On the three exponents of the isentropic change of the refrigerant R22

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The differential isentropic change of real gases is usually calculated by using the corresponding equation of ideal gases, with the isentropic exponent taken as the ratio of the specific heats at constant pressure and constant volume. A closer examination shows that there exist three isentropic exponents, having different values, corresponding to the three possible pairs of variables selected among temperature, pressure and volume. The numerical values of these exponents were calculated for the refrigerant R22. It was found that calculations performed with the conventional isentropic exponent can show significant deviations from the real values.

Keywords: *isentropic change, real gases, refrigerant R22, thermodynamics*

Introduction

The isentropic change of an ideal gas having a constant $k=c_p/c_v$ value is described by the well-known relations $pv^k=$constant, $Tv^{(k-1)}=$constant or $p^{(1-k)}T^k=$ constant. The small relations with $k=c_p/c_v$ are often used for real gases if small or differential isentropic changes are considered. A closer examination of the differential isentropic change shows that, for p, v, T systems, there are three different isentropic exponents corresponding to each pair formed from the variables p, v, T. These three exponents, named $k_{p,v}$, $k_{v,T}$, $k_{T,p}$ after the corresponding pair of variables used, are interconnected by one relation, and accordingly only two out of the three are independent. The numerical values of these exponents were calculated and are presented here for the refrigerant R22.

The deviations from the conventional $k=c_p/c_v$ values are considerable. It is pointed out that calculations with the classical $k=c_p/c_v$ exponent used for each pair of the p, v, T variables may lead to incorrect results. For some special cases $k_{p,v}\leqslant 1$, leading to isentropic changes with slope, on the p, v plane, less than or equal to the slope of the isothermal change.

General

In thermodynamics the existence is assumed of a single-valued analytic function s giving the entropy of the system considered; further, for p, v, T systems, there are three functions $s(p, T)$, $s(T, v)$ and $s(v, p)$.

From these functions the isentropic change can be determined as described below, thus obtaining relations among the p, v, T variables and their derivatives.

Pair *p, T*

For constant entropy, $\mathrm{d}s=0$ and

$$\mathrm{d}s=\left(\frac{\partial s}{\partial p}\right)_T \mathrm{d}p+\left(\frac{\partial s}{\partial T}\right)_p \mathrm{d}T=0$$

Further

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_s=\left(\frac{\partial p}{\partial T}\right)_s=-\left(\frac{\partial s}{\partial T}\right)_p\Big/\left(\frac{\partial s}{\partial p}\right)_T$$

It is known that $(\partial s/\partial T)_p=c_p/T$, and, from Maxwell's relations, that $(\partial s/\partial p)_T=-(\partial v/\partial T)_p$. Hence the above relation yields

$$\left(\frac{\partial p}{\partial T}\right)_s=\frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \tag{1}$$

This relation gives the dependence of $\mathrm{d}p$ and $\mathrm{d}T$ along an isentropic change. Similar relations are obtained for the other two pairs of variables.

Pair *v, T*

The constant entropy condition gives

$$\mathrm{d}s=\left(\frac{\partial s}{\partial v}\right)_T \mathrm{d}v+\left(\frac{\partial s}{\partial T}\right)_v \mathrm{d}T=0$$

and

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_s=\left(\frac{\partial v}{\partial T}\right)_s=-\left(\frac{\partial s}{\partial T}\right)_v\Big/\left(\frac{\partial s}{\partial v}\right)_T$$

It is again known that $(\partial s/\partial T)_v=c_v/T$. From Maxwell's relations, $(\partial s/\partial v)_T=(\partial p/\partial T)_v$, and the above relation is written as

$$\left(\frac{\partial T}{\partial v}\right)_s=-\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v \tag{2}$$

connecting the variables v, T for an isentropic change.

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Pair p, v

The corresponding relation between these two variables can be found from Eqs (1) and (2) as follows.

$$\left(\frac{\partial p}{\partial v}\right)_s=\frac{(\partial p/\partial T)_s}{(\partial v/\partial T)_s}=-\frac{(c_p/T)(\partial T/\partial y)_p}{(c_v/T)(\partial T/\partial p)_v}$$

$$=-\frac{c_p}{c_v}\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial p}{\partial T}\right)_v$$

It is further known that

$$\left(\frac{\partial v}{\partial p}\right)_T\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial p}{\partial T}\right)_v=-1$$

abd, therefore

$$\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial p}{\partial T}\right)_v=-1\Big/\left(\frac{\partial v}{\partial p}\right)_T=-\left(\frac{\partial p}{\partial v}\right)_T$$

Hence the relation becomes

$$\left(\frac{\partial p}{\partial v}\right)_s=\frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T \tag{3}$$

The three relations (1), (2) and (3) give the dependence of the different variables for an isentropic change.

Comparison with an ideal gas

For an ideal gas the isentropic change is given by the well-known relation $pv^k=\text{constant}$ if the $k=c_p/c_v$ exponent is constant. Using this relation and the equation of state of the ideal gas, $pv=RT$, we obtain the well-known equations that correspond to Eqs (1), (2) and (3) given above. Thus from $pv^k=\text{constant}$, we find $p^{(1-k)}T^k=\text{constant}$. After taking logarithms and differentiating, we find

$$(1-k)\frac{\mathrm{d}p}{p}+k\frac{\mathrm{d}T}{T}=0$$

or

$$\left(\frac{\partial p}{\partial T}\right)_{s,\mathrm{id}}=-\frac{k}{1-k}\frac{p}{T}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_{s,\mathrm{id}}=\frac{k}{k-1}\frac{p}{T} \tag{4}$$

Eq (4) for an ideal gas corresponds to the general relation (1).

In the same way, for the pair of variables v, T we find that the isentropic change of the ideal gas is given by the relation $Tv^{(k-1)}=\text{constant}$. After taking logarithms and differentiating, we obtain

$$\frac{\mathrm{d}T}{T}+(k-1)\frac{\mathrm{d}v}{v}=0$$

or

$$\left(\frac{\partial T}{\partial v}\right)_{s,\mathrm{id}}=-(k-1)\frac{T}{v} \tag{5}$$

Eq (5) for the ideal gas corresponds to the general relation (2) obtained above.

For the last pair of variables, p, v, we find, in the same way, from the relation $pv^k=\text{constant}$ that

$$\frac{\mathrm{d}p}{p}+k\frac{\mathrm{d}v}{v}=0$$

or

$$\left(\frac{\partial p}{\partial v}\right)_{s,\mathrm{id}}=-k\frac{p}{v} \tag{6}$$

This relation corresponds to Eq (3) of the general case.

Eqs (4), (5) and (6) can be obtained as limiting cases of Eqs (1), (2) and (3) if the corresponding values of the derivatives, $(\partial T/\partial v)_{p,\mathrm{id}}=p/R$, $(\partial p/\partial T)_{v,\mathrm{id}}=R/v$ and $(\partial p/\partial v)_{T,\mathrm{id}}=-p/v$, for the ideal gas are used, and further we use the relation $R=c_p-c_v$.

The three isentropic exponents

Let us consider now a real gas that is approximated, along a differential isentropic change, by the corresponding ideal gas.

Pair p, T

If the approximation is made by using the p, T pair of variables, then, from Eqs (1) and (4), we see the following.

The actual change is given by Eq (1), ie

$$\left(\frac{\partial p}{\partial T}\right)_s=\frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p$$

If we approximate by Eq (4) we must define an isentropic exponent $k_{p,T}$ as follows:

$$\left(\frac{\partial p}{\partial T}\right)_s=\frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p=\left(\frac{\partial p}{\partial T}\right)_{s,\mathrm{id}}=\frac{k_{p,T}}{k_{p,T}-1}\frac{p}{T}$$

Notation

A	Coefficient of terms in Eq (21)
c_p	Specific heat at constant pressure
c_v	Specific heat at constant volume
k	Isentropic exponent $\equiv c_p/c_v$
p	Pressure
R	Gas constant
s	Specific entropy
T	Temperature
v	Specific volume
X, Y	Reference functions of c_p
Z	Compressibility factor
ρ	Density

Subscripts

c	Critical state
p, v	Pair of variables pressure, specific volume
r	Reduced state
s	Constant entropy
s, id	Constant entropy, ideal gas
T, p	Pair of variables temperature, pressure
T, v	Pair of variables temperature, specific volume

It is clear that the exponent of the isentropic change in this case should be defined as

$$\frac{k_{p,T}}{k_{p,T}-1}=\frac{c_p}{p}\left(\frac{\partial T}{\partial v}\right)_p$$

or

$$k_{p,T}=\frac{1}{1-\dfrac{p}{c_p}\left(\dfrac{\partial v}{\partial T}\right)_p} \tag{7}$$

This value of $k_{p,T}$ should be used in Eq (4) if the differential change of the real gas has to be approximated by the equation of the ideal gas. Thus we obtain

$$\left(\frac{\partial p}{\partial T}\right)_s=\frac{k_{p,T}}{k_{p,T}-1}\frac{p}{T} \tag{8}$$

Pair T, v

For these variables, from Eqs (2) and (5) we find

$$\left(\frac{\partial T}{\partial v}\right)_s=-\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v=\left(\frac{\partial T}{\partial v}\right)_{s,\text{id}}=-(k_{T,v}-1)\frac{T}{v}$$

or, finally

$$k_{T,v}=1+\frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v \tag{9}$$

Hence, the description of the isentropic differential change of the real gas is given by the equation of the ideal gas, using the pair of variables T, v only in the way given by Eq (10), ie only if the $k_{T,v}$ exponent is used and

$$\left(\frac{\partial T}{\partial v}\right)_s=-(k_{T,v}-1)\frac{T}{v} \tag{10}$$

Pair p, v

Comparison of Eqs (3) and (6) gives

$$\left(\frac{\partial p}{\partial v}\right)_s=\frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T=\left(\frac{\partial p}{\partial v}\right)_{s,\text{id}}=-k\frac{p}{v}$$

Thus, for the third isentropic exponent $k_{p,v}$, *we find*[1,2]

$$k_{p,v}=-\frac{v\,c_p}{p\,c_v}\left(\frac{\partial p}{\partial v}\right)_T \tag{11}$$

and the corresponding isentropic differential change is described by the relation

$$\left(\frac{\partial p}{\partial v}\right)_s=-k_{p,v}\frac{p}{v} \tag{12}$$

Eqs (7), (9) and (11) give the values of the three isentropic exponents that describe the differential isentropic change if the conventional forms of the equations of the ideal gas are retained.

Comparison of the isentropic exponents

The numerical values of the isentropic exponent $k=c_p/c_v$ and of the three exponents $k_{p,T}$, k_{Tv}, $k_{p,v}$ defined by Eqs (7), (9) and (11) are different. This can be seen from their corresponding defining relations and from Figs 1 to 11 concerning the refrigerant R22.

Only in limiting cases do all four exponents take the same numerical value. This is the case when the behaviour of the real gas approximates that of the ideal gas. Generally this is not the case, and using Eqs (4), (5) and (6) instead of the correct ones (8), (10) and (12) leads to incorrect results even if the local value of $k=c_p/c_v$ is the correct one.

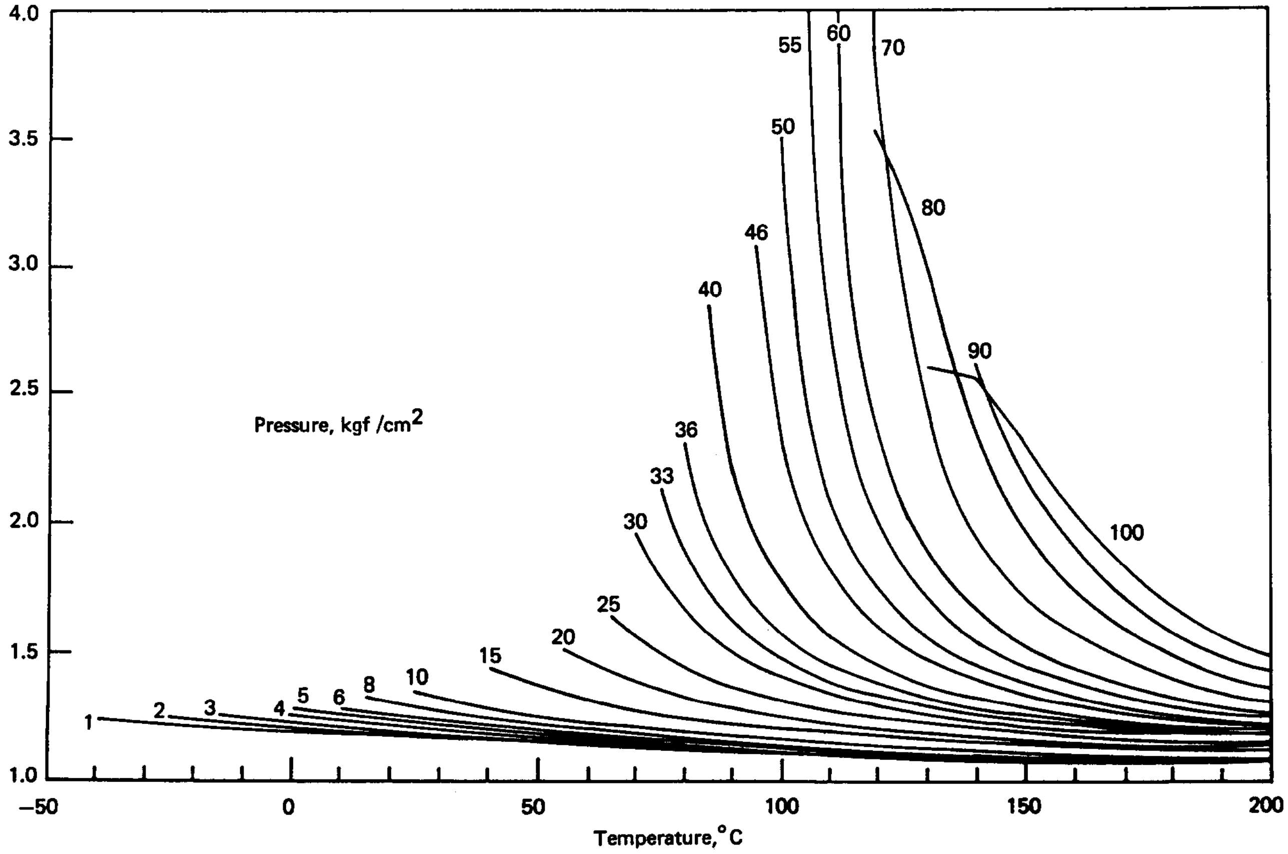

Fig 1 The conventional isentropic exponent $k=c_p/c_v$

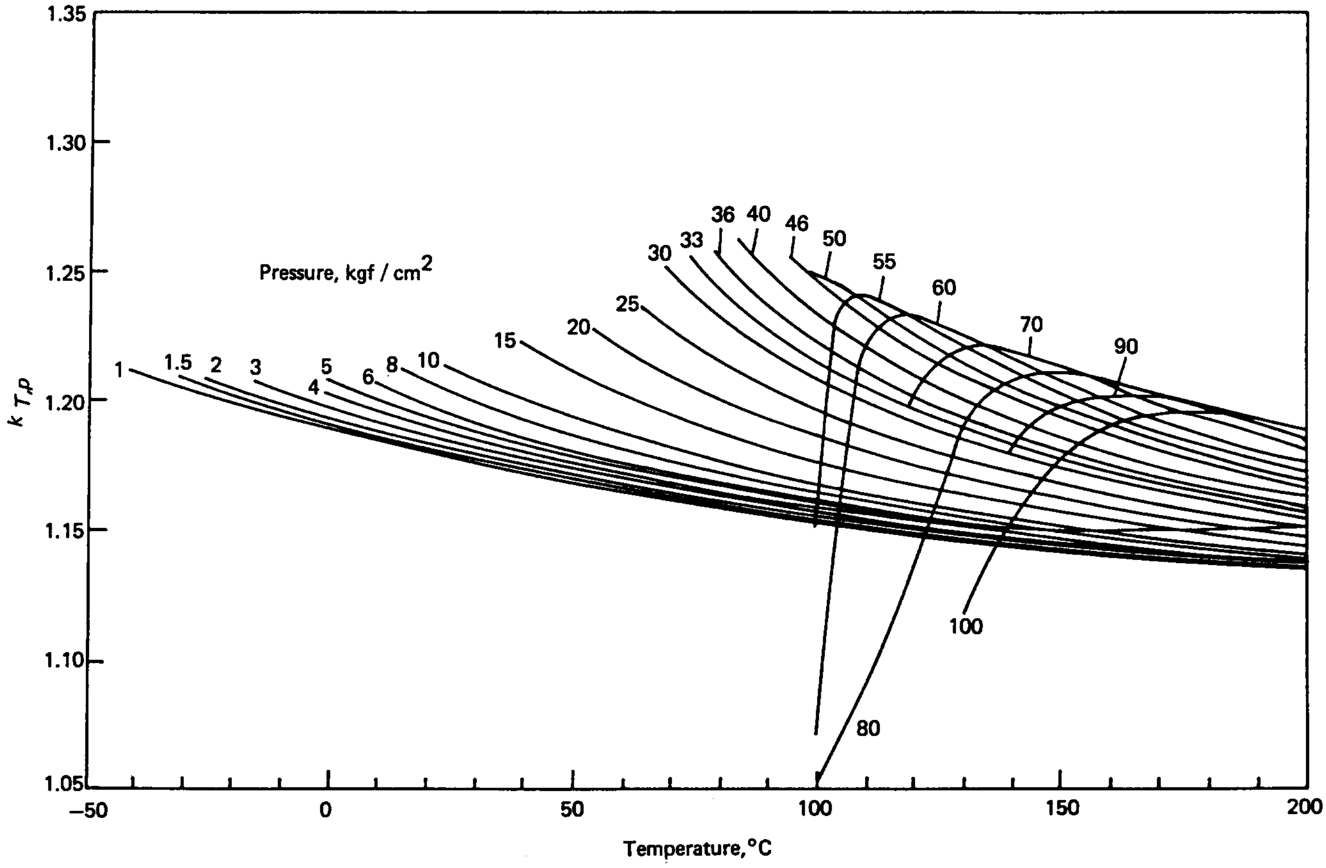

Fig 2 Variation of the $k_{T,p}$ *isentropic exponent of R22 with pressure and temperature. The exponent can take values less than 1 for temperatures of about 100°C*

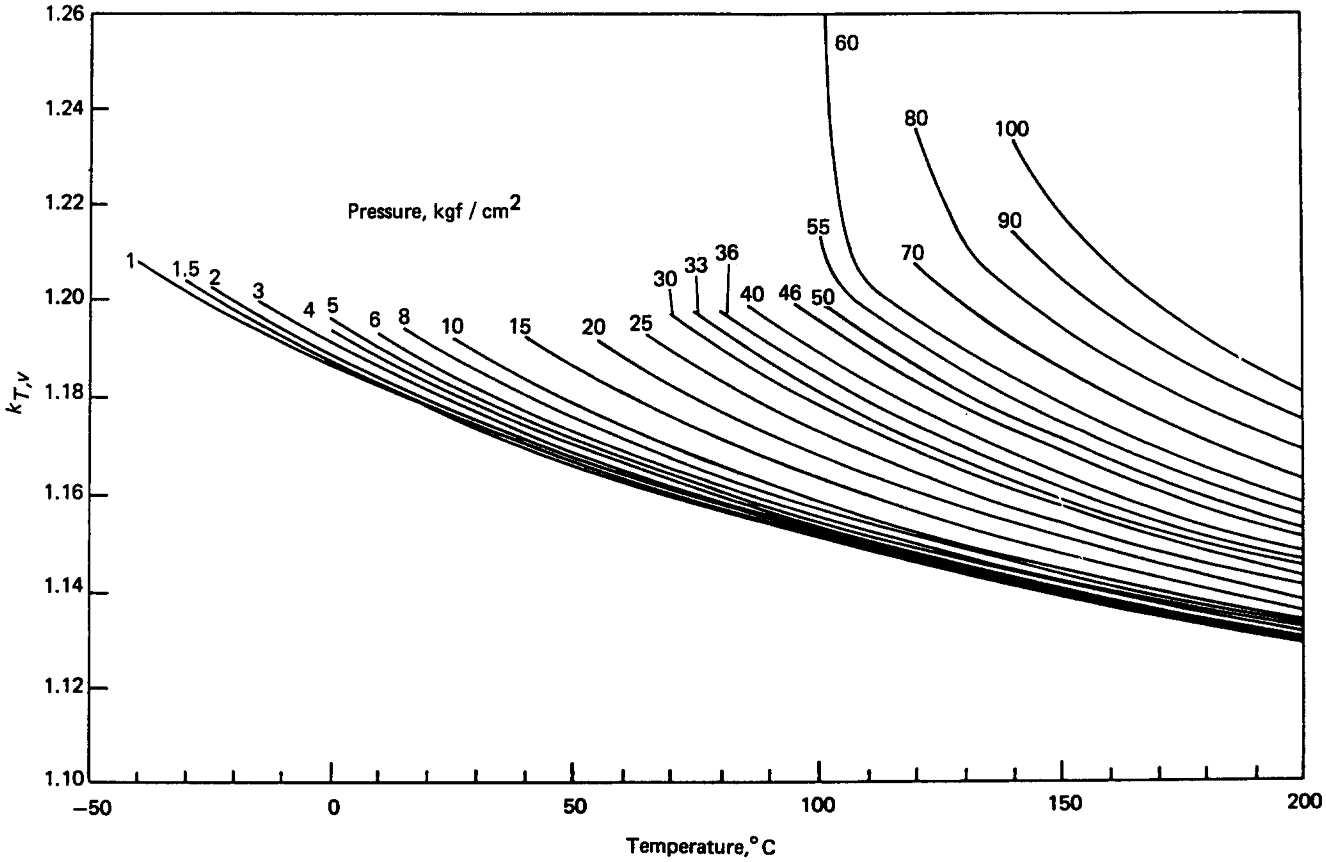

Fig *3 The* $k_{T,v}$ *isentropic exponent of R22*

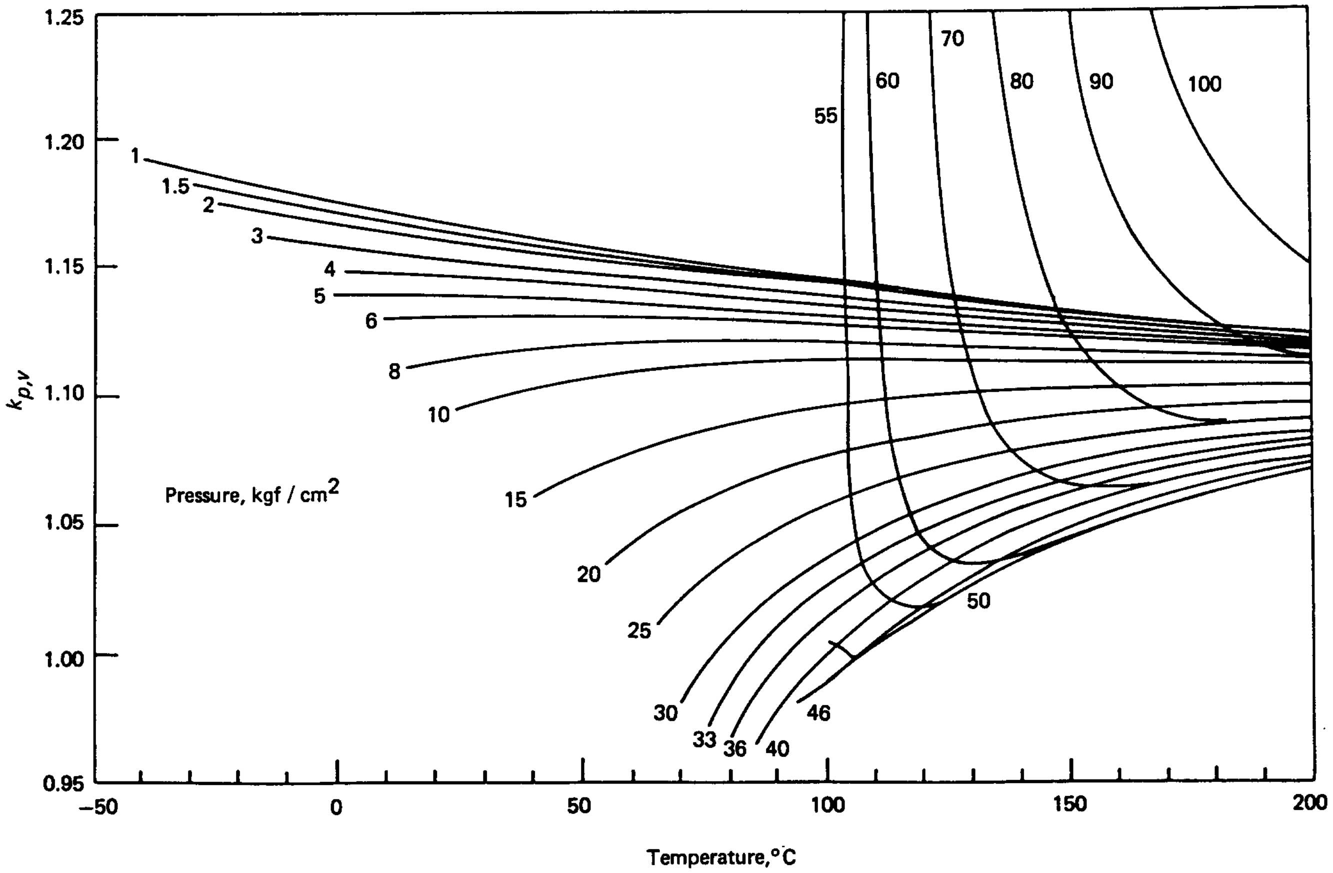

Fig 4 The $k_{p,v}$ *isentropic exponent of R22. For pressures near the critical pressure, the exponent takes high values*

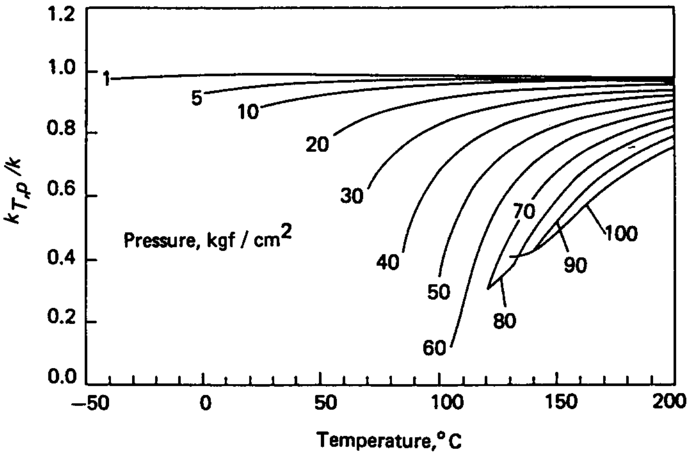

Fig 5 The reduced $k_{p,T}/k$ *isentropic exponent of R22*

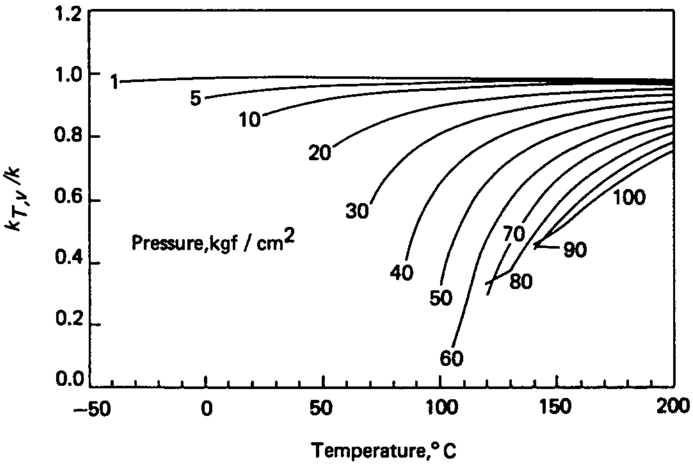

Fig 6 The reduced $k_{T,v}/k$ *isentropic exponent of R22*

The three isentropic $k_{p,T}$, $k_{T,v}$, $k_{p,v}$ are not independent of each other. This can be seen from the following. From Eqs (8), (10) and (12) we find

$$\left(\frac{\partial p}{p}\right)_s=\frac{k_{p,T}}{k_{p,T}-1}\left(\frac{\partial T}{T}\right)_s$$

$$\left(\frac{\partial T}{T}\right)_s=-(k_{T,v}-1)\left(\frac{\partial v}{v}\right)_s$$

$$\left(\frac{\partial v}{v}\right)_s=-\frac{1}{k_{p,v}}\left(\frac{\partial p}{p}\right)_s$$

and, by multiplication and elimination,

$$\frac{k_{p,T}}{k_{p,T}-1}(k_{T,v}-1)\frac{1}{k_{p,v}}=1$$

or

$$\frac{k_{p,v}}{k_{T,v}-1}=\frac{k_{p,T}}{k_{p,T}-1} \tag{13}$$

Thus knowing two out of the three isentropic exponents, we can calculate the third.

Another interesting relation, useful among others for check purposes, can be obtained by multiplying Eqs

(1), (2) and (3):

$$\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial v}{\partial p}\right)_s=\frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p\left(-\frac{T}{c_v}\right)\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{c_v}{c_p}\right)\left(\frac{\partial v}{\partial p}\right)_T$$

and, from the relation mentioned in the first paragraph:

$$\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial v}{\partial p}\right)_s=1 \tag{14}$$

To compare the deviations between calculating with the isentropic exponents $k=c_p/c_v$ instead of the appropriate choice from the $k_{p,T}$, $k_{T,v}$, $k_{p,v}$ exponents, we consider either the ratios of the exponents, ie

$$\frac{k_{p,T}}{k}=\frac{1}{1-\frac{p}{c_p}\left(\frac{\partial v}{\partial T}\right)_p}\frac{c_v}{c_p}=\frac{c_v}{c_p-p\left(\frac{\partial v}{\partial T}\right)_p} \tag{15}$$

$$\frac{k_{T,v}}{k}=\left\{1+\frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v\right\}\frac{c_v}{c_p}=\frac{c_v+v(\partial p/\partial T)_v}{c_p} \tag{16}$$

$$\frac{k_{p,v}}{k}=-\frac{v}{p}\frac{c_p}{c_v}\left(\frac{\partial p}{\partial T}\right)_T\frac{c_v}{c_p}=-\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_T \tag{17}$$

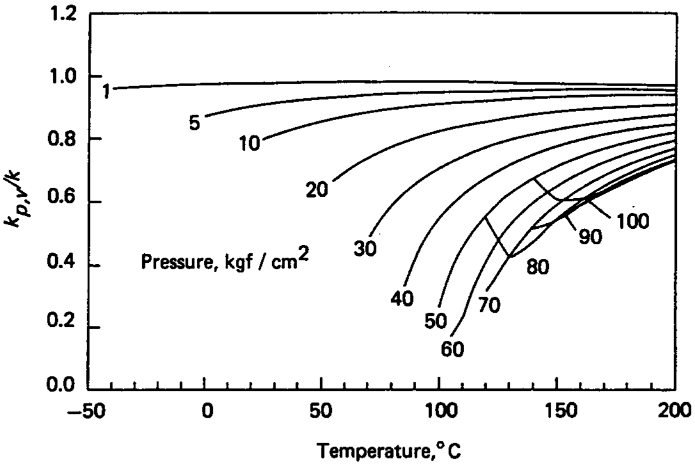

Fig 7 The reduced $k_{p,v}/k$ *isentropic exponent of R22*

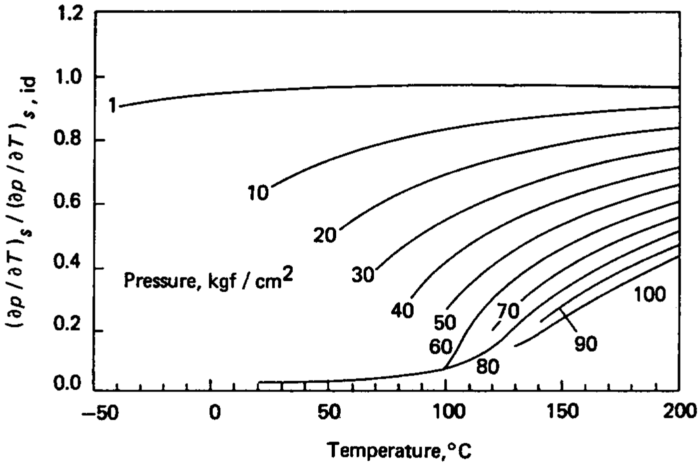

Fig 8 The reduced derivative $((\partial_p/\partial T)_s/(\partial p/\partial T)_{s,id}$ *of R22*

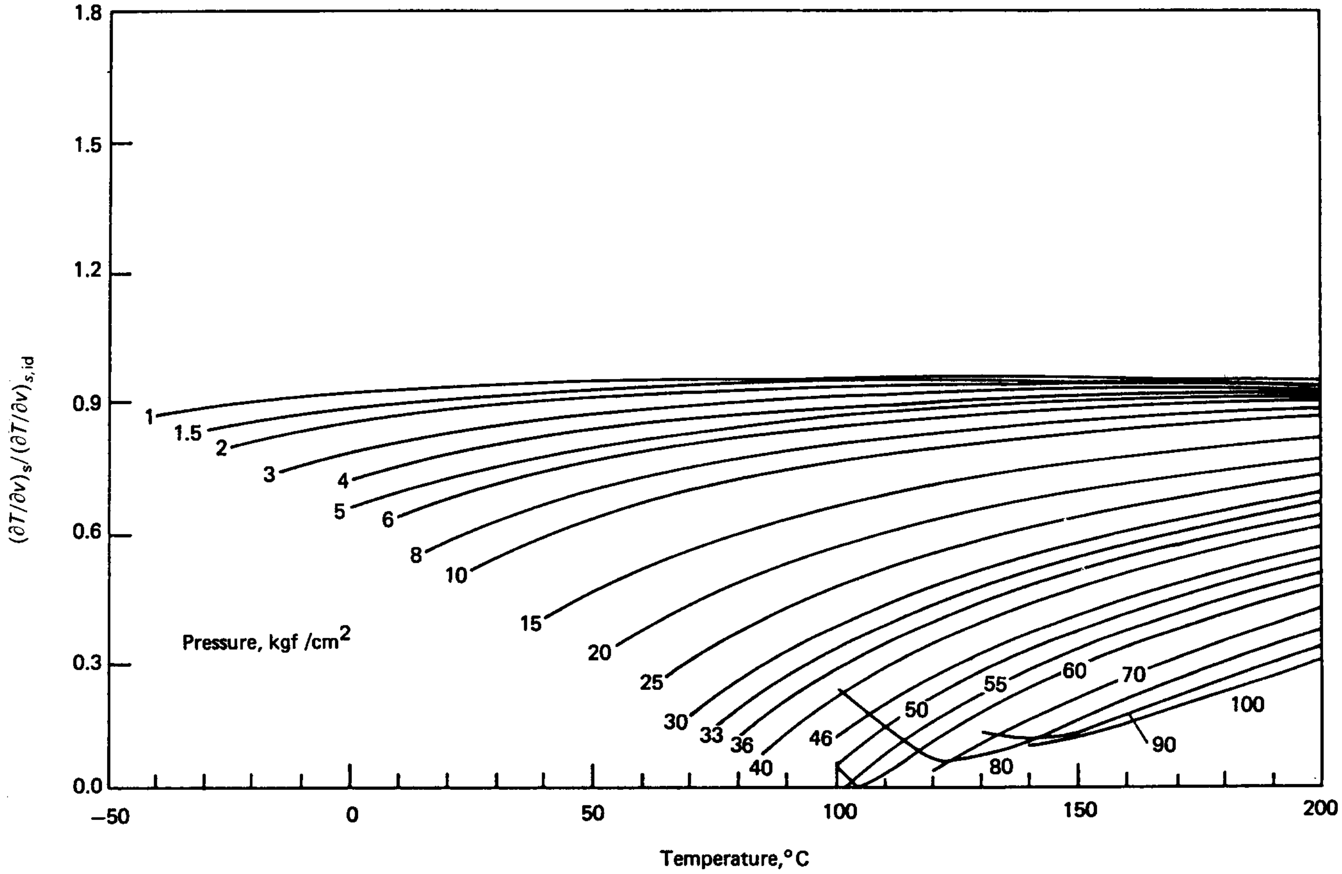

Fig 9 The reduced derivative $(\partial T/\partial v)_s/(\partial T/\partial v)_{s,id}$ *of R22*

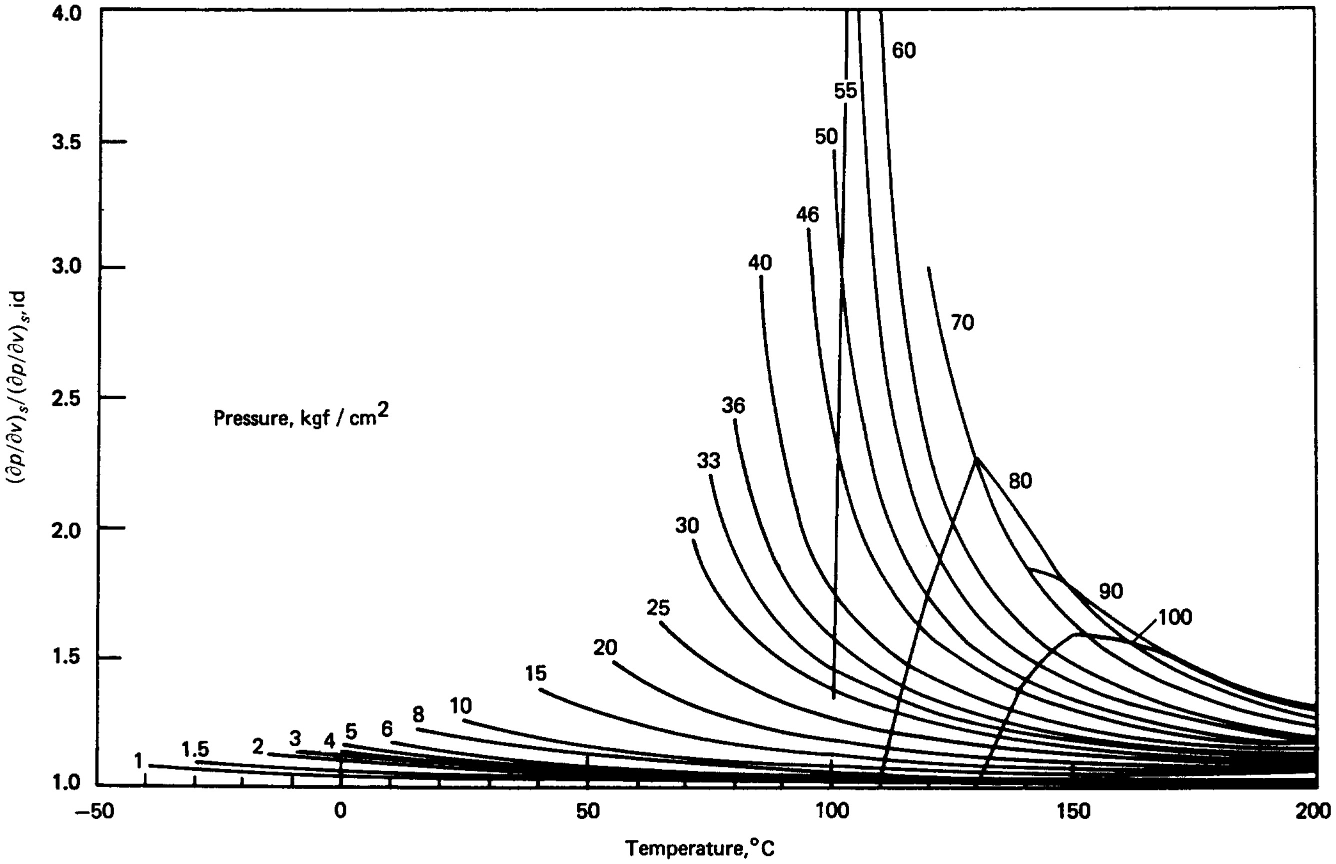

Fig 10 The reduced derivative $(\partial p/\partial v)_s/(\partial p/\partial v)_{s,id}$ of R22

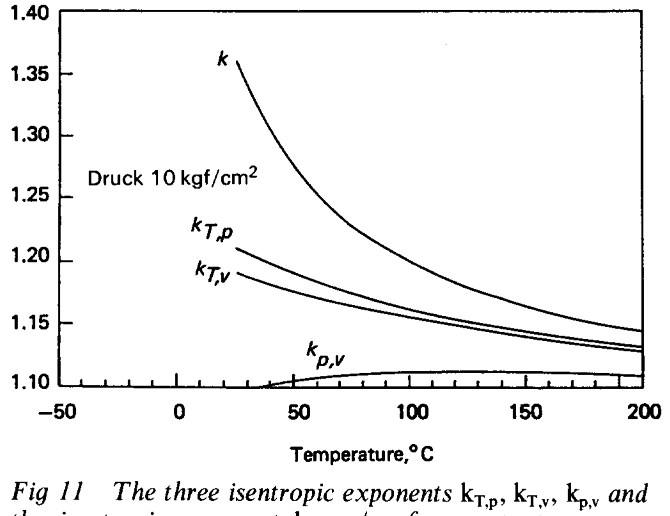

Fig 11 The three isentropic exponents $k_{T,p}$, $k_{T,v}$, $k_{p,v}$ and the isentropic exponent $k = c_p/c_v$ for constant pressure (10 kgf/cm^2) as functions of temperature

or the ratios of the slopes of the changes, namely

$$\frac{(\partial p/\partial T)_s}{(\partial p/\partial T)_{s,id}} = \frac{\{k_{p,T}/(k_{p,T}-1)\}(p/T)}{\{k/(k-1)\}(p/T)} = \frac{k_{p,T}}{k}\,\frac{k-1}{k_{p,T}-1} \qquad (18)$$

$$\frac{(\partial T/\partial v)_s}{(\partial T/\partial v)_{s,id}} = \frac{-(k_{T,v}-1)(T/v)}{-(k-1)(T/v)} = \frac{k_{T,v}-1}{k-1} \qquad (19)$$

$$\frac{(\partial p/\partial v)_s}{(\partial p/\partial v)_{s,id}} = \frac{-k_{p,v}(p/v)}{-k(p/v)} = \frac{k_{p,v}}{k} \qquad (20)$$

From the above relations we can see, with the help of Eqs (14) and (13) that

$$\frac{(\partial p/\partial T)_s}{(\partial p/\partial T)_{s,id}}\,\frac{(\partial T/\partial v)_s}{(\partial T/\partial v)_{s,id}}\,\frac{(\partial v/\partial p)_s}{(\partial v/\partial p)_{s,id}} = 1$$

Numerical values for the refrigerant R22

The refrigerant R22 was used as an example to show the numerical value of the three different $k_{p,T}$, $k_{T,v}$, and $k_{p,v}$ isentropic exponents and the deviations that are produced whenever we use only the one conventional k value.

The equation of state, and the values of the specific heats were calculated using the equations and data already known. The values of the derivatives needed for Eqs (7), (9) and (11) were found by taking the derivatives of the corresponding relations. The detailed equations, with the values of their numerous constants given in Table 1, are included in the Appendix.

Results and conclusions

From the relations obtained above, and from the figures, the following may be concluded.

- The differential isentropic changes of real gases cannot be calculated from the conventional isentropic exponent $k = c_p/c_v$ and the corresponding relations for an ideal gas.
- There exist three isentropic exponents $k_{p,T}$, $k_{T,v}$ and $k_{p,v}$ used in accordance with the appropriate pair of variables (p, T), (T, v) or (p, v) and the corresponding ideal gas relations. These exponents can be used to

Table 1 Values of numerical constants in Eq (A1)

$A_1 = 5.45762 \times 10^{-1}$
$A_2 = -1.39198$
$A_3 = -4.32562 \times 10^{-1}$
$A_4 = 2.214 \times 10^{-2}$
$A_5 = -1.307418 \times 10^{-1}$
$A_6 = 7.9211 \times 10^{-1}$
$A_7 = -1.67024 \times 10^{-1}$
$A_8 = 5.6743874 \times 10^{-1}$
$A_9 = -1.35071$
$A_{10} = -1.15487 \times 10^{-4}$
$A_{11} = 1.024567$
$A_{12} = 3.4435035 \times 10^{-1}$
$A_{13} = -4.082677 \times 10^{-1}$
$A_{14} = 8.30099 \times 10^{-2}$
$A_{15} = -1.899033 \times 10^{-1}$
$A_{16} = 8.821727 \times 10^{-2}$
$A_{17} = 1.90595 \times 10^{-2}$

$A_{18} = -3.76347 \times 10^{-2}$
$A_{19} = 3.329212 \times 10^{-2}$
$A_{20} = -3.794234 \times 10^{-2}$
$A_{21} = 7.86909 \times 10^{-3}$
$A_{22} = -4.626965 \times 10^{-3}$
$A_{23} = 2.336405 \times 10^{-2}$
$A_{24} = -2.066556 \times 10^{-3}$
$A_{25} = -1.0501834 \times 10^{-2}$
$A_{26} = 5.276995 \times 10^{-4}$
$A_{27} = 2.09547 \times 10^{-4}$
$A_{28} = 1.346363 \times 10^{-3}$

$A_{00} = 3.37055 \times 10^{-1}$
$A_{01} = 1.045219 \times 10^{-1}$
$A_{02} = 7.32804 \times 10^{-1}$
$A_{03} = -6.11404 \times 10^{-1}$
$A_{04} = 1.61807 \times 10^{-1}$

$B_{00} = 6.070732 \times 10^{2}$
$B_{01} = 4.643861$

$B_1 = -7.0340913$
$B_2 = 1.4030736$
$B_3 = -4.9605880$
$B_4 = 8.8828089$
$B_5 = -1.0600638 \times 10^{1}$

$R = 9.615469 \times 10^{-2}$ kJ/(kg K)

$P_c = 4.9880 \times 10^{3}$ kPa
$v_c = 1.949318 \times 10^{-3}$ m³/kg
$\rho_c = 5.130 \times 10^{2}$ kg/m³
$T_c = 3.69300 \times 10^{2}$ K
$Z_c = 2.738163 \times 10^{-1}$

calculate, stepwise numerically, the required isentropic change. For the refrigerant R22 the analytic expressions, and the corresponding values of the three exponents, are given here.

- Starting from a gas state, the differential isentropic change may be represented by the corresponding slopes $(\partial p/\partial T)_s$, $(\partial p/\partial v)_s$ or $(\partial T/\partial v)_s$. These values are given in a reduced form. For the reduction, the corresponding slopes of the same gas considered as ideal were used.
- Near the critical point (96.15°C) the isentropic exponent $k_{p,T}$ takes values less than 1, thus implying $(\partial p/\partial T)_s < 0$.
- Near the critical pressure (50.863 kgf/cm²) the isentropic exponent $k_{p,v}$ takes values less than 1.
- Near the critical point the three isentropic exponents take values as small as only 20% of the value of $k = c_p/c_v$.

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Appendix

The relevant equations are described briefly below. Input values are the temperature T and the specific volume v, while the pressure is calculated[3] from the compressibility Z:

$$Z = \frac{Pv}{RT} = \frac{P}{RT\rho} = Z_c \frac{P_r}{\mathrm{T}_r \rho_r}$$

$$= 1 + \left\{ A_1 + \frac{A_2}{T_r} + \frac{A_3}{T_r^4} + \frac{A_4}{T_r^6} \right\} \rho_r + \left\{ A_5 + \frac{A_6}{T_r} + \frac{A_7}{T_r^4} \right\} \rho_r^2$$

$$+ \left\{ A_8 + \frac{A_9}{T_r} + \frac{A_{10}}{T_r^2} + \frac{A_{11}}{T_r^4} \right\} \rho_r + \left\{ \frac{A_{12}}{T_r} + \frac{A_{13}}{T_r^4} \right\} \rho_r^4$$

$$+ \left\{ \frac{A_{14}}{T_r^2} + \frac{A_{15}}{T_r^3} + \frac{A_{16}}{T_r^4} + \frac{A_{17}}{T_r^6} \right\} \rho_r^5 + A_{18} \rho_r^6$$

$$+ \left\{ \frac{A_{19}}{T_r^2} + \frac{A_{20}}{T_r^6} \right\} \rho_r^7 + \frac{A_{21}}{T_r} \rho_r^8 + \left\{ \frac{A_{22}}{T_r^2} + \frac{A_{23}}{T_r^6} \right\} \rho_r^9$$

$$+ \left\{ \frac{A_{24}}{T_r} + \frac{A_{25}}{T_r^6} \right\} \rho_r^{10} + \left\{ \frac{A_{26}}{T_r} + \frac{A_{27}}{T_r^2} + \frac{A_{28}}{T_r^6} \right\} \rho_r^{11} \tag{A1}$$

with the constants having the numerical values of Table 1, and where P is in kPa, v in m³/kg, R in kJ/(kg K) and T in K.

The reduced specific heat c_p/R is given by Eq (A2) where the X and Y values are given by Eqs (A3) and (A4)

$$\frac{c_p}{R} = -\left\{ 12 \frac{A_3}{T_r^4} + 30 \frac{A_4}{T_r^6} \right\} \rho_r - 6 \frac{A_7}{T_r^4} \rho_r^2$$

$$-\left\{ \frac{2}{3} \frac{A_{10}}{T_r^2} + 4 \frac{A_{11}}{T_r^4} \right\} \rho_r^3 - 3 \frac{A_{13}}{T_r^4} \rho_r^4$$

$$-\left\{ \frac{2}{5} \frac{A_{14}}{T_r^2} + \frac{6}{5} \frac{A_{15}}{T_r^3} + \frac{12}{5} \frac{A_{16}}{T_r^4} + 6 \frac{A_{17}}{T_r^6} \right\} \rho_r^5$$

$$-\left\{ \frac{2}{7} \frac{A_{19}}{T_r^2} + \frac{30}{7} \frac{A_{20}}{T_r^6} \right\} \rho_r^7 - \left\{ \frac{2}{9} \frac{A_{22}}{T_r^2} + \frac{10}{3} \frac{A_{23}}{T_r^6} \right\} \rho_r^9$$

$$-3 \frac{A_{25}}{T_r^6} \rho_r^{10} - \left\{ \frac{2}{11} \frac{A_{27}}{T_r^2} + \frac{30}{11} \frac{A_{28}}{T_r^6} \right\} \rho_r^{11} + \frac{1}{R}$$

$$\times \{ (A_{00} - R) + A_{01} T_r + A_{02} T_r^2 + A_{03} T_r^3 + A_{04} T_r^4 \}$$

$$+ \frac{X^2}{Y} \tag{A2}$$

$$X = 1 + \left\{ A_1 - 3 \frac{A_3}{T_r^4} - 5 \frac{A_4}{T_r^6} \right\} \rho_r + \left\{ A_5 - 3 \frac{A_7}{T_r^4} \right\} \rho_r^2$$

$$+ \left\{ A_8 - \frac{A_{10}}{T_r^2} - 3 \frac{A_{11}}{T_r^4} \right\} \rho_r^3 - 3 \frac{A_{13}}{T_r^4} \rho_r^4$$

$$-\left\{ \frac{A_{14}}{T_r^2} + 2 \frac{A_{15}}{T_r^3} + 3 \frac{A_{16}}{T_r^4} + 5 \frac{A_{17}}{T_r^6} \right\} \rho_r^5 + A_{18} \rho_r^6$$

$$
\begin{aligned}
&-\left\{\frac{A_{19}}{T_r^2}+5\frac{A_{20}}{T_r^6}\right\}\rho_r^{\,7}-\left\{\frac{A_{22}}{T_r^2}5\frac{A_{23}}{T_r^6}\right\}\rho_r^{\,9}\\
&-5\frac{A_{25}}{T_r^6}\rho_r^{\,10}-\left\{\frac{A_{27}}{T_r^2}+5\frac{A_{28}}{T_r^6}\right\}\rho_r^{\,11}
\end{aligned}
\tag{A3}
$$

$$
\begin{aligned}
Y=1&+2\left\{A_1+\frac{A_2}{T_r}+\frac{A_3}{T_r^4}+\frac{A_4}{T_r^6}\right\}\rho_r+3\left\{A_5+\frac{A_6}{T_r}+\frac{A_7}{T_r^4}\right\}\rho_r^{\,2}\\
&+4\left\{A_8+\frac{A_9}{T_r}+\frac{A_{10}}{T_r^2}+\frac{A_{11}}{T_r^4}\right\}\rho_r^{\,3}+5\left\{\frac{A_{12}}{T_r}+\frac{A_{13}}{T_r^4}\right\}\rho_r^{\,4}\\
&+6\left\{\frac{A_{14}}{T_r^2}+\frac{A_{15}}{T_r^3}+\frac{A_{16}}{T_r^4}+\frac{A_{17}}{T_r^6}\right\}\rho_r^{\,5}+7A_{18}\rho_r^{\,6}\\
&+8\left\{\frac{A_{19}}{T_r^2}+\frac{A_{20}}{T_r^6}\right\}\rho_r^{\,7}+9\frac{A_{21}}{T_r}\rho_r^{\,8}+10\left\{\frac{A_{22}}{T_r^2}+\frac{A_{23}}{T_r^6}\right\}\rho_r^{\,9}\\
&+11\left\{\frac{A_{24}}{T_r}+\frac{A_{25}}{T_r^6}\right\}\rho_r^{\,10}+12\left\{\frac{A_{26}}{T_r}+\frac{A_{27}}{T_r^2}+\frac{A_{28}}{T_r^6}\right\}\rho_r^{\,11}
\end{aligned}
\tag{A4}
$$

The specific heat c_v/R is given further by Eq (A5)

$$
\begin{aligned}
\frac{c_v}{R}=&-\left\{12\frac{A_3}{T_r^4}+30\frac{A_4}{T_r^6}\right\}\rho_r-6\frac{A_7}{T_r^4}\rho_r^{\,2}\\
&-\left\{\frac{2}{3}\frac{A_{10}}{T_r^2}+4\frac{A_{11}}{T_r^4}\right\}\rho_r^{\,3}-3\frac{A_{13}}{T_r^4}\rho_r^{\,4}\\
&-\left\{\frac{2}{5}\frac{A_{14}}{T_r^2}+\frac{6}{5}\frac{A_{15}}{T_r^3}+\frac{12}{5}\frac{A_{16}}{T_r^4}6\frac{A_{17}}{T_r^6}\right\}\rho_r^{\,5}\\
&-\left\{\frac{2}{7}\frac{A_{19}}{T_r^2}+\frac{30}{7}\frac{A_{20}}{T_r^6}\right\}\rho_r^{\,7}-\left\{\frac{2}{9}\frac{A_{22}}{T_r^2}+\frac{10}{3}\frac{A_{23}}{T_r^6}\right\}\rho_r^{\,9}\\
&-3\frac{A_{25}}{T_r^6}\rho_r^{\,10}-\left\{\frac{2}{11}\frac{A_{27}}{T_r^2}+\frac{30}{11}\frac{A_{28}}{T_r^6}\right\}\rho_r^{\,11}+\frac{1}{R}\\
&\times\left[(A_{00}-R)+\right.A_{01}T_r+A_{02}T_r^{\,2}+A_{03}T_r^{\,3}+A_{04}T_r^{\,4}\}
\end{aligned}
\tag{A5}
$$

The derivatives required for calculating the different k values in Eqs (7), (9) and (11) are found by taking the derivatives of Eq (A1). The corresponding relations are as follows.

$$
\begin{aligned}
\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{v}\Bigg(Z-\Bigg[&\left\{A_2\frac{1}{T_r}+4A_3\left(\frac{1}{T_r}\right)^4+6A_4\left(\frac{1}{T_r}\right)^6\right\}\rho_r\\
&+\left\{A_6\frac{1}{T_r}+4A_7\left(\frac{1}{T_r}\right)^4\right\}\rho_r^{\,2}\\
&+\left\{A_9\frac{1}{T_r}+2A_{10}\left(\frac{1}{T_r}\right)^2+4A_{11}\left(\frac{1}{T_r}\right)^4\right\}\rho_r^{\,3}\\
&+\left\{A_{12}\frac{1}{T_r}+4A_{13}\left(\frac{1}{T_r}\right)^4\right\}\rho_r^{\,4}\\
&+\left\{2A_{14}\left(\frac{1}{T_r}\right)^2+3A_{15}\left(\frac{1}{T_r}\right)^3+4A_{16}\left(\frac{1}{T_r}\right)^4\right.\\
&\qquad\left.+6A_{17}\left(\frac{1}{T_6}\right)^6\right\}\rho_r^{\,5}\\
&+\left\{2A_{19}\left(\frac{1}{T_r}\right)^2+6A_{20}\left(\frac{1}{T_r}\right)^6\right\}\rho_r^{\,7}+A_{21}\frac{1}{T_r}\rho_r^{\,8}\\
&+\left\{2A_{22}\left(\frac{1}{T_r}\right)^2+6A_{23}\left(\frac{1}{T_r}\right)^6\right\}\rho_r^{\,9}\\
&+\left\{A_{24}\frac{1}{T_r}+6A_{25}\left(\frac{1}{T_r}\right)^6\right\}\rho_r^{\,10}\\
&+\left\{A_{26}\frac{1}{T_r}+2A_{27}\left(\frac{1}{T_r}\right)^2+6A_{28}\left(\frac{1}{T_r}\right)^6\right\}\rho_r^{\,11}\Bigg]\Bigg)
\end{aligned}
\tag{A6}
$$

$$
\left(\frac{\partial v}{\partial p}\right)_T=-v^2\left(\frac{\partial \rho}{\partial p}\right)_T
\tag{A7}
$$

with

$$
\begin{aligned}
\left(\frac{\partial p}{\partial \rho}\right)_T=RT\Bigg[1&+2\left\{A_1+\frac{A_2}{T_r}+\frac{A_3}{T_r^4}+\frac{A_4}{T_r^6}\right\}\rho_r\\
&+3\left\{A_5+\frac{A_6}{T_r}+\frac{A_7}{T_r^4}\right\}\rho_r^{\,2}\\
&+4\left\{A_8+\frac{A_9}{T_r}+\frac{A_{10}}{T_r^2}+\frac{A_{11}}{T_r^4}\right\}\rho_r^{\,3}\\
&+5\left\{\frac{A_{12}}{T_r}+\frac{A_{13}}{T_r^4}\right\}\rho_r^{\,4}\\
&+6\left\{\frac{A_{14}}{T_r^2}+\frac{A_{15}}{T_r^3}+\frac{A_{16}}{T_r^4}+\frac{A_{17}}{T_r^6}\right\}\rho_r^{\,5}+7A_{18}\rho_r^{\,6}\\
&+8\left\{\frac{A_{19}}{T_r^2}+\frac{A_{20}}{T_r^6}\right\}\rho_r^{\,7}+9A_{21}\frac{1}{T_r}\rho_r^{\,8}\\
&+10\left\{\frac{A_{22}}{T_r^2}+\frac{A_{23}}{T_r^6}\right\}\rho_r^{\,9}+11\left\{\frac{A_{24}}{T_r}+\frac{A_{25}}{T_r^6}\right\}\rho_r^{\,10}\\
&+12\left\{\frac{A_{26}}{T_r}+\frac{A_{27}}{T_r^2}+\frac{A_{28}}{T_r^6}\right\}\rho_r^{\,11}\Bigg]
\end{aligned}
\tag{A8}
$$

$$
\left(\frac{\partial v}{\partial T}\right)_p=-\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial p}\right)_T
\tag{A9}
$$