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GERG Round-Robin Test of Z-Meters, a Burnett Apparatus, and an Interferometric Device for *pVT* Measurements[1]

M. Jaeschke,[2] S. Audibert,[3] P. van Caneghem,[4] A. E. Humphreys,[5] R. Janssen-van Rosmalen,[6] and Q. Pellei[7]

The European Gas Research Group (GERG; Groupe Européen de Recherches Gazières) initiated a round-robin test of six Z-meters manufactured by Desgranges et Huot, a Burnett apparatus, and an interferometric device to back up the *pVT* data of the Z-meters. Two gas mixtures were measured. One mixture contained 49.7 mol% of methane and 50.3 mol% of nitrogen; the second mixture 81.3 mol% of methane, 16.4 mol% of ethane, and 2.3 mol% of propane. The test temperatures were mainly 280 and 300 K for the first mixture and 290 and 320 K for the second mixture. The maximum pressures were 8 MPa for Z-meters and 12 MPa for the Burnett apparatus and the grating interferometer. The experimental compressibility factors Z of the six Z-meters are generally in agreement within ±0.05%. The agreement with the reference data from the Burnett apparatus and the refractive index measurements is also within ±0.05%. Only two isotherms of the binary mixtures differ by about 0.1% from the other data. Recent natural gas measurements show substantially the same results.

KEY WORDS: Burnett apparatus; compressibility factor; density; ethane; methane; mixtures; nitrogen; refractive index; Z-meter.

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[2] Ruhrgas AG, Halterner Strasse 125, 4270 Dorsten, Federal Republic of Germany.

[3] Gaz de France, Centre de Recherches Gazières (CERSTA), 361 Avenue du Président Wilson, P.O. 93, 93211 La Plaine St. Denis Cedex, France.

[4] Distrigaz S.A., Digue du Canal 102, 1070 Bruxelles, Belgium.

[5] British Gas plc, London Research Station, Michael Road, London SW6 2AD, United Kingdom.

[6] Nederlandse Gasunie N.V., Energieweg 17, P.O. Box 19, 9700 MA Groningen, The Netherlands.

[7] SNAM S.p.A., Servizio Despacciamento e Misure, 20097 San Donato Milanese, Italy.

1. INTRODUCTION

In an effort to produce an accurate equation of state for natural gas mixtures, the European Gas Research Group (GERG; Groupe Européen de Recherche Gazières) has developed a unique data bank. The data bank combines sets of data from high-accuracy experimental compressibility factor measurements, made for pure gases and for binary and multicomponent mixtures by British Gas, Gaz de France, Gasunie and Ruhrgas, with similar data available from the published literature. The data bank was employed to develop an equation of state with a target uncertainty of less than 0.1% for predicted compressibility factors Z (p, T). A large proportion of the data, used mainly for the preliminary (1986) GERG virial equation [1], was obtained from tests with commercial "Z-meters" manufactured by Desgranges et Huot (DEH). The final GERG virial equation [2–4] is based on a data bank which also contains many high-accuracy data points measured by a Burnett apparatus or a grating interferometer.

GERG members recognized the importance of clarifying two factors upon which the performance of the GERG equation would depend, viz., (a) the level of agreement between Z-meters operated with slightly different methodologies and (b) the level of agreement between Z-meters and alternative methods of high-accuracy Z measurement. Obviously any systematic differences identified have implications for the accuracy of any equation ultimately developed. A particular problem for Z-meters was anticipated to be that the integrity of results might be prejudiced by adsorption or similar processes occurring during expansion within the apparatus. For this reason, GERG initiated a round-robin test of several Z-meters and other apparatus.

2. ROUND-ROBIN TEST

Two mixtures were used for the round-robin test:

(i) 49.7 mol% methane + 50.3 mol% nitrogen and

(ii) 81.3 mol% methane + 16.4 mol% ethane + 2.3 mol% propane.

Ruhrgas prepared the mixtures, each apportioned into seven samples and analyzed them. Some samples of the binary mixture were also analyzed by British Gas and Gasunie. The agreement for the analysis is within 0.15 mol%. Some samples of the tenary mixture were analyzed by Gaz de France and Gasunie. The agreement is within 0.05 mol%. The molar compositions of the sample gases tested using six DEH Z-meters from the laboratories of GERG members are listed in a GERG report [5]. Each individual sample of each mixture was only tested using one of the

Z-meters. The Z-meters used are discussed in the next section. Ruhrgas also employed a Burnett apparatus and a grating interferometer to provide further independent backup for the pVT data obtained using the Z-meters. One sample of each mixture was also tested at Texas A&M University, using another Burnett apparatus [6].

The test temperatures are mainly 280 and 300 K for the first mixture and 290 and 320 K for the second mixture. Additional measurements were made at various other temperatures. The maximum pressures were 8 MPa for the Z-meters and 12 MPa for the Burnett apparatus and the grating interferometer.

3. EXPERIMENTAL METHOD

3.1. The Z-Meter Apparatus

The DEH Z-meter is, in principle, an expansion-type meter, but unlike the conventional Burnett apparatus, the DEH Z-meter uses a single-step rather than a multiple-step expansion. The apparatus consists essentially of two vessels of volumes V_1 and V_2 ($V_1 < V_2$) and three valves (see Fig. 1). Z-meter operation occurs in two phases:

- (i) In phase 1, valves 1 and 3 are open and valve 2 is closed. Vessel V_1 is filled with the sample gas at pressure p_1 and temperature T and vessel V_2 is at atmospheric pressure p_2.
- (ii) In phase 2, valves 1 and 3 close, and valve 2 opens. The sample gas in vessel V_1 expands into vessel V_2, and when temperature stability is reestablished, the pressure p_3 in vessels V_1 and V_2 is measured.

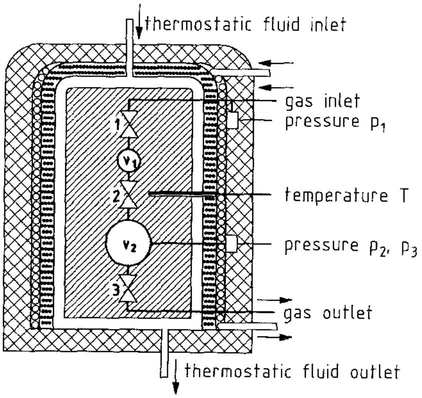

Fig. 1. Schematic of a DEH Z-meter. (1) Inlet valve; (2) expansion valve; (3) outlet valve.

The pressures measured before and after the expansion allow the calculation of the compressibility factor Z. The application of the equation of state to volumes V_1, V_2, and $V_3 = V_1 + V_2$ gives the compressibility factor Z_1, at pressure p_1 and temperature T in terms of the (unknown) "low-pressure" compressibility factors Z_2 and Z_3.

$$Z_1 = \frac{p_1}{(p_3/Z_3)(A+1) - (p_2/Z_2)\,A} \tag{1}$$

where

$$A = V_2/V_1$$

Equation (1) is valid only if the temperature before the expansion (phase 1) and after the expansion (phase 2) is the same. The volume ratio $A = V_2/V_1$ must be determined before the measurement by calibration of the Z-meter using a gas of known pVT behaviour.

For Z_2 and Z_3, values are obtained assuming a linear relation between the compressibility factor Z and pressure:

$$Z(p, T) = 1 + B(T)\,p \qquad \text{as} \quad p_2, p_3 < 0.3\ \text{MPa} \tag{2}$$

An approximation for $B(T)$ is obtained by assuming that the linear dependence in Eq. (2) holds at the high pressure p_1.

$$B(T) = (Z_1 - 1)/p_1 \tag{3}$$

An iterative scheme which takes $Z(p_2) = Z(p_3) = 1 (B = 0)$ as its starting point is used to solve Eqs. (1), (2), and (3) for $Z_1(p_1, T)$.

Some refinements used at the various laboratories when evaluating Z-meter results are presented separately [5]; those refinements have minor influences on the final Z_1 values.

The main features of all DEH Z-meters in the round-robin test are the same. Common features and differences of the Z-meters used are presented separately in a monograph [5] reviewing instrumentation and calibration methods. The volume ratio A calibration is particularly essential for the accuracy of the DEH Z-meter.

3.2. Determination of A

The determination of the volume ratio $A = V_2/V_1$ is the most important phase of Z-meter calibration. Rearranging Eq. (1) gives the following expression for A:

$$A = \frac{p_1/Z_1 - p_3/Z_3}{p_3/Z_3 - p_2/Z_2} \tag{4}$$

Equation (4) is used to determine A from the measurements of p_1, p_2, and p_3 made during a Z-meter calibration run and the known values of Z_1, Z_2, and Z_3 for the calibration gas. Hence, to calibrate the Z-meter volume ratio A, a gas whose pVT behaviour has been determined reliably and accurately fitted against an equation of state must be employed. Argon, nitrogen, helium, and methane are such gases, while the manufacturer favours nitrogen. For methane, the data of Kleinrahm et al. [7], Trappeniers et al. [8], and Douslin and Harrison [9] were used. The other reference data used for the calibration of the various Z-meters are given in Ref. 5.

The calibration measurements were carried out in exactly the same manner as the normal sample gas measurements.

3.3. Method of Measurement

Experimental data were produced by repeated measurements:

(i) at constant pressure p_1 and constant temperature,

(ii) at constant temperature and at pressures decreasing regularly from 7 to 3.5 MPa, and

(iii) at constant temperature and increasing or decreasing pressures (fixed pressure increments) between 2 MPa and 7 MPa;

e.g., measurement at increasing or decreasing pressures means in this case that after a full Z-meter cycle (phase 1 + phase 2), pressure p_1 was increased by a fixed increment Δp_1 before phase 1 of the next Z-meter cycle. This operation was repeated until a maximum pressure of $p_1 = 7$ MPa was attained. Pressure p_1 was then decreased by Δp_1 before each cycle, until a minimum pressure $p_1 = 2$ MPa was reached. Before the next Z-meter cycle, p_1 was again increased.

In the round-robin test, these measurements at increasing and decreasing pressures were often carried out with Z-meters fitted with computer-aided or computer-controlled data acquisition systems [5]. The accuracy of a Z-meter is not increased by computer control, but repeatability is likely to be improved by internal checks of the stability of the meter readings and therefore of the systems. Accuracy depends only on the devices used to measure pressures p_1, p_2, and p_3 and temperature and on the uncertainty in the determination of A.

3.4. Uncertainties

The accuracy of each Z-meter was estimated by each participant in the round-robin test by an error analysis for the variables used for the calculation of Z_1 by Eq. (1). The accuracy is better than ±0.15% and in most cases better than ±0.1% (see Table I). Tests were also made by running Z-meters on pure gases (nitrogen, helium and argon) and comparing the results with reference data. The differences between the reference data and measured values were in all cases below ±0.08%, suggesting that the accuracy of the Z-meters is indeed within the specified ±0.1%. Repeatability was even better, usually about ±0.03%.

For mixtures, the accuracy of the DEH Z-meter measurements is affected by the additional uncertainty of the sample gas analysis, which may produce a substantial uncertainty in Z, but this general problem is always encountered when mixtures are measured.

In addition, the accuracy of the DEH Z-meter measurements for mixtures may be affected by adsorption on vessel walls or valves and pipework of components near the saturation limit, an effect more likely to occur at relatively low temperature. The adsorption of gas during the operation of the Z-meter may cause some minor, but significant error in the experimental data. It was hoped that the GERG round-robin test would throw some light upon this problem. The round-robin Z-meter test data were to be verified by additional Burnett apparatus and grating interferometer measurements.

4. RESULTS

It would go beyond the scope of this paper to list all experimental density ρ or compressibility factor Z data. The actual temperature and pressure data and the associated ρ or Z data measured during the round-robin test of the different Z-meters are tabulated in a separate report [5] and integrated in the GERG databank. The data measured using the Texas A&M Burnett apparatus and the Ruhrgas apparatus and grating inter-

Table I. DEH Z-Meter Uncertainties

	Accuracy (%)	Repeatability (%)
British Gas	0.10	0.03
Distrigaz	0.035	0.02
Gasunie	0.10	0.03
Gaz de France	0.05	0.02
Ruhrgas[a]	0.15	0.06
SNAM	0.15	0.03

[a] With a reliability of 95%.

ferometer will be published elsewhere [6]. This section compares and discusses the results for the gas mixtures.

For the intercomparison, the data measured by the two Burnett apparatuses and by the grating interferometer were correlated and then used as the baseline for the comparison. The percentage differences between the compressibility factors predicted by the correlation (baseline) and the round-robin Z-meter data were employed for the evaluation.

4.1. Methane–Nitrogen Mixture

Figure 2 plots the results for the methane–nitrogen mixtures for the 280 to 284 K temperature range. The agreement between the different experimental data is excellent. Excepting one set of data, it is within ±0.05%.

The Gasunie data for 280 K differ systematically from the other data by about −0.1%. The 280 K isotherm shows a strange trend, as the measured compressibility factors do not extrapolate to unity at zero pressure. However, within the target uncertainty of ±0.1% (see Table I), the results still agree with the other Z-meter measurements.

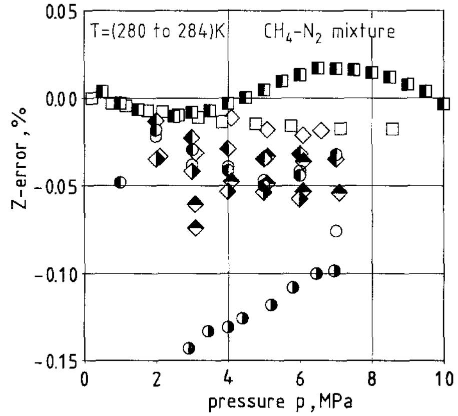

Fig. 2. Differences between maximum-likehood estimates (used as a baseline) and measurements of compressibility factors (Z-errors) for the methane–nitrogen mixture at 280 to 284 K. Z-meter data: (⬖) British Gas (1); (⬗) British Gas (1); (⬘) Distrigaz (1); (◇) SNAM (2); (◐) Gaz de France; (◑) Gasunie; (○) Ruhrgas. Burnett data: (□) Brugge [6]. Grating interferometer: (◧) Ruhrgas. (1) Measured at 283 K and (2) at 284 K (others at 280 K).

This good agreement between the various data sets (the same holds for the 290 to 293 K, the 300 to 303 K, and the 310 to 313 K temperature ranges [5]) is particularly satisfactory, as many of the compressibility factors used for correlating the GERG virial equation of state were measured by DEH Z-meters. Even though the data discussed in this paper were not part of the correlating work, the agreement between the experimental data and the data predicted by the GERG virial equation of state [3] is excellent and lies within the experimental error limits (see Fig. 3).

4.2. Methane–Ethane–Propane Mixture

The percentage differences between the compressibility factors calculated using a maximum-likelihood estimate (baseline) and the experimental data are plotted for the 290 to 293 K temperature range in Fig. 4. The different DEH Z-meter measurements are in excellent agreement within ±0.05% with the exception of a few data points measured by the Z-meter, e.g., at the Gaz de France and SNAM laboratories for pressures around 2 MPa. It is well known that the accuracy of the DEH Z-meter deteriorates in this pressure range.

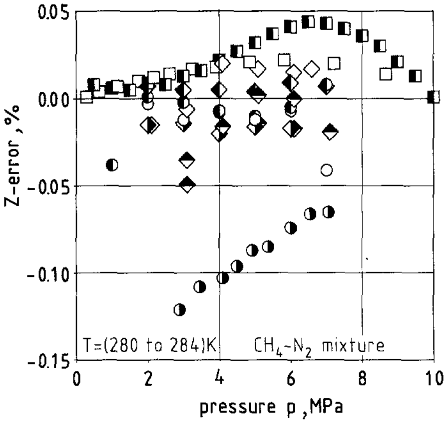

Fig. 3. Differences between predicted compressibility factors by the GERG-88 virial equation [3] and measured values (Z-errors) for the methane–nitrogen mixture at (280 to 284) K. Z-meter data: (⬖) British Gas (1); (⬗) British Gas (1); (⬘) Distrigaz (1); (◇) SNAM (2); (◐) Gaz de France; (◑) Gasunie; (○) Ruhrgas. Burnett data: (□) Brugge [6]. Grating interferometer: (◧) Ruhrgas. (1) Measured at 283 K and (2) at 284 K (others at 280 K).

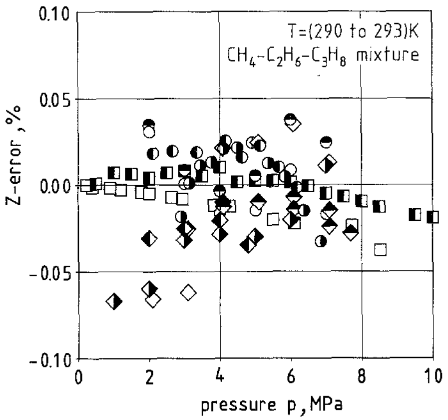

Fig. 4. Differences between maximum-likehood estimates used as a baseline and measurements of compressibility factors (Z-errors) for the methane–ethane–propane mixture at 290 to 293 K. Z-meter data: (⬖) British Gas (1)(*); (⬗) Gaz de France; (⬘) Distrigaz (1); (◇) SNAM (*); (◐) Gasunie (*); (◑) Gasunie; (○) Ruhrgas; (◓) Ruhrgas (*). Burnett data: (□) Brugge [6]. Grating interferometer: (◧) Ruhrgas. (1) Measured at 293 K; (*) second sample (others at 290 K).

Z-meter data measured by Distrigaz and British Gas with increasing and decreasing pressure increments do not indicate any substantial systematic differences. The experimental data for increasing and decreasing pressures agree within the specified repeatability (see Table I). However, for the Ruhrgas Z-meter measurements, some minor systematic differences can be identified. Even though this effect is really discernible only for the ternary mixture, it is for this reason that the standard deviations of the measured compressibility factors for the ternary mixture are higher than those for the binary mixture (see Fig. 5). These minor systematic differences for increasing pressure and decreasing pressure measurements may be due to adsorption. The effect of adsorption could cause a significant change of the gas composition in V_1 prior to or during expansion, with a consequent change in the true value of Z_1.

Although the data discussed above more or less answer the questions posed at the outset of the round-robin exercise (see Section 1), one question must still be answered. The question remains whether adsorption could cause a deterioration of the absolute accuracy as distinct from repeatability or reproducibility of the measured value of Z_1 for a natural gas mixture.

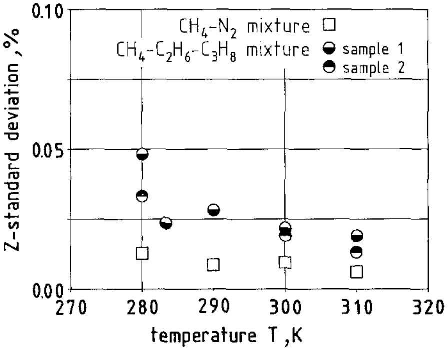

Fig. 5. Standard deviations for all Ruhrgas Z-meter measurements (increasing and decreasing pressure) of compressibility factors.

4.3. Natural Gas Mixtures

Systematic errors of DEH Z-meter measurements of natural gas mixtures can be detected only by comparing the results with other independent measurements using a different experimental device or by changing details of the experimental Z-meter technique. For each type of experiment, the precision or the repeatability could be considerably better than the disagreement between the results of different types of experiments.

British Gas, Distrigaz, and Ruhrgas investigated the so-called "hysteresis" problem for natural gases. Distrigaz observed no measurable effect [10]. British Gas analyzed hysteresis for a hydrogen-rich gas mixture (not forming part of the round-robin exercise) and observed no disagreement in excess of ±0.03% between the results for rising and falling pressures [11]. Early measurements using the computer-controlled Z-meter of Ruhrgas showed a strong hysteresis effect, showing differences of as much as 0.5% for runs with rising and falling pressure p_1 sequences [12]. The gas inlet system of the Z-meter was redesigned and is now accommodated in a thermostatic box maintained at high temperature (330 K) to prevent adsorption.

Figure 6 compares the compressibility factors measured by the Ruhrgas Z-meter for repeated rising and falling pressure runs with the compressibility factors of the same gas (Ekofisk gas), obtained from grating interferometer data by a maximum-likelihood fit (used as baseline). The maximum difference between the different Z-meter runs is 0.08%. Repeatability for the different runs is good, as the standard deviation for the average at each pressure point is less than ±0.03%. The results

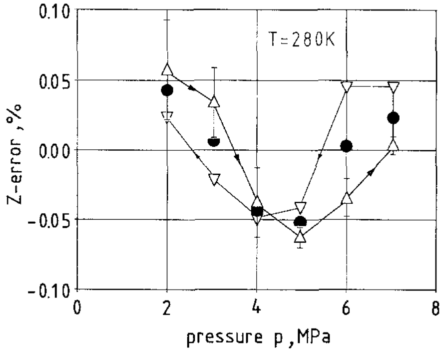

Fig. 6. Average differences between compressibility factors measured using rising or falling pressure increments (Ruhrgas Z-meter data): the baseline is the maximum-likelihood fit to grating interferometer data for the Ekofisk-type natural gas. (△) Rising pressure; (▽) falling pressure; (●) averaged values; (|) standard deviation.

averaged for increasing and decreasing pressures agree within ±0.05% (well within the stated accuracy of the Z-meter) with the results measured by the grating interferometer.

5. CONCLUSION

The round-robin test was carried out by measuring two mixtures. A binary mixture contained 49.70 mol% of methane and 50.30 mol% of nitrogen, while a ternary mixture contained 81.3 mol% of methane, 16.4 mol% of ethane, and 2.3 mol% of propane.

The DEH Z-meters used for the round-robin test are equipped with different pressure and temperature measuring devices. They are calibrated by slightly different methods and reference data.

The round-robin test was made with considerable differences between the details of experimental procedures and protocols. In spite of these differences and various modifications to the original DEH Z-meter, the agreement between the round-robin test compressibility factors measured by different Z-meters is, generally speaking, within ±0.05%. The agreement with the reference data is also within ±0.05%. Only two of the measured binary mixture isotherms differ by about 0.1% from the other data. This is an excellent result.

The results for the ternary mixture measured by increasing and decreasing pressure runs differ slightly (0.03%). Recent natural gas measurements show differences of up to 0.08% for these conditions. The compressibility factors, averaged for falling and rising pressure, differ by up to 0.05% from the data measured very accurately by a grating interferometer (accuracy of ±0.06% below 8 MPa). The uncertainty of natural gas mixture compressibility factors measured by Z-meters is therefore estimated to be about ±0.1%. The uncertainty of ±0.15% determined by Ruhrgas and SNAM is probably too pessimistic, but it is certainly extremely difficult to justify an uncertainty much better than specified by the manufacturer.

REFERENCES

1. A. Melvin, *Proc. 1989 Int. Gas Res. Conf., Toronto* (1987), pp. 438–448.
2. M. Jaeschke, S. Audibert, P. van Caneghem, A. E. Humphreys, R. Janssen, Q. Pellei, J. A. Schouten, and J. P. J. Michels, SPE 17766 and 17767, Gas Technology Symposium, Dallas (1988).
3. M. Jaeschke, S. Audibert, P. van Caneghem, A. E. Humphreys, R. Janssen-van Rosmalen, Q. Pellei, J. P. J. Michels, J. A. Schouten, and C. A. Ten Seldam, High Accuracy Compressibility Factor Calculation for Natural Gases and Similar Mixtures by Use of a Truncated Virial Equation. GERG Technical Monograph TM2 (1988) and Fortschritt-Berichte VDI Reihe 6, No. 231 (1989).
4. J. P. J. Michels, J. A. Schouten and M. Jaeschke, *Int. J. Thermophys.* **9**(6):985–992 (1988); J. A. Schouten, J. P. J. Michels, and M. Jaeschke, *Int. J. Thermophys* **11**(1):145–156 (1990).
5. M. Jaeschke, S. Audibert, P. van Caneghem, A. E. Humphreys, R. Janssen-van Rosmalen, and Q. Pellei, GERG Round-Robin Test of Z-Meters for pVT Measurements. GERG Technical Monograph TM 3 (1989) and Fortschritt-Berichte VDI Reihe 6, No. 238 (1989).
6. H. B. Brugge, Chih-An Hwang, K. N. Marsh, J. C. Holste, K. R. Hall, and M. Jaeschke, *J. Chem. Thermodyn.* (in press).
7. R. Kleinrahm, W. Duschek, W. Wagner, and M. Jaeschke, *J. Chem. Thermodyn.* **20**(5):621–631 (1988).
8. N. J. Trappeniers, T. Wassenaar, and J. C. Abels, *Physica* **98A**(1-2):289–297 (1979).
9. D. R. Douslin and R. H. Harrison, *J. Chem. Thermodyn.* **5**:491 (1973).
10. P. van Caneghem and P. Rombouts, Investigation of Hysteresis Effects in Operation of Desgranges & Huot Z-Meter with Ekofisk Gas, GERG Thermodynamics Committee Meeting, Essen (April 1986).
11. P. Cowan, P. J. McElroy, and A. E. Humphreys, Gas Mixture Compressibility Factors Using a Z-Meter, British Gas LRS T 927, London (Jan. 1988).
12. M. Jaeschke, Hysteresis in the DEH Z-Meter, GERG Thermodynamics Committee Meeting, Essen (April 1986).