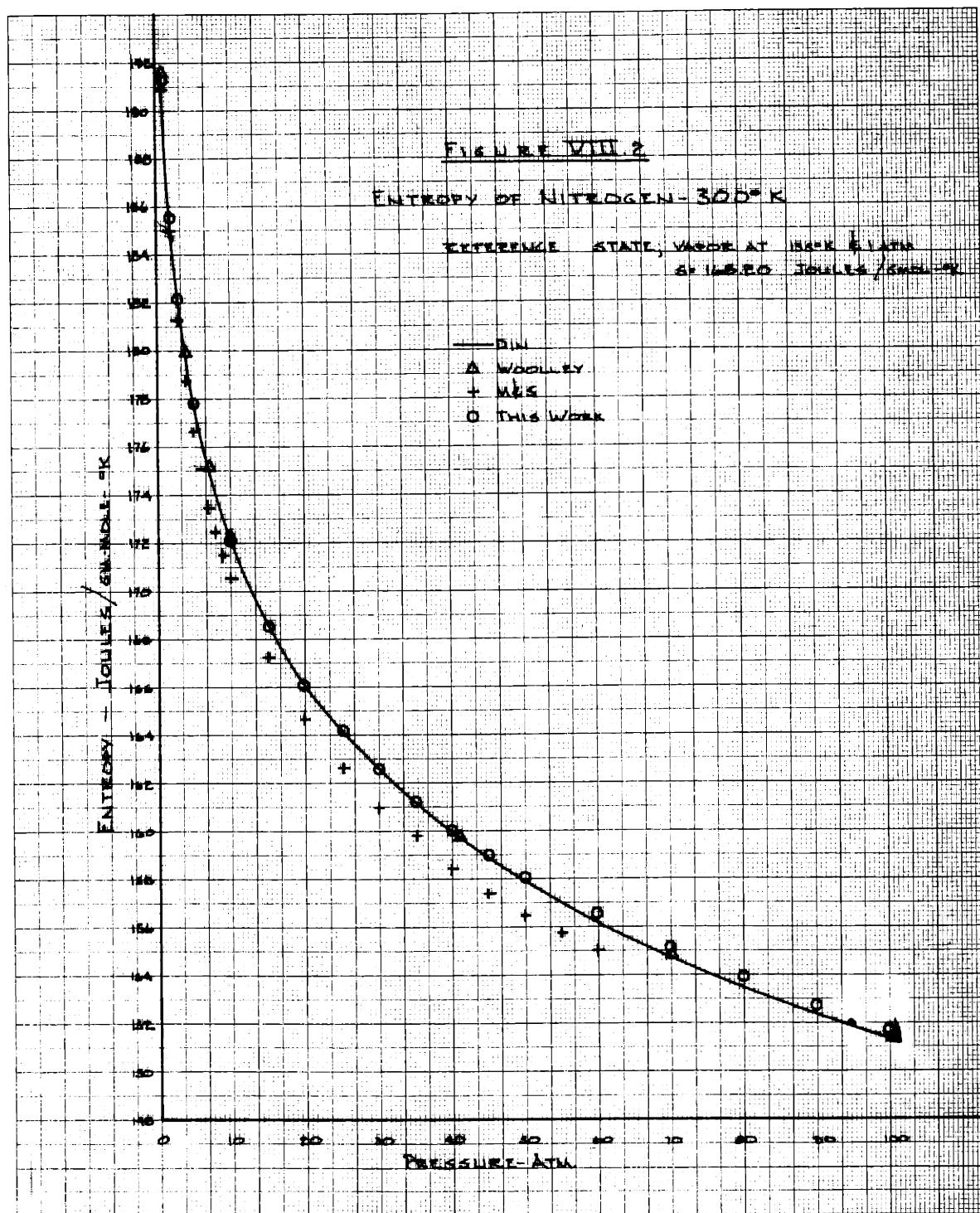
Most of the results for nitrogen will be presented as isotherms. The 140°K isotherm is close to the critical region, isotherms at 240° to 340°K cover a nonideal region, and at 500°K, the gas is nearly ideal. The highest pressure, for each isotherm, is 100 atm.

2. Entropy

Some of the results of the entropy calculation shown in Figure VIII.1 where entropy is plotted against pressure for five different temperatures and compared with other compilations. Except for the 140°K isotherm, which is in the critical region, all of the results agree well with each other. The values of Miller and Sullivan are slightly low except on the 140°K isotherm, where they are in agreement with Din's values. At the higher pressures, at 140°K, the results of Woolley, and of this work, are in poor agreement with Din's values.

In Figure VIII.2, the 300°K isotherm is replotted on a larger scale. In the more familiar units of calorie/gram-$^{\circ}$K, the entire scale would only be about 0.37 calorie/gram-$^{\circ}$K,

FIGURE VIII .1

ENTROPY OF NITROGEN

REFERENCE STATE: S = 168.20 FOR VAPOR
AT 350 K & 1 ATM.

FIGURE VII.2

ENTROPY OF NITROGEN - 300° K
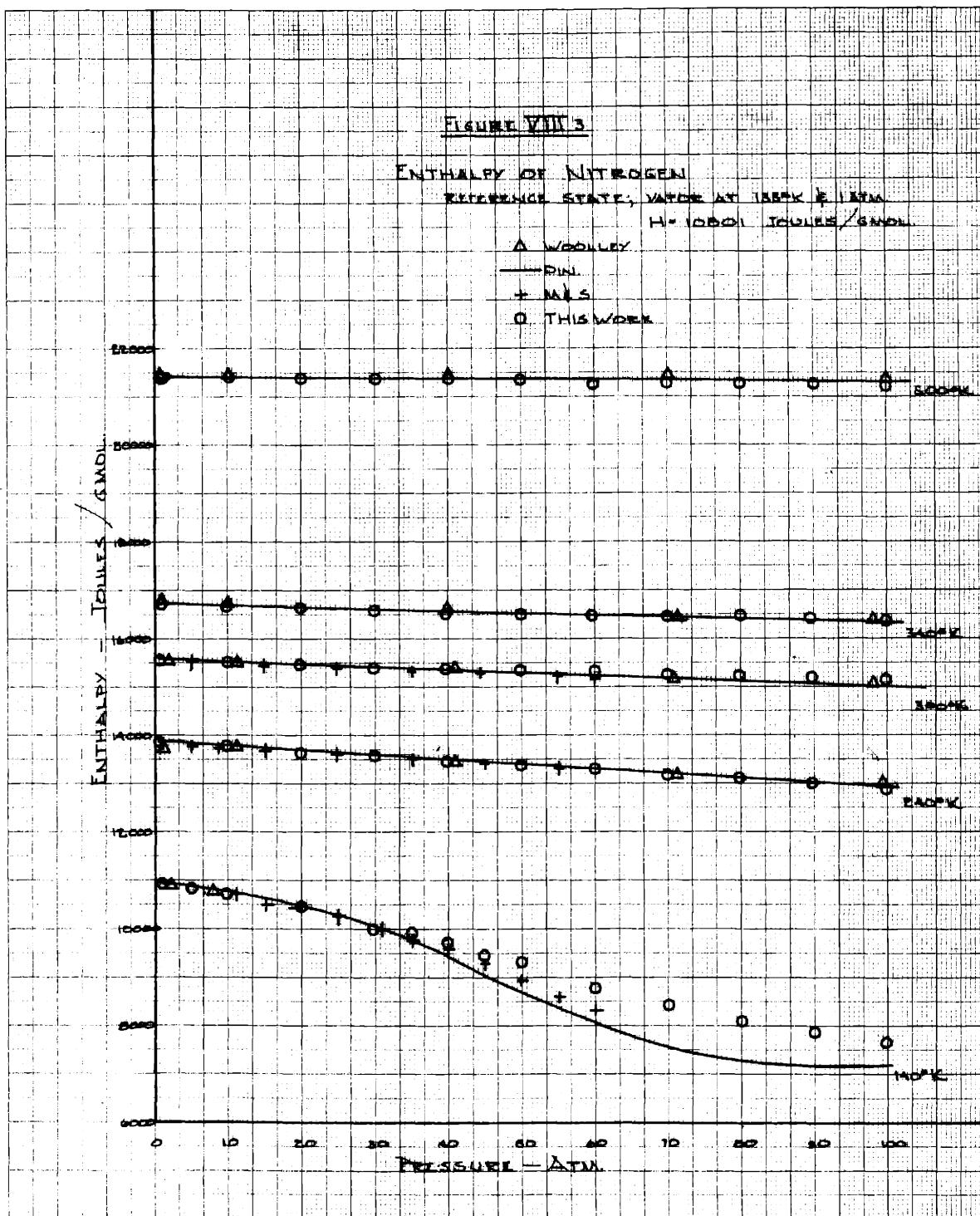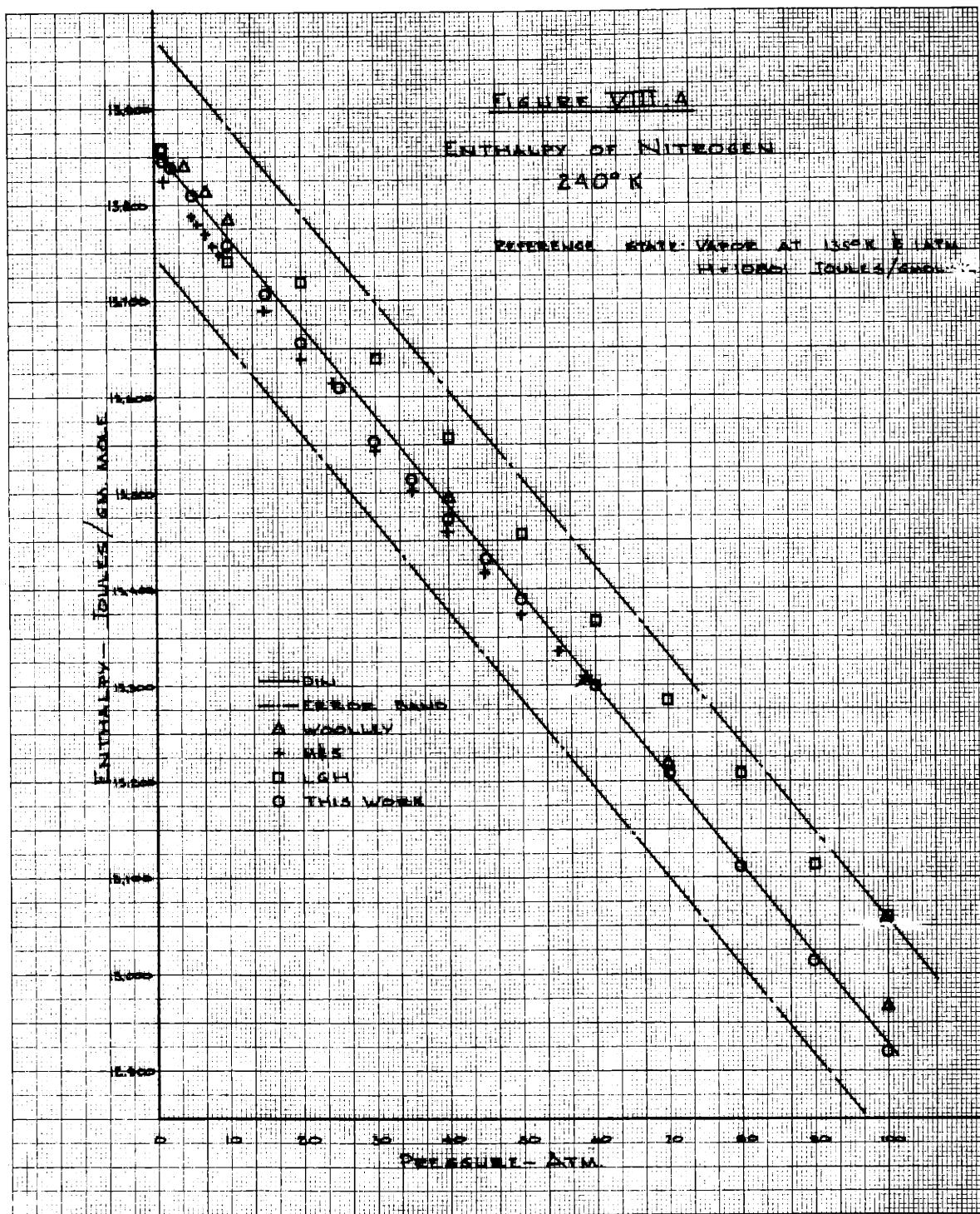
instead of about 44 joules/gram-mole-^{o}K, as it is. Even on
this large scale where differences are magnified, there is
good agreement amongst all of the values, except for those
of Miller and Sullivan, which are slightly lower than the
others. At the 300°K isotherm, the gas is out of the criti-
cal region but is non-ideal.

3. Enthalpy

Five isotherms for enthalpy are plotted in Figure
VIII.3, for the four different compilations. There is good
agreement among all values except for the 140°K isotherm.
For the 140°K, Woolley's results are only tabulated to ten
atmospheres. Above 60 atmospheres there is only Din's work
and this work. Up to 40 atmospheres, agreement is good for
all values. On Figure VIII.4, the 240°K isotherm is shown
on an enlarged scale. The entire enthalpy scale is 1000
joules/gram-mole, or about 15 BTU/lb. At this temperature,
the gas is above the critical region, but still non-ideal.
There is good agreement between Din, Woolley, Miller and
Sullivan, and the present work, the maximum difference being
about 50 joules/gram-mole or about 0.75 BTU/lb. In addition
to the above mentioned compilations, the results of Lyderson,
Greenkorn and Hougen's generalized correlation are also
shown. These points are not in as good agreement as the
others are amongst themselves, but are not bad considering
the large scale plot. The maximum deviation is only about
3 or 4 BTU/lb at 100 atmospheres.

Figure VIII 3

Enthalpy of Nitrogen
Reference State; Vapor at 135°K & 1 atm.
H = 10801 joules/gmol.

△ Woolley
——— DIN
+ MLS
○ This work

Figure VIII A

ENTHALPY OF NITROGEN

240° K

REFERENCE STATE: VAPOR AT 130°K & 1 ATM
H = 10841 JOULES/GMOL
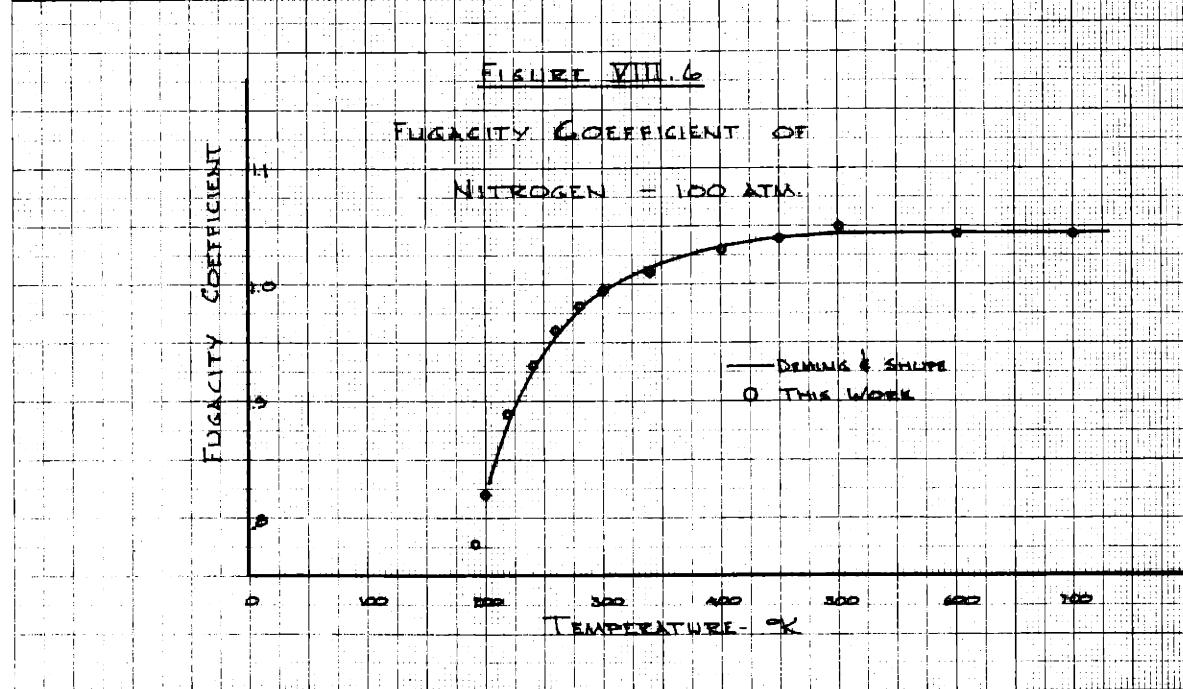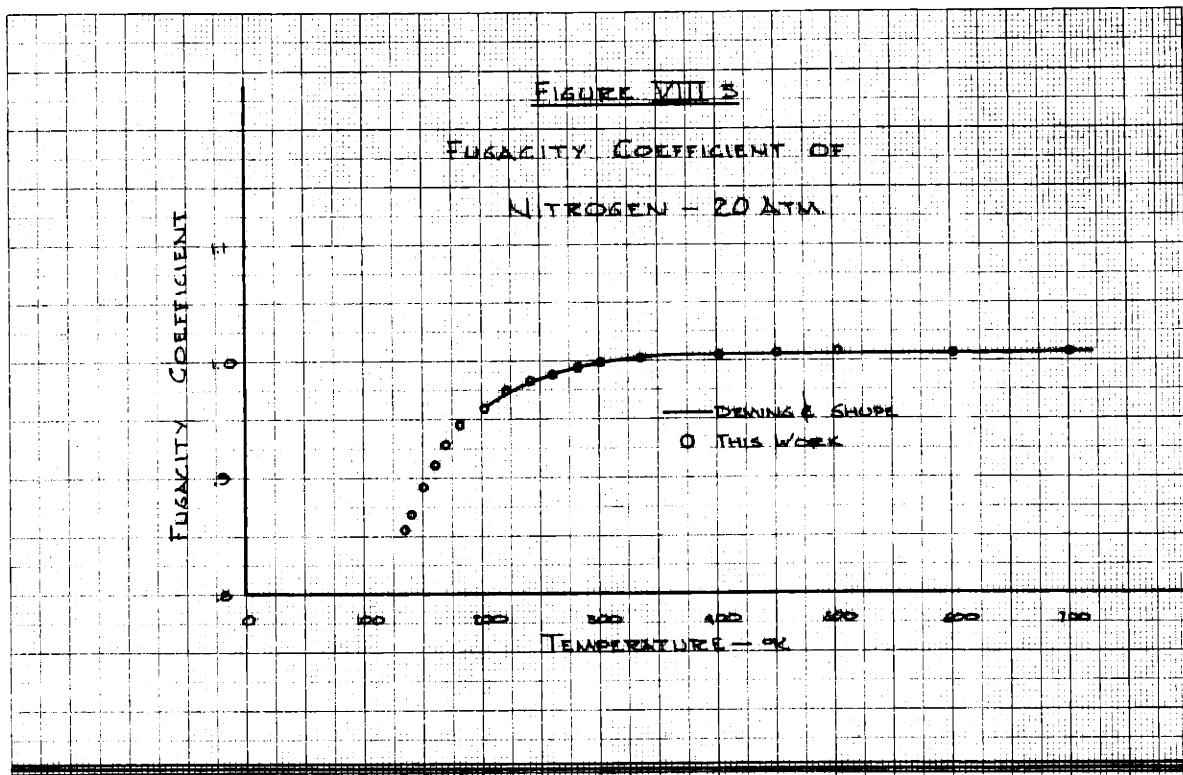
The two, almost parallel lines, which form an envelope around the plotted points, represent Din's estimate of the possible errors in enthalpy. These errors are due to errors in the measured data, as well as errors introduced in carrying out the calculations.
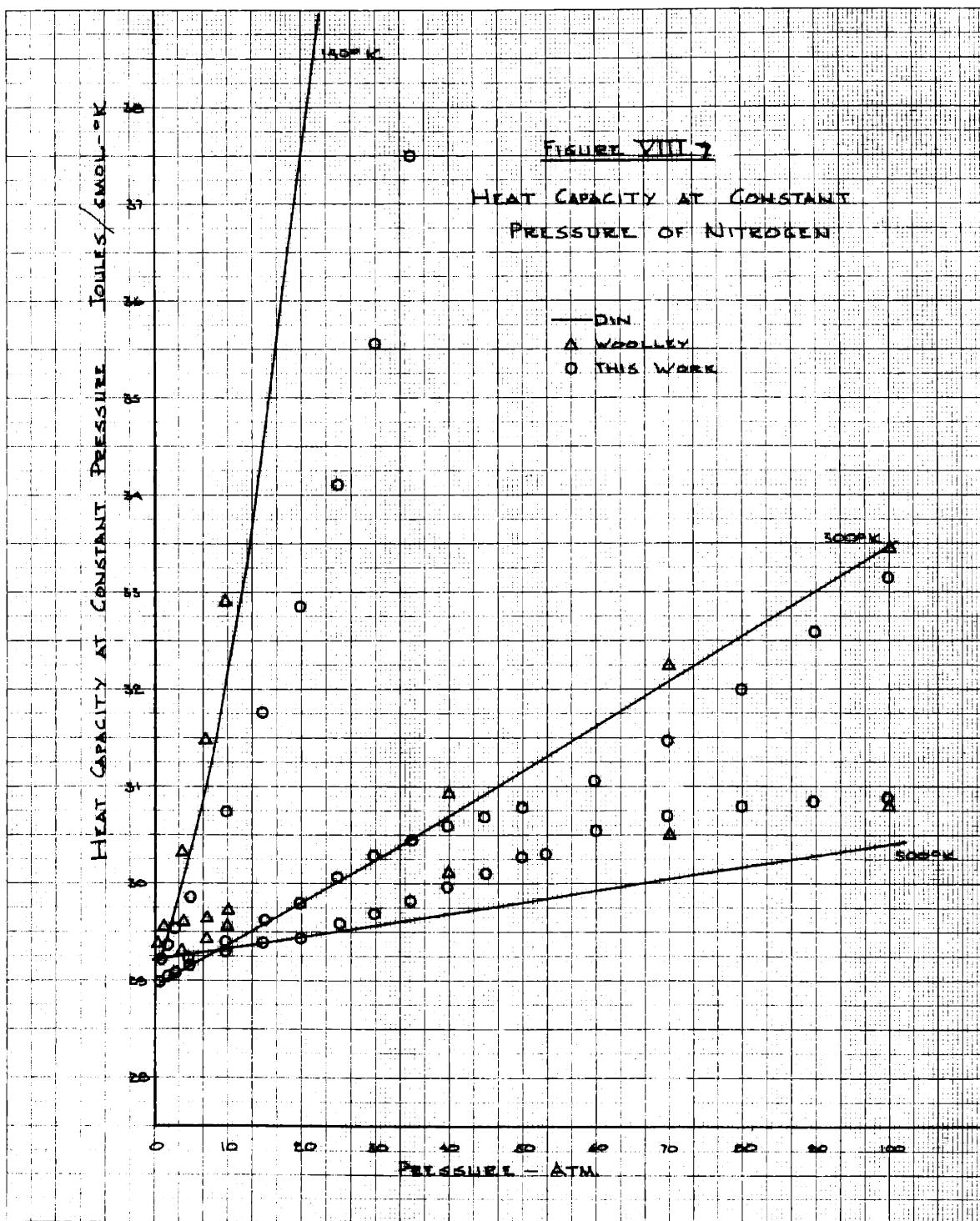
4. Fugacity Coefficient

The fugacity coefficients calculated in this work are compared with those calculated by Deming and Shupe (21). In Figures VIII.5 and VIII.6, the fugacity coefficient is plotted as a function of temperature for 20 atmospheres and 100 atmospheres. In both cases there is good agreement.

5. Heat Capacity at Constant Pressure

Heat capacities are plotted in Figure VIII.7 as a function of pressure for three temperatures. The entire scale of 10 joules/mole-^{O}K is equivalent to about 0.08 BTU/lb-^{O}R, or about 2.4 cal/mole-^{O}K. On the 140°K isotherm, the agreement is poor, with a difference of about 10 per cent at 20 atmospheres between this work and Din's. At this temperature, Woolley's tabulation only extends to ten atmospheres. Below ten atmospheres on the 140°K isotherm, and on the other isotherms, at all pressures, the differences are only two or three per cent among the three sets of points. At 300°K, Din's results and Woolley's results are in good agreement, while the results for this work are

FIGURE VIII.5

FUGACITY COEFFICIENT OF

NITROGEN - 20 ATM.

—— DEMING & SHUPE
O THIS WORK

FIGURE VIII.6

FUGACITY COEFFICIENT OF

NITROGEN - 100 ATM.

—— DEMING & SHUPE
O THIS WORK

Figure VIII 7

Heat Capacity at Constant Pressure of Nitrogen

low. At 500°K, this work and Woolley's are in good agreement, while Din's results are low, except at the lower pressures.
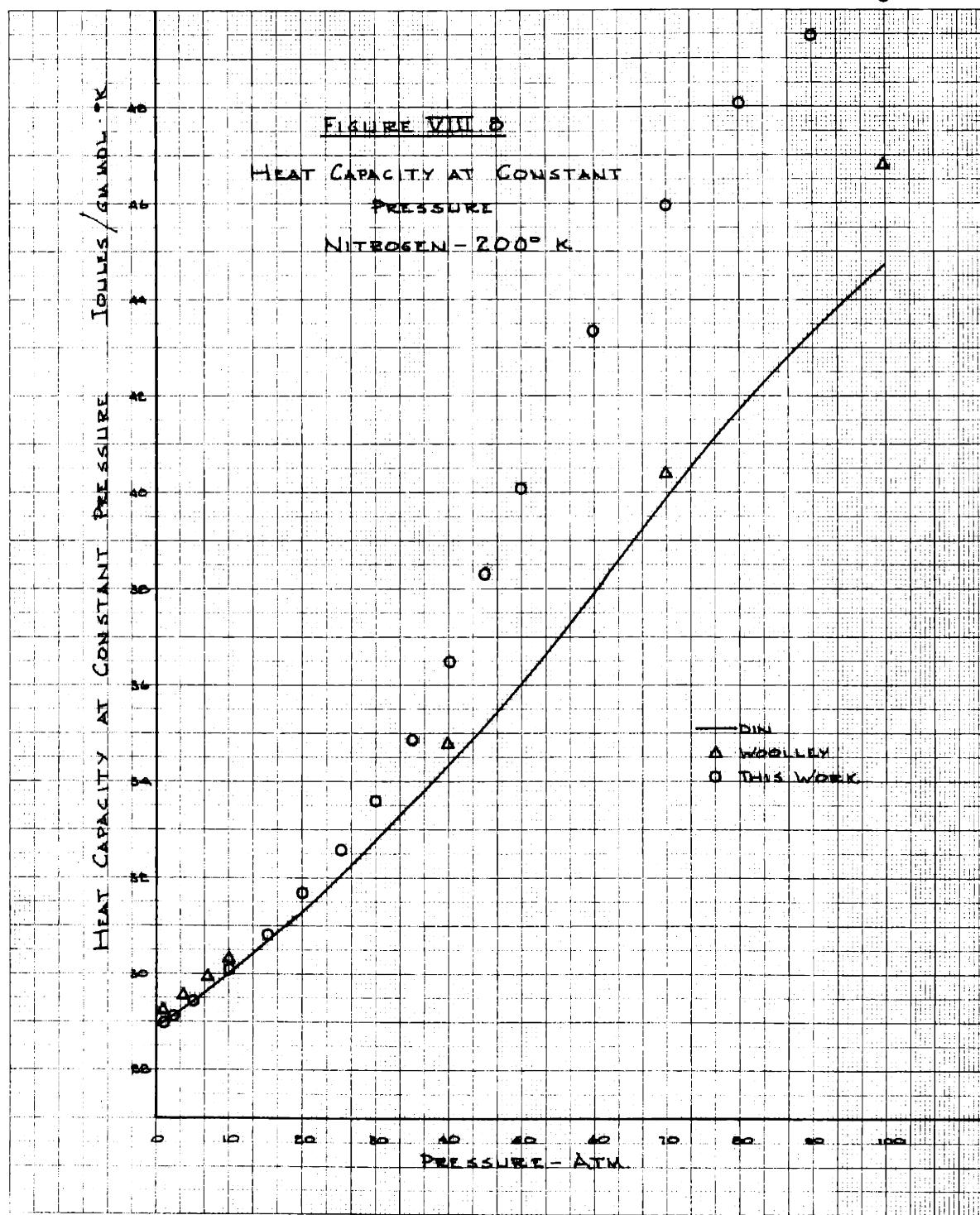
For the temperatures shown in Figure VIII.7, the agreement is fair. Those temperatures happened to give better agreement than most. In Figure VIII.8, the same type of plot is shown for 200°K. At this temperature the gas is very non-ideal. Din's results and Woolley's are in good agreement. At pressures higher than 40 atmospheres, the results of this work are high, with a maximum difference of about 10 per cent. Although not shown graphically, the results for other temperatures would be about the same. At the higher pressures, the differences are from about 2 per cent to 10 per cent.
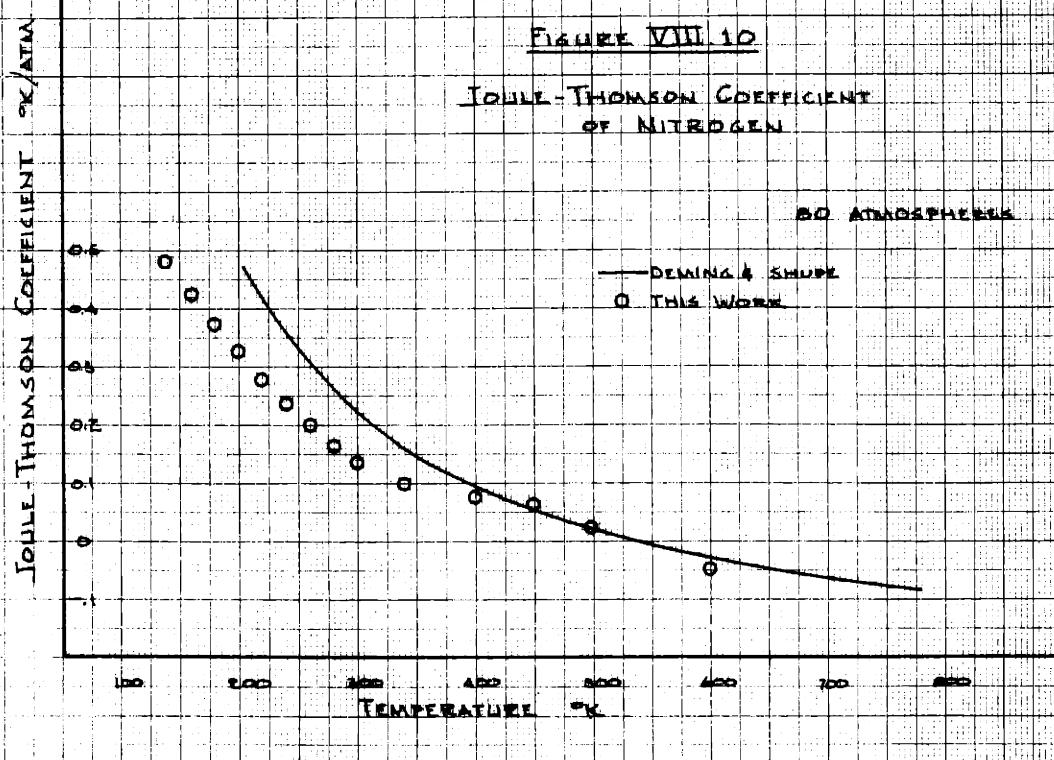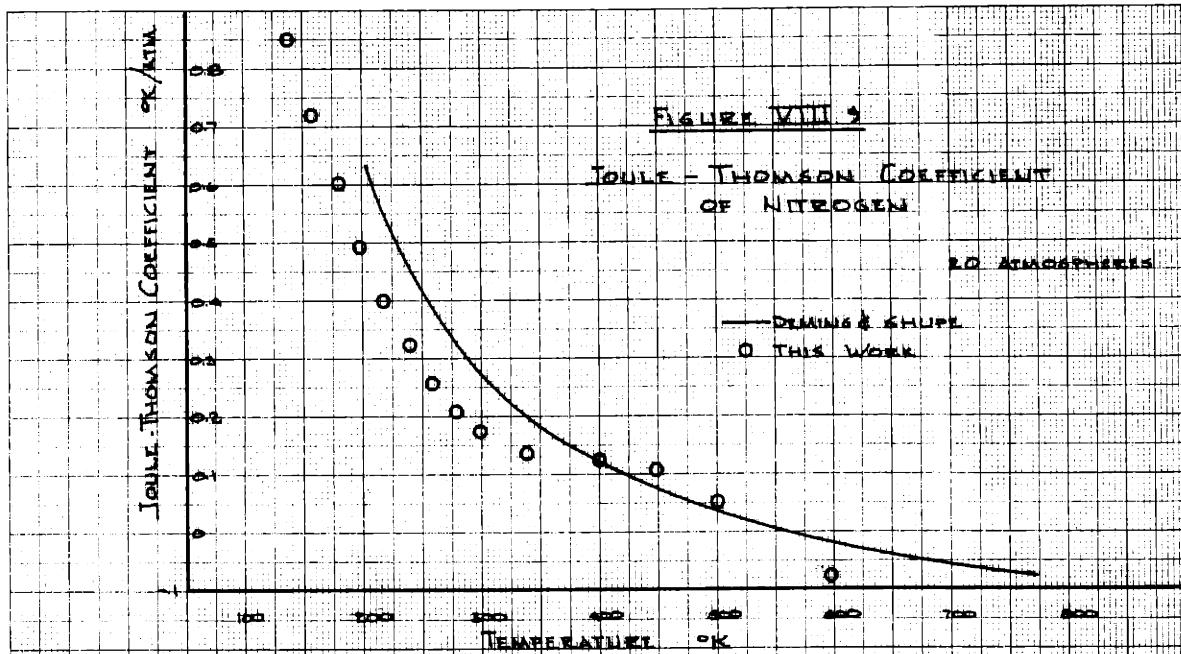
6. Joule-Thomson Coefficient

The Joule-Thomson coefficient is plotted against temperature for pressures of 20 atmospheres (in Figure VIII.9) and 80 atmospheres (in Figure VIII.10). In each plot a comparison is made between this work and the results calculated by Deming and Shupe (21).

The largest differences occur at the lower temperatures and are about 10 to 15 per cent. This is fair agreement considering that the Joule-Thomson coefficient is not very large at the pressures and temperatures considered. The absolute magnitude of the differences is only about 0.1-0.15 $^{\circ}$K/atm.

FIGURE VIII D

HEAT CAPACITY AT CONSTANT
PRESSURE
NITROGEN - 200° K.

FIGURE VIII 9

JOULE - THOMSON COEFFICIENT
OF NITROGEN

20 ATMOSPHERES

— DEMING & SHUPE
O THIS WORK

FIGURE VIII 10

JOULE - THOMSON COEFFICIENT
OF NITROGEN

80 ATMOSPHERES

— DEMING & SHUPE
O THIS WORK

D. <u>Discussion</u> <u>of</u> <u>Results</u>

1. Comparison of Different Compilations

The results calculated in this work have been compared
with Din's results, and, in some cases, with results calcu-
lated by Deming and Shupe. The calculated results were also
compared when possible with the results of Woolley and of
Miller and Sullivan. In addition, the results of the vari-
ous compilations have been compared amongst each other.
While all of the compilations are based on the same data,
there are differences in the final calculated thermodynamic
properties. These are due to the various methods used in
carrying out the calculations, each of which introduces
small errors due to numerical approximations and round-off
errors. For the most part, the results of each investiga-
tion, including this one, agreed well with each of the other
results equally well. There was no set of results that was
way out of line. Any two sets of results, when compared
with each other shows about the same magnitude of differ-
ences as any other two sets of results. This indicates that
the results calculated by the techniques used in this work
are as good as the results calculated by any of the other
techniques used by the other investigators.

2. Comparison of Different Thermodynamic Properties

By examining Figures VIII.1 to VIII.10, it is seen
that on some of the calculated thermodynamic properties,

better agreement is achieved than with other properties. The best agreement between this work and the others is achieved with the entropy, enthalpy and fugacity coefficient. The heat capacity and Joule-Thomson coefficient data are not in as good agreement. The reason for this becomes clear when one considers the method by which the various properties are calculated.

The fugacity coefficient, for example, is calculated by evaluating an integral of the form, $\int V dP$. Regardless of the actual numerical technique used, this integral can be evaluated quite accurately from the volumetric data. The entropy is calculated by evaluating an integral of the form, $\int (\partial V/\partial T)_P dP$. The accuracy of this integration depends on how well the derivative, $(\partial V/\partial T)_P$ can be evaluated. It has been shown in Section III, that the derivative can be approximated accurately by the techniques used in this work. Therefore, it is not surprising that the calculated entropies are in good agreement with all of the other compilations.

The isothermal change in enthalpy is calculated by integrating $\int \left[V - T(\partial V/\partial T)_P \right] dP$. Since the calculated integrals, $\int V dP$ and $\int (\partial V/\partial T)_P dP$, are of high accuracy, one might expect that the difference of the two integrals would also be accurate. However, evaluating the integral for calculating enthalpy involves taking the difference between two large terms which are nearly equal. Doing this frequently causes a serious loss of accuracy. Nevertheless, the

calculated enthalpies are in good agreement with the enthalpies reported by the other investigators.

The constant pressure heat capacity is calculated from an integral of the form, $\int(\partial^2 V/\partial T^2)_P dP$. The three sets of data (Din's, Woolley's and the present work) do not show as close an agreement among themselves, as for the other properties. This discrepency between the sets of results can be ascribed to the loss in accuracy in evaluating the second derivative, $(\partial^2 V/\partial T^2)_P$. In the present work, this is not too serious, as the heat capacity is an end result, and is not used to calculate enthalpies as in Din's work.

The heat capacity is, however, used in calculating the Joule-Thomson coefficient (as well as the specific heat at constant volume). Considering the method used in calculating the Joule-Thomson coefficient, it shows surprisingly good agreement when compared with the Joule-Thomson coefficients calculated by Deming and Shupe. For example, the Joule-Thomson coefficient is calculated from Equation (V.25)

$$\mu = \frac{1}{C_p} \left[T(\partial V/\partial T)_P - V \right] \tag{V.25}$$

Since it involves taking the difference between two large numbers, a loss of accuracy is introduced. In addition, it also uses a previously calculated value of C_p, which may be in error by about ten per cent. Nevertheless, the calculated Joule-Thomson coefficient is fairly accurate, based

on the comparison with the Joule-Thomson coefficients calculated by Deming and Shupe (21).

In addition to the thermodynamic properties shown graphically in Figures VIII.1 to VIII.10, the program calculates the specific heat at constant volume, C_v, as well as the ratio C_p/C_v, and the difference $C_p - C_v$. The constant volume heat capacity is calculated from Equation (V.34)

$$C_v = C_p + \frac{T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} \qquad (V.34)$$

The ratio and the difference of the heat capacities are then easily determined. Their accuracy will be determined by how well C_v is calculated. Due to the error in C_p, combined with the error in the other derivatives used in Equation (V.34), the resulting value of C_v can only be regarded as a rough estimate. Similarly, C_p/C_v can only be regarded as a rough estimate, but in the difference $C_p - C_v$, some of the error cancels out, as can be seen from Equation (V.34). However, since these three properties ($C_p - C_v$, C_p/C_v, C_v) are not as important as the others, and since they are of limited accuracy, the results are not presented.

IX. VAPOR PRESSURE AND SATURATED VAPOR PROPERTIES

A. Vapor Pressure

If the vapor pressure data are measured or are available from some other source, then the constants of the vapor pressure equation are calculated by the method of least squares as described in Section V. When vapor pressure data are not available, Riedel's (69) generalized correlation is used to calculate the vapor pressure curve. Riedel's correlation requires a knowledge of the critical pressure and temperature, and one other point on the vapor pressure curve.

In Din's tabulation, the vapor pressure data are tabulated at evenly spaced values of the pressure. These data were curve fit, and temperatures were calculated from the polynomial corresponding to the evenly spaced pressures by the Newton-Raephson method (32). The calculated temperatures were compared to the tabulated temperatures and there was a root mean square error of $0.006^{O}K$ for nine points. The temperatures in Din's tabulation are given to $0.01^{O}K$, so that the root mean square error is less than the precision of the data.

The vapor pressure curve for nitrogen was also calculated using Riedel's method based on the critical constants and the normal boiling point. In this case the resulting vapor pressures were compared at evenly spaced values of

the temperature, with the vapor pressure calculated by the least squares polynomial. The root mean square error for six calculated points was about 0.05 atmospheres. This corresponds to differences of about $0.3^{\circ}K$ at the normal boiling point to about $0.03^{\circ}K$ near the critical point, based on the slope of the vapor pressure curve.
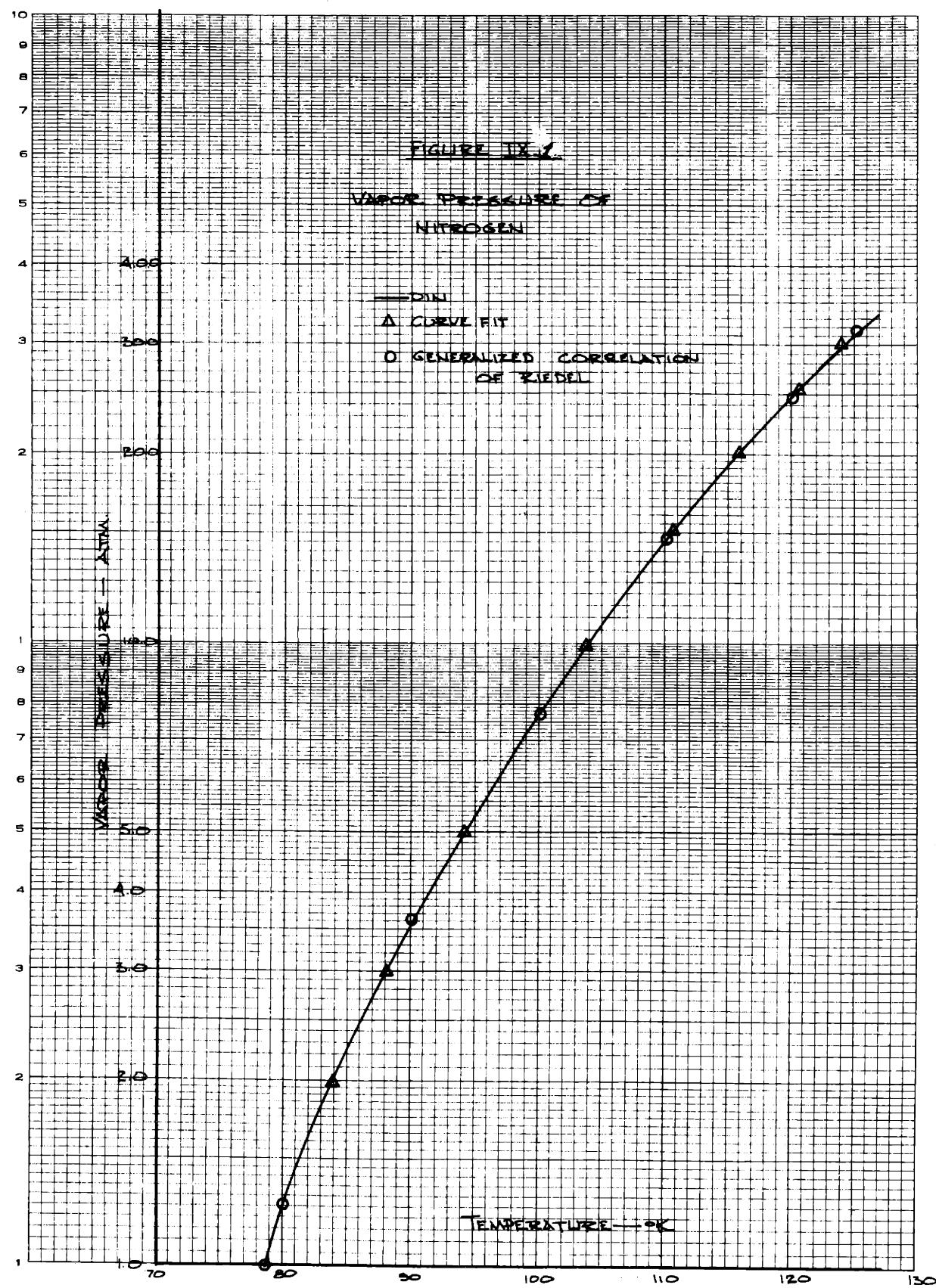
The results of both of these calculations are shown graphically in Figure IX.1. With the accuracy obtainable on a graph, there is no difference between either of the two methods and the original data of Din.

The calculation of vapor pressures are not necessary except when it is desired to extend the thermodynamic network to the saturation curve.

B. Saturated Vapor Properties

1. Calculation

The computor program operates along an isotherm. At a given temperature it calculates all of the thermodynamic properties as a function of pressure, starting at the lowest pressure and ending at the highest pressure of the tabulation. For each isotherm at which the thermodynamic properties are calculated, the highest pressure is input to the program. When the properties are calculated at that pressure, a cycle is completed and the program begins to calculate properties at the lowest pressure at the next highest temperature. However, when the vapor pressure is calculated, it becomes the

FIGURE IX.1

VAPOR PRESSURE OF NITROGEN

— DIN
△ CURVE FIT
○ GENERALIZED CORRELATION OF RIEDEL

VAPOR PRESSURE — ATM.

TEMPERATURE — °K
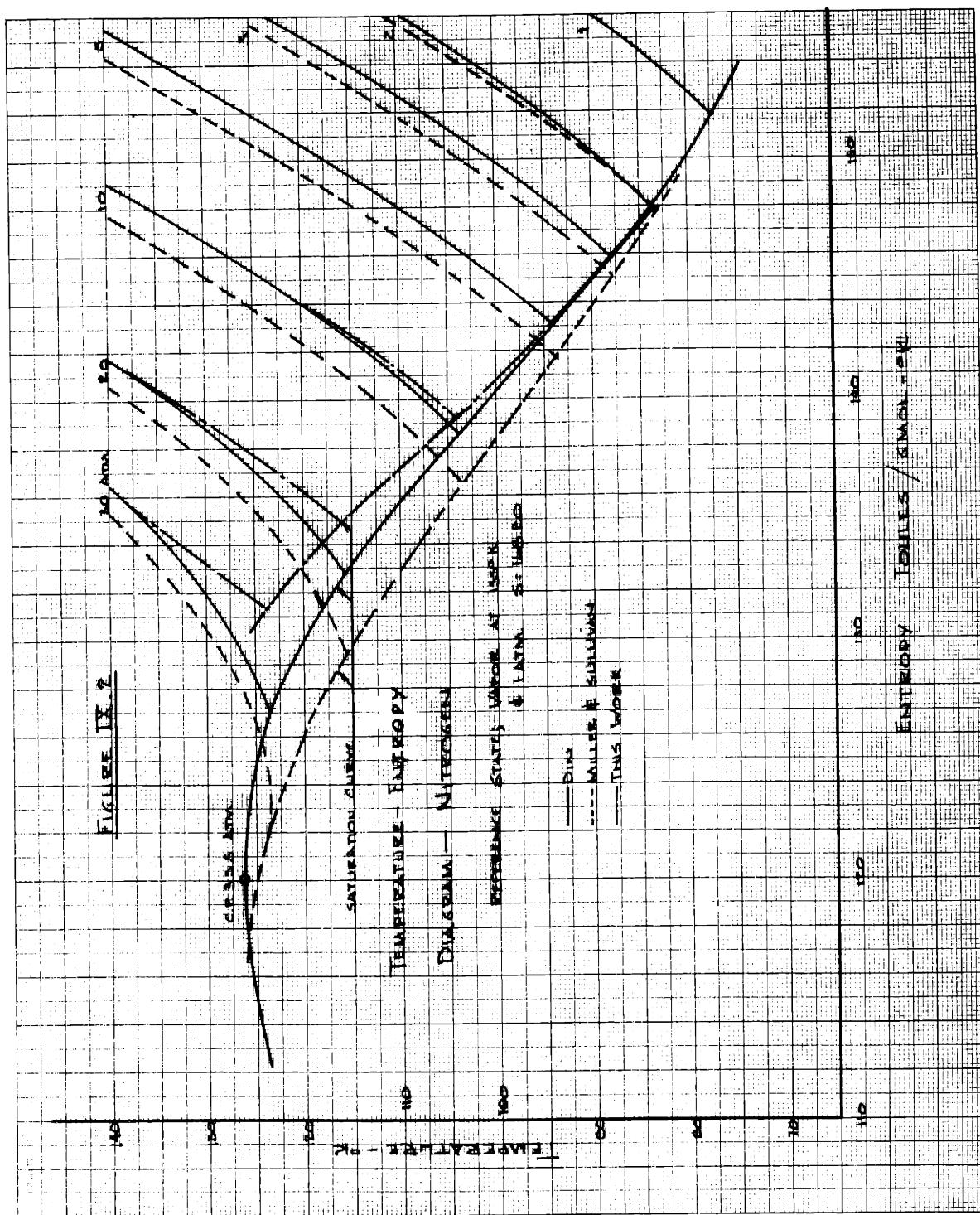
highest pressure for the isotherm, taking precedence over the pressures input to the program.

For example, suppose that the computor program is calculating the thermodynamic network at 100°K, and it has been instructed to calculate properties up to ten atmospheres, starting at one atmosphere and at intervals of one atmosphere. Previously, the vapor pressure has been calculated at 100°K and is 7.73 atm. Thus, 7.73 atm. replaces 10 atm. as the highest pressure for the 100°K isotherm and the thermodynamic properties are calculated at the following pressures: 1, 2, 3, 4, 5, 6, and 7.73 atmospheres.

2. Discussion of Results

In general, calculating the properties on the saturation curve will require an extrapolation unless experimental volumetric data are available for the saturated vapor. In the present results for nitrogen, specific volumes were extrapolated a few degrees along an isobar to the saturation curve, using the least squares polynomial. The full set of properties calculated for the saturated vapor would include specific volume, enthalpy, entropy, constant pressure, heat capacity, etc.

In Figure IX.2, the entropy is shown for the saturated vapor in form of a temperature-entropy diagram. The calculated results are compared with Din's results and with Miller and Sullivan's results. A few isobars near the saturation

FIGURE IX.2

SATURATION CURVE

TEMPERATURE-ENTROPY
DIAGRAM — NITROGEN

REFERENCE STATE; VALUES AT LIQUID
@ LATM = ZERO

——— DIN
- - - - MILLER & SULLIVAN
——— THIS WORK

curve are also included. For all three tabulations the reference value of entropy is taken as 168.20 joule/gmol-$^\circ$K at 135°K and one atmosphere, for the vapor.

On examination of Figure IX.2 it is seen that there is good agreement among the results of Din, Miller and Sullivan and the present work at the low pressures, both on the saturation curve and on the isobars near the saturation curve. At all temperatures on the one atmosphere isobar, there is perfect agreement among the three tabulations, extending to the saturation curve. This is shown by a single solid line in Figure IX.2. At two atmospheres, the entropy values calculated by Miller and Sullivan show a slight departure from those of Din and the present work. This is indicated by the dotted line in Figure IX.2. The same behavior is found for the three and five atmosphere isobars. The dotted line represents the entropy values calculated by Miller and Sullivan, and the solid line represents the entropy values of Din and of the present work. Up to five atmospheres, Din's entropy values are in perfect agreement with the entropy values of the present work, including the saturation curve. The entropy values of Miller and Sullivan are not in agreement, neither on the isobars nor the saturation curve.

At a pressure of ten atmospheres, the entropy values calculated in this work depart slightly from the entropy values calculated by Din, but only very close to the saturation curve. This behavior is shown by the dot-dash line in

Figure IX.2. The differences in the entropy values become greater as the pressure is increased and the critical pressure is approached. Agreement is good in the superheated gas region, but the isobars of the various investigators depart from each other as the saturation curve is reached. Thus, the saturation curves of the different investigators do not coincide at the higher pressures.

In general, Din's results and the results of this work are in better agreement with each other than either are with the results of Miller and Sullivan. The agreement is excellent, except at high pressures near the critical point. This is not too surprising since the specific volume, and its derivatives, changes rapidly near the critical, and any property calculated from $(\partial V/\partial T)_P$ would be relatively uncertain, regardless of the numerical method used.

X. EFFECT OF ERROR IN VOLUMETRIC DATA ON CALCULATED THERMODYNAMIC NETWORK OF NITROGEN

A. Introduction

By using Din's (23) volumetric data for nitrogen as input to the computor program, a thermodynamic network is calculated that is in good agreement with the one given by Din. Thus, it is shown that a thermodynamic network can be accurately calculated, by the techniques used in the present computor program. However, it is desirable that the calculated techniques be relatively insensitive to small random errors in the initial volumetric data, and it is desirable to also be able to calculate an accurate thermodynamic network from experimental data which is less accurate than the data tabulated by Din. In order to test these requirements, errors are purposely introduced into the volumetric data, which are input to the computor program, and the calculation is repeated. The resulting thermodynamic properties, based on the less accurate data, are compared with the corresponding thermodynamic properties calculated by using volumetric data without any induced errors.

In this section, Din's volumetric data is taken as a reference set of data. A thermodynamic network is calculated based on data of full precision and with no induced error. Other thermodynamic networks are calculated by

introducing errors into the volumetric data. The thermo-
dynamic network calculated by the computor program and using
Din's data of full precision is used as a standard. The
volumetric data is tabulated by Din to four or five signi-
ficant figures and is accurate to about 0.01 per cent, al-
though the accuracy and number of significant figures depend
on the pressure and temperature for which the specific volume
is tabulated.

B. Method Used to Simulate Error

1. Significant Figures

By rounding off the original volumetric data to a
smaller number of significant figures, a random error is
introduced. The original volumetric data contains four, and
in some regions, five significant figures. Thermodynamic
networks were calculated based on rounding the volumetric
data to four, three, and two significant figures. When the
data are rounded to four significant figures the correspond-
ing error varies from 0.1 to 0.01 per cent, depending on the
magnitude of the number rounded off. Similarly, data rounded
to three significant figures have a precision varying from
1.0 to 0.1 per cent, and data rounded to two significant
figures have a precision of from 1.0 to 10.0 per cent. When
introducing errors by rounding off, the errors are random.
They may be positive, negative, or zero, and the magnitude
of the error may vary from zero up to the maximum value. In

this manner, random errors are introduced into the original data.

2. Constant Percentage Error

Rounding off introduces a random error distribution which is not easily characterized. But introducing a constant percentage error is not as realistic since it is unlikely that the error in a set of experimental points will always be a constant percentage of the value. For example, suppose a certain quantity can be measured to an accuracy of 1.0 per cent. This is usually interpreted to mean that the error in a measurement may be as high as 1.0 per cent, but may have any value between zero and 1.0 per cent.

In the present work, it has been estimated in Section IV that specific volumes can be measured to within an accuracy of 1.0 per cent. By introducing an error of 1.0 per cent into the volumetric data, the most unfavorable case is considered. If a thermodynamic network is calculated from volumetric data that have in it errors of plus or minus 1.0 per cent, and the network is in good agreement with a corresponding network calculated from volumetric data that have no errors associated with it, it follows that a 1.0 per cent error in the volumetric data is of slight importance. In the present calculation an error of plus or minus 1.0 per cent is introduced into the data. In a real case the errors in the data will have some distribution between zero

and 1.0 per cent, so that the present case is the most un-favorable.
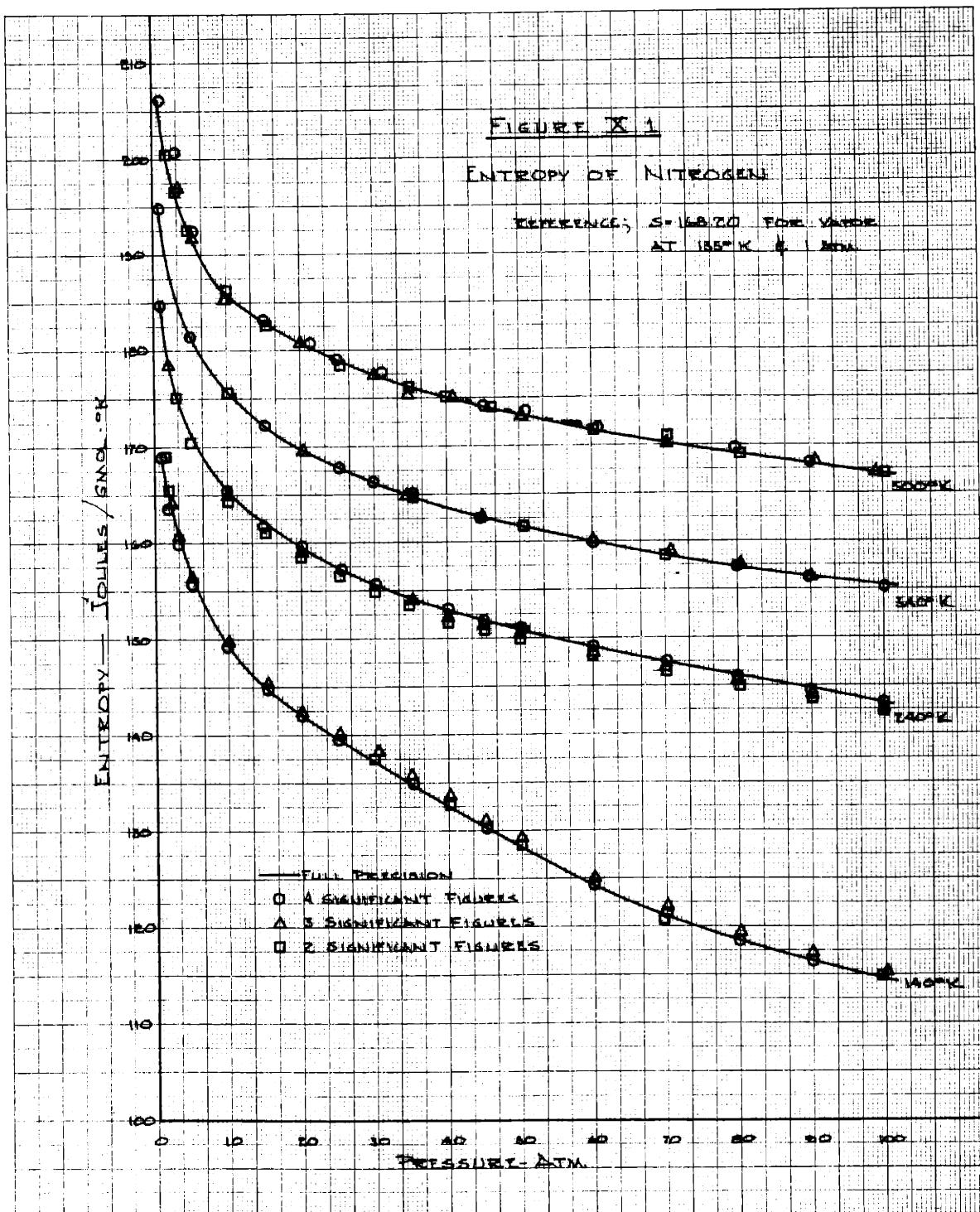
There are two ways in which the error is introduced into the data. In one case, called the "alternate" error, the first point of a set of data is changed by plus 1.0 per cent, the second point by minus 1.0 per cent, and so on alternately.

The other method is to introduce an error of plus or minus 1.0 per cent in each point depending on whether or not the least significant digit in the number is odd or even. If the least significant digit is odd, an error of plus 1.0 per cent is introduced. If the least significant digit is even, an error of minus 1.0 per cent is introduced. In this way, the errors are introduced in a nearly random manner, although the magnitude of the percentage error is constant.

C. Results of Calculations

1. Entropy
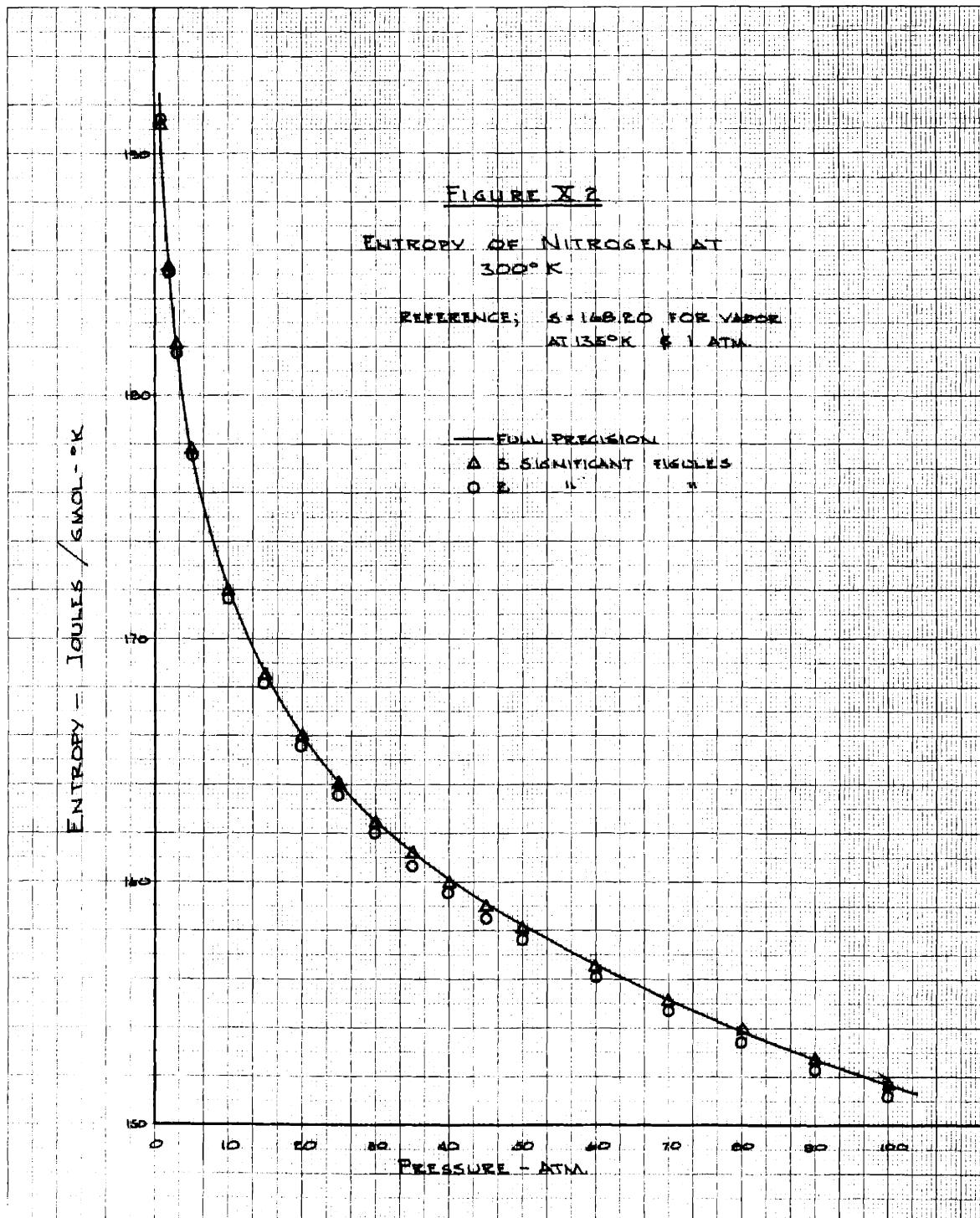
The errors introduced into the volumetric data have very little effect on the calculated entropy. Some results are shown graphically in Figure X.1 to X.4. In Figure X.1, the entropy calculated using the full precision volumetric data is shown as a solid curve for four temperatures. When the data is rounded to four significant figures, there is no significant variation in the calculated entropy. When the data is rounded to three significant figures, the calculated

FIGURE X 1

ENTROPY OF NITROGEN
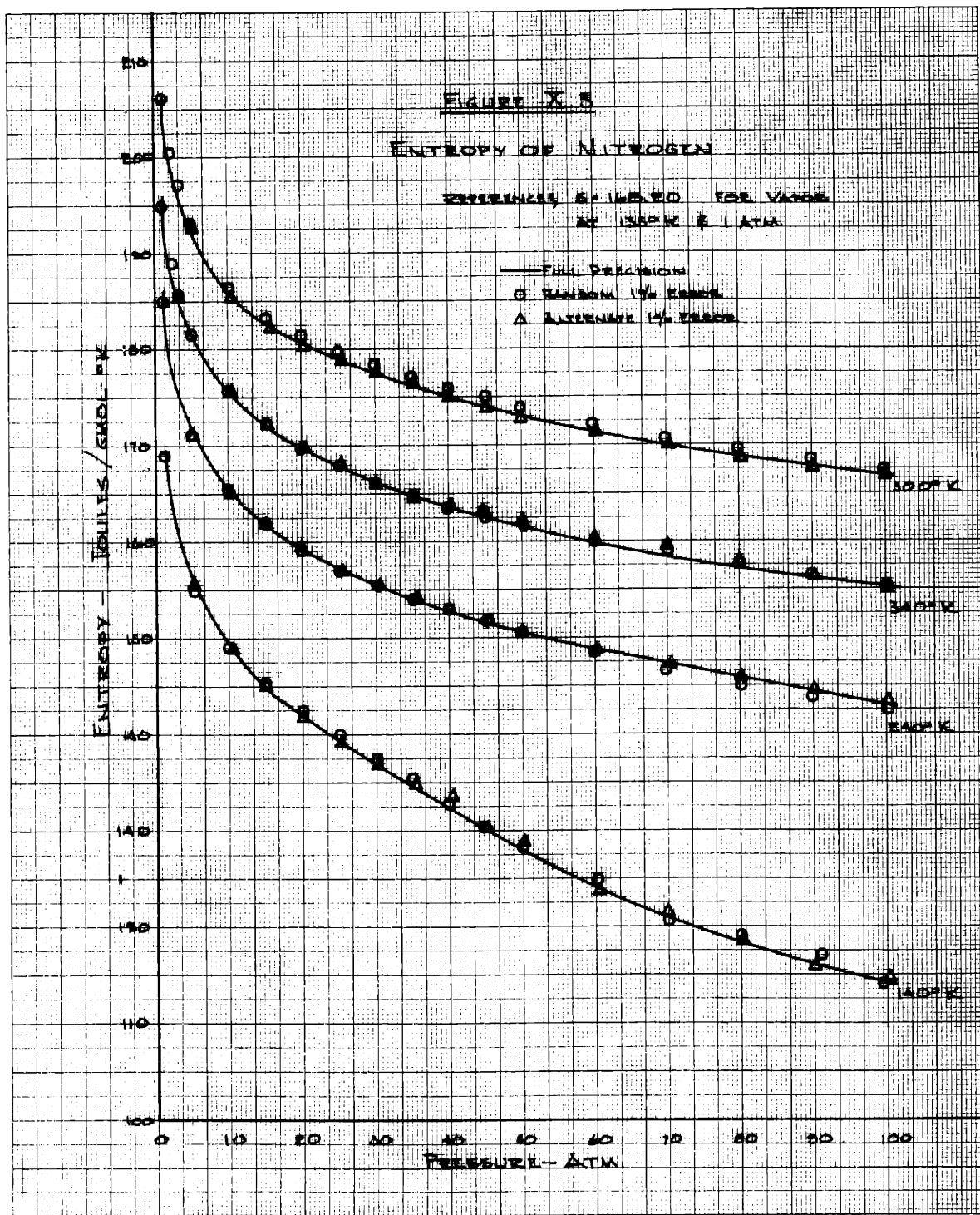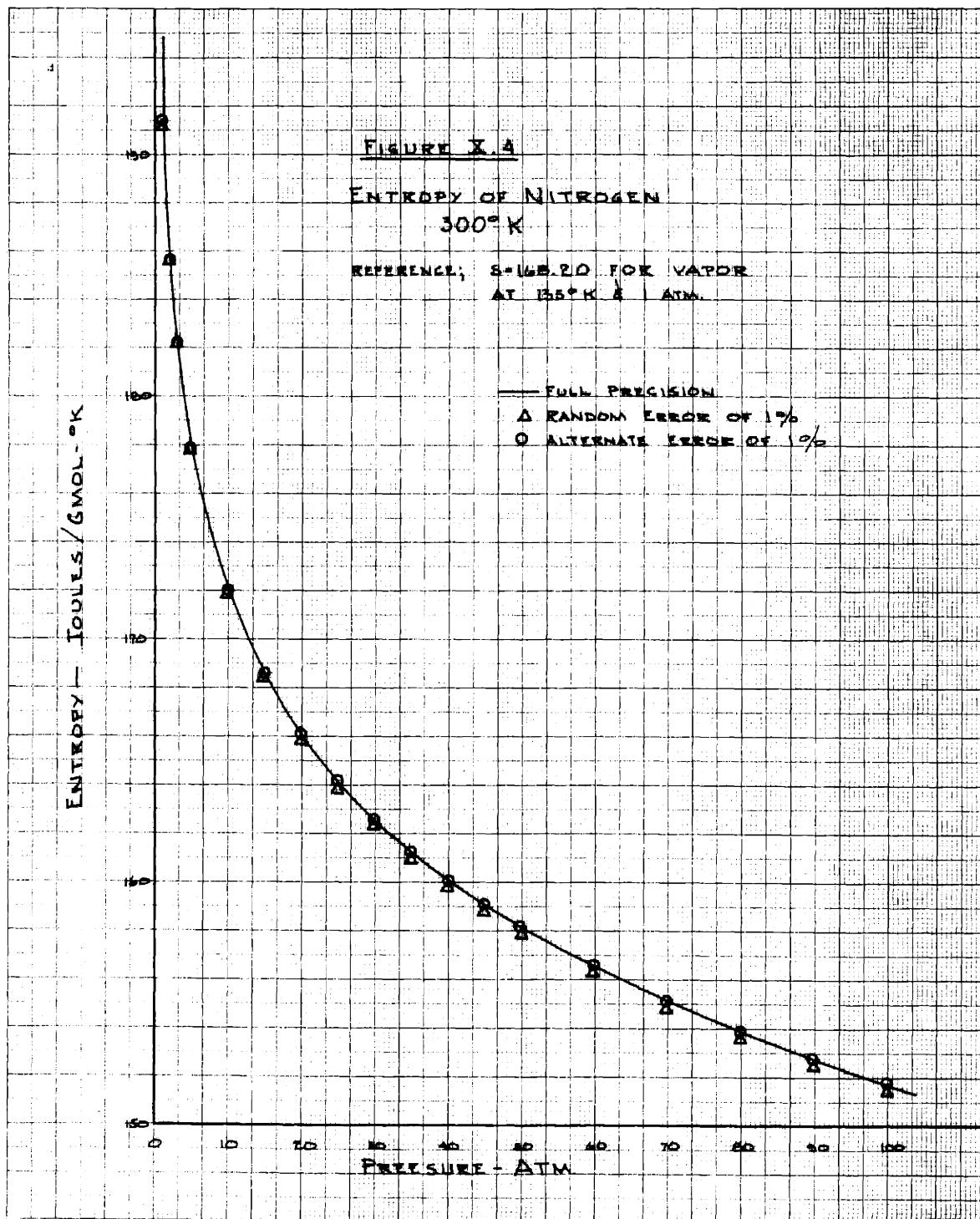
entropies show a very slight departure only on the 140°K and 240°K isotherms. When the entropy is calculated from data that has been rounded to only two significant figures, the only differences between the calculated entropies occur at 140°K.

In Figure X.2, the entropy-pressure curve for the 300°K isotherm is shown on an enlarged scale. The solid line, which is used as a reference, is calculated from the full precision data. The entropies calculated from the data rounded to four significant figures are not shown, as they fall exactly on the same curve. The entropies calculated from the data rounded to three significant figures depart only slightly from the reference curve, the maximum departure being only about 0.1 joule/gmol-°K. The entropies calculated from the data of two significant figures are also in excellent agreement, being low by only as much as 0.5 joules/gmol-°K at 100 atmospheres.

In Figure X.3, results are shown for four temperatures on an entropy-pressure diagram for entropies calculated from volumetric data with an error of 0.1 per cent. The reference curves represent the entropies calculated from the full precision volumetric data. The points shown are for the case of an alternate error of plus and minus 1.0 per cent, and for a random error of plus or minus 1.0 per cent. The agreement is excellent for all four isotherms, for both types of error. Figure X.4 contains the results for the 300°K isotherm plotted on an enlarged scale. Again,

FIGURE X 2

ENTROPY OF NITROGEN AT
300° K

REFERENCE; S = 148.20 FOR VAPOR
AT 135°K & 1 ATM.

——— FULL PRECISION
△ 3 SIGNIFICANT FIGURES
○ 2   "   "

Figure X.5
Entropy of Nitrogen

Figure X.4

ENTROPY OF NITROGEN
300° K

REFERENCE; S=165.20 FOR VAPOR
AT 135° K & 1 ATM.

—— FULL PRECISION
△ RANDOM ERROR OF 1%
O ALTERNATE ERROR OF 1%
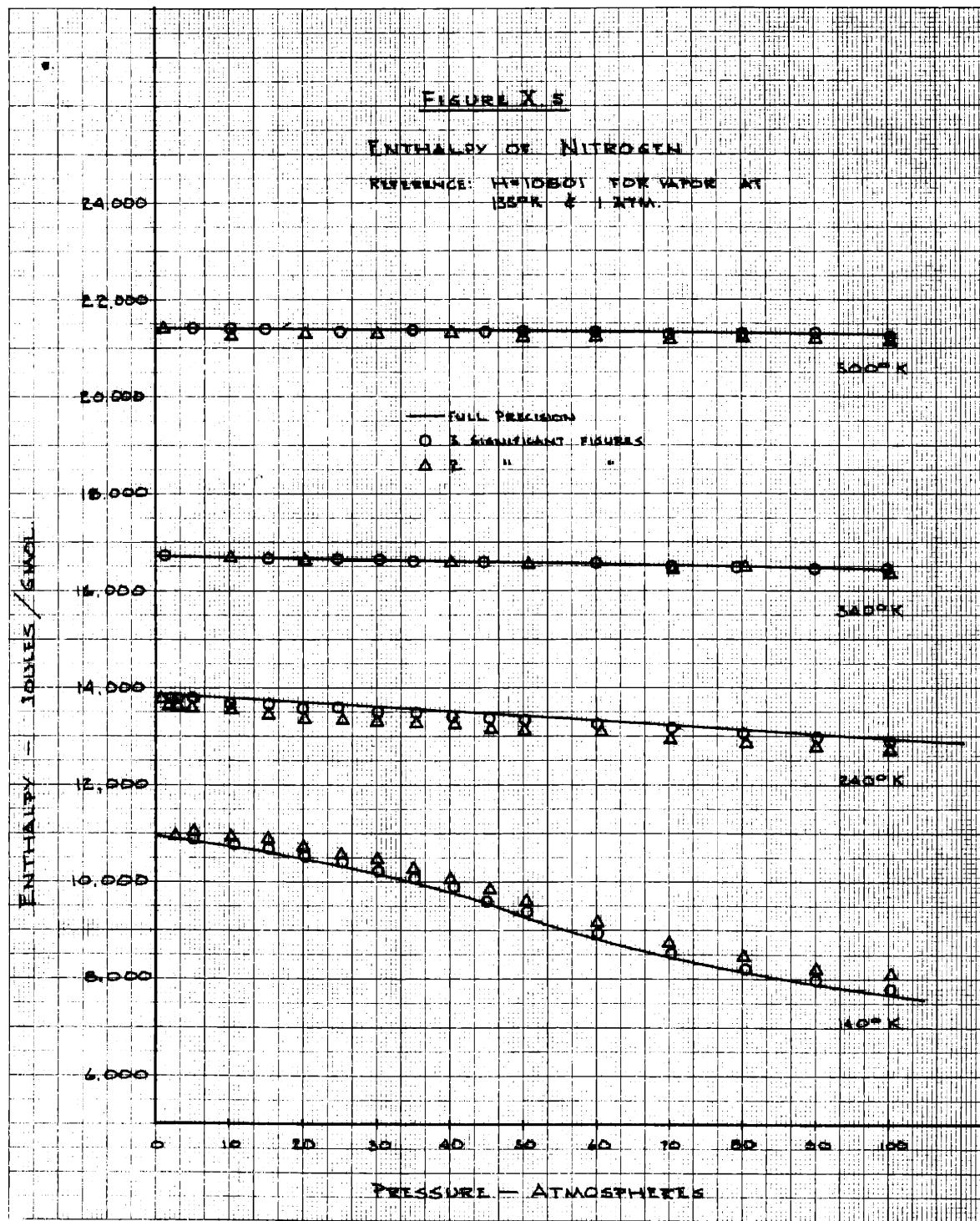
the results calculated with a 1.0 per cent error in the data
are in excellent agreement with the reference curve, calcu-
lated from the full precision data.
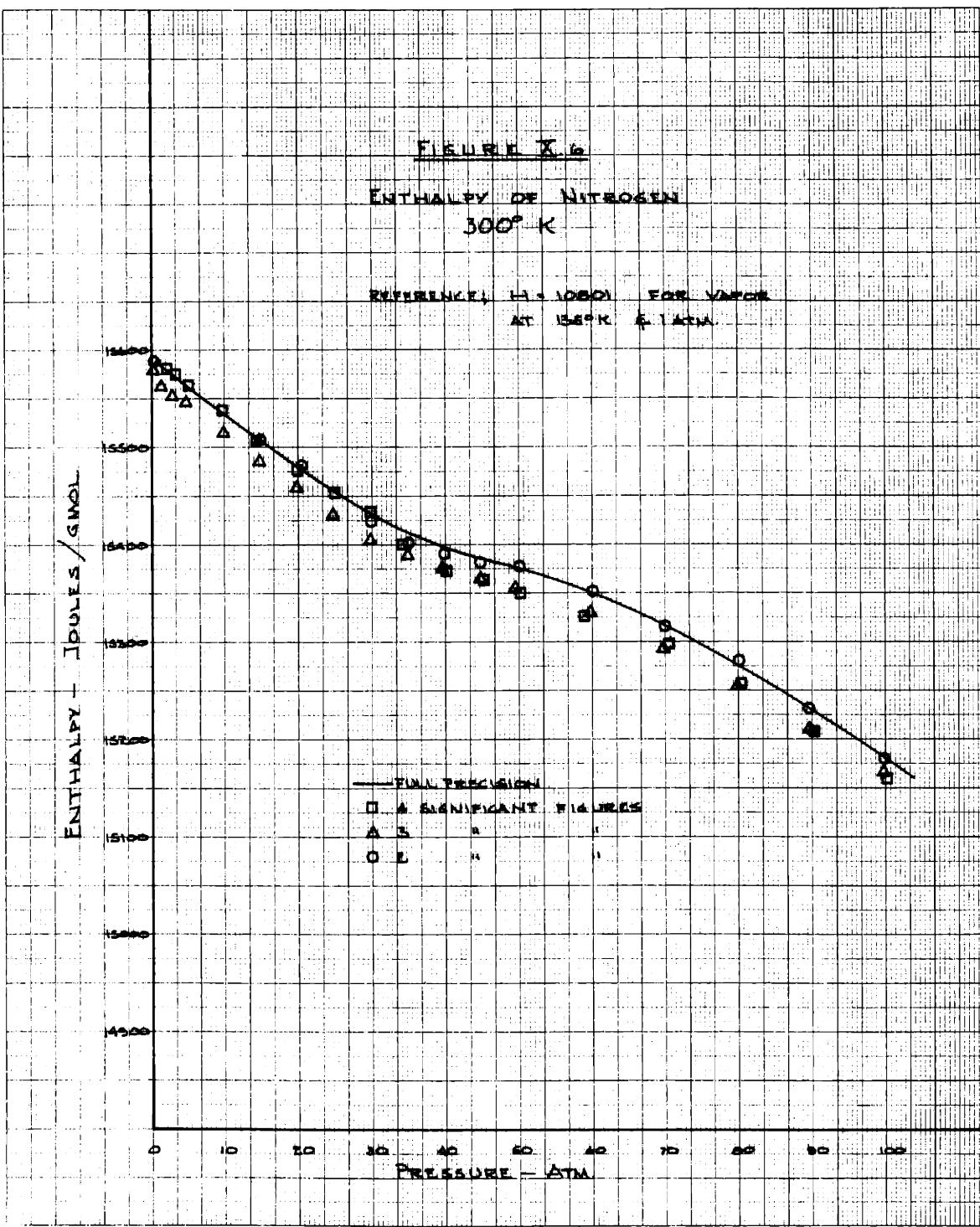
2. Enthalpy
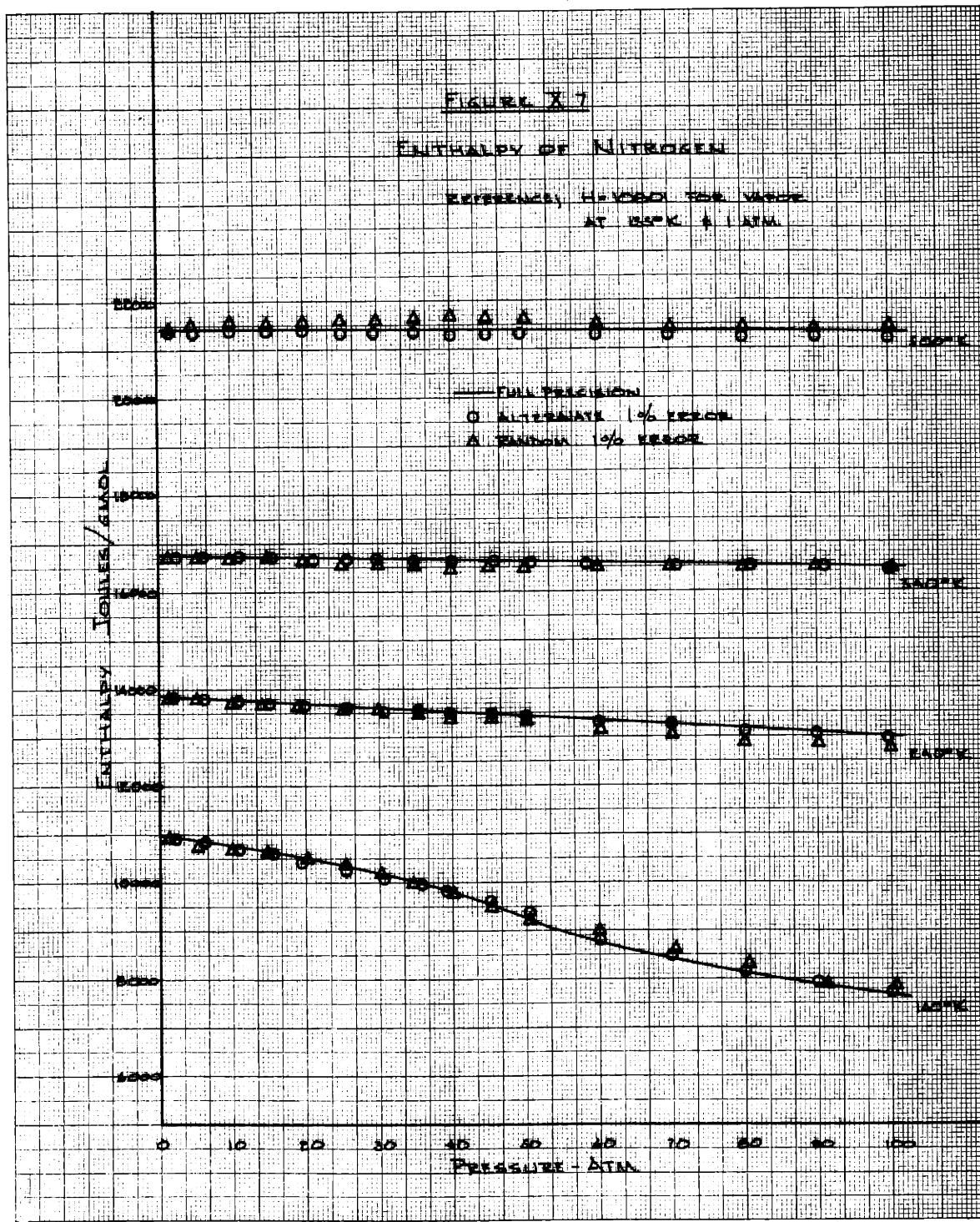
In Figure X.5 four isotherms are shown on a pressure-
enthalpy plot. The reference curves are calculated using the
full precision volumetric data. The enthalpies calculated
from the volumetric data rounded to four significant figures
are not shown, as they coincide exactly with the reference
curve. The enthalpies calculated from volumetric data
rounded to three significant figures, and from the data
rounded to two significant figures are in excellent agreement
with the reference curve.

Figure X.6 shows the $300^{\circ}K$ isotherm for an enthalpy-
pressure diagram on a greatly enlarged scale. There is ex-
cellent agreement between the reference curve, calculated
from full precision volumetric data, and the points calcu-
lated from volumetric data of two, three and four signifi-
cant figures.

When the points, which were calculated from volume-
tric data having errors of 1.0 per cent are compared with the
full precision reference curve, they are seen to be in good
agreement. Figure X.7 shows four isotherms on an enthalpy-
pressure diagram. The points calculated from volumetric
data with a random error of plus or minus 1.0 per cent, and

Figure X.5
Enthalpy of Nitrogen
Reference: H=10801 for vapor at 135°K & 1 atm.

FIGURE X.6

ENTHALPY OF NITROGEN
300° K

REFERENCE: H = 10801 FOR VAPOR
AT 136°K & 1 ATM.

FULL PRECISION
□ 4 SIGNIFICANT FIGURES
△ 3 " "
○ 2 " "

175

Figure X-7
Enthalpy of Nitrogen
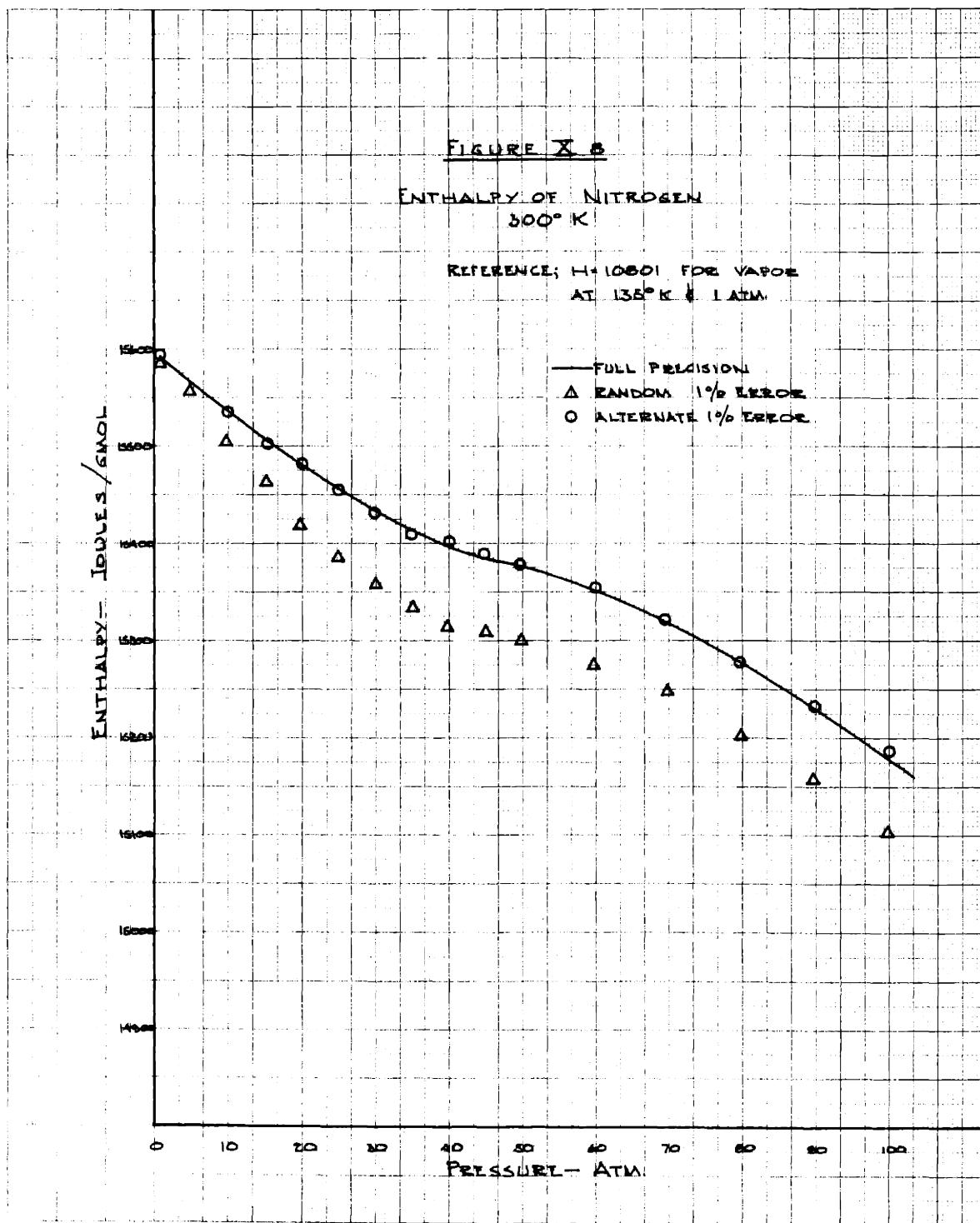
the points calculated from data with an alternate error of plus and minus one per cent, are compared with the full precision reference curve. Excellent agreement is obtained on all the isotherms shown.
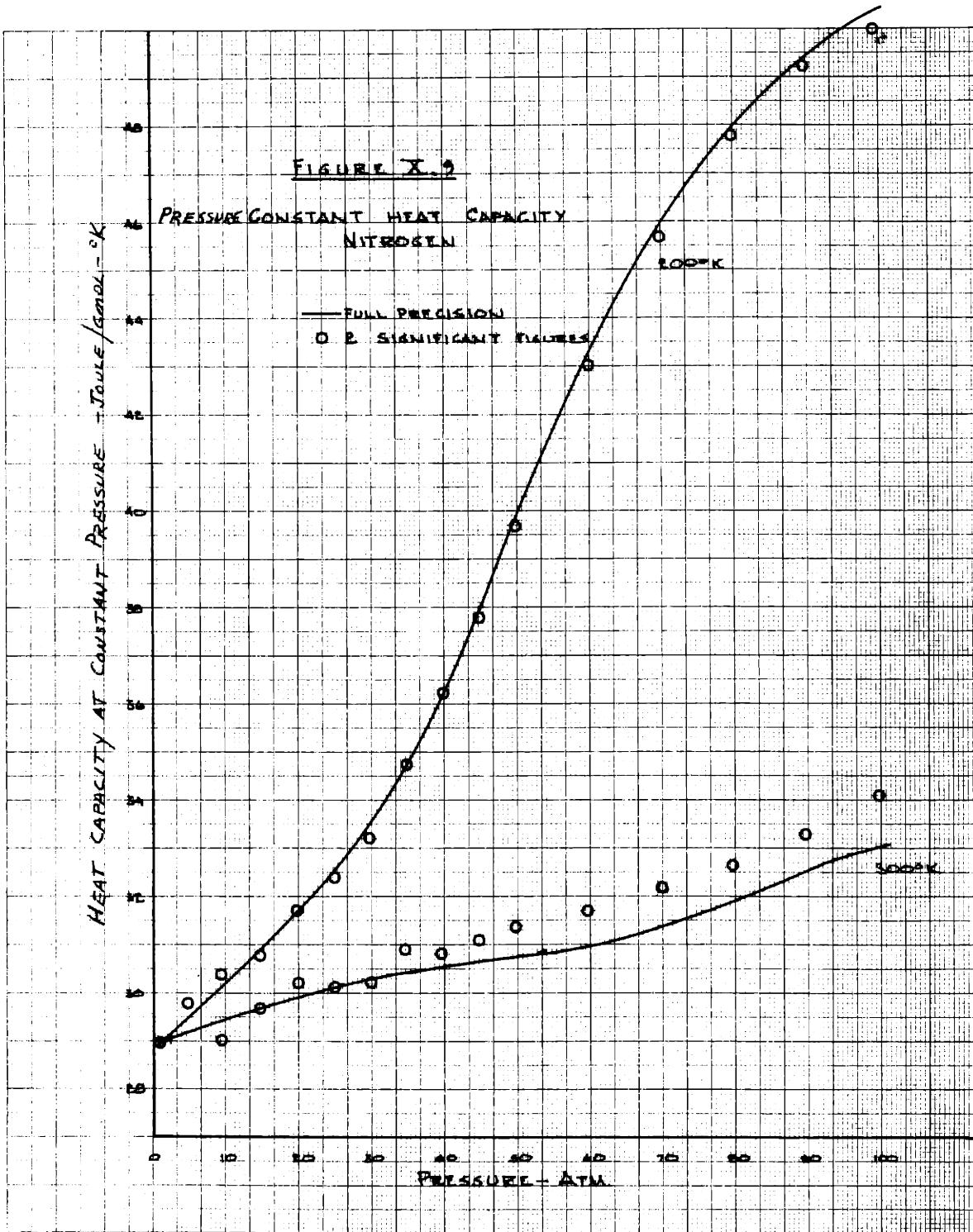
A large scale enthalpy-pressure plot is shown in Figure X.8 for the 300°K isotherm. The points calculated using volumetric data with alternate errors of plus and minus 1.0 per cent fall right on the reference curve. The points calculated from volumetric data having random errors of 1.0 per cent are low, but still in good agreement. The maximum deviation is about 75 joules/gmol, or less than 1.0 BTU/lb.

3. Constant Pressure Heat Capacity

Figure X.9 shows the heat capacity calculated from data of two significant figure accuracy compared with the heat capacity calculated from the full precision data. Two isotherms are shown and the agreement is excellent. On the 200°K isotherm the agreement is perfect. On the 300°K, there is a maximum departure of only about 3.0 per cent at 100 atmospheres. The heat capacities calculated from data of three and four significant figure accuracy are not shown as they are congruent with the reference curve.

Constant pressure heat capacities calculated from data with a random and alternate error of plus and minus 1.0 per cent are compared with heat capacities calculated from

FIGURE X 8

ENTHALPY OF NITROGEN
300° K

REFERENCE; H=10801 FOR VAPOR
AT 138° K & 1 ATM.

——— FULL PRECISION
△ RANDOM 1% ERROR
O ALTERNATE 1% ERROR

FIGURE X.5

PRESSURE CONSTANT HEAT CAPACITY
NITROGEN
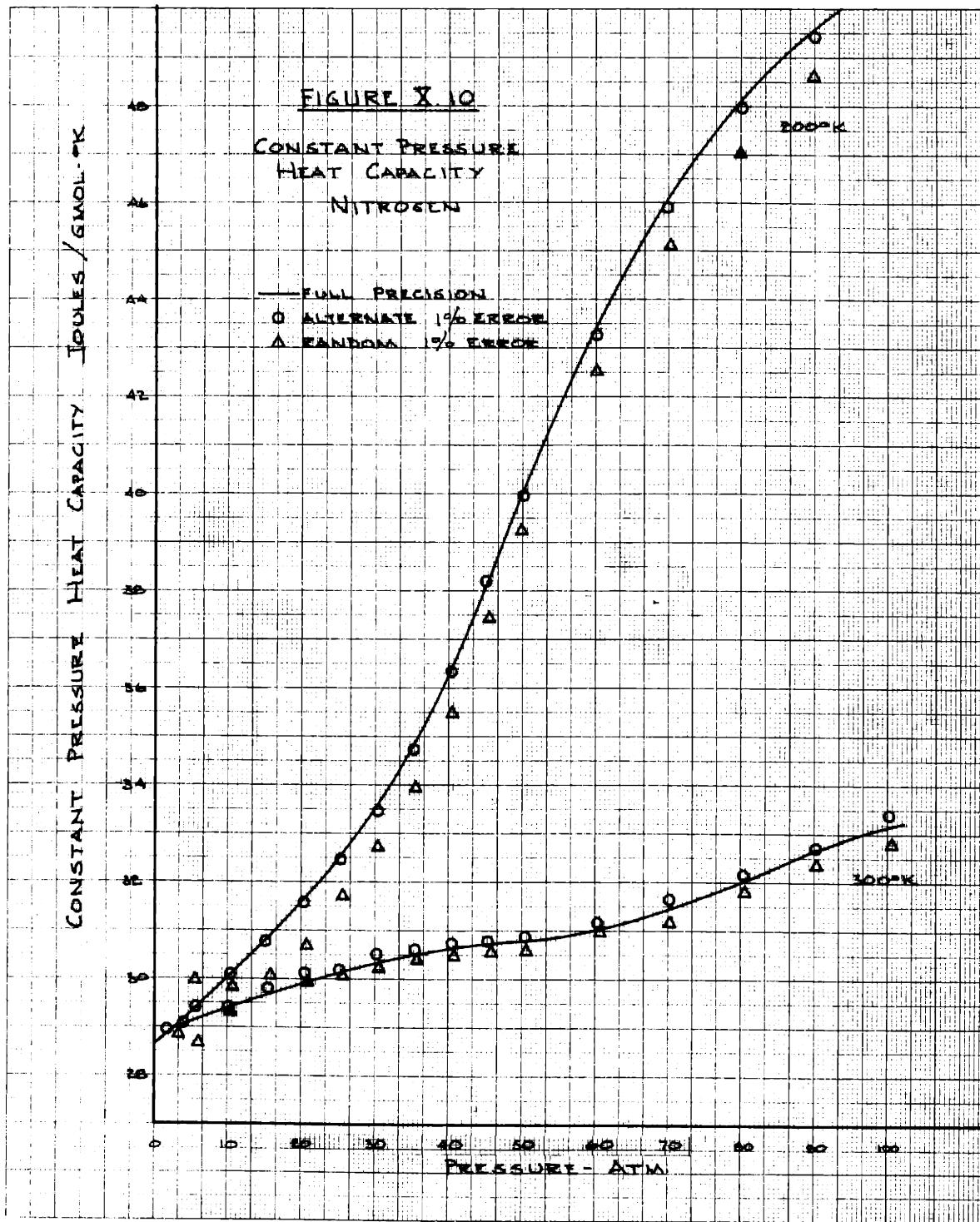
full precision volumetric data in Figure X.10. The heat
capacity is plotted against the pressure for the 200°K and
300°K isotherms. Again, the agreement is excellent, except
on the 200°K isotherm, where the heat capacities calculated
from the volumetric data with a random error of plus or
minus 1.0 per cent are about 2.0 per cent low.

D. Discussion of Results and Conclusions

It has been shown that the calculational techniques
used in the computor program are relatively insensitive to
small errors in the input data. Even when introducing var-
ious types of errors into the input data, the resulting cal-
culated thermodynamic network is in good agreement with a
thermodynamic network calculated from error free data. Re-
ferring to Section VIII, it can be seen that the difference
between the calculated thermodynamic network based on data
containing errors and the calculated thermodynamic network
based on error free data is less than the difference between
the calculated thermodynamic network using the computor pro-
gram and the thermodynamic networks calculated by Din (23),
Woolley (90), and Miller and Sullivan (57). This is an im-
portant point since it may be concluded that a thermodynamic
network of good accuracy may be calculated using the techni-
que presented here, even from data which have relatively
large errors.

FIGURE X.10

CONSTANT PRESSURE
HEAT CAPACITY
NITROGEN

—— FULL PRECISION
◯ ALTERNATE 1% ERROR
△ RANDOM 1% ERROR

The data which were accurate to only two significant figures were used to calculate a thermodynamic network, and good results were obtained. This corresponds to errors of greater than 1.0 per cent, and as high as 10.0 per cent. Using data which have an alternate error of plus and minus 1.0 per cent is unrealistic, but it is still an unfavorable case which gave good results. Using data with a random of error of 1.0 per cent is also a very unfavorable case that gave good results in the calculated thermodynamic network.

When it is said that experimental data have an accuracy of 1.0 per cent, what is implied is that 1.0 per cent is the maximum error, or that 1.0 per cent is the error at the 95 per cent confidence level. In any event, the true error has a distribution, and will usually be less than 1.0 per cent. In the present calculation using data with a random error, the maximum error of 1.0 per cent was introduced into each point of the data. When dealing with experimental data, the maximum error of 1.0 per cent would not be present in each point. The actual percentage error in each point would depend on the distribution of the error. Thus, carrying through the calculations with data having a random error of 1.0 per cent is more unfavorable than would be expected when dealing with experimental data of 1.0 per cent accuracy. Nevertheless, the resulting thermodynamic network was in good agreement when compared with a thermodynamic network calculated from error free data.

In Section IV, it was shown that the volumetric data can be measured to an accuracy of at least 1.0 per cent by the methods proposed. Thus, it is concluded that a thermodynamic network of good accuracy may be calculated from the data generated in an automatic manner, as proposed in Section IV. By combining the proposed experiment and the computor program devised, it is possible to achieve a thermodynamic network simply and conveniently, which will be of high accuracy.

XI. TEST FOR CONSISTENCY

A thermodynamic network may be consistent, but not accurate. However, if a thermodynamic network is accurate, it will also be consistent. Thus, consistency is a necessary condition for accuracy, but not a sufficient condition.

In the present work the thermodynamic network is calculated isothermally. At each temperature, all properties are calculated as a function of the pressure. In order to test for consistency, some of the properties may be calculated along an isobar, and compared with the same property calculated along an isotherm, both at the same final pressure and temperature. For example, consider the enthalpy. In the present program the enthalpy is calculated as a function of temperature at one atmosphere. This is considered as the reference line for enthalpy (one atmosphere). Then, at each temperature, the enthalpy is calculated as a function of pressure based on its value at the one atmosphere reference line. In order to test for consistency, it would be desirable to calculate the enthalpy as a function of temperature at some high pressure, and compare it with the enthalpy calculated in the standard manner, at the same temperature and pressure. This corresponds to calculating the change in enthalpy by two different paths, starting at P_1 and T_1 and ending at P_2 and T_2. Since the enthalpy is a state

function, the resulting H should be the same for each of the paths.
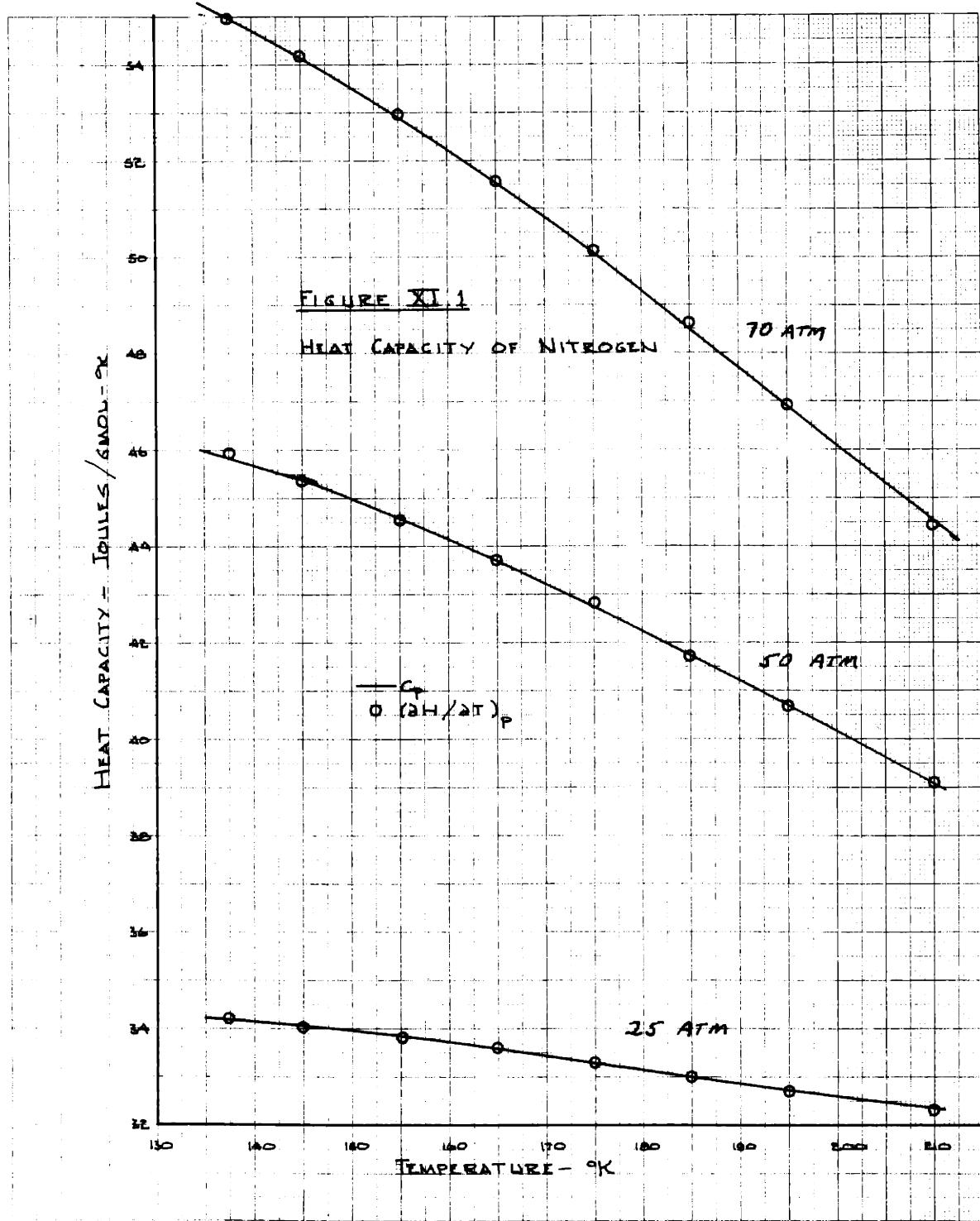
In the present work the alternate calculation of enthalpy can be easily done since high pressure heat capacities have already been calculated. However, instead of integrating the high pressure heat capacities with respect to temperature, it is also possible to differentiate the enthalpy with respect to temperature and compare it with the constant pressure heat capacity. This would be a more sensitive test since random variations would tend to cancel out in an integration, but may actually be amplified in a numerical differentiation. Since $(\partial H/\partial T)_P = C_p$, if there is agreement between the derivative and the independently calculated heat capacity, this would be a good test of consistency. The high pressure heat capacities are calculated independently from Equation (V.23), and are tabulated as part of the thermodynamic network.

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \qquad (V.23)$$

The derivative, $(\partial H/\partial T)_P$ is estimated by a central difference formula using the tabulated enthalpies.

$$\left(\frac{\partial H}{\partial T}\right)_{P,T(0)} = \frac{H_{T(1)} - H_{T(-1)}}{T(1) - T(-1)} \qquad (XI.1)$$

The results are shown in Figure XI.1 for three pressures. It is seen that the consistency condition is satisfied

FIGURE XI 1

HEAT CAPACITY OF NITROGEN

to better than 1.0 per cent, even with the crude approxima-
tion used in Equation (XI.1). Considering the sensitivity
of the test, this is excellent agreement.

XII. DISCUSSION OF RESULTS

A. Agreement with Other Compilations

As seen in Section VIII, the thermodynamic proper-
ties for nitrogen calculated in this work are in good agree-
ment with the corresponding properties calculated by Din (23),
Woolley (90) and Miller and Sullivan (57). Din's work is
selected as a standard for comparison, since it is the most
complete and thorough. In Section VIII, results were pre-
sented graphically so that a convenient, semi-quantitative
comparison could be made amongst the various sets of results.
The average differences in entropy and enthalpy were calcu-
lated between Din's tabulation and each of the others. The
points used in this calculation correspond to the points
plotted in Figures VIII.1 to VIII.4. The worst agreement is
found on the $140^{\circ}K$ isotherm, near the critical region. Thus,
comparisons were made both including the $140^{\circ}K$, and without
the $140^{\circ}K$ isotherm.

When the tabulated enthalpies of Miller and Sullivan
are compared with Din's values, there is an average devia-
tion of 26 joules/gmol, averaged over 30 points at $240^{\circ}K$
and $300^{\circ}K$ for pressures up to 60 atmospheres. When the $140^{\circ}K$
isotherm is included, the average overall deviation is 42
joules/gmol averaged over 45 points. For the entropy, the
values of Miller and Sullivan were in good agreement with

those of Din at 140°K. The overall average deviation was
1.09 joules/gmol-°K for 45 points. Woolley's enthalpy values
extend only up to 10 atmospheres at 140° and are not included
in the comparison. On four isotherms, from 240°K to 500°K
including pressures up to 100 atmospheres, 24 points are com-
pared with Din's work with an average deviation of 44 joules/
gmol. In Woolley's tabulation, entropies are included at
140°K. The overall deviation is 1.16 joules/gmol-°K averaged
over 30 points. If the values on the 140°K isotherm are
omitted, the average deviation is 0.182 joules/gmol-°K,
averaged over 24 points.

The results of this work are averaged over 80 points
in the temperature range 140°K to 500°K, and for pressures
up to 100 atmospheres. When the 140° isotherm is included
the average deviation from Din's enthalpy values is 91 joules/
gmol. With the 140°K isotherm omitted, the average devia-
tion is only 29 joules/gmol. For entropy, the average de-
viation is 0.62 joules/gmol-°K when the 140°K isotherm is
included and only 0.10 joules/gmol-°K when the 140°K isotherm
is omitted.

These deviations may be compared with the estimated
error as given by Din. At 150°K, the estimated magnitude of
the error in enthalpy is 150 to 400 joules/gmol, depending
on the pressure, and at 400°K it is about 250 joules/gmol
for pressures up to 100 atmospheres. At 150°K, the estimated
magnitude of the error in the entropy varies from 1.0 to
2.5 joules/gmol-°K, depending on the pressure. At 400°K,

the magnitude of the error is about 0.65 joules/gmol-$^{\circ}$K for pressures up to 100 atmospheres. The results are summarized in Table XII.1.

Table XII.1

Average Deviation of Thermodynamic Properties

Compared With Din's Tabulation

Source	Enthalpy-joules/gmol		Entropy-joules/gmol-$^{\circ}$K	
	Including 140°K isotherm	Not including 140°K isotherm	Including 140°K isotherm	Not including 140°K isotherm
Miller and Sullivan	42	26	1.09	--
Woolley	--	44	1.16	0.18
Present Work	91	29	.62	.10
Din's Estimate of Error at:				
150°K	150-400		1.0-2.5	
400°K	250		0.65	

The present program gives excellent results when calculating enthalpy and entropy, except near the critical region, shown by the 140°K isotherm, and also shown in Section IX. However, the results are not much different than those of

Miller and Sullivan, or Din. While the agreement is poor

near the critical region, when compared to Din's results, it

is not certain which of the results are really the more accu-

rate. For example, in Din's work a preliminary volume-entropy

diagram was constructed and it was found that isotherms at

$135^{\circ}K$ and $145^{\circ}K$ (which are above the critical temperature of

$126.2^{\circ}K$) were running inside the two phase boundary. In order

to correct this serious inconsistency, a reduction of 3.2

joule/gmol-$^{\circ}K$ was required for the value of the critical

entropy. The point to be made is that thermodynamic proper-

ties in the critical region are, at best uncertain, regard-

less of how they are calculated.

In the present work, the agreement is as good as can

be expected, even in the critical region if allowance is made

for the inherent difficulties in calculating thermodynamic

properties near the critical point. This is especially true

when different numerical techniques are used. In the present

case, a relatively large error is introduced in calculating

$(\partial V/\partial T)_P$ near the critical point. Since the isothermal changes

in enthalpy and entropy are calculated from the derivative,

which changes rapidly, the agreement is not as good as in

other regions of the thermodynamic network. The results are

confirmed by the calculation of the thermodynamic properties

of ethane, which are to be found in Appendix C.

B. <u>Accuracy</u> <u>of</u> <u>Initial</u> <u>Data</u>

A thermodynamic network was calculated for nitrogen using Din's full precision data. When an error of 1.0 per cent was introduced into Din's volumetric data and the calculation of the thermodynamic network repeated, the results agreed with the results calculated using the full precision data. The results were also in agreement with the results calculated from full precision volumetric data, when they were calculated from data that had been rounded, successively to four, three and two significant figures.

In Section X these results were presented graphically. Depending on the type of error, i.e., round-off or 1.0 per cent, the calculated results were in better or worse agreement with the results calculated using the full precision volumetric data. The poorest agreement between the full precision results and the results calculated from data having errors occurred when the data were rounded to two significant figures and when a random error of 1.0 per cent was introduced into the data.

Regardless of the type of error introduced into the data, the maximum difference, at $140^\circ K$, in the enthalpy calculated from the full precision data, and the enthalpy calculated from data having errors, either 1.0 per cent or two significant figures, was 200 joules/gmol. At other temperatures the differences in enthalpy were much less than 200 joules/gmol, and in many cases was completely negligible.

For the calculated entropy values, the situation is similar as for the enthalpy values. The poorest agreement was at $140^{\circ}K$. At $140^{\circ}K$ the difference between the entropy calculated using full precision data and the entropy calculated using data with a random error of 1.0 per cent or using data rounded to two significant figures, was about 1.0 joules/gmol-$^{\circ}K$. At other temperatures, the differences were much less, usually negligible.

For both enthalpy and entropy, the differences described above are of the same order of magnitude as the differences found between the properties calculated by Din and the properties calculated in this work using Din's full precision volumetric data. Also, these same differences are considerably less than the estimated errors in the enthalpy and entropy, as reported by Din and summarized in Table XII.1.

XIII. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. A thermodynamic network can be calculated automatically on a computor, directly from experimental data, using the computor program described in this work. The computor program is general, can be used for any gas and will produce a thermodynamic network of high accuracy.

2. The calculated thermodynamic network is less accurate near the critical region than in other regions, but is as accurate in the critical region as a thermodynamic network calculated by other methods suggested in the literature.

3. It is possible to measure automatically and with an accuracy of 1.0 per cent, using commercially available instruments, sufficient volumetric data for the generation of a complete thermodynamic network.

4. Using data of 1.0 per cent accuracy, it is possible to automatically calculate a thermodynamic network, using the computor program described here, of sufficient accuracy for engineering use. The data may be obtained from the literature or from the experiment described here.

5. By combining the proposed experiment and the computor program, it is possible to generate a thermodynamic network, automatically.

6. The preferred method for obtaining the heat capacity data is to measure the constant pressure heat capacity in a flow calorimeter.

B. Recommendations

1. Experimental

The experimental system discussed in Section IV should be further investigated. The crucial measurements are those of mass flow rate and volumetric flow rate. Based on the information available, these measurements could be combined so that densities could be measured to an accuracy of about 1.0 per cent over a range of pressures and temperatures. The complete useful range of these instruments should be further investigated so that the accuracy could be quantitatively evaluated as a function of the useful pressure and temperature ranges. This is important since it may require more than one mass flowmeter, and more than one volumetric flowmeter, in order to measure densities of sufficient accuracy over the desired range of pressure and temperature.

Another crucial part of the experiment is how well the pressure can be controlled. An investigation should be made to see if this can be done by using relatively simple pressure controllers, or whether a more complicated system as discussed in Section IV, may be required.

2. Analytical

The computor program has been checked out and is working satisfactorily. Some improvement should be made in calculating derivatives.

The derivative, $(\partial V/\partial T)_P$ is being calculated satisfactorily, but the derivative $(\partial^2 V/\partial T^2)_P$ requires a better evaluation, since the largest discrepencies occur in the calculation of the change in heat capacity with pressure. Presently, $(\partial^2 V/\partial T^2)_P$ is calculated by differentiating the least squares fifth degree polynomial twice. A better approximation may be obtained by using a polynomial of some other degree, or by using an interpolation polynomial.

The derivative $(\partial V/\partial P)_T$ should be calculated more accurately. It is used to calculate the constant pressure heat capacity from the sonic velocity and the volumetric data. It is being calculated by a five point interpolation formula. Other possibilities would be to use another interpolation polynomial or a least squares polynomial. A very interesting method, which should be investigated, is the method of Landis and Wilson (45). They divided the data into sets of points. Each set of points is represented by a cubic equation with the condition that the first and second derivatives be continuous at the junction points of the sets. The cubic polynomial may be fit to any number of points. In treating thermodynamic data, they found that seven points gave good results. This method may be generalized so that

polynomials of different degrees may be used on various number of points. This type of procedure should be investigated further with the aim of getting a better approximation to the derivative, $(\partial V/\partial P)_T$.

XIV. <u>APPENDICES</u>

Appendix A

Computor Program for Least Squares Curve Fit

The **FORTRAN** statements for the computor program that was used in calculating the coefficients of the least squares polynomial are presented and described below.

The program begins in the main section by printing out some identifying information at statement 200, and goes to the subroutine DVDT. In DVDT some control information is read in which indicates the total number of points to be curve fit (NI) and the scaling factor for temperatures (TSCALE). The factor TSCALE is used to normalize the temperatures so that overflow does not occur. Then, at statement 103 the set of volumes and temperatures to be curve fit are read in and stored and printed out for reference. Additional control information is read in at statement 113. M is the number of coefficients that will be calculated (which is equal to one plus the degree of the polynomial). NA is the first point, NB the last point and NC the number of points skipped, all referred to the original data. Using these parameters it is possible to select certain points to be curve fit from the original set of data. The degree of the polynomial is calculated at statement 115, and this information, together with the other parameters, is printed out for reference.

Control is then transferred to the subroutine SUB1, which sets up the coefficient matrix of the normal equations as described in Section II.A. The actual calculation is accomplished by the DO loops around statements 9 and 14.

In subroutine SUB2, the Crout reduction (17) is applied to the coefficient matrix, and the elements of an intermediate matrix are calculated. In subroutine SUB3, the coefficients of the least square polynomial are calculated from the intermediate matrix. The coefficients are the solution to the set of normal equations. The coefficients are calculated in statements 10 to 18. In statement 20, the coefficients are substituted back into the original equations to see if the original equations are satisfied. This test is made in statements 21 to 24. If the equations are satisfied, the actual coefficients are calculated from the normalized coefficients in statement 32. If the normal equations are not satisfied, control is transferred to statement 35. Statements 35 to 50 calculate a correction to the previously calculated coefficients. The new coefficients are tested again and if the normal equations are still not satisfied, statements 35 to 50 are repeated. This process is repeated until the corrected coefficients satisfy the normal equations to within a specified tolerance. Control is then transferred to subroutine SUB4.

In SUB4, specific volumes, and derivatives of specific volume with respect to temperature are calculated, as a

function of temperature. The calculated volumes are compared to the input volumes and the root mean square errors are calculated. The results of these calculation are printed out for reference.

Control is returned to DVDT at statement 118, which directs the program back to statement 113 to read more control data. Thus, the program can fit a given set of volume-temperature data to least square polynomials of various degrees.

When there is no more control data to be read, control is transferred to statement 99 and the entire calculation can be repeated with a new set of volume-temperature data. When there is no more data to be read, control is transferred back to the main program, a message is printed out, and the job is ended.

```
      PROGRAM FOR LEAST SQUARES CURVE FIT

D     DIMENSION AP(8,10),A(8,10),B(8),COF(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100)
      DIMENSION DER(100),ERR(6),ERRCOF(8,6),VCALC(100),WORD(12)
      COMMON AP,A,B,COF,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
      PRINT 200
200   FORMAT(1H1,19X46H CALC OF DV/DT, PROB NO. M2616, G. GRUBER 2152)
      CALL DVDT
      PRINT 201
201   FORMAT (1H1,19X32H END OF JOB, ALL CASES COMPLETED)
      CALL EXIT
      END

      SUBROUTINE DVDT
D     DIMENSION AP(8,10),A(8,10),B(8),COF(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100)
      DIMENSION DER(100),ERR(6),ERRCOF(8,6),VCALC(100),WORD(12)
      COMMON AP,A,B,COF,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
99    READ 100,(WORD(I),I=1,12)
100   FORMAT(12A6)
      READ 101,NO1,NO2,NO3,NI,P,R,TSCALE
101   FORMAT(4I3,3F18.6)
      TF(TSCALE) 103,119,103
103   READ 102, (V(I),T(I),I=1,NI)
102   FORMAT(4E18.6)
106   PRINT 107,(WORD(I),I=1,12)
107   FORMAT(1H1,19X12A6)
      PRINT 110,NI,(V(I),T(I),I=1,NI)
110   FORMAT(1H0,19X20H TOTAL DATA POINTS =I4/27X27H VOLUME        TEMP
     1ERATURE/(E40.6,E18.6))
      PRINT 112, P,R
112   FORMAT(1H0,19X 12H PRESSURE IS E18.6, 20H GAS CONSTANT (R) IS E18.
     16)
113   READ 114,M,NA,NB,NC,(ERR(J),J=1,5)
114   FORMAT (4I3,5F12.4)
      TF (M) 115,99,115
115   M1=M-1
      PRINT 116, NA,M1,NB,NC,(ERR(J),J=1,5)
116   FORMAT(1H1,19X15H FIRST POINT IS I3,23H DEGREE OF POLYNOMIAL =I2,
     121H LAST POINT IS NUMBER I3,13H INCREMENT IS I2/19X6H ERR =5F12.4)
      CALL SUB1
      CALL SUB2
      CALL SUB3
      CALL SUB4
118   GO TO 113
119   RETURN
      END

      SUBROUTINE SUB1
D     DIMENSION AP(8,10),A(8,10),B(8),COF(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100)
      DIMENSION DER(100),ERR(6),ERRCOF(8,6),VCALC(100),WORD(12)
      COMMON AP,A,B,COF,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
      DO 12 J=1,M
      DO 10 K=1,M
      A(J,K)=0.0
D9    DO 9I=NA,NB,NC
      A(J,K)=A(J,K)+(T(I)/TSCALE)**(J+K-2)
```

```
10    CONTINUE
D     A(J,M+2)=0.0
D     A(J,M+1)=0.0
D     DO 14 I=NA,NB,NC
      A(J,M+1)=A(J,M+1)+V(I)*(T(I)/TSCALE))**(J-1)
D14   A(J,M+2)=A(J,M+2)+(T(I)/TSCALE))**(J-1)
D     B(J)=A(J,M+1)
D     C(J)=A(J,M+2)
12    CONTINUE
      M2=M+2
      IF(NO1-1)18,16,18
16    PRINT 17,((A(J,K),K=1,M2),J=1,M)
17    FORMAT(1H0,19X27H COEFFICIENT MATRIX BY ROWS/(F34.6,4E18.6))
18    RETURN
      END

      SUBROUTINE SUB2
D     DIMENSION AP(8,10),A(8,10),B(8),COF(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100)
      DIMENSION DER(100),ERR(6),ERRCOF(8,6),VCALC(100),WORD(12)
      COMMON AP,A,B,COF,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
      DO 10 J=1,M
      DO 12 K=1,M2
D12   AP(J,K)=0.0
10    CONTINUE
      DO 14 J=1,M
      AP(J,1)=A(J,1)
D14   DO 16 K=2,M2
      AP(1,K)=A(1,K)/AP(1,1)
D16   DO 20 J=2,M
      DO 18 K=2,M
D     SUM=0.0
      IF(J-K)23,21,21
21    K1=K-1
      DO 22 L=1,K1
D22   SUM=SUM+AP(J,L)*AP(L,K)
D     AP(J,K)=A(J,K)-SUM
      GO TO 25
23    J1=J-1
      DO 24 L=1,J1
D24   SUM =SUM+AP(J,L)*AP(L,K)
      AP(J,K)=(A(J,K)-SUM)/AP(J,J)
25    CONTINUE
18    CONTINUE
20    CONTINUE
      DO 40 J=2,M
      J1=J-1
D     SUM=0.0
      DO 38 L=1,J1
D38   SUM=SUM+AP(J,L)*AP(L,M+1)
D40   AP(J,M+1)=(A(J,M+1)-SUM)/AP(J,J)
      DO 36 J=2,M
      J1=J-1
D     SUM=0.0
      DO 34 L=1,J1
D34   SUM=SUM+AP(L,M+2)*ARSF(AP(J,L))
D36   AP(J,M+2)=(SUM+A(J,M+2))/ARSF(AP(J,J))
      IF(NO2-1)44,41,44
41    PRINT 42, ((AP(J,K),K=1,M2),J=1,M)
42    FORMAT(1H0,19X22H SECOND MATRIX BY ROWS/(F40.8,4F20.8))
44    RETURN
```

```
      END
      SUBROUTINE SUB3
      DIMENSION AP(8,10),A(8,10),B(8,10),B(8),COF(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100)
      DIMENSION DER(100),ERR(6),ERRCOF(8,8),VCALC(100),WORD(12)
      COMMON AP,A,B,COF,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
      NCON1=0
      DO 10 K=1,M
      COF(K)=0.0
      COF(M)=AP(M,M+1)
      DO 18 K=1,M1
      MK=M-K
      DO 16 J=1,M
      COE(MK)=COE(MK)+COE(J)*AP(MK,J)
      COE(MK)=AP(MK,M+1)-COE(MK)
      DO 21 J=1,M
      RES(J)=0.0=B(J)
      DO 20 K=1,M
      RES(J)=RES(J)+COF(K)*A(J,K)
      RES(J)=RES(J)+COF(K)*A(J,K)
      DO 24 J=1,M
      RATIO(J)=ABSF(RES(J)/A(J,M+1))
      IF(RATIO(J)-0.000001) 22,22,35
      CONTINUE
      CONTINUE
      IF(NO2-1) 30,26,30
      PRINT 28,(RES(J),J=1,M)
      FORMAT(1H0,19X27H RESIDUALS FOR COEFFICIENTS/(E40.8,4E20.8))
      DO 32 K=1,M
      COE(K)=COE(K)/((TSCALE)**(K-1))
      PRINT 34,(COE(K),K=1,M)
      FORMAT(1H0,19X24H COEFFICIENTS FOR VOLUME/(E38.6,4E18.6))
      GO TO 53
      DO 36 J=1,M
      AIJ,M+1)=RES(J)
      AP(J,M+1)=0.0
      AP(1,M+1)=RES(1)/AP(1,1)
      DO 40 J=2,M
      J1=J-1
      DO 38 L=1,J1
      AP(J,M+1)=AP(J,L)*AP(L,M+1)+AP(J,M+1)
      AP(J,M+1)=A(J,M+1)-AP(J,M+1)
      DO 42 K=1,M
      DCOF(K)=0.0
      DCOF(M)=AP(M,M+1)
      DO 48 K=1,M1
      MK=M-K
      DO 46 J=1,M
      DCOF(MK)=DCOF(MK)+DCOF(J)*AP(MK,J)
      DCOF(MK)=AP(MK,M+1)-DCOF(MK)
      DO 50 K=1,M
      COE(K)=COE(K)=DCOF(K)
      NCON1=NCON1+1
      IF(NCON1-10) 19,19,51
      PRINT 52
      FORMAT(1H0,19X38H NO CONVERGENCE AFTER TEN TRIES ON COE)
      GO TO 26
      END
```

```
      SUBROUTINE SUB4
      DIMENSION AP(8,10),A(8,10),B(8,10),COE(8),C(8),DCOF(8),DELCOF(8),DLCO
     1E(8),RATIO(8),RES(8),T(100),V(100),VCALC(100),DER(100)
      DIMENSION ERR(6), ERRCOF(8,6), WORD(12), Q(100)
      COMMON AP,A,B,COE,C,ERR,M1,M2,M,NA,NR,NC,NI,NO1,NO2,NO3,T,V,TSCALE
      COMMON DUM1, DELCOE
      RT=0.0
      DO 10 I=NA,NR,NC
      VCALC(I)=0.0
      DO 8 K=1,M
      VCALC(I)=VCALC(I)+COE(K)*(T(I))**(K-1))
      RI=RI+(V(I)-VCALC(I))**2
      N=1+(NB-NA)/NC
      D=FLOATF(N-M)
      ERRCAL=SQRTF(RT/D)
      ERR(6)=ERRCAL
      DO 20 I=NA,NR,NC
      DER(I)=0.0
      DO 18 K=1,M
      DER(I)=DER(I)+(FLOATF(K-1)*(COF(K))*(T(I))**(K-2))
      CONTINUE
      EP=FLOATF(N-M)/FLOATF(N)
      ERMS=SQRTF(EP)*ERRCAL
      PRINT 34, ERRCAL
      FORMAT(1H0,19X45H RMS ERROR OF OBSERVED VALUES IF M IS CORRECT E18
     1.6)
      PRINT 36, ERMS
      FORMAT(1H0,19X58H RMS DEVIATION BETWEEN OBSERVED POINTS AND SMOOTH
     1 FUNCTION E18.6)
      PRINT 40,N
      FORMAT(1H0,19X 20H TOTAL POINTS USED = I3)
      PRINT 42, (T(I),V(I),VCALC(I),DER(I),I=NA,NR,NC)
      FORMAT (1H0,47H   VOLUME          VCALC         DER      TEMP
     1 /(E48.6,3F18.6))
      RETURN
      END
```

Appendix B

Description of Computor Program for Calculating
Thermodynamic Networks

This section will contain a detailed description of
the IBM 7094 computor program for calculating thermodynamic
networks. A FORTRAN listing is included, together with a
special table of nomenclature used in the program.

1. Main Portion of Program

The program begins in MAIN by reading in the name of
the substance and the units that will be used for the thermo-
dynamic variables. The standard units are for the engineer-
ing system, and the constants, A1-A4, and B correspond to
those units. The molecular weight of the gas is read in, and
the control integers, M1-M8, are also read. The control con-
stants specify the units, and conversions from the standard
units are carried out with stored conversion factors. The
proper conversion factors are selected according to the
values of M1-M7. These calculations take place from state-
ments 22-54. M8 is the control constant for the output op-
tion. The option is to have all of the output punched so
that it may be reproduced from a punched deck. After these
preliminary calculations, an identification is printed out
at statement 60, and control is transferred to SETUP.

The initial READ statements in SETUP call in the pressures and temperatures at which final values will be calculated and tabulated, and the number of points on each volumetric isobar. In the DO loop, the data points for each volumetric isobar are read in and curve fit until the volumetric data is exhausted. The curve fitting is accomplished by transferring control to CURFT. The basis for CURFT has already been described in Appendix A.

When the curve fitting of the volumetric data is completed, the process is continued with either sonic velocity data or heat capacity data, if present. If neither of these are present, control is transferred to statement 36 where the coefficients of a heat capacity polynomial are read in and stored.

After the bulk of the data has been read in and curve fit, and enthalpy and entropy at the reference temperature and pressure are read in and stored. The reference temperature and pressure are the first ones on the temperature-pressure matrix. Then, for each temperature on the matrix, the highest pressure is read in. The matrix is not necessarily square, and there may be some temperatures for which the matrix is to be truncated. Control is transferred to subroutine VAPR.

An identification is printed out at statement 2, and the program continues by reading in a set of vapor pressure data. When only two vapor pressure points are read in, one is the critical point and the vapor pressure curve is estimated

by Riedel's method (67, 69). When a complete set of data
is read in the points are curve fit and the coefficients are
printed out.

Then the temperatures are calculated at evenly spaced
values of the vapor pressure by using the Newton-Raphson
method (32). This occurs at statement 8 or 9 depending on
whether data were read in and curve fit or if the generalized
method was used. The statements starting on number 15 test
for convergance. When convergance is achieved the results
are printed and/or punched out at statements 105 and 106.

The vapor pressures are then calculated at evenly
spaced values of the temperature by either statement 121 or
122, depending on which equation is used. The calculated
vapor pressure replaces the highest pressure read in after
statement 32 in SETUP. This insures that the tabulation is
completed up to the saturation curve. The calculated vapor
pressure are also tabulated as output at statement 114 and/or
112. Control is transferred back to MAIN through SETUP.

In MAIN control is transferred to either HSTART or
HSTARK. If sonic velocities were read in control goes to
HSTART. If heat capacities or the coefficients of a heat
capacity polynomial were read in, control goes to HSTARK.

In HSTARK, the constant pressure heat capacity is
calculated at each temperature on the matrix by using either
the curve fit or input polynomial. Enthalpies and entropies
are calculated at the same temperatures at statements 30 and
35 by integrating the polynomial.

In HSTART, the constant pressure heat capacities are calculated from the sonic velocity and volumetric data. In order to calculate C_p at the reference pressure the sonic velocity, specific volume, $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ are required at the same reference pressure. Since the measurements of sonic velocity and specific volume will not have been made at the reference pressure, P_O, an interpolation must be carried out. This is done by the subroutines INTRP1 and INTRP2. For example, INTRP1 calculates the specific volume, and $(\partial V/\partial T)_P$ at P_O from values of the least square polynomial coefficients at surrounding pressures. The same is done for the sonic velocity using INTRP2. In addition, $(\partial V/\partial P)_T$ is calculated using INTDVP. These subroutines will be discussed in detail below.

The calculation of C_p at each temperature takes place at statement 40. At statements 7-50, the enthalpy and entropy are calculated using a Legendre-Gauss integration. Heat capacities are calculated at the required temperature for the integration (TA) by interpolation, using INTRP3.

The result, after passing through either HSTART or HSTARK, is a set of heat capacities, enthalpies and entropies at the reference pressure, and at each temperature on the pressure-temperature matrix. Control is then transferred back to MAIN.

At statement 122, the fugacity coefficient is set equal to unity at the reference pressure and control is transferred to PRNT. In PRNT, the thermodynamic network is

calculated for each constant temperature, and control is transferred back to MAIN to check the temperature. If there are still temperatures remaining on the pressure-temperature matrix, control is transferred back to PRNT. This process continues until all the temperatures have been used up.

In PRNT the calculation starts at the first pressure and temperature by calculating the volume, $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$. If sonic velocity data were input then the sonic velocity is evaluated by interpolation at P_o and T_o, and the heat capacity is calculated between statement 100 and 90. If heat capacity data were input, then control is transferred to statement 90 and the sonic velocity is calculated from the heat capacity. Starting at statement 89, the other properties are calculated. The calculated items are output and the calculation proceeds to the next highest pressure on the matrix at statement 30.

A check is made to see if the highest pressure for the temperature (PLA) is greater than the next pressure (P1) on the matrix. If it is the calculation continues at statement 5. If not, P1 is replaced by PLA and P1 is temporarily stored at P8 at statement 51. Usually PLA would be the vapor pressure at the temperature of the calculation. In any event, having selected the pressure for the next step, the calculation continues at statement 5, by calculating the pressure (PL) for the Legendre-Gauss integration. Then V, $(\partial V/\partial T)_P$ and $(\partial^2 V/\partial T^2)_P$ are evaluated at PL, and the first

term in the integration formula is calculated for the heat
capacity, entropy, enthalpy and fugacity coefficient. This
is completed at statement 16, and then the next pressure for
the Legendre-Gauss integration is evaluated. From statement
16 to 20, the process is repeated for the second term in
the integration formula, and the second term is added to the
first term. The process is repeated for the third term at
statement 20 to 24. After statement 24, the derivatives
are evaluated at P1 so that the sonic velocity can be cal-
culated from the heat capacity (statement 105), or the heat
capacity can be calculated from the sonic velocity (state-
ment 110). Then, at statement 106, the remaining parameters
are evaluated and output is performed at statement 111 and/or
112. At statement 200, the index for pressure is advanced
to the next pressure on the matrix. If there are more pres-
sures control goes back to statement 30, and the process is
repeated for the next pressure. If there are no more pres-
sures, control passes to statement 52 which returns control
to MAIN.

In MAIN, the index for temperature is advanced. When
there are more temperatures to be covered, control passes
back to PRNT and the entire process is repeated, starting
at the lowest pressure. When there are no more temperatures,
a message is printed at statement 130 signifying that the
calculation has been completed. The control passes back to
statement 1 to start reading data for the next thermodynamic
network, if any.

2. Interpolation Subroutines

   a. LGCFT

   This subroutine calculates the coefficients for a
five point Lagrangian interpolation formula. The informa-
tion supplied to it is the pressure, PA, at which it is
desired to interpolate to, a set of surrounding pressures,
P2, for which data are available, and an index which specifies
the P2 which is closest to PA. The subroutine then calcu-
lates the five coefficients from PA and the five nearest
pressures to PA.

   b. DLGCFT

   This subroutine calculates the five coefficients for
the Lagrangian differentiation polynomial. The calculation
is carried out in the same manner as was done in LGCFT,
except that the algebraic expressions in statement 10 to
50 in DLGCFT are the derivative of the corresponding expres-
sions in LGCFT.

   c. BRKT

   Given a point, Y, and an array, X(J7), this sub-
routine finds J7 such that $X(J7-1) < Y \leq X(J7)$. This sub-
routine is always used by the interpolation subroutine to
find the nearest surrounding set of pressures to the inter-
polating pressure.

d. INTDVP

This subroutine calculates the derivative $(\partial V/\partial P)_T$, or DVP1 in FORTRAN notation, at a given pressure P7. Upon entering INTDVP, control is immediately transferred to BRKT to find the index, J1, which specifies the five nearest pressures, P2, surrounding P7. If P7 falls near either of the extremes of the array P2, then the index, J1, is set so that there are at least two pressures on either side of P7 (statements 28 to 34). Having selected an index, J1, control is transferred to DLGCFT, where the coefficients are calculated and returned to INTDVP. The equation following statement 40 calculates $(\partial PV/\partial P)_T$ at the pressure P7, and control is returned to the program which originally called INTDVP, where $(\partial V/\partial P)_T$ is calculated from $(\partial PV/\partial P)_T$.

e. INTRP1

INTRP1 is used to calculate V, $(\partial V/\partial T)_P$ and $(\partial^2 V/\partial T^2)_P$ at a given pressure, P7. At each pressure, P2, for which the volumetric isobars were curve fit, the resulting polynomial coefficients were stored. In order to calculate the volume and its derivatives, at a given pressure, P7, and at any temperature, the volume (and derivatives) are first calculated at the temperature and the pressures P2. Then, the volumes, (and derivatives) are calculated at P7 using a Lagrangian interpolation.

Upon entering INTRP1, control is transferred to BRKT which returns the index J1 to INTRP1. If P2(J1) is near the

extremes of the array, then J1 is set so that there are at least two pressures on either side of P7 (statements 38 to 36). Having selected a J1, control is transferred to LGCFT (statement 42), which returns the value of the interpolating coefficients. The actual interpolation takes place in the statements following number 42. If it turns out that for a given P7, there is a P2 which equals P7, control is transferred to statement 60. In that case, an interpolation is not required and the volume (and derivatives) are calculated directly from the stored coefficients.

    f.   INTRP2

INTRP2 does the same thing for the sonic velocity that INTRP1 does for the specific volume. In this case, however, derivatives are not calculated.

    g.   INTRP3

While the other interpolation routines were used to interpolate on pressures, INTRP3 interpolates on temperatures. Its function is to find the constant pressure heat capacity at a given temperature, TA, from the heat capacities which are already known at a set of temperatures, T. Aside from the interchange of temperature and pressure, the interpolation is carried out in the same manner as in INTRP1 and INTRP2.

3. Input and Output

    a. Input

        The input to the program is on punched cards. The first card contains the name of the gas for which the thermo-dynamic network is being calculated, together with any other identifying information. The second card contains the units in which the thermodynamic network will be tabulated. The third card contains the molecular weight of the gas, and the fourth card contains the control constant M1-M8.

        The next card contains the number of pressures on the pressure-temperature matrix, followed by the values of the pressure. As many cards as required are used. The next group of cards contains the corresponding information for the temperatures on the matrix. Following this information is a card with the number of measured volumetric isobars, and the number of measured sonic velocity isobars. The integer for the number of measured sonic velocity isobars is also a control constant. For example, if that integer is 1, then it is understood that heat capacity data at one pressure replaces the sonic velocity data.

        The next group of cards contains a set of pairs of number. For each pair, the first number specifies the number of volume-temperature points on a measured isobar. The second number gives the value of the measured pressure for that isobar. As many pairs and cards as required are used. The following set of cards contains the volumetric data,

two points per card, using as many cards as required.

The next card contains the number of measured points and measured pressure, in pairs, for each measured sonic velocity isobar. If heat capacity data is to be read in, this card contains the number of heat capacity data points. The cards following contain the sonic velocity data, or heat capacity data, as the case may be.

The next card contains the value of the enthalpy and entropy, at the reference pressure and temperature. The following card, or cards, contains the values of the highest pressure for each temperature on the pressure-temperature matrix.

The next card contains the number of measured vapor pressure points, followed by the vapor pressure data. If a generalized correlation is used for the vapor pressure, only two pairs of points are read in, one being the critical pressure and critical temperature. This completes the input data.

    b.   Output

The first line to be printed out contains the name of the gas and any other identifying information.

Then, on a new page, the vapor pressure information is printed out in the following order:

    1.   A title identifying the output as vapor pressure data, and the name of the gas, included in the title.

213

2. The form of the vapor pressure equation.

3. The coefficients of the vapor pressure equation.

4. The vapor pressure and corresponding temperature tabulated at evenly spaced values of the vapor pressure, corresponding to the pressures on the pressure-temperature matrix.

5. The vapor pressure tabulated at evenly spaced values of the temperature, corresponding to the temperature on the pressure-temperature matrix.

In addition to being printed out, the above output may also be obtained on punched cards.

Following the vapor pressure output the tabulated thermodynamic network is given. The thermodynamic variables are tabulated at evenly spaced pressures at a constant temperature. The tabulation for each constant temperature starts on a new page, and as many pages as are required are used.

The format of each page is the same. The first line is the title, followed by the temperatures for that page. The next line gives the column headings, followed by the units used. When the standard output is used, consecutive lines are printed out, each line corresponding to a different pressure. The order of the columns is pressure, specific volume, enthalpy, entropy and heat capacity. When the optional output is used, these items are punched out on cards, together with additional output. For each pressure, three cards are

punched. On each card the first column is the pressure. The other columns are given as follows:

Card 1 - specific volume, enthalpy, entropy, constant pressure heat capacity

Card 2 - compressibility factor, residual volume, fugacity coefficient, Joule-Thomson coefficient

Card 3 - constant volume heat capacity difference between heat capacities $(C_p - C_v)$ ratio of heat capacities (C_p/C_v) sonic velocity

If desired, the punched cards are collated to give three tables for each temperature. Also, heading for each table are punched on cards and inserted at the head of each table.

4. Program Nomenclature

A	Matrix element in CURFT
A1-A4	Conversion factors
ALFA	Dimensionless slope of vapor pressure curve - defined in VAPR
AP	Matrix element in CURFT
B	Matrix element in CURFT
C	Matrix element in CURFT
C1-C6	General coefficients of fifth degree least-squares polynomial
CL1-CL5	Coefficients for 5 point Lagrangian interpolation formula
CP	Constant pressure heat capacity at local temperature and pressure
CP1	Constant pressure heat capacity at reference pressure
CPCV	Difference between heat capacity at constant pressure and heat capacity at constant volume
CS1-CS6	Coefficients of fifth degree least squares polynomial for the sonic velocity squared as a function of temperature
CV	Heat capacity at constant volume
CV1-CV6	Coefficients of fifth degree least squares polynomial for specific volume as a function of temperature
CVP1-CVP6	Coefficients for natural logarithm vapor pressure equation
CVP1A-CVP6A	Coefficients for common logarithm vapor pressure equation
DC	Error in least square polynomial coefficient
DCL1-DCL5	Coefficients for 5-point Lagrangian differentiation

DVP1	Derivative of volume with respect to pressure at constant temperature
DVT1	Derivative of volume with respect to temperature at constant pressure
DVT2	Second derivative of volume with respect to temperature at constant pressure
FUC	Fugacity coefficient
GAMMA	Ratio of heat capacity at constant pressure to heat capacity at constant volume
H	Enthalpy at local pressure and temperature
HO	Enthalpy at reference pressure and temperature
I	Index for temperature on pressure-temperature matrix
J	Index for pressure on pressure-temperature matrix
J1	Index for measured volumetric isobars
J4	Index for measured sonic velocity isobars
L6	Number of measured points on each sonic velocity isobar
M1-M7	Control constants for conversion of units
M8	Control constant for output option
N1	Number of pressures in the pressure-temperature matrix
N2	Number of measured volumetric isobars
N3	Number of temperatures in the pressure-temperature matrix
N4	Number of measured data points on each volumetric isobar
N5	Number of measured vapor pressure points
N9	Number of measured sonic velocity isobars
N10	Represents the number of elements of any array

N11	Number of measured data points on each volumetric isobar
N12	Number of measured data points on each sonic velocity isobar
N14	Number of measured heat capacity points
NI	Represents the number of elements of any array
PO	Reference pressure
P1	Pressure at which final results are calculated on pressure-temperature matrix
P2	Pressure at which volumetric isobars are measured
P3	Pressure at which sonic velocity isobars are measured
P5	Measured vapor pressure
P6	Calculated vapor pressure
P7	Pressure at which an interpolation is carried out to
P8	Temporary representation of P1
PA	Pressure at which an interpolation is carried out to
PB	Vapor pressure corresponding to TB
PC	Critical pressure
PL	Pressure for Legendre-Gauss integration
PLA	Highest pressure for each temperature on pressure-temperature matrix
R	Gas constant
RAT	Array element in CURFT
RES	Array element in CURFT
RV	Residual volume
S	Entropy

SO	Entropy at reference pressure and temperature
S1,S2	Temperature scaling factors in CURFT
SV	Calculated sonic velocity squared
SV2	Calculated sonic velocity
SV3	Measured sonic velocity or measured heat capacity
SV3S	Measured sonic velocity squared
T	Temperature at which final results are calculated on pressure-temperature matrix
TO	Reference temperature
T1	Temperature on vapor pressure curve corresponding to P1
T2	Temperature at which specific volumes are measured
T3	Temperature at which sonic velocity or heat capacity is measured
T5	Temperature corresponding to vapor pressure P5
TA	Temperature for Legendre-Gauss integration
TB	Temperature corresponding to T in PRNT
TB	Normal boiling temperature, or temperature corresponding to vapor pressure PB
TC	Critical temperature
TE	Error in calculated temperature on vapor pressure curve
TLP	Temperature times logarithm of vapor pressure
TP1, TP2	Successive approximation to T1
V1	Calculated specific volume at local pressure and temperature
V2	Measured specific volume
WM	Molecular weight

WORD1	General alphanumeric information
WORD2	Specifies units in alphanumeric form
X,X1	Dummy array names
XJT	Joule-Thomson coefficient
XLFUC	Logarithm of fugacity coefficient
Y,Y1	Dummy array names
Z	Compressibility factor

```
      PROGRAM FOR CALCULATING THERMODYNAMIC NETWORKS

      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,I,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC,M8,WORD1
      DIMENSION CP1(75),CS1(75),CS2(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     2 75),PI(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
      DIMENSION WORD1(12)
   1  READ 10,(WORD1(K),K=1,12)
      READ 10,(WORD2(K),K=1,12)
C     WORD(1-4) = SUBSTANCE, I.E., NITROGEN.
C     WORD2, 1=T,2=P,3-4=SPECIFIC VOLUME,5-6=ENTHALPY,7-8=ENTROPY,
C     9-10=HEAT CAPACITY,11-12=SONIC VELOCITY.
   10 FORMAT(12A6)
      A1=1./132.174*777.97)
      A2=1./132.174*144.)
      A3=A1/A2
      A4=A3
      READ 12, WM
   12 FORMAT (F10.4)
      R=10.73
      READ 22, M1,M2,M3,M4,M5,M6,M7,M8
   22 FORMAT (8I1)
C     IF M8= 0, PRINT, IF M8= 1, PUNCH AND PRINT.
C     IF M1=0, V=CUBIC FT., IF M1=1, V=LITER, IF M1=2, V=CC.
      IF(M1-1) 24,26,28
   26 R=R/7.035316
      A2=A2/.035316
      A4=A4*.035316
      A3=A3*.035316
      GO TO 24
   28 R=R*28316.77
      A4=A4/28316.77
      A3=A3/28316.77
      A2=A2*28316.77
C     IF M2 = 0, P = PSIA. IF M2 = 1, P = ATM.
   24 IF(M2-1) 30,32,30
   32 R=R/14.696
      A3=A3*14.696
      A4=A4*14.696
      A2=A2/14.696
C     IF M3=0, TEMP. IS DEG. R. IF M3=1, TEMP. IS DEG. K.
   30 IF(M3-1) 34,36,34
   36 R=R*1.8
C     IF M4=0, MASS IS IN POUNDS, IF M4=1, MASS IS IN GRAMS.
   34 IF(M4-1) 40,38,40
   38 R=R*453.5924
      A1=A1/453.5924
      A2=A2/453.5924
C     IF M5=0, SONIC VEL. = FT/SEC. IF M5=1, SONIC VEL. = METERS/SEC.
   40 IF(M5-1) 44,42,44
   42 A1=A1*(3.2080R43**2)
      A2=A2*(3.2080843**2)
C     IF M6=0, HEAT = BTU, IF M6=1, HEAT = CALORIES, IF M6=2, HEAT = JOULES.
   44 IF(M6-1) 50,48,46
   48 A3=A3*251.98
      A4=A4*251.98
      A1=A1*251.98
   46 GO TO 50
      A3=A3*1054.8
      A1=A1*1054.8
      A4=A4*1054.8
C     IF M7=0, UNIT IS MASS,    IF M7=1, UNIT IS MOLE.
   50 IF (M7-1) 54,52,60
   52 A1=A1*WM
      A2=A2*WM
      GO TO 60
   54 R=R/WM
   60 PRINT 14, (WORD1(K),K=1,12)
   14 FORMAT(19X12A6)
      CALL SETUP
      T(N0-1) 112,112,110
  110 CALL HSTART
      GO TO 118
  112 CALL HSTARK
  118 T=1
  122 FUC(I)=1.0
      XLFUC(I)=0.0
      CALL PRNT(T(I))
      T=T+I
      IF(I-N3) 122,122,130
  130 PRINT 20
   20 FORMAT (1H1,19X 14H JOB COMPLETED )
      GO TO 1
      END
      SUBROUTINE SETUP
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,I,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     2 75),PI(75),P2(75),P3(75),S(75),T(75),T1(75),L6(75),T3(75),SV3S(75)
      DIMENSION N4(75),N1,(P1(J),J=1,N1)
      READ 40, N3,(T(I),I=1,N3)
      READ 44,  N2,N9
      READ 46, (N4(J1),P2(J1),J1=1,N9)
      DO 20 J1=1,N2
      N1=N4(J1)
      READ 48, V2(I1),T2(I1),I=1,N11)
      CALL CURFT(V2,T2,CV1(J1),CV2(J1),CV3(J1),CV4(J1),CV5(J1),CV6(J1),
     1 T2(I1),N11)
   20 CONTINUE
C     IF N9 = 0 OR GREATER THEN 2, SON. VEL.-- IF N9=1, READ CP DATA..
C     IF N9 = 0, READ CP COEFFICIENTS.
      IF (N9-1) 36,34,22
   22 READ 46, (L6(J4),P3(J4),J4=1,N9)
      DO 30 J4=1,N9
      N17=L6(J4)
      READ 48, (SV3(I3),T3(I3),I3=1,N12)
      DO 28 I3=1,N12
      SV3S(I3)=SV3(I3)**2
      CALL CURFT(SV3S,T3,CS1(J4),CS2(J4),CS3(J4),CS4(J4),CS5(J4),CS6(J4),
     1 T3(I1),N12)
   30 CONTINUE
      GO TO 32
C     WHEN CP DATA IS READ, SV3=CP
   34 READ 56, N14,(SV3(I3),T3(I3),I3=1,N14)
C     CS1(I) ETC. ARE COEFFICIENTS FOR HEAT CAPACITY POLYNOMIAL
```

```
      CALL CURFT(SV3,T3,CS1(1),CS2(1),CS3(1),CS4(1),CS5(1),CS6(1),T3(1),
     1N14)
      GO TO 32
36    READ 58, CS1(1), CS2(1),CS3(1),CS4(1),CS5(1),CS6(1)
32    READ 50, H0,S0
      READ 52, (PLA(I),I=1,N3)
      CALL VAPR
40    FORMAT(I3,8F8.2/(9F8.2))
44    FORMAT (2I4)
46    FORMAT (5I4,F10.3))
48    FORMAT (4E18.6)
50    FORMAT (2E18.6)
52    FORMAT (9F8.2)
56    FORMAT (I4/(4E18.6))
58    FORMAT (4E18.6)
      RETURN
      END

      SUBROUTINE VAPR
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,T,J,J8,J9,N1,N2,N3,N,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC,M8,WORD1
      DIMENSION WORD1(12)
      DIMENSION CP1(75),CS1(75),CS2(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),TP1(75),TP2(75),XLFUC(75)
      DIMENSION P5(75),T5(75),TLP(75),P6(75)
      FIRSTF(TR)=36./TR+42.*LOGF(TR)-35.-(TR**6)
      SECF(TR)=.0364*FIRSTF(TR)-LOGF(TR)/2.30259
      THIRDF(TR)=.118*FIRSTF(TR)-7.*LOGF(TR)/2.30259
      FOURF(TR)= -36.0/(TC+TR*TR)+42.0*TR -6.0*(TR**5)/TC
      IF(M8-112)1,2
1     PUNCH 302,(WORD1(M),M=1,4)
2     PRINT 302,(WORD1(M),M=1,4)
302   FORMAT (1H1,19X 19H VAPOR PRESSURE OF  4A6)
      READ 60, N5,(P5(I8),T5(I8),I8=1,N5)
      N5=N5
      IF N5 = 2, READ PB, TR, PC, TC.
      IF(N5-2) 18,16,18
16    PC=P5(2)
      PB=P5(1)
      TC=T5(2)
      TB=T5(1)
      GO TO 300
18    DO 19 I8=1,N5
19    TLP(I8)=T5(I8)*LOGF(P5(I8))
      CALL CURFT(TLP,T5,CVP1,CVP2,CVP3,CVP4,CVP5,CVP6,T5(1),N5)
      CVP1A=CVP1/2.30259
      CVP2A=CVP2/2.30259
      CVP3A=CVP3/2.30259
      CVP4A=CVP4/2.30259
      CVP5A=CVP5/2.30259
      CVP6A=CVP6/2.30259
      IF(M8-1) 20,22,20
22    PUNCH 198, WORD2(1), WORD2(2)
      PUNCH 199
      PUNCH 200, CVP1A, CVP2A,CVP3A,CVP4A, CVP5A,CVP6A
20    PRINT 198, WORD2(1), WORD2(2)
      PRINT 199
      PRINT 200, CVP1A, CVP2A, CVP3A, CVP4A,CVP5A,CVP6A
      N8=0
```

```
      J=1
      GO TO 301
300   ALFA= -(LOGF(PB/PC)/2.32259+THIRDF(TB/TC))/SECF(TB/TC)
      J=1
301   TP1(J)=T5(1)
4     IF(TP1(J)-P5(N5)) 6,6,102
6     IF (J-1) 140,140,7
7     TP1(J)=T(J-1)
140   IF (N5-2) 8,9,8
8     TP2(J)=(-LOGF(TP1(J)) + 7.0*CVP1/TP1(J) + CVP2 -CVP4*(TP1(J)**2)
     1 -2.0*CVP5*(TP1(J)**3) -3.0*CVP6*(TP1(J)**4))/((CVP1/(TP1(J)**2)
     2-CVP3-2.0*CVP4*TP1(J)-3.0*CVP5*(TP1(J)**2)-4.0*CVP6*(TP1(J)**3))
      GO TO 15
9     TP2(J)=(LOGF(TP1(J)/PC)/2.30259 +THIRDF(TP1(J)/TC)+ALFA*SECF(TP
     11(J)/TC)
      TP2(J)=TP2(J)/(-ALFA-7.01*TC/(2.30259*TP1(J))+FOURF(TP1(J)/TC)
     1*(0.118+ 0.0364*ALFA))
      TP2(J)=TP2(J) =TP2(J)
15    N8=N8+1
      TE=ABSF(TP2(J)-TP1(J))
      IF(TE-.0001) 12,10,10
10    IF(N8-20)  11,11,12
11    TP1(J)=TP2(J)
      IF (N5-2) 8,9,8
12    T1(J)=TP2(J)
      J=J+1
      N8=0
      IF (J-N1) 4,4,14
14    J9=N1
      GO TO 105
102   J9=J -1
      IF(M8-1) 106,105,105
105   PUNCH 202,(P1(J8),T1(J8),J8=1,J9)
106   PRINT 202,(P1(J8),T1(J8),J8=1,J9)
      K=1
      I=1
118   IF(T(I)-T5(N5)) 120,210,210
120   IF(N5-2) 121,122,121
121   P6(I)=EXPF(CVP1/T(I)+CVP2+CVP3*T(I)+CVP4*(T(I)**2)+CVP5*T(I)*(T(I)
     1**2) +CVP6*(T(I)**2)*(T(I)**2))
      GO TO 123
122   P6(I)=PC*EXPF(-2.30259*(THIRDF(T(I)/TC)+ALFA*SECF(T(I)/TC))
123   PLA(I)=P6(I)
131   IF(K-1) 130,131,130
131   IF(M8-1) 110,111,110
111   PUNCH 204
110   PRINT 204
      K=K+1
130   IF(M8-1) 112,114,112
114   PUNCH 206,T(I),P6(I)
112   PRINT 206, T(I),P6(I)
      I=I+1
      IF(I-N3)  118,118,210
60    FORMAT(I4,7(4F18.6))
198   FORMAT(1H0,10X 42H VAPOR PRESSURE EQUATION, LOG RASF 104  T =     A6,6
      1H0 P = A6)
200   FORMAT (1H0, 19X 17H COEFFICIENTS ARE /(F40.6))
199   FORMAT(1H0,19X43H LOG(P) = A/T + R + CT + DTT + FTTT + FTTTT)
202   FORMAT(1H0,19X31H TEMPERATURE     TEMPERATURE//(F32.2,F19.3))
204   FORMAT(1H0,19X 31H TEMPERATURE     VAPOR PRESSURE)
206   FORMAT(1H0,F29.2,F21.4)
```

```fortran
210   RETURN
      END

      SUBROUTINE HSTARK
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,T,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T1(75),WORD2(12),XLFUC(75)
      T0=T(1)
      P0=P1(1)
      DO 40 I=1,N3
20    CP1(I)=CS1(1) + CS2(1)*T(I)+ CS3(1)*(T(I)**2)+CS4(1)*(T(I)**3)
     1+ CS5(1)*(T(I)**4) + CS6(1)*(T(I)**5)
30    H(I)=H0+CS1(I)*(T(I)-T0) + CS2(1)*(T(I)**2-T0**2)/2.0 + CS3(1)*
     1(T(I)**3-T0**3)/3.0 + CS4(1)*(T(I)**4-T0**4)/4.0 +CS5(1)*(T(I)**5
     2-T0**5)/5.0 + CS6(1)*(T(I)**6-T0**6)/6.0
35    S(I)=S0 + CS1(I)*LOGF(T(I)/T0) + CS2(1)*(T(I)-T0) +CS3(1)*(T(I)**2
     1-T0**2)/2.0 +CS4(1)*(T(I)**3-T0**3)/3. + CS5(1)*(T(I)**4-T0**4)/4.
     2 +CS6(1)*(T(I)**5-T0**5)/5.0
40    CONTINUE
      RETURN
      END

      SUBROUTINE HSTART
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,T,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC,M8,WORD1
      DIMENSION WORD1(12)
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
      T0=T(1)
      P0=P1(1)
      I=1
6     CONTINUE
      CALL INTRP2 (P0,SV,J4)
      CALL INTRP1(P0,V1,DVT1,DVT2,J1)
      CALL INTDVP (P0,DVP1,J1)
      DVP1=DVP1-(V1/P0)
40    CP1(I)=-A1*SV*T(I)*(DVT1/V1)**2)/(1.+A2*SV*DVP1/(V1**2))
      I=I+1
      IF(I-N3) 6,6,7
7     I=1
      P0=P1(1)
      I=1
8     I=I+1
10    TA=.1127015*T(I)  +.8872985*(T(I-1))
      CALL INTRP3 (TA,CP)
      H(I)=5.*CP
12    S(I)=5.*CP/TA
14    TA=.5*(T(I)+T(I-1))
      CALL INTRP3 (TA,CP)
16    H(I)=H(I)+8.*CP
18    S(I)=S(I)+8.*CP/TA
20    TA=.1127015*T(I-1)+.8872985*T(I)
      CALL INTRP3 (TA,CP)
22    H(I)=5.*CP+H(I)
24    H(I)=H(I-1)+H(I)*(T(I)-T(I-1))/18.
      S(I)=S(I-1)+S(I)*(T(I)-T(I-1))/18.
50    IF (I-N3) 8,50,50
      I=1
      RETURN
      END

      SUBROUTINE PRNT(TB)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,H0,T,J,JR,J9,N1,N2,N9,N9,PLA,P0,P1,P2,P3,R,S,S0,T,T0,T1
     2,WORD2,XLFUC,M8,WORD1
      DIMENSION WORD1(12)
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T1(75),WORD2(12),XLFUC(75)
      CALL INTRP1(P1(1),V1,DVT1,DVT2,J1)
      CALL INTDVP(P1(1),DVP1,J1)
      DVP1=DVP1-(V1/P1(1))
      IF(N9-1) 90,90,100
100   CONTINUE
      CALL INTRP2 (P1(1),SV,J4)
      CP=-A1*SV*TB*((DVT1/V1)**2)/(1.+A2*DVP1*SV/(V1**2))
      SV2=SQRTF(ABSF(SV))
      GO TO 89
90    CP=CP1(1)
      SV=-CP*(V1**2)/(A2*CP*DVP1+A1*TB*(DVT1**2))
      SV2=SQRTF(ABSF(SV))
89    CPCV=-A3*TB*(DVT1**2)/DVP1
      Z=P1(1)*V1/(R*TB)
      RV=(R*TB/P1(1))-V1
      XJT=(TB*DVT1-V1)*A3/CP
      CV=CP-CPCV
      GAMMA=CP/CV
      IF(M8-1) 300,302,300
302   PUNCH 79, WORD1(1),WORD1(2),WORD1(3),WORD1(4)
      PUNCH 80, T(1),WORD2(1)
      PUNCH 81,WORD2(2),WORD2(3),WORD2(4),WORD2(5),WORD2(6),WORD2(7),
     1WORD2(8),WORD2(9),WORD2(10)
      PUNCH 82, P1(1),V1,H(1),S(1),CP
      PUNCH 83, P1(1),Z,RV,FUC(1),XJT
      PUNCH 84, P1(1),CV,CPCV,GAMMA,SV2
300   PRINT 79, WORD1(1),WORD1(2),WORD1(3),WORD1(4)
      PRINT 80, T(1),WORD2(1)
      PRINT 81,WORD2(2),WORD2(3),WORD2(4),WORD2(5),WORD2(6),WORD2(7),
     1WORD2(8),WORD2(9),WORD2(10)
      PRINT 82, P1(1),V1,H(1),S(1),CP
      J=2
30    CONTINUE
      K3=0
      IF (PLA(I)-P1(J)) 51,5,5
51    P8=P1(J)
      P1(J)=PLA(I)
      K3=1
5     PL=.1127015*P1(J)  +.8872985*P1(J-1)
      CALL INTRP1 (PL,V1,DVT1,DVT2,J1)
      CP1(I)=CP1(I)-2.5*A3*TB*DVT2*(P1(J)-P1(J-1))/9.
      H(I)=H(I)+2.5*A3*(V1-TB *DVT1)*(P1(J)-P1(J-1))/9.
12    S(I)=S(I)-2.5*A4*DVT1*(P1(J)-P1(J-1))/9.
      XLFUC(I)=XLFUC(I)+2.5*(V1/(R*TB)  -1./PL)*(P1(J)-P1(J-1))/9.
16    PL=.5*(P1(J)+P1(J-1))
      CALL INTRP1 (PL,V1,DVT1,DVT2,J1)
      CP1(I)=CP1(I)-4.0*A3*TB*DVT2*(P1(J)-P1(J-1))/9.0
```

```
18    H(I)=H(I)+A3*4.0*(V1-TB   *DVT1)*(P1(J)   -P1(J-1))/9.
      S(I)=S(I)-A4*4.0*DVT1*(P1(J)-P1(J-1))/9.
20    XLFUC(I)=XLFUC(I)+4.0*(V1/(R*TR   )-1./PL)*(P1(J)-P1(J-1))/9.
      PL=.1127015*P1(J-1)+.8872985*P1(J)
      CALL INTRP1 (PL,V1,DVT1,DVT2,J1)
22    R(I)=H(I)+A3*7.5*(V1-TR  *DVT1)*(P1(J)-P1(J-1))/9.
      CP1(I)=CP1(I)-2.5*A3*TR*DVT2*(P1(J)-P1(J-1))/9.
      S(I)=S(I)-A4*2.5*DVT1*(P1(J)-P1(J-1))/9.
24    XLFUC(I)=XLFUC(I)+2.5*(V1/(R*TB)  -1./PL)*(P1(J)-P1(J-1))/9.
      FUC(I)=EXPF(XLFUC(I))
      CALL INTRP1(P1(J),V1,DVT1,DVT2,J1)
      CALL INTDVP(P1(J),DVP1,J1)
      DVP1=DVP1-(V1/P1(J))
      CALL INTRP2(P1(J),SV,J4)
110   TFIN9-1) 105,105,110
26    CP=-A1*SV*TR  *((DVT1/V1)**2)/(1.+A2*DVP1*SV/(V1**2))
      SV2=SQRTF(ABSF(SV))
      GO TO 106
105   CP=CP1(I)
      SV=-CP*(V1**2)/(A2*CP*DVP1+A1*TR*(DVT1**2))
106   SV2=SQRTF(ABSF(SV))
      Z=P1(J)*V1/(R*TB)
      RV=(R*TB/P1(J))-V1
      XJT=A3*TB*DVT1-V1)/CP
      CPCV=-A3*TR*(DVT1**2)/DVP1
      CV=CP-CPCV
      GAMMA=CP/CV
      TFIMB-1) II1,II2,II1
112   PUNCH 82,P1(J),V1,H(I),S(I),CP
      PUNCH 83,P1(J),Z,RV,FUC(I),XJT
      PUNCH 84, P1(J),CV,CPCV,GAMMA,SV2
111   PRINT 82,P1(J),V1,H(I),S(I),CP
      TF(K3-1) 200,205,200
205   P1(J)=P8
      RETURN
200   J8=J+1
      TF(J-N1) 30,30,52
79    FORMAT(11R1, 8X 29H THERMODYNAMIC PROPERTIES OF  4A6)
80    FORMAT(1H0,10X12HTEMPERATURE FR.,1X4A6)
81    FORMAT(1H0,7HH       PRESSURE    VOLUME       ENTHALPY          FN
1TROPY     CP       //10X A6,4X2A6,2X2A6,3X4A6/72X)
82    FORMAT(1F14,3,3E15.5,F11.5)
83    FORMAT(F14.3,F11.5,E18.6,2F11.5)
84    FORMAT(F14.3,2F12.6,F12.5,F12.4)
C     ORDER OF PUNCH IS P,V,H,S,CP FOLLOWED BY P,Z,RV,F/P,J-T COEFF.
C     FOLLOWED BY P,CV,CP-CV,CP/CV, SONIC VELOCITY.
52    RETURN
      END
      SUBROUTINE CURFT (Y1,X1,C1,C2,C3,C4,C5,C6,S1,N1)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
1,CV6,FUC,H,R0,T,J,JH,J9,N1,N7,N4,N9,PLA,P0,P1,P2,P3,R,S,SA,T,TA,T1
2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
275),P1(75),P2(75),P3(75),S(75),T1(75),WORD2(12),XLFUC(75)
      DIMENSION AP(6,7),A(6,7),Y(75),X1(75),B(6),C(6),RAT(6),RFS(6),DC(6)
      DIMENSION  Y1(75),X1(75)
      DO 2 I2=1,N1
      X1(I2)=X1(I2)
2     Y(I2)=Y1(I2)

      S2=S1
      DO 10 J2=1,6
      DO 12 K=1,7
12    A(J2,K)=0.0
10    CONTINUE
      DO24 J2=1,6
      DO 22 K=1,6
      DO 20 I2=1,N1
20    A(J2,K)=A(J2,K)+TX(I2)/S2)**(J2+K-2)
22    CONTINUE
      DO 26 I2=1,N1
      A(J2,7)=A(J2,7)+Y(I2)*((X(I2)/S2)**(J2-1))
26    B(J2)=A(J2,7)
24    CONTINUE
      DO 28 J2=1,6
28    AP(J2,1)=A(J2,1)
      DO 30 K=2,7
30    AP(1,K)=A(1,K)/A(1,1)
      DO 34 J2=2,6
      DO 32K=2,6
      SUM=0.0
      IF(J2-K) 38,36,36
36    K1=K-1
      DO 37 L=1,K1
37    SUM=SUM+AP(J2,L)*AP(L,K)
      AP(J2,K)=A(J2,K)-SUM
      GO TO 40
38    J3=J2-1
      DO 39 L=1,J3
39    SUM=SUM+AP(J2,L)*AP(L,K)
      AP (J2,K)=(A(J2,K)-SUM)/AP(J2,J2)
40    CONTINUE
32    CONTINUE
34    CONTINUE
      DO 136 J2=2,6
      J3=J2-1
      SUM=0.
      DO 140 L=1,J3
140   SUM=SUM+AP(J2,L)*AP(L,7)
136   AP(J2,7)=(A(J2,7)-SUM)/AP(J2,J2)
      N7=0
      DO 42 K=1,6
      C(K)=0.
42    C(6)=AP(6,7)
      DO 50 K=1,5
      MK=6-K
      DO 48 J2=1,6
      C(MK)=C(MK)+C(J2)*AP(MK,J2)
48    C(MK)=AP(MK,7)-C(MK)
      DO 52 J2=1,6
51    RES(J2)=B(J2)-C(1)*A(J2,1)-C(2)*A(J2,2)-C(3)*A(J2,3)-C(4)*A(J2,4)-
1C(5)*A(J2,5)-C(6)*A(J2,6)
      RAT(J2)=ARSF(RFS(J2)/A(J2,7))
      IF (RAT(J2)-0.1E-08) 55,60,60
55    CONTINUE
52    CONTINUE
53    C1=C(1)
      C2=C(2)/S2
      C3=C(3)/(S2**2)
      C4=C(4)/(S2**3)
```

```fortran
      C5=C(5)/(52**4)
      C8=C(8)/(52**5)
      RETURN
   60 DO 62 J2=1,6
D     A(J2,7)=RES(J2)
D62   AP(J2,7)=0.0
D     AP(1,7)=RES(1)/AP(1,1)
D     DO 66 J2=2,6
      J3=J2-1
      DO 64 L=1,J3
D64   AP(J2,7)=AP(J2,L)*AP(L,7)+AP(J2,7)
D66   AP(J2,7)=A(J2,7)-AP(J2,7)
      DO 68 K=1,6
D68   DC(K)=0.0
D     DC(6)=AP(6,7)
      DO 70 K=1,5
      MK=6-K
D     DO 89 J2=1,6
D69   DC(MK)=DC(MK)+DC(J2)*AP(MK,J2)
D70   DC(MK)=AP(MK,7)-DC(MK)
      DO 72 K=1,6
D72   C(K)=C(K)+DC(K)
      N7=N7+1
      IF(N7-10) 51,51,53
      END

      SUBROUTINE INTDVP(P7,DVP1,J1)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     2 75),P1(75),P2(75),P3(75),T(75),T1(75),WORD2(12),XLFUC(75)
      PRVLF(P,T,CV1,CV2,CV3,CV4,CV5,CV6)=P*(CV1+CV2*T+CV3*(T**2)+CV4*(T*
     1*3)+CV5*T*(T**3)+CV6*(T**2))/(T**3))
      CALL BRKT(P7,P2,N2,J1)
   28 IF (P7-P2(2)) 30,30,32
   30 J1=3
   32 IF (P7-P2(N2-2)) 40,36,34
   34 J1=N2-2
   40 CALL DLGCFT(P7,P2,DCL1,DCL2,DCL3,DCL4,DCL5,J1)
      DVP1=(DCL1*PRVLF(P2(J1-2),T(1),CV1(J1-2),CV2(J1-2),CV3(J1-2),CV4(J
     1-2),CV5(J1-2),CV6(J1-2))+DCL2* PRVLF(P2(J1-1),T(1),CV1(J1-1),CV2(
     2J1-1),CV3(J1-1),CV4(J1-1),CV5(J1-1),CV6(J1-1)+DCL3* PRVLF(P2(J1),
     3J1-1),CV3(J1),CV4(J1),CV5(J1),CV6(J1-1))+DCL4* PRVLF(
     4T(1),CV1(J1),T(1),CV1(J1),CV3(J1),CV4(J1),CV5(J1))+DCL4* PRVLF(
     5P2(J1+1),T(1),CV1(J1+1),CV4(J1+1),CV4(J1+1),CV5(J1+1),CV
     66(J1+1))+DCL5* PRVLF(P2(J1+2),T(1),CV1(J1+2),CV2(J1+2),CV3(J1+2),C
     7V4(J1+2),CV5(J1+2),CV6(J1+2)))/P7
      RETURN
      END

      SUBROUTINE INTRP1 (P7,V1,DVT1,DVT2,J1)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC,M8,WORD1
      DIMENSION WORD1(12)
      DIMENSION CP1(75),CS1(75),CS2(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     2 75),P1(75),P2(75),P3(75),T(75),T1(75),WORD2(12),XLFUC(75)
      PRVLF(P,T,CV1,CV2,CV3,CV4,CV5,CV6)=P*(CV1+CV2*T+CV3*(T**2)+CV4*(T*
```

```fortran
     1*3)+CV5*T*(T**3)+CV6*(T**2)+(T**3)}
      DRVLF(P,T,CV1,CV2,CV3,CV4,CV5,CV6)=P*(CV2+2.*CV3*T+3.*CV4*(T**2)+
     14.*CV5*(T**3)+5.*CV6*T*(T**3))
      DPRVF(P,T,CV3,CV4,CV5,CV6 )=P*(2.*CV3+6.*CV4*T+12.*CV5*T*T+20.*CV
     16*(T**3))
      CALL BRKT(P7,P2,N2,J1)
      IF (P7-P2(J1)) 38,60,41
   38 IF(P7-P2(N2-2)) 32,60,41
   41 J1=N2-2
      GO TO 42
   32 IF (P7-P2(2)) 36,60,42
   36 J1=3
   42 CALL LGCFT(P7,P2,CL1,CL2,CL3,CL4,CL5,J1)
      V1=(CL1*PRVLF(P2(J1-2),T(1),CV1(J1-2),CV2(J1-2),CV3(J1-2),CV4(J1-2
     1),CV5(J1-2),CV6(J1-2))+CL2*PRVLF(P2(J1-1),T(1),CV1(J1-1),CV2(J1-1)
     2,CV3(J1-1),CV4(J1-1),CV5(J1-1),CV6(J1-1))+CL3*PRVLF(P2(J1),T(1),CV
     3T(J1),CV2(J1),CV3(J1),CV4(J1),CV5(J1),CV6(J1))+CL4*PRVLF(P2(J1+1),
     4T(1),CV1(J1+1),CV3(J1+1),CV4(J1+1),CV5(J1+1),CV6(J1+1)+
     5CL5*PRVLF(P2(J1+2),T(1),CV1(J1+2),CV2(J1+2),CV3(J1+2),CV4(J1+2),CV
     65(J1+2),CV6(J1+2)))/P7
   30 DVT1=(CL1*DPRVLF(P2(J1-2),T(1),CV1(J1-2),CV2(J1-2),CV3(J1-2),CV4(J
     11-2),CV5(J1-2),CV6(J1-2))+CL2*DPRVLF(P2(J1-1),T(1),CV1(J1-1),CV2(J
     21-1),CV3(J1-1),CV4(J1-1),CV5(J1-1),CV6(J1-1))+CL3*DPRVLF(P2(J1),T(
     31),CV3(J1-1),CV4(J1),CV5(J1),CV6(J1))+CL4*DPRVLF(P2
     4J1+1),T(1),CV1(J1+1),CV2(J1+1),CV3(J1+1),CV4(J1+1),CV5(J1+1),CV6(J
     51+1))+CL5*DPRVLF(P2(J1+2),T(1),CV1(J1+2),CV3(J1+2),CV4(J1+2),CV4(J
     61+2),CV5(J1+2),CV6(J1+2)))/P7
   40 DVT2=(CL1*D2PRVLF(P2(J1-2),T(1),CV3(J1-2),CV4(J1-2),CV5(J1-2),CV6(J
     11-2))+CL2*D2PRVLF(P2(J1-1),T(1),CV3(J1-1),CV4(J1-1),CV5(J1-1),CV6(J
     21-1))+CL3*D2PRVLF(P2(J1),T(1),CV3(J1),CV4(J1),CV5(J1))+CL4*
     3D2PRVLF(P2(J1+1),T(1),CV4(J1+1),CV4(J1+2),CV5(J1+1),CV6(J1+1))+CL5*
     4D2PRVLF(P2(J1+2),T(1),CV4(J1+2),CV4(J1+2),CV5(J1+2),CV6(J1+2)))/P7
      RETURN
   60 V1=PRVLF(P2(J1),T(1),CV1(J1),CV1(J1),CV2(J1),CV3(J1),CV4(J1),CV5(J1),CV6(J
     11))/P2(J1)
      DVT1=DPRVLF(P2(J1),T(1),CV1(J1),CV2(J1),CV3(J1),CV4(J1),CV5(J1),CV
     16(J1))/P2(J1)
      DVT2=D2PRVLF(P2(J1),T(1),CV3(J1),CV4(J1),CV5(J1),CV6(J1))/P2(J1)
   70 RETURN
      END

      SUBROUTINE INTRP2 (P7,SV,J4)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,P0,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),PLA(
     2 75),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
      SNCF(T,CS1,CS2,CS3,CS4,CS5,CS6)=CS1+CS2*T+CS3*(T**2)+CS4*(T**3)+CS
     15*T*(T**3)+CS6*(T**2)+(T**3)
      CALL BRKT(P7,P3,N9,J4)
   30 IF(P7-P3(N9-2)) 32,60,36
   36 J4=N9-2
      GO TO 40
   32 IF(P7-P3(2)) 38,60,40
   38 J4=3
   40 CALL LGCFT(P7,P3,CL1,CL2,CL3,CL4,CL5,J4)
      SV=CL1*SNCF(T(1),CS1(J4-2),CS2(J4-2),CS3(J4-2),CS4(J4-2),CS5(J4-2)
     1,CS6(J4-2))+CL2*SNCF(T(1),CS1(J4-1),CS2(J4-1),CS3(J4-1),CS4(J4-1),
     2CS5(J4-1),CS6(J4-1),CS1(J4),CS2(J4),CS3(J4),CS4(J4)
```

```
     3,CS5(J4),CS6(J4))+CL4*SNCF(T(I),CS1(J4+1),CS2(J4+1),CS3(J4+1),CS4(
     4J4+1),CS5(J4+1),CS6(J4+1))+CL5*SNCF(T(I),CS1(J4+2),CS2(J4+2),CS3(J
     5+2),CS4(J4+2),CS5(J4+2),CS6(J4+2))
      RETURN
60    SV=SNCF(T(I),CS1(J4),CS2(J4),CS3(J4),CS4(J4),CS5(J4),CS6(J4))
70    RETURN
      END

      SUBROUTINE INTRP3 (TA,CP)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,PO,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
10    IF (TA-T(2)) 8,12,16
8     I1=3
      GO TO 21
16    IF (TA-T(N3-2)) 20,12,22
22    I1=N3-2
      GO TO 21
20    I1=I
21    CALL LGCFT(TA,T,CL1,CL2,CL3,CL4,CL5,I1)
      CP=CL1*CP1(I1-2)+CL2*CP1(I1-1)+CL3*CP1(I1)+CL4*CP1(I1+1)+CL5*CP1(I1
     1+2)
12    CP=CP1(I1)
14    RETURN
      END

      SUBROUTINE BRKT(Y,X,N10,J7)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,PO,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
      DIMENSION X(75)
      J7=1
20    IF(Y-X(J7))60,60,100
100   J7=J7+1
      IF(J7-N10)20,20,40
40    J7=N10
60    RETURN
      END

      SUBROUTINE LGCFT(PA,P2,CL1,CL2,CL3,CL4,CL5,J1)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,PO,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
10    CL1=(PA-P2(J1))*(PA-P2(J1-1))*(PA-P2(J1+1))*(PA-P2(J1+2))/((P2
     1(J1-2)-P2(J1))*(P2(J1-2)-P2(J1-1))*(P2(J1-2)-P2(J1+1))*(P2(J1-2)-P
     222(J1+2)))
20    CL2=(PA-P2(J1-2))*(PA-P2(J1))*(PA-P2(J1+1))*(PA-P2(J1+2))/((P2
     1(J1-1)-P2(J1-2))*(P2(J1-1)-P2(J1))*(P2(J1-1)-P2(J1+1))*(P2(J1-1)-P
     222(J1+2)))
30    CL3=(PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1+1))*(PA-P2(J1+2))/((
     1P2(J1)-P2(J1-2))*(P2(J1)-P2(J1-1))*(P2(J1)-P2(J1+1))*(P2(J1)-P2(J1
```

```
     2+2)))
40    CL4=(PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1))*(PA-P2(J1+2))/((P2
     1(J1+1)-P2(J1-2))*(P2(J1+1)-P2(J1-1))*(P2(J1+1)-P2(J1))*(P2(J1+1)-P
     22(J1+2)))
50    CL5=(PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1))*(PA-P2(J1+1))/((P2
     1(J1+2)-P2(J1-2))*(P2(J1+2)-P2(J1-1))*(P2(J1+2)-P2(J1))*(P2(J1+2)-P
     22(J1+1)))
      RETURN
      END

      SUBROUTINE DLGCFT(PA,P2,DCL1,DCL2,DCL3,DCL4,DCL5,J1)
      COMMON A1,A2,A3,A4,CP1,CS1,CS2,CS3,CS4,CS5,CS6,CV1,CV2,CV3,CV4,CV5
     1,CV6,FUC,H,HO,I,J,J8,J9,N1,N2,N3,N9,PLA,PO,P1,P2,P3,R,S,SO,T,TO,T1
     2,WORD2,XLFUC
      DIMENSION CP1(75),CS1(75),CS2(75),CS3(75),CS4(75),CS5(75),CS6(75),
     1CV1(75),CV2(75),CV3(75),CV4(75),CV5(75),CV6(75),FUC(75),H(75),PLA(
     275),P1(75),P2(75),P3(75),S(75),T(75),T1(75),WORD2(12),XLFUC(75)
10    DCL1=((PA-P2(J1-1))*(PA-P2(J1))*(PA-P2(J1+1))+(PA-P2(J1))*(PA-
     1P2(J1-1))+(PA-P2(J1+2))*(PA-P2(J1))+(PA-P2(J1-1))*(PA-P2(J1+2))+(P
     2A-P2(J1-1))*(PA-P2(J1+1))+(PA-P2(J1+2)))/((P2(J1-2)-P2(J1-1))*(P2(
     3J1-2)-P2(J1))*(P2(J1-2)-P2(J1+1))*(P2(J1-2)-P2(J1+2)))
20    DCL2=((PA-P2(J1))*(PA-P2(J1+1))+(PA-P2(J1-2))+(PA-P2(J1+2))*(PA
     1-P2(J1+1))*(PA-P2(J1+2))+(PA-P2(J1-2))*(PA-P2(J1+1))*(PA-P2(J1+2))+(
     2PA-P2(J1+1))*(PA-P2(J1-2))*(P2(J1-1)-P2(J1-2))/((P2(J1-1)-P2(J1))*(P2
     3(J1-1)-P2(J1+1))*(P2(J1-1)-P2(J1+2)))
30    DCL3=((PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1+1))*(PA-P2(J1-2))*
     1(PA-P2(J1-1))*(PA-P2(J1+2))*(PA-P2(J1+1))*(PA-P2(J1+2))*(PA-P2(J1+
     22))*(PA-P2(J1-1))+(P2(J1)-P2(J1-2))/((P2(J1)-P2(J1-1))*(P2(J1)-P2(J1-2))*
     3(P2(J1)-P2(J1-1))+(P2(J1)-P2(J1+1))*(P2(J1)-P2(J1+2)))
40    DCL4=((PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1))+(PA-P2(J1+2))*(P
     1A-P2(J1-1))*(PA-P2(J1+2))+(PA-P2(J1))*(PA-P2(J1-2))*(PA-P2(J1+2))+(
     2PA-P2(J1-1))*(PA-P2(J1+2))/((P2(J1+1)-P2(J1-2))*(P2(J1+1)-P2(J1-1))*(
     3J1+1)-P2(J1-1))*(P2(J1+1)-P2(J1))*(P2(J1+1)-P2(J1+2)))
50    DCL5=((PA-P2(J1-2))*(PA-P2(J1-1))*(PA-P2(J1))+(PA-P2(J1-2))*(PA
     1-P2(J1-1))*(PA-P2(J1+1))*(PA-P2(J1))*(PA-P2(J1+1))+(PA-P2(J1-1))+(
     2PA-P2(J1-1))*(PA-P2(J1))*(PA-P2(J1+1))/((P2(J1+2)-P2(J1-2))*(P2(J1
     3+2)-P2(J1-1))*(P2(J1+2)-P2(J1))*(P2(J1+2)-P2(J1+1)))
      RETURN
      END
```

Appendix C

Thermodynamic Properties of Ethane

1. Introduction

The calculation of the thermodynamic properties of ethane is discussed separately in this section for a number of reasons. First, it provides a sample calculation in the sense that it will show in detail how to prepare input for the computor program. The results presented will also tend to confirm and reinforce the conclusions drawn based on the results for nitrogen. Also, it will emphasize the fact that the computor program is general, and can be applied to the calculation of the thermodynamic properties of any gas. In addition, a more complete listing of computor output will be presented, and it will be seen that the computor output is a full thermodynamic network, requiring no further calculations.

The volumetric data for the calculations are taken from Tester (81). The results are compared with the results of Tester (81) and Rossini (73). Tester (81) used the volumetric data to calculate the residual volume as a function of pressure and temperature. The values of residual volume were plotted on a large scale graph and smoothed. Using smoothed values of the residual volume, the free energy was calculated

as a function of pressure at constant temperature. Then, the entropy was calculated as a function of pressure by differentiating the free energy with respect to temperature at constant pressure. Finally, the enthalpy is calculated from the free energy and entropy.

Rossini (73) used a volume residual which was the difference between the actual gas volume and the volume calculated by the Benedict-Webb Rubin equation of state for ethane (8). These calculated residuals are subsequently smoothed and isothermal changes in the thermodynamic properties are calculated from them.

In comparing the results among Tester's tabulation and Rossini's tabulation and the present work, all values have been adjusted to agree for the vapor at one atmosphere and the normal boiling point, 184.52°K. At these conditions, the entropy is 49.49 cal/gmol-$^{\circ}$K, and the enthalpy is 6386.5 cal/gmol, for the vapor.

2. Input

The input is shown in Table XIV.C.1 exactly as it would be used for the actual calculation. Some of the volumetric data have been omitted to conserve space. Each printed line represents a punched data card.

The first line contains the name of the gas and any other identifying information which will be printed with the output. The second line contains the units that will be

TABLE XIV.C.1

ETHANE   INPUT DATA FOR COMPUTOR PROGRAM
DEG K ATM   CC/GMOL   CAL/GMOL   CAL/GMOL-K CAL/GMOL-K M/SEC
     30.0680
21111111
018   1.00   2.00   3.00   4.00   5.00   6.00   7.00   8.00
      9.00   10.00   15.00   20.00   25.00   30.00   35.00   40.00   45.00
     50.00
033 184.52 190.00 200.00 210.00 220.00 230.00 240.00 250.00
     260.00 270.00 280.00 290.00 300.00 310.00 320.00 330.00 340.00
     350.00 360.00 370.00 380.00 390.00 400.00 410.00 420.00 430.00
     440.00 450.00 460.00 470.00 480.00 490.00 500.00
00180001
0033   001.0000032   002.0000031   003.0000030   004.0000029   005.000
0029   006.0000028   007.0000028   008.0000028   009.0000027   010.000
0026   015.0000025   020.0000023   025.0000023   030.0000022   035.000
0022   040.0000021   045.0000020   050.000
         0.147300+05   0.184520+03   0.151500+05   0.190000+03
         0.159910+05   0.200000+03   0.168450+05   0.210000+03
         0.176960+05   0.220000+03   0.185450+05   0.230000+03
         0.193920+05   0.240000+03   0.202370+05   0.250000+03
         0.210800+05   0.260000+03   0.219200+05   0.270000+03
         0.227580+05   0.280000+03   0.235950+05   0.290000+03
         0.244300+05   0.300000+03   0.252640+05   0.310000+03
         0.277590+05   0.340000+03   0.285880+05   0.350000+03
         0.310730+05   0.380000+03   0.319000+05   0.390000+03
         0.343780+05   0.420000+03   0.352030+05   0.430000+03
         0.376790+05   0.460000+03   0.385030+05   0.470000+03
         0.409760+05   0.500000+03
0033
         0.998000+01   0.184520+03   0.100800+02   0.190000+03
         0.102900+02   0.200000+03   0.105000+02   0.210000+03
         0.107200+02   0.220000+03   0.109400+02   0.230000+03
         0.111700+02   0.240000+03   0.114100+02   0.250000+03
         0.116600+02   0.260000+03   0.119200+02   0.270000+03
         0.121900+02   0.280000+03   0.124700+02   0.290000+03
         0.127500+02   0.300000+03   0.130400+02   0.310000+03
         0.139100+02   0.340000+03   0.142100+02   0.350000+03
         0.151100+02   0.380000+03   0.154100+02   0.390000+03
         0.157200+02   0.400000+03   0.160200+02   0.410000+03
         0.163200+02   0.420000+03   0.166200+02   0.430000+03
         0.175000+02   0.460000+03   0.177900+02   0.470000+03
         0.186600+02   0.500000+03
         0.638650+04   0.494900+02
    50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00
    50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00
    50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00   50.00
    50.00   50.00   50.00   50.00   50.00   50.00
0014
         0.100000+01   0.184520+03   0.133000+01   0.190000+03
         0.214620+01   0.200000+03   0.329700+01   0.210000+03
         0.485800+01   0.220000+03   0.691200+01   0.230000+03
         0.955100+01   0.240000+03   0.128500+02   0.250000+03
         0.169100+02   0.260000+03   0.218000+02   0.270000+03
         0.276500+02   0.280000+03   0.346500+02   0.290000+03
         0.430900+02   0.300000+03   0.485000+02   0.305500+03

used for temperature, pressure, volume, entropy, heat capacity and sonic velocity. These units are the same for the input as for the output. The next line contains the molecular weight of the gas. The following line contains eight control constants, each is an integer which may have the value 0, 1, or 2. The control constants specify the proper conversion factors to be used, depending on the units employed. Taken in order, the constants specify the following information: the volume is in cubic centimeters, the pressure is in atmospheres, the temperature is in degrees Kelvin, the unit of mass is the gram, the sonic velocity is in meters per second, the unit of thermal energy is the calorie and the basis for mass is the gram-mole, rather than the gram. The eighth constant refers to the printout. In this case it indicates that the optional output is desired and all values will be punched out.

The first number on the next line, or data card, is the number of pressures at which results will be printed out on the thermodynamic network. The next eight numbers on the same line indicate the values of these printout pressures. Additional pressures are punched nine to a card, and as many cards as required are used. This accounts for the next two lines.

The first number on the next line (033) indicates the number of temperatures at which results will be printed on the thermodynamic network. The following numbers specify the values of the temperatures, using as many cards as

required. Following the temperatures, the next card contains
two numbers, 18 and 1. The first number (0018) indicates
the number of measured pressures at which volumetric isobars
are input to the computor. The next number (0001) indicates
that heat capacity data will be input to the program. If
the second number has some value other than 0001, then it
indicates the number of sonic velocity isobars which will
be input to take the place of the heat capacity data. Of
the cards following, each contains five pairs of numbers.
The first number (0033 in this case) indicates the number of
volume-temperature data points on the isobar. The pressure
of the measured isobar is specified by the next number (1.000
in this case). This pair of points is repeated on as many
cards as required, there being 18 pairs on 4 cards in this
case.

Following this information, the volumetric data is
tabulated. There are two pairs of volume-temperature points
per card. As many cards as are required are used for each
isobar. Only some of the data for the one atmosphere isobar
is duplicated here. There are 33 points, contained on 17
cards, the last card having only one pair of points. The
data for the next isobar would start on a new line or card.

In this case, the heat capacity data is input after
the volumetric data. The number on the next card indicates
that there are 33 heat capacity data points, together with
the corresponding temperatures. It is assumed that the

pressure at which the heat capacity data is given is the same as the reference pressure, one atmosphere in this instance. Some of the heat capacity data follow, there being two heat capacities and temperatures on each card, using as many cards as required.

After the heat capacity data, the next line contains the values of enthalpy and entropy at the reference pressure and temperature. The following cards contain the highest pressure for each temperature that will be printed out. In this case there are 33 temperatures, and at each temperature, the highest pressure is 50 atmospheres. For temperatures below the critical temperature, the highest pressure will be the vapor pressure. However, these will be calculated during the operation of the program and are substituted, where applicable, for the pressure which were originally input.

The next card indicates that there are 14 vapor pressure data points in the input. The following cards contain the vapor pressure data, two vapor pressures with corresponding temperatures per card.

When it is desired to calculate another thermodynamic network, the input data for the next job follow the last vapor pressure card. If there are no more data cards, the job ends after the calculations are completed.

3. Output

The output for ethane is shown in Table XIV.C.2

and XIV.C.3 exactly as would come off the computor output
punched cards. After the output cards are received, they
are collated, and some punched cards containing titles are
added to the deck. The deck is put through an IBM accounting
machine which prints the contents of the punched cards on
paper.

Table XIV.C.2 contains the vapor pressure output.
The first line identifies the output as the vapor pressure
of ethane. The next line gives the units used for pressure
and temperature, and indicates that the logarithm is to the
base ten. The third line of output prints out the form of
the vapor pressure equation for convenience. This corres-
ponds to Equation (V.57). The next output lists the six
coefficients of the vapor pressure equation. Then the tem-
peratures corresponding to evenly spaced values of the vapor
pressure are tabulated. Finally, the vapor pressure is tab-
ulated at evenly spaced values of the vapor pressure.

Table XIV.C.3 lists the thermodynamic properties of
ethane. Only a few temperatures are shown. The complete
tabulation would include every temperature from $190^{o}K$ to
$500^{o}K$ at intervals of $10^{o}K$. At temperatures less than the
critical temperature, the tabulation extends up to the vapor
pressure. Thus, the properties of the vapor on the satura-
tion curve are included with the thermodynamic properties
of the superheated vapor. Above the critical temperature,
the tabulation has been ended at a pressure of 50 atmos-
pheres.

TABLE XIV.C.2

VAPOR PRESSURE OF ETHANE

VAPOR PRESSURE EQUATION, LOG BASE 10. T =DEG K , P = ATM

LOG(P) = A/T + B + CT + DTT + ETTT + FTTTT
COEFFICIENTS ARE

-.263721E 04
.435288E 02
-.333455E 00
.141872E-02
-.302562E-05
.258519E-08

VAPOR PRESSURE	TEMPERATURE
1.00	184.530
2.00	198.450
3.00	207.721
4.00	214.876
5.00	220.788
6.00	225.873
7.00	230.364
8.00	234.405
9.00	238.090
10.00	241.489
15.00	255.542
20.00	266.538
25.00	275.689
30.00	283.556
35.00	290.449
40.00	296.559
45.00	302.016

TEMPERATURE	VAPOR PRESSURE
184.52	.9995
190.00	1.3311
200.00	2.1463
210.00	3.2952
220.00	4.8569
230.00	6.9146
240.00	9.5523
250.00	12.8536
260.00	16.9034
270.00	21.7960
280.00	27.6532
290.00	34.6546
300.00	43.0883

TABLE XIV.C.3 B

THERMODYNAMIC PROPERTIES OF ETHANE

TEMPERATURE 250.0 DEG K

PRESSURE ATM	VOLUME CC/GMOL	ENTHALPY CAL/GMOL	ENTROPY CAL/GMOL-K	CP CAL/GMOL-K
1.000	.20231E 05	.70850E 04	.52719E 02	11.41652
2.000	.99750E 04	.70633E 04	.51283E 02	11.56172
3.000	.65936E 04	.70417E 04	.50418E 02	11.69852
4.000	.48402E 04	.70183E 04	.49781E 02	11.94304
5.000	.38094E 04	.69977E 04	.49260E 02	12.36830
6.000	.31189E 04	.69699E 04	.48815E 02	12.79198
7.000	.26262E 04	.69331E 04	.48415E 02	13.48421
8.000	.22580E 04	.69036E 04	.48061E 02	14.02671
9.000	.19692E 04	.68758E 04	.47746E 02	14.37290
10.000	.17346E 04	.68469E 04	.47451E 02	14.75534
12.854	.12303E 04	.67382E 04	.46612E 02	16.70307

PRESSURE ATM	COMP FACTOR	RESIDUAL VOLUME CC/GM-MOLE	FUGACITY COFF	J-T COFF K/ATM
1.000	.98636	.279821E 03	1.00000	1.86118
2.000	.97264	.280611E 03	.98644	1.85822
3.000	.95854	.283446E 03	.97298	1.89726
4.000	.94392	.287589E 03	.95953	2.07686
5.000	.92861	.292840E 03	.94606	2.24596
6.000	.91236	.299599E 03	.93249	2.22866
7.000	.89627	.303948E 03	.91886	2.36272
8.000	.88069	.305889E 03	.90530	1.96715
9.000	.86405	.309826E 03	.89183	1.96824
10.000	.84570	.316491E 03	.87832	2.01623
12.854	.77098	.365456E 03	.83769	2.80362

PRESSURE ATM	CV CAL/GMOL-K	CP-CV CAL/GMOL-K	CP/CV	SONIC VELOCITY M/SEC
1.000	9.313046	2.103574	1.22587	293.6374
2.000	9.334615	2.227103	1.23859	290.9843
3.000	9.331155	2.367360	1.25370	288.3462
4.000	9.354470	2.588569	1.27672	286.2436
5.000	9.491092	2.877210	1.30315	283.9069
6.000	9.686090	3.105890	1.32065	280.4880
7.000	9.911933	3.572275	1.32747	278.1766
8.000	10.566478	3.460236	1.34524	271.7274
9.000	10.684746	3.688653	1.36964	266.7110
10.000	10.773164	3.982176		260.7923
12.854	9.769885	6.933185	1.70965	255.3429

TABLE XIV.C.3A

THERMODYNAMIC PROPERTIES OF ETHANE

TEMPERATURE 230.0 DEG K

PRESSURE ATM	VOLUME CC/GMOL	ENTHALPY CAL/GMOL	ENTROPY CAL/GMOL-K	CP CAL/GMOL-K
1.000	.18541E 05	.68615E 04	.51787E 02	10.93774
2.000	.91014E 04	.68369E 04	.50339E 02	11.08336
3.000	.59502E 04	.68125E 04	.49463E 02	11.21677
4.000	.43583E 04	.67836E 04	.48803E 02	11.53199
5.000	.33944E 04	.67467E 04	.48238E 02	12.14379
6.000	.27574E 04	.67089E 04	.47752E 02	12.72323
6.915	.23113E 04	.66646E 04	.47317E 02	13.73026

PRESSURE ATM	COMP FACTOR	RESIDUAL VOLUME CC/GM-MOLE	FUGACITY COFF	J-T COEF K/ATM
1.000	.98254	.329426E 03	1.00000	2.01805
2.000	.96462	.333794E 03	.98245	2.18362
3.000	.94595	.339049E 03	.96514	2.28896
4.000	.92385	.359227E 03	.94745	2.83364
5.000	.89941	.379638E 03	.92900	3.23639
6.000	.87675	.387619E 03	.91045	3.11211
6.915	.84692	.417757E 03	.89266	3.85958

PRESSURE ATM	CV CAL/GMOL-K	CP-CV CAL/GMOL-K	CP/CV	SONIC VELOCITY M/SEC
1.000	8.831346	2.106393	1.23851	281.7208
2.000	8.806391	2.276965	1.25856	279.1247
3.000	8.766055	2.450713	1.27957	275.0338
4.000	8.677592	2.854402	1.32894	272.1266
5.000	8.682675	3.461117	1.39862	272.3559
6.000	9.033227	3.690005	1.40849	261.8549
6.915	8.324683	5.405578	1.64934	280.6180

TABLE XIV.C.3C

THERMODYNAMIC PROPERTIES OF ETHANE

TEMPERATURE 320.0 DEG K

PRESSURE ATM	VOLUME CC/GMOL	ENTHALPY CAL/GMOL	ENTROPY CAL/GMOL-K	CP CAL/GMOL-K
1.000	.26100E 05	.79490E 04	.55756E 02	13.32021
2.000	.12968E 05	.79362E 04	.54352E 02	13.41979
3.000	.85914E 04	.79233E 04	.53518E 02	13.52181
4.000	.63999E 04	.79105E 04	.52919E 02	13.60337
5.000	.50866E 04	.78981E 04	.52449E 02	13.65904
6.000	.42116E 04	.78859E 04	.52062E 02	13.73886
8.000	.31172E 04	.78574E 04	.51426E 02	13.76354
10.000	.24594E 04	.78302E 04	.50923E 02	13.96025
20.000	.11396E 04	.76941E 04	.49248E 02	15.40472
30.000	.69112E 03	.75212E 04	.48038E 02	17.73215
40.000	.45414E 03	.73077E 04	.46944E 02	21.46542
50.000	.29786E 03	.69061E 04	.45608E 02	37.49046

PRESSURE ATM	COMP FACTOR	RESIDUAL VOLUME CC/GM-MOLE	FUGACITY COEFF	J-T COEFF K/ATM
1.000	.99413	.154029E 03	1.00000	.95384
2.000	.98790	.158881E 03	.99400	.95872
3.000	.98172	.160011E 03	.98799	.95427
4.000	.97507	.163656E 03	.98191	.92966
5.000	.96872	.164252E 03	.97579	.89755
6.000	.96248	.164171E 03	.96971	.92285
8.000	.94986	.164557E 03	.95761	.96840
10.000	.93677	.166014E 03	.94561	.97643
20.000	.86811	.173130E 03	.88701	1.02065
30.000	.78972	.184024E 03	.82876	1.08268
40.000	.69191	.202217E 03	.77046	1.20060
50.000	.56726	.227227E 03	.70980	1.01664

PRESSURE ATM	CV CAL/GMOL-K	CP-CV CAL/GMOL-K	CP/CV	SONIC VELOCITY M/SEC
1.000	11.279575	2.040640	1.18091	328.4778
2.000	11.319311	2.100479	1.18557	327.2186
3.000	11.365120	2.156685	1.18976	325.5673
4.000	11.397106	2.206264	1.19358	323.8434
5.000	11.405589	2.253451	1.19757	322.4876
6.000	11.415497	2.323366	1.20353	321.0242
8.000	11.284912	2.478631	1.21964	318.9617
10.000	11.326925	2.633324	1.23248	316.6187
20.000	11.778597	3.626119	1.30786	299.4103
30.000	12.237704	5.494444	1.44898	283.5975
40.000	12.292731	9.172688	1.74619	258.2953
50.000	16.117573	21.372885	2.32606	242.1062

TABLE XIV.C.3D

THERMODYNAMIC PROPERTIES OF ETHANE

TEMPERATURE 400.0 DEG K

PRESSURE ATM	VOLUME CC/GMOL	ENTHALPY CAL/GMOL	ENTROPY CAL/GMOL-K	CP CAL/GMOL-K
1.000	.32723E 05	.91099E 04	.58984E 02	15.71693
2.000	.16314E 05	.91019E 04	.57593E 02	15.74122
3.000	.10844E 05	.90940E 04	.56774E 02	15.76829
4.000	.81114E 04	.90857E 04	.56188E 02	15.81806
5.000	.64707E 04	.90770E 04	.55728E 02	15.80797
6.000	.53764E 04	.90682E 04	.55350E 02	15.04672
8.000	.40075E 04	.90529E 04	.54750E 02	16.35506
10.000	.31871E 04	.90358E 04	.54275E 02	16.47609
20.000	.15444E 04	.89441E 04	.52727E 02	17.07276
30.000	.99655E 03	.88551E 04	.51758E 02	17.57880
40.000	.72172E 03	.87617E 04	.51012E 02	18.07503
50.000	.55638E 03	.86482E 04	.50347E 02	17.65091

PRESSURE ATM	COMP FACTOR	RESIDUAL VOLUME CC/GM-MOLF	FUGACITY COEF	J-T COEFF K/ATM
1.000	.99711	.947021E 02	1.00000	.49417
2.000	.99424	.944626E 02	.99716	.50390
3.000	.99133	.948514E 02	.99427	.50571
4.000	.98866	.930505E 02	.99143	.54270
5.000	.98585	.928947E 02	.98865	.55197
6.000	.98296	.932144E 02	.98572	.52901
8.000	.97691	.947036E 02	.98122	.51243
10.000	.97115	.946867E 02	.97567	.51459
20.000	.94121	.964754E 02	.94763	.50982
30.000	.91098	.973802E 02	.92013	.51924
40.000	.87965	.987306E 02	.89301	.54805
50.000	.84768	.999784E 02	.86564	.56629

PRESSURE ATM	CV CAL/GMOL-K	CP-CV CAL/GMOL-K	CP/CV	SONIC VELOCITY M/SEC
1.000	13.702893	2.014032	1.14698	363.2364
2.000	13.698862	2.042357	1.14909	362.4268
3.000	13.695580	2.072713	1.15134	361.8187
4.000	13.702406	2.115661	1.15440	361.3528
5.000	13.752191	2.145777	1.15603	350.9304
6.000	13.707671	2.239045	1.16334	365.7824
8.000	14.191420	2.163637	1.15246	350.7790
10.000	14.203204	2.272884	1.16003	353.0649
20.000	14.403282	2.669474	1.18534	348.2157
30.000	14.469143	3.109661	1.21492	340.3095
40.000	14.421476	3.653554	1.25334	329.5569
50.000	12.077059	5.573849	1.46152	395.3668

The first line of the output identifies the table as
being the thermodynamic properties of ethane. The next line
gives the temperature. For each temperature there are three
tables when the complete output is printed out. Otherwise,
the output would consist only of the first table, which gives
the specific volume, enthalpy, entropy, and heat capacity
as a function of pressure.

Below the critical temperature (305.5°K) the tabula-
tion ends at an uneven pressure. At 250°K, for example, the
tabulation ends with a pressure of 12.854 atmospheres. This
indicates that the vapor pressure at 250°K is 12.854 atmos-
pheres, and the properties listed are for the saturated vapor.

4. Results

a. Tabulated Results

The results for ethane have been tabulated for a
few temperatures. A complete network, for temperatures up
to 500°K, would involve about 30 temperatures, if a ten
degree spacing was used. The calculated thermodynamic net-
work has been stopped at 50 atmospheres and 500°K. However,
these limits have been used only for convenience, and the
thermodynamic network could have been extended up to any
pressure and temperature for which input data were available.

A partial tabulation is presented in Table XIV.C.3
for the purposes of illustrating the output, and so that all

of the calculated properties may be examined at a few temperatures.

b. Enthalpy

A pressure-enthalpy diagram is presented in Figure XIV.C.1. For greater clarity, some of the isotherms have been omitted, although the saturation curve is included. In the superheated region, comparisons are made among the results of Tester (81), Rossini (73) and the present work. On the saturation curve, comparison is made between the calculated results of the present work and Tester's results. There is excellent agreement among the three sets of enthalpy values, even with the relatively large scale used in Figure XIV.C.1.

c. Fugacity Coefficient

Some results for the fugacity coefficient, calculated in this work, are compared with the corresponding results of Tester (81) in Figure XIV.C.2. In the present calculation, the calculated fugacity coefficient, as a function of pressure, is correct only if the fugacity coefficient at the reference pressure is unity. If not, then the true fugacity coefficient is obtained by multiplying the calculated fugacity coefficient by the value of the true fugacity coefficient at the reference pressure. This is more fully explained in Section V.
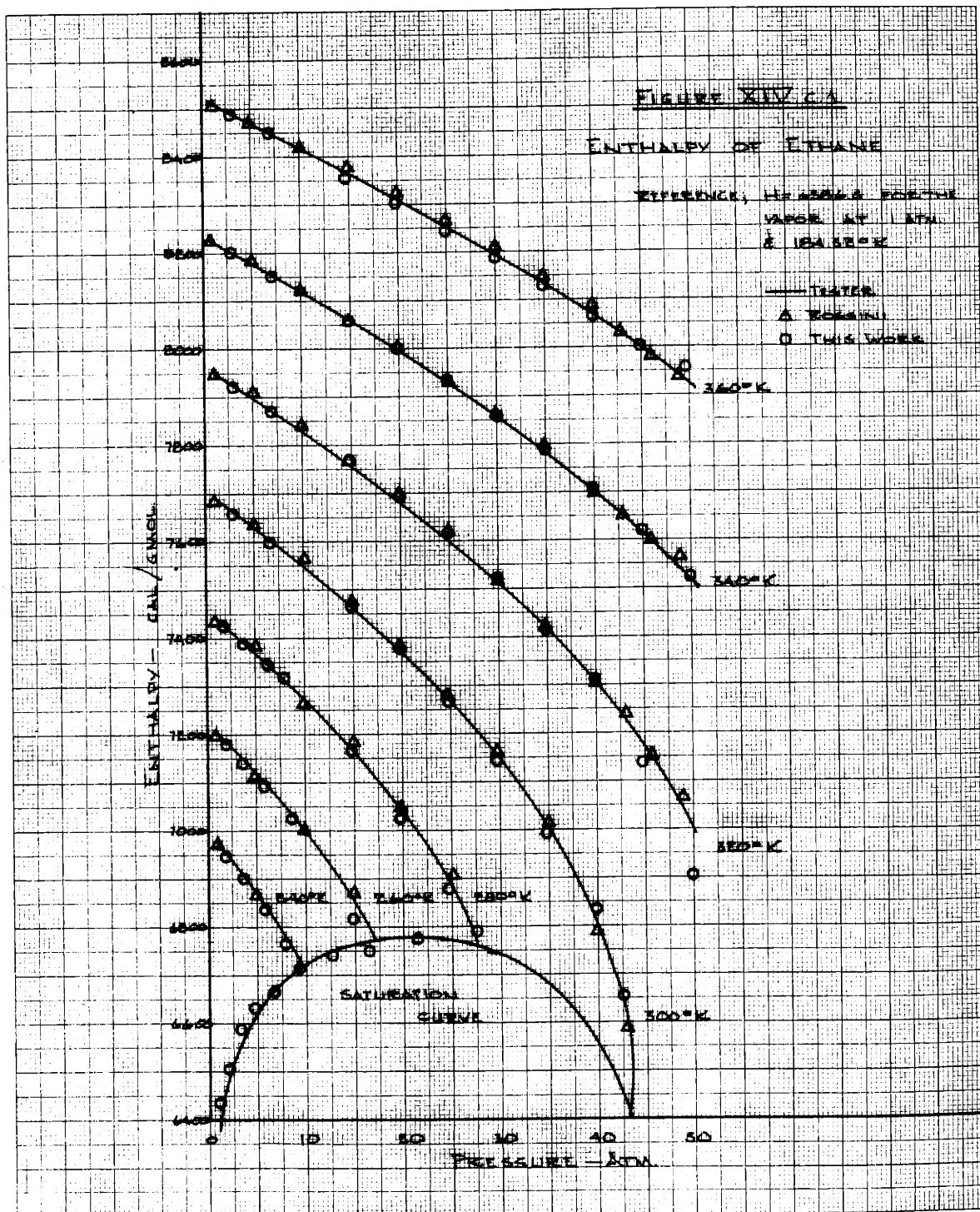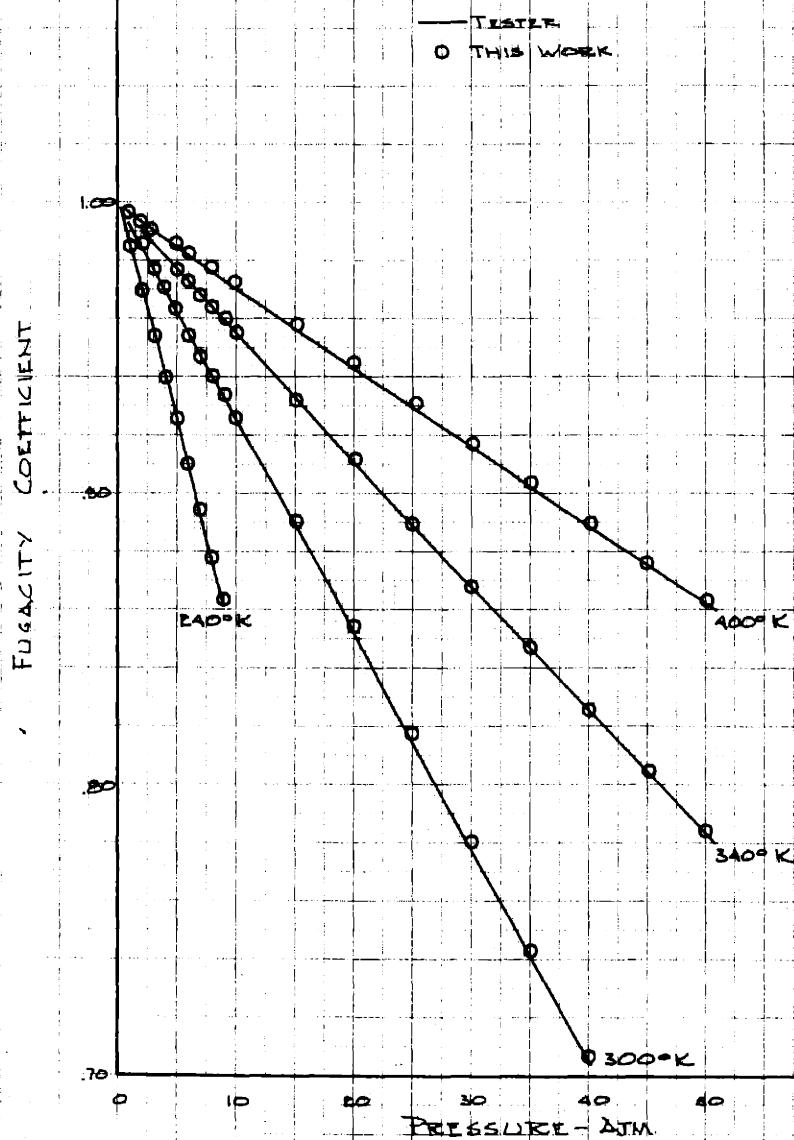
Figure XIV GA

ENTHALPY OF ETHANE

Reference, H = 8900.8 for the vapor at 1 atm & 184.550 K

——— Tester
△ Rossini
□ This Work

FIGURE XIV. C. 2.

FUGACITY COEFFICIENT OF ETHANE

——— TESTER.
O THIS WORK.

FUGACITY COEFFICIENT

PRESSURE — ATM.

In the present calculation for ethane, the reference pressure is one atmosphere. The true fugacity coefficient at one atmosphere was obtained from Tester's results. The fugacity coefficient at other pressures was then calculated by multiplying the calculated values by the true value at one atmosphere. This was done for each temperature shown in Figure XIV.C.2. Thus, at one atmosphere, at each temperature, Tester's values are forced into agreement with the present calculation. At the higher pressures, agreement is not forced, but is seen to be excellent, between the two sets of values.

5. Discussion of Results

The results shown graphically in Figure XIV.C.1 and XIV.C.2 are in excellent agreement. These include the calculated results of this work, Tester's results (81) and Rossini's results (73). For the results calculated in this work and tabulated in Table XIV.C.3, but not compared graphically, the agreement is also excellent.

These results confirm the conclusions obtained by comparing the calculated results for nitrogen with the results of Woolley (90), Din (23) and Miller and Sullivan (57). In general, the thermodynamic properties which are calculated by integrals of the form $\int V dP$ and $\int (\partial V/\partial T)_P dP$ are of high accuracy. These properties include the enthalpy, entropy and fugacity coefficient. For the variation of the constant

pressure heat capacity with pressure, which is calculated from an integral of the form $\int (\partial^2 V/\partial T^2)\, dP$, the accuracy is not quite as good. These results are analagous to the results obtained with nitrogen.

The calculated results for ethane are in slightly better agreement than the results for nitrogen, when both are compared with other thermodynamic networks. This can best be seen in Figure XIV.C.1. On the enthalpy-pressure diagram, the saturation curve calculated in this work is in almost perfect agreement with Tester's saturation curve up to about 30 atmospheres, or a reduced pressure of about 0.62 (critical pressure is 48.50 atmospheres). For nitrogen, the agreement between saturation curves is not as good as may be seen in Figure IX.2. The reason for the better agreement, in the case of ethane, is that the thermodynamic network covered a temperature range of about $300^\circ K$, whereas in the case of nitrogen, the range covered was almost $600^\circ K$. The consequence of this is that the volumetric data can be curve fit better using a smaller temperature range. This does not mean that a thermodynamic network must be limited to small temperature ranges in order to achieve high accuracy. When it is desired to calculate a thermodynamic network covering a large temperature range, the calculation may be divided up into two, or more, portions, each portion covering part of the temperature range. In this way, the high accuracy can be maintained.

Appendix D

Nomenclature

a	Sonic velocity
C_p	Heat capacity at constant pressure
C_v	Heat capacity at constant volume
E	Internal energy
f	Fugacity
H	Enthalpy
P	Pressure
R	Universal gas constant
S	Entropy
T	Temperature
V	Specific volume
Z	Compressibility factor
α	Residual volume
ρ	Density
μ	Joule-Thomson coefficient

Appendix E

Literature Citations

1. Amagat, E. H., Ann. Chim. Phys., 29, 68(1893)

2. Bahlke, W. H., and W. B. Kay, Ind. Eng. Chem., 24, 291 (1932)

3. Bartlett, E. P., et. al., J. Amer. Chem. Soc. 50, 1275(1928); 52, 1363(1930)

4. Beattie, J. A., and O. C. Bridgemen, J. Amer. Chem. Soc., 50, 3133(1928)

5. Benedict, M., G. B. Webb and L. C. Rubin, J. Chem. Phys., 8, 334(1940)

6. Bird, S. T., Potter Aeronautical Co., personal communication, November 8, 1962

7. Bridgeman, O. C., Phys. Rev. 34, 529(1929)

8. Brinkworth, J. H., Proc. Roy. Soc. (London), A107, 510(1925); A111, 124(1926)

9. Brough, H. W., W. C. Shlinger and B. H. Sage, Ind. Eng. Chem., 43, 2442(1951)

10. Budenholzer, R. A., B. H. Sage, and W. N. Lacey, Ind. Eng. Chem., 31, 369, 1288(1939); 32, 384(1940); 34, 878(1942)

11. Burnett, E. S., Rep. U. S. Bur. Mines, No. 4729(1950)

12. Chalfant, J. R., "Thermodynamic Networks for Cases" S. B. Thesis, Mass. Inst. Tech., Dept. of Chem. Eng., 1960

13. Chemcon, Inc., Medfield, Mass., Chem. Eng., 69, 104(March 19, 1962)

14. Collins, S. C., and F. G. Keyes, Proc. Amer. Acad. Arts Sci., 72, 283(1938)

15. Cornell, D., Chem. Eng., 69, 159(March 19, 1962)

16. Cox Instrument Co., Bulletin 1384-**D**

17. Crout, P. D., Trans., AIEE, <u>60</u>, 1235(1941)

18. Dauphinee, T. M., and S. B. Woods, Rev. Sci. Inst.,
     <u>26</u>, 693(1955)

19. Deming, W. E., and L. S. Deming, Phys. Rev., <u>45</u>,
     109(1934)

20. Deming, W. E., and L. E. Shupe, J. Amer. Chem. Soc.,
     <u>52</u>, 1382(1930); <u>53</u>, 843(1931)

21. Deming, W. E., and L. E. Shupe, Phys. Rev., <u>37</u>, 638(1931)

22. Deming, W. E., and L. E. Shupe, Phys. Rev., <u>37</u>, 2245
     (1931); <u>40</u>, 848(1932); <u>45</u>, 109(1934); <u>48</u>, 448(1935)

23. Din, F., "Thermodynamic Function of Gases", Vol. III,
     Chap. 2, "Nitrogen", ed. F. Din, London, Butterworths,
     1962, p. 72

24. Dixon, H. B., C. Campbell and A. Parker, Proc. Roy.
     Society (London), <u>A100</u>, 1(1921)

25. Edwards, R. G., "Computation of Thermodynamic Variables
     of a Homogeneous Gas by Analogue Techniques", S. B.
     Thesis, Mass. Inst. Tech., Dept. Chem. Eng., 1959

26. Ellington, R. T., and B. E. Eakin, Chem. Eng. Prog.,
     <u>59</u>, No. 11, 80(1963)

27. Eucken, A., and K. Von Lude, Zeit. Phys. Chem.,
     <u>B5</u>, 413(1929)

28. Fischer and Porter Co., Catalogue 310

29. Flow Corporation, Bulletin 17A

30. Gilkey, W. K., F. W. Gerard and M. E. Bixler, Ind.
     Eng. Chem., <u>23</u>, 364(1931)

31. Haxton, L. G. and R. A. Weiss, Rev. Sci. Inst.,
     <u>26</u>, 1085(1955)

32. Hildebrand, F. B., "Introduction to Numerical
     Analysis", McGraw-Hill, New York, 1956.

33. Holborn, L. and J. Otto, Z. Phys., <u>23</u>, 77(1924);
     <u>30</u>, 320(1924); <u>33</u>, 1(1925)

34. Hubbard, J. C. and A. H. Hodge, J. Chem. Phys.,
5, 974(1937)

35. International Business Machine Systems Reference
Library, File No. 7090-25, Form C28-6054-3, "IBM
7090/7094 Programming Systems, FORTRAN II Program-
ming", 1963

36. Johnson, D. P., and D. H. Newhall, Inst. and Cont.
Systems 35, 120(April, 1962)

37. Johnston, H. L., et. al., J. Amer. Chem. Soc. 68,
2373(1946)

38. Kang, T. L., and J. J. McKetta, A. I. Ch. E. Journal
7, 418(1961)

39. Keenan, J. H., Mech. Eng., 48, 144(1926)

40. Keenan, J. H., and F. G. Keyes, "Thermodynamic
Properties of Steam", New York, Wiley, 1936

41. Kells, L. F., S. R. Orfeo and W. H. Mears, Refrig.
Eng., 63, No. 10, 46(1955)

42. Keyes, F. G., Proc. Nat. Acad. Sci., 3, 323(1917)

43. Klock, F. G. Jr., Rev. Sci. Inst., 32, 612,771(1961)

44. Lagermann, R. T., and C. H. Knowles, J. Chem. Phys.,
32, 561(1960)

45. Landis, F., and E. N. Wilson, "Progress in Inter-
national Research on Thermodynamics and Transport
Properties", ed., J. F. Masi and D. H. Tsai, Academic
Press, 1962, "The Determination of Thermodynamic
Properties by Direct Differentiation Techniques", p.218

46. Li, Y. T. and S. Y. Lee, Mech. Eng. 77, 702(1955)

47. Lindsday, J. D. and G. G. Brown, Ind. Eng. Chem.,
27, 816(1935)

48. Lovejoy, D. R., Rev. Sci. Inst., 32, 4(1961)

49. Lyderson, A. L., R. A. Greenkorn and O. A. Hougen, U.
of Wisconsin, College of Engineering, Report No. 4,
"Generalized Thermodynamic Properties of Pure Fluids",
1955.

50. Mackay, B. H. and N. W. Krase, Ind. Eng. Chem., 22,
1062(1930); J. Amer. Chem. Soc. 52, 5111(1930)

51. Manganero, J. L., "The Generation of Thermodynamic Networks for Gases", S. B. Thesis, Mass. Inst. of Tech., Dept. of Chem. Eng., 1960

52. McHarness, R. C., B. J. Eisman and J. J. Martin, Refrig. Eng., 63, No. 9, 37(1955)

53. Michels, A., et. al., Physica 1, 587(1934); Phys. Z., 35, 97(1934); Physica 3, 585(1936)

54. Michels, A., R. J. Lunbeck and G. J. Wolkers, Physica 17, 801(1951); App. Sci. Res., A3, 197(1952)

55. Miesse, C. C., "Study of Mass Flow Meters", Armour Research Foundation, Project d173, July, 1959

56. Miller, E. W., "Turbine Flow Sensors in Gas Flow Measurements", Preprint 127-LA-61, ISA Fall Instrument and Automation Exhibit, Los Angeles, 1961

57. Miller, R. W., and J. D. Sullivan, U. S. Bureau of Mines, Tech. Paper 424, "Thermodynamic Properties of Oxygen and Nitrogen", 1928

58. Myers, W. R., Inst. and Cont. Systems, 35, 117 (April, 1962)

59. Noury, J. and A. Lacom, Proc. Conf. Therm. and Trans. Prop. of Fluids, London, 1957, pp. 34-42

60. Onnes, H. K., and A. Von Urk, Commun. Phys. Lab., Univ. Leiden, N6, 169d(1924)

61. Orlando, V. A., and F. B. Jennings, Trans. ASME, 76, 961(1954)

62. Partington, J. R., and A. B. Howe, Proc. Roy. Soc. (London), A105, 225(1924)

63. Potter Aeronautical Co., Union, N. J., Bulletin t-2a

64. Potter, J. H., and M. J. Levy, Second Symposium on Thermophysical Properties, January 24, 1962, "An Axial Flow Porous Plug Experiment."

65. Reamer, H. H., and B. H. Sage, Rev. Sci. Inst., 24, 362(1953)

66. Reamer, H. H., et. al., Trans. ASME, 80, 1004(1958)

67. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, New York, 1958

68. Richardson, E. G., Proc. Conf. Therm. Trans. Prop. of Fluids, London, 1957, pp. 34-42

69. Riedel, L., Chem.-Ing.-Tech., 26, 83(1954)

70. Robinson, H. M., and H. Bliss, Ind. Eng. Chem., 32, 396(1940)

71. Roebuck, J. R., Proc. Amer. Acad. Arts Sci., 60, 537(1925)

72. Roebuck, J. R., et. al., Proc. Amer. Acad. Arts Sci., 64, 287(1930); Phys. Rev., 43, 60(1933); 45, 332(1934); 46, 785(1934); 48, 450(1935); J. Amer. Chem. Soc., 64, 400(1942)

73. Rossini, F. D., Selected Values of Properties of Hydrocarbons, API Project 44, 1953

74. Sage, B. H., E. R. Kennedy and W. N. Lacey, Ind. Eng. Chem., 28, 601(1936)

75. Selleck, F. T., J. B. Opfell and B. H. Sage, Ind. Eng. Chem., 45, 1350(1953)

76. Shilling, W. G., and J. R. Partington, Phil. Mag., 6, 920(1928)

77. Smith, L. B., and R. S. Taylor, J. Amer. Chem. Soc., 45, 2107(1923); 48, 3122(1926)

78. Smith, P. W., J. Acoust. Soc. Amer., 25, 81(1953)

79. Spauschus, H. O., Rev. Sci. Inst., 32, 1297(1961)

80. Sullivan, J. J., "Temperature, Its Measurement and Control in Science and Industry", Vol. 3, part 2, ed. C. M. Herzfeld, Reinhold, New York, 1962, p. 329

81. Tester, H. E., "Thermodynamic Functions of Gases", Vol. 3, Chap. 3, "Ethane", ed. F. Din, London, Butterworths, 1962, p. 162

82. Van Itterbeck, A., and P. Mariens, Physica, 4, 207(1937)

83. Van Itterbeck, A., and O. Van Paemal, Physica, 5, 593, 845(1938)

84. Van Itterbeck, A., et. al., Appl. Sci. Res., A6, 15, 421(1956)

85. Van Ness, H. C., A. I. Ch. E. Journal, 1, 100(1955)

BIOGRAPHICAL NOTE

The author was born on February 4, 1937, in Brooklyn, New York, and attended the public schools in that city. He entered Brooklyn College in 1954 and spent two years there. He received his bachelors degree in chemical engineering from the City College of New York in 1959. He entered the Massachusetts Institute of Technology in 1959 and received his S.M. in chemical engineering, after attending the School of Chemical Engineering Practice, in 1961. From 1961 to 1962 he was employed by Aerojet-General Corporation, in Sacramento, California. In 1962 he returned to the Massachusetts Institute of Technology to complete the work for the Doctor of Science degree in chemical engineering.

On July 3, 1962 he was married to the former Miss Barbara Weinstein of New Bedford, Massachusetts. They have one child, a girl, Rebecca Ann, born on June 7, 1964.