

THE CALCULATION OF THE ISENTROPIC EXPONENT
FOR THE METERING OF NATURAL GAS

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SUMMARY

The International Standard ISO 5167 requires the use of the isentropic exponent parameter in fluid flow calculations involving orifice plates, nozzles and venturi tubes in circular cross section conduits running full. In contrast, standard practice in the oil and gas industry is to substitute the isentropic exponent by the ratio of the specific heat capacities.

Starting with an introduction to British Gas plc, its involvement in fiscal metering and the motivation for this work, this paper describes how an algorithm for the isentropic exponent was developed for use with hydrocarbon gases. The algorithm is based on procedures written by the American Petroleum Institute and was developed in conjunction with University College, London.

The use of the isentropic exponent in preference to the ratio of specific heat capacities in gas metering computations is justified and the consequent increase in accuracy quantified.

NOTATION

α	Flow coefficient	dimensionless
d	Diameter of orifice or throat of primary device at operating conditions.	m
Δp	Differential static pressure	Pa
p_1	Upstream static pressure	Pa
γ_s	Isentropic exponent	dimensionless
ρ_1	Upstream gas density	kg/m ³
q_m	Mass rate of flow	kg/s
V	Volume	m ³
S	Specific entropy	kJ/K.kg
T	Thermodynamic temperature	K
ω	Acentric factor	dimensionless
V_m	Molar volume	m ³ /kmole
T_c	Critical temperature	K
P_c	Critical pressure	kPa
$C_{p,m}$	Molar Isobaric Heat Capacity	kJ/K.mole
C_p	Isobaric specific heat capacity	kJ/K.kg
C_v	Isochoric specific heat capacity	kJ/K.kg
p	Pressure	kPa

The above terms are as defined in ISO 5167 where appropriate

1. THE BUSINESS AND STRUCTURE OF BRITISH GAS PLC

The primary business of British Gas is the purchase, transmission and sale of natural gas to domestic, industrial and commercial customers in Great Britain. The company also attaches great importance to the activities which support its gas marketing efforts, for example, appliance trading and customer service play a key role in supporting the domestic gas market. British Gas is also active in the exploration for and the production of hydrocarbons both offshore and onshore and is therefore an integrated company concerned with all aspects of the gas supply business. In addition expertise developed in the gas business is offered for sale overseas through the British Gas International Consultancy Service.

British Gas comprises a Headquarters and twelve Regions. The Headquarters is responsible for formulation of policies, for co-ordination and the direct management of centralised operations such as gas purchasing, exploration, bulk transmission of gas, negotiation of major industrial sales contracts and research and development. Regions are largely responsible for the important customer-related activities, including the distribution and sale of gas, the retailing, installation and servicing of gas appliances, meter reading and collection of accounts and the maintenance of emergency services.

1.2 SCALE OF OPERATION

The turnover of British Gas for the year 1987/88 was £7364 million. British Gas supplies well over one half of the energy used in British homes and a third of the energy used by industry and commerce apart from fuel for transport.

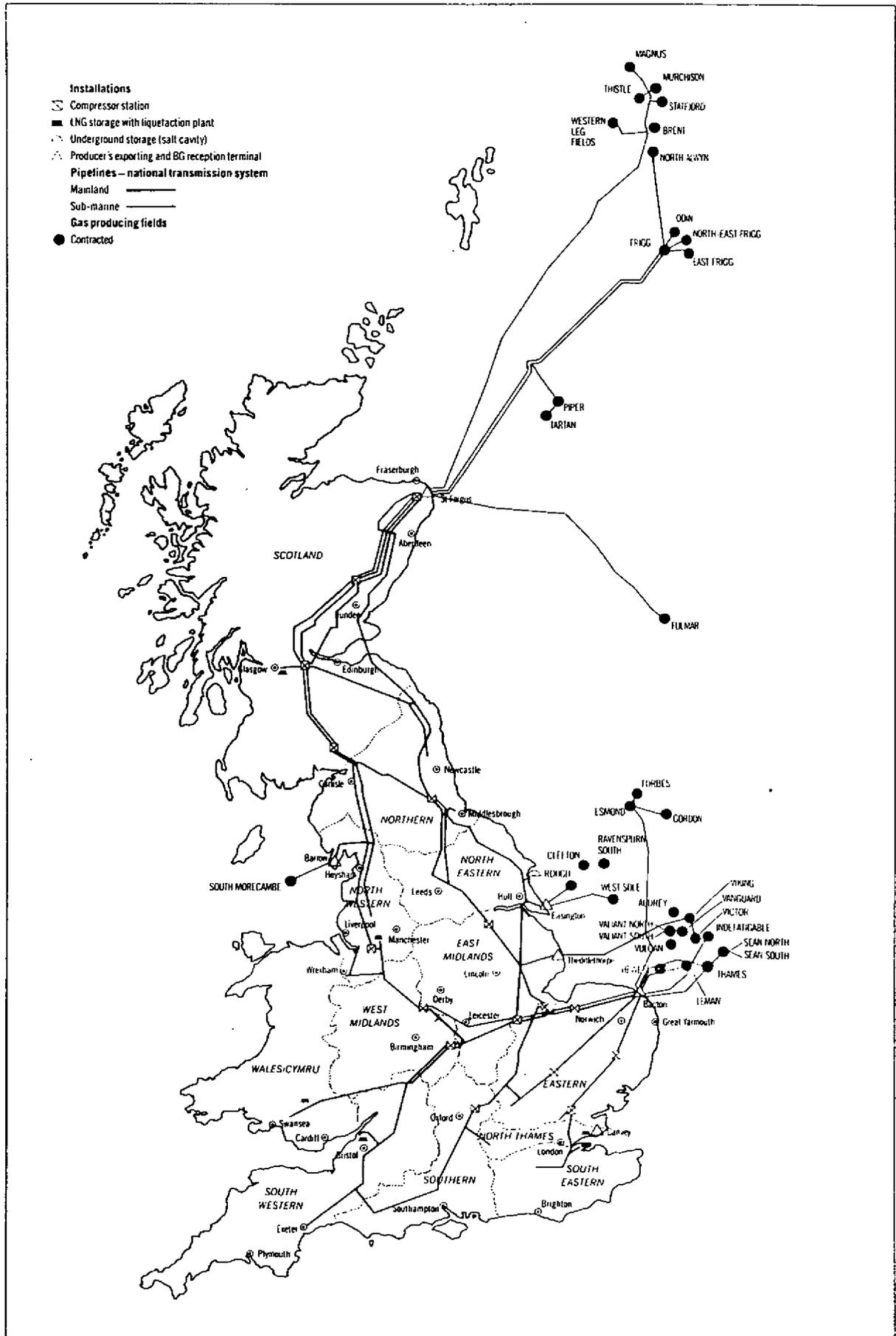
To meet the annual demand of 1.97 million million Megajoules (18706 million therms) the cost of gas purchased was £3,186 million - a significant sum in the equation of British Gas' finances. The majority of the gas is purchased from oil companies, although an increasing proportion, currently ten percent during periods of peak demand, is produced by British Gas owned and operated fields, the Morecambe Bay field being the largest.

The gas is transmitted to the Regions from reception terminals by the National Transmission System, shown in figure 1.

The National Transmission System comprises a network of some 5300km of high pressure pipeline stretching from the North of Scotland to Kent in the South East, Exeter in the South West to Swansea in South Wales.

The system operates at a pressure between 38 bar and 75 bar and is supported by fifteen compressor stations with compressors driven by industrial derivatives of high powered aircraft gas turbines typically Rolls Royce Avons and RB211s.

GAS SUPPLY AND TRANSMISSION



* The above map is indicative only.

FIGURE 1

2.1 METERING

Despite recent developments, in Morecambe Bay for example, the majority of gas brought on shore in the UK is owned by oil companies. From the oil company's reception terminal the gas is sold to British Gas for onward transmission to British Gas customers.

Where two parties are involved in this matter, the gas is metered with duplicated instrumentation - one set owned and operated by each party. The supplier, bringing the gas onshore will meter the gas for two reasons:

- a) To pay the duties owed to the Government on the gas.
- b) To charge British Gas for each unit of gas supplied.

This metering is referred to as fiscal metering.

British Gas also meter the received gas using the duplicated instrumentation in order to validate independently the sums of money paid to the supplier. Such metering is called Check Metering.

Where offshore gas storage is used fiscal metering is also required by the Department of Energy to meter the gas pumped offshore and the gas brought back onshore for tax to be paid on any net gas brought onshore.

In all of these cases the volumes passing through metering installations are very large - for example 1.6 million m³/hour - worth about £100,000/hr at the point of sale and therefore accurate metering is essential - an inaccuracy of a fraction of a percent can represent a considerable financial error between either the supplier and the purchaser or the supplier and the Department of Energy. Consequently the Gas and Oil Measurement Branch of the Department of Energy take an interest in, and lay down standards for, metering installations, actively pursuing compliance.

THE ORIFICE PLATE

All terminal gas metering installations are based on the orifice plate. The gas passes through the orifice plate causing a temporary differential pressure to occur across the plate due to the flow profile.

This differential pressure is proportional to the square of the flow and hence once all parameters are known, the flow rate of the gas can be computed from the differential pressure across the orifice plate.

To relate the actual flow through the installation to the differential pressure across the orifice plate caused by that flow it is necessary to know the pressure and temperature of the gas, its relative density, dynamic viscosity, molecular weight, density, isentropic exponent as well as the roughness of the pipe and the size of the orifice plate itself.

The differential pressure across the orifice plate, static pressure, relative density and temperature of the gas are constantly measured and the actual values are used in the calculation of flow. On line flow calculations are performed in a dedicated flow computer. The values of other parameters dependent on gas composition are placed in the computer for the calculation of the flow and only altered when a marked change of gas composition occurs.

The relationship between all these variables and the flow is given thus:

$$q_m = \alpha \epsilon \frac{\pi}{4} d^2 \sqrt{2 \Delta p \cdot \rho_1}$$

Where $\epsilon = 1 - (0.41 + 0.35\beta^4)\Delta p/\gamma_s p_1$

and α = flow coefficient

d = diameter of orifice or throat

Δp = differential static pressure across orifice

ρ_1 = upstream gas density

β = ratio of orifice or throat diameter to pipe diameter

γ_s = isentropic exponent

p_1 = upstream gas pressure

q_m = mass rate of flow

The above terms are as defined in ISO 5167.

One of these variables, the subject of this paper, is the isentropic exponent. It can be seen that the flow through the orifice plate is dependent on the isentropic exponent through the expansibility factor.

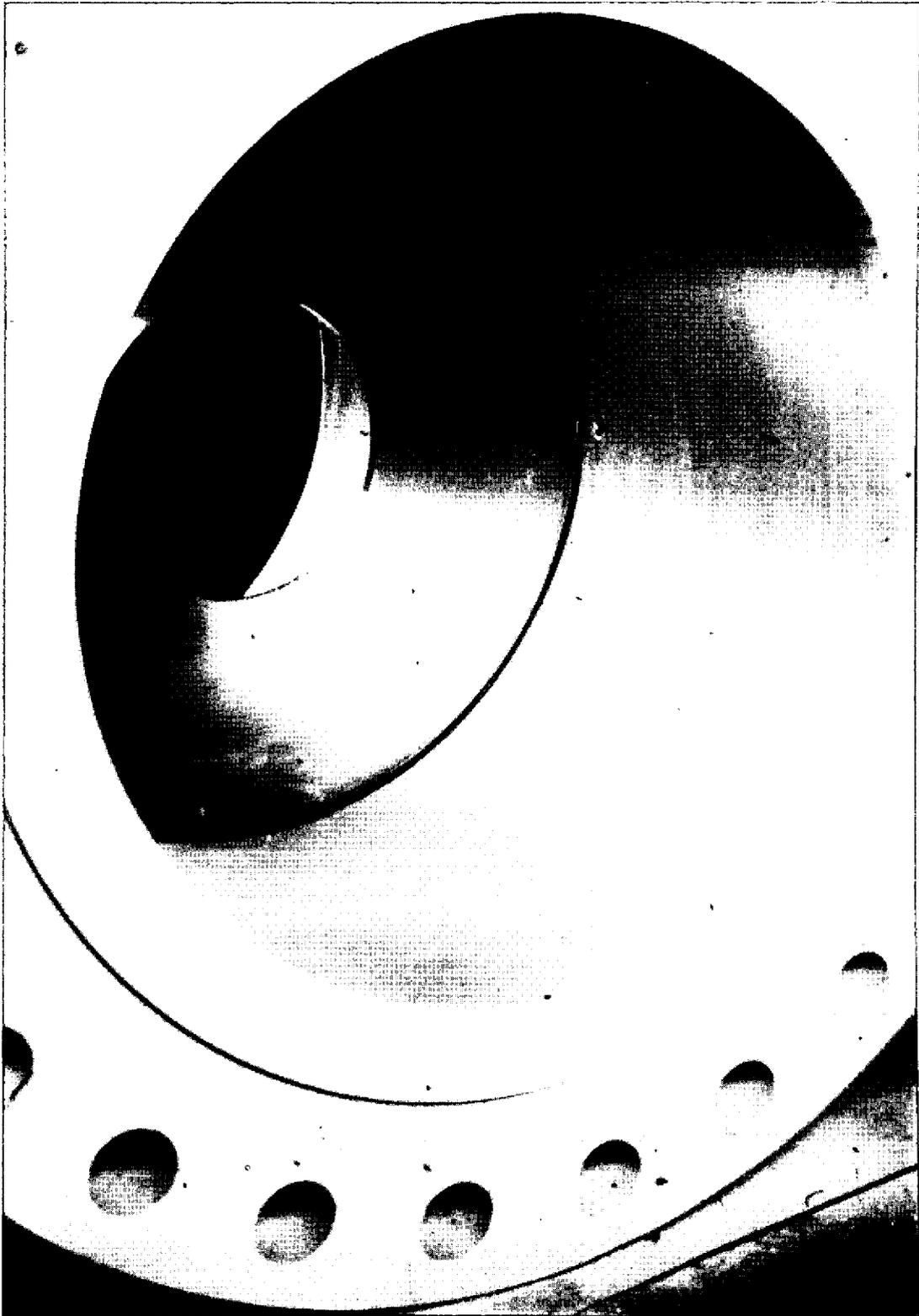


FIGURE 2
AN ORIFICE PLATE

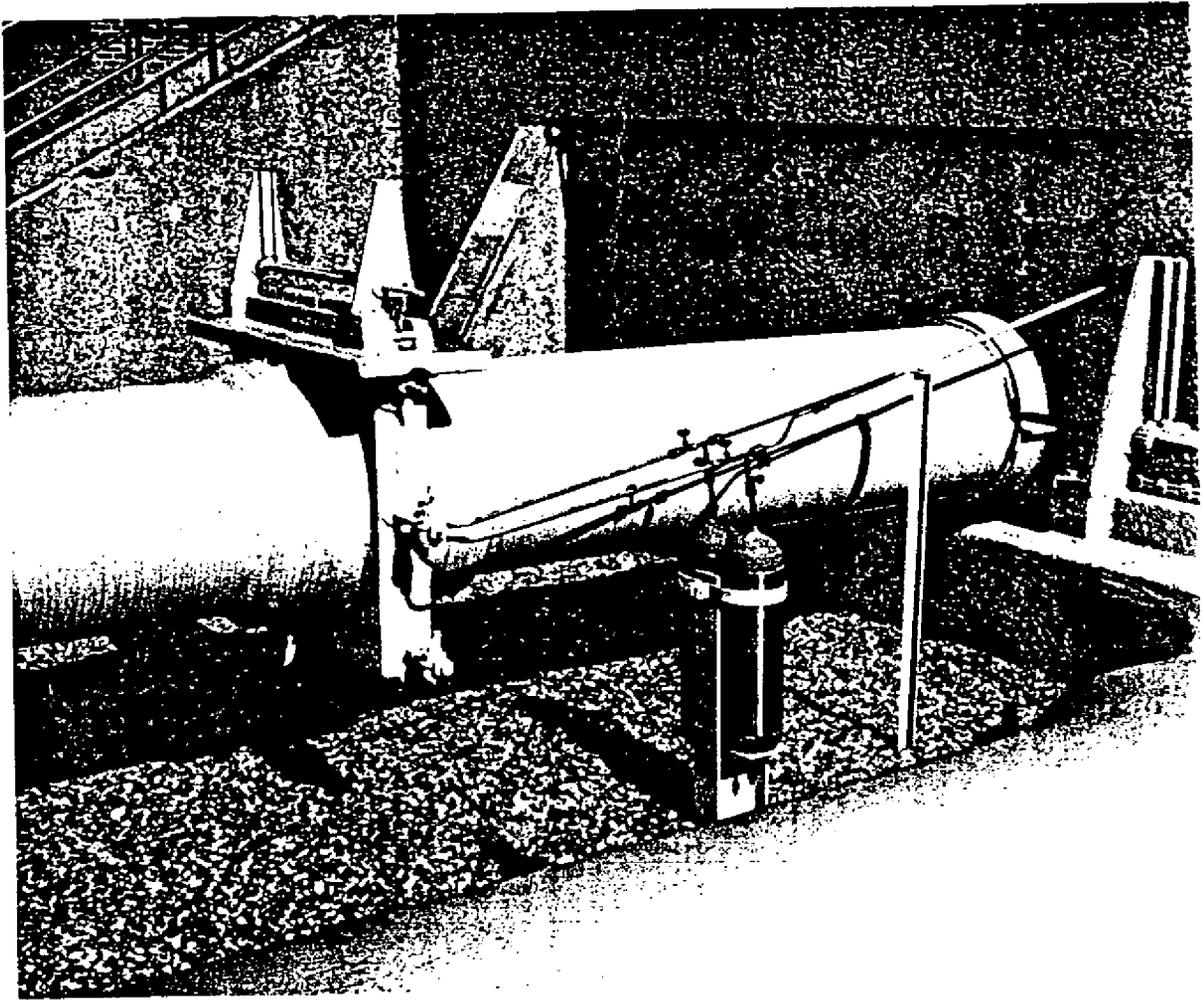


FIGURE 3

ORIFICE PLATE WITH DIFFERENTIAL TAPPINGS

3. THE MOTIVATION TO CALCULATE THE ISENTROPIC EXPONENT

BS 1042 and its International equivalent ISO 5167 state that although the isentropic exponent should be used in the above calculation of flow, it is recognised that there are many gases and vapours for which no values of the isentropic exponent are available. In such a case the standards state that the ratio of the specific heat capacities of the gas may be used in place of the isentropic exponent.

This use of the ratio of specific heat capacities rather than the isentropic exponent is widespread throughout the oil and gas industry. This follows because there is no Department of Energy approved method for the calculation of the isentropic exponent for many fluids and hence, in accordance with the standards, the industry reverts to the use of the ratio of the specific heat capacities. However preliminary calculations (Section 4) of the isentropic exponent for hydrocarbons have found that the exponent differs markedly - typically by 15% from the ratio of the specific heat capacities. This difference is typically equivalent to a 0.05% change in flow, and the financial effect can be very significant with a difference of £150,000 per annum for a typical metering installation.

There is therefore considerable motivation to determine accurately the isentropic exponent of natural gas mixtures within the oil and gas industry.

4. THE CALCULATION OF THE ISENTROPIC EXPONENT

Certain gases over a specific range of temperatures and pressures behave as ideal gases, where their compressibility factors are practically unity. The properties of ideal gases can be determined simply and as a result gases are often treated as if they were ideal gases, ie. their compressibility factors are taken as unity, the errors introduced being small and the advantages in simplifying calculations great. For an ideal gas, the isentropic exponent is simply the ratio of the isobaric specific heat capacity, (the specific heat capacity at constant pressure), C_p , to the isochoric specific heat capacity, (the specific heat capacity at constant volume), C_v . Both can be determined easily and hence the isentropic exponent for an ideal gas is found by a mere division. ISO 5167/BS 1042 allows gas mixtures to be treated as ideal gases if the real isentropic exponent cannot be determined and so the pseudo-isentropic exponent used in flow calculations is C_p/C_v , the ratio of specific heat capacities.

However, real gases - the gases met in the oil and gas industry - are not ideal gases, but gases with a non-constant value of compressibility. Therefore there are errors between the ratio of specific heat capacities, C_p/C_v , and the isentropic exponent.

To calculate accurately the isentropic exponent for natural gas it is first necessary to drop all assumptions that gas mixtures behave as ideal gases, and consider the mixture as a real gas whose compressibility will change with pressure and temperature.

Following discussions between the Department of Energy and British Gas it was agreed that the basis of all calculations should be the American Petroleum Institute (API) Technical Data Book. This data book contains a substantial selection of procedures for the calculation of a wide range of gas mixture parameters, but does not include a procedural method for determining the isentropic exponent.

British Gas ultimately required a computer program to calculate two parameters:

- 1) the ratio of specific heat capacities,
- 2) the isentropic exponent.

The values of the isochoric, C_v and isobaric, C_p , specific heat capacities required in (1) were thought to be necessary in the calculation of the isentropic exponent and thus were to be determined first. These heat capacities are calculated initially by treating the gas, whose properties are required, as an ideal gas and then correcting for pressure and temperature to determine the real gas specific heat capacities. The heat capacities are therefore a function of pressure and temperature for two reasons:

1. The ideal heat capacities are temperature dependent.
2. The density of the gas is a function of pressure and temperature. This affects the molar volume which influences the deviation between the ideal and real heat capacities, even though these properties are specific. ie in units of kJ/kg.K .

In order to obtain the ideal isobaric heat capacity for a mixture, the API Technical Data Book states that the individual component ideal heat capacities are weighted by their weight fractions and summed. The mixture isochoric heat capacity is found from the real mixture isobaric heat capacity.

The basic simplified steps to obtain the specific heat capacities to API procedures are shown in Figure 4.

The calculation of the specific heat capacities achieved the first stage towards the increased accuracy of flow metering as it gave British Gas a more accurate value of the ratio of the specific heat capacities by treating the gas as a real gas mixture and calculating to API procedures.

The next stage was to formulate an algorithm to calculate the isentropic exponent for a real gas mixture. The derivation of the algorithm was required since there is no explicit method for the calculation of the isentropic exponent in the API Technical Data Book. Nevertheless the mandate from the Department of Energy insisted that the final isentropic exponent algorithm should be to API procedures or in accordance with good oilfield practice and thus it was necessary that each term of the final algorithm should be sourced from these procedures. Further the Department of Energy required that the final algorithm should be certified by an independent authority recognised by the Oil and Gas Industry.

Early attempts by British Gas to formulate an algorithm were unsuccessful as literature researched on the subject did not provide a derivation for the isentropic exponent but conveniently skirted around the function merely stating that the exponent was a function of numerous variables. Therefore British Gas approached Professor M.L. McGlashan of University College, London who is a world authority in this field.

Professor McGlashan, in conjunction with British Gas, produced an exhaustive derivation of the isentropic exponent. This derivation forms the first part of Appendix A.

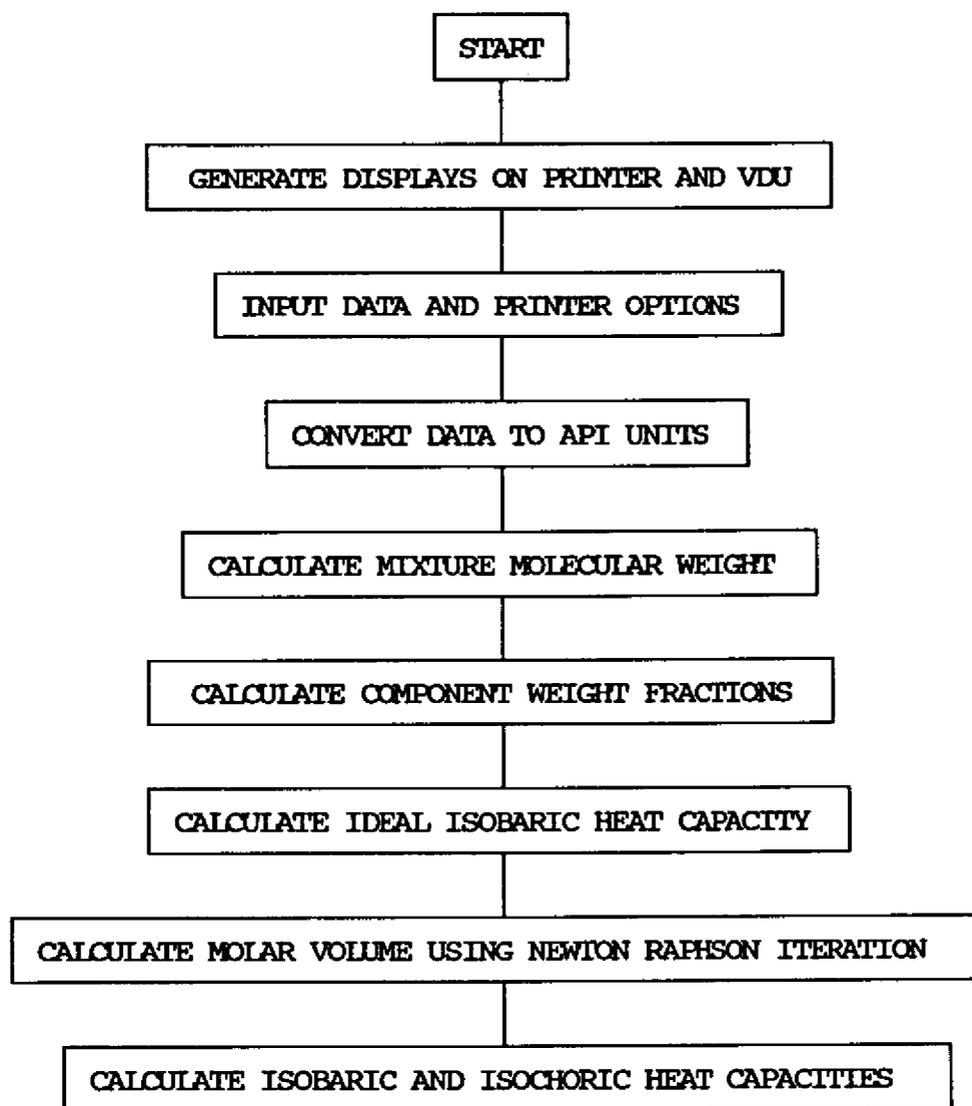


FIGURE 4

THE SIMPLIFIED STEPS TO OBTAIN THE SPECIFIC
HEAT CAPACITIES TO API PROCEDURES

The next aim was to link the terms in this equation to API procedures. Ideally each term in the isentropic exponent equation should be taken straight from an API procedure to satisfy the Department of Energy's requirements.

A further document was then produced linking each term of the isentropic exponent equation to an API procedure, although linking the partial differential terms to API procedures involved detailed analysis. The partial derivatives were available from the API procedures but these derivatives were not of the mixture under analysis but of a heavy reference fluid (octane) and a simple reference fluid. To determine properties of a mixture under analysis, the existing API procedures apply interpolation between the two reference fluid properties. The interpolation is based on the relative acentric factors.

Further work was therefore carried out on these interpolative procedures so that a partial derivative could be determined for the required mixture. As a result the API procedures were fully linked to the isentropic exponent algorithm. In all the analysis no approximations were made and therefore the final derivation of the isentropic exponent is exact.

British Gas are currently writing software titled 'VIPAN II' that will incorporate Professor McGlashan's algorithm, together with procedures employing the API interpolative techniques to determine the partial derivatives required from the API reference fluids. The final algorithm is derived in Appendix A and given in Figure 5.

$$\gamma_s = \frac{-V_m \cdot C_{p,m}}{p \cdot \left(\frac{\partial V_m}{\partial p}\right)_T \cdot C_{p,m} + T \cdot \left(\frac{\partial V_m}{\partial T}\right)_p \cdot p}$$

Where γ_s = Isentropic Exponent
 V_m = Molar Volume
 p = Pressure
 $C_{p,m}$ = Molar Isobaric Heat Capacity
 T = Thermodynamic Temperature (Temperature measured on an absolute scale).

Figure 5 - The Isentropic Exponent Algorithm

The accuracy of the final isentropic exponent value is dependent only on the accuracy of the API procedures. The API state that errors between the calculated and experimental specific heat ratios, on which the algorithm is based, rarely exceed two percent except in a critical region where errors in excess of ten percent can occur. This critical region is described within the API documentation and it is found that natural gas metering installation conditions are well outside this region. Strictly the final API procedure employed is only valid for pure hydrocarbon gases. The errors introduced by applying the procedure to Natural Gas Mixtures (which are predominantly methane) are thought to be small and this has been accepted by the Department of Energy.

Once finished, "VIPAN II" will be available for purchase together with the signed documentation prepared by Professor McGlashan. It is then intended that "VIPAN II" will be used to calculate the ratio of specific heat capacities and the isentropic exponent for fiscal metering installations.

5. CONCLUSION

British Gas, with assistance from University College, London, has developed a procedure for calculating the isentropic exponent to API procedures. It has been established that the isentropic exponent can differ markedly from the ratio of specific heat capacities that has hitherto dominated flow equations.

ISO 5167/BS 1042 states that the ratio of specific heat capacities is only to be used when the isentropic exponent is not available and hence the procedure developed has an important consequence for the oil and gas industry as it enables the isentropic exponent to be calculated for a much wider range of gas mixtures.

6. REFERENCES

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7. ACKNOWLEDGMENTS

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APPENDIX A

THE DERIVATION OF THE ISENTROPIC EXPONENT OF A REAL FLUID

Defining the isentropic exponent γ_S by

$$\gamma_S \stackrel{\text{def}}{=} -(\partial \ln p / \partial \ln V)_S = -(V/p)(\partial p / \partial V)_S, \quad (1)$$

where p denotes pressure, V volume and S entropy, we have, by use of "the rule for changing the variable held constant":

$$\begin{aligned} \gamma_S &= -(V/p) \{ (\partial p / \partial V)_T + (\partial p / \partial T)_V (\partial T / \partial V)_S \} \\ &= -(\partial \ln p / \partial \ln V)_T [1 + (\partial V / \partial p)_T (\partial p / \partial T)_V (\partial T / \partial V)_S], \end{aligned} \quad (2)$$

where T denotes thermodynamic temperature: and thence by use of "the -1 rule":

$$\gamma_S = -(\partial \ln p / \partial \ln V)_T [1 - ((\partial V / \partial T)_p / (\partial V / \partial T)_S)], \quad (3)$$

and by use of "the -1 rule" again:

$$\gamma_S = -(\partial \ln p / \partial \ln V)_T [1 + (\partial V / \partial T)_p (\partial S / \partial V)_T / (\partial S / \partial T)_V], \quad (4)$$

and thence, by use of the Maxwell relation: $(\partial S/\partial V)_T = (\partial p/\partial T)_V$:

$$\gamma_S = -(\partial \ln p/\partial \ln V)_T(1 + (\partial V/\partial T)_p(\partial p/\partial T)_V/(\partial S/\partial T)_V), \quad (5)$$

and by use of "the -1 rule" for a third time:

$$\gamma_S = -(\partial \ln p/\partial \ln V)_T[1 - \{(\partial V/\partial T)_p\}^2/(\partial V/\partial p)_T(\partial S/\partial T)_V], \quad (6)$$

which, by use of the definitions: of the isobaric expansivity

$\alpha \stackrel{\text{def}}{=} V^{-1}(\partial V/\partial T)_p$, of the isothermal compressibility

$\kappa_T \stackrel{\text{def}}{=} -V^{-1}(\partial V/\partial p)_T$, and of the heat capacity at constant volume

$C_V \stackrel{\text{def}}{=} T(\partial S/\partial T)_V$, becomes

$$\gamma_S = -(\partial \ln p/\partial \ln V)_T(1 + T\alpha^2V/\kappa_T C_V), \quad (7)$$

which, by virtue of the exact relation:

$$C_p = C_V + T\alpha^2V/\kappa_T,$$

where $C_p \stackrel{\text{def}}{=} T(\partial S/\partial T)_p$ denotes the heat capacity at constant pressure,

can be written in the form;

$$\gamma_S = -(\partial \ln p/\partial \ln V)_T C_p/C_V, \quad (8)$$

$$\gamma_S = -(\partial \ln p/\partial \ln V)_T C_p/(C_p - T\alpha^2V/\kappa_T), \quad (9)$$

$$\gamma_S = C_p/(p\kappa_T C_p - T\alpha^2pV). \quad (10)$$

Every equation above is exact. Every equation applies exactly to any homogeneous (one-phase) real fluid or fluid mixture. There are no approximations in any of the equations. In particular, none of them assumes that the fluid is a perfect gas, or that it is approximately a perfect gas. The concept of a "perfect gas" is nowhere used in the above derivation.

Substituting for α and κ_T in equation (10) and using equation (2), the isentropic exponent γ_s can be expressed in the exactly equivalent form:

$$\gamma_s = - V_m C_{p,m} / [p(\partial V_m / \partial p)_T C_{p,m} + T \{(\partial V_m / \partial T)_p\}^2 p], \quad (11)$$

where V_m denotes molar volume, T the thermodynamic temperature, p the pressure and $C_{p,m}$ molar heat capacity.

The independent variables are chosen throughout this analysis as T and p together with the $(C - 1)$ independent mole fraction x_i , or the $(C - 1)$ mass fractions w_i , of the C components of the gas mixture.

According to API Technical Data Book 6B1.8-1:

$$z = z^{(0)} + (\omega/\omega^{(h)})(z^{(h)} - z^{(0)}), \quad (12)$$

where

$$z \stackrel{\text{def}}{=} pV_m/RT, \quad (13)$$

so that

$$V_m = V_m^{(0)} + (\omega/\omega^{(h)})(V_m^{(h)} - V_m^{(0)}). \quad (14)$$

If we can calculate $V_m^{(0)}$ and $V_m^{(h)}$ then, given the recipe (equation API 2-0.2, p.2-1):

$$\omega = \sum_{i=1}^{i=C} X_i \omega_i^*, \quad (15)$$

where ω_i^* denotes the acentric factor of the pure substance i and the summation is over the C components of the mixture, and given that $\omega^{(h)} = 0.3978$, we can calculate V_m for any mixture.

It follows from equation (14) that

$$(\partial V_m / \partial p)_T = (\partial V_m^{(0)} / \partial p)_T + (\omega / \omega^{(h)}) \{ (\partial V_m^{(h)} / \partial p)_T - (\partial V_m^{(0)} / \partial p)_T \}, \quad (16)$$

and

$$(\partial V_m / \partial T)_p = (\partial V_m^{(0)} / \partial T)_p + (\omega / \omega^{(h)}) \{ (\partial V_m^{(h)} / \partial T)_p - (\partial V_m^{(0)} / \partial T)_p \}, \quad (17)$$

so that if we can calculate $(\partial V_m^{(0)} / \partial p)_T$, $(\partial V_m^{(h)} / \partial p)_T$, $(\partial V_m^{(0)} / \partial T)_p$, and $(\partial V_m^{(h)} / \partial T)_p$ then we can calculate $(\partial V_m / \partial p)_T$ and $(\partial V_m / \partial T)_p$ for any mixture.

According to API 6B1.8-2

$$z^{(i)} = f(V_R^{(i)}, T_R) = f(p_C V_m^{(i)} / RT_C, T / T_C), \quad (18)$$

so that

$$p = (RT / V_m^{(i)}) f(p_C V_m^{(i)} / RT_C, T / T_C). \quad (19)$$

Writing the function f explicitly we then obtain

$$\begin{aligned} p = & RT V_m^{(i)-1} \\ & + (b_1 T - b_2 T_C - b_3 T_C^2 T^{-1} - b_4 T_C^3 T^{-2}) (R^2 T_C p_C^{-1} V_m^{(i)-2}) \\ & + (c_1 T - c_2 T_C + c_3 T_C^3 T^{-2}) (R^3 T_C^2 p_C^{-2} V_m^{(i)-3}) \\ & + (d_1 T + d_2 T_C) (R^6 T_C^5 p_C^{-5} V_m^{(i)-6}) \\ & + c_4 \beta (R^3 T_C^5 p_C^{-2} V_m^{(i)-3} T^{-2}) \exp(-\gamma R^2 T_C^2 p_C^{-2} V_m^{(i)-2}) \\ & + c_4 \gamma (R^5 T_C^7 p_C^{-4} V_m^{(i)-5} T^{-2}) \exp(-\gamma R^2 T_C^2 p_C^{-2} V_m^{(i)-2}), \end{aligned} \quad (20)$$

where the parameters b_1 , b_2 , b_3 , b_4 , c_1 , c_2 , c_3 , c_4 , d_1 , d_2 , β , and

γ are displayed on API p.6-75 for "the simple fluid" $i = 0$, and for "the heavy referenc

By differentiation of (20) with respect to $V_m^{(i)}$ at constant T it follows that

$$\begin{aligned}
 (\partial p / \partial V_m^{(i)})_T &= -RTV_m^{(i)-2} \\
 &- 2(b_1T - b_2T_C - b_3T_C^2T^{-1} - b_4T_C^3T^{-2})(R^2T_C p_C^{-1}V_m^{(i)-3}) \\
 &- 3(c_1T - c_2T_C + c_3T_C^3T^{-2})(R^3T_C^2 p_C^{-2}V_m^{(i)-4}) \\
 &- 6(d_1T + d_2T_C)(R^6T_C^5 p_C^{-5}V_m^{(i)-7}) \\
 &- 3c_4\beta(R^3T_C^5 p_C^{-2}V_m^{(i)-4}T^{-2})\exp(-\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2}) \\
 &- 5c_4\gamma(R^5T_C^7 p_C^{-4}V_m^{(i)-6}T^{-2})\exp(-\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2}) \\
 &+ 2c_4\gamma(R^5T_C^7 p_C^{-4}V_m^{(i)-6}T^{-2})(\beta + \\
 &\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2})\exp(-\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2})
 \end{aligned} \tag{21}$$

and by differentiation of (20) with respect to T at constant $V_m^{(i)}$ it follows that

$$\begin{aligned}
 (\partial p / \partial T)_{V_m^{(i)}} &= RV_m^{(i)-1} \\
 &+ (b_1 + b_3T_C^2T^{-2} + 2b_4T_C^3T^{-3})(R^2T_C p_C^{-1}V_m^{(i)-2}) \\
 &+ (c_1 - 2c_3T_C^3T^{-3})(R^3T_C^2 p_C^{-2}V_m^{(i)-3}) \\
 &+ d_1(R^6T_C^5 p_C^{-5}V_m^{(i)-6}) \\
 &- 2c_4(R^3T_C^5 p_C^{-2}V_m^{(i)-3}T^{-3})(\beta + \\
 &\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2})\exp(-\gamma R^2T_C^2 p_C^{-2}V_m^{(i)-2}),
 \end{aligned} \tag{22}$$

from which $(\partial p / \partial V_m^{(i)})_T$ and $(\partial p / \partial T)_{V_m^{(i)}}$ can

be calculated for $i = 0$ and for $i = h$ given the same information as was used to calculate $V_m^{(0)}$ and $V_m^{(h)}$, and the values of $V_m^{(0)}$ and $V_m^{(h)}$.

Given that

$$(\partial V_m^{(i)}/\partial T)_P = -(\partial p/\partial T)V_m^{(i)}/(\partial p/\partial V_m^{(i)})_T,$$

and that

$$(\partial V_m^{(i)}/\partial p)_T = ((\partial p/\partial V_m^{(i)})_T)^{-1},$$

we can use (21) and (22) to calculate $(\partial V_m^{(0)}/\partial p)_T$, $(\partial V_m^{(h)}/\partial p)_T$, $(\partial V_m^{(0)}/\partial T)_P$, and $(\partial V_m^{(h)}/\partial T)_P$.

We can then use (16) and (17) to calculate $(\partial V_m/\partial p)_T$ and $(\partial V_m/\partial T)_P$ for our mixture.

Hence, using these and the existing API procedures, the isentropic exponent can be calculated using equation (11).