A correlation of the isentropic exponents of real gases

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In previous publications, three isentropic exponents, k_{pv}, k_{Tv}, k_{pT}, have been introduced, which when used in place of the classical isentropic exponent $k=c_p/c_v$ in the ideal gas isentropic change equations, the latter can describe very accurately the isentropic change of real gases. The present work provides a general method for determining the values of k_{pv}, k_{Tv}, k_{pT} within the ranges of reduced pressure $p_r=0$ to 10 and of reduced temperature $T_r=1$ to 3.5, thus allowing the calculation of the isentropic flow of those real gases for which no detailed thermodynamic data are available. The accuracy obtained is limited only by the accuracy of the generalized Lee-Kesler equation of state, which is employed in the method developed.

Keywords: real gases; isentropic change; isentropic exponents

Introduction

In previous publications[1,2,3] three isentropic exponents, k_{pv}, k_{Tv}, k_{pT}, have been introduced, which when used in place of the classical isentropic exponent $k=c_p/c_v$ (where c_p and c_v are the constant pressure and constant volume specific heats, respectively) in the ideal gas isentropic change equations, the latter can describe very accurately the isentropic change of a real gas, i.e.

$$pv^{k_{pv}}=\text{const.} \tag{1}$$

$$Tv^{(k_{Tv}-1)}=\text{const.} \tag{2}$$

$$p^{(1-k_{pT})}T^{k_{pT}}=\text{const.} \tag{3}$$

Therefore, small or differential isentropic changes of real gases may be calculated directly from the above equations. In the case of extended isentropic changes, the calculation should be performed step by step because, as is the case with k, the values of the new exponents depend on the state variables. The analytical expressions of the three exponents are[4–6]

$$k_{pv}=-\frac{v}{p}\frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T \tag{4}$$

$$k_{Tv}=1+\frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v \tag{5}$$

$$k_{pT}=\left(1-\frac{p}{c_p}\left(\frac{\partial v}{\partial T}\right)_p\right)^{-1} \tag{6}$$

Their values are not independent of each other; they are linked by the equation[4–6]

$$\frac{k_{pv}}{k_{Tv}-1}=\frac{k_{pT}}{k_{pT}-1} \tag{7}$$

The numerical values of k_{pv}, k_{Tv}, k_{pT} can be calculated by use of Equations 4, 5, and 6, provided that the thermal and caloric equations of state of the real gas under examination are accurately known. Unfortunately, this is seldom the case, since detailed thermodynamic data are available only for a few gases. It is, therefore, necessary to make approximations by using generalized equations of state as, for example, are the Pitzer[7] correlation, the Redlich-Kwong,[8] or the Redlich-Kwong-Soave[9,10] generalized equation of state and the Lee-Kesler[11] correlation. In previous publications,[12,13] the Redlich-Kwong and the Redlich-Kwong-Soave correlations have been employed for this purpose. In the present work the Lee-Kesler correlation is employed for developing a more accurate and general method for determining the values of k_{pv}, k_{Tv}, k_{pT} in the ranges of reduced pressure and temperature $p_r=0$ to 10, $T_r=1$ to 3.5, for those real gases for which not enough thermodynamic data are available. The accuracy of the method is limited only by the accuracy of the Lee-Kesler correlation, described later by Equations 8 to 16.

The usefulness of the three real gas exponents in engineering lies in the fact that they allow the use of the simple isentropic change equations of the ideal gas to be applied with great accuracy to real gases. The practical usefulness is also due to the frequent appearance of the classical exponent k in various relations encountered in fluid mechanics, gas dynamics, thermodynamics, heat transfer, theory of internal combustion engines and compressors, etc. For real gases, these relations become more accurate if k is replaced by the appropriate real gas exponent. Numerical examples[3] in real engineering situations showed that the use of the real gas exponents leads (under the conditions examined) to a 5% improvement in the accuracy of the calculated value of the blow-by rate in internal combustion engines, high-pressure compressors, or steam turbines, and to a 50% improvement in the calculated value of pressure or volume of the isentropic expansion or compression.

According to the Lee-Kesler[11] correlation, the compressibility factor Z of a real gas is approximated as

$$Z=\frac{pv}{RT}=Z_0+\frac{\omega}{0.3978}(Z_r-Z_0) \tag{8}$$

where p, v, T, ω, R stand for the pressure, the specific volume, the temperature, the acentric factor, and the constant of the real gas under examination, and

$$Z_0=\frac{p_r v_{0r}}{T_r}=1+\frac{B_0}{v_{0r}}+\frac{C_0}{v_{0r}^2}+\frac{D_0}{v_{0r}^5}+\frac{c_{04}}{T_r^3 v_{0r}^2}\left(\beta_0+\frac{\gamma_0}{v_{0r}^2}\right)\exp\left(-\frac{\gamma_0}{v_{0r}^2}\right) \tag{9}$$

$$Z_r=\frac{p_r v_{rr}}{T_r}=1+\frac{B_r}{v_{rr}}+\frac{C_r}{v_{rr}^2}+\frac{D_r}{v_{rr}^5}+\frac{c_{r4}}{T_r^3 v_{rr}^2}\left(\beta_r+\frac{\gamma_r}{v_{rr}^2}\right)\exp\left(-\frac{\gamma_r}{v_{rr}^2}\right) \tag{10}$$

In the above equations p_r $(=p/p_c)$ and T_r $(=T/T_c)$ are the reduced pressure and temperature, respectively, i.e., the pressure and temperature normalized by the corresponding critical values p_c, T_c. Properties v_{0r} and v_{rr} denote reduced volumes, whose values are different from the reduced volume v_r $(=v/v_c)$ corresponding to the pair of state variables p_r, T_r. Quantities B_0, C_0, D_0, B_r, C_r, D_r are defined as

$$B_0=b_{01}-\frac{b_{02}}{T_r}-\frac{b_{03}}{T_r^2}-\frac{b_{04}}{T_r^3} \tag{11}$$

$$B_r=b_{r1}-\frac{b_{r2}}{T_r}-\frac{b_{r3}}{T_r^2}-\frac{b_{r4}}{T_r^3} \tag{12}$$

$$C_0=c_{01}-\frac{c_{02}}{T_r}+\frac{c_{03}}{T_r^3} \tag{13}$$

$$C_r=c_{r1}-\frac{c_{r2}}{T_r}+\frac{c_{r3}}{T_r^3} \tag{14}$$

$$D_0=d_{01}+\frac{d_{02}}{T_r} \tag{15}$$

$$D_r=d_{r1}+\frac{d_{r2}}{T_r} \tag{16}$$

where coefficients b, c, d, β, γ are given in Table 1.

Isentropic exponent k_{pv}

Analytical calculation

The derivative $(\partial p/\partial v)_T$ in expression (4) is calculated by differentiation of the equation of state $pv=ZRT$, where the compressibility factor Z is taken from the Lee-Kesler correlation (8). After algebraic transformations, we get

$$k_{pv}=-\frac{c_p}{c_v}\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_T=\frac{c_p}{c_v}(N_0+\omega N_1) \tag{17}$$

Table 1 Constants contained in Equations 9 to 16

$b_{01}=0.1181193$	$c_{01}=0.0236744$	$d_{01}\times 10^4=0.155488$
$b_{02}=0.265728$	$c_{02}=0.0186984$	$d_{02}\times 10^4=0.623689$
$b_{03}=0.154790$	$c_{03}=0.0$	$\beta_0=0.65392$
$b_{04}=0.030323$	$c_{04}=0.042724$	$\gamma_0=0.060167$
$b_{r1}=0.2026579$	$c_{r1}=0.0313385$	$d_{r1}\times 10^4=0.48736$
$b_{r2}=0.331511$	$c_{r2}=0.0503618$	$d_{r2}\times 10^4=0.0740336$
$b_{r3}=0.027655$	$c_{r3}=0.016901$	$\beta_r=1.226$
$b_{r4}=0.203488$	$c_{r4}=0.041577$	$\gamma_r=0.03754$

where

$$N_0=1-\frac{T_r}{p_r}\left(\frac{\partial Z_0}{\partial v_{0r}}\right)_{T_r} \tag{18}$$

$$N_1=-\frac{1}{0.3978}\frac{T_r}{p_r}\left[\left(\frac{\partial Z_r}{\partial v_{rr}}\right)_{T_r}-\left(\frac{\partial Z_0}{\partial v_{0r}}\right)_{T_r}\right] \tag{19}$$

Derivatives $(\partial Z_0/\partial v_{0r})_{T_r}$ and $(\partial Z_r/\partial v_{rr})_{T_r}$ are calculated by differentiation of Equations 9 and 10, respectively:

$$\begin{aligned}\left(\frac{\partial Z_0}{\partial v_{0r}}\right)_{T_r}&=-\frac{B_0}{v_{0r}^2}-2\frac{C_0}{v_{0r}^3}-5\frac{D_0}{v_{0r}^6}-\frac{2c_{04}}{T_r^3 v_{0r}^3}\left(\beta_0+\frac{\gamma_0}{v_{0r}^2}\right)\exp\left(-\frac{\gamma_0}{v_{0r}^2}\right)\\&+\frac{c_{04}}{T_r^3 v_{0r}^2}\left(-2\frac{\gamma_0}{v_{0r}^3}\right)\exp\left(-\frac{\gamma_0}{v_{0r}^2}\right)\\&+\frac{2\gamma_0}{v_{0r}^3}\frac{c_{04}}{T_r^3 v_{0r}^2}\left(\beta_0+\frac{\gamma_0}{v_{0r}^2}\right)\exp\left(-\frac{\gamma_0}{\mathrm{v}_{0r}^2}\right)\end{aligned} \tag{20}$$

$$\begin{aligned}\left(\frac{\partial Z_r}{\partial v_{rr}}\right)_{T_r}&=-\frac{B_r}{v_{rr}^2}-2\frac{C_r}{v_{rr}^3}-5\frac{D_r}{v_{rr}^6}-\frac{2c_{r4}}{T_r^3 v_{rr}^3}\left(\beta_r+\frac{\gamma_r}{v_{rr}^2}\right)\exp\left(-\frac{\gamma_r}{v_{rr}^2}\right)\\&+\frac{c_{r4}}{T_r^3 v_{rr}^2}\left(-2\frac{\gamma_r}{v_{rr}^3}\right)\exp\left(-\frac{\gamma_r}{v_{rr}^2}\right)\\&+\frac{2\gamma_r}{v_{rr}^3}\frac{c_{r4}}{T_r^3 v_{rr}^2}\left(\beta_r+\frac{\gamma_r}{v_{rr}^2}\right)\exp\left(-\frac{\gamma_r}{\mathrm{v}_{rr}^2}\right)\end{aligned} \tag{21}$$

For the calculation of k_{pv} for the real gas of interest, given the values of p and T, the following steps are carried out:

(i) Calculate p_r $(=p/p_c)$ and T_r $(=T/T_c)$ using the critical values of p_c, T_c of the gas under examination.
(ii) Solve Equation 9 for v_{0r} and Equation 10 for v_{rr}.

Notation

c_p	Specific heat under constant pressure
c_v	Specific heat under constant volume
k	Classical isentropic exponent, $k=c_p/c_v$
k_{pv}	Real gas isentropic exponent corresponding to the pair of variables p, v
k_{Tv}	Real gas isentropic exponent corresponding to the pair of variables T, v
k_{pT}	Real gas isentropic exponent corresponding to the pair of variables p, T
M_0, M_1	Expressions defined by Equations 23 and 24, respectively
N_0, N_1	Expressions defined by Equations 18 and 19, respectively
p, p_c, p_r	Pressure, critical pressure, and reduced pressure, respectively
R	Gas constant
T, T_c, T_r	Temperature, critical temperature, and reduced temperature, respectively
v, v_c, v_r	Specific volume, critical specific volume, and reduced specific volume, respectively
v_{0r}, v_{rr}	Reduced specific volumes defined by Equations 2 and 3, respectively, different from the reduced specific volume v_r, which corresponds to the pair of variables p_r, T_r
Z	Compressibility factor
Z_0, Z_r	Expressions defined by Equations 2 and 3, respectively
B_0, C_0, D_0 B_r, C_r, D_r	Expressions defined by Equations 4 to 9
b_{0i}, c_{0i}, d_{0i}, β_0, γ_0 b_{ri}, c_{ri}, d_{ri}, β_r, γ_r	Constants (for $i=1$ to 4) given in Table 1
ω	Acentric factor

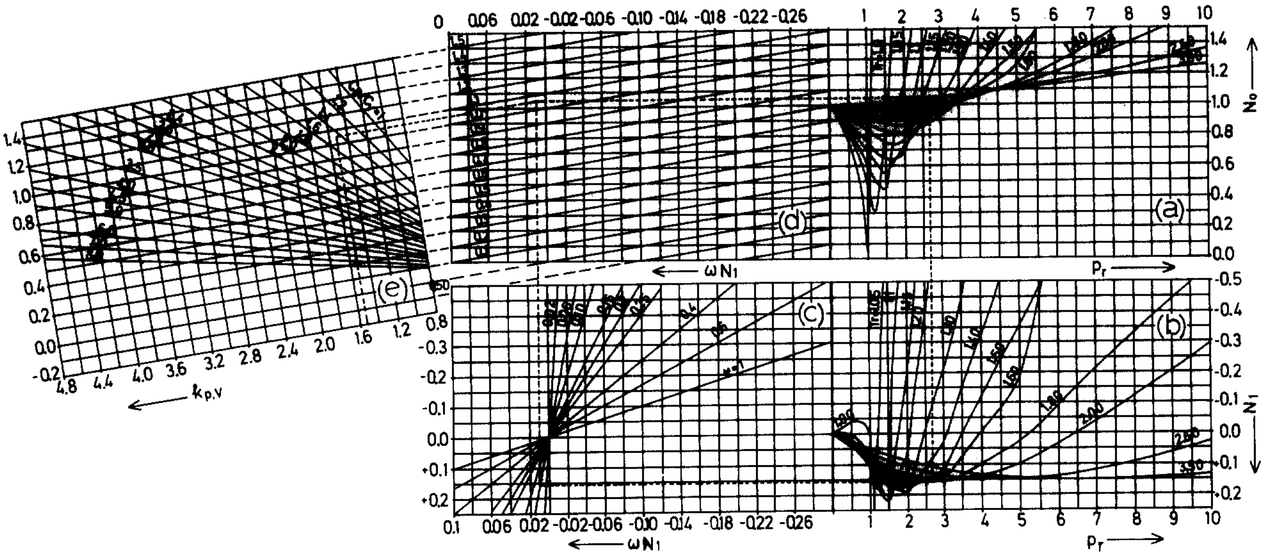

Figure 1 Graphical representation of the isentropic exponent k_{pv}

(iii) Calculate $(\partial Z_0/\partial v_{0r})_{T_r}$ and $(\partial Z_r/\partial v_{rr})_{T_r}$ from Equations 20 and 21, respectively, by using the calculated values of v_{0r} and v_{rr}.

(iv) Calculate N_0 and N_1 from Equations 18 and 19, respectively.

(v) Using properties c_p/c_v, ω of the gas under examination and the calculated values of N_0, N_1, calculate k_{pv} from Equation 17. If the exact value of c_p/c_v is not known, it may be approximated by the Lee-Kesler correlation, as described in Ref. 11.

Graphical representation

The values of k_{pv} for the gas of interest can be found directly by use of the nomograph of Figure 1, which has been elaborated on the basis of the procedure outlined above. Parts (a) and (b) of the nomograph give the values of N_0 and N_1, respectively, as a function of p_r with T_r as a parameter. In part (c) the value of N_1 (taken on the vertical axis) is multiplied by the appropriate value of ω, and the product ωN_1 is given on the horizontal axis. In part (d) the values of N_0 and ωN_1 (taken on the vertical and on the horizontal axes, respectively) are added, and their sum $(N_0+\omega N_1)$ is read on the inclined axes. Finally, part (e) multiplies the value of $N_0+\omega N_1$ by the appropriate value of c_p/c_v, so the product $(c_p/c_v)(N_0+\omega N_1)$, i.e., the value of k_{pv}, is directly given on the k_{pv}-axis.

An example of the use of the above nomograph is given by the dotted lines (Figure 1), which illustrate the calculation of k_{pv} for air ($\omega=0.035$, $p_c=37.66$ bar, $T_c=132.52$ K) at $p=100$ bar and $T=473$ K. For these values, $p_r=p/p_c=2.66$, $T_r=T/T_c=3.57$, and c_p/c_v (taken from Ref. 14) is 1.445. From the nomograph of Figure 1, $k_{pv}=1.510$. The exact value of k_{pv} at the same value of pressure and temperature is $k_{pv}=1.512$.[2] Therefore, the error observed in this example is about 0.1%. Additional tests made in the case of steam, refrigerants R12, R22, and ammonia, for which detailed thermodynamic data are available[15-19] gave results of a similar accuracy.

Isentropic exponent k_{Tv}

Analytical calculation

The derivative $(\partial p/\partial T)_v$ in expression (5) is calculated by differentiation of the equation of state $pv=ZRT$, with Z taken from Equation 8. After algebraic transformations, we get

$$k_{Tv}=1+\frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v=1+\frac{R}{c_v}\frac{v}{R}\left(\frac{\partial p}{\partial T}\right)_v=1+\frac{R}{c_v}(M_0+\omega M_1) \tag{22}$$

where

$$M_0=Z_0+T_r\left(\frac{\partial Z_0}{\partial T_r}\right)_{v_{0r}} \tag{23}$$

$$M_1=\frac{1}{0.3978}(Z_r-Z_0)+\frac{T_r}{0.3978}\left[\left(\frac{\partial Z_r}{\partial T_r}\right)_{v_{rr}}-\left(\frac{\partial Z_0}{\partial T_r}\right)_{v_{0r}}\right] \tag{24}$$

The derivatives $(\partial Z_0/\partial T_r)_{v_{0r}}$ and $(\partial Z_r/\partial T_r)_{v_{rr}}$ are calculated by differentiation of Equations 9 and 10, respectively:

$$\left(\frac{\partial Z_0}{\partial T_r}\right)_{v_{0r}}=\frac{1}{v_{0r}}\left(\frac{b_{02}}{T_r^2}+\frac{2b_{03}}{T_r^3}+\frac{3b_{04}}{T_r^4}\right)+\frac{1}{v_{0r}^2}\left(\frac{c_{02}}{T_r^2}-\frac{3c_{03}}{T_r^4}\right)$$
$$-\frac{1}{v_{0r}^5}\frac{d_{02}}{T_r^2}-\frac{3c_{04}}{T_r^4v_{0r}^2}\left(\beta_0+\frac{\gamma_0}{v_{0r}^2}\right)\exp\left(-\frac{\gamma_0}{v_{0r}^2}\right) \tag{25}$$

$$\left(\frac{\partial Z_r}{\partial T_r}\right)_{v_{rr}}=\frac{1}{v_{rr}}\left(\frac{b_{r2}}{T_r^2}+\frac{2b_{r3}}{T_r^3}+\frac{3b_{r4}}{T_r^4}\right)+\frac{1}{v_{rr}^2}\left(\frac{c_{r2}}{T_r^2}-\frac{3c_{r3}}{T_r^4}\right)$$
$$-\frac{1}{v_{rr}^5}\frac{d_{r2}}{T_r^2}-\frac{3c_{r4}}{T_r^4v_{rr}^2}\left(\beta_r+\frac{\gamma_r}{v_{rr}^2}\right)\exp\left(-\frac{\gamma_r}{v_{rr}^2}\right) \tag{26}$$

For the calculation of k_{Tv} for the real gas of interest, given the values of p and T, the following steps are carried out:

(i) Calculate p_r $(=p/p_c)$ and T_r $(=T/T_c)$ using the critical values p_c, T_c of the gas under examination.

(ii) Solve Equation 9 for v_{0r} and Equation 10 for v_{rr}.

(iii) Calculate $(\partial Z_0/\partial T_r)_{v_{0r}}$ and $(\partial Z_r/\partial T_r)_{v_{rr}}$ from Equations 25 and 26, respectively, by using the calculated values of v_{0r} and v_{rr}.

(iv) Calculate M_0 and M_1 from Equations 23 and 24, respectively.

(v) Calculate k_{Tv} from Equation 22 using properties R/c_v, ω of the gas under examination and the calculated values of M_0, M_1. If the exact value of c_v is not known, it may be approximated by the Lee-Kesler correlation, as described in Ref. 11.

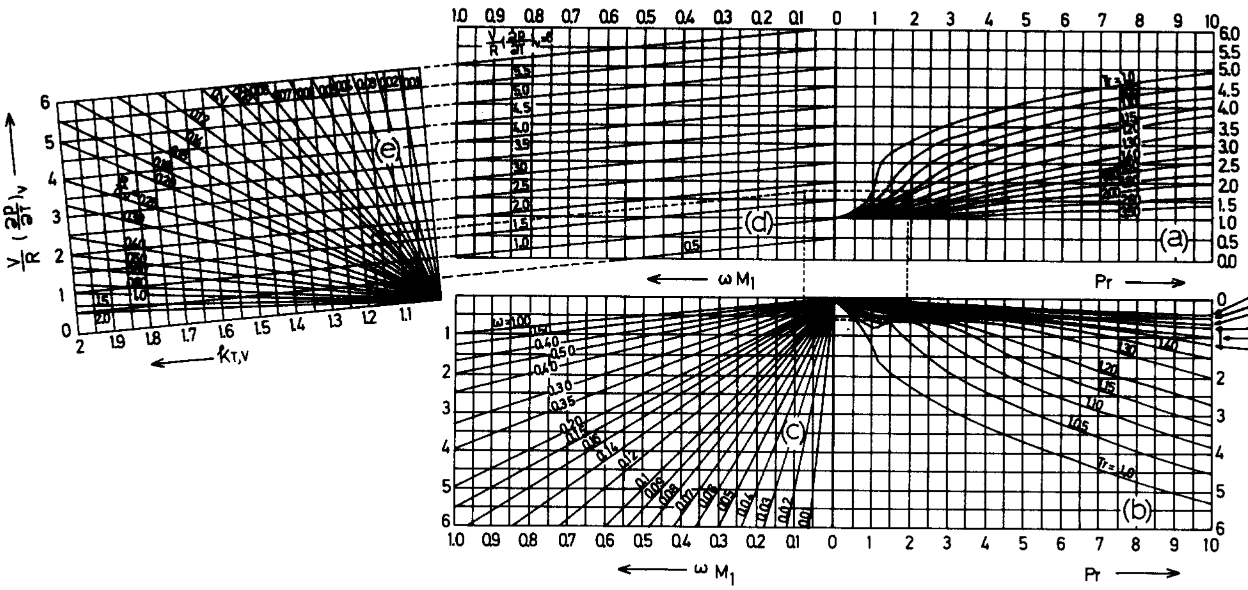

Figure 2 Graphical representation of the isentropic exponent k_{Tv}

Graphical representation

The values of k_{Tv} for the fluid of interest can be found directly by use of the nomograph of Figure 2, which has been elaborated on the basis of the procedure outlined above. Parts (a) and (b) of the nomograph give the values of M_0 and M_1, respectively, as a function of p_r, with T_r as a parameter. In part (c) the value of M_1 (on the vertical axis) is multiplied by the appropriate value of ω, and the product ωM_1 is given on the horizontal axis. In part (d) the values of M_0 and ωM_1 are added, and their sum $(M_0+\omega M_1)$ is given on the inclined axes. Finally, in part (e) the value of $M_0+\omega M_1$ is multiplied by the appropriate value of R/c_v and unity is added to the product $(R/c_v)(M_0+\omega M_1)$, so the value of $k_{Tv}=1+(R/c_v)(M_0+\omega M_1)$ is directly given on the k_{Tv}-axis.

An example of the use of the above nomograph is shown by the dotted lines (Figure 2), which illustrate the calculation of isentropic exponent k_{Tv} for the refrigerant R12 (for which $\omega=0.158$, $p_c=42.063\,\text{kgf/cm}^2$, $T_c=384.95\,K$) at $p=80\,\text{kgf/cm}^2$ and $T=443$ K. For these values, $p_r=p/p_c=1.90$, $T_r=T/T_c=1.15$, and R/c_v (taken from Ref. 17) is 0.0977. From the nomograph of Figure 2, $k_{Tv}=1.182$. The exact value of k_{Tv} at the same value of pressure and temperature is 1.180.[17] Therefore, the error observed in this example is about 0.2%. Other tests made in the case of air, steam, R22, and ammonia for which detailed thermodynamic data are available[14–19] gave results of a similar accuracy.

Isentropic exponent k_{pT}

The third isentropic exponent k_{pT} is calculated from Equation 7 with the values of k_{pv} and k_{Tv}, contained in this equation, calculated either analytically as described in the second and third sections, or by use of the nomographs of Figures 1 and 2 as outlined in the second and third sections, respectively.

Conclusion

A method has been presented for the calculation of the three real gas isentropic exponents, k_{pv}, k_{Tv}, k_{pT} in the ranges of reduced pressure $p_r=1$ to 10 and of reduced temperature $T_r=1$ to 3.5. The method is applicable to those real gases for which no detailed thermodynamic data are available. The accuracy obtained is limited only by the accuracy of the Lee-Kesler correlation, which is employed in the method developed. Applications of the method in the case of the air, steam, refrigerants R12, R22, and NH_3, for which detailed thermodynamic data are available, yielded results very close to the exact values, in the pressure and temperature ranges examined.

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