Standard GERG Virial Equation for Field Use

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M. Jaeschke · A. E. Humphreys

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Simplification of the Input Data Requirements for the GERG Virial Equation – an Alternative Means of Compressibility Factor Calculation for Natural Gases and Similar Mixtures

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in memory

of our friend and colleague

RUSSELL COULTHURST

Errata for GERG Monograph TM-2 (1988)

verso	below ISBN	insert "also published as - Fortschritt-Berichte VDI series 6 number 231"
page iii	page number list	"6" should read "5" "41" should read "40" "45" should read "44"
page iv	page number list	"92" should read "94" "113" should read "112" "114" should read "113"
page v	first line	"IMPLEMENTATION" is misspelled
page 17	ref [25] date	"1966" should read "1965"
	ref [60] date	"1935" should read "1936"
page 23	data counts	"73" should read "72" "493" should read "492"
page 36	ref [60] date	"1935" should read "1936"
page 57	penultimate line	first "is" should read "are"
page 61	fifth line down	delete second "in"
page 75	fourth line down	"80" should read "8"
page 77	18th line down	insert "the" before "GERG"
page 88	15th line down	"(N37)" should read "(N37, N79)"
page 92	18th line down	"factor" should read "factors"
page 97	figure 5.16	faulty printing of data point for 280 K at 11 MPa
page 112	fifth line up	insert "," before "firstly"
page 148	reference 33(a)	run together lines 2 and 3
page 149	reference 45	"1251" should read "1250"
page 158	first definition of N	incorrect line spacing of text

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Abstract

This Monograph provides a detailed account of the concept, development, performance and use of the Standard (or Simplified) GERG-88 Virial Equation for the accurate calculation of compressibility factors for natural gases. The equation has been developed from the Master (or Molar) GERG-88 Virial Equation - described fully in GERG Technical Monograph TM2 - and utilises a restricted set of input variables in place of the detailed (13 component) composition analysis required for the Master equation. The simplified input data requirement comprises any three from superior (gross) calorific value, relative density, carbon dioxide content (the usual set) and nitrogen content, together with pressure and temperature. Even with this minimal information, the equation predicts the compressibility factor Z(p,T) within the respective pressure and temperature ranges of 0 to 12 MPa (0 to 120 bar) and 265 to 335 K (-8 to 62 ^{o}C) with an expectation accuracy which, at about 0.1%, matches that of the Master equation. For mixtures containing manufactured (coke-oven) gas, the amount of hydrogen must also be known.

The principle involved in the new development is to consider any natural gas as a 3-component mixture containing carbon dioxide, nitrogen and an "equivalent hydrocarbon" CH which represents all of the alkane hydrocarbons collectively as a single pseudo-component. Given the mole fraction of either inert component, it turns out that both the mole fraction and the virial coefficients of the equivalent hydrocarbon may be inferred through knowledge of the superior calorific value and relative density of the whole natural gas, i.e. these two properties are sufficient to characterise the gas uniquely.

Coefficients used in the Standard GERG-88 Virial Equation have either been taken directly from those used in the Master equation or, for the equivalent hydrocarbon, derived from available data for actual natural gases. The resulting equation describes the set of some 4,500 data points, for natural gases in the GERG databank of compressibility factors, with a root-mean-square error of 0.049%.

Numerical values for all coefficients needed to implement the equation are given, together with flow diagrams showing the iterative structure of an efficient calculational procedure; computer program listings are provided.

The Standard GERG-88 Virial Equation was developed at the van der Waals Laboratorium of the University of Amsterdam, under contract to, and with specific guidance from, the Groupe Européen de Recherches Gazières.

Zusammenfassung

In dieser Monographie werden im Detail das Konzept, die Entwicklung, die Güte und der Gebrauch der Standard (oder Vereinfachten) GERG-88 Virial-Gleichung zur genauen Berechnung der Realgasfaktoren von Erdgasen beschrieben. Die Gleichung ist von der Master (oder Molaren) GERG-88 Virial-Gleichung, die ausführlich im GERG Technical Monograph TM2 beschrieben worden ist, abgeleitet worden. Sie benutzt nur einen reduzierten Satz von Eingabegrößen anstelle einer detaillierten Gasanalyse (13 Komponenten), die von der Master-Gleichung benötigt wird. Als vereinfachter Eingabedatensatz kommen dabei drei der folgenden Größen in Frage: der Brennwert, die relative Dichte, der Kohlendioxid-Anteil (dies sind die üblichen Eingabegrößen) und der Stickstoff-Anteil zusammen mit dem Druck und der Temperatur. Selbst mit dieser minimalen Information ist es möglich, mit der Gleichung den Realgasfaktor Z(p,T) innerhalb der Druck- und Temperaturbereiche von 0 bis 12 MPa (0 bis 120 bar) und 265 bis 335 K (-8 bis 62 $^{\circ}$C) mit einer Voraussagegenauigkeit von etwa 0,1% zu bestimmen. Damit ist diese Gleichung der Master-Gleichung ebenbürtig. Für Gemische, die Zumischungen von künstlich hergestellten Gasen (Kokereigas) enthalten, muß zusätzlich der Wasserstoffanteil bekannt sein.

Das wesentliche Prinzip dieser Neuentwicklung ist, jedes Erdgas als ein Drei-Komponenten-Gemisch zu betrachten, welches Kohlendioxid, Stickstoff und ein "äquivalentes Kohlenwasserstoffgas" CH enthält. Hierbei werden alle vorhandenen, gesättigten Kohlenwasserstoff gemeinsam durch diese einzelne Pseudokomponente, das CH-Gas, repräsentiert. Ist der Molanteil eines der inerten Gase bekannt, so läßt sich sowohl der Molanteil als auch die Virialkoeffizienten des äquivalenten Kohlenwasserstoffgases allein aus der Kenntnis des Brennwertes und der relativen Dichte für das ganze Erdgas ableiten; d.h., diese beiden Eigenschaften reichen aus, um das Gas vollständig zu charakterisieren.

Die Virialkoeffizienten, die in der Standard GERG Virial-Gleichung benutzt werden, sind entweder direkt von der Master GERG Virial-Gleichung übernommen oder für das äquivalente Kohlenwasserstoffgas aus den vorhandenen Daten für tatsächliche Erdgase abgeleitet worden. Die so aufgebaute Gleichung beschreibt die Realgasfaktoren für Erdgase aus der GERG-Datenbank von etwa 4500 Punkten mit einem mittleren quadratischen Fehler (rms-error) von 0,049%.

Alle Zahlenwerte für die Koeffizienten der Gleichung, die zur Implementierung notwendig sind, sind zusammen mit den Fließdiagrammen, die die iterative Struktur für eine effiziente Berechnungsprozedur aufzeigen, aufgeführt; die Listings der Computerprogramme werden mitgeliefert.

Die Standard GERG-88 Virial-Gleichung wurde vom Van der Waals Laboratorium der Universität von Amsterdam im Auftrag und unter der Leitung der "Groupe Européen de Recherches Gazières" entwickelt.

Acknowledgements

Once again it is our pleasure to record our thanks to GERG Programme Committee No.1, and especially to its former chairman Dr Alec Melvin, for recognising and responding to the urgent need of the international community of natural gas engineers (and others) for a new, accurate and reasonably simple method with which to predict compressibility factors for natural gas and similar mixtures, and for supporting the consequent efforts of GERG Working Group 1.1 in this area. Both the timeliness of the developments described in this and previous GERG Monographs from WG-1.1, and their success, are evidenced by the intention of the International Organization for Standardization (ISO) to incorporate the Standard GERG-88 Virial Equation into a new international standard method for the calculation of compressibility factor.

The Working Group could not have achieved its success without the detailed correlational work carried out under contract to GERG at the University of Amsterdam by Dr Jan Schouten and Dr Jan Michels.

Manfred Jaeschke
Tony Humphreys

August 1991

1 - INTRODUCTION

1.1 Compressibility Factor Calculation in the Natural Gas Industry

In reference (1)* a new equation, known now as the Master GERG-88 Virial Equation, was introduced as a means for the accurate calculation of the compressibility factors Z(p,T) of natural gases and similar mixtures for wide ranges of temperature T, pressure p and composition. The importance of such calculations in custody transfer, transmission and distribution applications, in particular for use in equations governing orifice plate and sonic nozzle metering, and in conversion of gas volumes to values at reference conditions, was emphasized.

The development of the Master GERG-88 Equation depended crucially upon a contracted collaboration between the Groupe Européen de Recherches Gazières (GERG), whose members carried out an extensive series of measurements on pure gases, binary, ternary, multicomponent and natural gas mixtures, and the van der Waals Laboratorium of the University of Amsterdam, where the correlational work was performed.

Given a sufficiently detailed compositional analysis, the accuracy achieved by the Master GERG-88 Equation is approximately 0.1% in the temperature range 265 to 335 K and pressures up to 12 MPa.

Despite the considerable technical advance represented by this achievement, it remains true that there are many situations in which such a detailed composition of a natural gas is not available. Consequently, it would perhaps be even more valuable to have an alternative equation of similar accuracy, but requiring fewer input parameters. The obvious candidates for such a restricted set of input parameters are superior calorific value (higher or gross heating value) and relative

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* Figures in parentheses refer to literature citations - see Section 9.

density (specific gravity), which are commonly available in the gas industry from direct measurements made for other purposes. This in itself is not a new idea, but no previous "restricted" or "simplified input" method has achieved sufficient accuracy to represent a mature and general challenge to the more traditional methods which use the detailed compositional analysis.

1.2 Current Restricted Input Methods

As indicated above, calculational methods employing a restricted set of input parameters have been developed previously. Whether such developments can be classified as successful or not depends upon the accuracy required for a particular application; however, in the context of current industry requirements for an accuracy of about 0.1%, no extant method can be considered as more than a somewhat limited success.

Some European gas utilities presently use modified versions of the AGA NX-19 method (2). In the case of lean natural gases with calorific values lower than that of methane, the compressibility factor is calculated using the AGA NX-19-mod technique (3), while the modification AGA NX-19-mod/3H (4) is employed for rich natural gases with calorific values higher than that of methane. Both modifications are used in custody transfer applications when only a simplified gas analysis consisting of superior calorific value, relative density and carbon dioxide content is available.

The agreement between compressibility factors predicted by the AGA NX-19-mod method and measured compressibility factors of lean natural gases (group L gases) is adequate for low pressures and high temperatures. The difference between predicted and measured compressibility factors increases as pressure rises, however, and may be as large as 0.7% for low temperatures (see Figure 1.1).

The AGA NX-19-mod/3H method was developed as a simple correction of the AGA NX-19-mod method, using a best fit for group H natural gas data. The correlation is only valid in the pressure range up to 9 MPa and in the temperature range between 263 and 303 K. In this range the difference between compressibility factors calculated by the AGA NX-19-mod/3H method and measured values for Ekofisk-type gas are less than 0.2%. However, for higher pressures and higher temperatures the difference may be as much as 1% (see Figure 1.2) (1).

More recently, a version of the GRI-SuperZ equation has been published, as part of the AGA-8-1985 report (5), which accepts a simplified set of input parameters instead of the more usual detailed compositional analysis. The GRI-SuperZ equation was developed by Starling (5), under contract to the Gas Research Institute (GRI) in Chicago. The simplified version of the SuperZ equation is based on the same set of input parameters as for the modified AGA NX-19 method. The compressibility factors calculated by the simplified GRI-SuperZ equation, using superior calorific value, relative density and carbon dioxide content as input data, are compared with experimental data for several typical natural gases in Figure 1.3 for the 270 K isotherm. It is clear that acceptable accuracy is only obtained by this method in the lower pressure range. In general the accuracy of the simplified GRI-SuperZ equation does not approach that of either the detailed analysis SuperZ equation or the Master GERG-88 equation. The equation is not valid for mixtures of natural gas and coke-oven gas, which contain hydrogen.

In view of the rather limited accuracy and applicability of the various equations mentioned, the (then) GERG Thermodynamics Committee decided to support the development of an equation of state for field use (i.e. one for which the relevant input data are readily available in operational situations) with a target uncertainty of 0.1% for predicted compressibility factors. The approach taken was firstly to develop an accurate equation state based upon knowledge of the detailed gas composition, and secondly to simplify this equation by reducing the input data requirements. The development of such a simplified equation is fully described and documented in this Monograph.

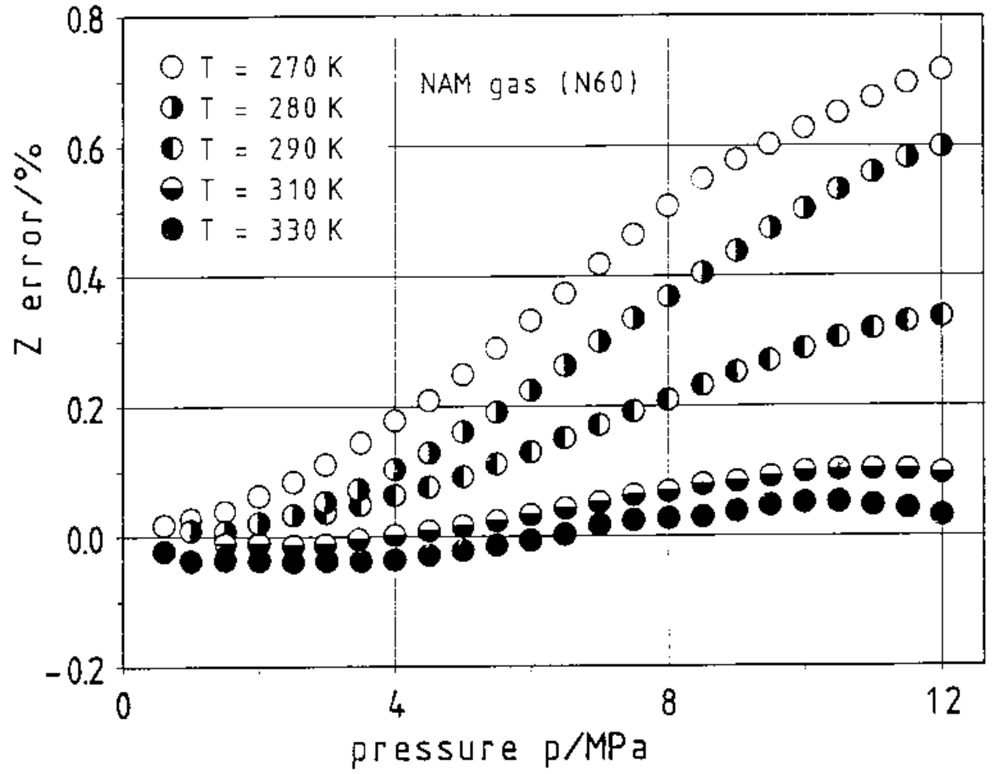

Figure 1.1 Z-Error (Deviation) Plot for a Lean Natural Gas (NAM gas). Calculated Z Values are from the AGA NX-19-mod Equation (3). (Reprinted from ref.1.)

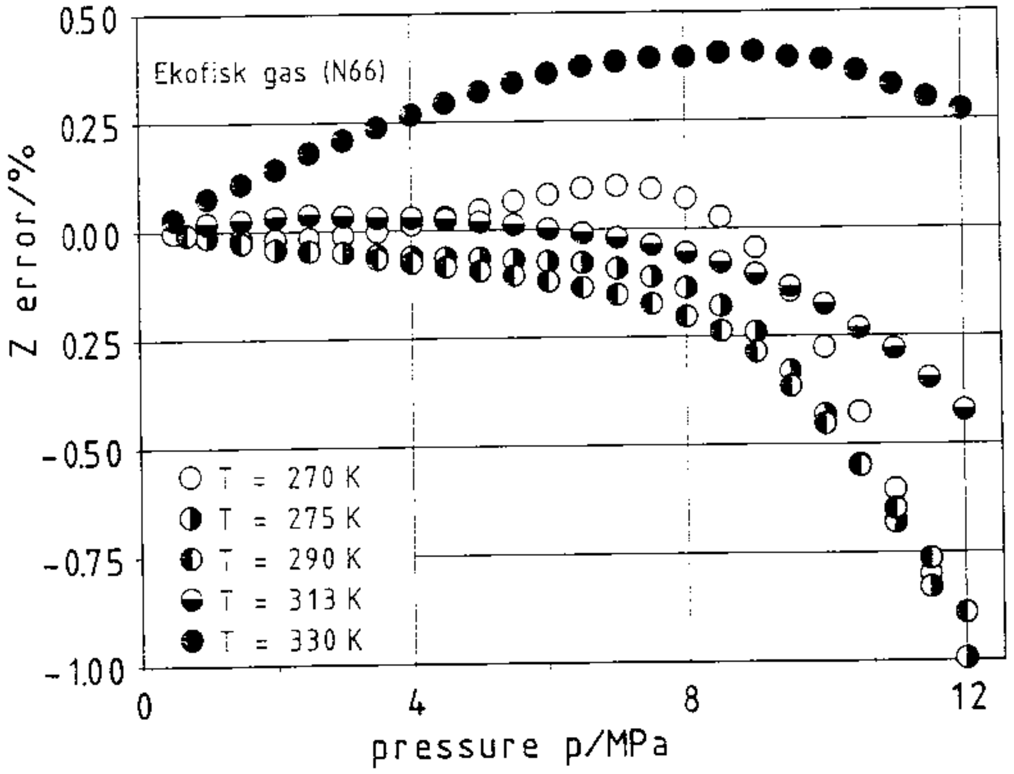

Figure 1.2 Z-Error Plot for a Rich Natural Gas of the Ekofisk Type. Calculated Z Values are from the AGA NX-19-mod/3H Equation (4).

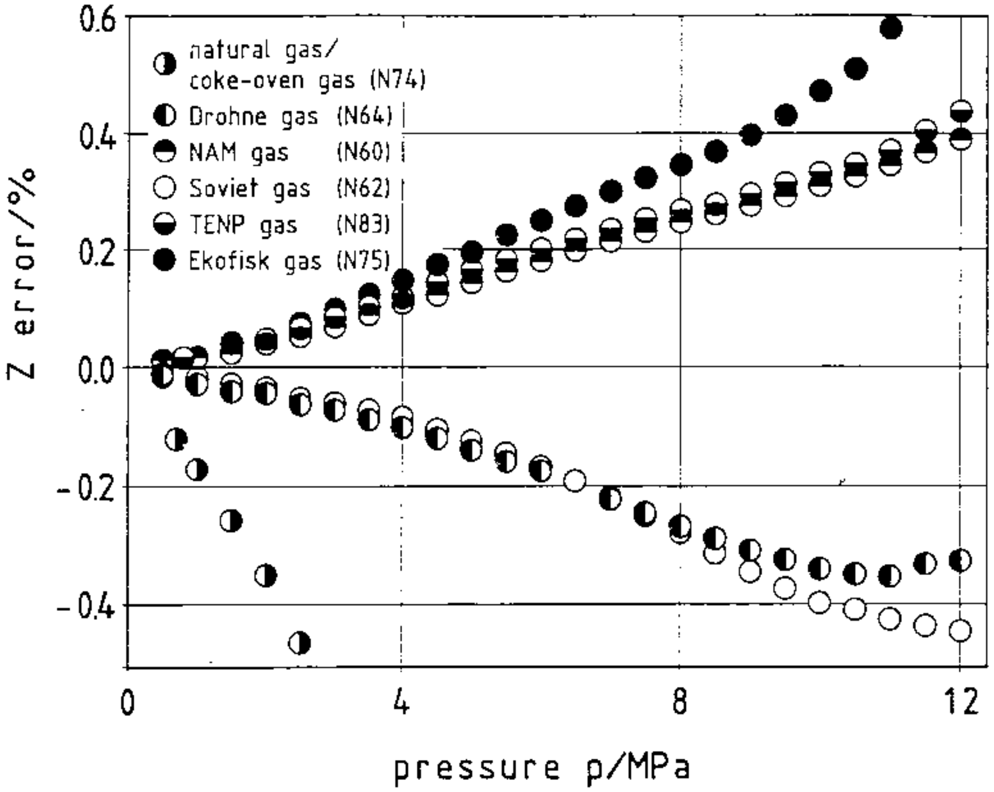

Figure 1.3 Influence of Pressure on Z-Error for the Simplified AGA-8 or GRI-SuperZ Equation based on a Restricted Gas Analysis (5) for several Natural Gases at 270 K.

$$Z\text{-Error} = (Z_{calc} - Z_{expt})/Z_{expt} \cdot 100\%$$

Sources of Z_{expt} are identified in the later text.

The resulting Standard GERG-88 Virial Equation is a simplified (restricted input) version of the original (detailed analysis input) Master GERG-88 Virial Equation; the latter is documented in a previous Monograph (1). Some aspects of the development and performance of the Standard GERG-88 Virial Equation have already been presented at the 10th Symposium on Thermophysical Properties in Gaithersburg and at a Gas Technology Symposium in Dallas (6), both held in 1988, and published respectively in the International Journal of Thermophysics (7) and SPE Production Engineering (8). A poster presentation was also made at the 1989 International Gas Research Conference (IGRC) in Tokyo (9).

1.3 **Specification for the Standard GERG Virial Equation**

The Standard GERG-88 Virial Equation can predict the compressibility factor when three of the following four properties of the gas are known -

* the superior (gross) calorific value H_S
* the relative density (specific gravity) d
* the mole fraction of nitrogen x_2, and
* the mole fraction of carbon dioxide x_3.

Throughout this Monograph, however, the selection as input parameters of calorific value, relative density and mole fraction of carbon dioxide is emphasized and recommended. This is because these are the three most amenable to direct measurement and, consequently, most commonly available. The other possible input parameter groups are discussed briefly in sub-section 5.5; the principles involved are entirely analogous.

It is also possible to use the calculation method for natural gases containing hydrogen admixture, but in this case the mole fraction of hydrogen needs additionally to be known. It is then also assumed that the presence of hydrogen implies the presence of a corresponding amount (i.e. a fixed ratio) of carbon monoxide, as is usually the case for coke-oven gases.

The following input parameter ranges were specified by the European Gas Research Group (GERG) for the Standard GERG Virial Equation (see Table 1.1). They are modelled on the specifications for the Master GERG-88 Virial Equation (1).

Table 1.1 Specification for the Standard GERG-88 Virial Equation

Maximum Uncertainty in Z	± 0.1%
Temperature Range	$265 \le T/K \le 335$
Pressure Range	$0 < p/MPa \le 12$
Reduced (simplified) Gas Analysis -	
Superior Calorific Value at N.T.P.[*]	$19 \le H_s/MJ\ m^{-3} \le 48$
Relative Density at N.T.P.[+]	$0.55 \le d \le 0.90$
Mole Fraction of Nitrogen	$0 \le x_2 \le 0.5$
Mole Fraction of Carbon Dioxide	$0 \le x_3 \le 0.3$
Mole Fraction of Hydrogen	$0 \le x_4 \le 0.1$

The ranges of conditions are limited to those of interest in metering on European transmission installations. The temperature range is 265 to 335 K and the pressure range up to 12 MPa. The property and composition specifications given in Table 1.1 are chosen to cover a wide variety of natural gases.

Although it is intended and anticipated that the simplified version of the GERG-88 Virial Equation will be valid for all generic natural gases (with or without coke-oven gas admixture), this may not be so for entirely manufactured gas mixtures. The reason for this proviso is that in natural gases the mole fraction of methane strongly predominates that of any other hydrocarbon; furthermore the mole fractions of the higher hydrocarbons diminish in a uniform and reasonably consistent pattern which does not vary substantially, even

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[*] Superior calorific value at the following reference conditions -
metering : $T = 273.15$ K, $p = 101.325$ kPa (N.T.P.)
combustion : $T = 298.15$ K

[+] Density is relative to dry air of standard composition at the following reference conditions -
temperature $T = 273.15$ K, pressure $p = 101.325$ kPa.

for markedly different natural gases. These features, which are essential in establishing a simple characterisation of an "equivalent hydrocarbon" for the paraffinic (alkane) part of the mixture, may not be valid for manufactured gas mixtures (see sub-section 2.2).

The concentration of each hydrocarbon is limited by the maximum allowable value applicable for the Master GERG-88 Virial Equation (1). These limits are summarized again in Table 1.2. The equation is only valid for nominally dry natural gases .

Table 1.2 Specification of the Gas Composition by Mole Fractions

1	CH_4	≥ 0.5	6	C_3H_8	≤ 0.05	11	C_6	≤ 0.001
2	N_2	≤ 0.5	7	CO	≤ 0.03	12	C_7	≤ 0.001
3	CO_2	≤ 0.3	8	C_4H_{10}	≤ 0.015	13	C_{8+}	≤ 0.001
4	C_2H_6	≤ 0.2	9	He	≤ 0.005			
5	H_2	≤ 0.1	10	C_5H_{12}	≤ 0.005			

Under these conditions the accuracy of the results predicted by the Standard GERG-88 Virial Equation using a restricted, or simplified, set of input data, is expected to be within 0.1%. This level of accuracy refers to normal situations where the equation is to predict true gas-phase compressibility factors, computations not being made near a phase-separation surface and particularly not in the vicinity of the gas-liquid critical point.

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2 - PRINCIPLES AND METHODOLOGY

2.1 Basic Concepts: The Three-Component Truncated Virial Equation

The real-gas behaviour of any gas is described by

$$Z = p/\rho_m RT \qquad (2.1)$$

where (in coherent SI units)

Z = compressibility (or compression) factor - dimensionless
p = pressure/Pa
ρ_m = molar density/mol m^{-3}
R = universal gas constant, 8.314510 J mol^{-1} K^{-1}, and
T = temperature/K.

In this Monograph we more commonly give p in MPa, ρ_m in kmol m^{-3} and R in MJ kmol^{-1} K^{-1} in order that other quantities, such as virial coefficients, may be expressed in more familiar units. The validity of the equation does not, of course, depend upon the choice of units.

The equation of state chosen here for predicting the compressibility factors for natural gases is a truncated version of the familiar virial series, i.e. a series in ascending powers of the density. Reasons for this choice have been given in detail previously (1).

The virial equation of state, truncated after the third term, has the form

$$Z(p,T) = 1 + B_{mix}(T)\cdot\rho_m + C_{mix}(T)\cdot\rho_m^2 \qquad (2.2)$$

In this equation $B_{mix}(T)$ and $C_{mix}(T)$ are the second and third virial coefficients, which are functions of temperature and composition only. The second and third virial coefficients respectively describe the effects of binary and ternary interactions between molecules; such interactions result in deviations from the ideal gas law (Z=1).

Expressions for the second and third virial coefficients are provided by statistical mechanics for a multicomponent mixture of arbitrary composition as follows -

$$B_{mix}(T) = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j B_{ij}(T) \qquad (2.3)$$

$$C_{mix}(T) = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} x_i x_j x_k C_{ijk}(T) \qquad (2.4)$$

where x_i, x_j and x_k represent the molar (or mole) fractions of the i-th, j-th and k-th components respectively.

For a binary mixture of species i and j equations (2.3) and (2.4) reduce to the expressions -

$$B_{mix}(T) = x_i^2.B_{ii} + 2x_i x_j.B_{ij} + x_j^2.B_{jj} \qquad (2.5)$$

$$C_{mix}(T) = x_i^3.C_{iii} + 3x_i^2 x_j.C_{iij} + 3x_i x_j^2.C_{ijj} + x_j^3.C_{jjj} \qquad (2.6)$$

In these equations B_{ij} represents the unlike interaction second virial coefficient, which is purely a function of the forces of interaction between a pair of dissimilar molecules; subscript i denotes species i and subscript j species j. Similarly C_{iij} represents the third virial coefficient for the 3-body interaction between two molecules of species i and one molecule of species j, and so on.

The virial coefficients of a mixture are thus obtained by combination of (a) the virial coefficients for the pure components, describing the interactions between like molecules (B_{ii}, B_{jj}, C_{iii}, C_{jjj} etc.), (b) those for the mixed interaction between the unlike molecules in binary systems (B_{ij}, C_{iij}, C_{ijj} etc.), and (c) C_{ijk} for the interaction between three unlike molecules in multicomponent mixtures. Virial coefficients of the type B_{ij} and C_{ijk} are functions of temperature, but not of pressure or composition.

By means of individual correlations of experimental gas density data on each isotherm for each natural gas for pressures up to 12 MPa, it was shown in ref.1 that a second order equation is just sufficient to describe accurately the density data, i.e. the virial equation could justifiably be truncated after the third term, the fourth and higher virial coefficients being omitted.

GERG Monograph TM2 (1) describes in detail the development of a truncated virial equation based upon the assumption that any natural gas can be adequately characterised by its composition, when this is taken to consist of 13 different components. A large amount of data concerning the volumetric behaviour of pure gases and their binary mixtures had to be taken into account in order to evaluate the necessary virial coefficients. Fortunately the contribution of many virial coefficients to the compressibility factor is very small, due either to low numerical values or to low component concentrations. Consequently, the contributions of those binary and ternary interactions having methane as one component, and those binary interactions between the components N_2, CO_2, H_2 and C_2H_6 are the most important to take into account.

The simplified version of the GERG-88 Virial Equation retains the truncated form, but does not require a gas mixture to be characterised by means of its detailed composition. It is based instead on the concept that the entire mixture may be represented and replaced by a 3-component mixture containing (in the absence of hydrogen) carbon dioxide, nitrogen and an "equivalent hydrocarbon" CH which represents all of the alkane hydrocarbons collectively as a single pseudo-component. The problem then is to adequately characterize the equivalent hydrocarbon in terms of known physical properties of the whole mixture. Results obtained from the Master GERG Virial Equation may be used in helping to evaluate the interactions between the three components present in the simplified treatment.

2.2 The Equivalent Hydrocarbon and its Characterisation

For this new, simplified, approach to the truncated virial equation, we identify the three components as follows -

component 1 - equivalent hydrocarbon gas - CH
component 2 - nitrogen - N_2
component 3 - carbon dioxide - CO_2.

As implied above, the equivalent hydrocarbon (abbreviated CH) must collectively represent all hydrocarbons present in the natural gas in such a way that its volumetric properties mimic those of the several components it replaces. The volumetric properties of the other components (N_2 and CO_2) are described in the usual way, i.e. in terms of their virial coefficients B and C. The latter are well-known from pVT-measurements (1). For the equivalent hydrocarbon CH, however, the virial coefficients have to be related to a quantity which is characteristic for a specific gas. Here, the molar heating value H_{CH} will be used as this characteristic property.

It is demonstrated in sub-section 3.4.3 that the second and third virial coefficients of the equivalent hydrocarbon gas may be taken as related to its molar heating value H_{CH} by

$$B_{CH}(T,H_{CH}) = \beta_{H0}(T) + \beta_{H1}(T).H_{CH} + \beta_{H2}(T).H_{CH}^2 \qquad (2.7)$$

$$C_{CH}(T,H_{CH}) = \epsilon_{H0}(T) + \epsilon_{H1}(T).H_{CH} + \epsilon_{H2}(T).H_{CH}^2 \qquad (2.8)$$

H_{CH} can be derived from the known superior (gross) calorific value H_s, relative density d and carbon dioxide content x_3 of the whole natural gas. Self-evidently, the experimentally accessible properties H_s and d are properties of the whole natural gas, not of the equivalent hydrocarbon. Consequently it has been necessary to develop relationships which enable the conversion of H_s and d to H_{CH} and M_{CH}, where M_{CH} is the molar mass of the equivalent hydrocarbon gas. The development and use of these relationships will be described in Section 5.

It should be emphasized that, although any natural gas may be described as a three-component system, the third pseudo-component is, in principle, different for each individual natural gas. For example, two distinct natural gases could have the same mole fractions of N_2, CO_2 and CH but, if H_S and d are different, the composition of the equivalent hydrocarbon is different and therefore H_{CH} has a different value.

The three-component model is useful only if the input data used to specify the third component (superior calorific value, relative density and mole fraction of carbon dioxide) characterise the volumetric behaviour of that component with sufficient accuracy. Because of the dominance of methane in natural gas mixtures and the observed regularity with which the proportions of higher hydrocarbons decrease towards the "tail" of a typical natural gas, it is likely, whatever the absolute concentrations of the component hydrocarbons, that adequate characterisation may be achieved. This matter will be considered more fully, and proper justification of these assertions given, in sub-section 3.4.3. However, for manufactured gas mixtures or natural gas/coke-oven gas mixtures, such regularities are not guaranteed, with the consequence that a correspondingly simple characterisation cannot be established.

2.3 <u>Natural Gases with Hydrogen or Carbon Monoxide Admixture</u>

For natural gas/coke-oven gas mixtures and natural gases without admixtures, it is possible to have the same reduced set of input data but a quite different composition of the "equivalent hydrocarbon gas". Table 2.1 gives an example of two such gases, which are quite similar to the gases N43 and N68 of the GERG databank N-file (10).

Both gases have the same reduced gas analysis, viz.

- mole fraction of CO_2 : 0.0171
- calorific value : 39.12 MJ m^{-3}
- relative density : 0.6296

Even the mole fractions of nitrogen are nearly identical for these gases, 0.0550 and 0.0537 respectively. However, the mole fractions of the hydrocarbons differ appreciably, as one mixture also contains 0.0440 mole fraction of hydrogen.

Table 2.1 Example of a Natural Gas and a Natural Gas/Coke-Oven Gas Mixture having Similar Reduced Analyses

Component		**Composition by Mole Percent**	
		Natural Gas	N.G./Coke-Oven Gas
Nitrogen	N_2	5.50	5.37
Carbon Dioxide	CO_2	1.71	1.71
Hydrogen	H_2	0	4.40
Carbon Monoxide	CO	0	0.38
Helium	He	0	0.02
Methane	CH_4	88.00	80.08
Ethane	C_2H_6	3.31	5.55
Propane	C_3H_8	0.92	1.69
Butanes	C_4H_{10}	0.33	0.55
Pentanes	C_5H_{12}	0.14	0.12
Hexanes	C_6H_{14}	0.05	0.03
Heptanes	C_7H_{16}	0.03	0.01
Octanes	C_8H_{18}	0.01	0.01
Ethylene	C_2H_4	0	0.08

Property*		
Gross Calorific Value/MJ m^{-3}	39.12	39.12
Relative Density	0.6294	0.6294
Density at N.T.P./kg m^{-3}	0.8137	0.8137
Molecular Weight	18.190	18.190

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* Properties calculated using ref.25(b) for the real gas.

Consequently the compressibility factors for these two gases are different and it is, in principle, not possible to describe the volumetric behaviour of the hydrocarbon-plus-hydrogen gas mixture with the basic "three-component" model.

A solution to this problem, however, is to use an additional fourth input parameter. As this Extended Standard GERG Virial Equation is intended primarily for use with natural gas/coke-oven gas mixtures, the hydrogen content may sensibly be chosen as the fourth input parameter. In the extended equation the natural gas/coke-oven gas mixture is then treated internally as a five-component system with -

component 4 - hydrogen - H_2
component 5 - carbon monoxide - CO.

The mole fraction of the fifth component, carbon monoxide, is assumed to bear a fixed ratio to the hydrogen content, in order to mimic the reality of coke-oven gas mixtures. The small amount of ethylene also generally present in such mixtures is not considered as a separate component; its volumetric behaviour is somewhat similar to that of carbon dioxide, to which component minor amounts are assigned in the Master GERG-88 Virial Equation. However, the input to the Standard GERG-88 Equation must also take into account its contribution to the calorific value, irrespective of whether the latter is directly measured or calculated from composition (see sub-sections 3.4.1, 3.4.2 and 3.5.3 for further details.

2.4 Temperature Dependence of Virial Coefficients

A second-order polynomial (i.e. quadratic) function has been used throughout this work to describe the variation with temperature of all second and third virial coefficients, viz.

$$B(T) = b^{(0)} + b^{(1)}T + b^{(2)}T^2 \qquad (2.9)$$

$$C(T) = c^{(0)} + c^{(1)}T + c^{(2)}T^2 \qquad (2.10)$$

The acceptability of this entirely empirical formulation was previously tested extensively in the temperature range 265 to 335 K (1). Comparison of the results of using second and third order polynomials to fit the virial coefficients from the research literature for methane gives no indication of any need to go beyond a second-order polynomial in temperature.

A quadratic dependence upon temperature has also been used for the quantities β_{Hq} and ϵ_{Hq} (where q=0,1,2) in equations (2.7) and (2.8).

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3 - EVALUATION OF VIRIAL COEFFICIENTS

3.1 GERG Contract with the van der Waals Laboratory

The development of the Master GERG-88 Virial Equation, in particular the correlation method used in generating second and third virial coefficients from selected data sets for pure gases and binary mixtures, is discussed in detail in the previous GERG Monograph TM2 (1). The correlational work was carried out at the van der Waals Laboratory in Amsterdam under a contract awarded by, and with specific guidance from, the European Gas Research Group (GERG).

The additional work necessary to achieve the simplification of the GERG virial equation, so as to be able to predict compressibility factors for natural gas mixtures using a reduced set of input data, was also carried out at the van der Waals Laboratory. The main reasons for taking the step of awarding a contract to this renowned institution were discussed previously (1).

3.2 Pure Component Second and Third Virial Coefficients

The pure component virial coefficients for N_2, CO_2, H_2 and CO are taken from the previous GERG Monograph (1). There the evaluation was made using a maximum-likelihood-surface fit for each pure gas, correlating the virial coefficients obtained from the fit of Z against ρ_m for each value of T (equation (3.1) below) to second-degree polynomials in temperature (equations (3.2) and (3.3)), viz.

$$Z(p,T) = 1 + B_{ii}(T) \cdot \rho_m + C_{iii}(T) \cdot \rho_m^2 \qquad (3.1)$$

$$B_{ii}(T) = b_{ii}^{(0)} + b_{ii}^{(1)} \cdot T + b_{ii}^{(2)} \cdot T^2 \qquad (3.2)$$

$$C_{iii}(T) = c_{iii}^{(0)} + c_{iii}^{(1)} \cdot T + c_{iii}^{(2)} \cdot T^2 \qquad (3.3)$$

where the subscripts ii and iii identify the i-th pure gaseous species.

For the evaluation of the coefficients for the pure components, the sources of data listed in Table 3.1 were used. The selection of the data was justified previously (1).

Table 3.1 Pure Gas Data Sets used for the Correlation

Nitrogen	Roe (1972)	ref.11
	Michels (1934)	ref.12
Carbon Dioxide	Michels (1936)	ref.13
Hydrogen	Jaeschke (1987)	ref.14
	Michels (1959)	ref.15
Carbon Monoxide	Michels (1952)	ref.16

The numerical values derived for the various b's and c's are given in Section 4, Tables 4.1 and 4.3 respectively, reproduced from the corresponding tables in ref.1.

Both the source data and other good quality experimental data have been compared back with values of Z calculated from the virial equation of state, taking for B(T) and C(T) the values given by these tables. The results of this comparison are summarized in Table 3.2. This clearly shows that, in the pressure and temperature ranges to be considered, the selected source data for each pure component can be described by equation (3.1) with a root-mean-square deviation (rms) within 0.021%, though for some other data (for carbon dioxide) the rms deviation is somewhat greater.

3.3 Unlike Interaction Second and Third Virial Coefficients of Systems containing Nitrogen, Carbon Dioxide, Hydrogen and Carbon Monoxide

The unlike interaction virial coefficients for a binary system can be expressed as a combination of the pure component virial coefficients and the virial coefficients of the mixture, as expressed by equations (2.5) and (2.6), viz.

$$B_{mix}(T) = x_i^2 . B_{ii} + 2x_i x_j . B_{ij} + x_j^2 . B_{jj} \qquad (2.5)$$

$$C_{mix}(T) = x_i^3 . C_{iii} + 3x_i^2 x_j . C_{iij} + 3x_i x_j^2 . C_{ijj} + x_j^3 . C_{jjj} . \qquad (2.6)$$

Table 3.2 Comparison of Calculated and Experimental Values for the Compressibility Factors of Pure Gases

Data Source ref.	**Pressure Range/MPa**	**Temperature Range/K**	**Number of Points**	**rms-% Deviation in Z(p,T)**
Nitrogen:				
Roe (11)	0- 5.6	277-291	10	0.003
Michels (12)	0- 6.4	273-323	24	0.004
Duschek (17)	0- 6.0	273-323	130	0.011
Jaeschke(14)				
Burnett	0- 6.0	273-313	72	0.012
Optical	0- 6.0	270-330	173	0.011
Crain (18)	0- 5.6	273	15	0.014
Carbon Dioxide:				
Michels (13)	0- 4.6	273-323	54	0.021
Holste (19)	0- 4.0	270-323	138	0.026
Jaeschke(14)				
Burnett	0- 4.0	273-320	124	0.040
Optical	0- 4.0	273-320	194	0.069
Hydrogen:				
Jaeschke(14)				
Burnett	0-10.5	273-353	43	0.004
Optical	0-12.0	273-353	72	0.005
Michels (15)	0- 4.3	248-348	26	0.006
Carbon Monoxide:				
Michels (16)	0- 4.8	273-323	20	0.005

The unlike interaction virial coefficients $B_{ij}(T)$, $C_{iij}(T)$ and $C_{ijj}(T)$ of the nitrogen + carbon dioxide and the nitrogen + hydrogen systems were evaluated previously (1). Assuming again that a quadratic function would be sufficient to correlate the interaction virial coefficients with temperature, nine independent variables appeared to be required for each binary mixture. However, as neither the quantity nor the quality of the experimental data was sufficient to obtain reliable values of all these variables, such a strict evaluation of parameters proved impossible. To resolve this problem, the correlation for the second virial coefficient $Bij(T)$ was kept intact, viz.

$$B_{ij}(T) = b_{ij}^{(0)} + b_{ij}^{(1)}.T + b_{ij}^{(2)}.T^2 \qquad (3.4)$$

but the total number of independent parameters was reduced to six by means of a secondary correlation between the third virial coefficients $C_{iij}(T)$ and $C_{ijj}(T)$, viz.

$$C_{iij}(T) - C_{ijj}(T) = [C_{iii}(T) - C_{jjj}(T)]/3. \qquad (3.5)$$

For the determination of the parameters for the two binary systems under consideration the sources of data listed in Table 3.3 were used. The principles applied in reaching this final selection of data sets was outlined previously (1).

The resulting numerical values of the set of parameters describing the temperature dependence of the unlike interaction virial coefficients are given in Section 4, Tables 4.1 and 4.3. In both cases the data (N=208 for N_2+CO_2 and N=339 for N_2+H_2) could be correlated with a root-mean-square deviation of just 0.025%.

For the nitrogen + hydrogen system it proved sufficient for present purposes to use a constant value for the second unlike interaction virial coefficient in the Standard GERG Virial Equation, and to take the third unlike interaction virial coefficients as zero at all temperatures. Furthermore, it proved unnecessary to take explicit account, through their four unlike interaction second and eight third virial coef-

Table 3.3 Binary Data Sets used for the Correlation

System	Data Source and ref.		Number of Mixtures
N_2+CO_2	Audibert (1987)	(20)	2
	Esper (1987)	(21,22)	1
	Jaeschke (1987)	(14)	2
	Reintsema (1982)	(23)	1
N_2+H_2	Jaeschke (1987)	(14)	4
	Michels (1948)	(24)	1

ficients, of the systems N_2+CO, CO_2+H_2, CO_2+CO and H_2+CO, and of all 24 possible unlike triple-interaction third virial coefficients $C_{ijk}(T)$. This is in contrast to the case for the Master GERG-88 Virial Equation, where at least some of the values were required (1).

3.4 Virial Coefficients for the Equivalent Hydrocarbon Gas

3.4.1 The GERG N-File of Natural Gas Compressibility Factors

The N-File is that part of the large databank of high-quality compressibility factor measurements (10), set up and maintained by GERG, containing data for natural gas and natural gas/coke-oven gas mixtures. The original 84 data sets, comprising 4486 data points (31 March 1988) have recently been supplemented by 12 data sets comprising 364 additional data points. These 96 data sets are used in verifying the performance of the Standard GERG-88 Virial Equation (see Section 6), in a similar way to which the original 84 data sets were used to assess the Master equation (1).

Table 3.4 gives the sources of these data sets, the number of data points available in each case and the "GERG Code". Table 3.5 gives a listing of the reduced (simplified) analysis for these natural gases, specifying the superior (gross) calorific value, the relative density and the mole fractions of carbon dioxide and hydrogen. The calorific values and rela-

Table 3.4 Listing of Codes for Natural Gases

Data-Reference	Gas	Gas Nr.	GERG CODE	No. of Points
Ruhrgas AG GERG Gas DEH03	EKOFISK-H	49	N 1	18
Ruhrgas AG GERG Gas DEH05	UDSSR-H	58	N 2	18
Ruhrgas AG GERG Gas DEH06	TENP-H	57	N 3	18
Ruhrgas AG GERG Gas DEH07	EPE-H	56	N 4	18
Ruhrgas AG GERG Gas DEH11	MIXTURE+H2-H	85	N 5	24
Ruhrgas AG GERG Gas DEH12	MIXTURE+H2-H	86	N 6	24
Ruhrgas AG GERG Gas DEH13	MIXTURE-H2-L	87	N 7	24
Ruhrgas AG GERG Gas DEH14	MIXTURE+H2-L	88	N 8	23
Lit.Achtermann [29](1982)	UDSSR-H	71	N 9	67
Lit.Achtermann [29](1982)	EKOFISK-H	70	N 10	68
Lit.Achtermann [29](1982)	TENP-H	64	N 11	69
Lit.Achtermann [29](1982)	EPE-H	65	N 12	69
Lit.Achtermann [29](1982)	UDSSR-H	71	N 13	74
Lit.Achtermann [29](1982)	EKOFISK-H	70	N 14	74
Lit.Achtermann [29](1982)	TENP-H	64	N 15	73
Lit.Achtermann [29](1982)	EPE-H	65	N 16	74
Lit.Achtermann [30](1981)	UDSSR-H	67	N 17	76
Lit.Achtermann [30](1981)	EKOFISK-H	69	N 18	68
Lit.Achtermann [30](1981)	TENP-H	66	N 19	73
Lit.Achtermann [30](1981)	EPE-H	68	N 20	77
Brit.Gas, Roe [11](1972)	SOUTH.N.SEA-H	37	N 21	12
Brit.Gas, Roe [11](1972)	BACTON-H	38	N 22	15
GazdeFrance GERG Gas GF008	GRONINGEN-L	30	N 23	18
GazdeFrance GERG Gas GF009	LACQ-H	31	N 24	12
GazdeFrance GERG Gas GF010	EKOFISK-H	34	N 25	10
GazdeFrance GERG Gas GF011	EKOFISK-H	35	N 26	5
GazdeFrance GERG Gas GF012	EKOFISK-H	36	N 27	5
Ned.Gasunie GERG Gas GU008	STATENZIJL-H	110	N 28	64
Ned.Gasunie GERG Gas GU009	URETERP-L	111	N 29	53
Ned.Gasunie GERG Gas GU010	AMBACHT-H	112	N 30	52
Ned.Gasunie GERG Gas GU011	PLACID-H	113	N 31	53
Ned.Gasunie GERG Gas GU012	MIDDENM.-H	114	N 32	54
Ned.Gasunie GERG Gas GU013	MID.MIX-L	115	N 33	64
Ned.Gasunie GERG Gas GU014	MID.ZECH.-L	116	N 34	52
Ned.Gasunie GERG Gas GU015	MID.ROTL.-M	117	N 35	55
Ned.Gasunie GERG Gas GU016	BOCHOLTZ-H	118	N 36	55
Ned.Gasunie GERG Gas GU017	EKOFISK-H	119	N 37	64
Ned.Gasunie GERG Gas GU018	GARYP-L	120	N 38	65
Ned.Gasunie GERG Gas GU019	GRAVENV.-H	121	N 39	55
Ned.Gasunie GERG Gas GU020	TIETJERK-L	122	N 40	54
Ned.Gasunie GERG Gas GU021	SLOCHTEREN-L	123	N 41	16
Ned.Gasunie GERG Gas GU022	SLOCHTEREN-L	124	N 42	44
Ned.Gasunie GERG Gas GU023	BALGZAND-H	125	N 43	66
Ned.Gasunie GERG Gas GU024	AMOCO-H	126	N 44	66
Ned.Gasunie GERG Gas GU025	ANNERVEEN-H	127	N 45	66
Ned.Gasunie GERG Gas GU026	ROSWINKEL-L	128	N 46	65
Ned.Gasunie GERG Gas GU027	SLEEN-ROSW.-M	129	N 47	65
Ned.Gasunie GERG Gas GU028	SLEEN-M	130	N 48	65
Ned.Gasunie GERG Gas GU038	STATENZIJL-H	274	N 49	33
Ned.Gasunie GERG Gas GU051	GRONINGEN-L	275	N 50	22

Table 3.4 Listing of Codes for Natural Gases

Data-Reference	Gas	Gas Nr.	GERG CODE	No. of Points
Ruhrgas AG GERG Gas BUR07	EPE-H	65	N 51	25
Ruhrgas AG GERG Gas OPT07	EPE-H	65	N 52	23
Ruhrgas AG GERG Gas BUR08	EPE-H	68	N 53	25
Ruhrgas AG GERG Gas OPT08	EPE-H	68	N 54	38
Ruhrgas AG GERG Gas BUR09	EPE-H	212	N 55	83
Ruhrgas AG GERG Gas OPT09	EPE-H	212	N 56	71
Ruhrgas AG GERG Gas BUR17	UDSSR+NAM-H	211	N 57	27
Ruhrgas AG GERG Gas OPT35	UDSSR+NAM-H	211	N 58	48
Ruhrgas AG GERG Gas BUR18	NAM-L	223	N 59	28
Ruhrgas AG GERG Gas OPT36	NAM-L	223	N 60	117
Ruhrgas AG GERG Gas BUR20	UDSSR-H	210	N 61	30
Ruhrgas AG GERG Gas OPT34	UDSSR-H	210	N 62	109
Ruhrgas AG GERG Gas BUR31	DROHNE-L	224	N 63	50
Ruhrgas AG GERG Gas OPT31	DROHNE-L	224	N 64	117
Ruhrgas AG GERG Gas BUR32	EKOFISK-H	225	N 65	54
Ruhrgas AG GERG Gas OPT32	EKOFISK-H	225	N 66	120
Ruhrgas AG GERG Gas BUR49	MIXTURE+H2-H	86	N 67	68
Ruhrgas AG GERG Gas BUR50	MIXTURE+H2-H	85	N 68	69
Ruhrgas AG GERG Gas BUR51	MIXTURE+H2-L	87	N 69	70
Ruhrgas AG GERG Gas BUR52	MIXTURE+H2-H	137	N 70	68
Ruhrgas AG GERG Gas BUR53	MIXTURE+H2-H	241	N 71	70
Ruhrgas AG GERG Gas BUR54	MIXTURE+H2-L	242	N 72	67
Ruhrgas AG GERG Gas BUR47	MIXTURE+H2-L	242	N 73	25
Ruhrgas AG GERG Gas OPT60	MIXTURE+H2-L	242	N 74	121
Ruhrgas AG GERG Gas OPT48	EKOFISK-H	240	N 75	132
Lit.Duschek [31](1989)	EKOFISK-H	278	N 76	135
Ned.Gasunie GERG Gas GU001	SLOCHTEREN-L	22	N 77	11
Ned.Gasunie GERG Gas GU002	STATENZIJL-H	23	N 78	19
Ned.Gasunie GERG Gas GU003	EKOFISK-H	16	N 79	21
Ned.Gasunie GERG Gas GU006	MID.ROTL.-M	62	N 80	44
Ned.Gasunie GERG Gas GU007	MID.ZECH.-L	63	N 81	42
Ruhrgas AG GERG Gas BUR48	TENP-H	243	N 82	45
Ruhrgas AG GERG Gas OPT61	TENP-H	243	N 83	123
British Gas GERG Gas BG004	BACTON+H2-H	283	N 84	37
Ned.Gasunie GERG Gas GU071	EKOFISK-H	344	N 85	48
Lit.Hannisdal [32](1987)	STATOIL-H	322	N 86	8
Lit.Ellington [33](1986)	GULF COAST-H	323	N 87	7
British Gas GERG Gas BG002	LEMAN BANK-H	321	N 88	40
British Gas GERG Gas BG007	HAMILTON-L	324	N 89	42
British Gas GERG Gas BG008	ARCO(THAMES)-H	325	N 90	35
British Gas GERG Gas BG009	S.MORECAMBE-L	326	N 91	32
British Gas GERG Gas BG010	FRIGG-H	327	N 92	26
British Gas GERG Gas BG011	BRENT-H	315	N 93	8
Ned.Gasunie GERG Gas GU072	EKOFISK-H	345	N 94	26
Ned.Gasunie GERG Gas GU073	EKOFISK-H	346	N 95	44
Ned.Gasunie GERG Gas GU074	ROSWINKEL-L	347	N 96	48

Table 3.5 Listing of Reduced Composition for Natural Gases

GERG CODE	Hs ** MJ/m3	d	CO2 Mol %	H2 Mol %
N 1	44.645	0.6691	1.929	0.002
N 2	40.248	0.5825	0.233	
N 3	40.286	0.6462	1.455	
N 4	44.070	0.6606	1.864	
N 5	39.112	0.6305	1.701	4.195
N 6	39.838	0.6402	1.713	2.309
N 7	34.406	0.5983	1.336	9.392
N 8	35.926	0.6235	1.264	4.289
N 9	40.254	0.5826	0.234	
N 10	44.679	0.6682	1.850	
N 11	40.276	0.6461	1.458	
N 12	44.078	0.6606	1.863	
N 13	40.254	0.5826	0.234	
N 14	44.679	0.6682	1.850	
N 15	40.276	0.6461	1.458	
N 16	44.078	0.6606	1.863	
N 17	40.241	0.5823	0.230	
N 18	44.683	0.6686	1.865	
N 19	40.296	0.6459	1.435	
N 20	44.081	0.6609	1.871	
N 21	41.281	0.6037	0.040	
N 22	40.615	0.5968	0.040	
N 23	35.019	0.6454	0.994	
N 24	40.083	0.6098	1.528	
N 25	44.821	0.6725	1.987	
N 26	44.810	0.6730	2.027	
N 27	44.888	0.6733	1.973	
N 28	41.866	0.6334	1.982	
N 29	32.717	0.7016	7.177	
N 30	40.095	0.6288	1.573	
N 31	39.592	0.6032	1.986	
N 32	39.831	0.6182	0.581	
N 33	30.448	0.8356	25.437	
N 34	36.197	0.7087	11.248	
N 35	29.062	0.8676	28.943	
N 36	40.069	0.6370	1.603	
N 37	44.816	0.6749	2.125	
N 38	34.172	0.6504	0.555	
N 39	41.436	0.6359	1.779	
N 40	35.029	0.6577	1.472	
N 41	35.336	0.6442	0.978	
N 42	35.267	0.6446	0.980	
N 43	39.466	0.6363	1.796	
N 44	40.151	0.6021	0.975	
N 45	39.913	0.6111	0.704	
N 46	30.621	0.6591	0.118	
N 47	28.728	0.6787	0.108	
N 48	18.749	0.7814	0.059	
N 49	42.378	0.6401	2.036	

** reference conditions: combustion at T1 = 25°C,
metering at T2 = 0°C, p2 = 101.325 kPa

Table 3.5 (cont) Listing of Reduced Composition for Natural Gases

GERG CODE	Hs ** MJ/m3	d	CO2 Mol %	H2 Mol %
N 50	35.255	0.6440	0.958	
N 51	44.078	0.6606	1.863	
N 52	44.078	0.6606	1.863	
N 53	44.081	0.6609	1.871	
N 54	44.081	0.6609	1.871	
N 55	44.088	0.6614	1.905	
N 56	44.088	0.6614	1.905	
N 57	38.766	0.5818	0.261	
N 58	38.766	0.5818	0.261	
N 59	36.560	0.6443	1.109	
N 60	36.560	0.6443	1.109	
N 61	39.782	0.5646	0.067	
N 62	39.782	0.5646	0.067	
N 63	35.824	0.6254	4.863	
N 64	35.824	0.6254	4.863	
N 65	44.223	0.6595	1.771	0.002
N 66	44.223	0.6595	1.771	0.002
N 67	39.838	0.6402	1.713	2.309
N 68	39.112	0.6305	1.701	4.195
N 69	34.406	0.5983	1.336	9.392
N 70	39.840	0.6400	1.708	2.277
N 71	39.112	0.6305	1.702	4.220
N 72	34.370	0.5980	1.339	9.492
N 73	34.370	0.5980	1.339	9.492
N 74	34.370	0.5980	1.339	9.492
N 75	43.596	0.6506	1.502	
N 76	44.653	0.6689	1.920	0.002
N 77	35.114	0.6449	0.989	
N 78	42.282	0.6374	1.856	
N 79	45.174	0.6759	1.882	0.001
N 80	29.082	0.8676	28.926	
N 81	36.210	0.7088	11.242	
N 82	40.226	0.6477	1.398	
N 83	40.226	0.6477	1.398	
N 84	32.271	0.4318	0.033	35.631
N 85	43.843	0.6504	1.455	
N 86	44.463	0.6493	0.790	
N 87	40.826	0.5835	0.599	
N 88	40.943	0.5859	0.060	
N 89	35.790	0.6107	0.210	
N 90	40.493	0.5937	0.320	
N 91	39.254	0.6376	0.600	
N 92	40.642	0.5783	0.300	
N 93	39.888	0.5866	0.850	
N 94	43.841	0.6504	1.440	
N 95	44.050	0.6530	1.438	
N 96	30.607	0.6587	0.132	

** reference conditions: combustion at T1 = 25°C,
metering at T2 = 0°C, p2 = 101.325 kPa

tive densities have been calculated from the detailed gas mixture compositions (see Table 3.6) by the method described in sub-section 3.4.2; note, however, that the CO_2 content listed in Table 3.6, for those gases containing hydrogen, includes the small amount of ethylene present, whereas the values of H_s given in Table 3.5 have separately taken into account the calorific value of ethylene, and the CO_2 content listed there corresponds to the actual composition.

3.4.2 Calculation of Calorific Value and Relative Density for N-File Natural Gases

The superior calorific value and relative density of any natural gas may best be calculated by the following method, as given in ISO draft proposal DP-6976 (25(b)).

The superior calorific value H_s for combustion at temperature T_1 of a gas metered at a temperature T_2 and pressure p_2 is given by -

$$H_s = [\sum_{j=1}^{N} x_j H_j^o(T_1)\ ]\cdot p_2/[RT_2 Z_{mix}(T_2,p_2)] \qquad (3.6)$$

where $H_j^o(T_1)$ is the ideal molar superior calorific value of component j at the combustion reference condition,

x_j is the mole fraction of component j, and

$Z_{mix}(T_2,p_2)$ is the compressibility factor of the mixture at the metering reference conditions.

The real-gas relative density (specific gravity) d of a gas metered at temperature T_2 and pressure p_2 is defined by -

$$d = [\sum_{j=1}^{N} x_j M_j\ ]\cdot \rho_m(T_2,p_2)/\rho_{air}(T_2,p_2) \qquad (3.7)$$

where M_j is the mass per mole of component j,

$\rho_{air}(T_2,p_2)$ is the mass density of dry air of standard composition

(ρ_{air}(273.15 K, 101.325 kPa) = 1.292923 kg m^{-3}), and

$\rho_m(T_2,p_2)$ is the molar density of the mixture, given by equation (2.1), viz.

Table 3.6 Listing of Compositions (by mole percent) for Natural Gases

GERG Code	CH_4	N_2	CO_2	C_2H_6	H_2	C_3H_8	CO	C_4H_{10}	HE	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
N 1	84.3346	0.4390	1.9285	8.8946	0.0015	3.1919		0.9844	0.0032	0.1825	0.0325	0.0061	0.0012
N 2	95.5340	1.6004	0.2331	1.8790		0.4926		0.1511		0.0587	0.0309	0.0168	0.0034
N 3	85.1473	5.6769	1.4546	5.4174		1.5968		0.5073		0.1449	0.0391	0.0138	0.0019
N 4	85.4814	0.6224	1.8643	8.0607		2.8624		0.8695		0.1891	0.0398	0.0096	0.0008
N 5	80.1984	5.4710	1.8292	5.5031	4.1947	1.6910	0.3826	0.5457	0.0229	0.1157	0.0296	0.0128	0.0033
N 6	82.1692	5.3302	1.7802	5.6763	2.3094	1.7778	0.2019	0.5667	0.0249	0.1175	0.0309	0.0116	0.0034
N 7	73.6405	10.0017	1.6182	3.3093	9.3919	0.7661	0.9067	0.2456		0.0744	0.0239	0.0149	0.0068
N 8	78.7092	10.3370	1.3977	3.5876	4.2885	0.8272	0.4137	0.2704	0.0417	0.0779	0.0257	0.0154	0.0080
N 9	95.5192	1.6052	0.2339	1.8835		0.4933		0.1518		0.0591	0.0326	0.0176	0.0038
N 10	84.4678	0.4278	1.8497	8.8604		3.1831		0.9668		0.1999	0.0369	0.0068	0.0008
N 11	85.1666	5.6760	1.4579	5.4022		1.5922		0.5061		0.1451	0.0385	0.0134	0.0020
N 12	85.4915	0.6122	1.8630	8.0626		2.8576		0.8709		0.1902	0.0404	0.0100	0.0016
N 13	95.5192	1.6052	0.2339	1.8835		0.4933		0.1518		0.0591	0.0326	0.0176	0.0038
N 14	84.4678	0.4278	1.8497	8.8604		3.1831		0.9668		0.1999	0.0369	0.0068	0.0008
N 15	85.1666	5.6760	1.4579	5.4022		1.5922		0.5061		0.1451	0.0385	0.0134	0.0020
N 16	85.4915	0.6122	1.8630	8.0626		2.8576		0.8709		0.1902	0.0404	0.0100	0.0016
N 17	95.5480	1.6032	0.2299	1.8724		0.4883		0.1497		0.0577	0.0312	0.0164	0.0032
N 18	84.4333	0.4293	1.8647	8.8669		3.1897		0.9697		0.2011	0.0377	0.0072	0.0004
N 19	85.1784	5.6680	1.4349	5.4163		1.5962		0.5071		0.1451	0.0387	0.0131	0.0022
N 20	85.4620	0.6137	1.8710	8.0768		2.8634		0.8712		0.1902	0.0405	0.0101	0.0011
N 21	92.2794	2.2937	0.0401	3.7252		0.9170		0.4361	0.0598	0.1483	0.0654	0.0115	0.0235
N 22	93.0357	2.6334	0.0402	3.1217		0.6420		0.2816	0.0399	0.1155	0.0436	0.0229	0.0235
N 23	81.2125	14.3770	0.9940	2.8090		0.3800		0.1292		0.0554	0.0237	0.0161	0.0031
N 24	90.8251	2.4630	1.5280	4.4050		0.6420		0.1129		0.0231	0.0003	0.0006	
N 25	83.9520	0.4040	1.9870	9.1380		3.2590		0.9890		0.2090	0.0473	0.0139	0.0008
N 26	83.8681	0.4050	2.0270	9.1800		3.2790		0.9760		0.2049	0.0459	0.0136	0.0005
N 27	83.7500	0.3940	1.9730	9.3490		3.3080		0.9680		0.1996	0.0447	0.0133	0.0004
N 28	88.9650	1.2330	1.9820	5.4550		1.6160		0.5130	0.0300	0.1630	0.0310	0.0120	
N 29	75.7200	13.7510	7.1770	2.5220		0.4110		0.1430	0.1580	0.0730	0.0230	0.0190	0.0030
N 30	87.9810	4.1240	1.5730	4.8020		0.9080		0.3140	0.0710	0.1550	0.0450	0.0260	0.0010
N 31	92.7220	1.8580	1.9860	2.7990		0.3430		0.1030	0.0500	0.1070	0.0150	0.0170	
N 32	88.8020	5.0460	0.5810	4.1500		0.8580		0.2990	0.0780	0.1220	0.0400	0.0220	0.0020

Table 3.6 (cont) Listing of Compositions (by mole percent) for Natural Gases

GERG Code	CH4	N2	CO2	C2H6	H2	C3H8	CO	C4H10	HE	C5H12	C6H14	C7H16	C8H18
N 33	68.7140	2.0650	25.4370	2.8070		0.5540		0.2020	0.0580	0.0990	0.0390	0.0240	0.0010
N 34	80.8760	2.9080	11.2480	3.7680		0.7040		0.2390	0.0660	0.1210	0.0430	0.0240	0.0030
N 35	65.6860	1.8580	28.9430	2.5520		0.5360		0.2010	0.0530	0.1020	0.0410	0.0270	0.0010
N 36	86.6460	4.9040	1.6030	4.9600		1.2440		0.4030	0.0440	0.1440	0.0340	0.0170	0.0010
N 37	84.0050	0.4230	2.1250	8.7790		3.2380		1.0790		0.2790	0.0590	0.0130	
N 38	79.3180	16.8100	0.5550	2.6710		0.4050		0.1280	0.0230	0.0540	0.0230	0.0130	
N 39	87.9700	2.4340	1.7790	5.5520		1.5120		0.4920	0.0410	0.1640	0.0360	0.0190	0.0010
N 40	79.6150	14.7670	1.4720	3.0380		0.6150		0.2330	0.0920	0.1040	0.0380	0.0230	0.0030
N 41	81.5920	13.7870	0.9780	2.9160		0.4120		0.1500	0.0470	0.0710	0.0250	0.0190	0.0030
N 42	81.4780	13.9310	0.9800	2.8990		0.3960		0.1480	0.0480	0.0680	0.0280	0.0200	0.0040
N 43	86.4450	5.4550	1.7960	4.7560		0.9140		0.3310	0.0850	0.1430	0.0460	0.0260	0.0030
N 44	92.3210	2.4480	0.9750	3.2850		0.5690		0.1850	0.0570	0.1000	0.0350	0.0230	0.0020
N 45	90.4400	4.0710	0.7040	3.5110		0.7500		0.2840	0.0520	0.1190	0.0410	0.0250	0.0030
N 46	75.1050	23.7320	0.1180	0.8670		0.0580		0.0190	0.0810	0.0120	0.0070	0.0010	
N 47	70.3170	28.5000	0.1080	0.8940		0.0560		0.0190	0.0870	0.0110	0.0070	0.0010	
N 48	45.2360	53.5570	0.0590	0.9510		0.0480		0.0130	0.1220	0.0080	0.0050	0.0010	
N 49	88.0480	1.0140	2.0360	6.2390		1.8390		0.6130	0.0230	0.1520	0.0260	0.0080	0.0020
N 50	81.5500	13.9300	0.9580	2.8630		0.4030		0.1440	0.0430	0.0650	0.0220	0.0210	0.0010
N 51	85.4915	0.6122	1.8630	8.0626		2.8576		0.8709		0.1902	0.0404	0.0100	0.0016
N 52	85.4915	0.6122	1.8630	8.0626		2.8576		0.8709		0.1902	0.0404	0.0100	0.0016
N 53	85.4620	0.6137	1.8710	8.0768		2.8634		0.8712		0.1902	0.0405	0.0101	0.0011
N 54	85.4620	0.6137	1.8710	8.0768		2.8634		0.8712		0.1902	0.0405	0.0101	0.0011
N 55	85.3453	0.6039	1.9051	8.1433		2.8692		0.8975	0.0139	0.1745	0.0345	0.0117	0.0011
N 56	85.3453	0.6039	1.9051	8.1433		2.8692		0.8975	0.0139	0.1745	0.0345	0.0117	0.0011
N 57	94.6077	3.7581	0.2609	1.0118		0.2128		0.0762	0.0343	0.0244	0.0086	0.0044	0.0008
N 58	94.6077	3.7581	0.2609	1.0118		0.2128		0.0762	0.0343	0.0244	0.0086	0.0044	0.0008
N 59	82.5198	11.7266	1.1093	3.4611		0.7645		0.2539	0.0538	0.0746	0.0225	0.0110	0.0029
N 60	82.5198	11.7266	1.1093	3.4611		0.7645		0.2539	0.0538	0.0746	0.0225	0.0110	0.0029
N 61	98.2722	0.8858	0.0668	0.5159		0.1607		0.0592	0.0157	0.0157	0.0055	0.0016	0.0009
N 62	98.2722	0.8858	0.0668	0.5159		0.1607		0.0592	0.0157	0.0157	0.0055	0.0016	0.0009
N 63	89.4525	5.3701	4.8625	0.2353		0.0163		0.0064	0.0544	0.0020	0.0003	0.0002	
N 64	89.4525	5.3701	4.8625	0.2353		0.0163		0.0064	0.0544	0.0020	0.0003	0.0002	

Table 3.6 (cont) Listing of Compositions (by mole percent) for Natural Gases

GERG Code	CH4	N2	CO2	C2H6	H2	C3H8	CO	C4H10	HE	C5H12	C6H14	C7H16	C8H18
N 65	85.4541	0.4275	1.7708	8.4983	0.0019	2.7421		0.8951	0.0038	0.1673	0.0315	0.0068	0.0008
N 66	85.4541	0.4275	1.7708	8.4983	0.0019	2.7421		0.8951	0.0038	0.1673	0.0315	0.0068	0.0008
N 67	82.1692	5.3302	1.7802	5.6763	2.3094	1.7778	0.2019	0.5667	0.0249	0.1175	0.0309	0.0116	0.0034
N 68	80.1984	5.4710	1.8292	5.5031	4.1947	1.6910	0.3826	0.5457	0.0229	0.1157	0.0296	0.0128	0.0033
N 69	73.6405	10.0017	1.6182	3.3093	9.3919	0.7661	0.9067	0.2456		0.0744	0.0239	0.0149	0.0068
N 70	82.2373	5.3206	1.7745	5.6871	2.2770	1.7596	0.1960	0.5597	0.0246	0.1174	0.0309	0.0119	0.0034
N 71	80.1543	5.4722	1.8318	5.4932	4.2203	1.7111	0.3863	0.5480	0.0230	0.1151	0.0297	0.0117	0.0033
N 72	73.5015	10.0214	1.6245	3.3152	9.4918	0.7657	0.9142	0.2458		0.0740	0.0241	0.0148	0.0070
N 73	73.5015	10.0214	1.6245	3.3152	9.4918	0.7657	0.9142	0.2458		0.0740	0.0241	0.0148	0.0070
N 74	73.5015	10.0214	1.6245	3.3152	9.4918	0.7657	0.9142	0.2458		0.0740	0.0241	0.0148	0.0070
N 75	85.9284	0.9617	1.5021	8.4563		2.3022		0.6985		0.1218	0.0228	0.0057	0.0005
N 76	84.3769	0.4233	1.9201	8.8749	0.0020	3.1776		1.0022	0.0031	0.1812	0.0310	0.0065	0.0012
N 77	81.3140	14.1790	0.9890	2.8290		0.3910		0.1400	0.0500	0.0620	0.0248	0.0192	0.0020
N 78	88.2210	1.1760	1.8560	6.1190		1.8840		0.5890	0.0250	0.0930	0.0230	0.0130	0.0010
N 79	83.4177	0.3379	1.8816	9.5284	0.0010	3.5694		1.0365	0.0028	0.1828	0.0327	0.0081	0.0011
N 80	65.6961	1.8530	28.9263	2.5547		0.5395		0.2045	0.0527	0.0995	0.0425	0.0299	0.0013
N 81	80.8753	2.9080	11.2419	3.7681		0.7038		0.2400	0.0657	0.1221	0.0448	0.0263	0.0040
N 82	84.4872	5.9990	1.3984	5.9271		1.5364		0.5089		0.1057	0.0251	0.0101	0.0021
N 83	84.4872	5.9990	1.3984	5.9271		1.5364		0.5089		0.1057	0.0251	0.0101	0.0021
N 84	57.6930	1.4200	0.0330	1.7800	35.6310	3.2000		0.1450		0.0420	0.0560		
N 85	85.9610	0.6370	1.4550	8.7390		2.3870		0.6680	0.0060	0.1220	0.0210	0.0040	
N 86	82.7100	0.6200	0.7900	14.7000		1.0400		0.1200		0.0100	0.0100		
N 87	96.5016	0.2501	0.5990	1.7490		0.4003		0.1999		0.2000	0.1001		
N 88	95.0220	1.1200	0.0600	2.9190		0.4900		0.1900	0.0240	0.0920	0.0410	0.0300	0.0120
N 89	87.4320	11.1140	0.2100	0.9100		0.1600		0.0500	0.0630	0.0280	0.0170	0.0090	0.0070
N 90	93.6200	2.1390	0.3200	2.9390		0.5500		0.2100	0.0410	0.0950	0.0470	0.0280	0.0110
N 91	85.2970	7.7470	0.6000	4.5080		1.0600		0.5000	0.0360	0.1720	0.0620	0.0150	0.0030
N 92	95.6160	0.5100	0.3000	3.4800		0.0440		0.0140	0.0040	0.0060	0.0100	0.0090	0.0070
N 93	94.2320	1.6100	0.8500	3.1500		0.1500			0.0080				
N 94	85.9230	0.6640	1.4400	8.7770		2.3800		0.6640	0.0060	0.1210	0.0210	0.0040	
N 95	85.9030	0.5890	1.4380	8.7660		2.3870		0.6690	0.0050	0.1220	0.0210	0.1000	
N 96	75.2030	23.6960	0.1320	0.7830		0.0590		0.0180	0.0860	0.0130	0.0080	0.0020	

$$\rho_m(T_2,p_2) = p_2/[RT_2Z_{mix}(T_2,p_2)]. \qquad (2.1)$$

Consequently, equation (3.7) reduces to

$$d = [\sum_{j=1}^{N} x_jM_j/M_{air}]\cdot Z_{air}(T_2,p_2)/Z_{mix}(T_2,p_2) \qquad (3.8)$$

where M_{air} = 28.9626 kg mol^{-1} is the mass per mole of dry air of standard composition, and

$Z_{air}(T_2,p_2)$ is the compressibility factor of dry air of standard composition

(Z_{air}(273.15 K, 101.325 kPa) = 0.99941 (ref.25(b))).

The compressibility factor $Z_{mix}(T_2,p_2)$ of the natural gas at the metering reference conditions is calculated from equation (3.9), using the so-called summation factors $\sqrt{b_j(T_2,p_2)}$, viz.

$$Z_{mix}(T_2,p_2) = 1 - [\sum_{j=1}^{N} x_j\sqrt{b_j(T_2,p_2)}]^2 \qquad (3.9)$$

where, in most cases, $b_j = 1 - Z_j$. For hydrogen and helium "pseudo" values of the summation factor $\sqrt{b}$ are assigned, because $Z > 1$ and $\sqrt{b}$ therefore cannot be evaluated directly. Equation (3.9) is specially formulated for the above purpose, and must not be used at pressures above normal atmospheric.

Values of the molar superior calorific value H_j^o(298.15 K), the summation factors $\sqrt{b_j(273.15 \text{ K}, 101.325 \text{ kPa})}$ and the molar mass M_j for individual pure substances have been taken from the ISO draft proposal DP-6976 (25(b)) or the first GERG Technical Monograph (26), and are listed for convenience in Table 3.7 for the main constituents of natural gases.

Equations (3.6) and (3.8) were used to determine the values of H_s and d for each of the gases in the N-file from their known compositions, as given in Table 3.6 and in GERG TM4 (10). As emphasized earlier, the "true" component concentrations must be used here, i.e. not those which result from the re-assignment of various minor components such as ethylene. For the purposes of development of the Standard GERG-88 Virial Equation, these values of H_s and d were thereafter

Table 3.7 Numerical Values of the Molar Mass M, Summation Factor $\sqrt{b}$ and Molar Superior Calorific Value H^{o} for Pure Gases

		M	$\sqrt{b}$	H^{o}
		kg $kmol^{-1}$		kJ mol^{-1}
Methane	CH_4	16.043	0.0490	890.63
Ethane	C_2H_6	30.070	0.1000	1560.69
Propane	C_3H_8	44.097	0.1453	2219.17
n-Butane	C_4H_{10}	58.123	0.2069	2877.40
iso-Butane	C_4H_{10}	58.123	0.2049	2868.20
mean Butane		58.123	0.2062	2874.20
n-Pentane	C_5H_{12}	72.150	0.2864	3535.77
iso-Pentane	C_5H_{12}	72.150	0.2510	3528.83
neo-Pentane	C_5H_{12}	72.150	0.2387	3514.61
mean Pentane		72.150	0.2682	3532.09
n-Hexane	C_6H_{14}	86.177	0.3286	4194.95
n-Heptane	C_7H_{16}	100.204	0.4123	4853.43
n-Octane	C_8H_{18}	114.231	0.5079	5511.80
n-Nonane	C_9H_{20}	128.258	0.6221	6171.15
n-Decane	$C_{10}H_{22}$	142.285	0.7523	6829.77
Nitrogen	N_2	28.0135	0.0224	0
Carbon Dioxide	CO_2	44.010	0.0819	0
Carbon Monoxide	CO	28.010	0.0265	282.98
Hydrogen	H_2	2.0159	-0.0040	285.83
Helium	He	4.0026	0.0006	0
Ethylene	C_2H_4	28.054	0.0866	1411.18
Benzene	C_6H_6	78.114	0.3017	3301.43

Reference conditions for $\sqrt{b}$: 0 °C and 101.325 kPa
Reference condition for H^{o}: 25 °C

Mean butane = 0.65 n-C_4 + 0.35 iso-C_4
Mean pentane = 0.49 n-C_5 + 0.50 iso-C_5 + 0.01 neo-C_5

treated as accurately known "pseudo-experimental" values.

3.4.3 Evaluation of Virial Coefficients for the Equivalent Hydrocarbon Gas

The principle of congruence, as originally formulated by Brønsted and Koefoed (27), states that the excess thermodynamic functions of a **liquid** mixture of n-alkanes depend only on the average chain-length, defined as $\Sigma x_i \mu_i$ (where x_i is the mole fraction of component i, μ_i is the number of carbon atoms per molecule, and the summation extends over all components). Barker and Linton extended the concept to include **gaseous** mixtures, and showed its applicability to the estimation of second virial coefficients (28).

Thus, for an equimolar mixture of methane and propane, the principle of congruence predicts a value of B equal to that of ethane at the same temperature. The same expectation also holds, for example, for a mixture of 67 mole percent CH_4 and 33 mole percent n-C_4H_{10}, or for 75 percent CH_4 plus 25 percent n-C_5H_{12}. In Table 3.8, values of B calculated from the data given in ref.1 are listed for C_2H_6 and these supposedly congruent simple mixtures for several temperatures. The table shows that application of the principle to these mixtures would give good first approximations to the rigorously calculated values of B, but also suggests that these would not be sufficiently accurate for direct application to the calculation of compressibility factors of natural gases at an accuracy of around 0.1%.

The principle of congruence also predicts the molar heating values H^o of alkanes and their mixtures reasonably well, though by no means perfectly. The values decrease regularly from H^o=1560.7 kJ mol^{-1} for C_2H_6, to H^o=1551.9 kJ mol^{-1} for (75+25) CH_4+C_5H_{12} (see Table 3.8). In general, the principle is obeyed significantly more closely for the molar heating value than for the second virial coefficient. In the case of heating value, an equivalent result also follows directly from the application, to the homologous series of n-alkanes, of the well-known chemical concept of group additivity.

Table 3.8 Second Virial Coefficient and Molar Calorific Value for C_2H_6 and for Congruent Mixtures of CH_4, C_3H_8, C_4H_{10} and C_5H_{12}

Components and Mole Fractions	**Second Virial Coefficient** $cm^3\ mol^{-1}$			
	t/°C = 0	20	40	60
1.00 C_2H_6	-221.8	-192.3	-167.3	-146.8
0.50 CH_4 + 0.50 C_3H_8	-209.6	-180.7	-156.3	-134.8
$0.6\dot{6}$ CH_4 + $0.3\dot{3}$ n-C_4H_{10}	-216.8	-181.8	-155.1	-136.9
0.75 CH_4 + 0.25 n-C_5H_{12}	-240.0	-199.5	-163.8	-132.0

	Molar Calorific Value $kJ\ mol^{-1}$
	t/°C = 25
1.00 C_2H_6	1560.7
0.50 CH_4 + 0.50 C_3H_8	1554.9
$0.6\dot{6}$ CH_4 + $0.3\dot{3}$ n-C_4H_{10}	1552.9
0.75 CH_4 + 0.25 n-C_5H_{12}	1551.9

The above observations raise the question of whether there may be a useful relationship between the molar heating value and the virial coefficients. Schouten et al (7) contended that no such relationship can be sufficiently general or sufficiently accurate to describe mixtures of methane with large amounts of higher hydrocarbons. For natural gases, however, the average chain-length is always within the range 1.00 to 1.25, and the molar heating value H_{CH} is, correspondingly, within the range 890 to 1030 kJ mol^{-1}. Consequently, Schouten et al (7) were able to argue that in this restricted range the principle might apply with much better precision. Moreover, the mole fraction ratios of the higher hydrocarbons are not entirely arbitrary; rather, there tends to be a somewhat regular decrease in mole fraction with increasing carbon number, whatever the total amount of non-methane hydrocarbons. The amount of C_4H_{10} is usually about one-third that of C_3H_8, the amount of C_5H_{12} roughly one-third that of C_4H_{10} etc. These two features favour the applicability of a general relation between the heating value and the virial coefficients, at least for that part of the natural gas consisting entirely of hydrocarbons i.e. excluding the inert gases.

In order to establish and demonstrate the validity of such a relationship between the virial coefficients and the molar heating value for the hydrocarbon content of natural gases, the following procedure was adopted -

(1) The second virial coefficient B_{CH} of an arbitrary (equivalent) hydrocarbon mixture of known composition was calculated from equation (2.3), using data for the various virial coefficients B_{ii} and B_{ij} as given in GERG Monograph TM2 (1), for several selected temperatures.

(2) The molar heating value H_{CH} of this hydrocarbon mixture was then calculated using the known calorific values of the pure hydrocarbons, from Table 3.7, in the equation

$$H_{CH} = \sum_{j=1}^{N} x_j H_j^o(T_1) . \qquad (3.10)$$

(3) This procedure was repeated for a large number of equivalent hydrocarbon mixtures. In fact the "arbitrary" compositions selected were those of the first 84 natural gases in the GERG databank N-file (10), with the inert components excluded.

(4) The second virial coefficients of these hydrocarbon mixtures were then plotted as a function of H_{CH} for each of the chosen temperatures. The results are shown in Figure 3.1. For convenience and clarity of presentation, a substantial proportion of the data points have been omitted from the figure. Those included, however, form a fully representative subset of the whole; points omitted are generally for mixtures of closely similar composition to those for which points are shown.

(5) The same procedure was carried out for the third virial coefficients of the same set of gases at the same temperatures; results are shown in Figure 3.2.

It turns out that in both cases the virial coefficient is, to a very good approximation, a quadratic function of the molar heating value H_{CH} of the equivalent hydrocarbon at each temperature, viz.

$$B_{CH}(T) = \beta_{H0}(T) + \beta_{H1}(T).H_{CH} + \beta_{H2}(T).H_{CH}^2 \qquad (2.7)$$

and $$C_{CH}(T) = \epsilon_{H0}(T) + \epsilon_{H1}(T).H_{CH} + \epsilon_{H2}(T).H_{CH}^2. \qquad (2.8)$$

Furthermore, the temperature dependence of the coefficients can be adequately described by the expressions

$$\beta_{Hq}(T) = b_{Hq}^{(0)} + b_{Hq}^{(1)}.T + b_{Hq}^{(2)}.T^2 \qquad (3.11)$$

and $$\epsilon_{Hq}(T) = c_{Hq}^{(0)} + c_{Hq}^{(1)}.T + c_{Hq}^{(2)}.T^2 \qquad (3.12)$$

where T is the temperature in kelvin and q = 0,1 and 2. The values obtained for the 18 coefficients $b_{Hq}^{(r)}$ and $c_{Hq}^{(r)}$ (r = 0, 1 and 2) are reported in Section 4. It needs to be emphasized

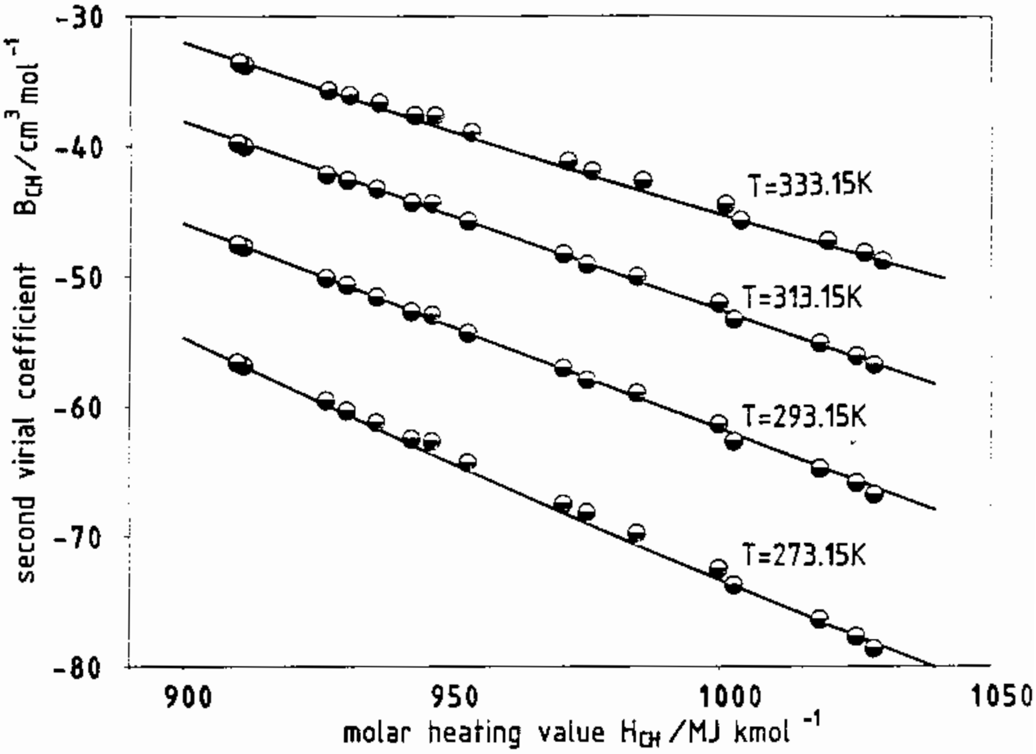

Figure 3.1 Second Virial Coefficient of the Equivalent Hydrocarbon Gas as a Function of Molar Heating Value.

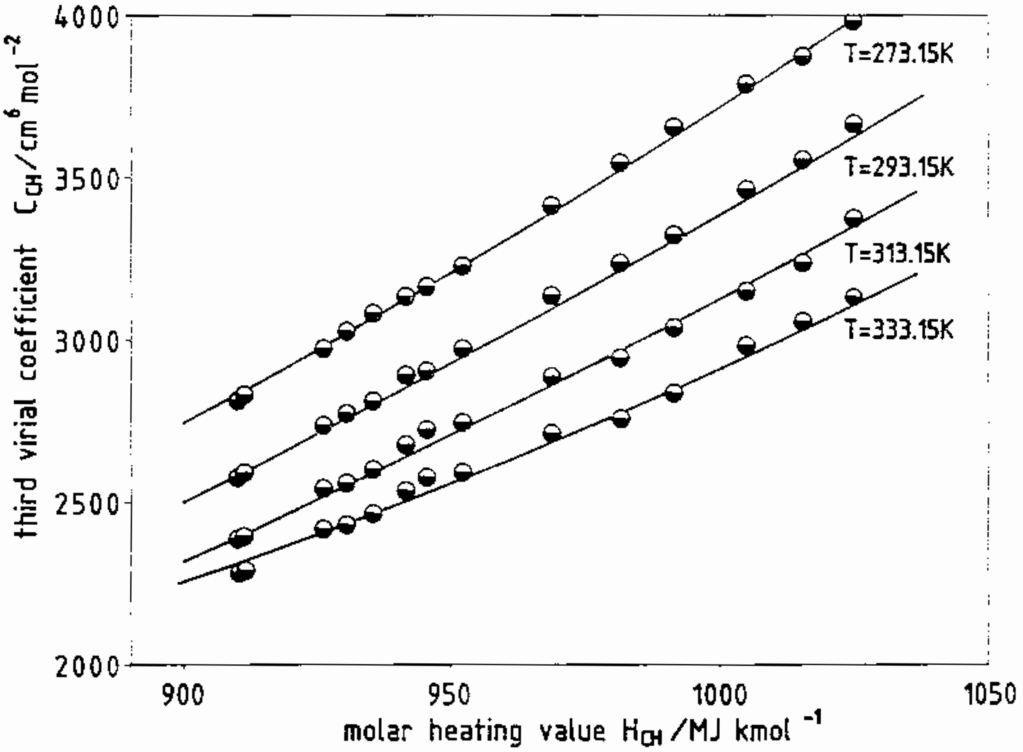

Figure 3.2 Third Virial Coefficient of the Equivalent Hydrocarbon Gas as a Function of Molar Heating Value.

that no volumetric (compressibility factor) data for the natural gases have been used to establish the relations (2.7) and (2.8), or to obtain the coefficients of equations (3.11) and (3.12). Rather, we have calculated these coefficients for hydrocarbon mixtures having the same characteristic distributions of components as those found in typical natural gases.

3.5 Unlike Interaction Virial Coefficients for the Equivalent Hydrocarbon Gas

3.5.1 Equivalent Hydrocarbon plus Carbon Dioxide or Nitrogen: Second Virial Coefficients

The determination of the unlike interaction virial coefficients between the equivalent hydrocarbon and both carbon dioxide and nitrogen will be described in this sub-section. As usual, these coefficients depend upon temperature, but in this case also on the composition of the hydrocarbon as characterised by its molar heating value. In principle, the coefficients can be calculated from the Master GERG Virial Equation (1) (in a similar way to that described above for the "pure" equivalent hydrocarbon) and fitted to power series in temperature T and molar heating value H_{CH}. This procedure is rather complicated for mixtures, however, and leads to expressions too elaborate for convenient use.

For $CH+CO_2$ another approach is to write the second unlike interaction virial coefficient, without loss of generality, as

$$B_{13}(T) = y_{13}(T) \cdot [B_{11}(T) . B_{33}(T)]^{\frac{1}{2}} \qquad (3.13)$$

where $B_{11} = B_{CH}$ and y_{13} is an arbitrary function of temperature and composition. It was shown previously (1) that this is an appropriate combining rule, with which to reduce the number of independent parameters in the temperature expansion of second interaction virial coefficients, only if y_{13} is a constant. Even in this case B_{13} is still dependent on temperature in a plausible fashion through B_{33} and B_{CH}, and on composition through B_{CH}. In fact a comparison with coefficients calculated from the Master GERG-88 Virial Equation shows agreement within experimental error if y_{13} is assigned the constant value

$$y_{13} = -0.865. \qquad (3.14)$$

The validity of the simple expression (3.14) is also supported by the following argument. The equivalent hydrocarbon consists mainly of CH_4 and C_2H_6; if equation (3.13) is applied to the cases of CH = CH_4 and CH = C_2H_6 and solved for y(T) in each case, the values found are both nearly independent of temperature and approximately equal to the constant value given in (3.14).

A different combination rule is required for the $CH+N_2$ interaction. This is because the second virial coefficient for nitrogen is small and changes sign in the temperature range under consideration. The second virial coefficient for $CH+N_2$ may be more satisfactorily expressed by a combination rule which uses an arithmetic average of the constituent virial coefficients rather than the quadratic mean used in equation (3.13). Thus we have

$$B_{12}(T) = y_{12}(T).[B_{11}(T) + B_{22}(T)]/2 \qquad (3.15)$$

with

$$y_{12}(T) = 0.72 + 1.875\ 10^{-5}.(320-T)^2. \qquad (3.16)$$

One might have anticipated that a simple expression like equation (3.14) might again have sufficed for y_{12}. However, it turns out that only a temperature-dependent value of the interaction parameter y_{12} yields sufficient agreement with accurate virial coefficients calculated directly from the Master GERG-88 Virial Equation for a representative set of equivalent hydrocarbon compositions.

3.5.2 Equivalent Hydrocarbon plus Carbon Dioxide or Nitrogen: Third Virial Coefficients

The third unlike interaction virial coefficients may be written in general as follows -

$$C_{ii1}(T) = y_{ii1}(T).[C_{iii}^2(T).C_{111}(T)]^{1/3} \quad (3.17)$$

and $$C_{i11}(T) = y_{i11}(T).[C_{iii}(T).C_{111}^2(T)]^{1/3} \quad (3.18)$$

with i = 2 (for N_2) or 3 (CO_2).

For CH_4+CO_2 and CH_4+N_2, each of the third unlike interaction virial coefficients may be calculated from the Master GERG-88 Virial Equation (1) at a selection of temperatures. When the values obtained are substituted into equations of the form of (3.17) and (3.18), it turns out that the dependence of y upon T is minimal. Furthermore, in each case, sufficient accuracy is retained in the resultant values of compressibility factor even under the simplifying assumption of $y_{ii1}(T) = y_{i11}(T)$. These results can be extended to the case where the equivalent hydrocarbon replaces methane, giving the working expressions

$$y_{113} = y_{133} = 0.92 \quad (3.19)$$

and $$y_{112} = y_{122} = 0.92 + 0.0013\ (T-270). \quad (3.20)$$

Finally, for the ternary interaction third virial coefficient we take

$$C_{123}(T) = y_{123}\ [C_{111}(T).C_{222}(T).C_{333}(T)]^{1/3} \quad (3.21)$$

with $$y_{123} = 1.10. \quad (3.22)$$

This is similar, but not identical, to the expression given in ref.1 for the CH_4+N_2+CO_2 interaction virial coefficient; previously the value y_{123}=1 was used.

3.5.3 Equivalent Hydrocarbon plus Hydrogen and Carbon Monoxide

The unlike interaction virial coefficients between the equivalent hydrocarbon and both hydrogen and carbon monoxide have been determined by following similar procedures to those described in the foregoing sub-sections. That is to say, the virial coefficients are fitted to the results obtained for natural gases containing hydrogen or coke-oven gas using the Master GERG Virial Equation. There is, however, a minor complication due to the presence of an appreciable amount of ethylene (C_2H_4) in the natural gas/coke-oven gas mixtures.

In the 13-component Master GERG-88 Virial Equation (1), the mole fraction of C_2H_4 is added to that of CO_2, since the virial coefficients of these species show closely similar behaviour. Since ethylene also contributes to the superior calorific value, however, this re-assignment must not be applied in the simplified-input version - the Standard GERG Virial Equation - when calculating the calorific value of the gas mixture. As the calorific value of ethylene is reasonably close to that of ethane, its mole fraction is now added to that of ethane. Another reason for this change in re-assignment is the fact that the proper input parameter for the Standard GERG Virial Equation, in operational use, is the mole fraction of carbon dioxide, not a value which sums the mole fractions of carbon dioxide and ethylene. Using the latter value in the correlation work for the virial coefficients would introduce a systematic error into the actual operational (field) use of the simplified equation.

This new re-assignment of ethylene changes compressibility factors predicted by the Master GERG-88 Virial Equation for the hydrogen-containing gases by more than 0.1% at the highest pressures. The expressions for $B_{14}(T)$ and $C_{114}(T)$ in the Standard version are constructed in such a way from the virial coefficients of the Master equation that this effect is compensated. The interaction second virial coefficient $B_{14}(T)$ is given as a function of temperature according to equation (3.4), the coefficients being as presented in Section 4. The third virial coefficient $C_{114}(T)$ is expressed using the combination rule given as equation (3.18), for $i = 4$, with the constant parameter y_{114} given by

$$y_{114} = 1.20. \tag{3.23}$$

A value for C_{144} turns out not to be necessary at the level of accuracy sought.

For the virial coefficients $B_{15}(T)$ and $C_{115}(T)$, for the equivalent hydrocarbon interaction with carbon monoxide, values for the methane plus carbon monoxide system, as given in ref.1 for the Master GERG-88 Virial Equation, have been selected. This approximation is quite adequate, as the overall contributions of these coefficients to the prediction of natural gas/coke-oven gas mixture compressibility factors is only minor. A value for C_{145} is unnecessary.

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4 - NUMERICAL VALUES

4.1 Second Virial Coefficients and Coefficients of the Expansion in Temperature

Numerical values of coefficients of the expansion in temperature of the second virial coefficient for both like and unlike interactions are listed in Table 4.1. Second virial coefficients calculated from these coefficients using equation (2.9), viz.

$$B(T) = b^{(0)} + b^{(1)}T + b^{(2)}T^2 \qquad (2.9)$$

are given in the SI unit m^3 $kmol^{-1}$ when the temperature T is in kelvin and, for the equivalent hydrocarbon gas, H_{CH} is in kJ mol^{-1}.

For a few selected temperatures (0, 20, 40 and 60 °C) numerical values of second virial coefficients are given in Table 4.2 in the more familiar units of cm^3 mol^{-1}. The virial coefficients given for the equivalent hydrocarbon gas and equivalent hydrocarbon gas mixtures are for the case where H_{CH} = 890.63 kJ mol^{-1} i.e. the equivalent hydrocarbon has the same molar calorific value as methane.

Second virial coefficients of an arbitrary three-component mixture, one component of which is of course the equivalent hydrocarbon pseudocomponent, are then calculated from equation (2.3), viz.

$$B_{mix}(T) = \sum_{i=1}^{3} \sum_{j=1}^{3} x_i x_j B_{ij}(T) \qquad (2.3)$$

where each B_{ij} is calculated from equation (2.9) using the coefficients given in Table 4.1, and x_i, x_j are the mole fractions of components i and j respectively. However, the mole fractions are not immediately available as input data for the Standard GERG Virial Equation; they first have to be derived from H_S and d as described in Section 5. If the mixture in question contains hydrogen and carbon monoxide in

Table 4.1 **Numerical Values of the Coefficients $b^{(0)}$, $b^{(1)}$ and $b^{(2)}$ for the Expansion in Temperature of the Second Virial Coefficients of Gases and of the Unlike Interaction Virial Coefficients**

Units of B are m^3 $kmol^{-1}$ when T is in kelvin.

	equation	i,j	$b^{(0)}$	$b^{(1)}$	$b^{(2)}$
CH,β_{H0}	(3.11)	1 1	$-4.25468\ 10^{-1}$	$2.86500\ 10^{-3}$	$-4.62073\ 10^{-6}$
CH,β_{H1}	(3.11)	1 1	$8.77118\ 10^{-4}$	$-5.56281\ 10^{-6}$	$8.81510\ 10^{-9}$
CH,β_{H2}	(3.11)	1 1	$-8.24747\ 10^{-7}$	$4.31436\ 10^{-9}$	$-6.08319\ 10^{-12}$
N_2	(3.2)	2 2	$-1.44600\ 10^{-1}$	$7.40910\ 10^{-4}$	$-9.11950\ 10^{-7}$
CO_2	(3.2)	3 3	$-8.68340\ 10^{-1}$	$4.03760\ 10^{-3}$	$-5.16570\ 10^{-6}$
H_2	(3.2)	4 4	$-1.10596\ 10^{-3}$	$8.13385\ 10^{-5}$	$-9.87220\ 10^{-8}$
CO	(3.2)	5 5	$-1.30820\ 10^{-1}$	$6.02540\ 10^{-4}$	$-6.44300\ 10^{-7}$
CH+N_2	(3.15)	1 2	$y = 0.72 + 1.875\ 10^{-5}\ (320-T)^2$		
CH+CO_2	(3.13)	1 3	$y = -0.865$		
CH+H_2	(3.4)	1 4	$-5.21280\ 10^{-2}$	$2.71570\ 10^{-4}$	$-2.50000\ 10^{-7}$
CH+CO	(3.4)	1 5	$-6.87290\ 10^{-2}$	$-2.39381\ 10^{-6}$	$5.18195\ 10^{-7}$
N_2+CO_2	(3.4)	2 3	$-3.39693\ 10^{-1}$	$1.61176\ 10^{-3}$	$-2.04429\ 10^{-6}$
N_2+H_2	(3.4)	2 4	$1.20000\ 10^{-2}$	0.00000	0.00000

Table 4.2 **Numerical Values of the Second Virial Coefficient in $cm^3\ mol^{-1}$ for Pure Gases and Mixed Interactions at Four Temperatures**

Pure Gases **Mixtures**	**Temperature/K**			
	273.15	**293.15**	**313.15**	**333.15**
CH^*	-53.43	-44.84	-37.53	-31.49
N_2	-10.26	-5.77	-2.01	1.02
CO_2	-150.89	-128.64	-110.53	-96.55
H_2	13.75	14.26	14.68	15.04
CO	-14.31	-9.55	-5.32	-1.59
$CH+N_2$	-24.24	-18.56	-14.25	-11.02
$CH+CO_2$	-77.67	-65.70	-55.71	-47.70
$CH+H_2$	3.40	6.00	8.40	10.60
CH+CO	-30.72	-24.90	-18.66	-12.01
N_2+CO_2	-51.97	-42.89	-35.44	-29.63
N_2+H_2	12.00	12.00	12.00	12.00

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* The equivalent hydrocarbon gas is here assigned a molar heating value of H_{CH} = 890.63 kJ mol^{-1}.

addition to nitrogen (i=2), carbon dioxide (i=3) and the equivalent hydrocarbon (i=1), then the summation is of course extended over these two extra components.

4.2 Third Virial Coefficients and Coefficients of the Expansion in Temperature

Numerical values of the coefficients of the expansion in temperature of the third virial coefficient for like, two-component and three-component triple interactions are listed in Table 4.3. Third virial coefficients calculated from these coefficients using equation (2.10), viz.

$$C(T) = c^{(0)} + c^{(1)}T + c^{(2)}T^2 \qquad (2.10)$$

are given in the SI unit $m^6\ kmol^{-2}$ when the temperature T is in kelvin and, for the equivalent hydrocarbon gas, H_{CH} is in $kJ\ mol^{-1}$.

For a few selected temperatures (0, 20, 40 and 60 °C) rounded numerical values of third virial coefficients are given in Table 4.4 in the more familiar units of $cm^6\ mol^{-2}$. The values for the equivalent hydrocarbon gas are again calculated for a molar calorific value corresponding to that of pure methane (H_{CH} = 890.63 $kJ\ mol^{-1}$).

Third virial coefficients of an arbitrary three (or five) component mixture are then calculated from equation (2.6), viz.

$$C_{mix}(T) = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} x_i x_j x_k C_{ijk}(T) \qquad (2.6)$$

where each C_{ijk} is calculated from equation (2.10) using the coefficients given in Table 4.3, and x_i, x_j, and x_k are the mole fractions of components i, j and k respectively, predetermined from the input data as shown in Section 5.

Table 4.3 Numerical Values of the Coefficients $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$ for the Expansion in Temperature of the Third Virial Coefficients of Gases and of the Unlike Interaction Virial Coefficients

Units of C are m^6 $kmol^{-2}$ when T is in kelvin.

	equation	$c^{(0)}$	$c^{(1)}$	$c^{(2)}$
CH, ϵ_{H0}	(3.12)	$-3.02488\ 10^{-1}$	$1.95861\ 10^{-3}$	$-3.16302\ 10^{-6}$
CH, ϵ_{H1}	(3.12)	$6.46422\ 10^{-4}$	$-4.22876\ 10^{-6}$	$6.88157\ 10^{-9}$
CH, ϵ_{H2}	(3.12)	$-3.32805\ 10^{-7}$	$2.23160\ 10^{-9}$	$-3.67713\ 10^{-12}$
N_2	(3.3)	$7.84980\ 10^{-3}$	$-3.98950\ 10^{-5}$	$6.11870\ 10^{-8}$
CO_2	(3.3)	$2.05130\ 10^{-3}$	$3.48880\ 10^{-5}$	$-8.37030\ 10^{-8}$
H_2	(3.3)	$1.04711\ 10^{-3}$	$-3.64887\ 10^{-6}$	$4.67095\ 10^{-9}$
$CH+CH+N_2$	(3.20)	$y = 0.92 + 0.0013\ (T-270)$		
$CH+CH+CO_2$	(3.19)	$y = 0.92$		
$CH+CH+H_2$	(3.23)	$y = 1.20$		
CH+CH+CO	(2.10)	$7.36748\ 10^{-3}$	$-2.76578\ 10^{-5}$	$3.43051\ 10^{-8}$
$CH+N_2+N_2$	(3.20)	$y = 0.92 + 0.0013\ (T-270)$		
$CH+N_2+CO_2$	(3.22)	$y = 1.10$		
$CH+CO_2+CO_2$	(3.19)	$y = 0.92$		
$N_2+N_2+CO_2$	(2.10)	$5.52066\ 10^{-3}$	$-1.68609\ 10^{-5}$	$1.57169\ 10^{-8}$
$N_2+CO_2+CO_2$	(2.10)	$3.58783\ 10^{-3}$	$8.06674\ 10^{-6}$	$-3.25798\ 10^{-8}$

Table 4.4 Numerical Values of the Third Virial Coefficient in cm^6 mol^{-2} for Pure Gases and Mixed Interactions at Four Temperatures

Pure Gases **Mixtures**	**Temperature/K**			
	273.15	**293.15**	**313.15**	**333.15**
CH*	2670	2480	2320	2210
N_2	1520	1410	1360	1350
CO_2	5340	5090	4770	4380
H_2	399	379	363	350
$CH+CH+N_2$	2045	1950	1897	1878
$CH+CH+CO_2$	3095	2897	2716	2552
$CH+CH+H_2$	1700	1590	1502	1434
CH+CH+CO	2370	2210	2070	1960
$CH+N_2+N_2$	1695	1616	1587	1594
$CH+N_2+CO_2$	3067	2871	2717	2590
$CH+CO_2+CO_2$	3899	3683	3453	3207
$N_2+N_2+CO_2$	2090	1930	1780	1650
$N_2+CO_2+CO_2$	3360	3150	2920	2660

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* The equivalent hydrocarbon gas is here assigned a molar heating value of H_{CH} = 890.63 kJ mol^{-1}.

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5 - CALCULATIONAL PROCEDURES

5.1 Relation between Molar Heating Value and Molar Mass

In sub-section 3.4 a relationship between the molar heating value H_{CH} and the virial coefficients B_{CH} and C_{CH} of the equivalent hydrocarbon has been developed. A similar relation can be obtained between the virial coefficients and the molar mass M_{CH} of the equivalent hydrocarbon, where

$$M_{CH} = \sum_{j=1}^{N} x_j M_j . \qquad (5.1)$$

The reason for this is that the molar heating values of alkane hydrocarbons increase in an essentially linear fashion with molar mass, leading to the expression

$$M_{CH} = -2.709328 + 0.021062199 . H_{CH} . \qquad (5.2)$$

Equation (5.2) is a correlation valid for the range of values found in natural gas mixtures, especially derived for the equivalent hydrocarbon part of natural gases (7). It is needed as part of the procedure, outlined briefly in the next sub-section and in more detail thereafter, by which x_{CH} and H_{CH} - and consequently the virial coefficients and compressibility factor Z of the whole gas - may be derived from H_s, d and x_3.

5.2 General Description of Iterative Procedures

The major task in the determination of $Z_{mix}(p,T)$ is clearly the evaluation of the molar heating value H_{CH} of the equivalent hydrocarbon, its mole fraction x_{CH} (or x_1) and the unmeasured mole fraction (usually) of nitrogen x_2. Once these are known the calculation of B_{CH}, and then Z_{mix}, may be carried out straightforwardly.

If the problem instead was to determine unknown values of H_s, x_3 and d from known values of H_{CH}, x_{CH} and x_2 (i.e. the inverse of the actual case), then this could be solved essentially directly, as follows -

(1) Use x_{CH} (x_1) and x_2 to find x_3 (sum=1);

(2) Use H_{CH} to find M_{CH} (equation (5.1));

(3) Use M_{CH}, with M_2 and M_3 as known physical constants, together with x_1, x_2 and x_3, to determine the mean molecular weight or molar mass M_{mix};

(4) Divide M_{mix} by the known value for M_{air}, to find d (actually the ideal value d^o, but that is a minor detail readily accommodated);

(5) Multiply d by the known mass density of air at reference conditions, so as to obtain the mass density of the whole natural gas mixture at reference conditions;

(6) Divide the mass density at reference conditions by M_{mix}, so as to obtain the molar density at reference conditions;

(7) Multiply H_{CH} by the molar density, so as to obtain H_s.

Although the above argument suggests that the inverse problem with which we are actually faced can indeed be solved, this cannot be achieved directly. This is because we do not know what value of either H_{CH} or the molar density to take at the first step of the reverse procedure; nor would we know the value of M_{mix} required at the second step. Instead, an iterative approach is required; a convenient version of such an iterative approach is outlined in this sub-section.

The calculation scheme for determining $Z_{mix}(p,T)$, given the values of p, T (or t), H_s, d and x_3 is a nested iteration technique. It is illustrated in the simplified flow diagram given as Figures 5.1 and 5.2.

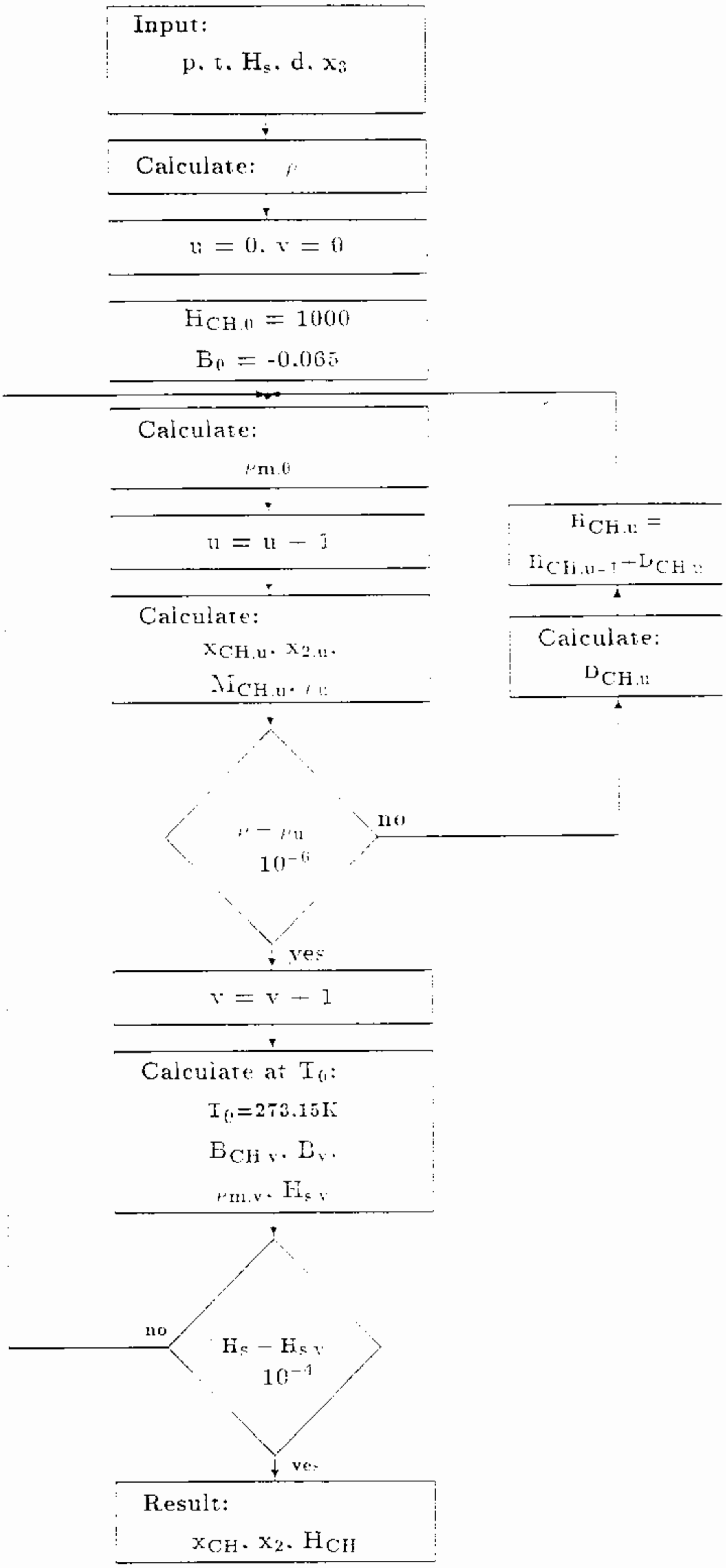

Figure 5.1 Flow Diagram: Intermediate Data Iteration

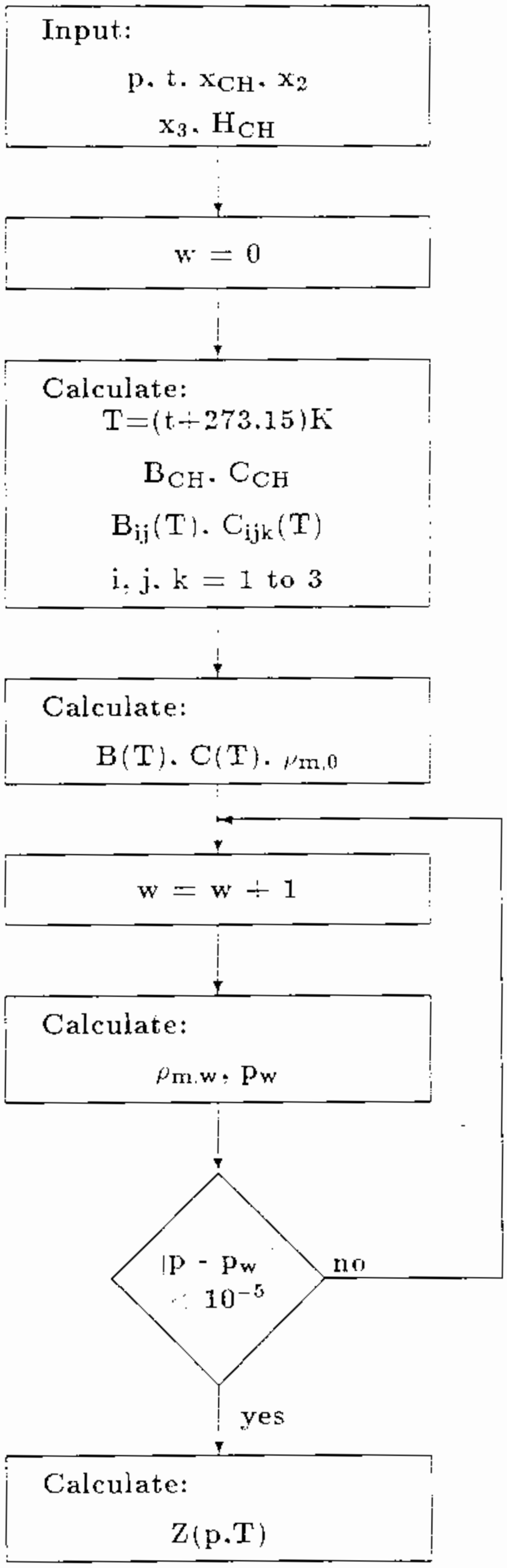

Figure 5.2 Flow Diagram: Compressibility Factor Calculation

The method first takes an assumed value B_0 for the second virial coefficient of the whole gas mixture and, holding this value fixed, reduces the difference between the known (experimental) value of the relative density d and a calculated value d_u (for the u-th iteration) by adjusting the value $H_{CH,u}$ of the molar heating value of the equivalent hydrocarbon. When this procedure has converged, within an acceptable limit, to the correct value of d, the prevailing value of $H_{CH,u}$ is used to calculate "first approximation" values of the equivalent hydrocarbon second virial coefficient $B_{CH,1}$ and, from this, the second virial coefficient B_1 of the whole gas and hence its superior calorific value $H_{s,1}$.*

A second convergence criterion is then applied to the difference between the known calorific value H_s and the calculated value $H_{s,1}$. If this is not satisfied, the value of B_0 is replaced by B_1 and the iteration on the relative density (or density, as illustrated in Figure 5.1 and used in the next sub-section) repeated, yielding an improved value of $H_{CH,u}$, whence new values $B_{CH,2}$, B_2 and $H_{s,2}$ emerge. This procedure is repeated until a value $H_{s,v}$ is found which satisfies the second convergence criterion on the v-th iteration.

When both convergence criteria are satisfied, the prevailing values of all parameters are taken to be the correct values, and the problem is essentially solved; that is, the values of H_{CH} and $x_1=x_{CH}$ which simultaneously give the correct values for d (or ρ) and H_s may be used to calculate $B_{CH}(T)$ and x_2 respectively, and hence Z(p,T) as indicated in Figure 5.2.

The detailed equations which apply in this iterative process are given in the next sub-section, together with all other necessary details.

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* An equivalent convergence test for the u-loop uses the difference between the mass density ρ and the value ρ_u from the u-th iteration. These quantities differ from the corresponding values of d and d_u only by the multiplying factor ρ_{air}.

5.3 Details of Procedures to Determine Compressibility Factor using the Standard Input Variables

Starting values for the iterative procedure outlined in the foregoing sub-section are not critical, provided that reasonably typical values are adopted; suitable values are

$$B_0(273.15\ \mathrm{K}) = -0.065\ \mathrm{m^3\ kmol^{-1}} \tag{5.3}$$

$$H_{CH,0}(298.15\ \mathrm{K}) = 1000\ \mathrm{MJ\ kmol^{-1}}. \tag{5.4}$$

From these values the calculation proceeds in a fairly straightforward fashion. Firstly, using the starting value B_0, a first iterative estimate (u=1, v=0) of the molar density $\rho_{m,v}$ of the whole natural gas is calculated from

$$\rho_{m,v} = 1/(V_m{}^o + B_v) \tag{5.5}$$

where $V_m{}^o = 22.414097\ \mathrm{m^3\ kmol^{-1}}$ is the molar volume of an ideal gas at 273.15 K and 101.325 kPa. This equation is simply a re-expressed form of the virial equation truncated after the second virial coefficient.

Next, the starting value $H_{CH,0}$ of the molar heating value of the equivalent hydrocarbon is used to make a first estimate (u=1) of its own mole fraction by use of the expression

$$x_{CH,u} = H_S/(H_{CH,u-1}\cdot\rho_{m,v}). \tag{5.6}$$

As the mole fraction x_3 of carbon dioxide is known, a first approximation $x_{2,u}$ (u=1) for the mole fraction of nitrogen may then be calculated from

$$x_{2,u} = 1 - (x_{CH,u} + x_3). \tag{5.7}$$

Next, we again use the value of $H_{CH,0}$ in equation (5.8) (a generalised form of (5.2)) so as to calculate a first approximation (u=1) to the molar mass of the equivalent hydrocarbon, viz.

$$M_{CH,u} = -2.709328 + 0.021062199.H_{CH,u-1}. \tag{5.8}$$

The (mass) density ρ_u of the whole gas may now be calculated from

$$\rho_u = \rho_{m,v} \cdot (x_{CH,u} \cdot M_{CH,u} + x_{2,u} \cdot M_2 + x_3 . M_3) \qquad (5.9)$$

where $M_2 = 28.0135$ kg kmol^{-1} is the molar mass of nitrogen, and $M_3 = 44.010$ kg mol^{-1} is the molar mass of carbon dioxide (25).

Finally, the first approximation ($u=1$) to the (mass) density may be compared with the known density ρ calculated from

$$\rho = d . \rho_{air} \qquad (5.10)$$

where $\rho_{air} = 1.292923$ kg m^{-3} is the mass density of air at 273.15 K and 101.325 kPa (25), and d the known relative density .

At this stage the first convergence criterion is applied. A suitable criterion is that the calculated (mass) density ρ_u should agree with the known (mass) density ρ within 10^{-6}, that is

$$|(\rho_u - \rho)| < 10^{-6} \qquad (5.11)$$

Alternatively, an exactly equivalent test can be applied to the difference between the calculated relative density d_u and the value d.

If this condition is not satisfied (as is very unlikely to be the case for $u=1$), then a new value is taken for $H_{CH,u}$ given by

$$H_{CH,u} = H_{CH,u-1} + D_{CH,u} \qquad (5.12)$$

where

$$D_{CH,u} = -H_{CH,u-1} \cdot (\rho_u - \rho)/\rho_{air} \qquad (5.13)$$

The iteration counter u is then re-set to u+1 and equations

(5.6) to (5.13) re-applied until the convergence criterion (5.11) is satisfied. Equation (5.13) is a convenient means of assuring reasonably rapid convergence (typically requiring 5 to 7 iterations), but alternative formulations are possible.*

The second stage now begins. Using the value of $H_{CH,u-1}$ established as an interim solution for H_{CH} from the first (u) iteration loop, a first approximation (v=1) for the second virial coefficient of the equivalent hydrocarbon is obtained from

$$B_{CH,v}(T_o) = \beta_{H0}(T_o) + \beta_{H1}(T_o)H_{CH,u-1} + \beta_{H2}(T_o)H^2_{CH,u-1} \qquad (5.14)$$

where $T_o = 273.15$ K, and the corresponding values of β_{Hq} (q=0,1,2) are known from equation (3.11) using the numerical values of constants given in Section 4, Table 4.1.

We may now calculate a revised (v=1) approximation for the second virial coefficient of the whole gas, using the expression

$$\begin{aligned} B_v(T_o) = {} & x^2_{CH,u}B_{CH,v}(T_o) + x^2_{2,u}B_{22}(T_o) + x^2_3B_{33}(T_o) \\ & + 2x_{CH,u}x_{2,u}B_{12,v}(T_o) + 2x_{CH,u}x_3B_{13,v}(T_o) \\ & + 2x_{2,u}x_3B_{23}(T_o). \end{aligned} \qquad (5.15)$$

In this equation, which is simply a specific case of equation (2.3), $x_{CH,u}$ and $x_{2,u}$ are obtained from the previous iteration on u, B_{22}, B_{33} and B_{23} are calculated from equation (3.2) using the constants given in Table 4.1, B_{12} is calculated from the combination rule given as equations (3.15) and (3.16), and B_{13} from the corresponding equations (3.13) and (3.14).

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* One such alternative formulation uses the expresssion

$$D_{CH,u} = (\rho_u - \rho)/(\rho_u - \rho_D) \qquad (5.13a)$$

where ρ_D is calculated from equations (5.3) to (5.9) using ($H_{CH,u-1}$ + 1) as input for the molar heating value.

The first (v=1) approximation to the normal molar density $\rho_{m,1}$ may now be calculated using equation (5.5), and equation (5.6) may then be used in the opposite sense to its previous application so as to obtain a predicted value $H_{s,v}$ for the superior calorific value from $\rho_{m,1}$, viz.

$$H_{s,v} = x_{CH,u} \cdot H_{CH,u-1} \cdot \rho_{m,v}. \tag{5.16}$$

The second convergence test is now applied. A suitable criterion is that the calculated superior calorific value $H_{s,v}$ should agree with the known superior calorific value H_s within 10^{-4}, i.e.

$$|(H_{s,v} - H_s)| < 10^{-4}. \tag{5.17}$$

If this condition is not satisfied (as, again, is very unlikely to be the case for v=1), then the value of B_0 is replaced by the current value $B_{v=1}(T_0)$ from equation (5.15), and the whole iteration procedure restarted from equation (5.6) using the current values of $H_{CH,u-1}$ and $\rho_{m,v}$.

Self-evidently, it is now simply a matter of repeating the process until both criteria (5.11) and (5.17) are satisfied simultaneously. With the starting values given by (5.3) and (5.4), no set of input parameters H_s, d and x_3 for which the Standard GERG-88 Virial Equation is valid has been found which fails to lead to satisfactory convergence within 20 iterations. The outer (second) loop usually converges very rapidly, normally requiring only 2 or 3 iterations.

Note that throughout the iterative procedure, all calculations have been carried out for the "normal" condition i.e. T_0 = 273.15 K, p_0 = 101.325 kPa; no reference has yet been made to the temperature and pressure at which it is actually required to know the compressibility factor. The final stage of the calculation addresses that matter (see Figure 5.2).

We now have set values for $x_1 = x_{CH}$, x_2, x_3 and H_{CH}. Given H_{CH} and T, we may calculate $B_{CH}(T)$ and $C_{CH}(T)$ using equations (2.7) and (2.8) respectively, using values of the coefficients β_{Hq} and ϵ_{Hq} calculated from equations (3.11) and (3.12) with the various constants $b_{Hq}^{(r)}$ and $c_{Hq}^{(r)}$ as given in Tables 4.1 and 4.3 respectively. Values for $B_{22}(T)$, $B_{33}(T)$, $B_{23}(T)$, $C_{222}(T)$, $C_{333}(T)$, $C_{223}(T)$ and $C_{233}(T)$ are all straightforward to calculate using the numerical values given in Tables 4.1 and 4.3, leaving only $B_{12}(T)$, $B_{13}(T)$, $C_{112}(T)$, $C_{113}(T)$, $C_{122}(T)$, $C_{133}(T)$ and $C_{123}(T)$ requiring evaluation. However, since we now know $B_{11}=B_{CH}(T)$ and $C_{111}=C_{CH}(T)$, even these fall out simply from equations (3.13) to (3.22), so that $B_{mix}(T)$ and $C_{mix}(T)$ may be calculated from equations (2.3) and (2.4) respectively for the present special case where N=3.

The very final stage is then to solve equations (2.1) and (2.2) simultaneously for the given value of pressure p. There are various equivalent ways by which this may be achieved. A simple iterative procedure (as described previously in ref.1) uses $Z_0=1$ as a starting value in (2.1), solves this equation for $\rho_{m,w}$ and puts this value into (2.2) so as to generate an improved estimate $Z_{w=1}$, which acts as a starting value for the next loop. Alternatively, as shown in Figure 5.2, the pressure p_w may now be calculated by re-entering $\rho_{m,w}$ and Z_w into equation (2.1). Either process converges to the correct value of Z both reliably and rapidly for all valid sets of conditions. An appropriate convergence criterion is that Z_w should change by less than 1 in at least 10^5 on successive iterations, or that the input pressure differs from the calculated value by a corresponding amount.

5.4 Procedure when Hydrogen and Carbon Monoxide are Present

The calculation procedure described in the previous sub-sections 5.2 and 5.3 has only to be modified slightly for natural gases containing admixture of hydrogen and carbon monoxide from coke-oven gases.

The mole fraction of hydrogen x_4 is required as the fourth input parameter. The mole fraction of carbon monoxide x_5 is then calculated using equation (5.18), which adopts and defines a fixed ratio between these two mole fractions, viz.

$$x_5 = 0.0964.x_4. \qquad (5.18)$$

The constant factor has been estimated from observations of the compositions of the several gases in the GERG databank (10) which contain these components.

The calculation method can then proceed in exactly the same way as described previously, except that equations (5.6), (5.7), (5.9), (5.15) and (5.16) need to be modified for the contributions of hydrogen and carbon monoxide, as follows (respectively) -

(a) $$x_{CH,u} = [H_s/H_{CH,u-1}\cdot\rho_{m,v}] - [(x_4H_4 + x_5H_5)/H_{CH,u-1}] \qquad (5.19)$$

where H_4 = 285.83 MJ $kmol^{-1}$ is the molar heating value of hydrogen, and H_5 = 282.98 MJ $kmol^{-1}$ is the molar heating value of carbon monoxide at 298.15 K (25).

The above equation is more recognisably correct if it is multiplied through $H_{CH,u}$ and the terms in x_4 and x_5 are taken to the left-hand side.

(b) $$x_{2,u} = 1 - (x_{CH,u} + x_3 + x_4 + x_5) \qquad (5.20)$$

(c) $$\rho_u = \rho_{m,v}\cdot(x_{CH,u}M_{CH,u} + x_{2,u}M_2 + x_3M_3 + x_4M_4 + x_5M_5) \qquad (5.21)$$

where M_4 = 2.0159 g mol^{-1} is the molar mass of hydrogen, and M_5 = 28.010 g mol^{-1} is the molar mass of carbon monoxide (25).

(d) $$B_v(T_o) = x_{CH,u}^2B_{CH,v} + 2x_{CH,u}x_{2,u}B_{12,v} + 2x_{CH,u}x_3B_{13,v} + 2x_{CH,u}x_4B_{14,v} + 2x_{CH,u}x_5B_{15,v} + x_{2,u}^2B_{22} + 2x_{2,u}x_3B_{23} + 2x_{2,u}x_4B_{24} + x_3^2B_{33} + x_4^2B_{44} + x_5^2B_{55} \qquad (5.22)$$

(e) $$H_{s,v} = (x_{CH,u}H_{CH,u-1} + x_4H_4 + x_5H_5)\cdot\rho_{m,v}. \qquad (5.23)$$

5.5 Procedures using Alternative Input Variables

The calculation procedure, for cases where input variables other than those comprising the normally recommended set are available, will be discussed for natural gases only. For natural gases with hydrogen admixture, the principles discussed in sub-section 5.4 must be applied in a rather self-evident manner.

5.5.1 Calorific Value, Relative Density and Mole Fraction of Nitrogen

The procedure is similar to that described in sub-section 5.3. However, equation (5.7) must be re-written as

$$x_{3,u} = 1 - (x_{CH,u} + x_2). \qquad (5.24)$$

The entire iteration procedure is unchanged, except that it gives the unknown value of x_3 instead of x_2 as previously.

5.5.2 Calorific Value, Mole Fractions of Carbon Dioxide and Nitrogen

When the mole fractions of carbon dioxide and nitrogen are available as input data, the mole fraction x_{CH} of the equivalent hydrocarbon may immediately be calculated as

$$x_{CH} = 1 - (x_2 + x_3). \qquad (5.25)$$

The iteration on u is started and carried out in a very similar fashion to that described in detail in sub-section 5.3. In this case, however, when a new value $x_{CH,u}$ becomes available from equation (5.6) a convergence test against the known value of x_{CH} is applied. A suitable criterion is

$$|(x_{CH,u} - x_{CH})| < 10^{-5}. \qquad (5.26)$$

This replaces condition (5.11), the (mass) density or relative density being unknown. The remaining procedure is similar to that described in 5.3. Indeed the outer iteration loop on v is essentially identical to that described, and uses condition (5.17) as the convergence criterion. Once this is satisfied, the final values of H_{CH} and ρ_m are available, and values of all properties given by equations (5.8) to (5.10) may be inferred, in addition to the virial coefficients and compressibility factor for any valid (p,T) condition.

Although the above is a viable scheme for carrying out the calculations for this set of input data, the inner (u) iteration loop is in fact not necessary. Input of the known values for H_S and x_{CH}, together with the initial (v=0) value $\rho_{m,v}$ from equation (5.5), enables $H_{CH,u-1}$ to be found directly from equation (5.6). By use of equations (5.14), (5.15) and (5.5), a new value for $\rho_{m,v}$ may then be found. The procedure may be carried out again with this new value, and repeated until satisfactory convergence on the value of H_{CH} is obtained. Once this is satisfied, all of the properties are available as before.

5.5.3 Relative Density, Mole Fractions of Carbon Dioxide and Nitrogen

A similar procedure to that described in sub-section 5.5.2 can be followed. The mole fraction x_{CH} of the equivalent hydrocarbon is again given by equation (5.25), but now the equations (5.6) and (5.7) do not appear in the inner (u) iteration loop; condition (5.11) is applied as the convergence criterion, and equations (5.12) and (5.13) used to move towards convergence. The outer (v) iteration loop then begins, and continues until the value of B_v calculated from equation (5.15) is in satisfactory (converged) agreement with the previous value B_{v-1} used in equation (5.5). When this is achieved, final values of H_{CH} and ρ_m are available, and the unmeasured value H_S may be found from equation (5.16), in addition to the virial coefficients and compressibility factor of the mixture for any valid (p,T) condition.

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6 - PERFORMANCE OF THE STANDARD GERG-88 VIRIAL EQUATION

6.1 Test Data and Input Parameters

From the GERG databank of high-quality compressibility factor measurements (10), the first 84 sets of data for natural gas and natural gas/coke-oven gas mixtures have been used for assessing the performance of the Standard GERG-88 Virial Equation of State. This analysis was carried out in a closely similar fashion to that previously adopted for the Master GERG Equation (1). The details concerning each individual data set, comprising a reference to the data source, the GERG coding and the number of experimental points, are given in Table 3.4. The reduced gas analyses for the natural gases are listed in Table 3.5, and the detailed gas compositions in Table 3.6. The reduced analyses, for which the calorific values and relative densities were calculated in accordance with international standard ISO-6976 (25(b)), were used together with the known temperature and pressure as input parameters for each data point.

Four different intercomparisons have been made, viz.

(a) A global comparison of the predicted values against all available experimental data for the natural gases listed in Table 3.4 (4486 data points);

(b) A comparison of the predicted values against the same set of experimental data for natural gases, but with these sub-divided and grouped into pressure and temperature domains;

(c) A comparison of the predicted data against experimental data for various types of natural gas. To accomplish this the experimental data were re-grouped according to gas composition, as follows -

Natural gases with mole fraction of N_2 ≥ 0.095, and no H_2
Natural gases with mole fraction of CO_2 ≥ 0.040
Natural gases with mole fraction of C_2H_6 ≥ 0.080
Natural gases with mole fraction of H_2 ≥ 0.020
Natural gases with N_2 and C_2H_6 each ≥ 0.040, and no H_2
Natural gases with mole fraction of CH_4 ≥ 0.940
Liquefied Natural Gases (LNG)*; and

(d) A graphical comparison of predicted values against experimental data (made as plots of relative deviation), along several isotherms, for six individual sets of data for natural gases, one belonging to each of the above selected composition groups.

6.2 Global Comparison against Test Data

For the comparison of values of compressibility factor Z_{calc} predicted by the Standard GERG-88 Virial Equation against experimental test data, the following quantities are used -

N = number of experimental data points
n = number of distinct data sets
ΔZ_i = relative error (or deviation) of Z for the i-th data point (equation (6.1) below)
b = bias of relative error (equation (6.2))
s = standard deviation (equation (6.3))
rms = root-mean-square error (equation (6.4)).

$$\Delta Z_i = (Z_{calc,i} - Z_{expt,i})/Z_{expt,i} \qquad (6.1)$$

$$b = \frac{1}{N} \sum_{i=1}^{N} \Delta Z_i \qquad (6.2)$$

$$s = \left[\frac{1}{N-1} \sum_{i=1}^{N} (\Delta Z_i - b)^2 \right]^{\frac{1}{2}} \qquad (6.3)$$

$$\text{rms} = \left[\frac{1}{N} \sum_{i=1}^{N} \Delta Z_i^2 \right]^{\frac{1}{2}} \qquad (6.4)$$

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* The liquefied natural gases do not belong to the set of natural gases listed in Table 3.4 - see sub-section 6.6.

The root-mean-square error for the difference between the compressibility factors predicted by the Standard GERG-88 Virial Equation and all the measured natural gas* compressibility factors for the first 84 data sets in the GERG databank is -

rms = ± 0.049% for pressures between 0 and 12 MPa (N=4486).

Figure 6.1 is a schematic plot of the correlation between the rms-error and pressure. The rms-errors are as follows for the two pressure ranges -

rms = ± 0.048% for pressures between 0 and 8 MPa (N=4043)
rms = ± 0.055% for pressures between 8 and 12 MPa (N=443).

Table 6.1 gives a more detailed breakdown of this global analysis for the first 84 data sets. It lists the number of data points, the bias, the standard deviation and the rms-error for the pressure ranges 0 to 8 and 0 to 12 MPa, the data being separated into sets (a) measured using a Desgranges et Huot (DEH) Z-Meter (used by Gaz de France, British Gas, Gasunie and Ruhrgas), (b) measured by Ruhrgas using their optical interferometry or Burnett apparatus, (c) otherwise reported in the research literature, and finally all the experimental data together. A comparison of the rms-error values for these different data sets leads to some interesting conclusions.

The rms-error for the data measured using the optical or Burnett apparatus in the pressure range up to 8 MPa is only 0.023%. The rms values are over twice as large for the data measured using a DEH Z-Meter and for the published literature data (10, 29-31). The larger rms-error for the Z-Meter set and for the literature set, as compared with the optical and Burnett set, corresponds to the generally acknowledged larger experimental uncertainties (except in the case of ref.31) for

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* Unless specifically noted otherwise, the term "natural gas(es)" or "natural gas mixtures" is here taken to include natural gas/coke-oven gas mixtures.

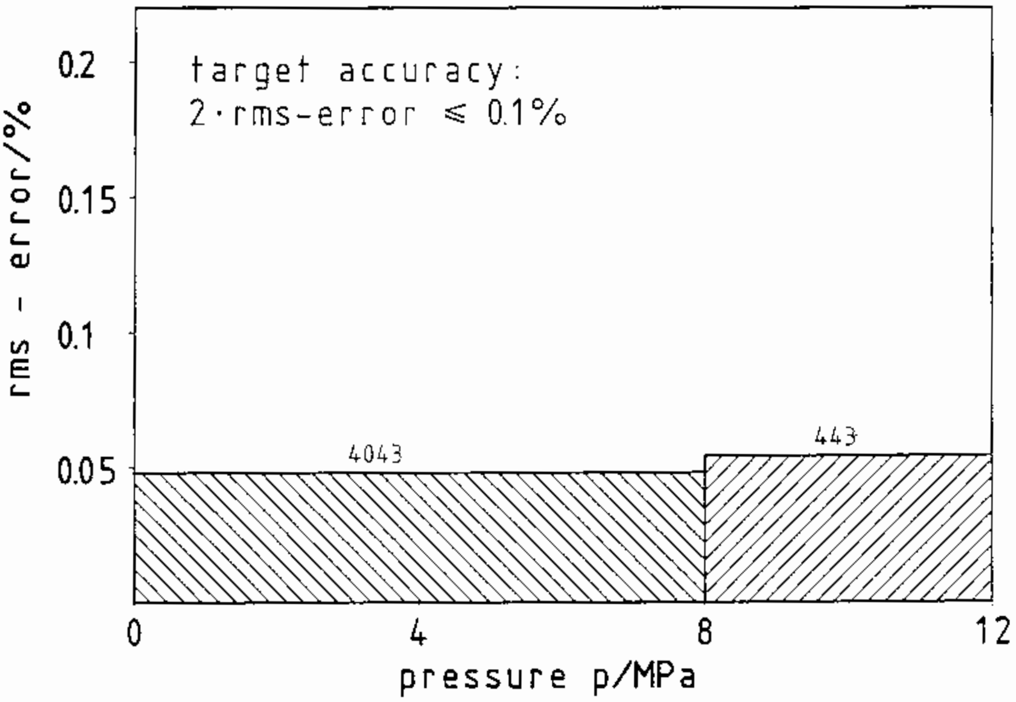

Figure 6.1 Root-Mean-Square Error for all Experimental Data Points in Two Distinct Pressure Ranges (0-8 and 8-12 MPa): Standard GERG Virial Equation.

these former measurements. Nevertheless, in all three cases the predicted values of Z agree within experimental uncertainty with the measured values. The same situation holds true for a comparison of the experimental data in the 8 to 12 MPa pressure range. Here the rms-error for the optical and Burnett set is only 0.050% whereas for the published set of data, measured to a maximum pressure of only 9 MPa and containing rather few data points, the rms-error is over 0.1%; this may again be explained by the larger uncertainties in the latter experiments.

One further minor feature worthy of note in Table 6.1 is an apparently remarkable improvement (over the equivalent table for the Master GERG Equation) in the DEH data set for the 8 to 12 MPa pressure range, notwithstanding that the entire set consists of just 6 points for a single gas at only just over 8 MPa. These experimental data are for a hydrogen-enriched natural gas (N84) containing over 35% hydrogen, and are predicted by the Standard GERG Equation equally as well as for the data for other gases with much lower hydrogen content (see also sub-section 6.4.4).

Table 6.2 gives a detailed breakdown of the same analysis for all 96 sets of data now in the GERG databank of compressibility factors. There is a noteworthy change of the results only in the subset (c), comprising data from the published literature, compared to the results in Table 6.1; in the 8 to 12 MPa pressure range the rms-error has increased to about 0.18% due to the inclusion of Hannisdal's data (32) for an ethane-rich natural gas. This data set will be discussed further in sub-section 6.4.3.

Figure 6.2 shows the rms-errors for six specific natural gases, varying widely in composition and calorific value, for pressures between 0 and 8 and between 8 and 12 MPa, as a function of superior (gross) calorific value. The compressibility factors for these natural gases were measured using the Ruhrgas optical interferometry apparatus. As the figure shows, the rms-error is always less than 0.04% for pressures not exceeding 8 MPa, and less than 0.05% for the high pres-

Table 6.1 Differences of predicted compressibility factors from measured values (Z-differences) for various groups of natural gas data in the temperature range of 265 K to 335 K: Standard GERG 88 virial equation, for 84 data sets

data set	pressure range /MPa	N points	n sets	b %	s %	rms %
DEH data	[0, 8)	1633	42	-0.011	0.056	0.057
(a)	[8,12]	6	1	0.006	0.022	0.021
	[0,12]	1639	42	-0.011	0.055	0.056
Ruhrgas data	[0, 8)	1411	27	0.008	0.022	0.023
(b)	[8,12]	412	27	-0.002	0.050	0.050
	[0,12]	1823	27	0.006	0.031	0.031
Literature data	[0, 8)	999	15	-0.010	0.060	0.060
[10,29-31]	[8,12]	25	6	-0.047	0.104	0.112
(c)	[0,12]	1024	15	-0.011	0.061	0.062
all data	[0, 8)	4043	84	-0.004	0.049	0.048
	[8,12]	443	34	-0.005	0.055	0.055
	[0,12]	4486	84	-0.004	0.049	0.049

Table 6.2 Differences of predicted compressibility factors from measured values (Z-differences) for various groups of natural gas data in the temperature range of 265 K to 335 K: Standard GERG 88 virial equation, for 96 data sets

data set	pressure range /MPa	N points	n sets	b %	s %	rms %
DEH data	[0, 8)	1982	52	-0.012	0.054	0.056
(a)	[8,12]	6	1	-0.006	0.022	0.021
	[0,12]	1988	52	-0.012	0.054	0.056
Ruhrgas data	[0, 8)	1411	27	0.008	0.022	0.023
(b)	[8,12]	412	27	-0.002	0.050	0.050
	[0,12]	1823	27	0.006	0.031	0.031
Literature data	[0, 8)	1012	17	-0.010	0.060	0.061
[10,29-33]	[8,12]	27	7	-0.004	0.186	0.183
(c)	[0,12]	1039	17	-0.009	0.066	0.067
all data	[0, 8)	4405	96	-0.005	0.049	0.049
	[8,12]	445	35	-0.002	0.066	0.066
	[0,12]	4850	96	-0.005	0.051	0.051

sure range. The NAM* gas, the natural gas/coke-oven gas mixture and the Ekofisk gas contain some 10% of nitrogen, hydrogen and ethane respectively. The Drohne gas contains some 5% of nitrogen and of carbon dioxide, and the TENP+ gas some 5% of nitrogen and of ethane, while the Soviet gas is practically pure methane.

The distribution of root-mean-square errors for the first 84 natural gases is plotted in Figure 6.3. For two-thirds of the natural gases the rms-error of the data is less than 0.05%. The data sets with an rms-error greater than 0.05% were measured - with the exception of one Ruhrgas interferometry set - either with a DEH Z-Meter or are from the literature. More detailed information about the bias, standard deviation and rms-error for each set of data is given in Table 6.3. One natural gas (N21) has a rms-error which is greater than 0.2%.

The distribution of the bias (mean relative error) between the Standard GERG-88 Virial Equation and the experimental data is plotted in Figure 6.4 for the entire (84 set) population of natural gases. This plot shows the equation to provide an excellent description of the real-gas behaviour of these gases; the distribution of biases is more or less symmetrical, and exceeds ±0.1% for gas N21 only.

The same distribution pattern is evident in Figure 6.5, which shows the relative deviation between the predicted compressibility factor and the measured compressibility factor for all 4486 data points. The agreement between the predicted compressibility factors and the measured values can again be seen to be very satisfactory. The predicted values differ only in some 220 cases (about 5% of the total) by more than ±0.1% from the measured values; 12 values exceed 0.25% relative error.

Consequently, the Standard GERG-88 Virial Equation can be said to predict the experimental compressibility factor data,

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* Nederlandse Aardolie Maatschappij
+ Trans Europa Naturgas Pipeline

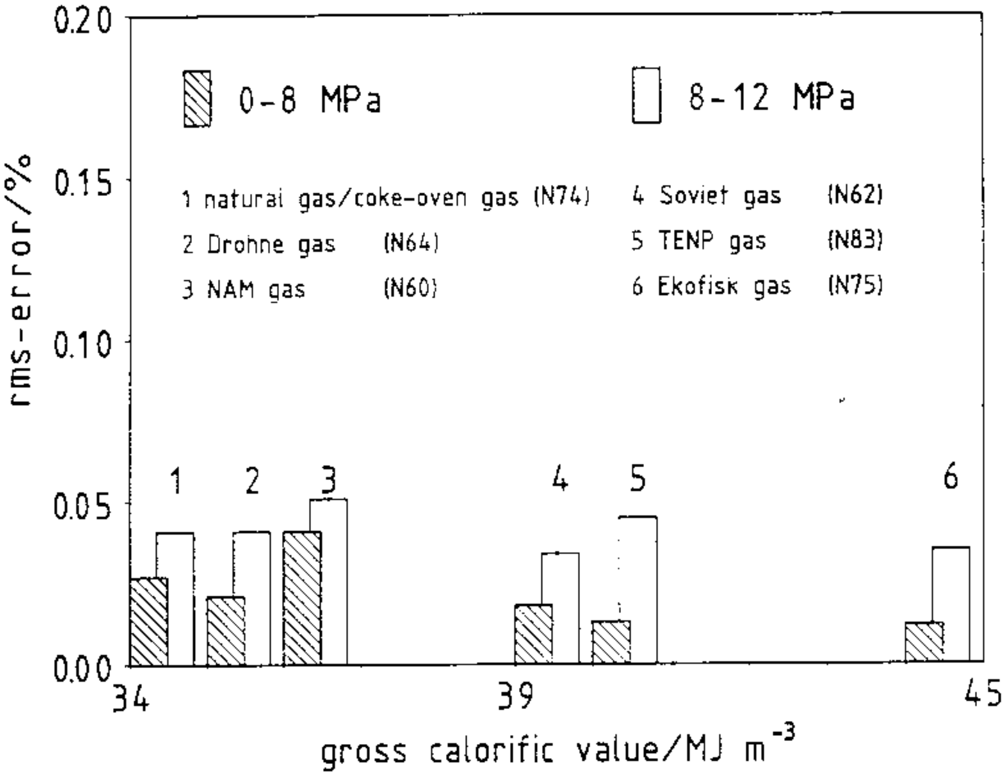

Figure 6.2 Root-Mean-Square Error for Six Specific Natural Gases in Two Distinct Pressure Ranges (0-8 and 8-12 MPa): Standard GERG Virial Equation.

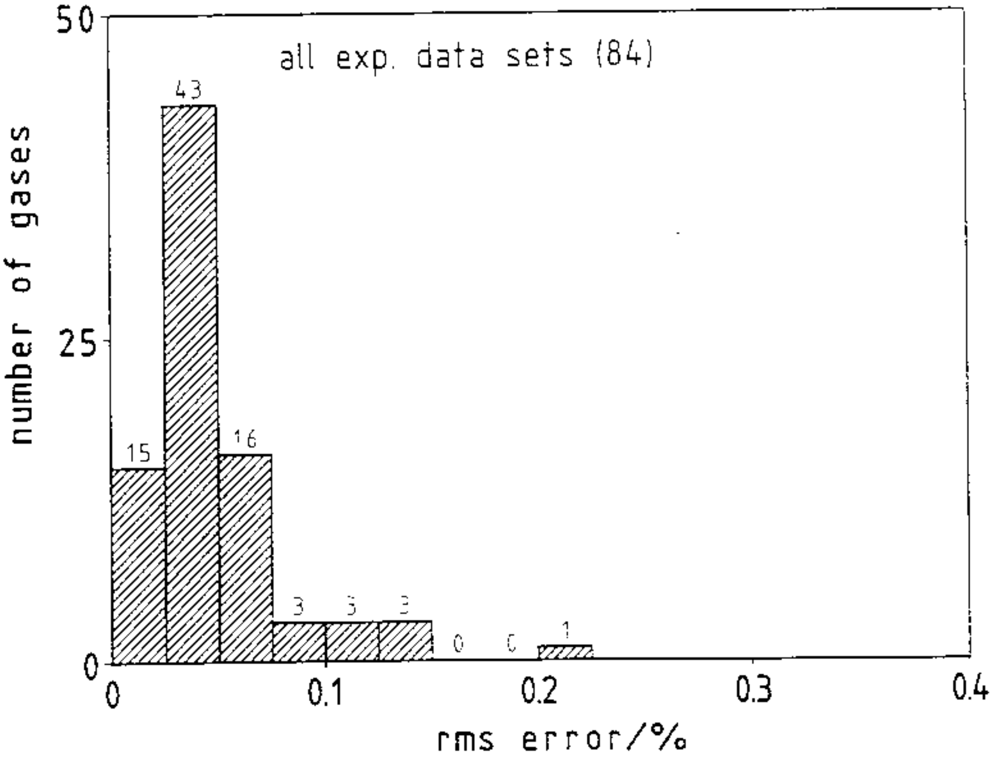

Figure 6.3 Root-Mean-Square Error Distribution of all Data sets for Natural Gases: Standard GERG Virial Equation.

Table 6.3 Statistical analysis of the Z-differences for the compressibility factors of each individual natural gas data set: Standard GERG 88 virial equation

temperature range in K (265,335)

pressure range in MPa (0,12)

GERG code	reference	N points	b %	s %	rms %
N 1	RG DEH 003	18	-0.095	0.052	0.108
N 2	RG DEH 005	16	-0.021	0.032	0.038
N 3	RG DEH 006	18	-0.094	0.039	0.102
N 4	RG DEH 007	18	-0.037	0.050	0.061
N 5	RG DEH 011	24	-0.028	0.041	0.049
N 6	RG DEH 012	24	-0.015	0.025	0.029
N 7	RG DEH 013	24	-0.040	0.030	0.049
N 8	RG DEH 014	23	-0.021	0.045	0.049
N 9	Achtermann	67	0.009	0.036	0.037
N 10	Achtermann	68	-0.022	0.044	0.049
N 11	Achtermann	69	-0.012	0.024	0.027
N 12	Achtermann	69	-0.008	0.027	0.028
N 13	Achtermann	74	0.007	0.020	0.022
N 14	Achtermann	74	0.022	0.055	0.059
N 15	Achtermann	73	0.005	0.075	0.075
N 16	Achtermann	74	0.001	0.051	0.060
N 17	Achtermann	76	0.020	0.045	0.049
N 18	Achtermann	68	-0.029	0.078	0.083
N 19	Achtermann	73	-0.041	0.069	0.079
N 20	Achtermann	77	-0.007	0.071	0.071
N 21	BG Roe	12	-0.159	0.135	0.205
N 22	BG Roe	15	-0.100	0.103	0.141
N 23	GF 008	18	-0.009	0.039	0.039
N 24	GF 009	12	-0.005	0.032	0.031
N 25	GF 010	10	0.013	0.078	0.075
N 26	GF 011	5	0.008	0.160	0.143
N 27	GF 012	5	0.017	0.177	0.159
N 28	GU 008	64	-0.037	0.028	0.047
N 29	GU 009	53	0.039	0.025	0.046
N 30	GU 010	52	-0.037	0.021	0.042
N 31	GU 011	53	-0.036	0.020	0.041
N 32	GU 012	54	-0.040	0.023	0.046
N 33	GU 013	64	0.000	0.048	0.048
N 34	GU 014	52	0.008	0.031	0.032
N 35	GU 015	55	0.059	0.043	0.073
N 36	GU 016	55	-0.036	0.021	0.042
N 37	GU 017	64	-0.099	0.071	0.121
N 38	GU 018	65	-0.021	0.031	0.037
N 39	GU 019	55	-0.002	0.020	0.020
N 40	GU 020	54	-0.051	0.025	0.057
N 41	GU 021	16	-0.045	0.012	0.046
N 42	GU 022	44	-0.050	0.054	0.073
N 43	GU 023	66	0.019	0.026	0.032
N 44	GU 024	66	-0.039	0.048	0.061
N 45	GU 025	66	0.008	0.039	0.040
N 46	GU 026	65	0.000	0.043	0.043
N 47	GU 027	65	0.015	0.024	0.029
N 48	GU 028	65	0.056	0.044	0.071
N 49	GU 038	33	0.050	0.022	0.055
N 50	GU 051	22	-0.031	0.010	0.033

Table 6.3 Statistical analysis of the Z-differences for the compressibility factors of each individual natural gas data set: Standard GERG 88 Virial equation

temperature range in K (265,335)

pressure range in MPa (0,12)

GERG code	reference	N points	b %	s %	rms %
N 51	RG BUR 007	25	0.037	0.026	0.045
N 52	RG OPT 007	23	0.055	0.031	0.063
N 53	RG BUR 008	25	0.011	0.028	0.030
N 54	RG OPT 008	38	-0.002	0.052	0.051
N 55	RG BUR 009	83	-0.007	0.025	0.026
N 56	RG OPT 009	71	-0.020	0.043	0.047
N 57	RG BUR 017	27	0.005	0.015	0.016
N 58	RG OPT 035	48	0.017	0.021	0.027
N 59	RG BUR 018	28	0.016	0.019	0.025
N 60	RG OPT 036	117	0.024	0.037	0.044
N 61	RG BUR 020	30	0.005	0.008	0.009
N 62	RG OPT 034	109	0.002	0.024	0.024
N 63	RG BUR 031	50	0.008	0.028	0.029
N 64	RG OPT 031	117	0.023	0.028	0.036
N 65	RG BUR 032	54	-0.004	0.018	0.018
N 66	RG OPT 032	120	-0.006	0.029	0.030
N 67	RG BUR 049	68	0.028	0.028	0.039
N 68	RG BUR 050	69	0.009	0.016	0.018
N 69	RG BUR 051	70	-0.005	0.013	0.013
N 70	RG BUR 052	68	0.029	0.035	0.045
N 71	RG BUR 053	70	0.001	0.014	0.014
N 72	RG BUR 054	67	-0.003	0.014	0.014
N 73	RG BUR 047	25	0.012	0.010	0.016
N 74	RG OPT 060	121	0.010	0.033	0.034
N 75	RG OPT 048	132	0.002	0.021	0.021
N 76	Duschek	135	-0.030	0.039	0.049
N 77	GU 001	11	0.036	0.065	0.072
N 78	GU 002	19	0.049	0.031	0.058
N 79	GU 003	21	-0.063	0.046	0.077
N 80	GU 006	44	0.048	0.048	0.067
N 81	GU 007	42	0.031	0.028	0.041
N 82	RG BUR 048	45	-0.005	0.014	0.015
N 83	RG OPT 061	123	-0.017	0.023	0.029
N 84	BG 004	37	-0.011	0.022	0.025
N 85	GU 071	48	0.017	0.038	0.041
N 86	HD EXP 001	8	0.193	0.232	0.291
N 87	EL DEH 004	7	-0.035	0.022	0.041
N 88	BG DEH 002	40	-0.067	0.027	0.072
N 89	BG DEH 007	42	0.000	0.020	0.020
N 90	BG DEH 008	35	-0.065	0.027	0.070
N 91	BG DEH 009	32	-0.075	0.040	0.085
N 92	BG DEH 010	26	-0.004	0.023	0.023
N 93	BG DEH 011	8	0.063	0.017	0.065
N 94	GU 072	26	-0.016	0.011	0.019
N 95	GU 073	44	-0.019	0.048	0.052
N 96	GU 074	48	0.022	0.024	0.032
Totals		4850	-0.005	0.051	0.051

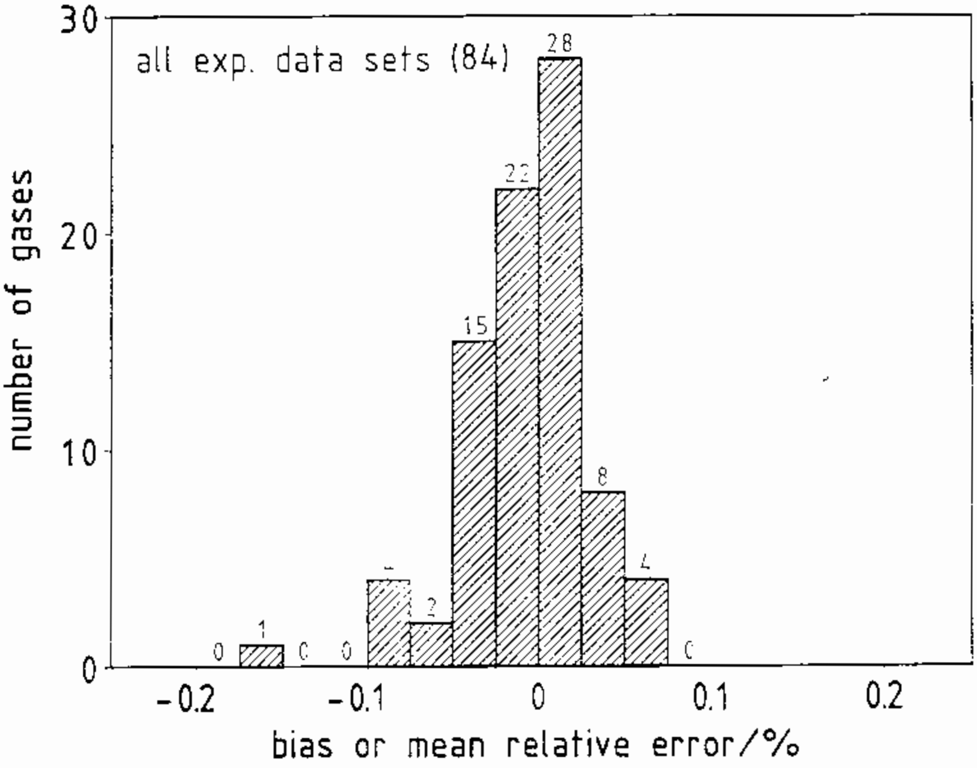

Figure 6.4 Average Error (Bias) Distribution of all Data Sets for Natural Gases: Standard GERG Virial Equation.

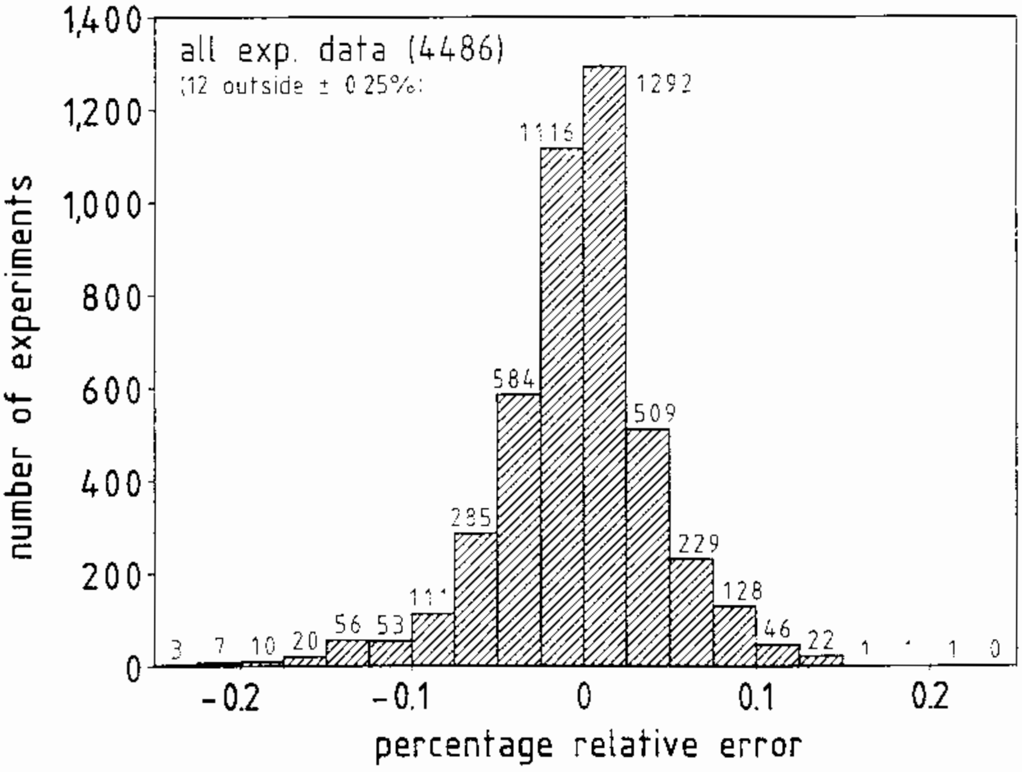

Figure 6.5 Percentage Relative Error Distribution for all Experimental Data Points for Natural Gases: Standard GERG Virial Equation.

at the 95% confidence level, within the target accuracy of ±0.1%. This performance compares favourably with that of the Master GERG-88 Virial Equation (1).

The Standard GERG Virial Equation may also be compared directly with the Master GERG Virial Equation using the rms-errors for the various natural gas data sets, as shown in Figures 6.6 and 6.7. The rms-errors for both the Standard and Master equations are plotted in Figure 6.6 for the 28 Gasunie data sets (measured using a DEH Z-Meter). Results are quite similar for both equations, but only two data sets have a rms-error greater than 0.075% for the Standard Equation compared to eight sets for the Master Equation. One reason for this is the improved prediction of high-nitrogen content gases by the Standard Equation; this matter is discussed further in sub-section 6.4.1. Nevertheless, within the experimental uncertainty of about ±0.1%, the measured Gasunie data agree well with the predicted values for both equations.

Figure 6.7 shows a similar comparison for the 27 sets of data measured by Ruhrgas using their optical interferometry or Burnett apparatus. As the uncertainties of these measurements are somewhat lower than ±0.1%, it is not unexpected that both equations give better agreement between measurement and calculation than for the data sets in Figure 6.6. Both equations give rms-errors within 0.05% for almost all the Ruhrgas data sets.

The performance of the Standard GERG-88 Virial Equation will be discussed in more detail in the following sub-sections.

6.3 Statistical Analysis of the Standard GERG Virial Equation by Pressure-Temperature Domains

The Standard GERG-88 Virial Equation can be assessed in more detail by comparing the results in particular domains of pressure and temperature. For this analysis, the experimental data for the first 84 data sets were grouped into pressure and temperature domains as follows -

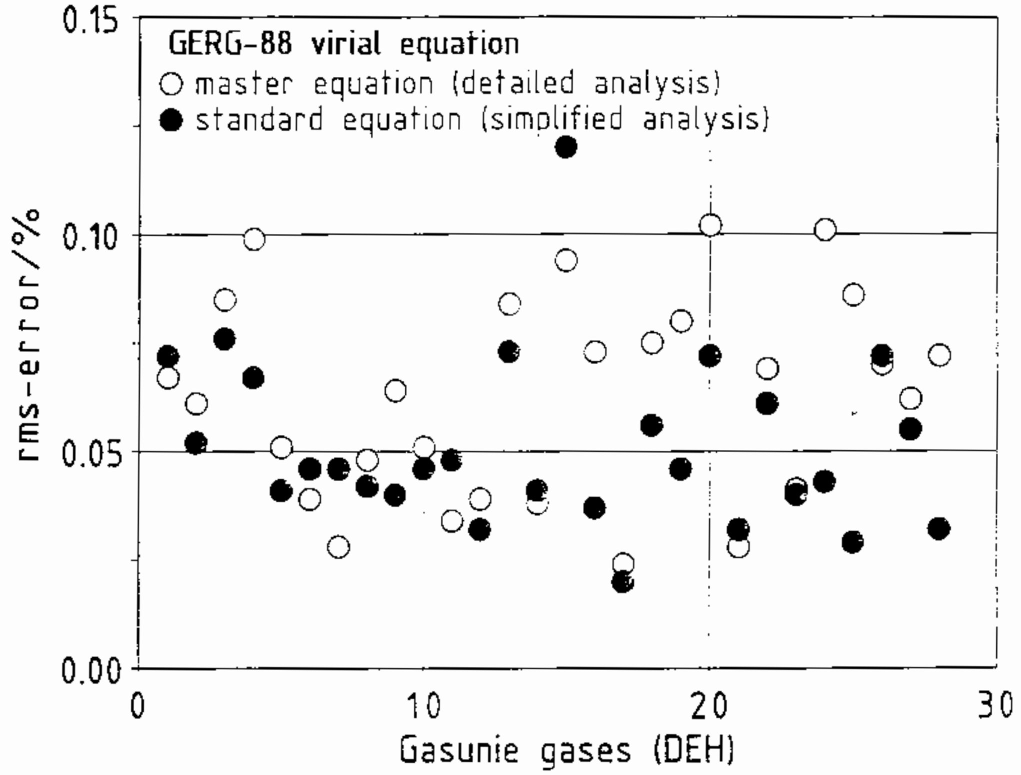

Figure 6.6 Root-Mean-Square Errors for 28 Data Sets Measured at Gasunie with the Desgranges et Huot Z-Meter, compared with the GERG-88 Virial Equations.

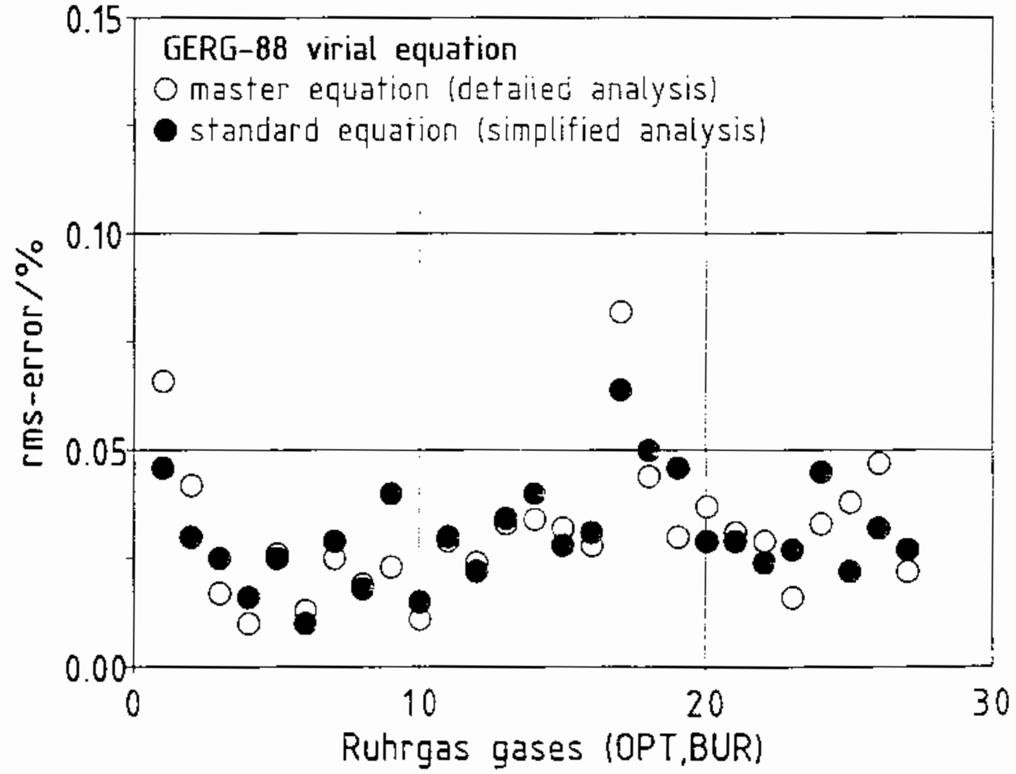

Figure 6.7 Root-Mean-Square Errors for 27 Data Sets Measured at Ruhrgas with the Burnett Apparatus or Optical Interferometer, compared with the GERG-88 Virial Equations.

Pressure/MPa	[0.2)	[2.4)	[4.5)	[5.6)
	[6.7)	[7.8)	[8.10) and	[10.12]
Temperature/K	[265.275)	[275.285)	[285.295)	[295.315)
			and	[315.335]

In this notation [2.4), for example, defines the pressure interval which includes 2 MPa exactly but excludes 4 MPa exactly (i.e. $2 \leq p/\text{MPa} < 4$) and [10.12] defines the interval which includes both 10 MPa and 12 MPa exactly. Again, only the first 84 data sets were used in this statistical analysis, so as to make it directly comparable with the corresponding analysis made in ref.1 for the Master GERG-88 Virial Equation.

Table 6.4 provides a statistical analysis of the Standard GERG Equation, broken down into these pressure-temperature domains, in terms of the quantities defined previously, viz.

N = number of experimental data points
n = number of distinct data sets
b = bias of relative error (mean relative deviation)
s = standard deviation
rms = root-mean-square error.

The mean relative deviations of the values predicted by the Standard GERG Virial Equation from the experimental data are summarized in column 5 of Table 6.4 for the various domains. The deviations tend slightly to the negative; the average bias for all data is -0.004%. The mean deviations are greatest at the higher pressures. The maximum value of the mean relative deviation, for any domain, is -0.04%.

The root-mean-square errors of the values predicted by the Standard GERG Virial Equation are summarized in column 7 of Table 6.4 and shown schematically in Figure 6.8. The rms-error ranges up to 0.06% for pressures up to 6 MPa. The maximum rms-errors are in the 6 to 8 MPa pressure range; the overall maximum rms-error of 0.102% is in the 265 to 275 K temperature domain. In this region the population of data points is dominated by values of compressibility factor measured using DEH Z-Meters. A similar analysis on the subset

Table 6.4 Statistical analysis of the Z-differences by pressure and temperature domains for all experimental natural gas compressibility factor data : Standard GERG 88 Virial equation for 84 data sets

temperature range /K	pressure range /MPa	N points	n sets	b %	s %	rms %
[265,275)	[0, 2)	245	32	0.021	0.043	0.048
[275,285)	[0, 2)	274	31	0.004	0.033	0.033
[285,295)	[0, 2)	276	36	-0.001	0.025	0.025
[295,315)	[0, 2)	159	27	0.002	0.009	0.009
[315,335]	[0, 2)	62	12	-0.002	0.006	0.006
[265,275)	[2, 4)	134	40	0.012	0.047	0.048
[275,285)	[2, 4)	244	67	-0.004	0.039	0.039
[285,295)	[2, 4)	227	68	-0.009	0.036	0.037
[295,315)	[2, 4)	158	53	0.009	0.031	0.032
[315,335]	[2, 4)	50	12	-0.004	0.008	0.009
[265,275)	[4, 5)	63	39	0.009	0.061	0.061
[275,285)	[4, 5)	329	66	-0.011	0.052	0.053
[285,295)	[4, 5)	279	67	-0.015	0.045	0.047
[295,315)	[4, 5)	150	53	0.009	0.042	0.043
[315,335]	[4, 5)	22	12	-0.004	0.012	0.012
[265,275)	[5, 6)	61	38	0.010	0.060	0.060
[275,285)	[5, 6)	256	63	-0.012	0.055	0.056
[285,295)	[5, 6)	225	64	-0.011	0.051	0.052
[295,315)	[5, 6)	122	51	0.008	0.047	0.047
[315,335]	[5, 6)	22	12	-0.002	0.014	0.014
[265,275)	[6, 7)	64	40	-0.025	0.094	0.096
[275,285)	[6, 7)	162	61	-0.030	0.066	0.073
[285,295)	[6, 7)	124	60	-0.015	0.054	0.056
[295,315)	[6, 7)	76	46	0.014	0.047	0.048
[315,335]	[6, 7)	22	12	-0.002	0.016	0.016
[265,275)	[7, 8)	50	34	-0.028	0.099	0.102
[275,285)	[7, 8)	63	36	-0.040	0.076	0.085
[285,295)	[7, 8)	65	37	-0.022	0.070	0.072
[295,315)	[7, 8)	39	24	0.022	0.033	0.039
[315,335]	[7, 8)	20	10	-0.001	0.019	0.019
[265,275)	[8,10)	49	22	-0.019	0.084	0.085
[275,285)	[8,10)	51	22	-0.008	0.054	0.054
[285,295)	[8,10)	50	23	0.005	0.044	0.044
[295,315)	[8,10)	57	24	0.034	0.031	0.046
[315,335]	[8,10)	38	12	-0.007	0.023	0.024
[265,275)	[10,12]	39	12	-0.030	0.078	0.082
[275,285)	[10,12]	35	10	-0.014	0.044	0.046
[285,295)	[10,12]	44	12	-0.022	0.040	0.045
[295,315)	[10,12]	43	16	0.029	0.043	0.052
[315,335]	[10,12]	37	11	-0.032	0.026	0.041
Totals		4486	84	-0.004	0.049	0.049

of data measured solely by Ruhrgas, using the optical or Burnett apparatus, shows a rms-error of less than 0.08% over the whole set of pressure-temperature domains, as shown in Table 6.5 and Figure 6.9.

The entire analysis given in sub-sections 6.2 and 6.3 is an averaged survey or overview of all natural gases. It could of course happen, however, that for particular types of natural gas (characterised either by composition or by physical properties) the predicted compressibility factors are less accurate than revealed by the above analysis. To investigate this possibility, results for the Standard GERG Virial Equation are compared below with the experimental data sets for several individual natural gases.

6.4 Accuracy of the Standard GERG Virial Equation for Six Groups of Natural Gases

The distributions of the relative deviation between the predicted and experimental compressibility factors are plotted for six groupings of natural gases in Figures 6.10 to 6.15, and are discussed below. The groups of gases are the first six of those defined in sub-section 6.1; a seventh group, comprising (gas phase) LNGs, is discussed in sub-section 6.6, together with results for synthetic gases prepared as "model" natural gases but truncated at some specific and relatively low carbon number.

The discussion for each group should be read in conjunction with Table 6.3 where the results are summarized for each natural gas in terms of the number of measured points N, the bias b, the standard deviation s and the root-mean-square deviation rms for the data set.

6.4.1 Group 1 - Natural Gases with $N_2 \geq 0.095$

The 13 gases containing more than 0.095 mole fraction (9.5%) nitrogen and no hydrogen are: N23, 29, 38, 40, 41, 42, 46, 47, 48, 50, 59, 60 and 77. Most of the gases were measured by Gasunie (N29 to N50 and N77); there is one gas from Gaz de

Table 6.5 Statistical analysis of the Z-differences by pressure and temperature domains for the natural gas compressibility factors measured with the Burnett or optical device : Standard GERG 88 Virial equation

temperature range /K	pressure range /MPa	N points	n sets	b %	s %	rms %
[265,275)	[0, 2)	90	17	0.005	0.011	0.012
[275,285)	[0, 2)	121	16	0.004	0.008	0.008
[285,295)	[0, 2)	110	17	0.001	0.010	0.010
[295,315)	[0, 2)	152	22	0.001	0.007	0.007
[315,335]	[0, 2)	61	11	-0.003	0.005	0.006
[265,275)	[2, 4)	63	17	0.019	0.016	0.025
[275,285)	[2, 4)	73	16	0.007	0.013	0.015
[285,295)	[2, 4)	70	17	0.003	0.017	0.017
[295,315)	[2, 4)	92	22	0.007	0.010	0.013
[315,335]	[2, 4)	48	11	-0.004	0.008	0.009
[265,275)	[4, 5)	31	17	0.031	0.018	0.036
[275,285)	[4, 5)	27	16	0.012	0.020	0.023
[285,295)	[4, 5)	29	17	0.005	0.043	0.023
[295,315)	[4, 5)	35	22	0.014	0.014	0.020
[315,335]	[4, 5)	20	11	-0.006	0.011	0.012
[265,275)	[5, 6)	25	17	0.037	0.026	0.045
[275,285)	[5, 6)	27	16	0.011	0.027	0.028
[285,295)	[5, 6)	28	17	0.009	0.026	0.027
[295,315)	[5, 6)	32	22	0.020	0.017	0.026
[315,335]	[5, 6)	21	11	-0.004	0.013	0.013
[265,275)	[6, 7)	26	17	0.030	0.038	0.048
[275,285)	[6, 7)	27	16	0.013	0.032	0.034
[285,295)	[6, 7)	27	17	0.006	0.035	0.035
[295,315)	[6, 7)	30	19	0.026	0.021	0.033
[315,335]	[6, 7)	21	11	-0.003	0.016	0.016
[265,275)	[7, 8)	23	15	0.023	0.055	0.058
[275,285)	[7, 8)	28	16	0.009	0.046	0.046
[285,295)	[7, 8)	26	16	0.015	0.040	0.042
[295,315)	[7, 8)	29	19	0.031	0.026	0.040
[315,335]	[7, 8)	19	9	-0.003	0.018	0.018
[265,275)	[8,10)	44	17	-0.012	0.076	0.076
[275,285)	[8,10)	43	16	-0.001	0.051	0.051
[285,295)	[8,10)	44	17	0.007	0.044	0.044
[295,315)	[8,10)	49	22	0.036	0.033	0.049
[315,335]	[8,10)	36	11	-0.009	0.022	0.023
[265,275)	[10,12]	38	11	-0.021	0.057	0.060
[275,285)	[10,12]	35	10	-0.014	0.044	0.046
[285,295)	[10,12]	43	11	-0.018	0.032	0.037
[295,315)	[10,12]	43	16	0.029	0.043	0.052
[315,335]	[10,12]	37	11	-0.032	0.026	0.041
Totals		1823	27	0.006	0.031	0.031

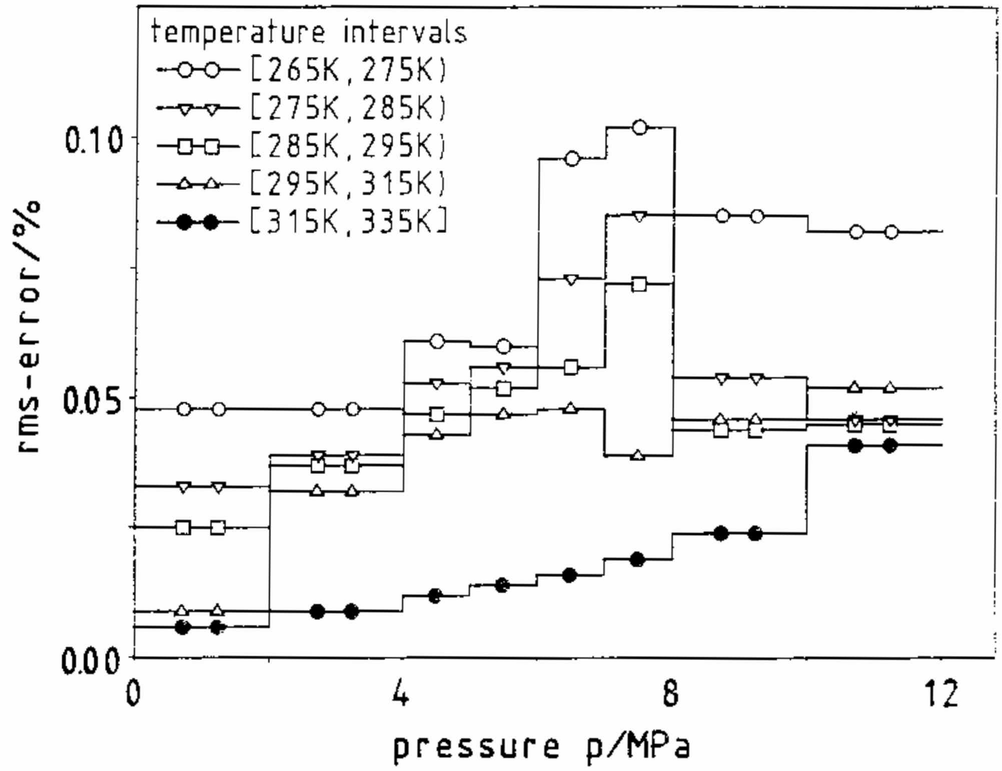

Figure 6.8 Root-Mean-Square Error for all Experimental Data Points for Natural Gases as a Function of Pressure for Various Temperature Domains: Standard GERG Virial Equation.

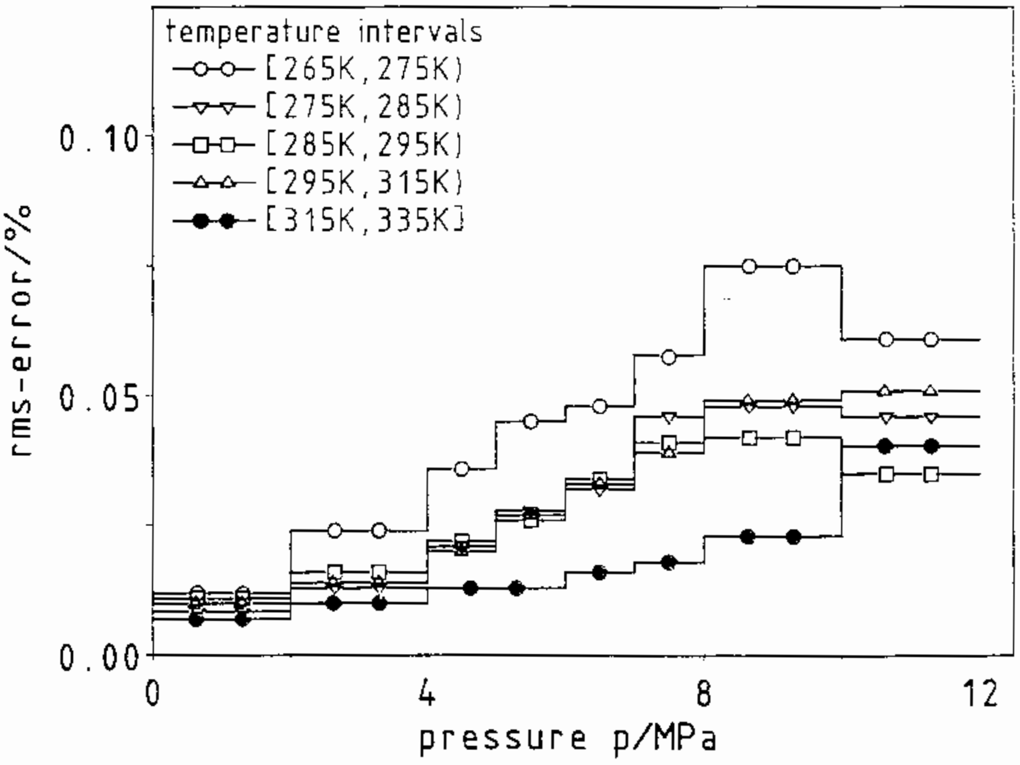

Figure 6.9 Root-Mean-Square Error for Experimental Data for Natural Gases Measured with the Burnett Apparatus or Optical Interferometer as a Function of Pressure for Various Temperature Domains: Standard GERG Virial Equation.

France (N23) and two from Ruhrgas (N59, 60).

The distribution of the relative deviations for these gases is relatively broad and symmetrical, as shown in Figure 6.10, although with a small bias to positive values. The calculated compressibility factor generally agrees with the experimental value within the target of 0.1%. The agreement between calculated and experimental compressibility factors is much better for the Standard GERG Virial Equation than was found to be the case for the Master Equation using the detailed gas analyses (1), viz.

	bias	rms-error
Standard Equation	+0.004%	±0.049%
Master Equation	-0.042%	±0.072%

A reason might be that inaccuracies in the gas composition are somewhat self-compensating when calorific value and relative density are calculated so as to provide the reduced gas analysis. Thus the effects of systematic errors in the gas composition, for example in the nitrogen content, might be diminished. This effect is especially noticeable for the gases N46 to 48, where the average bias has been reduced by 0.092% to a value of +0.024% for the Standard GERG Virial Equation; these three gases are the only natural gases in the Group 1 subset with a nitrogen content greater than 0.20 mole fraction, but they have only been investigated over limited temperature (280 to 300 K) and pressure (4 to 6½ MPa) ranges. This matter is discussed further in sub-section 7.3.6.

Recently an additional natural gas (N96) with a nitrogen mole fraction of 0.237 has been tested in the same temperature range for pressures up to 7.4 MPa. The point-by-point agreement with the Standard GERG-88 Virial Equation is better than ±0.01%. Furthermore another two natural gases, with sufficient nitrogen admixture to give mole fractions of 0.36 and 0.49 respectively, have been the subject of even more recent measurements at the Ruhrgas laboratories. The results are not yet available in the open literature, but show that, for pressures up to 8 MPa and temperatures between 270 and 320 K, agreement with the Standard GERG virial Equation is within 0.1%. For the pressure range 8 to 12 MPa, maximum deviations are between -0.3 and -0.4% at the extreme temperatures of 270 and 330 K.

Consequently, the overall conclusion must be that natural gases with high nitrogen content are represented with good accuracy by the Standard GERG-88 Virial Equation.

6.4.2 Group 2 - Natural Gases with $CO_2 \geq 0.040$

The eight natural gases containing more than 0.04 mole fraction (4%) carbon dioxide are N29, 33, 34, 35, 63, 64, 80, and 81; all except N63 and 64 (Ruhrgas) were measured by Gasunie.

The distribution of the relative deviations for these gases is slightly shifted to positive values; the maximum falls in the interval between zero and +0.025% (see Figure 6.11). This feature is caused largely by the data for two of the natural gases (N35 and 80) which show rms-errors of about 0.07% and mean deviations of +0.05 to +0.06%. The other gases all have rms-errors of less than 0.05% (see Table 6.3). However, the agreement of the data for N35 and 80 with predicted values to within 0.1% is rather important and significant, as these gases have a very high carbon dioxide content, some 29%. Unfortunately the data are limited to the temperature range 280 to 300 K and to pressures up to only 6.4 MPa.

Very recently a natural gas with sufficient carbon dioxide admixture to give a mole fraction of 0.266 has been investigated at the Ruhrgas laboratories. Again these results are not yet published, but show agreement within ±0.1% with the Standard GERG-88 Virial Equation for pressures up to only 4 MPa, for all temperatures between 270 and 330 K. The maximum differences increase with pressure - at 6 MPa, ±0.15%; 8 MPa, ±0.25% except for the 270 K isotherm; 10 MPa, ±0.4%. For the 270 K isotherm, measured only up to 9 MPa, the results show maximum differences as great as 0.9%. The Master GERG-88 Virial Equation agrees within ±0.1% up to 8 MPa.

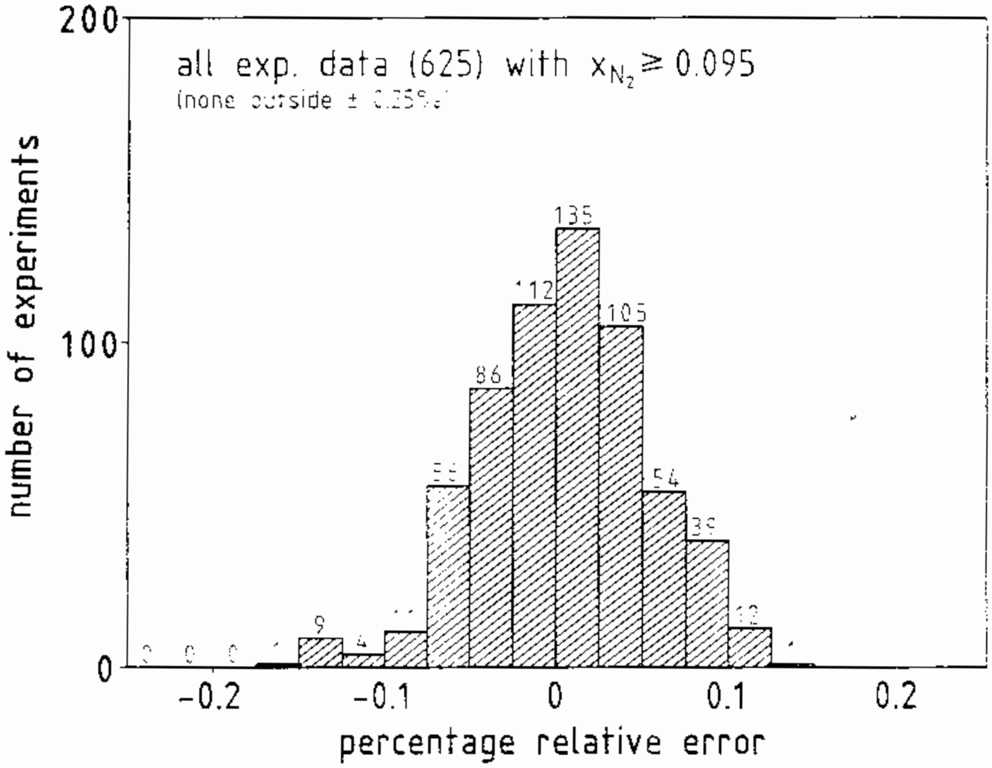

Figure 6.10 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 9.5% Nitrogen and no Hydrogen: Standard GERG Virial Equation.

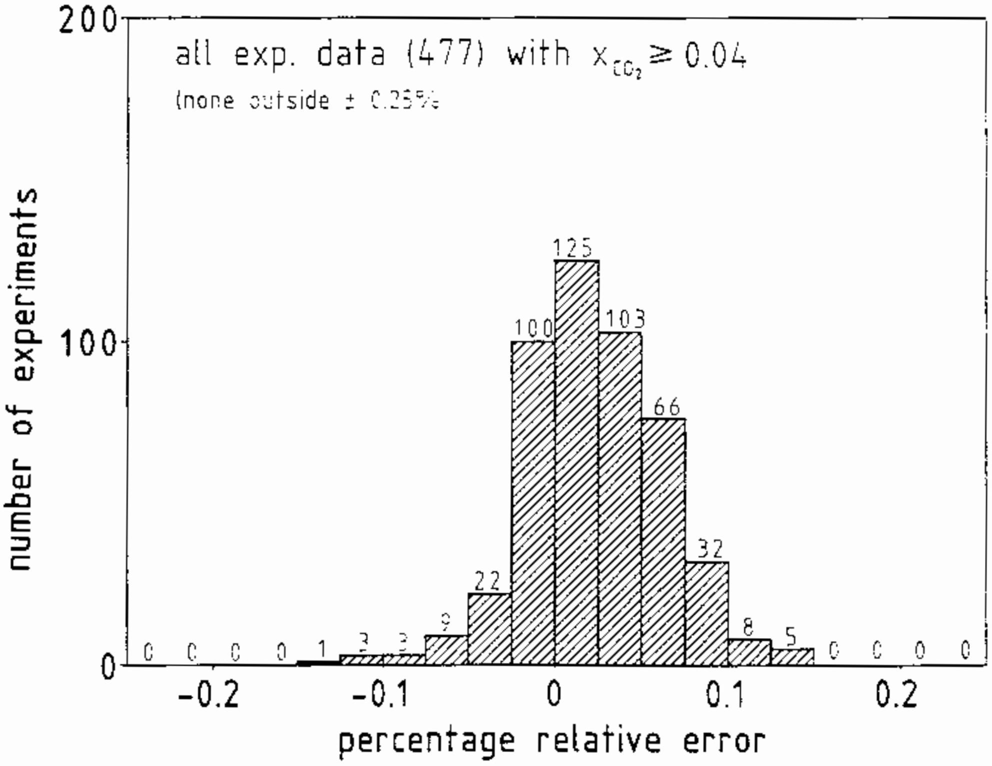

Figure 6.11 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 4% Carbon Dioxide: Standard GERG Virial Equation.

Despite these last observations, which demand some caution at medium-to-high pressures for very high carbon dioxide concentrations, the overall conclusion is that the compressibility factor for high carbon dioxide content natural gases is generally predicted by the Standard GERG-88 Virial Equation to well within the usual experimental uncertainty of ±0.1%.

6.4.3 Group 3 - Natural Gases with $C_2H_6 \geq 0.080$

The 23 natural gases containing more than 0.08 mole fraction (8%) ethane are N1, 4, 10, 12, 14, 16, 18, 20, 25, 26, 27, 37, 51, 52, 53, 54, 55, 56, 65, 66, 75, 76 and 79. Gases N51 to 56, 65, 66 and 75 were studied by Ruhrgas in the temperature range 270 to 330 K for pressures up to 12 MPa. The other gases were studied only in the temperature range 273 to 283 K and for pressures limited to 8 MPa; there are DEH Z-Meters measurements from Ruhrgas (N1, 4), Gaz de France (N25 to 27) and Gasunie (N37, 79), plus data from Achtermann et al (N10 to 20)(29,30) and Duschek et al (N76)(31).

The distribution of relative deviations for these gases is fairly symmetrical, as shown in Figure 6.12. The values on the far negative side are from DEH Z-Meter measurements and from the work of Achtermann et al (29,30). As the Gaz de France Z-Meter and Achtermann data sets yield only very small mean deviations (but relatively large rms-errors - see Table 6.3), there are necessarily data points with large positive deviations to compensate for the large negative deviations.

There seem to be inconsistencies in the data of Achtermann et al. For example, N14 shows large positive deviations for the 273 K isotherm. Furthermore, this isotherm cannot be fitted accurately with a second-order polynomial in density even if B and C are free parameters; consequently it seems that the deviations observed are almost certainly reflections of experimental error. In addition N12, 16 and 20 each has exactly the same composition, but at 273.15 K and 7.4 MPa the difference in the deviation between N12 and N16 is more than 0.15%, while N20 is somewhere in between. The same is true for N14, 18 and 10 respectively at 283.15 K and 7.4 MPa.

The more recent Ruhrgas measurements (N51 to 56, 65, 66 and 75) are predicted very well at all temperatures from 270 to 330 K and pressures up to 12 MPa, although for some of these (N54 to 56) there are negative deviations, with a maximum value of -0.15%, at 270 to 275 K and about 9 MPa.

The data of Duschek et al (31) for N76 are also very closely predicted at all temperatures from 273 to 323 K and pressures up to 8 MPa, although at 273 K the 7.5 and 8.0 MPa data points have negative deviations beyond -0.1%.

It is not clear why the deviations are relatively large (maximum deviation -0.32%) for N37; perhaps a careful re-analysis of the composition would be instructive. An Ekofisk natural gas (N85), close in composition to N37, has recently been the subject of new measurements at the Gasunie research laboratories; the new measurements show excellent agreement with the Standard GERG-88 Virial Equation. A Ekofisk natural gas containing 0.1% admixture of C_7H_{16} (N95) also has its measured compressibility factors well predicted by the equation.

The published data from Hannisdal (32) for a Statoil gas containing 14.7% ethane (N86), taken at a temperature of 303.12 K and pressures up to 12 MPa show a bias of 0.3% and an rms-error of 0.42%; the data are, however predicted much more closely by the Master GERG-88 Virial Equation (1) using the complete component analysis as input.

Very recently two further natural gases containing sufficient ethane admixture to give mole fractions of 0.117 and 0.190 have been subject to measurement in the Ruhrgas physics laboratories. For these two gas samples the experimental data agree with calculated values from the Standard GERG-88 Virial Equation only at very low pressures for temperatures between 270 and 330 K. For the gas with 11.7% ethane content the prediction is within 0.1% up to a maximum pressure of less than 5 MPa, and for the gas with 19.0% ethane up to only about 2 MPa. The differences increase to maximum values of about 0.4% and 1.0% respectively for the two gases at pressures of about 12 MPa, more or less independently of temperature. The agreement of the experimental data with the Master GERG-88 Virial Equation for these gases is again rather better.

For the gas with 11.7% ethane content, the Master Equation is within ±0.1% of measurement for temperatures between 280 and 330 K at all pressures up to 12 MPa; however, the 270 K isotherm exceeds that limit at 6 MPa and above. For the gas with 19.0% ethane, the agreement is within ±0.2% at all pressures up to 12 MPa, but only for temperatures between 290 and 330 K; at lower temperatures that limit is again exceeded above 6 MPa.

The overall conclusion seems to be that compressibility factors of gases rich in ethane are only predicted by the Standard GERG-88 Virial Equation within ±0.1% if the ethane content is less than about 10%.

6.4.4 <u>Group 4 - Natural Gases with $H_2 \geq 0.020$</u>

The 13 gas mixtures containing more than 0.02 mole fraction (2%) hydrogen are N5 to 8, N67 to 74 and N84. These gases were all derived from natural gases by admixture of either hydrogen or coke-oven gas.

The distribution of the relative deviations for these gases is quite symmetrical, as shown in Figure 6.13. There are only five scattered data points (for gases N8 and 70, studied by use of the DEH Z-Meter and a Burnett apparatus respectively) with deviations worse than ±0.1%. Consequently, gases containing up to 10% hydrogen may be said to have their compressibility factors predicted by the Standard GERG-88 Virial Equation well within the experimental uncertainty of about 0.1% for pressures up to 12 MPa. Even for the mixture N84, which contains over 35% hydrogen (and so is greatly out-of-range of the targetted applicability of the equation), the experimental data measured up to 8 MPa are predicted within 0.1%.

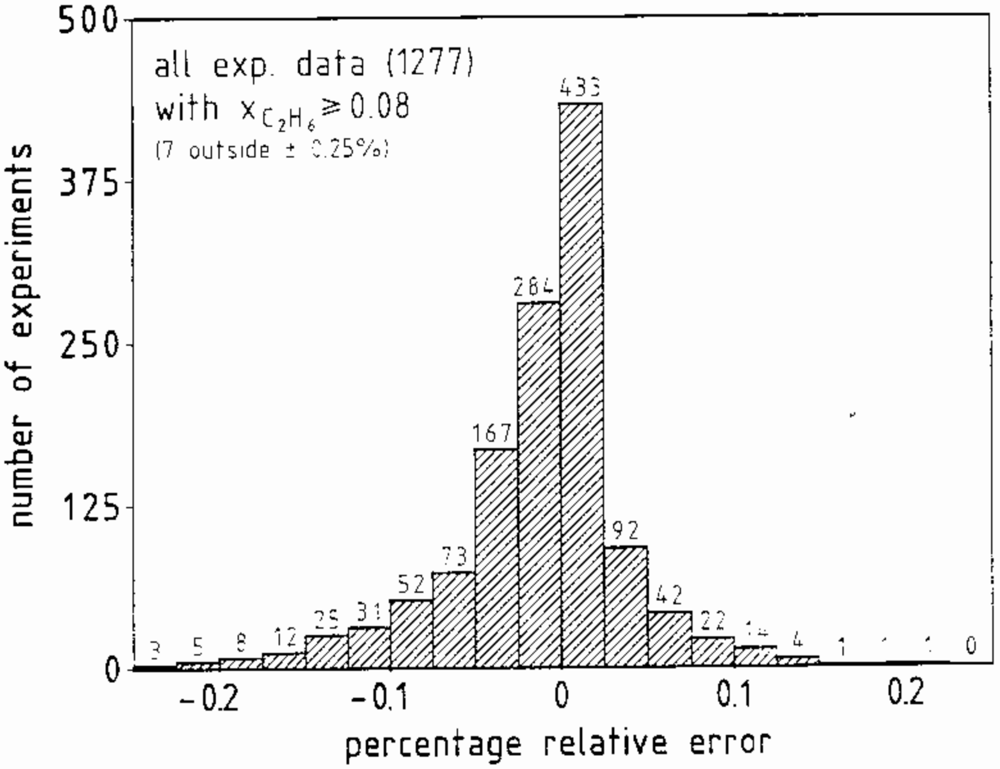

Figure 6.12 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 8% Ethane: Standard GERG Virial Equation.

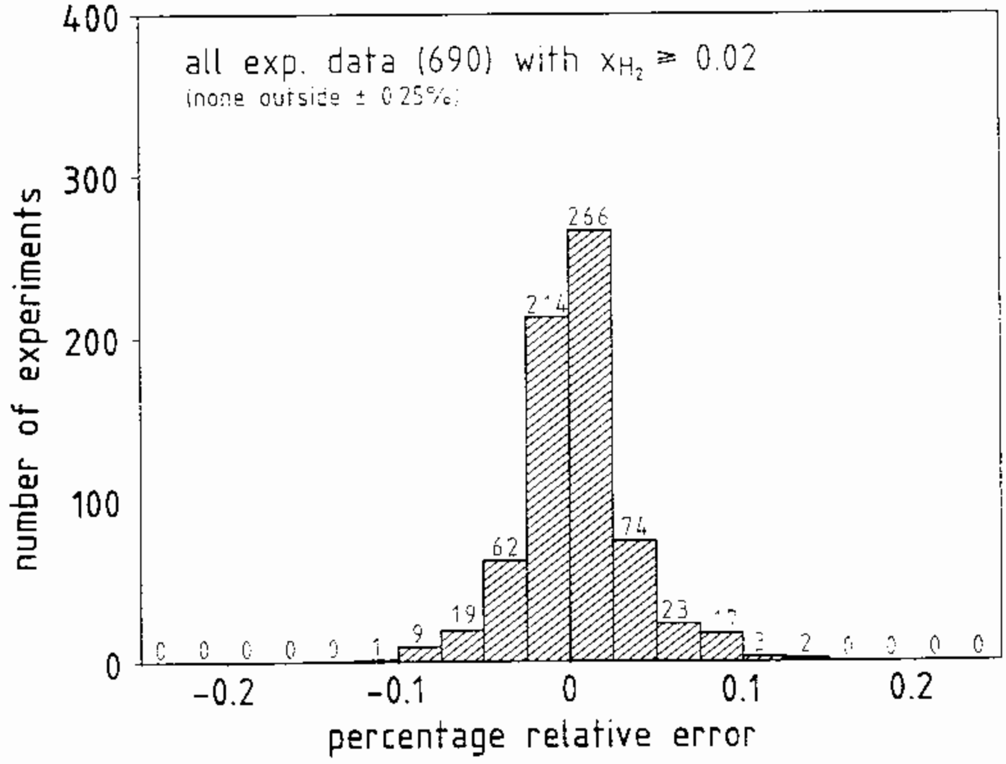

Figure 6.13 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 2% Hydrogen: Standard GERG Virial Equation.

6.4.5 Group 5 - Natural Gases with N_2 and C_2H_6 each ≥ 0.040

The ten gases which belong to this group and contain no hydrogen are N3, 11, 15, 19, 30, 32, 36, 43, 82 and 83.

The data sets for N3, 11, 15 and 19 were taken using separate samples of the same natural gas source. One data set (N3), studied by Ruhrgas using a DEH Z-Meter has a very high bias of -0.094%. The other data sets are from Achtermann et al (29,30). Gas N15 shows large positive deviations of greater than 0.1% at 273 K for 15 data points but, as before, this isotherm cannot be fitted satisfactorily by a second-order expansion in density even with B and C as free parameters; consequently the deviations are most probably due to experimental errors. At 293 K the data set for N19 shows large negative deviations, whereas the same isotherm for the N11 and N15 data sets are predicted quite well by the Standard GERG-88 Virial Equation.

As can be seen from Figure 6.14, the distribution of the relative deviations of the data points for these gases is fairly symmetrical; the maximum falls in the interval between zero and -0.025%. Despite the above comments, it is clear that the compressibility factors for these natural gases are generally predicted by the Standard GERG-88 Virial Equation to well within the experimental uncertainty of about ±0.1%.

The recent set of measurements made by British Gas on a natural gas (N91) belonging to this group has a bias of -0.075%. For all isotherms, even the low pressure data show a negative deviation of at least -0.05%. Although it would be useful to find an explanation of this observation, this new data set does not change the general conclusion that compressibility factors for this group of natural gases are predicted within ±0.1% by the Standard Equation.

6.4.6 Group 6 - Natural Gases with $CH_4 \geq 0.940$

The eight natural gases N2, 9, 13, 17, 57, 58, 61 and 62 each contain more than 0.940 mole fraction (94%) methane. All these gases have their compressibility factors predicted well by the Standard GERG-88 Virial Equation, even though the gases N9 and 17, studied by Achtermann et al (29,30), have a tendency towards positive deviations at 273 K.

The conclusion that the Standard GERG Equation provides an excellent description of lean natural gases, consisting mainly of methane, is clearly confirmed by Figure 6.15.

Four new data sets (N87, 88, 92 and 93) more recently added to the GERG databank (10) confirm this result. Although two of the three data sets provided by British Gas show consistent deviations at all temperatures and pressures (negative for N88, positive for N93), all of the data remain within the acknowledged uncertainty band of ±0.1%. There could be a very slight mis-adjustment of the Z-Meter, perhaps of the transducer used for measuring the low pressure after expansion. Alternatively the compositional analyses may be marginally less exact than is believed to be the case.

6.5 Performance for Specific Natural Gases

In another attempt to identify any systematic deviations of the compressibility factor values predicted by the Standard GERG-88 Virial Equation from the true values, six individual natural gases - one from each of the six composition groups discussed above - were chosen for examination in greater detail. The particular gases chosen for this study were selected because their compressibility factors have been measured using the optical interferometry and Burnett apparatus methods (up to pressures of 12 MPa), it consequently being expected that these data are as extensive and accurate as any available for natural gases at the present time.

The relative errors ΔZ_i, as defined by equation (6.1), for these gases are plotted for the pressure range up to 12 MPa,

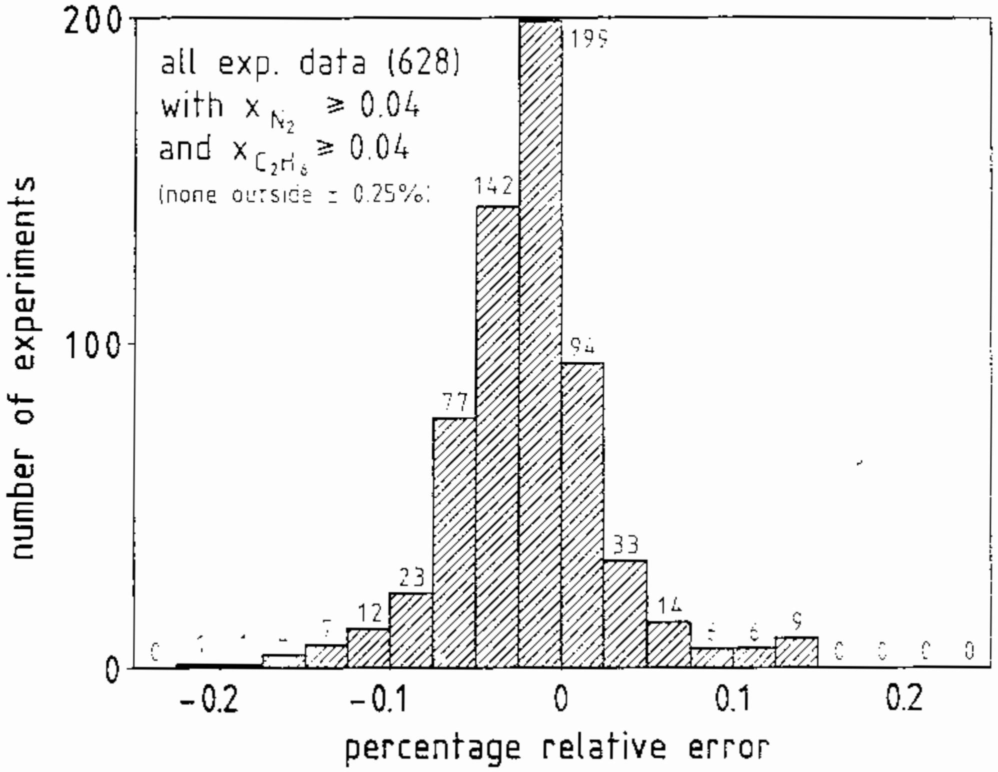

Figure 6.14 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 4% both of Nitrogen and of Ethane, and no Hydrogen: Standard GERG Virial Equation.

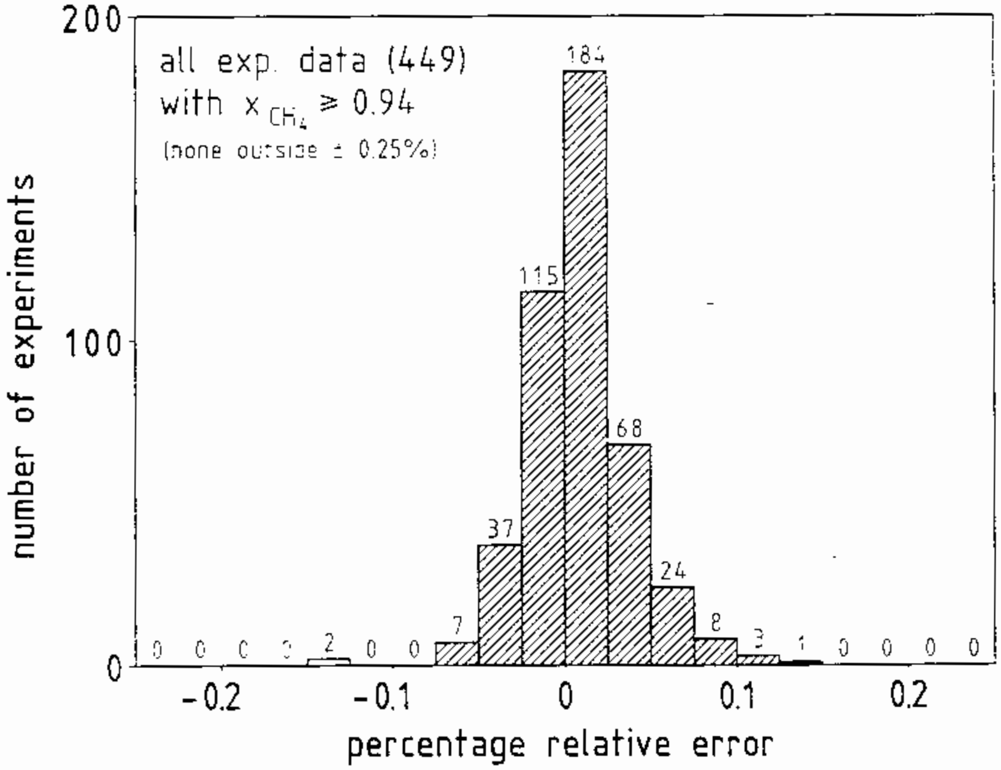

Figure 6.15 Percentage Relative Error Distribution of the Experimental Data for Natural Gases containing more than 94.0% Methane: Standard GERG Virial Equation.

with the temperature as parameter, in Figures 6.16 to 6.21. The gases are, in increasing order of calorific value -

(1) Figure 6.16: H-gas/coke-oven gas N74 $x(H_2)$ =0.095
(2) Figure 6.17: Drohne gas N64 $x(CO_2)$ =0.049
(Drohne gas is from Lower Saxony)
(3) Figure 6.18: NAM-gas N60 $x(N_2)$ =0.117
(NAM-gas is mainly Slochteren-type)
(4) Figure 6.19: Soviet gas N62 $x(CH_4)$ =0.983
(5) Figure 6.20: TENP-gas N83 $x(N_2)$ =0.060
$x(C_2H_6)$=0.059
(TENP-gas is a Slochteren-Ekofisk mixture)
(6) Figure 6.21: Ekofisk gas N75 $x(C_2H_6)$=0.085

The compressibility factors Z_{expt} of these gases have been measured at 270, 280, 290, 310 and 330 K. For most of the isotherms the maximum deviations are less than ±0.07% over the whole pressure range up to 12 MPa. For each isotherm the gases with some larger deviations are as follows -

270 K: H-gas/coke-oven gas; Drohne gas; NAM-gas; Ekofisk gas
280 K: NAM-gas; TENP-gas; Ekofisk gas
290 K: H-gas/coke-oven gas; TENP-gas
310 K: None
330 K: H-gas/coke-oven gas; Soviet gas; TENP gas.

The largest deviations for the various gases are often at pressures above 11.5 MPa. Only two points are outside the ±0.1% error band.

In the cases of only two gases do any deviations exceed ±0.07% (the estimated experimental uncertainty of these particular data) within the intermediate pressure range from about 6 to 10 MPa, for the NAM-gas at 270 and 280 K and for the H-gas/coke-oven gas mixture at 270 K. The deviations are, however, always below ±0.1%.

The deviation curves for these two gases (Figures 6.16 and 6.18) reveal some repetitive systematic pattern; both exhibit bell-shaped deviation curves with a maximum positive devi-

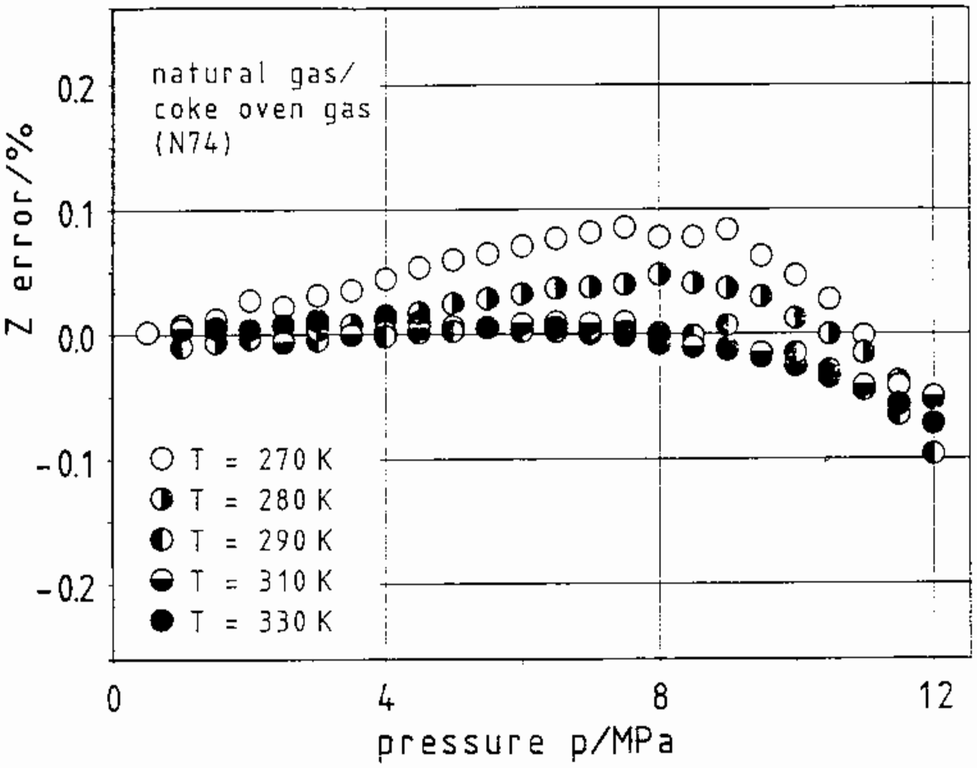

Figure 6.16 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for a H-Gas/Coke-Oven Gas (N74) with $x(H_2)=0.095$, for Five Isotherms.

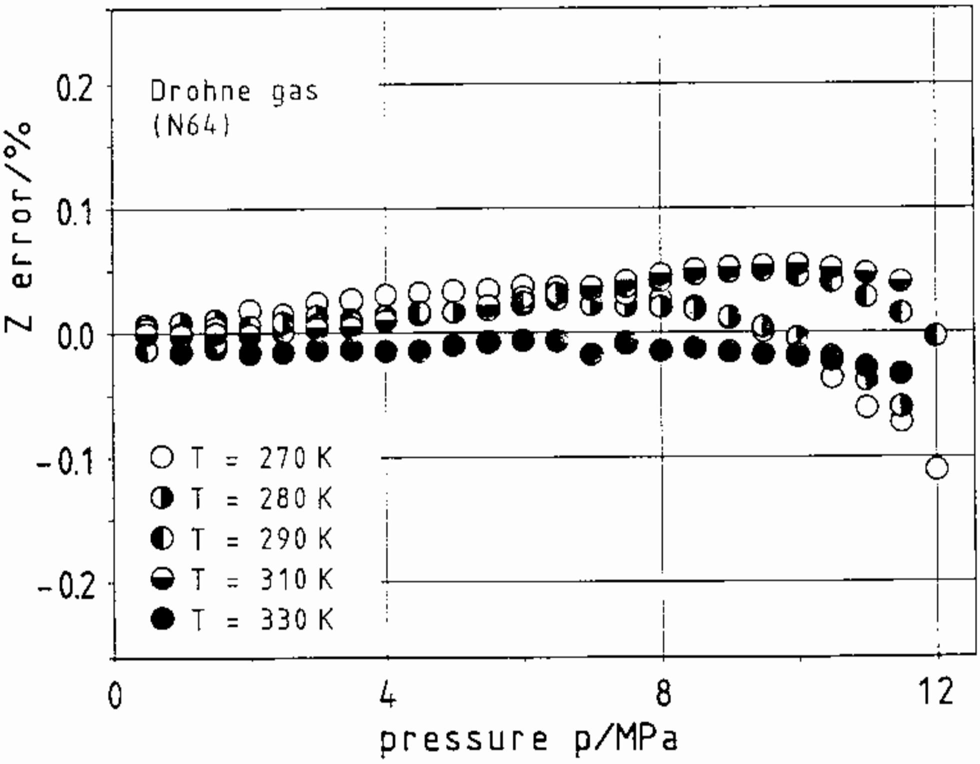

Figure 6.17 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for a Drohne Gas (N64) with $x(CO_2)=0.049$, for Five Isotherms.

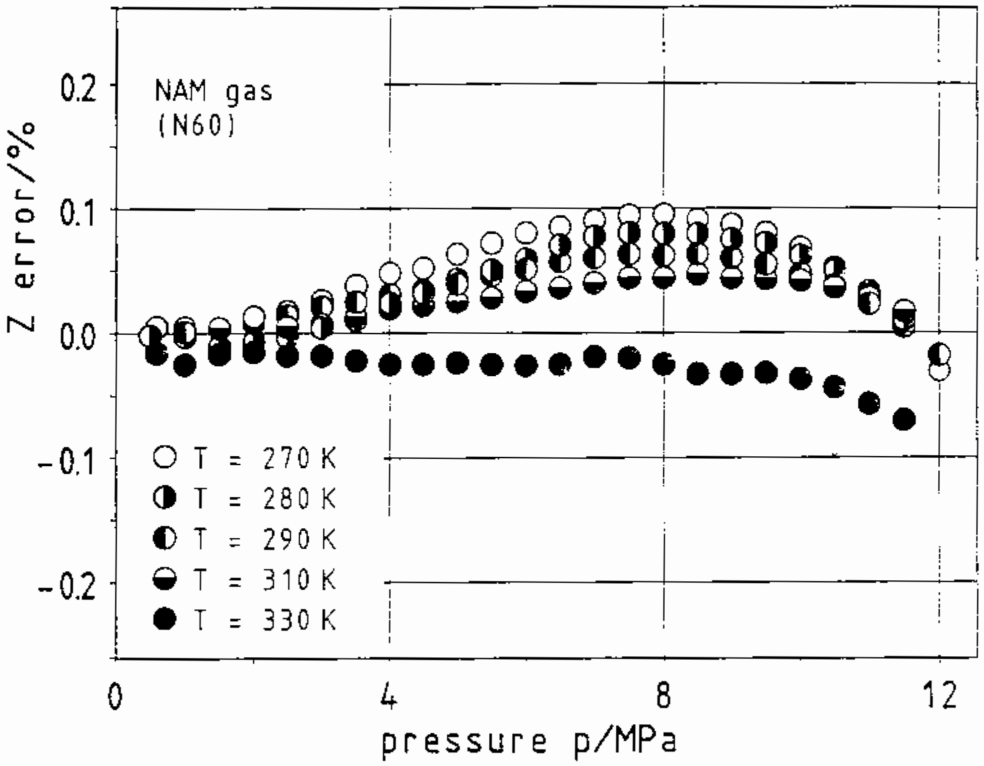

Figure 6.18 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for a NAM-Gas (N60) with $x(N_2)=0.117$, for Five Isotherms.

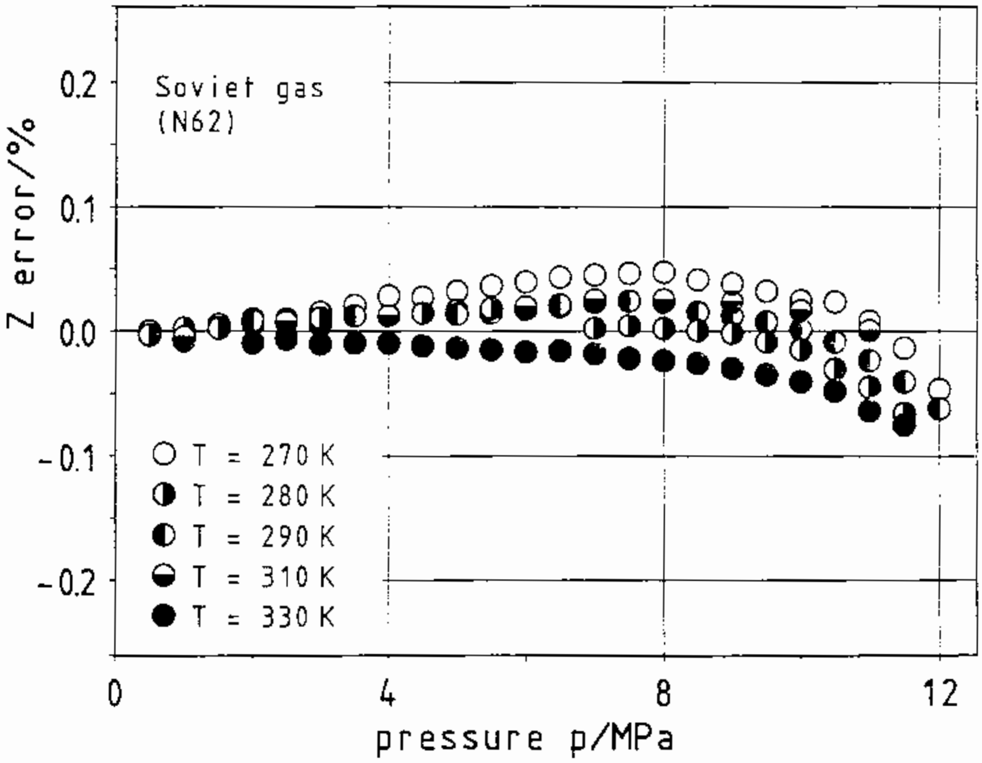

Figure 6.19 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for a Soviet Gas (N62) with x(CH4)=0.983, for Five Isotherms.

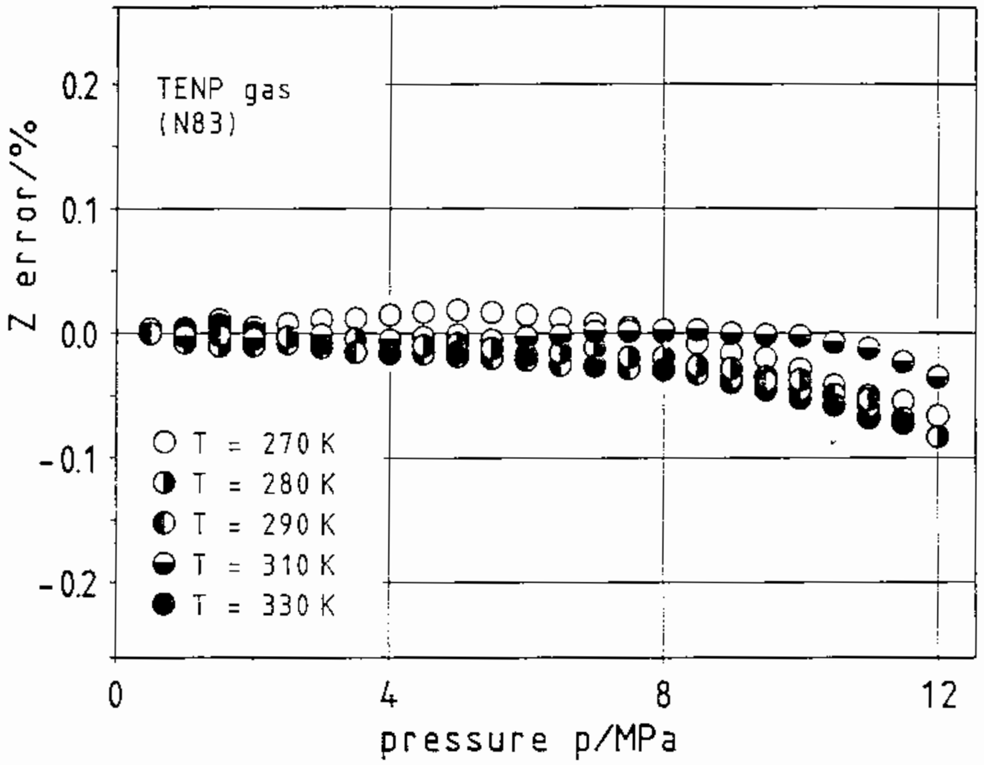

Figure 6.20 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for a TENP-Gas (N83) with $x(N_2)=0.060$ and $x(C_2H_6)=0.059$, for Five Isotherms.

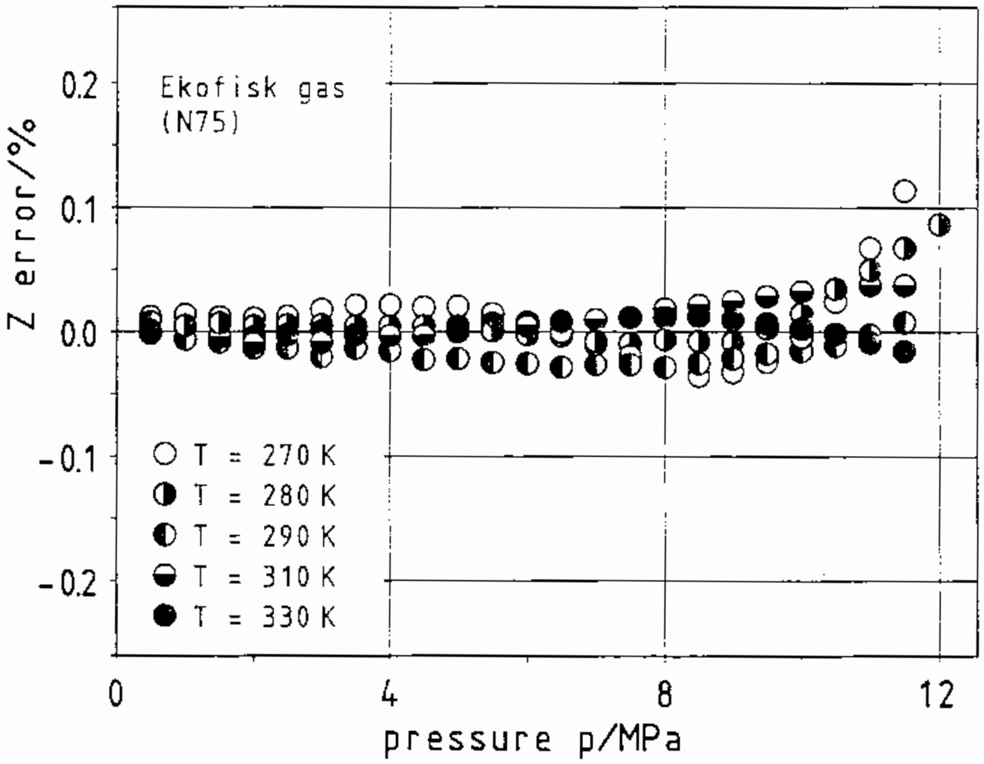

Figure 6.21 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for an Ekofisk Gas (N75) with $x(C_2H_6)=0.085$, for Five Isotherms.

ation around 8 MPa on the 270 K isotherm. For higher temperatures the deviation curves are flatter. The curves intersect the axis around 11 MPa and finally reach negative values approaching -0.1% at 12 MPa.

Similar bell-shaped deviation patterns were found for these gases for the Master GERG-88 Virial Equation, and were discussed in detail previously (1). The conclusion there, which now also applies to the Standard GERG-88 Virial Equation, was that the equation still provides the best compressibility factors for natural gases at pressures up to 12 MPa that can be achieved with a virial equation truncated after the third term.

6.6 Performance for Liquefied Natural Gas and Simulated Natural Gases

Two data sets for re-vaporised liquefied natural gases (LNGs) are available in the D-file, for multicomponent mixtures, of the GERG databank (10). The LNGs are assigned to this file because, as for the synthetic multicomponent gas mixtures therein, they contain no hydrocarbon above C5. The higher hydrocarbons are removed during the liquefaction process. The Standard GERG-88 Virial Equation does not apply automatically to such gases, or to any other synthetic gases prepared in such a way as to mimic or simulate natural gases if their paraffinic content is truncated at a similarly low carbon number.

The relative deviations (Z-errors), as defined by equation (6.1), for one of these gases (D19) are plotted in Figure 6.22 for the pressure range up to 12 MPa with the temperature as parameter. The composition of the two gases D19 and D20 are practically identical, and the quality of the (original) gas is similar to an Ekofisk gas, with a mole fraction of ethane of 0.087. The compressibility factors of the LNG D19 have been measured at 275, 290, 310 and 330 K. The deviations are within ±0.1% of predicted values of Z for pressures up to about 8 MPa only. For the lowest temperature isotherm, the deviations may be as large as 0.4% at 12 MPa.

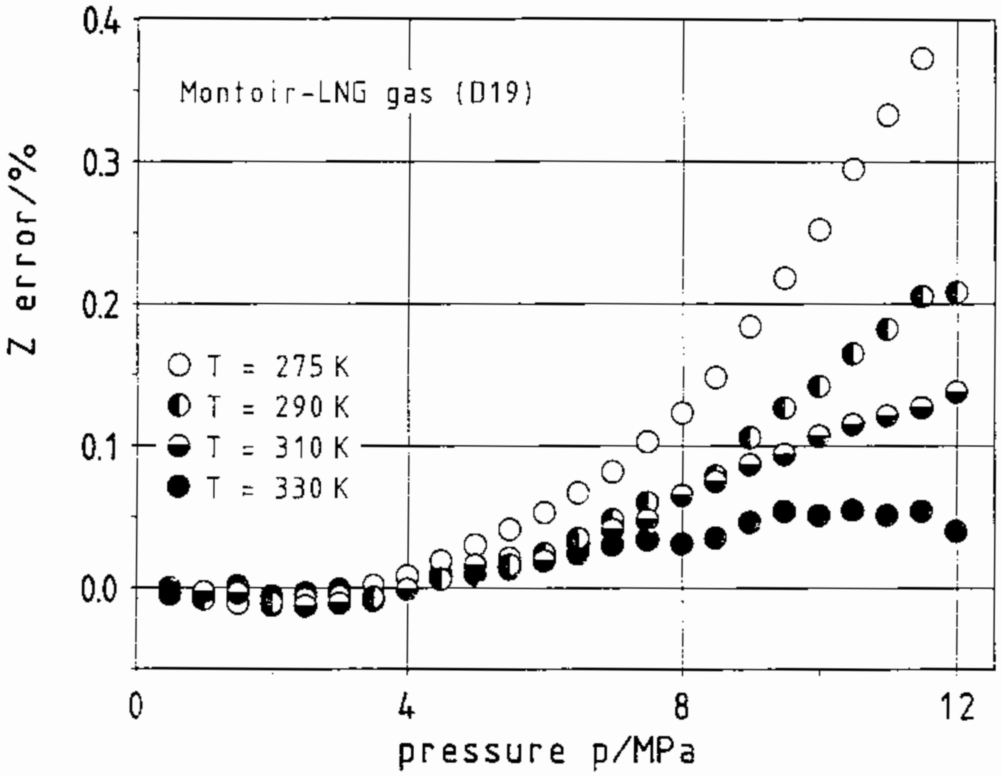

Figure 6.22 Z-Errors of Compressibility Factors, Calculated using the Standard GERG Virial Equation, compared with Measured Values for Montoir LNG (D19).

These large errors in Z for pressures above 8 MPa, and especially at 275 K seem, superficially, probably to be the result of incorrect values for the second and third virial coefficients for the equivalent hydrocarbon gas CH given by the Standard GERG Virial Equation. The latter are, in principle (see sub-sections 2.2 and 3.4.3), deficient for any type of gas which lacks the characteristic "tail" of a generic natural gas because of the way in which they were derived from the pVT (volumetric) behaviour of the paraffinic part of actual natural gases exhibiting a regular decrease in mole fractions of the higher hydrocarbons.

However, measurements have very recently been carried out at the Ruhrgas physics laboratories with five simulated natural gases, prepared gravimetrically at the National Institute of Standards and Technology (NIST) in Boulder (Colorado). These were subject to a round-robin exercise, organized by the Gas Research Institute (GRI) in Chicago, for four participants. Details of the Ruhrgas tests have been reported elsewhere (34). The results of all participants will be published as NIST report.

The experimental compressibility factor data obtained by Ruhrgas have been compared with values calculated from the Standard GERG-88 Virial Equation. Calculated and experimental values agree within ±0.1% for pressures up to 10 MPa throughout the complete temperature range investigated of 275 to 325 K. For pressures up to 12 MPa the agreement is still better than ±0.2%. A maximum error of +0.2% occurs at 275 K for the Ekofisk type simulated natural gas RG-2 which, apart from the hydrocarbon content being truncated at C5, has a composition similar to the natural gas N75; this gas is also similar in composition to the LNG D19 discussed previously.

We conclude from these experimental observations that the prognosis for simulated (or synthetic) natural gases is not as pessimistic as the LNG measurements might suggest, and that, even for gases truncated at around C5, the Standard GERG Equation retains its specified accuracy of ±0.1% for pressures up to 10 MPa.

6.7 Expected Accuracy of the Standard GERG Equation

The specifications given in Table 1.1 for the Standard GERG-88 Virial Equation called for an expectation accuracy of ±0.1% over a wide range of gas quality parameters and for an extensive pressure-temperature surface. These ranges are shown schematically in Figure 6.23(a). The corresponding ranges where the equation has been adequately tested, and is known to perform within specification, are shown in Figure 6.23(b). A more detailed discussion of performance, particularly for those regions where the sparseness of good quality test data prevents a definitive assessment thereof, is reserved for Section 7.

6.8 Comparison with Alternative Simplified Input Methods

In this sub-section we compare the Standard GERG-88 Virial Equation only with other methods which employ a simplified (reduced) set of input parameters. We have demonstrated repeatedly throughout the text of Section 6 that the uncertainty of prediction of the Standard GERG Equation is of a similar magnitude to that of the Master GERG Equation, and in ref.1 it was shown that the performance of the latter compares favourably with all other extant methods which use a detailed compositional analysis as input.

In sub-section 1.1 both the longer-standing (AGA NX-19 type (2-4)) and more recent (AGA-8 or GRI-SuperZ (5)) methods for the calculation of natural gas compressibility factors were discussed very briefly. Both methods use a simplified set of input parameters; at the level of accuracy and for the range of applicability now achieved by the GERG equation, only the Simplified SuperZ equation remains even moderately comparable with the Standard GERG Equation. For calculations with the Simplified SuperZ Equation, the same set of input variables (superior calorific value, relative density and mole fraction of carbon dioxide) has been used as for the Standard GERG-88 Virial Equation.

A comparison of the Simplified GRI-SuperZ Equation against

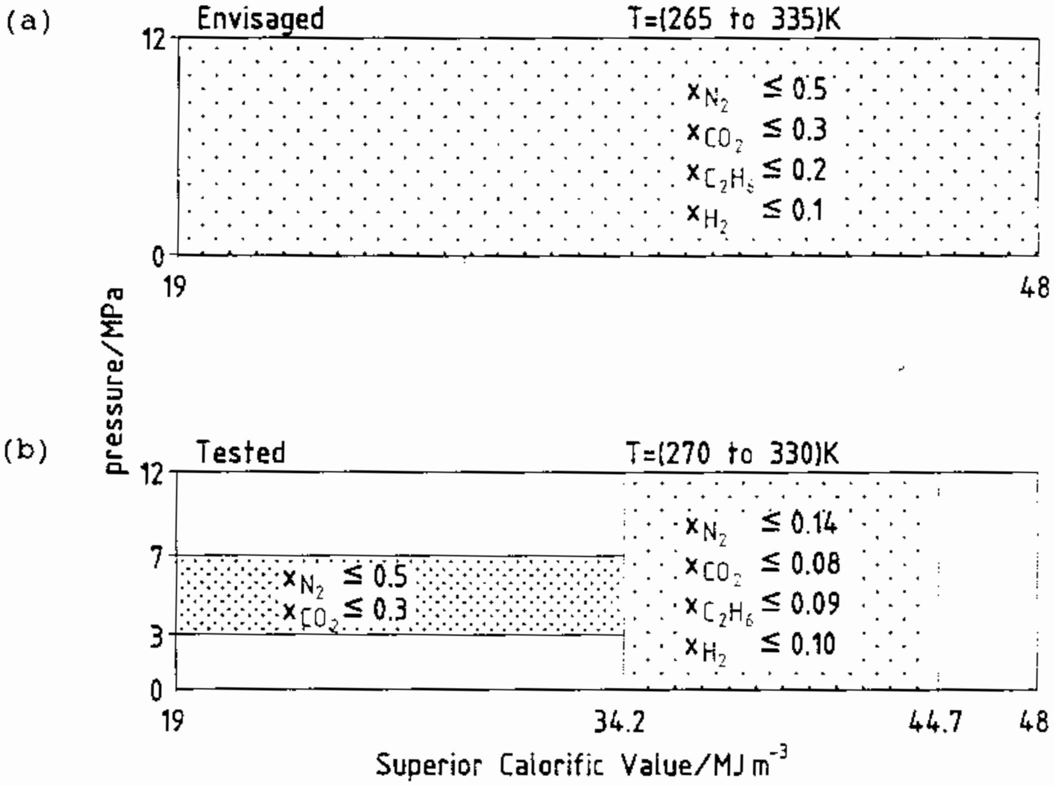

Figure 6.23 Specification of the Standard GERG-88 Virial Equation -

(a) Envisaged (see Table 1.1)
(b) Region Tested.

experimental data for the 270 K isotherm, for several specific natural gases, is shown as Figure 1.3. It is clear that for all five natural gases selected, the Z-error remains within ±0.1% only in the lower pressure range, below 4 MPa. At 12 MPa the Z-error reaches about ±0.4%. Furthermore, the equation is not valid for any mixture, such as natural gas with coke-oven gas admixture, containing hydrogen.

For the Standard GERG Virial Equation, the corresponding Z-errors, for the same gases, are within a spread of ±0.1%, as shown in Figure 6.24. That the Simplified SuperZ Equation is less accurate than the Standard GERG Equation as pressure increases can also be seen from trends in the root-mean-square errors for the natural gases (up to N84 in the GERG databank (10)) with experimental data measured using the Ruhrgas optical interferometer or Burnett apparatus. For this subset of natural gases, Table 6.6 and Figure 6.25 show that the rms-errors are higher by a factor of about six than those for the Standard GERG Equation shown in Table 6.5 and Figure 6.9, even though the results for natural gases containing coke-oven gas admixture have been excluded. Since, as noted above, the SuperZ equation is not properly applicable to such mixtures, their inclusion would only further unbalance the comparison in favour of the Standard GERG Equation.

Finally, it is notable that, although the detailed composition input version of the AGA-8 (alias GRI-SuperZ) Equation is currently undergoing revision so as to improve its performance, no such revision of the Simplified SuperZ is envisaged. This fact is an explicit recognition that both the concept and performance of the Standard GERG Virial Equation are superior to any present or near-future alternatives.

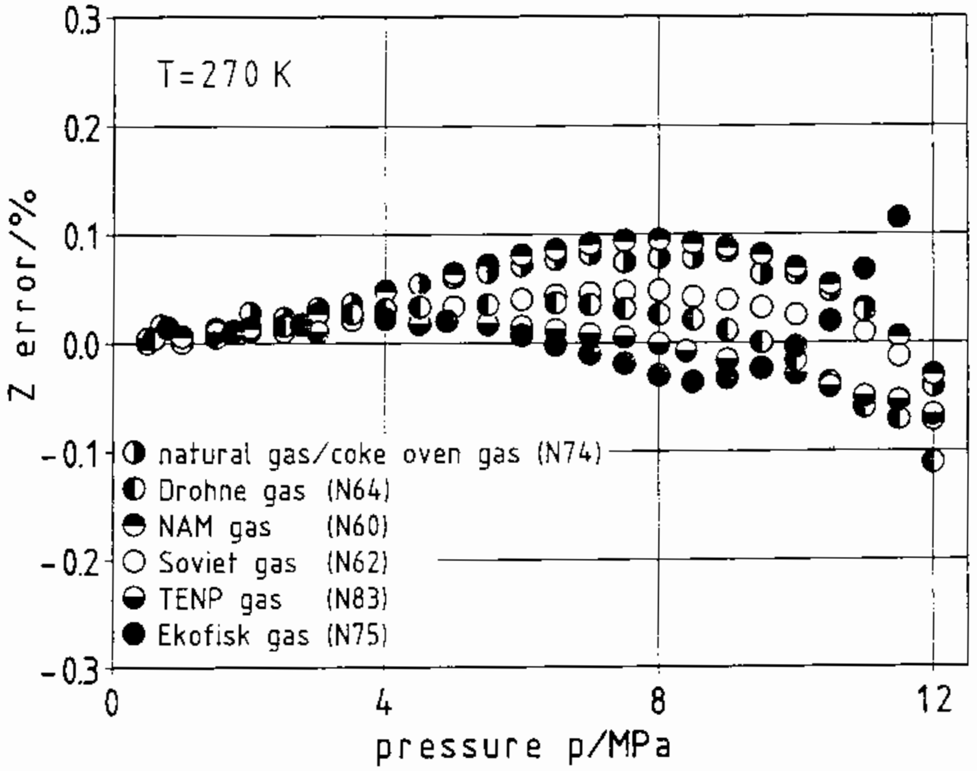

Figure 6.24 Influence of Pressure on Z-Error for the Standard GERG Virial Equation for Several Natural Gases at 270 K.

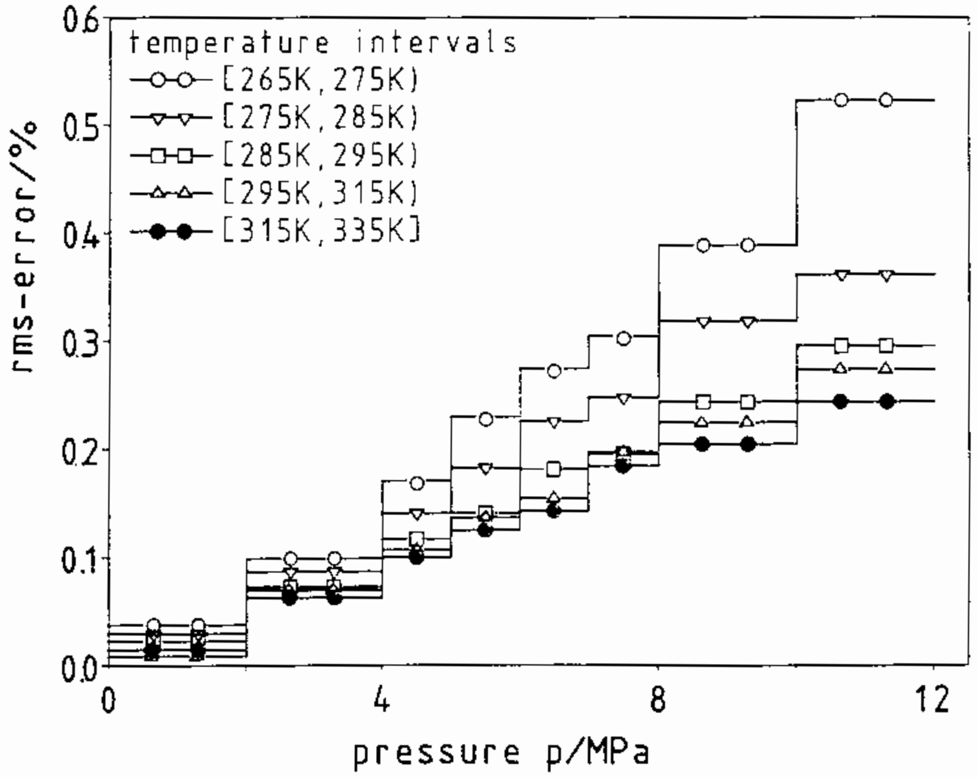

Figure 6.25 Root-Mean-Square Error for Experimental Data measured with the Burnett Apparatus or the Grating Interferometer as a Function of Pressure, for Various Temperature Domains, for Natural Gases contain no Hydrogen; GRI-SuperZ Equation.

Table 6.6 Statistical analysis of the Z-differences by pressure and temperature domains for compressibility factors measured with the Burnett or optical device for natural gas containing no hydrogen: GRI-SuperZ (AGA-8) equation simplified version.

temperature range /K	pressure range /MPa	N points	n sets	b %	s %	rms %
[265,275)	[0, 2)	38	10	0.027	0.027	0.038
[275,285)	[0, 2)	64	9	0.023	0.020	0.031
[285,295)	[0, 2)	56	10	0.018	0.022	0.028
[295,315)	[0, 2)	92	14	0.012	0.021	0.024
[315,335]	[0, 2)	57	10	0.017	0.019	0.026
[265,275)	[2, 4)	40	10	0.060	0.077	0.099
[275,285)	[2, 4)	45	9	0.063	0.065	0.090
[285,295)	[2, 4)	43	10	0.045	0.058	0.073
[295,315)	[2, 4)	57	14	0.049	0.051	0.070
[315,335]	[2, 4)	45	10	0.045	0.044	0.063
[265,275)	[4, 5)	19	10	0.120	0.125	0.171
[275,285)	[4, 5)	18	9	0.096	0.114	0.147
[285,295)	[4, 5)	21	10	0.076	0.091	0.117
[295,315)	[4, 5)	25	14	0.068	0.084	0.107
[315,335]	[4, 5)	17	10	0.080	0.061	0.100
[265,275)	[5, 6)	16	10	0.144	0.185	0.230
[275,285)	[5, 6)	19	9	0.141	0.129	0.189
[285,295)	[5, 6)	19	10	0.072	0.125	0.141
[295,315)	[5, 6)	22	14	0.095	0.101	0.137
[315,335]	[5, 6)	19	10	0.097	0.080	0.125
[265,275)	[6, 7)	18	10	0.179	0.216	0.275
[275,285)	[6, 7)	19	9	0.153	0.179	0.232
[285,295)	[6, 7)	19	10	0.126	0.135	0.182
[295,315)	[6, 7)	21	11	0.102	0.119	0.155
[315,335]	[6, 7)	20	10	0.099	0.107	0.143
[265,275)	[7, 8)	15	8	0.167	0.264	0.305
[275,285)	[7, 8)	21	9	0.140	0.220	0.256
[285,295)	[7, 8)	18	9	0.095	0.176	0.196
[295,315)	[7, 8)	20	11	0.151	0.131	0.198
[315,335]	[7, 8)	17	8	0.157	0.102	0.185
[265,275)	[8,10)	35	10	0.210	0.333	0.389
[275,285)	[8,10)	32	9	0.177	0.282	0.329
[285,295)	[8,10)	35	10	0.146	0.198	0.244
[295,315)	[8,10)	37	14	0.150	0.169	0.225
[315,335]	[8,10)	32	10	0.147	0.146	0.205
[265,275)	[10,12]	34	10	0.322	0.418	0.523
[275,285)	[10,12]	31	9	0.206	0.332	0.386
[285,295)	[10,12]	39	10	0.160	0.252	0.296
[295,315)	[10,12]	38	14	0.196	0.194	0.274
[315,335]	[10,12]	32	10	0.173	0.175	0.244
Totals		1265	19	0.100	0.174	0.201

7 - DISCUSSION AND CONCLUSIONS

7.1 General Comments on Overall Performance

The Standard GERG-88 Virial Equation has been tested very carefully for natural and coke-oven gases in the temperature range from 270 to 330 K, the pressure range up to 12 MPa, the superior calorific value range from 34.2 to 44.7 MJ m^{-3}, the relative density range from 0.55 to 0.69, and for the following concentration ranges -

mole fraction of nitrogen	$x(N_2)$	≤ 0.14
mole fraction of carbon dioxide	$x(CO_2)$	≤ 0.08
mole fraction of ethane	$x(C_2H_6)$	≤ 0.09
mole fraction of hydrogen	$x(H_2)$	≤ 0.10.

The analyses of the performance of the Standard GERG Virial Equation given in Section 6 can be summarized by the following conclusions -

(a) The Standard GERG Virial Equation predicts compressibility factors within ±0.1% for almost all natural gases, and for natural gas/coke-oven gas mixtures, for pressures up to 12 MPa and for temperatures between 270 and 330 K.

(b) At 270 K the equation exhibits some minor, apparently systematic, errors for several natural gases, as evidenced by the relative deviations of predicted compressibility factors from experimental values being sometimes greater than ±0.06% for data acknowledged to be of the highest quality. For NAM-gas (N60) (with some 12% nitrogen) and natural gas/coke-oven gas mixture (N73) (with some 10% hydrogen) the systematic error is about +0.03% for pressures above 6 MPa. For the Drohne type natural gas (N64) (with some 5% carbon dioxide) the systematic error is about -0.05% in the pressure range above 11 MPa.

(c) For the Ekofisk area gas (N75) (with some 9% ethane) there is a modest systematic error at both 270 and 280 K for pressures above 11 MPa. At 270 K and 12 MPa this has a maximum value of +0.08%, while at 280 K it is always below +0.03%.

(d) For gas compositions outside of the range tested with experimental data all the way up to 12 MPa, it is difficult to state confidently an upper limit to the maximum error for the Standard GERG Virial Equation. Supplementary test data, especially at the lower temperatures, are required for this purpose (see sub-section 7.2).

(e) Nevertheless, the equation has been partially tested with some experimental data for gases having higher concentrations of nitrogen and carbon dioxide, for example N46, N47 and N48 with 0.23 to 0.53 mole fraction N_2, and N33 and N35 with 0.25 and 0.28 CO_2. Within the limited temperature (280 to 300 K) and pressure (3 to 7 MPa) ranges for which data are available, the agreement is better than ±0.1%.

The overall general conclusion is that the virial equation presented in this Monograph, using a restricted set of input data comprising superior (gross) calorific value, relative density, mole fraction of carbon dioxide, pressure and temperature, gives a good description of the compressibility factors in the GERG databank for pressures up to 12 MPa and in the temperature region from 270 to 330 K. The remaining differences between the experimental and calculated compressibility factors are either due to experimental errors or to the inadequacy of an equation truncated after the second term in density, but these differences are, in any case, rather trivial.

7.2 Recommendations - Use and Misuse of the Standard GERG Virial Equation

Within the composition and physical property ranges quoted in the previous sub-section, the uncertainty of compressibility factor prediction is ±0.1% for temperatures from 270 to 330 K and pressures up to 12 MPa both for true natural gases and for gases containing coke-oven gas or hydrogen admixture.

For concentrations of nitrogen above 0.14 mole fraction or carbon dioxide above 0.08 the equation maintains this accuracy for temperatures between 280 and 300 K at pressures up to 7 MPa, but sufficient experimental data of adequate quality, with which to test the equation right up to the specified maximum concentrations of 0.5 and 0.3 mole fraction respectively, are not available.

The Standard GERG Virial Equation is very strictly only applicable for natural gases in the gas phase. The user should therefore be sure that computations are not made close to the phase-separation surface; for example, care is needed at low temperatures for natural gases with high ethane and/or carbon dioxide content. In doubtful cases, the dew-point curve should be estimated to ensure that the GERG equation is not being used inappropriately.

As explained more fully in ref.1, it may also be considered inappropriate to use a truncated virial expression such as the GERG equation in order to predict any thermodynamic quantity other than the compressibility factor or some directly related quantity such as the supercompressibility factor or the molar density.

It is always dangerous to extrapolate predictive methods beyond the ranges of input variables for which they were designed and tested, especially when constants of the equation(s) involved have been derived solely from experimental data taken within these ranges.

In the case of the Standard GERG Virial Equation, extrapolation upwards in pressure beyond 12 MPa is dangerous because of the truncation of the equation after the term containing the second power of the density; the neglected higher order terms must be expected to become of ever-increasing significance as pressure is increased. Furthermore, extrapolation outside of the specified 265 to 325 K temperature range (even at relatively low pressures) is also risky, because of the rather arbitrary assumption of a quadratic dependence of all virial coefficients upon temperature over this limited range of temperatures.

Extrapolation beyond the specified ranges of composition (and hence of calorific value and relative density) is risky too, because of the neglect by implication of some of the virial coefficients of nominally low mole fraction components. In particular, as mentioned earlier, extrapolation of the equation to high ethane or carbon dioxide content beyond the tested ranges is questionable, since at low temperatures such a gas might be close to the phase-separation surface.

Nevertheless, there is some suggestive evidence, but no guarantees, of how the Standard GERG-88 Virial Equation might be expected to extrapolate into regions for which it has not been properly tested and was not strictly intended.

7.2.1 Extrapolation beyond Pressure and Temperature Limits

For some natural gases and natural gas/coke-oven gas in the aforementioned ranges of composition, superior calorific value and relative density, available data of good quality extend beyond 12 MPa and up to nearly 30 MPa in the temperature range from 270 to 350 K. These data, for the Drohne, NAM, Soviet, TENP and Ekofisk natural gases, and for an H-gas/coke-oven gas mixture, were secured by Ruhrgas (36) using their optical interferometry apparatus.

Recently, as discussed in sub-section 6.6, experimental data have also become available for five simulated natural gases in the same pressure and temperature ranges. These measurements were taken by Ruhrgas (34) as part of a round-robin exercise organized by the Gas Research Institute. Further data for the same five gases will be published for temperatures down to 225 K after the completion of the round-robin test. The performance of the Standard GERG Equation in matching the results so far available is summarized in Figure 7.1.

The pressure-temperature surface (0 to 30 MPa, 225 to 400 K) is divided into four regions, with a particular uncertainty for the calculational accuracy being attributed to each such region, thus -

Region A	Uncertainty ≤ ±0.1%
B	±0.1% to ±0.2%
C	±0.2% to ±0.5%
D	±0.5% to ±3.0%.

In the 270 to 350 K temperature range, the regions shown in Figure 7.1 have been defined using the experimental data mentioned above, taking the worst case from the various natural gases. For temperatures below 270 K or above 350 K the uncertainty has been estimated from a comparison of the GERG equation with experimental data for pure methane.

The uncertainty is ±0.1% in region A. For the temperature range from 270 to 330 K the equation is within ±0.1% at least up to 12 MPa. For higher or lower temperatures the pressure limit has to be reduced in order to retain an uncertainty of ±0.1%. For higher pressures the uncertainty of the calculated compressibility factors increases; at 265 K and 350 K an uncertainty within ±0.2% is only retained up to a maximum pressure of 10 MPa.

7.2.2 Extrapolation beyond Specified Composition and Quality Limits

In the temperature range 270 to 350 K the Standard GERG Virial Equation has been tested comprehensively for gases within the ranges of composition, superior calorific value and relative density defined in sub-section 7.1. These ranges may be taken broadly to describe what is sometimes known as **pipeline or end-use quality natural gas**, although the terminology is not definitive. The estimated uncertainties involved in calculations of compressibility factors beyond these limits of quality are plotted in Figures 7.2 to 7.4 as pressure-composition surfaces for nitrogen, carbon dioxide and ethane respectively.

The uncertainty limits for **high-nitrogen** content natural gases given in Figure 7.2 are supported by the experimental

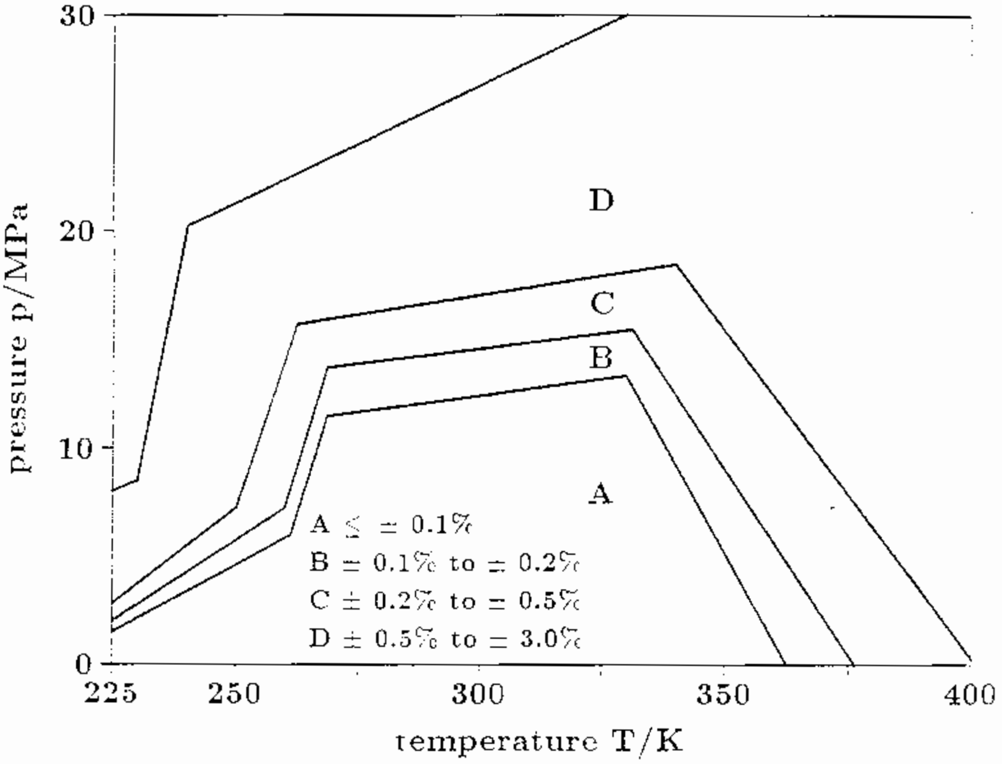

Figure 7.1 Uncertainty Limits for the Calculation of Compressibility Factor. The uncertainty limits given are expected to be valid for natural gases with $x(N_2) \leq 0.14$, $x(CO_2) \leq 0.08$, $x(C_2H_6) \leq .09$ and $x(H_2) \leq 0.10$, and for $34.2 \leq H_S/\mathrm{MJ\ m^{-3}} \leq 44.7$ and $0.55 \leq d \leq 0.69$.

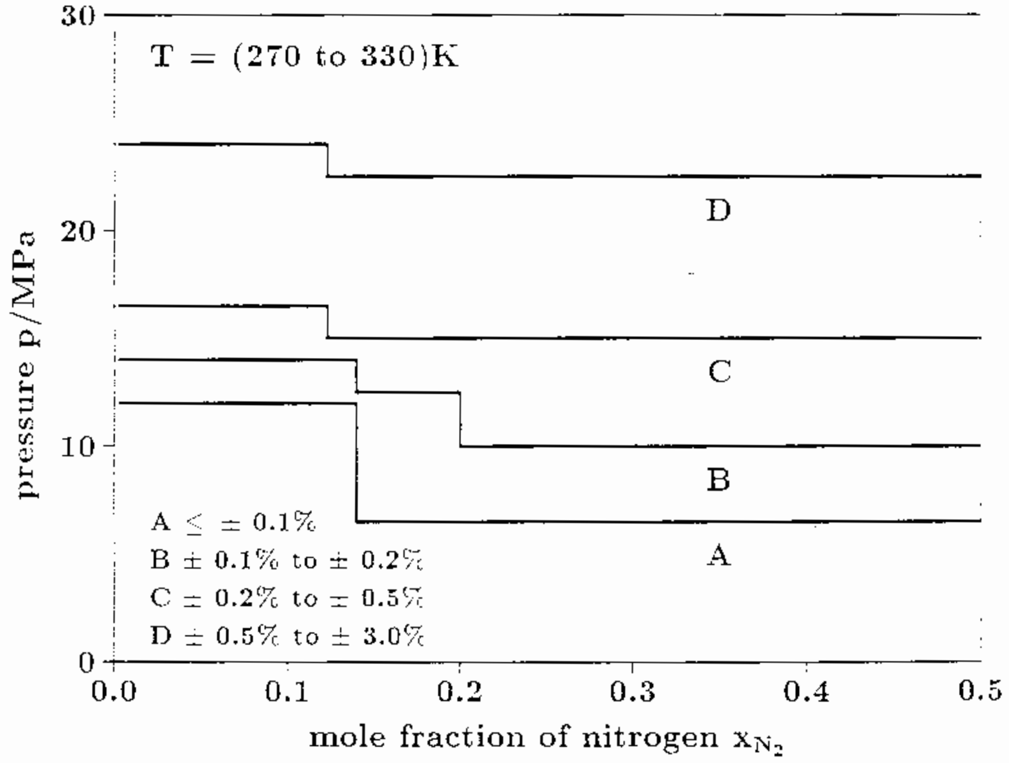

Figure 7.2 Uncertainty Limits for the Calculation of Compressibility Factors of Natural Gases with High Nitrogen Content.

data for natural gases N59, N60, N73 and N74 from the GERG databank (10) and for gas GU-1 from the GRI round-robin test (34) for mole fractions up to 0.14. The uncertainty limits for mole fractions of nitrogen in the range 0.14 to 0.50 have been estimated from the experimental results for binary CH_4+N_2 mixtures present in the GERG databank (10), viz. B12-8 ($x(N_2)=0.20$) and B12-22 ($x(N_2)=0.50$), for pressures up to 28 MPa. The uncertainty limits given are supported by natural gas data (N46 to N48) for pressures up to 6.5 MPa and temperatures of 280 to 300 K. Further work to establish the uncertainty limits more definitively is currently in progress at the Ruhrgas laboratories.

The ±0.1% estimated uncertainty limit for mole fractions $x(N_2)>0.14$ is applicable to pressures up to 6.5 MPa; the ±0.2% uncertainty limit applies up to about 10 MPa. The ±0.5% and ±3% uncertainty limits are practically independent of pressure throughout the whole composition range, and are reached at about 15 and 23 MPa respectively.

The estimated uncertainty limits for **high-carbon dioxide** content natural gases are shown in Figure 7.3. In the range up to 0.08 mole fraction these are based upon the experimental date for natural gases N53, N54, N63 and N64, and for gas GU-2 from the GRI round-robin test (34). The estimates for the range 0.08 to 0.30 mole fraction are based upon the binary CH_4+CO_2 mixture data present in the GERG databank (10), viz. B13-4 and B13-5, with a carbon dioxide mole fraction of 0.31. Several natural gas data sets (N33, N34, N35 and N80) in the 0.08 to 0.30 mole fraction range have been obtained by Gasunie. However, the pressure and temperature ranges are limited to only 3 to 6.5 MPa and 280 to 300 K respectively.

Each uncertainty limit shown is constant, independent of composition up to a carbon dioxide mole fraction of 0.08. For higher mole fractions the pressure at which a particular estimated uncertainty limit is reached decreases linearly with increasing mole fraction. At a pressure of 10 MPa the uncertainty limits of ±0.1% and ±0.2% in predicted compressibility factor are reached at mole fractions of about 0.13 and 0.18 respectively.

Figure 7.4 shows the estimated uncertainty limits for the pressure versus ethane content surface. For mole fractions up to 0.09 the limits have been derived from experimental data for the natural gases N59 to N66 and N75 (10).

For **higher ethane** concentrations, the uncertainty limits have been estimated from the experimental binary CH_4+C_2H_6 mixture data present in the GERG databank, viz. B14-8 and 9, B14-6 and 7, and B14-12 and 13, having ethane mole fractions of 0.08, 0.12 and 0.16 respectively. The pressure at which any particular estimated uncertainty limit, calculated from the relative errors of the predicted compressibility factors, is reached, decreases with increasing mole fraction. However, the relative errors for the binary mixture containing 0.08 mole fraction of ethane are, at the same pressure, much higher than the relative errors for natural gases with 0.08 ethane. The reason for apparent paradox is obvious. The virial coefficients calculated for this binary mixture from the Standard GERG Equation do not properly represent the true virial coefficients of the mixture, because the latter does not exhibit the "normal" distribution of hydrocarbons in a typical natural gas. This is a necessary condition for the equivalent hydrocarbon concept to be applicable.

To overcome this problem, the uncertainty limits calculated from the binary mixture data were "matched" at a mole fraction 0.09 to the equivalent result from the natural gas data. The uncertainty limits in the high-ethane composition range were then estimated by scaling the pressure-axis values by constant factors calculated from this procedure; thus, at an uncertainty limit of ±0.1%, by the factor 4.3; at ±0.2%, by 2.9; at ±0.5%, by 2.0; and at ±3% by 1.0.

The estimated uncertainty limits are constant for mole fractions of ethane up to about 0.09. The ±0.1% limit is reached at a pressure of about 12 MPa. For higher mole fractions the pressure at which each uncertainty limit is reached decreases

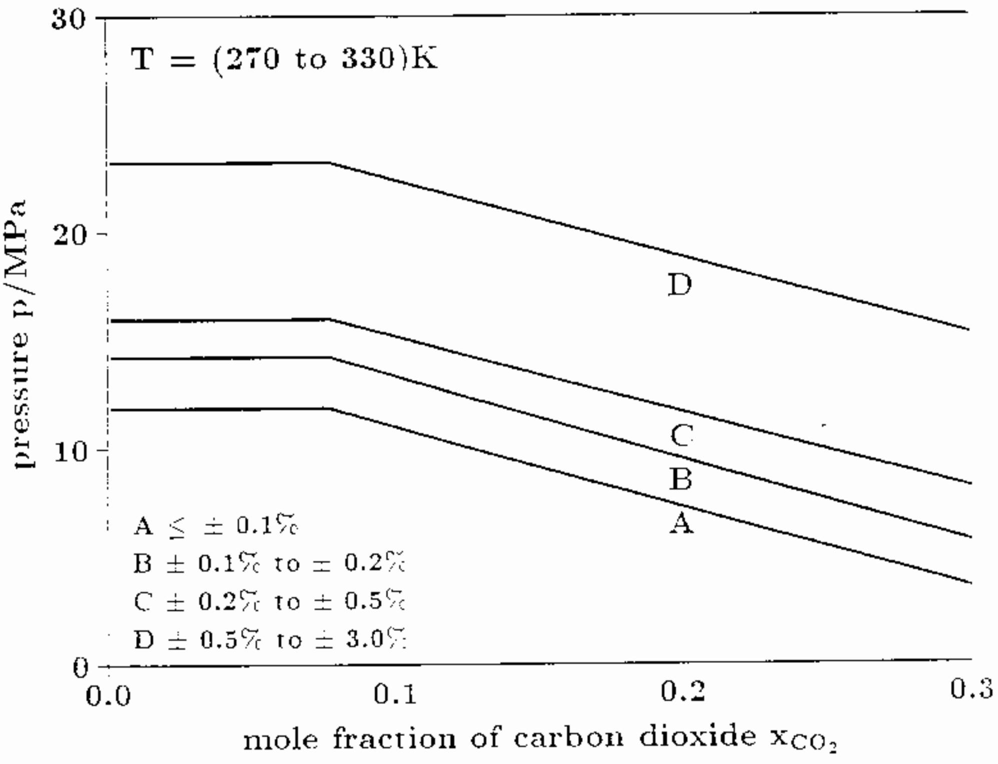

Figure 7.3 Uncertainty Limits for the Calculation of Compressibility Factors of Natural Gases with High Carbon Dioxide Content.

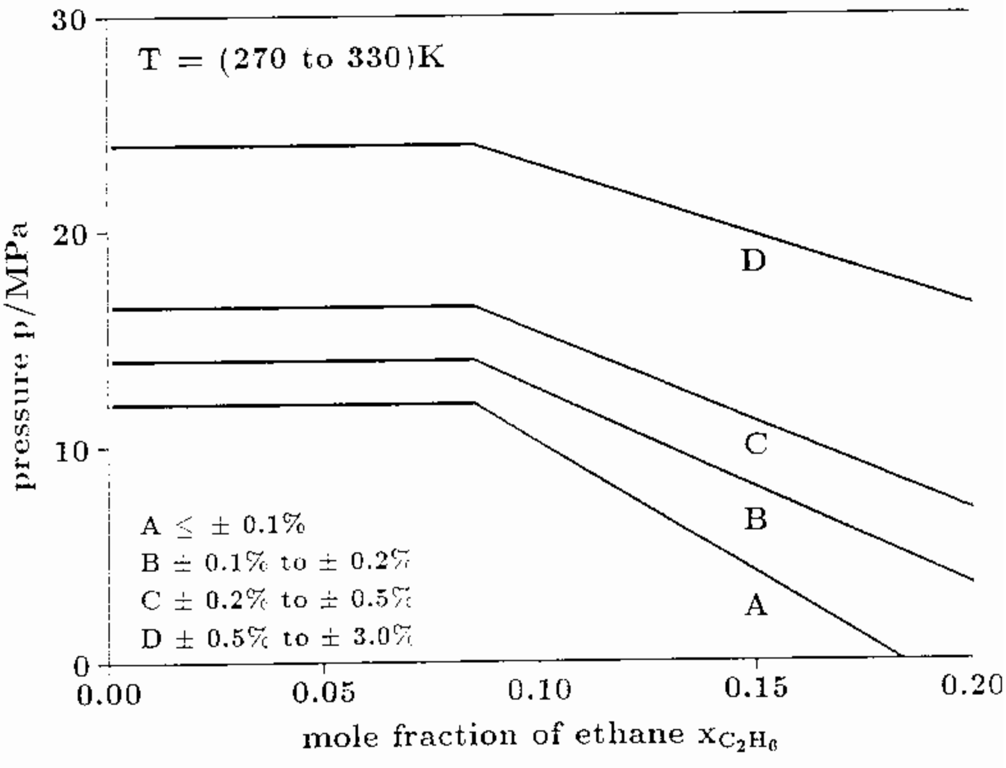

Figure 7.4 Uncertainty Limits for the Calculation of Compressibility Factors of Natural Gases with High Ethane Content.

linearly with increasing mole fraction. At a pressure of 10 MPa uncertainty limits of ±0.1% and ±0.2% are reached at mole fractions of about 0.10 and 0.13 respectively.

The overall results can be summarized as follows. For gases of a type categorised earlier in this sub-section as of pipeline quality, the uncertainty in compressibility prediction (For the temperature range 270 to 330 K) is ±0.1% at pressures up to 12 MPa and ±0.2% between 12 and 14 MPa. For gases beyond the designated limits of pipeline quality, only gases having mole fractions less than those listed below will have uncertainties within ±0.1% and ±0.2% respectively, at pressures up to 10 MPa and temperatures within the range 270 to 330 K --

component	maximum mole fraction for an uncertainty within -	
$(270 \le T/K \le 330, 0 \le p/MPa \le 10)$	±0.1%	±0.2%
nitrogen	0.14	0.50
carbon dioxide	0.13	0.18
ethane	0.10	0.13

7.3 Sensitivity to Input Variables

7.3.1 Inbuilt Uncertainties

The uncertainties of compressibility factors predicted by the Standard GERG-88 Virial Equation have been discussed in detail in the foregoing sub-sections. These uncertainties result from the uncertainties of both the like and unlike interaction virial coefficients used in the GERG equation of state. The uncertainties of the virial coefficients are attributable to the uncertainties of the experimental pVT (compressibility factor) data used in their evaluation and, for the unlike interaction coefficients, to the uncertainties in the compositions of the binary mixtures as well (9).

The uncertainties of gas analyses for natural gas test mixtures also contribute to the uncertainties in assessing the accuracy of prediction. The uncertainties $\delta Z_{expt}(pVT)$ resulting from the pVT measurements alone are, as for the pure gases, usually around ±0.07% for pressures up to about 8 MPa. The additional uncertainties $\delta Z_{expt}(x_i)$ attributable to the simplified (reduced) analysis input data, as deduced from the slightly uncertain detailed analysis data for the test gases, increases with pressure to about ±0.06% at 12 MPa. These features are shown in Figure 7.5; the expected overall uncertainty δZ_{calc} of ±0.1% is also shown.

These considerations indicate that even with a "perfect" set of input data for the operational application of the GERG Virial Equation, the expectation accuracy cannot be better than ±0.1%; the uncertainties associated with actual "imperfect" input data can only increase this uncertainty of prediction, and for field application it is essential to know the extent to which the achievable accuracy is likely to be further degraded in an operational environment. Consequently, the effects of uncertainties in superior calorific value, relative density, mole percentage of carbon dioxide, pressure and temperature on the uncertainty of compressibility factor prediction by the Standard GERG-88 Virial Equation are discussed below.

7.3.2 Calorific Value

The effect of uncertainty in the superior calorific value on the the uncertainty of compressibility factor prediction is shown in Figure 7.6 for three typical and distinct natural gases. These particular gases were chosen because of their substantially different compositions, which imply that the volumetric (pVT) behaviour of each is dominated by different interaction virial coefficients, as follows -

N60 NAM gas	~ 12% N_2	CH_4+N_2	interaction emphasized
N81 Middelie gas	~ 11% CO_2	CH_4+CO_2	
N66 Ekofisk gas	~ 9% C_2H_6	CH_4+C_2H_6	

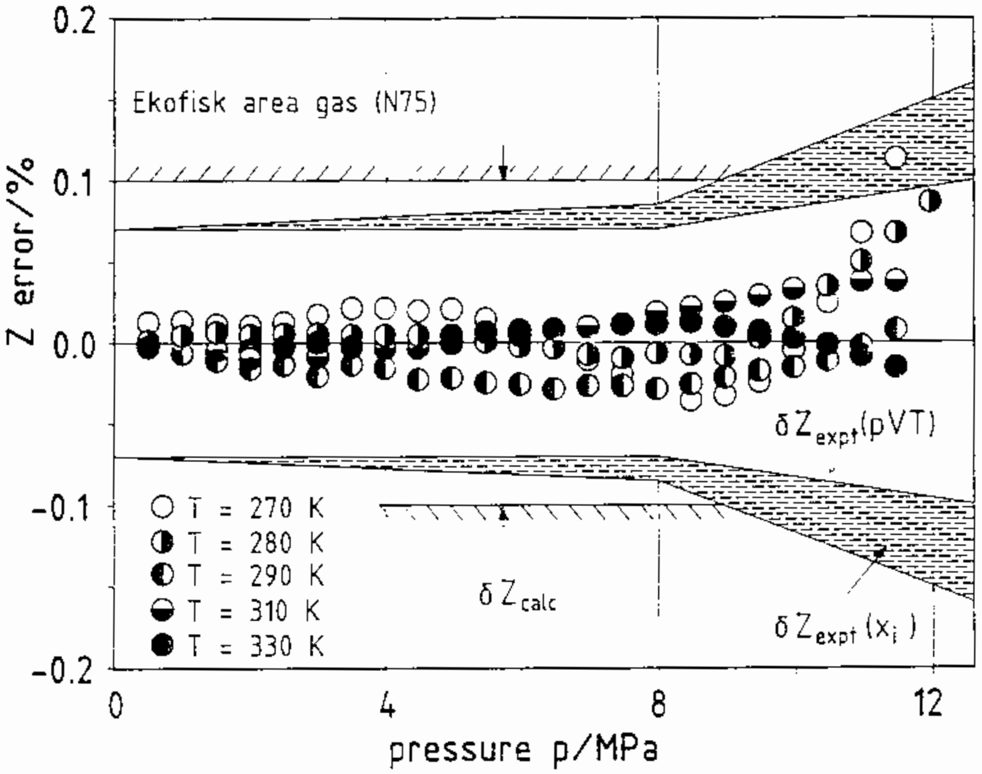

Figure 7.5 Effect of Uncertainties $\delta Z_{expt}(pVT)$ and $\delta Z_{expt}(x_i)$ in Source Data on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

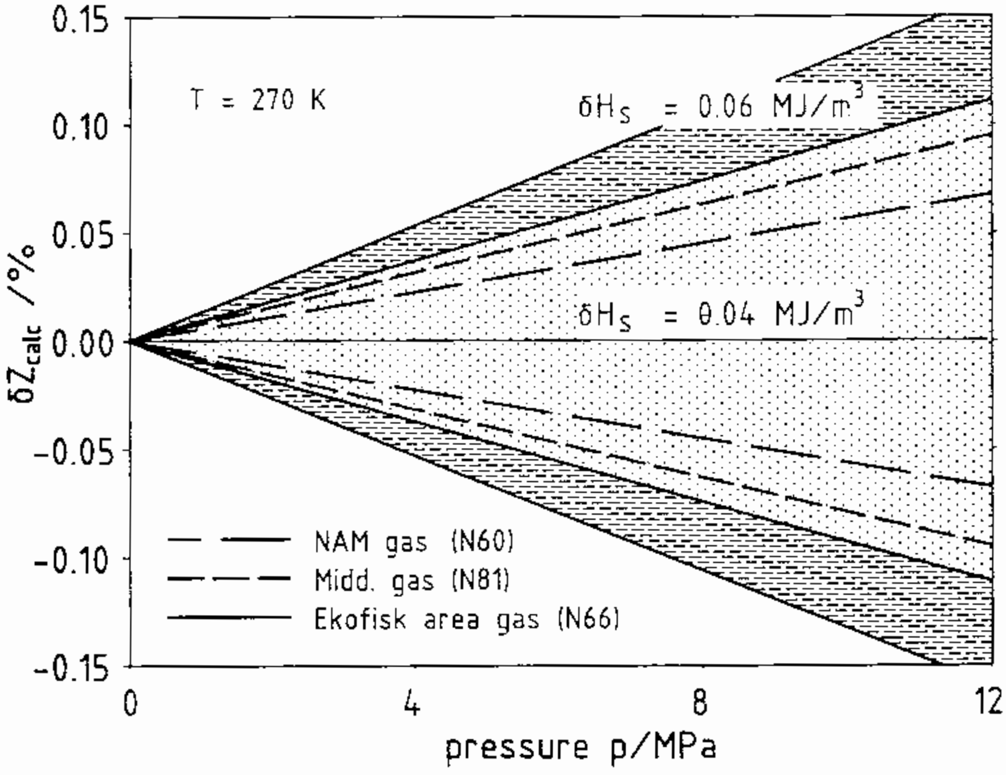

Figure 7.6 Effect of Uncertainty δH_S in Superior Calorific Value on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

The uncertainty in compressibility factor attributable to the uncertainty of in the measured superior calorific value is highest for the Ekofisk area gas and lower for the other natural gases. If the uncertainty of the measured superior calorific value is ±0.04 MJ m^{-3}, equivalent to approximately 0.1%, the maximum resulting uncertainty of the compressibility factor predicted by the Standard GERG Equation is ±0.1%, for high pressure and low temperature. For a pressure of less than 6 MPa, the extra uncertainty decreases to less than ±0.05%.

Thus the uncertainty δZ_{calc} increases approximately linearly with pressure for a given uncertainty in the measured calorific value. Although the effect is marginally greater at low temperatures, the dependence on temperature is weak. For Ekofisk area gas only, the outer boundary in Figure 7.6 shows the effect of ±0.06 MJ m^{-3} uncertainty in the calorific value.

In summary, the uncertainty of predicted compressibility factors increases with the uncertainty of the calorific value used as input data, as would be expected. Values for the sensitivity coefficient $S(Z/H_S)$ for the uncertainty δZ of the predicted compressibility factor resulting from the uncertainty δH_S of the measured calorific value, defined by the equation

$$\delta Z(\%) = S(Z/H_S).\delta H_S(\%) \qquad (7.1)$$

are given in Table 7.1. The uncertainty δH_S typically claimed in Europe for the calorific value measured measured under operational conditions in the field is usually between 0.10 and 0.25%, or about 0.04 to 0.10 MJ m^{-3}.

7.3.3 Relative Density

An analysis carried out in a manner exactly analogous to that described in sub-section 7.3.2, and for the same three typical natural gases, shows that the maximum effect of an uncertainty of ±0.2% in the measured relative density is a change of about ±0.1% in the predicted compressibility factor (see Figure 7.7). Again the uncertainty δZ increses with the uncertainty δd of the relative density and, for a given value of δd, linearly with pressure. Values for the sensitivity coefficient s(Z/d), defined by the equation

$$\delta Z(\%) = S(Z/d).\delta d(\%) \tag{7.2}$$

are listed in Table 7.1.

Typical values of the uncertainty δd range from about ±0.15 to ±0.30% for values of d obtained under operational conditions.

7.3.4 Concentrations of Inerts

The set of data normally recommended and required as input for the Standard GERG-88 Virial Equation includes a value for the carbon dioxide content, with the nitrogen content being determined as a by-product of the calculation procedure for compressibility factor.

Again for the same three test gases, as shown in Figure 7.8, an uncertainty of ±0.1% (molar) in the carbon dioxide content gives a maximum uncertainty in the predicted compressibility factor of ±0.1% at the highest pressures of 12 MPa. The uncertainty decreases with decreasing pressure and, self-evidently, for lower values of the uncertainty δx_3 of the molar percentage of carbon dioxide. Values for the sensitivity coefficient $S(Z/x_3)$ given in Table 7.1 have been derived according to the equation

$$\delta Z(\%) = S(Z/x_3).\delta x_3(\%,\text{molar}) \tag{7.3}$$

The effect of the uncertainty in composition of the other main inert component, nitrogen, on the uncertainty of prediction of compressibility factor by use of one of the alternative input data sets (for example, by the method given in sub-section 5.5.1) is expected to be of the same magnitude as for carbon dioxide.

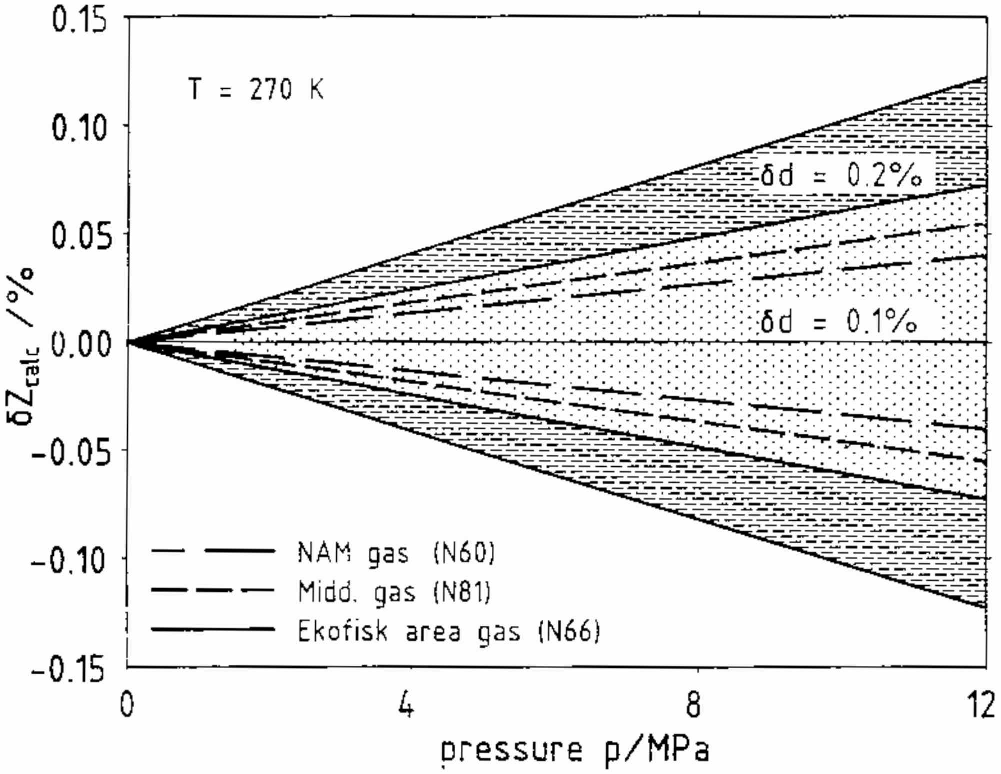

Figure 7.7 Effect of Uncertainty δd in Relative Density on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

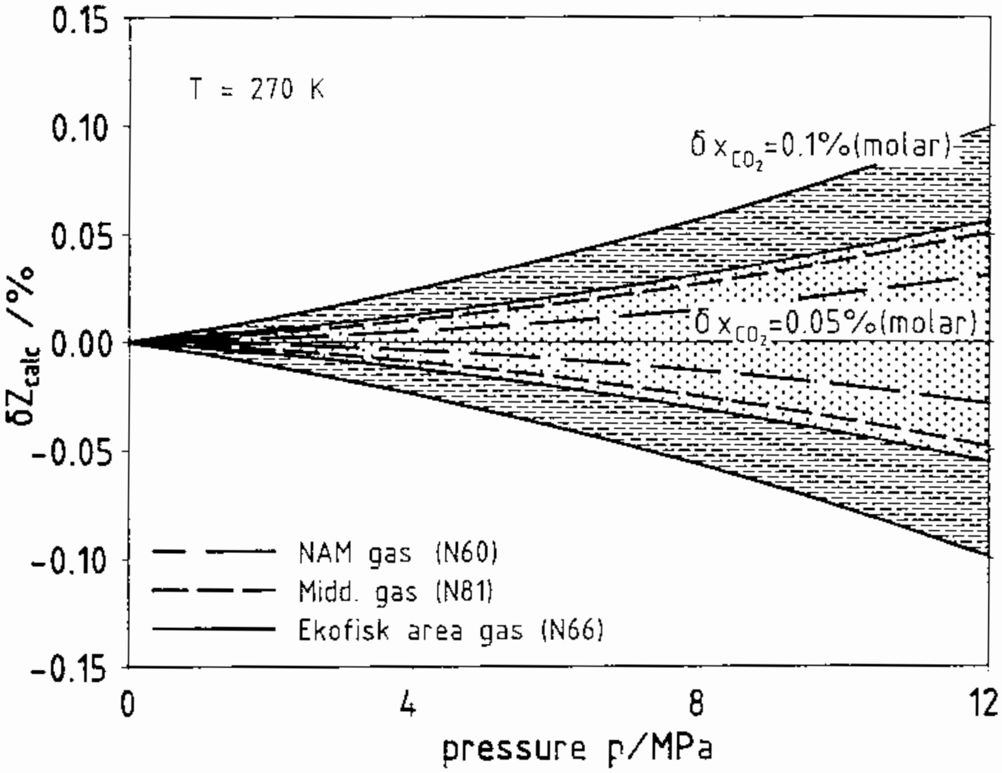

Figure 7.8 Effect of Uncertainty δx_3 in Carbon Dioxide Content on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

7.3.5 Temperature and Pressure

Any uncertainty in the temperature measurement used as input to the Standard GERG-88 Virial Equation propagates very strongly into an uncertainty in the predicted compressibility factor. This effect is illustrated in Figure 7.9 for the same three test gases as studied in previous sub-sections. The sensitivity coefficients S(Z/T) for the temperature dependence, defined by the equation

$$\delta Z(\%) = S(Z/T).\delta T(\%) \qquad (7.4)$$

are much higher than for any other of the input variables. An uncertainty in temperature of only ±0.2 K yields a maximum uncertainty in the compressibility factor of ±0.16% at high pressures for the Ekofisk area gas. For a fixed value of δT, the uncertainty δZ is more or less proportional to pressure, and at fixed pressure δZ is proportional to δT.

The effect of uncertainty in pressure on the uncertainty in compressibility factor follows a somewhat different pattern to that found for the other input variables, as shown in Figure 7.10. Over a wide range of pressures, up to about 8 MPa, there is only a weak dependence of δZ on pressure. For an uncertainty δp in pressure of ±0.02 MPa, the resulting uncertainty δZ in compressibility factor has an essentially constant value of about ±0.08% for the Ekofisk area gas.

Whereas, for the other input variables, the relative uncertainties $\delta Q(\%)$ were constant parameters, the relative uncertainty $\delta p(\%)$ in pressure in this case increases with decreasing pressure, and is greatest at $p \sim 0$; this factor leads to the distinctive pattern displayed by Figure 7.10.

7.3.6 Overall Sensitivity to Input Variables

The overall uncertainty in compressibility factors predicted by the Standard GERG-88 Virial Equation, resulting from the experimental uncertainties in the input variables required to perform the calculations, can be obtained by the combination

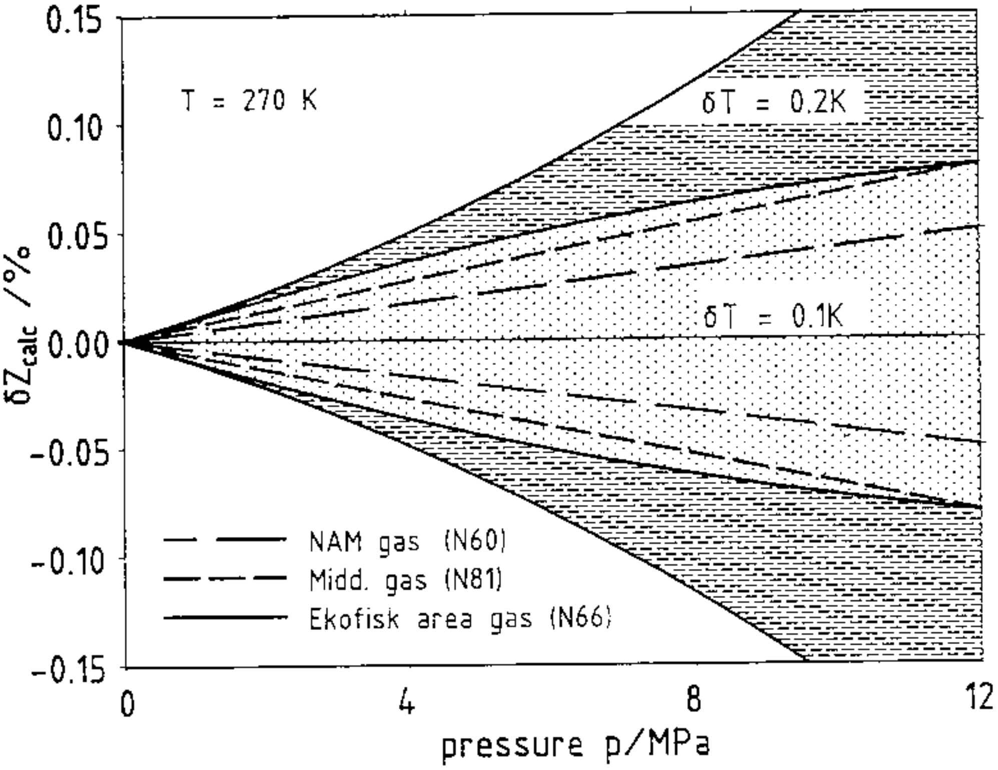

Figure 7.9 Effect of Uncertainty δT in Temperature on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

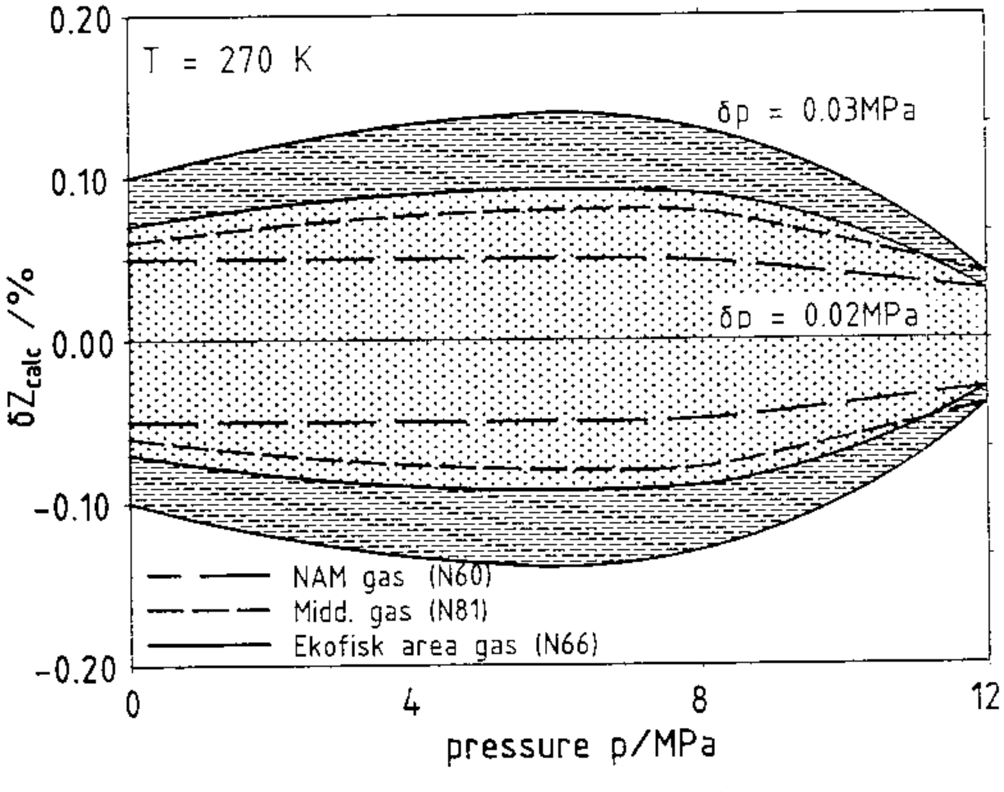

Figure 7.10 Effect of Uncertainty δp in Pressure on the Uncertainty of Prediction of Compressibility Factor by the Standard GERG Virial Equation.

in quadrature of the individual relative uncertainties discussed in the previous four sub-sections, as follows -

$$\delta Z(\%) = \{[S(Z/H_S).\delta H_S(\%)]^2 + [S(Z/d).\delta d(\%)]^2 + [S(Z/x_3).\delta x_3(\%,\text{molar})]^2 + [S(Z/T).\delta T(\%)]^2 + [S(Z/p).\delta p(\%)]^2\}^{\frac{1}{2}} \quad (7.5)$$

where S(Z/Q) is the sensitivity coefficient for the input variable Q; essentially each such quantity is the partial derivative of Z with respect to Q.

Approximate values for the sensitivity coefficients S(Z/Q), where $Q=H_S,d,x_3,T$ and p, are given in Table 7.1 for a natural gas containing about 6% nitrogen, 7½% carbon dioxide and 4½% ethane.

Table 7.1 Sensitivity Coefficients for the Standard GERG-88 Virial Equation to Errors in the Input Variables for a Natural Gas with H_S=36.61 MJ/m^3, d=0.6821, x_3=0.0766, for the temperature range 275 to 285 K

	p = 6 MPa	p = 12 MPa
$S(Z/H_S)$	0.28	0.75
S(Z/d)	0.22	0.40
$S(Z/x_3)$	0.33	0.73
S(Z/T)	0.70	1.55
S(Z/p)	0.15	0.15

Typical uncertainties of measurement (two standard deviations) are listed for the input variables in Table 7.2.

Except for the mole fraction (or percentage) of carbon dioxide, the values given in Table 7.2 summarize estimates from the various companies represented on the GERG Working Group 1.1; together they provide a general consensus view of the present capabilities of typical instrumentation used in field operations. Estimates for the uncertainty of the mole percentage of carbon dioxide, however, vary considerably, from 0.03 to 0.20%; the lower uncertainty value seems likely to be too optimistic.

Table 7.2 Typical Experimental Uncertainties of Input Variables

Calorific Value $\delta H_S = \pm 0.15\%$ or 0.06 MJ/m^3
Relative Density $\delta d = \pm 0.20\%$ or 0.0013
Mole Fraction of CO_2 $\delta x_3 = \pm 0.20\%$ molar
Temperature $\delta T = \pm 0.05\%$ or 0.15 K
Pressure $\delta p = \pm 0.30\%$ or 0.02 MPa at 6 MPa

For the calculation of the overall uncertainty of predicted compressibility factors according to equation (7.5), the uncertainties from Table 7.2 have been used together with the sensitivity coefficient values from Table 7.1. For the natural gas quoted in Table 7.1, the derived overall uncertainties are -

for $p = 6$ MPa --- $\delta Z = 0.10\%$
for $p = 12$ MPa --- $\delta Z = 0.22\%$

at temperatures in the range 275 to 285 K.

These overall uncertainty values, calculated for this particular natural gas, are typical of results also obtained for other natural gas compositions, even though the individual contributions to the overall uncertainty from the different input variables might vary.

Thus the final uncertainty of compressibility factors calculated from the Standard GERG-88 Virial Equation - summed up from the uncertainty of the calculation method (±0.1%) and the uncertainty caused by the uncertainties in the input variables - varies from about ±0.2% (at 6 MPa) to ±0.3% (at 12 Mpa).

These results are valid as long as each input variable is measured independently of the others. If, however, the calorific value and relative density are both determined by calculation (25) from the same detailed gas chromatographic analysis (which also includes the carbon dioxide content), then their values (and their concomitant uncertainties) are not independent variables, but instead are correlated. In consequence, equation (7.5) is no longer valid, and instead the correlated terms have to be replaced by an arithmetic summation before being combined in quadrature with the remaining independent terms, viz.

$$\delta Z(\%) = \{[S(Z/H_S).\delta H_S(\%) + S(Z/d).\delta d(\%) + S(Z/x_3).\delta x_3(\%)]^2 + [S(Z/T).\delta T(\%)]^2 + [S(Z/p).\delta p(\%)]^2\}^{\frac{1}{2}} \qquad (7.6)$$

Superficially this would seem bound to increase the overall uncertainty δZ, but in fact the details of a chromatographic analysis contain an implicit relationship between the relative signs of δH_S and δd; if both quantities bear the same sign, then the overall uncertainty increases, but if they are of opposite sign the overall uncertainty is reduced. In other words, depending upon which component in the natural gas analysis carries the most serious uncertainty, the final uncertainty in compressibility factor may be either somewhat greater or less than that calculated from equation (7.5); inaccuracy in the measurement of ethane or heavier hydrocarbons inevitably leads to δH_S and δd values of the same sign, whereas inaccuracy in the measurement of nitrogen or carbon dioxide leads to opposite signs and some compensation of measurement errors.

7.4 Use of Alternative Input Variables

The detailed analyses given in Section 6 demonstrate the performance of the Standard GERG-88 Virial Equation only for the set of input variables which comprise the preferred set, viz.

(1) Superior calorific value H_s
Relative density d
Mole fraction of carbon dioxide x_3
Mole fraction of hydrogen x_4.

It was, however, noted in Section 5 that the following alternative sets of input variables can also be used, viz.

(2) H_s d x_2 x_4
(3) H_s x_2 x_3 x_4
and (4) d x_2 x_3 x_4

where x_2 is the mole fraction of nitrogen.

An overall (global) comparison of the sort described in sub-section 6.2 has been carried out for each of these alternative procedures for the same set of test data (84 data sets, 4486 data points). The results are summarized in Table 7.3, and show that each set of input variables achieves a practically identical accuracy of prediction for compressibility factor.

Table 7.3 Comparison between Predicted and Measured Compressibility Factors; Standard GERG-88 Virial Equations using Four Alternative Input Variable Sets

Z-Differences for 84 data sets, 4486 points

Input variable set	Unknown input variable	Bias-%	Deviation rms-%
(1)	x_2	-0.004	0.049
(2)	x_3	-0.002	0.049
(3)	d	-0.007	0.050
(4)	H_s	+0.003	0.049

The mean deviation (bias) differs slightly, by up to 0.01%, between the various input variable sets, the outlying value occuring when calorific value H_S is unknown; the mean deviations for the remaining input variable sets agree within ±0.003%.

The point-to-point agreement for the four alternative input variable sets is better than 0.01% for a variety of natural gases, including those with a high content of nitrogen, carbon dioxide and hydrogen. For gases with a high content of ethane, however, maximum differences of up to 0.05% occur at high pressures between results for the preferred method (1) and method (4), for which the calorific value is unknown. The point-to-point agreement with method (1) for the remaining methods (2) and (3) is within ±0.025%.

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8 - COMPUTER IMPLEMENTATION OF THE STANDARD GERG-88 VIRIAL EQUATION

8.1 Calculation of Compressibility Factor

8.1.1 Input Data Requirements

The required input variables for predicting real-gas compressibility factors with the Standard GERG-88 Virial Equation (as implemented in the computer programs presented in sub-sections 8.2 and 8.3) are temperature t in degrees Celsius (which both programs convert internally to the temperature T in kelvin), the pressure in bar, the superior (gross) calorific value in MJ m^{-3} and relative density (both at appropriate reference conditions), and the molar content of carbon dioxide and hydrogen.

The Basic implementation also allows the temperature and pressure to be input in any of several other commonly used units, and the calorific value and relative density for any of several reference conditions. However, hydrogen-containing gases are not allowed in this implementation. For details of these options, see sub-section 8.2.

Neither the Basic nor the executable Fortran implementation allows the nitrogen content as one of the input variables i.e. the "alternative input" methods described in sub-sections 5.5.1 to 5.5.3 are not supported; however, the Fortran subroutine SGERG.FOR, discussed in sub-section 8.3, does include code appropriate for these purposes.

Numerical values for the compressibility factor of a natural gas with a known set of the aforementioned physical properties, at known pressure and temperature conditions (p,T), may be calculated in accordance with equation (2.2), viz.

$$Z(p,T) = 1 + B_{mix}(T) \cdot \rho_m + C_{mix}(T) \cdot \rho_m^2 \qquad (2.2)$$

where (equation (2.1))

$$\rho_m = p/ZRT \qquad (2.1)$$

Given values of $B_{mix}(T)$ and $C_{mix}(T)$, calculated by the intricate iteration procedure described in Section 5 (in particular sub-section 5.3), and knowing p, the easiest way of obtaining Z is to solve these two equations by further iteration, using Z=1 as a starting value in equation (2.1). This approach is used in both the Basic and Fortran implementations described below. Convergence to the true value of Z is usually quite rapid. Both programs use double-precision arithmetic.

For the Master GERG-88 Equation it is not too unreasonably difficult (though not recommended!) to carry out the calculation of B_{mix} and C_{mix}, and the subsequent calculation of Z, by hand. For the Standard GERG-88 Equation, however, the considerable complexity of the calculation of B_{mix} and C_{mix} makes it totally impracticable to use anything other than a validated computer program.

8.1.2 Calorific Value Reference Conditions

The reference conditions for which the Standard GERG-88 Virial Equation was developed, and which both computer programs use internally are those given in Table 1.1, viz.

Combustion at $T_1 = 298.15$ K ($t_1=25^oC$)
$p = 101.325$ kPa, and
Gas metered at $T_2 = 273.15$ K ($t_2=0^oC$)
$p = 101.325$ kPa.

The latter is also the reference condition for relative density.

Considerable care is needed to ensure that correctly referenced inputs are used for calorific value and relative density. Several countries normally use the above conditions, but others use alternative conditions; confusion because of this can occur readily, particularly since the unit of calorific value measurement in each case may still be MJ m^{-3}.

Table 8.1 is a guide to which of the major international gas trading countries use which reference conditions.

Table 8.1 Nationally Adopted Calorific Value Metric Reference Conditions

All values of the reference condition for pressure are equal at 101.325 kPa = 1.01325 bar

t_1 is the combustion reference temperature
t_2 is the gas metering reference temperature

	$t_1/^{\circ}C$	$t_2/^{\circ}C$
Australia	15	15
Austria	25	0
Belgium	25	0
Canada	15	15
Denmark	25	0
France	0	0
Germany	25	0
Ireland	15	15
Italy	25	0
Japan	0	0
Netherlands	25	0
Soviet Union	25	0 or 20
United Kingdom	15	15
United States of America	15	15

As indicated in sub-section 8.1.1, the Basic implementation allows the user a choice of reference conditions for which he may input the physical properties, but of course he must be sure that he definitively knows these before he can exercise that choice.

For the Fortran implementation there is no such choice; values must be entered for the "standard" reference conditions. Consequently, conversion factors need to be available for the user whose national (or local) convention differs from that used here. Appropriate conversion factors are given and briefly discussed in sub-section 8.1.4.

For those using non-metric measures of calorific value (i.e. Btu ft^{-3}), conversion both of the unit and of the reference condition is required. Again this may be carried out internally in the Basic implementation; further discussion is given in sub-section 8.1.4.

8.1.3 Units and Conversion Factors for Pressure and Temperature

If the input variables p an t are not in the favoured units of bar and °C, then conversions must be made in order to use the Fortran implementation. A selection of appropriate conversion factors is given in Table 8.2; the values quoted are identical to those available internally in the Basic implementation.

Table 8.2 Conversion Factors for Pressure and Temperature

Pressure:
to convert p/kPa to p/bar - multiply by 10^{-2}
to convert p/MPa to p/bar - multiply by 10
to convert p/atm to p/bar - multiply by 1.01325
to convert p/psia to p/bar - divide by 14.5038
to convert p/psig to p/bar - add 14.6959 and divide the result by 14.5038

Temperature:
to convert T/K to t/°C - subtract 273.15
to convert t/°F to t/°C - subtract 32 and divide the result by 1.8
to convert T/°R to t/°C - divide by 1.8 and subtract 273.15 from the result

8.1.4 Conversion between Reference Conditions

Because both superior calorific value and relative density are functions of the composition of a gas mixture, and because the thermophysical properties of the individual components depend upon temperature and pressure in individual ways, it is in principle impossible (without knowledge of the composition) to convert the calorific value and relative density, known at one set of reference conditions, to **exact** corresponding values for any other set of reference conditions.

However, because the relevant reference conditions are always thermodynamically close together, and because natural gases do not vary in their compositions by major amounts, it is possible in practice to give conversion factors which may be applied to any typical natural gas with essentially no loss of accuracy in the converted physical properties. Table 8.3 gives the conversion factors appropriate to the reference conditions appearing in Table 8.1.

Table 8.3 Conversion Factors for Calorific Value and Relative Density - Metric

Calorific Value: to convert H_S/MJ m^{-3} at t_1= 0°C, t_2= 0°C
to H_S/MJ m^{-3} at t_1=25°C, t_2= 0°C
multiply by 0.9974
to convert H_S/MJ m^{-3} at t_1=15°C, t_2=15°C
to H_S/MJ m^{-3} at t_1=25°C, t_2= 0°C
multiply by 1.0543

Relative Density: to convert d at t_2=15°C to d at t_2= 0°C
multiply by 1.0002

The values given in Table 8.3 are available within the Basic implementation of the Standard GERG-88 Equation. Also available therein are appropriate conversion factors for calorific values, quoted in Imperial units at non-metric reference conditions, for their transformation to values at the closest metric reference conditions. These are given in Table 8.4; the Imperial reference conditions quoted are those sometimes still encountered in the U.K. and U.S.A. respectively.

Table 8.4 Conversion Factors for Calorific Value and Relative Density - Imperial

Calorific Value: to convert H_s/Btu ft^{-3} at t_1=60°F, t_2=60°F
and p_2=1.01592 bar
to H_s/MJ m^{-3} at t_1=15°C, t_2=15°C
and p_2=1.01325 bar
divide by 26.86

to convert H_s/Btu ft^{-3} at t_1=60°F, t_2=60°F
and p_2=1.01560 bar (14.73 psia)
to H_s/MJ m^{-3} at t_1=15°C, t_2=15°C
and p_2=1.01325 bar
divide by 26.85

Relative Density: to convert d at t_2=60°F and
p_2=1.01592 or 1.01560 bar
to d at t_2=15°C and p_2=1.01325 bar
multiply by 1.0000

8.2 Basic Implementation - the Program ZGERG-88

The Basic program ZGERG-88 has primarily been written for use with IBM-compatible personal computers. Programming was mainly carried out on an Olivetti M24SP operating under MS-DOS 3.10 revision 3.13; the programming language was GW-BASIC 2.01 revision 1.02. The resulting source code, designated ZGERG-88.AEH, has been converted to executable code (approximately 79 kbyte) using the Microsoft Quickbasic compiler, version 2.02 revision 1.20. A complete listing of the source code is given as Table 8.5. The program incorporates the code described previously (1) for the Master GERG-88 Virial Equation, but does not require the presence of any associated data files as was previously the case.

Once ZGERG-88.EXE is loaded, all input information is solicited in a suitably user-friendly manner. Assuming that the user takes the "Standard Equation" option rather than the "Master Equation" option at the start, then all he has to provide is the temperature (with options of °C, °F, K or °R), the pressure (bar, MPa, atm, psia or psig), calorific value (MJ m^{-3} or Btu ft^{-3} for a variety of reference conditions), relative density (for either of two reference conditions) and carbon dioxide content (by mole fraction or mole percent). Conversions to the units and reference conditions used internally by the program are carried out in accordance with the appropriate conversion factors from those given in Tables 8.2 to 8.4.

There are several built-in error traps which, without crashing the program, identify faulty input, such as out-of-range selections for temperature, pressure, calorific value or relative density. Each error message may be either accepted or - at the user's own risk - ignored in order to extrapolate beyond the strict limits of applicability of the GERG equation. There is no facility in this implementation to carry out more than a single-point calculation with a single set of instructions, but a variety of continuation options, such as changing the pressure along an isotherm, changing the temperature along an isobar, and several others, are available.

Some example calculations are given in sub-section 8.4.

8.3 Fortran Implementation - the Subroutine SGERG

The Fortran implementation of the GERG-88 Virial Equation is essentially unchanged both in format and content from that described in the GERG Technical Monograph TM2 (1). Thus, the executable program GERG88.EXE, which is suitable for use on IBM-compatible personal computers, incorporates the Fortran 77 subprograms SGERG.FOR and MGERG.FOR. A complete listing of SGERG.FOR, constituting validated source code for the Standard (or Simplified) GERG Equation, is given as Table 8.6.* A listing of MGERG.FOR (for the Master GERG Equation) was given in ref.1. The intention is that users may either use the

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* The version of SGERG.FOR listed as Table 8.6 includes coding for the "alternative input" procedures discussed in sub-sections 5.5 and 7.4; however, the executable code GERG88.EXE does not support these procedures.

program GERG88.EXE as a stand-alone implementation, or alternatively may incorporate SGERG.FOR (and/or MGERG.FOR) into applications packages of their own.

Once GERG88.EXE is loaded, the necessary input data are requested in a user-friendly manner; the first few introductory screens of information which precede these requests are shown in Table 8.7. Note, however, that there is no provision for the input of data in units other than °C (temperature), bar (pressure) and MJ m^{-3} (calorific value), or at reference conditions other than those given in Table 1.1 ($t_1=25°C$, $t_2=0°C$) which apply in Germany and several other countries in continental Europe (see Table 8.1).

Some example calculations are given in sub-section 8.4.

8.4 Example Calculations

In this sub-section sample calculations are given for three typical gases, in each case for a set of five typical pressure/temperature conditions. Both the Basic and Fortran implementations are applied to natural gas N75 (Ekofisk type) from the GERG databank (10). In addition, calculations are given using the Basic implementation for N88 (Leman Bank gas), and using the Fortran implementation for N74 (which contains hydrogen from coke-oven gas admixture).

Input data are directly solicited during execution of both programs. Tables 8.8.1 and 8.8.2 illustrate the output formats of the respective programs. The numerical results of these examples may also provide a convenient check for the user of the correctness of any other implementation that may be used.

8.5 Program Availability

Both the Basic program ZGERG-88.EXE and the Fortran program GERG88.EXE are readily available upon request from either of the present authors as executable code. The Fortran subprograms SGERG.FOR and MGERG.FOR are also available. Exceptionally, the Basic source code ZGERG-88.AEH may be provided, but the complete Fortran source code GERG88 is not available.

The preferred medium on which program copies will be supplied is double-sided/double-density (360 kbyte) 5¼" flexible diskettes. Legal copies of the programs may only be obtained by contacting, in the first instance, either of the present authors. Their current addresses are -

Dr A.E.Humphreys

British Gas plc
Research and Technology Division
London Research Station
2 Michael Road
London sw6 2ad
England

and Dr M.Jaeschke

Ruhrgas A.G.
Applied Physics Section
Halterner Strasse 125
D-4270 Dorsten 21
Federal Republic of Germany.

Despite the willingness of GERG to make copies of the programs easily available, it should be recognised and respected that the copyrights of ZGERG-88.EXE, GERG88.EXE, MGERG.FOR and SGERG.FOR remain the property of the Groupe Européen de Recherches Gazières.

Table 8.5 Program Listing ZGERG-88.AEH

```
1000 REM GERG-88 equation
1005 ON ERROR GOTO 9000
1010 REM the original GERG-85 program was written by Pat Cowan
1020 REM extensive modifications and additions have been made since by AEH
1030 REM with contributions to GERG-87 by Sarah Kimpton
1040 REM simplified equation parts written entirely by AEH
1050 REM last update by AEH 20 Feb 91 correct minor logic fault in sgerg
1051 REM                              rho(air)=1.292923 not 1.292918
1052 REM                              mw(N2)=28.0135 not 28.0134
1060 SCREEN 0
1070 WIDTH 80
1080 KEY OFF
1090 DEFDBL B-H,M-Z
1100 DIM B(37),C(62),D(20),Z(20),X(111),Y(186)
1110 DIM YN(20),RD(20),RHO(20),DB(20),HS(20),BC(20)
1120 DIM BCH(20),DCH(20),HCH(20),MCH(20),YCH(20)
1130 R=.0831451
1140 T0=273.15
1150 OP$=" "
1160 CLS
1170 COLOR 5,0
1175 PRINT TAB(60) "program version date"
1176 PRINT TAB(60) "           20 Feb 91"
1177 COLOR 3,0
1180 PRINT:PRINT:PRINT
1190 PRINT "GERG VIRIAL EQUATION"
1200 PRINT "--------------------"
1210 PRINT
1220 PRINT "COPYRIGHT - Groupe Europeen de Recherches Gazieres, 1991
1230 PRINT
1240 PRINT "Legal copies of this program may only be obtained from"
1250 PRINT
1260 PRINT "   A E Humphreys     British Gas plc           (United Kingdom)"
1270 PRINT "   P van Caneghem    Distrigaz S A             (Belgium)"
1280 PRINT "   R Janssen         n v Nederlandse Gasunie   (Netherlands)"
1290 PRINT "   S Audibert        Gaz de France             (France)"
1300 PRINT "   M Jaeschke        Ruhrgas A G               (F R Germany)"
1310 PRINT "   Q Pellei          S.N.A.M. SpA              (Italy)"
1320 PRINT
1330 PRINT "at the addresses given in GERG Technical Monographs Number 2 (1988)"
1335 PRINT "and Number 5 (1991). Please report any program faults etc to AEH."
```

```
1340 PRINT:PRINT
1350 INPUT "                     .... press RETURN to begin .... ",IN$
1360 CLS
1370 COLOR 6,0
1380 PRINT:PRINT
1390 PRINT "Calculation of Compressibility Factor and Density for Natural Gases"
1400 PRINT "-------------------------------------------------------------------"
1410 PRINT
1420 PRINT "This program calculates  compressibility factors and  densities for"
1430 PRINT "natural gases of  known  molar composition  in accordance  with the"
1440 PRINT "GERG-88   equation ,  developed   primarily  by   J A Schouten  and"
1450 PRINT "J P J Michels of the van der Waals Laboratory of the  University of"
1460 PRINT "Amsterdam  under contract  to the  Groupe  Europeen  de  Recherches"
1470 PRINT "Gazieres."
1480 PRINT
1490 PRINT "The  expected accuracy is  +/- 0.1 percent  within the  temperature"
1500 PRINT "range  -8 to 62 deg C  and the  pressure  range  0 to 120 bar,  but"
1510 PRINT "these ranges may, with caution, be stretched."
1520 PRINT
1530 PRINT "There are also restrictions on the  range of compositions for which"
1540 PRINT "the equation  should be expected  to achieve the  target accuracy -"
1550 PRINT "these will be  flagged  if necessary  during program  execution, as"
1560 PRINT "will out-of-range inputs for temperature and pressure."
1570 PRINT
1580 INPUT "Press return key to continue ",IN$
1590 CLS
1600 PRINT:PRINT
1610 PRINT "If a complete  molar composition analysis is not available, you may"
1620 PRINT "instead calculate  compressibility factors  using as  input  a"
1630 PRINT "simplified analysis  comprising calorific value,  specific gravity"
1640 PRINT "and  carbon dioxide  content.  The  resultant  values  will  be  of"
1650 PRINT "similar accuracy  to those  obtained  from a full  molar  analysis."
1660 PRINT "(Note, however, that gases containing  hydrogen or  carbon monoxide"
1670 PRINT "are  not  permissible  in  this  implementation  of the  simplified"
1675 PRINT "analysis GERG virial equation.)"
1676 PRINT
1677 PRINT "The molar composition input version is known as the  MASTER GERG-88"
1678 PRINT "equation, and the simplified input version as the  STANDARD GERG-88"
1679 PRINT "equation."
1680 PRINT
1690 PRINT
1700 INPUT "Select master equation or standard equation input (m/s) ",A$
1710 IF A$="M" OR A$="m" OR A$="S" OR A$="s" THEN 1770
```

```
1720 GOTO 1690
1730 IF A$="S" OR A$="s" THEN 1760
1740 A$="S"
1750 GOTO 1770
1760 A$="M"
1770 PRINT
1780 S=1
1790 IF OP$="H" OR OP$="h" THEN 1810
1800 GOTO 1870
1810 IF F$="F" OR F$="f" THEN 1850
1820 IF F$="P" OR F$="p" THEN 1830
1830 F$="F"
1840 GOTO 1880
1850 F$="P"
1860 GOTO 1920
1870 INPUT "Select mole fraction or mole percent composition entry (f/p) ",F$
1880 MOL$=" fraction "
1890 IF F$="F" OR F$="f" THEN 1940
1900 IF F$="P" OR F$="p" THEN 1920
1910 GOTO 1870
1920 MOL$=" percent "
1930 S=100
1940 CLS
1950 IF A$="S" OR A$="s" THEN 4670
1960 PRINT "Select input unit to be used for temperature -"
1970 PRINT "   - you may choose by letter from (k) kelvin"
1980 PRINT "                                   (c) deg Celsius (centigrade)"
1990 PRINT "                                   (f) deg Fahrenheit"
2000 INPUT "                                   (r) deg Rankine   -- now -- ",T$
2010 IF T$="k" OR T$="K" THEN 2070
2020 IF T$="c" OR T$="C" THEN 2090
2030 IF T$="f" OR T$="F" THEN 2110
2040 IF T$="r" OR T$="R" THEN 2130
2050 PRINT
2060 GOTO 1960
2070 T$="kelvin"
2080 GOTO 2140
2090 T$="deg C"
2100 GOTO 2140
2110 T$="deg F"
2120 GOTO 2140
2130 T$="deg R"
2140 PRINT
```

```
2150 PRINT "Select input unit to be used for pressure -"
2160 PRINT "   - you may choose by letter from (m) megapascal"
2170 PRINT "                                   (b) bar"
2180 PRINT "                                   (s) standard atm"
2190 PRINT "                                   (a) psi absolute"
2200 INPUT "                                   (g) psi gauge     -- now -- ",P$
2210 IF P$="m" OR P$="M" THEN 2280
2220 IF P$="b" OR P$="B" THEN 2300
2230 IF P$="s" OR P$="S" THEN 2320
2240 IF P$="a" OR P$="A" THEN 2340
2250 IF P$="g" OR P$="G" THEN 2360
2260 PRINT
2270 GOTO 2140
2280 P$="MPa"
2290 GOTO 2370
2300 P$="bar"
2310 GOTO 2370
2320 P$="atm"
2330 GOTO 2370
2340 P$="psia"
2350 GOTO 2370
2360 P$="psig"
2370 CLS
2380 IF A$="S" OR A$="s" THEN 2930
2390 PRINT
2400 IF OP$="D" OR OP$="d" THEN 2930
2410 PRINT
2420 IF A$="S" OR A$="s" THEN 4790
2430 PRINT "Now enter the mole";MOL$;"of each component - "
2440 PRINT " (note - zeroes may be entered simply by pressing the return key)"
2450 PRINT
2460 INPUT "01 Methane         = ",X1
2470 IF X1/S>1 THEN 2490
2480 IF X1/S>=.5 THEN 2500
2490 GOSUB 4150
2500 INPUT "02 Nitrogen        = ",X2
2510 IF X2/S<=.5 THEN 2530
2520 GOSUB 4150
2530 INPUT "03 Carbon Dioxide  = ",X3
2540 IF X3/S<=.3 THEN 2560
2550 GOSUB 4150
2560 INPUT "04 Ethane          = ",X4
2570 IF X4/S<=.2 THEN 2590
```

```
2580 GOSUB 4150
2590 INPUT "05 Hydrogen         = ",X5
2600 IF X5/S<=.1 THEN 2620
2610 GOSUB 4150
2620 INPUT "06 Propane          = ",X6
2630 IF X6/S<=.05 THEN 2650
2640 GOSUB 4150
2650 INPUT "07 Carbon Monoxide = ",X7
2660 IF X7/S<=.03 THEN 2680
2670 GOSUB 4150
2680 INPUT "08 Butanes          = ",X8
2690 IF X8/S<=.015 THEN 2710
2700 GOSUB 4150
2710 INPUT "09 Helium           = ",X9
2720 IF X9/S<=.005 THEN 2740
2730 GOSUB 4150
2740 INPUT "10 Pentanes         = ",X10
2750 INPUT "11 Hexanes          = ",X11
2760 INPUT "12 Heptanes         = ",X12
2770 INPUT "13 Octanes-plus     = ",X13
2780 IF (X10+X11+X12+X13)/S<.005 THEN 2820
2800 GOSUB 4150
2810 REM test to ensure that 1.0001 > X > 0.9999
2820 X=(X1+X2+X3+X4+X5+X6+X7+X8+X9+X10+X11+X12+X13)/S
2830 IF X>=.9999 THEN 2850
2840 GOSUB 4380
2850 IF X<=1.0001 THEN 2880
2870 GOSUB 4380
2880 PRINT
2890 IF OP$="E" OR OP$="e" THEN 3340
2895 IF OP$="I" OR OP$="i" OR OP$="J" OR OP$="j" OR OP$="K" OR OP$="k" THEN 2910
2900 IF OP$<>" " THEN 2940
2910 PRINT "Getting GERG coefficients ..."
2920 GOSUB 4560
2930 PRINT
2940 PRINT "Enter the pressure in ";P$;
2950 INPUT " ",P
2960 IF P$="MPa" THEN 3010
2970 IF P$="bar" THEN 3080
2980 IF P$="atm" THEN 3030
2990 IF P$="psia" THEN 3050
3000 IF P$="psig" THEN 3070
3010 P=P*10
```

```
3020 GOTO 3080
3030 P=P*1.01325
3040 GOTO 3080
3050 P=P/14.5038
3060 GOTO 3080
3070 P=(P+14.6959)/14.5038
3080 IF P>0 THEN 3100
3090 GOSUB 4280
3100 IF P<=120 THEN 3140
3110 GOSUB 4280
3120 GOTO 3140
3130 PRINT
3140 IF OP$="A" OR OP$="a" THEN 3670
3150 PRINT "Enter the temperature in ";T$;
3160 INPUT " ",T
3170 IF T$="kelvin" THEN 3210
3180 IF T$="deg C" THEN 3260
3190 IF T$="deg F" THEN 3230
3200 IF T$="deg R" THEN 3250
3210 T=T-273.15
3220 GOTO 3260
3230 T=(T-32)/1.8
3240 GOTO 3260
3250 T=(T/1.8)-273.15
3260 IF T>=-8 THEN 3280
3270 GOSUB 4330
3280 IF T<=62 THEN 3300
3290 GOSUB 4330
3300 T=T+273.15
3314 IF A$="M" OR A$="m" THEN 3330
3315 IF OP$="F" OR OP$="f" THEN 4800
3320 GOTO 4790
3330 REM calculate virial coefficients for the gas mixture
3340 FOR I=1 TO 37
3350 B(I)=X(I)+X(37+I)*T+X(74+I)*T^2
3360 NEXT I
3370 FOR J=1 TO 62
3380 C(J)=Y(J)+Y(62+J)*T+Y(124+J)*T^2
3390 NEXT J
3400 B=0
3410 C=0
3420 B=X1^2*B(1)+X2^2*B(13)+X3^2*B(20)+X4^2*B(26)+X5^2*B(31)+X6^2*B(32)
3430 B=B+X7^2*B(34)+X8^2*B(35)+X9^2*B(36)+X10^2*B(37)
```

```
3440 B=B+2*X1*(X2*B(2)+X3*B(3)+X4*B(4)+X5*B(5)+X6*B(6)+X7*B(7)+X8*B(8))
3450 B=B+2*X1*(X10*B(9)+X11*B(10)+X12*B(11)+X13*B(12))
3460 B=B+2*X2*(X3*B(14)+X4*B(15)+X5*B(16)+X6*B(17)+X7*B(18)+X8*B(19))
3470 B=B+2*X3*(X4*B(21)+X5*B(22)+X6*B(23)+X8*B(24)+X10*B(25))
3480 B=B+2*X4*(X5*B(27)+X6*B(28)+X8*B(29)+X10*B(30))+2*X6*X8*B(33)
3490 B=B/(S*X)^2
3500 C=X1^3*C(1)+X2^3*C(28)+X3^3*C(45)+X4^3*C(54)+X5^3*C(59)+X6^3*C(60)
3510 C=C+X7^3*C(61)+X9^3*C(62)
3520 C=C+3*X1^2*(X2*C(2)+X3*C(3)+X4*C(4)+X5*C(5)+X6*C(6)+X7*C(7)+X8*C(8))
3530 C=C+3*X1^2*(X10*C(9)+X11*C(10)+X12*C(11))
3540 C=C+3*X2^2*(X1*C(12)+X3*C(29)+X4*C(30)+X5*C(31)+X6*C(32)+X7*C(33)+X8*C(34))
3550 C=C+3*X3^2*(X1*C(17)+X2*C(35)+X4*C(46)+X5*C(47)+X6*C(48))
3560 C=C+3*X4^2*(X1*C(20)+X2*C(39)+X3*C(49)+X5*C(55)+X6*C(56))
3570 C=C+3*X5^2*(X1*C(25)+X2*C(42)+X3*C(52)+X4*C(57))
3580 C=C+3*X6^2*(X1*C(26)+X2*C(43)+X3*C(53)+X4*C(58))+3*X7^2*(X1*C(27)+X2*C(44))
3590 C=C+6*X1*X2*(X3*C(13)+X4*C(14)+X5*C(15)+X6*C(16))
3600 C=C+6*X1*X3*(X4*C(18)+X6*C(19))
3610 C=C+6*X1*X4*(X5*C(21)+X6*C(22)+X8*C(23)+X10*C(24))
3620 C=C+6*X2*X3*(X4*C(36)+X5*C(37)+X6*C(38))
3630 C=C+6*X2*X4*(X5*C(40)+X6*C(41))
3640 C=C+6*X3*X4*(X5*C(50)+X6*C(51))
3650 C=C/(S*X)^3
3660 REM iterations to find Z
3670 M=1
3680 Z(0)=1
3690 D(M)=P/(Z(M-1)*R*T)
3700 Z(M)=1+B*D(M)+C*(D(M))^2
3710 IF ABS(Z(M-1)-Z(M))<.000001 THEN 3750
3720 M=M+1
3730 GOTO 3690
3740 REM the following section prints out the calculation results
3750 CLS
3760 PRINT:PRINT
3770 PRINT "The Compressibility Factor is";
3780 PRINT USING "\        \#.#####";" Z(T,p) = ";Z(M)
3790 PRINT
3800 PRINT "                              ";
3810 PRINT USING "\         \###.##";"    T/K = ";T
3820 PRINT "                              ";
3830 PRINT USING "\         \###.#####";"  p/bar = ";P
3840 PRINT
3850 PRINT "         The Molar Density is";
3860 PRINT USING "\        \#.#####";" D(T,p) =  ";D(M);" mol/L"
```

```
3870 PRINT
3880 PRINT
3890 RESTORE
3900 PRINT "Select by letter from the following continuation options -"
3910 PRINT
3920 PRINT "   (a) Retain gas analysis - change pressure along an isotherm"
3930 PRINT "   (b) Retain gas analysis - change temperature along an isobar"
3940 PRINT "   (c) Retain gas analysis - change pressure and temperature values"
3950 PRINT "   (d) Retain gas analysis - change pressure and temperature units"
3960 PRINT "   (e) Change gas analysis - retain pressure and temperature values"
3970 PRINT "   (f) Change gas analysis - change pressure and temperature values"
3980 PRINT "   (g) Change gas analysis - change pressure and temperature units"
3990 PRINT "   (h) Switch to/from mole percent from/to mole fraction input"
4000 PRINT "   (i) Switch between master and standard equation input"
4010 PRINT "   (j) Return to start of program"
4015 PRINT "   (k) Inspect ranges of validity and trace component assignments"
4020 INPUT "   (q) Quit program                                  -- now -- ",OP$
4030 CLS
4040 IF OP$="A" OR OP$="a" OR OP$="C" OR OP$="c" THEN 2930
4050 IF OP$="B" OR OP$="b" THEN 3130
4060 IF OP$="D" OR OP$="d" OR OP$="G" OR OP$="g" THEN 1940
4070 IF OP$="E" OR OP$="e" OR OP$="F" OR OP$="f" THEN 2410
4080 IF OP$="H" OR OP$="h" THEN 1770
4090 IF OP$="I" OR OP$="i" THEN 1730
4100 IF OP$="J" OR OP$="j" THEN 1360
4105 IF OP$="K" OR OP$="k" THEN 7010
4110 IF OP$="Q" OR OP$="q" THEN 4130
4120 GOTO 3900
4130 SYSTEM
4140 REM warnings that T, p, CV, SG and X values are outside validity limits
4150 PRINT
4160 COLOR 2,0
4170 PRINT "WARNING - COMPOSITION outside range of validity"
4180 L=1
4190 INPUT "Do you wish to ignore this warning (y/n)";W$
4200 COLOR 6,0
4210 IF W$="Y" OR W$="y" THEN 4260
4220 PRINT
4240 ON L GOTO 2430,2940,3140,4800,4800
4260 PRINT
4270 RETURN
4280 PRINT
4290 COLOR 2,0
```

```
4300 PRINT "WARNING - PRESSURE outside range of validity"
4310 L=2
4320 GOTO 4190
4330 PRINT
4340 COLOR 2,0
4350 PRINT "WARNING - TEMPERATURE outside range of validity"
4360 L=3
4370 GOTO 4190
4380 PRINT
4390 COLOR 2,0
4400 PRINT "WARNING - MOLE FRACTION SUM";X;"is not unity within +/- 0.0001"
4410 PRINT "If you choose to ignore this, all compositions will be normalised"
4420 L=1
4430 GOTO 4190
4440 PRINT
4450 COLOR 2,0
4460 PRINT "WARNING - CALORIFIC VALUE outside range of validity"
4470 L=4
4480 GOTO 4190
4490 PRINT
4500 COLOR 2,0
4510 PRINT "WARNING - SPECIFIC GRAVITY outside range of validity"
4520 L=5
4530 GOTO 4190
4540 REM this subroutine inputs the GERG-88 coefficients from data statements
4560 FOR I=1 TO 111
4570 READ X(I)
4590 NEXT I
4620 FOR I=1 TO 186
4630 READ Y(I)
4640 NEXT I
4660 RETURN
4670 REM simplified analysis section
4680 PRINT
4681 PRINT "Select input units to be used for calorific value -"
4682 PRINT "   - you may choose by letter from (b) btu(IT)/ft^3"
4683 INPUT "                                   (m) MJ/m^3        -- now -- ",Q$
4685 IF Q$="B" OR Q$="b" OR Q$="M" OR Q$="m" THEN 4690
4687 GOTO 4680
4690 PRINT
4691 PRINT "Select the reference conditions at which your dry-gas calorific"
4700 PRINT "value is defined - you may choose by letter from"
4710 PRINT
```

```
4711 IF Q$="M" OR Q$="m" THEN 4720
4712 PRINT "(a) Combustion at 60 deg F + Metering at 60 deg F + 1.01592 bar ";
4713 PRINT "( U.K )"
4714 U$="btu(IT)/ft^3"
4715 GOTO 4760
4720 PRINT "(a) Combustion at 15 deg C + Metering at 15 deg C + 1.01325 bar ";
4721 PRINT "( U.K, U.S,"
4722 PRINT TAB(67)"Aus )"
4723 U$="MJ/m^3"
4725 U=1
4730 PRINT "(b) Combustion at 25 deg C + Metering at  0 deg C + 1.01325 bar ";
4731 PRINT "( FRG, It,"
4732 PRINT TAB(67)"Bel, Ned )"
4750 PRINT "(c) Combustion at  0 deg C + Metering at  0 deg C + 1.01325 bar ";
4751 PRINT "( Fra, Jap )"
4755 GOTO 4765
4760 PRINT "(d) Combustion at 60 deg F + Metering at 60 deg F + 1.01560 bar ";
4761 PRINT "( U.S )"
4765 INPUT "                                                     -- now -- ",CV$
4770 CLS
4780 GOTO 1960
4790 IF OP$="B" OR OP$="b" OR OP$="C" OR OP$="c" THEN 5100
4795 IF OP$="F" OR OP$="f" THEN 2930
4800 PRINT
4805 PRINT "Enter the dry-gas calorific value in ";U$;
4806 INPUT " ",CV
4820 INPUT "Enter the dry-gas specific gravity ",SG
4860 IF CV$="A" OR CV$="a" THEN 4920
4870 IF CV$="B" OR CV$="b" THEN 5000
4880 IF CV$="C" OR CV$="c" THEN 4950
4890 IF CV$="D" OR CV$="d" THEN 4972
4900 GOTO 4680
4910 REM note 8/6/89 - conversion factor for sg may be better as 1.0003
4911 REM value of 1.0002+ is for ch4-rich gases - 1.0003+ for eg ekofisk
4920 IF Q$="M" OR Q$="m" THEN 4925
4922 U=26.86
4925 CV=1.0543*CV/U
4930 SG=1.0002*SG
4940 GOTO 5000
4950 CV=.9974*CV
4960 GOTO 5000
4972 U=26.85
4975 CV=1.0543*CV/U
```

```
4980 SG=1.0002*SG
4990 REM check cv sg and co2 for out of range
5000 IF CV>=19 THEN 5020
5010 GOSUB 4440
5020 IF CV<=48 THEN 5040
5030 GOSUB 4440
5040 IF SG>=.55 THEN 5060
5050 GOSUB 4490
5060 IF SG<=.9 THEN 5072
5070 GOSUB 4490
5072 PRINT "Enter the mole";MOL$;
5073 INPUT "of carbon dioxide ",Y3
5075 Y3=Y3/S
5080 IF Y3<=.3 THEN 5100
5090 GOSUB 4150
5100 IF OP$="B" OR OP$="b" THEN 5120
5102 TA=TO
5110 GOSUB 5680
5120 C222=(.78498/100)-((.39895*T)/10000)+((.61187*T*T)/10000000#)
5130 C333=(.20513/100)+((.34888*T)/10000)-((.83703*T*T)/10000000#)
5140 C223=(.552066/100)-((.168609*T)/10000)+((.157169*T*T)/10000000#)
5150 C233=(.358783/100)+((.806674*T)/100000!)-((.325798*T*T)/10000000#)
5160 C0=-.302488+((.195861*T)/100)-((.316302*T*T)/100000!)
5170 C1=(.646422/1000)-((.422876*T)/100000!)+((.688157*T*T)/10^8)
5180 C2=-(.332805/1000000!)+((.22316*T)/10^8)-((.367713*T*T)/10^11)
5190 IF OP$="B" OR OP$="b" THEN 5490
5192 VOL=R*T0/1.01325
5200 HCH(1)=1000
5210 DCH(1)=10
5220 BC(1)=-.065
5230 J=1
5240 I=1
5250 RHO(1)=1/(VOL+BC(1))
5260 MCH(I)=-2.709328+(.0210622*HCH(I))
5270 YCH(I)=CV/(HCH(I)*RHO(J))
5280 YN(I)=1-YCH(I)-Y3
5290 RD(I)=RHO(J)*((YCH(I)*MCH(I))+(YN(I)*28.0135)+(Y3*44.01))/1.292923
5300 IF ABS(RD(I)-SG)<.00001 THEN 5360
5310 IF I=1 THEN 5330
5320 DCH(I)=-HCH(I)*(RD(I)-SG)
5330 HCH(I+1)=HCH(I)+DCH(I)
5340 I=I+1
5350 GOTO 5260
```

```
5360 HCH=HCH(I)
5370 YCH=YCH(I)
5380 YN=YN(I)
5390 BCH(J)=B0+(B1*HCH)+(B2*HCH*HCH)
5400 B12=(.72+(1.875/100000!)*(320-T0)*(320-T0))*(BCH(J)+B22)/2
5410 B13=-.865*(BCH(J)*B33)^(1/2)
5420 BC(J+1)=(YCH*YCH*BCH(J))+(YN*YN*B22)+(Y3*Y3*B33)
5430 BC(J+1)=BC(J+1)+(2*YCH*YN*B12)+(2*YCH*Y3*B13)+(2*YN*Y3*B23)
5440 RHO(J+1)=1/(VOL+BC(J+1))
5450 HS(J)=YCH*HCH*RHO(J+1)
5460 IF ABS(HS(J)-CV)<.00001 THEN 5490
5470 J=J+1
5480 GOTO 5260
5490 TA=T
5500 GOSUB 5680
5510 BCH=B0+(B1*HCH)+(B2*HCH*HCH)
5520 B12=(.72+(1.875/100000!)*(320-T)*(320-T))*(BCH+B22)/2
5530 B13=-.865*(BCH*B33)^(1/2)
5540 B=(YCH*YCH*BCH)+(YN*YN*B22)+(Y3*Y3*B33)
5550 B=B+(2*YCH*YN*B12)+(2*YCH*Y3*B13)+(2*YN*Y3*B23)
5560 CCH=C0+(C1*HCH)+(C2*HCH*HCH)
5570 C112=(.92+.0013*(T-270))*(CCH*CCH*C222)^(1/3)
5580 C122=(.92+.0013*(T-270))*(CCH*C222*C222)^(1/3)
5590 C113=.92*(CCH*CCH*C333)^(1/3)
5600 C133=.92*(CCH*C333*C333)^(1/3)
5610 C123=1.1*(CCH*C222*C333)^(1/3)
5620 C=(YCH*YCH*YCH*CCH)+(YN*YN*YN*C222)+(Y3*Y3*Y3*C333)
5630 C=C+(3*YCH*YCH*YN*C112)+(3*YCH*YCH*Y3*C113)
5640 C=C+(3*YCH*YN*YN*C122)+(3*YCH*Y3*Y3*C133)
5650 C=C+(3*YN*YN*Y3*C223)+(3*YN*Y3*Y3*C233)
5660 C=C+(6*YCH*YN*Y3*C123)
5670 GOTO 3670
5680 B22=-.1446+((.74091*TA)/1000)-((.91195*TA*TA)/1000000!)
5690 B33=-.86834+((.40376*TA)/100)-((.51657*TA*TA)/100000!)
5700 B23=-.339693+((.161176*TA)/100)-((.204429*TA*TA)/100000!)
5710 B0=-.425468+((.2865*TA)/100)-((.462073*TA*TA)/100000!)
5720 B1=(.877118/1000)-((.556281*TA)/100000!)+((.88151*TA*TA)/10^8)
5730 B2=-(.824747/1000000!)+((.431436*TA)/10^8)-((.608319*TA*TA)/10^11)
5740 RETURN
7000 REM range of validity and minor component advice
7010 CLS
7020 PRINT "            Range of Validity     Trace Components to be included"
7030 PRINT "            -----------------     -------------------------------
```

```
7040 PRINT
7050 PRINT "Molar analysis - mole percent"
7060 PRINT "  Methane         50 to 100       None"
7070 PRINT "  Nitrogen         0     50       Oxygen Argon"
7080 PRINT "  Carbon Dioxide   0     30       Ethylene Acetylene Water H2S"
7090 PRINT "  Ethane           0     20       None"
7100 PRINT "  Hydrogen         0     10       None"
7110 PRINT "  Propane          0      5       Propylene Propadiene"
7120 PRINT "  Carbon Monoxide  0      3       None"
7130 PRINT "  Butanes          0      1.5     Butenes Butadienes"
7140 PRINT "  Helium           0      0.5     None"
7150 PRINT "  Pentanes         0      0.5     Benzene Pentenes Cyclopentane"
7160 PRINT "  Hexanes          0      0.1     Ethylbenzene Xylenes Cyclohexane"
7170 PRINT "  Heptanes         0      0.1     Toluene Methylcyclohexane"
7180 PRINT "  Octanes-plus     0      0.1     All higher hydrocarbons"
7190 PRINT
7200 PRINT "Standard (simplified) analysis         Both versions"
7210 PRINT "  Calorific Value    19 to 48 MJ/m^3     Temperature -8 to 62 deg C"
7220 PRINT "  Specific Gravity .55   .90             Pressure     0    120 bar"
7225 PRINT "  Carbon Dioxide      0    30 percent"
7230 PRINT
7240 INPUT "Press return key to use program ",GO$
7245 CLS
7247 IF GO$<>"" THEN 4130
7250 GOTO 1690
8001 DATA -.298675E+0
8002 DATA -.213606E+0
8003 DATA -.356120E+0
8004 DATA -.499337E+0
8005 DATA -.328913E-1
8006 DATA -.554110E+0
8007 DATA -.687290E-1
8008 DATA -.138708E+1
8009 DATA -.771367E+0
8010 DATA -.775140E+0
8011 DATA -.209989E+1
8012 DATA -.239409E+1
8013 DATA -.144600E+0
8014 DATA -.339693E+0
8015 DATA -.263553E+0
8016 DATA +.184506E-1
8017 DATA -.431268E+0
8018 DATA -.122189E+0
```

```
8019 DATA +.907220E-1
8020 DATA -.868340E+0
8021 DATA -.112000E+1
8022 DATA -.757226E-1
8023 DATA -.126372E+1
8024 DATA -.188108E+1
8025 DATA -.202135E+1
8026 DATA -.107320E+1
8027 DATA -.174834E+0
8028 DATA -.142020E+1
8029 DATA -.283644E+1
8030 DATA -.331426E+1
8031 DATA -.110596E-2
8032 DATA -.259920E+1
8033 DATA -.435393E+1
8034 DATA -.130820E+0
8035 DATA -.708016E+1
8036 DATA +.206740E-1
8037 DATA -.111580E+2
8038 DATA +.133425E-2
8039 DATA +.104585E-2
8040 DATA +.144963E-2
8041 DATA +.205755E-2
8042 DATA +.158947E-3
8043 DATA +.185897E-2
8044 DATA -.239381E-5
8045 DATA +.689575E-2
8046 DATA +.143827E-2
8047 DATA +.184050E-2
8048 DATA +.979707E-2
8049 DATA +.112199E-1
8050 DATA +.740910E-3
8051 DATA +.161176E-2
8052 DATA +.106233E-2
8053 DATA -.111895E-3
8054 DATA +.184597E-2
8055 DATA +.521240E-3
8056 DATA -.198016E-2
8057 DATA +.403760E-2
8058 DATA +.576913E-2
8059 DATA +.356052E-3
8060 DATA +.584661E-2
8061 DATA +.926431E-2
8062 DATA +.954081E-2
8063 DATA +.464810E-2
8064 DATA +.103728E-2
8065 DATA +.575230E-2
8066 DATA +.136800E-1
8067 DATA +.152019E-1
8068 DATA +.813385E-4
8069 DATA +.119650E-1
8070 DATA +.213786E-1
8071 DATA +.602540E-3
8072 DATA +.363100E-1
8073 DATA -.513060E-4
8074 DATA +.535740E-1
8075 DATA -.159761E-5
8076 DATA -.131159E-5
8077 DATA -.158061E-5
8078 DATA -.230786E-5
8079 DATA -.916521E-7
8080 DATA -.147793E-5
8081 DATA +.518195E-6
8082 DATA -.940171E-5
8083 DATA +.125744E-5
8084 DATA -.400000E-6
8085 DATA -.125373E-4
8086 DATA -.143976E-4
8087 DATA -.911950E-6
8088 DATA -.204429E-5
8089 DATA -.110155E-5
8090 DATA +.303122E-6
8091 DATA -.208060E-5
8092 DATA -.437181E-6
8093 DATA +.456313E-5
8094 DATA -.516570E-5
8095 DATA -.813744E-5
8096 DATA -.357678E-6
8097 DATA -.747500E-5
8098 DATA -.124525E-4
8099 DATA -.121639E-4
8100 DATA -.560520E-5
8101 DATA -.150332E-5
8102 DATA -.640000E-5
8103 DATA -.181244E-4
8104 DATA -.189007E-4
8105 DATA -.987220E-7
8106 DATA -.152910E-4
8107 DATA -.287483E-4
8108 DATA -.644300E-6
8109 DATA -.503829E-4
8110 DATA +.724000E-7
8111 DATA -.684970E-4
8201 DATA +.927260E-2
8202 DATA +.889649E-2
8203 DATA +.117576E-1
8204 DATA +.160923E-1
8205 DATA +.233159E-3
8206 DATA +.892850E-2
8207 DATA +.736748E-2
8208 DATA +.227707E+0
8209 DATA +.320344E-1
8210 DATA +.320344E-1
8211 DATA +.320344E-1
8212 DATA +.874115E-2
8213 DATA +.900338E-2
8214 DATA +.449508E-2
8215 DATA +.360589E-2
8216 DATA -.187767E-1
8217 DATA +.877002E-2
8218 DATA -.176574E-2
8219 DATA -.623055E-1
8220 DATA -.827905E-2
8221 DATA -.116095E-2
8222 DATA -.189480E+0
8223 DATA -.189480E+0
8224 DATA -.189480E+0
8225 DATA -.308914E-2
8226 DATA -.848395E-1
8227 DATA +.436399E-2
8228 DATA +.784980E-2
8229 DATA +.552066E-2
8230 DATA -.136584E-1
8231 DATA -.650954E-2
8232 DATA +.674630E-2
8233 DATA +.615912E-2
8234 DATA -.101202E+0
8235 DATA +.358783E-2
8236 DATA -.768174E-5
```

```
8237 DATA +.269108E-2
8238 DATA -.301719E-1
8239 DATA -.369750E-1
8240 DATA -.297743E-3
8241 DATA -.506529E-1
8242 DATA -.877711E-2
8243 DATA -.859670E-1
8244 DATA +.418924E-2
8245 DATA +.205130E-2
8246 DATA +.154623E+0
8247 DATA +.843475E-2
8248 DATA -.594074E-1
8249 DATA +.133240E+0
8250 DATA -.516317E-2
8251 DATA -.944235E-1
8252 DATA +.810002E-2
8253 DATA -.149820E+0
8254 DATA -.621000E-1
8255 DATA +.843800E-2
8256 DATA -.144234E+0
8257 DATA +.294870E-1
8258 DATA -.216734E+0
8259 DATA +.104711E-2
8260 DATA -.270290E+0
8261 DATA +.190870E-2
8262 DATA 0
8263 DATA -.376132E-4
8264 DATA -.410784E-4
8265 DATA -.447615E-4
8266 DATA -.638586E-4
8267 DATA +.102923E-4
8268 DATA +.190637E-4
8269 DATA -.276578E-4
8270 DATA -.139926E-2
8271 DATA -.691674E-4
8272 DATA -.691674E-4
8273 DATA -.691674E-4
8274 DATA -.443880E-4
8275 DATA -.355487E-4
8276 DATA +.530233E-6
8277 DATA -.145437E-4
8278 DATA +.142145E-3
8279 DATA -.167108E-4
8280 DATA +.597684E-4
8281 DATA +.459485E-3
8282 DATA +.121913E-3
8283 DATA +.263812E-4
8284 DATA +.139040E-2
8285 DATA +.139040E-2
8286 DATA +.139040E-2
8287 DATA +.254973E-4
8288 DATA +.605618E-3
8289 DATA -.100358E-4
8290 DATA -.398950E-4
8291 DATA -.168609E-4
8292 DATA +.106972E-3
8293 DATA +.519104E-4
8294 DATA -.365557E-5
8295 DATA -.272612E-4
8296 DATA +.723716E-3
8297 DATA +.806674E-5
8298 DATA +.385226E-4
8299 DATA -.596904E-5
8300 DATA +.222387E-3
8301 DATA +.289620E-3
8302 DATA +.168641E-4
8303 DATA +.363400E-3
8304 DATA +.639925E-4
8305 DATA +.579776E-3
8306 DATA -.126365E-4
8307 DATA +.348880E-4
8308 DATA -.965716E-3
8309 DATA -.355786E-4
8310 DATA +.430798E-3
8311 DATA -.807996E-3
8312 DATA +.579276E-4
8313 DATA +.671721E-3
8314 DATA -.484242E-4
8315 DATA +.994385E-3
8316 DATA +.508050E-3
8317 DATA -.265166E-4
8318 DATA +.101275E-2
8319 DATA -.197083E-3
8320 DATA +.143604E-2
8321 DATA -.364887E-5
8322 DATA +.171040E-2
8323 DATA +.420040E-5
8324 DATA 0
8325 DATA +.493066E-7
8326 DATA +.603723E-7
8327 DATA +.505481E-7
8328 DATA +.779273E-7
8329 DATA -.227208E-7
8330 DATA -.979363E-7
8331 DATA +.343051E-7
8332 DATA +.221564E-5
8333 DATA 0
8334 DATA 0
8335 DATA 0
8336 DATA +.696584E-7
8337 DATA +.467680E-7
8338 DATA -.152576E-7
8339 DATA +.204722E-7
8340 DATA -.221855E-6
8341 DATA -.151577E-9
8342 DATA -.123785E-6
8343 DATA -.733765E-6
8344 DATA -.239958E-6
8345 DATA -.512600E-7
8346 DATA -.238860E-5
8347 DATA -.238860E-5
8348 DATA -.238860E-5
8349 DATA -.439625E-7
8350 DATA -.954102E-6
8351 DATA +.660155E-8
8352 DATA +.611870E-7
8353 DATA +.157169E-7
8354 DATA -.179369E-6
8355 DATA -.887528E-7
8356 DATA -.234530E-7
8357 DATA +.391226E-7
8358 DATA -.121618E-5
8359 DATA -.325798E-7
8360 DATA -.817506E-7
8361 DATA +.540142E-8
8362 DATA -.350693E-6
8363 DATA -.494852E-6
8364 DATA -.330680E-7
8365 DATA -.577241E-6
```

```
8366 DATA -.107591E-6
8367 DATA -.877215E-6
8368 DATA +.136268E-7
8369 DATA -.837030E-7
8370 DATA +.156362E-5
8371 DATA +.450909E-7
8372 DATA -.691157E-6
8373 DATA +.129643E-5
8374 DATA -.105347E-6
8375 DATA -.108080E-5
8376 DATA +.745489E-7
8377 DATA -.152037E-5
8378 DATA -.885260E-6
8379 DATA +.381345E-7
8380 DATA -.163277E-5
8381 DATA +.334778E-6
8382 DATA -.221182E-5
8383 DATA +.467095E-8
8384 DATA -.250010E-5
8385 DATA -.156800E-7
8386 DATA 0
9000 PRINT
9001 PRINT "Unidentified error - program terminated ..."
9002 PRINT
9999 END
```

Table 8.6 Listing of Fortran Subroutine SGERG.FOR

```
C***********************************************************************
C   last update: 04.11.91                        H.M. Hinze / M. Jaeschke
C
C  ******************* GERG-88  VIRIAL  EQUATION  ********************
C                           SUBROUTINE  SGERG
C
C   'SGERG'      CALCULATES THE COMPRESSIBILITY OF NATURAL GASES USING
C                A SIMPLIFIED GASANALYSIS
C
C   COPYRIGHT - GROUPE EUROPEEN DE RECHERCHES GAZIERES, 1988
C                LEGAL COPIES OF THIS PROGRAM MAY ONLY BE OBTAINED FROM THE
C                MEMBERS  OF  THE  GERG  WORKING  GROUP  ON COMPRESSIBILITY
C                FACTORS  OF  NATURAL  GAS  AS  GIVEN IN THE GERG TECHNICAL
C                MONOGRAPH TM 5 (1991).
C
C                The calculations are based on  three  of  the  first  four
C                following input parameters  for the gas analysis  and  the
C                input for H2:
C                                                          (Valid ranges:)
C                -1-  X2: molar fraction N2                ( 0.0  -> 0.5 )
C                -2-  X3: molar fraction CO2               ( 0.0  -> 0.3 )
C                -3-  HS: calorific value in MJ/m^3(s.t.p.) (  19  ->  48 )
C                -4-  RM: relative mass vs. air    (s.t.p.) ( 0.55 -> 0.9 )
C                -5-  X5: molar fraction H2                ( 0.0  -> 0.1 )
C
C                *** (X2 +X3): molar fraction (N2 + CO2)   ( 0.0  -> 0.5 )
C
C                s.t.p. : metering   at T  =  0.0 C  ,  P = 1.01325 bar
C                       : combustion at T  = 25.0 C
C
C                further input parameters used are:
C
C                     P : pressure in bar                  ( 0    -> 120 )
C                     TC: temperature in deg. Celsius      (-8.15 ->61.85)
C                     N : switch                           ( 1    ->  4  )
C
C                The "switch" N indicates which of the first four parameters
C                is NOT used for the calculations. Thus, the discarded para-
C                meter must correspond with a dummy parameter in the calling
C                program. For N=1,N=2 and N=3 a CALCULATED value for respec-
C                tively X2, X3 and HS is returned.
C
C                calculated values:
C
C                     Z : compressibility factor
C                     D : molar density in mol/m**3
C
C   ****  For some compilers the SAVE option has to be set explicitly  ****
C
C   SYNTAX :     CALL SGERG(X2,X3,HS,RM,X5,P,TC,N,Z,D)
C
C                The coefficients used in this program  are conform with the
C                values of subroutine GAS682, from July 20,1988, appended to
C                report 8807, Van der Waals Laboratory, Amsterdam.
C
C                        J.P.J. Michels   &   J.A. Schouten
C                                  August 16, 1991
C
C                Values for the gas constant, molar masses, calorific values
C                and the density of air are conform with ISO/DIS 6976 (1991).
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
```

```
C
      SUBROUTINE SGERG(X2,X3,HS,RM,X5,P,TC,N,Z,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      IF(N.LT.1.OR.N.GT.4)                STOP ' ERROR IN SWITCH '
      IF(P.LT.0.0 .OR. P.GT.120.0)        STOP ' PRESSURE OUT OF RANGE'
      IF(TC.LT.-8.15 .OR. TC.GT.61.85)    STOP ' TEMPERATURE OUT OF RANGE'
      IF(N.EQ.1)CALL SGERG1(P,TC,X2,X3,X5,HS,RM,Z,D)
      IF(N.EQ.2)CALL SGERG2(P,TC,X2,X3,X5,HS,RM,Z,D)
      IF(N.EQ.3)CALL SGERG3(P,TC,X2,X3,X5,HS,RM,Z,D)
      IF(N.EQ.4)CALL SGERG4(P,TC,X2,X3,X5,HS,RM,Z,D)
      RETURN
      END
C     *************************************************************************
      SUBROUTINE  SGERG1(P,TC,Q2,Q3,Q5,QM,RM,Z,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /RBLOK/ AMOL,HS
      COMMON /XBLOK/ X1,X2,X3,X11,X12,X13,X22,X23,X33
     >               ,X5,X7,X15,X17,X25,X55,X77
      COMMON /MBLOK/ GM1R0,GM1R1,GM2,GM3,GM5,GM7,FA,FB,RL,TO,H5,H7,R
      HS = QM
      X3 = Q3
      X5 = Q5
      IF(RM.LT.0.55 .OR. RM.GT.0.90)STOP    'REL. MASS OUT OF RANGE'
      IF(X3.LT.0.0  .OR. X3.GT.0.30)STOP    'CO2 OUT OF RANGE'
      IF(HS.LT.19.0 .OR. HS.GT.48.0)STOP    'CALOR. VALUE OUT OF RANGE'
      IF((0.55+0.97*X3-0.39*X5).GT.RM)STOP  'CONFLICTING INPUT'
      SM = RM*RL
      X7  = X5*0.0964D0
      X33 = X3*X3
      X55 = X5*X5
      X77 = X7*X7
      BEFF= -0.065D0
      H   = 1000.0D0
      AMOL= 1.0D0/(FA+BEFF)
      K   = 0
      KK = 0
 1    CALL SMBER(H,SMT1)
      IF(ABS(SM-SMT1) .GT. 1.D-6) THEN
            CALL SMBER(H+1.0D0,SMT2)
            DH= (SM-SMT1)/(SMT2-SMT1)
            H = H+DH
            KK = KK+1
               IF(KK.GT.20)STOP  ' NO CONVERGENCY  #1'
            GO TO 1
      END IF
      X11 = X1*X1
      X12 = X1*X2
      X13 = X1*X3
      X22 = X2*X2
      X23 = X2*X3
      X25 = X2*X5
      X15 = X1*X5
      X17 = X1*X7
      CALL B11BER(TO,H,B11)
      CALL BBER(TO,B11,BEFF)
      AMOL= 1.0D0/(FA+BEFF)
      HSBER = X1*H*AMOL+(X5*H5+X7*H7)*AMOL
      IF(ABS(HS-HSBER).GT.1.0D-4) THEN
            K = K+1
            IF(K.GT.20)STOP   'NO CONVERGENCY  #2'
            GO TO 1
      END IF
```

```
      IF(X2.GT.0.5)   STOP    'CALC. N2 OUT OF RANGE'
      IF(X2+X3.GT.0.5)STOP    'N2 + CO2 OUT OF RANGE'
      IF(X2.LT.-0.01 .OR. (0.55+.4*X2+0.97*X3-0.39*X5).GT.RM)
     +                STOP    'CONFLICTING RESULT FOR N2'
      Q2 = X2
      T = TC+T0
      CALL B11BER(T,H,B11)
      CALL BBER(T,B11,B)
      CALL CBER(T,H,C)
      CALL ITER(P,T,B,C,V,Z)
      D = 1.0D0/V
      END
      SUBROUTINE SMBER(H,SM)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /RBLOK/ AMOL,HS
      COMMON /XBLOK/ X1,X2,X3,X11,X12,X13,X22,X23,X33
     >              ,X5,X7,X15,X17,X25,X55,X77
      COMMON /MBLOK/ GM1R0,GM1R1,GM2,GM3,GM5,GM7,FA,FB,RL,T0,H5,H7,F
      GM1= GM1R0-GM1R1*H
      X1 = (HS-(X5*H5+X7*H7)*AMOL)/H/AMOL
      X2 = 1.0D0-X1-X3-X5-X7
      SM = (X1*GM1+X2*GM2+X3*GM3+X5*GM5+X7*GM7)*AMOL
      END
C     **************************************************************
      SUBROUTINE  SGERG2(P,TC,Q2,Q3,Q5,QM,RM,Z,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /RBLOK/ AMOL,HS
      COMMON /XBLOK/ X1,X2,X3,X11,X12,X13,X22,X23,X33
     >              ,X5,X7,X15,X17,X25,X55,X77
      COMMON /MBLOK/ GM1R0,GM1R1,GM2,GM3,GM5,GM7,FA,FB,RL,T0,H5,H7,F
      HS = QM
      X2 = Q2
      X5 = Q5
      IF(RM.LT.0.55 .OR. RM.GT.0.90)STOP    'REL. MASS OUT OF RANGE'
      IF(X2.LT.0.0  .OR. X2.GT.0.50)STOP    'N2 OUT OF RANGE'
      IF(HS.LT.19.0 .OR. HS.GT.48.0)STOP    'CALOR. VALUE OUT OF RANGE'
      IF((0.55+0.41*X2-0.39*X5).GT.RM)STOP  'CONFLICTING INPUT'
      SM = RM*RL
      X7  = X5*0.0964D0
      X22 = X2*X2
      X25 = X2*X5
      X55 = X5*X5
      X77 = X7*X7
      BEFF=-0.065D0
      H   = 1000.0D0
      AMOL= 1.0D0/(FA+BEFF)
      KK = 0
 1    CALL SMBR(H,SMT1)
      IF(ABS(SM-SMT1) .GT. 1.D-6) THEN
            CALL SMBR(H+1.0D0,SMT2)
            DH= (SM-SMT1)/(SMT2-SMT1)
            H = H+DH
            KK = KK+1
               IF(KK.GT.20)STOP   'NO CONVERGENCY  #1'
            GO TO 1
      END IF
      X11 = X1*X1
      X12 = X1*X2
      X13 = X1*X3
      X33 = X3*X3
      X23 = X2*X3
      X15 = X1*X5
      X17 = X1*X7
```

```
      K = 0
      CALL B11BER(T0,H.B11)
      CALL BBER(T0,B11,BEFF)
      AMOL= 1.0D0/(FA+BEFF)
      HSBER = X1*H*AMOL+(X5*H5+X7*H7)*AMOL
      IF(ABS(HS-HSBER).GT.1.0D-4) THEN
            K = K-1
            IF(K.GT.20)STOP   'NO CONVERGENCY  #2'
            GO TO 1
      END IF
      IF(X3.GT.0.3)   STOP    'CALC. CO2 OUT OF RANGE
      IF(X2+X3.GT.0.5)STOP    'N2 - CO2 OUT OF RANGE'
      IF(X3.LT.-0.01 .OR. (0.55+.4*X2+0.97*X3-0.39*X5).GT.RM)
     +                STOP    'CONFLICTING RESULT FOR CO2'
      Q3 = X3
      T = TC+T0
      CALL B11BER(T.H,B11)
      CALL BBER(T.B11,B)
      CALL CBER(T.H.C)
      CALL ITER(P.T,B,C.V.Z)
      D = 1.0D0/V
      END
C     **********************************
      SUBROUTINE SMBR(H.SM)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /RBLOK/ AMOL.HS
      COMMON /XBLOK/ X1,X2.X3.X11.X12.X13.X22.X23.X33
     >               .X5.X7,X15.X17.X25.X55.X77
      COMMON /MBLOK/ GM1R0.GM1R1.GM2.GM3.GM5.GM7.FA.FB.RL,T0,H5.H7,R
      GM1= GM1R0+GM1R1*H
      X1 = (HS-(X5*H5+X7*H7)*AMOL)/H/AMOL
      X3 = 1.0D0-X1-X2-X5-X7
      SM = (X1*GM1+X2*GM2+X3*GM3+X5*GM5+X7*GM7)*AMOL
      END
C     ******************************************************************
      SUBROUTINE  SGERG3(P.TC.Q2,Q3.Q5.HS.RM.Z,D)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /XBLOK/ X1,X2.X3,X11.X12.X13.X22.X23,X33
     >               ,X5,X7,X15,X17,X25.X55,X77
      COMMON /MBLOK/ GM1R0.GM1R1,GM2.GM3,GM5,GM7,FA.FB.RL,T0,H5.H7,R
      DATA BM0/.0838137D0/.BM1/-.00851644D0/.
     +     WD0/134.2153D0/.WD1/  1067.943D0/
      X2 = Q2
      X3 = Q3
      X5 = Q5
      IF(RM.LT.0.55 .OR. RM.GT.0.90)STOP    'REL. MASS OUT OF RANGE'
      IF(X2.LT.0.0  .OR. X2.GT.0.50)STOP    'N2 OUT OF RANGE'
      IF(X3.LT.0.0  .OR. X3.GT.0.30)STOP    'CO2 OUT OF RANGE'
      IF((0.55+0.41*X2+0.97*X3-0.39*X5).GT.RM)STOP  'CONFLICTING INPUT'
      IF(X2+X3 .GT. 0.50)           STOP    'N2+CO2 OUT OF RANGE'
      SM = RM*RL
      X7 = X5*0.0964D0
      X1 = 1.0D0-X2-X3-X5-X7
      X11= X1*X1
      X12= X1*X2
      X13= X1*X3
      X22= X2*X2
      X23= X2*X3
      X33= X3*X3
      X15= X1*X5
      X17= X1*X7
      X25= X2*X5
      X55= X5*X5
      X77= X7*X7
```

```
      B11= -.065D0
      K = 0
 1    CALL BBER(TO,B11,BEFF)
      AMOL= 1.0D0/(FA+BEFF)
      X2M = X2*AMOL*GM2
      X3M = X3*AMOL*GM3
      X5M = X5*AMOL*GM5
      X7M = X7*AMOL*GM7
      X1M = SM-X2M-X3M-X5M-X7M
      GM1 = X1M/(X1*AMOL)
      B11B = BM0 - BM1*GM1
      IF(ABS(B11B-B11).GT.1.0D-5) THEN
            K = K+1
            IF(K.GT.20)STOP  ' NO CONVERGENCY  #1'
            B11 = B11B
            GO TO 1
      END IF
      B11 = B11B
      DCH= GM1/(FB+B11)
      H  = WD0 - WD1*DCH
      T  = TC+T0
      CALL B11BER(T.H.B11)
      CALL BBER(T.B11.B)
      CALL CBER(T.H.C)
      CALL ITER(P.T,B.C.V.Z)
      D = 1.0D0/V
      HS=(X1*H+X5*H5+X7*H7)*AMOL
      RETURN
      END
C     ********************************************************************
      SUBROUTINE  SGERG4(P.TC.Q2.Q3.Q5.HS.RM.Z,D)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /XBLOK/ X1.X2,X3.X11.X12.X13.X22.X23,X33
     >              .X5.X7,X15,X17.X25.X55.X77
      COMMON /MBLOK/ GM1R0,GM1R1.GM2.GM3.GM5.GM7,FA.FB.RL,TO.H5.H7.R
      X2 = Q2
      X3 = Q3
      X5 = Q5
      IF(X2.LT.0.0 .OR. X2.GT.0.50)     STOP 'N2 OUT OF RANGE'
      IF(X3.LT.0.0 .OR. X3.GT.0.30)     STOP 'CO2 OUT OF RANGE'
      IF(X2+X3 .GT. 0.50)               STOP 'N2 + CO2 OUT OF RANGE'
      X7 = X5*0.0964D0
      X1 = 1.0D0-X2-X3-X5-X7
      X11= X1*X1
      X12= X1*X2
      X13= X1*X3
      X22= X2*X2
      X23= X2*X3
      X33= X3*X3
      X15= X1*X5
      X17= X1*X7
      X25= X2*X5
      X55= X5*X5
      X77= X7*X7
      H = HS/X1*22.35D0
```

```
      K = 0
 1    CALL B11BER(T0,H,B11)
      CALL BBER(T0.B11,B)
      AMOL = 1.0D0/(B+FA)
      HBER=(HS-(X5*H5+X7*H7)*AMOL)/AMOL/X1
      IF(ABS(H-HBER).GT.1.0D-1) THEN
            K = K+1
            IF(K.GT.20)STOP  ' NO CONVERGENCY  #1'
            H = HBER
            GO TO 1
      END IF
      H = HBER
      T= TC+T0
      CALL B11BER(T,H.B11)
      CALL BBER(T.B11.B)
      CALL CBER(T.H,C)
      CALL ITER(P.T,B.C.V.Z)
      D = 1.0D0/V
      RETURN
      END
C     ******************************************************************
      SUBROUTINE B11BER(T.H.B11)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /BBLOK/ BR11H0(3), BR11H1(3). BR11H2(3). BR22(3). BR23(3).
     +               BR33(3), BR15(3). BR17(3). BR55(3). BR77(3), B25
      T2=T*T
      B11=BR11H0(1) + BR11H0(2)*T - BR11H0(3)*T2
     +  +(BR11H1(1) + BR11H1(2)*T - BR11H1(3)*T2)*H
     +  +(BR11H2(1) - BR11H2(2)*T - BR11H2(3)*T2)*H*H
      END
C     ******************************************************************
      SUBROUTINE BBER(T.B11.BEFF)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /BBLOK/ BR11H0(3). BR11H1(3). BR11H2(3). BR22(3). BR23(3).
     +               BR33(3), BR15(3). BR17(3), BR55(3). BR77(3), B25
      COMMON/ZETA/   Z12.Z13,Y12.Y13,Y123.Y115
      COMMON /XBLOK/ X1,X2.X3,X11.X12.X13.X22.X23,X33
     >              ,X5,X7.X15,X17.X25,X55.X77
      T2=T*T
      B22=BR22(1) + BR22(2)*T - BR22(3)*T2
      B23=BR23(1) + BR23(2)*T + BR23(3)*T2
      B33=BR33(1) + BR33(2)*T + BR33(3)*T2
      B15=BR15(1) + BR15(2)*T - BR15(3)*T2
      B55=BR55(1) + BR55(2)*T + BR55(3)*T2
      B17=BR17(1) + BR17(2)*T + BR17(3)*T2
      B77=BR77(1) + BR77(2)*T + BR77(3)*T2
      BA13= B11*B33
      IF (BA13 .LT. 0.0) STOP  ' NO SOLUTION'
      ZZZ=Z12+(320.0D0-T)**2*1.875D-5
      BEFF =  X11*B11 + X12*ZZZ*(B11+B22) - 2.0D0*X13*Z13*DSQRT(BA13)
     >        +X22*B22 +    2.0D0*X23*B23  - X33*B33        + X55*B55
     > +2.0D0*X15*B15 -    2.0D0*X25*B25  - 2.0D0*X17*B17 + X77*B77
      END
C     ******************************************************************
```

```
      SUBROUTINE CBER(T.H.CEFF)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /CBLOK/ CR111H0(3). CR111H1(3). CR111H2(3). CR222(3).
     +               CR223(3). CR233(3),  CR333(3). CR555(3), CR117(3)
      COMMON /ZETA/  Z12.Z13,Y12.Y13.Y123.Y115
      COMMON /XBLOK/ X1.X2.X3.X11,X12.X13.X22.X23.X33
     >              ,X5.X7.X15.X17.X25,X55.X77
      T2=T*T
      C111=CR111H0(1) - CR111H0(2)*T - CR111H0(3)*T2
     +    +(CR111H1(1) - CR111H1(2)*T - CR111H1(3)*T2)*H
     +    +(CR111H2(1) - CR111H2(2)*T - CR111H2(3)*T2)*H*H
      C222 = CR222(1) -   CR222(2)*T -   CR222(3)*T2
      C223 = CR223(1) -   CR223(2)*T -   CR223(3)*T2
      C233 = CR233(1) -   CR233(2)*T -   CR233(3)*T2
      C333 = CR333(1) -   CR333(2)*T -   CR333(3)*T2
      C555 = CR555(1) -   CR555(2)*T -   CR555(3)*T2
      C117 = CR117(1) -   CR117(2)*T -   CR117(3)*T2
      CA112=C111*C111*C222
      CA113=C111*C111*C333
      CA122=C111*C222*C222
      CA123=C111*C222*C333
      CA133=C111*C333*C333
      CA115=C111*C111*C555
      IF (CA112.LT.0.0  .OR.  CA113.LT.0.0  .OR.  CA122.LT.0.0
     +     .OR.  CA123.LT.0.0  .OR.  CA133.LT.0.0 .OR. CA115. LT. 0.0)
     -     STOP  ' NO SOLUTION'
      D3REP=1.0D0/3.0D0
      CEFF=X1*X11*C111 -3.0D0*X11*X2*(CA112)**D3REP*(Y12+(T-270.0D0)
     -    *0.0013D0)
     +    + 3.0D0*X11*X3  *(CA113)**D3REP  *Y13
     +    + 3.0D0*X1*X15  *(CA115)**D3REP  *Y115
     +    + 3.0D0*X1*X22  *(CA122)**D3REP  *(Y12-(T-270.0D0)*0.0013D0)
     +     +6.0D0*X1*X2*X3*(CA123)**D3REP  *Y123
     +     +3.0D0*X1*X33  *(CA133)**D3REP  *Y13
     +     +X22*X2*C222 - 3.0D0*X22*X3*C223 - 3.0D0*X2*X33*C233
     +     +X3*X33*C333 -       X5*X55*C555 - 3.0D0*X11*X7*C117
      RETURN
      END
C     ******************************************************************
      SUBROUTINE ITER(P,T.B.C,V,Z)
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /MBLOK/ GM1R0.GM1R1,GM2.GM3,GM5.GM7.FA.FB,RL,T0,H5,H7,R
      RT = R*T
      RTP= RT/P
      V  = RTP+B
      KK = 0
  5   V  = RTP*(1.0D0+B/V+C/V**2)
      KK = KK+1
      IF (KK .GT. 20) STOP  ' NO CONVERGENCY #3'
      Z  = 1.0D0+B/V+C/V**2
      PA = RT/V*Z
      IF(ABS(PA-P) .GE. 1.D-5)GO TO 5
      RETURN
      END
C     ******************************************************************
```

```
      BLOCK DATA
      IMPLICIT DOUBLE PRECISION (A-H.O-Z)
      COMMON /BBLOK/ BR11H0(3), BR11H1(3). BR11H2(3). BR22(3). BR23(3).
     +               BR33(3), BR15(3), BR17(3), BR55(3), BR77(3), B25
      COMMON /CBLOK/ CR111H0(3). CR111H1(3). CR111H2(3). CR222(3),
     +               CR223(3). CR233(3).  CR333(3). CR555(3). CR117(3)
      COMMON /ZETA/  Z12.Z13.Y12.Y13.Y123.Y115
      COMMON /MBLOK/ GM1R0.GM1R1.GM2.GM3.GM5.GM7.FA.FB.RL.TO.H5.H7,R
      DATA BR11H0/-0.425468D0, 0.286500D-2. -.462073D-5 /,
     +     BR11H1/0.877118D-3, -.556281D-5. 0.881514D-8 /,
     +     BR11H2/-.824747D-6, 0.431436D-8. -.608319D-11/,
     +     BR22 / -.144600D0 , 0.740910D-3, -.911950D-6 /,
     +     BR23 / -.339693D0 , 0.161176D-2. -.204429D-5 /,
     +     BR33 / -.868340D0 , 0.403760D-2. -.516570D-5 /,
     +     BR15 / -.521280D-1, 0.271570D-3. -.25    D-6 /,
     +     BR17 / -.687290D-1. -.239381D-5, 0.518195D-6 /,
     +     BR55 / -.110596D-2, 0.813385D-4. -.987220D-7 /,
     +     BR77 / -.130820D0 , 0.602540D-3. -.644300D-6 /,
     +     B25  / 0.012D0
      DATA CR111H0/ -.302488D0 , 0.195861D-2. -.316302D-5 /.
     +     CR111H1/ 0.646422D-3, -.422876D-5. 0.688157D-8 /,
     +     CR111H2/ -.332805D-6, 0.223160D-8. -.367713D-11/.
     +     CR222 /  0.784980D-2, -.398950D-4. 0.611870D-7 /,
     +     CR223 /  0.552066D-2, -.168609D-4, 0.157169D-7 /.
     +     CR233 /  0.358783D-2. 0.806674D-5. -.325798D-7 /,
     +     CR333 /  0.205130D-2. 0.348880D-4. -.837030D-7 /,
     +     CR555 /  0.104711D-2. -.364887D-5.  .467095D-8 /,
     +     CR117 /  0.736748D-2. -.276578D-4.  .343051D-7 /
      DATA  Z12 /   0.72D0 /, Z13 /  -.865D0 /,
     +      Y12 /   0.92D0 /, Y13 /  0.92D0/. Y123 /1.10D0/,
     +      Y115/   1.2D0/
      DATA GM1R0/-2.709328D0/, GM1R1/.021062199D0/,
     +     GM2  /  28.0135D0/, GM3  /      44.010D0/.
     +     GM5  /   2.0159D0/, GM7  /      28.010D0/,
     +     FA   /22.414097D0/, FB   /  22.710811D0/,
     +     RL   / 1.292923D0/, TO   /      273.15D0/,
     +     H5   /   285.83D0/, H7   /      282.98D0/
     +     R    /0.0831451D0/
      END
```

Errata for GERG Monograph TM-5 (1991)

STANDARD GERG VIRIAL EQUATION FOR FIELD USE

Page 155

The Fortran program listing given contains, on this page, the incorrect value 0.881514D-8 (line 10); the correct value is 0.881510D-8, as given in Table 4.1 (page 43), in the Basic program line 5720 (page 143) and in references (6), (7) and (8). Consequently the example calculations given in Table 8.8.2 are very slightly incorrect (not more than 3.10^{-5} in Z). For example 1 (N75), correct implementations of the SGERG method must conform with the example calculations shown in Table 8.8.1 for the same gas. For example 2 (N74), the correct compressibility factor/molar density (kmol m^{-3}) pairs are as follows: 0.88515/ 3.0183, 0.90101/ 2.8594, 0.83541/ 6.1673, 0.91465/2.7195 and 0.99274/2.2950.

Table 8.7 Introductory Text Generated by GERG88.EXE

```
This program will be run on a IBM compatible PC (AT).   Please insert the disk
and start the program  :

                                   GERG88

(at first a describing text will be displayed, please press RETURN to continue)


===============================================================================
GERG-88 VIRIAL EQUATION

Calculation of the density and the compressibility factor of natural gases
from a detailed molar composition or from a simplified analysis
================================================ ==============================


COPYRIGHT - Groupe Europeen de Recherches Gazieres, 1988/1991
Legal copies  of this program  may only be obtained  from  the members of the
GERG Working Group on Compressibility Factors of Natural Gas at the following
addresses as given in GERG Technical Monographs TM 2 (1988) and TM 5 (1991).

(Return)

-------------------------------------------------------------------------------
Dr. M. Jaeschke                    Dr. S. Audibert
c/o Ruhrgas AG                     c/o Gaz de France
                                       DETN - CERSTA
Halterner Strasse 125
D-4270 Dorsten 21 (F.R.Germany)    361 . Avenue du President Wilson . BP 33
                                   F-93211 La Plaine St. Denis Cedex (France)
-------------------------------------------------------------------------------
Mme. P. van Canegnem               Dr. A.E. Humphreys
c/o S.A. Distrigaz                 c/o British Gas plc
                                       London Research Station
Digue du Canal 102                 Michael Road
B-1070 Bruxelles (Belgium)         GB-London SW6 2AD (United Kingdom)
-------------------------------------------------------------------------------
Mrs. Dr. R. Janssen-van Rosmalen   Mr. Ing. Q. Pellei
c/o Nederlandse Gasunie N.V.       c/o S.N.A.M. SpA.
                                       Servizio Despacciamento e Misure
Energieweg 17
P.O. Box 19                        I-20097 San Donato Milanese (Italy)
NL-9700 MA Groningen (Netherlands)
-------------------------------------------------------------------------------

(Return)

This program calculates compressibility factors and molar densities for natural
gases from a known molar composition or from the input of four parameters (mole
fractions of carbon dioxide and hydrogen, relative density and calorific value:
i.e. simplified  analysis), in  accordance  with  the  GERG-88  virial equation
( MGERG , May 1988  or  SGERG, July 1988 / August 1991, respectively) developed
primarily by  J.A. Schouten and J.P.J. Michels  of the Van der Waals Laboratory
of the University of Amsterdam under contract to the Groupe Europeen de Recher-
ches Gazieres.

The target accuracy is  +/- 0.1 % within the temperature range  -8.15 to  61.85
deg C (265 to 335 K) and a pressure range 0 to 120  bar (12 MPa).


(Return)
```

```
Ranges for percentage molar composition :

                methane                            >=  50 %
                nitrogen                           <=  50 %
                carbon dioxide + ethylene          <=  30 %
                ethane                             <=  20 %
                hydrogen                           <=  10 %
                propane                            <=   5 %
                carbon monoxide                    <=   3 %
                butanes                            <= 1.5 %
                helium                             <= 0.5 %
                pentanes - benzene                 <= 0.5 %
                hexanes  - e-benzene               <= 0.1 %
                heptanes - toluene                 <= 0.1 %
                octanes  - higher                  <= 0.1 %
(Return)

Ranges for simplified analysis :

mole percentage of carbon dioxide                  <=  30 %
mole percentage of hydrogen                        <=  10 %
density.relative to air at N.T.P.  *)              0.55 to 0.90
gross calorific value   at N.T.P.  *)              19 to 48 MJ/m3

*)note: density, relative to air at the following reference conditions
        temperature  T = 0.00 deg.C , pressure P = 1.01325 bar (N.T.P).

        gross calorific value, at the following reference conditions
        metering   : T = 0.00 deg.C , P = 1.01325 bar (N.T.P.)
        combustion : T = 25.00 deg.C
(Return)

The GERG-88 virial equation  was  tested very carefully in the tempera-
ture range from 270 to 335 K , the pressure range up to  12 MPa and for
pipeline quality gas covering  the  following concentrations and ranges
for the relative density and the gross calorific value :

        nitrogen                :       <=  14 %
        carbon dioxide          :       <=   8 %
        ethane                  :       <=   9 %
        hydrogen                :       <=  10 %
        relative density        :       0.55 to 0.69
        gross calorific value   :       31    to  45  MJ/m3

The expected uncertainty  limits  for  calculation  of  compressibility
factor beyond this limit  of  pipeline quality gas is discussed in GERG
Technical Monograph TM 5 (1991).

The restrictions of the input data on the  range  of  compositions  and
simplified (reduced) gas analysis will  be flagged  if necessary during
program execution, as  will  out-of-range  inputs  for  temperature and
pressure.
(Return)

Select
  MASTER GERG-88 VIRIAL EQUATION   (molar composition)                (m)
  STANDARD GERG-88 VIRIAL EQUATION (simplified analysis)              (s)
  EXIT (program end)                                                  (x)
                                                          your choice:
```

(if m is selected :)

```
*******************************************************************************
              GERG-88 VIRIAL EQUATION       (molar composition)
              CALCULATION OF THE COMPRESSIBILITY OF NATURAL GAS
              MOLAR COMPOSITION             MGERG  .  MAY 1988
*******************************************************************************

Select fractional or percentage molar composition (f/p):

Enter gas composition in mole fraction/percent (must enter "0" for zeroes):

              METHANE                       :
              NITROGEN                      :
              CARBON DIOXIDE - ETHENE       :
              ETHANE                        :
              HYDROGEN                      :
              CARBON MONOXIDE               :
              PROPANE                       :
              BUTANES                       :
              HELIUM                        :
              PENTANES - BENZENE            :
              HEXANES  - EBENZENE           :
              HEPTANES - TOLUENE            :
              OCTANES  - HIGHER             :

Do you wish to modify these compositions?

Do you wish to save the results on a datafile?
       (if answer Y) please give a name of the datafile:
                     enter a title of the listing (max. 50 characters):

Enter pressure in bar:

Enter temperature in deg.C:


Results :     GAS PRESSURE                  :           - bar
              GAS TEMPERATURE               :             °C
              COMPRESSIBILITY FACTOR Z      :
              MOLAR DENSITY                 :             kmol/m**3


Select        new pressure and temperature     p
              modify last analysis             a
              new molar composition            m
              new simplified analysis          s
              EXIT                             x

                  Please make your choice .
```

(if s is selected:)

```
********************************************************************************
                STANDARD GERG-88 VIRIAL EQUATION
                CALCULATION OF THE COMPRESSIBILITY OF NATURAL GAS
                SIMPLIFIED ANALYSIS          SGERG  . AUGUST 1991
********************************************************************************

Select fractional or percentage molar composition (f/p):

Enter simplified analysis:

                MOLE FRACTION/PERCENTAGE OF CARBON DIOXIDE  :
                MOLE FRACTION/PERCENTAGE OF HYDROGEN        :
                DENSITY, RELATIVE TO AIR    AT N.T.P.       :
                GROSS CALORIFIC VALUE AT N.T.P. IN MJ/m**3  :

Do you wish to modify these parameters?

Do you wish to save the results on a datafile?
        (if answer Y) please give a name of the datafile:
                      enter a title of the listing (max. 50 characters):

Enter pressure in bar:

Enter temperature in deg.C:


Results:        GAS PRESSURE                        :             bar
                GAS TEMPERATURE                     :             °C
                COMPRESSIBILITY FACTOR     Z        :
                MOLAR DENSITY                       :             kmol/m**3



Select          new pressure and temperature      p
                modify last analysis              a
                new molar composition             m
                new simplified analysis           s
                EXIT                              x

                     Please make your choice :
```

(if x is selected:)

Exit , the program will be ended.

Table 8.8.1 Example Results for (Basic) ZGERG-88.EXE

```
GERG VIRIAL EQUATION
--------------------

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Legal copies of this program may only be obtained from

    A E Humphreys      British Gas plc              (United Kingdom)
    P van Caneghem     Distrigaz S A                (Belgium)
    R Janssen          N V Nederlandse Gasunie      (Netherlands)
    N Audibert         Gaz de France                (France)
    M Jaeschke         Ruhrgas A G                  (F R Germany)
    G Pellei           S.N.A.M. S p A               (Italy)

at the addresses given in GERG Technical Monographs Number 2 (1988)
and Number [illegible]            [illegible]    [illegible] program faults etc to AEH


                        Press RETURN to begin ...


Calculation of Compressibility Factor and Density for Natural Gases
-------------------------------------------------------------------

This program calculates  compressibility factors and  densities for
natural gases of  known  molar composition  in accordance  with the
GERG-88   equation ,  developed   primarily  by   J A Schouten  and
J P J Michels of the van der Waals Laboratory of the  University of
Amsterdam  under contract  to the  Groupe  Europeen  de  Recherches
Gazieres.

The  expected accuracy is  +/- 0.1 percent  within the  temperature
range  -8 to 62 deg C  and the  pressure  range  0 to 120 bar,  but
these ranges may, with caution, be stretched.

There are also restrictions on the  range of compositions for which
the equation  should be expected  to achieve the  target accuracy -
these will be  flagged  if necessary  during program  execution, as
will out-of-range inputs for temperature and pressure.

Press return key to continue


If a complete  molar composition analysis is not available, you may
instead  calculate  compressibility  factors  using  as  input  a
simplified analysis  comprising  calorific value,  specific gravity
and  carbon dioxide  content.  The  resultant  values  will  be  of
similar accuracy  to those  obtained  from a full  molar  analysis.
(Note, however, that gases containing  hydrogen or  carbon monoxide
are  not  permissible  in  this  implementation  of the  simplified
analysis GERG virial equation.)

The molar composition input version is known as the  MASTER GERG-88
equation, and the simplified input version as the  STANDARD GERG-88
equation.


Select master equation or standard equation input (m/s) S

Select mole fraction or mole percent composition entry (f/p) P
```

```
Select input units to be used for calorific value -
   - you may choose by letter from (b) btu(IT)/ft^3
                                   (m) MJ/m^3          -- now -- M

Select the reference conditions at which your dry-gas calorific
value is defined - you may choose by letter from

(a) Combustion at 15 deg C + Metering at 15 deg C + 1.01325 bar ( U.K, U.S,
                                                                  Aus )
(b) Combustion at 25 deg C - Metering at  0 deg C + 1.01325 bar ( FRG, It,
                                                                  Bel, Ned )
(c) Combustion at  0 deg C + Metering at  0 deg C + 1.01325 bar ( Fra, Jap )
                                                      -- now -- B


 Select input unit to be used for temperature -
    - you may choose by letter from (k) kelvin
                                    (c) deg Celsius (centigrade)
                                    (f) deg Fahrenheit
                                    (r) deg Rankine    -- now -- C

 Select input unit to be used for pressure -
    - you may choose by letter from (m) megapascal
                                    (b) bar
                                    (s) standard atm
                                    (a) psi absolute
                                    (g) psi gauge      -- now -- B


 Enter the pressure in bar 60.120
 Enter the temperature in deg C -3.15

 Enter the dry-gas calorific value in MJ/m^3 43.5956
 Enter the dry-gas specific gravity 0.6506
 Enter the mole percent of carbon dioxide 1.5021


 The Compressibility Factor is Z(T,p) = 0.79292

                                  T/K =  270.00
                                p/bar =   60.12000

         The Molar Density is D(T,p) = 3.37744 mol/L


 Select by letter from the following continuation options -

    (a) Retain gas analysis - change pressure along an isotherm
    (b) Retain gas analysis - change temperature along an isobar
    (c) Retain gas analysis - change pressure and temperature values
    (d) Retain gas analysis - change pressure and temperature units
    (e) Change gas analysis - retain pressure and temperature values
    (f) Change gas analysis - change pressure and temperature values
    (g) Change gas analysis - change pressure and temperature units
    (h) Switch to/from mole percent from/to mole fraction input
    (i) Switch between master and standard equation input
    (j) Return to start of program
    (k) Inspect ranges of validity and trace component assignments
                                                        -- now -- C
    (q) Quit program
```

```
Enter the pressure in bar 59.988
Enter the temperature in deg C 6.85

The Compressibility Factor is Z(T,p)  = 0.82144

                                          T/K =  280.00
                                        p/bar =   59.98800

         The Molar Density is D(T,p)  = 3.13683 mol/L


Enter the pressure in bar 119.968
Enter the temperature in deg C 6.85


The Compressibility Factor is Z(T,p)  = 0.68946

                                          T/K =  280.00
                                        p/bar =  119.96800

         The Molar Density is D(T,p)  = 7.47409 mol/L


Enter the pressure in bar 60.118
Enter the temperature in deg C 16.85


The Compressibility Factor is Z(T,p)  = 0.84465

                                          T/K =  290.00
                                        p/bar =   60.11800

         The Molar Density is D(T,p)  = 2.95185 mol/L


Enter the pressure in bar 60.191
Enter the temperature in deg C 56.85


The Compressibility Factor is Z(T,p)  = 0.90831

                                          T/K =  330.00
                                        p/bar =   60.19100

         The Molar Density is D(T,p)  = 2.41516 mol/L


Select by letter from the following continuation options -

   (a) Retain gas analysis - change pressure along an isotherm
   (b) Retain gas analysis - change temperature along an isobar
   (c) Retain gas analysis - change pressure and temperature values
   (d) Retain gas analysis - change pressure and temperature units
   (e) Change gas analysis - retain pressure and temperature values
   (f) Change gas analysis - change pressure and temperature values
   (g) Change gas analysis - change pressure and temperature units
   (h) Switch to/from mole percent from/to mole fraction input
   (i) Switch between master and standard equation input
   (j) Return to start of program
   (k) Inspect ranges of validity and trace component assignments
   (q) Quit program                                       -- now -- G
```

```
Select input units to be used for calorific value -
   - you may choose by letter from (b) btu(IT)/ft^3
                                   (m) MJ/m^3          -- now -- M

Select the reference conditions at which your dry-gas calorific
value is defined - you may choose by letter from

(a) Combustion at 15 deg C + Metering at 15 deg C + 1.01325 bar ( U.K, U.S,
                                                                  Aus )
(b) Combustion at 25 deg C + Metering at  0 deg C + 1.01325 bar ( FRG, It,
                                                                  Bel, Ned )
(c) Combustion at  0 deg C + Metering at  0 deg C + 1.01325 bar ( Fra, Jap )
                                                           -- now -- A


 Select input unit to be used for temperature -
    - you may choose by letter from (k) kelvin
                                    (c) deg Celsius (centigrade)
                                    (f) deg Fahrenheit
                                    (r) deg Rankine    -- now -- K

 Select input unit to be used for pressure -
    - you may choose by letter from (m) megapascal
                                    (b) bar
                                    (s) standard atm
                                    (a) psi absolute
                                    (g) psi gauge      -- now -- M


 Enter the pressure in MPa 5.0306
 Enter the temperature in kelvin 283.50

 Enter the dry-gas calorific value in MJ/m^3 38.83
 Enter the dry-gas specific gravity 0.5858
 Enter the mole percent of carbon dioxide 0.06


 The Compressibility Factor is Z(T,p) = 0.88733

                                  T/K =  283.50
                                p/bar =    50.30600

         The Molar Density is D(T,p) = 2.40515 mol/L


 Select by letter from the following continuation options -

    (a) Retain gas analysis - change pressure along an isotherm
    (b) Retain gas analysis - change temperature along an isobar
    (c) Retain gas analysis - change pressure and temperature values
    (d) Retain gas analysis - change pressure and temperature units
    (e) Change gas analysis - retain pressure and temperature values
    (f) Change gas analysis - change pressure and temperature values
    (g) Change gas analysis - change pressure and temperature units
    (h) Switch to/from mole percent from/to mole fraction input
    (i) Switch between master and standard equation input
    (j) Return to start of program
    (k) Inspect ranges of validity and trace component assignments
    (q) Quit program                                      -- now -- C
```

```
Enter the pressure in MPa 2.0339
Enter the temperature in kelvin 293.06


The Compressibility Factor is Z(T,p)  = 0.95905

                                   T/K =  293.06
                                 p/bar =    20.33900

        The Molar Density is D(T,p)  = 0.87035 mol/L


Enter the pressure in MPa 5.9906
Enter the temperature in kelvin 293.06


The Compressibility Factor is Z(T,p)  = 0.88366

                                   T/K =  293.06
                                 p/bar =    59.90600

        The Molar Density is D(T,p)  = 2.78222 mol/L


Enter the pressure in MPa 2.0428
Enter the temperature in kelvin 303.00


The Compressibility Factor is Z(T,p)  = 0.96372

                                   T/K =  303.00
                                 p/bar =    20.42800

        The Molar Density is D(T,p)  = 0.84138 mol/L


Enter the pressure in MPa 4.5056
Enter the temperature in kelvin 313.08


The Compressibility Factor is Z(T,p)  = 0.93166

                                   T/K =  313.08
                                 p/bar =    45.05600

        The Molar Density is D(T,p)  = 1.85783 mol/L


Select by letter from the following continuation options -

   (a) Retain gas analysis - change pressure along an isotherm
   (b) Retain gas analysis - change temperature along an isobar
   (c) Retain gas analysis - change pressure and temperature values
   (d) Retain gas analysis - change pressure and temperature units
   (e) Change gas analysis - retain pressure and temperature values
   (f) Change gas analysis - change pressure and temperature values
   (g) Change gas analysis - change pressure and temperature units
   (h) Switch to/from mole percent from/to mole fraction input
   (i) Switch between master and standard equation input
   (j) Return to start of program
   (k) Inspect ranges of validity and trace component assignments
   (q) Quit program                                     -- now -- Q
```

Table 8.8.2 Example Results for (Fortran) GERG88.EXE

```
           EXAMPLE 1 (s)   N75

***************************************************************************
           STANDARD GERG-88  VIRIAL  EQUATION
           CALCULATION OF THE COMPRESSIBILITY OF NATURAL GAS
           SIMPLIFIED ANALYSIS          SGERG  , AUGUST 1991
***************************************************************************


           MOLE PERCENTAGE OF CARBON DIOXIDE    :     1.5021
           MOLE PERCENTAGE OF HYDROGEN          :     0.0000
           DENSITY, RELATIVE TO AIR AT N.T.P.   :    0.65060
           GROSS CALORIFIC VALUE    AT N.T.P.   :    43.5956 MJ/m**3


           GAS PRESSURE                         :    60.1200 bar
           GAS TEMPERATURE                      :      -3.15 °C
           COMPRESSIBILITY FACTOR      Z        :    0.79292
           MOLAR DENSITY                        :    3.3774  kmol/m**3

           GAS PRESSURE                         :    59.9880 bar
           GAS TEMPERATURE                      :       6.85 °C
           COMPRESSIBILITY FACTOR      Z        :    0.82145
           MOLAR DENSITY                        :    3.1366  kmol/m**3

           GAS PRESSURE                         :   119.9680 bar
           GAS TEMPERATURE                      :       6.85 °C
           COMPRESSIBILITY FACTOR      Z        :    0.68949
           MOLAR DENSITY                        :    7.4738  kmol/m**3

           GAS PRESSURE                         :    60.1180 bar
           GAS TEMPERATURE                      :      16.85 °C
           COMPRESSIBILITY FACTOR      Z        :    0.84466
           MOLAR DENSITY                        :    2.9518  kmol/m**3

           GAS PRESSURE                         :    60.1910 bar
           GAS TEMPERATURE                      :      56.85 °C
           COMPRESSIBILITY FACTOR      Z        :    0.90832
           MOLAR DENSITY                        :    2.4151  kmol/m**3
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          EXAMPLE 2 (s)   N74

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          STANDARD GERG-88  VIRIAL  EQUATION
          CALCULATION OF THE COMPRESSIBILITY OF NATURAL GAS
          SIMPLIFIED ANALYSIS         SGERG  , AUGUST 1991
**********************************************************************************


          MOLE PERCENTAGE OF CARBON DIOXIDE     :     1.3390
          MOLE PERCENTAGE OF HYDROGEN           :     9.4916
          DENSITY, RELATIVE TO AIR  AT N.T.P.   :    0.59800
          GROSS CALORIFIC VALUE     AT N.T.P.   :    34.3700 MJ/m**3


          GAS PRESSURE                          :    59.9760 bar
          GAS TEMPERATURE                       :      -3.15 °C
          COMPRESSIBILITY FACTOR     Z          :    0.88516
          MOLAR DENSITY                         :    3.0183  kmol/m**3

          GAS PRESSURE                          :    59.9800 bar
          GAS TEMPERATURE                       :       6.85 °C
          COMPRESSIBILITY FACTOR     Z          :    0.90102
          MOLAR DENSITY                         :    2.8594  kmol/m**3

          GAS PRESSURE                          :   119.9480 bar
          GAS TEMPERATURE                       :       6.85 °C
          COMPRESSIBILITY FACTOR     Z          :    0.83543
          MOLAR DENSITY                         :    6.1672  kmol/m**3

          GAS PRESSURE                          :    59.9750 bar
          GAS TEMPERATURE                       :      16.85 °C
          COMPRESSIBILITY FACTOR     Z          :    0.91465
          MOLAR DENSITY                         :    2.7194  kmol/m**3

          GAS PRESSURE                          :    59.9930 bar
          GAS TEMPERATURE                       :      56.85 °C
          COMPRESSIBILITY FACTOR     Z          :    0.95275
          MOLAR DENSITY                         :    2.2949  kmol/m**3
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10 - NOMENCLATURE

Symbol	First Use	SI Unit	Meaning
b	page 62	-	Bias, or mean relative deviation, of a set of data; defined by equation 6.2.
$b^{(0)}$	page 15	$m^3\ mol^{-1}$	Zero-th order (constant) term in the expansion of B in temperature (equations 2.9, 3.2).
$b^{(1)}$	page 15	$m^3\ mol^{-1}\ K^{-1}$	Coefficient of the first order (linear) term in the expansion of B in temperature (equations 2.9, 3.2).
$b^{(2)}$	page 15	$m^3\ mol^{-1}\ K^{-2}$	Coefficient of the second order (quadratic) term in the expansion of B in temperature (equations 2.9, 3.2).
B	page 9	$m^3\ mol^{-1}$	(Also use $m^3/kmol, cm^3/mol$). Second virial coefficient (equations 2.2, 2.3).
$c^{(0)}$	page 15	$m^6\ mol^{-2}$	Zero-th order (constant) term in the expansion of C in temperature (equations 2.10, 3.3).
$c^{(1)}$	page 15	$m^6\ mol^{-2}\ K^{-1}$	Coefficient of the first order (linear) term in the expansion of C in temperature (equations 2.10, 3.3).
$c^{(2)}$	page 15	$m^6\ mol^{-2}\ K^{-2}$	Coefficient of the second order (quadratic) term in the expansion of C in temperature (equations 2.10, 3.3).
C	page 9	$m^6\ mol^{-2}$	(Also use $m^6/kmol$, cm^6/mol). Third virial coefficient (equations 2.2, 2.4).
d	page 6	-	Density relative to air of standard composition at $0\ ^oC$, 101.325 kPa.
D_{CH}	page 50	$J\ mol^{-1}$	(Also use kJ/mol). Iteration increment for molar heating value; defined by equation 5.13

Symbol	First Use	SI Unit	Meaning
H^o	page 26	$J\ mol^{-1}$	(Also use kJ/mol). Ideal molar superior heating (calorific) value of the whole natural gas or of a pure chemical species - reference condition 25 °C.
H_{CH}	page 12	$J\ mol^{-1}$	(Also use kJ/mol). Molar superior heating (calorific) value of the equivalent hydrocarbon - reference condition 25 °C.
H_S	page 6	$J\ m^{-3}$	(Also use MJ/m^3). Superior (gross) calorific value for the whole natural gas - reference conditions; combustion at 25 °C, metering at 0 °C, 101.325 kPa.
M	page 12	$kg\ mol^{-1}$	(Also use kg/kmol). Mass per mole.
n	page 62	-	Number of distinct data sets.
N	page 10	-	Number of components in a mixture.
N	page 20	-	Number of experimental points in a set.
p	page 1	Pa	(Also use MPa, kPa, bar, atm, psia). (Absolute) pressure.
Q	page 116	varies	Physical quantity (usually H_S, d, x, p or T).
R	page 9	$J\ mol^{-1}\ K^{-1}$	(Also use MJ/kmol K). Universal gas constant. (R = 8.314510 J/mol K).
rms	page 18	-	Fractional (or percentage) root-mean-square deviation of a data set; defined by equation 6.4.
s	page 62	-	Standard deviation of a data set; defined by equation 6.3.
S(Z/Q)	page 113	-	Sensitivity coefficient of Z to the physical quantity Q; defined by equations 7.1 to 7.3.
t	page 33	°C	Celsius (also use Fahrenheit °F) temperature; t/°C = T/K - 273.15.
T	page 1	K	Thermodynamic (absolute) temperature.
V_m	page 53	$m^3\ mol^{-1}$	Molar volume ($=1/\rho_m$).
x	page 6	-	Mole fraction.

Symbol	First Use	SI Unit	Meaning
y	page 37	-	Interaction coefficient.
Z	page 1	-	Compressibility (or compression) factor; defined by equation 2.1.
β_{H0}	page 12	$m^3\ mol^{-1}$	Zero-th order (constant) term in the expansion of B_{CH} (equation 2.7).
β_{H1}	page 12	$m^3\ J^{-1}$	Coefficient of the first order (linear) term in the expansion of B_{CH} (equation 2.7).
β_{H2}	page 12	$m^3\ mol\ J^{-2}$	Coefficient of the second order (quadratic) term in the expansion of B_{CH} (equation 2.7).
ϵ_{H0}	page 12	$m^6\ mol^{-2}$	Zero-th order (constant) term in the expansion of C_{CH} equation 2.8).
ϵ_{H1}	page 12	$m^6\ mol^{-1}\ J^{-1}$	Coefficient of the first order (linear) term in the expansion of C_{CH} (equation 2.8).
ϵ_{H2}	page 12	$m^6\ J^{-2}$	Coefficient of the second order (quadratic) term in the expansion of C_{CH} (equation 2.8).
μ	page 32	-	Number of carbon atoms per molecule.
ρ	page 26	$kg\ m^{-3}$	(Mass) density.
ρ_m	page 9	$mol\ m^{-3}$	(Also use $kmol/m^3$, mol/L). Molar density.
δQ	page 111	varies	Uncertainty of the physical quantity Q (e.g. Z, H_s, d).
ΔZ	page 62	-	Relative deviation (or error) of a single data point; defined by equation 6.1 (also known as "Z-Error").
$\sqrt{b}$	page 30	-	Summation factor.

Additional Subscripts

Symbol	First Use	Meaning
i	page 10	Identifier of i-th component in a mixture.
i	page 62	Identifier of i-th data point in a set.
j	page 10	Identifier of j-th component in a mixture.

Symbol	First Use	Meaning
k	page 10	Identifier of k-th component in a mixture.
ij	page 10	For the binary interaction of component i with component j.
ijk	page 10	For the ternary interaction of components i, j and k.
o	page 50	Value at the base condition.
q	page 16	Dummy subscript; $q = 0,1,2$.
u,v,w	page 50	Iteration counters.
air	page 26	For dry air of standard composition.
calc	page 5	Calculated.
expt	page 5	Experimental.
mix	page 9	For a mixture.
CH	page 12	For the equivalent hydrocarbon.
D	page 55	Special value of ρ used in equation 5.13a.
1	page 37	For the equivalent hydrocarbon.
1	page 26	For the combustion reference condition.
2	page 6	For nitrogen.
2	page 26	For the metering reference condition.
3	page 6	For carbon dioxide.
4	page 7	For hydrogen.
5	page 41	For carbon monoxide.

Additional Superscripts

Symbol	First Use	Meaning
o	page 49	For the ideal gas state.
r	page 37	Dummy superscript; $r = 0,1,2$.