## THE UNIVERSITY OF CALGARY

# EXPERIMENTAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF NITROGEN, ARGON, AND THEIR MIXTURES AT $0{ }^{\circ} \mathrm{C}$, AND ASSESSMENT OF CERTAIN COMMONLY USED EQUATIONS OF STATE IN THE LIGHT OF THESE DATA 

## BY

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## A THESIS <br> SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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## ABSTRACT

An experimental procedure is developed and carried out to determine the compressibility factor (Z), the isothermal compressibility coefficient (K), the speed of sound (a), and the ratio of specific heats $\left(C_{p} / C_{v}\right)$ for Nitrogen, Argon and their mixtures. The measurements which are made at $0{ }^{\circ} \mathrm{C}$ and for pressures from the atmospheric to 25 MPa , are in good agreement with currently available published information.

The procedure comprises precise calibration and monitoring of the various measured parameters during the tests, and the use of digital recording techniques for manipulation of the data.

The observations are compared with predictions by four equations of state, namely, the Hybrid-Virial, the Benedict-Webb-Rubin, the Redlich-Kwong-Soave, and the Peng-Robinson. The comparisons are extensively documented in tables and graphs.

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a
speed of sound.

$$
B-W-R \text { coefficient. }
$$

$B-W-R$ coefficient / specific volume.
B-W-R coefficient.
Second virial coefficient.
B-W-R coefficient.
$B-W-R$ coefficient.
Specific heat at constant pressure.
Specific heat at constant volume.
Third virial coefficient.
Boltzmann constant.
Isothermal compressibility coefficient.
Coefficient used in $P-R, R-K-S$ equations.
Pressure.
Gas constant.
Standard deviation.
Time.
Temperature.
Specific volume.
Volume.
Acentric factor.
Dimensionless density for the rigid sphere potential.

| X | Value of property used in calculation of standard deviation. |
| :---: | :---: |
| $\mathrm{x}^{\prime}$ | Fitted value of property used in calculation of standard deviation. |
| Z | Compressibility factor. |
| $a$ | Variable used in $B-W-R, R-K-S$ and $P-R$ equations of state. |
| $\delta$ | Binary interaction coefficient. |
| $\varphi$ | Potential energy. |
| $\gamma$ | Ratio of specific heats: |
| $\rho$ | Density. |
| $\sigma$ | Low velocity collision diameter. |
| $\theta$ | Potential constant |

Superscripts:

* Quantity reduced by means of combination of molecuiar parameters.

Subscripts:
c Quantity at the critical point.
h Hard molecule.

- Ideal gas properties.

LJ Lennard-Jones coefficient.
$r$ Quantity reduced by means of combination of critical constants.

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## INTRQDUCTION

### 1.1 OBJECTIVES

The objective of this study is to obtain precise measurements of certain thermodynamic properties, namely, the compressibility factor (Z), the isothermal compressibility coefficient ( $K$ ), the speed of sound (a) and the ratio of specific heats $\left(C_{p} / C_{v}\right)$ for nitrogen, argon and for binary mixtures of these gases and to present these observations compared to values predicted by certain selected equations of state. The binary mixtures studied contained Nitrogen mole fractions of 85.6\%, 52.4\%, and $22.5 \%$.

For each composition, the properties concerned are determined only on the $0{ }^{\circ} \mathrm{C}$ isotherm and at pressures up to 25 MPa. The results obtained are compared with experimental data from other sources.

The equations of state selected for examination are: the Hybrid Virial Equation of State $\langle 15,18,20,29,42,53\rangle$; the Benedict-Webb-Rubin Equation of State $\langle 1,23,53\rangle$; The Redlich-Kwong-Soave Equation of State $\langle 23,28,44,49,53\rangle$ and the Peng-Robinson Equation of State $\langle 23,28,33,34,35,36,49\rangle$. All but the first. of these equations enjoy widespread use by the oil and gas industry.

In this thesis, the methods used in obtaining and analyzing the data as well as the equipment utilized have been highlighted.

## I. 2 PRELIMINARY DISCUSSION

Equations of state are an estimate of the way nature behaves, relating pressure, density and temperature. Attempts have been made to conceive the perfect equation of state capable of serving three primary purposes <53>, namely:
I) To represent PVT data reliably enough so that these data can be differentiated and integrated to calculate derived slope properties.
2) To predict gas properties for pure components and gas mixtures using a minimum of experimental data.
3) To predict vapour-liquid equilibria of mixtures especially at high pressures.

This is accomplished by assuming a functional form which seems to be justified but contains unknown constants. These unknown constants are provided by experiments. The most ambitious of these equations call upon two fitted constants. The most frequently used data for determining these constants are the pressure, temperature and density at the critical point. Such equations of state or extensions of them, e.g. Rediich-Kwong-Soave, Peng-Robinson, naturally find their closest adherents among
those primarily concerned with properties near the saturated vapour line. In no case should one expect these equations to be accurate everywhere.

One objective of this thesis, is to show, with a reliable and accurate set of observations, the limitations of some equations of state in their predictions of thermodynamic properties, specifically applied to the gases, temperature and pressure range concerned here. A more general evaluation of the performance of these equations would fall outside the scope of this examination.

METHOD

### 2.1 OUTLINE OF THE METHOD

The test procedure can be divided into two nearly independent operations which are aimed at obtaining data to provide the compressibility factor (Z) and the isothermal compressibility coefficient (K), and to provide the speed of sound (a) and the ratio of specific heats ( $\mathrm{Cp} / \mathrm{Cv}$ ).

The isothermal compressibility coefficient ( $K$ ) is calculated from pressure measurements obtained by allowing the test gas to expand from a certain known volume $V_{1}$ to another known volume $\left(\mathrm{V}_{1}+\mathrm{V}_{2}\right)$. The compressibility coefficient (Z) is calculated in a similar way by expanding the.gas from volume $V_{2}$ to a third known volume $\left(V_{2}+V_{3}\right)$, sufficiently large that the contents obey the Ideal Gas Law.

The speed of sound in the gas is calculated by measuring the time taken by a decompression wave front to travel over a known distance. The decompression wave is generated by bursting a diaphragm at the top end of the test tube (T-tube) which contains the gas under a prescribed pressure. Pressure transducers, at precisely located stations in the tube, record the passage of the decompression wave in the form of pressure-time data.

The ratio of specific heats ( $C p / C v$ ) is obtained by using the observed speed of sound (a), the density ( $\rho$ ), and the isothermal compressibility coefficient (K).

### 2.2 APPARATUS

A schematic diagram of the apparatus employed in the experimental work is shown in Figure 2.1 .

The system consists of four main components: (1) the gas supply and gas mixing station; (2) the test tube and expansion volumes; (3) high vacuum pump; and (4) the electronic data acquisition, display and analysis systems.
(1) The gas supply and mixing station is a simple arrangement of high pressure bottles, commercial type IH rated at 41000 kPa ( 6000 psi ). When in test mode, the working bottle containing the test gas is . directly connected to the gas intake line of the apparatus through a pressure regulator and $a$ valve. When in mixing mode, the working bottle is disconnected from the apparatus and connected to another bottle from which the appropriate amount of gas is drawn to provide the desired mixture. In order to enhance the transfer of gas from one bottle to another, the receiving bottle is cooled and the delivery bottle is heated by drenching the bottles with cold and hot water respectively. Significant pressure changes were


Figure 2.1
realized by this method allowing better use of the supply gas. Pressure levels are monitored using a pressure transducer attached to the connection line.
(2) The test tube (T-tube) was designed and tested hydrostatically to 60 MPa , while tubing and connections used throughout are rated to 100 MPa . The test tube section is made of 316 stainless steel pipe (schedule $10,7.798 \mathrm{~mm}$ i.d., and 10.287 mm o.d.) arranged in an inverted $T$ shape with a diaphragm holder and a quick opening ball-valve at the top of the vertical section. The diaphragm-holder arrangement permits rapid replacement of diaphragms after each test; it also divides the vertical section of the $T$-tube into two parts, the upper section being isolated from the atmosphere by the ball-valve. Opening the ball-valve lowers the pressure in the upper section of the tube suddenly, which causes the diaphragm to burst. Several types of diaphragm materials were tested for use in the experiment and cellophane was selected because it's rupture generates decompression waves with the sharpest leading edge. The shattering effect, observed with bursting of the cellophane, provides a large cross sectional area for the flow of the escaping gases and therefore a greater 'instantaneous' pressure drop, which leads to a stronger decompression wave. The
ball-valve used in the top of the $T$-tube was selected for the same reasons described above, i.e. to provide the greatest possible cross sectional area upon opening.

Pressure-welding was used in the construction of the $T$-tube. Pressure transducer taps are located at the junction of the $T$-tube and also at each end of the horizontal section. The volume of the T-tube section was measured to be $72.67 \times 10^{-6} \mathrm{~m}^{3}$.

There are two expansion volumes connected in series with the $T$-tube, namely, $\mathrm{V}_{2}$ and $\mathrm{V}_{3}$. Expansion volume $V_{2}$, used in the first expansion of the gas, as described in the Section 2.3, is subjected to pressures of the same order as that of the supply pressure and of the $T$-tube pressure, and is composed of three parallel sections of coiled 3.13 mm O.D. (1/8 inch nominal size) stainless steel tubing together with accompanying block valves and thermocouple fittings. This three-section design allows for a faster temperature equalization of the test gas during experiments. The expansion volume $\mathrm{V}_{2}$ was measured to be $19.911 \times 10^{-6} \mathrm{~m}^{3}$.

Expansion volume $V_{3}$ is a large chamber designed to receive the final expansion of the gas. The magnitude of $V_{3}$ is selected to be such that the Ideal Gas Law applies with high accuracy to the gases discharged into it. The working pressures in volume $V_{3}$
vary typically from 0.1 kPa to 150 kPa , it was hydrostatically tested to 250 kPa . This chamber is made of a section of carbon steel pipe of nominal diameter 100.16 mm closed at both ends by blind flanges with appropriate gaskets to ensure high vacuum sealing. The measured volume of $V_{3}$ is $5104.34 \times 10^{-6} \mathrm{~m}^{3}$.

- The T-tube and expansion volumes $V_{2}$ and $V_{3}$ are immersed in a constant temperature bath consisting of an insulated box of approximate dimensions 800 mm L x $230 \mathrm{~mm} \mathrm{H} \times 290 \mathrm{~mm} \mathrm{~W}$, containing melting ice and water. A pump type stirrer was attached to the box to ensure temperature equalization in the box and also to provide adequate supply of cold bath water to cool the exposed parts of the apparatus.
(3) The vacuum pump is used throughout most phases of the experiment to evacuate the entire apparatus prior to loading of the gas and also to provide high vacuum in volumes $V_{2}$ and $V_{3}$ for the tests. This pump is a Speedvac model VDC ED500 2-stage high vacuum pump (Edwards High Vacuum Ltd., England). It is capable of achieving vacuum of better than $10^{-3}$ Torr. The pump is connected to volume $V_{3}$ through a sealed $6.25 \mathrm{~mm}(1 / 4$ inch nominal size) copper tubing.
(4) The data acquisition, monitoring and display
instrumentation used in this experiment can be divided for description purposes into three parts: (a) Temperature monitoring; (b) Static pressure monitoring; (c) Pressure-time data acquisition system.
(a) Temperature monitoring of the gas is done by five thermocouples located in the $T$-tube, in volumes $V_{2}$ and $V_{3}$ and in the bath water. These temperature observations are displayed on five channels of a data-logger (Fluke Model 2200B). The thermocouples were calibrated in a constant temperature bath of melting ice prior to commencing the experiments. Calibration curves are shown in Appendix A, Figures A.19 to A. 24.
(b) Three pressure transducers are used to monitor the steady pressure in the $T$-tube and expansion volumes. The high pressures present in the $T$-tube and volume $V_{2}$ are observed using two strain gage transducers, one with a range 0 to $103.4 \mathrm{MPa}(0-15000 \mathrm{psi})$ and the other with a range 0 to $20.68 \mathrm{MPa}(0-3000 \mathrm{psi})$. Both tranducers are accurate to $0.1 \%$ of full-scale. (see. Section 2.5 for specifications of the pressure transducers). The low pressures occurring in the volumes $V_{2}$ and $V_{3}$ are monitored using an absolute pressure transducer (strain gage type) with 0 to 345 kPa (0 - 50 psia), also with accuracy of $0.1 \%$ of full-scale. All three transducers were calibrated at
various temperatures and over a wide range of pressures to establish the calibration curves used in correcting the pressure readings. The calibration curves are shown in Appendix A.

A Pirani type gage <60> is used to measure the high vacuum present after evacuation of the apparatus. The bottom end of the scale of the Pirani gage was calibrated to guarantee the same level of vacuum at the end of every evacuation procedure. (calibration is described in Section 2.5) This gage works on the principle that the thermal conductivity of gases varies almost linearly with pressure at very low pressures.
(c) Transients in pressure, which are generated by bursting the diaphragm, are measured using piezoelectric transducers. These transducers are located at the bottom of the vertical tube section and at one end of the horizontal section of the $T$-tube. Their arrangement is such as to ensure that the decompression wave encounters the face of each transducer head-on. This provides the sharp and clean signal necessary to define accurately the time of arrival of the decompression wave front at the measuring stations.

The signals from the piezoelectric transducers are amplified by charge amplifiers (Kistler model 504E) and fed to a high speed digitizing oscilloscope
(Tektronix model 5223). The analog-to-digital conversion rate of the oscilloscope is 1 MHz , permitting a resolution of 2 microseconds, operating on two channels. The analog-to-digital converter of the oscilloscope provides the digitized data in a 10 bit format so that the resolution is better than $0.1 \%$ of full-scale. This high resolution in both pressure and time is fundamental in determining precisely the relative time of arrival of the decompression wave at the measuring stations. The digitized data in the format described above are stored in the oscilloscope memory which can hold 1016 data points per channel; these data points are taken at 2 microseconds intervals but interpolated by the oscilloscope digital system to provide data at 1 microsecond intervals. The total time span allowable in memory at this rate is slightly greater than one millisecond.

The digitizing oscilloscope was fitted with and IEEE-488 digital interface $\langle 50,51,52,61\rangle$ to allow the transfer of data to a computer for processing and analysis. An HP-9816 desk-top computer was programmed to retrieve the data from the oscilloscope, temporarily store and then transfer the data to a Harris 800B computer where it was finally processed. Communication between the HP-9816 and the Harris 800 B computer was established using RS-232 ports on both machines and
proper interface programming.
The data acquisition system described above was developed, tested and programmed entirely within the scope of work of this investigation.

### 2.3 EXPERIMENTAL PROCEDURE

2.3.1 ISOTHERMAL COMPRESSIBILITY COEFFICIENT (K) MEASUREMENTS

The isothermal compressibility coefficient is defined by:

$$
1 / \mathrm{K}=-\mathrm{V}(\partial \mathrm{P} / \partial \mathrm{V})_{\mathrm{T}}=\rho(\partial \mathrm{P} / \partial \rho) \quad \ldots .2 .1
$$

A direct experimental determination of $K$ is obtained by replacing $(\partial P / \partial V)_{T}$ by $(\Delta P / \Delta V)$, where $\Delta V$ is the increase in volume of the gas (in a controlled expansion) and $\Delta P$ is the observed change in isothermal pressure consequent on this expansion.

In principle, the error arising from this approximation may be reduced without limit by decreasing $\Delta V$ indefinitely: in practice, a lower limit on $\Delta V$ is set by increasing uncertainty in $\Delta P$ and by the increase in the required time and effort as $\Delta V$ is reduced. The compromise adopted was to design $\left(\Delta V / V_{1}\right)$ to be small (here no more than 0.25), and to call upon Taylor's theorem to provide a correction to the approximate form.

Accordingly, the gas in the $T$-tube (at state
$\mathrm{P}_{1}, \mathrm{~V}_{1}, \mathrm{~T}_{0}$ ) is allowed access to a small, pre-evacuated chamber of volume $V_{2}$. When thermal equilibrium is reached, the gas pressure $\left(P_{2}\right)$ is noted. The gas state is now $\left(\mathrm{P}_{2}, \mathrm{~V}_{1}+\mathrm{V}_{2}, \mathrm{~T}_{0}\right)$ so that the uncorrected approximate form of $I / K$ at some pressure $P^{\prime}$ between $P_{1}$ and $P_{2}$ is:

$$
I / K\left(P^{\prime}, T_{0}\right)=-V^{\prime}\left(P_{2}-P_{1}\right) / V_{2}
$$

where $V^{\prime}$ is the gas volume corresponding to $P^{\prime}$. Thus, if $V^{\prime}$ is chosen to be the mid-volume point, 2.2 becomes:

$$
1 / K\left(P_{m}, T_{0}\right)=-\left(0.5+\left(V_{1} / V_{2}\right)\right)\left(P_{2}-P_{1}\right)
$$

where $P_{m}$ is the equilibrium pressure at the mid-volume $\left(V_{1}+0.5 V_{2}\right)$. This choice of $V^{\prime}$ satisfies the requirement of Rolle's theorem and it is therefore not surprising that the relevant correction derived from Taylor's theorem is very small. This advantage is partly offset by the fact that whereas the other observations of thermal property values are made at the pressure $\mathrm{P}_{2}$ (e.g. $\mathrm{Z}\left(\mathrm{P}_{2}, \mathrm{~T}_{\mathrm{o}}\right)$, here the measurement is at a higher pressure $P_{m}$. For this reason, the volume $V^{\prime}$ was alternatively assigned to the end value $\left(\mathrm{V}_{1}+\mathrm{V}_{2}\right)$ where the pressure is $\mathrm{P}_{2}$, so that 2.2 becomes:

$$
1 / K\left(P_{2}, T_{0}\right)=-\left(1+\left(V_{1} / V_{2}\right)\right)\left(P_{2}-P_{1}\right)
$$

In this case the correction derived from Taylor's theorem is, of course, greater than before. However, the corrected values derived from these two forms are found to be well within uncertainties when they are referred to the same. state ( $\mathrm{P}_{2}, \mathrm{~T}_{\mathrm{o}}$ ).

In summary, the correction relations for the observed K values are:
$1 / K\left(P_{m} \cdot T_{o}\right)_{\text {corrected }}=\left(1 / K_{a}\right)+\left(V_{I}^{3} / 6\right)\left(x^{2}(1+x)\left(\partial^{3} P / \partial V^{3}\right)_{T}\right)$ .... 2.5
where $V^{\prime}=V_{1}+\left(V_{2} / 2\right)$
$I / K\left(P_{2}, T_{o}\right)=\left(I / K_{b}\right)+V_{1} x\left(\left(\partial^{2} P / \partial V^{2}\right)_{T}-(2 / 3) V_{1} x\left(\partial^{3} P / \partial V^{3}\right)_{T}\right) V^{\prime}$
.... 2.6
where $V^{\prime}=V_{1}+V_{2}, x=V_{2} / 2 V_{1}$ and where the derivatives are obtained from fits of pressure to volume.

The experimental determinations of $K$ described above are nearly unbiassed in that any bias can only arise in the relatively small correction component. A much more convenient determination, but also more biased, arises from the compressibility factor definition described above. Thus, by definition:

$$
1 / K\left(P, T_{0}\right)=\rho(\partial P / \partial \rho)=P /(1-d \ln Z / d \ln P) \quad \ldots 2.7
$$

and since $Z$ has the form:

$$
z=1+\sum_{j=1,3} q_{j} P^{j}
$$

then:
$1 / K\left(P_{o}, T_{o}\right)=P\left(1+\Sigma_{j=1,3} q_{j} P^{j}\right) /\left(1-\Sigma_{j=1,3}(j-1) q_{j} P^{j}\right)$
.... 2.8
where $q_{j=1,3}$ are constants.

These three forms of $K$ are determined and compared. It may be seen that the form just considered is dependent only on $Z(P)$. It is in very good agreement with the two other forms, 2.5 and 2.6 .

### 2.3.2 GAS COMPRESSIBILITY FACTOR (Z)

It will be recalled that after the gas expands from $V_{1}$ to $\left(V_{1}+V_{2}\right)$, the equilibrium pressure is $P_{2}$.

The valve separating the volumes $V_{I}$ and $V_{2}$, is now closed and the contents of $V_{2}$ are allowed to expand into the volume $V_{3}$. The $\left(V_{3} / V_{2}\right)$ ratio is 265.05 so that the equilibrium pressure $P_{3}$ obtained after this expansion is about one atmosphere or less in all cases and $Z\left(P_{3}\right)$ is approximately unity. Thus, the equilibrium isothermal states before and after the expansion are connected by the relation:

$$
\mathrm{Z}_{2}=\mathrm{P}_{2} \mathrm{~V}_{2} /\left(\mathrm{P}_{3}\left(\mathrm{~V}_{2}+\mathrm{V}_{3}\right)\right)
$$

The initial pressure in volume $V_{3}$ was set sufficiently low that the residual mass in $V_{3}$ prior to the expansion could be neglected. The simplicity and accuracy of expression 2.9 above is the result of this precaution. At the end of each test, volumes $V_{3}$ and $V_{2}$ are evacuated in preparation for another test. Volume $V_{1}$ is kept isolated and is now at pressure $\mathrm{P}_{2}$; the remaining gas after each test is thus used for the next test without reloading. This allows for a better use of the available gas supply.

### 2.3.3 SPEED OF SOUND MEASUREMENTS

The observed speed of sound is defined to be the time of travel of the head of a decompression wave between two chosen points divided by the distance separating these points. The decompression wave is generated in the $T$-tube by bursting a diaphragm located in its upper section.

The measurement points are located at the T-tube junction, at the bottom of the vertical section, and at each end of the horizontal section. Piezoelectric pressure transducers at these locations detect the passage of the head of the decompression wave in the form of a sharp decay in the pressure level. The first, transducer, at the $T$-tube junction point, is also used to trigger the data acquisition equipment.

A digitizing oscilloscope $\langle 45,50\rangle$ is used to display and store the pressure-time trace produced by the
pressure transducers. This data is then transfered to a computer for later processing. The digitizing oscilloscope has a pre-triggering feature that allows the recording of events prior to the trigger signal. Once the oscilloscope is set for operation, it continuously records data until receiving the triggering signal. At this point it saves a prescribed number of data points recorded prior to the triggering signal and stops recording data once the available memory space is full. This time-record in memory now contains data that allows precise determination of the time of arrival of the decompression wave. Because both channels are triggered simultaneously by the arrival of the wave at the first transducer, the time records permit calculation of the time difference by simple subtraction (Detailed description of the digitizing oscilloscope data files is provided in Section 2.4.1.).

Due to the spherical nature of the expansion wave <38> which will travel in all directions with the speed of sound in the medium, a correction in the assumed distance of travel relative to the distance between the two transducers is necessary in order to account for the 'corner effect' at the junction of the vertical and horizontal sections of the $T$-tube as depicted in Figure 2.2. The decompression wave front as when it arrives at the edge of the vertical leg of the $T$-tube, is nearly planar. At this point, the wave still has to travel one tube

Figure 2.2
THE 'T' TUBE - CORNER EFFECT

diameter before encountering the first transducer located at the junction of the $T$-tube. In the time taken to travel down a distance equal to one tube diameter it will also have travelled the same distance along the horizontal section.

At this point, the decompression wave is a corner centered wave travelling towards the other transducer. Again referring to Figure 2.2, it is evident that the actual length travelled by the wave corresponding to the time as measured by the transducer signals is not the geometric distance between the transducers, but less. This was confirmed by extensive preliminary tests done with the pure gases Argon and Nitrogen at low pressures where the speed of sound data closely approximates the ideal gas values.

The effective separation 'l', calculated, on the basis of the findings above and the geometric arrangement of the test tube (T-tube), is found to be 292.50 mm . This value is used as a constant in the calculation of the speed of sound for all the gas mixtures studied.
2.3.4 MEASUREMENTS OF THE RATIO OF SPECIFIC HEATS

The ratio of specific heats, (Cp/Cv), is determined from the observed properties $a, k$, and $Z$ using the expression:

$$
(\mathrm{Cp} / \mathrm{Cv})=\mathrm{a}^{2} \rho \mathrm{~K}
$$

The computation of ( $\mathrm{Cp} / \mathrm{Cv}$ ) is strongly dependent on the accuracy of each of the variables envolved in the formulation. A discussion on the accuracy of the ratio of specific heats can be found in Section 2.6.2.

### 2.4 DATA MANAGEMENT

2.4.1 OBSERVED DATA FILES

Two types of data files are produced in the course of an experiment with a certain gas or gas mixture. (I) Files containing pressure data from the expansions, namely $P_{1} i, P_{1} f, P_{2} i, P_{2} f$ and Patm which are used in determining the compressibility factor (Z) and isothermal compressibility coefficient ( $K$ ) as described in section 2.3.1 and 2.3.2.; (2) Files of Pressure-Time data obtained from the rupture of the diaphragm and which are used to calculate the speed of sound in the gas or mixture.
(1) Tables 3.1.1, 3.2.1, 3.3.1, 3.4.1, 3.5.1 of Chapter 3, list the observed pressure data collected for the 5 mixtures under study. A total of 5 files were produced. These data files, when created in the computer, contained two initial lines with information on the gas or gas mixture under test as well as the transducers calibration constants to be used in the calculations.
(2) The Pressure-Time data files are generated from data stored in each of the channels of the digitizing oscilloscope. Two files are necessary to calculate the speed of sound for each test point, one from each channel. A typical data file provided by the digitizing oscilloscope contains 1024 'l0 bit words'. The first eight 'words' constitute a header with information pertinent to the data, i.e. channel number, type of file (ASCII or BINARY) $\langle 50,51,52,61\rangle$ and the data point at which the trigger was detected. The next 1016 words contain the pressure data as received and digitized by the analog-to-digital converter of the oscilloscope. Data points are obtained at constant time intervals which are selectable from the oscilloscope time-base setting. More than 300 time-pressure data files were generated.

### 2.4.2 MANAGEMENT OF DATA

Figure 2.3 shows a block diagram of the database and functional relations between the various programs. The data base consists of a group of 7 computer programs written in Fortran on a Harris 800B computer and serve the purpose of performing the necessary calculations on the data as well as, through the use of extensive computer graphics, to generate plots and tables. for presentation.

The $Z$ program and $K$ program are used to calculate

Figure 2.3

## DATABASE FLOW DIAGRAM


the compressibility factor $Z$ and isothermal compressibility coefficient $K$ as described in Section 2.3. The programs also generate the graphs of properties presented in Chapter 3. The $\boldsymbol{\gamma}$ program uses the speed of sound values calculated from the pressure time files by the (a) program, together with the values of isothermal compressibility coefficient $k$ produced by the $K$ program. Graphs of ( $C p / C v$ ) vs. pressure are created by the program and shown in Chapter 3.

The programs called Virial, Bwr, Rks and $\operatorname{Pr}$ calculate the properties $Z, K, a$, and ( $C p / C v$ ) from equations of state for the range of pressures under consideration. A total of 80 files of calculated properties were created. The comparison plots program, using the observed properties data calculated from the $Z, K, \quad a \quad$ and (Cp/Cv) programs, together with the corresponding properties calculated from the equations of state programs, produces the graphs for study of performance of equations of state shown in Chapter 5.

The three table programs are used to present the observed data and calculated properties in tabular form. A total of 25 graphs of observed data points, 15 tables and 20 comparison graphs are produced by the database.

### 2.5 CALIBRATION

2.5.1 CALIBRATION OF PRESSURE TRANSDUCERS

Three types of pressure transducers are used in
the apparatus. These are piezoelectric, strain gage and Pirani type transducers.

The piezoelectric transducers are used in determining the time of travel of a decompression wave inside a tube as it goes past two transducers separated by a precisely known distance. Because of time being the only parameter of interest in the experiment, the piezoelectric transducers are not calibrated in amplitude although a verification was carried out on the performance of the charge amplifiers (Kistler type 601A) for different time constants.

The strain gage type transducers are used to determine non-transient pressure levels in the apparatus. The performance of these transducers is of great importance in determining the overall accuracy of most of the thermodynamic parameters. A total of three strain gage transducers used in the apparatus, two located in the upper section of the $T$-tube and one in the expansion volume $V_{3}$. The two gages used for high pressure have ranges of 0 to 103.4 MPa ( 0 - 15000 psi ) and 0 to $20.69 \mathrm{MPa}(0-3000 \mathrm{psi})$ respectively. The low pressure transducer located in the $V_{3}$ volume has a range of 0 to $345 \mathrm{kPa}(0-50 \mathrm{psi}$ absolute). These transducers are listed below:
I) $\mathrm{DJ}-\mathrm{TRANSBAR} \quad 0-20.68 \mathrm{MPa}(0-3000 \mathrm{psi}$ gage).
II) SENSOTEC SUPER TJE 0-103.4 MPa (0-15000 psi gage). III) MICROGAGE $0-345 \mathrm{kPa}(0-50 \mathrm{psi}$ absolute).

For T-tube measurements at low pressures, the low range transducer ( $0-20.60 \mathrm{MPa}$ ) is chosen as the primary gage while above 20 MPa , the high range pressure transducer is used.

The uncertainty of all three transducers is declared by the manufacturers to be $0.1 \%$ of full-scale: this includes linearity, hysterisis and repeatability defects. These values were used only as guidelines when purchasing the units. Very early, during the course of the experiments, it became clear that calibration curves for each transducer at various temperatures were necessary. Figures A.l to A. 18 in Appendix A show calibration curves for the three transducers.

The calibration parameters are obtained by plotting the pressure readings from a previously calibrated gage and the pressure readings from the transducer. Calibration tests were performed, in the case of the two high pressure transducers, using a dead-weight tester, and in the case of the absolute pressure transducer, a mercury manometer with resolution of 0.05 mm of mercury. The transducers were placed in a controlled environment set to various temperatures so as to investigate the effect of temperature on the calibration constant. In the case of the transducers concerned, no significant variations in the calibration constant were encountered.

All three transducers demonstrated a high degree
of linearity at all temperatures. The Microgage absolute pressure transducer exhibited non-linearity near $10^{-4}$ Torr. This could be easily explained by its construction. This kind of transducer consists of a sealed chamber which has been evacuated (to 0.001 Torr usually in the case of industrial models) separated from the test gas environment by a metallic diaphragm which has a strain gage welded to it. The strain gage will pick up the dimensional variations in the diaphragm and the system electronics will translate these variations into a signal proportional to pressure.

Because the vacuum attained in the experiments was roughly 0.0001 Torr, that is, lower even than the vacuum in the sealed chamber of the transducer, a considerable amount of 'non-linearity' is observed at the very low end of the pressure range for this transducer. This non-linearity did not affect the results of the experiments because the pressure level in volumes $\left(V_{2}, V_{3}\right)$ was monitored by a Pirani high vacuum gage.

The Pirani $\langle 6,60\rangle$ gage high vacuum transducer was especially calibrated for the measurement of very low absolute pressures with the aid of a McLeod $\langle 6,60\rangle$ gage. The Mcleod gage is capable of resolving pressures down to 0.0001 Torr and is used to calibrate the low end of the scale of the Pirani gage at about 0.0001 Torr.

For all transducers, the slope of the calibration curve, which can be associated with the 'gain' is
adjustable on the amplifier/display unit. The slope varies slightly with temperature and although the variations recorded were small, of the order of $0.001 \mathrm{kPa} / \mathrm{kPa}$ they were accounted for in processing the data.

The intercept value, also known as the 'zero' or 'offset', is a major source of concern. Distortions in the dimensions and flexibility of the diaphragm are affected by temperature. Moreover, a minute variation in the temperature of the environment can cause relatively large variations in the preformance of the various electronic components. Both factors contribute to the degree of difficulty encountered in determining the offset which can vary during the course of a series of experiments and must be annotated at the begining and at the end of each session. It has proven to be of great value to leave the electronic equipment permanently on power, or to turn them on many hours prior to commencing the tests to minimize the 'zero' fluctuations. The 'zeros' were made part of the data transferred to the computer for use in further processing of the pressure data.

Special attention was paid to control the temperature of the transducers themselves by maintaining their bodies immersed in the test bath.

Depending on the pressure ratios involved in some of the stages of the experiments, the temperature in the gas being tested will vary quite significantly, therefore
affecting the pressure tranaducers' readings. Temperature was monitored at various stations and time was allowed for stabilization before any pressure data was collected.

The true pressure, corrected and within the tolerances allowed by the instrumentation is then expressed as <6>:

$$
P_{o}=\left(P_{r}-O f f\right) / s l o p e
$$

In 2.11 above $P_{o}$ is the true value of the variable pressure, $P_{r}$ is the pressure reading, Off is the offset and slope is the 'gain' or multiplier for the correction.
2.6 UNCERTAINTIES
2.6.1 RESOLUTION

The chambers of volume $\mathrm{V}_{1}, \mathrm{~V}_{2}$, and $\mathrm{V}_{3}$ were chosen so that a significant pressure drop is obtained at each expansion of the gas under test so that the uncertainty associated with pressure change is small compared with the magnitude of this pressure change.

These volumes were measured by the following two methoảs:

1) The absolute values were measured by measuring the mass of each volume section when dry, and then filled with distilled water. The difference in weight and the known density of the water at the test temperature provided the volume.
2) The relative ratios $V_{1} / V_{2}, \sim V_{2} / V_{3}$ and $V_{1} /\left(V_{2}+V_{3}\right)$ were confirmed by expanding pure nitrogen from one volume to another at sufficiently low pressures that the Ideal Gas Law is precise. Since the process is isothermal, volume ratios are inversely proportional to the (observed) pressure ratios.

The digitizing oscilloscope used to collect the time data for the calculation of the speed of sound was set to a time scale such that the distance between the two decompression waves, as shown by the traces, occupied about $80 \%$ of the full-scale. The absolute value of the pressure readings,(for the purpose of calculating the speed of sound) was of no significance. The emphasis in this part of the experiment was on achieving a clean and sharp pressure trace. Accordingly it is extremely important to ensure a high signal-to-noise ratio associated with the pressure time trace. This was done by optimizing the performance of the data acquisition system through varying, in combination, the amplitude scale of the oscilloscope and the amplification factor of the charge amplifier. An optimum setting for the above scales was reached by trial and error. In addition, the shielding of the cables used to transmit the charge signal from the transducers to the charge amplifiers was tested before each test session.

The rise time of the piezoelectric transducers utilized in the speed of sound experiments is 3
microseconds. This is the time the transducer takes to respond to an instantaneous pressure change. Because this delay is common to the response characteristics of the transducers, it is cancelled out when calculating time differences. Because of the rise time being very small, of the order of the analog-to-digital converter sampling interval, the uncertainty in the rise time is considered to be neglegible and was not accounted for in this investigation.

### 2.6.2 UNCERTANTIES IN OBSERVED VALUES

Uncertainties are calculated for the observed thermodynamic properties, namely (i) the compressibility factor $Z$, (ii) the isothermal compressibility coefficient $l / K$, the speed of sound $a$, and the ratio of specific heats ( $\mathrm{Cp} / \mathrm{Cv}$ ).
i. Uncertainty in the values of the compressibility factor Z:

$$
Z=\left(P_{2} / P_{3}\right)\left(V_{2} /\left(V_{2}+V_{3}\right)\right)
$$

which can be written as:

```
    Z = (Pressure ratio).(Volume ratio)
```

    Pressure ratio \(=P_{2} / P_{3}\)
    Volume ratio \(=P_{i} / P_{j}\)
    The volume ratio is measured as described in

Section 2.6.1 using a ratio of low pressures in an expansion $\left(P^{i} / P^{j}\right)$. The uncertainty in the pressure measurements is 0.1\% based on the measured accuracy of the transducer. The uncertainty in both the volume ratio and the pressure ratio is $0.14 \%$. The uncertainty in $Z$ is therefore $0.2 \%$.
ii. Uncertainty in the values of the isothermal compressibility coefficient $1 / K$ is calculated based on its definition:

$$
I / K=\rho \frac{d P}{d \rho}
$$

The density $\rho$ is calculated from the following expression:

$$
\rho=\frac{\mathrm{P}}{\mathrm{ZRT}}
$$

The uncertainties in the density, $d P / d \rho$, and $l / K$ are $0.22 \%, 0.49 \%$, and $0.54 \%$ respectively.
iii. Uncertainty in the speed of sound measurements. The speed of sound values are calculated from:

$$
a=x / t, \quad x \text { in } m m, \text { and } t \text { in } \mu s
$$

The uncertainties in the measurements of length and time are $0.066 \%$ and $0.31 \%$ respectively. For the observed values of speed of sound, the uncertainty is
therefore 0.31\%.
iv. Uncertainty in the calculated ratio of specific heats from measured properties can be estimated considering the expression for ( $\mathrm{Cp} / \mathrm{Cv}$ ) :

$$
(\mathrm{Cp} / \mathrm{Cv})=\mathrm{a}^{2} \rho \mathrm{~K} \quad \ldots .2 .15
$$

The uncertainty in ( $C P / C v$ ) calculated from the parameters in the expression above is $0.59 \%$

Table 2.1 UNCERTAINTIES IN THE OBSERVED VALUES

## Property

Speed of sound
Compressibility factor
Density
Isot. Compr. Coeff
Ratio of Specific heats

Uncertainty
$0.31 \%$
$0.20 \%$
$0.22 \%$
$0.54 \%$
$0.59 \%$

## OBSERVATIONS

3.1 SUMMARY OF OBSERVATIONS

The tables and figures presented here contain experimental values exclusively. These thermodynamic property data are determined by methods described earlier from the primary measurements. All data are related to pressure on the $0{ }^{\circ} \mathrm{C}$ isothermal and are fitted by third degree polynomials in pressure using the method of least squares. The data are presented in 25 figures and 15 tables.

The body of results is presented in 5 groups, each corresponding to a different mixture, from pure Nitrogen to pure Argon. Each group consists of a table of experimental data, a table of thermal properties ( $Z$ and $K$ ), a table of caloric properties $(a$ and $(C p / C v))$, and 6 graphs depicting $Z, \rho, K, a$, and $(C p / C v)$.
3.2 COMPARISON WITH DATA FROM OTHER SOURCES. The data available for comparison are sparse, however, they confirm the results obtained in this study. Crain and Sonntag $\langle 3\rangle$ give $Z$ and density data for Nitrogen and Argon, as well as for approximately the same mixture compositions adopted here. Contributions from R. B.

Stewart $\langle 47,48\rangle$ for $Z$, density, and for ( $C p / C v$ ) in pure Nitrogen and Argon are also included, no $K$ data were available for comparison.

Speed of sound data for Nitrogen and Argon according to El-Hakeen $\langle 16,17\rangle$ and M. A. Sharif <41> are also presented for comparison.

### 3.2.1 COMPRESSIBILITY FACTOR

Figure 3.1.1 shows $Z$ vs. $P$ for pure Nitrogen. It can be seen the Crain and Sonntag values differ by no more $0.3 \%$ at 25 MPa .

Figure 3.5 .1 shows $Z$ vs. $P$ for pure Argon. The agreement is good in general. The last observed data point, at 30 MPa , seems to be in error, generating an uncertainty in the fitted curve. (This data point was kept in the graph for consistency of presentation). Inspection of the graph shows a remarkable agreement, except for the last data point.

The mixtures referred to in the data obtained from the literature for comparison differ slightly in composition from the mixtures tested in this investigation. The analysis of the results should therefore be made more on a qualitative basis than a quantitative one.

Figure 3.2 .1 shows $Z$ vs. $P$ for a mixture of $85.6 \%$ $\mathrm{N}_{2}$ and $14.4 \% \mathrm{Ar}$. Some divergency, of the order of $0.4 \%$ is evident at 15 MPa , otherwise the agrement is excellent.

Figure 3.3 .1 shows $Z$ vs. $P$ for a mixture of $52.4 \%$ $N_{2}$ and 47.6\% Ar. Maximum departure from the comparison data in the literature is noted to be of the order of $0.2 \%$ maximum at 20 MPa .

Figure 3.4 .1 shows $Z$ vs. $P$ for a mixture of $22.5 \%$ $N_{2}$ and $77.5 \% \mathrm{Ar}$. A relatively higher discrepancy , of about $0.5 \%$ is noted at 16 MPa .

### 3.2.2 ISOTHERMAL COMPRESSIBILITY COEFFICIENT

For clarity, the inverse of the isothermal compressibility coefficient, was chosen for presentation. This variable $1 / K$ is proportional to, and is expressed in the same units as the pressure $P$. It can be shown that:

$$
1 / \mathrm{K}=\rho(\mathrm{dP} / \mathrm{d} \rho) \quad \ldots . .3 .1
$$

or

$$
1 / K=\rho R T(Z+\rho \mathrm{dz} / \mathrm{d} \rho) \text { or } \mathrm{P}(1+(\rho / Z) \mathrm{dz} / \mathrm{d} \rho) \quad \ldots .3 .2
$$

For comparison purposes the plots of $1 / \mathrm{K}$, Figures 3.1.3, $3.2 .3,3.3 .3,3.4 .3$, and 3.5 .3 , include the values calculated from two independent measurements, that is, expression 3.1 , which is based on the fitted $Z$ data, and by expressions 2.5 and 2.6 which are based on the measurements of $P$ and $V$. Section 2.3 .1 presents the details of this computation. (Figures 3.1.3, 3.2.3, 3.3.3, 3.4.3, 3.5.3)

It can be seen from the functional form of $1 / K$, (Expression 3.2) that the slope of the curve must
approximate unity as pressure decreases. Accordingly, the coefficient of $P$ in the equation of the fitted curve presented in the figures, should closely approximate unity.

### 3.2.3 DENSITY

The data points shown in the graphs of density vs. $P$ were calculated from fitted points of the observed compressibility factor $Z$ data by making use of the expression:

$$
\rho=\mathrm{P} / \mathrm{RT} \mathrm{Z}
$$

.... 3.3
It is evident that as pressure $P$ tends to zero, the value of $d \rho / d P$ must tend to $1 / R T$. In the equations of the fitted curve presented in the graphs, the coefficient of $P$ is nearly equal to $1 / R T$ in all cases. This is an indication of the accuracy of the initial slope of the $\rho$ vs. $P$ curves. (The units of $I / R T$ and of the second coefficient of the equation describing the fit of the observed data are $\mathrm{s}^{2} / \mathrm{m}^{2} \times 1000$. The values of $1 / R T$ will be referred to in this section in these units.)

Figure 3.1.2 shows the density vs. pressure for pure Nitrogen. Density data from R. B. Stewart and from Crain-Sonntag are included for comparison. Deviations of the order of $10 \%$ maximum at 25 MPa are noted between the data from Crain-Sonntag and the observed fitted points. However, the observed data compares extremely well with the data from R. B. Stewart. The numerical value of $1 / R T$ which
is equal to 12.33493 compares well with the second coefficient 12.33 from the equation of the fitted curve.

Figure 3.2.2 shows density vs. pressure for a mixture of $85.6 \%$ nitrogen and $14.4 \%$ argon. The observed data correlates well with the data from Crain-Sonntag up to 15 MPa . Above this pressure, however, some divergency is present, with a maximum of $10 \%$ at 23 MPa . The value of $1 / R T$ is 12.9 and the second coefficient from the equation of the fitted curve is 12.8 which shows a very good agreement.

Figure 3.3.2 shows density vs. pressure for a mixture of $52.4 \%$ nitrogen and $47.6 \%$ argon. The data from Crain-Sonntag shows little difference from the observed data up to a pressure of 20 MPa . At 24 MPa , however, a departure of about $8 \%$ is observed. The calculation of $1 / R T$ gives 14.4 while the second coefficient of the equation of the fitted curve is l4.3. Again there is no significant difference between the two values.

Figure 3.4.2 shows density vs. pressure for a mixture of $22.5 \%$ nitrogen and $77.5 \%$ argon. There are no significant departures of the data from Crain-Sonntag from the observed data. The value of $1 / R T$ is 16.1 and the second coefficient of the equation of the fitted curve is 16.0 , which shows very good agreement.

Figure 3.5.2 shows density vs. pressure for pure argon. There are slight differences between the data from Crain-Sonntag and the observed values starting at 10 MPa.

These departures reach $6 \%$ at about 25 MPa . The value of the expression $1 / R T$ is 17.6 whereas the value of the second coefficient of the equation of the fitted data is 17.3 showing a departure in the slope of about $1.6 \%$.

### 3.2.4 SPEED OF SOUND

Figures $3.2 .4,3.3 .4$ and 3.4 .4 show the speed of sound for the mixtures containing mole fractions of $85.6 \%$, 52.4\% and $22.5 \%$ nitrogen respectively. The graphs also show a curve fitted to the observed data values. The sets of data present very little scatter (see Table 3.6).

The speed of sound data of the pure gases, nitrogen and argon, are presented in Figures 3.1.4 and 3.5.4, respectively. In these figures, the observed data is shown together with the data from El-Hakeen $\langle I 7\rangle$ and $M$. A. R. Sharif <4l>. The agreement is excellent throughout. The scatter in the observed data is clearly small.

### 3.2.5 RATIO OF SPECIFIC HEATS

The values of the observed ratio of specific heats presented in this work were calculated as decribed in 2.3.4 and equation 2.12. The results presented here compare well with the available data from the literature at low and moderately high pressures.

Figure 3.1.5 shows observed ratios of specific heats for pure Nitrogen. Data from R. B. Stewart <48> and
A. van Itterbeek <55> are presented for comparison. The agreement between observed data and data from other researchers is excellent up to 15 MPa . The intercept value of the fitted curve agrees with the ideal gas ratio of specific heats.

Figure $3.2 .5,3.3 .5$ and 3.4 .5 shows observed ratios of specific heats for mixtures containing nitrogen mole fractions of $85.6 \%$, $52.4 \%$ and 22.5\%. There are no data available for comparison with these observations.

Figure 3.5 .5 shows the observed ratios of specific heats for pure argon. The observed data agrees well with the data from R. B. Stewart <48> which was available for pressures up to 10 MPa . The intercept value coincides with the ratio of specific heats calculated for argon as an ideal gas.
3.3 STANDARD DEVIATION OF THE OBSERVED DATA

The tables presented here were calculated using expression 3.5 below. It contains the values of the normalized standard deviation determined from all data points, for the compressibility factor and the speed of sound of all gases concerned.
$s=\sqrt{\sum\left(\left(x-x^{\prime}\right) / x^{\prime}\right)^{2} /(n-1)}$
where $x^{\prime}$ is the fitted value.
The values of standard deviation for both
properties, are reasonably within the predicted uncertainty estimated (see Section 2.6.2) and indicate minimal scatter.

## Table 3.6

STANDARD DEVIATION OF OBSERVED COMPRESSIBILITY FACTOR DATA

| Pure Nitrogen | $-0.098 \%$ |
| :--- | :--- |
| $85.6 / 14.4 \% \mathrm{~N} 2 / \operatorname{Ar}$ | $0.091 \%$ |
| $52.4 / 47.6 \% \mathrm{~N} 2 / \mathrm{Ar}$ | $0.158 \%$ |
| $22.5 / 77.5 \% \mathrm{~N} 2 / \operatorname{Ar}$ | $0.151 \%$ |
| Pure Argon | $0.290 \%$ |

STANDARD DEVIATION OF OBSERVED SPEED OF SOUND DATA

| Pure Nitrogen | $0.207 \%$ |
| :--- | :--- |
| $85.6 / 14.4 \% \mathrm{~N} 2 / \mathrm{Ar}$ | $0.216 \%$ |
| $52.4 / 47.6 \% \mathrm{~N} 2 / \mathrm{Ar}$ | $0.324 \%$ |
| $22.5 / 77.5 \% \mathrm{~N} 2 / \operatorname{Ar}$ | $0.143 \%$ |
| Pure Argon | $0.321 \%$ |

Table 3.1.1
把PERIMENTAL VALUES USED IN DERIVATION OF COMP. FACTOR (Z) AND ISOT.COMP.COEF (K) TEMP. 273.15 K GAS COMP.NITROGEN $99.89 \%$

| P1i | P1f | P2i | $P 2 \mathrm{f}$ | Patm |
| :---: | :---: | :---: | :---: | :---: |
| $0.9499 \mathrm{E}+00$ | $0.7499 \mathrm{E}+00$ | 0.1000E-08 | 0.3406E-02 | 0.8853E-01 |
| $0.1204 \mathrm{E}+01$ | $0.8499 \mathrm{E}+00$ | 0.1000E-08 | 0.4120E-02 | $0.8853 \mathrm{E}-01$ |
| $0.1523 E+01$ | $0.1204 \mathrm{E}+01$ | 0.1000E-08 | 0.5113E-02 | 0.8854E-01 |
| $0.1923 \mathrm{E}+01$ | $0.1523 \mathrm{E}+01$ | 0.1000E-08 | 0.6347E-02 | $0.8858 \mathrm{E}-01$ |
| $0.2430 \mathrm{E}+01$ | $0.1923 E+01$ | 0.1000E-08 | 0.7878E-02 | 0.8857E-01 |
| $0.3072 \mathrm{E}+01$ | $0.2430 \mathrm{E}+01$ | 0.1000E-08 | 0.9814E-02 | 0.8855E-01 |
| $0.3882 \mathrm{E}+01$ | $0.3072 \mathrm{E}+01$ | 0.1000E-08 | 0.1225E-01 | 0.8352E-01 |
| $0.4903 \mathrm{E}+01$ | $0.3881 \mathrm{E}+01$ | $0.1000 \mathrm{E}-08$ | 0.1535E-01 | $0.8848 \mathrm{E}-01$ |
| $0.6195 \mathrm{E}+01$ | $0.4903 E+01$ | 0.1000E-08 | 0.1931E-01 | 0.8845E-01 |
| $0.6556 \mathrm{E}+01$ | $0.5188 \mathrm{E}+01$ | 0.1000e-08 | 0.2040E-01 | 0.8857E-01 |
| $0.7834 \mathrm{E}+01$ | $0.6195 \mathrm{E}+01$ | 0.1000ㅌ-08 | 0.2426E-01 | 0. 8 E25E-01 |
| $0.8300 \mathrm{E}+01$ | $0.6558 \mathrm{E}+01$ | 0.1000E-08 | 0.2563E-01 | 0.8357E-01 |
| $0.9932 E+01$ | $0.7834 \mathrm{E}+01$ | 0.1000E-08 | 0.3055E-01 | 0.8822E-01 |
| $0.1055 \mathrm{E}+02$ | $0.8300 \mathrm{E}+01$ | 0.1000E-08 | 0.3239E-01 | $0.8358 \mathrm{E}-01$ |
| $0.1268 \mathrm{E}+02$ | $0.9832 \mathrm{E}+01$ | 0.1000E-08 | 0.3852E-01 | 0.8823E-01 |
| $0.1348 \mathrm{E}+02$ | $0.1055 \mathrm{E}+02$ | 0.1000E-08 | 0.4089E-01 | $0.8857 \mathrm{E}-01$ |
| $0.1627 \mathrm{E}+02$ | $0.1266 E+02$ | 0.1000E-08 | $0.4861 \mathrm{E}-01$ | $0.8825 \mathrm{E}-01$ |
| $0.1741 \mathrm{E}+02$ | $0.1348 \mathrm{E}+02$ | 0.1000E-08 | 0.5161E-01 | $0.8855 \mathrm{E}-01$ |
| $0.2242 \mathrm{E}+02$ | $0.1696 E+02$ | 0.1000E-08 | 0.6352E-01 | 0.8824E-01 |
| $0.2290 \mathrm{E}+02$ | $0.1726 \mathrm{E}+02$ | 0.1000E-08 | $0.6467 \mathrm{E}-01$ | 0.8955E-01 |
| $0.3083 \mathrm{E}+02$ | 0.2246E+02 | 0.1000E-08 | 0.8099E-01 | 0.8826E-01 |
| $0.3136 \mathrm{E}+02$ | $0.2297 \mathrm{E}+02$ | 0.1000E-08 | 0.8249E-01 | 0.8935E-01 |
| $0.8048 \mathrm{E}+00$ | $0.3186 E+02$ | 0.1000E-08 | $0.1052 E+00$ | 0.8853E-01 |

Pli - initial pressure in $T$ tube
Pif - final pressure in $T$ tube and VZ
P2i - initial pressure in V2
p2f - final pressure in V2 and V3
ALL PRESSURES IN MPa.

Table 3.1.2


Table 3.1.3


Figure 3.1.1


Figure 3.1.2


Figure 3.1 .3


Figure 3.1.4


Figure 3.1.5


Table 3.2.1
EXPERIMENTAL VALUES USED IN DERIVATION OF COMP. FACTOR (Z) AND ISOT.COMP.COEF (K) TEMP. 273.15 K GAS COMP. $14.4 \%$ Ar $85.6 \%$ NZ

| P1i | P1 $\mathbf{I}$ | $P \mathcal{i}$ | $P \mathcal{I}$ | $P a t m$ |
| :---: | :---: | :---: | :---: | :---: |
| $0.8551 \mathrm{E}+00$ | $0.6641 \mathrm{E}+00$ | 0.1000E-08 | 0.2947E-02 | $0.8818 \mathrm{E}-01$ |
| $0.1088 E+01$ | $0.8551 \mathrm{E}+00$ | $0.1000 \mathrm{E}-08$ | 0.3680E-02 | $0.8818 \mathrm{E}-01$ |
| $0.1428 E+01$ | $0.1102 \mathrm{E}+01$ | 0.1000E-08 | 0.4626E-02 | 0.8821E-01 |
| $0.1838 \mathrm{E}+01$ | $0.1428 \mathrm{E}+01$ | 0.1000E-08 | 0.5867E-02 | $0.8825 \mathrm{E}-01$ |
| $0.2373 \mathrm{E}+01$ | $0.1842 E+01$ | $0.1000 \mathrm{E}-08$ | 0.7467E-02 | 0.9825E-01 |
| $0.3064 \mathrm{E}+01$ | $0.2373 E+01$ | 0.1000E-08 | $0.9513 \mathrm{E}-02$ | 0.8826E-01 |
| $0.3940 \mathrm{E}+01$ | $0.3064 \mathrm{E}+01$ | 0.1000E-08 | 0.1218E-01 | 0.8827E-01 |
| $0.5072 \mathrm{E}+01$ | $0.3840 E+01$ | 0.1000E-08 | $0.1556 \mathrm{E}-01$ | 0.8830E-01 |
| $0.6531 \mathrm{E}+01$ | $0.5072 \mathrm{E}+01$ | 0.1000E-08 | 0.1998E-01 | 0.8E32E-01 |
| 0.8420E+01 | $0.6531 E+01$ | 0.1000E-08 | $0.2568 \mathrm{E}-01$ | $0.8834 \mathrm{E}-01$ |
| 0.1089E+02 | $0.8420 \mathrm{E}+01$ | 0.1000E-08 | $0.3303 \mathrm{E}-01$ | $0.8835 \mathrm{E}-01$ |
| $0.1419 \mathrm{E}+02$ | $0.1080 \mathrm{E}+02$ | 0.1000E-08 | 0.4255E-01 | $0.8836 \mathrm{E}-01$ |
| $0.1872 \mathrm{E}+02$ | 0.1419E+02 | $0.1000 \mathrm{E}-08$ | 0.5470E-01 | $0.8838 \mathrm{E}-01$ |
| $0.2538 \mathrm{E}+02$ | $0.1872 \mathrm{E}+02$ | 0.1000E-08 | $0.7054 \mathrm{E}-01$ | 0.8844E-01 |
| $0.2611 \mathrm{E}+02$ | $0.1919 \mathrm{t}+02$ | 0.1000E-08 | $0.7217 \mathrm{E}-01$ | $0.8815 \mathrm{E}-01$ |
| $0.2611 \mathrm{E}+02$ | $0.2611 \mathrm{E}+02$ | 0.1000E-08 | $0.9301 \mathrm{E}-01$ | $0.8817 \mathrm{E}-01$ |
| , |  |  |  |  |
|  |  |  | . . |  |
|  |  |  | . |  |

Pli - initial pressure in tube
Plf - final pressure in $T$ tube and VZ
P2i - initial pressure in V2
PZf - final pressure in VZ and V3
ALL PRESSURES IN MPa.

Table 3.2 .2


Table 3.2 .3


Figure 3.2.1.


Figure 3.2 .2


Figure 3.2.3


Figure 3.2 .4


Figure 3.2.5



Table 3.3.1
EXPERIMENTAL VALUES USED IN DERIVATION OF COMP. FACTOR (Z) AND ISOT.COMP.COEF (K) TEMP. 273.15 K GAS COMP. $47.6 \%$ Ar $52.4 \% \mathrm{NZ}$

| P1 i | $P 1 \mathbf{f}$ | $P \geq$ i | $P \geq \mathbf{f}$ | $P a t m$ |
| :---: | :---: | :---: | :---: | :---: |
| $0.1026 \mathrm{E}+01$ | $0.8140 \mathrm{E}+00$ | 0.1000E-08 | $0.3694 \mathrm{E}-02$ | $0.8943 \mathrm{E}-01$ |
| $0.1290 \mathrm{E}+01$ | 0.1022E+01 | 0.1000E-08 | $0.4523 \mathrm{E}-02$ | 0.8944E-01 |
| 0.1623E+01 | 0.1290E+01 | 0.1000E-08 | $0.5514 \mathrm{E}-02$ | $0.8944 \mathrm{E}-01$ |
| $0.2033 E+01$ | $0.1623 E+01$ | 0.1000E-08 | 0.6848E-02 | 0.8945E-01 |
| $0.2554 \mathrm{E}+01$ | $0.2033 E+01$ | 0.1000E-08 | $0.8327 \mathrm{E}-02$ | $0.8945 \mathrm{E}-01$ |
| $0.3204 \mathrm{E}+01$ | $0.2554 E+01$ | 0.1000E-08 | 0:1043E-01 | $0.8945 \mathrm{E}-01$ |
| $0.4020 \mathrm{E}+01$ | $0.3204 \mathrm{E}+01$ | 0.1000E-08 | 0.1285E-01 | $0.8945 \mathrm{E}-01$ |
| $0.5038 E+01$ | $0.4020 \mathrm{E}+01$ | 0.1000E-08 | 0.1610E-01 | 0.8945E-01 |
| $0.6316 \mathrm{E}+01$ | $0.5045 \mathrm{E}+01$ | 0.1000E-08 | 0.2022E-01 | 0.8945E-01 |
| $0.7917 \mathrm{~F}+01$ | $0.6316 \mathrm{E}+01$ | $0.1000 \mathrm{E}-08$ | $0.2525 E-01$ | 0. E945E-01 |
| 0.9932E+01 | $0.7921 \mathrm{E}+01$ | 0.1000E-08 | $0.3166 E-01$ | 0.8948E-01 |
| $0.1247 E+02$ | $0.9935 E+01$ | 0.1000E-08 | 0.3868E-01 | 0.8948E-01 |
| $0.1580 \mathrm{t}+02$ | $0.1248 E+02$ | 0.1000E-08 | 0.4983E-01 | 0.8948E-01 |
| $0.2031 \mathrm{E}+02$ | $0.1583 \mathrm{E}+02$ | $0.1000 \mathrm{E}-08$ | 0.6283E-01 | 0.8950E-01 |
| $0.2330 \mathrm{E}+02$ | $0.1788 \mathrm{E}+02$ | 0.1000E-08 | 0.7107E-01 | $0.8943 \mathrm{E}-01$ |
| $0.2686 E+02$ | $0.2038 \mathrm{E}+02$ | 0.1000E-08 | 0.7818E-01 | 0.8951E-01 |
| $0.2690 E+02$ | $0.2690 \mathrm{E}+02$ | $0.1000 \mathrm{E}-08$ | $0.1001 E+00$ | 0.9943E-01 |
|  |  |  |  | - |

Pli - initial pressure in tube
Plf - final pressure in $T$ tube and V2
P2i - initial pressure in VZ
P2f - final pressure in V2 and V3
ALL PRESSURES IN MPa.

Table 3.3 .2
OBSERVED THERMAL PROPERTIES GAS COMPOSITION: $47.6 \%$ Ar $52.4 \%$ NZ ISOTHERMAL TEMPERATURE : 273.15 K

| $P$ | $\rho$ | $Z$ | K |
| :---: | :---: | :---: | :---: |
|  |  |  |  |
| $0.8140 \mathrm{E}+00$ | $0.1176 \mathrm{E}+02$ | $0.9939 \mathrm{E}+00$ | $0.1269 \mathrm{E}+01$ |
| $0.1022 \mathrm{E}+01$ | $0.1480 \mathrm{E}+02$ | $0.9936 \mathrm{E}+00$ | $0.1006 \mathrm{E}+01$ |
| $0.1290 \mathrm{E}+01$ | $0.1871 \mathrm{E}+02$ | $0.9900 \mathrm{E}+00$ | $0.7954 \mathrm{E}+00$ |
| $0.1623 \mathrm{E}+01$ | $0.2360 \mathrm{E}+02$ | $0.9886 \mathrm{E}+00$ | $0.6311 \mathrm{E}+00$ |
| $0.2033 \mathrm{E}+01$ | $0.2964 \mathrm{E}+02$ | $0.8862 \mathrm{E}+00$ | $0.5037 \mathrm{E}+00$ |
| $0.2554 \mathrm{E}+01$ | $0.3736 \mathrm{E}+02$ | $0.9850 \mathrm{E}+00$ | $0.4012 \mathrm{E}+00$ |
| $0.3204 \mathrm{E}+01$ | $0.4706 \mathrm{E}+02$ | $0.9815 \mathrm{E}+00$ | $0.3203 \mathrm{E}+00$ |
| $0.4020 \mathrm{E}+01$ | $0.5932 \mathrm{E}+02$ | $0.8745 \mathrm{E}+00$ | $0.2557 \mathrm{E}+00$ |
| $0.5045 \mathrm{E}+01$ | $0.7484 \mathrm{E}+02$ | $0.9698 \mathrm{E}+00$ | $0.2042 \mathrm{E}+00$ |
| $0.6316 \mathrm{E}+01$ | $0.9424 \mathrm{E}+02$ | $0.9621 \mathrm{E}+00$ | $0.1632 \mathrm{E}+00$ |
| $0.7921 \mathrm{E}+01$ | $0.1189 \mathrm{E}+03$ | $0.9573 \mathrm{E}+00$ | $0.1299 \mathrm{E}+00$ |
| $0.9935 \mathrm{E}+01$ | $0.1498 \mathrm{E}+03$ | $0.9538 \mathrm{E}+00$ | $0.1027 \mathrm{E}+00$ |
| $0.1249 \mathrm{E}+02$ | $0.1887 \mathrm{E}+03$ | $0.9518 \mathrm{E}+00$ | $0.8022 \mathrm{E}-01$ |
| $0.1583 \mathrm{E}+02$ | $0.2383 \mathrm{E}+03$ | $0.9549 \mathrm{E}+00$ | $0.6100 \mathrm{E}-01$ |
| $0.1798 \mathrm{E}+02$ | $0.2691 \mathrm{E}+03$ | $0.9578 \mathrm{E}+00$ | $0.5217 \mathrm{E}-01$ |
| $0.2038 \mathrm{E}+02$ | $0.3020 \mathrm{E}+03$ | $0.9735 \mathrm{E}+00$ | $0.4448 \mathrm{E}-01$ |

Table 3.3 .3


Figure 3.3.1


Figure 3.3.2


Figure 3.3.3


Figure 3.3.4


Figure 3.3 .5


Table 3.4.1
EXPERIMENTAL VALUES USED IN DERIVATION OF COMP. FACTOR (Z) AND ISOT.COMP.COEF (K) TEMP.-273.15 K GAS COMP.:77.5\% Ar $22.5 \%$ N2


Pli - initial pressure in $T$ tube
Pif - final pressure in $T$ tube and VZ
P2i - initial pressure in V2
P2f - final pressure in $V 2$ and V3
ALL PRESSURES IN MPa.

Table 3.4.2
OBSERVED THERMAL PROPERTIES GAS COMPOSITION• $77.5 \%$ AT $22.5 \% \mathrm{NZ}$ ISOTHERMAL TEMPERATURE : 273.15 K


Table 3.4 .3
OBSERVED CALORIC PROPERTIES GAS COMPOSITION: $77.5 \%$ Ar $22.5 \%$ NZ ISOTHERMAL TEMPERATURE - 273.15 K

| $P$ | $\rho$ | $a$ | $\gamma$ |
| :---: | :---: | :---: | :---: |
|  |  |  |  |
| $0.2206 E+00$ | $0.3495 E+01$ | $0.3125 E+03$ | $0.1562 E+01$ |
| $0.2344 E+00$ | $0.3715 E+01$ | $0.3125 E+03$ | $0.1582 \mathrm{E}+01$ |
| $0.3654 \mathrm{E}+00$ | $0.5799 \mathrm{E}+01$ | $0.3125 \mathrm{E}+03$ | $0.1567 \mathrm{E}+01$ |
| $0.3930 \mathrm{E}+00$ | $0.6239 \mathrm{E}+01$ | $0.3125 \mathrm{E}+03$ | $0.1568 \mathrm{E}+01$ |
| $0.5309 \mathrm{E}+00$ | $0.8441 \mathrm{E}+01$ | $0.3125 \mathrm{E}+03$ | $0.1573 \mathrm{E}+01$ |
| $0.6964 \mathrm{E}+00$ | $0.1109 \mathrm{E}+02$ | $0.3138 \mathrm{E}+03$ | $0.1579 \mathrm{E}+01$ |
| $0.1413 \mathrm{E}+01$ | $0.2269 \mathrm{E}+02$ | $0.3138 \mathrm{E}+03$ | $0.1605 \mathrm{E}+01$ |
| $0.2131 \mathrm{E}+01$ | $0.3445 \mathrm{E}+02$ | $0.3152 \mathrm{E}+03$ | $0.1630 \mathrm{E}+01$ |
| $0.3516 \mathrm{E}+01$ | $0.5761 \mathrm{E}+02$ | $0.3166 \mathrm{E}+03$ | $0.1679 \mathrm{E}+01$ |
| $0.5192 \mathrm{E}+01$ | $0.8622 \mathrm{E}+02$ | $0.3186 \mathrm{E}+03$ | $0.1738 \mathrm{E}+01$ |
| $0.6950 \mathrm{E}+01$ | $0.1168 \mathrm{E}+03$ | $0.3207 \mathrm{E}+03$ | $0.1800 \mathrm{E}+01$ |
| $0.1051 \mathrm{E}+02$ | $0.1798 \mathrm{E}+03$ | $0.3279 \mathrm{E}+03$ | $0.1926 \mathrm{E}+01$ |
| $0.1382 \mathrm{E}+02$ | $0.2380 \mathrm{E}+03$ | $0.3417 \mathrm{E}+03$ | $0.2040 \mathrm{E}+01$ |
| $0.1724 \mathrm{E}+02$ | $0.2969 \mathrm{E}+03$ | $0.3567 \mathrm{E}+03$ | $0.2149 \mathrm{E}+01$ |
| $0.2068 \mathrm{E}+02$ | $0.3533 \mathrm{E}+03$ | $0.3750 \mathrm{E}+03$ | $0.2237 \mathrm{E}+01$ |
| $0.2324 \mathrm{E}+02$ | $0.3922 \mathrm{E}+03$ | $0.3800 \mathrm{E}+03$ | $0.2276 \mathrm{E}+01$ |

Figure 3.4.1


Figure 3.4.2


Figure 3.4.3


Figure 3.4.4


Figure 3.4 .5


Table 3.5.1
EXPERIMENTAL VALUES USED IN DERIVATION OF COMP. FACTOR (Z) AND ISOT.COMP.COEF (K) TEMP. 273.15 K GAS COMP.. ARGON $99.99 \%$


Pli - initial pressure in T tube
P1f - final pressure in $T$ tube and VZ
P2i - initial pressure in VZ
P2f - final pressure in V2 and V3
ALL PRESSURES IN MPa.

Table 3.5 .2
OBSERVED THERMAL PROPERTIES
GAS COMPOSITION: ARGON $99.99 \%$ ISOTHERMAL TEMPERATURE: 273.15 K

| $P$ | $\rho$ | $Z$ | K |
| :---: | :---: | :---: | :---: |
|  |  |  |  |
| $0.2130 \mathrm{E}+01$ | $0.3820 \mathrm{E}+02$ | $0.9768 \mathrm{E}+00$ | $0.4851 \mathrm{E}+00$ |
| $0.2762 \mathrm{E}+01$ | $0.4982 \mathrm{E}+02$ | $0.8726 \mathrm{E}+00$ | $0.3749 \mathrm{E}+00$ |
| $0.3818 \mathrm{E}+01$ | $0.6950 \mathrm{E}+02$ | $0.9699 \mathrm{E}+00$ | $0.2724 \mathrm{E}+00$ |
| $0.4895 \mathrm{E}+01$ | $0.8988 \mathrm{E}+02$ | $0.8601 \mathrm{E}+00$ | $0.2134 \mathrm{E}+00$ |
| $0.6222 \mathrm{E}+01$ | $0.1154 \mathrm{E}+03$ | $0.9535 \mathrm{E}+00$ | $0.1687 \mathrm{E}+00$ |
| $0.7886 \mathrm{E}+01$ | $0.1479 \mathrm{E}+03$ | $0.9403 \mathrm{E}+00$ | $0.1336 \mathrm{E}+00$ |
| $0.9990 \mathrm{E}+01$ | $0.1895 \mathrm{E}+03$ | $0.8236 \mathrm{E}+00$ | $0.1055 \mathrm{E}+00$ |
| $0.1094 \mathrm{E}+02$ | $0.2084 \mathrm{E}+03$ | $0.9209 \mathrm{E}+00$ | $0.9618 \mathrm{E}-01$ |
| $0.1270 \mathrm{E}+02$ | $0.2436 \mathrm{E}+03$ | $0.9160 \mathrm{E}+00$ | $0.8225 \mathrm{E}-01$ |
| $0.1387 \mathrm{E}+02$ | $0.2669 \mathrm{E}+03$ | $0.9125 \mathrm{E}+00$ | $0.7479 \mathrm{E}-01$ |
| $0.1620 \mathrm{E}+02$ | $0.3131 \mathrm{E}+03$ | $0.9083 \mathrm{E}+00$ | $0.6277 \mathrm{E}-01$ |
| $0.1765 \mathrm{E}+02$ | $0.3415 \mathrm{E}+03$ | $0.8094 \mathrm{E}+00$ | $0.5671 \mathrm{E}-01$ |
| $0.1917 \mathrm{E}+02$ | $0.3705 \mathrm{E}+03$ | $0.9098 \mathrm{E}+00$ | $0.5126 \mathrm{E}-01$ |
| $0.2307 \mathrm{E}+02$ | $0.4421 \mathrm{E}+03$ | $0.9210 \mathrm{E}+00$ | $0.4032 \mathrm{E}-01$ |

[^0]Table 3.5 .3


Figure 3.5.1


Figure 3.5.2


Figure 3.5.3


Figure 3.5.4


Figure 3.5 .5


## EQUATIONS OF STATE FOR DENSE GASES

4.1 EQUATIONS OF STATE

An equation of state, more properly, a thermal equation of state for gases is any suitable function $f(P, V, T)=0$ which provides one of the properties concerned in terms of the other two. The large number of equations of state proposed over the past century is a clear indication that all dense gas equations of state remain suspect in functional form and imprecise in regard to certain properties or at certain pressures. These equations can be divided into families, according to their functional forms, with the main ones being the two-constant equation, the multiple-constant equation and the virial equation family.
4.2 TWO CONSTANT EQUATIONS OF STATE

Most two-constant equations of state are extensions of the Van der Wals equation introduced in 1873.

The general form of this equation is:

$$
P=R T /(v-b)-a / v^{2}
$$

This equation takes into account repulsive and attractive forces between molecules in its two separate terms and uses the critical point properties, ( $P_{C}, V_{C}, T_{C}$ ) to define the constants "a" and "b". These constants are defined by noting that the critical isotherm passes through a point of inflection at the critical point $\left(P_{C}, V_{C}\right)$. The requirements $\left(d P / \partial V=0=d^{2} P / \partial V^{2}\right)$ at $P_{C}, V_{c}$ define "a" and "b" as follows:

$$
b=R T_{C} / 8 P_{C} ; a=27\left(R T_{C}\right)^{2} / 64 P_{C} \quad \ldots 44.2
$$

The Redlich-Kwong equation of state
introduced modifications to the second term of the Van der Waals equation, so as to allow for temperature dependence, viz;

$$
P=R T /(v-b)-a /\left(T^{1 / 2} v(v+b)\right)
$$

The most widely used form of the Redlich-Kwong equation includes a further modification introduced by Georgio Soave in $1972\langle 46\rangle$. The term $\left(a / T^{1 / 2}\right.$ ) was replaced by a general temperature dependent term $a(T)$. The resultant form of the equation becomes:

$$
P=R T /(v-b)-a(T) /(v(v+b))
$$

where $a(T)=a_{i} a\left(T_{r}, w\right)$

The parameters for the $i^{\text {th }}$ component of a mixture can be written as follows:

$$
\begin{array}{cc}
a_{i}=a_{i}\left(T_{C}\right) a_{i}\left(T_{r}, W\right) & \ldots 4.5 \\
b_{i}=0.08664 R_{C} / P_{C} & \ldots 4.6 \\
& a_{i}\left(T_{C}\right)=0.42747 \mathrm{R}^{2} T_{C}^{2} / P_{C} \\
& a_{i}\left(T_{r}, w\right)=\left(1+m\left(1-T_{r} 1 / 2\right)\right)^{2} \\
\text { and } & m=0.480+1.574 \mathrm{w}-0.176 \mathrm{w}^{2}
\end{array}
$$

in which $w$ is the acentric factor $\langle 46\rangle$.
This equation uses the Van der Waals mixing rules for an n-component mixture which can be stated as: $\langle 37,46,53\rangle$

$$
\begin{array}{cc}
a_{m}=\sum \sum x_{i} x_{j} a_{i j} & \ldots 44.10 \\
a_{i j}=\left(a_{i} a_{j}\right)^{1 / 2}\left(1-\delta_{i j}\right) & \ldots 4.11
\end{array}
$$

where $\boldsymbol{\delta}_{i j}$ is the binary interaction coefficient.
and

$$
\mathrm{b}=\Sigma \mathrm{x}_{\mathrm{i}} \mathrm{~b}_{\mathrm{i}}
$$

$$
\ldots 4.12
$$

An important modification of the attractive term of the Redlich-Kwong equation (in reality a modification to the Van der Waals equation) is that by Peng and Robinson (1976) with their addition of the term $b(v-b)$ in the denominator $\langle 33,34,35,36\rangle$. The Peng-Robinson equation <34> of state therefore appears as follows:

$$
P=R T /(v-b)-a(T) / i(v(v+b)+b(v-b)))
$$

where $\quad a(T)=0.45724 R^{2} T_{C}{ }^{2} / P_{C}$ and $b=0.07780 R T_{C} / P_{C}$

The parameters for the $i^{\text {th }}$ component of a mixture can be written as follows:

$$
\begin{array}{rc}
a_{i}\left(T_{C}\right)=0.45724 R_{T}^{2} T_{C}^{2} / P_{C} & \ldots 44.14 \\
a_{i}=a_{i}\left(T_{C}\right) a\left(T_{r}, W\right) & \ldots .4 .15 \\
b_{i}=0.07780 R T_{C} / P_{C} & \ldots 4.16 \\
a_{i}\left(T_{r i}, w\right)=\left(I+m_{i}\left(1-T_{r} 1 / 2\right)\right)^{2} & \ldots 4.17
\end{array}
$$

and

$$
m=0.37464+1.54226 w-0.26992 w^{2}
$$

The mixing rules used in determining the parameters for an $n$-component mixture using this equation are:

$$
\begin{aligned}
& a=\Sigma \Sigma x_{i} x_{j} a_{i j} \\
& b=\Sigma x_{i} b_{i}
\end{aligned}
$$

in which:

$$
a_{i j}=\left(1-\delta_{i j}\right) a_{i}^{1 / 2} a_{j}^{1 / 2}
$$

and $\delta_{i j}$ is is an empirically determined binary interaction coefficient related to components i and j.

These equations may be called attracting hard sphere equations of state since the repulsive term is fixed.

### 4.3 MULTIPLE CONSTANT EQUATIONS OF STATE

Multiple-constant equations of state, such as the 8-constant Benedict-Webb-Rubin equation, are virtually 'fits' to observed data.

The Benedict-Webb-Rubin equation of state $\langle 1,18,23\rangle$ has the form:

$$
\begin{align*}
& \mathrm{P}=\rho_{\mathrm{RT}}+\left(\mathrm{B}_{\mathrm{O}} \mathrm{RT}-\mathrm{A}_{\circ}-\mathrm{C}_{\mathrm{O}} / \mathrm{T}^{2}\right) \rho^{2}+(\mathrm{BRT}-\mathrm{A}) \rho^{3}+\mathrm{A} a \rho^{6}+ \\
& +\mathrm{C} \rho^{3}\left(1+\boldsymbol{\gamma} \rho^{2}\right) \mathrm{e}^{-\boldsymbol{\gamma} \rho^{2} / \mathbb{T}^{2}}
\end{align*}
$$

The set of constants derived from observed data may not be unique in the sense that several sets of
constants can represent the data.
The mixing rules which make use of the parameters of the single components can be written as 〈l>:

$$
\begin{aligned}
& B_{o}=(1 / 8) \sum \sum X_{i} X_{j}\left(B_{o i}^{l / 3}+B_{o j}^{l / 3}\right)^{3} \quad \ldots 4.23 \\
& A_{0}=\left(\sum_{x_{i}}\left(A_{0 i}\right)^{I / 2}\right)^{2} \quad \ldots . .4 .24 \\
& C_{0}=\left(\Sigma x_{i}\left(C_{0 i}\right)^{1 / 2}\right)^{2} \ldots 4.25 \\
& B=\left(\Sigma x_{i}\left(B_{i}\right)^{1 / 3}\right)^{3} \quad \ldots . .4 .26 \\
& A=\left(\Sigma \mathrm{x}_{\mathrm{i}}\left(\mathrm{~A}_{\mathrm{i}}\right)^{1 / 3}\right)^{3} \quad \ldots . .4 .27 \\
& C=\left(\Sigma \mathrm{x}_{\mathrm{i}}\left(\mathrm{C}_{\mathrm{i}}\right)^{\mathrm{l} / 3}\right)^{3} \quad \ldots .{ }^{4.28} \\
& \boldsymbol{a}=\left(\Sigma_{\mathrm{x}_{\mathrm{i}}}\left(\boldsymbol{a}_{\mathrm{i}}\right)^{1 / 3}\right)^{3} \quad \ldots \ldots \text {... } 4.29 \\
& \boldsymbol{\gamma}=\left(\boldsymbol{\Sigma} \mathrm{x}_{\mathrm{i}}\left(\boldsymbol{\gamma}_{\mathrm{i}}\right)^{1 / 2}\right)^{2} \\
& \text {.... } 4.30
\end{aligned}
$$

Also worthy of mention is a related member of the multiple-constant family of equations of state, the 5-constant Beattie-Bridgeman equation (1927)<18>, which has the form:

$$
P v^{2}=R T\left(1-c / v T^{3}\right)\left(v+B_{o}-b B_{0} / v\right)-A_{0}(1-a / v)
$$

4.4 THE VIRIAL EQUATION OF STATE

The virial equation of state expresses the compressibility factor $Z$ of $a \operatorname{las}$ as a power series. in density called the Leiden form, and as a power series in pressure called the Berlin form.

The Leiden <53> form of the virial equation of state is as follows:

$$
Z=I+B(T) / v+C(T) / v^{2}+D(T) / v^{3}+\ldots . \ldots 4.32
$$

The temperature dependent coefficients $B(T), C(T)$, etc, have their formulation in statistical mechanics applied to molecular collisions controlled by an assumed functional form of the intermolecular force. This functional form contains (in the Lennard-Jones force model), two unknown constants. These are determined from moderately non-ideal gas data. .

The range of applicability of the virial equation of state is'restricted to moderate densities because the higher virial coefficients remain unknown. The coefficients of the series are functions of both temperature and molecular co-volume "b", which is dependent only on the low-velocity collision diameter of the molecules.

Various intermolecular potential energy functions have been proposed including the non-attractive hard sphere potential, the Sutherland potential, the Buckingham potential, and the Lennard-Jones (6-12) potential.

For the hard sphere potential, the calculated second, third and fourth virial coefficients take the form:

$$
\begin{array}{ll}
B=(2 \Pi / 3) N_{a} \sigma_{h}^{3}=b_{h} & \ldots 4.33 \\
C=0.625 b_{h}^{2}
\end{array}
$$

$$
\mathrm{D}=0.2869 \mathrm{~b}_{\mathrm{h}}^{3}
$$

where $b_{h}$ is the hard sphere co-volume and $N_{a}$ is the number of molecules in the system.

The Lennard-Jones (6-12) function for the potential energy between a pair of like molecules is:

$$
\varphi(r)=4 \mathrm{k} \theta\left(\left(\sigma_{\mathrm{LJ}} / r\right)^{12}-\left(\sigma_{\mathrm{LJ}} / r\right)^{6}\right) \quad \ldots .4 .36
$$

where $k$ is the Boltzmann constant and $\sigma_{\text {LJ }}$ is the low velocity collision diameter. The term $k \theta$ is the minimum potential energy and is located at $r=2^{1 / 6} \sigma_{\text {LJ }}$. The constants $\sigma_{I J}$ and $\theta$ are characteristic of the chemical species of the colliding molecules, and when determined from equation of state data ( $P, V, T$ ) completely define, in principle, the equation of state of the gas concerned.

The generalized universal second ( ${ }^{*}$ ) and third (C*) virial coefficients and their temperature derivatives for the Lennard-Jones potential (6-12) are tabulated as a function of $T^{*}(T / \theta)\langle 18\rangle$. Their definitions are:

$$
B^{*}\left(T^{*}\right)=B(T) / b_{L J}
$$

$C^{*}\left(T^{*}\right)=C(T) / b_{L J}{ }^{2}$
$B_{n}^{*}\left(T^{*}\right)=T^{*}{ }^{n}\left(d^{n} B^{*} / \mathrm{CT}^{*}{ }^{*}\right)$

$$
C_{n}^{*}\left(T^{*}\right)=T^{*} n\left(d^{n} C^{*} / d T^{*} n\right)
$$

where $b_{L J}$ is the co-volume ( 4 times the volume of 1 mole of molecules) defined for a molar system as:
$\mathrm{b}=4 \mathrm{~N}_{\mathrm{a}}(4 / 3) \pi\left(\sigma_{\mathrm{LJ}} / 2\right)^{3}=(2 \pi / 3) \mathrm{N}_{\mathrm{a}} \sigma_{\mathrm{LJ}}{ }^{3} \quad \ldots 4.41$ when $N_{a}$ is the Avogadro number and $\sigma_{\text {IJ }}$ is the "low velocity collision diameter" of the molecule.

In this study, a "hybrid" virial equation of state is used for comparison with observations. This equation designed by Groves 〈I4〉, makes use of the second and third terms of the virial equation determined from the soft-molecule Lennard-Jones (6-12) potential and of the fourth and fifth term of the rigid sphere potential. The hybrid virial equation of state then has the functional form:

$$
\mathrm{Z}=1+\mathrm{B}^{*}\left(\mathrm{~T}^{*}\right) \mathrm{w}_{\mathrm{LJ}}+\mathrm{C}^{*}\left(\mathrm{~T}^{*}\right) \mathrm{w}_{\mathrm{LJ}}^{2}+0.2869 \mathrm{w}_{\mathrm{h}}^{3}+0.115 \mathrm{w}_{\mathrm{h}}^{4}
$$

where $w$ is the dimensionless density defined as $w=b_{L J} / v$ for the Lennard-Jones potential and $w=b_{h} / v$ for the rigid sphere potential. The hard-molecule co-volume is determined by defining the hard molecule diameter $\sigma_{h}$ to be equal to the most probable distance of closest approach of two molecules in a collision. Accordingly, from the $L J(6-12)$
potential relation:

$$
b_{h} / b_{I J J}=w_{h} / w_{L J}=\left(2 /\left(1+\sqrt{1+T^{*}}\right)\right)^{1 / 2}
$$

The mixing rules, used to determine the coefficients, define a mixture-representative hypothetical pure gas having the potential constants $\sigma_{\text {LJ (mix) }}$ and $\theta_{\text {LJ (mix) }}$. Once $\sigma_{\mathrm{IJ}(\mathrm{mix})}$ and $\boldsymbol{\theta}_{\text {(mix) }}$ are established, the parameters $b_{I J}(m i x)$ and $T^{*}$ (mix) are calculated according to their definitions given above and the virial coefficients are then determined.

The mixing rules for an $n$-component mixture are as
follows:

$$
\sigma_{(\text {mix })}=\Sigma_{j} \Sigma_{i} x_{i} x_{j}\left(\sigma_{i j}\right)
$$

and

$$
\theta_{(\text {mix })}=\Sigma_{j} \Sigma_{i x_{i} x_{j}} \theta_{i j}
$$

where: $\quad \theta_{i j}=\left(\theta_{i} \theta_{j}\right)^{1 / 2}$
and $\quad \sigma_{i j}=\left(\sigma_{i i}+\sigma_{j j}\right) / 2$
.... 4.47

## CHAPTER V

## RESULTS FROM THE SELECTED EQUATIONS OF STATE

5.1 INTRODUCTION

This chapter presents the predictions from each of the equations of state under investigation. The properties $Z, K, a$ and $(C p / C v)$ were calculated for each equation and are presented in graphs together. with fitted observed data. Tables of percentage error in the prediction of the properties $Z, a$ and ( $\mathrm{Cp} / \mathrm{Cv}$ ) are provided in Section 5.3. In Section 5.4, the virial form of these equations is derived and the coefficients calculated for each one. of the mixtures. Virial coefficients are also estimated from the observed fitted data for comparison.
5.2 COMPARISON GRAPHS

The comparison graphs are organized in 5 groups covering the gases concerned, from pure nitrogen, to pure argon. Each group contains 4 plots of the properties $Z, K$, a, and (Cp/Cv), Figures 5.1.1 to 5.5 .5 respectively.
5.3 TABLE OF PERCENTAGE ERRORS

Tables 5.1 to 5.4 below, show the percentage error in the prediction of properties $Z, a$, and ( $C p / C v$ ), in comparison with the observed data. The errors were
calculated for 5 pressures in the range from 5 to 25 MPa and for each of the gases.
5.4 VIRIAL FORM OF THE SELECTED EQUATIONS OF STATE

The derived virial form of each one of the selected equations of state used in this study are presented below. The coefficients in the tables that follow each derivation are calculated directly from the equations and incorporate the parameter (b) as defined in each equation. A direct comparison of coefficients between equations and for each gas can therefore be made once $Z$ is expressed as a function of molar density in every case.

Only the second virial coefficients were calculated for the Benedict-Webb-Rubin equation of state case. The third and fourth coefficients involve complex functions of density, and are not presented here.

The coefficients obtained from the least squares fit of the observed compressibility factor data are shown in section 5.4.5. These are coefficients of the data in virial form, and can be used in a qualitative way to show the major points of divergency between the values predicted from the various equations of state and the observed data.

### 5.4.1 THE HYBRID VIRIAL EQUATION OF STATE

$Z=I+B{ }^{*} b \rho+C b^{*} \rho^{2}+0.2869 b_{h}^{3} \rho^{3}+0.115 b_{h}^{4} \rho^{4} \quad \ldots 5.1$
Values of the second, third, fourth and fifth coefficients of the hybrid virial equation.

For pure Nitrogen:

$$
-359.62 \times 10^{-6} 1.856 \times 10^{-6} 1.828 \times 10^{-9} 1.360 \times 10^{-12}
$$

For a $85.6 \% / 14.4 \%$ N2/Ar mixture:

$$
-402.86 \times 10^{-6} 1.560 \times 10^{-6} 1.432 \times 10^{-9} .0 .951 \times 10^{-12}
$$

For a $52.4 \% / 47.6 \% \mathrm{~N} 2 / \operatorname{Ar}$ mixture:

$$
-476.10 \times 10^{-6} 1.070 \times 10^{-6} 0.793 \times 10^{-9} 0.433 \times 10^{-12}
$$

For a $22.5 \% / 77.5 \%$ N2/Ar mixture:
$-517.51 \times 10^{-6} 0.781 \times 10^{-6} 0.480 \times 10^{-9} 0.221 \times 10^{-12}$
For pure Argon:
$-538.64 \times 10^{-6} \quad 0.623 \times 10^{-6} 0.333 \times 10^{-9} 0.136 \times 10^{-12}$
5.4.2 THE VIRIAL FORM OF THE BENEDICT-WEBB-RUBIN EQUATION OF STATE
$Z=P V / R T=.1+\left(B_{0}-A_{0} / R T-C_{0} / R T^{3}\right) \rho+\left(B-A / R T+C / R T^{3} e^{-\gamma \rho^{2}}\right) \rho^{2}$.
$+\left(\mathrm{C} / \mathrm{RT}^{3}\right) \mathrm{e}^{-\gamma \rho^{2}} \rho^{4}+a \mathrm{~A} \rho^{5} / \mathrm{RT}$

The values of the second virial coefficient for the various mixtures follows:

$$
\begin{aligned}
& \text { Pure Nitrogen }-395.80 \times 10^{-6} \\
& 85.6 \% \text { Nitrogen }-415.96 \times 10^{-6} \\
& 52.4 \% \text { Nitrogen }-465.84 \times 10^{-6} \\
& 22.5 \% \text { Nitrogen }-515.59 \times 10^{-6} \\
& \text { Pure Argon } \\
& -558.59 \times 10^{-6}
\end{aligned}
$$

5.4.3 VIRIAL FORM OF THE REDLICH-KWONG-SOAVE EQUATION OF STATE

$$
\begin{aligned}
& P=\frac{R T}{V-b}-\frac{a(T)}{V(v+b)} \\
& Z=\frac{1}{1-W}-\frac{a(T)}{R T b(1+W)} \\
& \text { call } F(T)=\frac{a(T)}{R T b}
\end{aligned}
$$

$$
\begin{aligned}
& Z=1+(1-F(T)) w+(1+F(T)) w^{2}+(1-F(T)) w^{3}+(1+F(T)) w^{4} \\
& \text { or: }
\end{aligned}
$$

$$
\begin{array}{r}
Z=1+(1-F(T)) b \rho+(1+F(T)) b^{2} \rho^{2}+(1-F(T)) b^{3} \rho^{3}+(1+F(T)) b^{4} \rho^{4} \\
\ldots .5 .3
\end{array}
$$

Values of the second, third, fourth and fifth coefficients of the virial form.

For pure Nitrogen:

$$
-0.0069 \quad 1.618 \times 10^{-3}-4.984 \times 10^{-6} \quad 1.159 \times 10^{-6}
$$

For a $85.6 \% / 14.4 \% \mathrm{~N} 2 / \mathrm{Ar}$ mixture:

$$
-0.0087 \quad 1.592 \times 10^{-3}-5.979 \times 10^{-6} \quad 1.085 \times 10^{-6}
$$

For a $52.4 \% / 47.6 \% \mathrm{~N} 2 /$ Ar mixture:

$$
-0.0130 \quad 1.528 \times 10^{-3}-7.895 \times 10^{-6} \quad 0.925 \times 10^{-6}
$$

For a $22.5 \% / 77.5 \%$ N2/Ar mixture:

$$
-0.0170 \quad 1.474 \times 10^{-3}-9.186 \times 10^{-6} \quad 0.795 \times 10^{-6}
$$

For pure Argon:

$$
-0.0200 \quad 1.431 \times 10^{-3}-9.901 \times 10^{-6} \quad 0.704 \times 10^{-6}
$$

5.4.4 VIRIAL FORM OF THE PENG-ROBINSON EQUATION OF STATE

$$
\begin{aligned}
& P=\frac{R T}{v-b}-\frac{a(T)}{V(v+b)+b(v-b)} \\
& Z=\frac{P V}{R T}=\frac{1}{1-w}-\frac{a(T)}{R T b} \frac{W}{1-w(w-2)} \\
& F(T)=\frac{a(T)}{R T b}
\end{aligned}
$$

or:
$Z=1+(1-F(T)) b \rho+(1+2 F(T)) b^{2} \rho^{2}+(1-5 F(T)) b^{3} \rho^{3}+(1+12 F(T)) b^{4} \rho^{4}$ .... 5.4

Values of the second, third, fourth and fifth coefficients of the virial form.

For pure Nitrogen:

$$
-0.0170 \quad 2.547 \times 10^{-3}-0.104 \times 10^{-3} \quad 7.140 \times 10^{-6}
$$

For a $85.6 \% / 14.4 \%$ N2/Ar mixture:

$$
-0.0180 \quad 2.527 \times 10^{-3}-0.103 \times 10^{-3} \quad 6.830 \times 10^{-6}
$$

For a $52.4 \% / 47.6 \%$ N2/Ar mixture:

$$
-0.0228 \quad 2.466 \times 10^{-3}-0.098 \times 10^{-3} \quad 6.031 \times 10^{-6}
$$

For a $22.5 \% / 77.5 \% \mathrm{~N} 2 / \mathrm{Ar}$ mixture:

$$
-0.0265 \quad 2.404 \times 10^{-3}-0.094 \times 10^{-3} \quad 5.337 \times 10^{-6}
$$

For pure Argon:

$$
-0.0293 \quad 2.360 \times 10^{-3}-0.089 \times 10^{-3} \quad 4.838 \times 10^{-6}
$$

5.4.5 COEFFICIENTS OF $Z \mathrm{x}$ DENSITY

These coefficients were obtained from fitting the observed compressibility factors (Z) against density using -96-
the leást squares method.

For pure Nitrogen

$$
-422.7 \times 10^{-6} 2.67 \times 10^{-6}-3.58 \times 10^{-9} 8.39 \times 10^{-12}
$$

For a $85.6 \% / 14.4 \% \mathrm{~N} 2 /$ Ar mixture:

$$
-526.7 \times 10^{-6} 2.83 \times 10^{-6}-4.37 \times 10^{-9} 8.34 \times 10^{-12}
$$

For a $52.4 \% / 47.6 \%$ N2/Ar mixture:

$$
-552.8 \times 10^{-6} 1.82 \times 10^{-6}-2.73 \times 10^{-9} 3.95 \times 10^{-12}
$$

For a 22.5\%/77.5\% N2/Ar mixture:
$-535.0 \times 10^{-6} 1.14 \times 10^{-6}-9.50 \times 10^{-10} 1.62 \times 10^{-12}$
For pure Argon:

$$
-582.5 \times 10^{-6} 1.20 \times 10^{-6}-1.26 \times 10^{-9} 1.20 \times 10^{-12}
$$

## HYBRID VIRIAL EQUATION QF STATE

PERCENTUAL ERROR IN THE PREDICTION OF
COMPRESSIBIIITY FACTOR ( $Z$ )

MOLE FRACTION NITROGEN

5 PRESSURES (MPa)

| $99.99 \%$ | 0.06 | 0.35 | 0.86 | 1.52 | 2.26 |
| ---: | ---: | ---: | ---: | ---: | ---: |
| $86.60 \%$ | 0.25 | 0.48 | 0.81 | 1.32 | 2.05 |
| $52.40 \%$ | 0.04 | 0.19 | 0.53 | 1.09 | 1.89 |
| $23.50 \%$ | -0.27 | -0.37 | -0.24 | 0.19 | 0.97 |
| $00.00 \%$ | -0.13 | -0.48 | -0.70 | -0.35 | 0.99 |

PERCENTUAL ERROR IN THE PREDICTION OF SPEED OF SOUND (a)

MOLE
FRACTION
NITROGEN

| $99.99 \%$ | 0.25 | 0.61 | 1.06 | 1.49 | 1.84 |
| :--- | ---: | ---: | ---: | ---: | ---: |
| $86.60 \%$ | -0.41 | -0.36 | -0.05 | 0.54 | 1.40 |
| $52.40 \%$ | -1.32 | -1.48 | -1.34 | -0.59 | 0.96 |
| $23.50 \%$ | -2.05 | -2.03 | -1.90 | -1.85 | -2.04 |
| $00.00 \%$ | 0.40 | 0.31 | 0.19 | 0.56 | 1.79 |

PERCENTUAL ERROR IN THE PREDICTION OF RATIO OF SPECIFIC HEATS (Cp/Cv)

MOLE
FRACTION NITROGEN

| $99.99 \%$ | 0.53 | 0.31 | -1.11 | -3.70 | -7.47 |
| ---: | ---: | ---: | ---: | ---: | ---: |
| $86.60 \%$ | 0.13 | -0.26 | -0.77 | -1.29 | -1.74 |
| $52.40 \%$ | -0.14 | -0.70 | -0.67 | 0.18 | 2.23 |
| $23.50 \%$ | -1.14 | -1.03 | -1.36 | -2.92 | -6.42 |
| $00.00 \%$ | 0.66 | 1.88 | 2.86 | 2.17 | -1.37 |

TABLE 5.2

## BENEDICT-WEBB-RUBIN EQUATION OF STATE

PERCENTUAL ERROR IN THE PREDICTION OF COMPRESSIBILITY FACTOR (Z)

| MOLE |  |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: | ---: |
| FRACTION | PRESSURES (MPa) |  |  |  |  |
| NITROGEN | 5 | 10 |  | 15 | 20 |
|  |  |  |  |  | 25 |
| $99.99 \%$ | -0.10 | -0.12 | -0.12 | -0.10 | -0.09 |
| $86.60 \%$ | 0.11 | 0.18 | 0.26 | 0.42 | 0.71 |
| $52.40 \%$ | -0.03 | 0.29 | 0.90 | 1.70 | 2.56 |
| $23.50 \%$ | -0.29 | -0.07 | 0.53 | 1.39 | 2.34 |
| $00.00 \%$ | -0.16 | -0.29 | -0.22 | 0.28 | 1.45 |

PERCENTUAL ERROR IN THE PREDICTION OF SPEED OF SOUND (a)

MOLE
FRACTION NITROGEN
99.99?
$86.60 \%$
$52.40 \%$
23.50\%
$00.00 \%$
$-0.17$
PRESSURES (MPa)
5
10
15
20
25

PERCENTUAL ERROR IN THE PREDICTION OF RATIO OF SPECIFIC HEATS (Cp/Cv)

| MOLE |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| FRACTION |  |  | RES |  |  |
| NITROGEN | 5 | 10 | 15 | 20 | 25 |
| 99.99\% | -0.09 | -0.25 | -0.91 | -2.21 | -4.27 |
| 86.60\% | -0.20 | -0.88 | -1.04 | -0.59 | 0.65 |
| $52.40 \%$ | -0.47 | -2.24 | -2.91 | -1.99 | 1.25 |
| 23.50\% | -2.40 | -4.42 | -6.39 | -8.60 | -11.38 |
| 00.00\% | -2. 26 | -3.98 | -5.32 | -7.21 | -10.41 |

## REDLICH-KWONG-SOAVE EQUATION OF STATE

PERCENTUAL ERROR IN THE PREDICTION OF COMPRESSIBILITY FACTOR (Z)

MOLE
FRACTION NITROGEN
99.99\%
86.60 \%
$52.40 \%$
$23.50 \%$
$00.00 \%$

| PRESSURES (MPa) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 5 | 10 | 15 | 20 | 25 |
| 0.84 | 1.63 | 2.22 | 2.54 | 2.54 |
| 1.08 | 1.96 | 2.55 | 2.84 | 2.85 |
| 0.87 | 1.92 | 2.92 | 3.58 | 3.66 |
| 0.42 | 1.31 | 2.37 | 3.13 | 3.15 |
| 0.38 | 1.00 | 1.82 | 2.64 | 3.25 |
| PERCENTUAL ERROR IN THE PREDICTION OF SPEED OF SOUND (a) |  |  |  |  |
| PRESSURES (MPa) |  |  |  |  |
| 5 | 10 | 15 | 20 | 25 |
| 0.97 | 1.10 | 0.37 | -0.92 | -2.53 |
| 0.92 | 0.92 | 0.27 | -0.73 | -1.83 |
| 0.89 | 1.05 | 0.68 | 0.15 | 0.23 |
| -0.04 | 0.49 | 0.42 | -0.58 | -2.65 |
| 1.11 | 1.50 | 1.31 | 0.78 | 0.13 |

PERCENTUAL ERROR IN THE PREDICTION OF RATIO OF SPECIFIC HEATS ( $\mathrm{Cp} / \mathrm{Cv}$ )

| MOLE |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| FRACTION | PRESSURES (MPa) |  |  |  |  |
| NITROGEN | 5 | 10 | 15 | 20 | 25 |
| - |  |  |  |  |  |
| 99.99\% | -0.35 | -0.72 | -3.00 | -5.80 | -8.60 |
| $86.60 \%$ | 1.07 | -0.24 | -1.82 | -2.72 | -2.08 |
| 52.40\% | 2.60 | 0.88 | -0.73 | -0.63 | -2.85 |
| $23.50 \%$ | 1.55 | 0.18 | -2.41 | -5.13 | -7.27 |
| 00.00\% | 1.09 | 0.41 | -1.48 | -3.90 | -6.93 |

## TABLE 5.4

## PENG-ROBINSON EOUATION OF STATE

PERCENTUAL ERROR IN THE PREDICTION OF COMPRESSIBILITY FACTOR (Z)

| MOLE |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| FRACTION |  |  | JRES ( |  |  |
| NITROGEN | 5 | 10 | 15 | 20 | 25 |
| 99.99\% | -1.09 | -1.71 | -2.14 | -2.53 | -3.03 |
| 86.60\% | -0.84 | -1.40 | -1.85 | -2.27 | -2.77 |
| $52.40 \%$ | -1.03 | -1. 45 | -1.54 | -1.64 | -2.10 |
| 23.50\% | -1.46 | -2.05 | -2.13 | -2.17 | -2.68 |
| 00.00\% | -1.49 | -2.37 | -2.71 | -2.72 | -2.68 |

PERCENTUAL ERROR IN THE PREDICTION OF SPEED OF SOUND (a)

MOLE

| FRACTION | PRESSURES (MPa) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| NITROGEN | 5 | 10 | 15 | 20 | 25 |
|  |  |  |  |  |  |
| $99.99 \%$ | -0.50 | -1.31 | -2.60 | -4.21 | -6.21 |
| $86.60 \%$ | -0.54 | -1.47 | -2.69 | -4.02 | -5.35 |
| $52.40 \%$ | -0.54 | -1.31 | -2.27 | -3.15 | -3.79 |
| $23.50 \%$ | -1.41 | -1.81 | -2.47 | -3.81 | -6.09 |
| $00.00 \%$ | -0.25 | -0.77 | -1.55 | -2.44 | -3.33 |

PERCENTUAL ERROR IN THE PREDICTION OF RATIO OF SPECIFIC HEATS (Cp/Cv)

MOLE FRACTION NITROGEN

| $99.99 \%$ | 0.96 | 0.19 | -1.94 | -4.69 | -7.49 |
| ---: | ---: | ---: | ---: | ---: | ---: |
| $86.60 \%$ | 1.70 | 0.71 | -0.71 | -1.53 | -0.85 |
| $52.40 \%$ | 3.29 | 1.91 | 0.52 | 0.75 | 4.31 |
| $23.50 \%$ | 2.29 | 1.34 | -0.98 | -3.59 | -5.79 |
| $00.00 \%$ | 1.88 | 1.72 | 0.18 | -2.10 | -4.77 |

Figure 5.1.1


Figure 5.1 .2


Figure 5.1.3


Figure 5.1.4


Figure 5.2.1


Figure 5.2.2


Figure 5.2.3


Figure 5.2:4


Figure 5.3.1


Figure 5.3.2


Figure 5.3.3


Figure 5.3.4


Figure 5.4.1

| COMPARISON BETWEEN OBSERVED DATA AND PREDICTIONS BY EQUATIONS OF STATE |  |  |
| :---: | :---: | :---: |
|  |  |  |
| GAS COMPOSITION: $77.5 \%$ Ar $22.5 \% \mathrm{NZ}$ SYMBOL LEGEND |  |  |

Figure 5.4.2


Figure 5.4.3


Figure 5.4.4


Figure 5.5.1


Figure 5.5.2


Figure 5.5.3


Figure 5.5.4


# CHAPTER VI 

## DISCUSSION

### 6.1 PERFORMANCE OF THE SELECTED EQUATIONS OF STATE

In this chapter, a brief discussion of the performance of the equations of state will be carried out. This discussion is limited to a presentation highlighting the areas of agreement or disagreement between the experimental results and the properties determined by the equations of state.

There are three sources of error in an equation of state: in the constants, in the structure, or in the mixing rules. In regard to errors arising from error either in the constants or structure, it is necessary to discuss the predictions of properties for pure gases. Until this is done, there is no possibility of rationally discussing the error that can be ascribed to the mixing rules.

The information for this inquiry lies in the comparative performance figures of Section 5.2, together with the table of errors in Section 5.3, and the coefficients for the four equations when expanded as a virial form in Section 5.4.
6.1.2 THE HYBRID VIRIAL EQUATION OF STATE.

The virial equation of state has in its functional form the feature of providing the investigator with a reasonably clear understanding of the influence of its parameters. This equation can be written as a polynomial series expressing the compressibility factor $Z$ as a function of specific volume $v$ (or density), temperature $T$, plus parameters $\sigma$ and $\theta$ which define the intermolecular forces potential for the gas concerned. The parameter $\theta$ and the temperature $T$ are used to define the dimensionless temperature $\mathrm{T}^{*}$ which determines all the virial cofficients $B^{*}, C^{*}$, etc. The parameter $\sigma$ determines the molecular co-volume b.

The second virial coefficient $B^{*}$. has been determined very precisely from experimental data, it relates to the influence of temperature on a two-body-collision between the molecules. In the $\mathrm{B}^{\star} \mathrm{vs}$. $\mathrm{T}^{*}$ relation, for temperatures below the Boyle point, $T^{*}=3.42$, for a Lennard-Jones potential, attractive forces are predominant between the molecules and for temperatures above this point, repulsive forces dominate. Also as the temperature increases, the value of $B^{*}$ levels off. The mean kinetic energy of the molecules in free movement in a gas is proportional to the temperature. Thus at low temperatures, (low velocities), when two molecules approach, there is sufficient time for the influence of
attraction to predominate whereas at high temperatures (high velocities), the potential surrounding the molecule is disregarded by the molecules in its trajèctory, with the molecules behaving as if in a hard-sphere type of collision.

The Hybrid Virial equation of state performed well in the prediction of the compressibility $Z$ at low pressures up to 15 MPa . Beyond that, the predictions seem to be considerably higher than the observations. There is very good agreement between the predicted and the measured values of speed of sound (a) in all the mixtures, and over the pressure range. Moreover, the predictions of the ratio of specific heats agree well with the measurements for most cases up to 20 MPa .

Also, the second and third coefficients of the hybrid virial equation agree in magnitude with the coefficients obtained from the $Z$ vs. $\rho$ relation fitted to the observed compressibility data.

### 6.1.3 THE BENEDICT-WEBB-RUBIN EQUATION OF STATE.

This equation of state did well in predicting the values of the compressibility factor (Z). No great departures were noted for any of the mixtures in the range of test pressures.

It should be noted that there is good agreement between the second coefficients of the virial form of the
$B-W-R$ equation and those of the hybrid virial, for all mixtures.

In the prediction of speed of sound the calculated results from this equation of state were out no more than 2.6\%. The errors are shown to increase towards higher concentrations of Argon.

The values of the ratio of specific heats as calculated from the equation of state compare poorly with the measured properties: errors reach ll\%.
6.1.4 THE REDLICH-KWONG-SOAVE EQUATION OF STATE.

The compressibility factor (Z) values calculated with the R-K-S compared poorly with measured values. There is a slight increase in the percentage error in the mixtures towards the $50 / 50 \%$ mixture and also with the increase in pressure.

The predicted values of speed of sound departed slightly from the measured values at pressures above 20 MPa, reaching 2.6\%. However, these erors seem to be about the same for all compositions, which could be interpreted as support for the mixing rules.

The prediction of values for the ratio of specific heats from this equation followed the same general pattern described above for the speed of sound, with an increased percentage error at moderate pressures. This seems to indicate that the deviations apparent in the speed of sound
are a result of discrepancies in the prediction of ( $C_{p} / C_{v}$ ). There is (apparently due to the similarity in the functional form) some coincidence in magnitude of the second and third virial coefficients of the virial form of the $R-K-S$ equation and the corresponding coefficients of the $P-R$ equation.
6.1.5 THE PENG-ROBINSON EQUATION OF STATE.

The compressibility factor values as predicted by the Peng-Robinson equation showed the greatest departure (of all the equations concerned) from experimentally measured values. When assessing the mixing rules, no indications were found of deterioration of the calculated values with the different mixtures. The maximum errors for the most part were around $3 \%$.

Starting from low values of pressure, there is a significant amount of error in the calculated values of the speed of sound using this equation. Although there are no signs of any change in the magnitude with different mixtures, the errors increase steeply with pressure, reaching about 6\%.

The discrepancies in $C_{p} / C_{V}$ closely approached $7.5 \%$ at high pressures for the values of the ratio of specific heats. There were no apparent changes in this error for different mixtures, when considered at the same pressures. It should be noted that the coefficients of the
virial forms of both the $P-R$ and $R-K-S$ equations are much greater than the corresponding ones of the Hybrid Virial equation.
6.2 RECOMENDATIONS FOR FUTURE STUDY.

During the course of this study, a number of lessons were learned. Some of these refer to the specific techniques utilized and some are of a more general nature. It seems appropriate to incorporate this experience with the recommendations for future study.

In the measurement of the speed of sound using the decompression wave front velocity it was found that although the design of a $T$ shaped tube is desirable for this purpose from the point of view of allowing the head of the decompression wave a head-on encounter with the first pressure transducer, it will also introduce a considerable error due to the 'corner effect' which has to be accounted for.

The total length of the tube, i.e. the distance between the two transducers is dictated by the total time available for capture of the time-pressure signal by the digitizing instrument at the maximum rate, in this case, this time is slightly over one millisecond. The typical time difference between arrival of the decompression wave at the two stations of 850 microseconds allows optimized use of the time base taking full advantage of its accuracy.

A serious attempt was made to examine the characteristic pressure-time trace during expansions with a view to determining the isentropic compressibility coefficient and consequently from it, the ratio of specific heats. This trace, shown in Figure A22 exhibits initially a very sharp drop in the pressure and a subsequent rise to an intermediate pressure. The rising part of the curve seemed to follow the relation:

$$
\left(t-t_{f}\right) /\left(t_{i}-t_{f}\right)=e^{-T / F} \quad \ldots 6.1
$$

The above equation is used to relate time and temperature during the quenching process of a cylinder. The model applied here was that of a cylinder, in this case the gas contained inside the stainless steel tubing of the apparatus, suddenly subjected to a medium of higher temperature (the final temperature of an isentropic expansion of the gas is considerably lower than that of the tubing). It was assumed that the pressure, as a first approximation would be proportional to temperature and as a result follow the same relation.

The treatment of the pressure time trace, included the writing of various digital filter programs to eliminate the noise present in the trace. This noise, common to digitizing instruments has the amplitude of plus or minus one least-significant-bit of the analog-digital converter and a frequency corresponding to the digitizing frequency being used. The digital filtering technique worked to the
satisfaction of the author. However, the asymptotic nature of the 'heating curve', and limitations in the time available for this part of the study, made it impossible to determine the lowest point in the curve which would yield the isentropic compressibility coefficient. Nevertheless, it was noted that the curve obtained from the equation above does follow the ascending part of the pressure-time trace with some degree of accuracy. The use of a fast response thermocouple, together with a more adequate model using temperature-time characteristics of the process should allow determination of this important parameter by this method.

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## APPENDIX A

This appendix contains the calibration curves of the pressure transducers utilized in this investigation, and tables of constants used in the calculations.

Figure AI


Figure A2

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Figure A3


Figure A4


Figure A5


## Figure A6



Figure A7


Figure A8


Figure A9


## Figure Al0



Figure All

'Figure Al2


Figure Al3



Figure Al5


Figure Al6

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Figure Al7


Figure Al8


## Figure Al9



Figure A20


Figure A21


MIXTURES


## Table A2 - CONSTANAS USED IN THE <br> BENEDICT-WFBB-RUBIN EQUATION OF STATE

MIXIURES

|  |  | 1 | 2 | 3 | 4 | 5 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 100\% Nitrogen | 85.6\% N 214.48 Ar | 52.4\% $\mathrm{N} 247.6 \% \mathrm{Ar}$ | 22.5\% N 2 77 . $5 \% \mathrm{Ar}$ | 100\% Argon |
|  | $\mathrm{A}\left(\mathrm{m}^{3} / \mathrm{kg}\right) \mathrm{kPa}$ | $0.1157 \times 10^{-3}$ | $0.1036 \times 10^{-3}$ | $78.4819 \times 10^{-6}$ | $58.7835 \times 10^{-6}$ | $45.8340 \times 10^{-6}$ |
| 亩 | $\mathrm{A}^{\mathrm{O}}\left(\mathrm{m}^{3} / \mathrm{kg}\right)^{2} \mathrm{kPa}$ | 0.136050 | 0.1215612 | 0.0912648 | 0.067688 | $0.5226 \times 10^{-1}$ |
| 1 | $\mathrm{B}\left(\mathrm{m}^{3} / \mathrm{kg}\right)^{2}$ | $0.2966 \times 10^{-5}$ | $0.2733 \times 10^{-5}$ | $0.2196 \times 10^{-5}$ | $0.1712 \times 10^{-5}$ | $0.1349 \times 10^{-5}$ |
|  | $B^{\circ}\left(\mathrm{m}^{3} / \mathrm{kg}\right)$ | $0.1454 \times 10^{-2}$ | $0.1325 \times 10^{-2}$ | $0.1027 \times 10^{-2}$ | $0.7599 \times 10^{-3}$ | $0.5578 \times 10^{-3}$ |
|  | $\mathrm{C}\left(\mathrm{m}^{3} / \mathrm{kg}\right)^{3} \mathrm{~K}^{2} \mathrm{kPa}$ | $0.3357 \times 10^{+1}$ | $0.2992 \times 10^{+1}$ | $0.2229 \times 10^{+1}$ | $0.1639 \times 10^{+1}$ | 1.25448 |
|  | $\mathrm{C}^{0}\left(\mathrm{~m}^{3} / \mathrm{kg}\right)^{2} \mathrm{~K}^{2} \mathrm{kPa}$ | $0.1040 \times 10^{+4}$ | $0.1009 \times 10^{+4}$ | $0.9396 \times 10^{+3}$ | $0.8788 \times 10^{+3}$ | $0.8344 \times 10^{+3}$ |
|  | $\boldsymbol{\gamma}\left(\mathrm{m}^{3} / \mathrm{kg}\right)^{2}$ | $0.5786 \times 10^{-8}$ | $0.4535 \times 10^{-8}$ | $0.2366 \times 10^{-8}$ | $0.1131 \times 10^{-8}$ | $0.5582 \times 10^{-9}$ |
|  | $a\left(\mathrm{~m}^{3} / \mathrm{kg}\right)^{3}$ | $0.6753 \times 10^{-5}$ | $0.5026 \times 10^{-5}$ | $0.2014 \times 10^{-5}$ | $0.4604 \times 10^{-6}$ | $0.1465 \times 10^{-7}$ |

## TABLE OF PHYSICAI CONSTANTS

|  | Nitrogen | Argon |
| :---: | :---: | :---: |
| Critical Temperature (K) | 126.1 | 150.9 |
| Critical Pressure (kPa) | 3394.0 | 4898.0 |
| Specific Heats (ideal) : |  |  |
| $C_{V}{ }^{\circ}(\mathrm{kJ} / \mathrm{kmol} \mathrm{K})$ | 20.7856 * | 12.4656* |
| $C_{p}{ }^{\circ}(\mathrm{kJ} / \mathrm{kmol} \mathrm{K})$ | 29.10* | 20.78 * |
| Molecular Weight ( $\mathrm{kg} / \mathrm{kmol}$ ) | 28.0134 | 39.948 |
| Acentric Factor | 0.0403 | -0.0038 |

[^1]


[^0]:    P (MPa) - test pressure
    $\rho(k g / m 3)$ - Density
    Z - Compressibility factor
    K (1/4Pa) - Isothermal Compressibility

[^1]:    Values taken from reference <4>

    * Values taken from reference <l9>

