NASA SP-3014

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

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Entropy, enthalpy, pressure, and speed of sound of carbon dioxide computed for wide ranges of temperature and density are presented graphically. The temperature range is 250° K $\leq T \leq 25{,}000^\circ$ K ($\Delta T = 250^\circ$ K). The density range is $-7.0 \leq \log \rho/\rho_o \leq +3.0$ ($\Delta\log \rho/\rho_o = 0.2$)

AUTHOR

INTRODUCTION

The equilibrium thermodynamic properties of carbon dioxide (i.e., entropy, enthalpy, pressure, and speed of sound) have been computed on an electronic digital computer for wide ranges of temperature and density. The temperature range is 250° K $\leq T \leq 25{,}000^\circ$ K ($\Delta T = 250^\circ$ K). The density range is $-7.0 \leq \log \rho/\rho_o \leq +3.0$ ($\Delta\log \rho/\rho_o = 0.2$), where ρ_o is the density at standard temperature and pressure.

The computations are based on the following assumptions. The species present in the mixture are CO_2, O_2, CO, O, O^+, O^{++}, C, C^+, C^{++}, e^-. Each species behaves as an ideal gas. The thermodynamic properties of polyatomic species are approximated by the rigid rotator-harmonic oscillator model with constants appropriate to the lowest electronic state. Only the first few excited electronic states are considered.

SYMBOLS

a	speed of sound, cm/sec
a_o	speed of sound at standard temperature and pressure, cm/sec
b_j	a constant for each species (eq. (5))
C_i	number of atoms/mole of type i at standard temperature and pressure
c	speed of light, cm/sec
c_i	concentration of the jth species, moles/g
E_{jl}	energy of the lth electronic level of the jth species, cm^{-1}

F_j	Gibb's free energy of the jth species, cal/mole
ΔF_i	change in Gibb's free energy for ith reaction, cal/mole
g_{jl}	degeneracy of the lth electronic level of the jth species
H	total enthalpy (zero enthalpy at zero temperature), cal/mole
H_j	enthalpy of the jth species, cal/mole
h	Planck's constant, erg-sec
h_j^o	energy of formation of the jth species, cal/mole
K_i	equilibrium constant for the ith reaction, $(\text{atm cm}^3/\text{mole})^{-\beta_i}$
k	Boltzmann's constant, ergs/°K
L_o	Avogadro's number
m_j	mass of the jth species, g
m_{ij}	number of i atoms in jth species
$(mw)_j$	mass of one mole of jth species, g
n_j	number of atoms in jth species
p	pressure, dyn/cm^2
p_o	pressure of one atmosphere, dyn/cm^2
R	gas constant for cold carbon dioxide (for physical units see table IV)
$\mathfrak{R}$	universal gas constant, cal/mole °K
$\mathfrak{R}'$	universal gas constant, atm cm^3/mole °K
$\mathfrak{R}''$	universal gas constant, ergs/mole °K
S	total entropy, cal/mole °K
S_j	entropy of the jth species, cal/mole °K
T	temperature, °K
T_o	standard temperature 273.16° K
x_j	mole fraction of jth species
Z	compressibility factor (moles of mixture per cold mole)

β_i	summation over j of all β_{ij}'s
β_{ij}	difference in the stoichiometric coefficients of the jth species in the ith reaction (coefficient on right side of chemical equation minus coefficient on left side)
γ	isentropic exponent
γ_o	isentropic exponent at standard temperature and pressure
θ_{r_j}	characteristic rotational temperature of the jth species, $^{\circ}$K
$\theta_{vj\ell}$	characteristic vibrational temperature of the ℓth mode of the jth species, $^{\circ}$K
ρ	density, g/cm^3
ρ_j	density of the jth species, g/cm^3
ρ_o	density at standard temperature and pressure, g/cm^3

METHOD OF COMPUTATION

The thermodynamic properties of each species are given by the following equations (cf. ref. 1).

For all species except carbon dioxide the free energy is

$$\frac{F_j}{\mathfrak{R}T} = -\left[b_j + \frac{5 + 2(n_j - 1)}{2}\,\ell n\,T + (n_j - 1)\,\ell n\left(\frac{1}{1 - e^{-\theta_{vj}/T}}\right) + \ell n\left(\frac{\sum_{\ell=1}^{10} g_{j\ell}\, e^{-hcE_{j\ell}/kT}}{g_{j\ell=1}}\right)\right] + \frac{h_j^{\,o}}{\mathfrak{R}T} \tag{1}$$

The free energy of carbon dioxide is

$$\frac{F_{CO_2}}{\mathfrak{R}T} = -\left[b_{CO_2} + \frac{7}{2}\,ln\,T - \sum_{l=1}^{4} ln\left(1 - e^{-\theta_{vCO_2 l}/T}\right)\right] \tag{2}$$

For all species except carbon dioxide the enthalpy is

$$\frac{H_j}{\mathfrak{R}T} = \left[\frac{5 + 2(n_j - 1)}{2}\right] + \frac{(n_j - 1)(\theta_{vj}/T)}{\left(e^{\theta_{vj}/T} - 1\right)} + \frac{1}{\mathfrak{R}''T}\,\frac{\sum_{l=1}^{10} hcE_{jl}L_o g_{jl} e^{-hcE_{jl}/kT}}{\sum_{l=1}^{10} g_{jl} e^{-hcE_{jl}/kT}} + \frac{h_j{}^o}{\mathfrak{R}T} \tag{3}$$

The enthalpy of carbon dioxide is

$$\frac{H_{CO_2}}{\mathfrak{R}T} = \frac{7}{2} + \sum_{l=1}^{4} \frac{\theta_{vCO_2 l}/T}{\left(e^{\theta_{vCO_2 l}/T} - 1\right)} \tag{4}$$

The constant b_j is

$$b_j = \frac{3}{2}\,ln\left(\frac{2\pi m_j k}{h^2}\right) + ln\left(\frac{k}{p_o}\right) - (n_j - 1)\,ln\,\theta_{r_j} + ln\,g_{j\,l=1} \tag{5}$$

The entropy is

$$\frac{S_j}{\mathfrak{R}} = \frac{(H_j - F_j)}{\mathfrak{R}T} \tag{6}$$

The pressure is

$$p_j = \frac{p_j \mathfrak{R}T}{(mw)_j} \tag{7}$$

The values of the physical constants which were used in the above equations are tabulated in tables I, II, and III.

The thermodynamic properties of the mixture may be found from those of the individual species, according to the equations,

$$p = \sum_{j=1}^{10} p_j \tag{8}$$

$$\frac{H}{RT_o} = Z \sum_{j=1}^{10} x_j \frac{H_j}{\mathcal{R}T} \frac{T}{T_o} \tag{9}$$

$$\frac{S}{R} = Z \sum_{j=1}^{10} x_j \left[\frac{S_j}{\mathcal{R}} - \ln\left(\frac{p_j}{p_o}\right)\right] \tag{10}$$

$$x_j = \frac{c_j}{\sum_{i=1}^{10} c_i} \tag{11}$$

The c_j's in the above equations must be determined with the help of the chemical reaction equations and their associated equilibrium constants. In principle, any set of chemical reaction equations which contain each species at least once may be solved for the c_j's. In practice it is best to select a set of chemical reaction equations which are ordered according to reaction energies. The set used in these calculations is shown below.

CHEMICAL REACTIONS

$2CO_2 = 2CO + O_2$

$CO = C + O$

$O_2 = O + O$

$O = O^+ + e^-$

$O^+ = O^{++} + e^-$

$C = C^+ + e^-$

$C^+ = C^{++} + e^-$

No matter what set is selected, the equilibrium constants, K_i, may be evaluated from the free energies of the constituent species and the following equations

$$\frac{\Delta F_i}{\mathcal{R}T} = \sum_{j=1}^{10} \beta_{ij} \frac{F_j}{\mathcal{R}T} \tag{12}$$

$$K_i = (\mathcal{R}'T)^{-\beta_i} e^{-\Delta F_i/\mathcal{R}T} \tag{13}$$

$$\beta_i = \sum_{j=1}^{10} \beta_{ij} \tag{14}$$

$$K_i = \rho^{\beta_i} \prod_{j=1}^{10} c_j^{\beta_{ij}} \tag{15}$$

Three additional equations which insure the conservation of the basic species C, O, and e^- are necessary.

$$\sum_{j=1}^{10} m_{ij} c_j = C_i \tag{16}$$

The term m_{ij} is the number of i particles contained in the jth species. The term C_i is the mass fraction of the ith species in the mixture at some reference state (e.g., standard temperature and pressure).

The speed of sound has been evaluated by numerical differentiation of the thermodynamic data. The basic equation defining the speed of sound is

$$a^2 = \left.\frac{\partial p}{\partial \rho}\right|_S \tag{17}$$

Since the numerical data do not contain pressure as a function of density with entropy as a parameter, it is necessary to expand equation (17) to give

$$a^2 = \left.\frac{\partial p}{\partial \rho}\right|_T - \left.\frac{\partial p}{\partial T}\right|_\rho \left[\frac{(\partial S/\partial \rho)|_T}{(\partial S/\partial T)|_\rho}\right] \tag{18}$$

This equation contains only partial derivatives with respect to T and ρ which are the independent variables in the present computations. All four of the partial derivatives in equation (18) were evaluated numerically.

The compressibility is given by

$$Z = \frac{p(mw)_j}{\rho \mathfrak{R} T} \tag{19}$$

The isentropic exponent is given by

$$\gamma = \frac{a^2 \rho}{p} \tag{20}$$

RESULTS

The results are presented in figures 1 through 9. Figure 1 provides the key to all of the data given in figure 2. Figure 2 contains the detailed results of the calculations. Lines of constant temperature and pressure are plotted in the enthalpy-entropy plane. Lines of constant density and sound speed ratio are plotted on the facing page for each of the 17 regions shown in figure 1.

Figure 3 contains plots of the mole fractions of each species as a function of temperature for eleven values of the density ratio. Figures 4 through 9 show the pressure, enthalpy, entropy, speed of sound, compressibility, and isentropic exponent as functions of temperature for eleven values of the density ratio.

The values of gas constant, as well as the density, and speed of sound at standard temperature and pressure are shown in several systems of physical units in table IV to facilitate use of the charts.

DISCUSSION

The assumptions which are made in these calculations are not uniformly valid over the entire ranges of temperature and density. At the highest densities the assumption that each species behaves individually as an ideal gas is bad. At the highest temperatures, above say $15{,}000^\circ$ K, an insufficient number of the higher electronic energy levels may have been included. In the medium temperature range the rigid rotator-harmonic oscillator approximation based on the lowest electronic level of the molecule will introduce an error.

The errors mentioned in the preceding paragraph may appreciably influence the values of the mole fractions shown in figure 3. In the case of the overall thermodynamic variables these errors are less serious. A check against the results of reference 2 shows differences of only 1 percent in the equilibrium thermodynamic variables in spite of the rigid rotator-harmonic oscillator approximation used here.

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4. Herzberg, Gerhard: Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules. Second ed., D. Von Nostrand Co., Inc., New York, 1945.

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TABLE I.- FUNDAMENTAL PHYSICAL CONSTANTS

Universal gas constant:

$\Re$ = 1.98647 cal/mole °K

$\Re'$ = 82.0561 atm cm^3/mole °K

$\Re''$ = 8.3134×10^7 erg/mole °K

Planck's constant:

$h = 6.6256\times10^{-27}$ erg-sec

Boltzmann's constant:

$k = 1.38054\times10^{-16}$ erg/°K

Pressure of one atmosphere:

$p_o = 1.013\times10^6$ dyn/cm^2

Avogadro's number:

$L_o = 6.02252\times10^{23}$ molecules/mole

Speed of light:

$c = 2.99793\times10^{10}$ cm/sec

TABLE II.- ATOMIC CONSTANTS USED IN PROGRAM[a]

Species	n_j	$(mw)_j$	b_j	θ_{vj}, °K	θ_{r_j}, °K	h_j^o, kcal/mole
O_2	2	32.000 (1)	1.21618 (1)	2256 (1)	4.16 (1)	93.964 (2)
O	1	16.000 (1)	2.1032 (1)	---	---	105.96 (2)
O^+	1	16.000 (1)	1.8794 (1)	---	---	419.88 (2)
O^{++}	1	16.000	.4939	---	---	1230.5 (2)
e^-	1	5.4847×10^{-4} (1)	-14.23517 (1)	---	---	0
CO_2	---	44.011	1.8948	1932.1 (4) 960.1 960.1 3380.0	1.124 (4)	0
CO	2	28.011	.3118	3082 (3)	2.779	19.782 (2)
C	1	12.011	.0637	---	---	169.99 (2)
C^+	1	12.011	.7569	---	---	429.77 (2)
C^{++}	1	12.011	.0637	---	---	991.956 (2)

[a] Numbers in ( ) refer to references from which the physical constants were taken. Those physical constants without reference numbers were computed for this report.

TABLE III.- ELECTRONIC ENERGY LEVELS[a]

Species	Energy level, cm^{-1}	Degeneracy	Species	Energy level, cm^{-1}	Degeneracy
O_2	0	3	O^{++}	0	1
	7918	2		113.4	3
	13195	1 (1)		306.8	5 (5)
	36096	3		20271	5
	49802	3		43183.5	1
				60312.1	5
CO	0	1			
	48687.5	6	C	0	1
	55901	3 (3)		16.4	3
	62299.4	6		43.5	5 (5)
	65074.8	2		10193.7	5
				21648.4	1
O	0	5		33735.2	5
	159	3			
	227	1 (1)	C^+	0	2
	15868	5		64	4
	33792	1		43000.2	2 (5)
				43021.8	4
O^+	0	4		43050.7	6
	26808	6			
	26829	4 (1)	C^{++}	0	1
	40467	4		52315	1
	40468	2		52338	3 (5)
				52394.8	5

[a] Numbers in ( ) refer to references from which the physical constants were taken.

TABLE IV.- CONSTANTS FOR CARBON DIOXIDE

Gas constant for carbon dioxide:

$$R = 1.125\times10^{3}\ \mathrm{ft^2/sec^2\ {}^{o}R}$$

$$R = 1.881\times10^{6}\ \mathrm{cm^2/sec^2\ {}^{o}K}$$

$$R = 1.881\times10^{2}\ \mathrm{m^2/sec^2\ {}^{o}K}$$

Density at standard temperature and pressure:

$$\rho_o = 0.3810\times10^{-2}\ \mathrm{slugs/ft^3}$$

$$\rho_o = 0.1964\times10^{-2}\ \mathrm{g/cm^3}$$

$$\rho_o = 0.1964\times10^{1}\ \mathrm{kg/m^3}$$

Sound speed at standard temperature and pressure:

$$a_o = 0.8435\times10^{3}\ \mathrm{ft/sec}$$

$$a_o = 0.2571\times10^{5}\ \mathrm{cm/sec}$$

$$a_o = 0.2571\times10^{3}\ \mathrm{m/sec}$$

Isentropic exponent at standard temperature and pressure:

$$\gamma_o = 1.281$$

Product of gas constant for carbon dioxide and standard temperature:

$$RT_o = 0.5532\times10^{6}\ \mathrm{ft^2/sec^2}$$

$$RT_o = 0.5138\times10^{9}\ \mathrm{cm^2/sec^2}$$

$$RT_o = 0.2388\times10^{5}\ \mathrm{cal/g}$$

$$RT_o = 0.2210\times10^{2}\ \mathrm{Btu/lbm}$$

$$RT_o = 0.9991\times10^{8}\ \mathrm{J/kg}$$

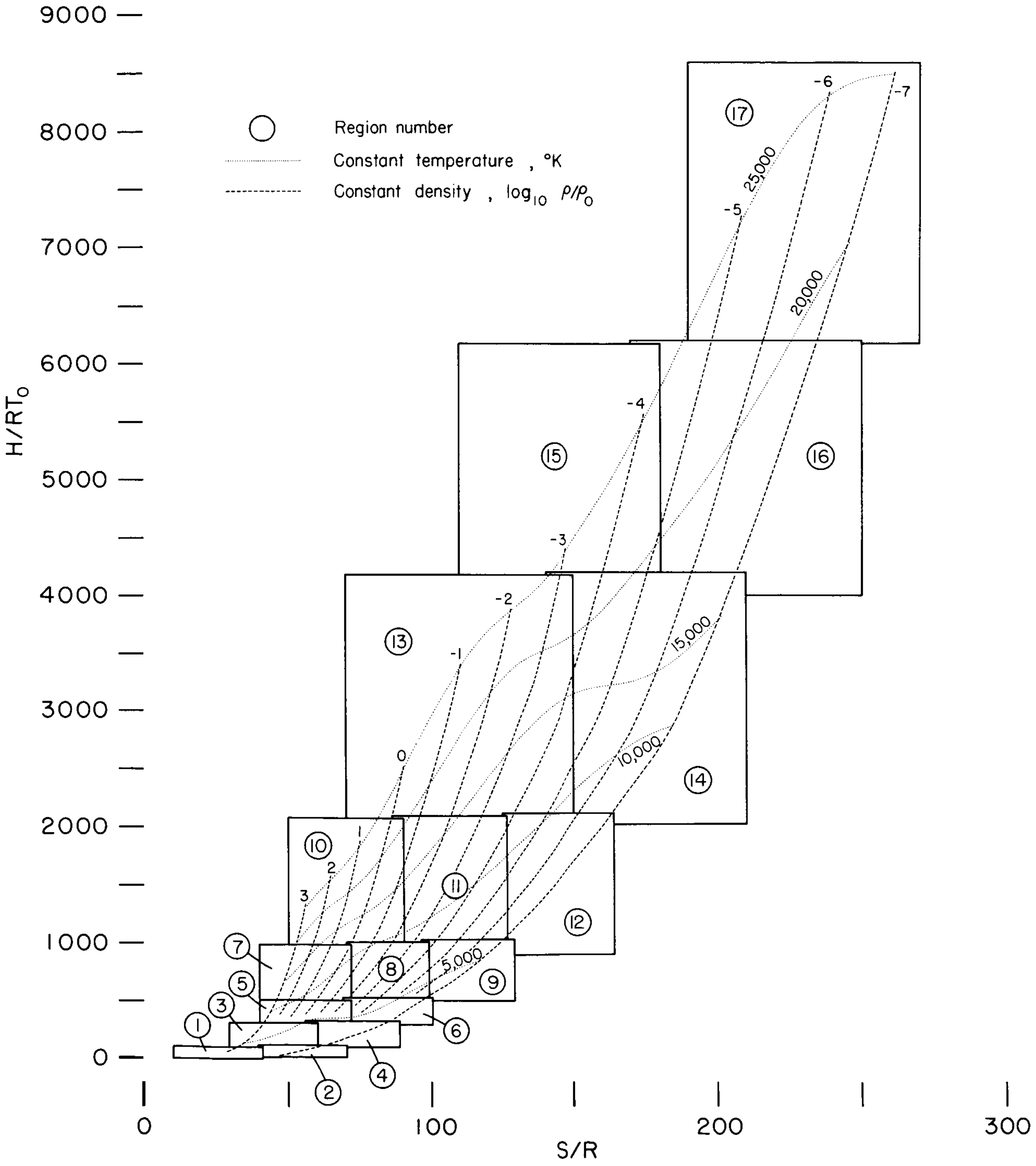
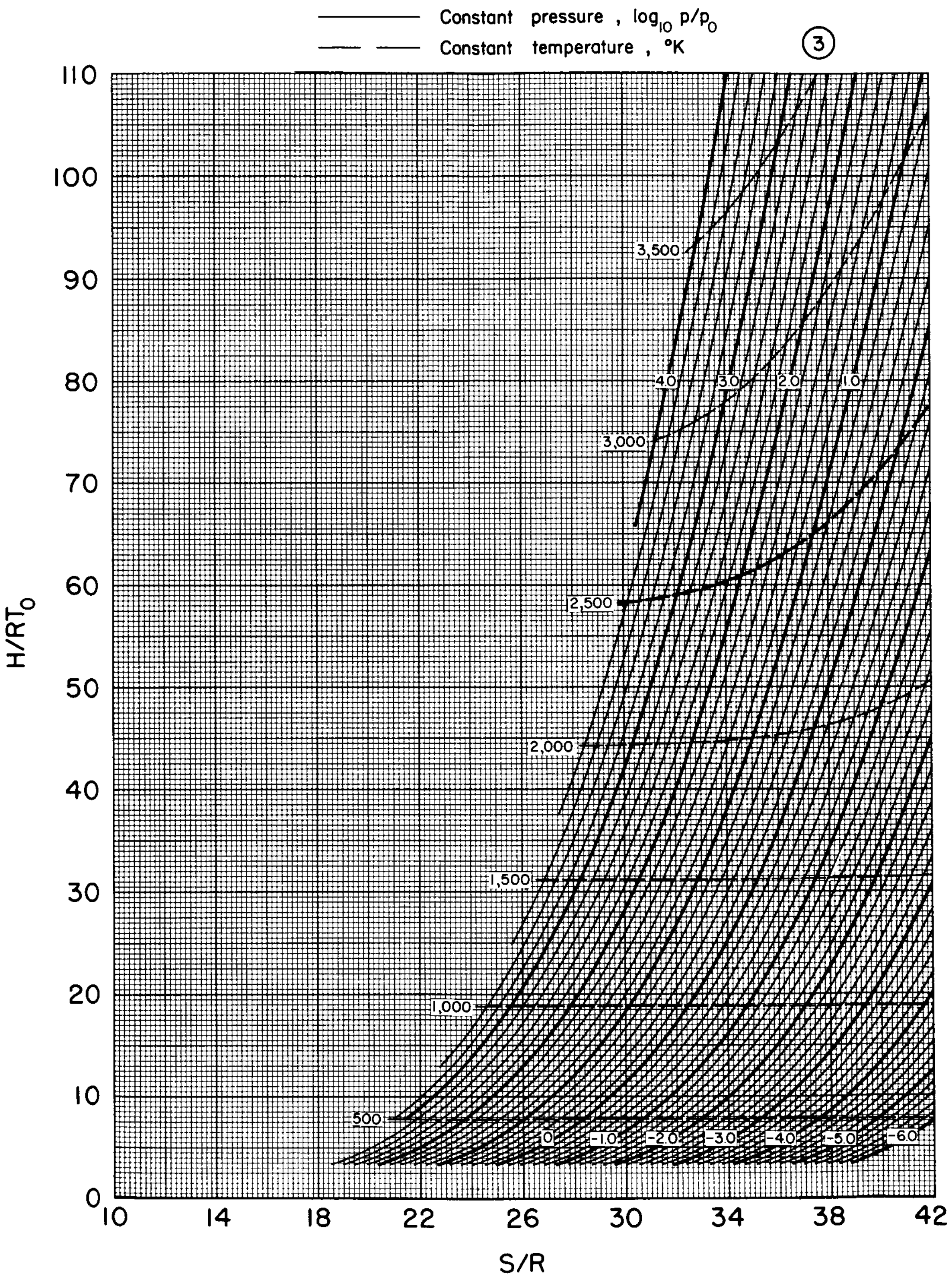


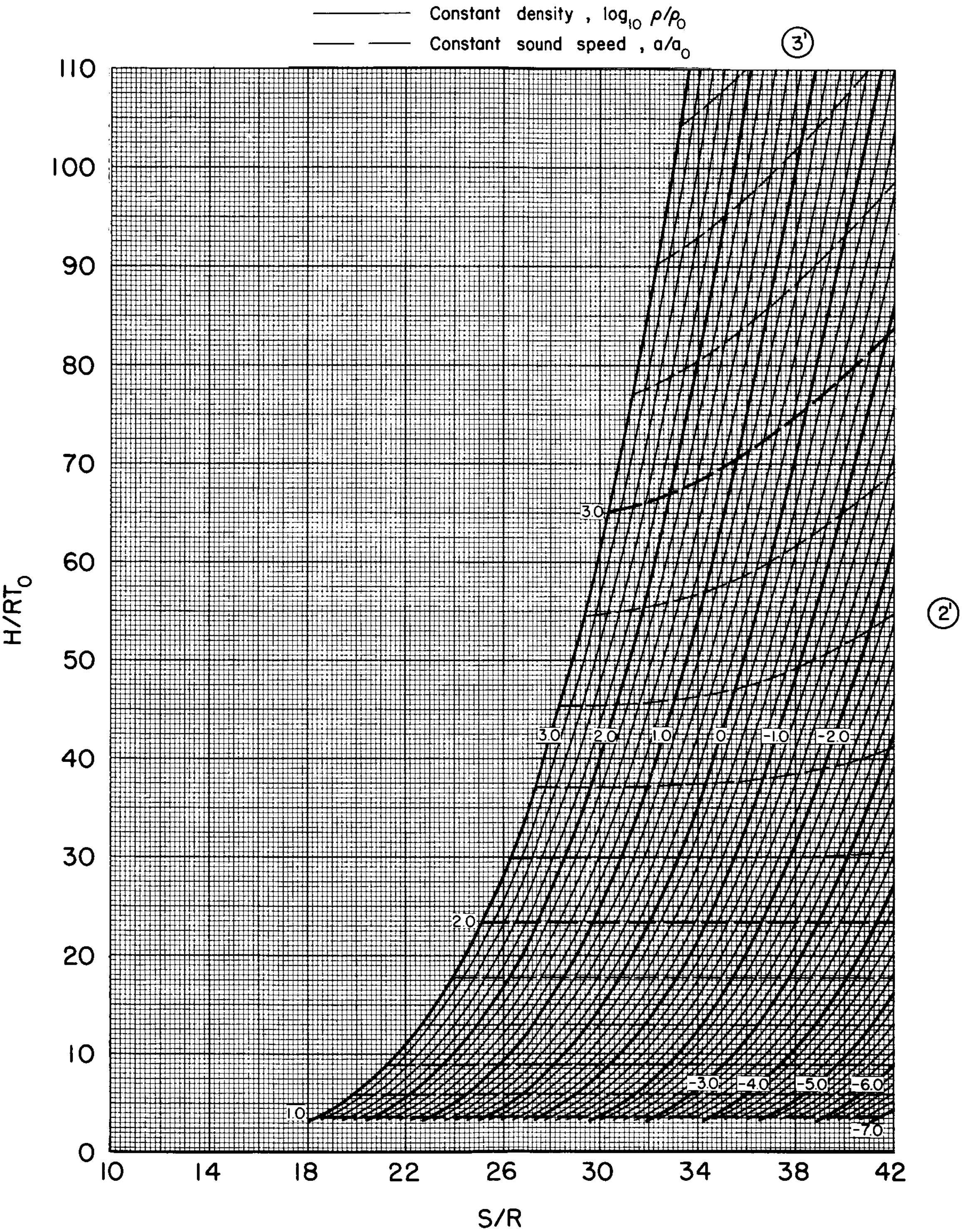
Figure 1.- Key to presentation of thermodynamic data for carbon dioxide.



②

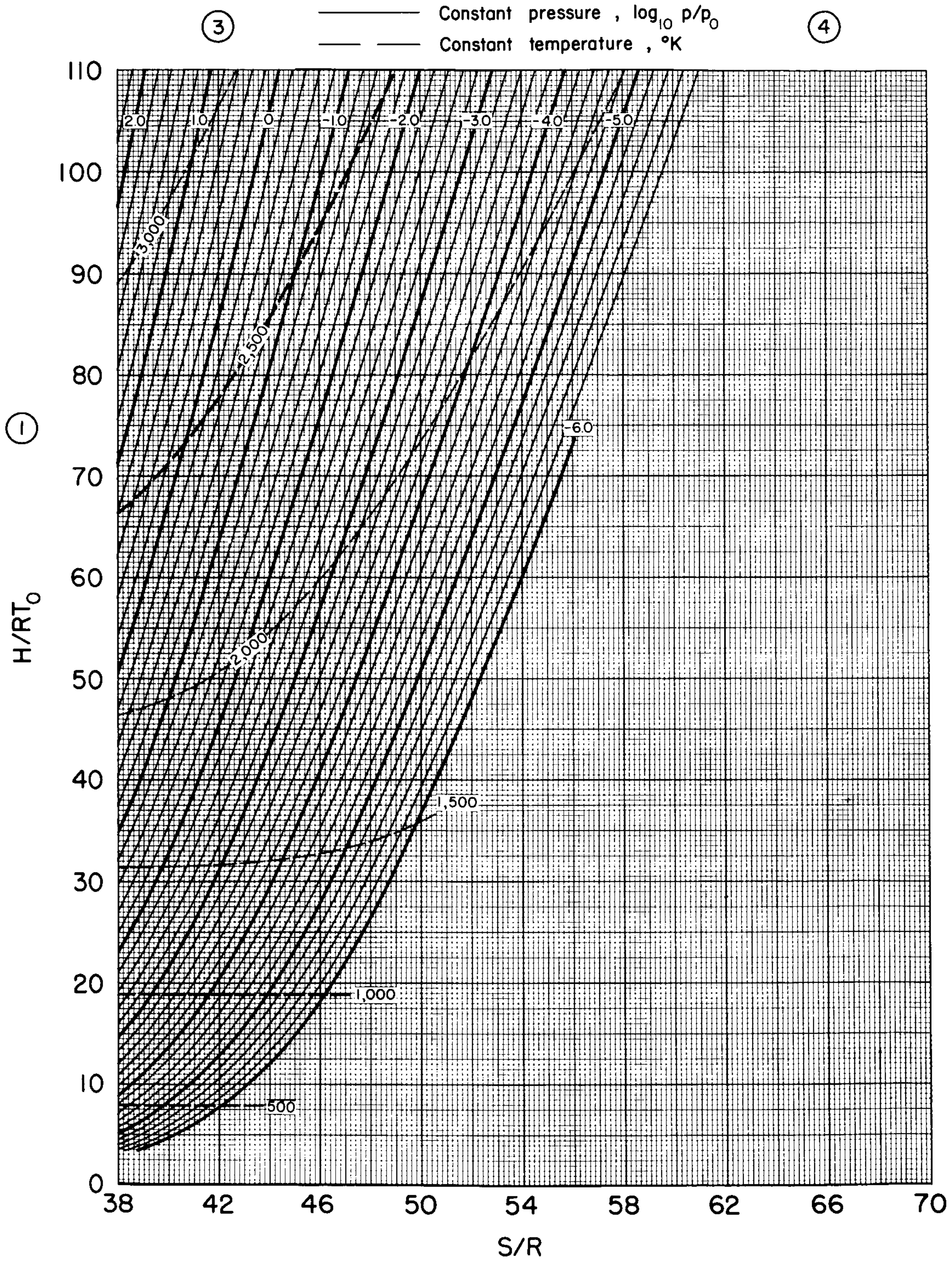
(a) Region 1

Figure 2.- Thermodynamic data for carbon dioxide.



(a) Region 1 - Concluded.

Figure 2.- Continued.



(b) Region 2

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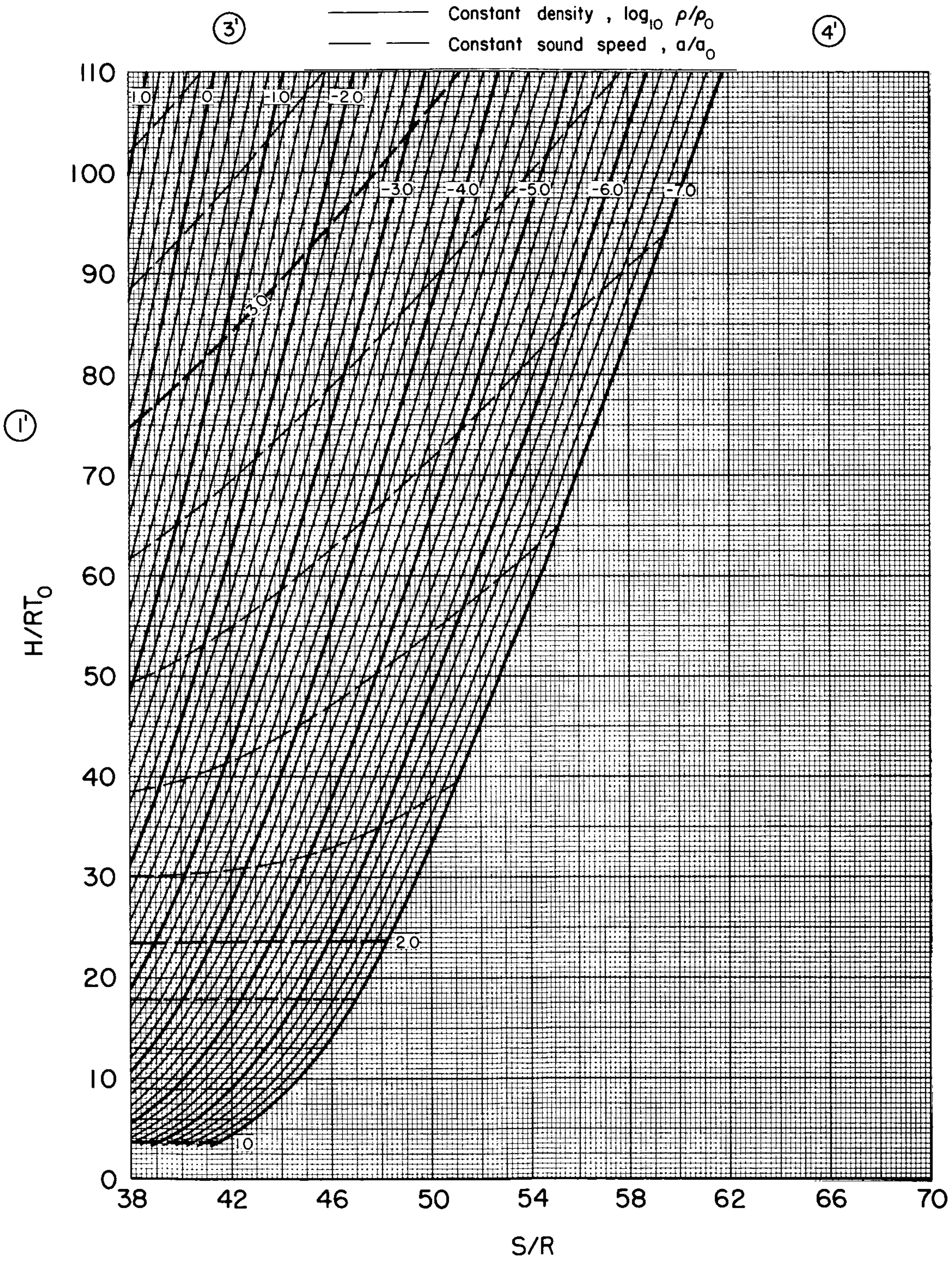

(b) Region 2 - Concluded.

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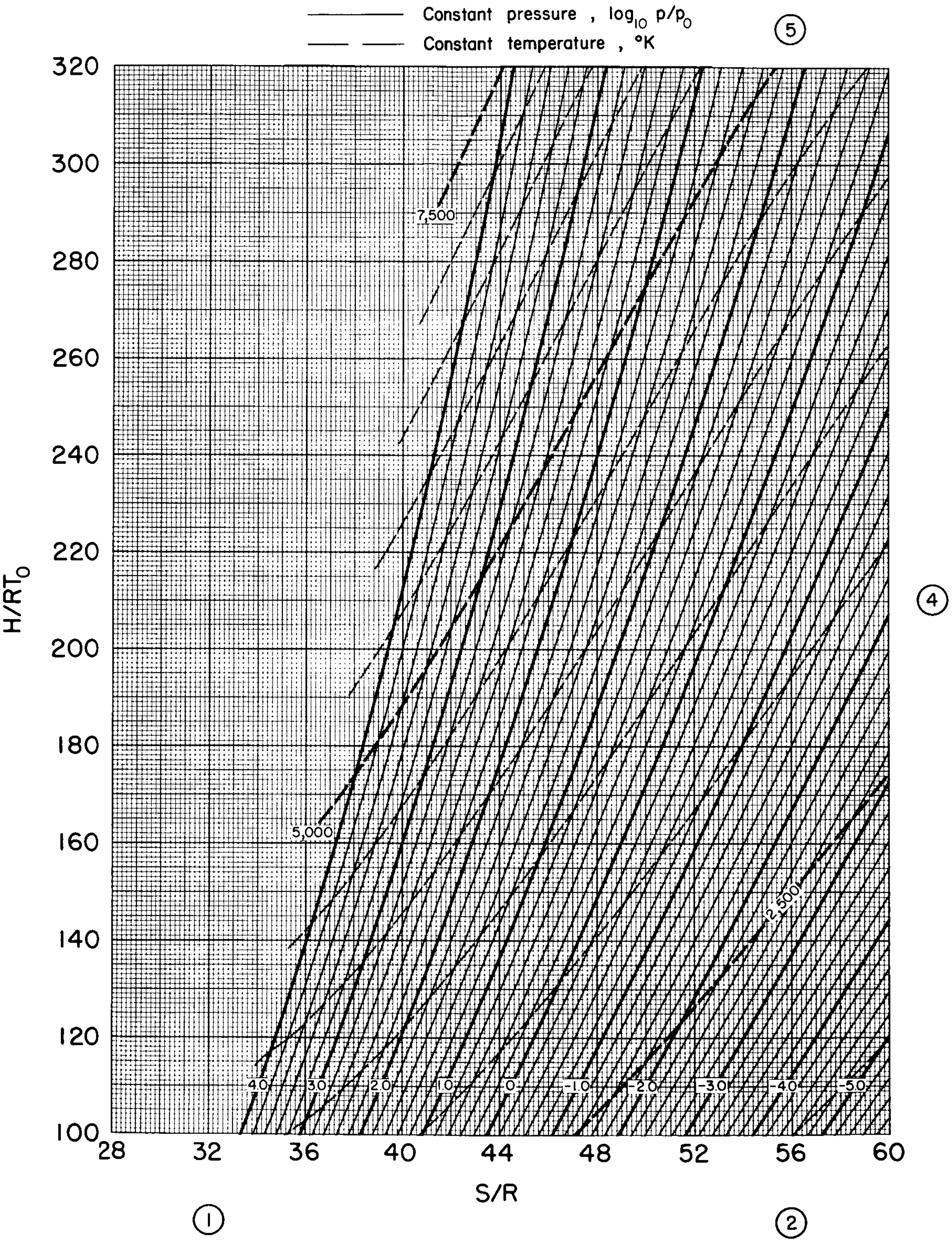

(c) Region 3

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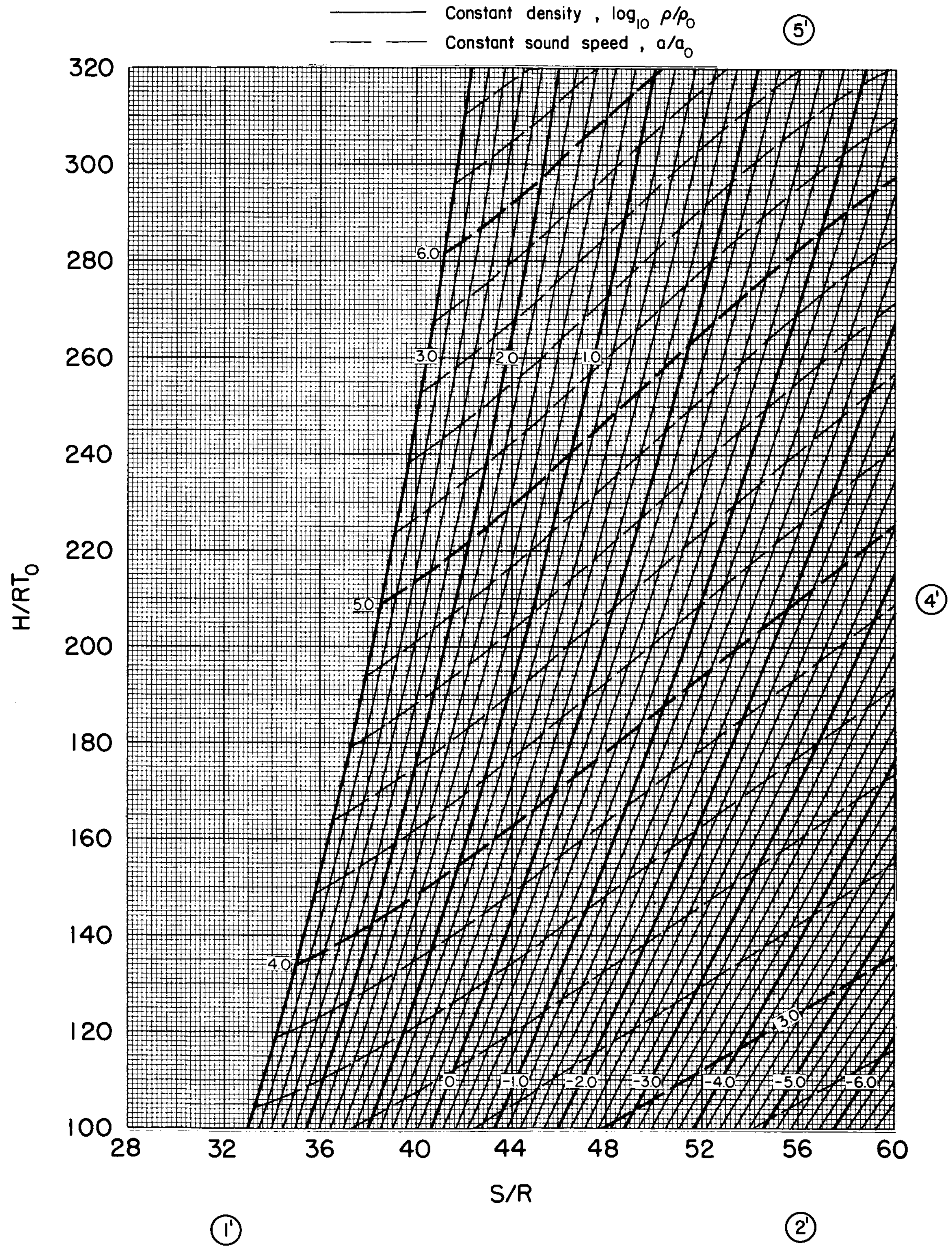
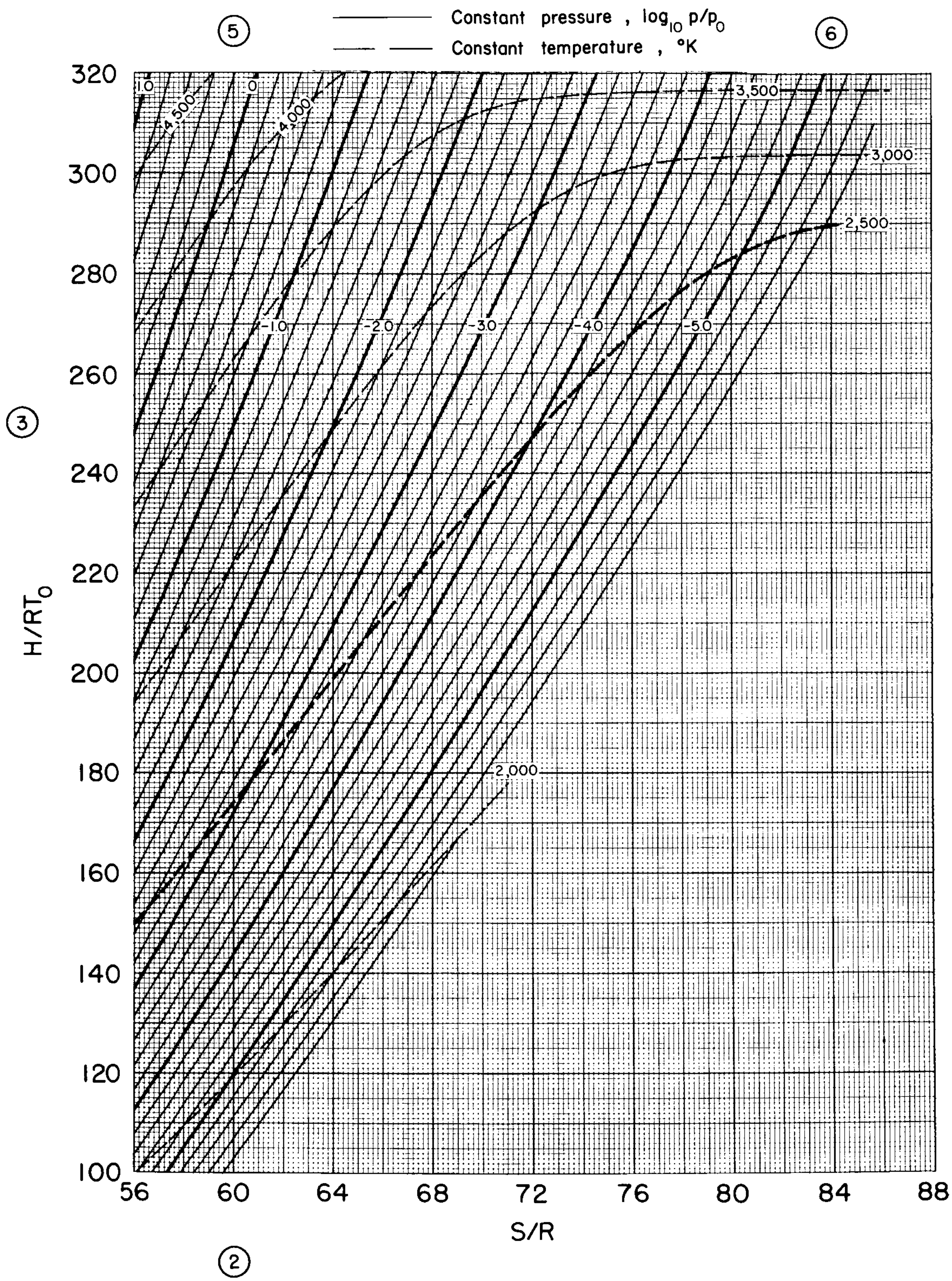


(c) Region 3 - Concluded.

Figure 2.- Continued



(d) Region 4

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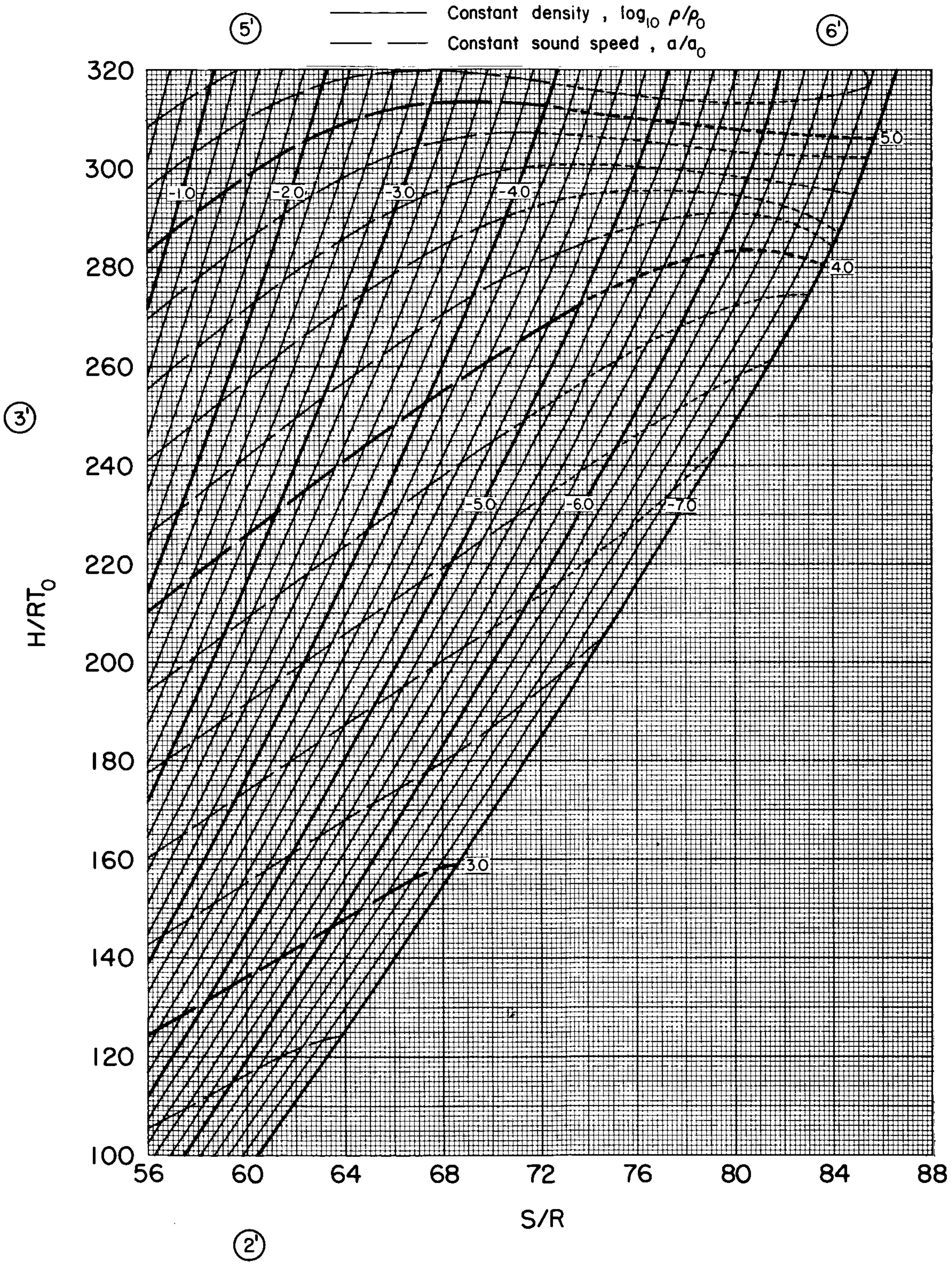

(d) Region 4 - Concluded.

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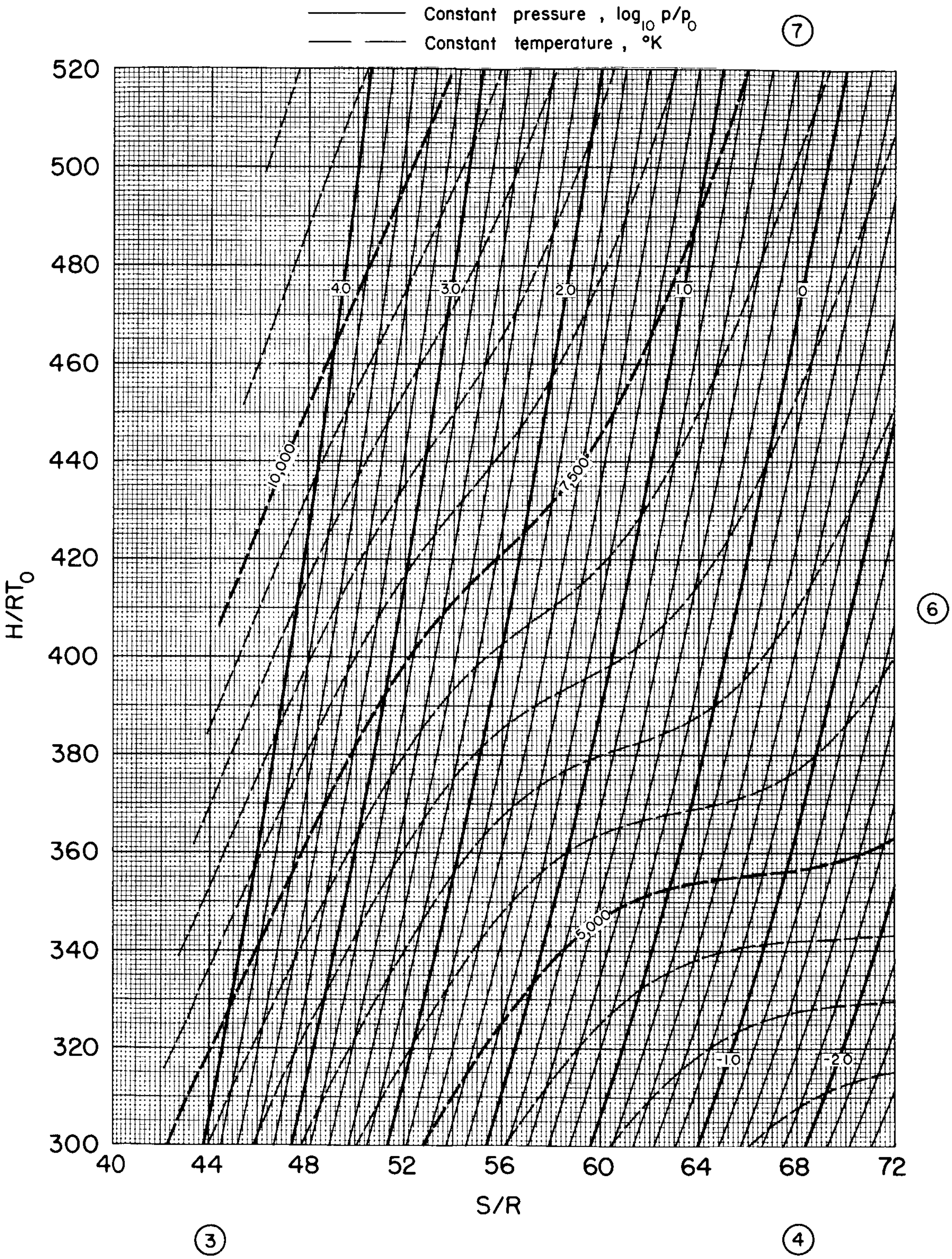

(e) Region 5

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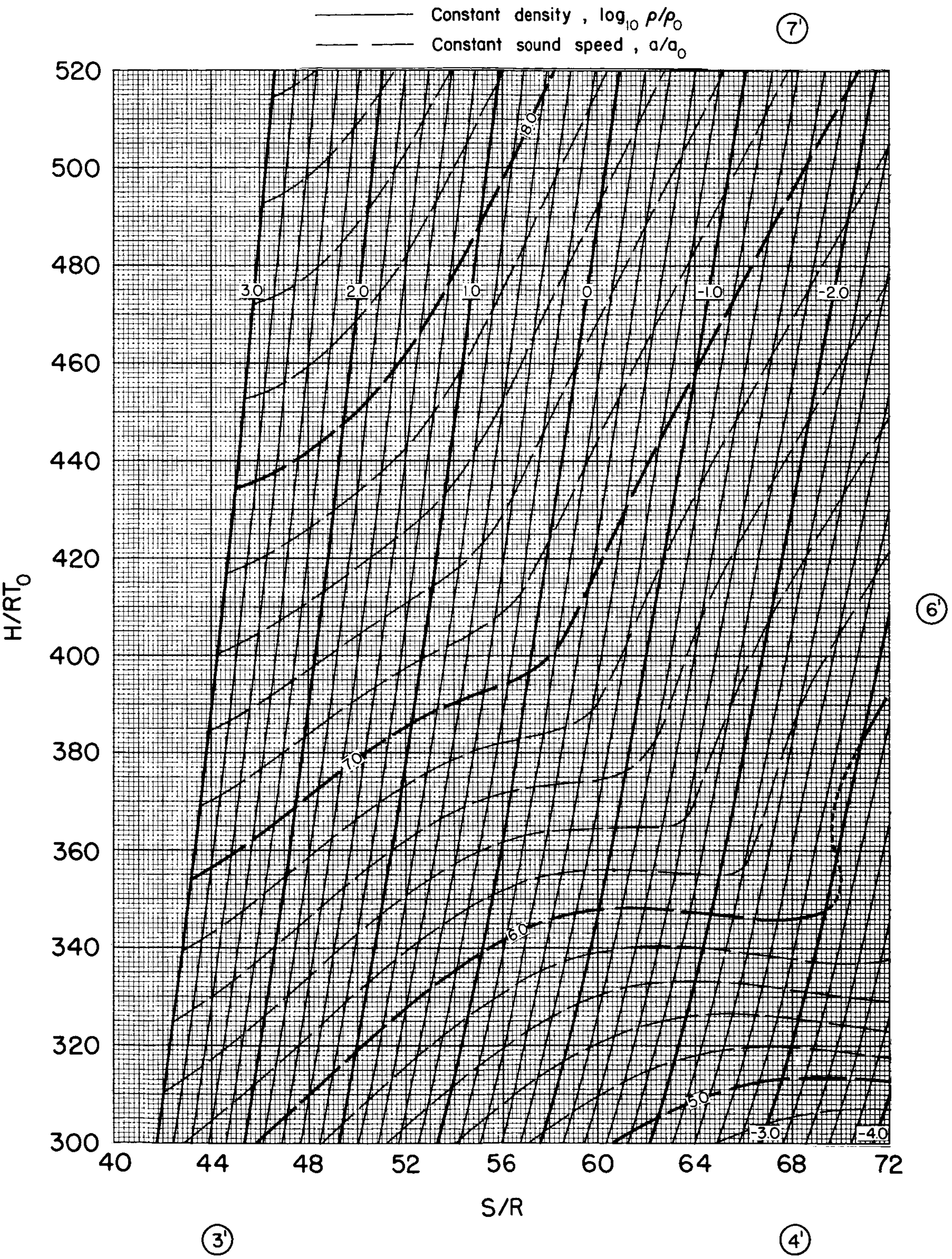

(e) Region 5 - Concluded.

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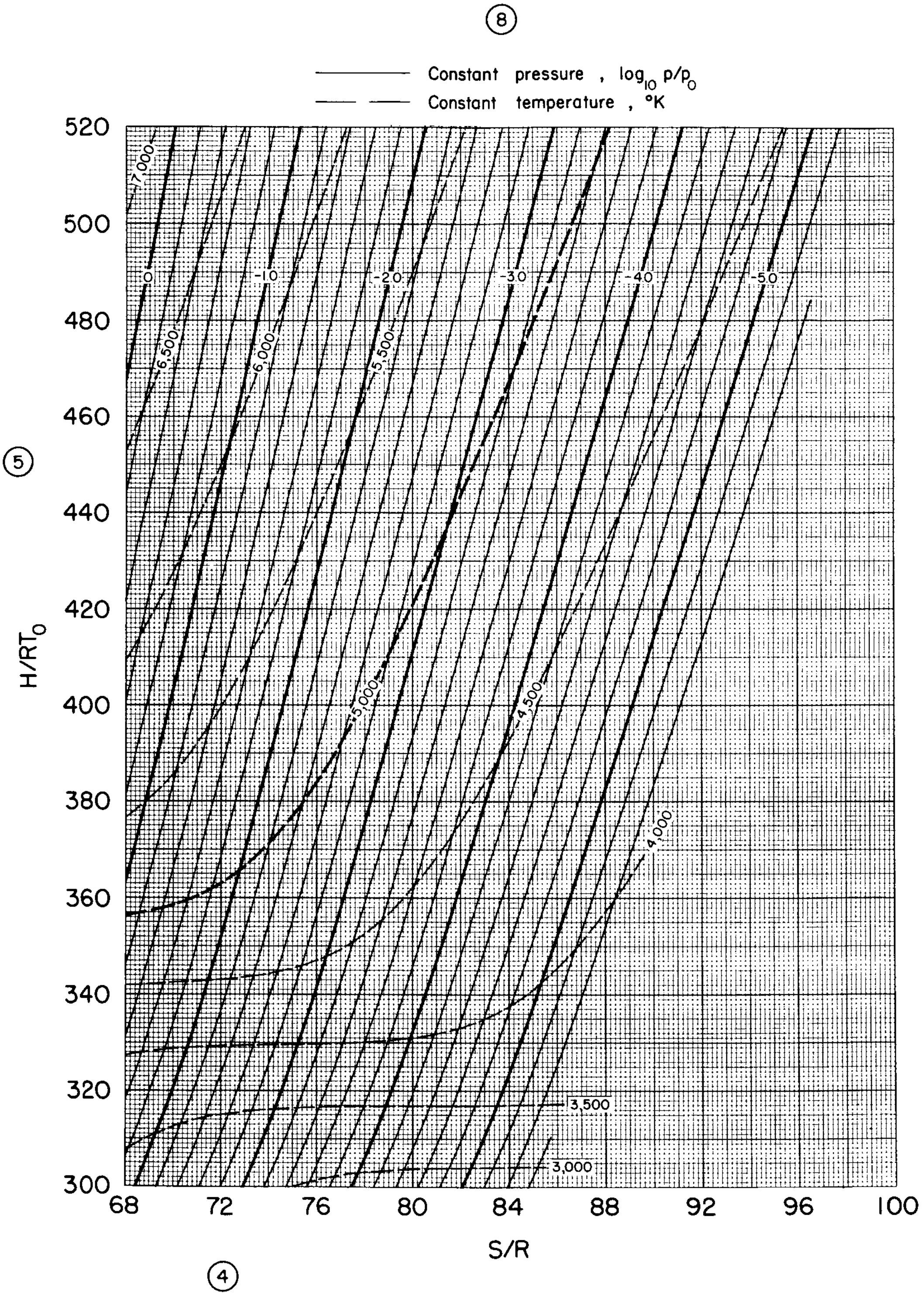

(f) Region 6

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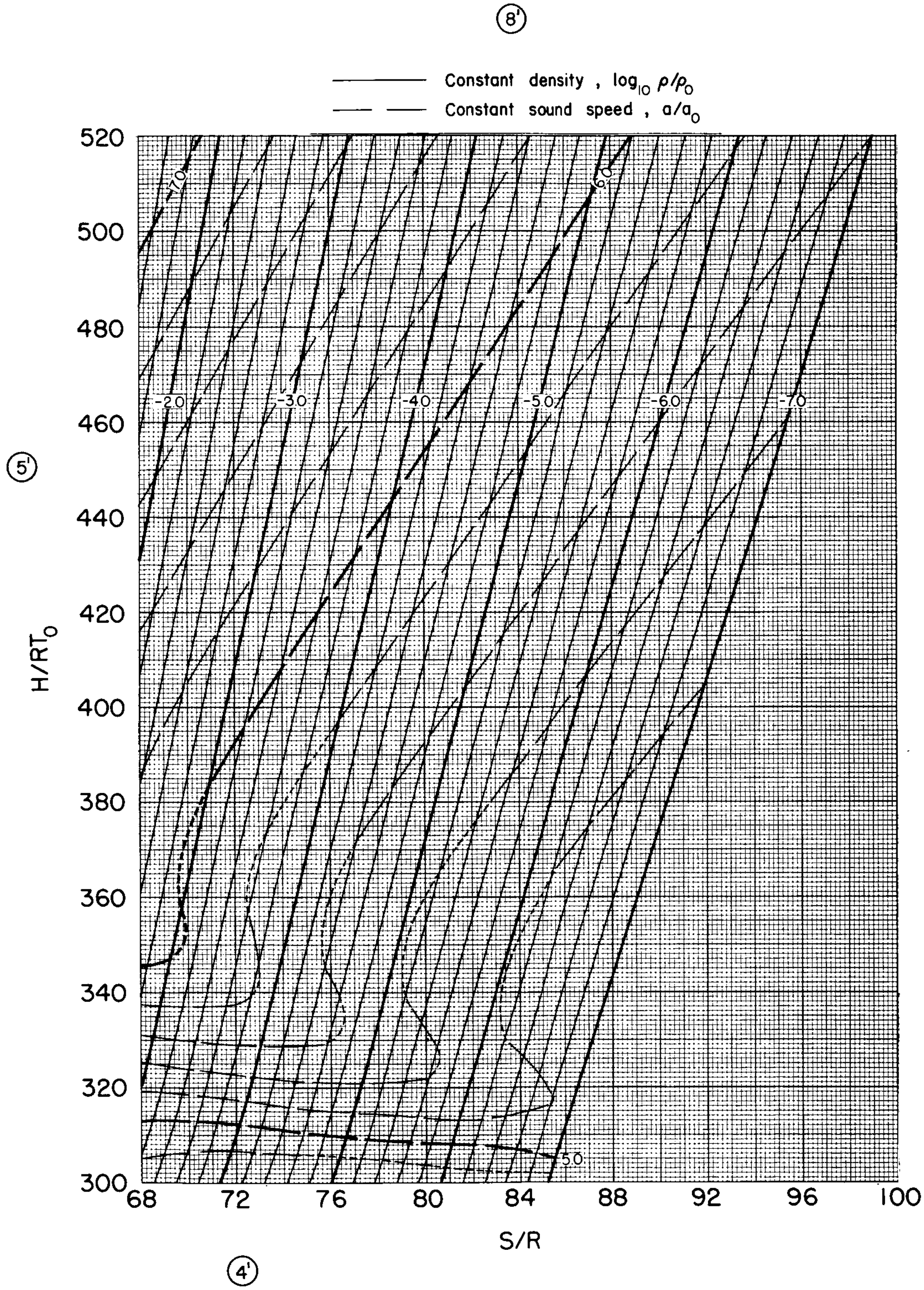

(f) Region 6 - Concluded.

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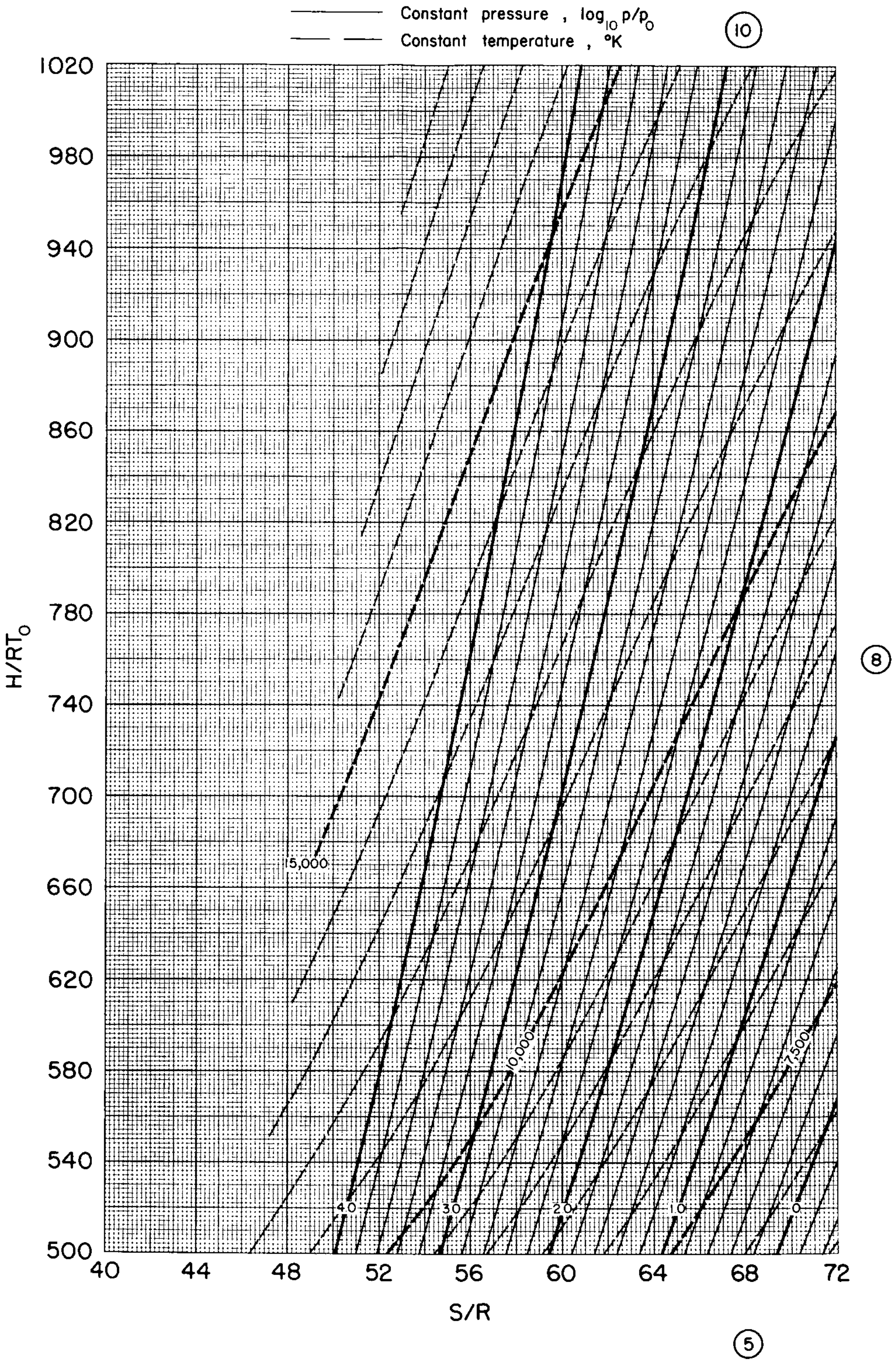

(g) Region 7

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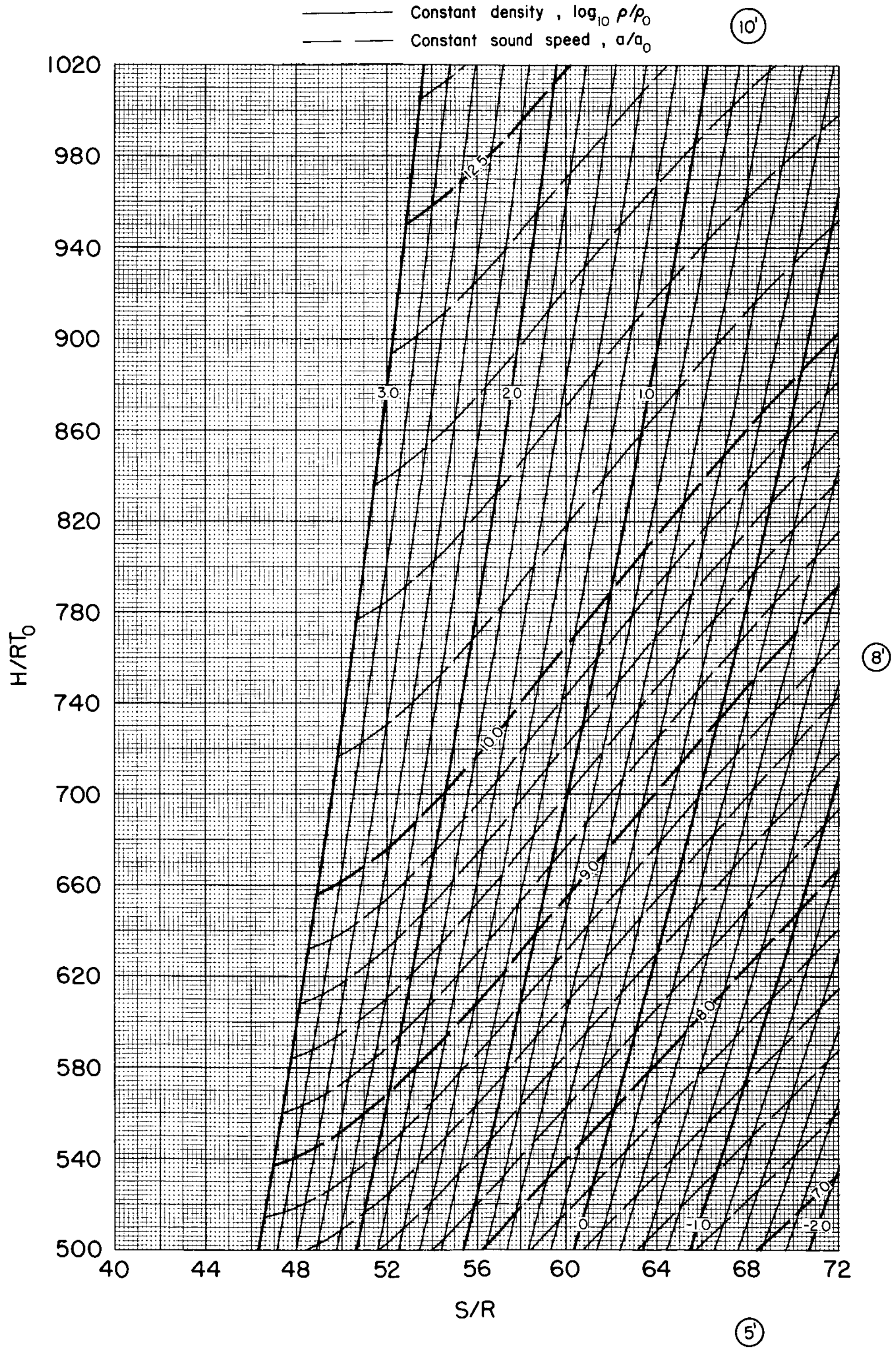
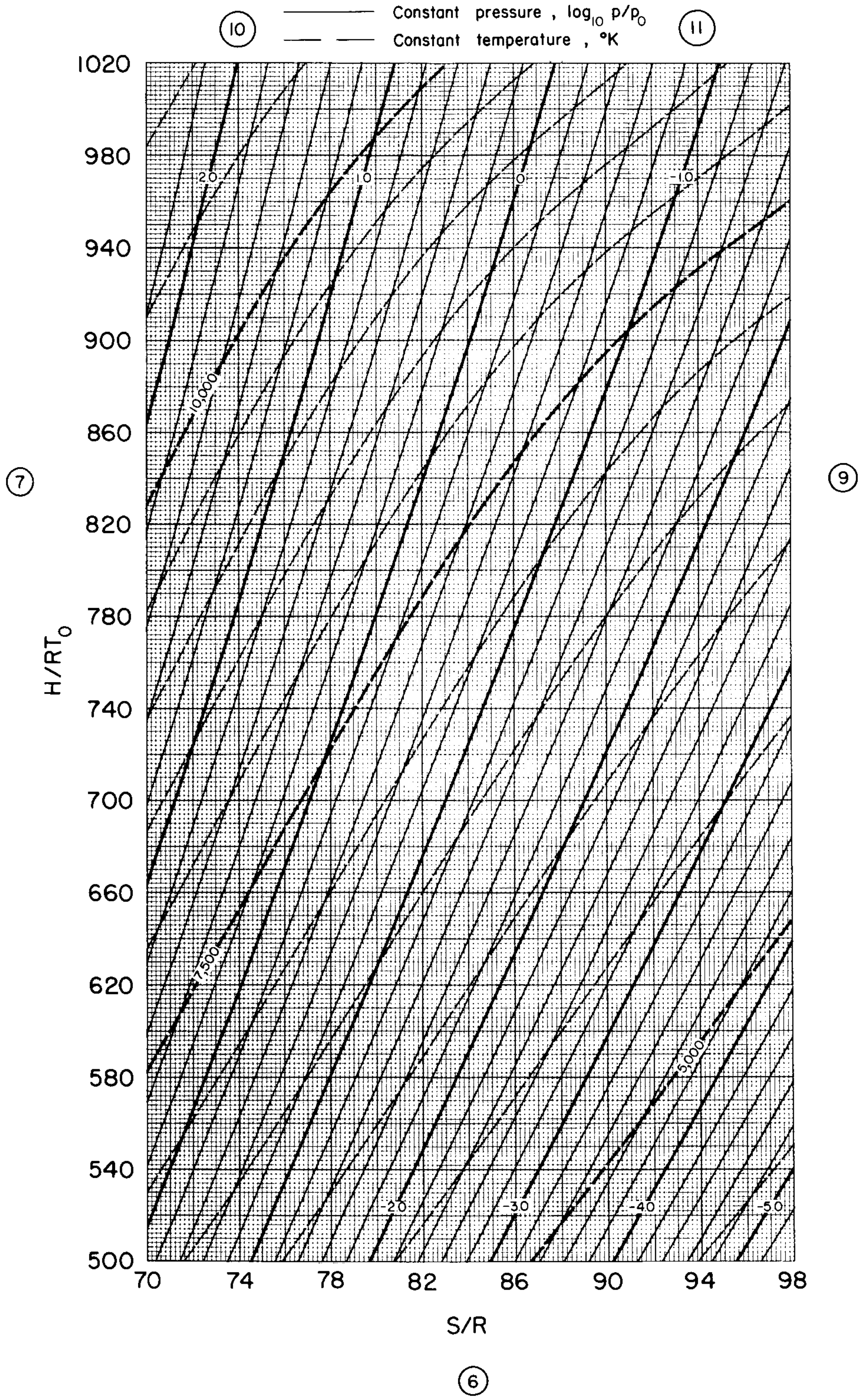


(g) Region 7 - Concluded.

Figure 2.- Continued



(h) Region 8

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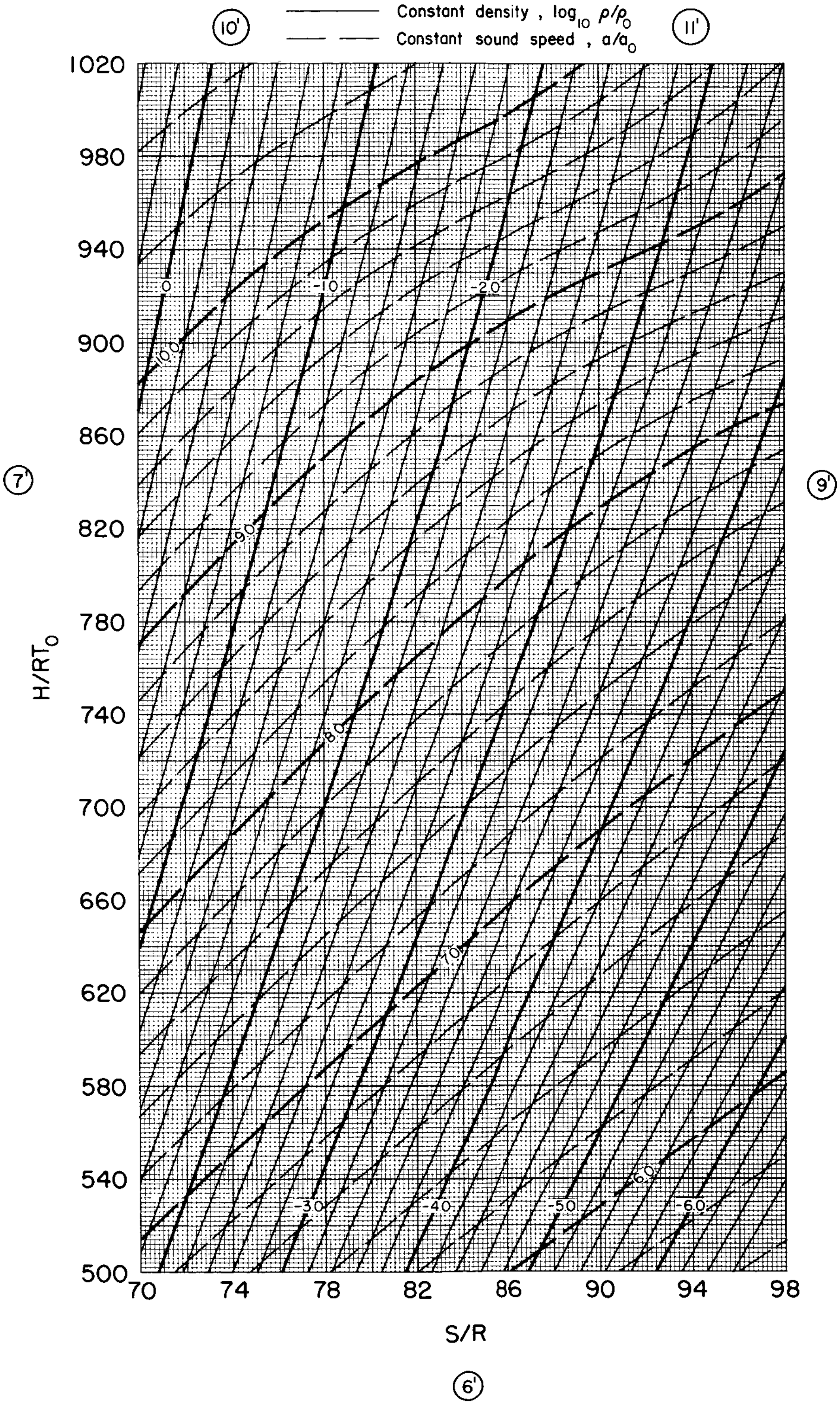

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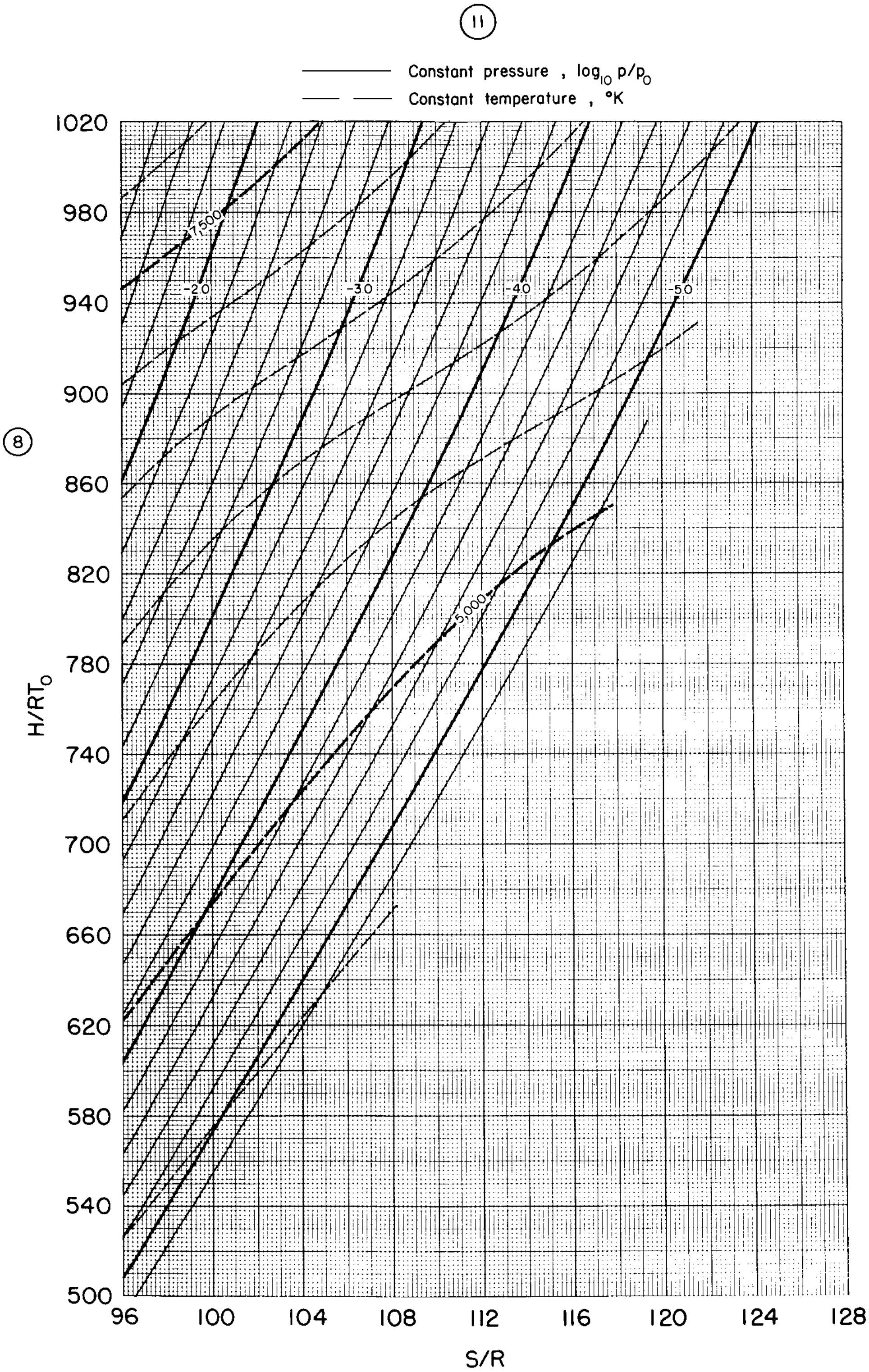

(i) Region 9

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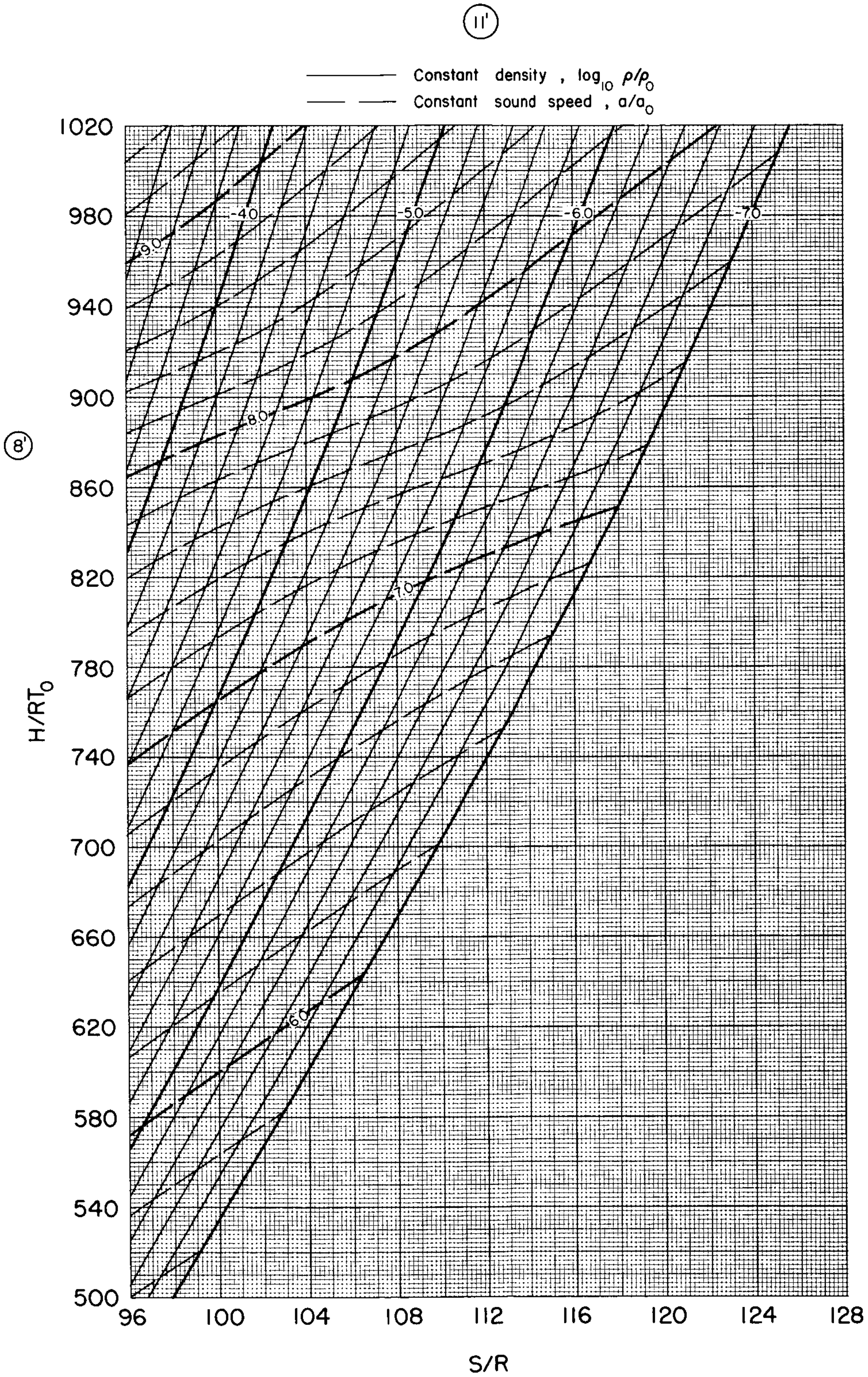

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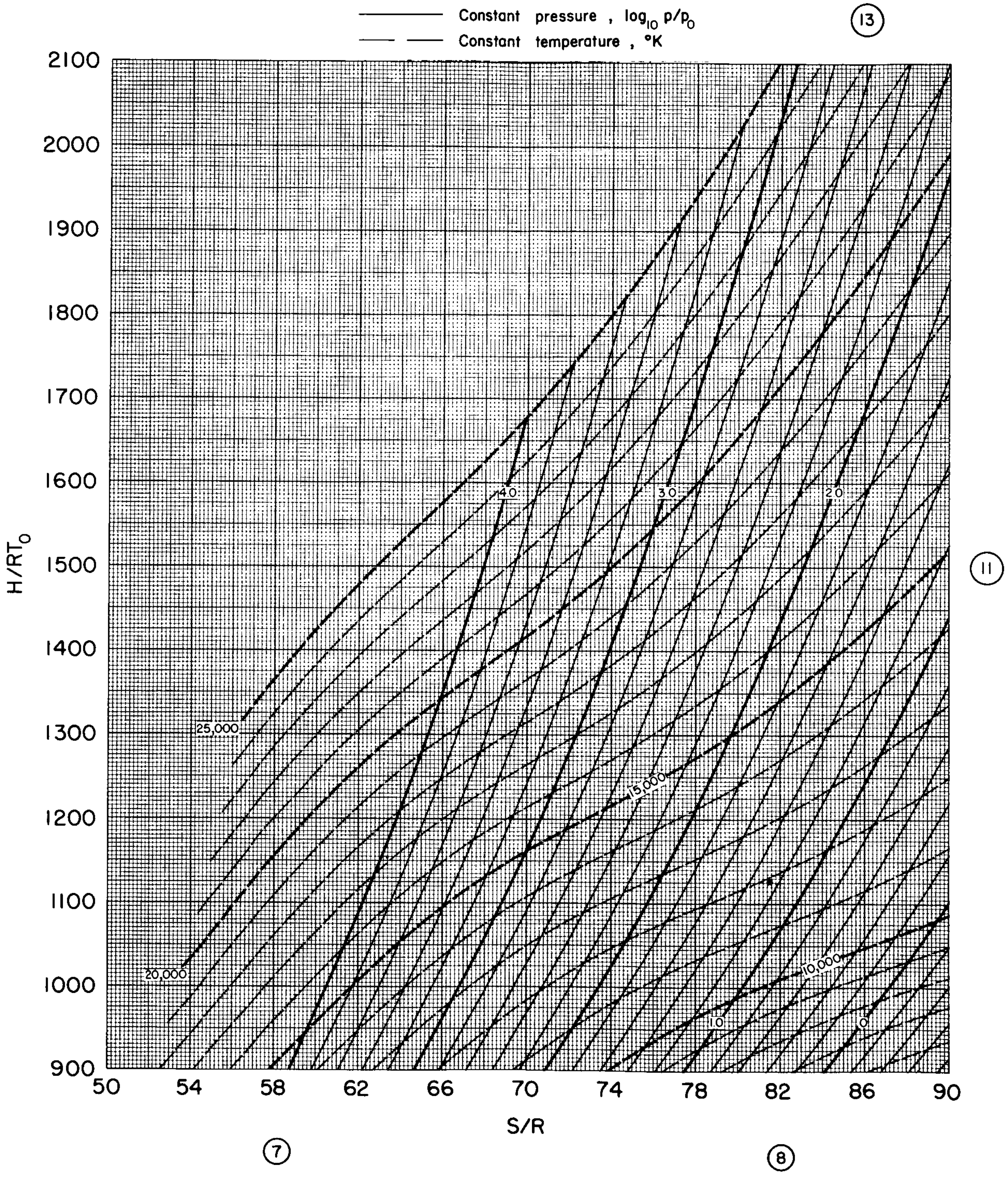

(j) Region 10

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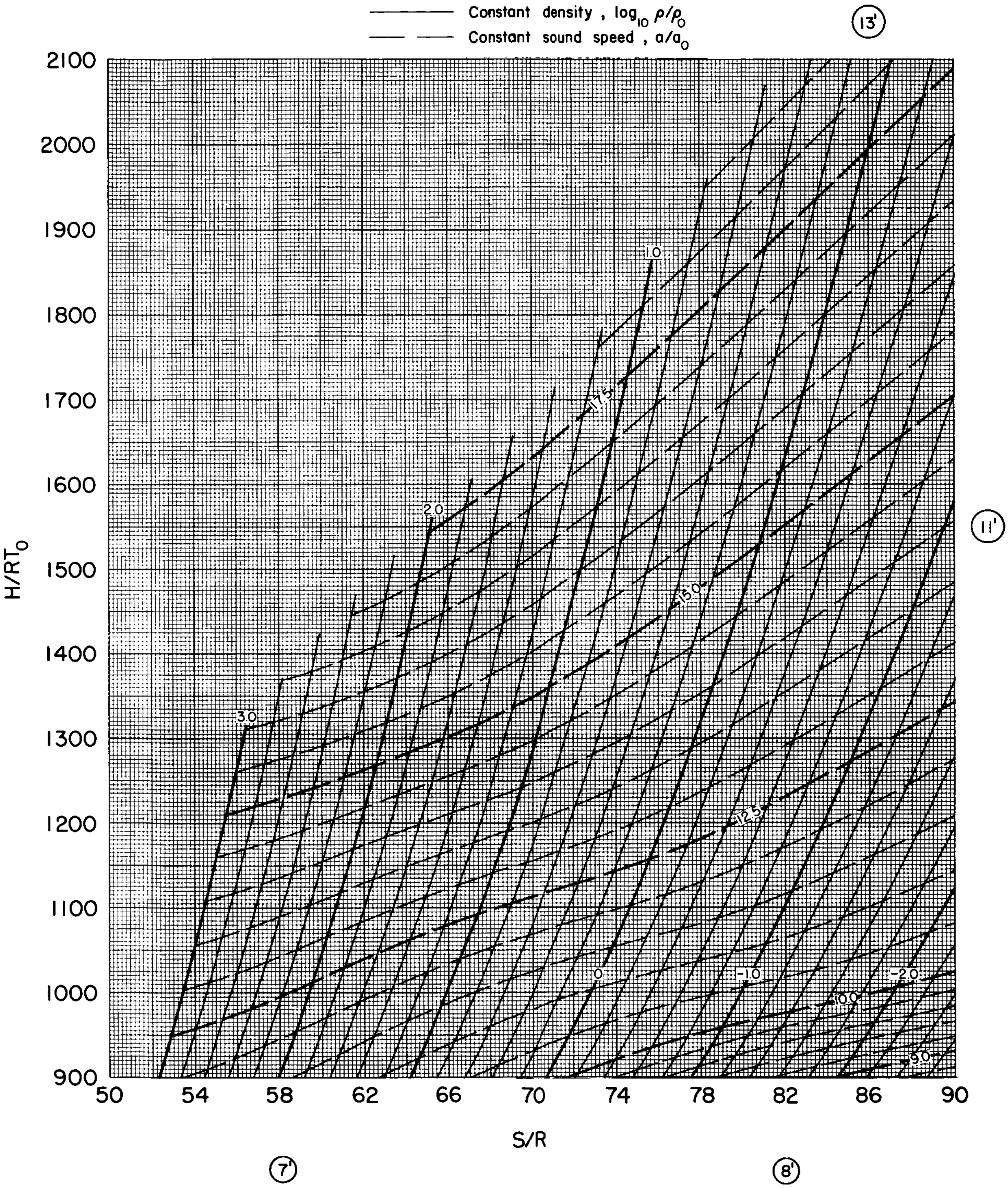

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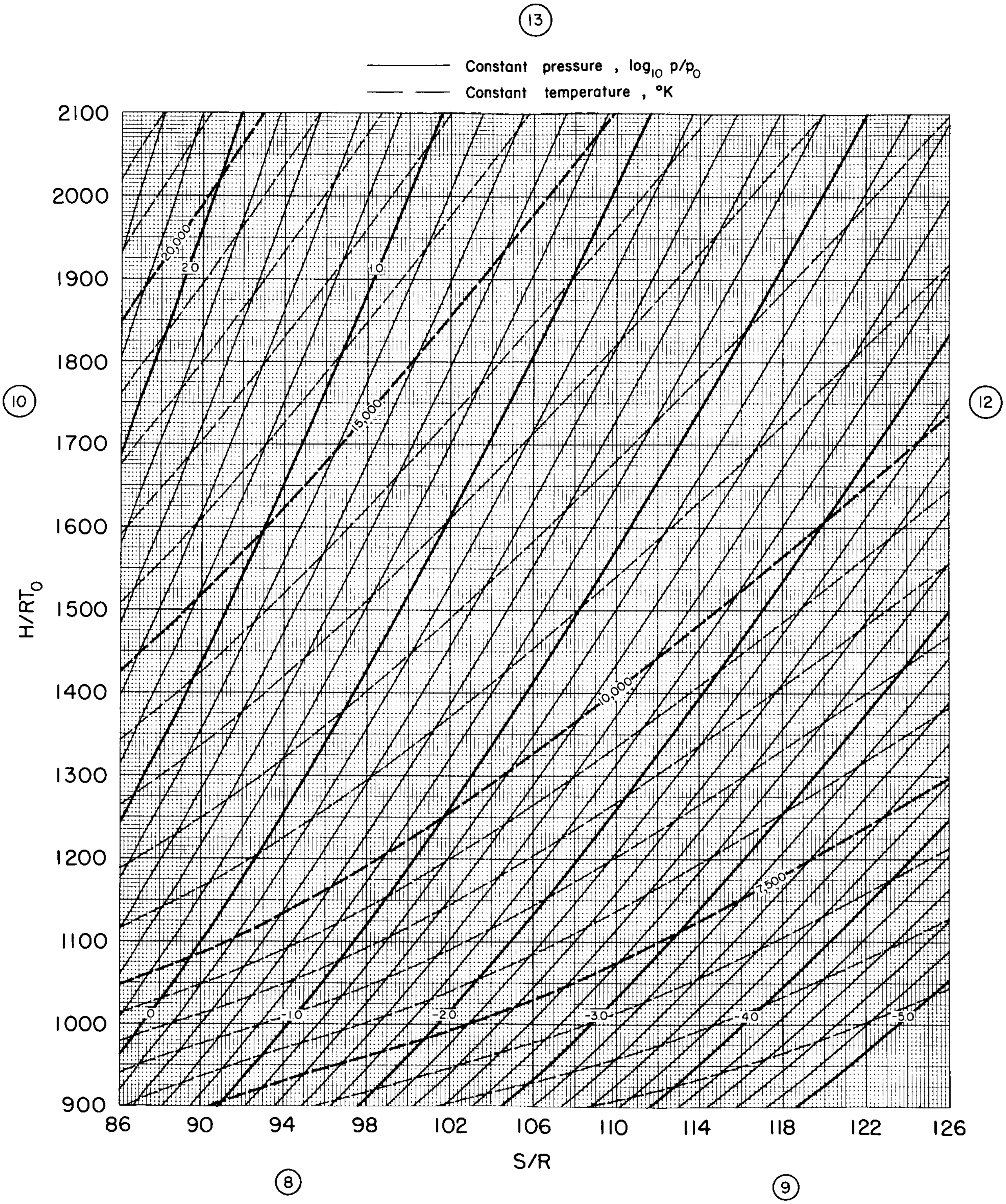

(k) Region 11

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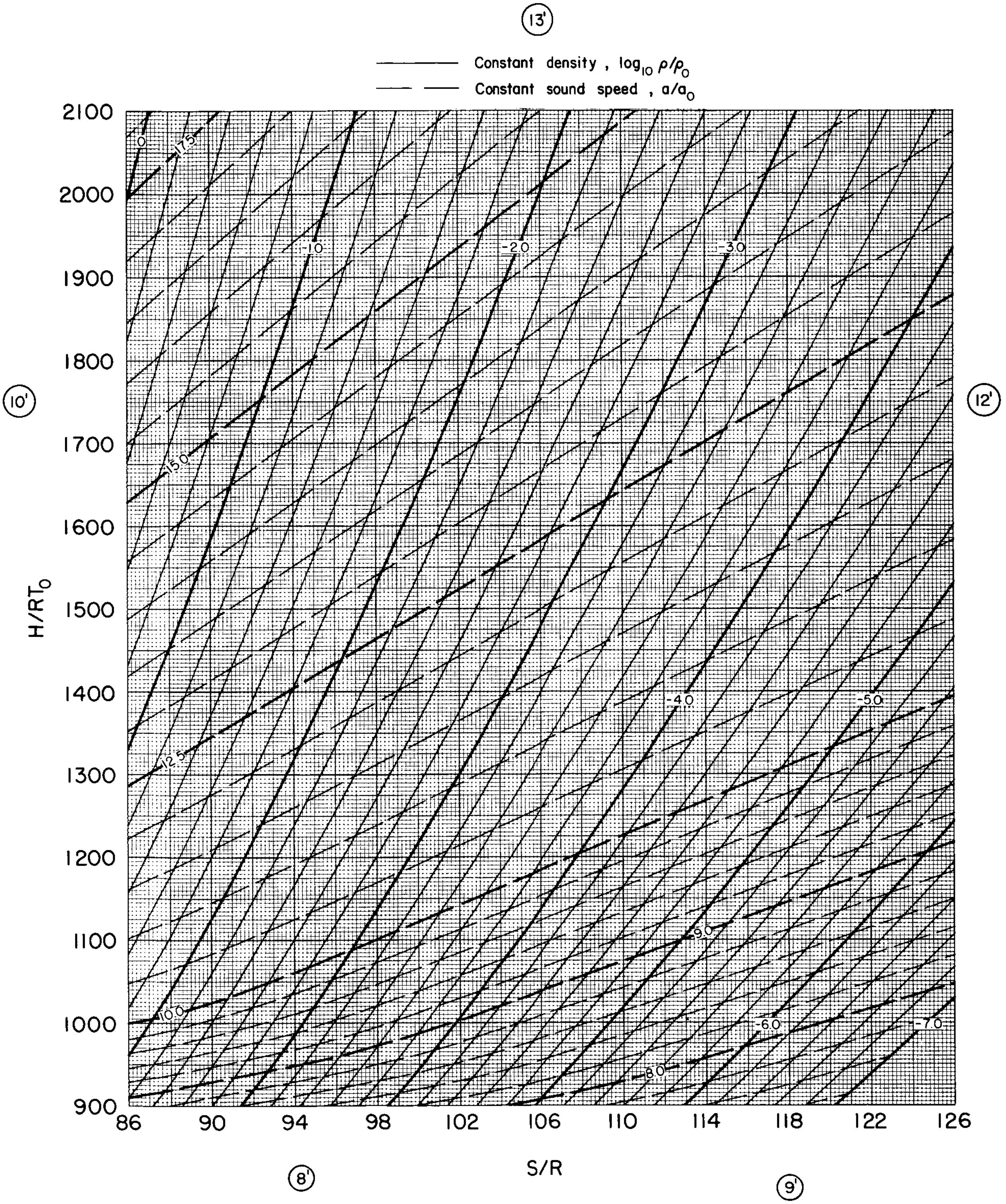

(k) Region 11 - Concluded.

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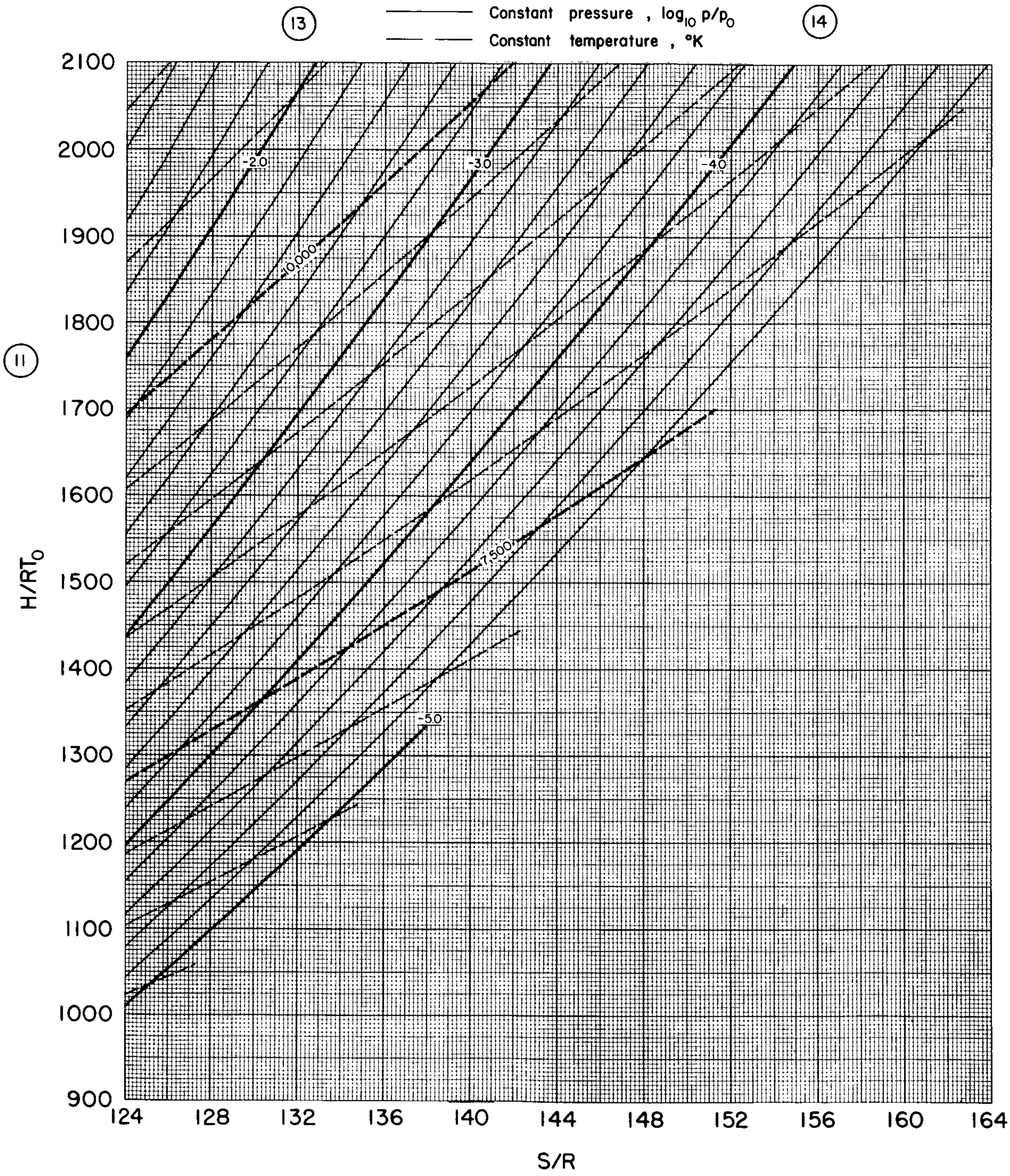

(l) Region 12

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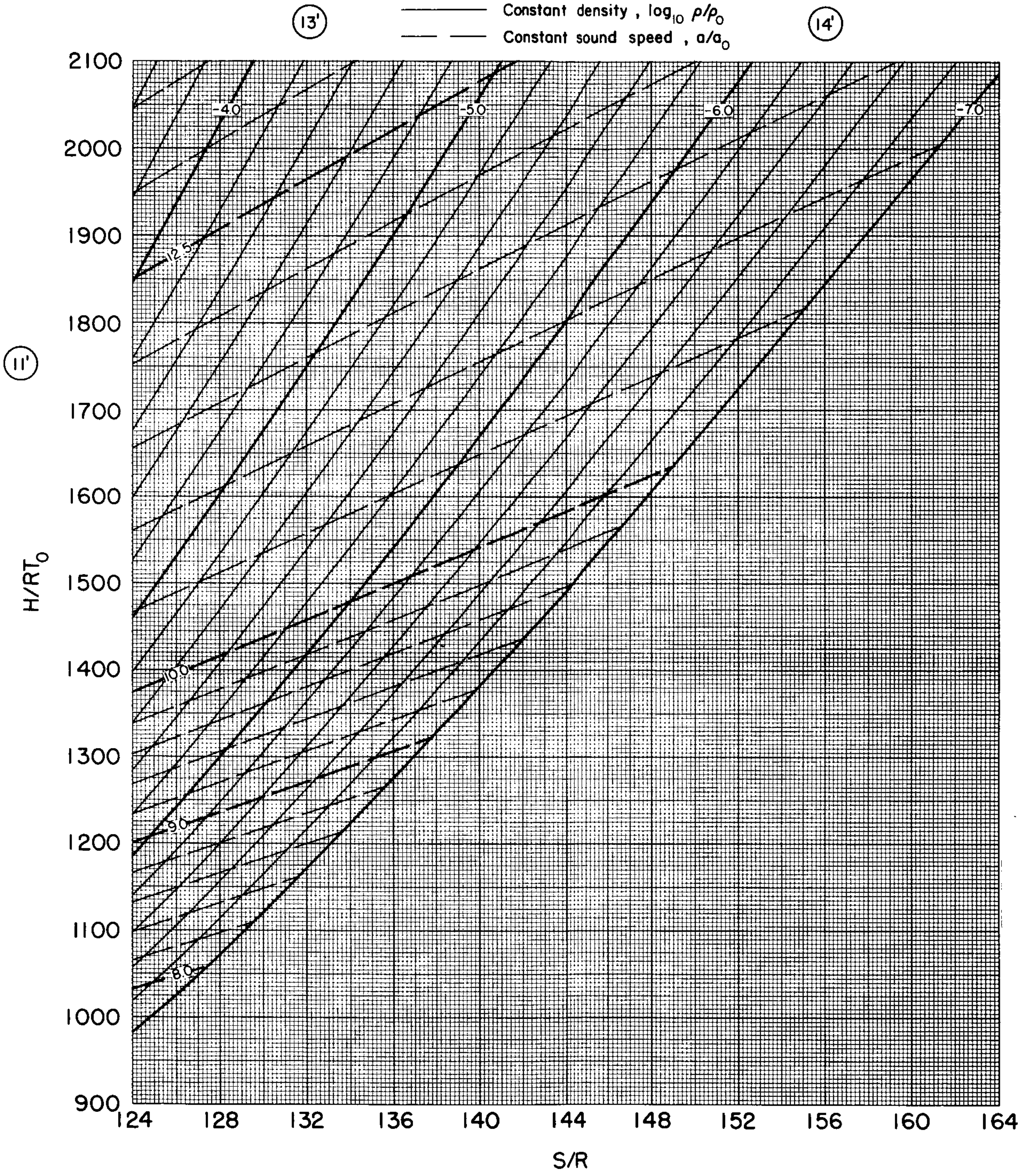

(*l*) Region 12 - Concluded.

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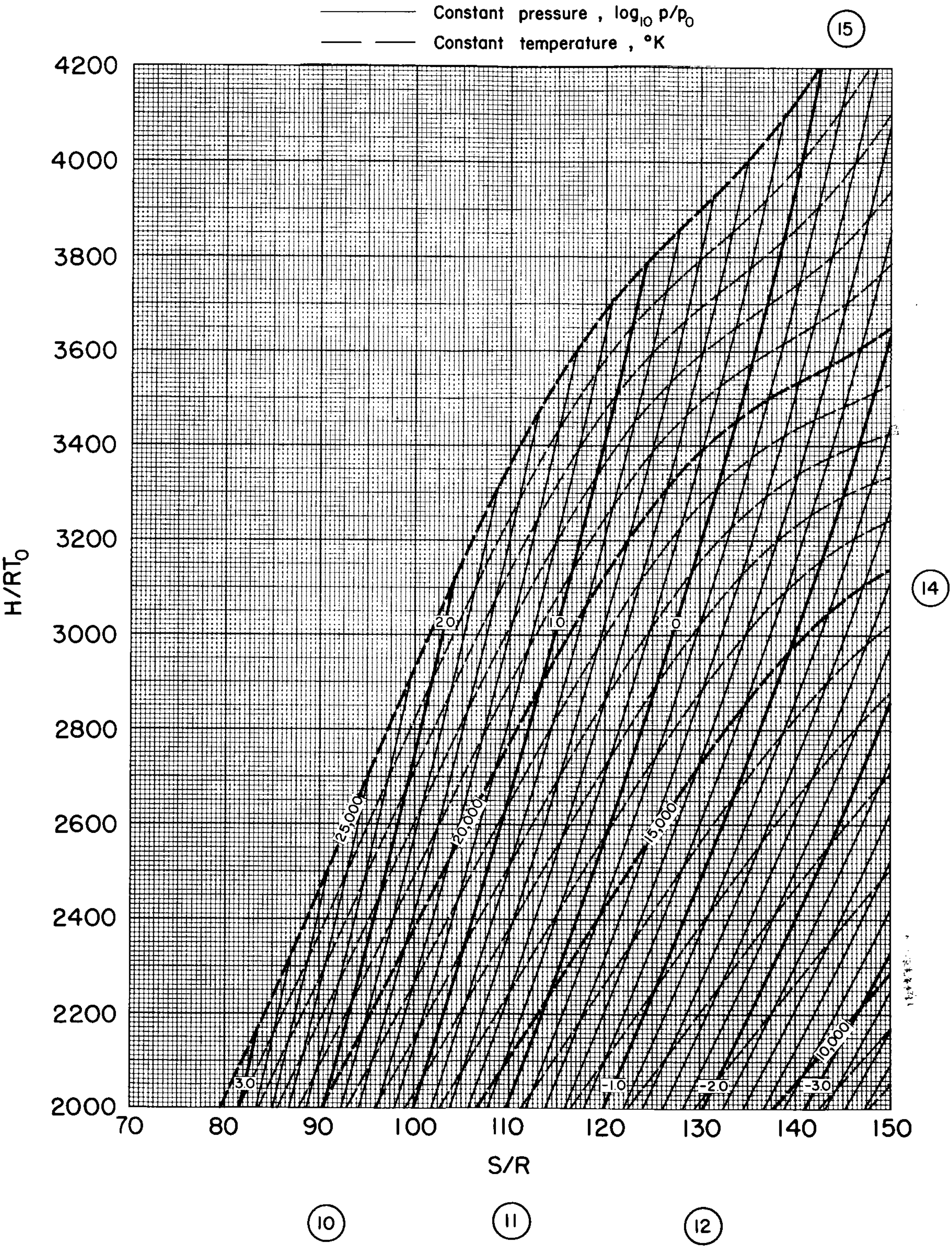
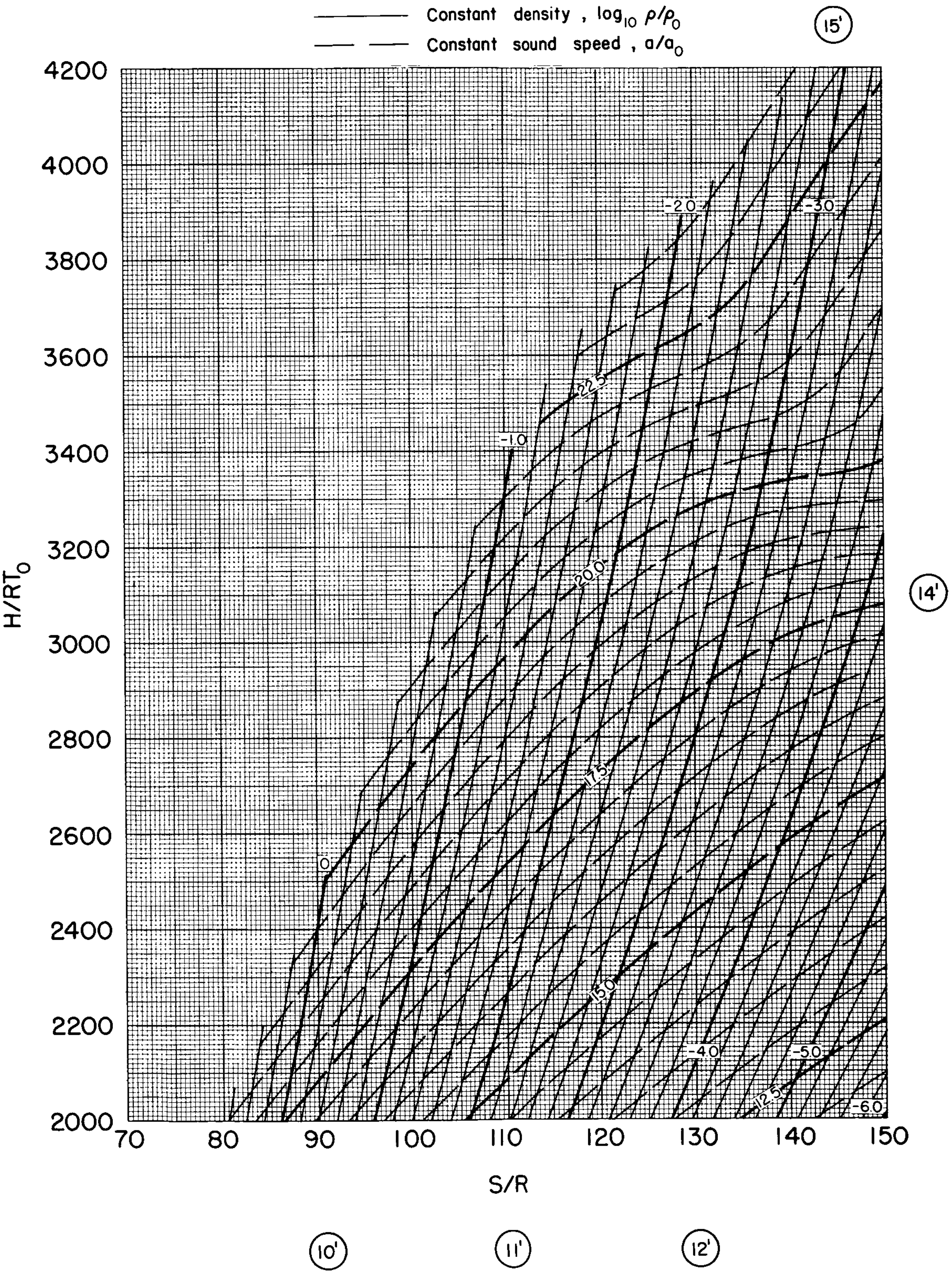


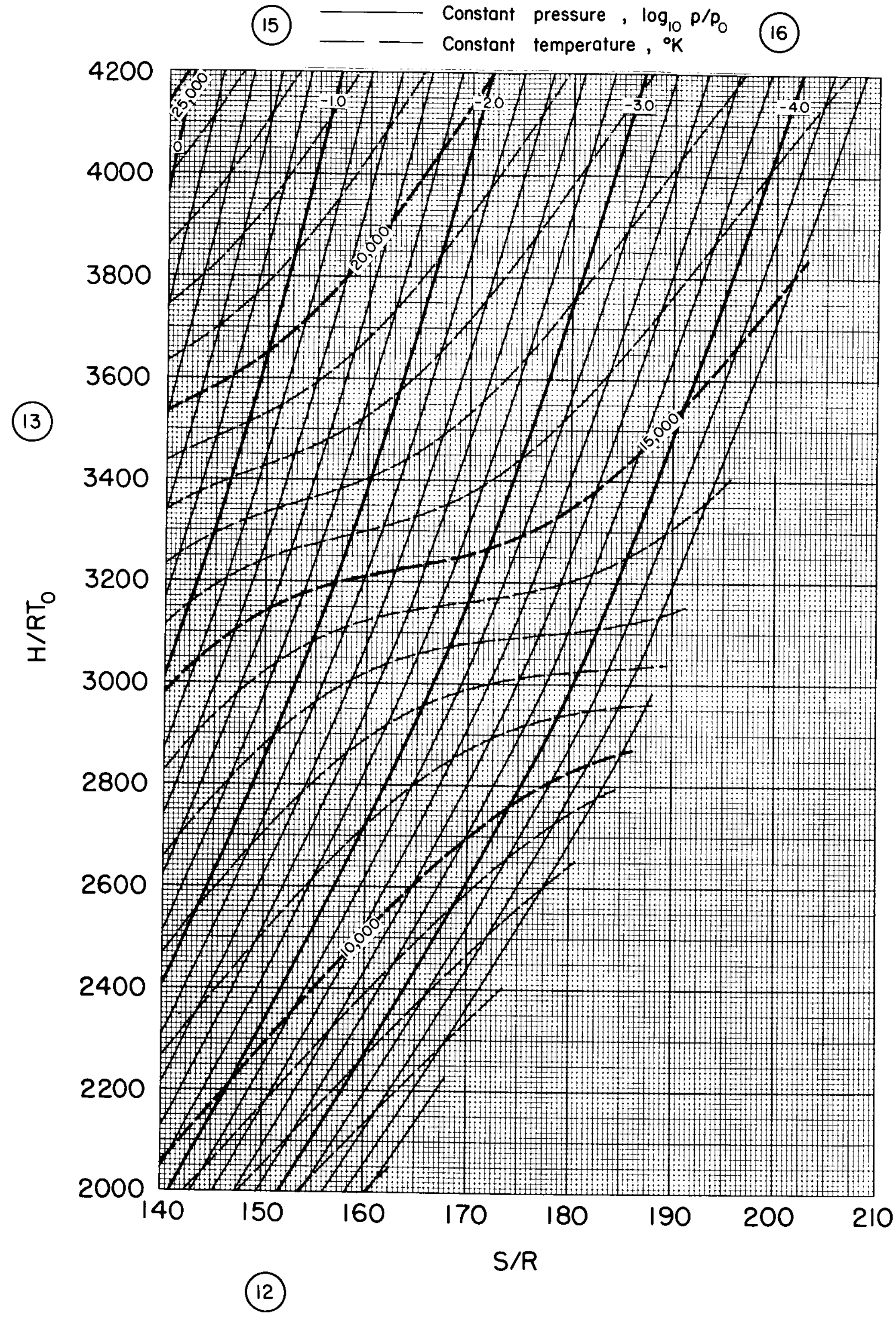
(m) Region 13

Figure 2.- Continued.



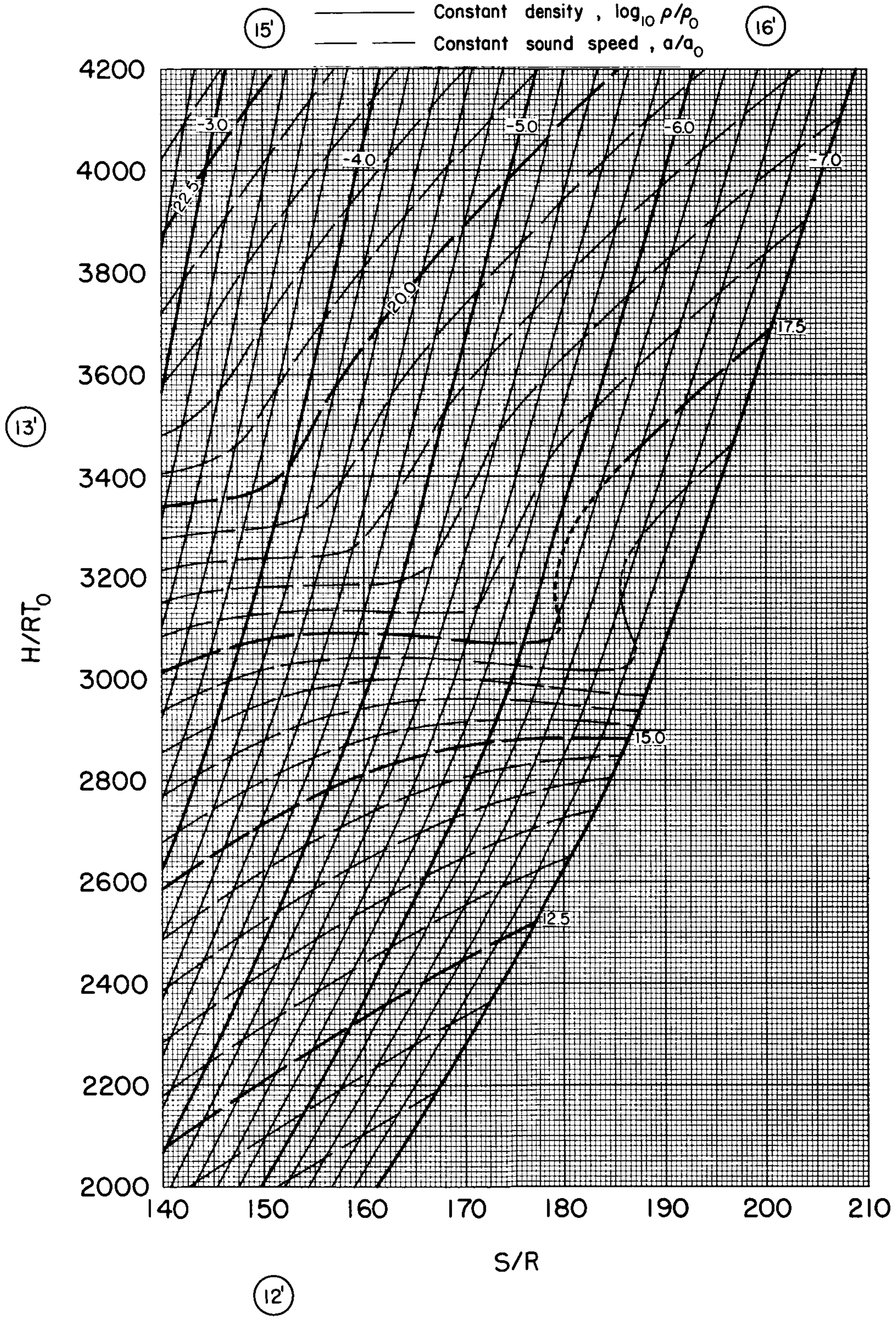
(m) Region 13 - Concluded.

Figure 2.- Continued.



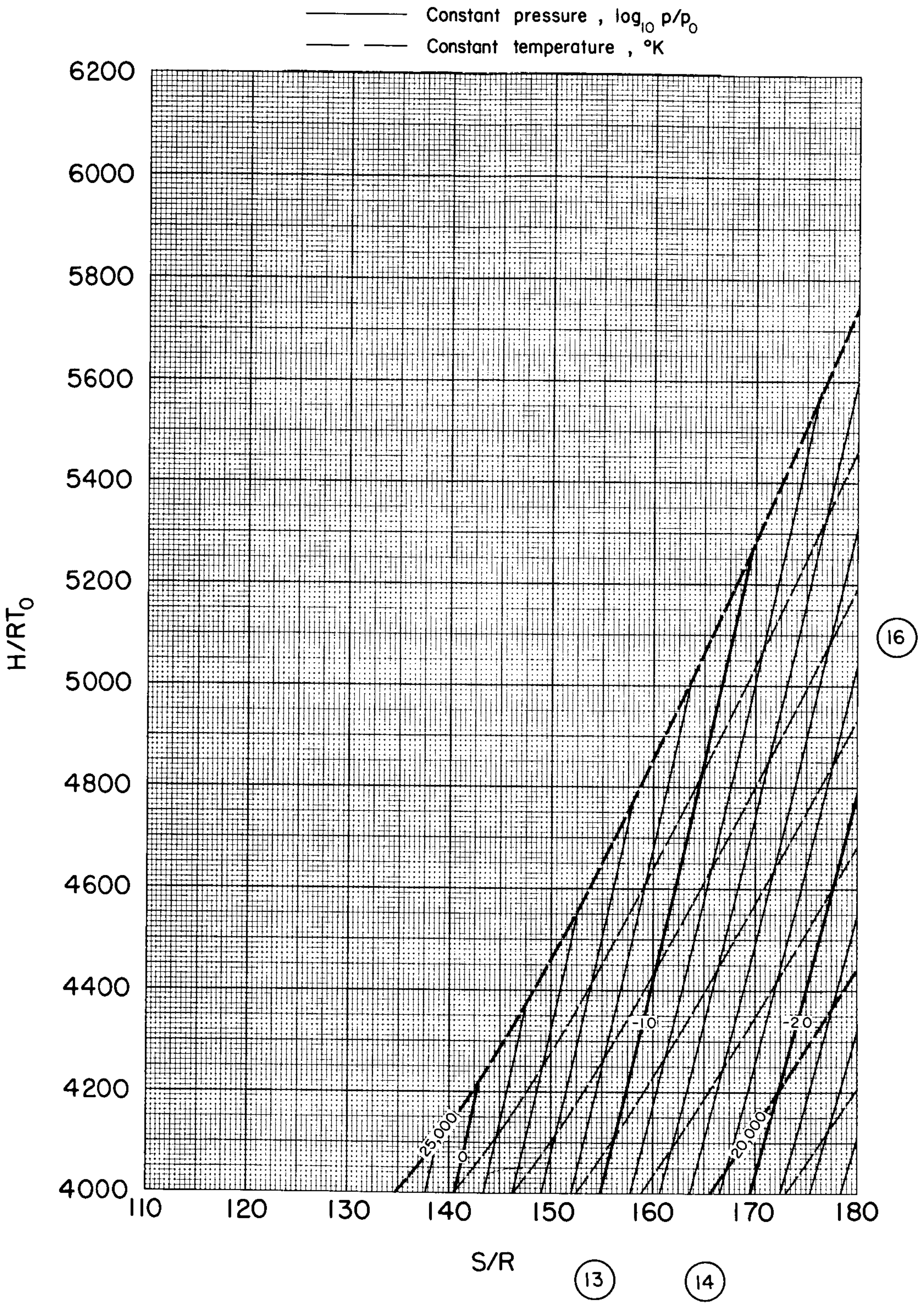
(n) Region 14

Figure 2.- Continued.



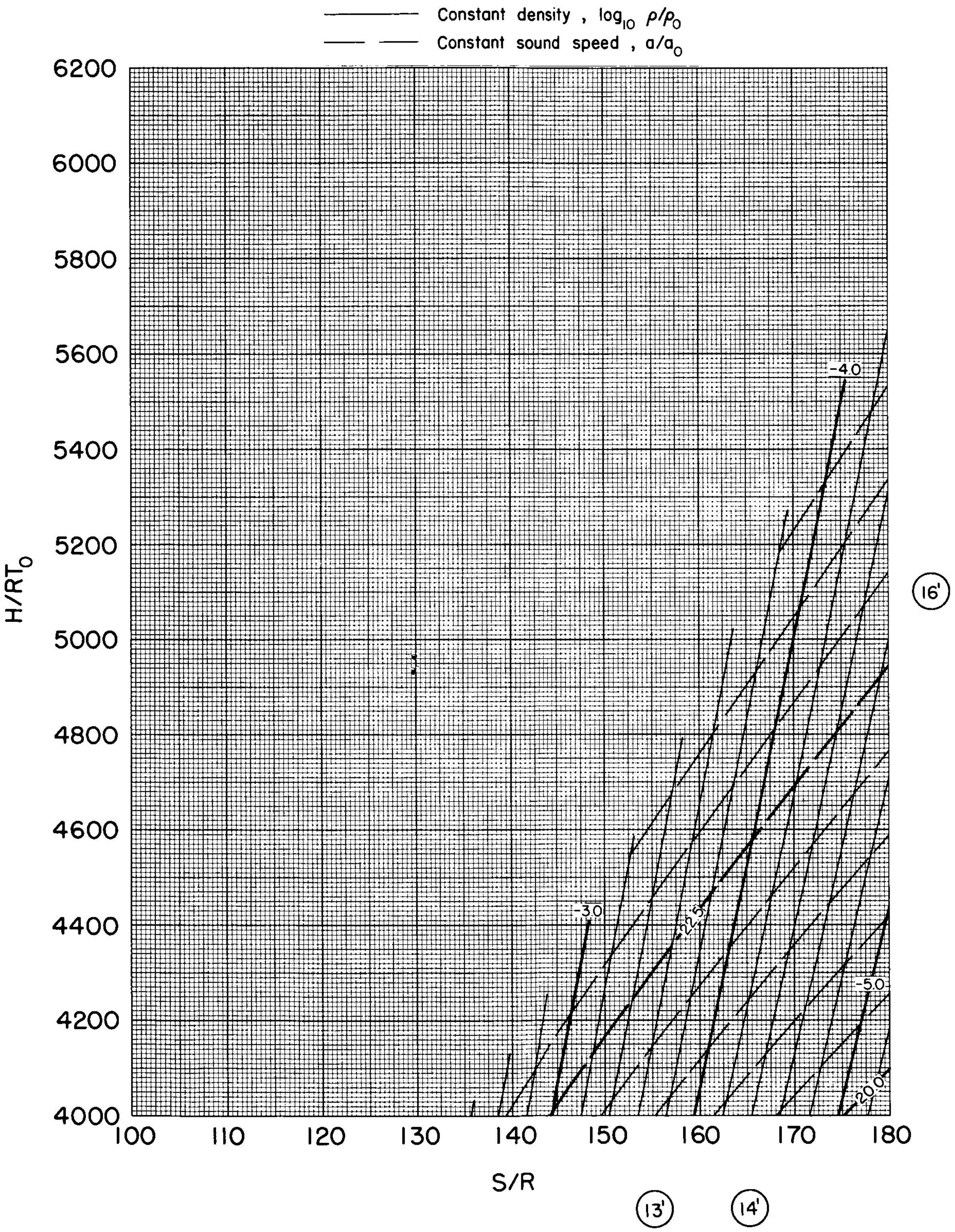
(n) Region 14 - Concluded.

Figure 2.- Continued.



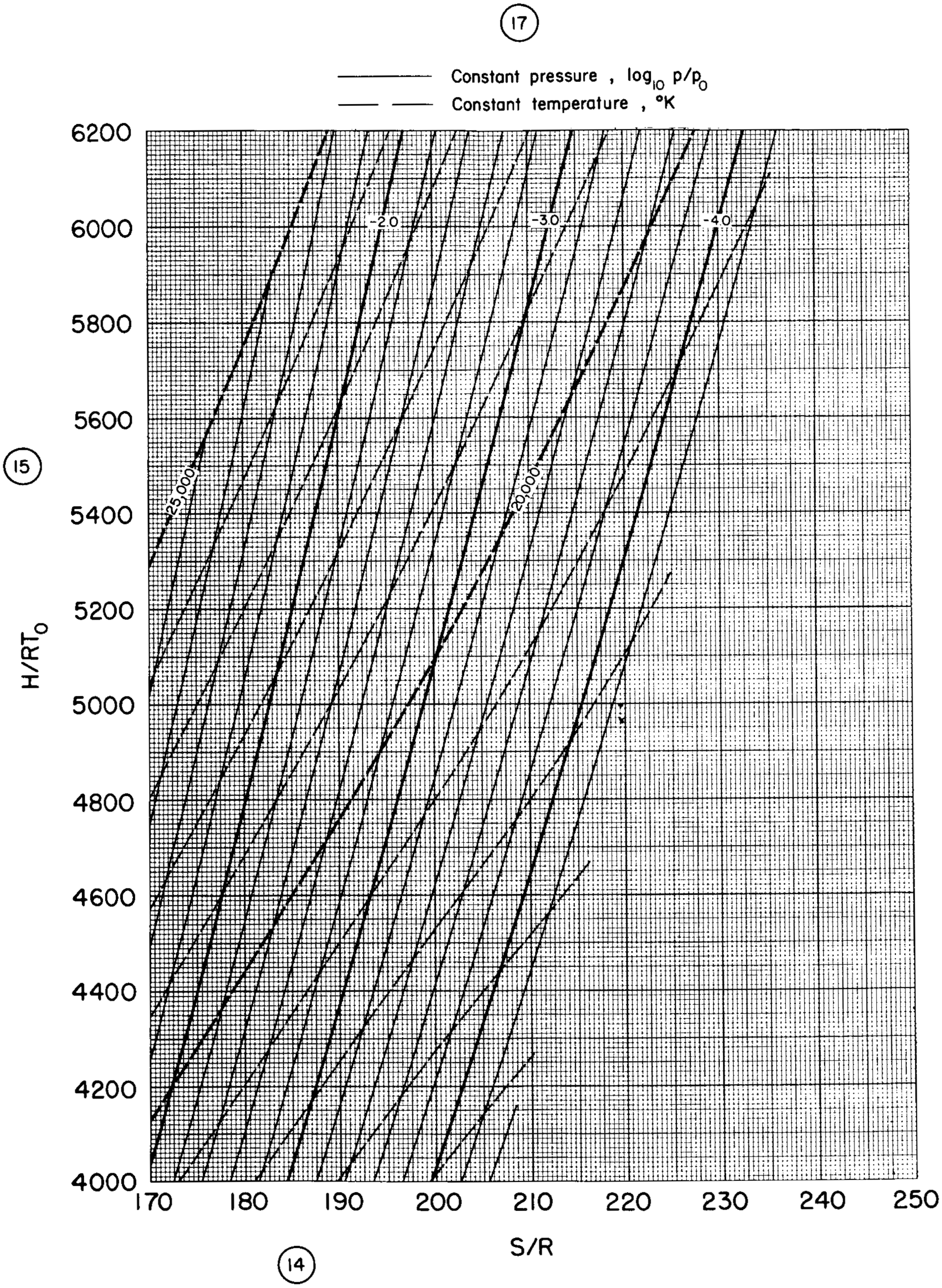
(o) Region 15

Figure 2.- Continued.



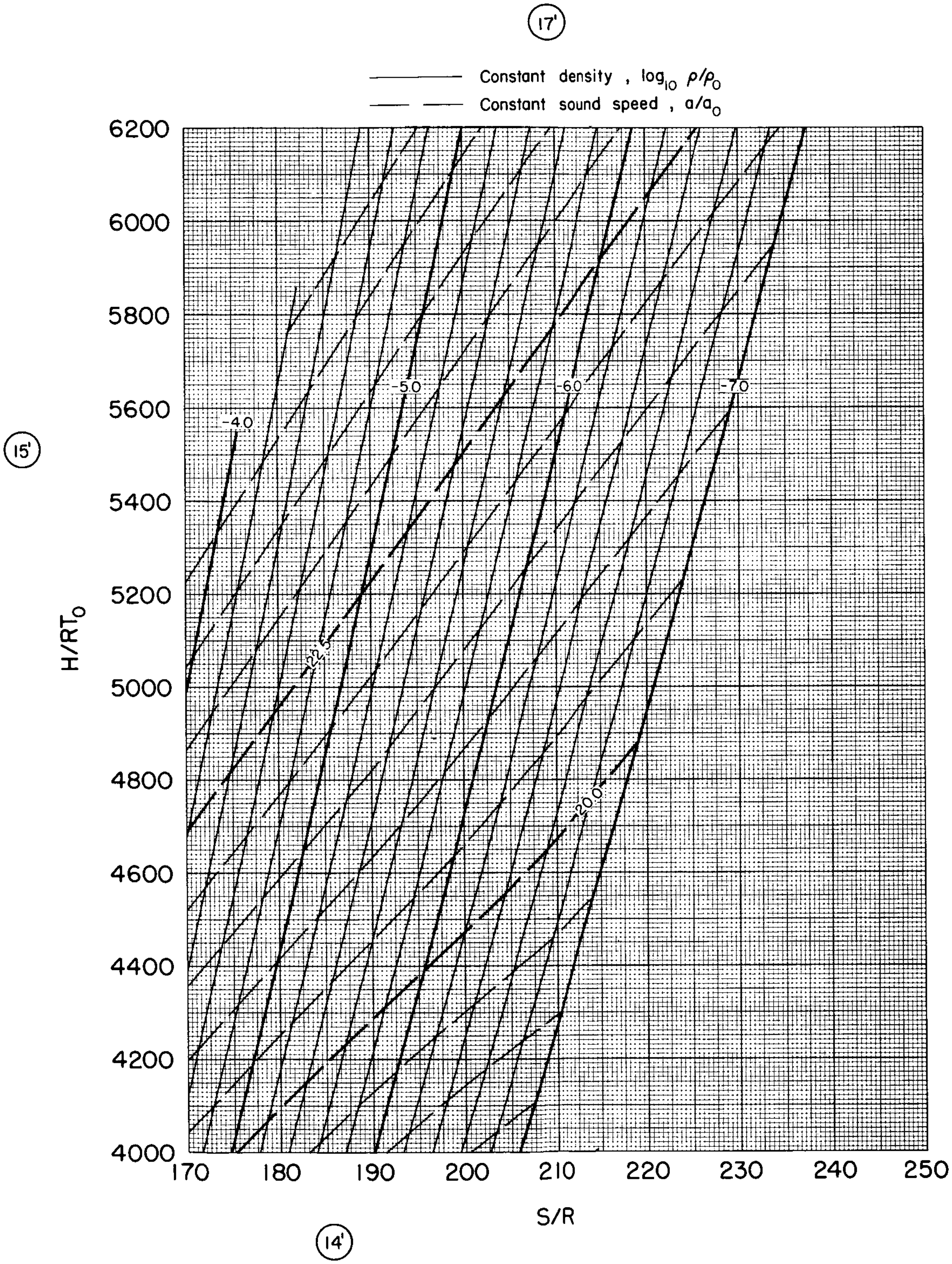
(o) Region 15 - Concluded.

Figure 2.- Continued.



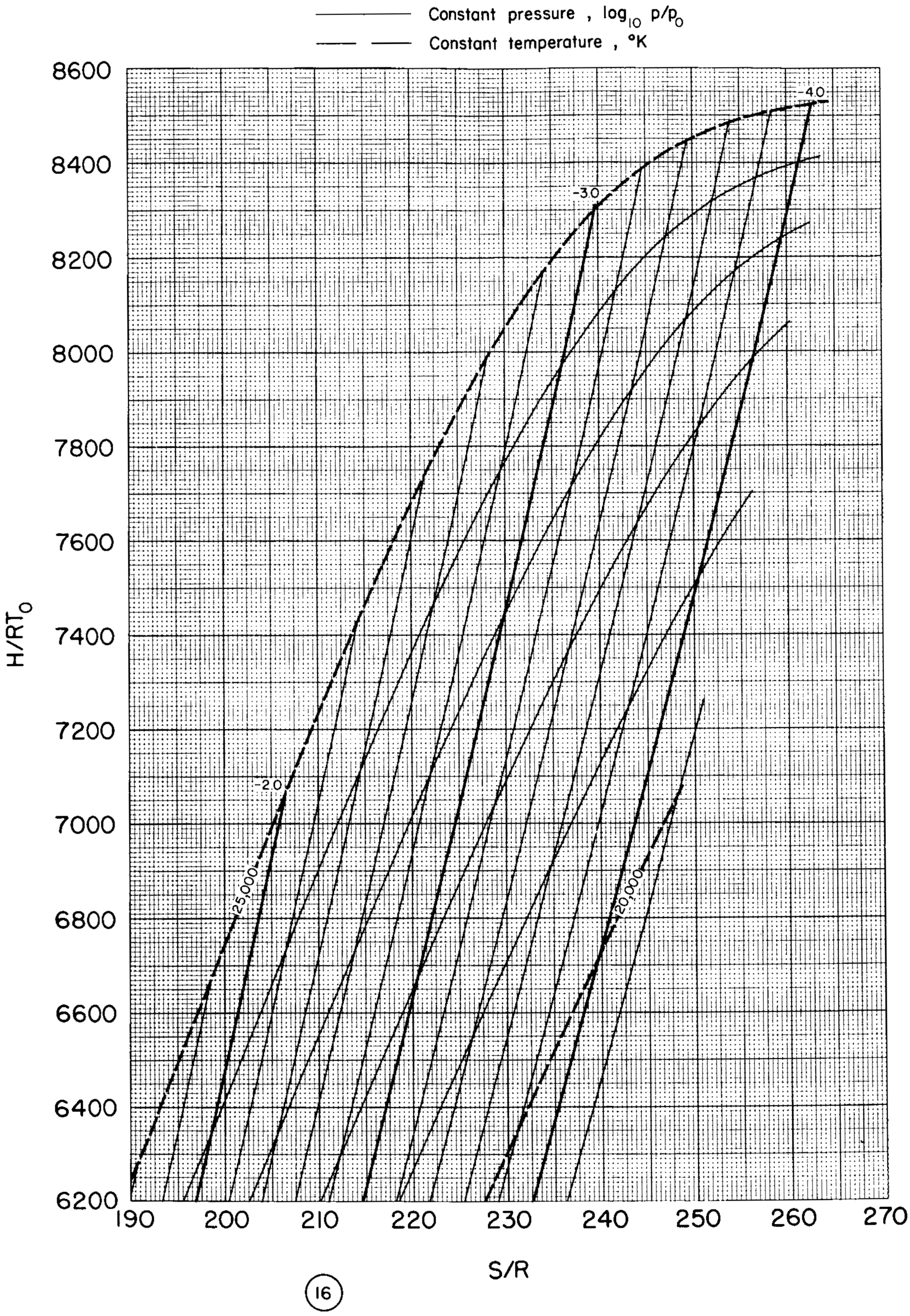
(p) Region 16

Figure 2.- Continued.



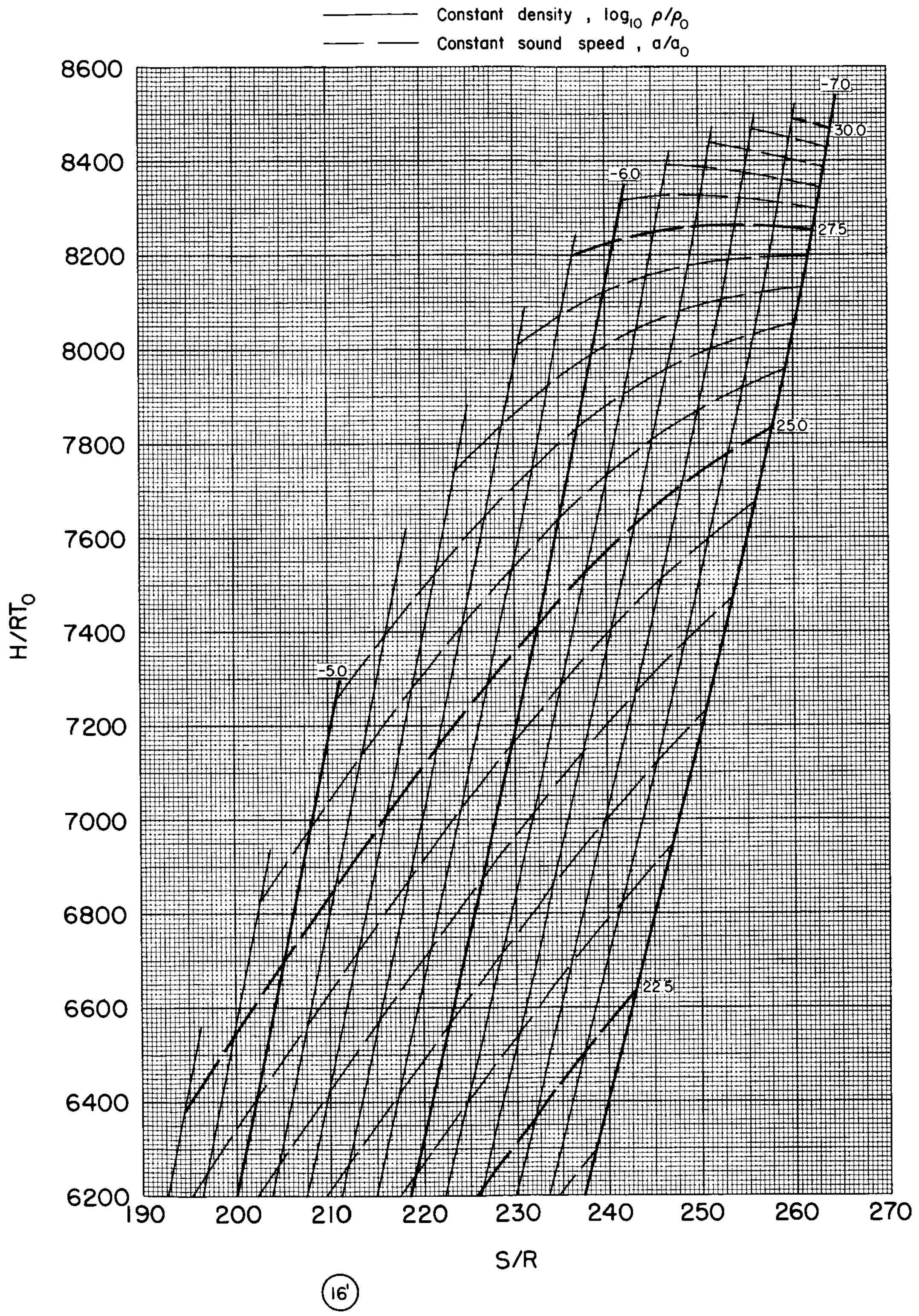
(p) Region 16 - Concluded.

Figure 2.- Continued.



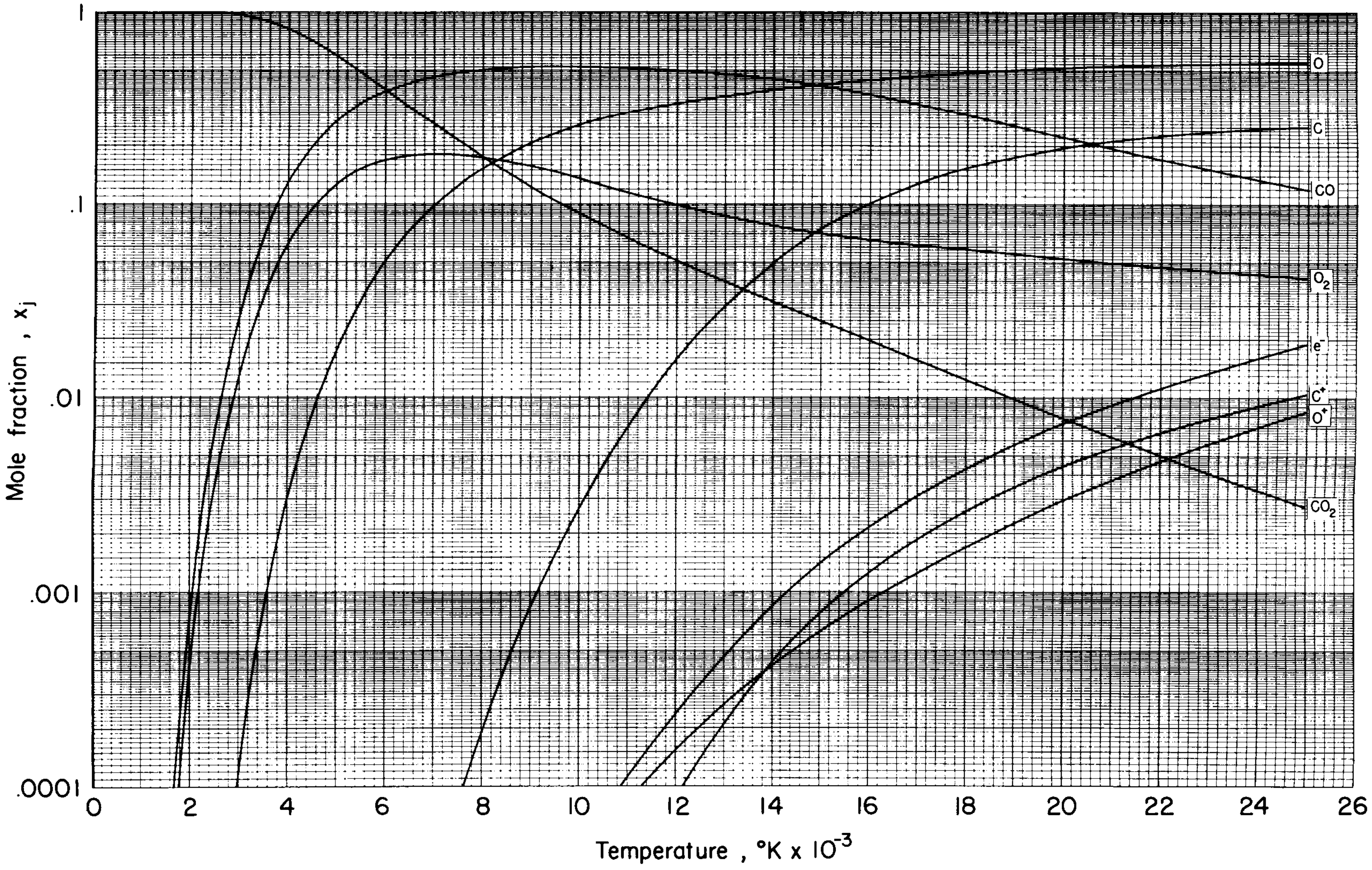
(q) Region 17

Figure 2.- Continued.



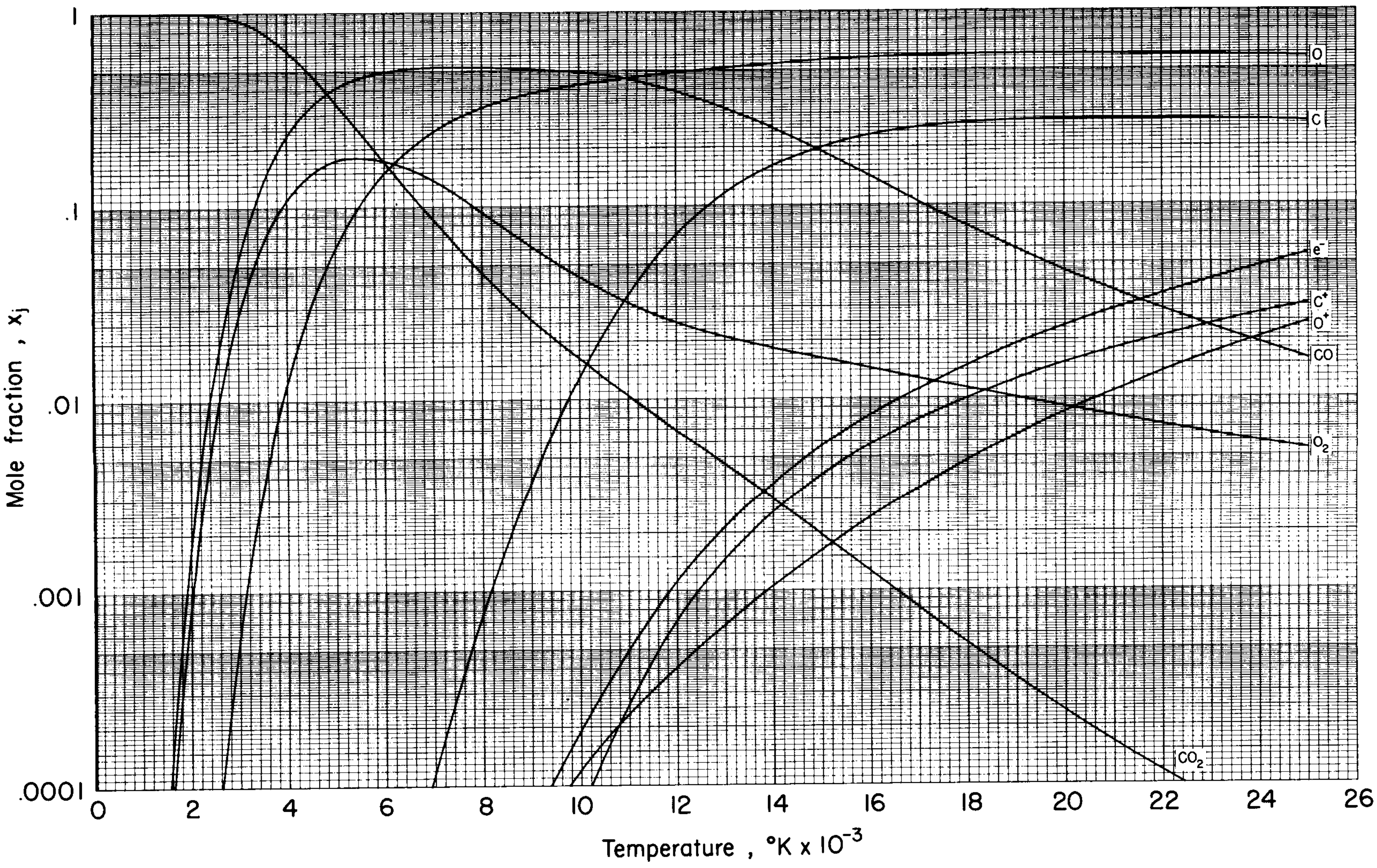
(q) Region 17 - Concluded.

Figure 2.- Concluded.



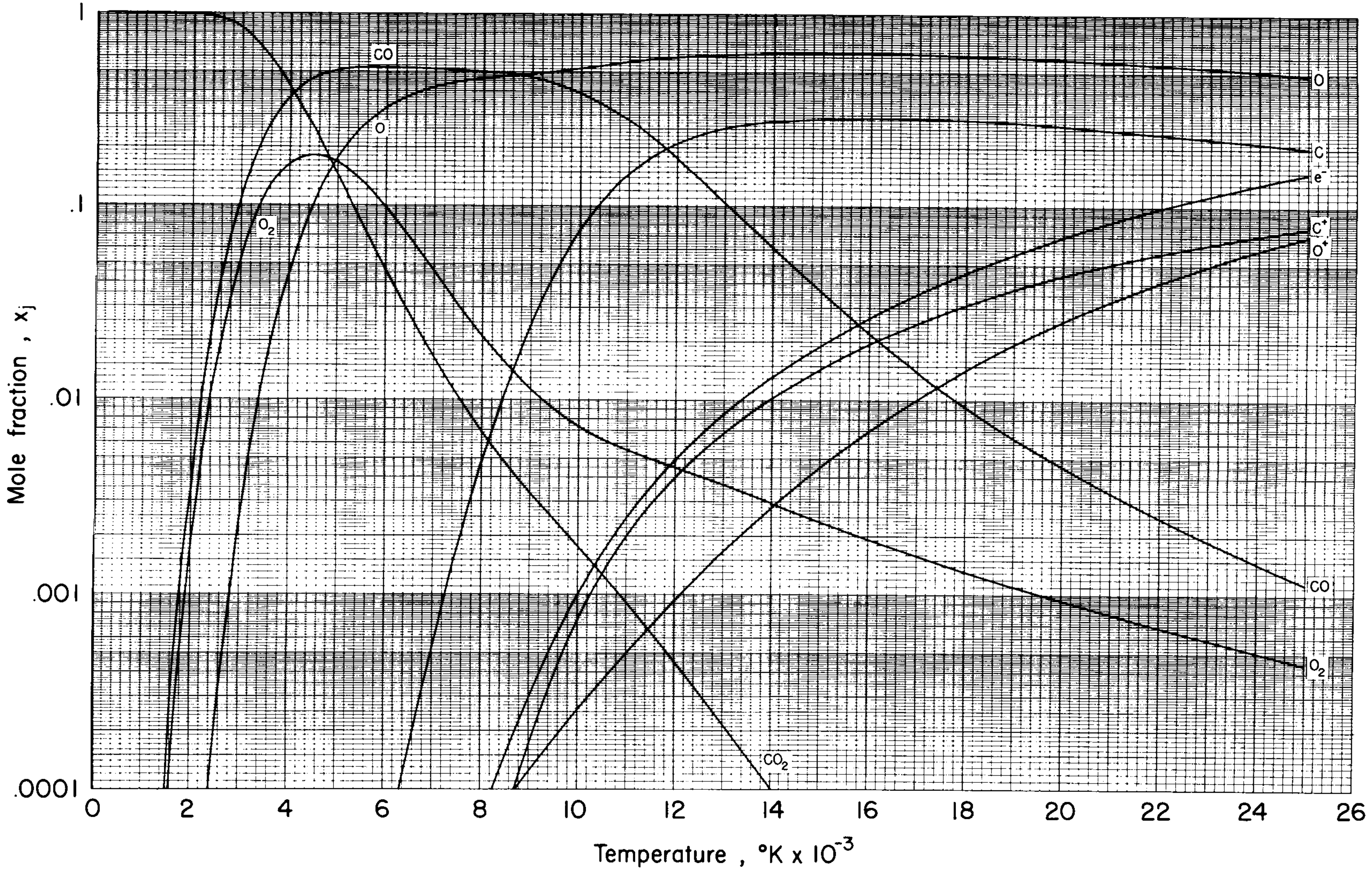
(a) $\rho/\rho_0 = 10^3$

Figure 3.- Equilibrium composition of carbon dioxide.



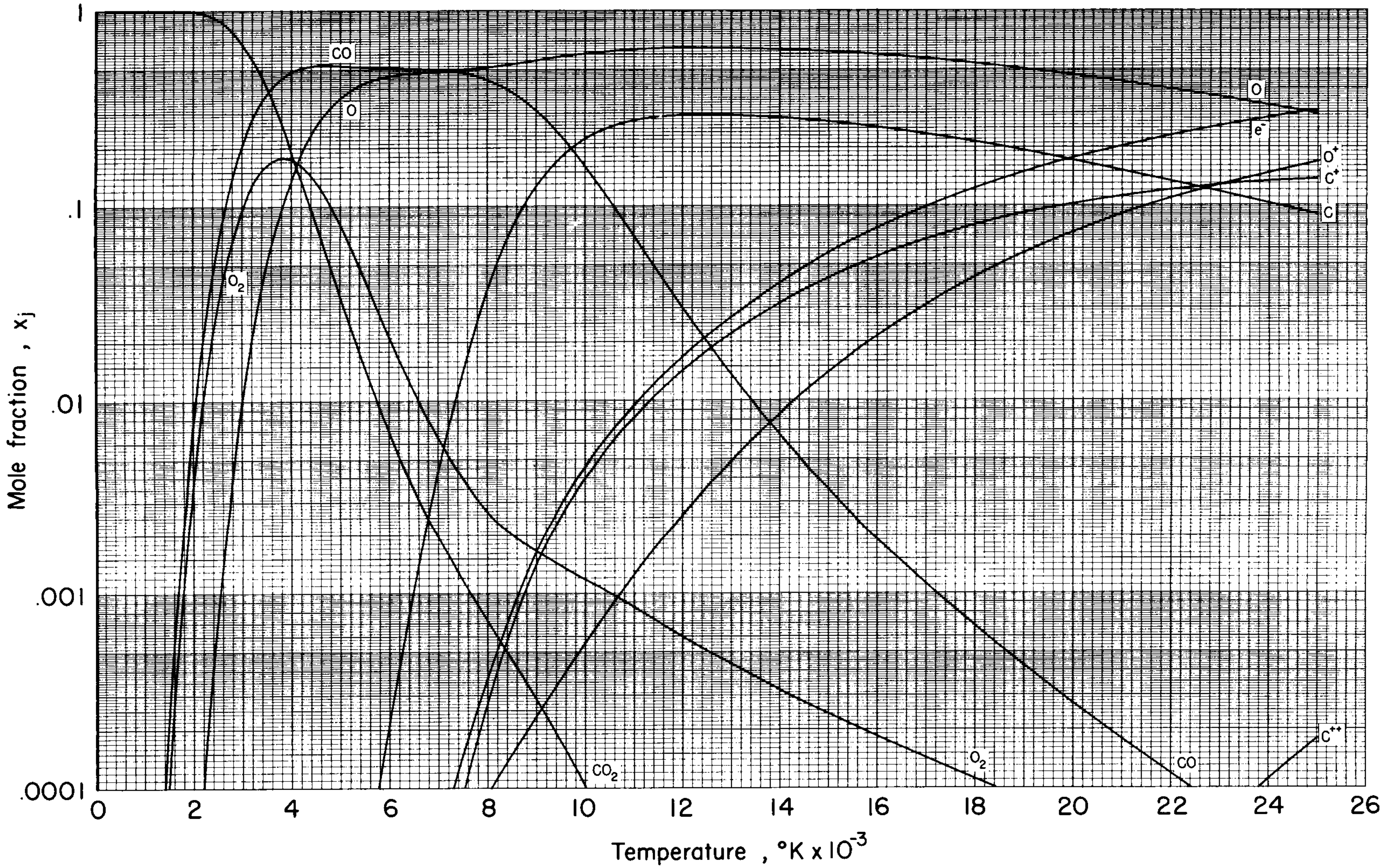
(b) $\rho/\rho_0 = 10^2$

Figure 3.- Continued.



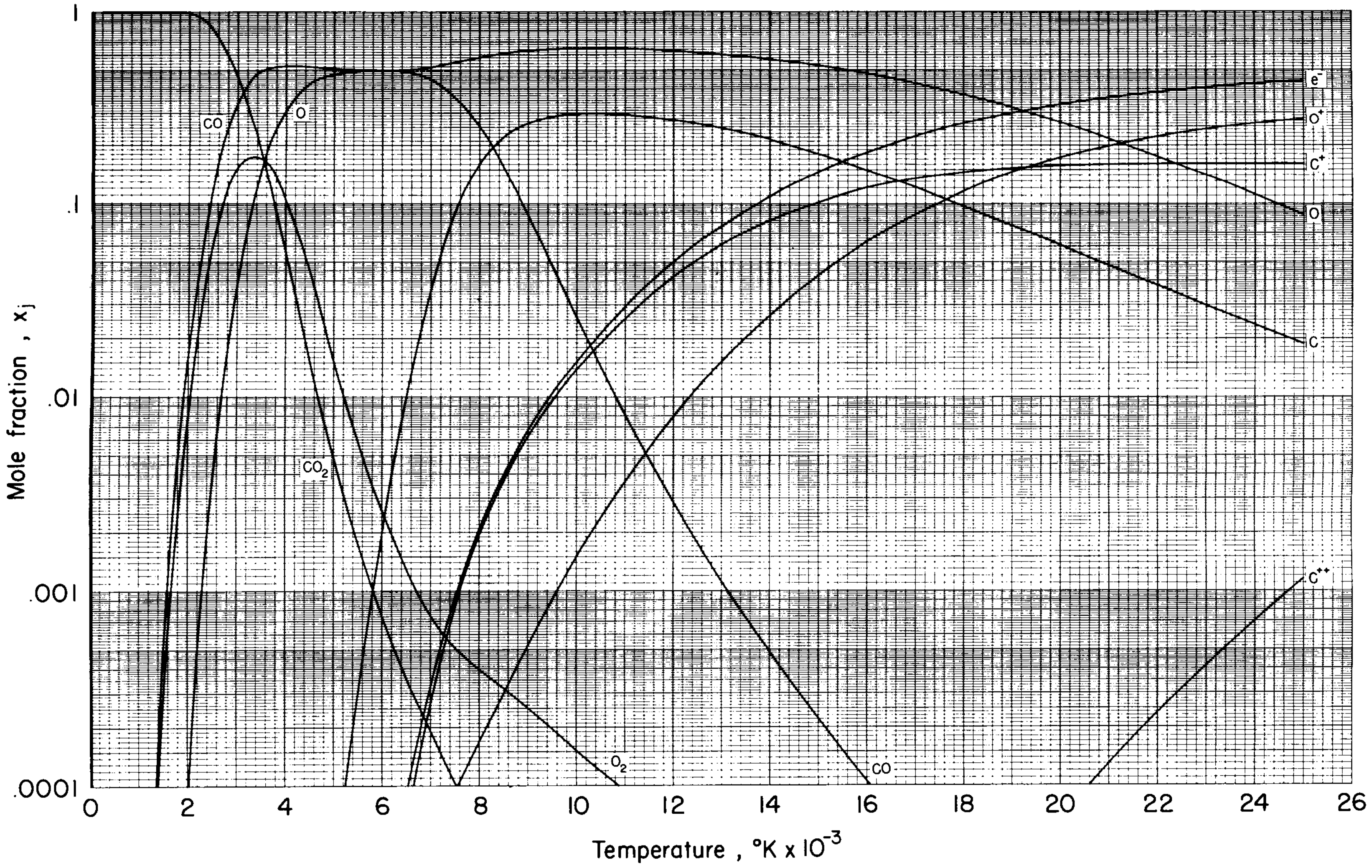
(c) $\rho/\rho_0 = 10^1$

Figure 3.- Continued.



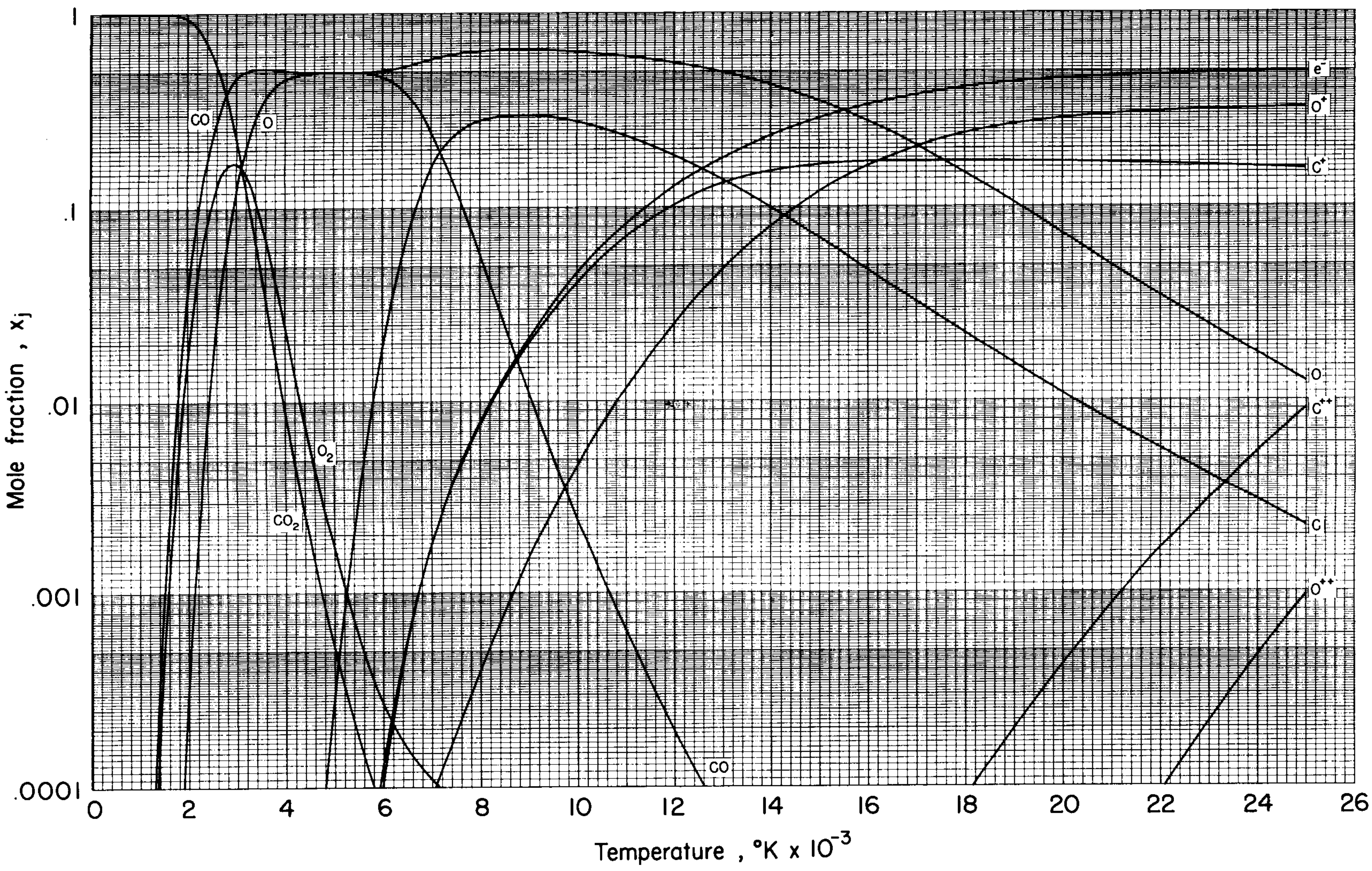
(d) $\rho/\rho_O = 1$

Figure 3.- Continued.



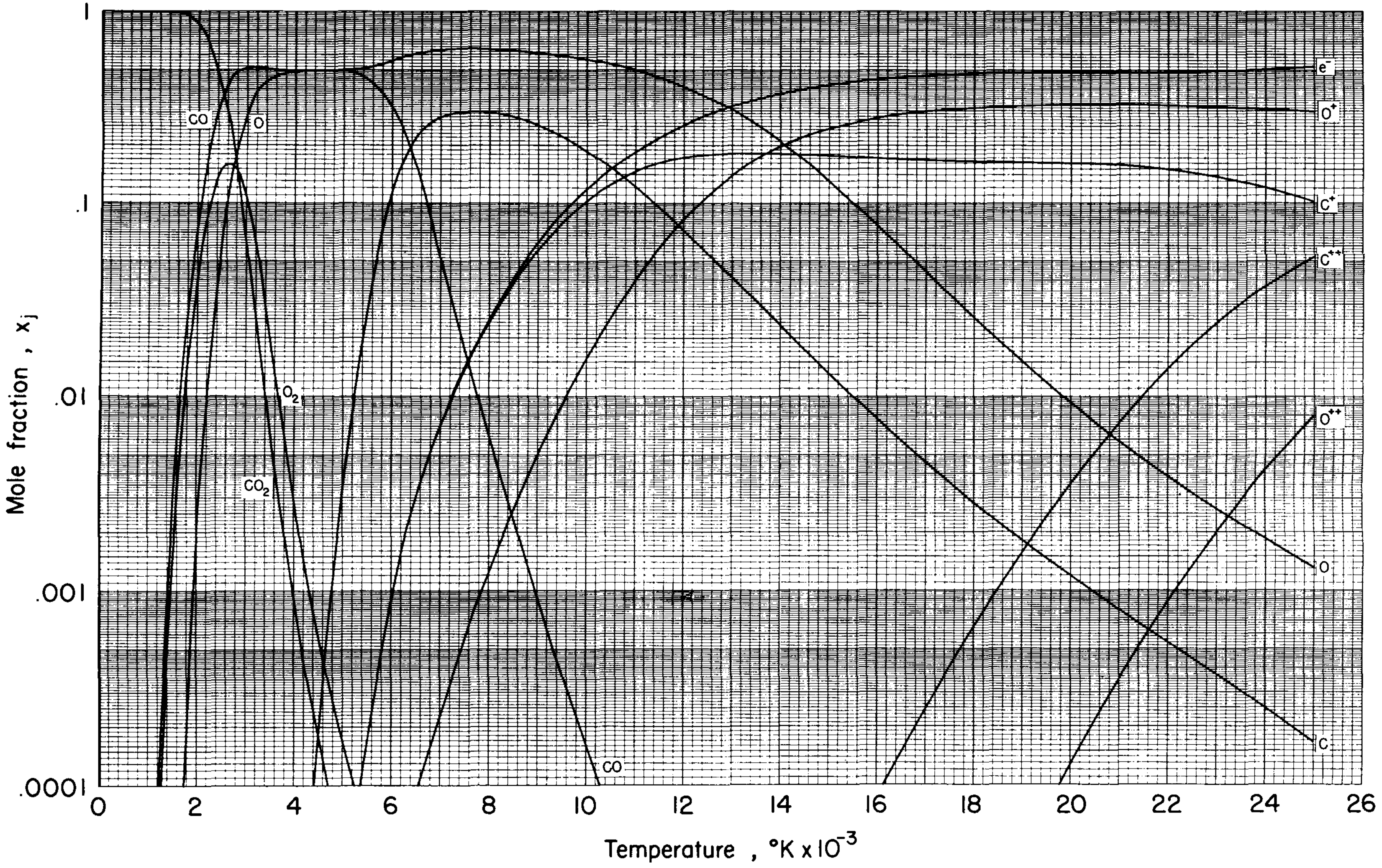
(e) $\rho/\rho_o = 10^{-1}$

Figure 3.- Continued.



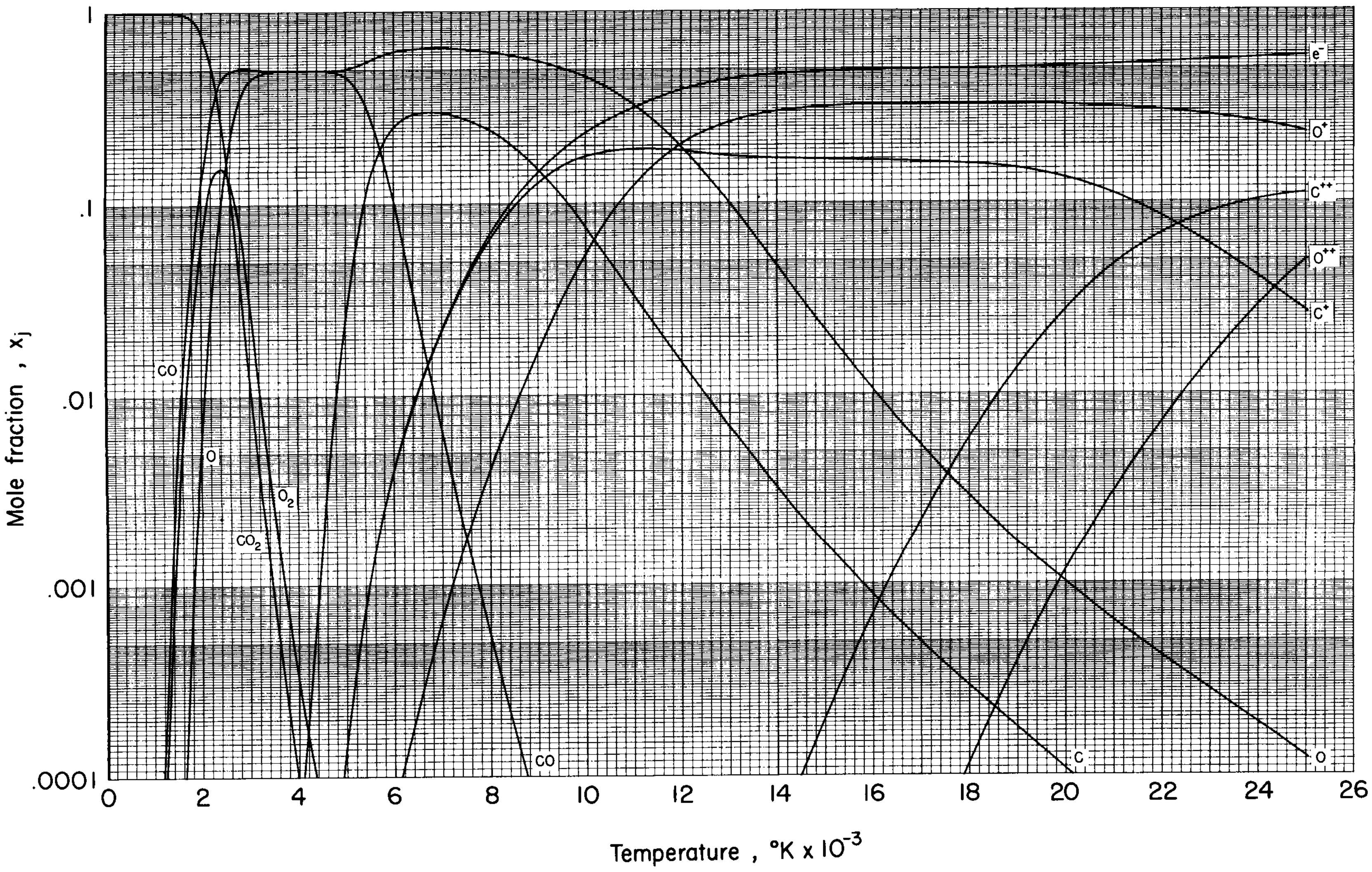
(f) $\rho/\rho_O = 10^{-2}$

Figure 3.- Continued.



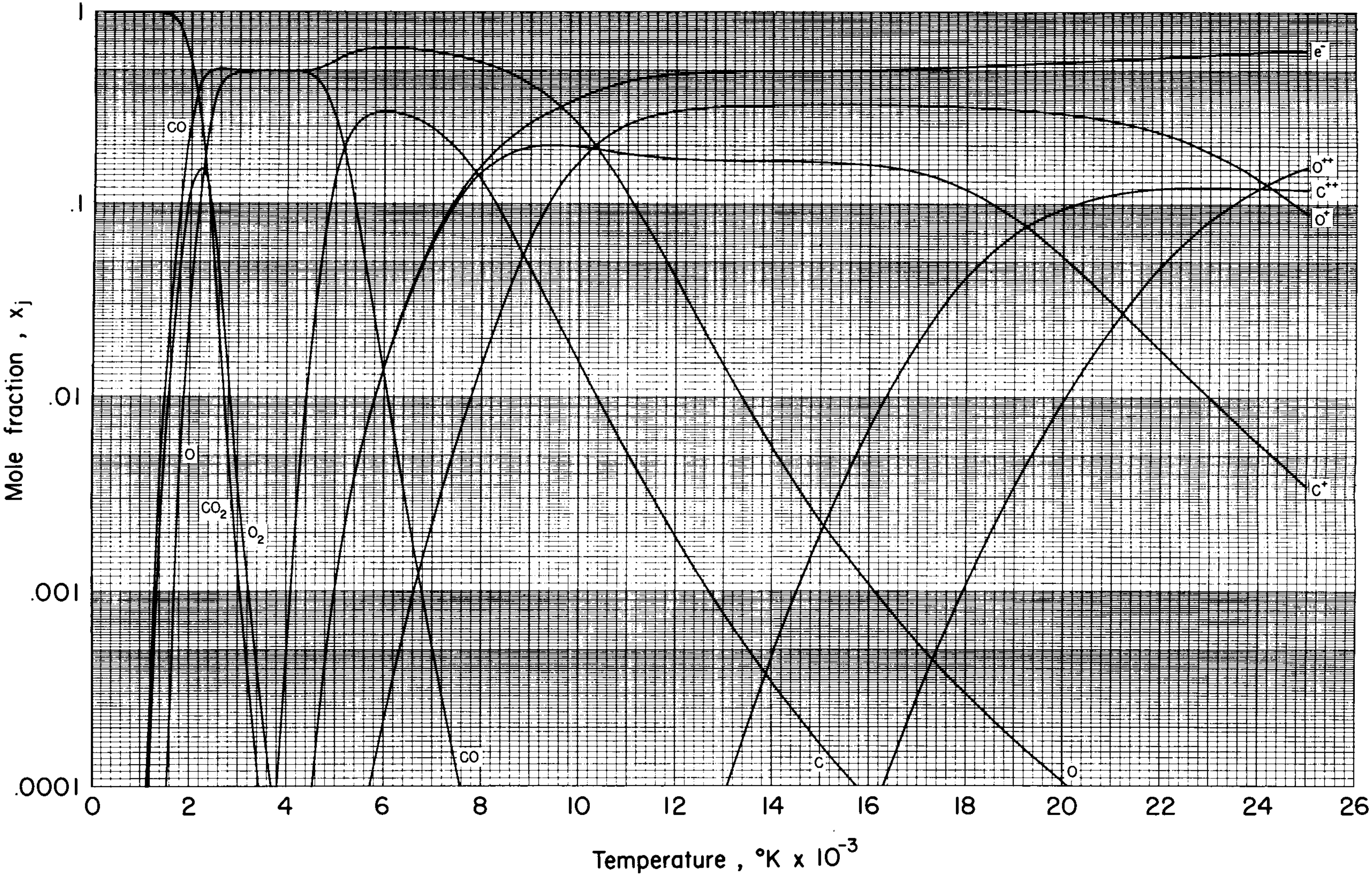
(g) $\rho/\rho_o = 10^{-3}$

Figure 3.- Continued.



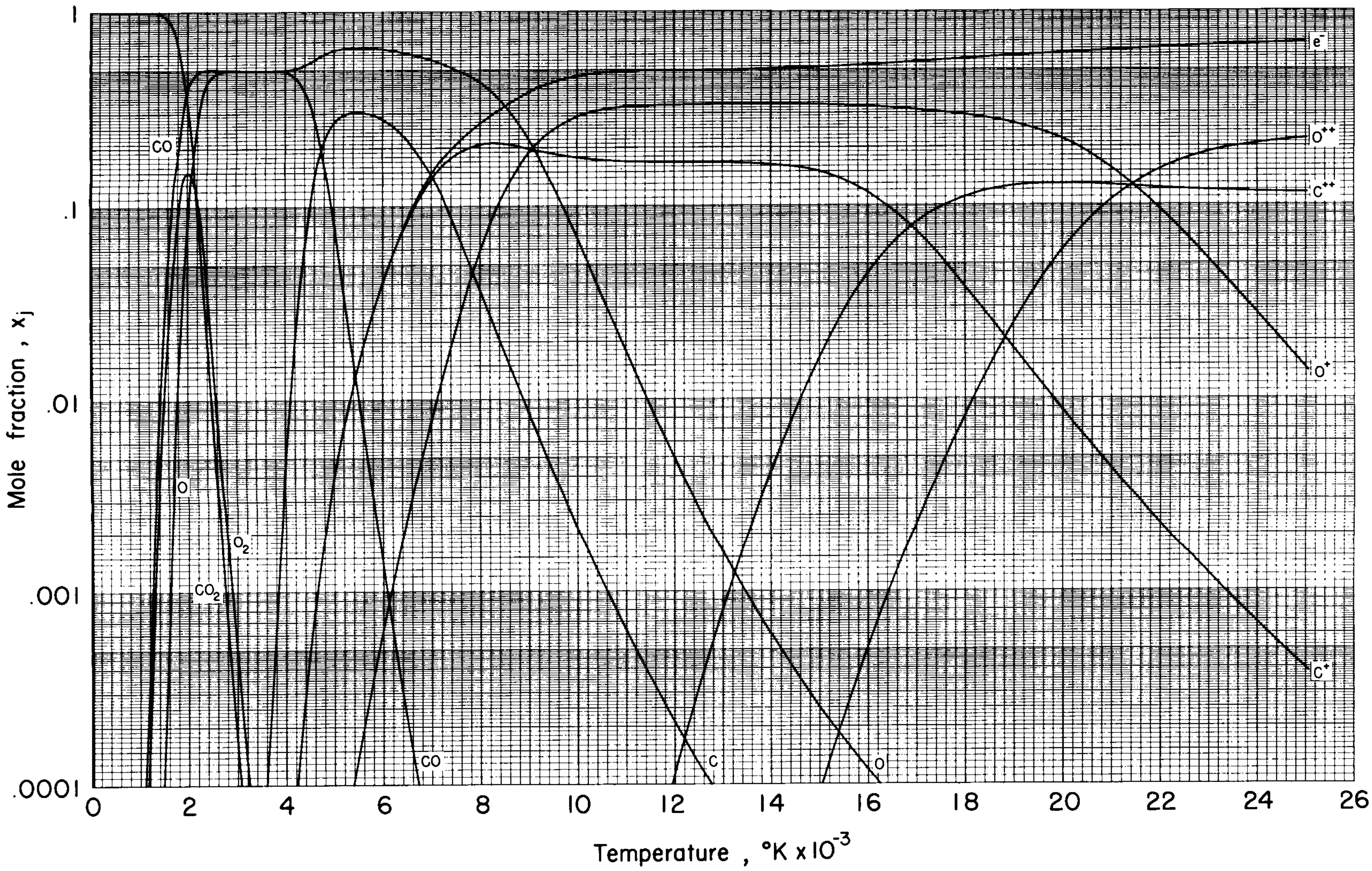
(h) $\rho/\rho_O = 10^{-4}$

Figure 3.- Continued.



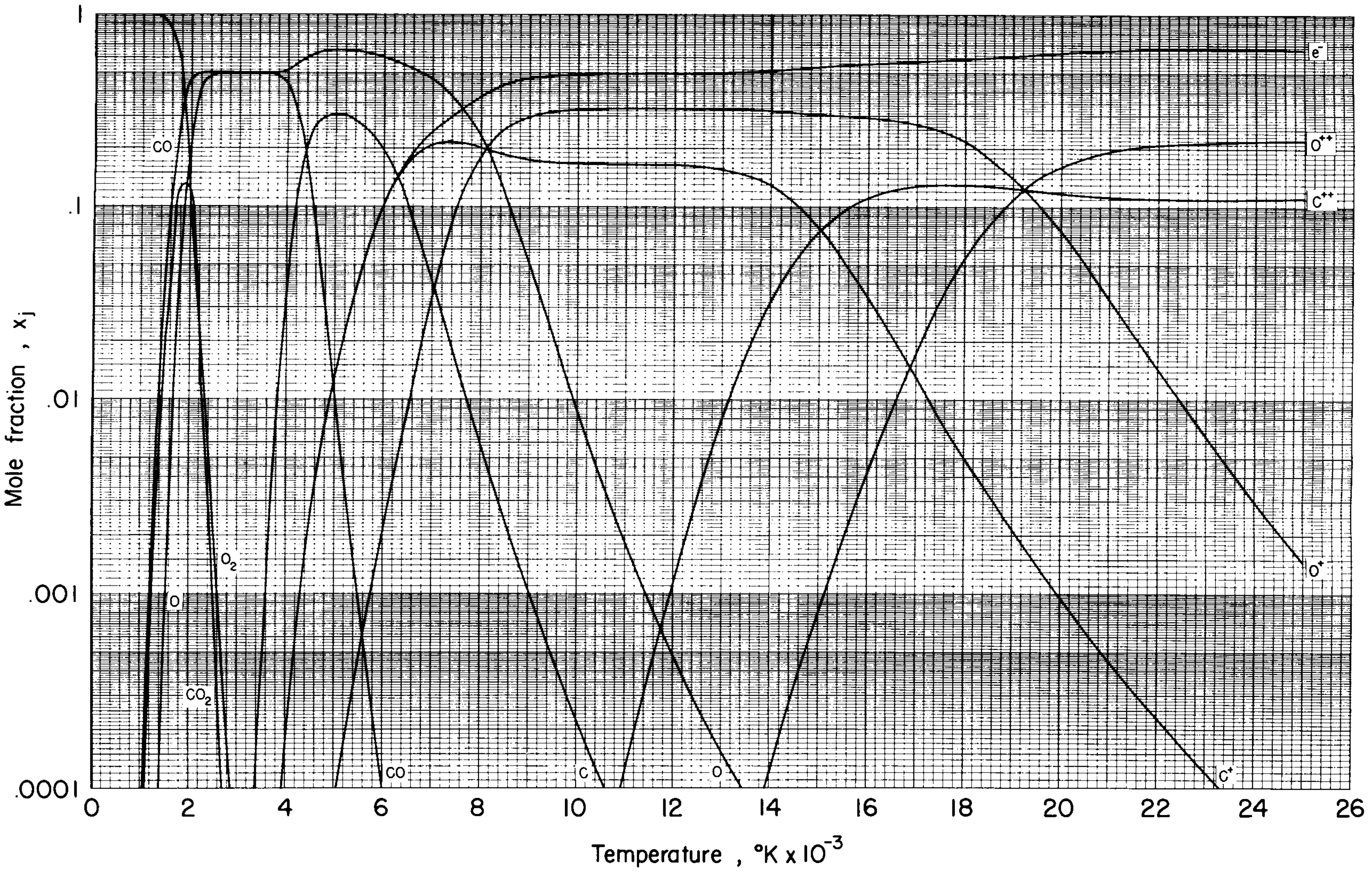
(i) $\rho/\rho_o = 10^{-5}$

Figure 3.- Continued.



(j) $\rho/\rho_o = 10^{-6}$

Figure 3.- Continued.



(k) $\rho/\rho_o = 10^{-7}$

Figure 3.- Concluded.

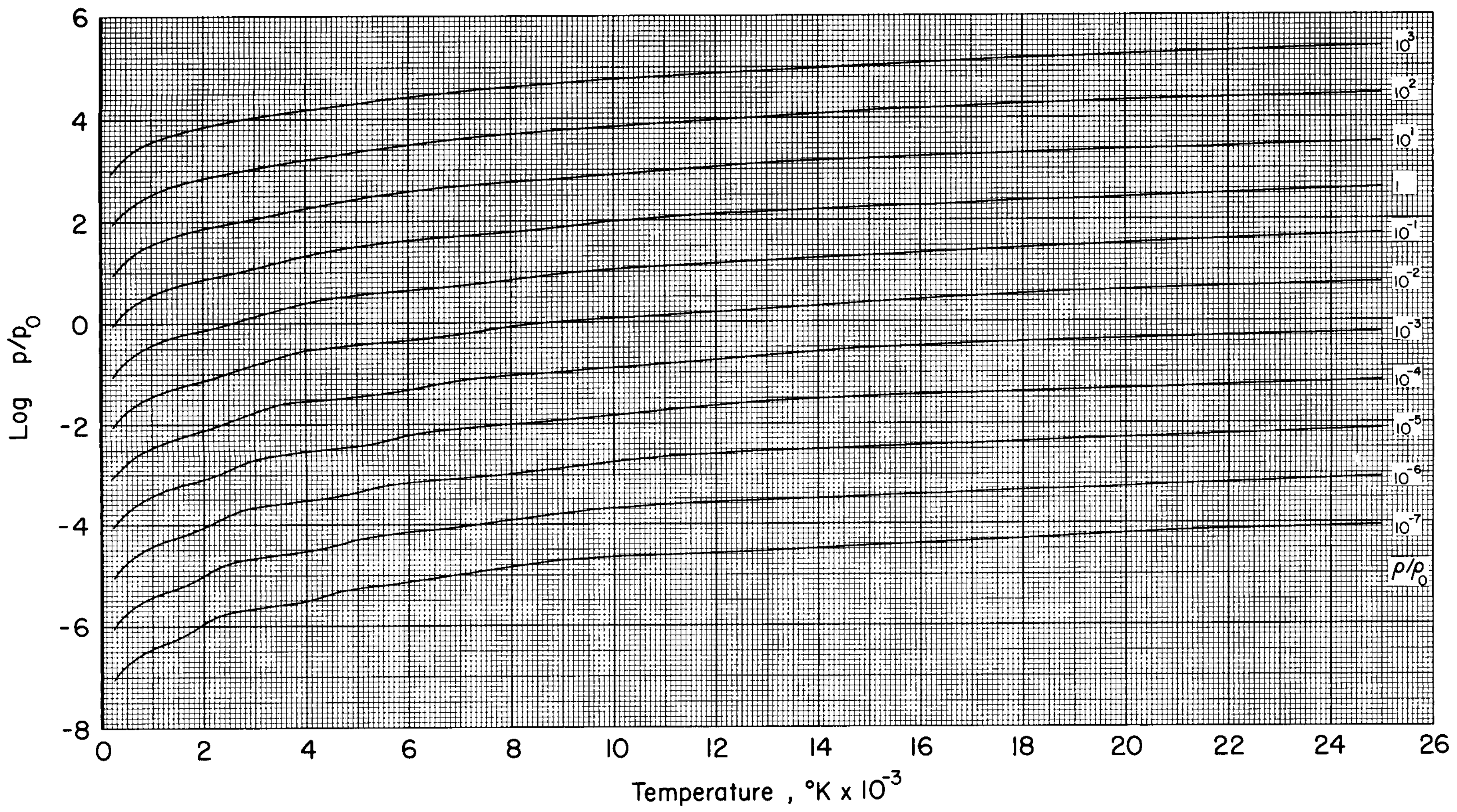


Figure 4.- Pressure as a function of temperature.

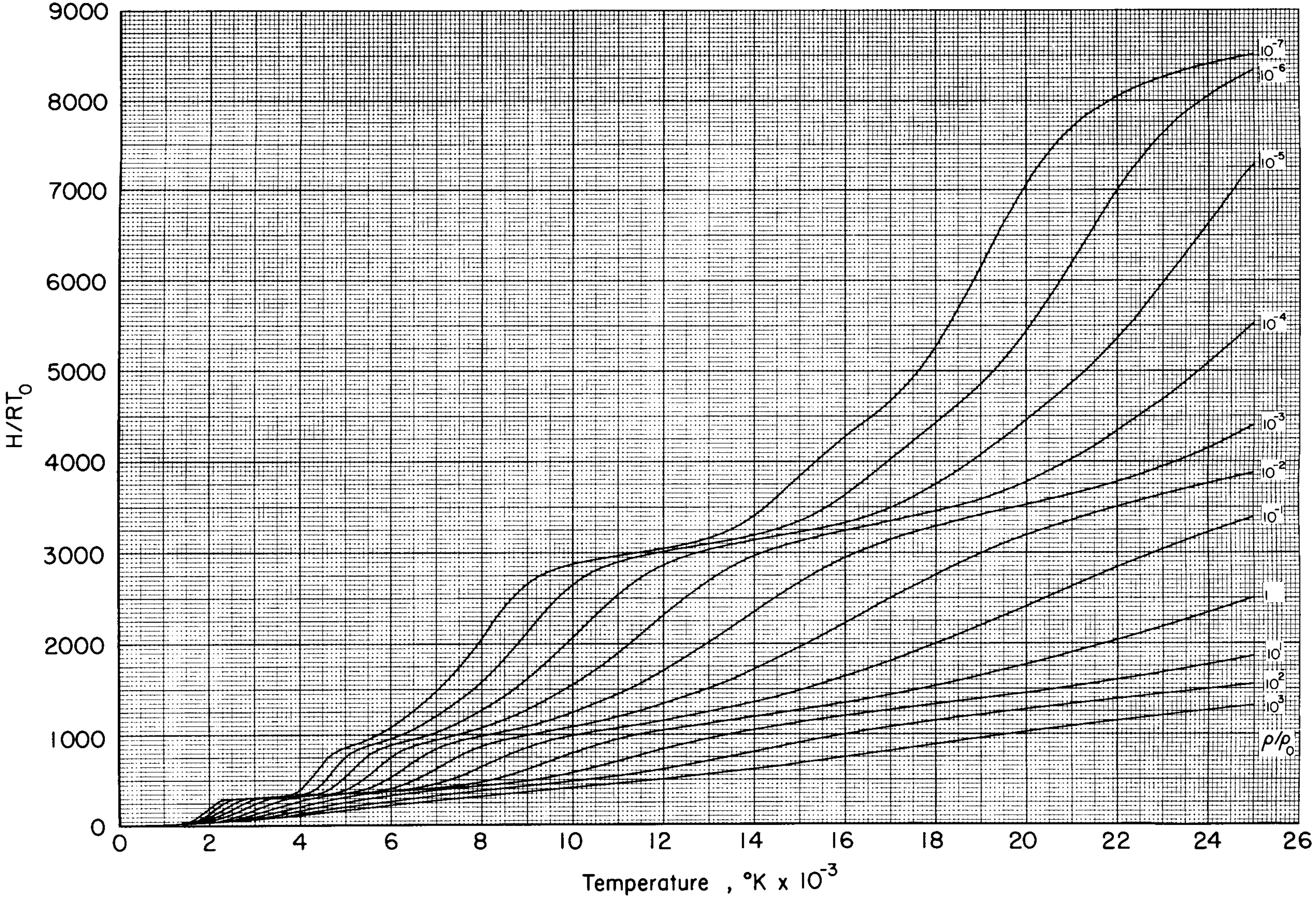


Figure 5.- Enthalpy as a function of temperature.

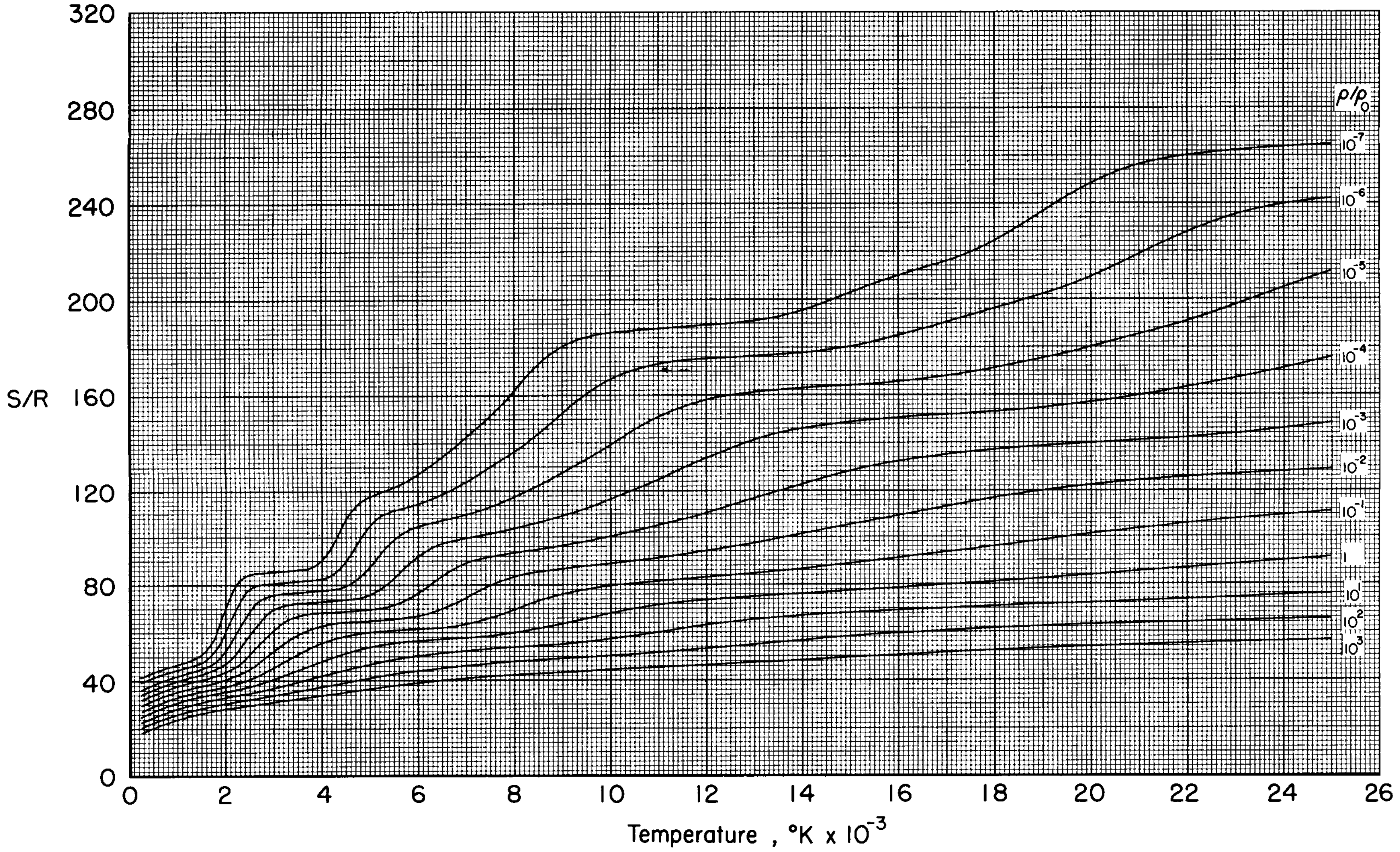


Figure 6.- Entropy as a function of temperature.

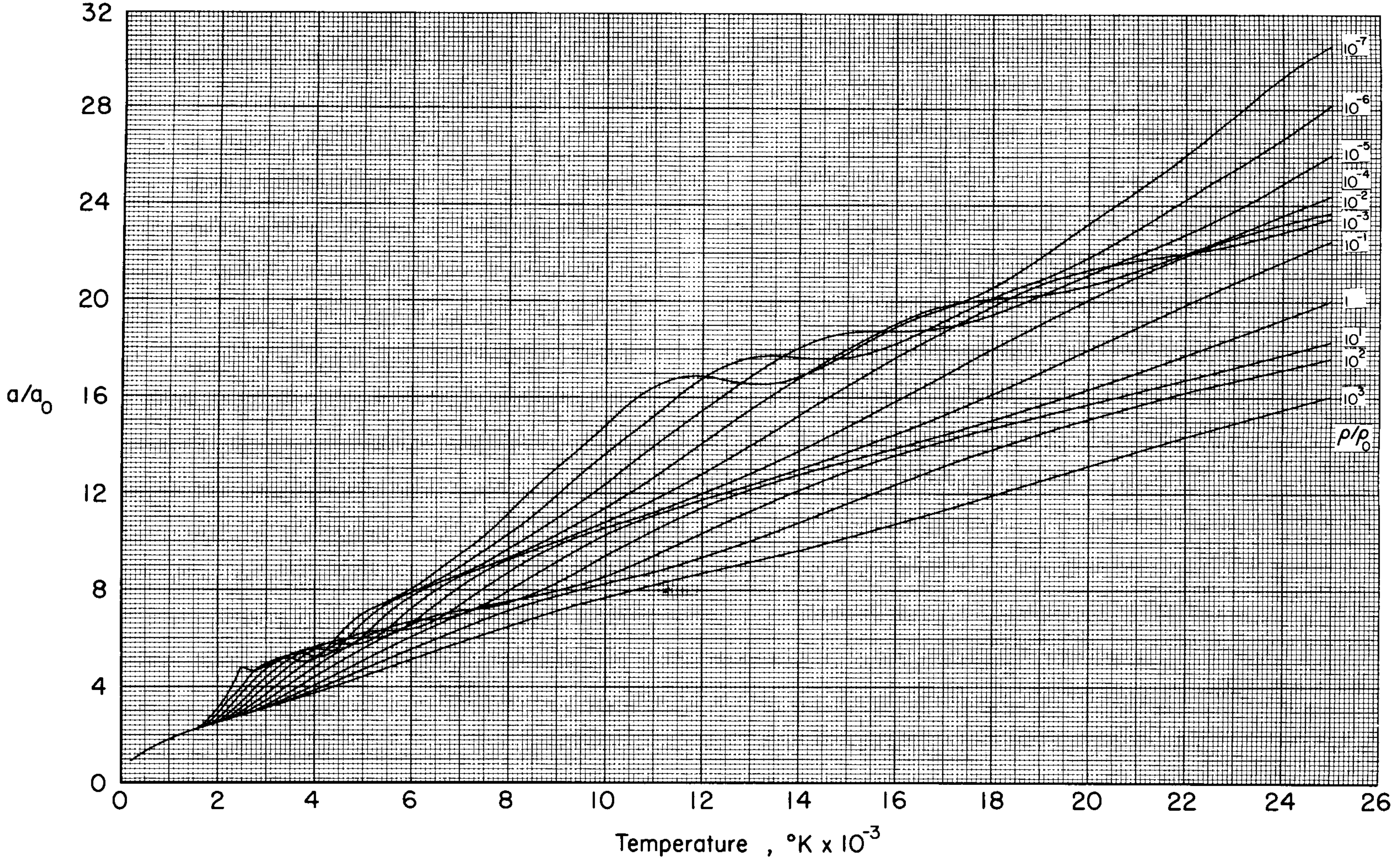


Figure 7.- Sound-speed ratio as a function of temperature.

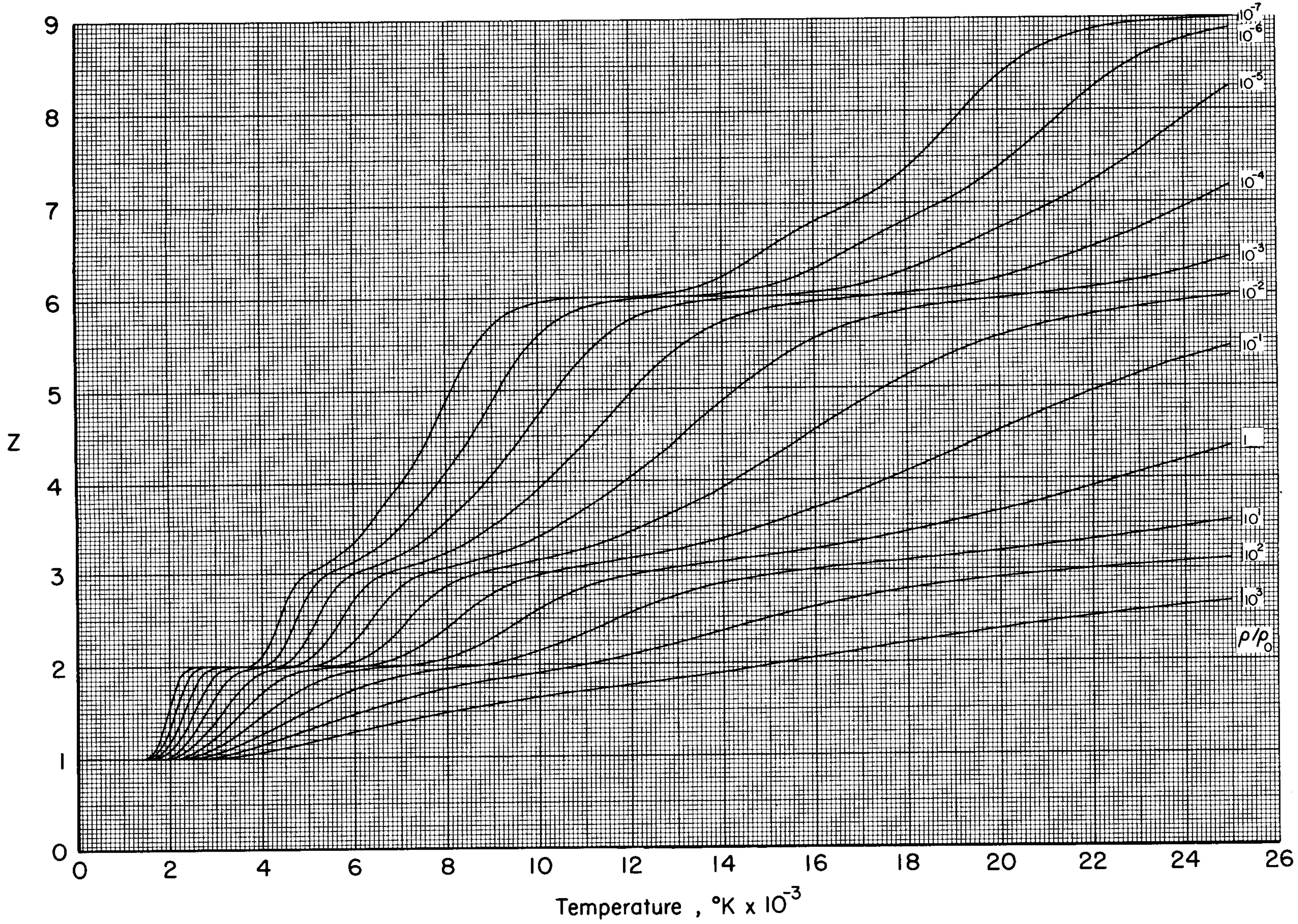
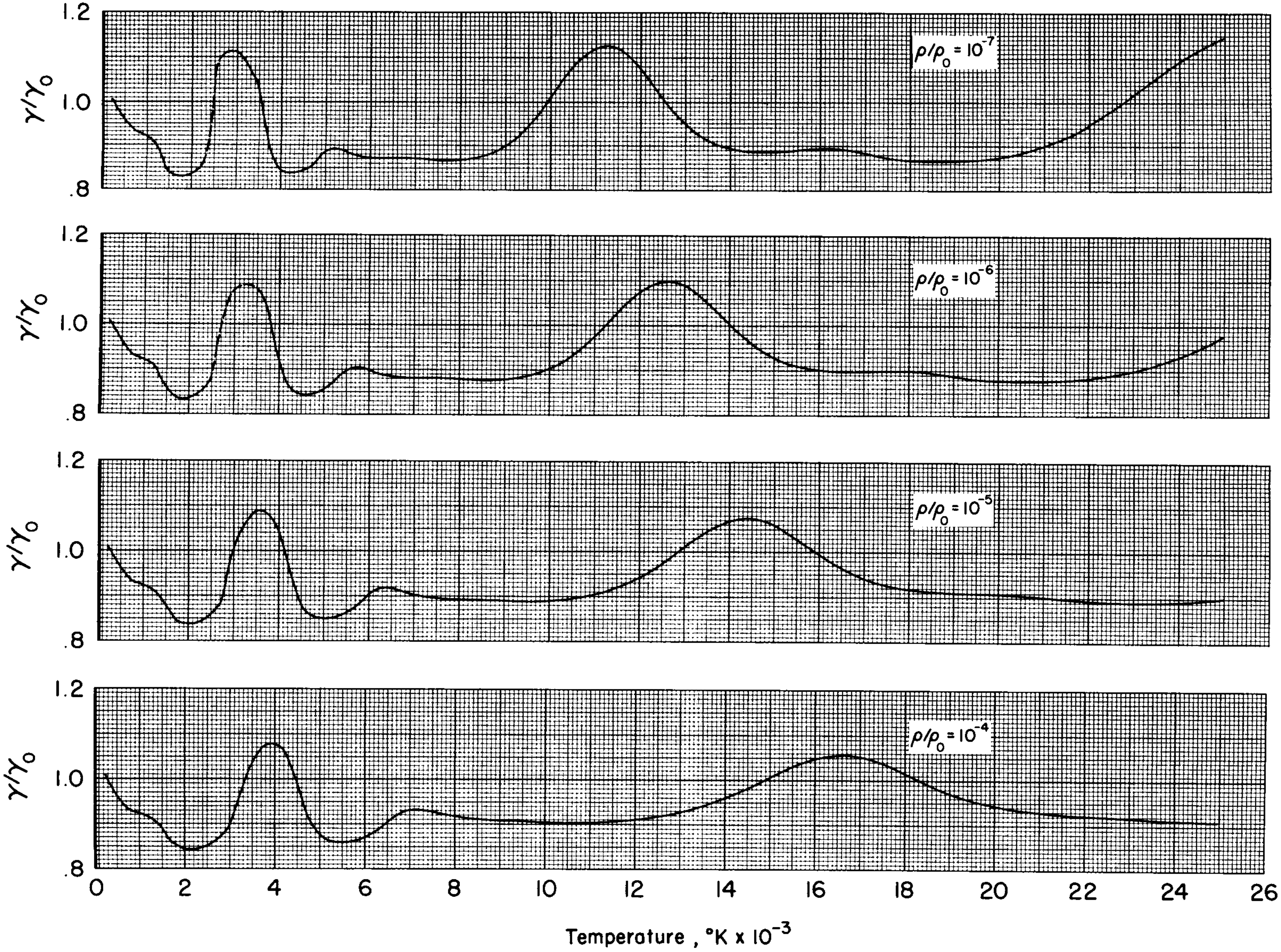
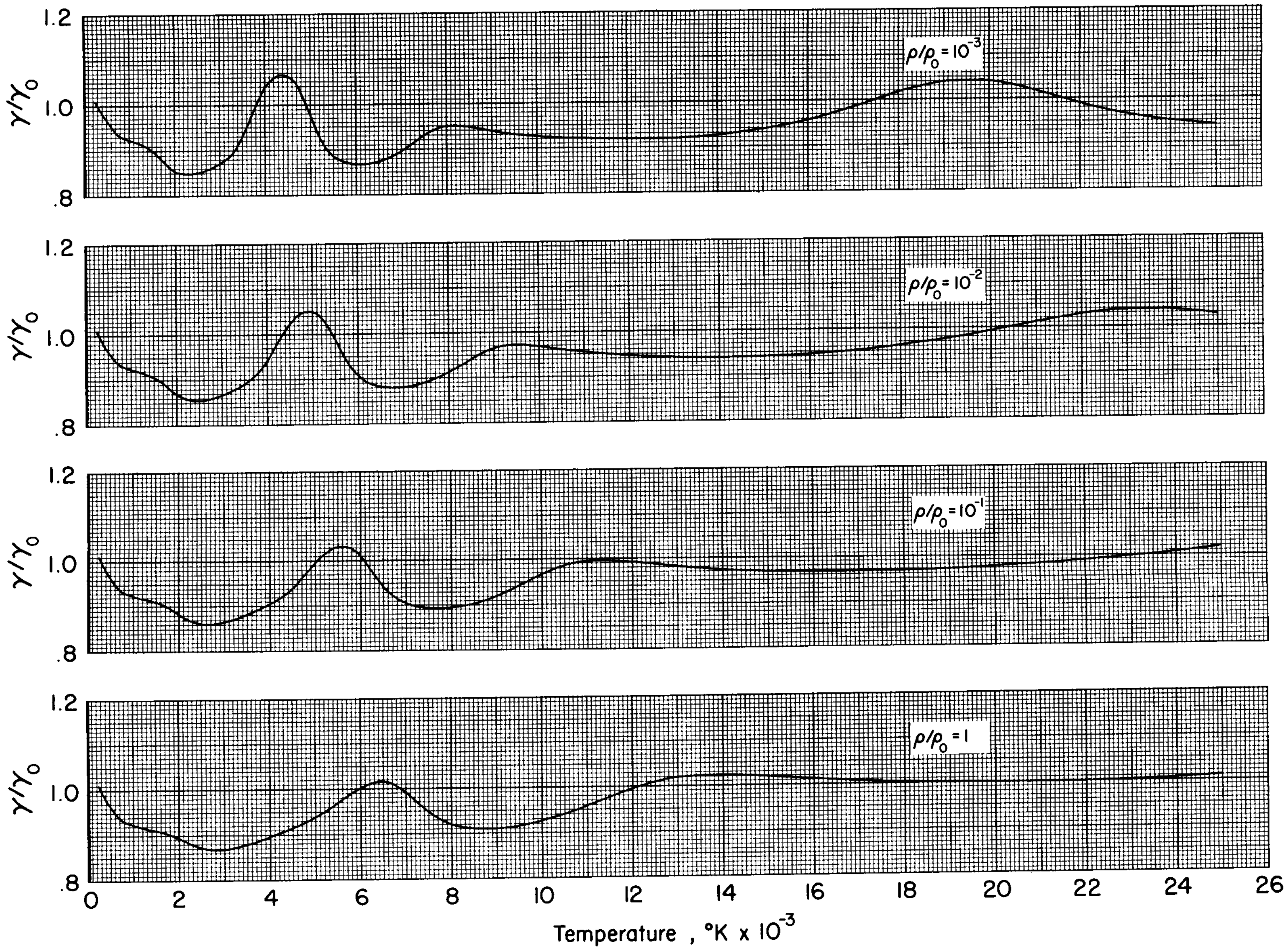


Figure 8.- Compressibility factor as a function of temperature.



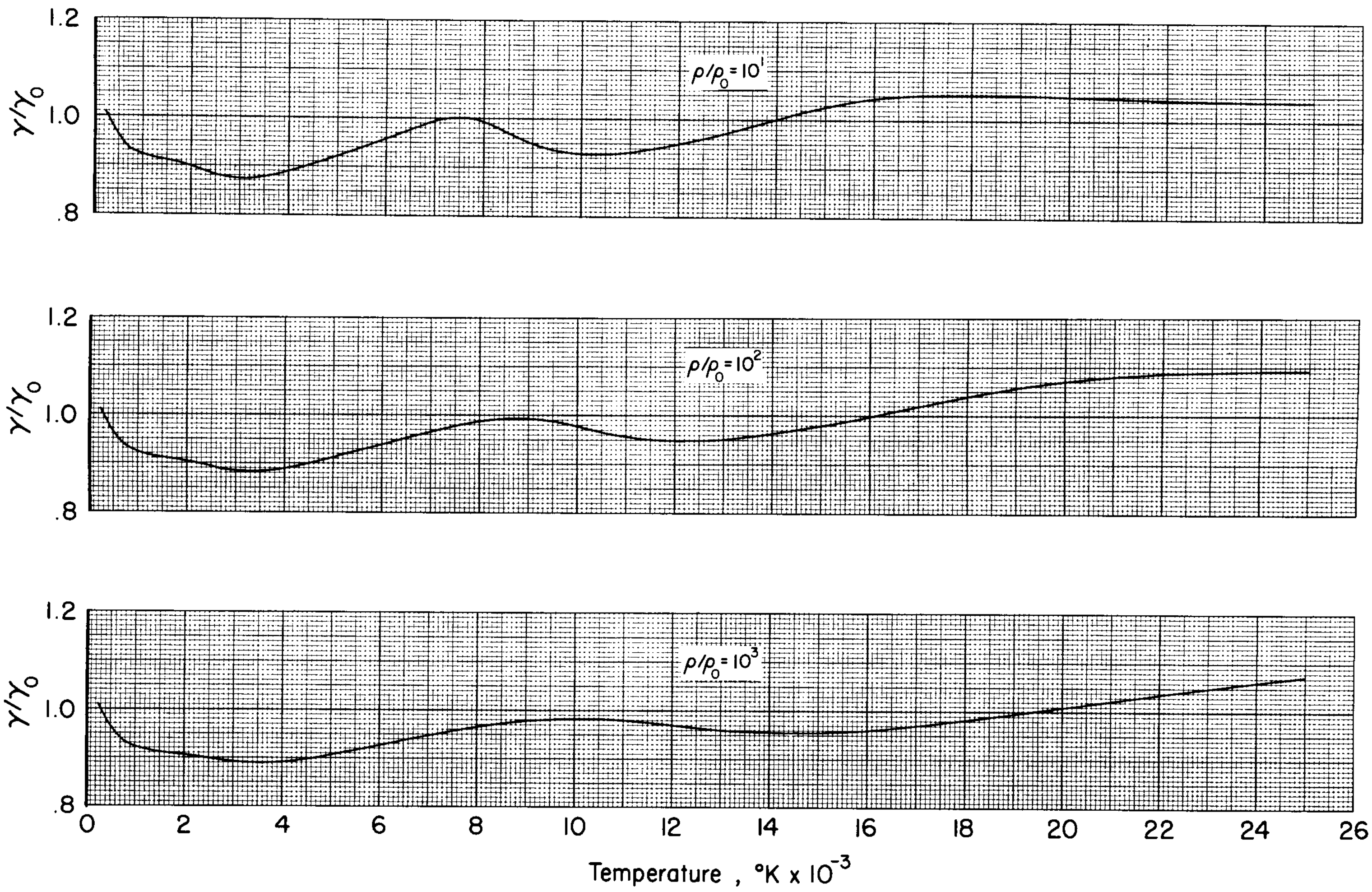
(a) $\rho/\rho_o = 10^{-7}$ to 10^{-4}; $\gamma_o = 1.281$

Figure 9.- Isentropic exponent as a function of temperature.



(b) $\rho/\rho_0 = 10^{-3}$ to 1; $\gamma_0 = 1.281$

Figure 9.- Continued.



(c) $\rho/\rho_0 = 10^1$ to 10^3; $\gamma_0 = 1.281$

Figure 9.- Concluded.