G. Emanuel.[3] The authors utilize the Redlich-Kwong (R-K) thermal equation of state and a polynomial in temperature T for the zero-pressure specific heat c_p^+ to examine nonideal behavior of methane for isentropic nozzle flow. Nonideal behavior occurs as the state of the gas approaches the coexistence curve, particularly in the vicinity of the critical point. At the end of the paper, there is a useful discussion by M. Vinokur. Additional comments are presented here.

The R-K state equation may be superior to van der Waals' equation, but is also subject to the same criticisms (Emanuel, 1987). For example, one can show that the compressibility factor at the critical point, Z_c, equals 1/3 for the R−K equation, whereas the experimental methane value is 0.28631 (Friend et al., 1989) This agreement is not good and would be worse for the many polyatomic gases whose Z_c value is below that of methane. As with the van der Walls equation (Emanuel, 1987), there is a multiplicity of critical-point solutions for the two free parameters, a and b, in the R-K equation. Bober and Chow utilize the form

$$a=\frac{\alpha R^2 T_c^{5/2}}{9p_c},\ b=\frac{RT_c}{3\alpha p_c}$$

where it can be shown that

$$\alpha = 1 + 2^{1/3} + 2^{2/3} = 3.8473$$

An alternative solution would be

$$a=\frac{1}{3}\,\alpha R T_c^{3/2} v_c,\ b=\frac{v_c}{\alpha}$$

With either set, the R-K equation is

$$p_r=\frac{3\alpha T_r}{\alpha v_r - 1}-\frac{\alpha^2}{T_r^{1/2} v_r(\alpha v_r + 1)}$$

in reduced variables. The equation for the entropy is also readily written in terms of reduced variables. The isentrope solution is then independent of the choice made for a and b. However, when reverting back to dimensional variables, there is a difference, and it is uncertain which a, b set provides the most realistic isentrope.

While a paper by Tsien is referenced, readers should be alerted to its errors, listed in Tsien (1947).

As noted, the zero-pressure specific heat c_p^+ is represented by a polynomial in T, as is frequently done. An alternative approach is to utilize an harmonic oscillator approximation for the vibrational modes of a polyatomic molecule (Emanuel, 1987). In terms of the constant volume, zero-pressure, specific heat c_v^+, this also yields closed-form results for both the $\int c_v^+ dT$ and $\int (c_v^+/T)dT$ integrals that appear in the internal energy, entropy fundamental equations.

Evaluation of nonideal gas flows, isentropic or otherwise, is most accurately achieved with computerized thermodynamic properties. (An introductory presentation, along with additional references, can be found in Emanuel (1987) and Stewart et al. (1986).) One reason for this is that no state equation, such as van der Waals or the R-K equation, can represent the non-analytic critical-point behavior of real fluids (Emanuel, 1987). This is true even though all free parameters in the state equation are evaluated using critical point properties. Consequently, the nonideal trend exhibited by Bober and Chow in Fig. 12 for the polytropic exponent n may not be appropriate for methane.

A more important reason is that the computerized approach is based on extensive experimental data, including coexistence curve data and data in the vicinity of the critical point. Methane has been treated in this manner by Friend et al. (1989).

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Additional References

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Authors' Closure

The authors would like to thank Dr. Leung for pointing out his previous work on the subject of nonideal gas flows. As he mentioned in his discussion, our analysis of nonideal gas flows through converging-diverging nozzles was more extensive than the work of Leung and Epstein. We were also pleased to see that for the critical flow parameters cited in his discussion, our work is in good agreement with theirs as well, as the experimental work of Johnson. However, it should be noted that their generalized charts of G/G^{id} versus $P_{r,0}$ for various values of $T_{r,0}$ do not account for the possibility that the flow may become two-phase before critical flow conditions are reached. For example, when stagnation conditions for methane at a $(T_{r,0},\ P_{r,0})$ = (1.1, 2.0) were used in our program, the liquid state was reached at a Mach number equal to 0.675. Therefore, the Redlich-Kwong equation was not valid all the way to the choked nozzle condition. The curves for $T_{r,0}$ of 1.05 and 1.0 are even less likely to be valid.

The authors would also like to thank Dr. Emanuel for providing additional useful information regarding the behavior of nonideal gas flows, especially near the critical point. For such cases, the use of computerized thermodynamic properties, as suggested by Dr. Emanuel, is an alternative which one may choose when a high degree of accuracy is required.