

REAL-GAS EFFECTS IN THE EXPANSIBILITY FACTOR FOR SUBSONIC  
DIFFERENTIAL PRESSURE FLOW METERS AT HIGH PRESSURE

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ABSTRACT

General and exact expressions for the expansibility factor, including arbitrary real-gas corrections, are derived. Further analyses are provided by the introduction of the equation of state on virial form, in which the second and third virial coefficients are calculated from a prototype cubic equation of state.

Important cancellations between real-gas effects, which put equations of state to a severe test at high pressure, are revealed.

The exact result raises doubts about the general applicability of the current ISO standard in a high accuracy approach for orifice measurements of gases with arbitrary composition, at high as well as at low pressure.

## 1. INTRODUCTION

The international standard <sup>1</sup> for natural gas flow measurements by orifices, nozzles and venturi tubes is based on a polytropic equation of state for the isentropic gas flow. This description is exact for an ideal gas. For custody transfer at pressures typically exceeding 100 bar, the polytropic approach is not justified even at supercritical temperatures, if high measurement accuracy is an objective.

Essentially two methods for the inclusion of real-gas effects have been presented in the literature. The first one <sup>2</sup> underlies the polytropic approach, assuming that real-gas effects can be taken into account by defining an isentropic exponent  $\kappa$ . Obviously, such an exponent is pressure-dependent, complicating calculations by creating the necessity for using different exponents in different ranges of pressure. Also, it is not obvious that the theory of flow through contractions can be consistently modified by ad hoc changes of the isentropic exponent. The recommended practice <sup>1</sup> is to replace  $\kappa$  by the ratio  $\gamma$  between specific heats if  $\kappa$  is not known. This may have contributed to the widespread misconception of identifying  $\kappa$  with  $\gamma$ . The second approach <sup>3</sup>, introduced for sonic nozzles, is based on a full treatment of the thermodynamics of the isentropic flow problem, rigorous to the extent that the compressibility (i.e., the equation of state) is well known. This excellent method, employing iterative solution of the entropy and enthalpy equations, has a drawback in a lack of clarity and overview for the practical user, since the results are given by tables and graphs rather than simple formulas.

This paper first develops general expressions for the expansibility factor. The principle of corresponding states is then used to obtain composition-independent predictions for the isentropic equation of state, by calculating virial coefficients from a prototype cubic equation of state, chosen for simplicity as much as for accuracy. Explicit expressions for the expansibility factor, as well as predictions of a general kind, are then obtained by low order corrections to ideality. This paper has thus a didactic purpose, in addition to pointing out the direction for further research.

## 2. THE EXPANSIBILITY FACTOR

Consider an adiabatic real gas flow without energy loss through an orifice, nozzle or venturi tube, with velocity  $u$  depending on the flow cross-section  $A$ . Assume that equilibrium thermodynamics applies, and that changes in thermodynamical states are reversible<sup>4</sup>. Conservation of energy is then given as usual by the Bernoulli equation<sup>5</sup>

$$\frac{1}{2} u_1^2 + H(p_1) = \frac{1}{2} u_2^2 + H(p_2) \quad (1)$$

where  $H(p)$  is the isentropic enthalpy per mass unit,  $H_0$  being an indefinite constant contribution:

$$H(p) - H_0 = \int_0^p \frac{dp}{\rho} \quad (2)$$

The density  $\rho$  and the pressure  $p$  is related through an isentropic equation of state, to be considered in detail later. Subscript <sub>1</sub> will refer to a point upstream of the flow obstacle, while subscript <sub>2</sub> refers to the center of the orifice or nozzle. The standard derivation of the expression for mass flow rate  $\dot{m}$  based on eq. (1) gives then

$$\dot{m} = A_2 C \varepsilon \sqrt{\frac{2 \rho_1 \Delta p}{1 - \beta^4}} \quad (3)$$

where

$$\Delta p = p_1 - p_2 \quad (4)$$

is the differential pressure,  $\beta$  is the ratio of the least hardware limitation of flow radius to pipe radius upstream, and  $C$  is the discharge coefficient which will not be discussed in any detail in the present paper. The expansibility factor  $\varepsilon$  includes real-gas effects in a completely general way, when written on the form

$$\epsilon^2 = \left(\frac{\rho_2}{\rho_1}\right)^2 \frac{\rho_1}{\Delta p} \frac{1 - \beta^4}{1 - \left(\frac{\rho_2}{\rho_1}\right)^2 \beta^4} \{ H(p_1) - H(p_2) \} \quad (5)$$

For a flow arrangement where  $\Delta p$  is a considerable fraction of the upstream pressure, one now proceeds by calculating  $H(p)$  explicitly by an equation of state. In particular, it can be calculated to an arbitrary order in the virial expansion to be introduced in subsequent sections. However, for arbitrary forms of the equation of state this does not necessarily lead to simple analytical expressions.

A considerable simplification occurs in the limit where  $\Delta p$  is small compared to the upstream pressure  $p_1$ . We expand  $H(p)$  in a Maclaurin series in  $\Delta p$  around  $p_1$ , using first the integral definition of  $H(p)$  in eq. (2). Using also

$$\begin{aligned} \left(\frac{\rho_2}{\rho_1}\right)^2 &= 1 - \frac{2}{\rho_1} \left(\frac{\partial \rho_1}{\partial p_1}\right)_s \Delta p \\ &+ \left[ \frac{1}{\rho_1^2} \left(\left(\frac{\partial \rho_1}{\partial p_1}\right)_s\right)^2 + \frac{1}{\rho_1} \left(\frac{\partial^2 \rho_1}{\partial p_1^2}\right)_s \right] (\Delta p)^2 + \dots \end{aligned} \quad (6)$$

we arrive by a straightforward calculation at the result

$$\begin{aligned} \epsilon &= 1 - \left(\frac{3}{4} + \frac{\beta^4}{1 - \beta^4}\right) \frac{1}{\rho_1} \left(\frac{\partial \rho_1}{\partial p_1}\right)_s \Delta p \\ &+ \left[ \left(-\frac{11}{96} + \frac{5}{4} \frac{\beta^4}{1 - \beta^4} + \frac{3}{2} \frac{\beta^8}{(1 - \beta^4)^2}\right) \frac{1}{\rho_1^2} \left(\left(\frac{\partial \rho_1}{\partial p_1}\right)_s\right)^2 \right. \\ &\left. + \left(\frac{5}{12} + \frac{1}{2} \frac{\beta^4}{1 - \beta^4}\right) \frac{1}{\rho_1} \left(\frac{\partial^2 \rho_1}{\partial p_1^2}\right)_s \right] (\Delta p)^2 + O((\Delta p)^3) \end{aligned} \quad (7)$$

Note that each order in  $\Delta p$  in eq. (7) incorporates real-gas effects in an exact way, independent of the form of the equation of state. Eq. (7) and the developments based on it may be the most important results of this paper from a practical point of view. Later in the paper we will also consider briefly the general situation where  $\Delta p$  is large enough that general expressions like eq. (5) apply, by treating integrated versions of the isentropic equation of state.

For the product of compressibility and differential pressure there are the alternative expressions <sup>4</sup>

$$\frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_s \Delta p = \frac{\Delta p}{\rho c^2} \quad (8)$$

and (using eq. (A-1))

$$\frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_s \Delta p = \left( 1 - \frac{p}{Z} \left( \frac{\partial Z}{\partial p} \right)_T \right) \frac{\Delta p}{\gamma p} \quad , \quad Z = \frac{pV}{RT} \quad (9)$$

with

$$\gamma = \frac{c_p}{c_v} \quad , \quad c_{p,v} = c_{p,v}(p,T) \quad (10)$$

Eq. (8), where  $c$  is the velocity of sound, relates the compressibility to experimentally measurable quantities. Eq. (9) relates real-gas effects explicitly and exactly to  $Z$  factor expressions by equations of state, in a way valid both for orifices, nozzles and venturi tubes:

$$\varepsilon = 1 - \left( \frac{3}{4} + \frac{\beta^4}{1 - \beta^4} \right) \left( 1 - \frac{p}{Z} \left( \frac{\partial Z}{\partial p} \right)_T \right) \frac{\Delta p}{\gamma p_1} + \dots \quad (11)$$

The prescribed regulation <sup>6</sup> for orifice measurement of fiscal custody transfer of gas specifies  $\Delta p < 0.5$  bar. At pressures of order 100 bar and above in orifice measurements, there is then no reason to study more than the lowest order correction in  $\Delta p/p_1$ .

Our result can now be compared to the standard expression for  $\varepsilon$  for orifice measurements <sup>1</sup>, the expansion parameter of which including  $\kappa$  (defined by the isentropic equation of state on a polytropic form) instead of  $\gamma$ :

$$\varepsilon^{ISO} = 1 - (0.41 + 0.35 \beta^4) \frac{\Delta p}{\kappa p_1} \quad (12)$$

$$p\rho^{-\kappa} = \text{constant} \quad , \quad \kappa = \kappa(p,T) \quad (13)$$

One objective of this paper will be to demonstrate that  $\kappa$  is a function of both  $p$  and  $T$ , and that the standard treatment<sup>1</sup> includes real-gas effects in a way which is unclear at best.

For now we consider briefly the ideal-gas limit, where<sup>4</sup>

$$\kappa^{\text{IDEAL}} = \gamma_0 = \frac{c_p^*}{c_v^*}, \quad c_{p,v}^* = c_{p,v}^*(T) \quad (14)$$

Eq. (11) with  $Z \equiv 1$  and  $\gamma = \gamma_0$  should reproduce eq. (12); however, it does not. We will comment on this in the discussion section.

To be able to proceed with the development leading to eqs. (7) and (11), in the next section we will first introduce virial expansion predictions for the isentropic equation of state.

### 3. THE ISENTROPIC EQUATION OF STATE BY A VIRIAL EXPANSION

The isentropic equation of state is obtained by simultaneous integration of eqs. (A-1) and (A-2). Note that T in eq. (A-1) varies with pressure as given by eq. (A-2). Formally, the result has been expressed in eq. (13). This equation of state receives real-gas contributions from the specific heats as well as from the isothermal derivative in eq. (A-1). It is immediately clear that

$$\kappa \neq \gamma \quad (15)$$

except for the case of an ideal gas.

[Note that we specifically exclude the near-critical region from the range of validity of this approach, and not only because of convergence problems: The equation of state in this region is given by power laws due to universality, which are not reproduced by 'classical' equations of state to which the virial coefficients are often fitted. Universality predictions for the operation of differential pressure meters will be addressed elsewhere <sup>7</sup> .]

By eqs. (10), (14), and (A-4) through (A-8), the lowest order real-gas corrections to the specific heat ratio are given by

$$\begin{aligned} \gamma &= \gamma_0 \frac{1 + (c_p^* - c_p^*)/c_p^*}{1 + (c_v^* - c_v^*)/(c_p^* - R)} \\ &= \gamma_0 \left\{ 1 + \frac{1}{c_p^*} \left[ -T \frac{\partial^2 B_2}{\partial T^2} p - \frac{1}{RT^2} \left( 1 - T \frac{\partial}{\partial T} + \frac{T^2}{2} \frac{\partial^2}{\partial T^2} \right) (B_3 - B_2^2) p^2 + \dots \right] \right. \\ &\quad \left. + \frac{1}{c_p^* - R} \left[ \left( T \frac{\partial^2 B_2}{\partial T^2} + 2 \frac{\partial B_2}{\partial T} \right) \left( p - \frac{B_2}{RT} p^2 \right) + \frac{1}{2RT} \left( T \frac{\partial^2 B_3}{\partial T^2} + 2 \frac{\partial B_3}{\partial T} \right) p^2 + \dots \right] \right\} \end{aligned} \quad (16)$$

Similarly, the lowest order corrections in the right-hand-side partial derivatives in eqs. (A-1) and (A-2) are found to be

$$\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{\rho}{p} \left\{ 1 - \frac{B_2}{RT} p + \frac{3B_2^2 - 2B_3}{(RT)^2} p^2 + \dots \right\} \quad (17)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \left\{ 1 + \frac{1}{R} \frac{\partial B_2}{\partial T} p + \frac{T \frac{\partial}{\partial T} - 1}{(RT)^2} (B_3 - B_2^2) p^2 + \dots \right\} \quad (18)$$

Eqs. (A-1) and (A-2) can now be integrated, if we know the temperature dependence of  $B_2$  and  $B_3$ . The equations are coupled in the sense that the temperature's dependence on pressure at constant entropy on the right-hand side of eq. (A-1) is given by eq. (A-2). Note that if we seek only the first order correction to ideality in the isentropic equation of state by incorporating only  $B_2$  in eq. (1), it will suffice to use the ideal-gas version of eq. (A-2) in the integration: Lowest-order corrections in eq. (A-2), if inserted into eq. (A-1), lead to contributions of order  $(B_2)^2$ , which are of the same order in pressure as the neglected  $B_3$  contributions.

We do not address here the question of radii of convergence for the expansions. However, we assume that low order terms of the pressure-explicit expansion can be used at supercritical temperatures even above the critical pressure to obtain order-of-magnitude estimates of real-gas effects, and in any case to disclose the general form of the corrections. Table 1 shows a numerical example for a model natural gas using a (not completely realistic) cubic equation of state, for which there is fairly fast convergence (possibly of an asymptotic kind) even at 150 bar.

The calculation of real-gas effects in the isentropic equation of state requires an accurate knowledge of the general equation of state, since first and second temperature derivatives of  $B_2$  are required. By induction, even superbly comprehensive<sup>3</sup> treatments of the thermodynamics of the flow problem will have a superficial accuracy only, if an inaccurate equation of state serves as a starting point.

#### 4. LOW ORDER ISENTROPIC RELATIONS FROM A CUBIC EQUATION OF STATE

Cubic equations of state<sup>8</sup> were originally introduced in petroleum technology to facilitate two-phase equilibrium calculations. They are usually two-parameter expressions, which implies that their phenomenological accuracy corresponds to relating the second and third virial coefficients to critical parameters by the principle of corresponding states. The various cubic equations in use<sup>8</sup> are distinguished by different values of the critical Z factor,  $Z_c$ . Cubic equations are often used also at supercritical temperatures even above the critical pressure (as will be done here), although even the best ones lose their high accuracy when the pressure exceeds the critical value<sup>9</sup>.

For explicit predictions by the approach of the previous section, we use the van der Waals equation:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (19)$$

$$a = \frac{9}{8} RT_c v_c, \quad b = \frac{1}{3} v_c, \quad Z_c = \frac{3}{8} \quad (20,21,22)$$

$$B_2 = b - \frac{a}{RT}, \quad B_3 = b^2 \quad (23,24)$$

i.e.,

$$A_2(T) = \frac{1}{RT} \left( b - \frac{a}{RT} \right) = \frac{1}{8} \left( 1 - \frac{27}{8} \frac{T_c}{T} \right) \frac{T_c}{T} \frac{1}{p_c} \quad (25)$$

$$A_3(T) = \frac{a}{(RT)^3} \left( 2b - \frac{a}{RT} \right) = \frac{27}{256} \left( 1 - \frac{27}{16} \frac{T_c}{T} \right) \left( \frac{T_c}{T} \right)^3 \frac{1}{p_c} \quad (26)$$

Behind this particular choice lies the unholy motive of simplicity: Contrary to most other cubic equations, the van der Waals equation leads to rational numbers as coefficients, and its a parameter does not depend on temperature. An eventual loss of accuracy compared to

the results by more refined cubic equations is not thought to be decisive for the lowest order predictions of the present paper, especially when also the gain in clarity is considered.

In Table 1, estimates of  $A_2$  and  $A_3$  are given for a set of parameter values<sup>10</sup> for a model natural gas at a supercritical temperature. If higher orders converged as fast, the  $A_2$  and  $A_3$  terms would give  $Z$  with less than 5 % deviation even at 150 bar. Provided, of course, that the expansion can be trusted under these extreme conditions.

For the van der Waals equation,  $c_v - c_v^* \cong 0$ , by eqs. (19) and (A-5). In this particular case one can then compute the remaining real-gas corrections in eq. (16) by eq. (A-3), to any order in the virial expansion (which is the reason why eq. (A-3) has been reproduced in this paper).

By eqs. (16), (17), (18), and (20) through (24), one finds for eqs. (A-1) and (A-2), with two orders included in the pressure-explicit form of the virial expansion:

$$\left(\frac{\partial \rho}{\partial p}\right)_s = \frac{1}{\rho_0} \frac{\rho}{p} \{1 + C_2(T) p + C_3(T) p^2 + \dots\} \quad (27)$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{R}{c_p} \frac{T}{p} \{1 + D_2(T) p + D_3(T) p^2 + \dots\} \quad (28)$$

Integrated along an isentropic path, and neglecting the slow<sup>4 10</sup> temperature variation of  $c_p^*$  and  $c_v^*$ :

$$p \rho^{-\gamma_0} \{1 + E_2(T) p + \dots\} = \text{constant} \quad (29)$$

$$\frac{T_0}{T} = \left(\frac{p_0}{p}\right)^{R/c_p^*} \{1 + O(p/p_c)\} \quad (30)$$

In eq. (30),  $p_0$  and  $T_0$  are ideal-gas reference values. For our purposes it suffices to present the ideal-gas version of the  $p$ - $T$  relationship, since only the first order correction has been used in eq. (29). The coefficients are

$$\begin{aligned}
 C_2(T) &= \frac{a}{(RT)^2} \left(1 - 2\frac{R}{c_p}\right) - \frac{b}{RT} \\
 &= \left(\frac{27}{64} \left(1 - 2\frac{R}{c_p}\right) \frac{T_c}{T} - \frac{1}{8}\right) \frac{T_c}{T} \frac{1}{p_c}
 \end{aligned} \tag{31}$$

$$C_3(T) = -3 A_2(T) C_2(T) - \frac{2}{(RT)^2} \left[ b^2 + \frac{R}{c_p} a C_2(T) \right] \tag{32}$$

$$D_2(T) = \frac{a}{(RT)^2} \left(1 - 2\frac{R}{c_p}\right) \tag{33}$$

$$\begin{aligned}
 D_3(T) &= D_2(T) \left\{ -3 A_2(T) - \frac{\frac{b}{RT} + 2\frac{R}{c_p} D_2(T)}{1 - 2\frac{R}{c_p}} \right\}
 \end{aligned} \tag{34}$$

$$E_2(T) = \frac{a}{(RT)^2} - \frac{1}{1 - \frac{R}{c_p}} \frac{b}{RT} \tag{35}$$

In eq. (35), the dependence on  $T$  is understood to be transformed into a dependence on  $p$  by insertion from eq. (30). The  $R/c_p^*$  factors distinguishing eq. (35) from eq. (31) show that the temperature variation enters the real-gas corrections to the isentropic equation of state in a non-trivial way.

Table 2 shows typical values of the coefficients, calculated with the same set of parameters as in Table 1. A fortuitous cancellation takes place in eq. (31) between real-gas contributions from  $\gamma$  and the other real-gas contributions; with the  $\gamma$  contributions neglected one would get for  $C_2$  the value of  $A_2$  (Table 1) with the opposite sign. Note that this cancellation is a parameter-dependent quirk of Nature for the model natural gas used, which depends also on the choice of equation of state. However, the general form of eq. (31) shows that there will be some degree of cancellation also for other cubic equations of state, which stresses the importance of making a wise choice. (For our particular choice,  $C_3$  contributions are seen to be more important than the  $C_2$  contributions from about 100 bar on.)

Anyway, the importance of taking also the isentropic temperature variation properly into account is clearly demonstrated by Table 2: In eqs. (32) through (35) there is no such strong cancellation.

A comparison of eq. (13) to the combination of eqs. (29) and (35) serves to demonstrate that  $\kappa$  is a function also of pressure, with a considerable variation as the pressure grows from the ideal-gas state to the values of concern to us in this paper.

Eventually in this section, we calculate the isentropic enthalpy per mass unit from eqs. (2), (29) and (30) by once more neglecting the temperature variation of the ideal-gas specific heats:

$$H(p) - H_0 = \frac{\gamma_0}{\gamma_0 - 1} \frac{p}{\rho} \{1 + F_2(T) p + \dots\} \quad (36)$$

$$F_2(T) = \frac{1 - 2\frac{R}{c_p^*}}{2\gamma_0 - 1 - 2\gamma_0\frac{R}{c_p^*}} \frac{a}{(RT)^2} - \frac{1}{2\gamma_0 - 1 - \gamma_0\frac{R}{c_p^*}} \frac{b}{RT} \quad (37)$$

The dependence of  $T$  on  $p$  at any point along the isentropic path is once more assumed to be given by eq. (30). A numerical estimate of  $F_2(T)$  (Table 2) shows considerable cancellations, as in  $C_2(T)$ . (Notice that  $R/c_p^*$  can be expressed by  $\gamma_0$ , to simplify some coefficients. We have kept the form  $R/c_p^*$  to trace the origin of the various terms.)

A more comprehensive approach in the case where  $H(p) - H_0$  is not adequately given by the lowest order in  $\Delta p/p_1$ , would be to include the temperature variation<sup>10</sup> of  $c_p^*$  and  $c_v^*$  via the pressure in the integrations to obtain eqs. (29) and (36). This would probably necessitate numerical integration. Still, it would be a point to bear in mind in an analysis of the large- $\Delta p$  case, since this temperature variation would influence the amount of cancellation in eqs. (35) and (37).

In the present paper we will leave the development of the general case at this stage. For the remainder of this presentation we will once again consider the limit of small  $\Delta p/p_1$  values.

### 5. $\epsilon$ BY A VIRIAL EXPANSION OF A CUBIC EQUATION AT SMALL $\Delta p$

In preceding sections we have found a general expression for the expansibility factor for small  $\Delta p/p_1$ , as well as an approximation by two virial coefficients for the pressure derivative of the isentropic equation of state. By the results found for the magnitude of  $A_2$  and  $A_3$  (Table 1), we will now apply the combined approach for supercritical temperatures at the pressures of interest, above the critical pressure. We insert eq. (27) into eq. (7) in the limit of small differential pressure:

$$\epsilon = 1 - \left( \frac{3}{4} + \frac{\beta^4}{1 - \beta^4} \right) (1 + C_2(T_1) p_1 + C_3(T_1) p_1^2 + \dots) \frac{\Delta p}{\gamma_0 p_1} + O((\Delta p/p_1)^2) \quad (38)$$

This expression does not lend itself easily to a direct comparison with the fit (12), in which  $\kappa$  is supposed to include all real-gas effects in an unclear way. Our expression (38), on the other hand, separates out real-gas effects in a tidy way, and keeps the clearly defined and parametrized<sup>10</sup> ideal-gas value  $\gamma_0$  as part of the expansion parameter.

Eqs. (31) and (38) show that for a given temperature, a given differential pressure, and a given critical pressure, the  $C_2(T)$  term leads to a constant contribution to  $\epsilon$ , independent of the total pressure. The magnitude of this contribution is strongly dependent on the equation of state, due to the cancellations in  $C_2(T)$ . The corresponding contribution to  $\epsilon$  from the  $C_3(T)$  term is proportional to the absolute pressure  $p_1$ , for given values of all other parameters and variables.

By Table 2, the  $C_2(T)$  and the  $C_3(T)$  terms contribute with opposite signs, for the equation of state and the parameter values considered in this paper. The  $C_3(T)$  contribution is even larger than that from  $C_2(T)$  in absolute magnitude, for  $p_1$  larger than about 100 bar. This is due to the cancellations in  $C_2(T)$ , and does not reflect any convergence problems in the virial expansion.

## 6. DISCUSSION

The low order results have revealed cancellation effects, which delimits the approach's accuracy, but which will be present in disguise also in superficially more sophisticated procedures. The low order approach, including the blessing of a composition-independent formalism, is a convenient way to analyze these effects. In a forthcoming paper<sup>11</sup> we will study the equation-specific effects, via predictions by other equations of state for the virial coefficients.

For a subsonic nozzle or a venturi tube, the ISO standard's expression<sup>1</sup> for the expansibility coefficient  $\epsilon$  is reproduced by the ideal-gas limit of eq. (36) inserted into eq. (5). This holds for any value of the ratio  $\Delta p/p_1$ . Then, the present standard's formalism cannot include real-gas effects, except in an approximate and non-rigorous way via the variation of  $\kappa$  with pressure. In particular, as was shown by numerical values in Table 2, there are cancellations between real-gas effects in eq. (27), which shows the advice<sup>1</sup> to use  $\gamma$  if  $\kappa$  is not known, to be untenable.

However, the standard's expression for  $\epsilon$  for orifice plates at small  $\Delta p/p_1$  is not reproduced by our exact results even in the ideal-gas limit. What may cause this discrepancy?

Obviously, real-gas effects may be expected at high pressure also in the discharge coefficient  $C$ , in the orifice and classical nozzle (as different from the venturi nozzle) cases: The jet cross-section downstream of the mechanical contraction will bounce up again from its minimum value at the vena contracta, which should depend also on non-ideal effects in the compressibility. If we assume that the discrepancy is not simply due to a bad fit, we may thus offer this explanation: The fit (12) may include real-gas effects and more general compressibility effects also from the discharge coefficient  $C$ , and possibly also the effects of a permanent pressure fall due to dissipative losses. Concerning contributions of order  $(\Delta p/\gamma_0 p_1)^2$ , eq. (7) shows that in the ideal-gas limit they would contribute to the  $\beta$ -independent part of the discrepancy between eqs. (12) and (38) with the opposite sign of what is observed.

We would argue that real-gas effects as well as general compressibility effects in  $\epsilon$  and  $C$  should be analyzed separately during the quest for an understanding of the effects. Concerning dissipative losses, it would seem logically most consistent to include any such effects in the discharge coefficient. And for a classical nozzle, one might expect to have the same type of non-ideal effects (thermodynamical as well as hydrodynamical) as for an orifice. Why, then, does the ISO standard <sup>1</sup> adopt different formalisms for  $\epsilon$  for orifices and classical nozzles in the limit of small  $\Delta p/p_1$ ?

It follows that improvements of differential pressure metering accuracy for natural gas at high pressure will involve, as a basis, a complete theoretical and phenomenological reanalysis of the various meters. For a consistent treatment of real-gas effects, the polytropic approach should be abandoned, and the formalism of the present paper involving ideal-gas values like  $\gamma_0$  as well as corrections derivable from (or correlatable by) equations of state should be introduced. As far as possible, a composition-independent formalism should be used. Any real-gas effects in the discharge coefficients should be treated separately from those in the expansibility factors.

A completely new experimental program will be needed for the final correlation of the basic results to metering practice. These experiments should be designed so as to distinguish real-gas effects in  $C$  from those in  $\epsilon$ . Furthermore, they should distinguish clearly effects of dissipative losses from the other types of non-ideal effects.

## 7. CONCLUSION

The prediction of the real-gas expansibility factor at high pressure provides a decisive test of the reliability of equations of state, since cancellations in low order virial coefficients are involved. Further analyses can be instructively simplified by the low order approach's composition-independent formalism.

In particular, the polytropic approach with the replacement of the isentropic exponent by the specific heat ratio, is a fundamentally inconsistent part of an approach to high accuracy at high pressure.

The exact result for the expansibility factor is in basic disagreement with an ISO standard expression for orifice measurements, in the combined limit of small real gas contributions and small relative differential pressure. An analysis of possible real-gas effects and compressibility effects in general in the discharge coefficient, should enter future analyses of this discrepancy.

New calibration experiments, designed to distinguish between real gas compressibility effects in the expansibility factor and in the discharge coefficient, as well as dissipative effects, will be needed in the final correlation of this new and systematic approach to actual metering practice at high pressure.

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APPENDIX: STANDARD THERMODYNAMICAL RESULTS

We denote molar values for intensive variables by small letters. The three basic thermodynamical relations to be used are <sup>4 8</sup>

$$\left(\frac{\partial g}{\partial p}\right)_s = \frac{c_v}{c_p} \left(\frac{\partial g}{\partial p}\right)_T \quad (\text{A-1})$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{c_p} \left(\frac{\partial v}{\partial T}\right)_p, \quad gv = M \quad (\text{A-2})$$

$$c_p - c_v = - \frac{T \left(\frac{\partial p}{\partial T}\right)_v^2}{\left(\frac{\partial v}{\partial T}\right)_T} \quad (\text{A-3})$$

The deviation of  $c_p$  and  $c_v$  from the ideal-gas values  $c_p^*$  and  $c_v^*$  is given by <sup>7</sup>

$$c_p - c_p^* = - \int_0^p T \left(\frac{\partial^2 v}{\partial T^2}\right)_p dp \quad (\text{A-4})$$

$$c_v - c_v^* = \int_0^v T \left(\frac{\partial^2 p}{\partial T^2}\right)_v dv \quad (\text{A-5})$$

The paper uses virial coefficients from the volume-explicit as well as the pressure-explicit version of the virial equation of state:

$$\frac{pv}{RT} = 1 + \frac{B_2}{v} + \frac{B_3}{v^2} + \dots, \quad B_i = B_i(T) \quad (\text{A-6})$$

$$= 1 + A_2 p + A_3 p^2 + \dots$$

$$A_2 = B_2/RT \quad (\text{A-7})$$

$$A_3 = (B_3 - B_2^2)/(RT)^2 \quad (\text{A-8})$$

NOMENCLATURE

a	Coefficient in the van der Waals' equation of state
$A_2, A_3$	Virial coefficients, pressure-explicit representation ( $A_2$ also used for contraction area)
b	Coefficient in the van der Waals' equation of state
$B_2, B_3$	Virial coefficients
c	Velocity of sound
$c_p, c_p^*$	Molar specific heat at constant pressure, * for ideal gas
$c_v, c_v^*$	Molar specific heat at constant volume, * for ideal gas
C	Discharge coefficient
$C_2, C_3$	Coefficients in $(\partial g/\partial p)_s$
$D_2, D_3$	Coefficients in $(\partial T/\partial p)_s$
$E_2$	Coefficient in isentropic equation of state
$F_2$	Coefficient in isentropic enthalpy per mass unit
H, $H_0$	Isentropic enthalpy per mass unit, 0 denoting indefinite additive contribution
IDEAL	(As superscript) ideal gas value
ISO	(As superscript) ISO standard value
$\dot{m}$	Mass flow rate
M	Molar mass
O	Order
p, $p_c$	Pressure (also int. variable), c for critical value
$p_0$	Reference pressure
$p_1, p_2$	Pressure, indices denoting locations
R	Molar gas constant
s	Molar entropy
T, $T_0, T_c$	Temperature, 0 and c for reference and critical values
$u_1, u_2$	Flow velocity, indices denoting locations
v	Molar volume
Z, $Z_c$	Gas deviation factor, c for value at critical point
$\beta$	Diameter ratio
$\Delta$	Difference operator
$\epsilon$	Expansibility factor
$\gamma, \gamma_0$	Specific heat ratio, 0 for ideal gas value
$\kappa$	Isentropic (polytropic) exponent
$\rho, \rho_1, \rho_2$	Density, indices denoting locations

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TABLES

97 mole% C1, 3 mole% C2	
$T_c = 194.1 \text{ K}$	$p_c = 46.1 \text{ bar}$
At $T = 273.15 \text{ K}$ :	
$\frac{c_p^*}{R} = 4.16$	$\gamma_0 = 1.316$
$A_2 = -1/(371 \text{ bar})$	$A_3 = -1/(532 \text{ bar})^2$

Table 1: Numerical example for given composition and temperature, assuming a van der Waals gas

$C_2 = 1/(2120 \text{ bar})$	$C_3 = -1/(463 \text{ bar})^2$
$D_2 = 1/(417 \text{ bar})$	$D_3 = 1/(441 \text{ bar})^2$
$E_2 = 1/(480 \text{ bar})$	
$F_2 = 1/(1070 \text{ bar})$	

Table 2: Coefficients in expressions leading to isentropic equation of state and isentropic enthalpy, parameters as in Table 1