

THE UNIVERSITY OF CALGARY

DETERMINATIONS OF SPEED OF SOUND
FROM DECOMPRESSION WAVE FRONT VELOCITY
IN MODERATELY DENSE GASES
AND MEASUREMENT OF THE ASSOCIATED
ISOTHERMAL COMPRESSIBILITY COEFFICIENT
AND COMPRESSIBILITY FACTOR

BY

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A THESIS

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DEPARTMENT OF MECHANICAL ENGINEERING

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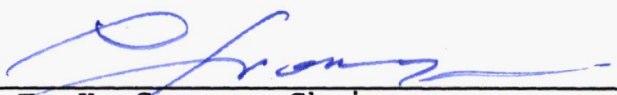
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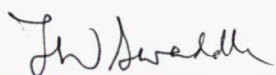
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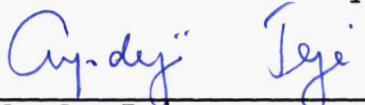
The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "Determinations of Speed of Sound from Decompression Wave Front Velocity in Moderately Dense Gases and Measurement of the Associated Isothermal Compressibility Coefficient and Compressibility Factor", submitted by Md. Ali Rob Sharif in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering.



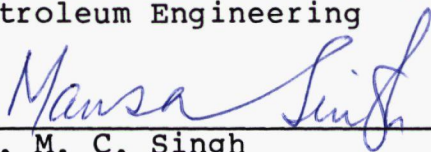
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ABSTRACT

An apparatus is designed and developed for simultaneous measurement of the speed of sound, the compressibility factor and the isothermal compressibility coefficient in moderately dense gases. The speed of sound is obtained by measuring the velocity of a decompression wave front initiated by the rupture of diaphragm in a decompression tube.

Measurements are made at 273.15 K and 298.15 K, for carbon dioxide gas at pressures up to 4.5 MPa and for argon and nitrogen gas at pressures up to 35 MPa. These measurements are found to be in good agreement with available published data.

These observations, together with certain thermodynamic properties directly derived from them, are compared with predictions using the van der Waals, the Benedict-Webb-Rubin and a virial equation of state.

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NOMENCLATURE*

<u>SYMBOL</u>	<u>EXPLANATION</u>
a	Speed of sound
a_{vdw}	Constant for van der Waals equation of state
a^0	Speed of sound at ideal gas state
A	Constant for Benedict-Webb-Rubin equation of state
A_0	Constant for Benedict-Webb-Rubin equation of state
b_h	Force constant for hard molecule assumption; defined in Eq. (3.2.10)
b_{LJ}	Force constant for Lennard-Jones (6-12) potential; defined in Eq. (3.2.12)
b_{vdw}	Constant for van der Waals Equation of state
B	Constant for Benedict-Webb-Rubin equation of state
B_0	Constant for Benedict-Webb-Rubin equation of state
B^*	Reduced second virial coefficient
B_n^*	Temperature derivative of order n of reduced second virial coefficient multiplied by the reduced temperature T^* raised to the power n
c_p	Specific heat at constant pressure
c_{pR}	Deviation of specific heat at constant pressure from that of ideal gas state
c_p^0	Constant pressure specific heat at ideal gas state

*other symbols, with more localized use, are defined in the text.

NOMENCLATURE (continued)

<u>SYMBOL</u>	<u>EXPLANATION</u>
c_v	Specific heat at constant volume
c_{vR}	Deviation of specific heat at constant volume from that of ideal gas state
c_v^0	Constant volume specific heat at ideal gas state
C	Constant for Benedict-Webb-Rubin equation of state
C_0	Constant for Benedict-Webb-Rubin equation of state
C^*	Reduced third virial coefficient
C_n^*	Temperature derivative of order n of the reduced third virial coefficient multiplied by the reduced temperature T^* raised to the power n
k	Boltzmann's constant
M	Molecular weight
m	Mass
N	Avogadro's Number
p	Pressure
p_c	Critical pressure
R	Gas constant per unit mass
s	Specific entropy
t	Time
T	Absolute temperature
T_c	Absolute critical temperature
T_r	Reduced temperature; T/T_c
T^*	Reduced temperature; T/θ
u	Velocity

NOMENCLATURE (continued)

<u>SYMBOL</u>	<u>EXPLANATION</u>
v	Specific volume
v_c	Critical specific volume
V	Total volume
x	Displacement or distance
z	Compressibility factor
z_c	Compressibility factor at the critical point
α	Constant for Benedict-Webb-Rubin equation of state
β	Coefficient of volumetric expansion at constant pressure
γ	Ratio of specific heats or constant for Benedict-Webb-Rubin equation of state
γ^0	Ratio of specific heats at ideal gas state
θ	Potential well depth temperature defined in Eq. (3.2.12)
ρ	Density
κ	Isothermal compressibility
κ^0	Isothermal compressibility at ideal gas state
ϵ	Depth of potential well
σ_h	Collision diameter of the molecules for hard molecule potential
σ_{LJ}	Force constant for Lennard-Jones (6-12) potential
ω_h	Dimensionless density for hard molecule potential
ω_{LJ}	Dimensionless density for Lennard-Jones (6-12) potential
ω_{vdw}	Dimensionless density for van der Waals equation of state

I INTRODUCTION

The main purpose of this study is to measure the speed of sound in moderately dense gases and to use these measurements to evaluate certain thermal equations of state.

Quite often the equations of state, due to the bias arising from incorrect functional form, fail to predict slope properties even when they reproduce a satisfactory correlation among the thermal equation of state properties (p, ρ, T) . It is thus necessary, while appraising an equation of state, to examine how well it predicts, not only the integral properties (p, ρ, T) but also the slope properties.

The speed of sound measurements are, therefore, supplemented by simultaneous measurement of isothermal compressibility coefficients and densities. Thus at each observed state the direct measured properties are: pressure (p) , temperature (T) , density (ρ) , isothermal compressibility (κ) and speed of sound (a) . These observations allow direct deduction of the compressibility factor $(Z = p/\rho RT)$, the ratio of specific heats $(\gamma = a^2 \rho \kappa)$ and the property $[\rho(\partial Z/\partial \rho)_T = (1/p\kappa - 1)Z]$. These slope properties a , κ , γ and $\rho(\partial Z/\partial \rho)_T$ are particularly significant in that they are determined directly by measurement, i.e., not by differentiation, and are therefore free from bias. Finally

the equations of state are evaluated by comparing calculated properties with the measured properties and those directly derived from them.

Measurements are confined to three gases, namely, carbon dioxide, argon and nitrogen, to two isotherms, 0°C and 25°C and to pressures up to 4.5 MPa in carbon dioxide and up to 35 MPa in argon and nitrogen.

Argon is chosen not only because it is monatomic and therefore described by spherically symmetric intermolecular potentials, but also because of the wealth of thermodynamic measurements on argon available for comparison with the measurements described here. Nitrogen is chosen to assess the possible deterioration of equation of state predictions for nitrogen relative to argon arising from the non-spherical shape of the nitrogen molecule. Carbon dioxide is chosen for its high critical temperature and therefore its strongly non-ideal behavior even at moderate pressures, at the temperatures concerned.

Due to the limitations of time, measurements are done only at two temperatures. The pressure range is limited to 35 MPa due to the cost of very high pressure equipment and instrumentation.

The equations of state chosen for evaluation are; 1) van der Waals equation, 2) Benedict-Webb-Rubin equation and 3) a virial equation. The van der Waals equation is chosen because it is a two-constant equation having a simple analytic form and is used mainly for instructional purposes. The Benedict-Webb-Rubin equation is chosen because it is a popular and frequently-used equation of state, especially in oil and gas applications, and is claimed to be very accurate. The virial equation is chosen because it has a sound theoretical basis.

An apparatus is developed for simultaneous measurement of speed of sound, isothermal compressibility and density. The whole apparatus is immersed in a liquid bath to maintain constant temperature accurately. The temperature is measured at several points via calibrated thermocouples while the pressure is measured via static pressure transducers connected to digital read-out units.

The speed of sound is determined from the velocity of a decompression wave front. The high pressure gas is charged in a tube having a diaphragm at one end. A decompression wave is initiated by the rupture of the diaphragm. The travel time of the decompression wave is detected by several piezoelectric transient pressure transducers placed along the tube. The distance between two such transducers divided

by the travel time, provides the velocity of the decompression wave front which is equal to the velocity of sound in the charged gas at the particular pressure and temperature.

Before the diaphragm is ruptured, the high pressure gas is given access to a pre-evacuated small chamber. The ratio of the increase in volume to the decrease in pressure is used to determine the isothermal compressibility. The leaked gas in this small chamber is then expanded to a large pre-evacuated chamber making the gas so dilute that its mass can be computed using the ideal gas relation. This mass divided by the known volume of the small chamber, provides the gas density.

Various other experimental techniques have been used to measure the speed of sound in gases at various combinations of pressure and temperature covering low, moderate and high densities. Almost all of the measurements described in the literature were obtained using ultrasonic techniques.

However, the speed of sound measured by ultrasonic techniques is frequency-dependent and therefore requires correction before it can be said to represent the thermodynamic speed of sound. These corrections include that for Kirchhoff's tube wall effect [1.1]* and absorption and boundary layer

*Numbers in the square bracket represents reference numbers

effects [1.2]. "One must distinguish between the velocity of sound at zero frequency which is a thermodynamically defined quantity and the velocity at any other frequency which depends upon the relaxation time and other rate constants" [1.3,p369]. The speed of sound obtained from the decompression wave front velocity however, is free from such corrections and therefore represents the thermodynamic speed of sound.

In chapter 2, a review of literature on the thermodynamic properties of the gases concerned is given. Chapter 3 contains the required shock tube theory together with a detailed description of the equations of state chosen for evaluation. Experimental procedure is given in chapter 4. The results of the experiments are presented in chapter 5 which is followed by a discussion in chapter 6.

II REVIEW OF LITERATURE

Among the numerous publications available in the literature, only those relevant to the thermodynamic properties and the range of pressures and temperatures studied in this research are discussed here. In Sec. 2.1 the general references are discussed while topics covering measurements of $p\rho T$ data are discussed in Sec. 2.2. Finally in Sec. 2.3, topics concerned with measurement of speed of sound are discussed. In this context, it should be noted that no suitable experimental data for isothermal compressibility (κ) are available for comparison with the values measured in this study.

2.1 General References

An extensive bibliography on thermodynamic properties for several gases and their mixtures is given in [2.1 and 2.2], which serves as an excellent source of reference. The general references for the specific gases are as follows.

2.1.1 Carbon Dioxide. Empirical equations of state are developed in [2.3, 2.4 and 2.5] for carbon dioxide, for a wide range of pressures and temperatures, using available published property data. Tables of property data computed from the developed equations are also given in [2.3 and

2.4] along with an extensive bibliography on thermodynamic properties of carbon dioxide.

2.1.2 Argon. Empirical equations of state are also developed for argon in [2.6 and 2.7] for a wide range of temperatures and pressures using available published data. Tabulations of the property data computed by the developed equations along with an extensive bibliography on the thermodynamic properties of argon can also be found in [2.6 and 2.7]. A detailed bibliography on theoretical, experimental and compilation studies on the thermodynamic properties of argon as of 1964 can be found in [2.8].

2.1.3 Nitrogen. In [2.9] an empirical equation of state for nitrogen is reported for a temperature range of 63 K to 2000 K and pressures to 1000 MPa, determined by least-squares-fitting of published data. Reference [2.9] also contains tabulations of properties calculated by the fitted equation as well as an extensive bibliography on thermodynamic properties of nitrogen.

2.2 Measurement of ppT Data

There are several standard techniques available for measuring ppT data in gases. Some of these are described in [2.1 and 2.2]. These techniques are compilations of various methods which have been used for measurement of ppT

data and are not described here. Various sources from which $p\rho T$ data are collected for comparison with the observed data of this study are discussed below.

2.2.1 Carbon Dioxide. Michels et al. [2.10] measured $p\rho T$ data of carbon dioxide between 0°C and 150°C and pressures from 16 to 250 atmospheres. MacCormack and Schneider [2.11] measured thermodynamic properties of gaseous carbon dioxide at temperatures from 0°C to 600°C and pressures up to 50 atmospheres. Vukalovich et al. [2.12] measured densities of carbon dioxide at temperatures from 0°C to 35°C and pressures up to 30 MPa. The $p\rho T$ data collected from these three references are used for comparison of the observed data in this study. However, data for both 0°C and 25°C are reported only in [2.10]. In the other two papers, measurements are not reported for 25°C .

2.2.2 Argon. Michels et al. [2.13] measured $p\rho T$ data for argon between 0°C and 150°C and pressures up to 2900 atmospheres. Data for both 0°C and 25°C are reported in this paper and are taken for comparison. Kestin and Liedenfrost [2.14] measured densities of argon and several other gases over a range of pressures and temperatures to determine the viscosity of these gases. Their density data at 0°C (measurements at 25°C are not reported) are also taken for comparison.

2.2.3 Nitrogen. Smith and Taylor [2.15] measured $p\rho T$ data to formulate an equation of state for pure nitrogen. Verschoyle [2.16] measured the $p\rho T$ data of hydrogen, nitrogen and their mixtures at 0°C and 20°C up to a pressure of 220 atmospheres. Bartlett et al. [2.17] also measured the compressibility factors of hydrogen, nitrogen and of a 3:1 mixture of these gases at temperatures between 0°C and 400°C and pressures to 1000 atmospheres. Michels et al. [2.18 and 2.19] measured $p\rho T$ data for nitrogen between 0°C and 150°C and pressures from 20 to 3000 atmospheres. Density data from these papers are chosen for comparison. However, except for Michels et al., data for 25°C are not presented in the other three papers.

2.3 Measurement of Speed of Sound

As mentioned earlier, almost all previous investigators have called on ultrasonic techniques using an acoustic interferometer. In an acoustic interferometer, resonance is generated in a confined column of fluid. One end of the column is excited by an electronically driven vibrating transducer or crystal so as to produce plane sound waves. The known length of the resonating fluid column is an integral multiple of the half wavelength of the sound wave and the ultrasonic speed of sound is equal to the product of the

wavelength and the frequency of vibration. In some cases (variable path interferometry) resonance is established by varying the length of the column whereas in other cases (fixed path interferometry) the column length is fixed and the frequency of vibration is varied.

In 1937 Hodge [2.20] measured ultrasonic speeds of sound at 27°C in several gases over a pressure range of 1 to 100 atmospheres using a variable path acoustic interferometer and in 1957 van Itterbeek et al. [2.21] measured the speed of sound in high pressure gases using a similar interferometer of higher precision.

Improvements in precision accompanied advancements in electronics. In 1970 Gammon and Douslin [2.22] used a significantly improved variable path interferometer to measure, with high precision, speeds of sound in compressed helium for temperatures from -175°C to 150°C and pressures from 10 to 150 atmospheres. In 1976 an even more precise variable path acoustic interferometer (0.002 per cent error) was used by Quinn et al. [1.2] to measure the speed of sound in argon at 273.16 K for a pressure range from 30 to 200 kPa.

In 1963 a different form of the variable path interferometer was developed by Lestz [2.23] based on the

principle that sound pressures at any two points are in phase provided that these two points are separated by a distance equal to an integral number of wavelengths. Phase is determined from simultaneous viewing of the input voltage to a loudspeaker at one end of the interferometer tube and of the output voltage from a movable microphone. The position of the microphone is adjusted until its output is in phase with the input to the speaker. The zero-phase difference condition is readily determined with a cathode ray oscilloscope. From the initial zero-phase position, the microphone is moved through one cycle until the two signals are again in phase. The distance traversed by the microphone is then equal to one wavelength, which, when multiplied by the input frequency of the loudspeaker, provides the speed of sound. In 1965 El-Hakeem [2.24] refined this and measured the speed of sound in nitrogen and argon for pressures up to 70 atmospheres.

In fixed path acoustic interferometry, two transducers are flush mounted at the end faces of a tube of accurately known length. One of the transducers acts as an input ultrasonic wave generator and the other one as the receiver. As the frequency of the input signal to the interferometer is varied, peaks are observed in the amplitude of the output signal corresponding to frequencies at which standing wave

resonance occurs. The speed of sound (a) is then calculated from $a = 2d\Delta f$, where (d) is the fixed distance between the transducers and (Δf) is the frequency difference between the successive resonances. Street and Constantino [2.25] used this technique for measuring speeds of sound in liquid argon at pressures up to 3400 atmospheres. The fixed path interferometer is particularly suited to high pressure applications since fewer adjustments are necessary. Liebenberg et al. [2.26] measured the speed of sound in argon at pressures up to 1300 MPa using this method and expressed the intention of extending these measurements to pressures up to 4000 MPa. In 1974, Garland and Williams [2.27] used a different variation of the fixed path interferometer. Instead of using the traditional longitudinal resonator, a transverse annular resonator was used in order to determine the resonant frequency in an azimuthal mode. An important feature of this method is the fact that low frequencies of the order of 1 kHz can be used.

The speed of sound in a gas can be measured most simply by sending a sound pulse through it and measuring its time of travel over a known distance. This method was used by Vereschagin et al. [2.28] in 1975. They developed an apparatus for adiabatically compressing a gas to high pressures (up to 3000 MPa) and high temperatures (>2000 K) for a period

of 1 to 2 milliseconds. A sound pulse is transmitted through this highly compressed gas and is detected by a transducer placed at a known distance from the emitter. However, accurate measurement of the time of travel has proved to be difficult and generally a repeating pulse technique is used which is similar to the fixed path interferometer. The difference is that in this case the emitting crystal or transducer sends an acoustic pulse which reflects between the receiving and emitting crystals several times which can be seen on an oscilloscope screen. By adjusting the repetition frequency of the input pulses, the acoustic pulse sequences belonging to different input pulses can be made to interfere constructively. When the time between consecutive input pulses is equal to the time required for an acoustic pulse to make a round trip from the detecting crystal to the emitting crystal and back, constructive interference of the received acoustic pulses occurs. The speed of sound (a) is then given by $a = 2df$ where (d) is the distance between the crystal surfaces and (f) is the pulse repetition frequency. Younglove [2.29] measured the speed of sound in fluid para-hydrogen by this method in 1965. Also Tsumura and Starty [2.30] in 1977 used this method to measure the speed of sound in saturated and compressed fluid ethane.

Lacram [2.31] used an optical method to measure the ultrasonic speed of sound in several gases for a wide range of pressures and temperatures. His method is based on the principle that if a fluid is subjected to a plane wave of frequency (f), planes of maximum and minimum density are produced in the fluid at any given instant and the distance between two consecutive planes of either maximum or minimum density is the wavelength. Thus, if a monochromatic parallel beam of light of wave length (λ) is passed through the fluid, fringes may be observed. When these fringes are photographed by a camera of focal length (d), the velocity of the ultrasonic wave is given by the relation $a = f\lambda d/i$ where (i) is the distance between two consecutive fringes on the photograph.

The determination of the speed of sound using decompression wave velocity has received little attention. In 1951 Glass [2.32] used it to measure the speed of sound in air, argon, carbon dioxide and helium at 0°C , for a pressure range of 1 to 5 atmospheres. He used streak photography to determine the path of the head of the decompression wave travelling into the high pressure chamber of a shock tube. The image path is a straight line whose slope provides the velocity of the head of the decompression wave which is equated to the speed of sound. After Glass,

no significant application of this method was undertaken until 1978 by Groves et al. [2.33]. In an attempt to study the effect of sudden rupture of a gas pipe line carrying high pressure natural gas, the decompression wave velocity in natural gases, pure methane and argon at 25°F and 1250 psi was measured. The spontaneous rupturing of the pipe line was idealized by the rupturing of a diaphragm in a shock tube. The arrival of the decompression wave was sensed by transient pressure transducers. The ratio of the distance between two consecutive transducers to the travel time of the head of the decompression wave from one transducer to the other provided the velocity.

Groves' method of measuring the decompression wave front velocity is used in this study, with a few modifications, to obtain the speed of sound in gases.

Relevant references on speed of sound data are discussed below.

2.3.1 Carbon Dioxide. A detailed list of references on speed of sound data and on molecular absorption in carbon dioxide at high pressures is given in [2.3,p141]. There are also some references on speed of sound measurements in carbon dioxide in [2.4]. However, "almost all the studies on the speed of sound have been made in the critical region

and have been concerned with the physics of the propagation of sound under dispersive conditions rather than with the determination of speed of sound as a thermodynamic property" [2.4,p32]. The only available data for comparison with the measured values in this study are taken from [2.34 and 2.35]. These data are, however, for 25°C only. The data of Hodge [2.20] which are at a slightly higher temperature (27°C), are also taken into consideration to show the consistency of the measured speed of sound at 25°C. No suitable speed of sound data at 0°C are available for comparison.

2.3.2 Argon. Lacam [2.31] measured speeds of ultrasound in argon, nitrogen and other gases at temperatures from 25°C to 200°C and pressures to 1100 atmospheres. His data for argon at 25°C are taken for comparison. Speeds of sound in argon were also measured by van Itterbeek et al. [2.36] at -98.9°C, -44.4°C, -36.7°C, -24.9°C, 0.6°C, and 26.6°C and for pressures up to 70 atmospheres. Their data for argon at 0.6°C are compared with the speed of sound in argon at 0°C measured in this study. El-Hakeem [2.24] measured speeds of sound in argon and nitrogen at 0°C and 21.11°C for pressures up to 70 atmospheres. His data for argon at 0°C are also taken for comparison.

2.3.3 Nitrogen. Lacam's [2.31] data for nitrogen at 25°C and El-Hakeem's data [2.24] for nitrogen at 0°C are

taken for comparison. Speeds of sound in nitrogen were also measured by van Itterbeek et al. [2.21] at -44.0°C , -24.43°C , -0.05°C and 25.57°C for pressures up to 65 atmospheres. Their data for -0.05°C and 25.57°C are also taken for comparison with the measured speed of sound in nitrogen at 0°C and 25°C of this study.

III THEORETICAL CONSIDERATIONS

The decompression wave front velocity apparatus, to be described in detail in chapter 4, is best appreciated by preliminary consideration of shock tubes. Accordingly, the shock tube theory and decompression wave theory are now reviewed. This is followed by a consideration of the equations of state used here to calculate the speed of sound and other thermodynamic properties for comparison with the values observed.

3.1 Shock Tube Theory

A simple shock tube [3.1,p8] is essentially a long straight tube of uniform cross section containing a thin diaphragm which separates a high pressure gas zone from a low pressure zone (Fig. 3.1.1). When the diaphragm is ruptured either by a cutter, or by increasing the gas pressure difference across it until it bursts spontaneously, a shock wave travels into the low pressure zone and a decompression wave fan travels into the high pressure zone.

In ideal shock tube theory the shock wave is assumed to form instantaneously and the waves are assumed to be plane, and to travel at uniform velocities within each of the uniform state regions (1), (2), (3) and (4) shown in

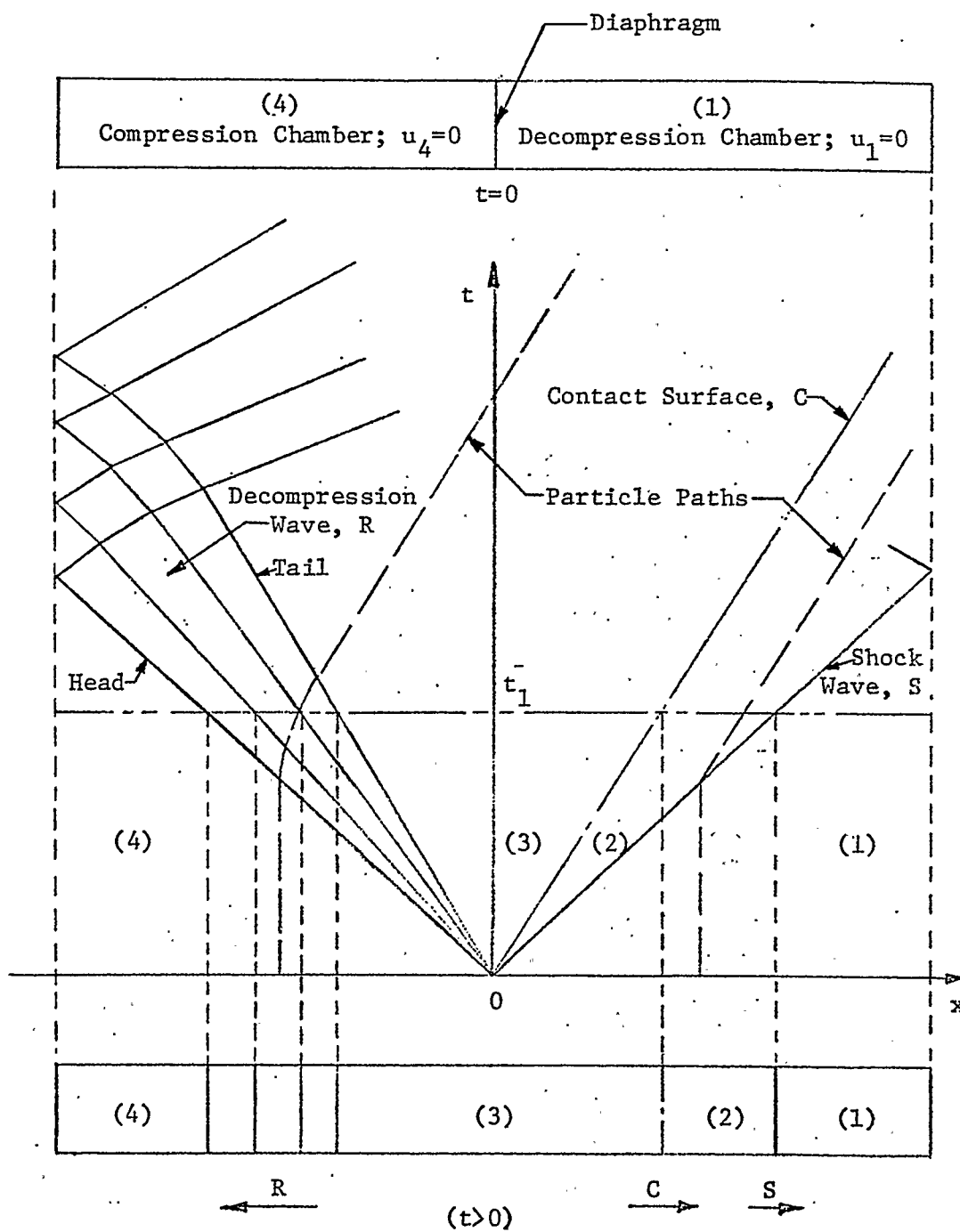


Fig. 3.1.1 The Wave System Produced by Bursting a Diaphragm in a Shock Tube.

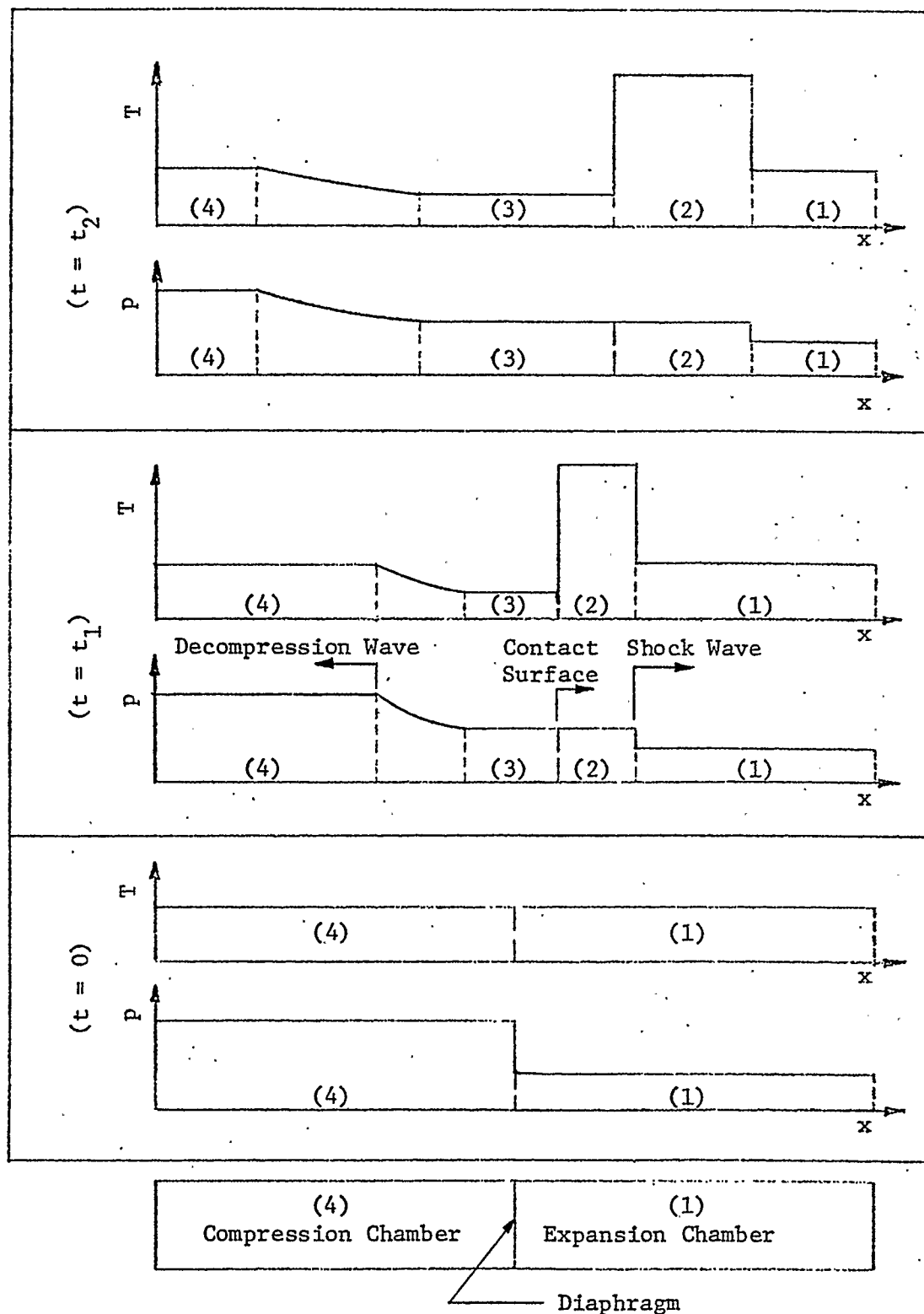


Fig. 3.1.2 Pressure and Temperature Distribution in a Simple Shock Tube after Diaphragm is Ruptured.

Fig. 3.1.1 [2.32a]. The region covered by the rarefaction or decompression wave fan is the only region which is not uniform. At the head of the decompression wave the flow speed is zero and the thermodynamic properties are same as in region (4). At the tail of the decompression wave, after isentropic expansion, the gas acquires the steady velocity and thermodynamic properties of region (3).

The equation for conservation of mass for one-dimensional, unsteady, inviscid flow is given by;

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + \rho \frac{\partial u}{\partial x} = 0 \quad \dots\dots\dots (3.1.1)$$

The equation for conservation of momentum is given by;

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + \frac{1}{\rho} \frac{\partial p}{\partial x} = 0 \quad \dots\dots\dots (3.1.2)$$

The speed of sound is defined by;

$$a^2 = \left(\frac{\partial p}{\partial \rho} \right)_s \quad \dots\dots\dots (3.1.3)$$

where s is entropy so that for isentropic flow;

$$dp = a^2 d\rho \quad \dots\dots\dots (3.1.4)$$

Using Eq.(3.1.4) the equation for conservation of momentum takes the form;

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + \frac{a^2}{\rho} \frac{\partial \rho}{\partial x} = 0 \quad \dots\dots\dots (3.1.5)$$

Multiplying Eq. (3.1.1) by a/ρ and adding it to and subtracting it from Eq. (3.1.5) leads to the following two equations;

$$\left(\frac{\partial u}{\partial t} + \frac{a}{\rho} \frac{\partial \rho}{\partial t}\right) + (u+a) \left(\frac{\partial u}{\partial x} + \frac{a}{\rho} \frac{\partial \rho}{\partial x}\right) = 0$$

$$\left(\frac{\partial u}{\partial t} - \frac{a}{\rho} \frac{\partial \rho}{\partial t}\right) + (u-a) \left(\frac{\partial u}{\partial x} - \frac{a}{\rho} \frac{\partial \rho}{\partial x}\right) = 0$$

which may be rewritten in the form;

$$\frac{\partial}{\partial t} [u+g(\rho)] + (u+a) \frac{\partial}{\partial x} [u+g(\rho)] = 0 \quad \dots\dots\dots(3.1.6)$$

$$\frac{\partial}{\partial t} [u-g(\rho)] + (u-a) \frac{\partial}{\partial x} [u-g(\rho)] = 0 \quad \dots\dots\dots(3.1.7)$$

where $g(\rho) = \int_{\rho_0}^{\rho} \frac{a}{\rho} d\rho$ is a thermodynamic property defined by ρ and s . The quantities $u+g(\rho)$ and $u-g(\rho)$ are the Reimann invariants denoted by P and Q respectively [3.1,p35]. Eqs. (3.1.6) and (3.1.7) therefore take the form;

$$\frac{\partial P}{\partial t} + (u+a) \frac{\partial P}{\partial x} = 0 \quad \dots\dots\dots (3.1.8)$$

$$\frac{\partial Q}{\partial t} + (u-a) \frac{\partial Q}{\partial x} = 0 \quad \dots\dots\dots (3.1.9)$$

These two equations define two families of special curves called the characteristic curves. If a curve exists in the distance-time (x,t) plane which has the slope $dx/dt = u+a$ then Eq. (3.1.8) can be written as;

$$\frac{\partial P}{\partial t} + \frac{dx}{dt} \frac{\partial P}{\partial x} = 0, \text{ i.e., } \frac{\partial P}{\partial t} dt + \frac{\partial P}{\partial x} dx = 0$$

which is an exact differential, i.e., $dP = 0$ so that $P = \text{constant}$.

In other words, in the (x,t) plane the curves along which $P = u+g(\rho)$ is constant have the slope $dx/dt = u+a$. These are called the P characteristic curves and represent the motion of a compression wave.

Similarly it can be shown that there exists another set of curves in the (x,t) plane along which $Q = u-g(\rho)$ is constant which has the slope $dx/dt = u-a$. These are called the Q characteristic curves and represent the motion of a decompression wave. The rate of advance of these waves is given by $u+a$ and $u-a$ respectively so that this rate of propagation relative to the flow speed u at every point under consideration is given by $\pm a$, i.e., the front of such a characteristic travels at the speed of sound relative to the gas. These characteristic paths are therefore properly called sound waves, Mach waves or characteristic lines. In particular, the decompression waves shown to be travelling to the left in Fig. 3.1.1 represent Q characteristics whose slopes are equal to $u-a$ [3.1 and 3.2]. The first characteristic line (head of the decompression wave) travelling into the gas at rest ($u = 0$) therefore propagates at the speed of sound [2.32a,p4].

3.2 Dense Gas Equations of State

The two functional relations;

$$p = p(\rho, T) : (\text{thermal equation of state}) \dots\dots (3.2.1)$$

$$U = U(\rho, T) : (\text{caloric equation of state}) \dots\dots (3.2.2)$$

taken together, constitute a complete equation of state for a pure substance, i.e., they are necessary and sufficient for the determination of all thermodynamic properties at the state (ρ, T) . However, particularly for gases, it is common practice to refer to the thermal equation of state as the equation of state with the understanding that the internal energy relation [Eq. (3.2.2)] is well known.

The equation of state for a very dilute gas, i.e., the well known ideal gas law, may be taken as the starting point for the present discussion. Here;

$$Z = p/\rho RT = 1 : \text{thermal equation of state}$$

$$\text{and } U = U^0(T) : \text{caloric equation of state}$$

where $U^0(T)$ is the precisely known ideal gas state internal energy value supplied by statistical mechanics applied to spectroscopic measurements of the rotation, vibration and electronic excitation of the molecules of the gas. The function (Z) describing the compressibility factor constitutes the essential difference among the various dense (i.e., non-ideal) gas equations of state.

The equation of state for a dense gas may be expressed as;

$$p = \rho RTZ; Z = Z(\rho, T) \quad : \text{thermal equation}$$

$$U(\rho, T) = U^O(T) + U_R(\rho, T) \quad : \text{caloric equation}$$

where $Z \neq 1$ except at one particular point on each (low temperature) isotherm while U^O is the ideal gas state internal energy component and U_R is the real or additional internal energy component arising from intermolecular forces and from the finite size of the molecules, both of which are justifiably neglected in the ideal gas equation of state. The real component of the internal energy (U_R) is determined from the general relation;

$$\left(\frac{\partial U_R}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_\rho - p = \rho RT^2\left(\frac{\partial Z}{\partial T}\right)_\rho$$

so that the calculated internal energy and other energy related properties such as speed of sound may be expected to be sensitive to the functional form of the equation of state $Z(\rho, T)$ even when the calculated values of $Z(\rho, T)$ accurately reflect observed values of Z .

Over the years, various equations of state have been developed, both analytically and empirically, for dense gases. However, no equation, regardless of its complexity, is wholly satisfactory for all conditions of temperature and density [3.3].

In this study three equations of state are chosen for comparison of the calculated thermodynamic properties with those observed here. These are;

1. The van der Waals equation of state
2. A virial equation of state
3. The Benedict-Webb-Rubin equation of state.

These equations and the expressions for calculation of the relevant thermodynamic properties are described below. The detailed procedure for computation of thermodynamic properties from these equations is given in appendix A1.

3.2.1 The van der Waals Equation of State. The van der Waals [3.4] equation may be written as;

$$\left(p + \frac{a_{vdw}}{v^2}\right)(v - b_{vdw}) = RT \quad \dots\dots\dots (3.2.3)$$

where a_{vdw} and b_{vdw} are constants accounting for the attractive forces among the molecules of the gas and the finite volume of the gas particles respectively. The constants a_{vdw} and b_{vdw} are determined from the p, v, T properties at the critical point using the definition of the critical point namely;

$$\left(\frac{\partial p}{\partial v}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c} = 0$$

From this condition it follows that;

$$\left. \begin{aligned} a_{vdw} &= (27/8)RT_c^2 b_{vdw} \\ b_{vdw} &= v_c/3 \end{aligned} \right\} \dots\dots\dots (3.2.4)$$

and the expression for the compressibility factor Z is seen to be;

$$Z = \frac{P}{\rho RT} = \frac{1}{1 - \omega_{vdw}} - \frac{27/8}{T_r} \omega_{vdw} \quad \dots\dots\dots (3.2.5)$$

where ω_{vdw} is a dimensionless density and is equal to b_{vdw}/v and $T_r = T/T_c$, T_c being the critical temperature.

The following relations can be derived from Eq. (3.2.5).

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} \frac{1}{1 - \omega_{vdw}} \quad \dots\dots\dots (3.2.6)$$

$$\kappa = \frac{1}{\frac{P}{Z} \left[\frac{1}{(1 - \omega_{vdw})^2} - \frac{27}{4T_r} \omega_{vdw} \right]} \quad \dots\dots\dots (3.2.7)$$

$$c_v = c_v^0(T); \quad c_{vR} = 0 \quad \dots\dots\dots (3.2.8)$$

Eqs. (3.2.5) through (3.2.8) can be used to calculate other desired thermodynamic properties.

3.2.2 Virial Equation of State. The experimental p v isotherm may be represented over wide ranges of pressures and temperatures by a power series relation;

$$\frac{pv}{RT} = Z = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots \quad \dots\dots\dots (3.2.9)$$

referred to as a virial equation of state. The temperature dependent functions $B(T)$, $C(T)$, ... are called the second, third, ... virial coefficients. These coefficients have

functional forms determined by the nature of the assumed intermolecular potential energy function. The computation requires statistical mechanics and results in dimensionless (i.e., universal) functions. The unknown constants are determined experimentally.

The range of validity of the virial expansion is limited by the convergence of the series, which diverges at about the density of the liquid. Hence the primary application of the virial equation of state is in the study of gases at low and moderate densities [1.3,p132].

In the simplest case, molecules are assumed to be force-free rigid spheres. For this model virial coefficients up to the fifth have been known for several years [1.3,p157]. The sixth and seventh virial coefficients also have now been calculated and the eighth virial coefficient has been estimated [2.1,p186]. These hard molecule coefficients are;

Second;	$B = \frac{2}{3} \pi N \sigma_h^3 = b_h$	[1.3 and 2.1]	} ... (3.2.10)
Third;	$C = 0.625 b_h^2$	[1.3 and 2.1]	
Fourth;	$D = 0.2869 b_h^3$	[1.3]	
Fifth;	$E = (0.115 \pm 0.005) b_h^4$	[1.3]	
Fifth;	$E = (0.1104 \pm 0.00006) b_h^4$	[2.1]	
Sixth;	$F = (0.0386 \pm 0.0004) b_h^5$	[2.1]	
Seventh;	$G = (0.0138 \pm 0.0004) b_h^6$	[2.1]	
Eighth;	$H \approx 0.005 b_h^7$	[2.1]	

where N is the Avogadro's number and σ_h is the diameter of the hard molecule which can be obtained from kinetic theory of gases [1.3,p15] or from experimental data. Stuart [3.5,p36] provides a listing of collision diameters for rigid spheres as determined from different types of experimental data. The virial coefficients for rigid molecules are, of course, independent of temperature. Thus, the rigid sphere approximation is good only at very high temperatures where the attraction between molecules becomes unimportant [1.3,p157]. However, experimental values of the virial coefficients demonstrate temperature dependence and at low temperatures differ significantly from the hard molecule case. More sophisticated intermolecular potential energy functions which have been proposed include the square-well potential, the Sutherland potential, the Lennard-Jones potential and the Buckingham potential. For non-polar molecules, the most commonly used intermolecular potential function is the Lennard-Jones (6-12) potential;

$$\phi(r) = 4\varepsilon[(\sigma_{LJ}/r)^{12} - (\sigma_{LJ}/r)^6] \quad \dots\dots\dots(3.2.11)$$

where σ_{LJ} is the low velocity collision diameter and is equal to the value of r for which $\phi(r) = 0$, and ε is the maximum energy of attraction (or depth of potential well) which occurs at $r = 2^{1/6} \sigma_{LJ}$. The parameters σ_{LJ} and ε having the dimensions of length and energy respectively are

constants characteristic of the chemical species of the colliding molecules [1.3,p22]. A pictorial representation of the Lennard-Jones potential energy function along with the hard molecule or rigid sphere potential function is shown in Fig. (3.2.1). The generalized second and third virial coefficients and their temperature derivatives for the Lennard-Jones (6-12) potential, defined below, are tabulated in [1.3,p1114-1117].

$$\left. \begin{aligned} B^*(T^*) &= B(T) / \left(\frac{2}{3} N \pi \sigma_{LJ}^3 \right) = B(T) / b_{LJ} \\ C^*(T^*) &= C(T) / b_{LJ}^2 \\ B_n^*(T^*) &= T^{*n} (d^n B^* / dT^{*n}) \\ C_n^*(T^*) &= T^{*n} (d^n C^* / dT^{*n}) \\ T^* &= T / (\epsilon / k) = T / \theta \end{aligned} \right\} \dots\dots\dots (3.2.12)$$

where k is the Boltzmann constant, b_{LJ} is the covolume and θ is the potential well depth temperature. The pair (b_{LJ}, θ) are the so called force constants and are determined from experimental $B(T)$ data [2.1,p250]. Once found, this pair of constants fully determines the thermal equation of state. However, the analytical $C^*(T^*)$ values do not agree well with observed values of $C(T) / b_{LJ}^2$ [1.3,p171 and 2.1,p254].

The fourth and higher virial coefficients for the Lennard-Jones (6-12) potential have also been calculated [3.6,3.7] but their experimental verification is so far

incomplete. Accordingly, since the fourth and fifth virial coefficients are well established for the rigid sphere potential, Groves [3.8] has designed a hybrid virial equation of state which takes the soft molecule terms of the virial equation using the Lennard-Jones (6-12) potential with the hard molecule terms from the hard molecule virial. In this hybrid virial equation the second and third virial coefficients are taken from the Lennard-Jones (6-12) potential and the fourth and fifth virial coefficients are taken from the hard molecule assumption. Thus the hybrid virial equation of state is given by;

$$\begin{aligned}
 Z = \frac{pV}{RT} &= 1 + \frac{B^*(T^*)b_{LJ}}{v} + \frac{C^*(T^*)b_{LJ}^2}{v^2} + \frac{0.2869b_h^3}{v^3} + \frac{0.115b_h^4}{v^4} \\
 &= 1 + B^*(T^*)\omega_{LJ} + C^*(T^*)\omega_{LJ}^2 + 0.2869\omega_h^3 + 0.115\omega_h^4 \quad \dots (3.2.13)
 \end{aligned}$$

where ω_{LJ} is a dimensionless density for Lennard-Jones (6-12) potential defined by $\omega_{LJ} = b_{LJ}/v$ and ω_h is a dimensionless density for hard molecules defined by $\omega_h = b_h/v$. This hybrid virial is found to predict satisfactory values of the compressibility factor at the critical point (Z_c). It can be shown that for the hard molecule virial the internal energy is the same as the ideal gas value. On the other hand the compressibility factor Z obtained from the truncated Lennard-Jones (6-12) virial is significantly lower than the

observed values. The hybrid equation takes advantage of the contribution to the internal energy by the soft Lennard-Jones (6-12) molecules and partly corrects the too low value of Z given by the truncated Lennard-Jones (6-12) virial. The diameter σ_h may be defined to be the distance of closest approach in a collision having the average collision energy kT [1.3,p157]. Thus, with reference to Fig. 3.2.2, σ_h is the value of r at which the potential function $\phi(r) = kT$. Thus;

$$kT = 4\epsilon[(\sigma_{LJ}/\sigma_h)^{12} - (\sigma_{LJ}/\sigma_h)^6]$$

From which;

$$\frac{\sigma_h}{\sigma_{LJ}} = \left[\frac{2}{1 + \sqrt{(1 + T^*)}} \right]^{1/6} \dots\dots\dots (3.2.14)$$

and therefore;

$$\frac{\omega_h}{\omega_{LJ}} = \frac{b_h}{b_{LJ}} = \left(\frac{\sigma_h}{\sigma_{LJ}} \right)^3 = \left[\frac{2}{1 + \sqrt{(1 + T^*)}} \right]^{1/2}$$

i.e. $b_h = b_{LJ} \left[\frac{2}{1 + \sqrt{(1 + T^*)}} \right]^{1/2} \dots\dots\dots (3.2.15)$

where an average temperature over the temperature range concerned may be used to define a fixed value of b_h for Eq. (3.2.15).

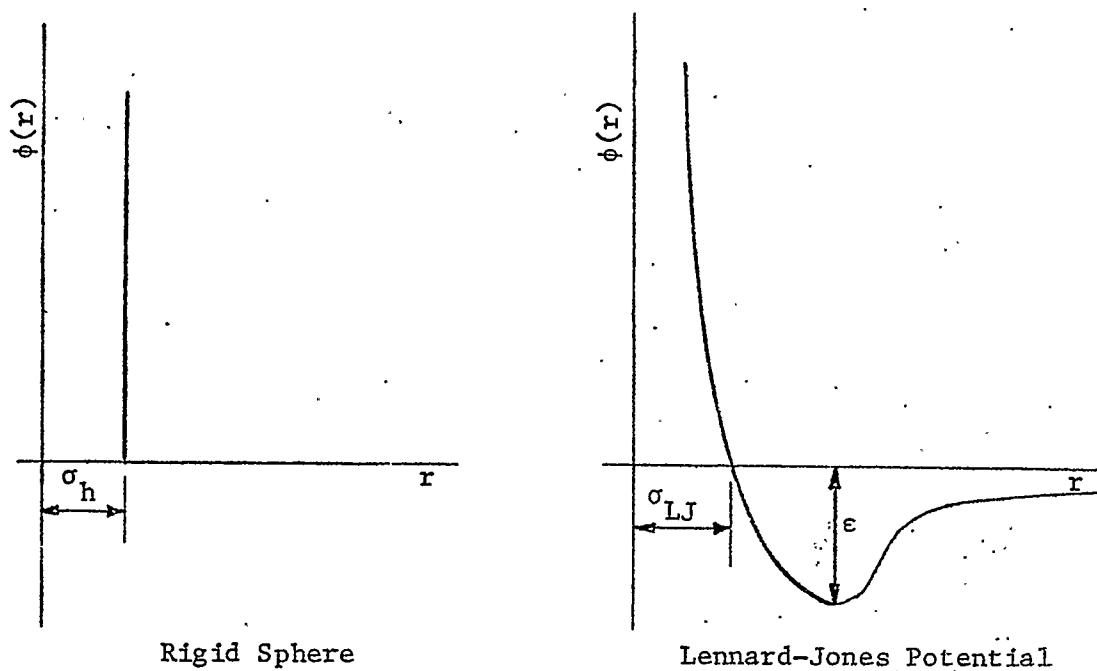


Fig. 3.2.1 Pictorial Representation of Hard Molecule or Rigid Sphere and Lennard-Jones (6-12) Potential Energy Function.

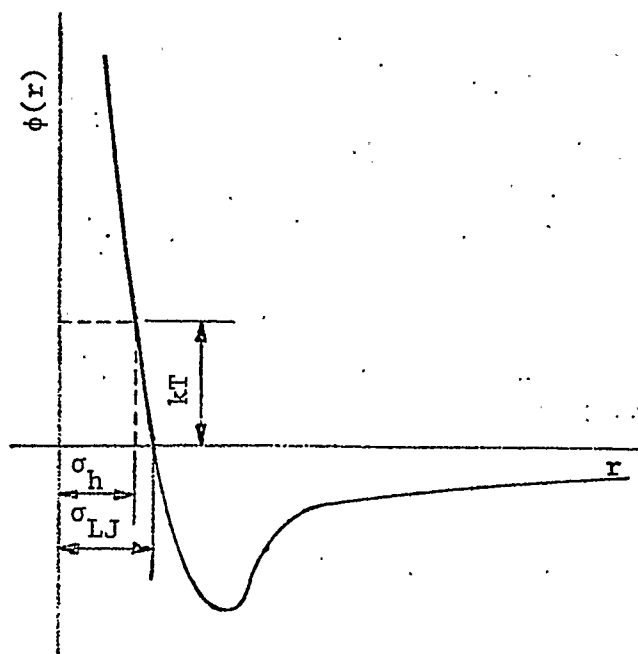


Fig. 3.2.2 Illustration of σ_h as the Value of r at which $\phi(r) = kT$ for Lennard-Jones Potential.

The following relations can be derived from Eq. (3.2.13);

$$\left(\frac{\partial p}{\partial T}\right)_v = ZR \frac{\omega_{LJ}}{b_{LJ}} + \frac{R}{b_{LJ}} (B_1^* \omega_{LJ}^2 + C_1^* \omega_{LJ}^3) \dots\dots\dots (3.2.16)$$

$$\kappa = \frac{1}{p[1 + (1/Z)(B_1^* \omega_{LJ} + 2C_1^* \omega_{LJ}^2 + 3 \times 0.2869 \omega_h^3 + 4 \times 0.115 \omega_h^4)]} \dots\dots\dots (3.2.17)$$

$$c_{vR} = -R\omega_{LJ}[(2B_1^* + B_2^*) + \left(\frac{\omega_{LJ}}{2}\right)(2C_1^* + C_2^*)] \dots\dots\dots (3.2.18)$$

Eqs. (3.2.16) through (3.2.18) and Eq. (3.2.13) are used to calculate other desired thermodynamic properties. The Lennard-Jones (6-12) potential constants for the gases used are given in Table A1.2.1.

3.2.3 The Benedict-Webb-Rubin Equation of State. This is an empirical equation with eight constants obtained by fitting the equation to experimental values. When expressed as a virial it has the form;

$$Z = \frac{pV}{RT} = 1 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3})\rho + (B - \frac{A}{RT} + \frac{C}{RT^3} e^{-\gamma\rho^2})\rho^2 \\ + (\gamma\frac{C}{RT^3})e^{-\gamma\rho^2}\rho^4 + \alpha\frac{A}{RT}\rho^5 \dots\dots\dots (3.2.19)$$

where the eight constants A , A_o , B , B_o , C , C_o , α and γ are determined from pure gas data. The constants for the gases used are taken from [3.9] and presented in Table A1.2.2. The following relations can be derived from Eq. (3.2.19)

which are used to compute the desired thermodynamic properties;

$$\left(\frac{\partial p}{\partial T}\right)_v = R\rho \left[1 + (B_o + \frac{2C_o}{RT^3})\rho + (B - \frac{2C}{RT^3} e^{-\gamma\rho^2})\rho^2 - \gamma \frac{2C}{RT^3} e^{-\gamma\rho^2} \rho^4\right]. \quad (3.2.20)$$

$$\kappa = \frac{1}{\frac{p}{Z} \left[1 + 2(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3})\rho + 3(B - \frac{A}{RT} + \frac{C}{RT^3} e^{-\gamma\rho^2})\rho^2 + 3(\gamma \frac{C}{RT^3}) e^{-\gamma\rho^2} \rho^4 + 6\alpha \frac{A}{RT} \rho^5 - 2\gamma^2 \frac{C}{RT^3} e^{-\gamma\rho^2} \rho^6\right]} \quad \dots\dots\dots (3.2.21)$$

$$c_{vR} = \frac{1}{RT^3} [6C_o\rho + 3C e^{-\gamma\rho^2} \rho^2 + 6 \frac{C}{\gamma} (e^{-\gamma\rho^2} - 1)] \quad \dots\dots\dots (3.2.22)$$

IV EXPERIMENTAL METHOD

4.1 Outline of the Method

4.1.1 Measurement of Decompression Wave Front Velocity.

The decompression wave is generated by bursting a diaphragm in a tube filled with the chosen gas at a known pressure and temperature. The front of the wave travels from the rupture point at the speed of sound in the undisturbed gas and is detected by piezoelectric transducers*. A typical set of pressure-time signals from these transducers is shown in Fig. 4.1.1. These signals are recorded on magnetic tape. These records are digitized by an analog-to-digital converter and the digitized data are transferred directly to a computer (desk-top 48 K Apple II) for analysis. A digitizing interval of 1 microsecond was adopted.

For the purpose of analysis every signal is divided into two zones as shown in Fig. 4.1.2. The first is the constant pressure zone where the pressure is seen to remain essentially constant (except for noise and drift) until the decompression wave front arrives. The second demonstrates a decaying pressure signal which describes the pressure of the decompression wave fan as it traverses the transducer.

*"Kistler" quartz transducers, type 601A

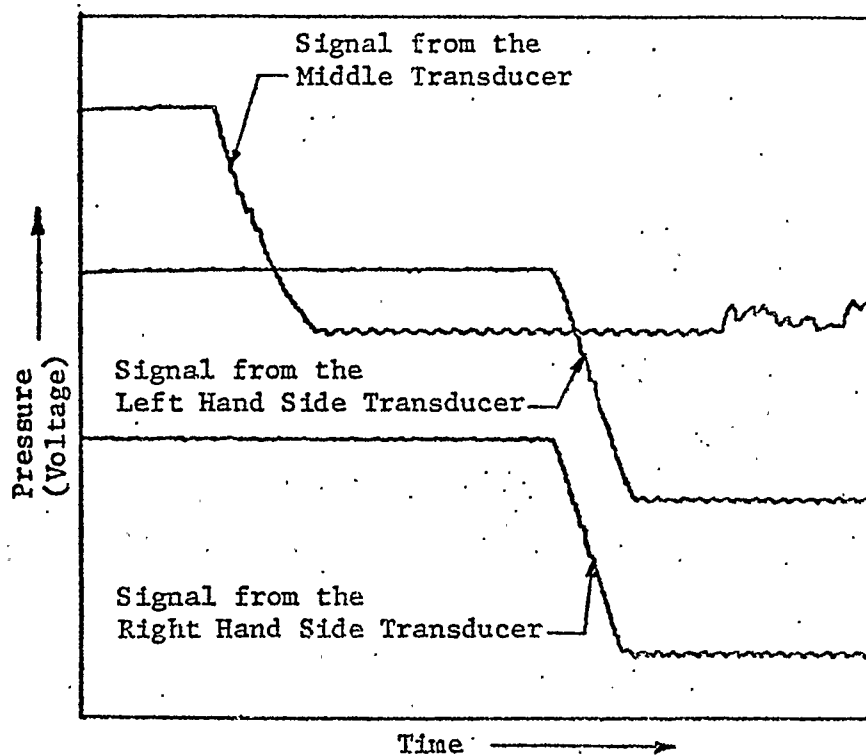


Fig. 4.1.1 A Typical Set of Pressure (Voltage) - Time Signal from the Piezoelectric Transducers; as Viewed on the Oscilloscope Screen and Recorded by xy Plotter.

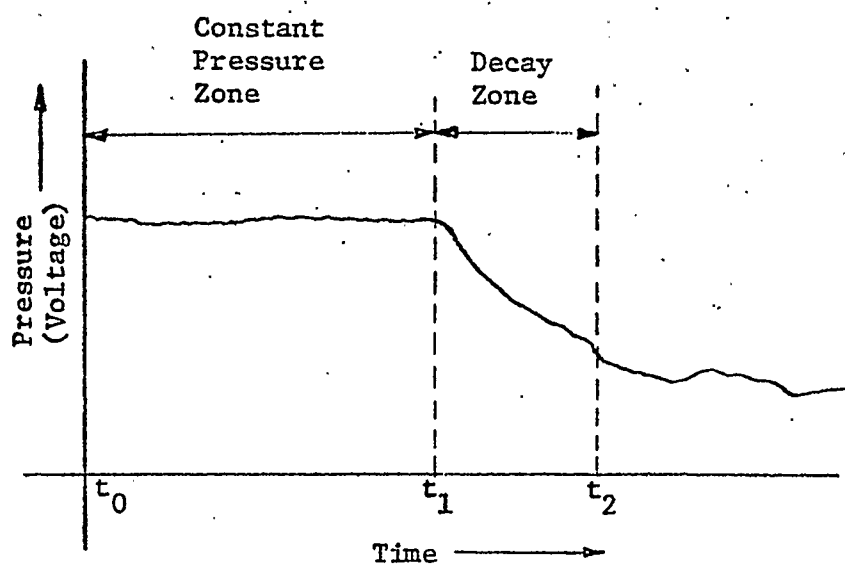


Fig. 4.1.2 Signal Description.

The digitized record from the constant pressure zone is fitted by a straight line. The decaying zone signal is fitted by a second degree polynomial. This particular polynomial was chosen from the examination of standard deviations of the fits of a variety of candidate fitting functions $p(t)$ when applied to several data sets. These candidate equations included first, second and third degree polynomials, exponentials, power functions and a logarithmic second degree polynomial [of the form $\ln p = C_0 + C_1(\ln t) + C_2(\ln t)^2$].

In order to determine the time of arrival (t_1) of the head of the decompression wave at a particular transducer position, the signal is first displayed on an oscilloscope from which an initial estimate of t_1 (see Fig. 4.1.2) is obtained. The digitized $p(t)$ data from t_0 to t_1 are fitted by least squares to obtain the linear equation in the constant pressure zone; $p(t) = b_0 + b_1 t$. A time t_2 , also chosen from the oscilloscope display, defines the time beyond which the decaying signal ceases to be smooth. The digitized data from t_1 to t_2 are fitted to obtain the pressure-time polynomial; $p(t) = a_0 + a_1 t + a_2 t^2$. The intersection of these two curves is taken to be the improved arrival time (t_1) of the head

of the decompression wave. Thus;

$$p(t_1) = b_o + b_1 t_1 = a_o + a_1 t_1 + a_2 t_1^2$$

$$\text{i.e., } t_1 = \frac{-(a_1 - b_1) \pm \sqrt{(a_1 - b_1)^2 - 4a_2(a_o - b_o)}}{2a_2} \quad \dots (4.1.1)$$

Using this improved value of t_1 , the process is repeated until no significant change in t_1 occurs. This final t_1 is taken to be the arrival time of the head of the decompression wave at the particular transducer position concerned. The velocity of the head of the decompression wave (i.e., the speed of sound) is then taken to be $\Delta x / \Delta t$ where Δx is the distance between two transducers and Δt is the difference in times of arrival of the decompression wave at these two transducers.

4.1.2 Measurement of the Isothermal Compressibility.

The isothermal compressibility κ may be defined by;

$$\kappa = -(1/V)(\partial V / \partial p)_T \quad \dots (4.1.2)$$

In the measurement of κ , the gas at pressure p_{1i} in the decompression tube is leaked into a relatively small pre-evacuated chamber of accurately known volume V_2 . After thermal equilibrium is established with the surrounding liquid bath in which the apparatus is immersed, decrease Δp in pressure is noted. The value of κ is therefore given by;

$$\kappa(p_\kappa, T) = -\frac{1}{V_1 + V_2/2} \frac{V_2}{\Delta p} ; \quad p_\kappa = p_{1i} - \frac{\Delta p}{2} \quad \dots (4.1.3)$$

where V_1 is the original volume of the gas and T is the temperature of the isotherm, i.e., of the bath.

4.1.3 Measurement of Density. Gas density is measured by expanding the mass of the gas previously leaked into the space of known volume V_2 (see above) into an additional large volume V_3 . Since the gas is now very dilute, the ideal gas equation of state may be applied in order to determine the mass (m) of the gas which was originally leaked into the small chamber. The gas density is therefore m/V_2 .

4.2 Apparatus

A schematic diagram of the apparatus is given in Fig. 4.2.1 and a photographic view is given in Plate 4.2.1. The apparatus consists of (i) a decompression wave tube equipped with pressure and temperature sensors designed to measure the speed of sound in the contained gas; (ii) a coil made of 1/8 inch OD stainless steel tubing used as the expansion chamber in the measurement of isothermal compressibility; (iii) a large cylindrical vessel designed to aid in the measurement of the gas density; (iv) a constant-temperature bath in which these gas-containing components are immersed; (v) high pressure gas bottles and (vi) electronic recording, display and analysing equipment.

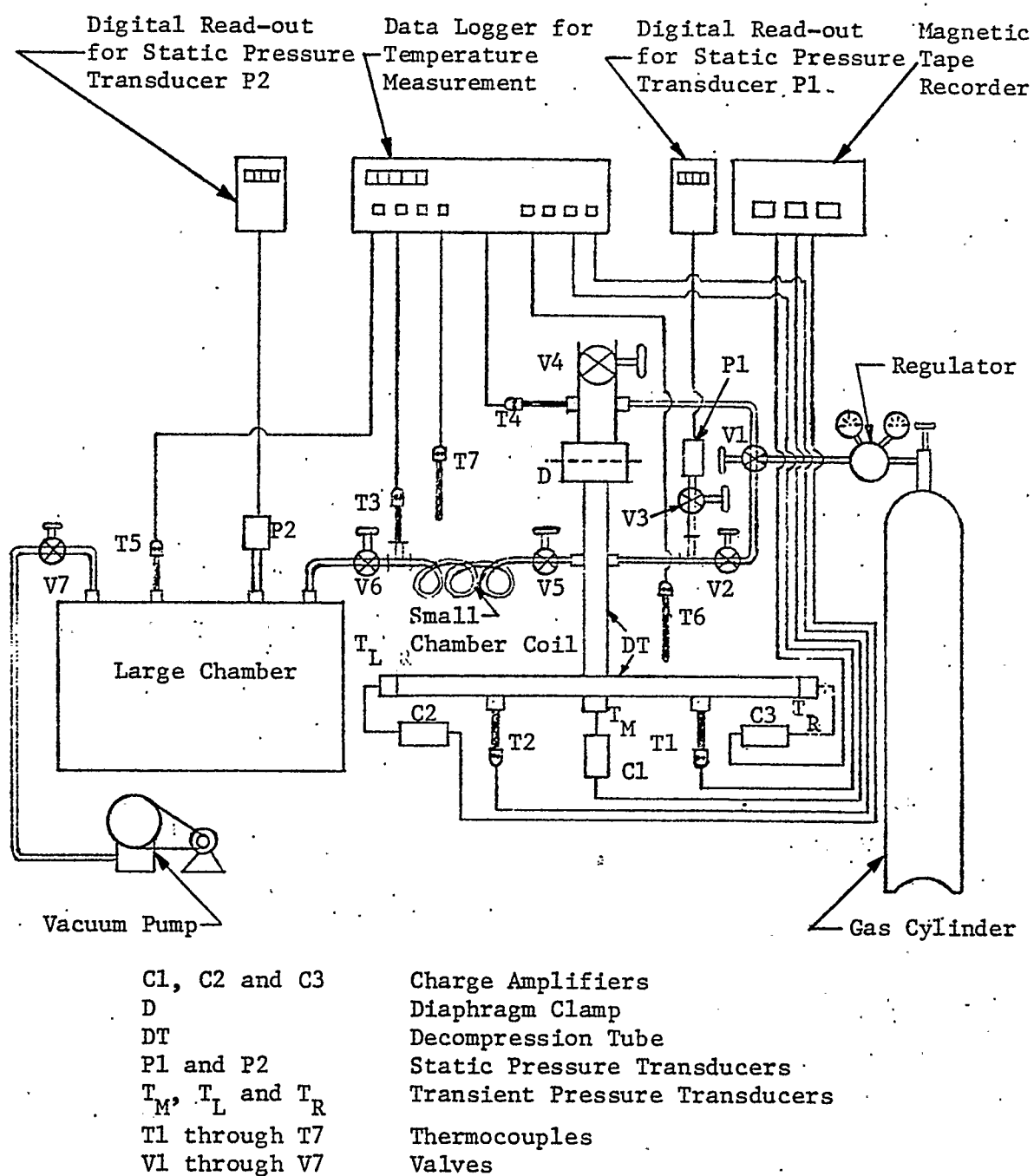


Fig. 4.2.1 Schematic Diagram of the Apparatus.

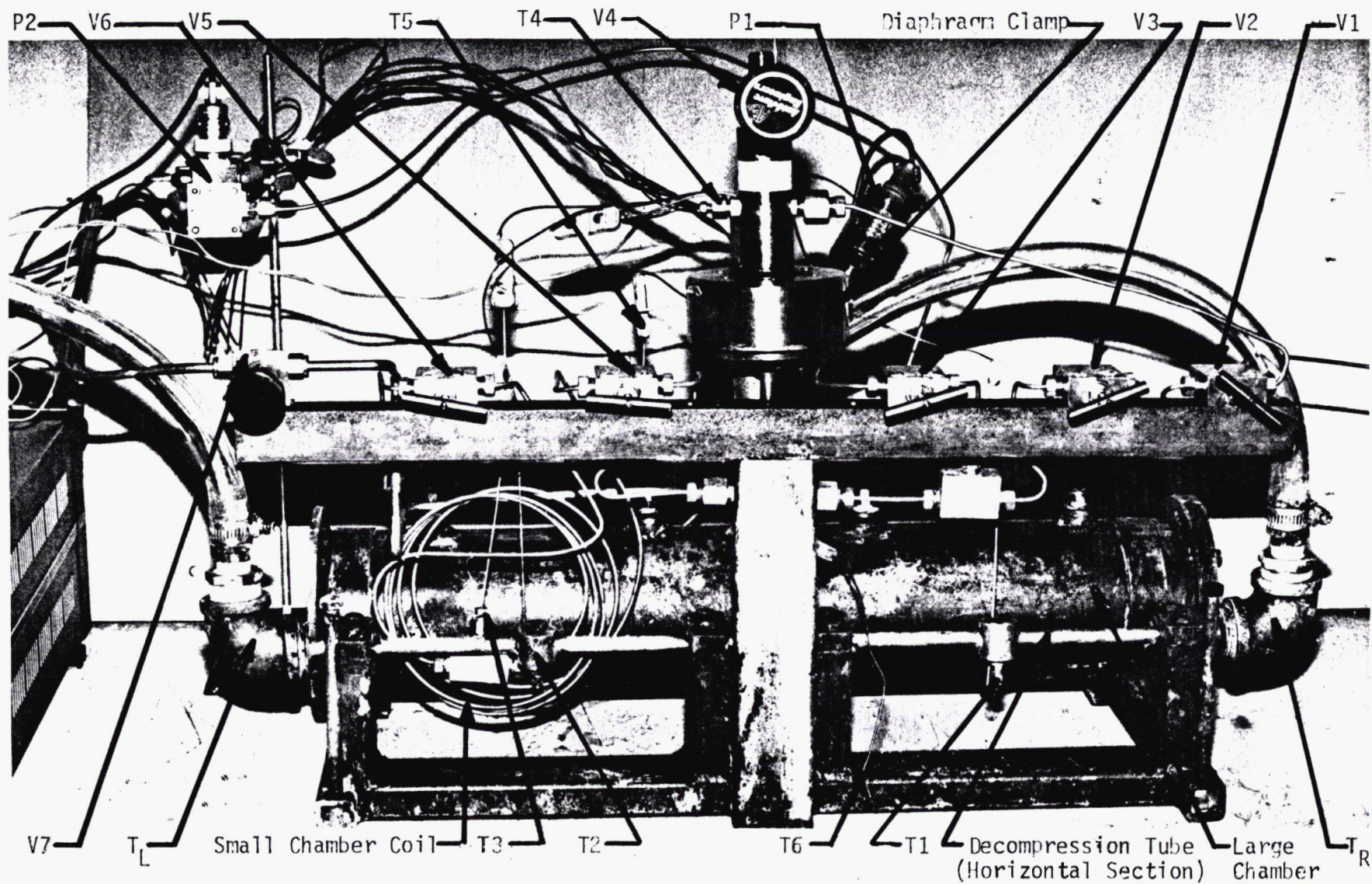


Plate 4.2.1 Photograph of the Apparatus.
 (for notations see Fig. 4.2.1)

The decompression wave tube, 7.798 mm ID and 10.287 mm OD is made from 316 stainless steel (1/8 inch nominal size pipe of schedule 10 is used). As shown in Plate 4.2.2, this tube is shaped like an inverted T with a diaphragm-clamp at the top of the vertical section. The diaphragm is designed according to Gaydon [4.1] and the details are shown in Fig. 4.2.2. The vertical section of the tube is welded to the middle of the horizontal section. A transducer (designated T_M) is mounted flush with the tube wall in the horizontal section of this T-junction normal to the axis of the vertical section. Two other transducers (designated T_L and T_R) are mounted flush with the end faces of the horizontal section of the tube.

This arrangement of transducers in the T-shaped decompression tube facilitates high accuracy in the measurement of decompression wave front velocity. When the diaphragm is ruptured a decompression wave travels down the vertical section of the tube, undergoes a normal reflection at the front surface of the transducer T_M and then splits into two decompression waves moving left and right along the horizontal section where normal reflection occurs again at the front surfaces of the transducers T_L and T_R . Thus each encounter of the wave with a transducer is essentially head on, so that all parts of the sensitive element of the

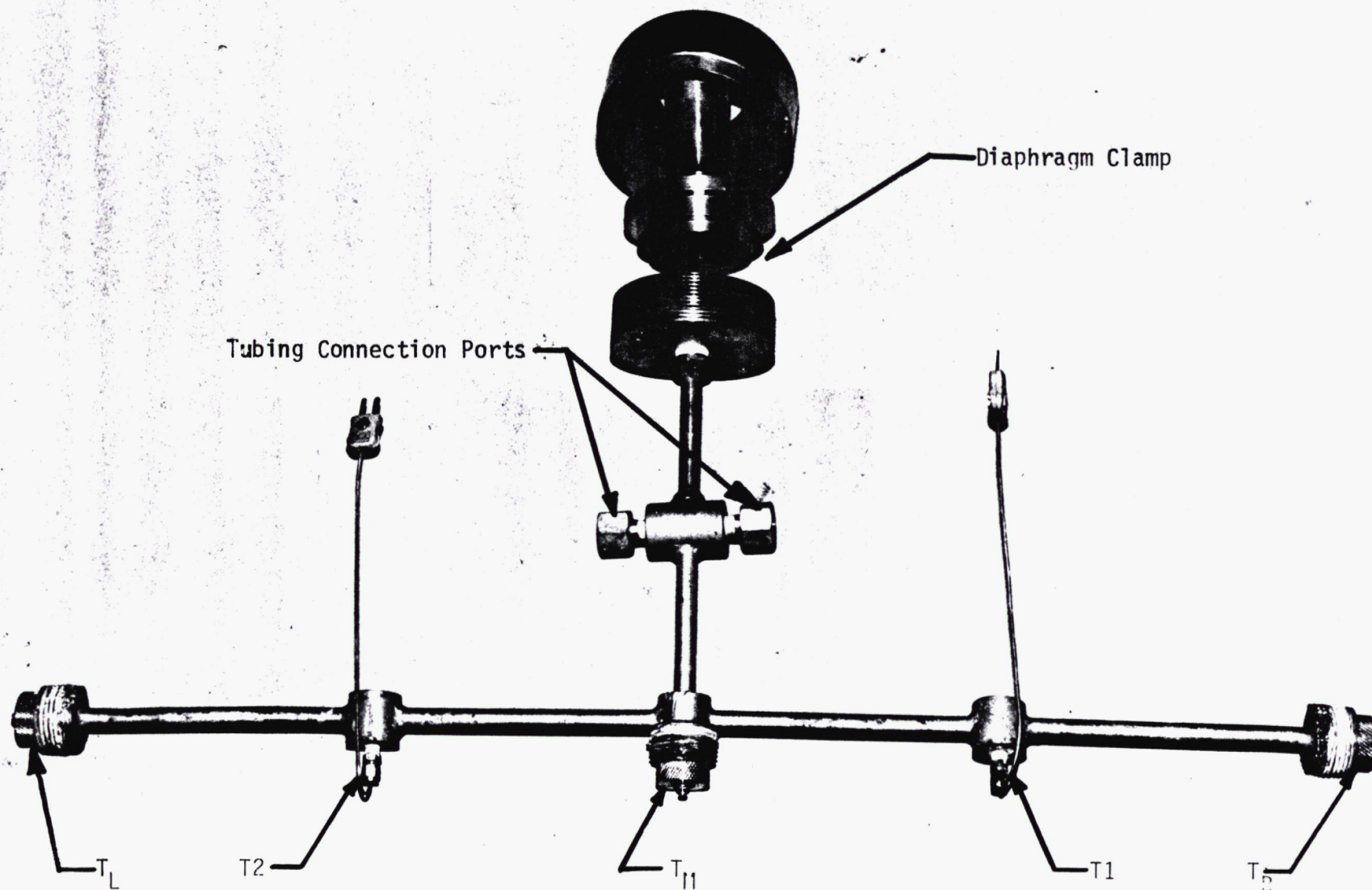


Plate 4.2.2 Closeup View of the Decompression Tube.
(for notations see Fig. 4.2.1)

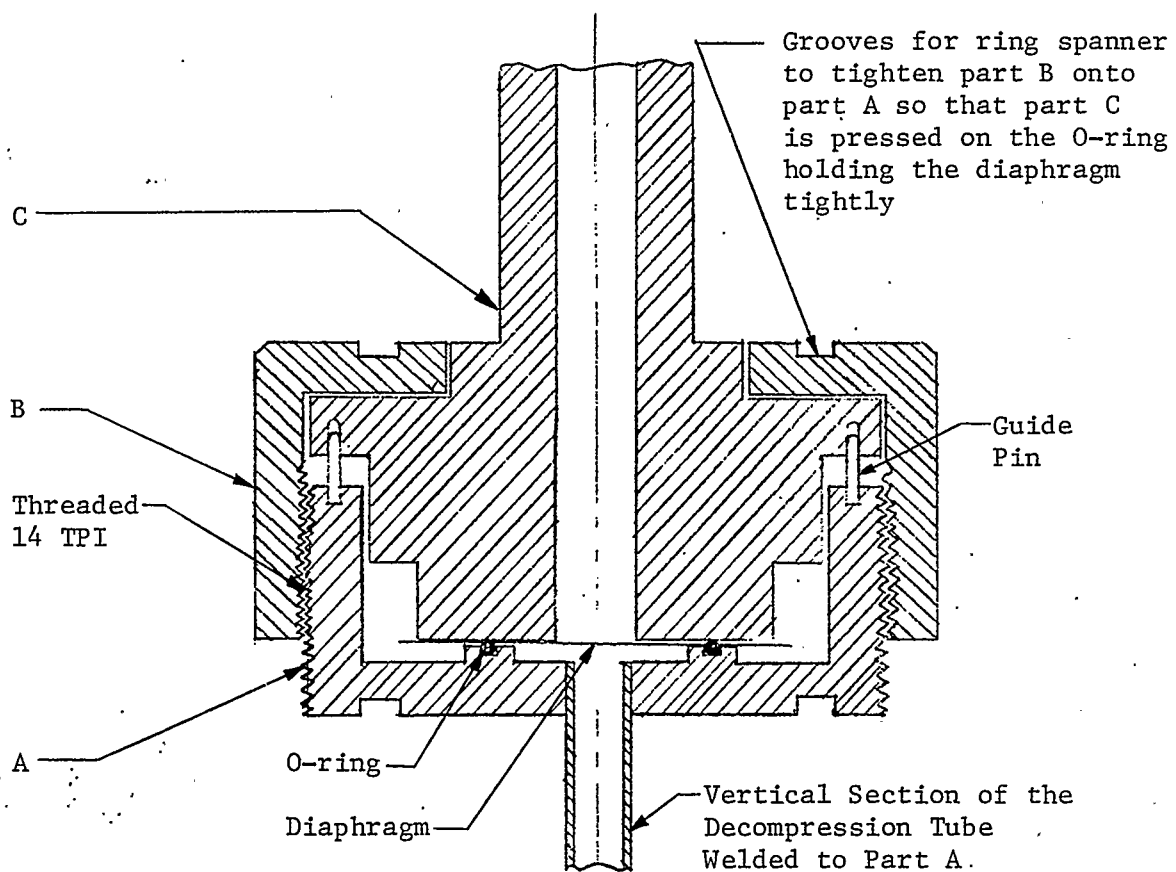


Fig. 4.2.2 Details of the Diaphragm Clamp.

transducers experience the same pressure simultaneously. This not only allows precise definition of the effective distance between transducers but also enables precise determination of the arrival time of the front of the decompression wave (indicated by an abrupt decrease in the pressure signal from the transducers). This abruptness (and therefore the determination of time of arrival) is further enhanced by the doubling effect of normal reflection on pressure decrease in the gas adjacent to the transducer elements.

The gas is drawn from the high pressure supply through 1/8 inch OD stainless steel tubing. This is fed to both sides of the diaphragm through ports in the vertical section of the tube. The coil-shaped expansion chamber, mentioned above, has an internal volume of only about 10 % of the main tube. One end of this is connected to the vertical section of the T-tube and the other end is connected through a valve to the large cylinder which has an internal volume about 1000 times that of the internal volume of the coil.

As shown in Fig. 4.2.1, seven high pressure valves V1 through V7 are connected to the tubing for operation and control, thermocouples T1 through T7 are used to measure the temperature at seven chosen points and two static pressure

transducers P1 and P2 are used to measure the static pressures in the decompression wave tube and the large tank respectively.

For measurement on a chosen isotherm all gas-containing chambers within the diaphragm are immersed in a temperature controlled liquid bath.

The connecting tubing and the valves V1 through V6 are rated for 100 MPa and hydraulic tests show the decompression tube to have a rating of at least 60 MPa.

Three gases are studied namely; carbon dioxide, argon and nitrogen. These gases, of 99.998 % purity, were supplied by Matheson Gas Co in gas cylinders. Argon and nitrogen were supplied at pressures of about 40 MPa while carbon dioxide was supplied at pressures of about 5.5 MPa.

4.3 Procedure

The diaphragm is emplaced. Then the entire system including the connected tubing and the large chamber is evacuated. Here, the valves V1 and V4 are closed and all other valves are open. The system is then flushed by repeatedly introducing a small amount of gas (via V1) and then evacuating. The final post-evacuation pressure p_{2i} registered by transducer P2 (generally 1kPa) is noted. The gas is then loaded into the decompression tube until the desired pressure is reached (V1 opened, V5 closed). With valve V1 now closed,

the gas is fully contained. Thermal equilibrium with the bath is reached within 10 minutes. When this has been attained the pressure p_{1i} registered by the transducer P1 is noted. This is the initial pressure inside the decompression tube. With valve V6 closed, V5 is opened so that a small fraction of the gas leaks into the expansion coil. After about 5 minutes, thermal equilibrium is established and the pressure p_{1f} registered by transducer P1 is noted. Valve V6 is now opened (with V5, V7 closed) so that the high pressure gas in the coil expands into the large chamber. After a few minutes, when thermal equilibrium is established the pressure p_{2f} exhibited by transducer P2 is noted.

The decompression wave is now initiated by opening valve V4 sharply (with V2 closed). As a result the pressure on the outer side of the diaphragm decreases so that a strong pressure difference across the diaphragm is rapidly established. Accordingly, the diaphragm (a thin sheet of mylar about 0.025 mm thick) bursts abruptly and a decompression wave travels downward along the vertical section of the tube as described earlier. The signal from the transducers T_M , T_L and T_R are recorded on a magnetic tape at a speed of 60 in/sec for later analysis.

4.4 Measurement Details

4.4.1 Temperature Measurement. Temperatures are measured via J-type (iron/constantan) thermocouples. Seven thermocouples are used for this purpose. Gas temperatures within the left and right arms of the horizontal section of the T-tube are obtained via thermocouples T1 and T2. The gas temperature in the coil and in the large cylinder are measured via thermocouples T3 and T5 respectively, while the temperature of the bath is measured via T6 and room temperature is measured via T7. The temperature of the gas external to the diaphragm is measured via T4. These thermocouples are connected to a "Fluke 2240B" data-logger which provides digital temperature read-out with a resolution of 0.1°C .

The thermocouples are calibrated against a high-precision quartz thermometer in a variable temperature oven over the range -45°C to 110°C in steps of 5°C . These observations are fitted by a linear relation using the method of least squares to obtain the coefficients of the linear calibration relation;

$$T = C_0 + C_1 T' \quad \text{..... (4.4.1)}$$

where T' is the apparent temperature registered by a thermocouple and T is the corrected temperature. These coefficients are given in Table 4.4.1.

Table 4.4.1 Thermocouple-Calibration Coefficients.

Thermocouple	C_0	C_1
	$^{\circ}\text{C}$	
T1	-0.568149	1.02296
T2	0.295812	1.01473
T3	0.156424	1.03290
T4	-0.135006	0.99783
T5	-0.534654	1.01942
T6	-0.446854	0.99839
T7	-1.080440	1.00003

Observations are made only at 0°C and 25°C . The 0°C isotherm is maintained by melting ice in distilled water (in the bath) while the 25°C isotherm is maintained by a "Thermomix" temperature-controller equipped with a heating element and a thermostat, using a 60 % (by weight) solution of ethylene glycol in distilled water.

For each gas-load, the temperature ascribed to the gas is taken to be the average of the corrected temperatures given by the thermocouples immersed in the bath namely; T1, T2, T3, T5 and T6. This average temperature is seen to vary for different sets of readings for the same isotherm. The maximum variation for the 0°C isotherm is $\pm 0.1^{\circ}\text{C}$ and that for the 25°C isotherm is $\pm 0.2^{\circ}\text{C}$. This variation is due in part to round-off of temperature readings presented by the data-logger.

4.4.2 Pressure Measurement. The pressure in the main tube is measured using a "Sensotech TJE" pressure transducer (P1), having a range of 0 to 15,000 psig with accuracy rated to within 0.1 %, connected to a "Sensotech 450D" signal conditioner which provides digital readings of pressure in psig units with a resolution of 1 psi.

The pressure in the large (low pressure) chamber is measured using a "Validyne DP15-42" differential pressure transducer (P2), having a range of ± 140 kPa with a rated accuracy of 0.25 %, connected to a "Validyne CD223" digital transducer indicator which provides digital pressure readings in kPa units with a resolution of 0.01 kPa.

Atmospheric pressure is measured using a "Penwalt-FA112150" precision aneroid dial type barometer (located near the apparatus) having a resolution of 0.05 kPa.

4.4.3 Volume Measurements. Precise values of the internal volume of the main decompression tube, the coil and the large low pressure chamber and the connected tubing are required in order to determine accurate values of gas density and isothermal compressibility. For convenience, the internal volume of the main tube along with the tubing, i.e., the volume from valve V1 to V5 (Fig.4.2.1), is designated as V_1 ; the internal volume of the coil, i.e., the volume

from valve V5 to V6, is designated V_2 while the volume of the large cylinder, from valve V6 to V7, is designated V_3 .

The internal volumes V_1 , V_2 and V_3 are determined by disconnecting each segment (including valves) and weighing them first empty and then filled with distilled water at a known temperature. The difference in mass divided by the density of water at the temperature concerned gives the volume. Weights are obtained using a (digital) balance and the density of the distilled water is obtained by interpolation using recent data [4.2,p6-10]. The procedure is repeated several times for each segment resulting in the average values given below;

$$(T\text{-tube}) \quad V_1 = 55.2234 \text{ ml} \pm 0.053 \text{ ml at } 22.0^\circ\text{C}$$

$$(Coil) \quad V_2 = 6.5146 \text{ ml} \pm 0.005 \text{ ml at } 18.1^\circ\text{C}$$

$$(Large Chamber) \quad V_3 = 5106.5407 \text{ ml} \pm 5.240 \text{ ml at } 19.5^\circ\text{C}$$

4.5 Working Formulae for Deriving Density, Isothermal Compressibility and Decompression Wave Front Velocity

4.5.1 Nomenclature.

p_{1i} : pressure in the main tube after the gas is loaded (and before valve V5 is opened).

p_{1f} : pressure in the main tube and the expansion coil (after the valve V5 is opened with V6 closed).

p_{2i} : initial (vacuum) pressure in the coil and the large chamber (before valve V5 is opened).
 p_{2f} : final pressure in the large chamber and coil after the high pressure contents of the coil are shared with the large chamber (after valve V6 is opened with V5 closed).
 p_{atm} : atmospheric pressure
 m_{2i} : initial mass of gas (at pressure p_{1f}) in the coil.
 m_{2f} : final mass of gas (at pressure p_{2f}) in the coil after the high pressure contents of the coil are shared with the large chamber.
 m_{3i} : initial mass of gas (at pressure p_{2i}) in the large chamber.
 m_{3f} : final mass of gas (at pressure p_{2f}) in the large chamber after the high pressure contents of the coil are shared with the large chamber.
 T : absolute temperature of the gas.
 ρ : gas density in the coil before discharge to the large chamber which is also the density of the gas in the main tube at pressure p_{1f} .
 R : gas constant per unit mass.
 x_{ML} : distance of the face of the left hand transducer from the center of the middle transducer.
 x_{MR} : distance of the face of the right hand

transducer from the center of the middle transducer.

t_M : time of arrival of the wave front at the middle transducer with respect to some arbitrary reference time.

t_L : time of arrival of the wave front at the left hand transducer with respect to the same reference time.

t_R : time of arrival of the wave front at the right hand transducer with respect to the same reference time.

v_{ML} : the average velocity of the decompression wave front from the middle to the left hand transducer.

v_{MR} : the average velocity of the decompression wave front from the middle to the right hand transducer.

4.5.2 Density of the Gas . The volume of the large chamber was chosen sufficiently large so that the ideal gas law can be applied with high accuracy throughout. Accordingly, the ideal gas equation of state applies to the contents of V_3 throughout. It also applies to the residual mass m_{2f} in V_2 .

Since;

$$\begin{aligned} m_{2i} + m_{3i} &= m_{2f} + m_{3f} \\ \text{then } m_{2i} &= (m_{3f} - m_{3i}) + m_{2f} \\ &= (1/RT)[V_3(p_{2f} - p_{2i}) + V_2 p_{2f}] \end{aligned}$$

Therefore;

$$\begin{aligned} \rho &= m_{2i}/V_2 \\ &= (1/RT)[(1 + V_3/V_2)(p_{2f} - p_{2i}) + p_{2i}] \end{aligned}$$

so that for the values of V_2 and V_3 given above

$$\rho(p_{1f}, T) = (1/RT)[784.861(p_{2f} - p_{2i}) + p_{2i}] \quad \dots (4.5.1)$$

4.5.3 Isothermal Compressibility. The isothermal compressibility is given by Eq. (4.1.2). Since $V_2/V_1 \approx 0.1$, according to Eq. (4.1.3) κ is approximated by;

$$\kappa = - \frac{1}{V_1 + V_2/2} \frac{V_2}{p_{1f} - p_{1i}}$$

which is taken to be applicable at the average pressure $(p_{1f} + p_{1i})/2$. Accordingly, for the values V_1 and V_2 given earlier;

$$\kappa(p_k, T) = -16.1567/(p_{1f} - p_{1i}) \text{ MPa}^{-1} \quad \dots (4.5.2).$$

4.5.4 Decompression Wave Front Velocity. Distances x_{ML} and x_{MR} are measured accurately by a vernier calliper having a resolution of 0.03 mm. The average values from several measurements are;

$$x_{ML} = 300.16 \text{ mm}$$

$$x_{MR} = 300.25 \text{ mm}$$

Therefore;

$$v_{ML} = x_{ML}/(t_L - t_M)$$

$$v_{MR} = x_{MR}/(t_R - t_M)$$

From signal analysis the values of t_M , t_L and t_R are obtained in microsecond units while the distances are in millimeter units. Accordingly;

$$v_{ML} = 300.16 \times 10^3/(t_L - t_M) \text{ m s}^{-1}$$

$$v_{MR} = 300.25 \times 10^3/(t_R - t_M) \text{ m s}^{-1}$$

The average of v_{ML} and v_{MR} is taken to be the velocity of the decompression wave front ,i.e., to be the speed of sound (a) at the particular pressure and temperature, i.e.;

$$a(p_{1f}, T) = (v_{ML} + v_{MR})/2 \text{ m s}^{-1} \dots\dots (4.5.3)$$

V RESULTS

5.1 Preliminary Measurements of Sound Speed

The measurement technique is first calibrated by measuring decompression wave front velocities at ideal gas states in the gases concerned and in air. The velocities obtained are required to be very nearly equal to ideal gas state speeds of sound, namely to;

$$a^o = (\gamma^o_{RT})^{1/2} \quad \text{..... (5.1.1)}$$

Measurements are made at "room temperatures" so that the observed speed of sound values are pertinent to a range of temperatures from 20°C to 22°C. The results of these measurements for air, nitrogen, carbon dioxide and argon for pressures up to 350 kPa are given in Table 5.1.1 and plotted in Fig. 5.1.1. Since the temperature varies slightly, only normalized values of the speed of sound (obtained by dividing the observed speed of sound by the ideal gas value at the same temperature) are given in the Table. This mode of presentation eliminates the spurious effect of variation in room temperature.

For carbon dioxide, the speed of sound is also measured at room temperatures for higher pressures (up to 4.5 MPa)

and the observed normalized values of speed of sound are given in Table 5.1.2 and plotted in Fig. 5.1.2.

5.2 Primary Observations

All primary observations of the experimental readings for the three gases and the two isotherms concerned are presented in Tables 5.2.1 through 5.2.6. These readings are used to derive the observed values of density, isothermal compressibility and speed of sound using Eqs. (4.5.1), (4.5.2) and (4.5.3) respectively.

5.3 Observed Thermodynamic Properties

The observed density, isothermal compressibility and speed of sound along with the fitted values (obtained by least squares fitting) are given in Tables 5.2.1 through 5.2.6.

For density data it is found that, a third degree polynomial;

$$\rho = \sum_{j=0}^3 C_{\rho j} p^j \quad \text{..... (5.3.1)}$$

best fits to the observed values. The constants $C_{\rho j}$ and the standard deviations of the fit are presented in Table 5.3.7.

Similarly, for speed of sound, a third degree polynomial;

$$a = \sum_{j=0}^3 C_{aj} p^j \quad \text{..... (5.3.2)}$$

is found to give the best fit to the observed values. The constants C_{aj} and the standard deviations of the fit are presented in Table 5.3.8.

However, for isothermal compressibility a simple polynomial in pressure is not suitable as a fitting function because isothermal compressibility is inversely proportional to the pressure and equals the inverse of pressure at the ideal gas state. Accordingly, a logarithmic polynomial;

$$\ln \kappa = \sum_{j=0}^5 C_{\kappa j} (\ln p)^j \quad \text{..... (5.3.3)}$$

is adopted. The constants $C_{\kappa j}$ and the standard deviations of the fit are presented in Table 5.3.9.

The primary observed properties (ρ , κ , a) are plotted in Figs. 5.3.1 through 5.3.18 relative to pressures together with their fitted values and the comparable data available.

The fitted values of the observed properties are used to derive the compressibility factor Z , the ratio of specific heats γ and the property $\rho \partial Z / \partial \rho$ at corresponding pressures

using the relations;

$$Z = p/\rho RT \quad \dots (5.3.4)$$

$$\gamma = a^2 \rho \kappa \quad \dots (5.3.5)$$

$$\rho \partial Z / \partial \rho = (1/p\kappa - 1)Z \quad \dots (5.3.6)$$

The values of Z and $\rho \partial Z / \partial \rho$ and the normalized values a/a^0 , κ/κ^0 and γ/γ^0 are presented in Tables 5.4.1 through 5.4.30 and plotted in Figs. 5.4.1 through 5.4.30.

5.4 Comparison with Equations of State

The observed thermodynamic properties of particular interest such as Z , κ/κ^0 , γ/γ^0 , a/a^0 and $\rho \partial Z / \partial \rho$ are compared to calculated values using the van der Waals, the hybrid virial and the Benedict-Webb-Rubin equations of state. A comparison of these calculated values with the observed (fitted) values at corresponding pressures is given in Tables 5.4.1 through 5.4.30. In these tables, observed and calculated quantities are given together with the percentage deviations of calculated values from observed values. In regard to the property $\rho \partial Z / \partial \rho$, the deviations (rather than the percentage deviation) from the observed values are given because the percentage deviation tends to infinity as the observed value of $\rho \partial Z / \partial \rho$ tends to zero. Similar comparisons are presented in Figs. 5.4.1 through 5.4.30.

Table 5.1.1 The Ratio of Observed to Ideal Gas State Speed of Sound (a/a^0) for Various Gases at Low Pressure and Room Temperatures.

Gas	Pressure kPa	Temperature K	a/a^0	Percent Deviation $(a - a^0)/a^0 \times 100$
Air	156.85	295.00	1.0070	0.70
	187.50	294.20	0.9924	-0.76
	191.58	294.55	1.0003	0.03
	212.50	294.30	0.9983	-0.17
	225.70	294.65	0.9961	-0.39
	237.50	294.00	0.9907	-0.03
	260.48	294.40	1.0026	0.26
	262.50	294.40	0.9915	-0.85
	287.50	294.50	1.0049	0.49
	313.80	294.70	0.9963	-0.37
	338.80	294.70	0.9971	-0.29
Nitrogen	189.00	294.40	1.0015	0.15
	214.00	294.20	1.0083	0.83
	225.50	294.45	0.9954	-0.46
	238.90	294.10	0.9975	-0.25
	259.68	294.75	1.0099	0.99
	263.90	293.90	1.0018	0.18
	295.25	294.15	0.9917	-0.83
	313.90	294.20	1.0055	0.55
	364.10	294.40	0.9960	-0.40
Carbon Dioxide	157.65	295.55	1.0012	0.12
	188.60	295.40	0.9929	-0.71
	192.53	294.30	1.0052	0.52
	212.90	295.30	1.0097	0.97
	226.60	293.30	0.9961	-0.39
	237.90	295.30	1.0024	0.24
	263.70	295.60	0.9938	-0.62
	288.70	294.50	0.9974	-0.26
	295.55	295.00	0.9936	-0.64
	313.70	294.50	0.9944	-0.56
	338.60	295.20	0.9914	-0.86
	350.71	295.30	0.9910	-0.90
Argon	152.15	294.29	1.0013	0.13
	167.39	295.00	1.0021	0.21
	173.28	295.12	0.9982	-0.18
	192.36	294.83	1.0056	0.56
	221.92	294.83	1.0044	0.44
	239.40	294.83	0.9976	-0.24
	263.56	295.02	0.9942	-0.58
	294.49	295.10	0.9928	-0.72
	313.62	294.21	1.0024	0.24
	338.19	294.35	1.0012	0.12
	356.53	294.55	0.9997	-0.03

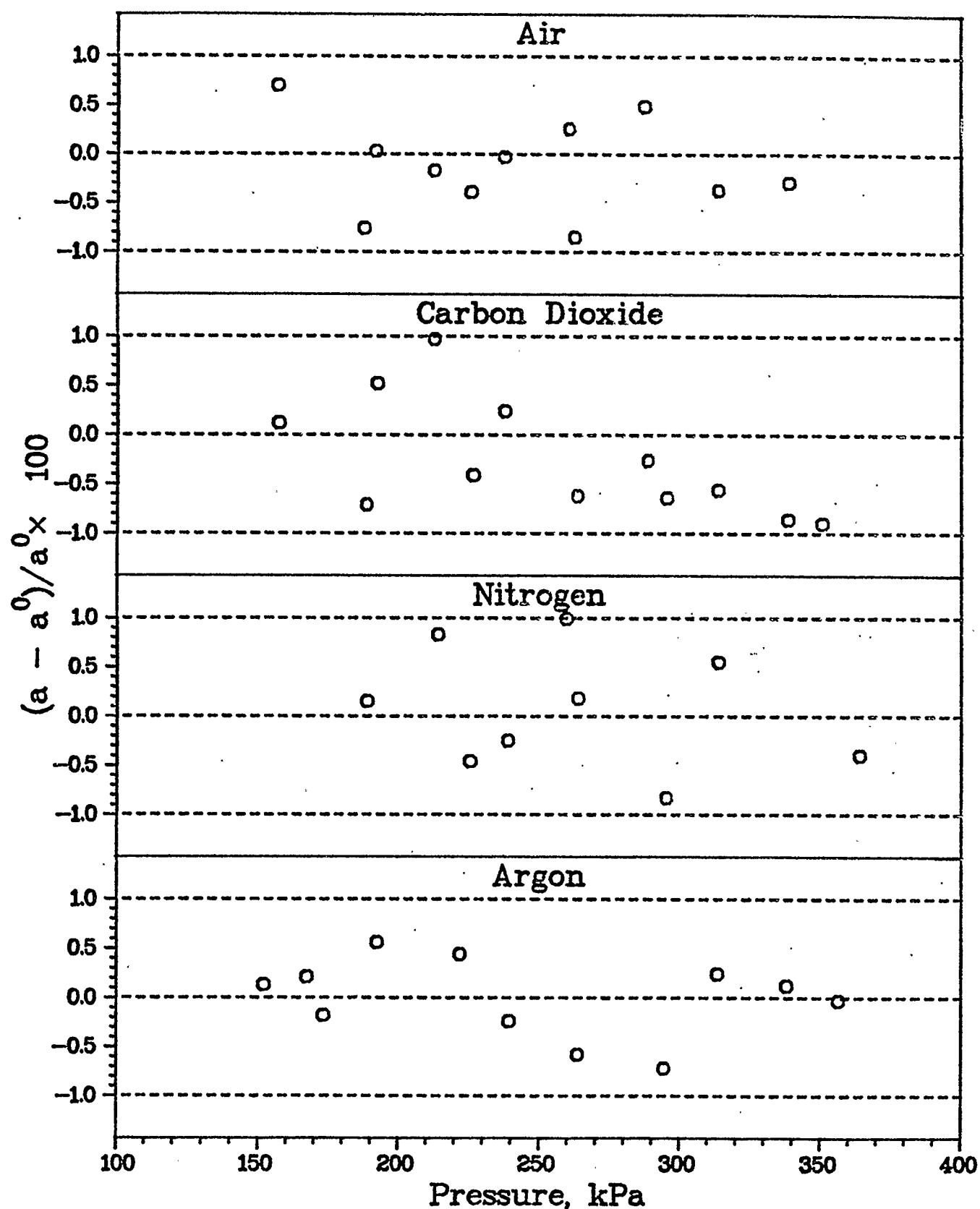


Fig. 5.1.1 Percent Deviation of Observed from Ideal Gas State Speed of Sound for Several Gases at Low Pressures and Room Temperatures (293 K - 295 K).

Table 5.1.2 The Ratio of Observed to Ideal Gas State Speed of Sound (a/a^0) for Carbon Dioxide at Room Temperatures and Pressures upto 4.5 MPa.

Pressure MPa	Temperature K	a/a^0
0.6388	294.10	0.9777
0.7778	294.20	0.9742
0.9145	294.60	0.9673
1.0524	294.40	0.9623
1.1904	294.40	0.9623
1.3652	294.00	0.9569
1.6048	293.50	0.9501
1.8792	294.30	0.9434
2.1564	293.90	0.9231
2.5009	294.20	0.9122
2.8460	294.30	0.9037
3.1908	294.60	0.8818
3.5355	294.80	0.8670
3.8804	295.50	0.8501
4.2253	295.00	0.8376
4.5701	295.50	0.8251

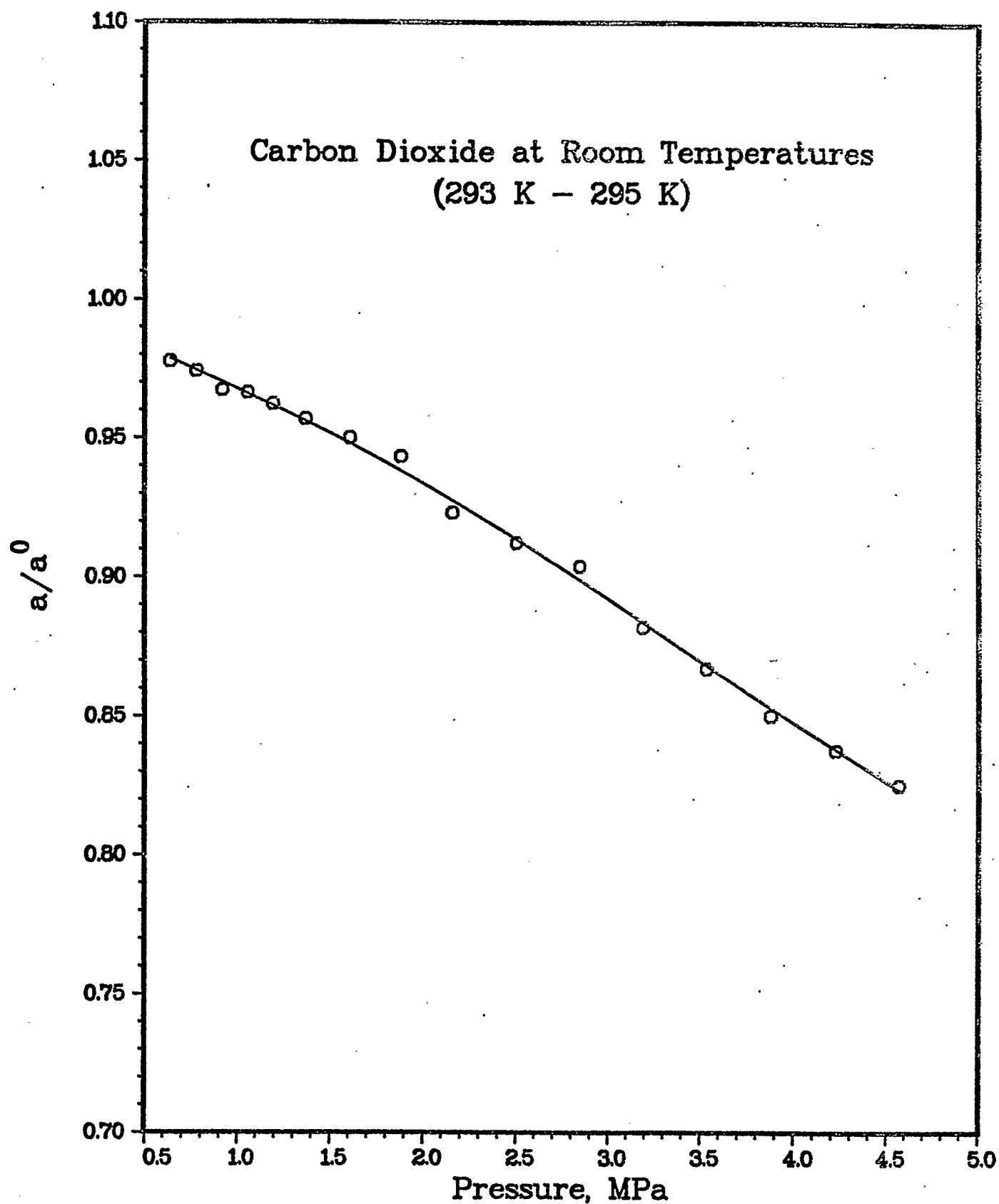


Fig. 5.1.2 Ratio of Observed to Ideal Gas State Speed of Sound for Carbon Dioxide at Room Temperatures (293 K - 295 K).

Table 5.2.1 Primary Observations for Carbon Dioxide at 273.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_M	t_L	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
142.0	132.0	-88.73	-87.36	90.19	252.1	1457.8	1460.2
180.0	160.0	-88.69	-87.04	90.17	258.2	1480.1	1483.4
215.0	191.0	-88.70	-86.69	90.17	245.3	1476.8	1472.2
241.0	218.0	-88.68	-86.36	90.18	250.6	1493.8	1494.2
278.0	252.0	-88.69	-85.99	90.21	251.7	1513.6	1516.9
312.0	284.0	-88.68	-85.63	90.20	244.6	1518.8	1521.2
343.0	313.0	-88.67	-85.20	90.20	242.8	1532.5	1532.9
379.0	346.0	-88.68	-84.71	90.19	243.3	1555.1	1558.5
404.0	372.0	-88.68	-84.40	90.16	239.7	1560.0	1564.4
437.0	401.0	-88.64	-83.88	90.16	240.0	1583.6	1587.0

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined
in Sec. 4.5.1.

Table 5.2.2 Primary Observations for Carbon Dioxide at 298.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_M	t_L	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
151.0	135.0	-87.63	-86.27	88.48	219.5	1367.0	1367.7
168.0	151.0	-87.63	-86.10	88.48	223.4	1374.3	1374.7
223.0	199.0	-87.63	-85.63	88.48	219.6	1383.0	1384.3
276.0	248.0	-87.64	-85.13	88.48	224.5	1402.1	1400.5
334.0	303.0	-87.61	-84.50	88.49	220.2	1411.8	1412.1
391.0	355.0	-87.63	-83.82	88.49	212.3	1421.1	1421.0
437.0	398.0	-87.64	-83.29	88.49	213.0	1436.1	1436.3
493.0	451.0	-87.59	-82.61	88.50	224.6	1464.9	1465.3
546.0	502.0	-87.63	-81.90	88.50	231.8	1490.3	1490.8
608.0	562.0	-87.60	-80.90	88.50	202.1	1484.8	1485.2
656.0	609.0	-87.65	-80.13	88.50	218.9	1521.2	1522.6
700.0	653.0	-87.64	-79.39	88.51	202.3	1529.3	1530.0

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined
in Sec. 4.5.1.

Table 5.2.3 Primary Observations for Argon at 273.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_M	t_L	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
163.0	144.0	-87.09	-85.70	87.49	200.2	1170.1	1175.4
225.0	201.0	-87.12	-85.21	87.49	201.3	1175.0	1175.3
282.0	252.0	-87.06	-84.73	87.49	198.3	1169.6	1174.9
349.0	312.0	-87.10	-84.19	87.45	210.5	1184.0	1182.3
409.0	363.0	-87.09	-83.69	87.46	205.2	1174.1	1174.4
452.0	405.0	-87.12	-83.35	87.46	195.4	1163.8	1164.1
502.0	450.0	-87.13	-82.90	87.44	202.7	1164.7	1170.0
575.0	511.0	-87.16	-82.35	87.59	212.9	1178.1	1182.4
693.0	619.0	-87.13	-81.39	87.57	203.8	1168.5	1168.8
780.0	708.0	-87.12	-80.50	87.83	197.9	1154.9	1153.2
890.0	799.0	-87.14	-79.70	87.83	196.8	1159.7	1156.0
1002.0	895.0	-87.15	-78.64	87.81	199.9	1156.5	1159.8
1110.0	1003.0	-87.21	-77.74	87.82	194.3	1142.9	1148.2
1493.0	1342.0	-87.20	-74.28	87.89	200.1	1138.8	1145.0
1802.0	1621.0	-87.22	-71.69	87.80	202.1	1126.5	1126.8
2121.0	1896.0	-87.19	-68.83	87.80	193.4	1101.4	1101.7
2464.0	2216.0	-87.21	-65.67	87.81	190.2	1075.4	1078.7
2827.0	2523.0	-87.21	-62.87	87.80	186.8	1051.0	1051.2
3160.0	2802.0	-87.20	-60.02	87.89	188.4	1030.2	1034.5
3489.0	3085.0	-87.25	-57.29	87.87	200.2	1015.4	1019.6
3851.0	3394.0	-87.23	-54.76	87.90	191.3	985.2	983.5
4236.0	3712.0	-87.21	-52.11	87.89	189.2	962.1	968.3
4637.0	4015.0	-87.16	-49.49	87.81	190.1	930.2	934.4
5060.0	4329.0	-87.20	-47.62	87.80	188.2	909.0	909.2
5489.0	4672.0	-87.22	-45.09	87.81	189.7	886.2	886.4

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined
in Sec. 4.5.1.

Table 5.2.4 Primary Observations for Argon at 298.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_M	t_L	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
179.0	159.0	-87.94	-86.41	89.27	192.2	1121.6	1122.9
236.0	208.0	-87.95	-85.96	89.27	213.5	1146.6	1148.9
350.0	313.0	-88.12	-85.24	89.27	202.6	1124.0	1123.2
439.0	393.0	-88.17	-84.52	89.30	190.7	1113.2	1114.5
548.0	489.0	-88.08	-83.56	89.35	197.3	1124.4	1126.7
652.0	586.0	-88.18	-82.79	89.27	190.8	1111.5	1110.8
768.0	688.0	-88.06	-81.74	89.25	199.0	1110.9	1118.1
899.0	803.0	-88.07	-80.69	89.25	212.3	1135.4	1139.6
1002.0	902.0	-87.68	-79.39	88.69	208.2	1120.5	1120.8
1075.0	963.0	-87.63	-78.70	88.69	207.3	1109.1	1113.4
1445.0	1286.0	-87.62	-75.62	88.64	205.6	1108.6	1105.8
1577.0	1415.0	-87.62	-74.47	88.60	206.4	1106.0	1106.3
1770.0	1595.0	-87.70	-72.72	88.89	204.8	1090.2	1090.4
2008.0	1800.0	-87.76	-70.79	88.80	203.1	1070.2	1078.4
2232.0	1997.0	-87.59	-68.98	88.73	205.4	1075.4	1072.6
2610.0	2363.0	-87.58	-65.58	88.71	200.9	1040.5	1044.7
2953.0	2630.0	-87.62	-63.32	88.70	199.4	1022.7	1028.9
3289.0	2882.0	-87.84	-61.19	88.96	198.3	1018.8	1013.0
3548.0	3183.0	-87.90	-58.53	88.96	200.1	994.1	996.4
3994.0	3516.0	-87.94	-55.53	88.92	198.3	968.9	977.1
4375.0	3789.0	-87.93	-53.39	88.92	195.2	951.2	951.4
4708.0	4126.0	-87.92	-50.87	88.92	196.9	933.5	930.8
5047.0	4381.0	-87.94	-49.05	88.93	194.7	905.7	913.0
5473.0	4688.0	-87.91	-46.89	88.90	193.1	890.7	895.9

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined
in Sec. 4.5.1.

Table 5.2.5 Primary Observations for Nitrogen at 273.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_M	t_L	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
206.0	184.0	-87.28	-85.53	88.59	235.3	1120.7	1123.9
275.0	244.0	-87.32	-85.05	88.56	234.9	1122.2	1119.4
337.0	300.0	-87.29	-84.51	88.45	230.7	1113.5	1113.8
399.0	357.0	-87.29	-84.00	88.44	243.8	1127.8	1128.0
452.0	399.0	-87.29	-83.65	88.43	229.5	1110.0	1110.2
517.0	461.0	-87.39	-83.14	88.84	211.7	1084.9	1088.2
560.0	500.0	-87.58	-83.01	88.86	225.4	1102.3	1105.5
782.0	697.0	-87.67	-81.31	88.88	220.7	1089.3	1089.5
1025.0	907.0	-87.80	-79.51	88.88	222.0	1085.4	1081.6
1408.0	1267.0	-87.83	-76.19	88.94	219.6	1059.1	1063.3
1718.0	1531.0	-87.83	-74.16	88.95	212.2	1034.4	1034.7
2035.0	1808.0	-87.79	-71.64	88.95	209.3	1010.1	1012.3
2379.0	2102.0	-87.76	-69.16	88.89	208.4	991.8	994.0
2719.0	2396.0	-87.78	-66.87	88.85	215.6	979.4	976.7
2975.0	2617.0	-87.84	-65.11	88.83	207.8	951.8	952.1
3311.0	2902.0	-87.80	-63.02	88.84	195.2	915.5	918.8
3698.0	3213.0	-87.81	-60.98	88.85	199.8	899.8	897.0
4046.0	3496.0	-87.76	-58.94	88.85	207.1	887.1	887.3
4425.0	3792.0	-87.83	-57.05	88.85	195.2	856.9	859.1
4843.0	4132.0	-87.78	-54.45	88.89	198.6	833.2	835.4
5218.0	4416.0	-87.80	-53.52	88.82	200.1	820.4	820.5
5479.0	4601.0	-87.81	-52.95	88.83	201.2	810.7	810.9

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined in Sec. 4.5.1.

Table 5.2.6 Primary Observations for Nitrogen at 298.15 K.

P_{1i}	P_{1f}	P_{2i}	P_{2f}	P_{atm}	t_L	t_M	t_R
psig	psig	kPag	kPag	kPa	μs	μs	μs
175.0	152.0	-88.12	-86.64	89.30	202.2	1045.6	1049.8
235.0	209.0	-88.11	-86.17	89.25	218.6	1067.3	1062.6
310.0	279.0	-88.15	-85.57	89.22	234.6	1077.7	1077.9
416.0	369.0	-87.69	-84.34	88.45	220.1	1057.8	1061.1
496.0	446.0	-87.70	-83.61	88.48	225.2	1068.6	1063.8
567.0	506.0	-87.71	-83.11	88.49	196.2	1030.3	1032.5
625.0	561.0	-87.69	-82.61	88.49	209.2	1042.9	1048.2
718.0	641.0	-87.65	-81.90	88.49	218.9	1049.2	1052.4
798.0	712.0	-87.75	-81.32	88.49	212.6	1039.4	1039.7
997.0	891.0	-87.73	-79.61	88.45	235.3	1050.8	1056.1
1139.0	1014.0	-87.74	-78.63	88.86	217.5	1036.2	1032.5
1302.0	1166.0	-87.71	-77.32	88.94	198.2	1005.0	1005.3
1448.0	1282.0	-87.72	-76.31	88.94	181.3	978.7	983.9
1622.0	1456.0	-87.70	-74.80	88.94	205.4	996.3	996.5
1826.0	1623.0	-87.71	-73.41	88.93	201.3	983.3	983.6
1981.0	1760.0	-87.72	-72.25	88.94	196.4	968.0	969.2
2179.0	1926.0	-87.72	-71.03	88.93	188.3	954.0	955.2
2392.0	2118.0	-87.70	-69.34	88.93	212.9	962.0	967.2
2583.0	2282.0	-87.70	-68.08	88.93	210.7	953.6	953.8
2783.0	2464.0	-87.73	-66.77	88.94	235.7	969.7	968.0
3099.0	2718.0	-87.69	-64.87	88.94	198.2	910.5	911.7
3336.0	2935.0	-87.72	-63.39	88.94	230.1	931.4	931.6
3590.0	3146.0	-87.69	-61.92	88.95	223.1	911.5	911.7
3852.0	3350.0	-87.71	-60.02	88.95	222.2	895.2	898.4
4029.0	3491.0	-87.71	-59.92	88.94	203.0	870.0	874.2
4212.0	3651.0	-87.72	-58.39	88.95	218.3	877.2	877.4
4423.0	3822.0	-87.69	-57.47	88.83	217.8	864.9	862.1
4670.0	4021.0	-87.68	-55.98	88.80	225.3	860.5	863.7
4917.0	4217.0	-87.69	-55.10	88.80	215.8	842.4	842.6
5160.0	4415.0	-87.68	-54.65	88.81	219.2	837.9	839.0
5431.0	4618.0	-87.69	-52.78	88.81	204.3	810.0	810.2
5636.0	4787.0	-87.68	-51.80	88.81	225.3	822.0	822.2

Note: P_{1i} , P_{1f} , P_{2i} , P_{2f} , P_{atm} , t_M , t_L and t_R are defined
in Sec. 4.5.1.

Table 5.3.1 Observed Thermodynamic Properties along with the Fitted Values for Carbon Dioxide at 273.15 K.

Pressure!	Density		Speed of Sound		Pressure!	Isothermal	
p	ρ		a		p_{κ}	κ	
MPa	kg m^{-3}		m s^{-1}		MPa	MPa^{-1}	
	Observed	Fitted	Observed	Fitted		Observed	Fitted
1.0003	20.8636	20.8244	248.7325	248.4719	1.0348	1.6157	1.6190
1.1933	25.1224	25.3374	245.3480	246.1517	1.2623	0.8079	0.7954
1.4071	30.5994	30.4513	244.2207	243.5325	1.4898	0.6732	0.7042
1.5932	35.3149	35.0417	241.4308	241.1995	1.6725	0.7025	0.6736
1.8277	41.0917	41.0688	237.5810	238.1733	1.9173	0.6214	0.6249
2.0483	46.4181	47.0457	235.3734	235.2219	2.1448	0.5770	0.5772
2.2482	52.8023	52.7703	232.7273	232.4459	2.3517	0.5386	0.5398
2.4758	60.4107	59.7041	228.5462	229.1515	2.5895	0.4896	0.5054
2.6550	65.1202	65.5163	226.9911	226.4461	2.7653	0.5049	0.4833
2.8549	72.4263	72.4095	223.1439	223.3005	2.9790	0.4488	0.4552

Note: (1) The observed properties are derived from the primary observations of Table 5.2.1 by Eqs. (4.5.1) through (4.5.3) and the fitted values are calculated by Eqs. (5.3.1) through (5.3.3).

(2) The pressure p_{κ} is defined in Eq. (4.5.2).

Table 5.3.2 Observed Thermodynamic Properties along with the Fitted Values for Carbon Dioxide at 298.15 K.

Pressure!		Density		Speed of Sound		Pressure!		Isothermal						
p		ρ		a		p _κ		Compressibility						
MPa		kg m ⁻³		m s ⁻¹		MPa		MPa ⁻¹						
		Observed	Fitted	Observed	Fitted			Observed	Fitted					
1.0193	!	18.9696	!	18.9937	!	261.5281	!	261.6447	!	1.0744	!	1.0098	!	1.0237
1.1296	!	21.3361	!	21.1816	!	260.7897	!	260.7123	!	1.1882	!	0.9504	!	0.9239
1.4605	!	27.8818	!	27.9389	!	257.8885	!	257.9064	!	1.5433	!	0.6732	!	0.6933
1.7984	!	34.9662	!	35.1800	!	255.0945	!	255.0078	!	1.8949	!	0.5770	!	0.5761
2.1776	!	43.3602	!	43.7830	!	251.8943	!	251.6830	!	2.2845	!	0.5212	!	0.5026
2.5361	!	53.1231	!	52.4464	!	248.3516	!	248.4377	!	2.6602	!	0.4488	!	0.4536
2.8326	!	60.6418	!	60.0478	!	245.4178	!	245.6562	!	2.9670	!	0.4143	!	0.4212
3.1980	!	69.4232	!	70.0164	!	241.9952	!	242.0792	!	3.3428	!	0.3847	!	0.3886
3.5496	!	79.8700	!	80.2945	!	238.4866	!	238.4532	!	3.7013	!	0.3672	!	0.3648
3.9633	!	93.3760	!	93.3330	!	233.9972	!	233.9152	!	4.1219	!	0.3512	!	0.3473
4.2874	!	104.8300	!	104.3222	!	230.3876	!	230.1258	!	4.4494	!	0.3438	!	0.3426
4.5907	!	115.0286	!	115.2689	!	226.1612	!	226.3708	!	4.7528	!	0.3438	!	0.3464

Note: (1) The observed properties are derived from the primary observations of Table 5.2.2 by Eqs. (4.5.1) through (4.5.3) and the fitted values are calculated by Eqs. (5.3.1) through (5.3.3).

(2) The pressure p_{κ} is defined in Eq. (4.5.2).

Table 5.3.4 Observed Thermodynamic Properties along with the Fitted Values for Argon at 298.15 K.

Pressure!		Density		Speed of Sound		Pressure!		Isothermal	
p		ρ		a		p_{κ}		Compressibility	
MPa		kg m^{-3}		m s^{-1}		MPa		MPa^{-1}	
		Observed		Observed				Observed	
		Fitted		Fitted				Fitted	
1.1855	!	19.3772	!	19.2562	!	322.7731	!	322.9929	!
1.5234	!	25.1930	!	24.8265	!	321.3224	!	323.1921	!
2.2473	!	36.4454	!	36.8294	!	325.9447	!	323.7058	!
2.7989	!	46.1527	!	46.0349	!	325.1856	!	324.1760	!
3.4609	!	57.2021	!	57.1452	!	323.3993	!	324.8292	!
4.1296	!	68.1869	!	68.4313	!	326.1749	!	325.5862	!
4.8328	!	79.9723	!	80.3614	!	327.9077	!	326.4862	!
5.6257	!	93.3755	!	93.8804	!	324.4666	!	327.6271	!
6.3077	!	104.8986	!	105.5576	!	328.9989	!	328.7137	!
6.7283	!	113.0274	!	112.7787	!	332.0943	!	329.4317	!
8.9552	!	151.8570	!	151.1922	!	332.9589	!	333.8286	!
9.8446	!	166.3053	!	166.5847	!	333.6427	!	335.8575	!
11.0859	!	189.5280	!	188.0754	!	339.0119	!	338.9412	!
12.4993	!	214.6862	!	212.5108	!	344.5839	!	342.8004	!
13.8574	!	235.4498	!	235.9021	!	345.6088	!	346.8470	!
16.3809	!	278.3358	!	278.9558	!	356.6553	!	355.2095	!
18.2218	!	307.4319	!	309.8668	!	363.2612	!	361.9689	!
19.9595	!	337.0929	!	338.5277	!	367.1709	!	368.8322	!
22.0348	!	371.5458	!	371.9426	!	377.5333	!	377.6113	!
24.3307	!	409.9720	!	407.6624	!	387.5090	!	388.0185	!
26.2129	!	437.0045	!	435.7969	!	397.0308	!	397.0596	!
28.5365	!	468.7605	!	468.8796	!	408.2912	!	408.8084	!
30.2946	!	492.0396	!	492.5501	!	420.0695	!	418.0986	!
32.4113	!	519.0236	!	519.3156	!	428.7332	!	429.7053	!
	!		!		!		!		!

Note: (1) The observed properties are derived from the primary observations of Table 5.2.4 by Eqs. (4.5.1) through (4.5.3) and the fitted values are calculated by Eqs. (5.3.1) through (5.3.3).

(2) The pressure p_{κ} is defined in Eq. (4.5.2).

Table 5.3.5 Observed Thermodynamic Properties along with the Fitted Values for Nitrogen at 273.15 K.

Pressure!	Density		Speed of Sound		Pressure!	Isothermal	
p	ρ		a		p_{κ}	Compressibility	
MPa	kg m^{-3}		m s^{-1}		MPa	MPa^{-1}	
	Observed	Fitted	Observed	Fitted		Observed	Fitted
1.3572	16.9582	16.7698	338.4396	338.6944	1.4331	0.7344	0.7279
1.7709	21.9882	22.0456	338.8597	339.1903	1.8777	0.5212	0.5369
2.1569	26.9319	26.9664	339.9909	339.7152	2.2844	0.4367	0.4341
2.5498	31.8699	31.9728	339.5487	340.3104	2.6946	0.3847	0.3650
2.8394	35.2534	35.6609	340.8983	340.7878	3.0221	0.3049	0.3245
3.2673	41.1596	41.1062	343.1400	341.5525	3.4603	0.2885	0.2832
3.5362	44.2619	44.5254	341.7142	342.0688	3.7431	0.2693	0.2620
4.8945	61.5870	61.7534	345.5681	345.0875	5.1875	0.1901	0.1904
6.3424	80.2581	80.0107	348.4580	349.0292	6.7492	0.1369	0.1472
8.8245	112.6854	110.9374	356.6977	357.3969	9.3106	0.1146	0.1063
10.6447	132.3550	133.2190	365.0453	364.7147	11.2894	0.0864	0.0864
12.5546	156.3882	156.1387	374.3553	373.3588	13.3371	0.0712	0.0715
14.5815	180.0832	179.8457	382.6584	383.5003	15.5365	0.0583	0.0596
16.6086	202.4756	202.8113	393.7255	394.5186	17.7220	0.0500	0.0505
18.1323	220.0479	219.5173	403.4066	403.3027	19.3664	0.0451	0.0449
20.0973	239.9831	240.2730	415.8134	415.1735	21.5072	0.0395	0.0389
22.2415	259.7193	261.7978	429.7112	428.7016	23.9135	0.0333	0.0334
24.1927	279.0037	280.2590	441.3983	441.4136	26.0888	0.0294	0.0294
26.2336	297.9982	298.3099	452.9206	454.9959	28.4157	0.0255	0.0258
28.5778	322.6622	317.3107	472.2288	470.7965	31.0289	0.0227	0.0224
30.5358	331.8575	331.6430	483.9123	484.0256	33.3006	0.0201	0.0200
31.8113	337.5220	340.1755	492.4459	492.6021	34.8381	0.0184	0.0185

Note: (1) The observed properties are derived from the primary observations of Table 5.2.5 by Eqs. (4.5.1) through (4.5.3) and the fitted values are calculated by Eqs. (5.3.1) through (5.3.3).

(2) The pressure p_{κ} is defined in Eq. (4.5.2).

Table 5.3.6 Observed Thermodynamic Properties along with the Fitted Values for Nitrogen at 298.15 K.

Pressure!	Density		Speed of Sound		Pressure!	Isothermal	
p	κ		a		p_κ	Compressibility	
MPa	kg m^{-3}		m s^{-1}		MPa	MPa^{-1}	
	Observed	Fitted	Observed	Fitted		Observed	Fitted
1.1373	13.1429	12.5791	355.0524	354.5933	1.2166	0.7025	0.7051
1.5302	17.2233	17.1843	354.6965	355.1716	1.6199	0.6214	0.6225
2.0128	22.9033	22.8251	356.0187	355.9512	2.1197	0.5212	0.4977
2.6326	29.7296	30.0428	357.6531	357.0624	2.7946	0.3438	0.3755
3.1635	36.2951	36.2002	356.9531	358.1104	3.3359	0.3231	0.3103
3.5772	40.8170	40.9816	359.4294	358.9872	3.7875	0.2649	0.2704
3.9564	45.0816	45.3510	358.9381	359.8365	4.1770	0.2525	0.2433
4.5080	51.0336	51.6835	360.8559	361.1481	4.7734	0.2098	0.2110
4.9975	57.0706	57.2789	363.0147	362.3863	5.2940	0.1879	0.1892
6.2316	72.0533	71.2799	366.9230	365.8075	6.5970	0.1524	0.1505
7.0801	80.8305	80.8132	367.5052	368.3990	7.5110	0.1293	0.1316
8.1282	92.1808	92.4774	372.0119	371.8564	8.5970	0.1188	0.1145
8.9279	101.2288	101.2898	375.2476	374.6765	9.5002	0.0973	0.1032
10.1276	114.4308	114.3600	379.5133	379.1876	10.6999	0.0973	0.0909
11.2790	126.8480	126.7251	383.8075	383.8155	11.9788	0.0796	0.0805
12.2236	137.2065	136.7313	388.7531	387.8169	12.9855	0.0731	0.0736
13.3681	148.0358	148.6796	391.7463	392.8960	14.2403	0.0639	0.0662
14.6919	162.8805	162.2477	399.3594	399.0630	15.6365	0.0590	0.0593
15.8226	174.0692	173.6113	404.0310	404.5578	16.8603	0.0537	0.0542
17.0775	185.8802	185.9678	409.4598	410.8782	18.1772	0.0506	0.0494
18.8287	202.4580	202.7379	421.0902	420.0429	20.1422	0.0424	0.0433
20.3249	215.8241	216.6047	427.9940	428.1454	21.7073	0.0403	0.0392
21.7797	228.5817	229.6578	436.0131	436.2222	23.3103	0.0364	0.0356
23.1862	245.4434	241.8549	444.9994	444.1801	24.9168	0.0322	0.0325
24.1583	246.5482	250.0321	448.6592	449.7474	26.0130	0.0300	0.0306
25.2615	260.1393	259.0530	455.5311	456.1154	27.1955	0.0288	0.0287
26.4404	268.1046	268.3787	464.9163	462.9606	28.5122	0.0269	0.0268
27.8124	281.2146	278.8088	471.4146	470.9527	30.0497	0.0249	0.0249
29.1637	289.1491	288.6207	479.0091	478.8210	31.5769	0.0231	0.0231
30.5289	293.1334	298.0523	484.7722	486.7354	33.0972	0.0217	0.0216
31.9285	309.7741	307.2015	495.5348	494.7794	34.7312	0.0199	0.0201

Note: (1) The observed properties are derived from the primary observations of Table 5.2.6 by Eqs. (4.5.1) through (4.5.3) and the fitted values are calculated by Eqs. (5.3.1) through (5.3.3).

(2) The pressure p_κ is defined in Eq. (4.5.2).

Table 5.3.7 Density-Fitting Polynomial Coefficients and
Standard Deviations of the Fit.

Gas	Temp K	$C_{\rho 0}$ kg m ⁻³	$C_{\rho 1}$ kg m ⁻³ MPa ⁻¹	$C_{\rho 2}$ kg m ⁻³ MPa ⁻²	$C_{\rho 3}$ kg m ⁻³ MPa ⁻³	Standard Deviation of $\rho_{\text{obs}} - \rho_{\text{fit}}$ kg m ⁻³
Carbon Dioxide	273.15	-2.5608	24.4870	-2.0416	0.9327	0.3646
Carbon Dioxide	298.15	-0.0900	17.9870	0.4837	0.2335	0.4170
Argon	273.15	-0.0824	17.5770	0.2067	-0.0060	1.2145
Argon	298.15	-0.1101	16.2130	0.1074	-0.0035	1.0326
Nitrogen	273.15	-0.5394	12.7490	0.0063	-0.0022	1.4880
Nitrogen	298.15	-0.8127	11.8130	-0.0323	-0.0011	1.5051

Table 5.3.8 Sound Speed-Fitting Polynomial Coefficients and Standard Deviations of the Fit.

Gas	Temp K	C_{a0} m s^{-1}	C_{a1} $\text{m s}^{-1} \text{MPa}^{-1}$	C_{a2} $\text{m s}^{-1} \text{MPa}^{-2}$	C_{a3} $\text{m s}^{-1} \text{MPa}^{-3}$	Standard Deviation of $a_{\text{obs}} - a_{\text{fit}}$ m s^{-1}
Carbon Dioxide	273.15	260.26	-11.8840	0.3593	-0.2560	0.5144
Carbon Dioxide	298.15	270.38	-8.8079	0.3462	-0.1124	0.1548
Argon	273.15	309.01	-0.2026	0.1547	-0.0010	1.0983
Argon	298.15	322.50	0.2774	0.1167	-0.0007	1.5239
Nitrogen	273.15	337.56	0.5454	0.2147	-0.0025	0.8398
Nitrogen	298.15	353.21	1.0196	0.1738	-0.0021	0.8669

Table 5.3.9 Isothermal Compressibility-Fitting Polynomial Coefficients and Standard Deviations of the Fit.

Gas	Temp K	C_{k0}	C_{k1}	C_{k2}	C_{k3}	C_{k4}	C_{k5}	Standard Deviation of $\kappa_{obs} - \kappa_{fit}$ MPa ⁻¹
Carbon Dioxide	273.15	0.7426	-8.4853	26.6090	-41.2540	30.0230	-8.3503	0.0174
Carbon Dioxide	298.15	0.0804	-0.6529	-2.2577	4.4877	-3.3433	0.8806	0.0127
Argon	273.15	-0.0554	-0.6366	-0.5599	0.3644	-0.0959	0.0078	0.0090
Argon	298.15	0.0396	-1.3239	0.6079	-0.4317	0.1377	-0.0167	0.0088
Nitrogen	273.15	0.1023	-1.1762	-0.0039	0.0970	-0.0397	0.0037	0.0079
Nitrogen	298.15	-0.3763	0.4418	-1.7276	0.9136	-0.2209	0.0193	0.0081

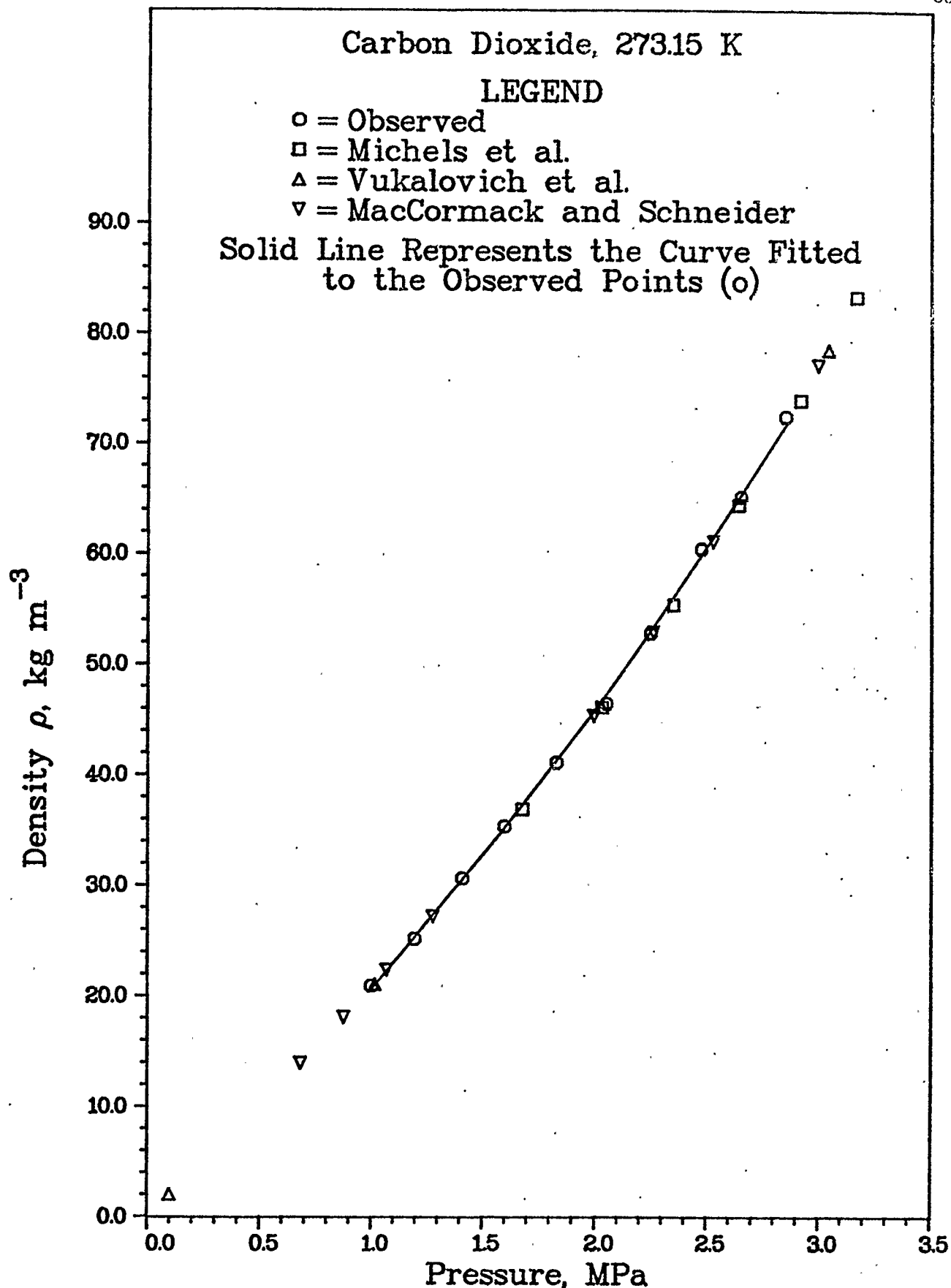


Fig. 5.3.1 Observed Density Versus Pressure for Carbon Dioxide Compared with the Data of Michels et al. [2.10], Vukalovich et al. [2.12] and MacCormack and Schneider [2.11] at 273.15 K.

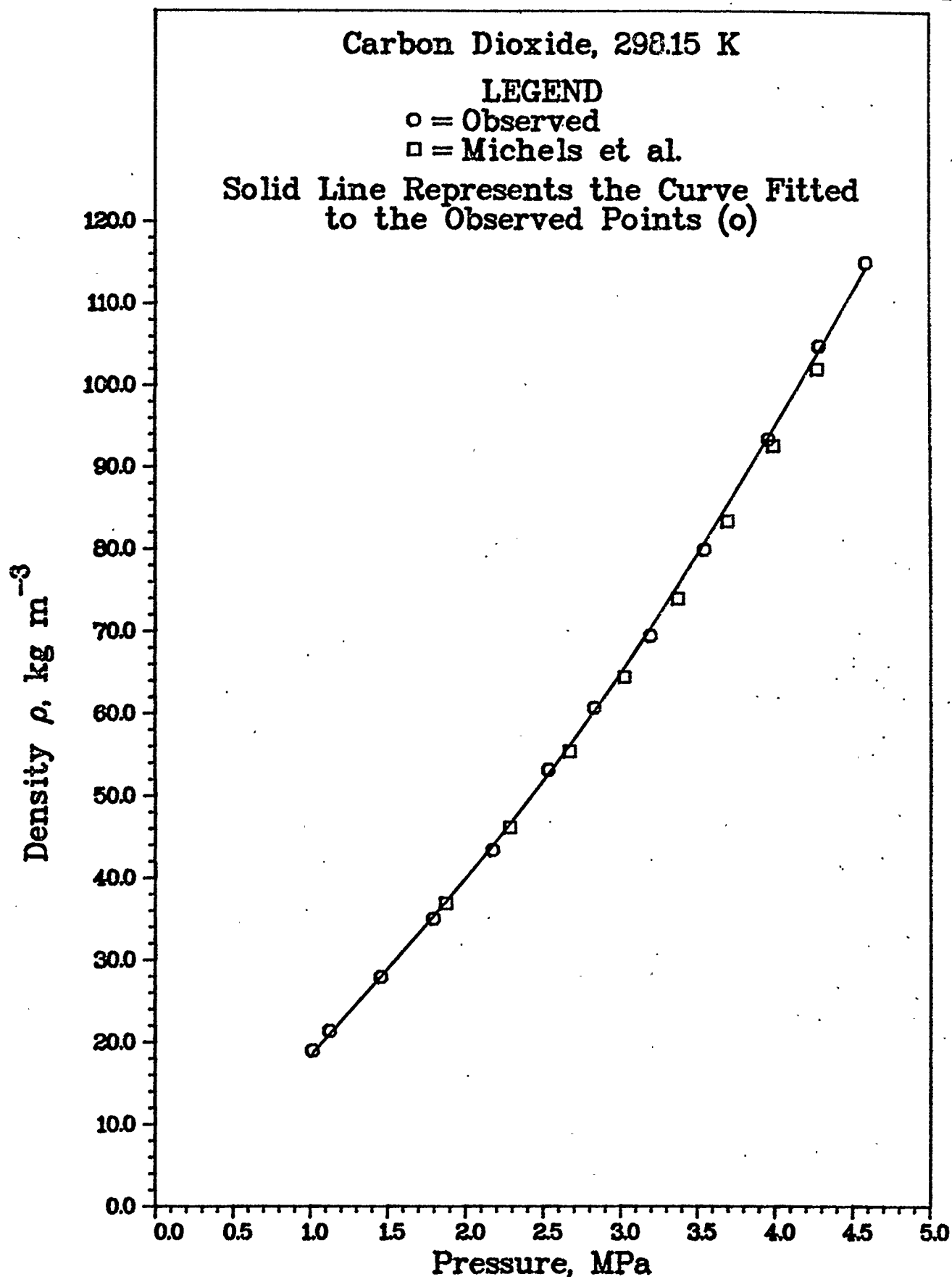


Fig. 5.3.2 Observed Density Versus Pressure for Carbon Dioxide Compared with the Data of Michels et al. [2.10] at 298.15 K.

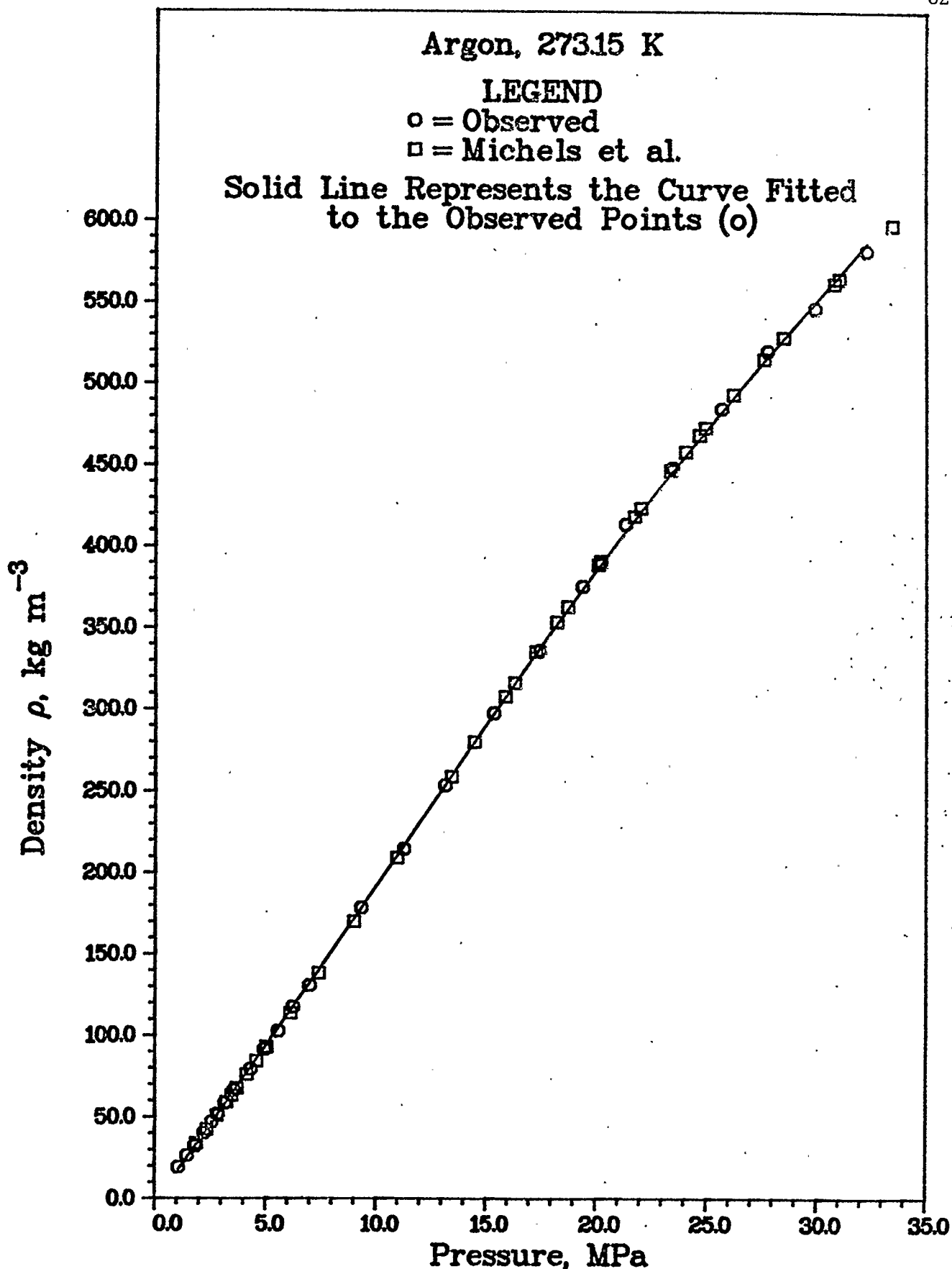


Fig. 5.3.3 Observed Density Versus Pressure for Argon Compared with the Data of Michels et al. [2.13] at 273.15 K.

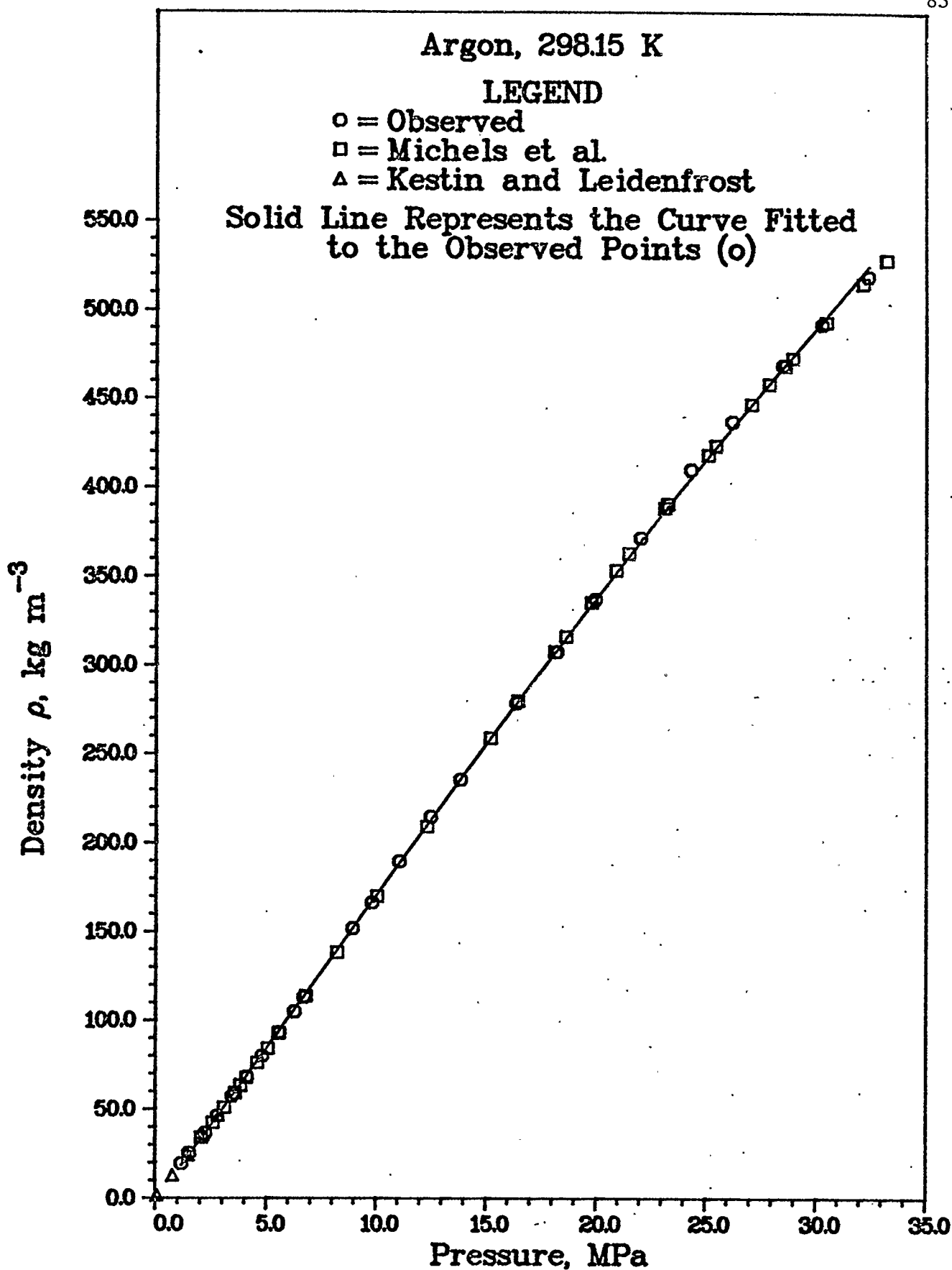


Fig. 5.3.4 Observed Density Versus Pressure for Argon Compared with the Data of Michels et al. [2.13] and Kestin and Liedenfrost [2.14] at 298.15 K.

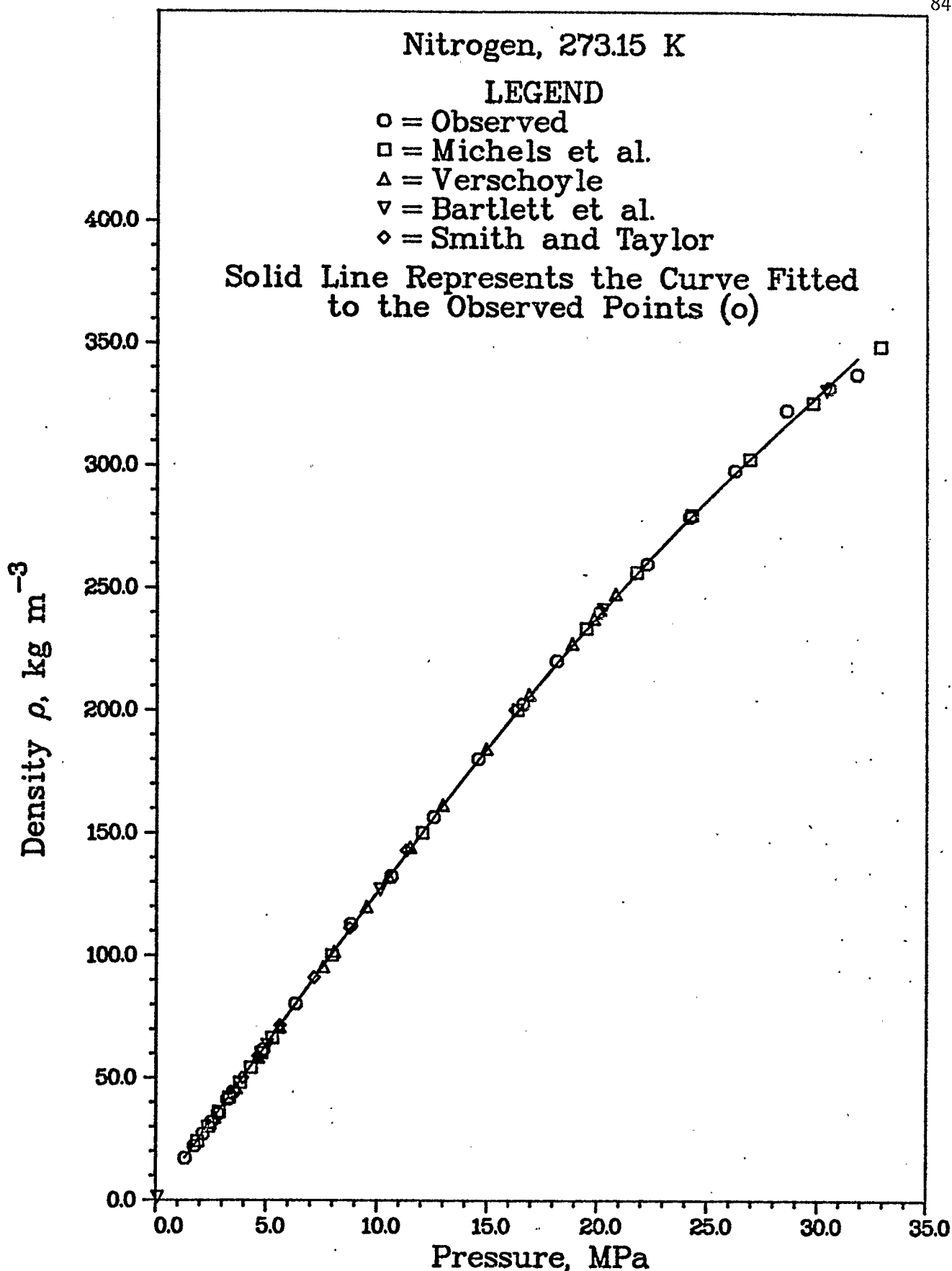


Fig. 5.3.5 Observed Density Versus Pressure for Nitrogen Compared with the Data of Michels et al. [2.18,2.19], Verschoyle [2.16], Bartlett et al. [2.17] and Smith and Taylor [2.15] at 273.15 K.

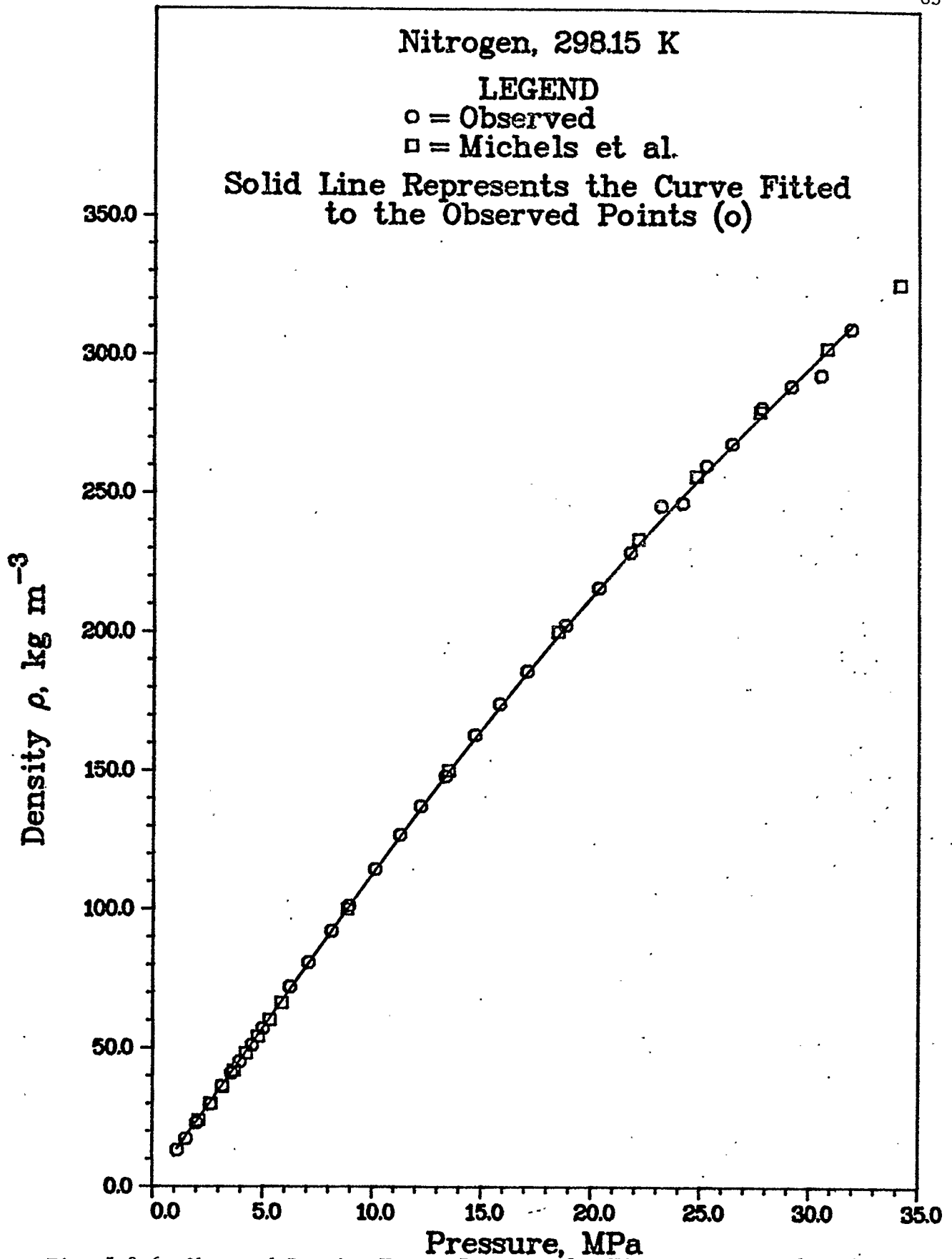


Fig. 5.3.6 Observed Density Versus Pressure for Nitrogen Compared with the Data of Michels et al. [2.18,2.19] at 298.15 K.

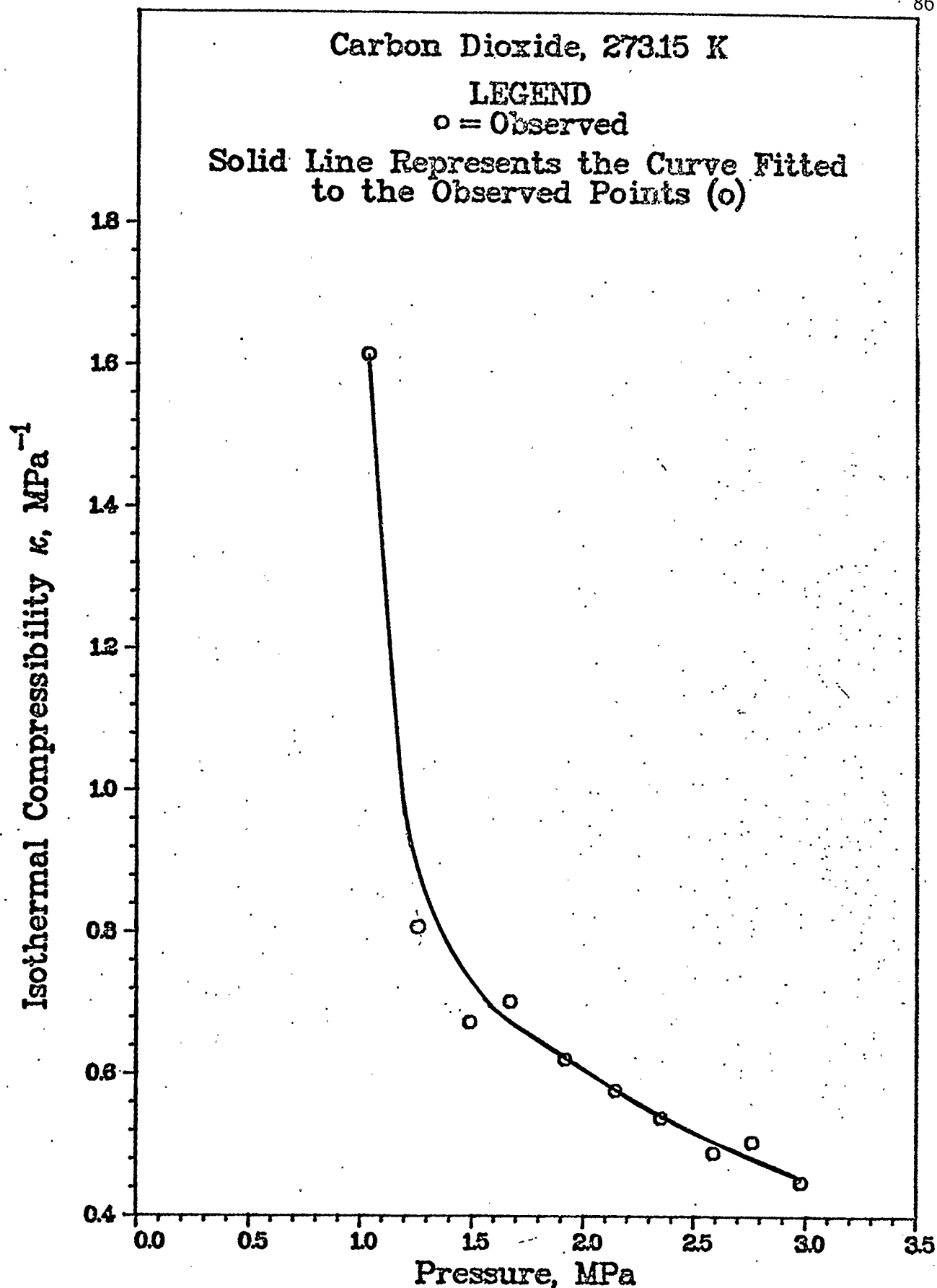


Fig. 5.3.7 Observed Isothermal Compressibility Versus Pressure for Carbon Dioxide at 273.15 K.

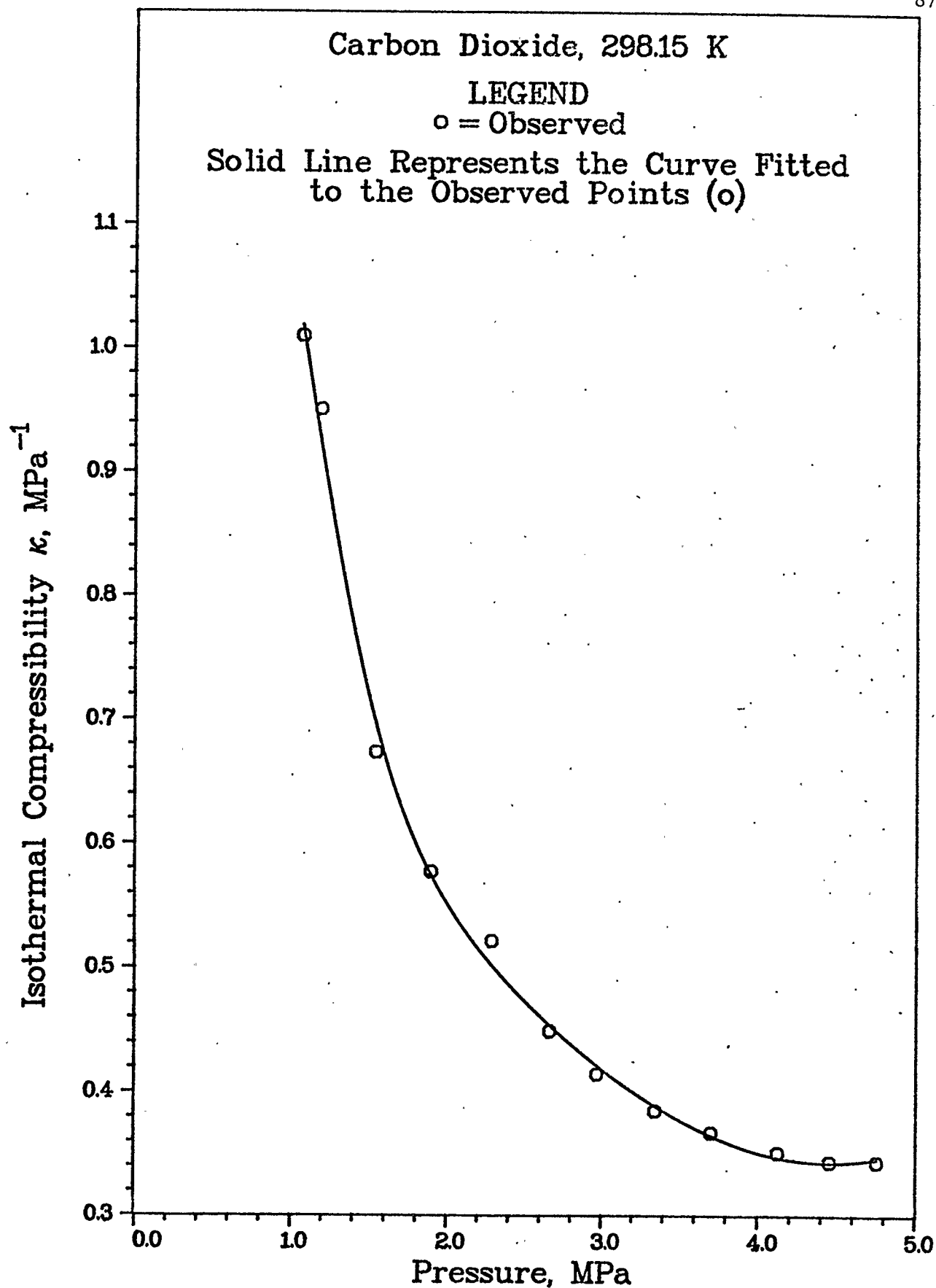


Fig. 5.3.8 Observed Isothermal Compressibility Versus Pressure for Carbon Dioxide at 298.15 K.

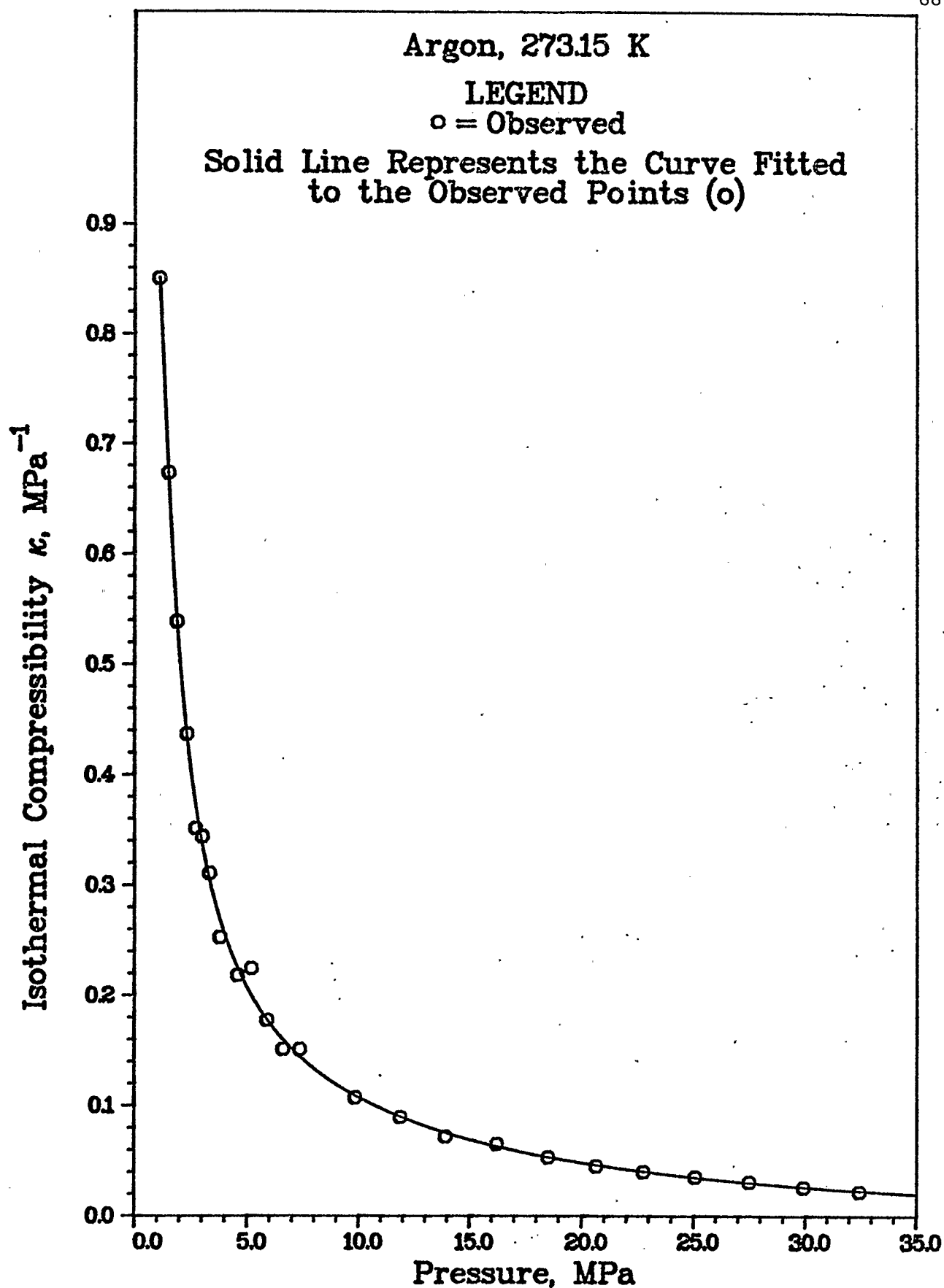


Fig. 5.3.9 Observed Isothermal Compressibility Versus Pressure for Argon at 273.15 K.

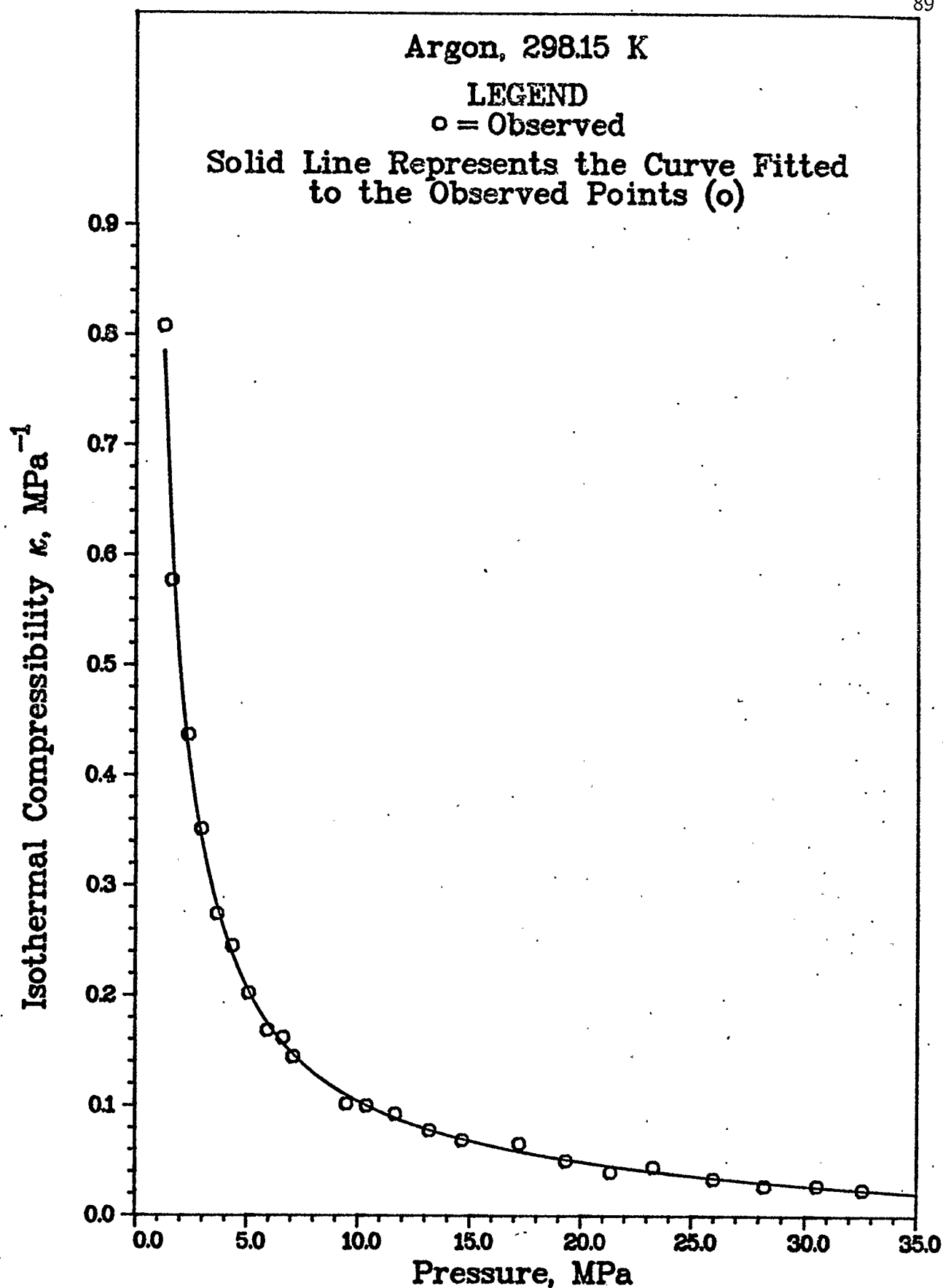


Fig. 5.3.10 Observed Isothermal Compressibility Versus Pressure for Argon at 298.15 K.

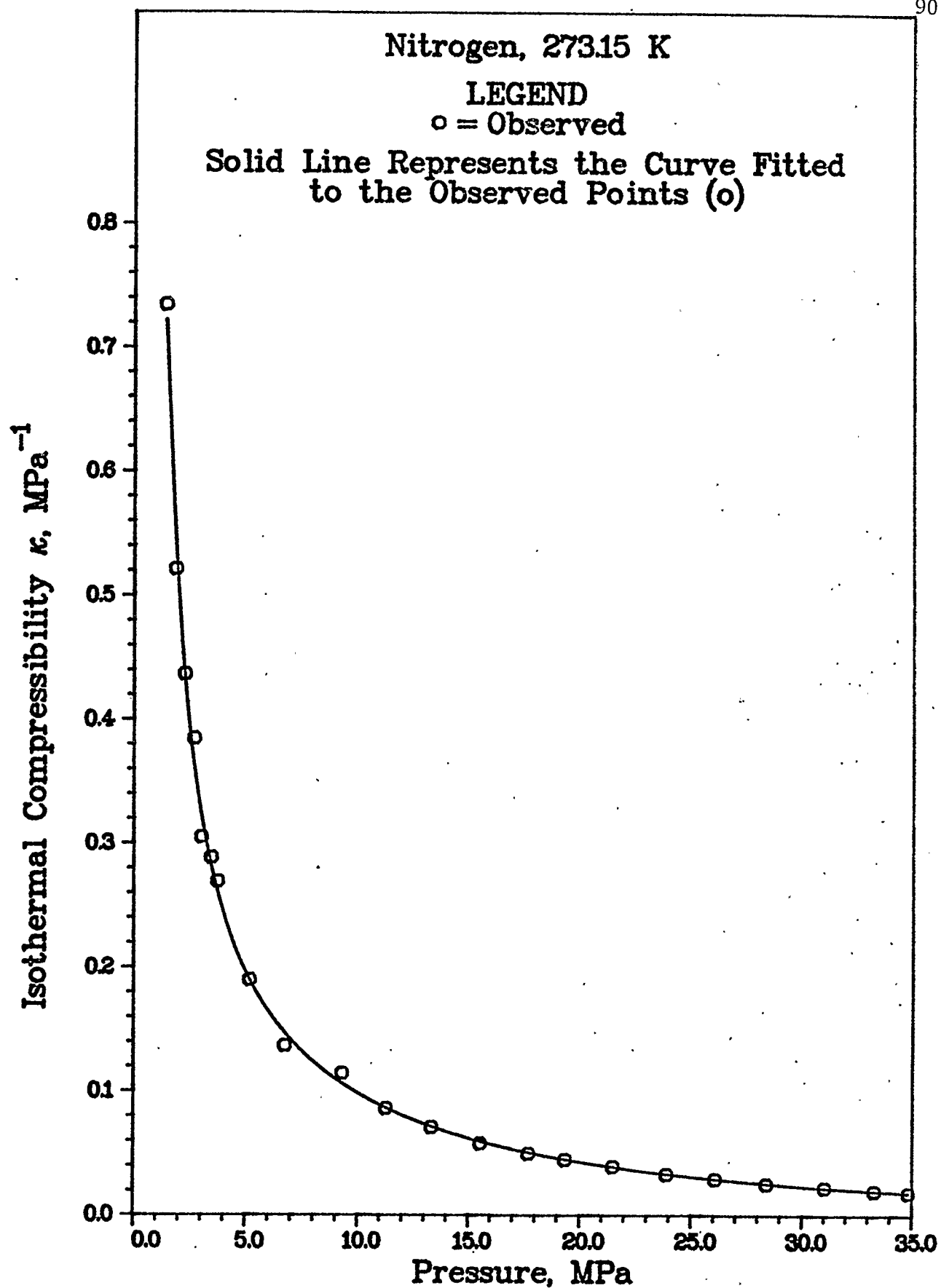


Fig. 5.3.11 Observed Isothermal Compressibility Versus Pressure for Nitrogen at 273.15 K.

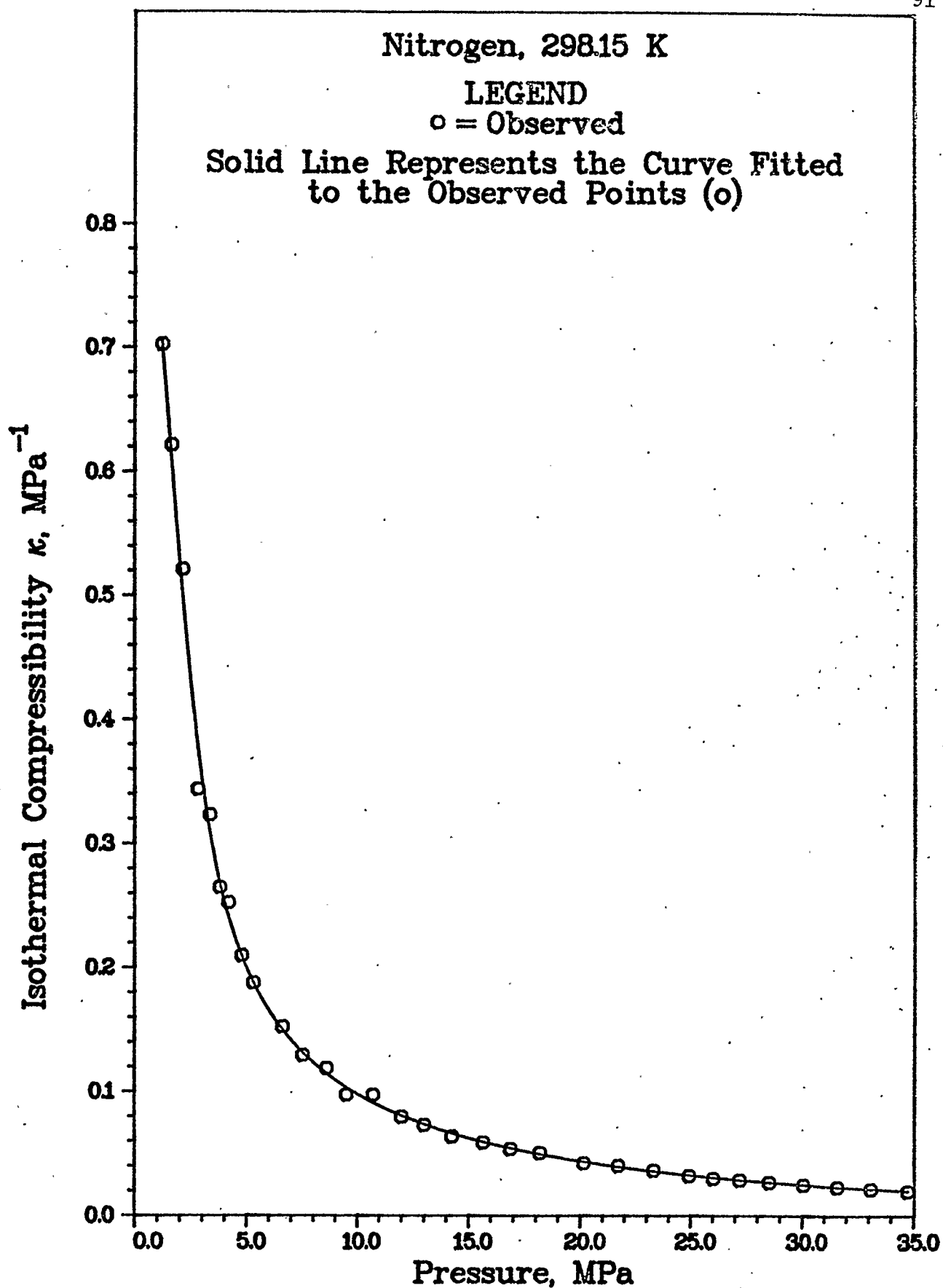


Fig 5.3.12 Observed Isothermal Compressibility Versus Pressure for Nitrogen at 298.15 K.

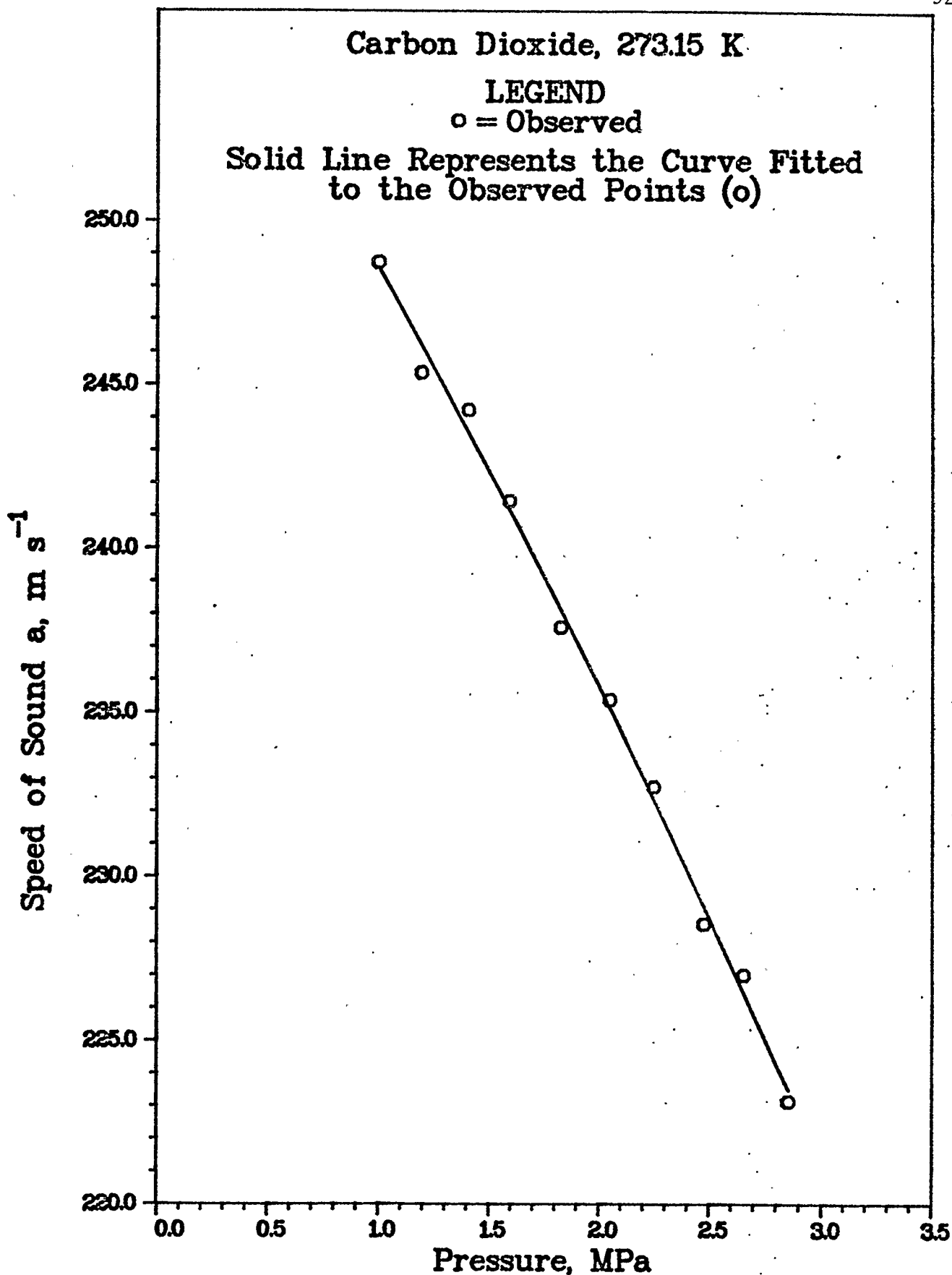


Fig. 5.3.13 Observed Speed of Sound Versus Pressure for Carbon Dioxide at 273.15 K.

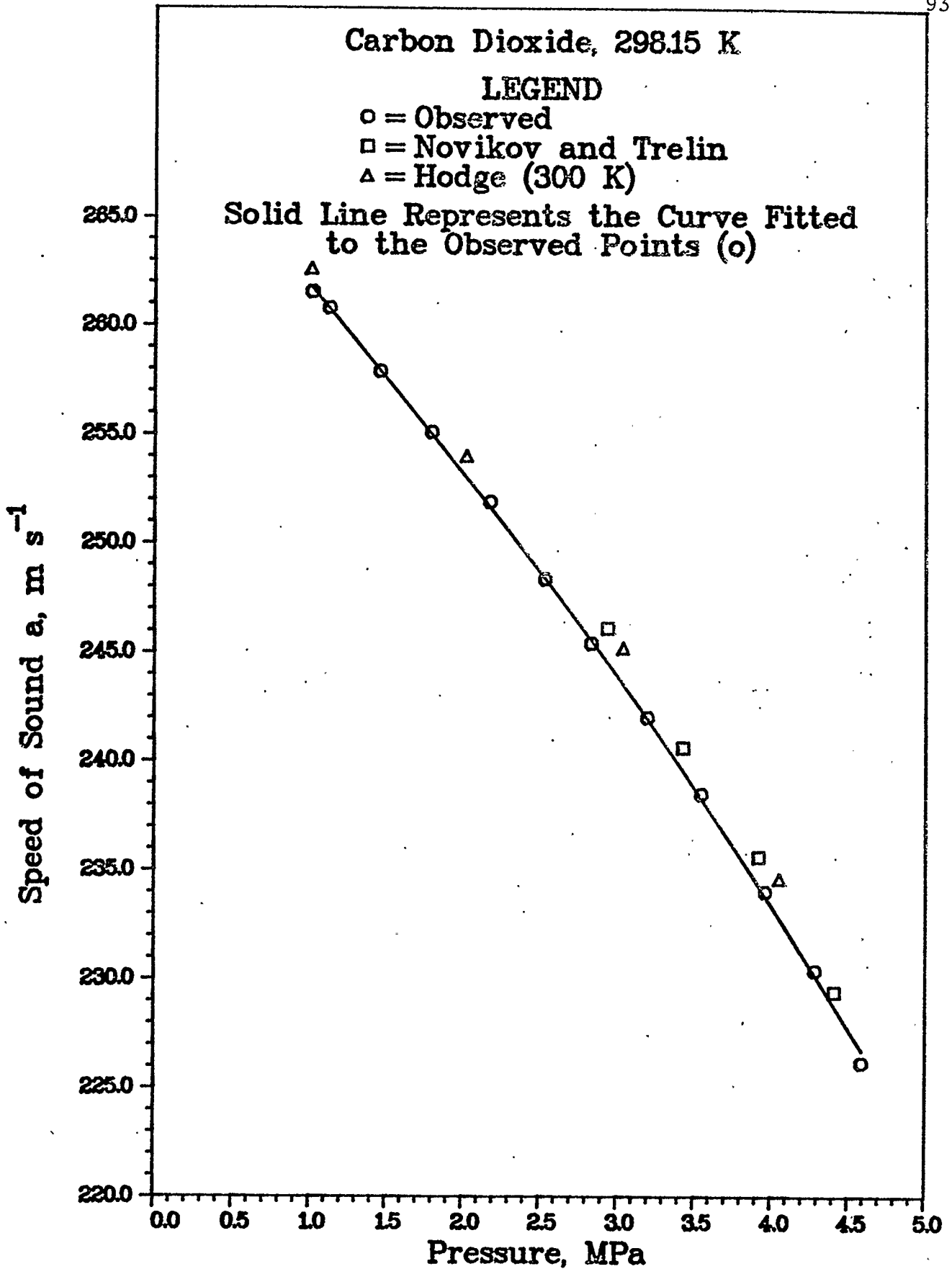


Fig. 5.3.14 Observed Speed of Sound Versus Pressure for Carbon Dioxide Compared with the Data of Novikov and Trelin [2.34,2.35] and Hodge [2.20] at 298.15 K.

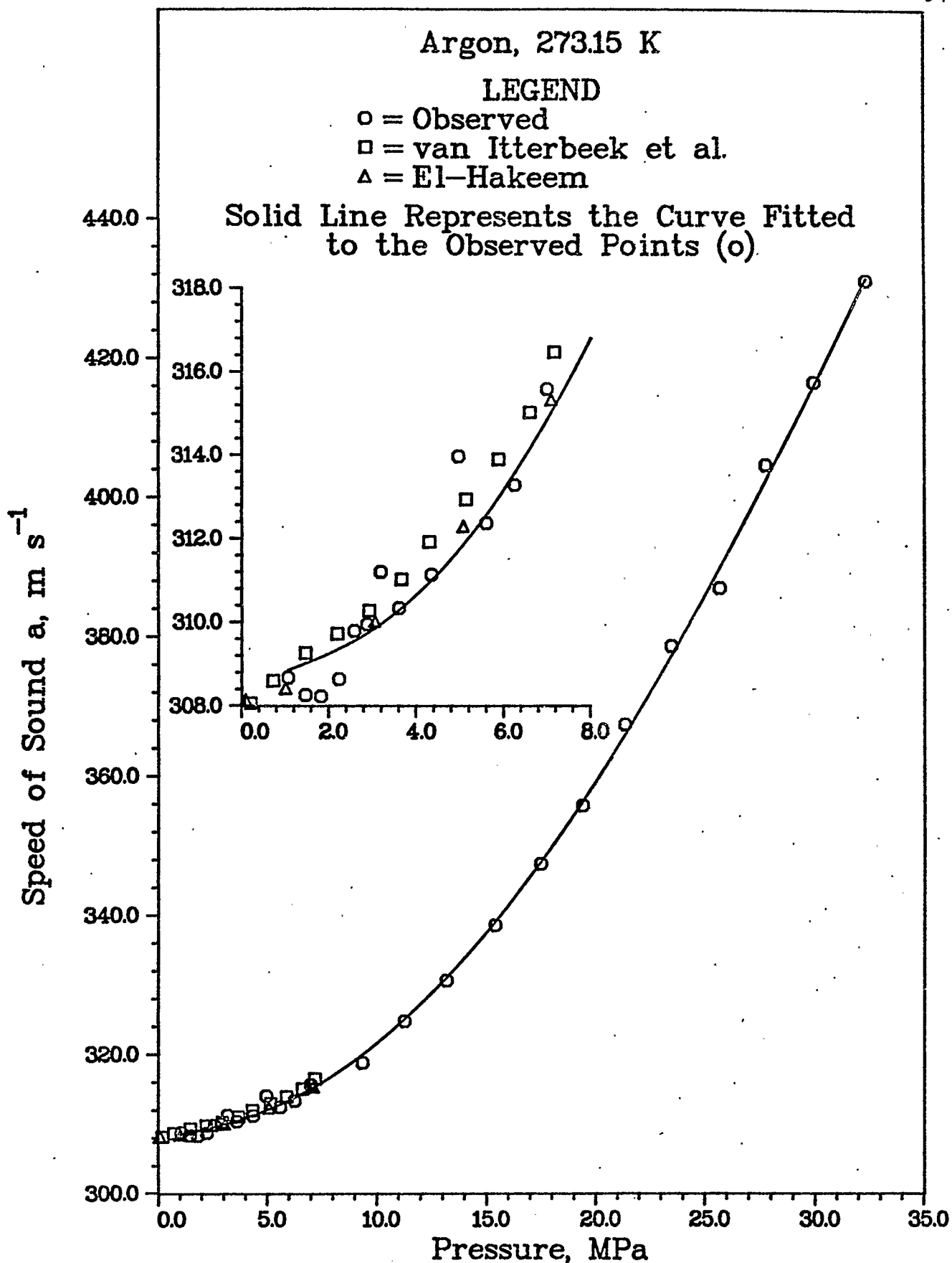


Fig. 5.3.15 Observed Speed of Sound Versus Pressure for Argon Compared with the Data of van Itterbeek et al. [2.36] and El-Hakeem [2.24] at 273.15 K.

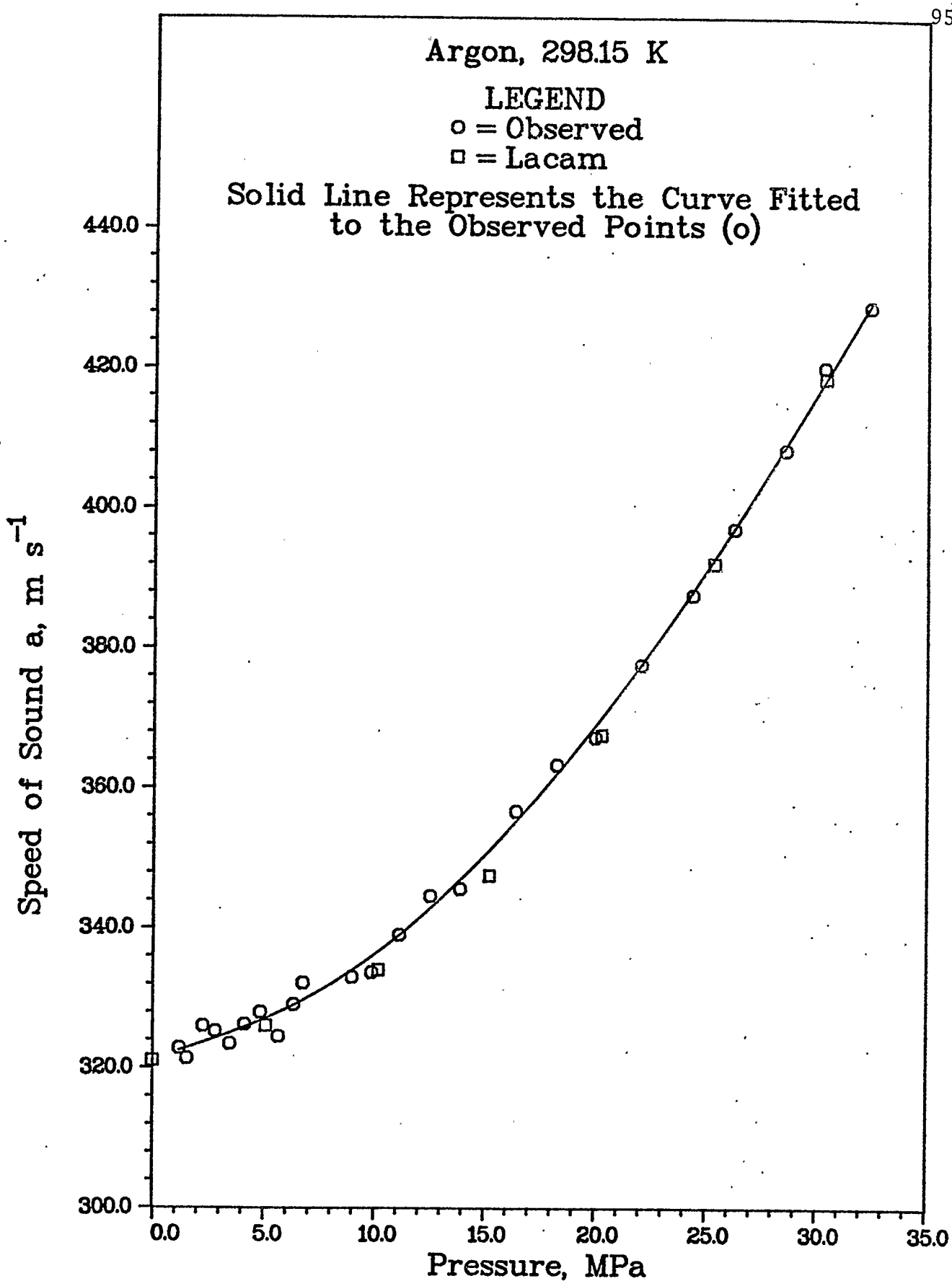


Fig. 5.3.16 Observed Speed of Sound Versus Pressure for Argon Compared with the Data of Lacam [2.31] at 298.15 K.

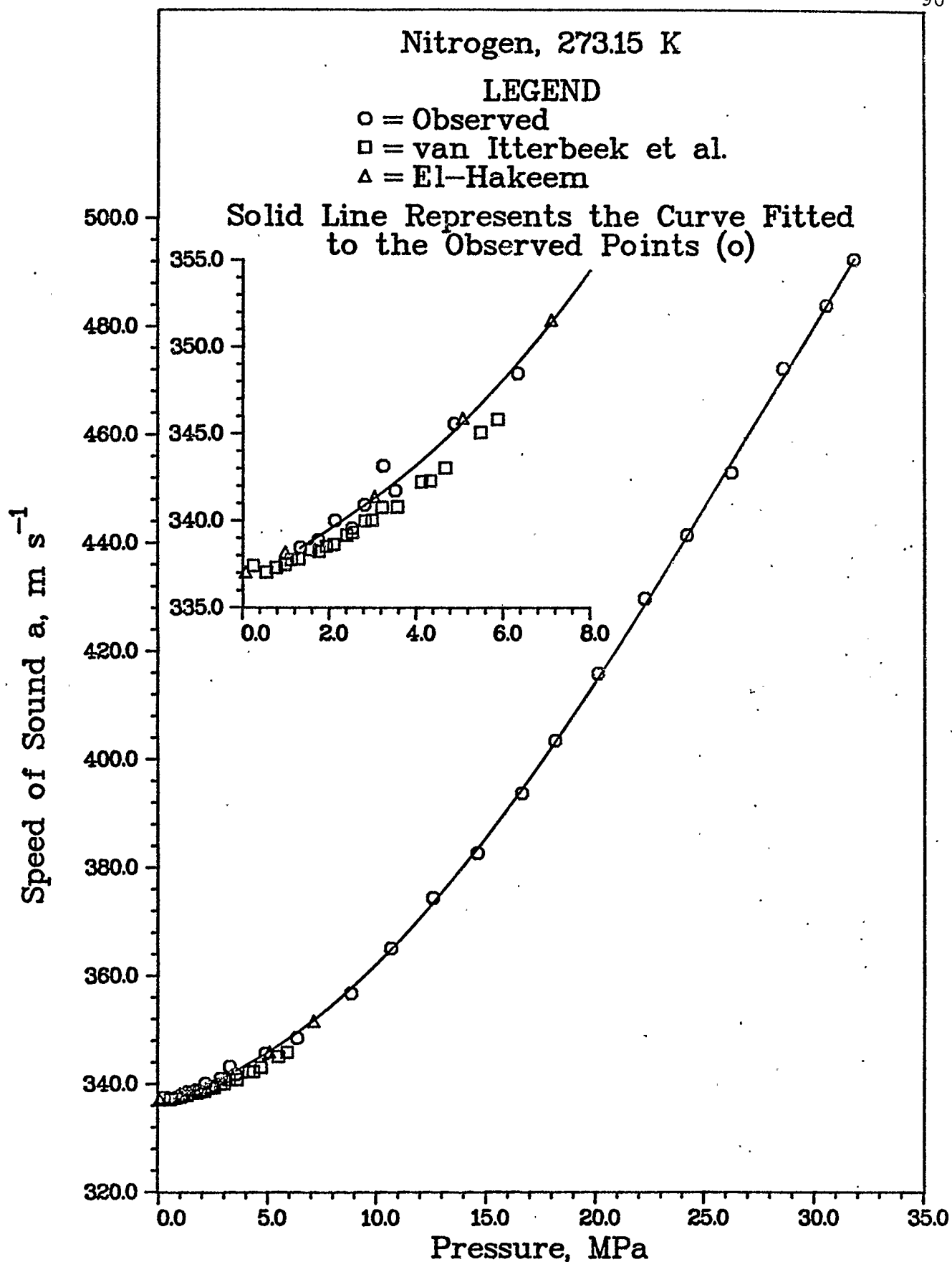


Fig. 5.3.17 Observed Speed of Sound Versus Pressure for Nitrogen Compared with the Data of van Itterbeek et al. [2.21] and El-Hakeem [2.24] at 273.15 K.

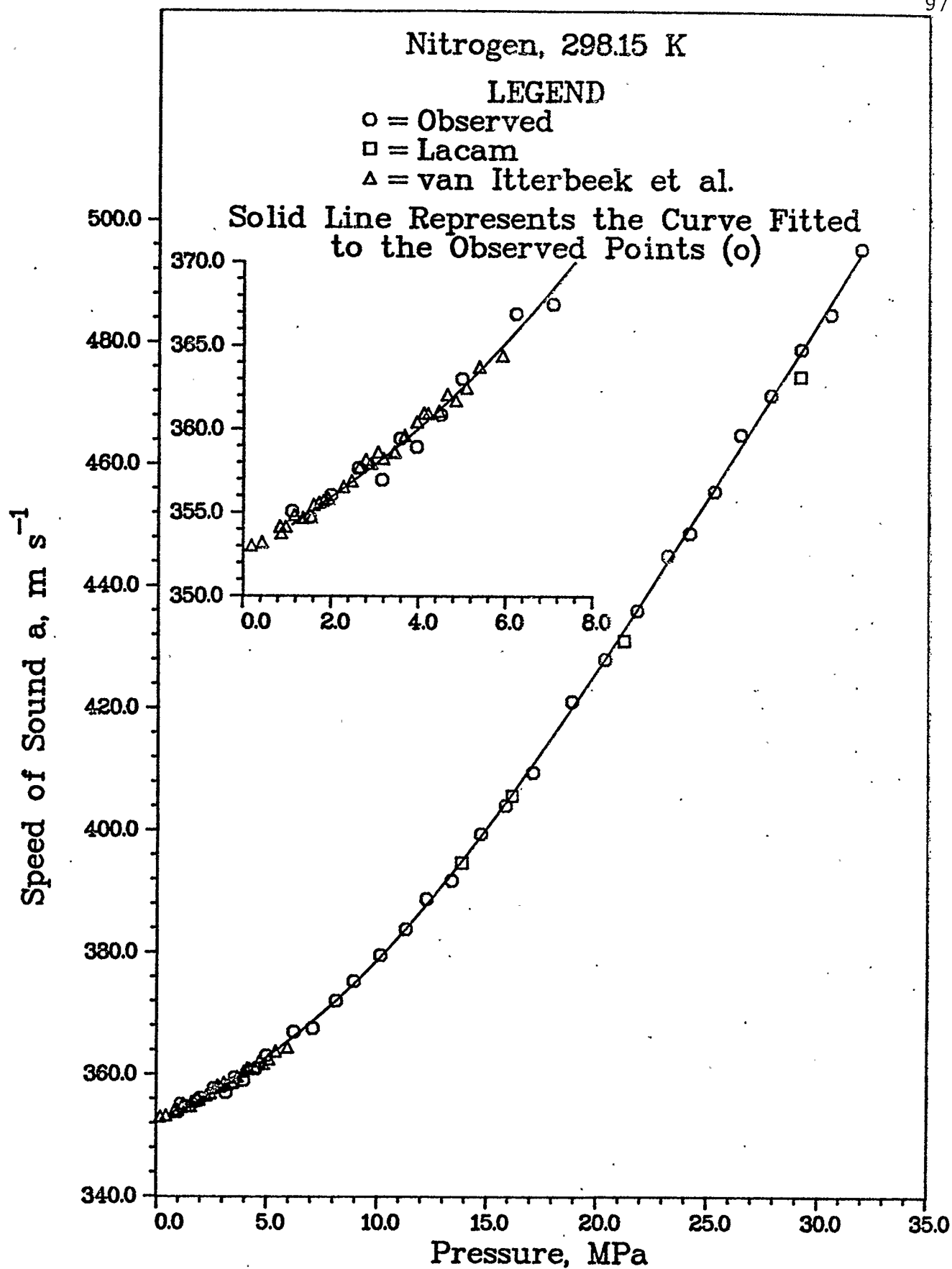


Fig. 5.3.18 Observed Speed of Sound Versus Pressure for Nitrogen Compared with the Data of Lacam [2.31] and van Itterbeek et al. [2.21] at 298.15 K.

Table 5.4.2 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

		van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
		Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	Z	Z	Deviation	Z	Deviation	Z	Deviation	
			from		from		from	
			Observed		Observed		Observed	
1.0193	0.9514	0.9673	1.6754	0.9539	0.2661	0.9464	-0.5271	
1.1296	0.9460	0.9637	1.8725	0.9488	0.2918	0.9404	-0.5968	
1.4605	0.9284	0.9526	2.6029	0.9330	0.5004	0.9218	-0.7063	
1.7984	0.9084	0.9410	3.5906	0.9166	0.9037	0.9024	-0.6619	
2.1776	0.8839	0.9278	4.9613	0.8977	1.5588	0.8799	-0.4574	
2.5361	0.8592	0.9149	6.4841	0.8792	2.3274	0.8577	-0.1758	
2.8326	0.8378	0.9040	7.8998	0.8636	3.0794	0.8388	0.1142	
3.1980	0.8108	0.8902	9.7961	0.8438	4.0646	0.8143	0.4372	
3.5496	0.7845	0.8766	11.7437	0.8240	5.0379	0.7898	0.6758	
3.9633	0.7535	0.8600	14.1355	0.8000	6.1743	0.7592	0.7547	
4.2874	0.7297	0.8466	16.0257	0.7804	6.9482	0.7335	0.5269	
4.5907	0.7080	0.8337	17.7494	0.7615	7.5596	0.7081	0.0143	

Table 5.4.3 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Argon at 273.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	Z	Z	Deviation	Z	Deviation	Z	Deviation
			from Observed		from Observed		from Observed
1.0803	0.9903	0.9894	-0.0879	0.9899	-0.0407	0.9896	-0.0686
1.4733	0.9862	0.9856	-0.0604	0.9863	0.0120	0.9859	-0.0279
1.8250	0.9827	0.9822	-0.0519	0.9831	0.0429	0.9827	-0.0040
2.2386	0.9786	0.9782	-0.0412	0.9794	0.0856	0.9789	0.0298
2.5902	0.9753	0.9748	-0.0507	0.9763	0.1031	0.9758	0.0494
2.8798	0.9726	0.9720	-0.0582	0.9738	0.1203	0.9732	0.0651
3.1901	0.9697	0.9691	-0.0656	0.9711	0.1415	0.9705	0.0848
3.6108	0.9660	0.9651	-0.0973	0.9674	0.1492	0.9669	0.0970
4.3554	0.9597	0.9580	-0.1728	0.9612	0.1590	0.9608	0.1160
4.9693	0.9548	0.9524	-0.2548	0.9562	0.1516	0.9559	0.1192
5.5967	0.9500	0.9466	-0.3539	0.9514	0.1427	0.9512	0.1298
6.2586	0.9453	0.9407	-0.4844	0.9464	0.1152	0.9464	0.1186
7.0032	0.9403	0.9342	-0.6506	0.9410	0.0747	0.9413	0.1078
9.3406	0.9270	0.9148	-1.3116	0.9262	-0.0914	0.9275	0.0584
11.2641	0.9188	0.9007	-1.9752	0.9167	-0.2298	0.9188	0.0029
13.1602	0.9131	0.8886	-2.6819	0.9098	-0.3572	0.9128	-0.0366
15.3665	0.9093	0.8776	-3.4904	0.9056	-0.4118	0.9090	-0.0295
17.4831	0.9086	0.8705	-4.1942	0.9052	-0.3698	0.9087	0.0076
19.4068	0.9103	0.8675	-4.7063	0.9082	-0.2352	0.9111	0.0893
21.3580	0.9143	0.8676	-5.1039	0.9140	-0.0382	0.9160	0.1886
23.4885	0.9213	0.8716	-5.3947	0.9232	0.2078	0.9240	0.2914
25.6810	0.9313	0.8796	-5.5533	0.9356	0.4646	0.9347	0.3665
27.7700	0.9434	0.8903	-5.6275	0.9498	0.6748	0.9470	0.3799
29.9350	0.9585	0.9042	-5.6670	0.9664	0.8198	0.9615	0.3166
32.2998	0.9780	0.9222	-5.7044	0.9864	0.8539	0.9792	0.1259

Table 5.4.4 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Argon at 298.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	Z	Z	Deviation	Z	Deviation	Z	Deviation
			from Observed		from Observed		from Observed
1.1855	0.9878	0.9913	0.3545	0.9926	0.4876	0.9919	0.4153
1.5234	0.9859	0.9889	0.3024	0.9906	0.4744	0.9897	0.3877
2.2473	0.9820	0.9837	0.1773	0.9863	0.4355	0.9851	0.3185
2.7989	0.9792	0.9799	0.0671	0.9831	0.3964	0.9818	0.2612
3.4609	0.9759	0.9752	-0.0708	0.9794	0.3624	0.9779	0.2056
4.1296	0.9728	0.9706	-0.2246	0.9759	0.3152	0.9742	0.1393
4.8328	0.9697	0.9659	-0.3911	0.9722	0.2612	0.9704	0.0748
5.6257	0.9665	0.9608	-0.5939	0.9684	0.1918	0.9665	0.0036
6.3077	0.9638	0.9564	-0.7654	0.9652	0.1480	0.9634	-0.0452
6.7283	0.9623	0.9538	-0.8828	0.9633	0.1082	0.9615	-0.0795
8.9552	0.9553	0.9407	-1.5331	0.9548	-0.0485	0.9533	-0.2131
9.8446	0.9531	0.9358	-1.8111	0.9521	-0.1055	0.9507	-0.2519
11.0859	0.9505	0.9298	-2.1828	0.9488	-0.1782	0.9477	-0.2952
12.4993	0.9483	0.9234	-2.6251	0.9460	-0.2375	0.9454	-0.3074
13.8574	0.9469	0.9181	-3.0409	0.9444	-0.2603	0.9441	-0.2953
16.3809	0.9463	0.9108	-3.7567	0.9440	-0.2475	0.9443	-0.2132
18.2218	0.9475	0.9076	-4.2131	0.9459	-0.1731	0.9464	-0.1131
19.9595	0.9499	0.9063	-4.5893	0.9493	-0.0622	0.9500	0.0105
22.0348	0.9546	0.9073	-4.9562	0.9555	0.0966	0.9561	0.1579
24.3307	0.9618	0.9111	-5.2687	0.9648	0.3073	0.9649	0.3262
26.2129	0.9695	0.9166	-5.4537	0.9740	0.4649	0.9736	0.4275
28.5365	0.9812	0.9260	-5.6247	0.9873	0.6259	0.9861	0.4996
30.2946	0.9917	0.9347	-5.7437	0.9987	0.7085	0.9965	0.4887
32.4113	1.0062	0.9472	-5.8631	1.0135	0.7249	1.0103	0.4071

Table 5.4.5 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Nitrogen at 273.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	Z	Z	Deviation	Z	Deviation	Z	Deviation
			from Observed		from Observed		from Observed
1.3572	0.9907	0.9902	-0.0529	0.9941	0.3416	0.9940	0.3302
1.7709	0.9891	0.9873	-0.1840	0.9925	0.3457	0.9923	0.3250
2.1569	0.9877	0.9846	-0.3135	0.9911	0.3443	0.9909	0.3252
2.5498	0.9864	0.9819	-0.4516	0.9898	0.3442	0.9896	0.3197
2.8394	0.9855	0.9800	-0.5583	0.9889	0.3404	0.9886	0.3188
3.2673	0.9843	0.9772	-0.7183	0.9876	0.3368	0.9873	0.3076
3.5362	0.9836	0.9755	-0.8219	0.9869	0.3323	0.9866	0.3065
4.8945	0.9809	0.9673	-1.3912	0.9841	0.3213	0.9836	0.2788
6.3424	0.9795	0.9594	-2.0540	0.9826	0.3133	0.9818	0.2374
8.8245	0.9804	0.9483	-3.2750	0.9838	0.3417	0.9820	0.1608
10.6447	0.9836	0.9425	-4.1802	0.9878	0.4320	0.9848	0.1219
12.5546	0.9892	0.9389	-5.0886	0.9950	0.5839	0.9900	0.0807
14.5815	0.9975	0.9380	-5.9632	1.0057	0.8207	0.9979	0.0401
16.6086	1.0082	0.9404	-6.7267	1.0193	1.0989	1.0082	0.0026
18.1323	1.0177	0.9442	-7.2194	1.0313	1.3330	1.0173	-0.0373
20.0973	1.0317	0.9518	-7.7478	1.0487	1.6430	1.0307	-0.0994
22.2415	1.0492	0.9633	-8.1854	1.0698	1.9635	1.0473	-0.1840
24.1927	1.0669	0.9764	-8.4836	1.0906	2.2197	1.0637	-0.2978
26.2336	1.0872	0.9924	-8.7234	1.1138	2.4478	1.0825	-0.4339
28.5778	1.1127	1.0133	-8.9307	1.1418	2.6165	1.1054	-0.6516
30.5358	1.1355	1.0325	-9.0665	1.1662	2.7000	1.1258	-0.8553
31.8113	1.1510	1.0459	-9.1337	1.1824	2.7282	1.1395	-1.0006

Table 5.4.6 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Nitrogen at 298.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	Z	Z	Deviation	Z	Deviation	Z	Deviation
			from Observed		from Observed		from Observed
1.1373	0.9934	0.9942	0.0851	0.9979	0.4553	0.9976	0.4266
1.5302	0.9926	0.9923	-0.0287	0.9973	0.4743	0.9969	0.4357
2.0128	0.9919	0.9900	-0.1891	0.9967	0.4878	0.9962	0.4323
2.6326	0.9912	0.9872	-0.4061	0.9961	0.4983	0.9954	0.4250
3.1635	0.9907	0.9849	-0.5895	0.9958	0.5109	0.9950	0.4325
3.5772	0.9905	0.9831	-0.7483	0.9956	0.5148	0.9947	0.4221
3.9564	0.9904	0.9815	-0.9014	0.9955	0.5149	0.9946	0.4192
4.5080	0.9904	0.9793	-1.1222	0.9955	0.5149	0.9944	0.4064
4.9975	0.9906	0.9774	-1.3293	0.9957	0.5105	0.9945	0.3973
6.2316	0.9916	0.9732	-1.8555	0.9966	0.5067	0.9953	0.3699
7.0801	0.9929	0.9706	-2.2500	0.9978	0.4942	0.9961	0.3267
8.1282	0.9950	0.9678	-2.7377	0.9999	0.4936	0.9979	0.2903
8.9279	0.9970	0.9660	-3.1112	1.0019	0.4928	0.9996	0.2622
10.1276	1.0007	0.9639	-3.6771	1.0056	0.4854	1.0028	0.2072
11.2790	1.0049	0.9625	-4.2223	1.0100	0.5058	1.0064	0.1517
12.2236	1.0089	0.9619	-4.6610	1.0141	0.5166	1.0099	0.1029
13.3681	1.0144	0.9618	-5.1867	1.0198	0.5281	1.0147	0.0250
14.6919	1.0214	0.9626	-5.7606	1.0273	0.5748	1.0209	-0.0503
15.8226	1.0281	0.9640	-6.2352	1.0343	0.6042	1.0267	-0.1331
17.0775	1.0361	0.9664	-6.7242	1.0429	0.6583	1.0339	-0.2132
18.8287	1.0484	0.9713	-7.3497	1.0561	0.7306	1.0447	-0.3514
20.3249	1.0599	0.9768	-7.8407	1.0683	0.7920	1.0549	-0.4724
21.7797	1.0719	0.9833	-8.2697	1.0810	0.8531	1.0654	-0.6100
23.1862	1.0841	0.9906	-8.6206	1.0940	0.9178	1.0761	-0.7336
24.1583	1.0930	0.9963	-8.8511	1.1034	0.9506	1.0839	-0.8336
25.2615	1.1034	1.0032	-9.0804	1.1143	0.9868	1.0929	-0.9499
26.4404	1.1149	1.0112	-9.3054	1.1263	1.0225	1.1030	-1.0700
27.8124	1.1288	1.0211	-9.5442	1.1407	1.0525	1.1151	-1.2178
29.1637	1.1429	1.0317	-9.7272	1.1553	1.0813	1.1273	-1.3609
30.5289	1.1577	1.0430	-9.9059	1.1702	1.0837	1.1400	-1.5248
31.9285	1.1732	1.0552	-10.0573	1.1860	1.0906	1.1534	-1.6861

Table 5.4.7 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

		van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
		Calculated	Percent		Calculated	Percent	Calculated	Percent
Pressure	Observed	Calculated	Deviation		Calculated	Deviation	Calculated	Deviation
MPa	κ/κ^0	κ/κ^0	from		κ/κ^0	from	κ/κ^0	from
			Observed			Observed		Observed
1.0003	1.0699	1.0430	-2.5128		1.0662	-0.3476	1.0822	1.1526
1.1933	1.0909	1.0525	-3.5192		1.0817	-0.8469	1.1022	1.0376
1.4071	1.1154	1.0636	-4.6414		1.1001	-1.3737	1.1265	0.9972
1.5932	1.1382	1.0738	-5.6563		1.1173	-1.8328	1.1498	1.0176
1.8277	1.1699	1.0874	-7.0497		1.1410	-2.4671	1.1825	1.0736
2.0483	1.2035	1.1010	-8.5141		1.1655	-3.1540	1.2173	1.1507
2.2482	1.2378	1.1142	-9.9873		1.1900	-3.8619	1.2532	1.2415
2.4758	1.2822	1.1301	-11.8647		1.2207	-4.7984	1.3003	1.4092
2.6550	1.3217	1.1435	-13.4807		1.2474	-5.6186	1.3432	1.6283
2.8549	1.3711	1.1595	-15.4364		1.2807	-6.5940	1.3991	2.0405

Table 5.4.8 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	κ/κ^0	κ/κ^0	Deviation	κ/κ^0	Deviation	κ/κ^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.0193	1.0517	1.0348	-1.6103	1.0499	-0.1710	1.0589	0.6865
1.1296	1.0607	1.0389	-2.0534	1.0560	-0.4468	1.0663	0.5270
1.4605	1.0872	1.0519	-3.2457	1.0752	-1.0999	1.0898	0.2423
1.7984	1.1151	1.0661	-4.3918	1.0967	-1.6530	1.1165	0.1221
2.1776	1.1491	1.0832	-5.7347	1.1229	-2.2764	1.1500	0.0749
2.5361	1.1860	1.1008	-7.1857	1.1504	-3.0048	1.1862	0.0174
2.8326	1.2212	1.1164	-8.5836	1.1753	-3.7600	1.2201	-0.0929
3.1980	1.2721	1.1372	-10.6009	1.2091	-4.9541	1.2680	-0.3225
3.5496	1.3307	1.1592	-12.8849	1.2455	-6.4045	1.3222	-0.6353
3.9633	1.4141	1.1880	-15.9913	1.2940	-8.4965	1.4001	-0.9920
4.2874	1.4921	1.2129	-18.7097	1.3372	-10.3830	1.4755	-1.1118
4.5907	1.5765	1.2386	-21.4333	1.3824	-12.3135	1.5626	-0.8791

Table 5.4.9 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Argon at 273.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	κ/κ^0	κ/κ^0	Deviation	κ/κ^0	Deviation	κ/κ^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.0803	1.0097	1.0107	0.0986	1.0101	0.0379	1.0103	0.0582
1.4733	1.0157	1.0146	-0.1116	1.0136	-0.2050	1.0138	-0.1822
1.8250	1.0208	1.0180	-0.2721	1.0168	-0.3947	1.0170	-0.3737
2.2386	1.0265	1.0221	-0.4321	1.0204	-0.5981	1.0206	-0.5746
2.5902	1.0310	1.0255	-0.5336	1.0234	-0.7359	1.0235	-0.7258
2.8798	1.0345	1.0283	-0.5988	1.0258	-0.8426	1.0258	-0.8368
3.1901	1.0380	1.0313	-0.6443	1.0283	-0.9378	1.0282	-0.9433
3.6108	1.0425	1.0353	-0.6868	1.0316	-1.0462	1.0313	-1.0723
4.3554	1.0494	1.0423	-0.6729	1.0372	-1.1629	1.0365	-1.2288
4.9693	1.0542	1.0479	-0.5941	1.0413	-1.2224	1.0402	-1.3263
5.5967	1.0584	1.0535	-0.4620	1.0451	-1.2545	1.0436	-1.3973
6.2586	1.0619	1.0591	-0.2659	1.0487	-1.2447	1.0466	-1.4381
7.0032	1.0648	1.0650	0.0152	1.0521	-1.1960	1.0493	-1.4536
9.3406	1.0672	1.0798	1.1853	1.0568	-0.9777	1.0521	-1.4163
11.2641	1.0619	1.0862	2.2851	1.0526	-0.8724	1.0473	-1.3736
13.1602	1.0509	1.0853	3.2735	1.0410	-0.9459	1.0361	-1.4093
15.3665	1.0314	1.0732	4.0534	1.0174	-1.3599	1.0152	-1.5727
17.4831	1.0066	1.0490	4.2165	0.9860	-2.0448	0.9883	-1.8150
19.4068	0.9796	1.0169	3.8105	0.9520	-2.8220	0.9594	-2.0630
21.3580	0.9483	0.9764	2.9622	0.9141	-3.6012	0.9272	-2.2277
23.4885	0.9102	0.9259	1.7259	0.8714	-4.2597	0.8900	-2.2221
25.6810	0.8676	0.8709	0.3803	0.8279	-4.5705	0.8513	-1.8790
27.7700	0.8244	0.8187	-0.6971	0.7885	-4.3583	0.8149	-1.1487
29.9350	0.7776	0.7670	-1.3687	0.7503	-3.5169	0.7787	0.1460
32.2998	0.7251	0.7148	-1.4151	0.7123	-1.7675	0.7414	2.2546

Table 5.4.10 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Argon at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	κ/κ^0	κ/κ^0	Deviation	κ/κ^0	Deviation	κ/κ^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.1855	1.0070	1.0087	0.1686	1.0072	0.0242	1.0079	0.0899
1.5234	1.0108	1.0111	0.0315	1.0092	-0.1570	1.0099	-0.0858
2.2473	1.0181	1.0162	-0.1847	1.0132	-0.4764	1.0141	-0.3927
2.7989	1.0232	1.0200	-0.3085	1.0161	-0.6937	1.0170	-0.6016
3.4609	1.0287	1.0245	-0.4106	1.0192	-0.9213	1.0202	-0.8262
4.1296	1.0335	1.0288	-0.4546	1.0221	-1.1000	1.0230	-1.0163
4.8328	1.0379	1.0332	-0.4555	1.0249	-1.2549	1.0255	-1.1905
5.6257	1.0420	1.0378	-0.4010	1.0274	-1.4004	1.0277	-1.3692
6.3077	1.0448	1.0415	-0.3196	1.0291	-1.5040	1.0292	-1.4977
6.7283	1.0462	1.0436	-0.2515	1.0300	-1.5467	1.0298	-1.5708
8.9552	1.0497	1.0527	0.2863	1.0312	-1.7619	1.0296	-1.9172
9.8446	1.0493	1.0550	0.5452	1.0301	-1.8258	1.0279	-2.0389
11.0859	1.0470	1.0567	0.9257	1.0270	-1.9136	1.0239	-2.2050
12.4993	1.0422	1.0564	1.3599	1.0208	-2.0517	1.0172	-2.4000
13.8574	1.0354	1.0534	1.7432	1.0125	-2.2100	1.0085	-2.5962
16.3809	1.0175	1.0404	2.2458	0.9908	-2.6271	0.9874	-2.9542
18.2218	1.0004	1.0244	2.3971	0.9705	-2.9920	0.9684	-3.1967
19.9595	0.9813	1.0042	2.3348	0.9485	-3.3455	0.9483	-3.3669
22.0348	0.9551	0.9746	2.0430	0.9195	-3.7261	0.9222	-3.4432
24.3307	0.9223	0.9364	1.5317	0.8855	-3.9932	0.8917	-3.3139
26.2129	0.8926	0.9022	1.0752	0.8570	-3.9847	0.8661	-2.9633
28.5365	0.8530	0.8582	0.6104	0.8222	-3.6059	0.8346	-2.1550
30.2946	0.8212	0.8247	0.4299	0.7967	-2.9860	0.8111	-1.2278
32.4113	0.7809	0.7853	0.5612	0.7671	-1.7632	0.7837	0.3569

Table 5.4.11 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Nitrogen at 273.25 K.

			van der Waals				Benedict-Webb-Rubin	
			Calculated	Percent	Calculated	Percent	Calculated	Percent
Pressure	Observed			Deviation		Deviation		Deviation
MPa	κ/κ^0		κ/κ^0	from	κ/κ^0	from	κ/κ^0	from
			Observed	Observed		Observed		Observed
1.3572	1.0062	1.0097	0.3440	1.0054	-0.0754	1.0054	-0.0746	
1.7709	1.0081	1.0124	0.4272	1.0066	-0.1479	1.0067	-0.1385	
2.1569	1.0095	1.0149	0.5375	1.0076	-0.1878	1.0077	-0.1812	
2.5498	1.0107	1.0173	0.6564	1.0083	-0.2389	1.0085	-0.2198	
2.8394	1.0114	1.0191	0.7597	1.0087	-0.2634	1.0088	-0.2528	
3.2673	1.0122	1.0215	0.9201	1.0090	-0.3116	1.0093	-0.2849	
3.5362	1.0125	1.0230	1.0374	1.0092	-0.3275	1.0094	-0.3077	
4.8945	1.0124	1.0293	1.6698	1.0080	-0.4344	1.0087	-0.3675	
6.3424	1.0090	1.0339	2.4638	1.0032	-0.5775	1.0050	-0.3989	
8.8245	0.9964	1.0348	3.8551	0.9866	-0.9866	0.9917	-0.4716	
10.6447	0.9822	1.0290	4.7680	0.9678	-1.4661	0.9771	-0.5222	
12.5546	0.9635	1.0160	5.4487	0.9432	-2.1104	0.9579	-0.5857	
14.5815	0.9401	0.9944	5.7756	0.9127	-2.9164	0.9340	-0.6456	
16.6086	0.9136	0.9655	5.6834	0.8796	-3.7227	0.9076	-0.6593	
18.1323	0.8921	0.9397	5.3392	0.8539	-4.2821	0.8866	-0.6188	
20.0973	0.8629	0.9028	4.6246	0.8208	-4.8815	0.8585	-0.5133	
22.2415	0.8299	0.8597	3.5857	0.7856	-5.3343	0.8275	-0.2947	
24.1927	0.7995	0.8197	2.5219	0.7552	-5.5362	0.7993	-0.0273	
26.2336	0.7681	0.7785	1.3494	0.7254	-5.5539	0.7704	0.2985	
28.5778	0.7333	0.7333	0.0020	0.6939	-5.3674	0.7382	0.6729	
30.5358	0.7062	0.6980	-1.1587	0.6697	-5.1639	0.7125	0.8910	
31.8113	0.6898	0.6763	-1.9536	0.6551	-5.0319	0.6963	0.9370	

Table 5.4.12 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	κ/κ^0	κ/κ^0	Deviation	κ/κ^0	Deviation	κ/κ^0	Deviation
			!from		!from		!from
			!Observed		!Observed		!Observed
1.1373	1.0072	1.0056	-0.1611	1.0017	-0.5424	1.0020	-0.5174
1.5302	1.0093	1.0074	-0.1872	1.0021	-0.7138	1.0024	-0.6802
2.0128	1.0115	1.0095	-0.1988	1.0022	-0.9170	1.0027	-0.8700
2.6326	1.0137	1.0120	-0.1693	1.0021	-1.1417	1.0027	-1.0851
3.1635	1.0149	1.0139	-0.0983	1.0017	-1.2961	1.0023	-1.2430
3.5772	1.0155	1.0152	-0.0258	1.0011	-1.4183	1.0019	-1.3401
3.9564	1.0158	1.0164	0.0617	1.0004	-1.5156	1.0012	-1.4415
4.5080	1.0158	1.0178	0.1980	0.9991	-1.6432	1.0000	-1.5549
4.9975	1.0154	1.0189	0.3431	0.9976	-1.7534	0.9987	-1.6475
6.2316	1.0125	1.0206	0.8015	0.9927	-1.9553	0.9943	-1.7986
7.0801	1.0092	1.0210	1.1663	0.9882	-2.0839	0.9903	-1.8683
8.1282	1.0037	1.0204	1.6611	0.9815	-2.2153	0.9844	-1.9193
8.9279	0.9986	1.0190	2.0425	0.9755	-2.3115	0.9793	-1.9322
10.1276	0.9894	1.0156	2.6438	0.9652	-2.4411	0.9705	-1.9073
11.2790	0.9791	1.0105	3.2060	0.9540	-2.5618	0.9611	-1.8362
12.2236	0.9697	1.0051	3.6480	0.9440	-2.6553	0.9527	-1.7486
13.3681	0.9572	0.9969	4.1501	0.9309	-2.7521	0.9418	-1.6061
14.6919	0.9416	0.9854	4.6539	0.9145	-2.8728	0.9284	-1.4022
15.8226	0.9275	0.9739	5.0070	0.8999	-2.9742	0.9163	-1.2036
17.0775	0.9110	0.9593	5.3065	0.8832	-3.0540	0.9025	-0.9349
18.8287	0.8872	0.9365	5.5519	0.8592	-3.1547	0.8825	-0.5352
20.3249	0.8665	0.9149	5.5833	0.8385	-3.2318	0.8650	-0.1768
21.7797	0.8463	0.8926	5.4722	0.8185	-3.2799	0.8478	0.1715
23.1862	0.8271	0.8701	5.1971	0.7996	-3.3302	0.8311	0.4831
24.1583	0.8142	0.8542	4.9151	0.7867	-3.3829	0.8196	0.6668
25.2615	0.8000	0.8361	4.5087	0.7723	-3.4564	0.8067	0.8400
26.4404	0.7856	0.8166	3.9515	0.7575	-3.5832	0.7929	0.9326
27.8124	0.7699	0.7941	3.1489	0.7407	-3.7971	0.7772	0.9468
29.1637	0.7560	0.7724	2.1642	0.7247	-4.1346	0.7619	0.7766
30.5289	0.7436	0.7509	0.9781	0.7094	-4.6026	0.7467	0.4214
31.9285	0.7331	0.7294	-0.5046	0.6942	-5.3072	0.7315	-0.2157

Table 5.4.13 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	γ/γ^0	γ/γ^0	Deviation	γ/γ^0	Deviation	γ/γ^0	Deviation
			from Observed		from Observed		from Observed
1.0003	1.0563	1.0274	-2.7326	1.0554	-0.0826	1.0736	1.6354
1.1933	1.0770	1.0335	-4.0350	1.0688	-0.7571	1.0918	1.3730
1.4071	1.0994	1.0407	-5.3356	1.0849	-1.3144	1.1139	1.3234
1.5932	1.1195	1.0474	-6.4431	1.1003	-1.7176	1.1353	1.4121
1.8277	1.1468	1.0562	-7.8973	1.1216	-2.2015	1.1654	1.6261
2.0483	1.1760	1.0652	-9.4204	1.1439	-2.7300	1.1979	1.8610
2.2482	1.2065	1.0739	-10.9938	1.1664	-3.3225	1.2315	2.0726
2.4758	1.2473	1.0845	-13.0524	1.1952	-4.1747	1.2758	2.2880
2.6550	1.2850	1.0935	-14.9036	1.2207	-5.0029	1.3166	2.4573
2.8549	1.3338	1.1041	-17.2181	1.2529	-6.0668	1.3699	2.7075

Table 5.4.14 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	γ/γ^0	γ/γ^0	Deviation	γ/γ^0	Deviation	γ/γ^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.0193	1.0433	1.0222	-2.0202	1.0426	-0.0637	1.0528	0.9088
1.1296	1.0502	1.0249	-2.4122	1.0480	-0.2072	1.0595	0.8889
1.4605	1.0729	1.0333	-3.6929	1.0652	-0.7132	1.0812	0.7704
1.7984	1.0996	1.0426	-5.1881	1.0847	-1.3513	1.1059	0.5704
2.1776	1.1348	1.0539	-7.1317	1.1094	-2.2398	1.1374	0.2267
2.5361	1.1744	1.0656	-9.2656	1.1356	-3.3017	1.1717	-0.2279
2.8326	1.2126	1.0761	-11.2554	1.1601	-4.3269	1.2043	-0.6841
3.1980	1.2674	1.0903	-13.9770	1.1943	-5.7692	1.2510	-1.2954
3.5496	1.3291	1.1054	-16.8336	1.2323	-7.2856	1.3046	-1.8469
3.9633	1.4145	1.1253	-20.4485	1.2848	-9.1661	1.3827	-2.2452
4.2874	1.4919	1.1427	-23.4041	1.3336	-10.6132	1.4598	-2.1540
4.5907	1.5735	1.1609	-26.2224	1.3865	-11.8845	1.5503	-1.4755

Table 5.4.15 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Argon at 273.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	γ/γ^0	γ/γ^0	Deviation	γ/γ^0	Deviation	γ/γ^0	Deviation
			!from !Observed		!from !Observed		!from !Observed
1.0803	1.0226	1.0192	-0.3284	1.0242	0.1541	1.0176	-0.4927
1.4733	1.0329	1.0265	-0.6174	1.0333	0.0365	1.0242	-0.8464
1.8250	1.0420	1.0331	-0.8510	1.0415	-0.0523	1.0301	-1.1378
2.2386	1.0528	1.0412	-1.1049	1.0515	-0.1264	1.0373	-1.4704
2.5902	1.0620	1.0480	-1.3154	1.0600	-0.1900	1.0436	-1.7323
2.8798	1.0696	1.0540	-1.4623	1.0671	-0.2295	1.0488	-1.9450
3.1901	1.0777	1.0603	-1.6134	1.0749	-0.2617	1.0544	-2.1629
3.6108	1.0887	1.0691	-1.7995	1.0854	-0.3002	1.0621	-2.4397
4.3554	1.1081	1.0851	-2.0766	1.1046	-0.3157	1.0761	-2.8845
4.9693	1.1241	1.0987	-2.2630	1.1209	-0.2860	1.0880	-3.2141
5.5967	1.1403	1.1132	-2.3782	1.1377	-0.2268	1.1003	-3.5101
6.2586	1.1574	1.1289	-2.4654	1.1557	-0.1475	1.1134	-3.7999
7.0032	1.1764	1.1470	-2.5017	1.1762	-0.0150	1.1284	-4.0807
9.3406	1.2345	1.2072	-2.2100	1.2413	0.5476	1.1762	-4.7254
11.2641	1.2800	1.2594	-1.6131	1.2933	1.0394	1.2150	-5.0786
13.1602	1.3220	1.3110	-0.8324	1.3409	1.4292	1.2516	-5.3280
15.3665	1.3666	1.3681	0.1122	1.3886	1.6107	1.2903	-5.5846
17.4831	1.4041	1.4160	0.8475	1.4247	1.4704	1.3222	-5.8362
19.4068	1.4330	1.4507	1.2366	1.4484	1.0772	1.3461	-6.0611
21.3580	1.4565	1.4761	1.3464	1.4641	0.5247	1.3655	-6.2506
23.4885	1.4747	1.4920	1.1743	1.4730	-0.1150	1.3810	-6.3558
25.6810	1.4844	1.4968	0.8371	1.4749	-0.6395	1.3916	-6.2548
27.7700	1.4841	1.4930	0.5987	1.4716	-0.8405	1.3974	-5.8449
29.9350	1.4732	1.4826	0.6397	1.4648	-0.5668	1.3996	-4.9940
32.2998	1.4478	1.4667	1.3065	1.4549	0.4928	1.3989	-3.3789

Table 5.4.16 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Argon at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure MPa	Observed γ/γ^0	Calculated γ/γ^0	Percent Deviation from Observed	Calculated γ/γ^0	Percent Deviation from Observed	Calculated γ/γ^0	Percent Deviation from Observed
1.1855	1.0199	1.0176	-0.2231	1.0216	0.1638	1.0156	-0.4221
1.5234	1.0272	1.0228	-0.4293	1.0279	0.0678	1.0202	-0.6819
2.2473	1.0426	1.0341	-0.8164	1.0416	-0.0995	1.0301	-1.1971
2.7989	1.0543	1.0429	-1.0840	1.0521	-0.2071	1.0379	-1.5595
3.4609	1.0683	1.0538	-1.3542	1.0651	-0.3040	1.0473	-1.9671
4.1296	1.0823	1.0651	-1.5865	1.0783	-0.3735	1.0570	-2.3418
4.8328	1.0969	1.0773	-1.7897	1.0923	-0.4219	1.0673	-2.6964
5.6257	1.1133	1.0913	-1.9760	1.1083	-0.4504	1.0791	-3.0675
6.3077	1.1271	1.1036	-2.0837	1.1222	-0.4354	1.0895	-3.3397
6.7283	1.1356	1.1114	-2.1322	1.1308	-0.4233	1.0958	-3.5015
8.9552	1.1792	1.1537	-2.1640	1.1763	-0.2481	1.1297	-4.1958
9.8446	1.1960	1.1710	-2.0865	1.1942	-0.1489	1.1433	-4.4075
11.0859	1.2187	1.1956	-1.8970	1.2188	0.0047	1.1619	-4.6595
12.4993	1.2434	1.2234	-1.6046	1.2456	0.1756	1.1825	-4.8940
13.8574	1.2658	1.2499	-1.2598	1.2699	0.3217	1.2017	-5.0615
16.3809	1.3039	1.2964	-0.5729	1.3101	0.4751	1.2348	-5.3013
18.2218	1.3282	1.3269	-0.0978	1.3348	0.4967	1.2564	-5.4079
19.9595	1.3481	1.3521	0.2932	1.3542	0.4547	1.2745	-5.4587
22.0348	1.3678	1.3764	0.6270	1.3722	0.3213	1.2933	-5.4449
24.3307	1.3838	1.3959	0.8768	1.3862	0.1726	1.3105	-5.3006
26.2129	1.3919	1.4061	1.0168	1.3937	0.1292	1.3218	-5.0347
28.5365	1.3953	1.4120	1.1945	1.3986	0.2388	1.3327	-4.4862
30.2946	1.3926	1.4125	1.4299	1.3997	0.5094	1.3390	-3.8509
32.4113	1.3829	1.4093	1.9085	1.3990	1.1663	1.3445	-2.7778

Table 5.4.17 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Nitrogen 273.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure MPa	Observed γ/γ^0	Calculated γ/γ^0	Percent Deviation from Observed	Calculated γ/γ^0	Percent Deviation from Observed	Calculated γ/γ^0	Percent Deviation from Observed
1.3572	1.0233	1.0165	-0.6639	1.0216	-0.1673	1.0193	-0.3864
1.7709	1.0309	1.0217	-0.8887	1.0283	-0.2519	1.0254	-0.5354
2.1569	1.0380	1.0267	-1.0913	1.0346	-0.3286	1.0311	-0.6658
2.5498	1.0451	1.0318	-1.2706	1.0411	-0.3868	1.0369	-0.7838
2.8394	1.0503	1.0356	-1.3961	1.0458	-0.4265	1.0412	-0.8655
3.2673	1.0579	1.0413	-1.5680	1.0528	-0.4799	1.0476	-0.9766
3.5362	1.0626	1.0449	-1.6669	1.0572	-0.5049	1.0516	-1.0377
4.8945	1.0858	1.0636	-2.0404	1.0795	-0.5796	1.0719	-1.2763
6.3424	1.1095	1.0842	-2.2847	1.1028	-0.6062	1.0936	-1.4305
8.8245	1.1472	1.1199	-2.3796	1.1401	-0.6173	1.1297	-1.5213
10.6447	1.1725	1.1457	-2.2879	1.1643	-0.7006	1.1546	-1.5272
12.5546	1.1967	1.1709	-2.1564	1.1861	-0.8879	1.1787	-1.5053
14.5815	1.2197	1.1946	-2.0577	1.2047	-1.2299	1.2017	-1.4744
16.6086	1.2397	1.2141	-2.0646	1.2190	-1.6695	1.2215	-1.4694
18.1323	1.2528	1.2256	-2.1678	1.2270	-2.0565	1.2345	-1.4612
20.0973	1.2669	1.2366	-2.3956	1.2345	-2.5599	1.2485	-1.4517
22.2415	1.2786	1.2432	-2.7663	1.2395	-3.0599	1.2607	-1.4029
24.1927	1.2859	1.2456	-3.1336	1.2420	-3.4165	1.2692	-1.2991
26.2336	1.2899	1.2449	-3.4894	1.2428	-3.6483	1.2756	-1.1118
28.5778	1.2897	1.2410	-3.7778	1.2425	-3.6596	1.2801	-0.7454
30.5358	1.2855	1.2361	-3.8445	1.2414	-3.4324	1.2818	-0.2899
31.8113	1.2806	1.2323	-3.7747	1.2404	-3.1370	1.2821	0.1137

Table 5.4.18 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	γ/γ^0	γ/γ^0	Deviation	γ/γ^0	Deviation	γ/γ^0	Deviation
			!from !Observed		!from !Observed		!from !Observed
1.1373	1.0276	1.0115	-1.5702	1.0147	-1.2590	1.0132	-1.4040
1.5302	1.0345	1.0155	-1.8349	1.0197	-1.4271	1.0178	-1.6173
2.0128	1.0427	1.0206	-2.1221	1.0260	-1.5977	1.0234	-1.8491
2.6326	1.0529	1.0271	-2.4477	1.0341	-1.7857	1.0307	-2.1100
3.1635	1.0613	1.0328	-2.6839	1.0410	-1.9157	1.0370	-2.2926
3.5772	1.0677	1.0373	-2.8500	1.0463	-2.0023	1.0419	-2.4196
3.9564	1.0734	1.0414	-2.9850	1.0512	-2.0674	1.0464	-2.5198
4.5080	1.0814	1.0474	-3.1449	1.0583	-2.1394	1.0529	-2.6377
4.9975	1.0883	1.0528	-3.2632	1.0645	-2.1905	1.0587	-2.7239
6.2316	1.1046	1.0666	-3.4433	1.0798	-2.2480	1.0731	-2.8541
7.0801	1.1150	1.0761	-3.4906	1.0900	-2.2406	1.0828	-2.8859
8.1282	1.1270	1.0877	-3.4830	1.1023	-2.1954	1.0947	-2.8623
8.9279	1.1356	1.0966	-3.4319	1.1112	-2.1463	1.1036	-2.8169
10.1276	1.1474	1.1097	-3.2877	1.1240	-2.0398	1.1165	-2.6928
11.2790	1.1577	1.1220	-3.0877	1.1353	-1.9327	1.1285	-2.5216
12.2236	1.1655	1.1316	-2.9092	1.1440	-1.8455	1.1379	-2.3655
13.3681	1.1740	1.1428	-2.6614	1.1537	-1.7274	1.1489	-2.1383
14.6919	1.1828	1.1548	-2.3658	1.1637	-1.6187	1.1608	-1.8574
15.8226	1.1895	1.1643	-2.1171	1.1713	-1.5312	1.1704	-1.6017
17.0775	1.1961	1.1738	-1.8662	1.1787	-1.4587	1.1803	-1.3191
18.8287	1.2038	1.1852	-1.5467	1.1874	-1.3654	1.1930	-0.8981
20.3249	1.2093	1.1931	-1.3402	1.1933	-1.3241	1.2027	-0.5478
21.7797	1.2137	1.1992	-1.1908	1.1980	-1.2940	1.2111	-0.2152
23.1862	1.2173	1.2037	-1.1186	1.2016	-1.2910	1.2182	0.0741
24.1583	1.2193	1.2060	-1.0915	1.2036	-1.2845	1.2228	0.2830
25.2615	1.2213	1.2079	-1.0954	1.2056	-1.2878	1.2274	0.5021
26.4404	1.2232	1.2092	-1.1405	1.2072	-1.3121	1.2318	0.7010
27.8124	1.2249	1.2099	-1.2249	1.2085	-1.3351	1.2363	0.9281
29.1637	1.2263	1.2097	-1.3574	1.2095	-1.3667	1.2399	1.1128
30.5289	1.2276	1.2088	-1.5320	1.2101	-1.4217	1.2431	1.2606
31.9285	1.2287	1.2072	-1.7464	1.2104	-1.4897	1.2456	1.3742

Table 5.4.19 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.0003	0.9590	0.9725	1.4120	0.9650	0.6207	0.9594	0.0419
1.1933	0.9500	0.9669	1.7839	0.9579	0.8278	0.9510	0.1024
1.4071	0.9399	0.9606	2.2056	0.9498	1.0537	0.9413	0.1465
1.5932	0.9309	0.9550	2.5923	0.9427	1.2662	0.9326	0.1823
1.8277	0.9192	0.9478	3.1140	0.9336	1.5663	0.9213	0.2284
2.0483	0.9079	0.9409	3.6330	0.9248	1.8584	0.9102	0.2487
2.2482	0.8971	0.9345	4.1637	0.9166	2.1749	0.8996	0.2820
2.4758	0.8844	0.9270	4.8114	0.9071	2.5716	0.8871	0.3069
2.6550	0.8740	0.9209	5.3670	0.8995	2.9177	0.8767	0.3090
2.8549	0.8619	0.9140	6.0450	0.8908	3.3476	0.8646	0.3104

Table 5.4.20 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

Pressure MPa	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation
			!from !Observed		!from !Observed		!from !Observed
1.0193	0.9713	0.9775	0.6405	0.9733	0.2093	0.9700	-0.1299
1.1296	0.9678	0.9750	0.7469	0.9704	0.2690	0.9667	-0.1183
1.4605	0.9573	0.9673	1.0480	0.9614	0.4285	0.9563	-0.1043
1.7984	0.9463	0.9594	1.3803	0.9522	0.6198	0.9454	-0.0913
2.1776	0.9343	0.9501	1.6917	0.9417	0.7880	0.9328	-0.1619
2.5361	0.9223	0.9411	2.0342	0.9316	1.0127	0.9205	-0.1930
2.8326	0.9119	0.9335	2.3642	0.9233	1.2472	0.9099	-0.2248
3.1980	0.8987	0.9238	2.7929	0.9129	1.5776	0.8963	-0.2623
3.5496	0.8852	0.9143	3.2834	0.9029	2.0033	0.8828	-0.2740
3.9633	0.8683	0.9026	3.9451	0.8912	2.6387	0.8659	-0.2763
4.2874	0.8543	0.8931	4.5445	0.8822	3.2688	0.8519	-0.2809
4.5907	0.8404	0.8839	5.1795	0.8739	3.9894	0.8382	-0.2647

Table 5.4.21 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Argon at 273.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.0803	1.0005	0.9989	-0.1574	1.0019	0.1375	0.9984	-0.2143
1.4733	1.0008	0.9986	-0.2195	1.0027	0.1914	0.9980	-0.2813
1.8250	1.0011	0.9984	-0.2734	1.0035	0.2383	0.9977	-0.3377
2.2386	1.0017	0.9982	-0.3479	1.0046	0.2914	0.9975	-0.4193
2.5902	1.0022	0.9981	-0.4091	1.0056	0.3375	0.9975	-0.4690
2.8798	1.0029	0.9981	-0.4786	1.0065	0.3573	0.9975	-0.5343
3.1901	1.0035	0.9981	-0.5381	1.0075	0.3976	0.9977	-0.5823
3.6108	1.0046	0.9982	-0.6360	1.0089	0.4286	0.9979	-0.6642
4.3554	1.0071	0.9987	-0.8383	1.0118	0.4662	0.9988	-0.8260
4.9693	1.0094	0.9993	-1.0035	1.0146	0.5108	0.9999	-0.9438
5.5967	1.0120	1.0001	-1.1725	1.0176	0.5575	1.0014	-1.0484
6.2586	1.0154	1.0013	-1.3878	1.0212	0.5721	1.0034	-1.1842
7.0032	1.0196	1.0030	-1.6242	1.0257	0.5949	1.0061	-1.3249
9.3406	1.0358	1.0113	-2.3640	1.0430	0.6954	1.0183	-1.6907
11.2641	1.0525	1.0218	-2.9151	1.0612	0.8252	1.0325	-1.9028
13.1602	1.0718	1.0360	-3.3427	1.0826	1.0040	1.0500	-2.0298
15.3665	1.0976	1.0577	-3.6340	1.1118	1.2930	1.0749	-2.0716
17.4831	1.1258	1.0840	-3.7164	1.1437	1.5865	1.1026	-2.0634
19.4068	1.1539	1.1125	-3.5861	1.1755	1.8719	1.1307	-2.0132
21.3580	1.1851	1.1453	-3.3585	1.2099	2.0921	1.1615	-1.9897
23.4885	1.2217	1.1851	-2.9932	1.2492	2.2526	1.1974	-1.9881
25.6810	1.2620	1.2296	-2.5679	1.2911	2.3030	1.2361	-2.0523
27.7700	1.3026	1.2743	-2.1732	1.3315	2.2201	1.2743	-2.1731
29.9350	1.3471	1.3221	-1.8543	1.3737	1.9711	1.3146	-2.4138
32.2998	1.3982	1.3755	-1.6201	1.4195	1.5205	1.3592	-2.7882

Table 5.4.22 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Argon at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation
			from		from		from
			Observed		Observed		Observed
1.1855	1.0012	1.0001	-0.1123	1.0033	0.2119	0.9998	-0.1398
1.5234	1.0018	1.0002	-0.1613	1.0044	0.2589	0.9999	-0.1900
2.2473	1.0033	1.0005	-0.2755	1.0068	0.3532	1.0003	-0.2952
2.7989	1.0045	1.0009	-0.3589	1.0089	0.4378	1.0009	-0.3567
3.4609	1.0069	1.0016	-0.5246	1.0116	0.4670	1.0019	-0.4962
4.1296	1.0091	1.0025	-0.6547	1.0145	0.5384	1.0033	-0.5766
4.8328	1.0121	1.0036	-0.8414	1.0179	0.5701	1.0049	-0.7068
5.6257	1.0156	1.0051	-1.0361	1.0221	0.6381	1.0074	-0.8051
6.3077	1.0190	1.0067	-1.2067	1.0260	0.6822	1.0099	-0.8960
6.7283	1.0214	1.0078	-1.3284	1.0284	0.6844	1.0116	-0.9629
8.9552	1.0349	1.0154	-1.8846	1.0436	0.8453	1.0228	-1.1719
9.8446	1.0409	1.0193	-2.0788	1.0506	0.9320	1.0283	-1.2091
11.0859	1.0507	1.0256	-2.3851	1.0611	0.9891	1.0371	-1.2984
12.4993	1.0626	1.0341	-2.6841	1.0744	1.1100	1.0484	-1.3360
13.8574	1.0752	1.0437	-2.9308	1.0883	1.2223	1.0606	-1.3550
16.3809	1.1011	1.0653	-3.2515	1.1173	1.4705	1.0867	-1.3064
18.2218	1.1221	1.0843	-3.3664	1.1406	1.6503	1.1081	-1.2480
19.9595	1.1432	1.1047	-3.3719	1.1643	1.8447	1.1301	-1.1500
22.0348	1.1705	1.1319	-3.2942	1.1942	2.0208	1.1580	-1.0706
24.3307	1.2027	1.1655	-3.0968	1.2290	2.1863	1.1908	-0.9888
26.2129	1.2309	1.1952	-2.8977	1.2586	2.2504	1.2190	-0.9689
28.5365	1.2673	1.2343	-2.6009	1.2959	2.2584	1.2548	-0.9836
30.2946	1.2961	1.2653	-2.3793	1.3247	2.2053	1.2826	-1.0446
32.4113	1.3321	1.3038	-2.1219	1.3596	2.0621	1.3166	-1.1639

Table 5.4.23 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Nitrogen at 273.15 K.

	!	!	van der Waals	!	Hybrid Virial	!	Benedict-Webb-Rubin	!
	!	!	!	!	!	!	!	!
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent	
MPa	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation	
			from		from		from	
			Observed		Observed		Observed	
1.3572	1.0053	0.9984	-0.6835	1.0050	-0.0276	1.0038	-0.1443	
1.7709	1.0067	0.9982	-0.8456	1.0070	0.0251	1.0054	-0.1325	
2.1569	1.0084	0.9980	-1.0284	1.0088	0.0418	1.0070	-0.1426	
2.5498	1.0102	0.9980	-1.2120	1.0109	0.0713	1.0087	-0.1488	
2.8394	1.0115	0.9979	-1.3429	1.0125	0.0993	1.0101	-0.1366	
3.2673	1.0138	0.9981	-1.5515	1.0151	0.1290	1.0123	-0.1502	
3.5362	1.0154	0.9982	-1.6919	1.0168	0.1364	1.0138	-0.1537	
4.8945	1.0243	0.9998	-2.3946	1.0266	0.2254	1.0224	-0.1855	
6.3424	1.0359	1.0030	-3.1726	1.0393	0.3238	1.0337	-0.2128	
8.8245	1.0607	1.0130	-4.4943	1.0663	0.5245	1.0577	-0.2873	
10.6447	1.0825	1.0243	-5.3770	1.0901	0.7029	1.0788	-0.3424	
12.5546	1.1083	1.0402	-6.1422	1.1186	0.9292	1.1038	-0.4074	
14.5815	1.1383	1.0616	-6.7423	1.1521	1.2155	1.1330	-0.4634	
16.6086	1.1711	1.0875	-7.1423	1.1885	1.4846	1.1649	-0.5277	
18.1323	1.1970	1.1098	-7.2886	1.2173	1.6949	1.1902	-0.5694	
20.0973	1.2325	1.1418	-7.3612	1.2559	1.8971	1.2243	-0.6650	
22.2415	1.2724	1.1804	-7.2306	1.2992	2.1067	1.2632	-0.7254	
24.1927	1.3102	1.2182	-7.0242	1.3392	2.2157	1.2996	-0.8088	
26.2336	1.3505	1.2597	-6.7201	1.3815	2.2923	1.3387	-0.8737	
28.5778	1.3974	1.3096	-6.2844	1.4300	2.3296	1.3845	-0.9264	
30.5358	1.4366	1.3523	-5.8714	1.4703	2.3438	1.4232	-0.9325	
31.8113	1.4622	1.3805	-5.5882	1.4963	2.3325	1.4486	-0.9283	

Table 5.4.24 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Percent	Calculated	Percent	Calculated	Percent
MPa	a/a^0	a/a^0	Deviation	a/a^0	Deviation	a/a^0	Deviation
			!from		!from		!from
			!Observed		!Observed		!Observed
1.1373	1.0076	1.0000	-0.7526	1.0054	-0.2207	1.0043	-0.3250
1.5302	1.0092	1.0002	-0.8956	1.0074	-0.1808	1.0061	-0.3106
2.0128	1.0115	1.0005	-1.0894	1.0101	-0.1338	1.0084	-0.3089
2.6326	1.0146	1.0010	-1.3392	1.0139	-0.0706	1.0115	-0.3007
3.1635	1.0176	1.0016	-1.5716	1.0173	-0.0328	1.0146	-0.2924
3.5772	1.0201	1.0022	-1.7549	1.0201	-0.0022	1.0171	-0.2969
3.9564	1.0225	1.0028	-1.9297	1.0227	0.0231	1.0196	-0.2862
4.5080	1.0263	1.0039	-2.1831	1.0268	0.0526	1.0233	-0.2949
4.9975	1.0299	1.0050	-2.4171	1.0307	0.0811	1.0268	-0.3035
6.2316	1.0395	1.0084	-2.9875	1.0412	0.1630	1.0364	-0.3005
7.0801	1.0468	1.0114	-3.3836	1.0492	0.2261	1.0437	-0.3001
8.1282	1.0566	1.0157	-3.8709	1.0597	0.2941	1.0534	-0.3012
8.9279	1.0646	1.0196	-4.2297	1.0683	0.3501	1.0614	-0.3030
10.1276	1.0773	1.0262	-4.7399	1.0820	0.4401	1.0741	-0.3000
11.2790	1.0905	1.0337	-5.2074	1.0963	0.5321	1.0871	-0.3114
12.2236	1.1018	1.0406	-5.5507	1.1086	0.6176	1.0983	-0.3190
13.3681	1.1163	1.0500	-5.9412	1.1242	0.7080	1.1126	-0.3349
14.6919	1.1339	1.0621	-6.3294	1.1433	0.8289	1.1298	-0.3583
15.8226	1.1495	1.0735	-6.6135	1.1603	0.9365	1.1452	-0.3738
17.0775	1.1673	1.0874	-6.8453	1.1798	1.0709	1.1629	-0.3788
18.8287	1.1935	1.1087	-7.1029	1.2081	1.2235	1.1885	-0.4169
20.3249	1.2165	1.1287	-7.2192	1.2331	1.3613	1.2111	-0.4447
21.7797	1.2394	1.1494	-7.2612	1.2578	1.4884	1.2337	-0.4603
23.1862	1.2616	1.1707	-7.2068	1.2823	1.6443	1.2560	-0.4440
24.1583	1.2780	1.1860	-7.1976	1.2994	1.6735	1.2717	-0.4962
25.2615	1.2959	1.2039	-7.0970	1.3189	1.7710	1.2896	-0.4897
26.4404	1.3155	1.2236	-6.9825	1.3398	1.8472	1.3089	-0.4984
27.8124	1.3382	1.2472	-6.7982	1.3643	1.9515	1.3318	-0.4789
29.1637	1.3606	1.2712	-6.5699	1.3885	2.0532	1.3545	-0.4482
30.5289	1.3833	1.2959	-6.3183	1.4129	2.1427	1.3776	-0.4106
31.9285	1.4061	1.3217	-6.0059	1.4380	2.2697	1.4015	-0.3279

Table 5.4.25 Comparison of Observed Values of the Property $\rho \partial Z / \partial \rho$ with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

	!	!	van der Waals	!	Hybrid Virial	!	Benedict-Webb-Rubin
	!	!	!	!	!	!	!
Pressure	Observed	Calculated	Deviation	Calculated	Deviation	Calculated	Deviation
MPa	$\rho \partial Z / \partial \rho$	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from
	!	!	Observed	!	Observed	!	Observed
1.0003	-0.0514	-0.0396	0.0118	-0.0583	-0.0069	-0.0705	-0.0191
1.1933	-0.0688	-0.0475	0.0213	-0.0701	-0.0013	-0.0847	-0.0159
1.4071	-0.0876	-0.0565	0.0311	-0.0832	0.0044	-0.1006	-0.0130
1.5932	-0.1037	-0.0643	0.0394	-0.0948	0.0089	-0.1147	-0.0110
1.8277	-0.1236	-0.0743	0.0493	-0.1096	0.0140	-0.1329	-0.0093
2.0483	-0.1420	-0.0839	0.0581	-0.1237	0.0183	-0.1502	-0.0082
2.2482	-0.1585	-0.0928	0.0657	-0.1368	0.0217	-0.1664	-0.0079
2.4758	-0.1769	-0.1031	0.0738	-0.1519	0.0250	-0.1851	-0.0082
2.6550	-0.1913	-0.1113	0.0800	-0.1640	0.0273	-0.2004	-0.0091
2.8549	-0.2073	-0.1206	0.0867	-0.1777	0.0296	-0.2178	-0.0105

Table 5.4.26 Comparison of Observed Values of the Property $\rho\partial Z/\partial\rho$ with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Deviation	Calculated	Deviation	Calculated	Deviation
MPa	$\rho\partial Z/\partial\rho$	$\rho\partial Z/\partial\rho$	from	$\rho\partial Z/\partial\rho$	from	$\rho\partial Z/\partial\rho$	from
			Observed		Observed		Observed
1.0193	-0.0467	-0.0325	0.0142	-0.0453	0.0014	-0.0526	-0.0059
1.1296	-0.0532	-0.0361	0.0171	-0.0503	0.0029	-0.0584	-0.0052
1.4605	-0.0725	-0.0470	0.0255	-0.0653	0.0072	-0.0760	-0.0035
1.7984	-0.0922	-0.0584	0.0338	-0.0808	0.0114	-0.0941	-0.0019
2.1776	-0.1142	-0.0713	0.0429	-0.0983	0.0159	-0.1148	-0.0006
2.5361	-0.1351	-0.0837	0.0514	-0.1149	0.0202	-0.1346	0.0005
2.8326	-0.1525	-0.0942	0.0583	-0.1287	0.0238	-0.1512	0.0013
3.1980	-0.1741	-0.1075	0.0666	-0.1459	0.0282	-0.1721	0.0020
3.5496	-0.1951	-0.1204	0.0747	-0.1624	0.0327	-0.1925	0.0026
3.9633	-0.2202	-0.1361	0.0841	-0.1818	0.0384	-0.2169	0.0033
4.2874	-0.2402	-0.1486	0.0916	-0.1968	0.0434	-0.2364	0.0038
4.5907	-0.2591	-0.1606	0.0985	-0.2106	0.0485	-0.2549	0.0042

Table 5.4.27 Comparison of Observed Values of the Property $\rho \partial Z / \partial \rho$ with those Derived from Equations of State. For Argon at 273.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Deviation	Calculated	Deviation	Calculated	Deviation
MPa	$\rho \partial Z / \partial \rho$	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from
			Observed		Observed		Observed
1.0803	-0.0152	-0.0104	0.0048	-0.0098	0.0054	-0.0101	0.0051
1.4733	-0.0189	-0.0141	0.0048	-0.0132	0.0057	-0.0135	0.0054
1.8250	-0.0220	-0.0173	0.0047	-0.0162	0.0058	-0.0164	0.0056
2.2386	-0.0255	-0.0211	0.0044	-0.0195	0.0060	-0.0197	0.0058
2.5902	-0.0284	-0.0243	0.0041	-0.0223	0.0061	-0.0223	0.0061
2.8798	-0.0307	-0.0268	0.0039	-0.0244	0.0063	-0.0245	0.0062
3.1901	-0.0330	-0.0294	0.0036	-0.0266	0.0064	-0.0267	0.0063
3.6108	-0.0360	-0.0329	0.0031	-0.0296	0.0064	-0.0294	0.0066
4.3554	-0.0408	-0.0389	0.0019	-0.0344	0.0064	-0.0338	0.0070
4.9693	-0.0443	-0.0436	0.0007	-0.0379	0.0064	-0.0369	0.0074
5.5967	-0.0475	-0.0480	-0.0005	-0.0411	0.0064	-0.0397	0.0078
6.2586	-0.0504	-0.0524	-0.0020	-0.0440	0.0064	-0.0422	0.0082
7.0032	-0.0530	-0.0570	-0.0040	-0.0466	0.0064	-0.0443	0.0087
9.3406	-0.0567	-0.0677	-0.0110	-0.0498	0.0069	-0.0459	0.0108
11.2641	-0.0544	-0.0715	-0.0171	-0.0458	0.0086	-0.0415	0.0129
13.1602	-0.0472	-0.0699	-0.0227	-0.0358	0.0114	-0.0318	0.0154
15.3665	-0.0321	-0.0598	-0.0277	-0.0154	0.0167	-0.0136	0.0185
17.4831	-0.0106	-0.0407	-0.0301	0.0128	0.0234	0.0107	0.0213
19.4068	0.0154	-0.0144	-0.0298	0.0459	0.0305	0.0386	0.0232
21.3580	0.0482	0.0210	-0.0272	0.0859	0.0377	0.0719	0.0237
23.4885	0.0918	0.0698	-0.0220	0.1363	0.0445	0.1143	0.0225
25.6810	0.1457	0.1306	-0.0151	0.1945	0.0488	0.1634	0.0177
27.7700	0.2058	0.1974	-0.0084	0.2549	0.0491	0.2151	0.0093
29.9350	0.2777	0.2749	-0.0028	0.3217	0.0440	0.2732	-0.0045
32.2998	0.3677	0.3679	0.0002	0.3986	0.0309	0.3416	-0.0261

Table 5.4.28 Comparison of Observed Values of the Property $\rho \partial Z / \partial \rho$ with those Derived from Equations of State. For Argon at 298.15 K.

		van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
		Calculated	Deviation		Calculated	Deviation	Calculated	Deviation
Pressure	Observed	Calculated	Deviation		Calculated	Deviation	Calculated	Deviation
MPa	$\rho \partial Z / \partial \rho$	$\rho \partial Z / \partial \rho$	from		$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from
			Observed			Observed		Observed
1.1855	-0.0077	-0.0085	-0.0008		-0.0072	0.0005	-0.0077	0.0000
1.5234	-0.0108	-0.0108	0.0000		-0.0090	0.0018	-0.0097	0.0011
2.2473	-0.0171	-0.0157	0.0014		-0.0129	0.0042	-0.0137	0.0034
2.7989	-0.0214	-0.0192	0.0022		-0.0155	0.0059	-0.0164	0.0050
3.4609	-0.0261	-0.0232	0.0029		-0.0185	0.0076	-0.0194	0.0067
4.1296	-0.0304	-0.0271	0.0033		-0.0212	0.0092	-0.0219	0.0085
4.8328	-0.0343	-0.0310	0.0033		-0.0237	0.0106	-0.0241	0.0102
5.6257	-0.0380	-0.0349	0.0031		-0.0259	0.0121	-0.0261	0.0119
6.3077	-0.0405	-0.0381	0.0024		-0.0273	0.0132	-0.0272	0.0133
6.7283	-0.0419	-0.0399	0.0020		-0.0281	0.0138	-0.0277	0.0142
8.9552	-0.0454	-0.0470	-0.0016		-0.0289	0.0165	-0.0274	0.0180
9.8446	-0.0452	-0.0488	-0.0036		-0.0278	0.0174	-0.0258	0.0194
11.0859	-0.0433	-0.0498	-0.0065		-0.0249	0.0184	-0.0222	0.0211
12.4993	-0.0390	-0.0493	-0.0103		-0.0193	0.0197	-0.0160	0.0230
13.8574	-0.0326	-0.0466	-0.0140		-0.0117	0.0209	-0.0080	0.0246
16.3809	-0.0150	-0.0353	-0.0203		0.0088	0.0238	0.0121	0.0271
18.2218	0.0026	-0.0216	-0.0242		0.0289	0.0263	0.0309	0.0283
19.9595	0.0228	-0.0038	-0.0266		0.0516	0.0288	0.0519	0.0291
22.0348	0.0517	0.0237	-0.0280		0.0837	0.0320	0.0807	0.0290
24.3307	0.0896	0.0619	-0.0277		0.1249	0.0353	0.1172	0.0276
26.2129	0.1252	0.0994	-0.0258		0.1625	0.0373	0.1505	0.0253
28.5365	0.1750	0.1532	-0.0218		0.2135	0.0385	0.1954	0.0204
30.2946	0.2169	0.1986	-0.0183		0.2551	0.0382	0.2320	0.0151
32.4113	0.2722	0.2591	-0.0131		0.3078	0.0356	0.2790	0.0068

Table 5.4.29 Comparison of Observed Values of the Property $\rho \partial Z / \partial \rho$ with those Derived from Equations of State. For Nitrogen at 273.15 K.

	!	!	van der Waals	!	Hybrid Virial	!	Benedict-Webb-Rubin	
	!	!	!	!	!	!	!	
Pressure	Observed	Calculated	Deviation	Calculated	Deviation	Calculated	Deviation	
MPa	$\rho \partial Z / \partial \rho$	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from	$\rho \partial Z / \partial \rho$	from	
	!	!	Observed	!	Observed	!	Observed	
1.3572	-0.0054	-0.0095	-0.0041	-0.0053	0.0001	-0.0053	0.0001	
1.7709	-0.0071	-0.0121	-0.0050	-0.0065	0.0006	-0.0066	0.0005	
2.1569	-0.0084	-0.0145	-0.0061	-0.0074	0.0010	-0.0075	0.0009	
2.5498	-0.0095	-0.0167	-0.0072	-0.0081	0.0014	-0.0083	0.0012	
2.8394	-0.0102	-0.0183	-0.0081	-0.0085	0.0017	-0.0086	0.0016	
3.2673	-0.0109	-0.0205	-0.0096	-0.0088	0.0021	-0.0091	0.0018	
3.5362	-0.0113	-0.0219	-0.0106	-0.0090	0.0023	-0.0092	0.0021	
4.8945	-0.0114	-0.0275	-0.0161	-0.0078	0.0036	-0.0084	0.0030	
6.3424	-0.0086	-0.0314	-0.0228	-0.0031	0.0055	-0.0048	0.0038	
8.8245	0.0033	-0.0319	-0.0352	0.0134	0.0101	0.0082	0.0049	
10.6447	0.0177	-0.0266	-0.0443	0.0329	0.0152	0.0231	0.0054	
12.5546	0.0378	-0.0148	-0.0526	0.0600	0.0222	0.0436	0.0058	
14.5815	0.0648	0.0053	-0.0595	0.0962	0.0314	0.0704	0.0056	
16.6086	0.0974	0.0337	-0.0637	0.1395	0.0421	0.1027	0.0053	
18.1323	0.1256	0.0606	-0.0650	0.1765	0.0509	0.1302	0.0046	
20.0973	0.1667	0.1025	-0.0642	0.2291	0.0624	0.1699	0.0032	
22.2415	0.2174	0.1574	-0.0600	0.2921	0.0747	0.2184	0.0010	
24.1927	0.2688	0.2150	-0.0538	0.3536	0.0848	0.2671	-0.0017	
26.2336	0.3279	0.2824	-0.0455	0.4218	0.0939	0.3227	-0.0052	
28.5778	0.4024	0.3688	-0.0336	0.5039	0.1015	0.3920	-0.0104	
30.5358	0.4699	0.4470	-0.0229	0.5752	0.1053	0.4546	-0.0153	
31.8113	0.5165	0.5009	-0.0156	0.6227	0.1062	0.4975	-0.0190	

Table 5.4.30 Comparison of Observed Values of the Property $\rho\partial Z/\partial\rho$ with those Derived from Equations of State. For Nitrogen at 298.15 K.

	van der Waals			Hybrid Virial		Benedict-Webb-Rubin	
Pressure	Observed	Calculated	Deviation	Calculated	Deviation	Calculated	Deviation
MPa	$\rho\partial Z/\partial\rho$	$\rho\partial Z/\partial\rho$	from	$\rho\partial Z/\partial\rho$	from	$\rho\partial Z/\partial\rho$	from
			Observed		Observed		Observed
1.1373	-0.0029	-0.0055	-0.0026	-0.0017	0.0012	-0.0020	0.0009
1.5302	-0.0054	-0.0073	-0.0019	-0.0021	0.0033	-0.0024	0.0030
2.0128	-0.0080	-0.0093	-0.0013	-0.0022	0.0058	-0.0026	0.0054
2.6326	-0.0108	-0.0117	-0.0009	-0.0021	0.0087	-0.0027	0.0081
3.1635	-0.0125	-0.0135	-0.0010	-0.0017	0.0108	-0.0022	0.0103
3.5772	-0.0136	-0.0148	-0.0012	-0.0011	0.0125	-0.0018	0.0118
3.9564	-0.0142	-0.0158	-0.0016	-0.0004	0.0138	-0.0011	0.0131
4.5080	-0.0146	-0.0172	-0.0026	0.0009	0.0155	0.0000	0.0146
4.9975	-0.0146	-0.0181	-0.0035	0.0024	0.0170	0.0013	0.0159
6.2316	-0.0126	-0.0197	-0.0071	0.0073	0.0199	0.0057	0.0183
7.0801	-0.0097	-0.0200	-0.0103	0.0120	0.0217	0.0098	0.0195
8.1282	-0.0045	-0.0193	-0.0148	0.0189	0.0234	0.0158	0.0203
8.9279	0.0006	-0.0180	-0.0186	0.0252	0.0246	0.0211	0.0205
10.1276	0.0102	-0.0147	-0.0249	0.0361	0.0259	0.0305	0.0203
11.2790	0.0213	-0.0100	-0.0313	0.0487	0.0274	0.0407	0.0194
12.2236	0.0317	-0.0048	-0.0365	0.0602	0.0285	0.0501	0.0184
13.3681	0.0460	0.0029	-0.0431	0.0757	0.0297	0.0626	0.0166
14.6919	0.0645	0.0143	-0.0502	0.0960	0.0315	0.0787	0.0142
15.8226	0.0819	0.0258	-0.0561	0.1150	0.0331	0.0938	0.0119
17.0775	0.1029	0.0410	-0.0619	0.1381	0.0352	0.1118	0.0089
18.8287	0.1348	0.0660	-0.0688	0.1731	0.0383	0.1392	0.0044
20.3249	0.1642	0.0909	-0.0733	0.2058	0.0416	0.1647	0.0005
21.7797	0.1946	0.1183	-0.0763	0.2397	0.0451	0.1913	-0.0033
23.1862	0.2253	0.1480	-0.0773	0.2744	0.0491	0.2188	-0.0065
24.1583	0.2473	0.1701	-0.0772	0.2994	0.0521	0.2385	-0.0088
25.2615	0.2729	0.1968	-0.0761	0.3286	0.0557	0.2620	-0.0109
26.4404	0.3009	0.2271	-0.0738	0.3609	0.0600	0.2880	-0.0129
27.8124	0.3341	0.2647	-0.0694	0.3996	0.0655	0.3198	-0.0143
29.1637	0.3675	0.3042	-0.0633	0.4389	0.0714	0.3525	-0.0150
30.5289	0.4017	0.3464	-0.0553	0.4796	0.0779	0.3869	-0.0148
31.9285	0.4370	0.3917	-0.0453	0.5224	0.0854	0.4235	-0.0135

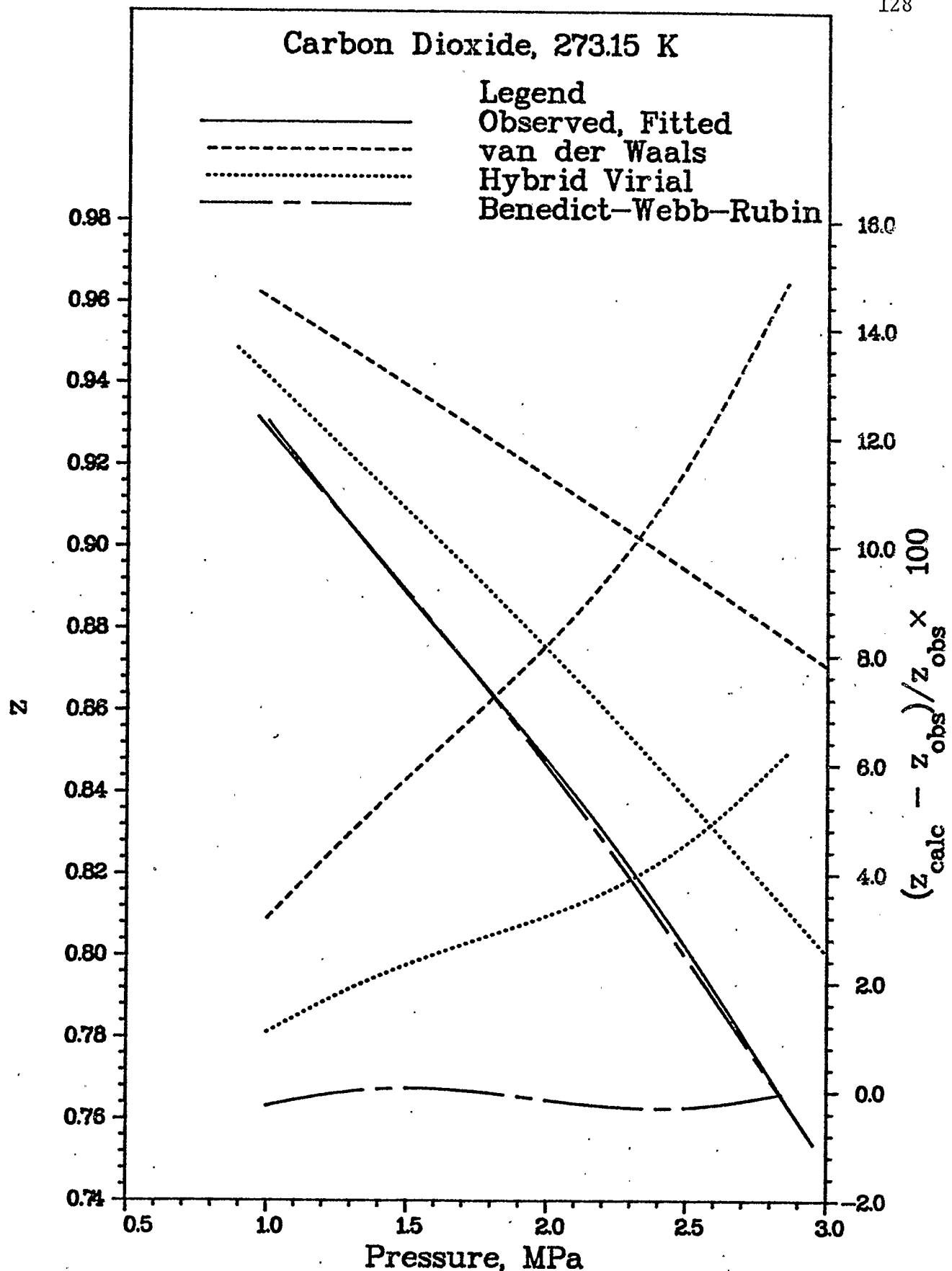


Fig. 5.4.1 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

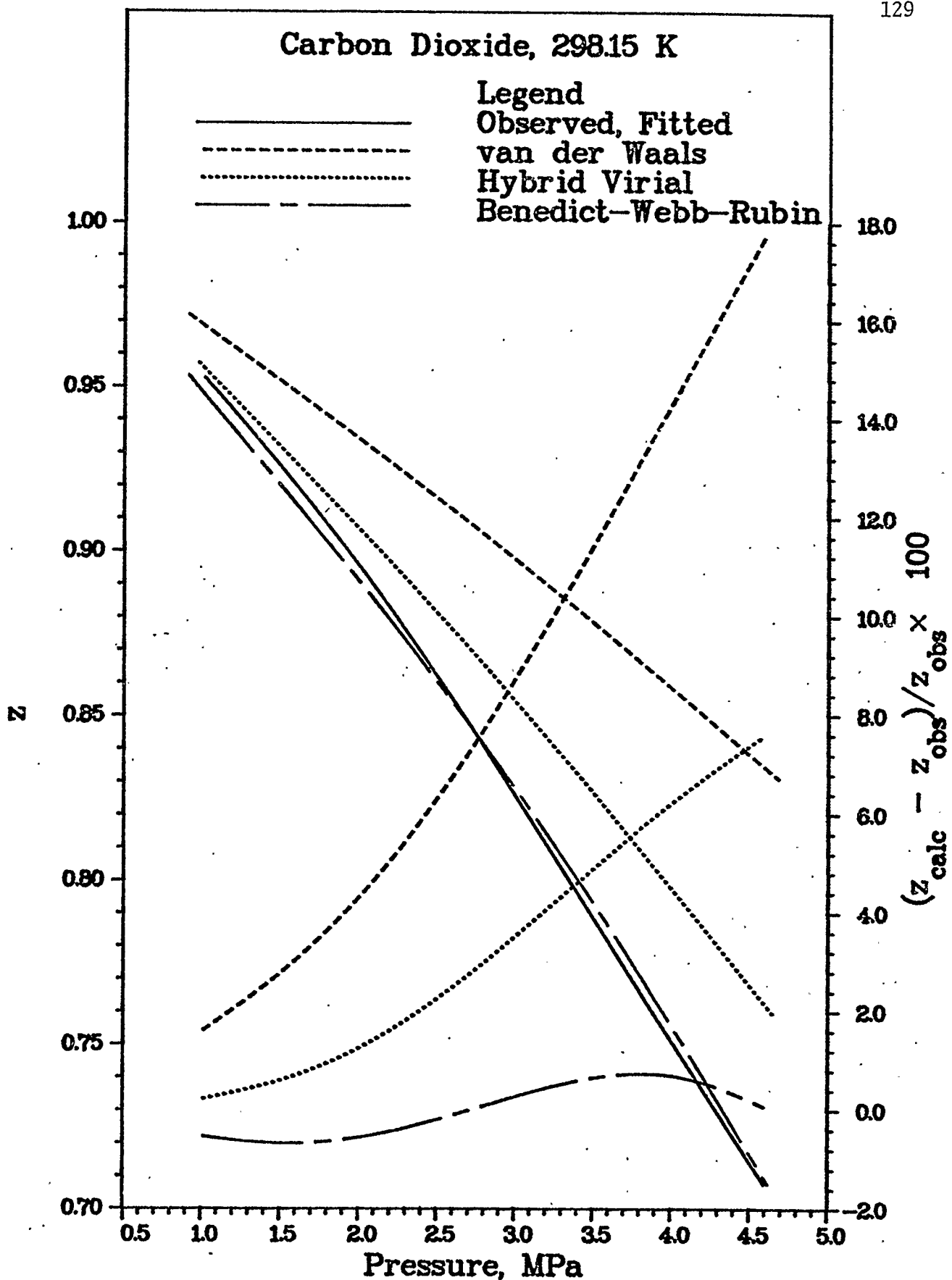


Fig. 5.4.2 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

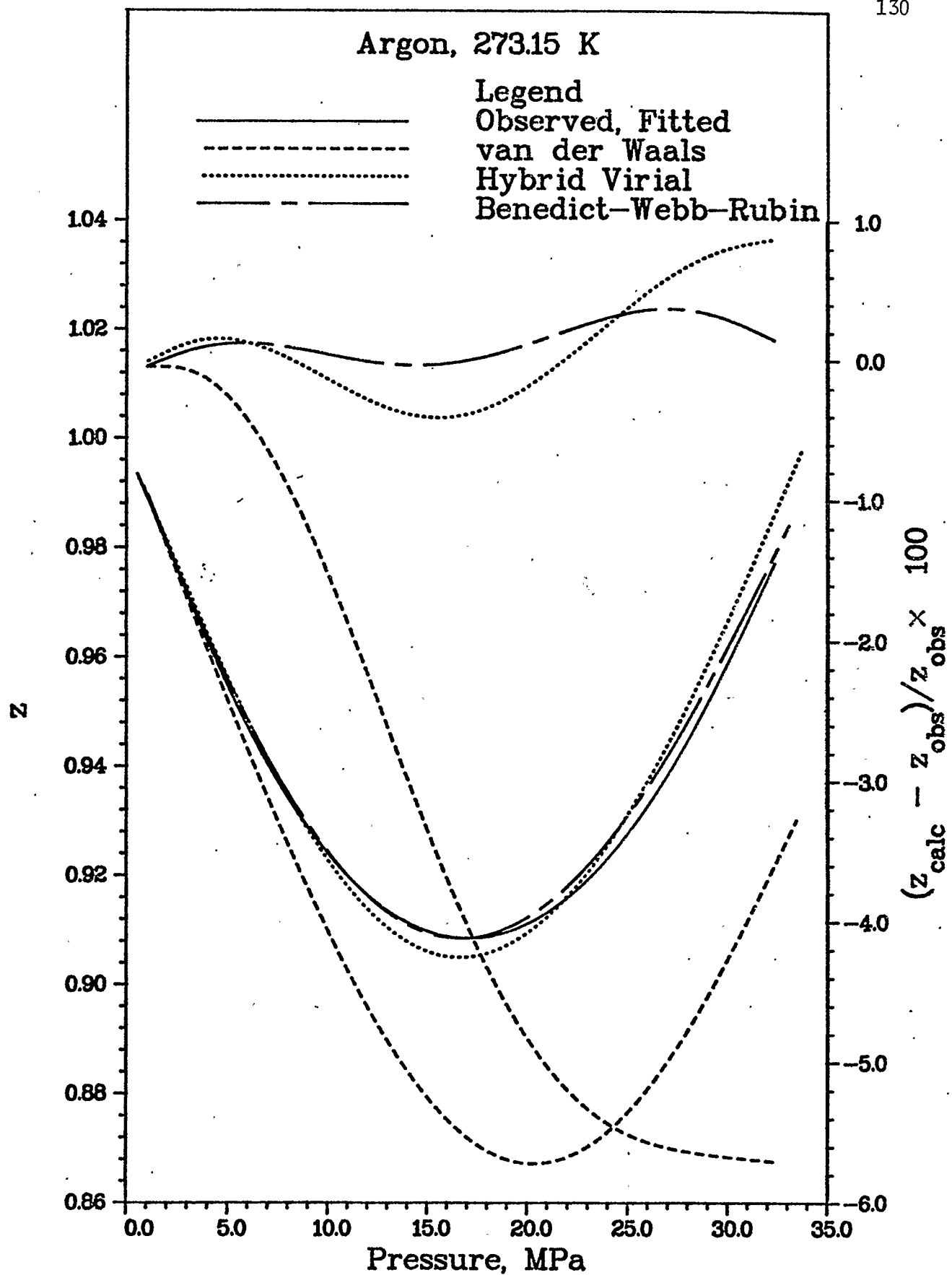


Fig. 5.4.3 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Argon at 273.15 K.

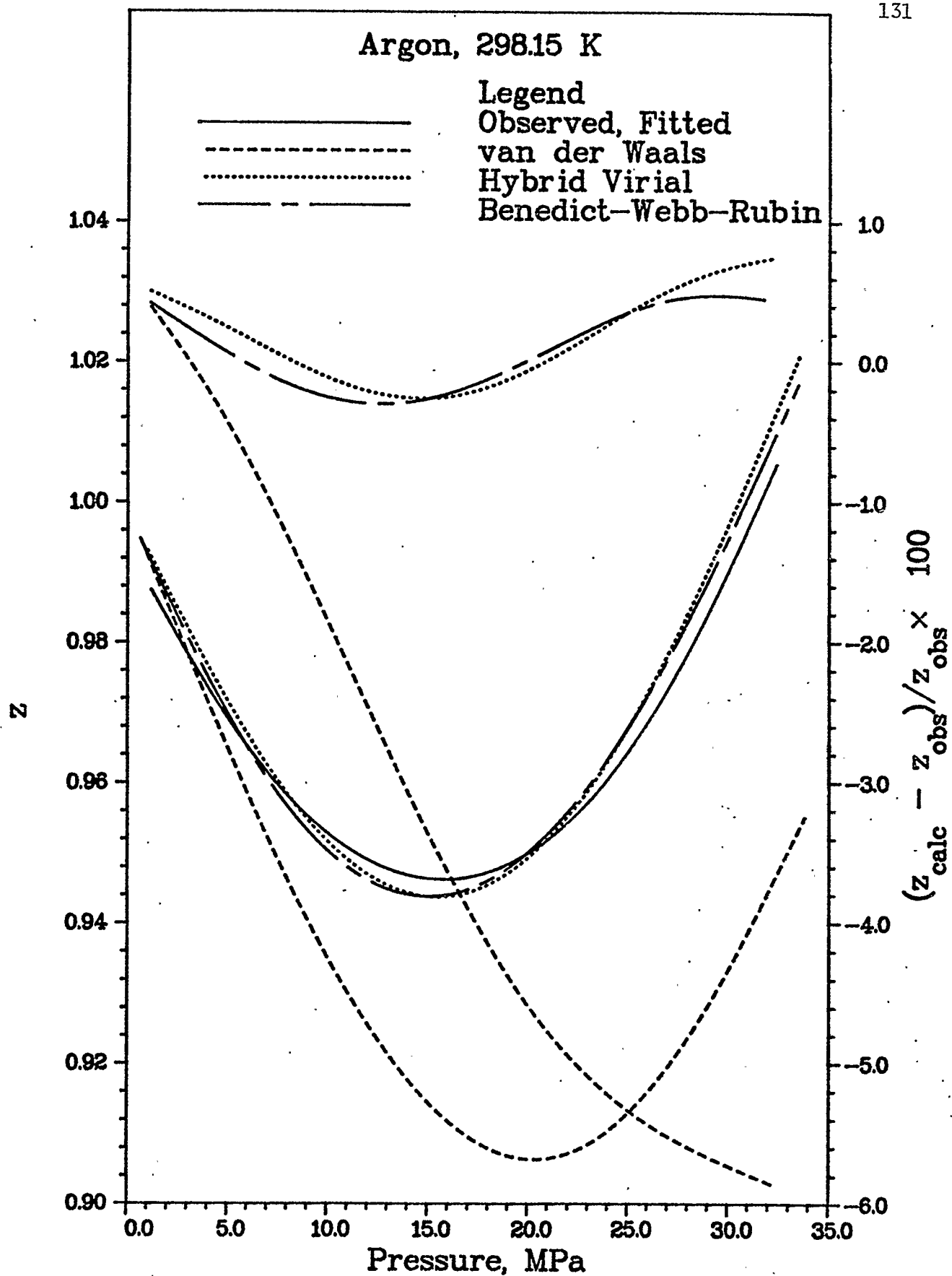


Fig. 5.4.4 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Argon at 298.15 K.

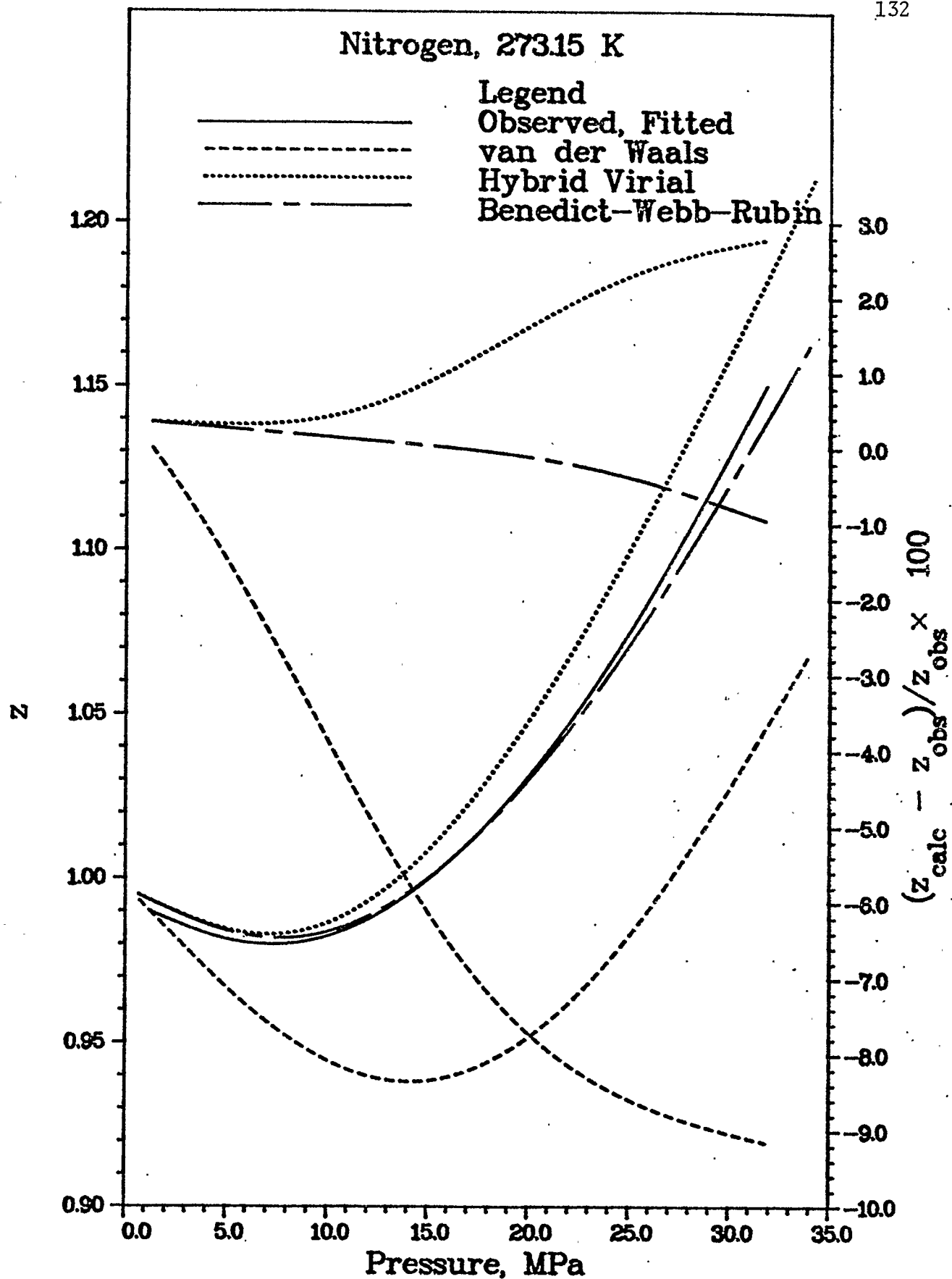


Fig. 5.4.5 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Nitrogen at 273.15 K.

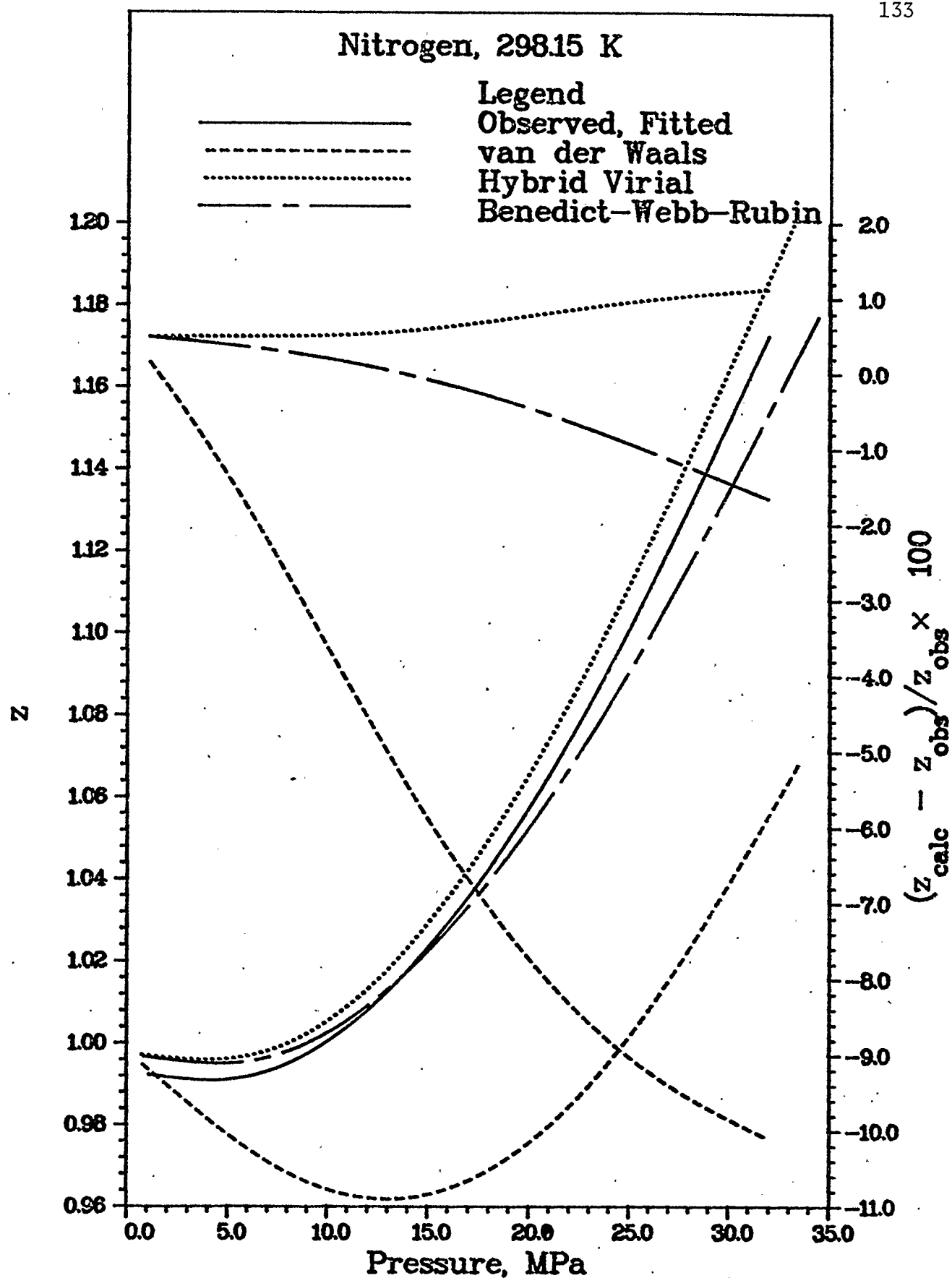


Fig. 5.4.6 Comparison of Observed Compressibility Factors (Z) with those Derived from Equations of State. For Nitrogen at 298.15 K.

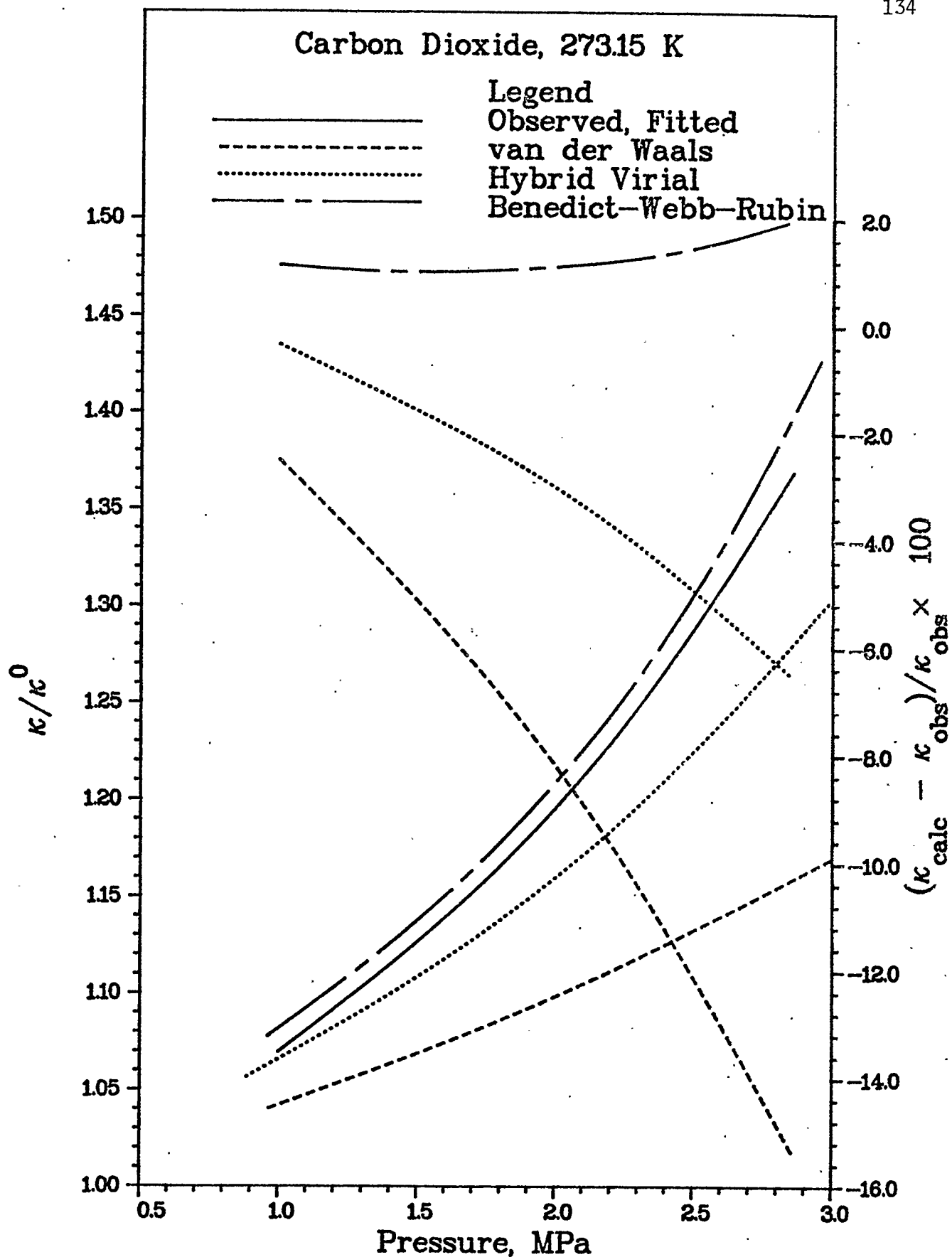


Fig. 5.4.7 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

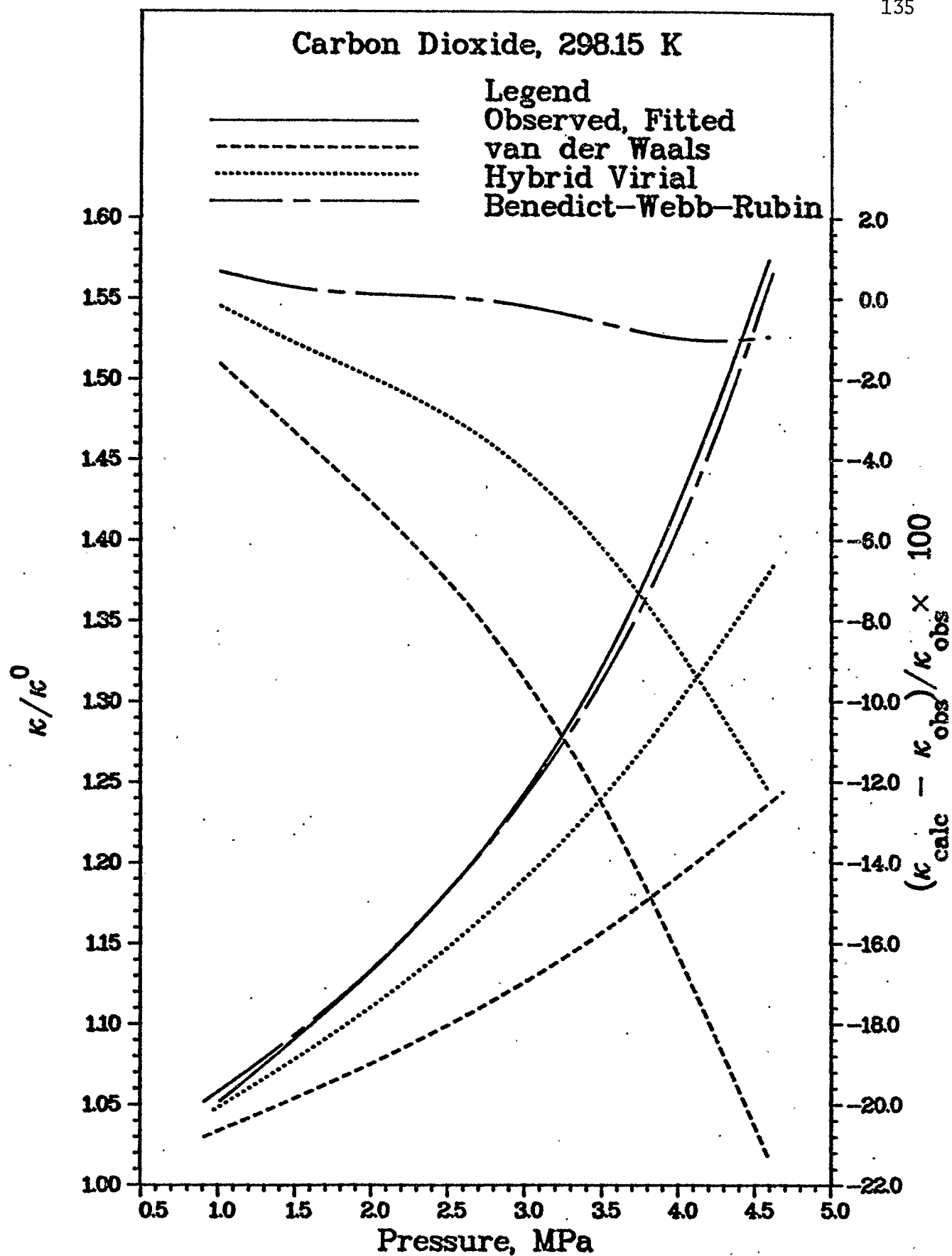


Fig. 5.4.8 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ_0) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

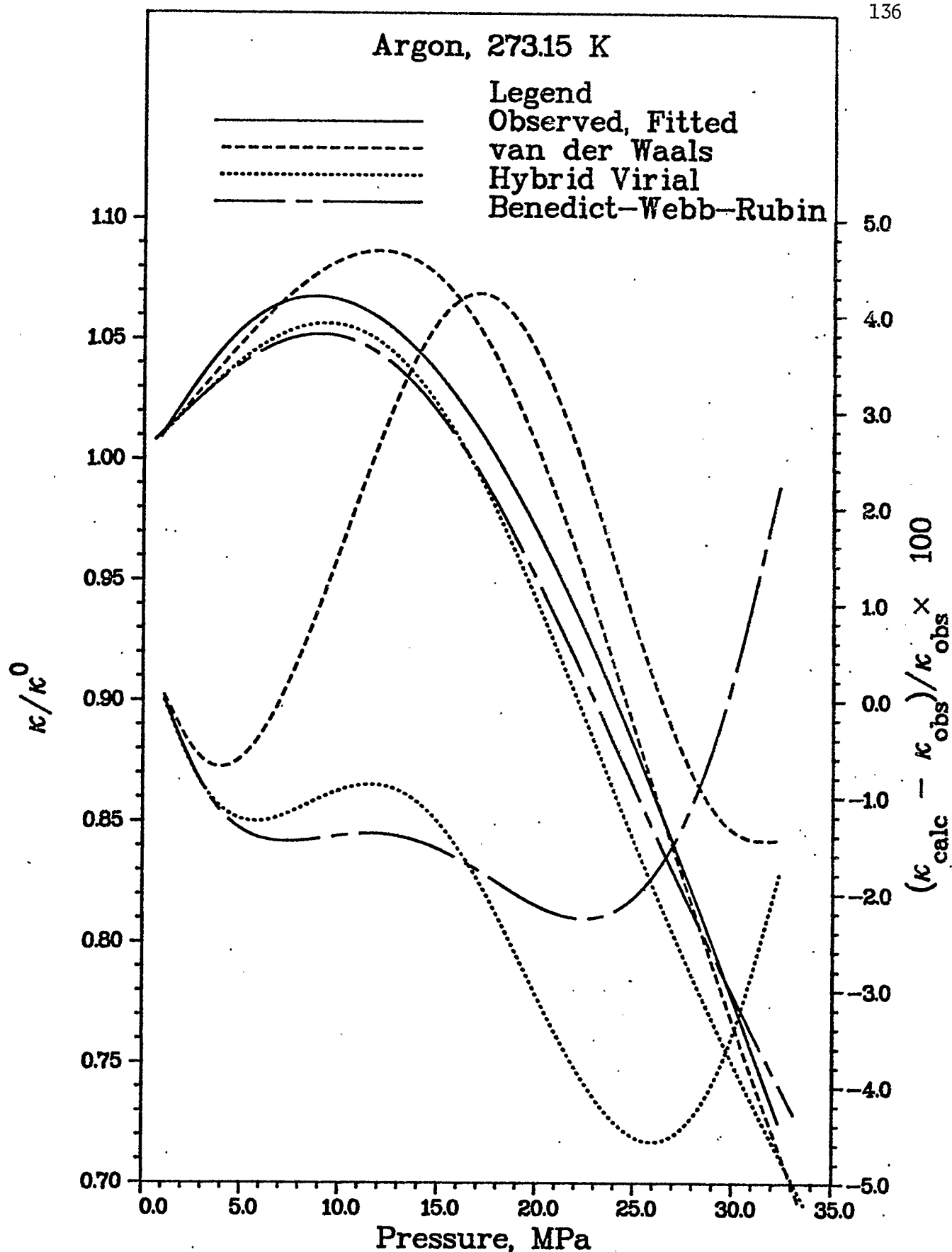


Fig. 5.4.9 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ_0) with those Derived from Equations of State. For Argon at 273.15 K.

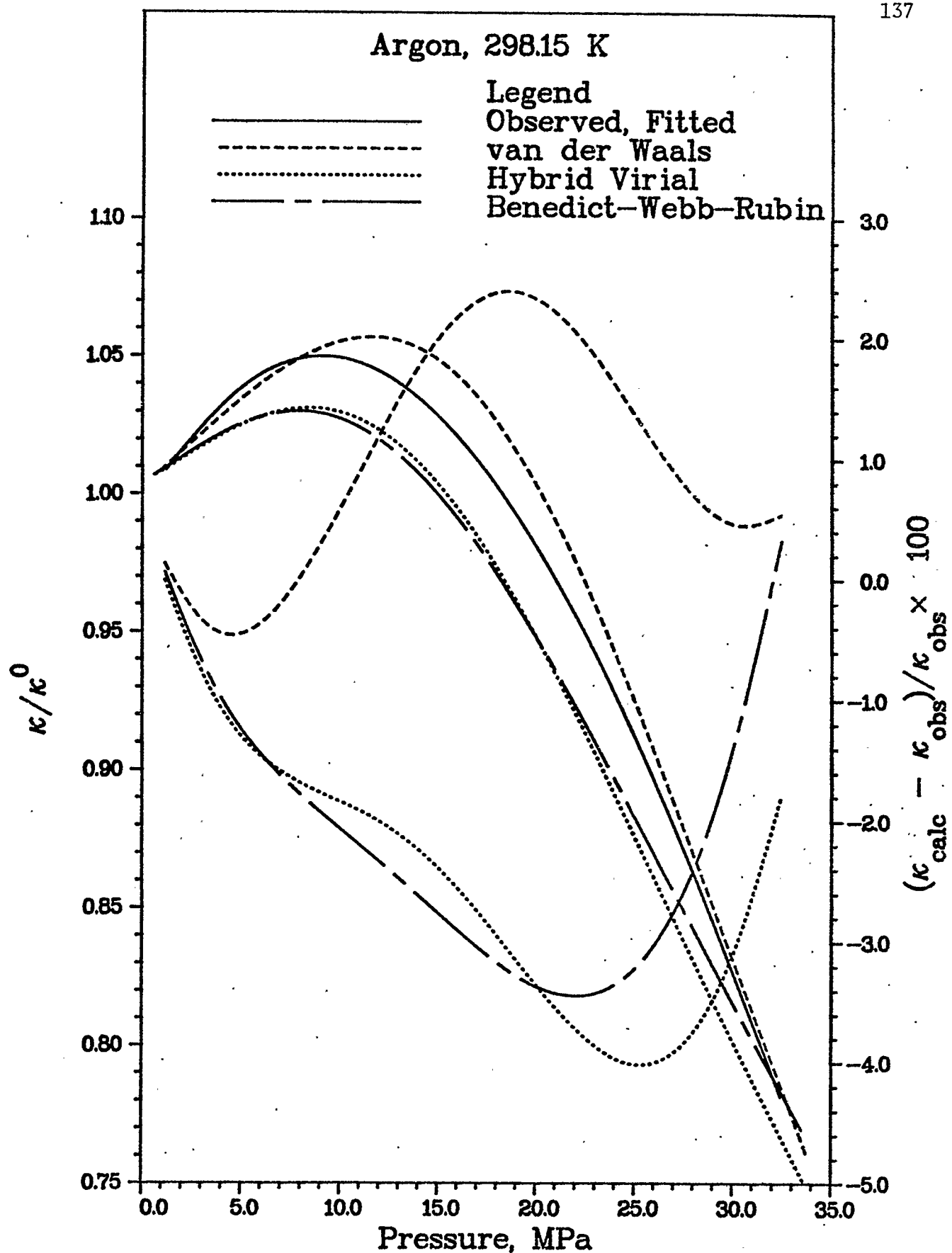


Fig. 5.4.10 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Argon at 298.15 K.

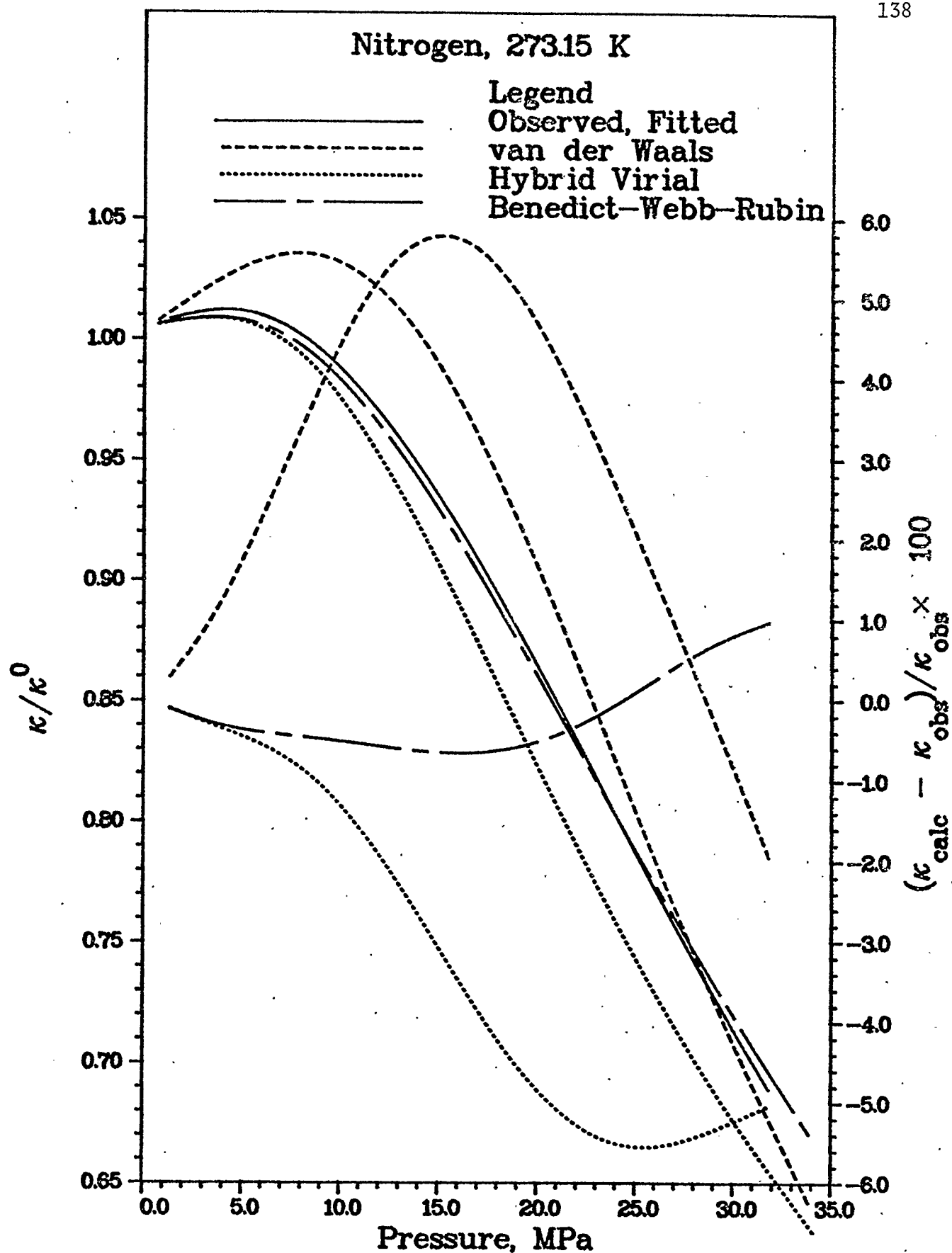


Fig. 5.4.11 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ_0) with those Derived from Equations of State. For Nitrogen at 273.15 K.

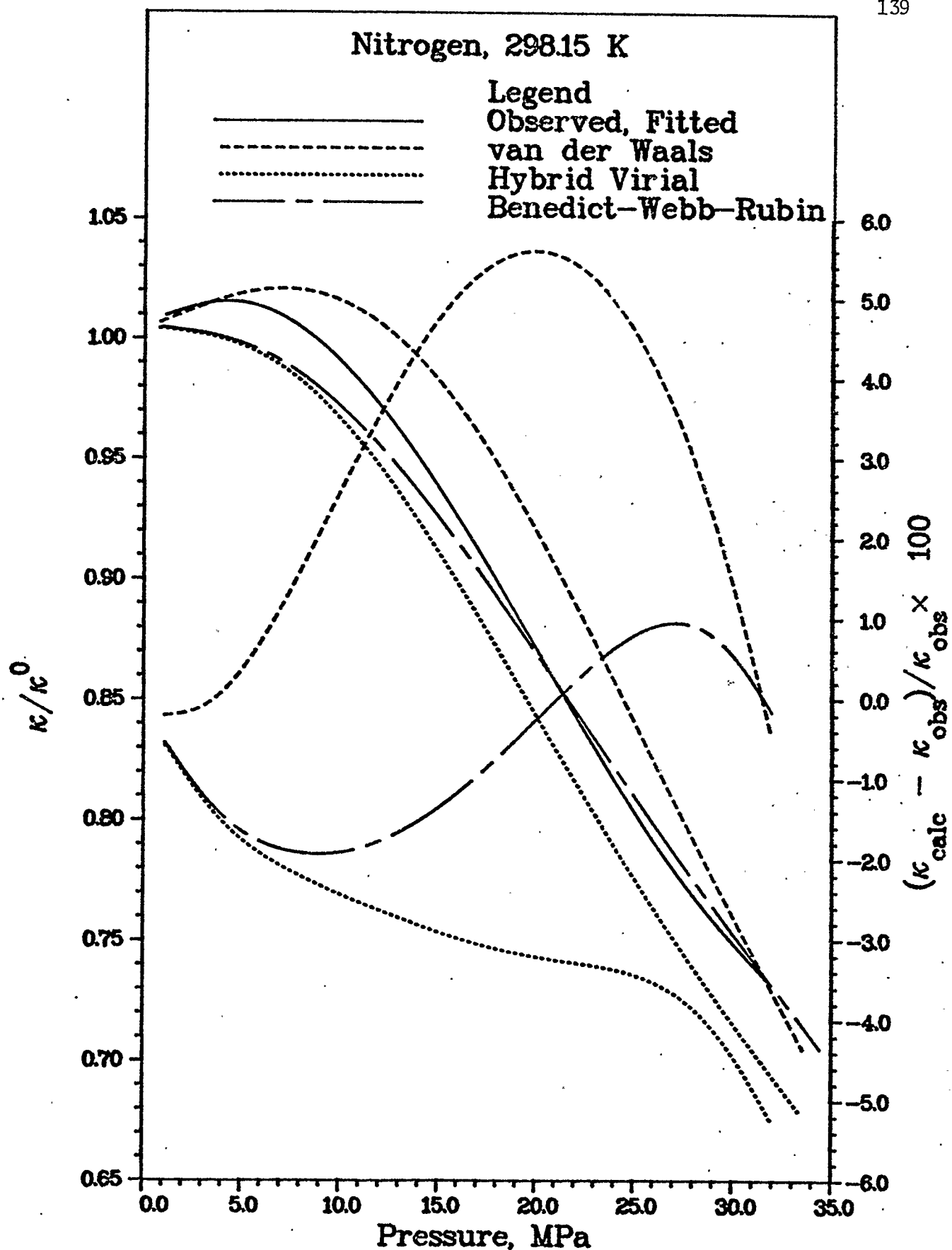


Fig. 5.4.12 Comparison of Observed Normalized Isothermal Compressibilities (κ/κ^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

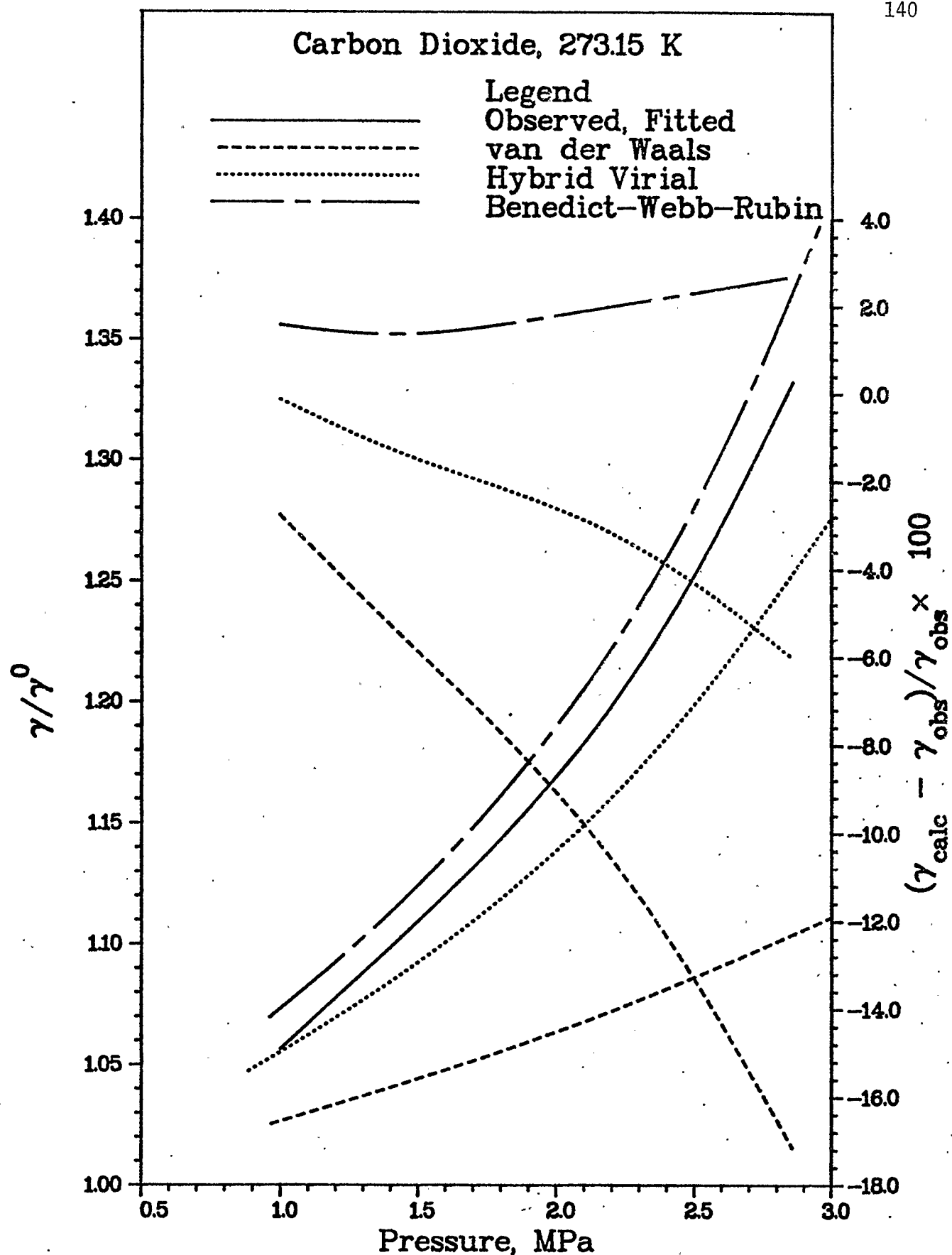


Fig. 5.4.13 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

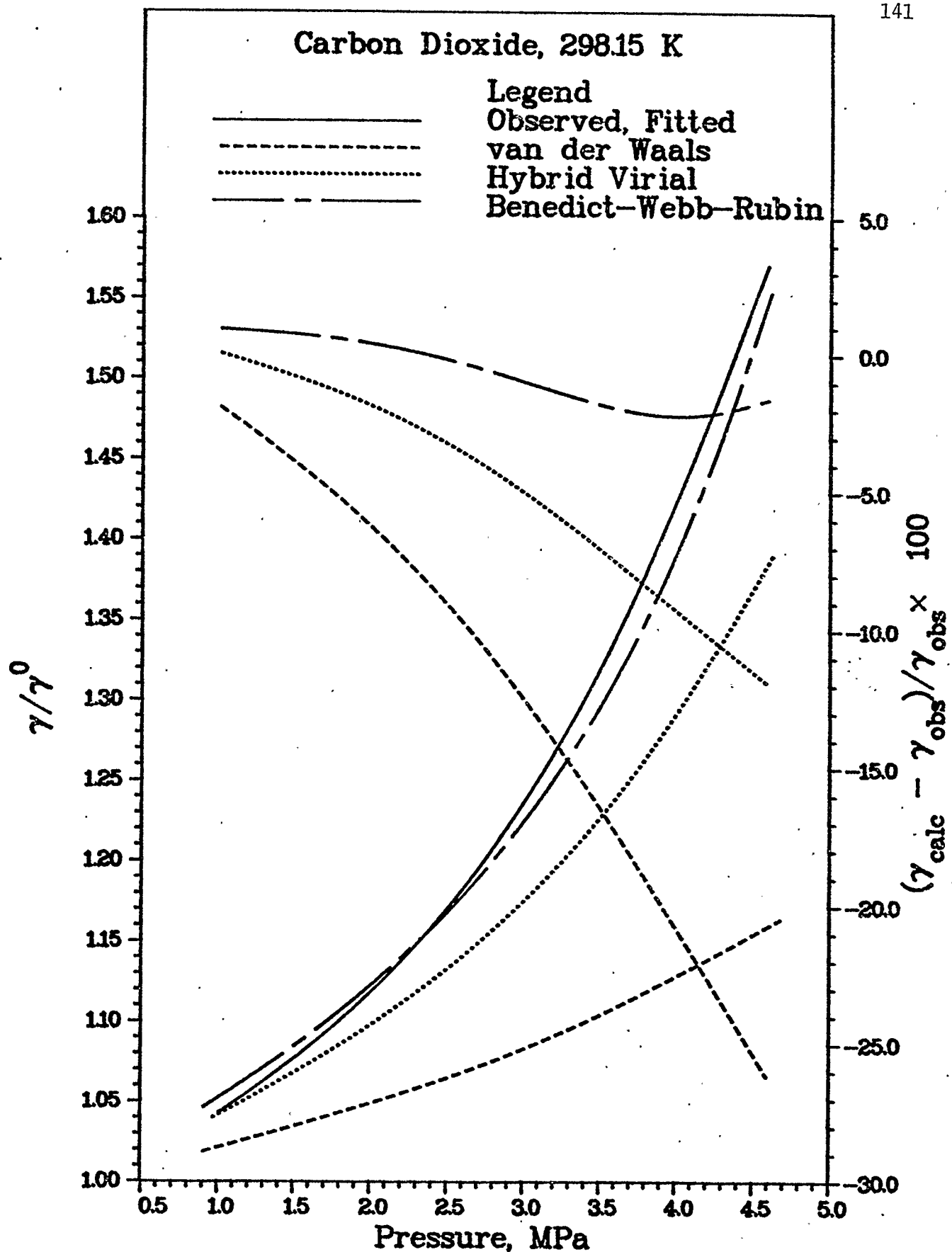


Fig. 5.4.14 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

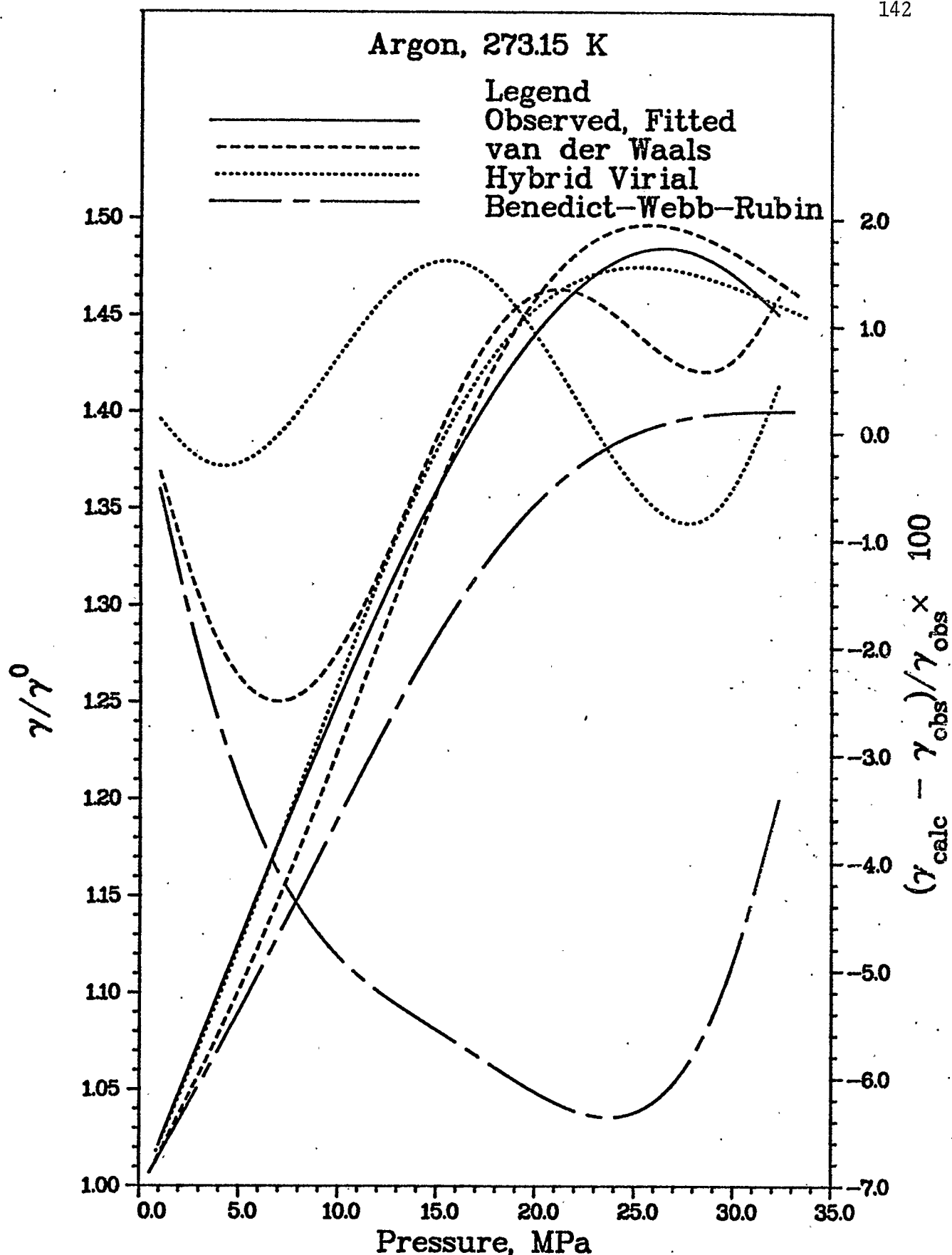


Fig. 5.4.15 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Argon at 273.15 K.

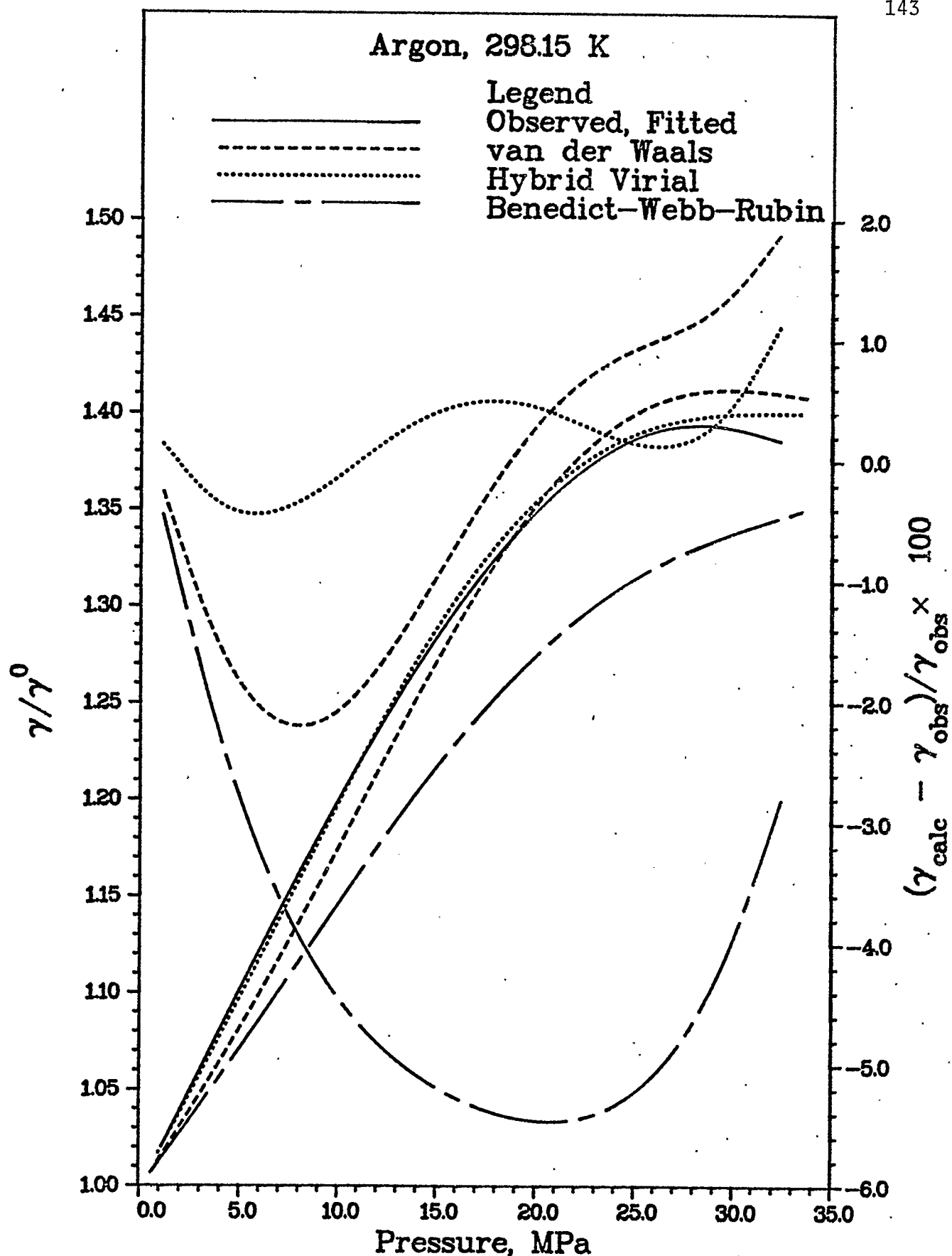


Fig. 5.4.16 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Argon at 298.15 K.

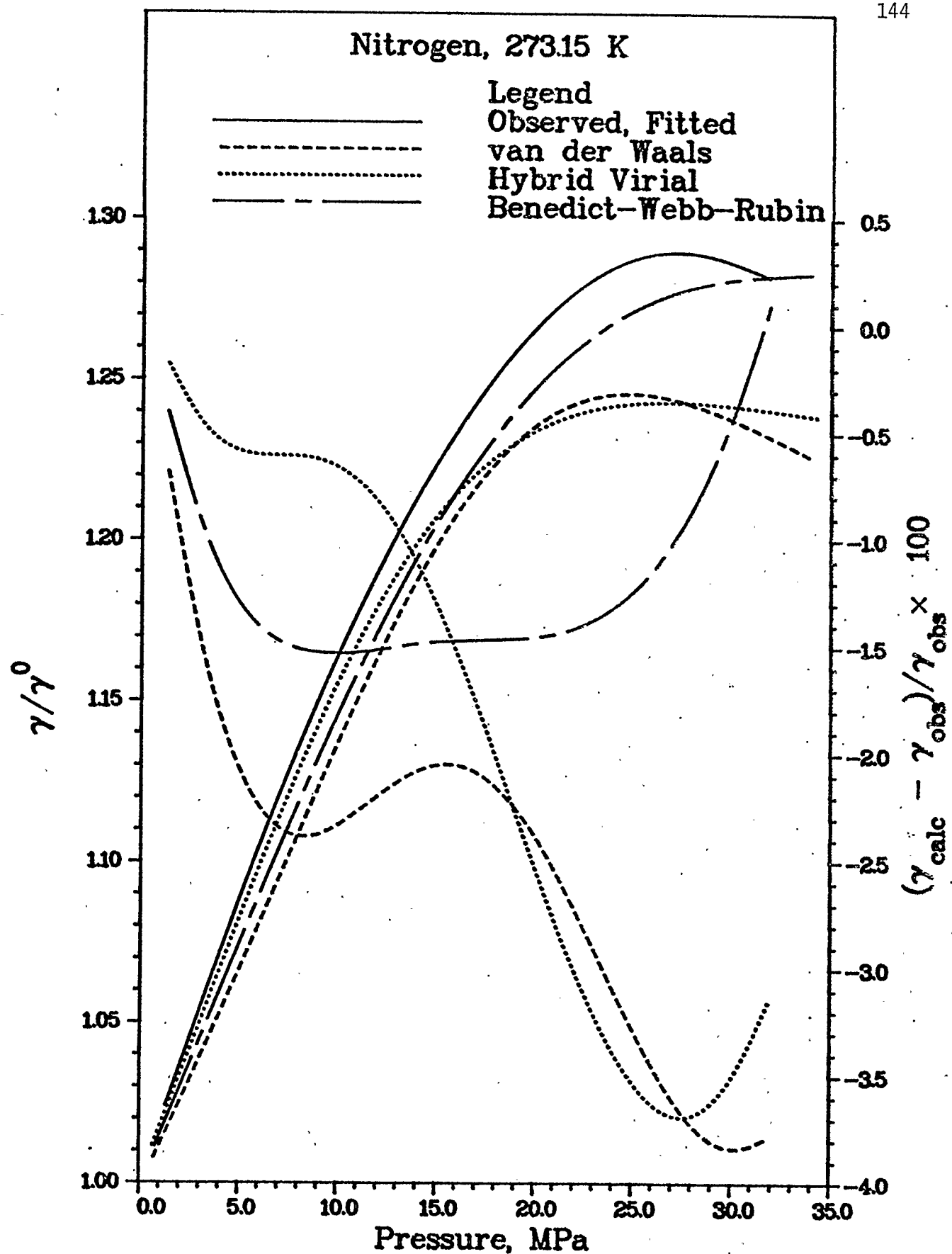


Fig 5.4.17 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Nitrogen at 273.15 K.

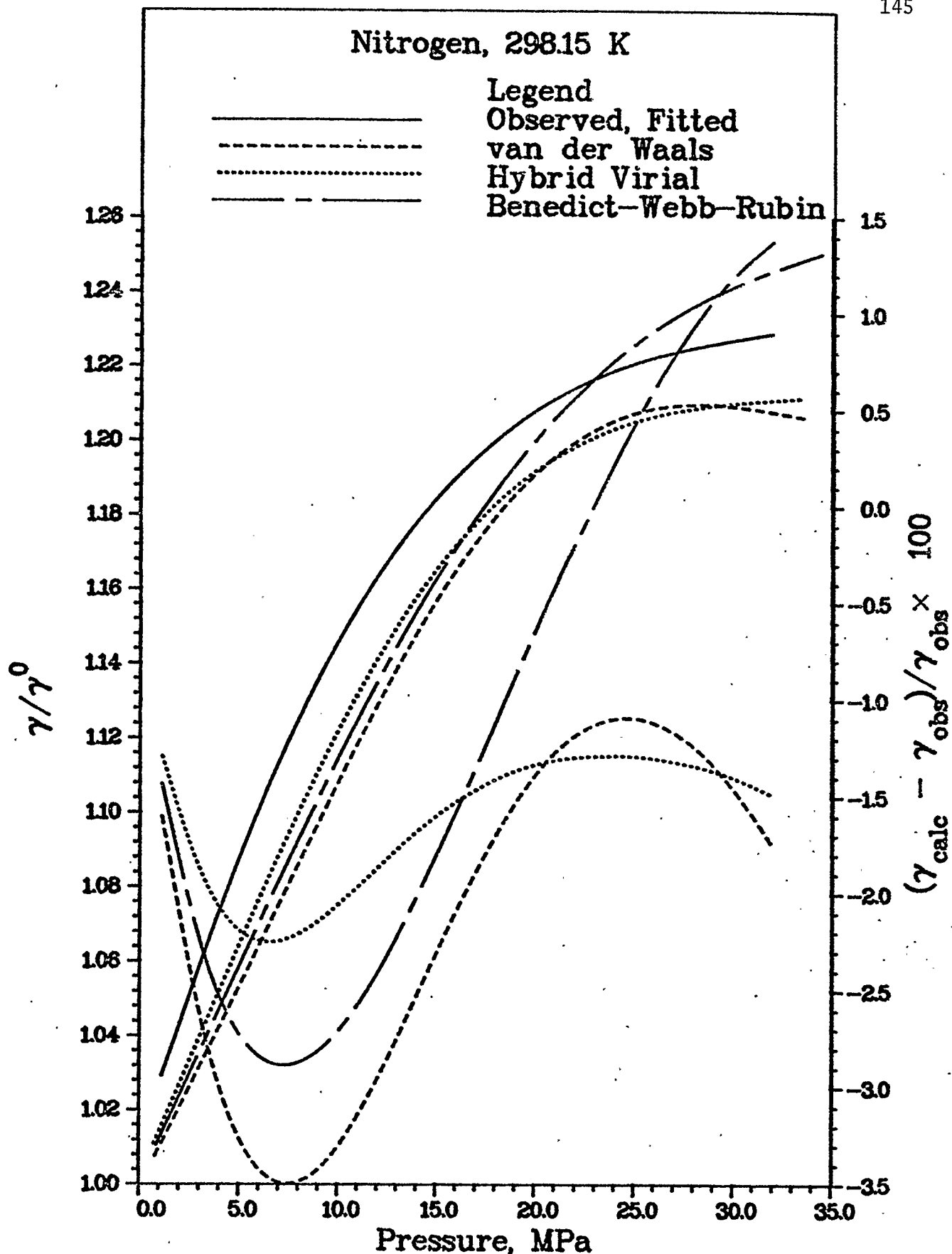


Fig. 5.4.18 Comparison of Observed Normalized Ratios of Specific Heats (γ/γ^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

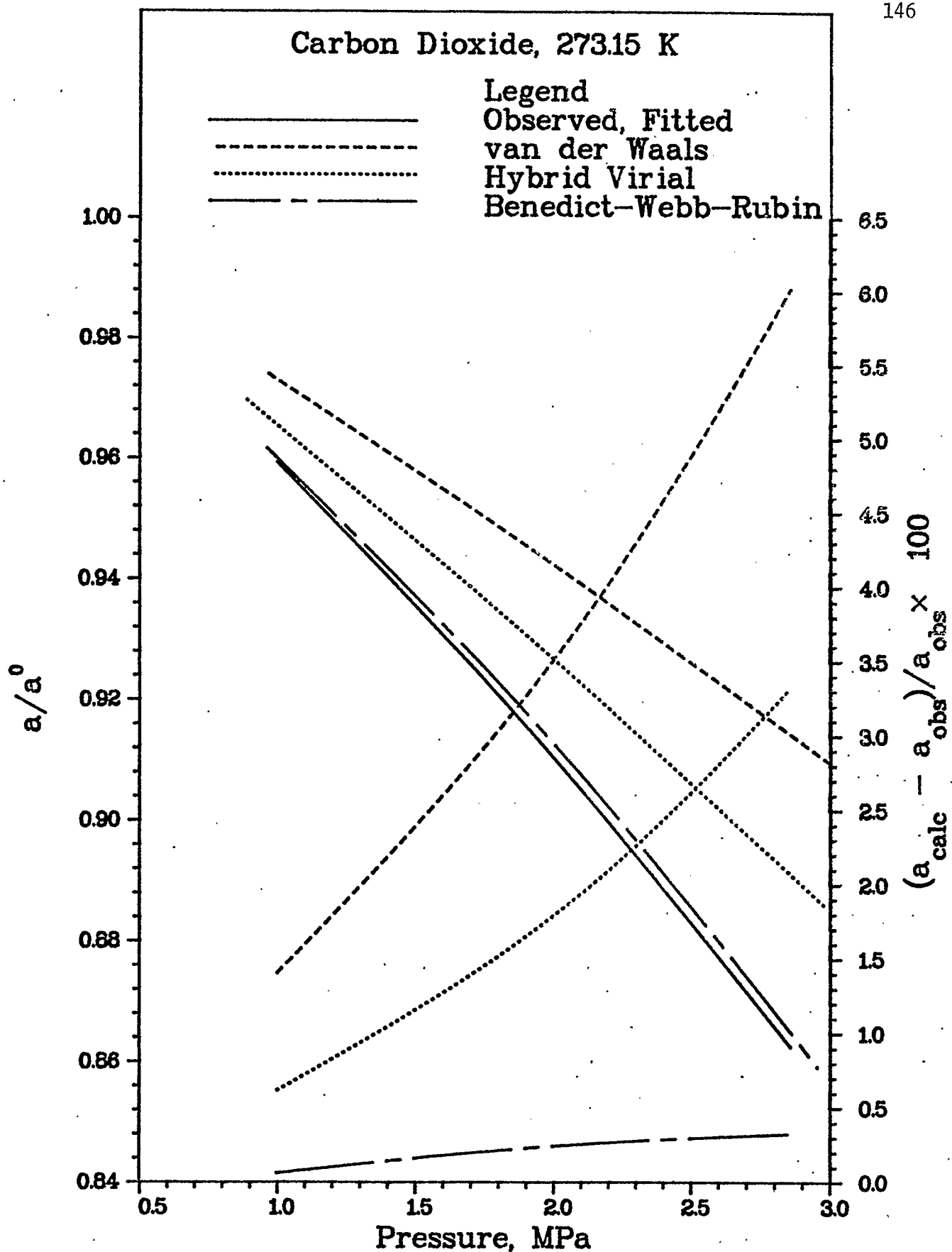


Fig. 5.4.19 Comparison of Observed normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

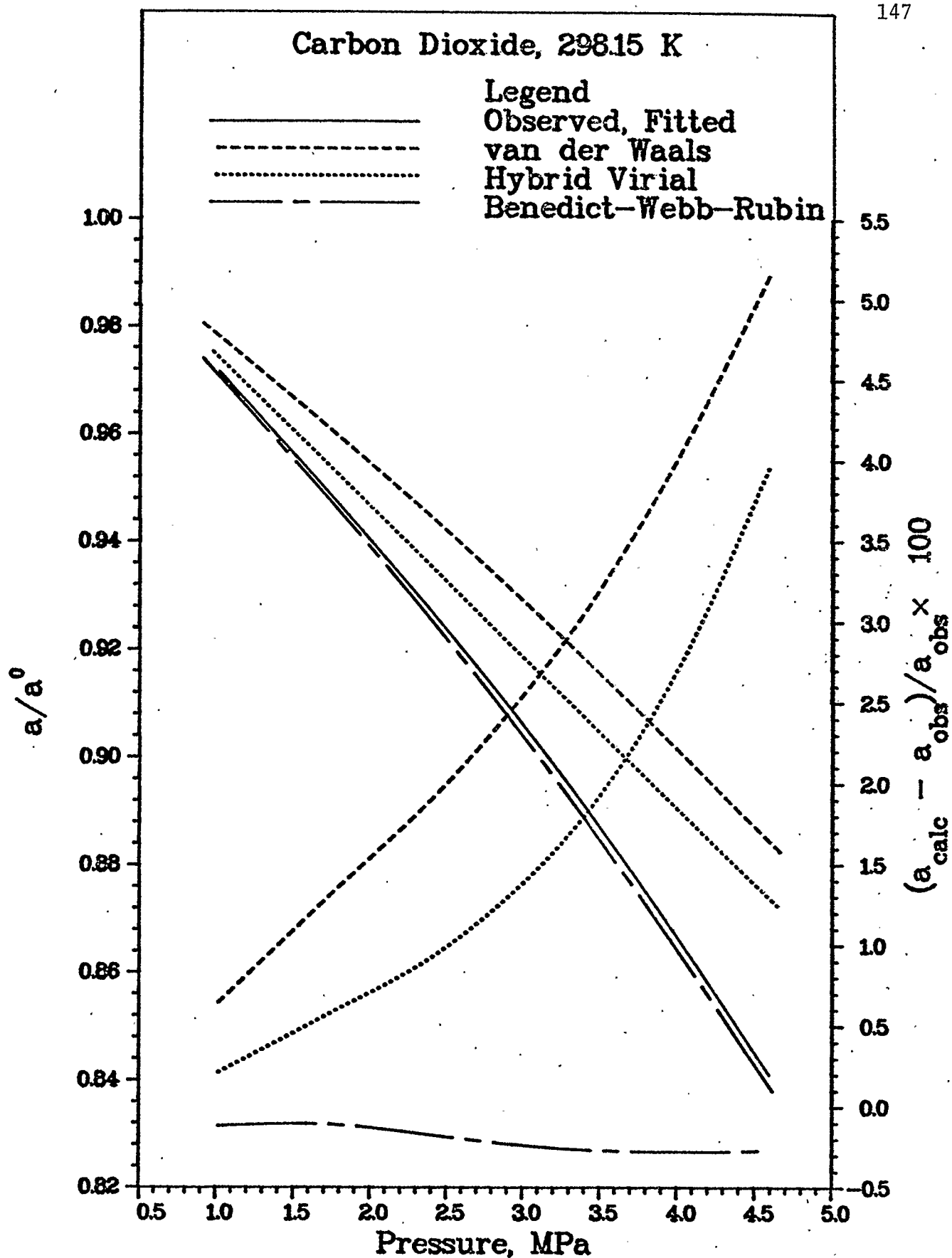


Fig. 5.4.20 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State.. For Carbon Dioxide at 298.15 K.

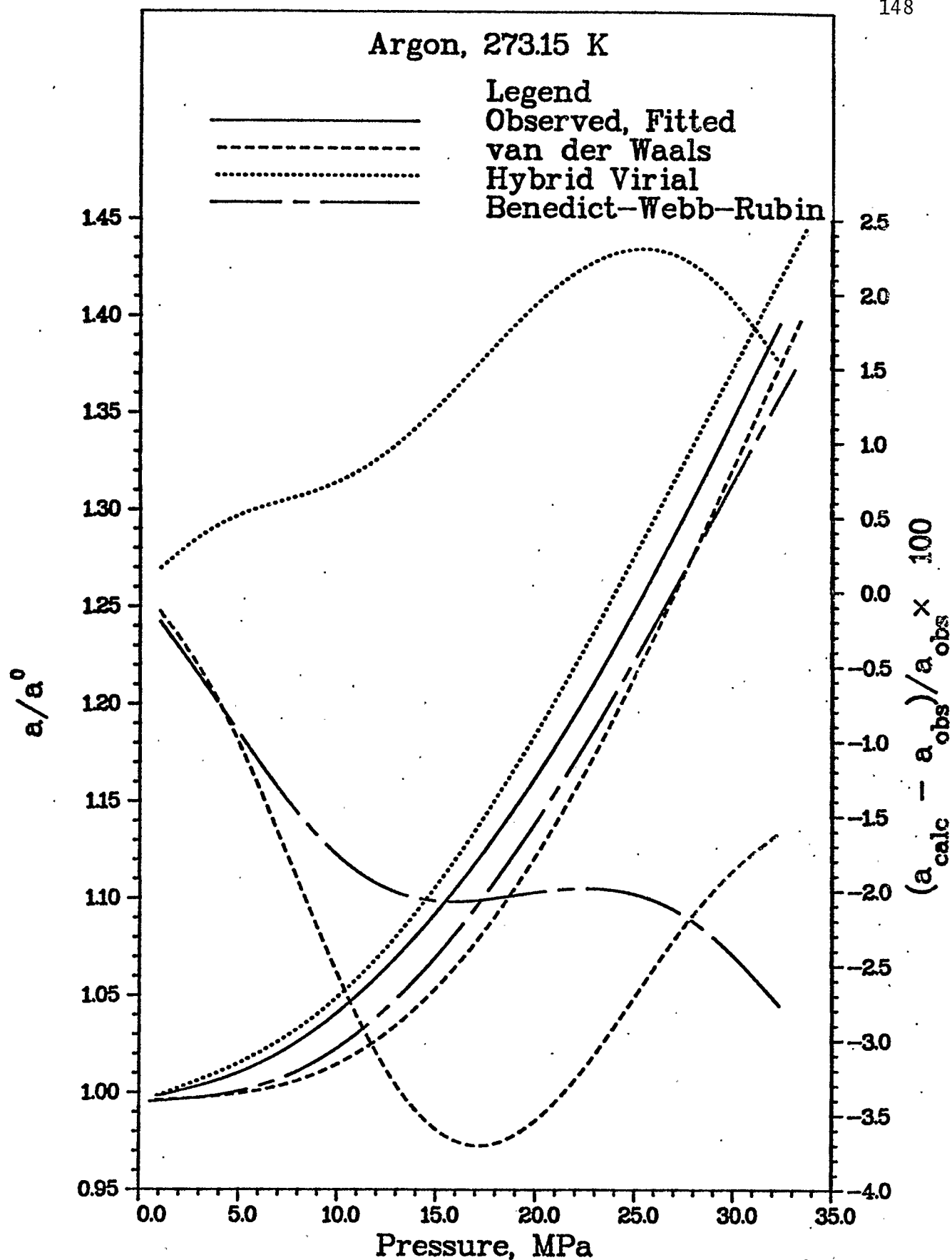


Fig. 5.4.21 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Argon at 273.15 K.

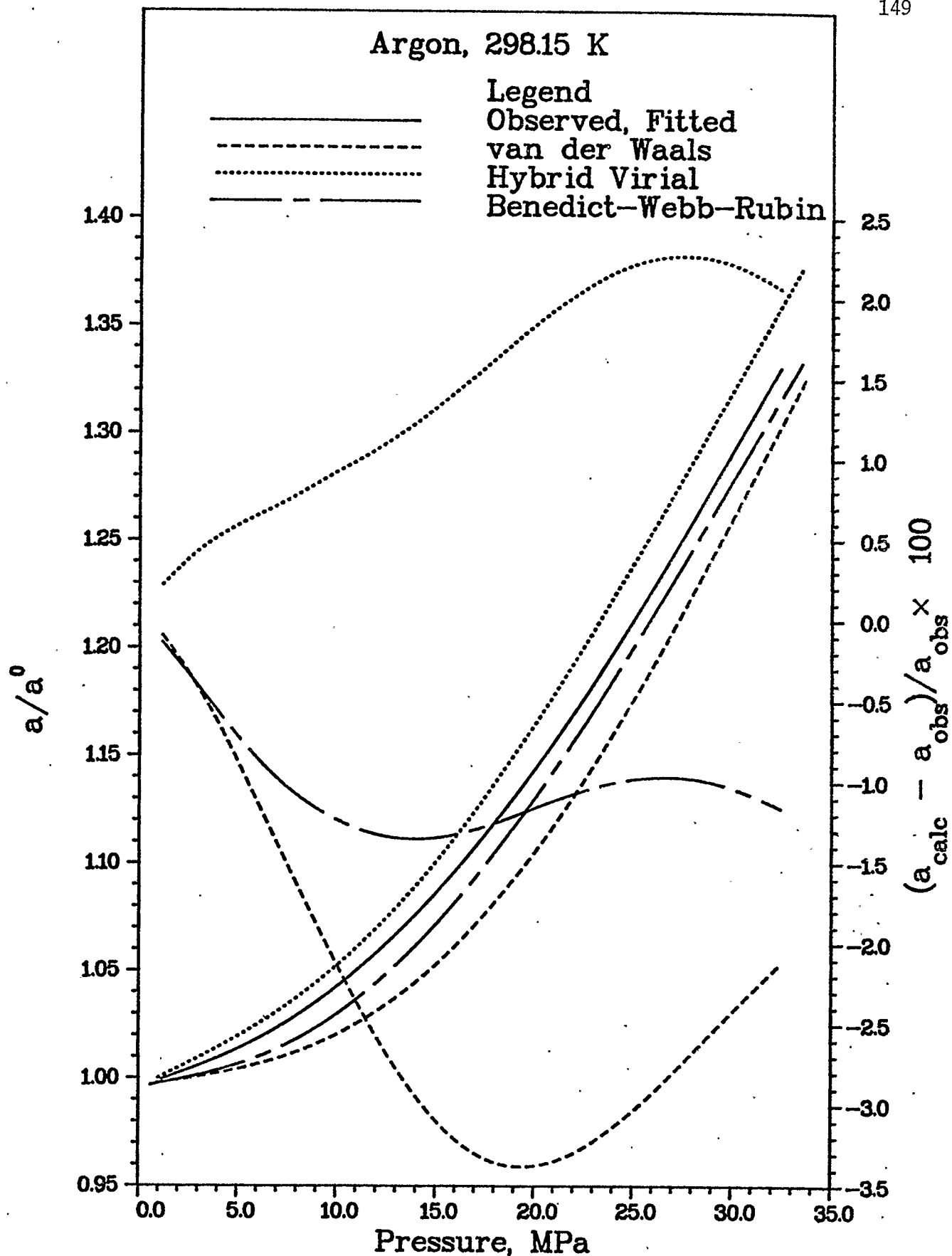


Fig. 5.4.22 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Argon at 298.15 K.

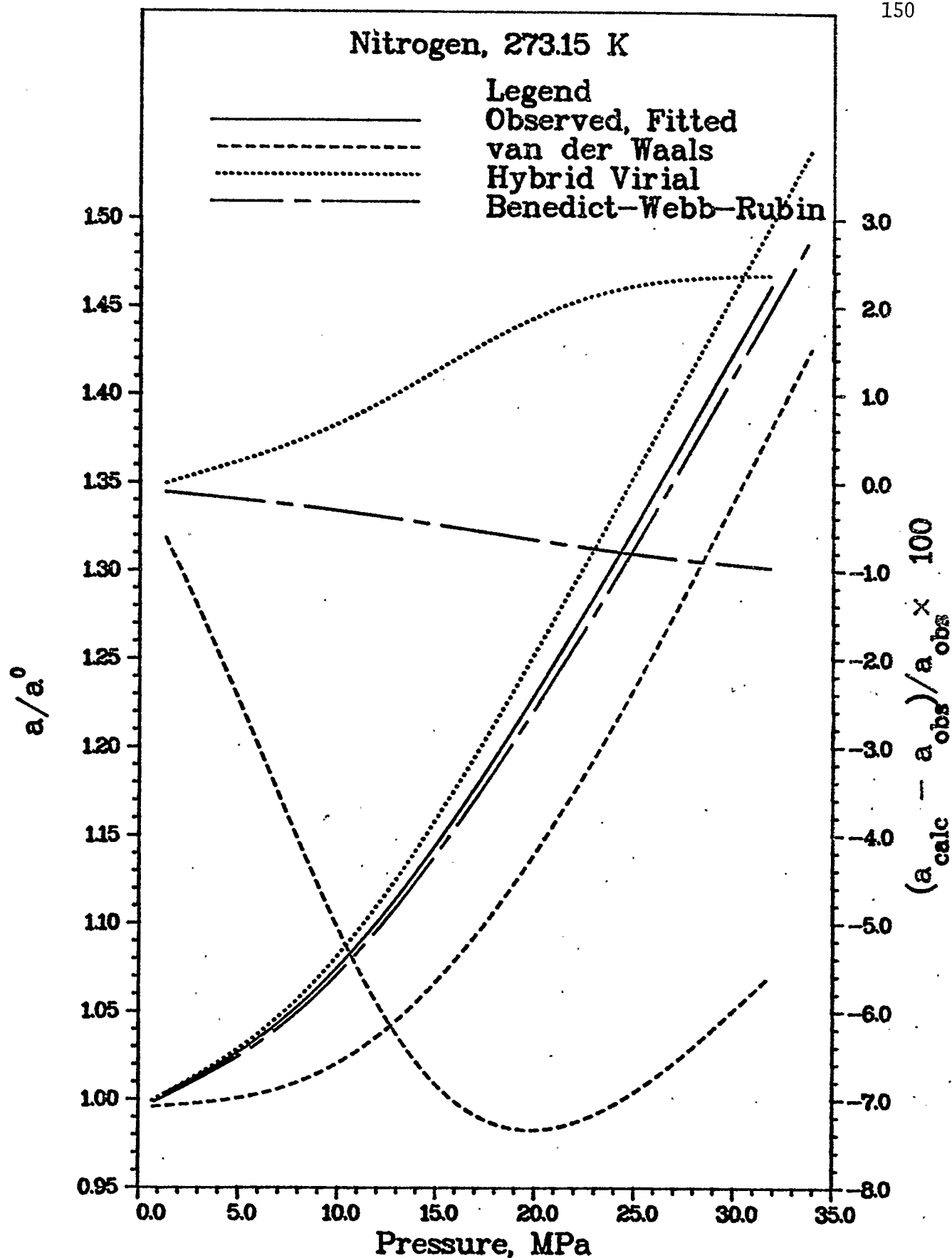


Fig. 5.4.23 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Nitrogen at 273.15 K.

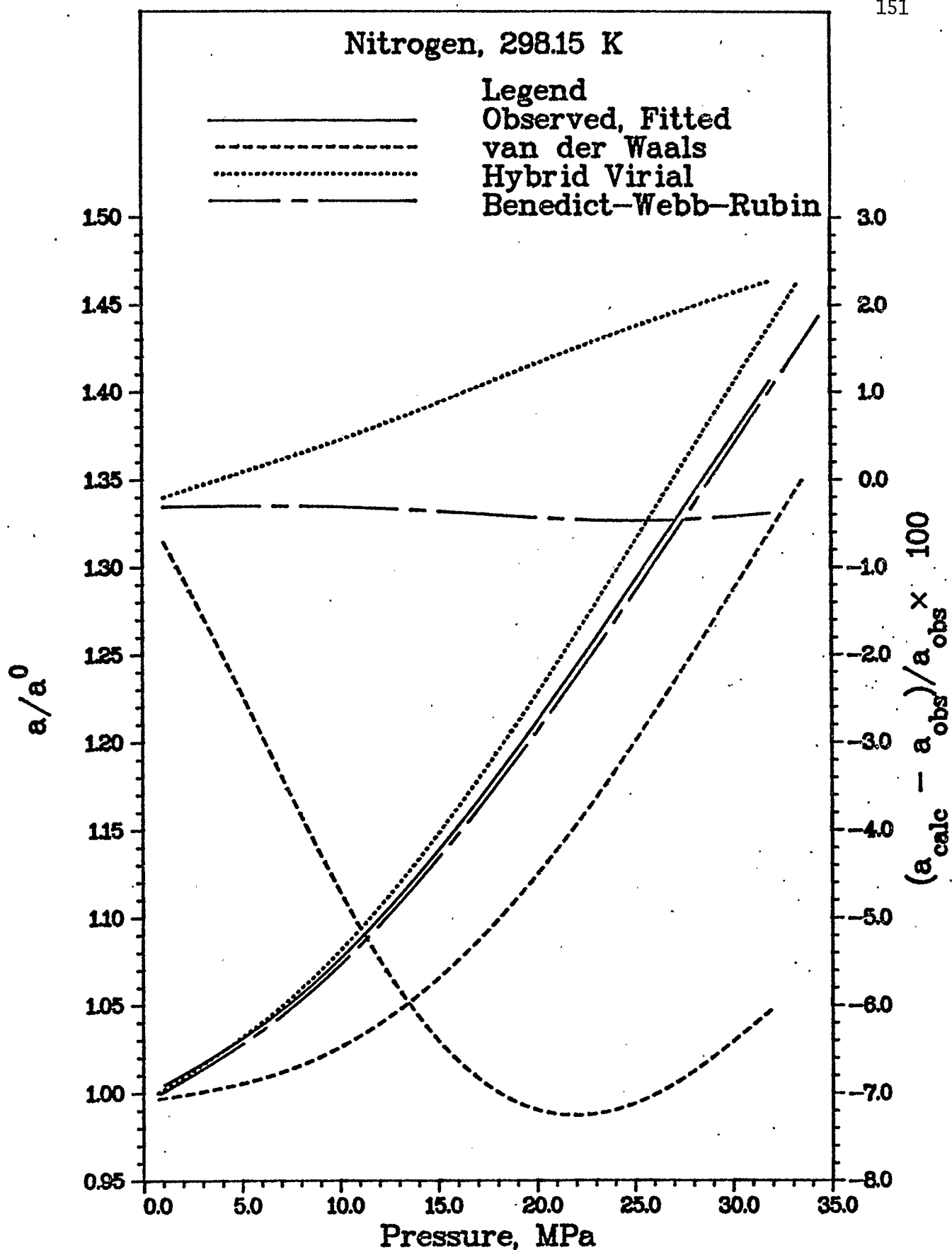


Fig. 5.4.24 Comparison of Observed Normalized Speeds of Sound (a/a^0) with those Derived from Equations of State. For Nitrogen at 298.15 K.

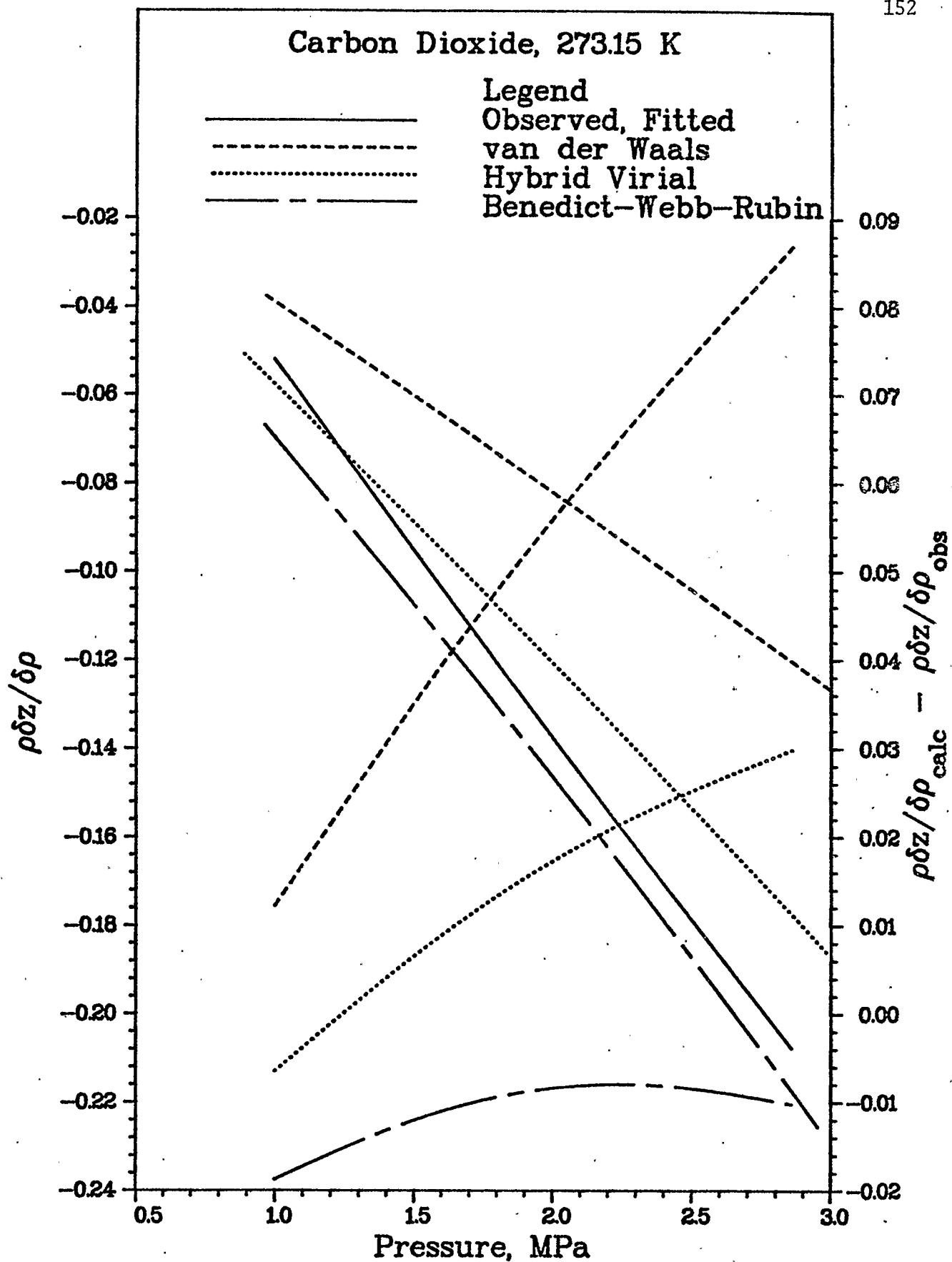


Fig 5.4.25 Comparison of Observed Values of the Property $\rho \frac{\partial Z}{\partial \rho}$ with those Derived from Equations of State. For Carbon Dioxide at 273.15 K.

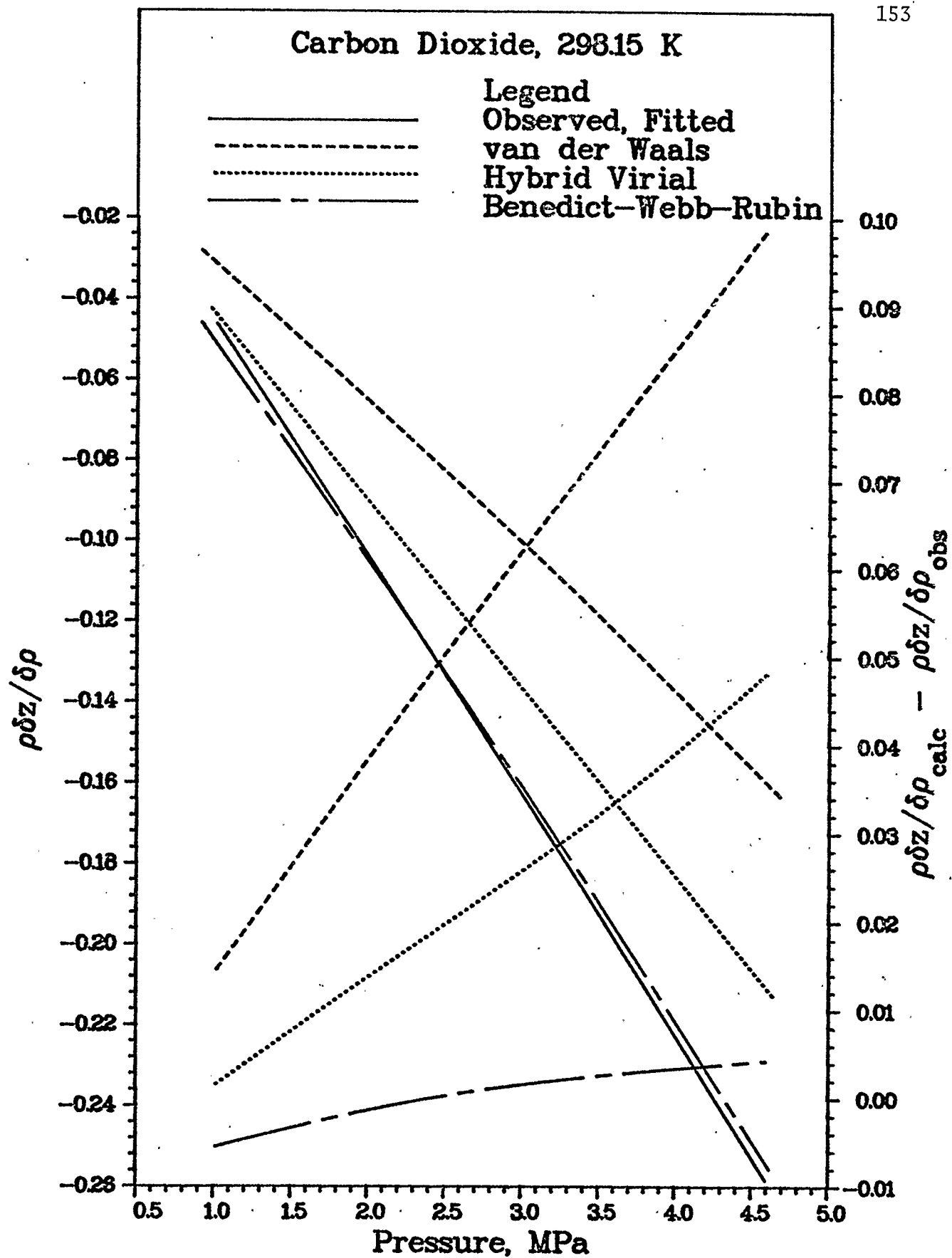


Fig. 5.4.26 Comparison of Observed Values of the Property $\rho \delta Z / \delta \rho$ with those Derived from Equations of State. For Carbon Dioxide at 298.15 K.

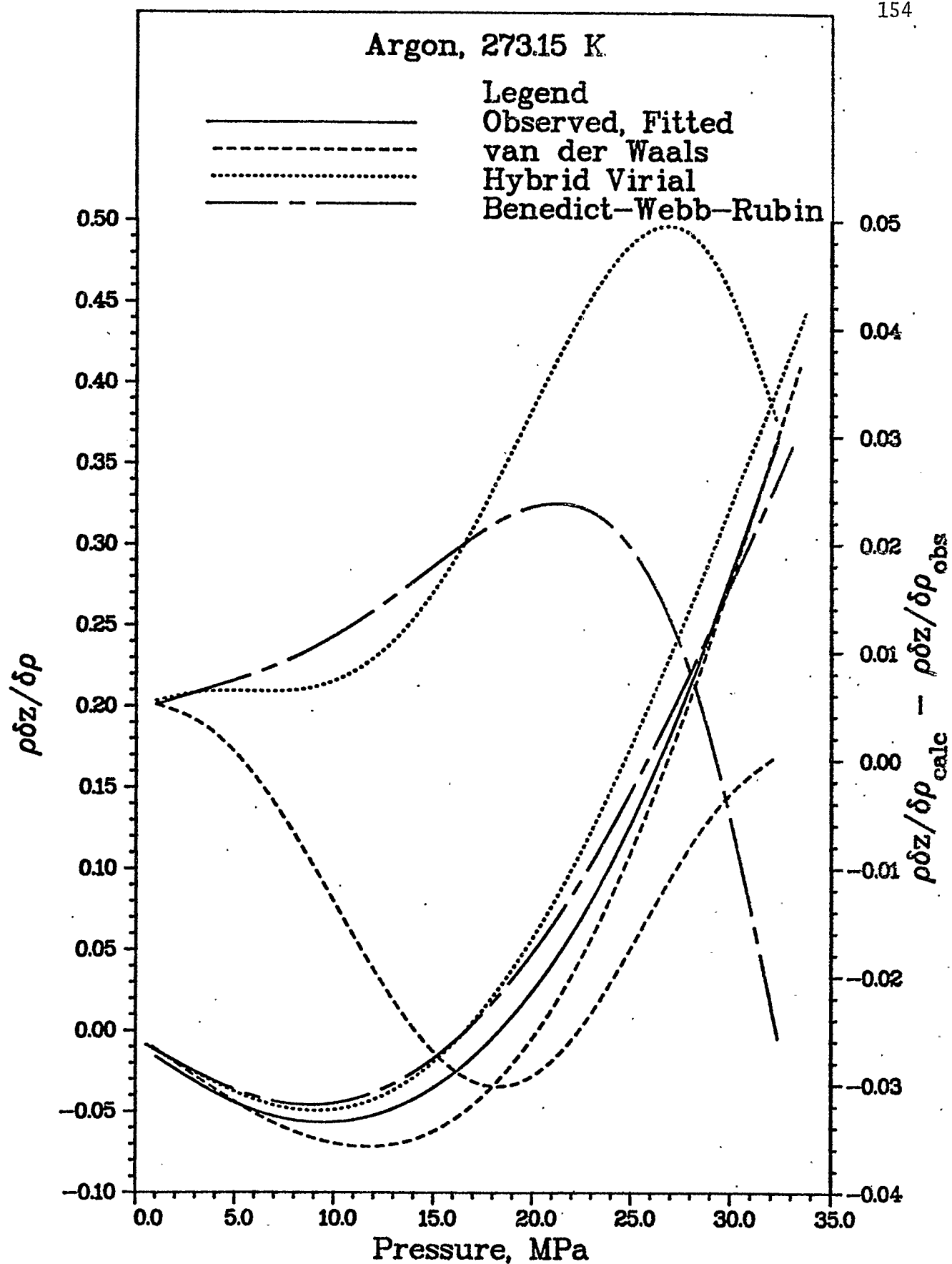


Fig. 5.4.27 Comparison of Observed Values of the Property $\rho\delta z/\delta\rho$ with those Derived from Equations of State. For Argon at 273.15 K.

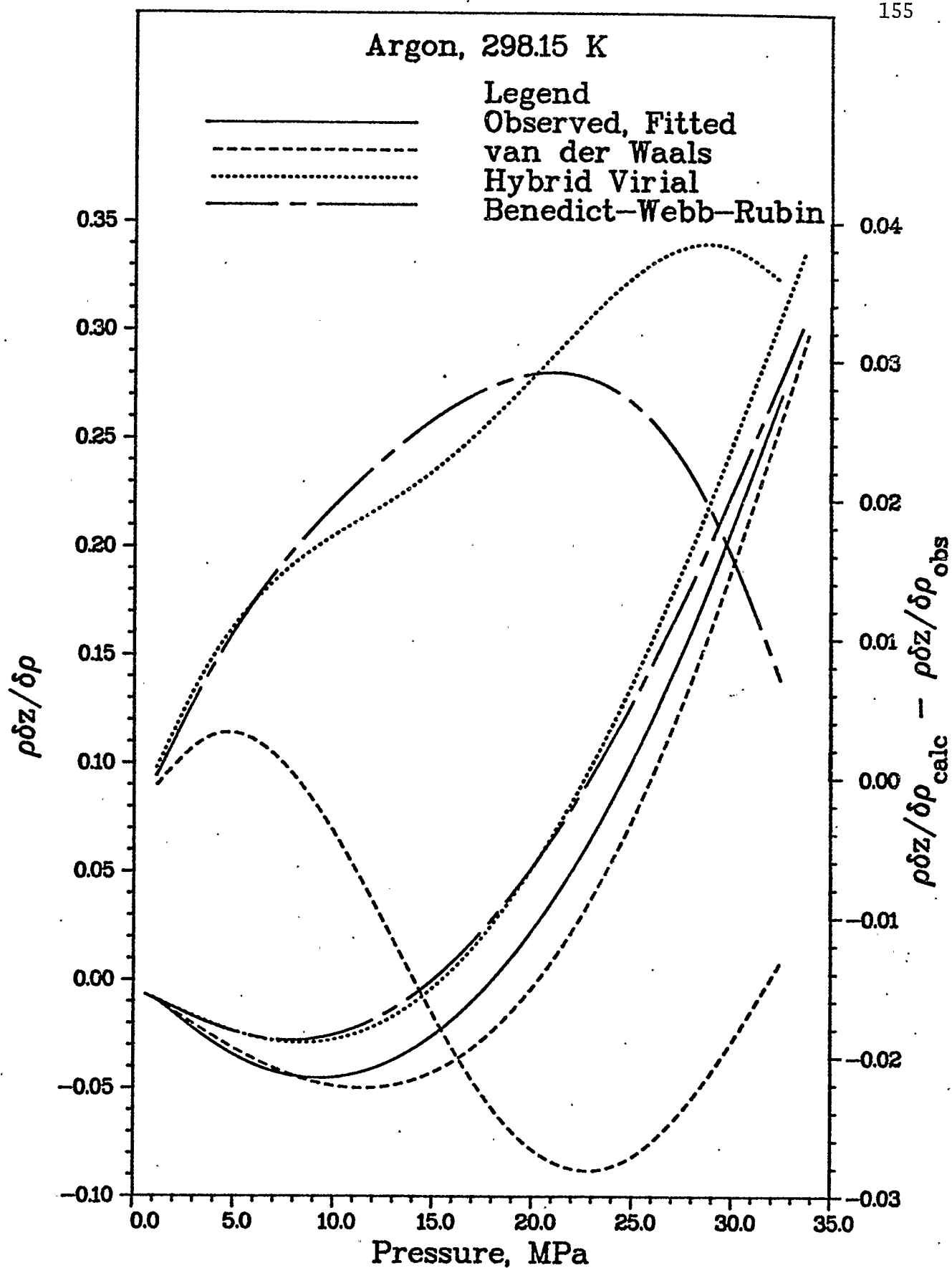


Fig. 5.4.28 Comparison of Observed Values of the Property $\rho \partial Z / \partial \rho$ with those Derived from Equations of State. For Argon at 298.15 K.

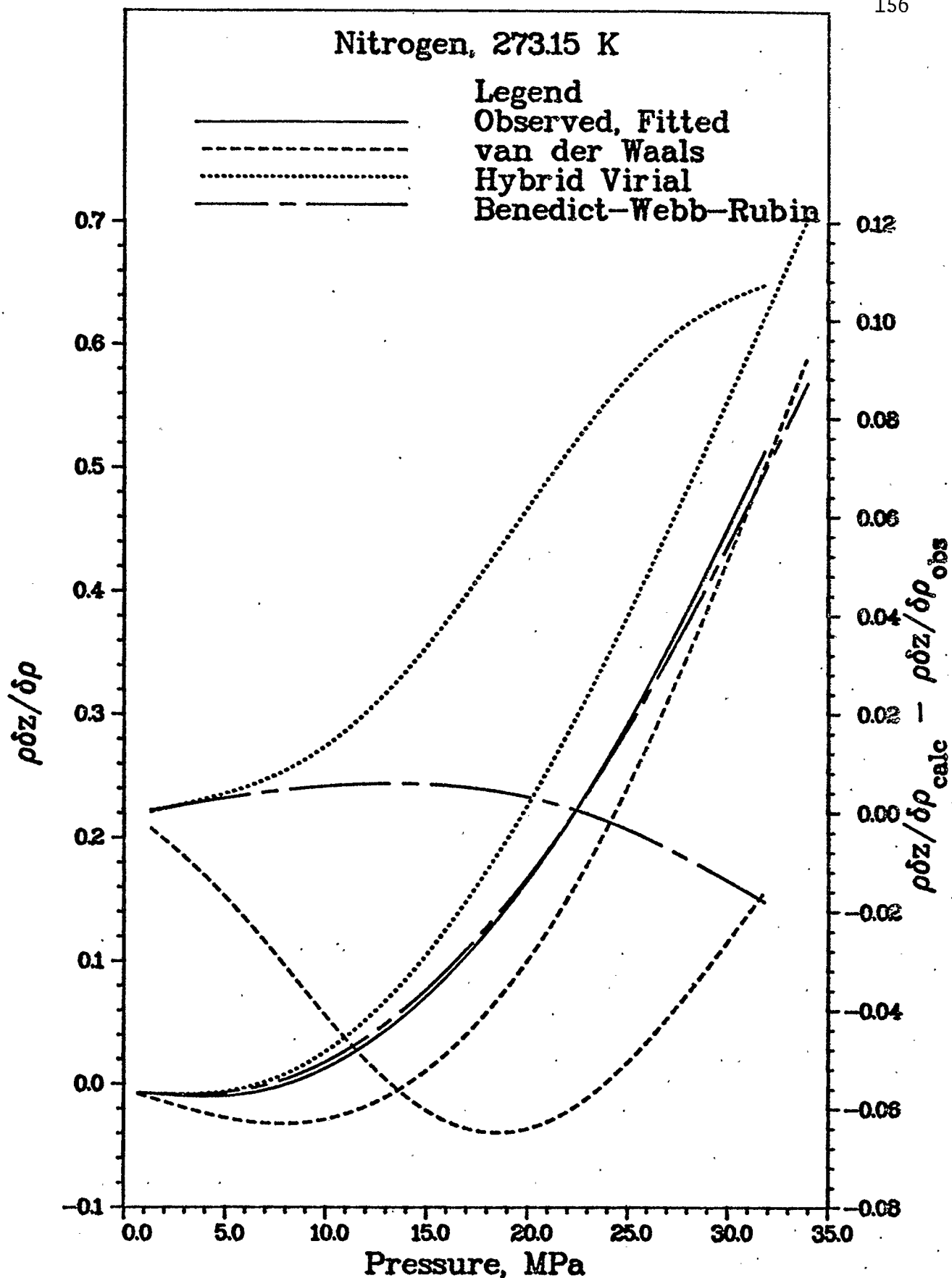


Fig. 5.4.29 Comparison of Observed Values of the Property $\rho \frac{\partial Z}{\partial \rho}$ with those Derived from Equations of State. For Nitrogen at 273.15 K.

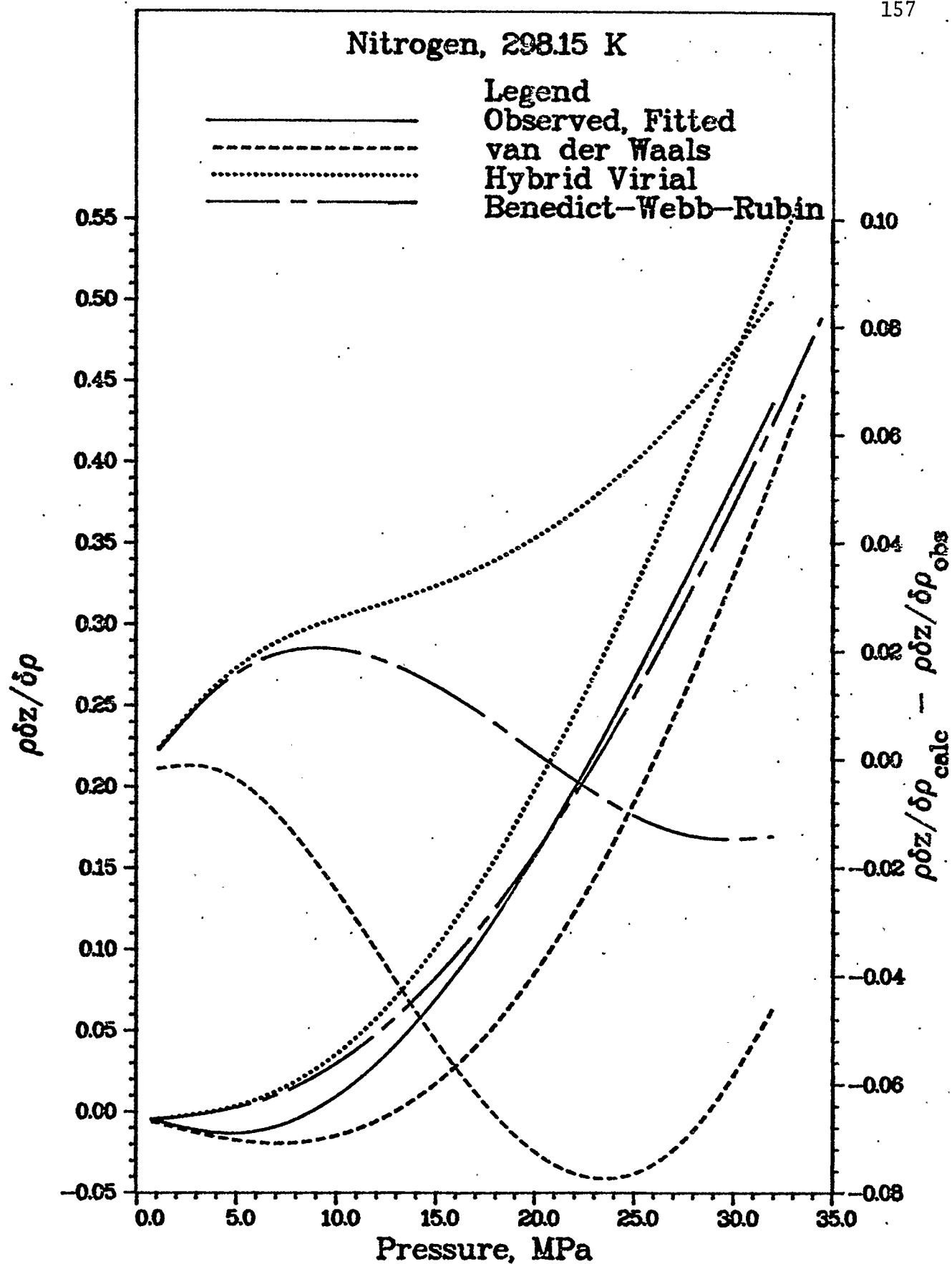


Fig. 5.4.30 Comparison of Observed Values of the Property $\rho \frac{dZ}{d\rho}$ with those Derived from Equations of State. For Nitrogen at 298.15 K.

VI DISCUSSION

The present discussion is confined to the gases concerned at the thermodynamic states at which measurements were made, namely, to carbon dioxide, argon and nitrogen at 0°C and 25°C only at pressures from 1 to 35 MPa in argon and nitrogen but in carbon dioxide confined to the range 1 to 3 MPa at 0°C and 1 to 4.5 MPa at 25°C. The 35 MPa upper limit in the case of nitrogen and argon was determined by the gas cylinder delivery pressure. For carbon dioxide, whose critical temperature is 31.06°C, the upper limit was determined by the dew-point line. The decision to limit pressures to not less than 1 MPa was determined by the relative unsuitability of the pressure sensors at lower pressures, by less consistent diaphragm rupturing at these pressures - both of which contribute to decreased accuracy - together with the fact that the low pressure region, being only slightly non-ideal, is of relatively low interest in this study.

In this chapter, measurement uncertainties are presented, agreement of the measured properties with other published data are discussed and relevant properties calculated by the van der Waals, the Benedict-Webb-Rubin and the hybrid virial equations of state are compared with those observed in an attempt to assess the validity of the equations.

6.1 Uncertainty Analysis of the Measurement System

The uncertainty w_R of a value $R = R(x_1, x_2, \dots)$ deduced from a set of independent measurements x_1, x_2 , etc. having independent uncertainties w_1, w_2 , etc. is given by [6.1];

$$w_R = \pm \left[\left(\frac{\partial R}{\partial x_1} w_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} w_2 \right)^2 + \dots \right]^{1/2} \quad \dots \quad (6.1.1)$$

This relation is used to estimate uncertainties in the density, isothermal compressibility and speed of sound data.

6.1.1 Uncertainty in Density Measurements. As mentioned in Sec. 4.5.2 the density is derived from the relation;

$$\rho = (1/RT) [(1 + V_3/V_2) (p_{2f} - p_{2i}) + p_{2i}]$$

The pressure p_{2i} is found to be very small compared to the first term in the square bracket above and is neglected in the computation of uncertainty as is V_2 in respect to V_3 so that uncertainties in density may be determined adequately from the approximate relation;

$$\rho \approx (1/RT) (V_3/V_2) \Delta p \quad \dots \quad (6.1.2)$$

where $\Delta p = p_{2f} - p_{2i}$. Uncertainties in temperatures, in the volumes (V_2, V_3) and in the pressure difference (Δp) are known to be about 0.07%, 0.1%, and 0.35% respectively so that the uncertainty in measured densities is about 0.4%. It may be noted that the main contributor to this uncertainty is that arising from pressure.

6.1.2 Uncertainty in Isothermal Compressibility Measurements. In the expression for isothermal compressibility;

$$\kappa = - \frac{1}{1 + \frac{V_2/2}{V_1}} \frac{V_2/V_1}{p_{1f} - p_{1i}}$$

the value $(V_2/2)/V_1$ is only about 0.05, so that ignoring it for simplicity, the uncertainty in κ may be determined acceptably using the approximate relation;

$$\kappa \approx - (V_2/V_1)/\Delta p \quad \dots \quad (6.1.3)$$

where $\Delta p = p_{1f} - p_{1i}$. Uncertainties in volume are about 0.1% and the uncertainty in Δp is about 0.14% (for transducer P1) so that the uncertainty in isothermal compressibility data is not more than 0.2%.

In addition an error in κ , rather than an uncertainty, arises from the approximation;

$$\kappa(p_\kappa, T) = - \frac{1}{V(p_\kappa)} \left(\frac{\partial V}{\partial p} \right)_T \text{ at } p_\kappa \approx - \frac{1}{V_1 + V_2/2} \frac{V_2}{p_{1f} - p_{1i}}$$

where $p_\kappa = (p_{1f} + p_{1i})/2$. The error introduced by the approximation $(\partial V/\partial p)_{\text{at } p_\kappa} \approx V_2/(p_{1f} - p_{1i})$ can be shown, by Taylor's theorem, to be very small (of the order of -0.01% maximum). The error due to the approximation $V(p_\kappa) \approx V_1 + V_2/2$, increases sharply with pressure and is greater at the lower temperature (273.15 K). For carbon

dioxide it is only about -0.005% at the mid range and increases to about -0.14% at maximum pressure (3 MPa). For argon and nitrogen (where the maximum pressure is much greater) the mid range error is only about 0.02% but increases to about 0.6% at the maximum pressure involved.

6.1.3 Uncertainty in Speed of Sound Measurements. The speed of sound is given by the relation;

$$a = x_{ML}/(t_L - t_M) \text{ or } x_{MR}/(t_R - t_M)$$

which can be rewritten as;

$$a = x_{ML}/\Delta t \text{ or } x_{MR}/\Delta t \quad \dots (6.1.4)$$

where $\Delta t = t_L - t_M$ or $t_R - t_M$. The uncertainty in x_{ML} or x_{MR} is about 0.17% and that in Δt is about 0.7% so that the uncertainty in speed of sound data is about 0.73%. The main contributor to the uncertainty is obviously the uncertainty in time Δt . This is due mainly to the tape recorder.

At low pressures, the measured speed of sound should be very nearly equal to the calculated ideal gas state value. This expectation is realized within uncertainty limits by the speed of sound data given earlier. From Table 5.1.1 and Fig. 5.1.1 it may be seen that at low pressures (about 0.1 MPa to 0.35 MPa) the maximum deviation of the measured speeds of sound from ideal gas state values is less than

1%, while the deviation of the average [i.e., $1 - (a/a^0)_{\text{average}}$] is not more than 0.2% for those gases (air, nitrogen, and argon) which are close to ideal at these temperatures and pressures. Since the ideal gas state sound speed is the thermodynamic equilibrium defined value, this close agreement provides effective experimental confirmation that a decompression wave front moves through still gas at a speed equal to the thermodynamic speed of sound in the gas ahead of the front. It also indicates that a similar accuracy in measured speeds of sound will apply at higher pressures as well.

6.2 Comparison of the Observations with Published Data

The available published data on the thermodynamic properties of interest are plotted in Figs. 5.3.1 through 5.3.18. It will be seen that in general, the observations agree very well with the data of other investigators and such deviations as exist, exhibit no coherent pattern. This supports the experimental procedure used in regard to precision and freedom from bias. Further support in regard to precision is provided by the fact that, in all cases, the standard deviation of the scatter of the observed data from the fitted curve is well within the limits of experimental uncertainty.

6.2.1 Density.

a) Carbon Dioxide: Figs. 5.3.1 and 5.3.2 show a high degree agreement of the data of this study with those of other investigators. However, at 298.15 K, the data of Michels et al. [2.10] are slightly less than the observed data at higher pressures.

b) Argon: From Figs. 5.3.3 and 5.3.4 it is seen that the agreement of the observed data with those of other workers is excellent for both isotherms.

c) Nitrogen: Observed densities are again in excellent agreement with other data as may be seen from Figs. 5.3.5 and 5.3.6.

6.2.2 Isothermal Compressibility. As mentioned earlier, suitable published data of other investigators on isothermal compressibility are not available for comparison.

6.2.3 Speed of Sound.

a) Carbon Dioxide: No suitable published data are available for comparison with the speed of sound observations of this study for carbon dioxide at 0°C. At 25°C the data of Novikov and Trelin [2.34,2.35] (see Fig. 5.3.14) are about 0.5 m s⁻¹ to 1.5 m s⁻¹ greater than the data of this study. Hodge's data [2.20] (at 27°C) agree

better with Novikov and Trelin (at 25°C). However, the data of this study are in close agreement with Hodge's values when the latter are adjusted to 25°C.

b) Argon: Observed values of the speed of sound in argon at 0°C (see Fig. 5.3.15) are more scattered (around the fitted curve) at lower pressures. The data of van Itterbeek et al. [2.36] are about 0.5 m s^{-1} higher than the corresponding values from the fitted curve. The reported temperature of van Itterbeek's data is however 0.6°C higher so that it is valid to conclude that van Itterbeek's data is in agreement. El-Hakeem's data [2.24] at 0°C agree well with the fitted curve. No other data at higher pressure are available for comparison. At 25°C Lacam's data [2.31] (see Fig. 5.3.16) are significantly lower (by about 2 m s^{-1} to 3 m s^{-1}) than the values of the fitted curve at pressures from 5 to 20 MPa. At other pressures they agree well with the fitted curve. The low pressure scatter of the observed data is again evident.

c) Nitrogen: For nitrogen at 0°C (see Fig. 5.3.17) van Itterbeek's [2.21] data are slightly lower than the observed fitted values. El-Hakeem's data [2.24] however, agree well with the fitted curve. Comparable data at pressures higher than 8 MPa are not available. At 25°C (see Fig. 5.3.18) agreement of fitted observed values with the data of Lacam

[2.31] and van Itterbeek et al. [2.21] is good. Here, scatter in the observations at low pressure is much less evident.

6.3 Comparison of the Observed Thermodynamic Properties with those Derived from Equations of State

This discussion is assisted by consideration of general relations for the foundation parameters, namely;

$$p = \rho RTZ(\rho, T) \quad \dots\dots (6.3.1)$$

$$1/\kappa = \rho RT[Z + \rho(\partial Z/\partial \rho)_T] \quad \dots\dots (6.3.2)$$

$$\frac{\gamma - 1}{\gamma^0 - 1} = \frac{c_v^0}{c_v} \frac{[Z + T(\partial Z/\partial T)_\rho]^2}{Z + \rho(\partial Z/\partial \rho)_T} \quad \dots\dots (6.3.3)$$

$$a^2/RT = [Z + \rho(\partial Z/\partial \rho)_T] + (R/c_v)[Z + T(\partial Z/\partial T)_\rho]^2 \quad \dots\dots (6.3.4)$$

6.3.1 The van der Waals Equation. The performance of this equation of state is significantly worse than the other two equations in regard to every property concerned for all three gases and for both isotherms. In view of its simplicity, its total dependence on only two constants (the critical point values T_c and ρ_c) and its well known failure to provide a realistic value of Z even at the critical state which defines the equation, this is not surprising.

a) Compressibility Factor (Z): The values of Z calculated from this equation are worse for carbon dioxide

than for argon and nitrogen even at the same dimensionless density values (see Figs. 5.4.1 through 5.4.6). This appears to be due to the relatively high value of T_C for carbon dioxide (304.21 K) which enhances structural flaws in the temperature dependent term for carbon dioxide whereas for argon ($T_C = 150.7$ K) and nitrogen ($T_C = 126.3$ K) the deviation is much less significant. For carbon dioxide this equation provides the highest values of Z among both observed values and those calculated from other the two equations of state, while for argon and nitrogen this equation provides the lowest values of Z . The behaviour of other properties can be readily appreciated by this (Z) behaviour.

b) Normalized Isothermal Compressibility (κ/κ^0):

(See Figs. 5.4.7 through 5.4.12) The equation values of κ/κ^0 for carbon dioxide are the lowest among those presented while for argon and nitrogen they are the highest (excepting the low pressure region for argon). This is completely consistent with the behaviour of Z and of $\rho(\partial Z/\partial \rho)_T$ [refer to Eq. (6.3.2) and see Figs. 5.4.25 through 5.4.30].

c) Normalized Ratio of Specific Heats (γ/γ^0):

(See Figs. 5.4.13 through 5.4.18) The equation values of γ/γ^0 are less than those observed except for argon at moderately high pressures (≥ 20 MPa). The agreement is best for argon (within 2% at all pressures) and is worst for carbon dioxide.

This can be appreciated by comparing with the virial equation, which exhibits the best performance in argon and nitrogen and is significantly better than the van der Waals equation in carbon dioxide. From Eq. (6.3.3) it is seen that the dominant term is that involving the gradient of TZ with temperature ($Z + T\partial Z/\partial T$). This term is independent of temperature and is too low by the van der Waals equation at most state points concerned here. For the 0°C isotherm in carbon dioxide at a dimensionless density $\omega_0 = 0.1$ (about 2.24 MPa) an approximate calculation indicates $(\gamma-1)_{\text{vdw}}/(\gamma-1)_{\text{virial}} \approx 0.7$. On the same isotherm and at the same dimensionless density in nitrogen (about 3.4 MPa) a similar calculation gives $(\gamma-1)_{\text{vdw}}/(\gamma-1)_{\text{virial}} \approx 0.96$. These rough values are in fair agreement with the plotted curves.

d) Normalized Speed of Sound (a/a^0): (See Figs.5.4.19 through 5.4.24) The equation values of a/a^0 are very similar in behaviour to that of Z. This is to be expected since;

$$a/a^0 = [(\gamma/\gamma^0)(Z + \rho(\partial Z/\partial \rho)_T)]^{1/2}$$

where Z dominates in the range of interest. For carbon dioxide the equation values are as much as 6% too high. For argon the agreement is best (errors less than 3.5%) while for nitrogen the errors are up to about 7%.

6.3.2 The Hybrid Virial Equation. In general the agreement of the calculated properties with those observed, although not very good, is much better than van der Waals' equation. Comparison of the observed and calculated properties plotted in Figs. 5.4.1 through 5.4.30 indicates certain conclusions as to the validity of the hybrid virial equation and the pair of constants (b_{LJ}, θ) defining it for a given gas. These are;

a) The tabulated Lennard-Jones (6-12) potential-well-depth-temperature, for carbon dioxide ($\theta = 205$ K) is probably too low. This deduction is consistent with (low pressure range) calculated values for carbon dioxide of Z (too high), absolute value of the slope of Z (too high), κ/κ^0 (too low) and a/a^0 (too high). For argon and nitrogen these errors are relatively insignificant at comparable pressures. A plot of second virial coefficients $B(T)$ for carbon dioxide against temperature, can be found in [1.3,p202] along with the experimental second virial coefficients of MacCormack and Schneider [2.11]. (The values of the force constants used here for carbon dioxide are taken from this reference). From this plot it may be seen that the calculated $B(T)$ is higher by about 5% or more than the experimental $B(T)$ of MacCormack and Schneider [2.11] around 350 K. This also explains the high values of calculated

Z and the large deviation of properties dominated by Z for carbon dioxide. Similar plots may also be found for argon and nitrogen in [1.3], from which it may be seen that the agreement of Lennard-Jones $B(T)$ values is quite good with experimental $B(T)$ values. This explains why properties calculated by the virial equation agree very well with observed properties at lower pressure ranges for nitrogen and argon. An additional important point is that observations in carbon dioxide were near to the critical point, where both the van der Waals and the virial equation are relatively inaccurate.

b) The application of this two-constant spherically-symmetric-potential-based equation to non-spherical molecules appears to be inaccurate at least in regard to the third virial coefficient, C^* . The second virial coefficient is relatively insensible to molecular shape [1.3,p206]. The agreement of calculated Z with observed Z values is very good for (spherical) argon at all pressures. For (non-spherical) nitrogen, however, the error in Z is low at low pressures (where B^* is more influential) but steadily increases with increasing pressure (where C^* has greater influence). The same applies for other properties where Z dominates.

6.3.3 The Benedict-Webb-Rubin Equation. Among the three equations studied, the agreement of properties calculated

by the Benedict-Webb-Rubin equation with observed values is best. For Z and properties dominated by Z the agreement is, in general, excellent. This is as expected because the Benedict-Webb-Rubin equation is purely an empirical equation (with eight adjustable constants) formulated by fitting to thermodynamic property data.

From the comparison presented in Figs. 5.4.1 through 5.4.30, it may be seen that, among the three gases, the agreement of the slope properties for argon is not as good as for the other two gases. The large number of constants makes this difficult to explain. Argon is a non polar spherically symmetric molecule and it is therefore quite unexpected that predictions for argon are not as good as those for carbon dioxide and nitrogen. However, since the Benedict-Webb-Rubin equation is a fit to data, insensitivity to molecular shape is to be expected.

It may also be mentioned that in properties where temperature derivatives of TZ dominate, like (γ/γ^0) and to some extent, a/a^0 , the agreement of the Benedict-Webb-Rubin equation is considerably poorer than that of the virial equation. A flaw in one or more temperature terms in this equation is therefore indicated.

6.4 Recommendations for Further Study

1. Measurements at higher pressure ranges are needed to study the deviations of equation of state predictions from experimental values at very high pressures. The present apparatus is designed for pressures up to 40 MPa. It can be redesigned and modified for measuring properties at much higher pressure ranges.

2. Measurements at several closely spaced isotherms are required to obtain observed temperature-derivative properties such as $(\partial p / \partial T)_\rho$, $(\partial \rho / \partial T)_p$, $(\partial Z / \partial T)_\rho$ etc.

3. During the measurement of isothermal compressibility (by expanding the gas in the T-tube into the small chamber coil), the pressure quickly falls to a minimum as the valve is opened, and then rises slowly to the equilibrium pressure as demonstrated in Fig. 6.4.1. The initial decrease in pressure is due to adiabatic expansion. Measurement of this minimum pressure should provide an independent estimate of γ .

4. The bias error in the measurement of isothermal compressibility at higher pressure ranges can be reduced significantly using a smaller expansion chamber at these pressures.

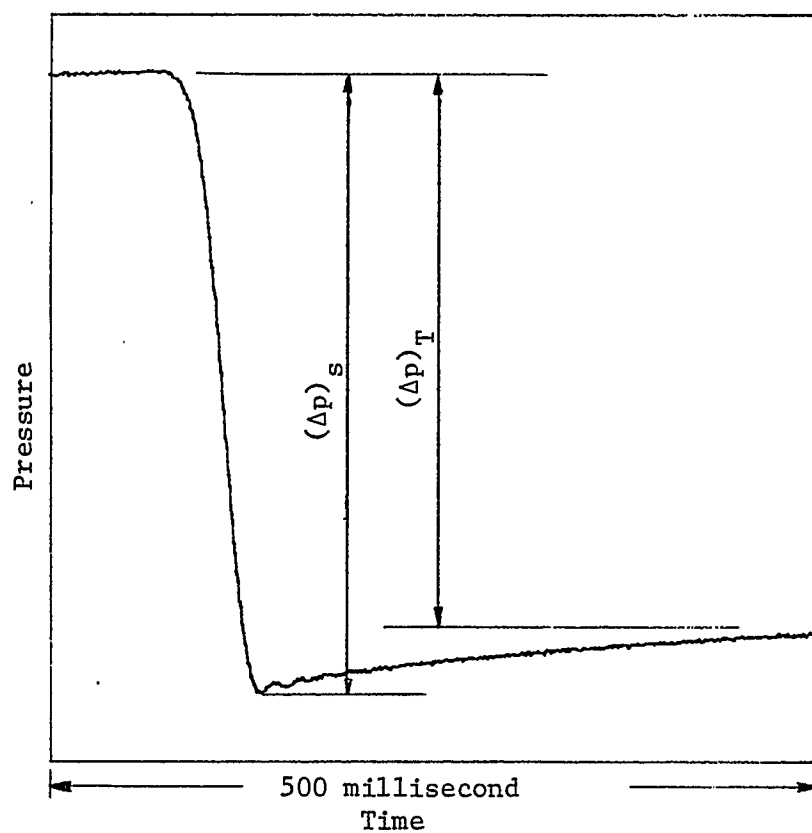


Fig. 6.4.1 Pressure Variation in the Decompression Tube Immediately after the valve connecting the Coil and the Decompression Tube is Opened; as seen on the oscilloscope and recorded by xy plotter.

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APPENDIX A1

A1.1 Details of Computation of Thermodynamic Properties by Equations of State

The computation of the desired thermodynamic properties are done by computer. The SI units are used throughout. The stepwise procedure for computation is given below.

1. Read the required constants for the particular equation, eg., molecular weight M in general; b_{LJ} , θ and b_h (estimated by Eq. (3.2.15) for an average temperature over the temperature range concerned) for hybrid virial equation; v_c and T_c for van der Waals equation ($b_{vdw} = v_c/3$); A , A_0 , B , B_0 , C , C_0 , α and γ for Benedict-Webb-Rubin equation.

2. Compute gas constant $R = \bar{R}/M$, $\bar{R}$ is the universal gas constant.

3. Read the temperature at which the computation is to be done.

4. For hybrid virial equation compute $T^* = T/\theta$ and interpolate the values of B^* , B_1^* , B_2^* , C^* , C_1^* and C_2^* from the tabulated values [1.3,p1114-1117] at the computed T^* . For van der Waals equation compute $T_r = T/T_c$.

5. Interpolate c_p^0 from the tabulated values (Table A1.2.3) for the given temperature.

6. Compute $c_v^0 = c_p^0 - R$

7. Compute $\gamma^0 = c_p^0 / c_v^0$

8. Compute $a^0 = (\gamma^0 RT)^{1/2}$

9. Assume an initial density ρ

10. Compute ω (for hybrid virial equation $\omega_{LJ} = \rho b_{LJ}$ and $\omega_h = \rho b_h$; for van der Waals equation $\omega_{vdw} = \rho v_c/3$; for Benedict-Webb-Rubin equation computation of ω is not required).

11. Compute Z

12. Compute $p = \rho RTZ = (\omega/b) RTZ$

13. Compute κ and $(\partial p / \partial T)_v$

14. Compute volume expansivity $\beta = \kappa (\partial p / \partial T)_v$

15. Compute c_{vR}

16. Compute $c_v = c_v^0 + c_{vR}$

17. Compute $c_p = c_v + T\beta^2 / \rho\kappa$

18. Compute $\gamma = c_p / c_v$

19. Compute $a = \gamma / \rho\kappa$

20. Compute $\rho (\partial Z / \partial \rho)_T = (1 / p\kappa - 1)Z$

21. Compute $\kappa^0 = 1/p$

22. Compute κ / κ^0

23. Compute γ / γ^0

24. Compute a / a^0

25. Increase ρ by some suitable step.

26. Repeat from step 10 until desired range of density or pressure is covered.

27. Read new T and repeat from step 4.

The expressions for Z , $(\partial p / \partial T)_V$, κ , and c_{VR} for the equations used are given in Sec. 3.2.

A1.2 Tables of Necessary Constants and Properties

Universal gas constant $R = 8314.3 \text{ J kmol}^{-1} \text{ K}^{-1}$

Avogadro's number $N = 6.0225 \times 10^{26} \text{ molecules kmol}^{-1}$

Boltzmann's constant $k = 1.3803 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$

Table A1.2.1 Molecular Weights, Critical Constants and Force Constants for the Gases used.

Gas	Molecular Weight M	p_c Pa	v_c $\text{m}^3 \text{ kg}^{-1}$	T_c K	b^* $\text{m}^3 \text{ kg}^{-1}$	θ^* K
Carbon Dioxide	44.0100	7383500.0	0.0021552	304.21	0.0019325	205.0
Argon	39.9480	4865000.0	0.0019493	150.70	0.0012466	119.8
Nitrogen	28.0134	3417000.0	0.0032206	126.30	0.0022996	95.9

* values are taken from [1.3] and reported after unit conversion.

Table A1.2.2 Benedict-Webb-Rubin Equation of State
Constants for the Gases Used.*

Constants	Carbon Dioxide	Argon	Nitrogen
A $(\text{m}^3 \text{kg}^{-1})^3 \text{Pa}$	0.162630 E 00	0.458340 E-01	0.115704 E 00
A ₀ $(\text{m}^3 \text{kg}^{-1})^2 \text{Pa}$	0.143211 E 03	0.522663 E 02	0.136050 E 03
B $(\text{m}^3 \text{kg}^{-1})^2$	0.212920 E-05	0.134907 E-05	0.296617 E-05
B ₀ $(\text{m}^3 \text{kg}^{-1})$	0.113383 E-02	0.557800 E-03	0.145440 E-02
C $(\text{m}^3 \text{kg}^{-1})^3 \text{K}^2 \text{Pa}$	0.177335 E 05	0.125448 E 04	0.335750 E 04
C ₀ $(\text{m}^3 \text{kg}^{-1})^2 \text{K}^2 \text{Pa}$	0.724928 E 07	0.834404 E 06	0.104061 E 07
α $(\text{m}^3 \text{kg}^{-1})^3$	0.993641 E-09	0.558252 E-09	0.578615 E-08
γ $(\text{m}^3 \text{kg}^{-1})^2$	0.278489 E-05	0.146524 E-07	0.675374 E-05

* values are taken from [3.9] and reported after unit conversion.

Table A1.2.3 Constant Pressure Specific Heat
at Ideal Gas State for the
Gases Used.

Temperature K	c_p^o $J\ kg^{-1}\ K^{-1}$		
	Carbon Dioxide ^a	Argon ^b	Nitrogen ^c
220.00	757.33	522.32	661.06
230.00	768.92		661.06
240.00	780.28		661.06
250.00	791.41		661.08
260.00	802.54		661.10
270.00	813.45		661.12
273.15	816.86		661.14
280.00	824.36		661.18
290.00	835.04		661.23
298.15	843.67		661.31
300.00	845.49		661.33
310.00	855.71		661.42
320.00	865.94		661.55
330.00	875.94		661.72
340.00	885.48		661.93
350.00	895.02		662.16
360.00	904.34		662.44
370.00	913.20		662.74
380.00	922.06		663.12
390.00	930.70		663.52
400.00	939.10		663.99

^a values are taken from [2.4] and tabulated after unit conversion.

^b for Argon c_p^o is virtually constant for the temperature range concerned and the reported value is taken from [2.7].

^c values are taken from [2.9] and tabulated after unit conversion.