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THE EQUILIBRIUM THERMODYNAMIC PROPERTIES OF A HIGH-TEMPERATURE NITROGEN—ALKALI-METAL VAPOR MIXTURE

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SUMMARY

A study has been made of the equilibrium thermodynamic properties of nitrogen, seeded with alkali-metal vapor, at high temperatures (1000° K to 20 000° K), moderate pressures (0.003 to 3 atmospheres), and 0- to 5-percent seeding. It was found that because of the low ionization potentials of the seed materials, their ionization could represent a significant energy sink in regions where nitrogen is essentially chemically inactive. In addition, the increased number density of electrons resulting from ionization of the seed material causes a delay, until a higher temperature, in the ionization of nitrogen. These two effects tend to produce, for a given seed material, rather well-defined temperature-pressure regions in which even small degrees of seeding produce fairly large variations in some thermodynamic properties. In other regions, if proper allowances are made for the change in the average atomic weight of the mixture (and consequently, a change in the gas constant of the mixture) caused by the mass fraction of seed material, the effect of seeding is found to be very small even for as much as 5-percent seeding.

In general, it was found that the effect of seeding on the thermodynamic properties of the mixture tends to become more pronounced at lower pressures. Also, as might be expected, the effect usually becomes more pronounced as the seeding percentage is increased. In addition, certain properties (the specific heats and, to a lesser degree, enthalpy and internal energy) are significantly more sensitive to seeding than others (entropy, speed of sound, departure coefficient, for example). Although the most pronounced effects are associated with cesium seeding, effects caused by potassium and sodium seeding are very similar and only slightly less pronounced.

A computational procedure is presented whereby the thermodynamic properties of this mixture may be computed for arbitrary degrees of seeding. This procedure is readily adaptable to high-speed computer use and should be useful as a subroutine in connection with step-by-step integration solutions of high-enthalpy gas flow problems. Included in this procedure is an approximate general method of treating electronic excitation and variable principal quantum number cutoff. This method permits the calculation

of excitation to high principal quantum numbers without a large increase in computation time.

INTRODUCTION

In recent years there has been a considerable amount of research with high-temperature plasma devices, such as plasma accelerators and magnetohydrodynamics (MHD) generators. Some of these utilize a nitrogen—alkali-metal vapor mixture as the working fluid because the addition of a small amount of alkali-metal vapor can result in a large increase in the electrical conductivity of the gas. Usually, an equilibrium solution of the equations governing the operation and performance of these devices requires a high-speed computer program using the thermodynamic properties of the gas mixture in connection with a step-by-step integration procedure. In addition, some of these devices (see, for example, ref. 1) produce gas enthalpies corresponding to those associated with reentry velocities and can be used in this area to study heat transfer and related problems. Although there are available a number of calculations of the thermodynamic properties of high-temperature nitrogen (refs. 2 to 7, for example), little data on the thermodynamic properties of a high-temperature nitrogen—alkali-metal vapor mixture are available. It is therefore desirable to develop expressions that will accurately describe the properties of this mixture and that will be in a form easily adapted for use with a computer program.

In this paper expressions for the thermodynamic properties of a high-temperature (up to 20 000° K) nitrogen—alkali-metal vapor mixture are developed by using a partition function analysis. This method is similar to, for example, that employed by Drellishak, et al. (ref. 2) for nitrogen, oxygen, and argon and by Ahtye and Peng for nitrogen (ref. 3). The reactions considered are the dissociation and single ionization of nitrogen and the single ionization of the alkali-metal vapor.

Expressions are obtained for the following conventional properties: entropy, enthalpy, internal energy, specific heats at constant pressure and volume, departure coefficient, density, and speed of sound. In addition, expressions are obtained for the logarithmic partial derivatives of the departure coefficient with respect to temperature and pressure $R\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_p\right]$ and $R\left[1 - \frac{p}{Z}\left(\frac{\partial Z}{\partial p}\right)_T\right]$, quantities which are fundamental to real-gas flow problems and appear as a consequence of the dissociation and ionization reactions.

A treatment of the electronic excitation partition function and its first and second derivatives is presented. Included in this treatment are an estimation and compilation of unobserved energy levels and the development of a simple closed-form expression to estimate the high principal quantum number contribution to the partition function. A method, which is a simplification of the method suggested in reference 8, of treating the problem of a variable principal quantum number cutoff is discussed. This method permits the easy handling of a variable cutoff without the usually associated large increase in computation time.

An outline is presented herein of a computer program which calculates the thermodynamic properties of a nitrogen—alkali-metal mixture as a function of temperature, pressure, and degree of seeding. This program, as presented, may be conveniently adapted for use as a subroutine in connection with computer programs used to solve real-gas high-enthalpy flow problems.

Because they are commonly used as seed materials a rather extensive study has been made of the effect of cesium, potassium, and sodium seeding on the thermodynamic properties. It is shown that in certain temperature-pressure regions, even the addition of small amounts of seed material (1 to 2 percent) may cause large variations (20 to 40 percent) in some of these properties. Results are presented for a temperature range of 1000° K to 20 000° K, at pressures of 0.003, 0.01, 0.03, 0.1, 0.3, 1, and 3 atmospheres, and for degrees of seeding from 0 to 5 percent.

SYMBOLS

a	speed of sound, m/s
$\bar{a}$	number of parent configurations
c_p	specific heat at constant pressure, J/kg-°K
c_v	specific heat at constant volume, J/kg-°K
e	electron
E(i)	internal energy of ith species, J/m^3
E	total internal energy, J/kg
f(T,n)	any general function of temperature and principal quantum number cutoff
g_ν	statistical weight of νth state
h	Planck's constant, J-sec
H	total enthalpy, J/kg

k	Boltzmann constant, J/°K
$K_W = m_X/m_N$	
K_c	degree of seeding (see eq. (7))
$K_c^1 = \frac{K_c}{1 + K_c}$	
$K_r(Y)$	dimensionless equilibrium constant
m_i	mass of a particle of species i, kg
m	principal quantum number
n_i	number density of species i, particle/m^3
n	principal quantum number cutoff
n_t	total number density, particles/m^3
n_o	reference quantum number
N_2	nitrogen molecule
N	nitrogen atom, also nitrogen generally
N^+	singly ionized nitrogen atom
$N(n)$	last term in excitation partition function summation
p_i	partial pressure of species i, N/m^2
p	total pressure, N/m^2
p_o	atmospheric pressure, N/m^2
$P = p/p_o$, atm	
q	effective charge

$Q_j(i)$	partition function of ith species
$Q(i)$	total partition function of ith species
R	mixture gas constant, J/kg-^{o}K
S(i)	entropy of species i, J/m^3-^{o}K
S	total entropy, J/kg-^{o}K
T	temperature, ^{o}K
V	volume, kT/p, m^3
X	alkali-metal atom, also an alkali metal generally
X^+	singly ionized alkali-metal atom
Y	type of gas
Z	departure coefficient, $p/\rho RT$

$$Z_T = R\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_p\right], \text{ J/kg-}^{o}\text{K}$$

$$Z_p = R\left[1 - \frac{p}{Z}\left(\frac{\partial Z}{\partial p}\right)_T\right], \text{ J/kg-}^{o}\text{K}$$

α_r	degree of reaction (r = 1,2,3)

$$\beta_o = \frac{5}{2} + \epsilon_{rot}\left(N_2\right) + \epsilon_v\left(N_2\right) + \epsilon_e\left(N_2\right) + 2K_c\left[\frac{5}{2} + \epsilon_e(X)\right]$$

$$\beta_r = T\,\frac{\partial}{\partial T}\left[\log_e K_r(Y)\right]$$

$$\gamma = \left(\frac{\partial \log_e p}{\partial \log_e \rho}\right)_S$$

$$\Delta = 2K_c\left(\frac{1 + \alpha_2}{1 + \alpha_1}\right)$$

$\epsilon_j(i) = T\left(\frac{\partial}{\partial T} \log_e Q_j(i)\right)_V$

$\theta_D(Y)$	characteristic temperature of dissociation, $^{\circ}$K

$\theta_o(i) = \frac{\text{Reference energy of ith species}}{k}$, $^{\circ}$K

$\theta_r(Y)$	characteristic temperature of reaction r, $^{\circ}$K
θ_ν	characteristic temperature of energy level ν, $^{\circ}$K
θ_v	characteristic temperature of vibration, $^{\circ}$K
θ_{rot}	characteristic temperature of rotation, $^{\circ}$K
θ_H	Rydberg constant, $^{\circ}$K

$\mu_o = \left[\frac{\partial}{\partial T}\left(\beta_o T\right)\right]_p$

$\mu_r = \left[\frac{\partial}{\partial T}\left(\beta_r T\right)\right]_p$

ν	summation index of excited states
ρ	total density, kg/m^3

$\sigma_j(i) = \left[\frac{\partial}{\partial T}\left(T\epsilon_j(i)\right)\right]_p$

ω	general seeded thermodynamic variable
ω_o	general unseeded thermodynamic variable

Subscripts:

i	species $\left(N_2, N, N^+, X, X^+, e\right)$
j	energy forms: translational t, rotational rot, vibrational v, and electronic excitation e
r	reaction number (=1,2,3)

EQUATION OF STATE

This paper considers a mixture of nitrogen and an alkali vapor in a pressure-temperature region (see fig. 1) where the principal reactions r are

$$N_2 \rightleftarrows N + N \qquad (r = 1) \qquad (1)$$

$$X \rightleftarrows X^+ + e \qquad (r = 2) \qquad (2)$$

$$N \rightleftarrows N^+ + e \qquad (r = 3) \qquad (3)$$

and X denotes any alkali-metal atom. It is assumed that each species i $\left(i\right.$ being $\left.N_2, N, N^+, X, X^+, e\right)$ obeys an ideal gas equation

$$p_i = n_i kT$$

where p_i is the partial pressure and n_i the number density of species i. (The validity of this assumption is discussed in ref. 8 where it is shown that for the range of temperature and pressure considered herein, the assumption is well justified.) The total gas pressure p then becomes

$$p = \sum_i p_i = \sum_i n_i kT \qquad (4)$$

The total gas mass density ρ is the sum of the species mass densities so that

$$\rho = \sum_i n_i m_i$$

where m_i is the mass of a particle of species i. If it is noted that $\frac{1}{2} m_{N_2} = m_N \approx m_{N^+}$, $m_X \approx m_{X^+}$, $n_e m_e << \rho$, and K_w is defined $K_w \equiv \frac{m_X}{m_N}$, equation (4) may be written as

$$p = \rho RTZ \qquad (5)$$

where

$$R \equiv \frac{k}{2m_N\left(1 + K_w K_c\right)} \qquad (6a)$$

$$Z \equiv \frac{2 \sum_i n_i}{2n_{N_2} + n_N + n_{N^+}} \tag{6b}$$

The quantity K_c is the degree of seeding and may be defined in terms of number densities as

$$K_c \equiv \frac{n_X + n_{X^+}}{2n_{N_2} + n_N + n_{N^+}} \qquad \left(0 \leqq K_c < \infty\right) \tag{7}$$

Some authors may prefer to define a slightly different degree of seeding K_c^1 as

$$K_c^1 \equiv \frac{n_X + n_{X^+}}{\left(2n_{N_2} + n_N + n_{N^+}\right) + \left(n_X + n_{X^+}\right)} \qquad \left(0 \leqq K_c^1 \leqq 1\right)$$

but for small degrees of seeding, the choice of definition is unimportant since

$$K_c^1 = \frac{K_c}{K_c + 1} \approx K_c$$

In general, the alkali-metal vapors (lithium, sodium, potassium, rubidium, and cesium) have a relatively high vapor temperature and a low characteristic temperature of dissociation. As a result, even at temperatures close to the liquid-vapor saturation line, the vapor is essentially completely dissociated. (See, for example, cesium, ref. 9.) In addition, the characteristic temperature of second ionization is on the order of, or much greater than, the corresponding characteristic temperature of second ionization for nitrogen. Therefore in the pressure-temperature region shown in figure 1, the predominant reaction involving the alkali metals is $X \rightleftarrows X^+ + e$. Values of K_w and the characteristic temperatures of dissociation and first and second ionization are presented in table I.

PARTITION FUNCTIONS

The theory of partition functions as a consequence of Maxwell-Boltzmann statistics and its application to equilibrium computations for gas mixtures have been discussed in many references (for example, refs. 8 and 10 to 14). For this reason, partition functions and the related number density equations are introduced with a minimum of theoretical explanation.

The partition functions $Q_j(i)$ for species i possessing energy of the form j are

$$Q_t(i) = \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} V \tag{8a}$$

$$Q_e(i) = \sum_{\nu=1}^{N(n)} g_\nu e^{-\frac{\theta_\nu}{T}} \tag{8b}$$

$$Q_{rot}(N_2) = \frac{T}{\theta_{rot}} \tag{8c}$$

$$Q_v(N_2) = \left(1 - e^{-\frac{\theta_v}{T}}\right)^{-1} \tag{8d}$$

where $Q_{rot}(N_2)$ is the classical limit of the rotation partition function and $Q_v(N_2)$ is the harmonic oscillator partition function. The energy forms are translation, electronic excitation, rotation, and vibration and the θ values are characteristic temperatures of electronic excitation $\left(\frac{\text{Energy of level } \nu}{k}\right)$, rotation, and vibration. (See table I.) The only species containing energy in rotation and vibration is, of course, N_2. The total partition function $Q(i)$ for species i is

$$Q(i) = \prod_j Q_j(i)$$

Partition functions $Q_{rot}(N_2)$ and $Q_v(N_2)$ are written in a rather simple form which ignores such real gas effects as anharmonic vibration and vibration-rotation coupling. In reference 15 it is shown that for equilibrium computations of gas thermodynamic properties in the pressure-temperature region considered herein, these effects are small (generally 1 percent or less) and they were therefore ignored.

Since in the partition function $Q_e(i)$ the quantity $N(n)$ is a function of the cutoff principal quantum number n, which is, for a given species i, dependent generally on temperature and electron and ion densities (ref. 16), $Q_e(i)$ is not a function of temperature alone. However, a discussion of the excitation partition function is presented in appendix A where it is shown that

$$\left(\frac{\partial}{\partial T} \log_e Q_e(i)\right)_V \approx \left(\frac{\partial}{\partial T} \log_e Q_e(i)\right)_n$$

and that

$$\left\{\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial}{\partial T}\log_e Q_e(i)\right)_V\right]\right\}_p \approx \left\{\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial}{\partial T}\log_e Q_e(i)\right)_n\right]\right\}_n$$

The evaluation of the thermodynamic properties of the gas mixture involves evaluation of the terms

$$\left[T\frac{\partial}{\partial T}\log_e Q(i)\right]_V = \left[T\frac{\partial}{\partial T}\sum_j \log_e Q_j(i)\right]_V$$

and

$$\left\{\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial}{\partial T}\log_e Q(i)\right)_V\right]\right\}_p = \left\{\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial}{\partial T}\sum_j \log_e Q_j(i)\right)_V\right]\right\}_p$$

The differentiation may be performed to obtain

$$T\left[\frac{\partial}{\partial T}\log_e Q(i)\right]_V = \frac{3}{2} + \epsilon_e(i) + \epsilon_v(i) + \epsilon_{rot}(i) \tag{9}$$

where

$$\epsilon_e(i) = \frac{\sum_{\nu=1}^{N(n)} g_\nu\left(\frac{\theta_\nu}{T}\right)e^{-\frac{\theta_\nu}{T}}}{Q_e(i)} \qquad (i \neq e)$$

$$\epsilon_v(i) = \frac{\theta_v}{T}\left(e^{\frac{\theta_v}{T}} - 1\right)^{-1} \qquad (i = N_2)$$

$$\epsilon_v(i) = 0 \qquad (i \neq N_2)$$

$$\epsilon_{rot}(i) = 1 \qquad (i = N_2)$$

$$\epsilon_{rot}(i) = 0 \qquad (i \neq N_2)$$

and to obtain

$$\left\{\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial}{\partial T}\log_e Q(i)\right)_V\right]\right\}_p = \frac{3}{2} + \sigma_{rot}(i) + \sigma_v(i) + \sigma_e(i) \tag{10}$$

where

$$\sigma_{rot}(i) = \epsilon_{rot}(i)$$

$$\sigma_e(i) = \frac{\sum_{\nu=1}^{N(n)} g_\nu \left(\frac{\theta_\nu}{T}\right)^2 e^{-\frac{\theta_\nu}{T}}}{Q_e(i)} - \epsilon_e^2(i) \qquad (i \neq e)$$

$$\sigma_v(i) = \epsilon_v^2(N_2) e^{\frac{\theta_v}{T}} \qquad (i = N_2)$$

$$\sigma_v(i) = 0 \qquad (i \neq N_2)$$

As is shown in appendix A, the quantities $Q_e(i)$, $\epsilon_e(i)$, and $\sigma_e(i)$ are functions of both temperature and principal quantum number cutoff n. Shown in figures 2 to 4, 5 to 7, and 8 to 10 are $Q_e(i)$, $\epsilon_e(i)$, and $\sigma_e(i)$, respectively, plotted against temperature for various values of n. For the alkali metals, as is suggested by equations (A3) to (A6), for higher values of n, these quantities become functions of $T/\theta_2(X)$ only and therefore for each quantity only one plot is needed to describe cesium, potassium, and sodium (and presumably also lithium and rubidium).

EQUILIBRIUM CONSTANTS

For each of the equilibrium reactions 1, 2, and 3, a dimensionless equilibrium constant may be defined as $\frac{kT}{p_o}$ times a function of the number densities of the species involved. This function may be related to the ratio of the respective total partition functions to obtain

$$\frac{p_o}{kT} K_1(N) \equiv \frac{n_N^2}{n_{N_2}} = \frac{Q^2(N)}{VQ(N_2)} e^{-\frac{\theta_1(N)}{T}} \tag{11a}$$

$$\frac{p_o}{kT} K_2(X) \equiv \frac{n_{X^+} n_e}{n_X} = \frac{Q(X^+)\, Q(e)}{VQ(X)} e^{-\frac{\theta_2(X)}{T}} \tag{11b}$$

$$\frac{p_o}{kT} K_3(N) \equiv \frac{n_{N^+} n_e}{n_N} = \frac{Q(N^+)\, Q(e)}{VQ(N)} e^{-\frac{\theta_3(N)}{T}} \tag{11c}$$

where $K_r(Y)$ is the dimensionless equilibrium constant, and $\theta_r(Y)$ is the characteristic temperature, for reaction r involving species of gas Y = (nitrogen, N or alkali metal, X). The quantity $\theta_r(Y)$ is defined in terms of the net energy change $\Delta\epsilon_r(Y)$ for reaction r, as $\theta_r(Y) \equiv \frac{\Delta\epsilon_r(Y)}{k}$. By using equations (8a) to (8d), the $K_r(Y)$ values may be expressed as

$$K_1(N) = \left(\frac{\pi m_N k}{h^2}\right)^{3/2}\left(\frac{k}{p_o}\right)\left(\frac{\theta_{rot}}{T}\right)\left(1 - e^{-\frac{\theta_v}{T}}\right)T^{5/2}\,\frac{Q_e{}^2(N)}{Q_e(N_2)}\,e^{-\frac{\theta_1(N)}{T}}$$

$$K_2(X) = 2\left(\frac{2\pi m_e k}{h^2}\right)^{3/2}\left(\frac{k}{p_o}\right)T^{5/2}\,\frac{Q_e(X^+)}{Q_e(X)}\,e^{-\frac{\theta_2(X)}{T}}$$

$$K_3(N) = 2\left(\frac{2\pi m_e k}{h^2}\right)^{3/2}\left(\frac{k}{p_o}\right)T^{5/2}\,\frac{Q_e(N^+)}{Q_e(N)}\,e^{-\frac{\theta_3(N)}{T}}$$

where $Q_e(e) = 2\ \left(\epsilon_e(e) = \sigma_e(e) = 0\right)$. Shown in figure 11 are values of $K_r(Y)$ plotted against temperature for various pressures and $K_c = 0.01$.

Some important derivatives which will be needed later are given by

$$\beta_1 \equiv T\,\frac{\partial}{\partial T}\Big[\log_e K_1(N)\Big]_V = \frac{5}{2} - \epsilon_{rot}(N_2) - \epsilon_v(N_2) - \epsilon_e(N_2) + 2\epsilon_e(N) + \frac{\theta_1(N)}{T} \qquad (12a)$$

$$\beta_2 \equiv T\,\frac{\partial}{\partial T}\Big[\log_e K_2(X)\Big]_V = \frac{5}{2} - \epsilon_e(X) + \epsilon_e(X^+) + \frac{\theta_2(X)}{T} \qquad (12b)$$

$$\beta_3 \equiv T\,\frac{\partial}{\partial T}\Big[\log_e K_3(N)\Big]_V = \frac{5}{2} - \epsilon_e(N) + \epsilon_e(N^+) + \frac{\theta_3(N)}{T} \qquad (12c)$$

and

$$\mu_1 \equiv \frac{\partial}{\partial T}\Big[\left(T\beta_1\right)\Big]_p = \frac{5}{2} - \sigma_{rot}(N_2) - \sigma_v(N_2) - \sigma_e(N_2) + 2\sigma_e(N) \qquad (13a)$$

$$\mu_2 \equiv \frac{\partial}{\partial T}\Big[\left(T\beta_2\right)\Big]_p = \frac{5}{2} - \sigma_e(X) + \sigma_e(X^+) \qquad (13b)$$

$$\mu_3 \equiv \frac{\partial}{\partial T}\Big[\left(T\beta_3\right)\Big]_p = \frac{5}{2} - \sigma_e(N) + \sigma_e(N^+) \qquad (13c)$$

DETERMINATION OF SPECIES CONCENTRATIONS

In general, thermodynamic properties can be expressed as functions of any two of the three variables – temperature, pressure, and density. The equilibrium properties of a particular species are conventionally described by the temperature and it is primarily through the solution of the number density equations (11a) to (11c) that the pressure or density dependence is introduced. Since it is the more conventional property and since in most applications it is more easily measured, pressure rather than density was chosen herein as the second independent variable.

Equations (11a) to (11c) and (7) together with expressions for charge neutrality

$$n_e = n_{X^+} + n_{N^+}$$

and species conservation

$$n_t = \sum_i n_i = \frac{p}{kT}$$

form a set of six equations in the six variables n_i. If for the reactions $r = 1,2,3,$ respectively, a degree of reaction $\alpha_r\left(0 < \alpha_r < 1\right)$ is defined as

$$\alpha_1 \equiv \frac{n_N}{2n_{N_2} + n_N}$$

$$\alpha_2 \equiv \frac{n_{X^+}}{n_X + n_{X^+}}$$

$$\alpha_3 \equiv \frac{n_{N^+}}{n_N + n_{N^+}}$$

the set of six equations can be reduced to three equations

$$\frac{K_1(N)}{P} = \frac{2\alpha_1}{1 - \alpha_1}\left(\frac{2}{Z}\right)\left[\frac{\alpha_1 - \alpha_1\alpha_3}{1 - \alpha_3\left(1 - \alpha_1\right)}\right] \tag{14a}$$

$$\frac{K_2(X)}{P} = \frac{\alpha_2}{1 - \alpha_2}\left(\frac{2}{Z}\right)\left[K_c\alpha_2 + \frac{\alpha_1\alpha_3}{1 - \alpha_3\left(1 - \alpha_1\right)}\right] \tag{14b}$$

$$\frac{K_3(N)}{P} = \frac{\alpha_3}{1 - \alpha_3}\left(\frac{2}{Z}\right)\left[K_c\alpha_2 + \frac{\alpha_1\alpha_3}{1 - \alpha_3\left(1 - \alpha_1\right)}\right] \tag{14c}$$

where $P = \frac{p}{p_o}$ and

$$Z = 1 + 2K_c\left(1 + \alpha_2\right) + \frac{\alpha_1 + 2\alpha_1\alpha_3}{1 - \alpha_3\left(1 - \alpha_1\right)}$$

It is shown in appendix B and illustrated in figure 1 that reactions 1 and 2 may occur in overlapping temperature-pressure regions, but that reaction 3 becomes significant $\left(\alpha_3 \neq 0\right)$ only in temperature-pressure regions where reactions 1 and 2 are essentially complete $\left(\alpha_1 \approx \alpha_2 \approx 1\right)$. Therefore α_1, α_2, and α_3 may be expressed to a high degree of accuracy as

$$\alpha_1 = \left[1 + 4\frac{P}{(1 + \Delta)K_1(N)}\right]^{-1/2} \tag{15}$$

$$\alpha_2 = \left(\frac{1 + \alpha_1}{4}\right)\frac{K_2(X)}{K_cP}(1 + \Delta)\left[\sqrt{1 + \frac{8K_cP}{\left(1 + \alpha_1\right)\left(1 + \Delta\right)K_2(X)}} - 1\right] \tag{16}$$

$$\alpha_3 = \frac{K_c\left(P + 2K_3(N)\right)}{2\left(P + K_3(N)\right)}\left\{\sqrt{1 + \frac{4\left(1 + 2K_c\right)\left(P + K_3(N)\right)K_3(N)}{K_c^2\left[P + 2K_3(N)\right]^2}} - 1\right\} \tag{17}$$

where $\Delta \equiv 2K_c\frac{1 + \alpha_2}{1 + \alpha_1}$. Note that in this form, equations (15) and (16) are still coupled, but, since $K_c < \Delta < 4K_c$ and usually $K_c << 1$, equations (15) and (16) are very insensitive to Δ and an iteration solution will therefore rapidly converge. Since the $K_r(Y)$ terms are functions of pressure (through the principal quantum number cutoff, n), an iteration solution on n is also necessary. However, since the solution of equations (15), (16), and (17) is very weakly coupled to n $\left(\text{through } n_e^{-1/4}\right)$, this iteration procedure also rapidly converges. It follows that for a given temperature, pressure, and degree of seeding, α_1, α_2, and α_3 are uniquely determined and the quantities $\frac{n_i}{2n_{N_2} + n_N + n_{N^+}}$ may be obtained from the following relationships:

$$\frac{n_i}{2n_{N_2} + n_N + n_{N^+}} = \begin{Bmatrix} \frac{1 - \alpha_1}{2} & (i = N_2) \\ \alpha_1 - \alpha_1\alpha_3 & (i = N) \\ \alpha_1\alpha_3 & (i = N^+) \\ K_c(1 - \alpha_2) & (i = X) \\ K_c\alpha_2 & (i = X^+) \\ K_c\alpha_2 + \alpha_1\alpha_3 & (i = e) \end{Bmatrix} \tag{18}$$

The number density n_i of species i is then given by

$$n_i = \frac{n_i}{2n_{N_2} + n_N + n_{N^+}} \frac{2}{Z} \frac{p}{kT}$$

and

$$Z = 1 + \alpha_1 + 2K_c(1 + \alpha_2) + 2\alpha_1\alpha_3 \tag{19}$$

It is interesting to note the effect of electronic excitation on the solution for α_r. Equations (15) to (17) were solved ($K_c = 0.01$) by using $K_r(Y)$ values which were insensitive to electronic excitation (all $Q_e(i)$ values were set equal to their ground-state degeneracy $q_{\nu=0}$) and the values of α_r obtained are shown in figure 12 for pressures of 0.01 and 1 atmospheres. Note that for small values of α_r, the effect is negligible but that as α_r approaches 1, the effect becomes apparent. This effect is caused by excitation becoming an appreciable energy sink at high temperatures.

The first derivatives of α_r are obtained from equations (B6) to (B8) in appendix B. To obtain the first partial derivatives of α_3, equation (B8) may be differentiated directly to obtain

$$\frac{T}{\beta_3}\left(\frac{\partial\alpha_3}{\partial T}\right)_p = -p\left(\frac{\partial\alpha_3}{\partial p}\right)_T \tag{20a}$$

$$\frac{T}{\beta_3}\left(\frac{\partial\alpha_3}{\partial T}\right)_p \equiv \phi_3 \tag{20b}$$

but, because of the coupling, the first derivatives of α_1 and α_2 must be obtained from the differentiation of equations (B6) and (B7) and the simultaneous solution of the equations

$$\left(\frac{\partial\alpha_a}{\partial T}\right)_p = \left(\frac{\partial\alpha_a}{\partial T}\right)_{p,\alpha_b} + \left(\frac{\partial\alpha_a}{\partial\alpha_b}\right)_{T,p}\left(\frac{\partial\alpha_b}{\partial T}\right)_p$$

$$\left(\frac{\partial\alpha_a}{\partial p}\right)_T = \left(\frac{\partial\alpha_a}{\partial p}\right)_{T,\alpha_b} + \left(\frac{\partial\alpha_a}{\partial\alpha_b}\right)_{T,p}\left(\frac{\partial\alpha_b}{\partial p}\right)_T$$

where $r = a = 1$ when $r = b = 2$ and $r = a = 2$ when $r = b = 1$. By performing the indicated operations and simplifying, it is possible to obtain

$$\left(\frac{\partial\alpha_1}{\partial T}\right)_p = \frac{\beta_1}{T}\phi_4\phi_1 - 2\frac{K_c}{T}\phi_5\left(\beta_1 - \beta_2\right) \tag{20c}$$

$$\left(\frac{\partial\alpha_1}{\partial p}\right)_T = -\frac{1}{p}\phi_4\phi_1 \tag{20d}$$

$$\left(\frac{\partial\alpha_2}{\partial T}\right)_p = \frac{\beta_2}{T}\phi_4\phi_2 + \frac{\phi_5}{T}\left(\beta_1 - \beta_2\right) \tag{20e}$$

$$\left(\frac{\partial\alpha_2}{\partial p}\right)_T = -\frac{1}{p}\phi_4\phi_2 \tag{20f}$$

(The equations for ϕ_1 to ϕ_5 are given in appendix B.)

Note that the indicated differentiation leading to equations (20a) to (20f) has been performed under the assumption that for $0 < \alpha_r < 1$, the quantities $Q_e(i)$ (and therefore $K_r(Y)$) are weak functions of pressure $\left(\frac{p}{K_r(Y)}\left(\frac{\partial K_r(Y)}{\partial p}\right)_T << 1\right)$. This assumption has been verified numerically as would be expected since generally it is only for $\alpha_r \approx 1$ that $K_r(Y)$ becomes pressure dependent. (See figs. 11 and 12.)

INTERNAL ENERGY, ENTHALPY, AND ENTROPY

In terms of the total partition function, the internal energy per unit volume for species i is given by

$$E(i) = n_i kT^2 \left[\frac{\partial}{\partial T} \log_e Q(i)\right]_V + n_i k\theta_o(i)$$

where

$$\theta_o(i) = 0 \qquad (i = N_2, X)$$

$$\theta_o(i) = \frac{1}{2}\theta_1(N) \qquad (i = N)$$

$$\theta_o(i) = \theta_2(X) \qquad (i = X^+)$$

$$\theta_o(i) = \frac{1}{2}\theta_1(N) + \theta_3(N) \qquad (i = N^+)$$

$$\theta_o(i) = 0 \qquad (i = e)$$

(Values of $\theta_r(Y)$ are given in table I.)

Note that the reference energy is taken to be zero for the nitrogen molecules N_2 and alkali-metal atoms X. It was felt that in most engineering applications, the seed material would be introduced into the system at high enough temperatures to assure the material would be in a monatomic vapor form. Therefore, the reference state for the enthalpy H and internal energy E was taken to be a gas mixture of N_2 and X. If it is desired to reference an enthalpy H' and internal energy E' to a gas mixture of N_2 and X_2, it may be done with the following relation:

$$H' - H = K_c R\theta_D(X) = E' - E$$

The total gas energy per unit mass E is therefore

$$E = \frac{\sum\limits_i E(i)}{\rho} = \frac{\sum\limits_i E(i)}{\sum\limits_i n_i m_i}$$

which becomes

$$E = 2RT \sum_i \frac{n_i}{2n_{N_2} + n_N + n_{N^+}} \left\{\left[T \frac{\partial}{\partial T} \log_e Q(i)\right]_V + \frac{\theta_o(i)}{T}\right\} \tag{21}$$

where R is defined by equation (6a).

The gas enthalpy H is simply determined by

$$H = E + \frac{p}{\rho} = E + RTZ \tag{22a}$$

With the use of equations (18), (11a) to (11c), and (12a) to (12c), H may be expressed as

$$H = RT\left(\beta_o + \alpha_1\beta_1 + 2\alpha_1\alpha_3\beta_3 + 2K_c\alpha_2\beta_2\right) \tag{22b}$$

where

$$\beta_o \equiv \frac{5}{2} + \epsilon_{rot}(N_2) + \epsilon_V(N_2) + \epsilon_e(N_2) + 2K_c\left[\frac{5}{2} + \epsilon_e(X)\right]$$

The entropy per unit volume S(i) of species i is

$$S(i) = n_i k\left(\log_e \frac{Q(i)}{Vn_i} + 1\right) + n_i k\left[T \frac{\partial}{\partial T} \log_e Q(i)\right]_V$$

so that the total entropy per unit mass S is

$$S = 2R\sum_i \frac{n_i}{2n_{N_2} + n_N + n_{N^+}}\left\{\log_e \frac{Q(i)}{Vn_i} + \left[T\frac{\partial}{\partial T} \log_e Q(i)\right]_V\right\} + RZ$$

or from equations (21) and (22a)

$$S = \frac{H}{T} + 2R\sum_i \frac{n_i}{2n_{N_2} + n_N + n_{N^+}}\left[\log_e \frac{Q(i)}{Vn_i} - \frac{\theta_o(i)}{T}\right]$$

SPECIFIC HEATS AND SPEED OF SOUND

The specific heat at constant pressure c_p is defined as $\left(\frac{\partial H}{\partial T}\right)_p$ so that from equations (13a) to (13c) and (22),

$$\frac{c_p}{R} = \mu_o + \alpha_1\mu_1 + 2\alpha_1\alpha_3\mu_3 + 2K_c\alpha_2\mu_2 + T\beta_1\left(\frac{\partial\alpha_1}{\partial T}\right)_p$$

$$+ 2T\beta_3\left[\alpha_1\left(\frac{\partial\alpha_3}{\partial T}\right)_p + \alpha_3\left(\frac{\partial\alpha_1}{\partial T}\right)_p\right] + 2K_c\beta_2 T\left(\frac{\partial\alpha_2}{\partial T}\right)_p$$

where

$$\mu_o \equiv \left[\frac{\partial}{\partial T}\left(\beta_o T\right)\right]_p$$

$$\mu_o = \frac{5}{2} + \sigma_{rot}(N_2) + \sigma_V(N_2) + \sigma_e(N_2) + 2K_c\left[\frac{5}{2} + \sigma_e(X)\right]$$

The specific heat at constant volume c_v may be obtained from the relationship (ref. 13)

$$c_p - c_v = -\frac{T}{\rho V}\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial V}{\partial p}\right)_T^{-1} = \frac{T}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_p^2\left(\frac{\partial \rho}{\partial p}\right)_T^{-1} \tag{23}$$

so that

$$c_p - c_v = Z\,\frac{{Z_T}^2}{Z_p}$$

where

$$Z_T \equiv R\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_p\right] = R\,\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$Z_p \equiv R\left[1 - \frac{p}{Z}\left(\frac{\partial Z}{\partial p}\right)_T\right] = -R\,\frac{p}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

and where the partial derivatives in equation (23) are obtained from equation (5).

The speed of sound is given by

$$a^2 = \frac{p}{\rho}\left(\frac{\partial \log_e p}{\partial \log_e \rho}\right)_S = \gamma RTZ \tag{24}$$

where

$$\gamma \equiv \left(\frac{\partial \log_e p}{\partial \log_e \rho}\right)_S = \frac{c_p}{c_v}\left(\frac{R}{Z_p}\right) \tag{25}$$

Equation (25) is easily obtained from the differentiation of equation (5), the definition of an isentropic process, and the identity

$$\frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_p = -\rho\left(\frac{\partial H}{\partial p}\right)_T$$

The quantities Z_T and Z_p can be obtained from equations (19) and (20a) to (20f) as

$$\frac{Z_T}{R} = 1 + \frac{1}{Z}\left[\left(1 + 2\alpha_3\right)\beta_1\phi_1\phi_4 + 2\alpha_1\beta_3\phi_3 + 2K_c\beta_2\phi_2\phi_4\right]$$

$$\frac{Z_p}{R} = 1 + \frac{1}{Z}\left[\left(1 + 2\alpha_3\right)\phi_1\phi_4 + 2\alpha_1\phi_3 + 2K_c\phi_2\phi_4\right]$$

As previously mentioned, the equilibrium flow solution of the equations governing the performance of plasma accelerators and MHD generators is usually accomplished with a computer by using a step-by-step integration procedure. The choice of what thermodynamic properties are required at each step in the integration is, of course, dependent upon the form in which the flow equations are written. If, for one-dimensional MHD accelerator (or generator) flow, these equations are written as suggested in reference 17, practically all the real gas effects are explicitly contained in the property β which is, in terms of the variables used herein,

$$\beta = \gamma Z \frac{Z_T}{c_p}$$

This quantity β is more than a convenient arrangement of terms and is, in fact, the real gas analog of the ideal gas term $\frac{c_p}{c_v} - 1$.

RESULTS AND DISCUSSION

The addition of a small amount of alkali-metal seed material into a nitrogen gas produces several rather distinct effects. Because of the low ionization potential and small partial pressure of the seed material, a greatly increased number density of electrons can be realized in a low-enthalpy temperature-pressure region. Shown in figure 13 is the resulting number density of electrons obtained by seeding with various amounts of cesium, and in figure 14 the cesium electron densities are compared with those obtained by sodium and potassium seeding. Much of the ionization of the alkali metals occurs in temperature-pressure regions where nitrogen is chemically inactive and, therefore, in these regions represents a significant energy sink. In addition, the increased number density of electrons resulting from this ionization causes a delay, until a higher temperature, in the ionization of the nitrogen atoms. Also, the addition of a seed material with a mass fraction $K_W K_C$ will cause a reduction in the mixture gas constant R (see eq. (6a)) and all quantities explicitly containing R. This effect, although important (especially for cesium with $K_W \approx 10$), is easily taken into account and for this reason it is more advantageous to study the seeding-induced variation in some thermodynamic properties ω by actually considering the property ω/R. If proper allowances are made for changes in the gas constant, it is found that the specific heats (and to a lesser degree, enthalpy, internal energy, and the parameter β) are significantly more sensitive to seeding than others such as entropy, speed of sound, Z_T/R, γ, and Z. $\left(Z_p/R\right.$ is almost completely insensitive.$\left.\right)$ The seeding-induced variations in c_p/R, H/R, β, Z_T/R, S/R, Z, and γ are shown in figures 15 to 21 for cesium seeding. In each case the quantity shown plotted is ω/ω_0 or $(\omega/R)/(\omega/R)_0 = (1 + K_W K_C)(\omega/\omega_0)$ where ω_0 is the corresponding property for unseeded nitrogen. Generally, as might be expected, the variations induced by sodium and potassium seeding are very similar but are less pronounced and occur at slightly higher temperatures. This effect is illustrated in figure 22 for the specific heat c_p/R at pressures of 0.003 and 0.3 atmosphere. Shown in figures 23 to 29 are plots of $\omega_o = c_p$, H, β, Z_T, S, Z, and γ. From figures 15 to 29 and values of K_w (see table I), values of ω may be obtained for various degrees of seeding.

As a further note of explanation it should be emphasized that in figures 15, 16, 18, and 19, the quantity plotted is $(1 + K_w K_c)\frac{\omega}{\omega_o}$ and that to obtain the actual value of ω/ω_o, the factor $(1 + K_w K_c)$ must be taken into account. For example (from fig. 15), at a pressure of 0.03 atmosphere and a value of $K_c = 0.05$, the quantity $\left[c_p/(c_p)_o\right](1 + K_w K_c)$ is approximately 1.8 for $T = 3500^o$ K while at $T = 7500^o$ K this same quantity is only 0.8. Since for cesium with $K_c = 0.05$ the quantity $(1 + K_w K_c) \approx 1.47$, the actual values of $c_p/(c_p)_o$ are 1.22 and 0.54.

As mentioned previously, the partition function analysis employed herein is similar to that used in references 2 and 3. There are, however, some significant differences. In reference 3, Ahtye and Peng assume that reactions $r = 1$ and $r = 3$ are independent and they use an approximate method of fairing to compute from one region of reaction to another. In addition, they assume a constant principal quantum number partition function cutoff of $n = 5$. In contrast, Drellishak, et al. (ref. 2) include: a variable cutoff (only up to $n = 32$, however), no assumptions of independence of reaction, lowering of the ionization potential, and a more exact model of the N_2 molecules. It may be seen that in comprehensiveness, for unseeded nitrogen, these two analyses bracket the analysis used herein. The data in table II are presented so that a comparison may be made of these analyses.

As mentioned in the section "Determination of Species Concentrations" the solution for α_r requires an iteration procedure involving $Q_e(i)$. Because of the form of $Q_e(i)$ this iteration procedure would normally be very time consuming. However, in connection with the discussion in appendix A, this iteration may be rapidly completed, for a fixed temperature and pressure, by computing $Q_e(i)_1$ and then simply correcting the value of $Q_e(i)$ at each iteration by computing $Q_e(i)_2$ (eq. (A4)).

It has been mentioned previously (for example, ref. 15) that a constant cutoff of $n = 5$ is usually considered to be sufficiently accurate for the computation of thermodynamic properties. As a check on this assumption and by using a computer program similar to that presented in appendix C, certain thermodynamic properties were computed by using a constant value of $n = 5$ (values for the species N were taken from ref. 15) and these properties were compared with those obtained by the more accurate variable cutoff method (appendix A). These comparisons are presented in table III for unseeded nitrogen and also for 5-percent cesium seeding ($n = 5$ was also used for the cesium atoms although a larger n would have been more appropriate). As may be seen, fairly large differences may occur. Inclusion of a reduced ionization potential would slightly reduce this effect but because of the present uncertainty in what the actual ionization potential reduction should be, it was not included in the calculations.

CONCLUDING REMARKS

Equations describing the thermodynamic properties of a high-enthalpy nitrogen, alkali-metal vapor mixture may be expressed in relatively simple form. This is true even if such non-ideal gas effects as electronic excitation and the associated variable quantum number partition function cutoff are included. The resulting expressions lend themselves well for use as a computer program subroutine (an outline of which is presented herein) for supplying thermodynamic data in connection with step-by-step integration procedures.

In certain high-temperature devices using nitrogen seeded with an alkali-metal vapor, it is usually assumed that because of a lack of data on nitrogen—alkali-metal mixtures and since the degree of seeding is small, the thermodynamic properties of this mixture are essentially those of nitrogen. It is found, however, that in certain temperature-pressure regions, 1/2- to 1-percent cesium seeding, for example, can change certain properties (such as the specific heats) by as much as 10 to 20 percent. In general, these effects become more pronounced at low pressures and/or high degrees of seeding. Although the largest effects are associated with cesium seeding, these effects become only slightly smaller for potassium and sodium seeding.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., February 28, 1967,
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APPENDIX A

ELECTRONIC EXCITATION PARTITION FUNCTIONS

There are several problems encountered in the evaluation of the electronic excitation partition function $Q_e(i)$ and its derivatives $\epsilon_e(i)$ and $\sigma_e(i)$. The first of these is that in references 18 to 20, particularly at high principal quantum numbers, many predicted energy levels have not been observed and are therefore not tabulated. For the alkali-metal atoms and also the nitrogen atom, failure to include these unobserved energy levels can generate, at high temperature, significant differences in $Q_e(i)$ and its derivatives. For the ions X^+ and N^+, however, this effect is not important at temperatures below at least 20 000° K. To estimate the missing energy levels for the alkali-metal atoms it was assumed that for high principal quantum numbers and even at relatively low principal quantum numbers but high azimuthal quantum numbers, an energy state θ_ν with principal quantum number m was hydrogen-like and could be, with reasonable accuracy, estimated by

$$\theta_\nu = \theta_2(X) - \frac{\theta_H}{m^2} \tag{A1}$$

where $\theta_H = 157\ 890^\circ$ K. For the nitrogen atom, missing energy levels have been estimated by Drellishak, et al. (ref. 8) and have been published (ref. 2) up to a principal quantum number of 32.

A survey of methods for treating the excitation partition function and determining the principal quantum number cutoff is presented in reference 16. Based on the theory of Lewis and Margenau (which was also used in ref. 8) the principal quantum number cutoff n is given by

$$n \approx 30(q + 1)^{1/2}\left[\frac{\left(\frac{T}{10^4}\right)}{\left(\frac{n_e}{10^{22}}\right)}\right]^{1/4} \tag{A2}$$

where $q = 0$ for an atom and $q = 1$ for an ion. The equation is made dimensionless for easy reference so that at $T = 10^4\ ^\circ K$ and $n_e = 10^{22}\ m^{-3}$, $n \approx 30(q + 1)^{1/2}$.

Equation (A2) is valid as written only for a mixture of neutrals and equal numbers of electrons and single ions. Shown in figure 30 are values of n for the temperature-pressure region considered and degrees of seeding of $K_c = 0.01$ (X = Cesium) and $K_c = 0$.

APPENDIX A

For the alkali and nitrogen atoms the evaluation of the electronic excitation partition function as written in equation (8b) requires, particularly at large values of n, a large amount of input data (for example, at $n = 20$, for cesium $N(n) = 199$) and a correspondingly long computational time. Because of the functional dependence of $Q_e(i)$ and n, the determination of n is accomplished with an iteration procedure (see the section "Determination of Species Concentrations") and it is extremely important that the time required to compute $Q_e(i)$ be reduced to a minimum. With this in mind it is advantageous to write

$$Q_e(i) = \sum_{\nu=1}^{N(n)} g_\nu e^{-\frac{\theta_\nu}{T}} = Q_e(i)_1 + Q_e(i)_2 \tag{A3}$$

where

$$Q_e(i)_1 \equiv \sum_{\nu=1}^{N(n_o)} g_\nu e^{-\frac{\theta_\nu}{T}}$$

and is a function of temperature only, and where

$$Q_e(i)_2 = \sum_{\nu=N(n_o)+1}^{N(n)} g_\nu e^{-\frac{\theta_\nu}{T}} = \sum_{m=n_o+1}^{n} \bar{a}(2m^2)e^{-\left(\frac{\theta_I - \frac{\theta_H}{m^2}}{T}\right)}$$

and is a function of both temperature and n. The quantity θ_I represents either $\theta_2(x)$ or $\theta_3(N)$ and $\bar{a}$ is the number of parent configurations ($\bar{a} = 1$ for the alkali-metal atoms and $\bar{a} = 9$ for the nitrogen atoms). The quantity $Q_e(i)_1$ is a summation over all energy states with a principal quantum number m such that $m \leqq n_o$ and $Q_e(i)_2$ is the contribution to $Q_e(i)$ resulting from a summation over the states where $n_o < m \leqq n$. The principal quantum number n_o is chosen so that all states with $m > n_o$ will be approximately hydrogen-like and also so that for a particular m the energy states for each azimuthal quantum number will differ by very small amounts of energy. The total contribution to $Q_e(i)_2$ for each principal quantum number greater than n_o is then approximately

$$2m^2 e^{-\frac{\theta_I - \frac{\theta_H}{m^2}}{T}}$$

where $2m^2$ is the sum of degeneracies for all azimuthal quantum numbers.

APPENDIX A

A simple expression may be obtained for $Q_e(i)_2$ if, in addition, n_o is chosen so that

$$\left(\frac{\theta_H}{n_o^2 T}\right)^2 << 1$$

and $\Delta\theta_m$ is defined so that

$$\Delta\theta_m \equiv \left(\theta_I - \frac{\theta_H}{m^2}\right) - \left(\theta_I - \frac{\theta_H}{n_s^2}\right) = \theta_H\left(\frac{1}{n_s^2} - \frac{1}{m^2}\right)$$

where n_s is some reference term $n_o < n_s < n$. The quantity $Q_e(i)_2$ may now be written as

$$Q_e(i)_2 = 2\bar{a}e^{-\frac{\theta_s}{T}} \sum_{m=n_o+1}^{n} m^2 e^{-\frac{\Delta\theta_m}{T}}$$

$$\theta_s \equiv \theta_I - \frac{\theta_H}{n_s^2}$$

Since

$$\left(\frac{\Delta\theta_m}{T}\right)^2 = \left[\theta_H\left(\frac{1}{n_s^2} - \frac{1}{m^2}\right)\right]^2 < \left(\frac{\theta_H}{n_o^2 T}\right)^2 << 1$$

$Q_e(i)_2$ may be written as

$$Q_e(i)_2 \approx 2\bar{a}e^{-\frac{\theta_s}{T}} \sum_{m=n_o+1}^{n} m^2\left(1 - \frac{\Delta\theta_m}{T}\right)$$

If the reference term n_s is chosen (thereby defining $\Delta\theta_m$) so that

$$\sum_{m=n_o+1}^{n} m^2\left(\frac{\Delta\theta_m}{T}\right) \equiv 0$$

and, if the definition of $\Delta\theta_m$ is recalled,

$$\sum_{m=n_o+1}^{n} m^2 \frac{\Delta\theta_m}{T} = \sum_{m=n_o+1}^{n} m^2 \frac{\theta_H}{T}\left(\frac{1}{n_s^2} - \frac{1}{m^2}\right) \equiv 0$$

Then n_s^2 becomes

$$n_s^2 = \frac{\sum\limits_{m=n_o+1}^{n} m^2}{n - n_o} = \frac{2\left(n^2 + nn_o + n^2\right) - 3\left(n + n_o\right) + 1}{6}$$

and $Q_e(i)_2$ becomes

$$Q_e(i)_2 = 2\bar{a}e^{-\frac{\theta_s}{T}}\left(n - n_o\right)n_s^2 \tag{A4}$$

Equation (A4) provides a simple and accurate manner of estimating the contribution to $Q_e(i)$ caused by higher quantum numbers. For both the nitrogen and alkali-metal atoms, n_o was taken as 15 although for the higher temperatures considered, an n_o less than 15 could have been used with sufficient accuracy for the alkali metals. Shown in table IV are the values of g_ν and θ_ν used to evaluate $Q_e(i)_1$. In many cases approximately equal energy states have been combined to reduce the amount of input data. The data are based on all energy levels with a principal quantum number less than or equal to 15. For the ions it is sufficiently accurate to take $Q_e(i)_2 \equiv 0$.

The quantities $\epsilon_e(i)$ and $\sigma_e(i)$ can be obtained in a manner similar to that used to obtain equations (A3) and (A4) and they are

$$\epsilon_e(i) = \frac{\sum\limits_{\nu=1}^{N(n_o)} g_\nu\left(\frac{\theta_\nu}{T}\right)e^{-\frac{\theta_\nu}{T}} + \left(\frac{\theta_s}{T}\right)Q_e(i)_2}{Q_e(i)} \tag{A5}$$

and

$$\sigma_e(i) = \frac{\sum\limits_{\nu=1}^{N(n_o)} g_\nu\left(\frac{\theta_\nu}{T}\right)^2 e^{-\frac{\theta_\nu}{T}} + \left(\frac{\theta_s}{T}\right)^2 Q_e(i)_2}{Q_e(i)} - \epsilon_e^2(i) \tag{A6}$$

APPENDIX A

The excitation of species N_2 becomes significant only in temperature-pressure regions where $n_{N_2} << n_t$ and therefore over the whole temperature-pressure region, it was sufficiently accurate to assume that

$$Q_e(N_2) = 1$$

$$\epsilon_e(N_2) = \sigma_e(N_2) = 0$$

By chain rule differentiation it is easily established that for a general function $f(T,n)$ of temperature and principal quantum number cutoff n,

$$\left(\frac{\partial f}{\partial T}\right)_{p \text{ or } \rho} = \left(\frac{\partial f}{\partial T}\right)_n + \frac{n}{4T}\left(\frac{\partial f}{\partial n}\right)_T \left[1 - \left(\frac{\partial \log_e n_e}{\partial \log_e T}\right)_{p \text{ or } \rho}\right] \qquad \text{(A7)}$$

where $n = \text{Constant}\ (T/n_e)^{1/4}$ and is treated as a continuous, rather than discrete, variable. For the three functions $Q_e(i)$, $\epsilon_e(i)$, and $\sigma_e(i)$ which are of the form $f(T,n)$, the second term in equation (A7) is generally much smaller than the first. Therefore, at a given temperature and n

$$\left(\frac{\partial f(T,n)}{\partial T}\right)_{p \text{ or } \rho} \approx \left(\frac{\partial f(T,n)}{\partial T}\right)_n$$

APPENDIX B

SIMPLIFICATION OF THE NUMBER DENSITY EQUATIONS

The number density equations written in terms of α_r are given by equations (14a) to (14c). The equations in this form contain none of the usual assumptions of independence of reaction. (See, for example, ref. 3.) By combining equations (14a) and (14c), it is possible to obtain

$$\alpha_3 = \frac{1}{1 + \sqrt{\frac{K_1(N)}{K_3(N)}\left(\frac{1 - \alpha_1}{2\alpha_1}\right)\left\{\left[1 - \alpha_3\left(1 - \alpha_1\right)\right]\frac{K_c}{\alpha_3} + 1\right\}}} \tag{B1}$$

and in a similar manner equations (14b) and (14c) together produce

$$\alpha_3 = \frac{1}{1 + \frac{K_2(X)}{K_3(N)}\left(\frac{1 - \alpha_2}{\alpha_2}\right)} \tag{B2}$$

Equations (B1) and (B2), respectively, provide the useful inequalities

$$\alpha_3\left(1 - \alpha_1\right) < \sqrt{2\frac{K_3(N)}{K_1(N)}\alpha_1\left(1 - \alpha_1\right)} < \frac{\sqrt{2}}{2}\sqrt{\frac{K_3(N)}{K_1(N)}} \tag{B3}$$

and

$$\alpha_3\left(1 - \alpha_2\right) < \frac{K_3(N)}{K_2(X)} \tag{B4}$$

In addition, an inspection of equations (14a) to (14c) reveals that for $K_r(Y) >> P$, the corresponding reaction r is essentially complete $\left(\alpha_r \approx 1\right)$. Therefore from equations (B3), (B4), and figure 11, it follows that in the regions of reaction $\left(0 < \alpha_r < 1\right)$,

$$\alpha_3\left(1 - \alpha_2\right) << 1$$

$$\alpha_3\left(1 - \alpha_1\right) << 1$$

which is true only, if for $0 < \alpha_1 < 1$ and $0 < \alpha_2 < 1$, then $\alpha_3 \approx 0$ or, if for $0 < \alpha_3 < 1$ then $\alpha_1 \approx 1$ and $\alpha_2 \approx 1$.

APPENDIX B

Although it may be expected that reaction 2 will become significant at lower temperatures than reaction 1, this is not necessarily so. By using conditions (B5), equations (14a) and (14b) may be combined to provide

$$\frac{1 - \alpha_1}{\alpha_1^2} = \frac{2K_2(X)}{K_c K_1(N)} \frac{1 - \alpha_2}{\alpha_2^2} \tag{B5}$$

This relation in connection with figure 11 illustrates that, particularly at larger values of K_c, reaction 1 may become significant in regions where reaction 2 is not essentially complete. (See fig. 1.)

Based on this discussion, equations (15) to (17) were obtained from the following equations:

$$\frac{\alpha_1^2}{1 - \alpha_1} = \frac{K_1(N)}{4P}\left[1 + \alpha_1 + 2K_c\left(1 + \alpha_2\right)\right] \tag{B6}$$

$$\frac{\alpha_2^2}{1 - \alpha_2} = \frac{K_2(X)}{2K_c P}\left[1 + \alpha_1 + 2K_c\left(1 + \alpha_2\right)\right] \tag{B7}$$

$$\frac{\alpha_3\left(\alpha_3 + K_c\right)}{1 - \alpha_3} = \frac{K_3(N)}{P}\left(1 + \alpha_3 + 2K_c\right) \tag{B8}$$

The quantities ϕ_1 to ϕ_5 are given by

$$\phi_1 \equiv \frac{\alpha_1\left(1 - \alpha_1\right)}{2 - \alpha_1}$$

$$\phi_2 \equiv \frac{\alpha_2\left(1 - \alpha_2\right)}{2 - \alpha_2}$$

$$\phi_3 \equiv \frac{\alpha_3\left(\alpha_3 + K_c\right)\left(1 - \alpha_3\right)\left(1 + \alpha_3 + 2K_c\right)}{\left(-K_c\alpha_3^2 + 4K_c\alpha_3 + 2\alpha_3 + K_c + 2K_c^2\right)}$$

$$\phi_4 \equiv \frac{\left[1 + \alpha_1 + 2K_c\left(1 + \alpha_2\right)\right]\left(2 - \alpha_1\right)\left(2 - \alpha_2\right)}{2\left[2 - \alpha_2 + 2K_c\left(2 - \alpha_1\right)\right]}$$

$$\phi_5 \equiv \frac{\alpha_1\alpha_2\left(1 - \alpha_1\right)\left(1 - \alpha_2\right)}{2\left[2 - \alpha_2 + 2K_c\left(2 - \alpha_1\right)\right]}$$

APPENDIX C

COMPUTER PROGRAM OUTLINE

As mentioned in the text, many high-enthalpy gas flow problems require, for a solution, a high-speed computer program using the thermodynamic properties of the gas in connection with a step-by-step integration procedure. This outline is presented in the hope that it might be useful either as a subroutine to supply all necessary thermodynamic variables at each step in the integration or for preparing tables of thermodynamic properties.

(1) Read in fundamental and gas dependent constants, including π, k, h, m_n, m_e, p_o, θ_{rot}, θ_v, $\theta_r(Y)$, θ_H, and K_w.

(2) Read in excitation constants g_ν and θ_ν for $\nu = 1$ to $\nu = N(n_o)$ for each species. (See table IV for values of g_ν and θ_ν.)

(3) Enter subroutine with values of K_c, T, and $P\left(= \frac{p}{p_o}\right)$.

(4) Compute $\sum_{\nu=1}^{N(n_o)} g_\nu \left(\frac{\theta_\nu}{T}\right)^b e^{-\frac{\theta_\nu}{T}}$ (b = 0, 1, 2) for each species.

(5) Start the iteration on n by choosing an initial $n = n_1$ $\left(n_1 = 20\right)$ and computing $Q_e(i)$ from equation (A3), and $K_r(Y)$. (See section "Equilibrium Constants.")

(6) Start iteration on Δ by choosing $\Delta = \Delta_1$ $\left(\Delta_1 = 2K_c\right)$ and computing α_1 (eq. (15)) and α_2 (eq. (16)).

(7) Compute $\Delta\left(= 2K_c \frac{1 + \alpha_2}{1 + \alpha_1}\right)$. If $\Delta = \Delta_1$, go to step 8; if $\Delta \neq \Delta_1$, set $\Delta_1 = \Delta$ and go to step 6.

(8) Compute α_3 (eq. (17)), Z (eq. (19)), and n_e (eq. (18)).

(9) Compute n (eq. (A2)). If $n = n_1$, go to step 10; if $n \neq n_1$ set $n_1 = n$ and go to step 5.

(10) With the correct values of α_r and n, compute $\epsilon_e(i)$ (from eq. (A5)), $\sigma_e(i)$ (from eq. (A6)), ϵ_v, σ_v (see section "Partition Functions"), ϵ_{rot}, and σ_{rot}.

(11) Compute R (eq. (6a)), $\beta_{1,2,3}$ (eqs. (12a), (12b), and (12c)), $\mu_{1,2,3}$ (eqs. (13a), (13b), and (13c)), $\left(\frac{\partial \alpha_r}{\partial T}\right)_p$ (eqs. (20a), (20c), and (20e)), $\left(\frac{\partial \alpha_r}{\partial p}\right)_T$ (eqs. (20b), (20d), and (20f)), β_o, and μ_o (see definition).

(12) Compute any of the desired properties from among the following: ρ (eq. (5)); n_i (eq. (18)); H, E, and S (see section "Internal Energy, Enthalpy, and Entropy"); c_p, Z_T, Z_p, γ, a, and β (see section "Specific Heats and Speed of Sound").

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TABLE I.- CHARACTERISTIC TEMPERATURES FOR DISSOCIATION AND IONIZATION

$\left[\theta_{rot} = 5.784^{\circ}\ K;\quad \theta_{V} = 3395^{\circ}\ K\right]$

Gas, Y	K_W	Characteristic temperature of –		
		Dissociation, °K	First ionization, °K	Second ionization, °K
Nitrogen, N	-----	113 220	168 730	343 560
Lithium, Li	0.4954	11 950	62 550	877 550
Sodium, Na	1.641	8 470	59 630	548 790
Potassium, K	2.791	5 965	50 350	369 150
Rubidium, Rb	6.102	5 690	48 460	319 130
Cesium, Cs	9.488	5 220	45 180	291 280

TABLE II.- COMPARISON OF PRESENT RESULTS WITH REFERENCE RESULTS

$T, ^{\circ}K$	Z			H, J/kg			c_p, J/kg-°K		
	Present paper	Reference 2	Reference 3	Present paper	Reference 2	Reference 3	Present paper	Reference 2	Reference 3
P = 0.01 atmosphere									
2 000	1.000	1.000	1.000	0.2303×10^7	0.2314×10^7	0.2302×10^7	1.273×10^3	1.281×10^3	1.273×10^3
4 000	1.009	1.009	1.009	.5220	.5257	.5222	2.461	2.507	2.459
6 000	1.774	1.765	1.773	3.494	3.468	3.489	20.08	22.31	19.90
8 000	2.045	2.045	2.045	4.940	4.939	4.932	6.158	6.194	5.741
10 000	2.481	2.484	2.482	7.885	7.864	7.838	27.43	27.08	26.92
12 000	3.530	3.546	3.554	14.52	14.52	14.49	26.33	26.66	26.83
14 000	3.904	3.927	3.939	17.30	17.33	17.34	6.509	6.571	6.583
16 000	3.958	3.982	3.992	18.23	18.29	18.28	3.711	4.123	3.670
P = 1.0 atmosphere									
2 000	1.000	1.000	1.000	0.2303×10^7	0.2314×10^7	0.2302×10^7	1.273×10^3	1.281×10^3	1.273×10^3
4 000	1.001	1.001	1.001	.4938	.4981	.4937	1.432	1.457	1.433
6 000	1.121	1.118	1.121	1.183	1.180	1.182	8.364	8.162	8.346
8 000	1.839	1.830	1.839	4.104	4.076	4.092	11.30	11.63	10.69
10 000	2.040	2.040	2.040	5.367	5.369	5.343	5.494	5.483	4.524
12 000	2.243	2.246	2.244	7.005	7.027	6.953	12.18	12.18	11.62
14 000	2.727	2.735	2.735	10.40	10.47	10.28	21.59	21.72	21.28
16 000	3.353	3.352	3.385	14.74	14.82	14.67	19.20	19.00	19.71
18 000	3.723	3.711	3.778	17.59	17.62	17.63	9.866	9.626	10.21
20 000	3.861	3.849	3.923	19.04	19.10	19.14	5.512	5.847	5.518

TABLE III.- COMPARISON OF DATA BASED ON BOTH A FIXED AND A VARIABLE PRINCIPAL QUANTUM NUMBER CUTOFF

(a) Unseeded

T, ^{o}K	n_e, m^{-3}		Z		H, J/kg		c_p, J/kg-^{o}K	
	n = 5	Variable n	n = 5	Variable n	n = 5	Variable n	n = 5	Variable n
P = 0.01 atmosphere								
2 000	-------------	-------------	1.000	1.000	0.2303×10^{7}	0.2303×10^{7}	1.273×10^{3}	1.273×10^{3}
4 000	-------------	-------------	1.009	1.009	.5220	.5220	2.461	2.461
6 000	5.276×10^{18}	5.276×10^{18}	1.774	1.774	3.494	3.494	20.08	20.08
8 000	$.2099 \times 10^{21}$	$.2099 \times 10^{21}$	2.045	2.045	4.936	4.940	6.061	6.158
10 000	1.427	1.423	2.483	2.481	7.841	7.885	26.94	27.43
12 000	2.674	2.651	3.554	3.530	14.49	14.52	26.82	26.33
14 000	2.581	2.557	3.939	3.904	17.34	17.30	6.585	6.509
16 000	2.287	2.269	3.989	3.958	18.27	18.23	3.686	3.711
P = 1.0 atmosphere								
2 000	-------------	-------------	1.000	1.000	0.2303×10^{7}	0.2303×10^{7}	1.273×10^{3}	1.273×10^{3}
4 000	-------------	-------------	1.001	1.001	.4938	.4938	1.432	1.432
6 000	-------------	-------------	1.121	1.121	1.183	1.183	8.364	8.364
8 000	0.1953×10^{22}	0.1953×10^{22}	1.839	1.839	4.103	4.104	11.28	11.30
10 000	1.772	1.771	2.040	2.040	5.357	5.367	5.333	5.494
12 000	6.671	6.652	2.244	2.243	6.955	7.005	11.71	12.18
14 000	14.09	13.97	2.735	2.727	10.29	10.40	21.31	21.59
16 000	18.76	18.51	3.384	3.353	14.68	14.74	19.69	19.20
18 000	19.18	18.87	3.776	3.723	17.62	17.59	10.20	9.866
20 000	17.97	17.69	3.918	3.861	19.12	19.04	5.585	5.512

(b) 5-percent seeded

T, ^{o}K	n_e, m^{-3}		Z		H, J/kg		c_p, J/kg-^{o}K	
	n = 5	Variable n	n = 5	Variable n	n = 5	Variable n	n = 5	Variable n
P = 0.01 atmosphere								
2 000	0.1054×10^{20}	0.1054×10^{20}	1.100	1.100	0.1666×10^{7}	0.1666×10^{7}	0.9342×10^{3}	0.9359×10^{3}
4 000	13.05	12.55	1.195	1.191	.4706	.4705	2.259	2.232
6 000	6.144	5.982	1.989	1.986	2.556	2.555	13.01	13.02
8 000	4.966	4.896	2.218	2.216	3.419	3.420	3.568	3.605
10 000	15.37	15.32	2.656	2.654	5.408	5.436	18.98	19.29
12 000	26.93	26.71	3.752	3.728	10.03	10.05	18.49	18.15
14 000	25.83	25.60	4.139	4.104	11.99	11.97	4.575	4.524
16 000	22.88	22.70	4.189	4.157	12.64	12.61	2.608	2.625
P = 1.0 atmosphere								
2 000	0.0106×10^{22}	0.0106×10^{22}	1.100	1.100	0.1663×10^{7}	0.1663×10^{7}	0.9161×10^{3}	0.9172×10^{3}
4 000	3.129	3.020	1.120	1.119	.3774	.3801	1.373	1.407
6 000	8.015	7.252	1.317	1.307	.9606	.9576	6.315	6.273
8 000	4.442	4.144	2.046	2.039	2.968	2.964	7.166	7.190
10 000	4.038	3.889	2.214	2.209	3.721	3.722	3.277	3.341
12 000	7.889	7.825	2.410	2.407	4.797	4.825	8.240	8.524
14 000	14.67	14.55	2.916	2.907	7.138	7.205	14.95	15.14
16 000	18.96	18.72	3.580	3.547	10.19	10.23	13.64	13.31
18 000	19.23	18.94	3.975	3.922	12.23	12.20	7.069	6.842
20 000	17.98	17.72	4.118	4.060	13.27	13.21	3.926	3.878

TABLE IV.- CHARACTERISTIC TEMPERATURES FOR ELECTRONIC EXCITATION

(a) Atoms

Index	Nitrogen, N		Cesium, Cs		Potassium, K		Sodium, Na	
ν	g_ν	θ_ν	g_ν	θ_ν	g_ν	θ_ν	g_ν	θ_ν
1	4	0	2	0	2	0	2	0
2	10	27 662	6	16 614	6	18 739	6	24 414
3	6	41 495	10	20 946	12	30 862	2	37 035
4	12	119 910	2	26 670	6	35 559	10	41 974
5	6	124 010	6	31 491	12	39 433	6	43 554
6	12	126 810	10	32 538	14	40 471	2	47 770
7	22	136 290	16	35 182	6	41 732	30	49 877
8	12	137 420	16	37 335	44	43 885	2	52 333
9	14	139 290	34	38 830	6	44 708	48	53 356
10	6	140 710	16	39 941	66	45 916	66	55 233
11	10	143 390	62	40 837	18	46 734	8	55 607
12	22	149 210	90	41 909	98	47 237	98	56 434
13	86	150 910	120	42 689	270	48 200	288	57 464
14	22	153 650	326	43 445	192	48 790	192	58 063
15	32	154 990	242	43 793	242	49 046	242	58 325
16	104	158 420	288	44 036	288	49 263	288	58 536
17	54	160 380	338	44 219	338	49 430	338	58 700
18	40	162 100	392	44 358	392	49 561	392	58 830
19	416	162 670	450	44 470	450	49 666	450	58 935
20	608	164 590						
21	966	165 700						
22	2552	166 710						
23	3366	167 200						
24	6570	167 560						

(b) Ions

Index	Nitrogen, N^+		Cesium, Cs^+		Potassium, K^+		Sodium, Na^+	
ν	g_ν	θ_ν	g_ν	θ_ν	g_ν	θ_ν	g_ν	θ_ν
1	1	0	1	0	1	0	1	0
2	3	70.65	10	152 560	9	234 310	9	381 770
3	5	188.9	14	155 160	12	237 200	3	386 700
4	5	22 036	3	159 630	3	239 510	3	421 890
5	1	47 030	14	161 770	16	244 650	15	428 140
6	5	67 865	7	163 620	12	247 190	9	430 480
7	15	132 720	10	172 710	3	263 600	4	432 330
8	9	157 140	4	176 600	12	268 360	1	444 400
9	5	207 460	3	177 890	8	270 380	25	459 120
10	12	214 460	3	182 040	12	272 920	23	477 320
11	3	223 200	12	185 150	1	280 240	24	479 020
12	3	236 840	15	187 410	8	306 080	15	508 620
13	21	240 210	1	191 580	13	309 940		
14	9	245 510	3	203 670	8	311 740		
15	5	250 660	9	206 480	16	312 710		
16	1	256 500	12	214 390	12	316 050		
17	41	269 020	27	220 490	8	320 920		

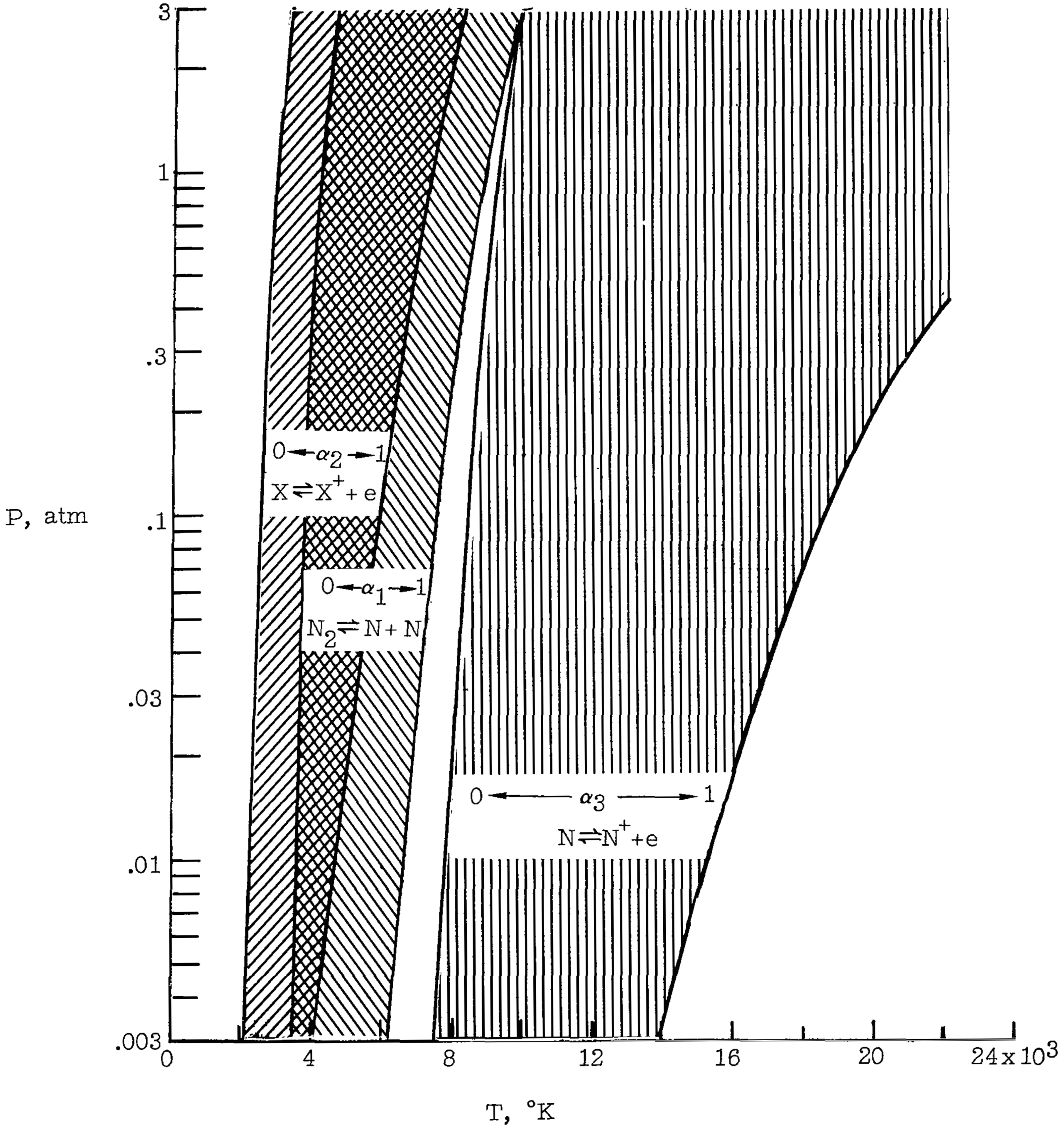

Figure 1.- The temperature-pressure regions of reaction ($0 < \alpha_r < 1$) for 1-percent cesium seeding.

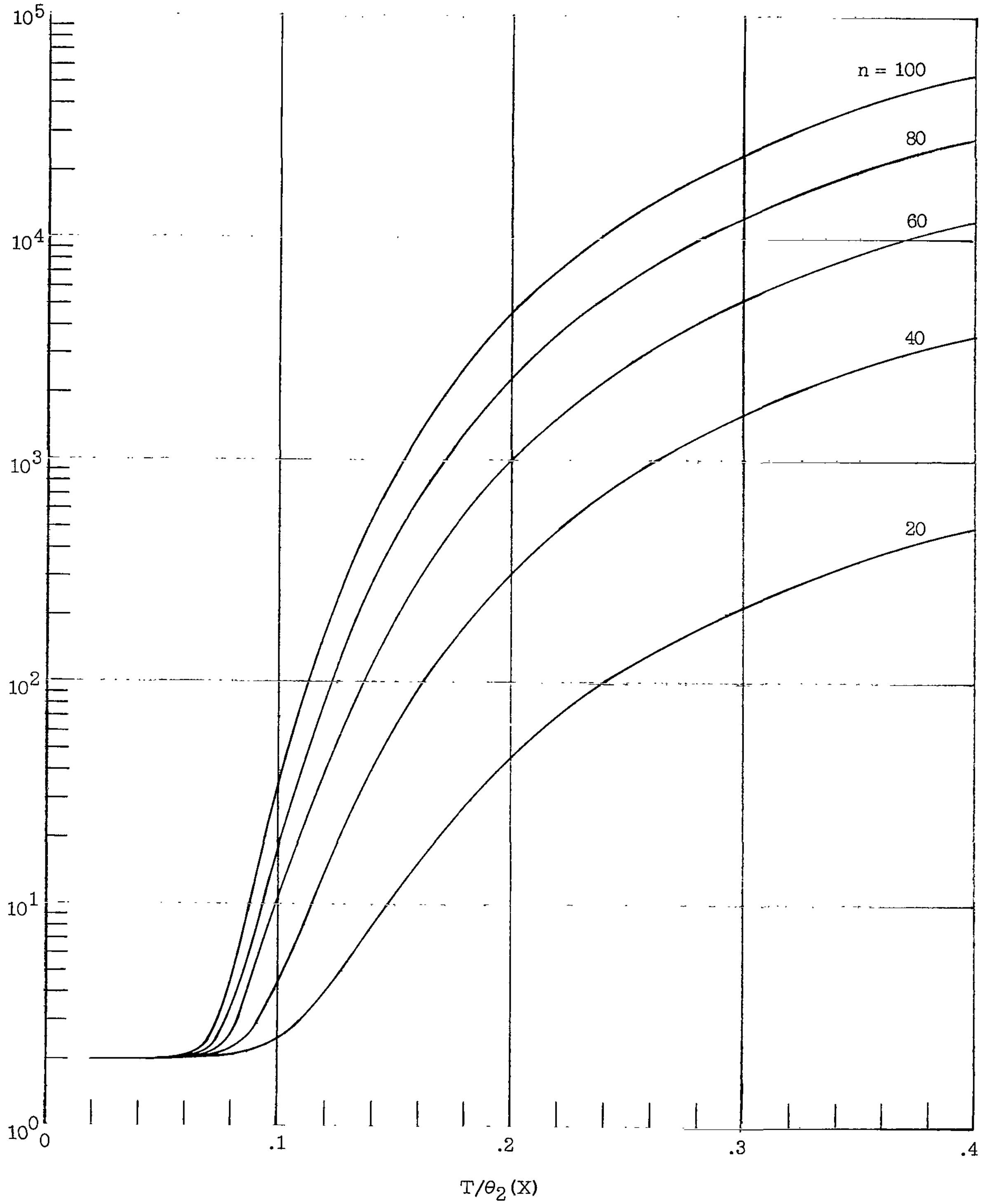

Figure 2.- The electronic excitation partition function $Q_e(i)$ for the alkali-metal atoms.

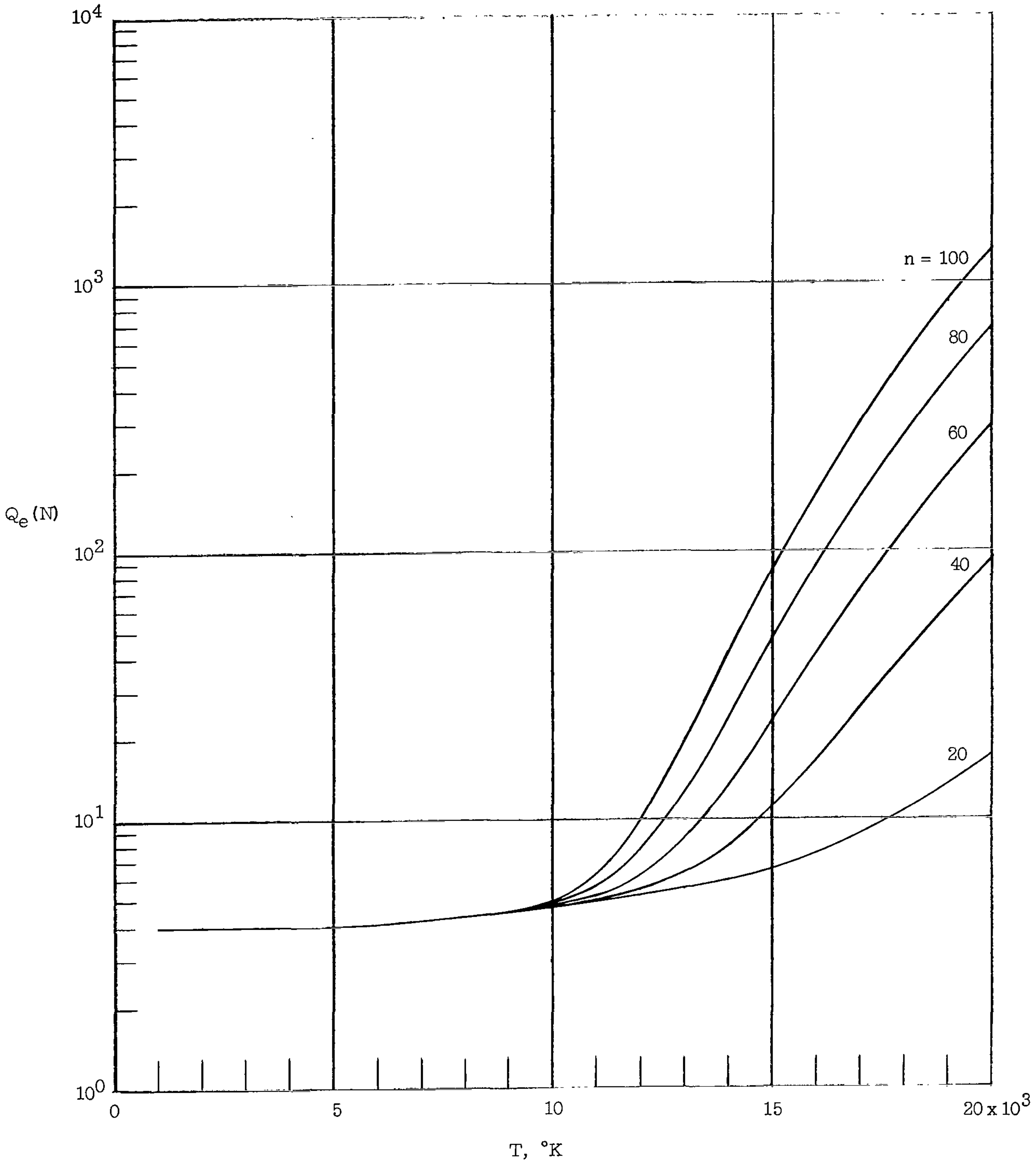

Figure 3.- The electronic excitation partition function $Q_e(i)$ for the nitrogen atoms.

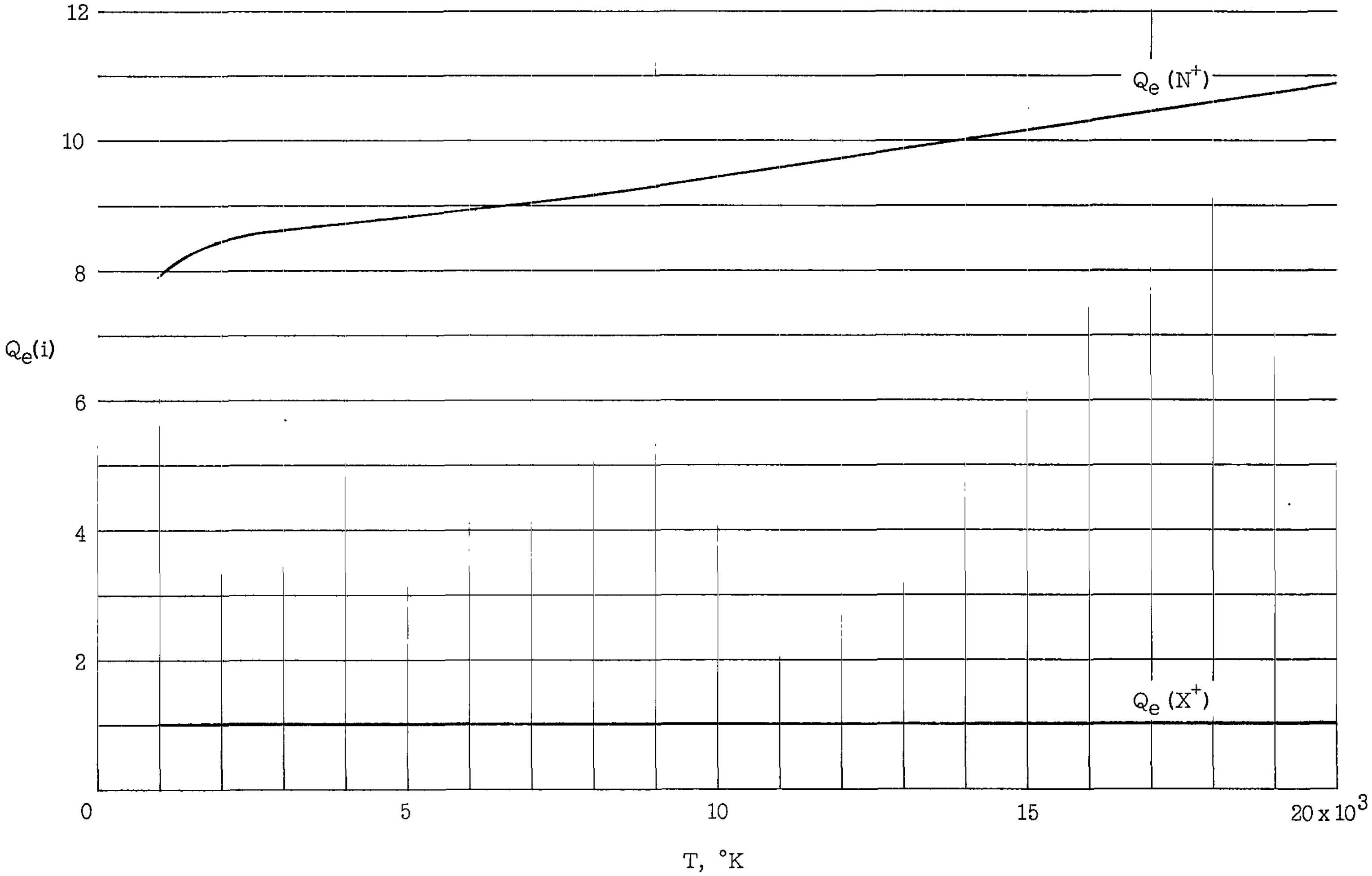

Figure 4.- The electronic excitation partition function $Q_e(i)$ for the nitrogen and alkali-metal ions.

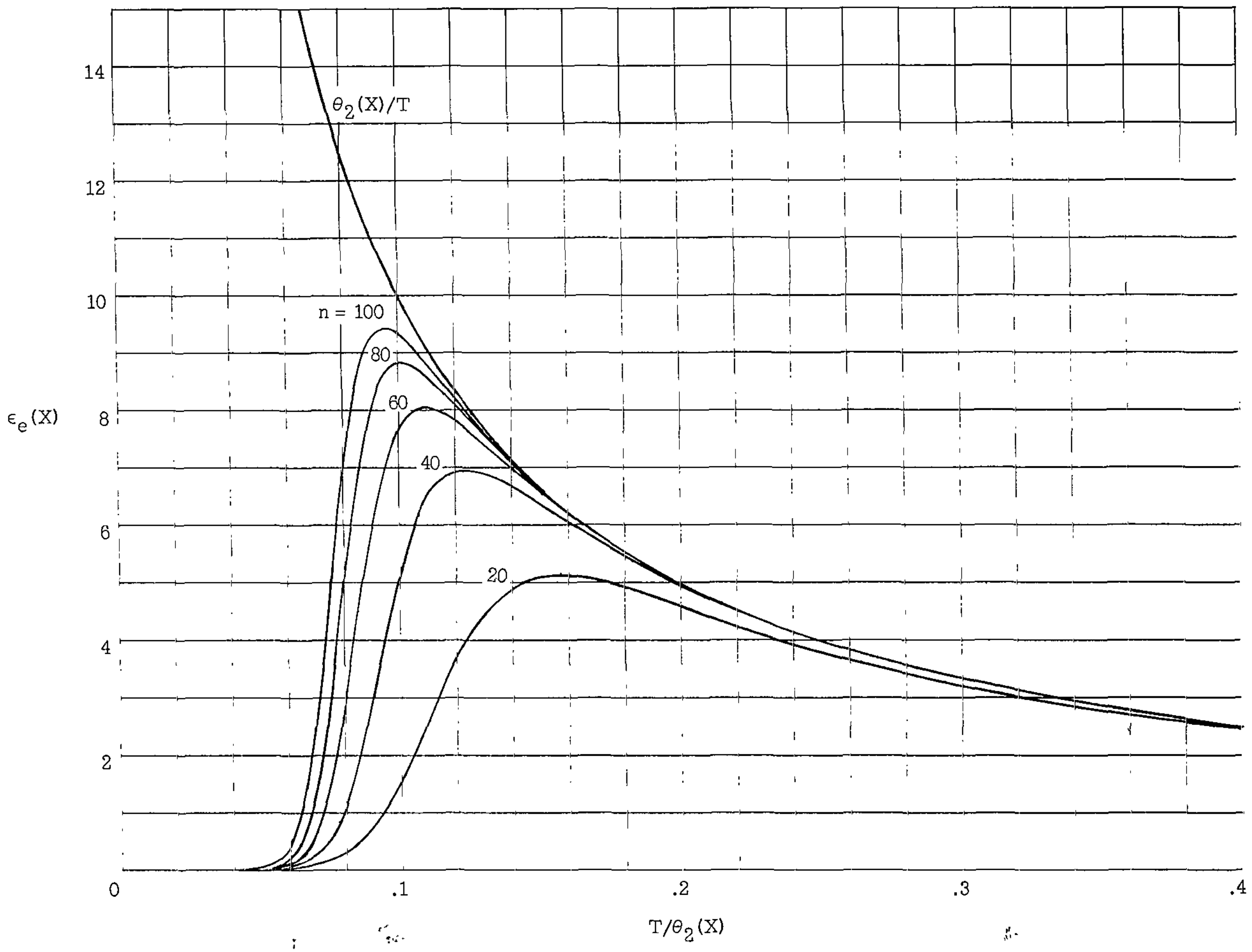

Figure 5.- The electronic excitation partition function derivative $\varepsilon_e(i)$ for the alkali-metal atoms.

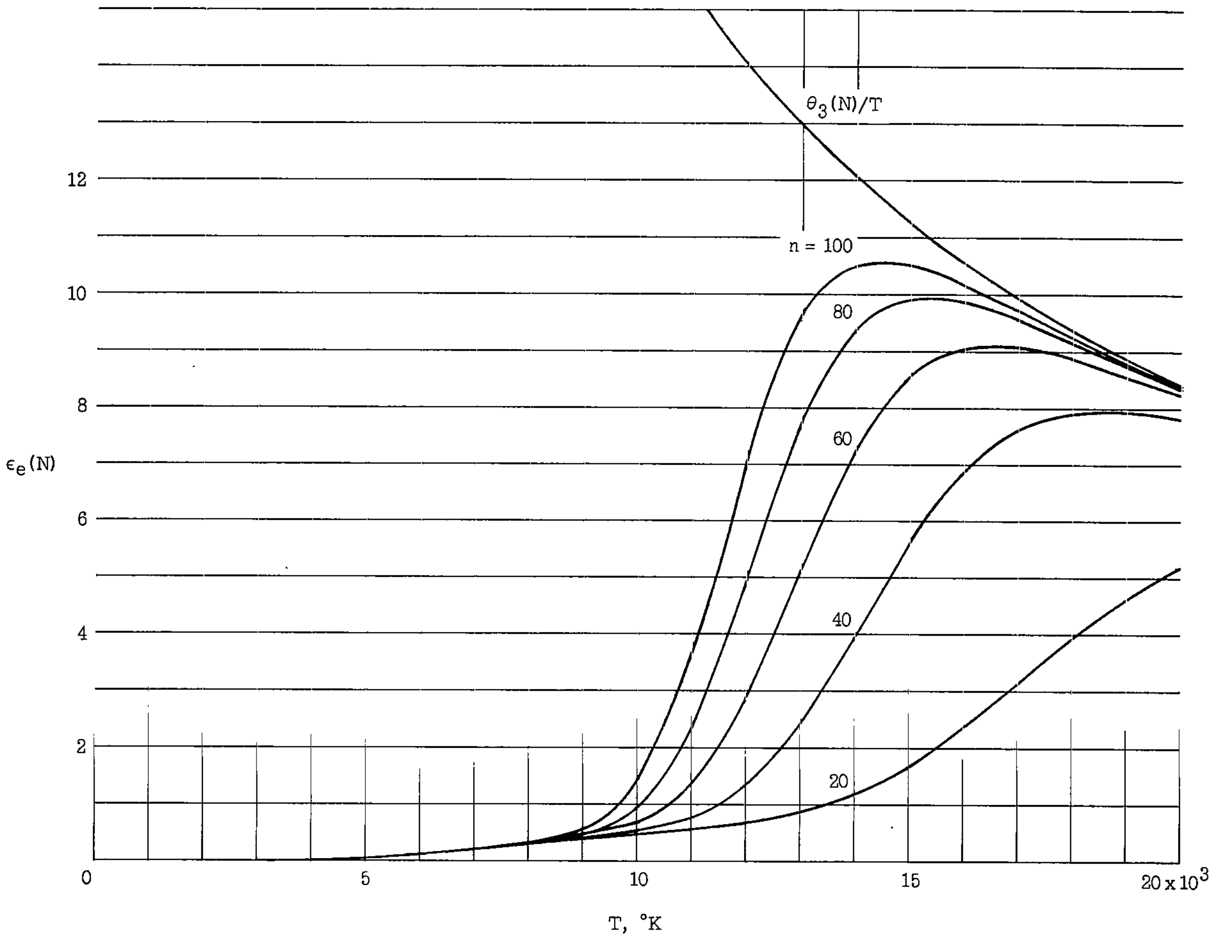

Figure 6.- The electronic excitation partition function derivative $\varepsilon_e(i)$ for the nitrogen atoms.

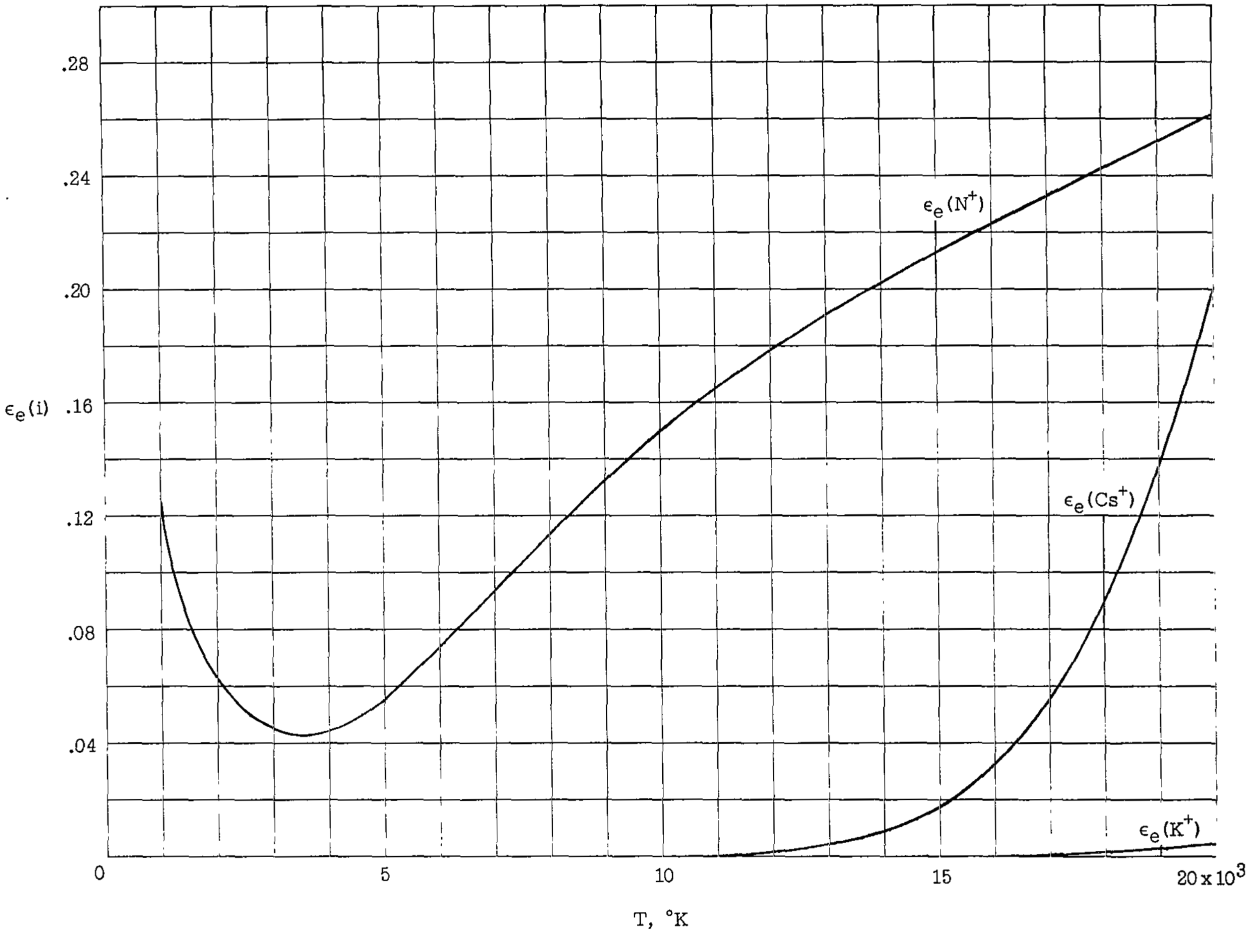

Figure 7.- The electronic excitation partition function derivative $\varepsilon_e(i)$ for the nitrogen and alkali-metal ions.

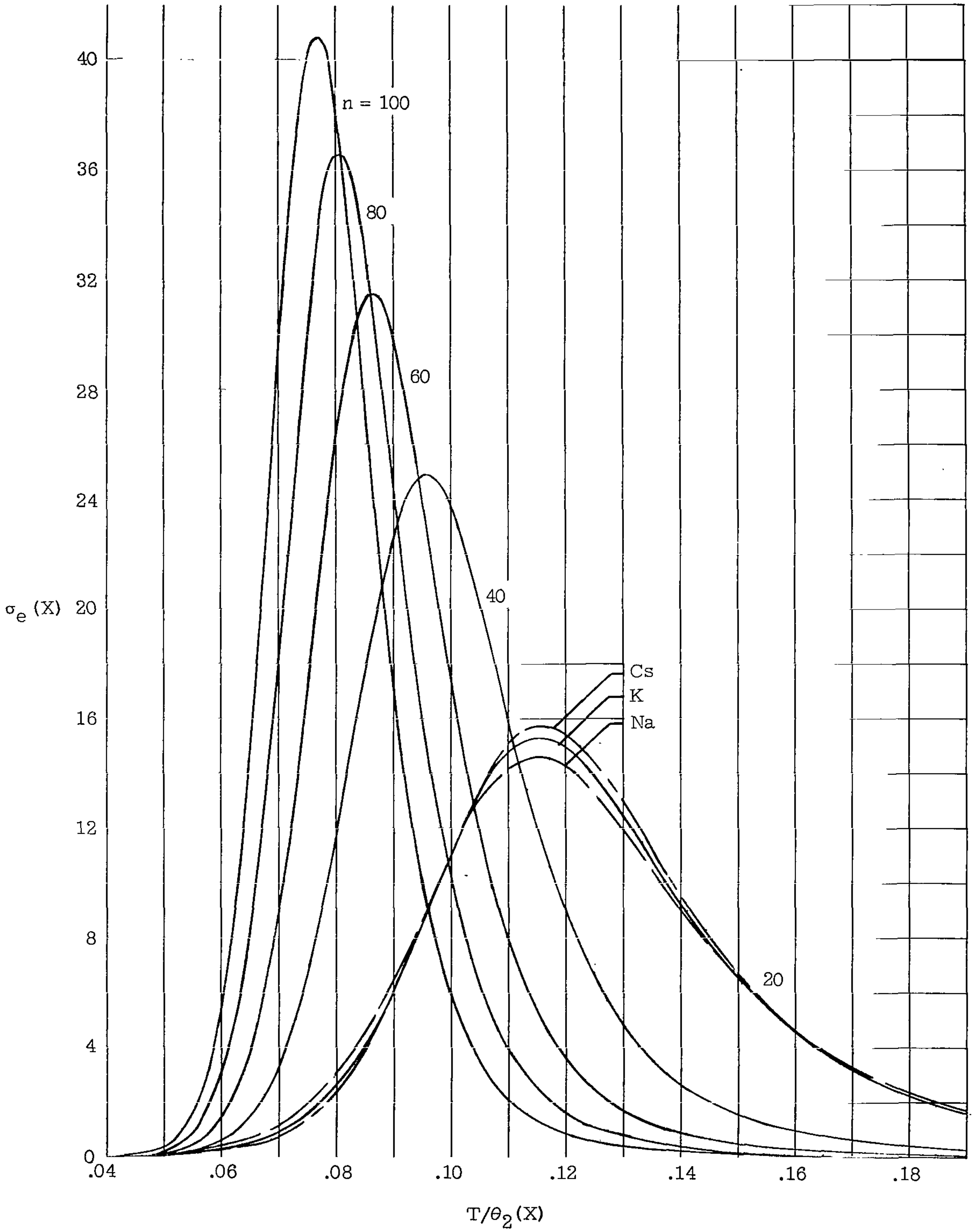

Figure 8.- The electronic excitation partition function derivative $\sigma_e(i)$ for the alkali-metal atoms.

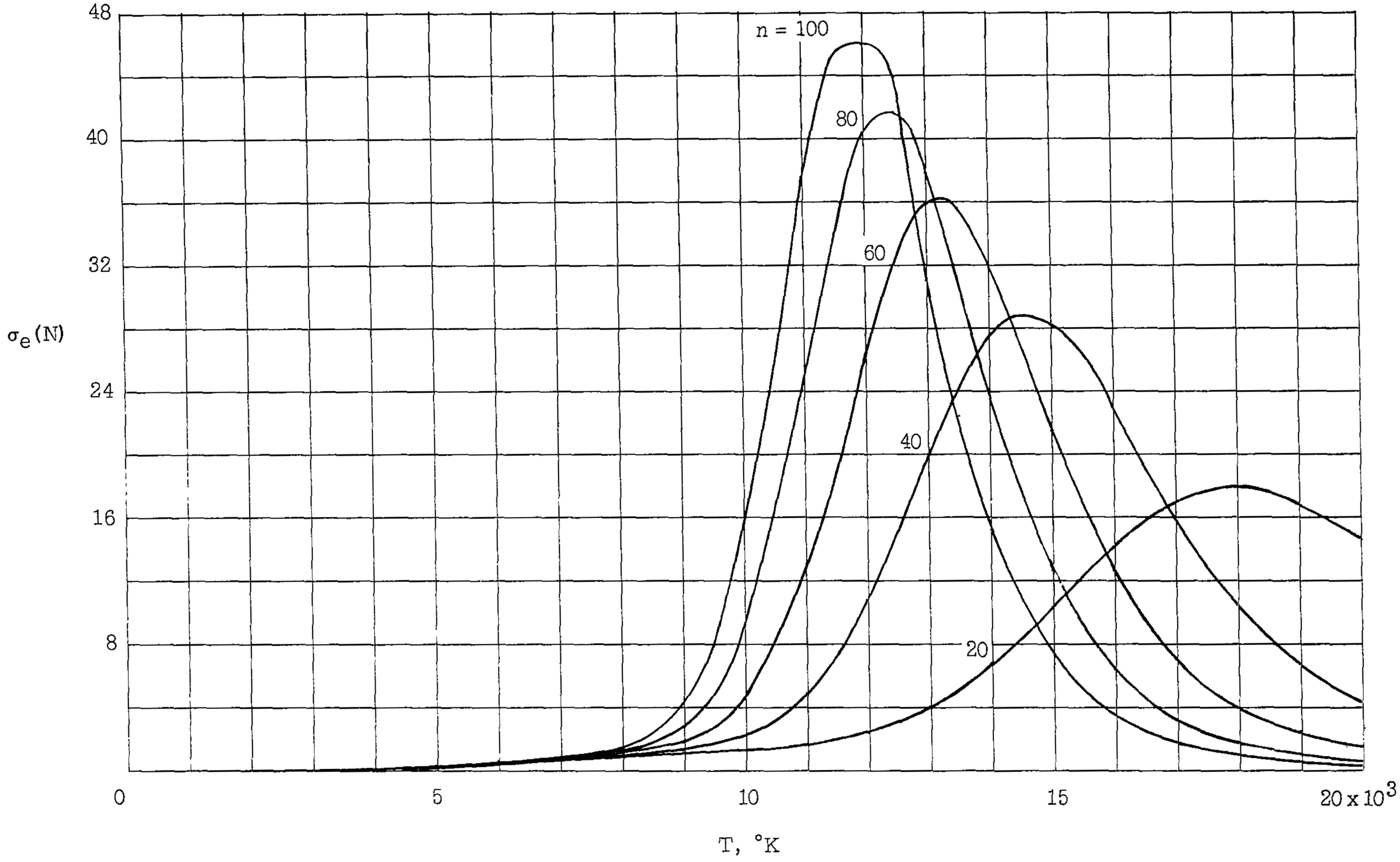

Figure 9.- The electronic excitation partition function derivative $\sigma_e(i)$ for the nitrogen atoms.

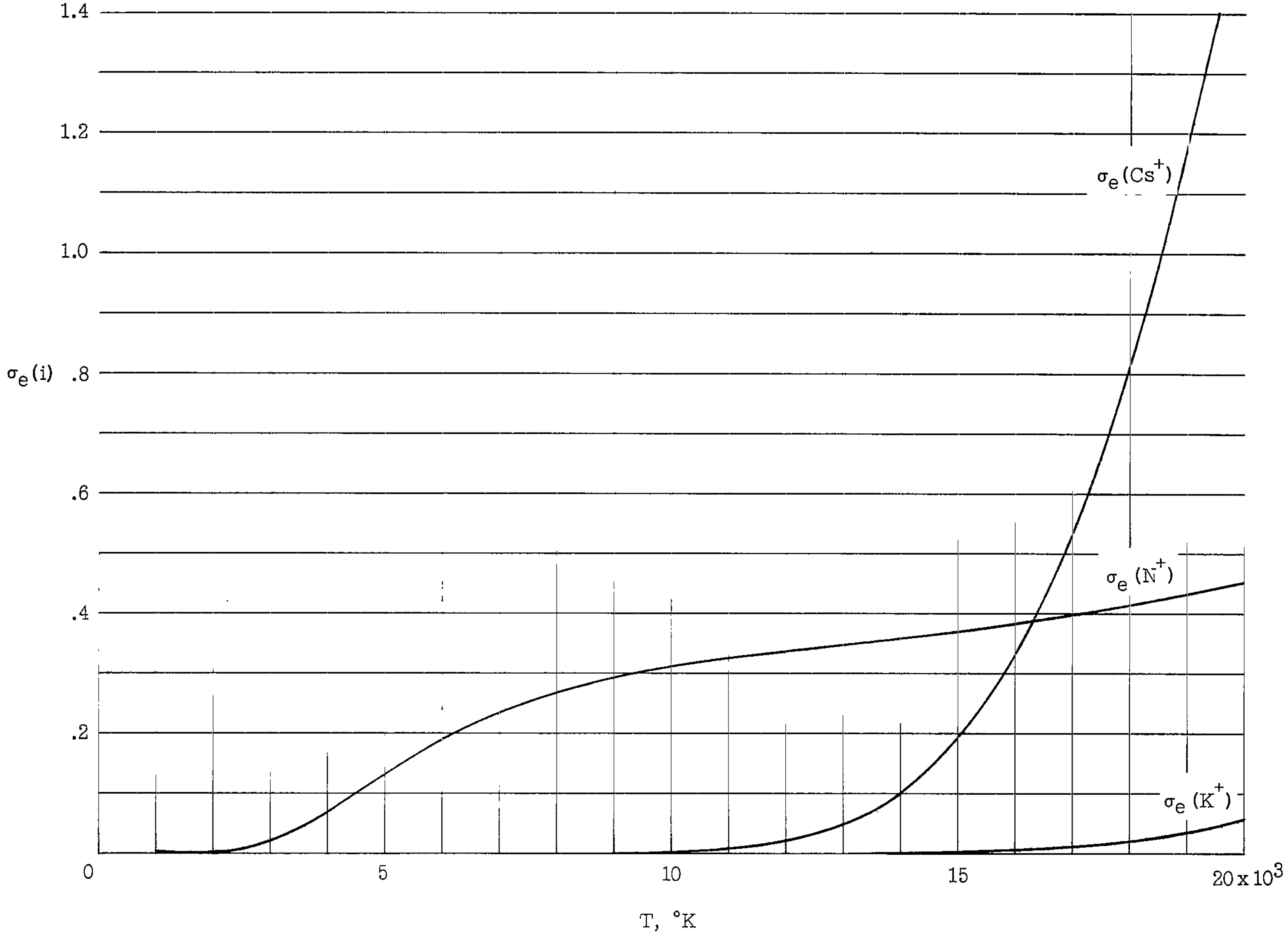

Figure 10.- The electronic excitation partition function derivative $\sigma_e(i)$ for the nitrogen and alkali-metal ions.

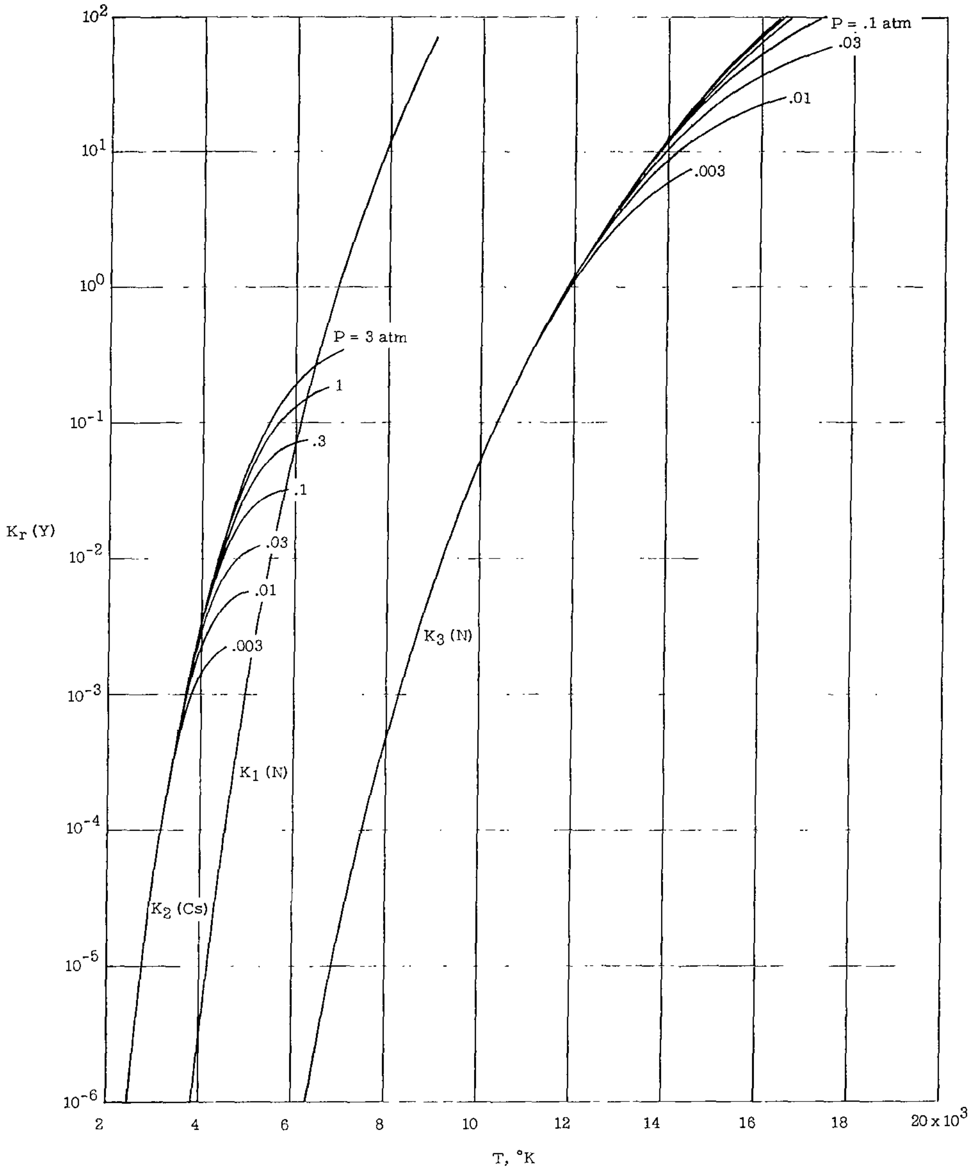

Figure 11.- The equilibrium constants $K_r(Y)$ for $r = 1, 2,$ and 3. $K_c = 0.01$.

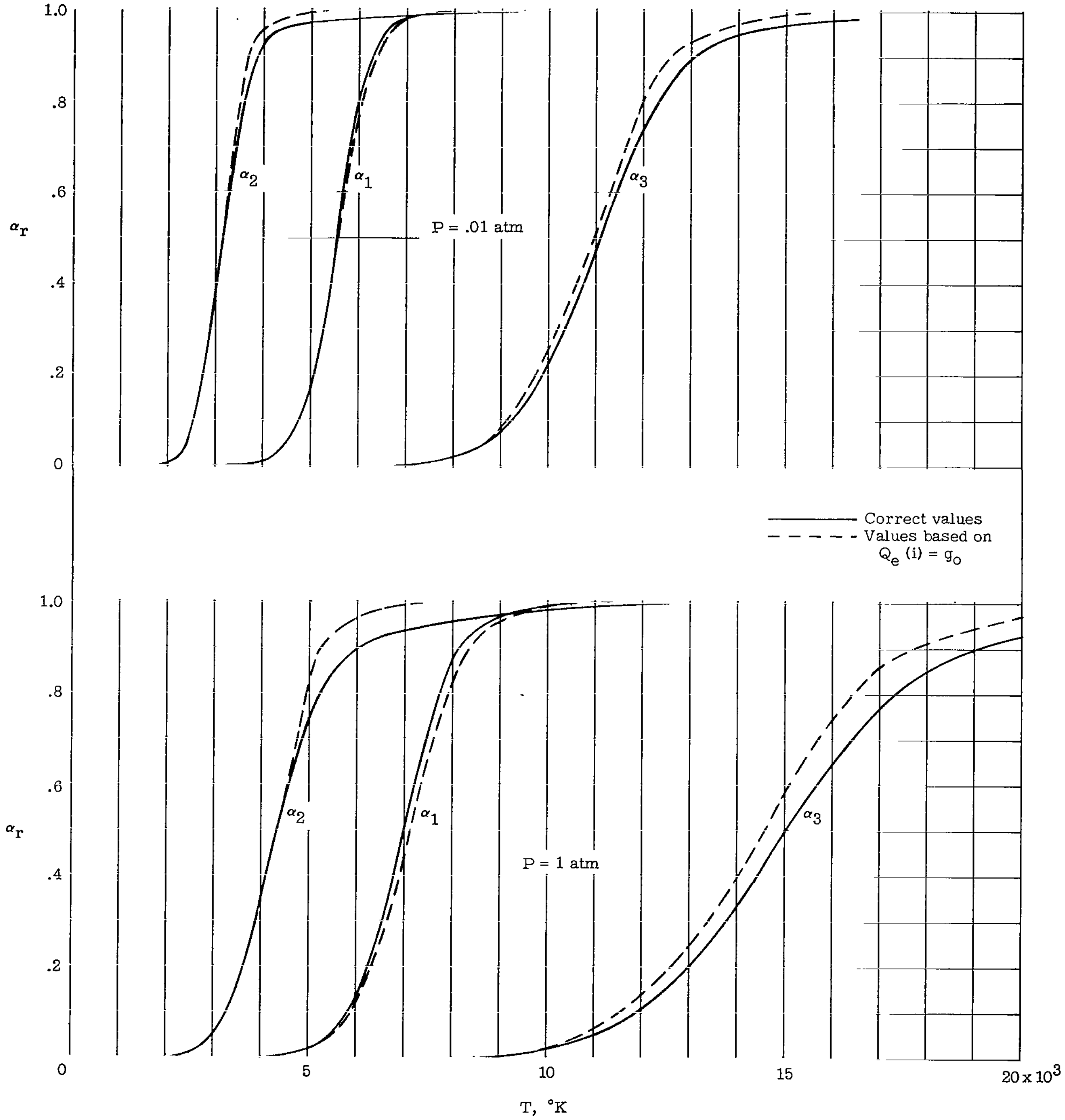

Figure 12.- Computation of the degree of reaction α_r with and without excitation considered. K_c = 0.01.

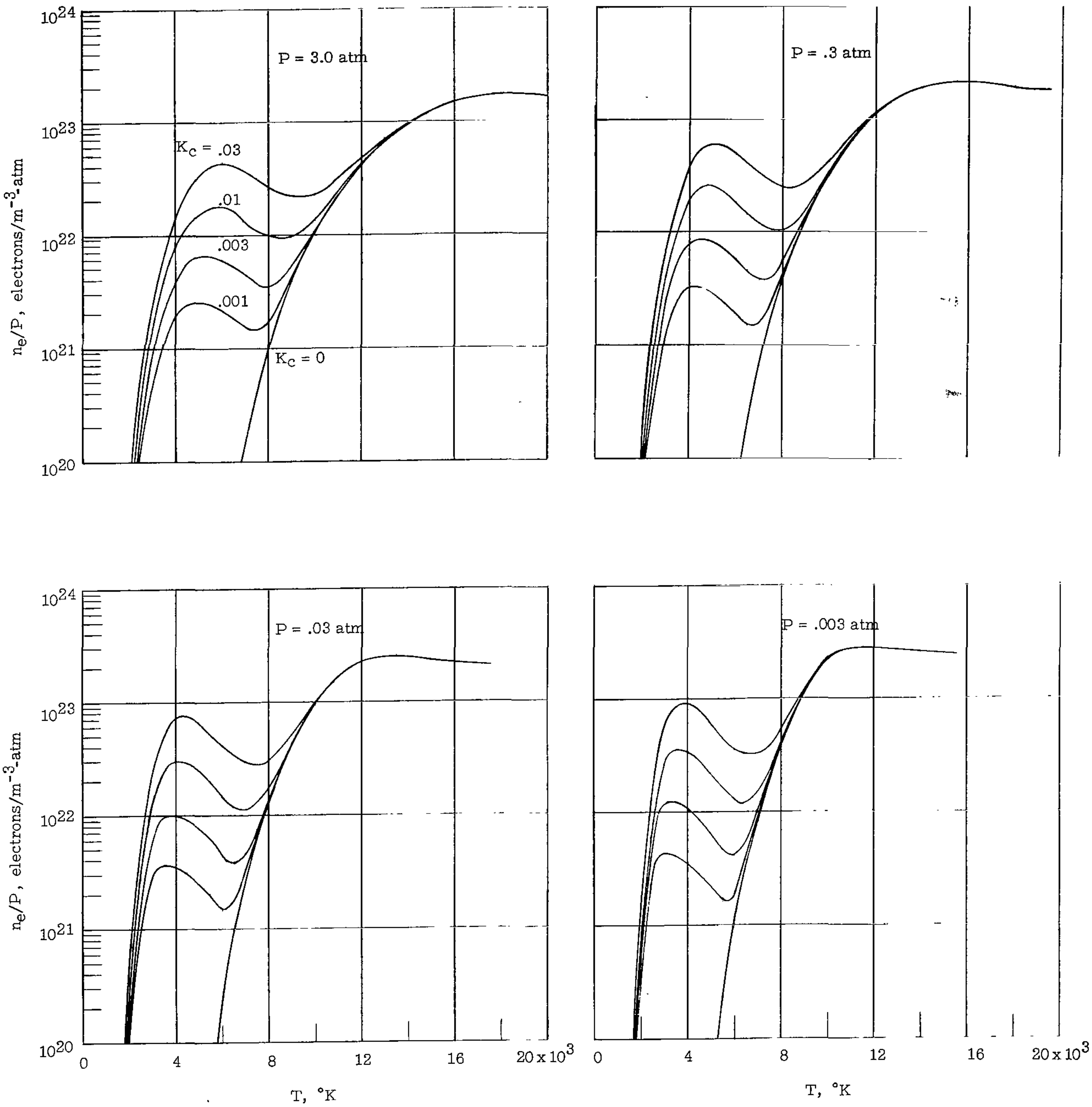

Figure 13.- The electron density for cesium-seeded nitrogen.

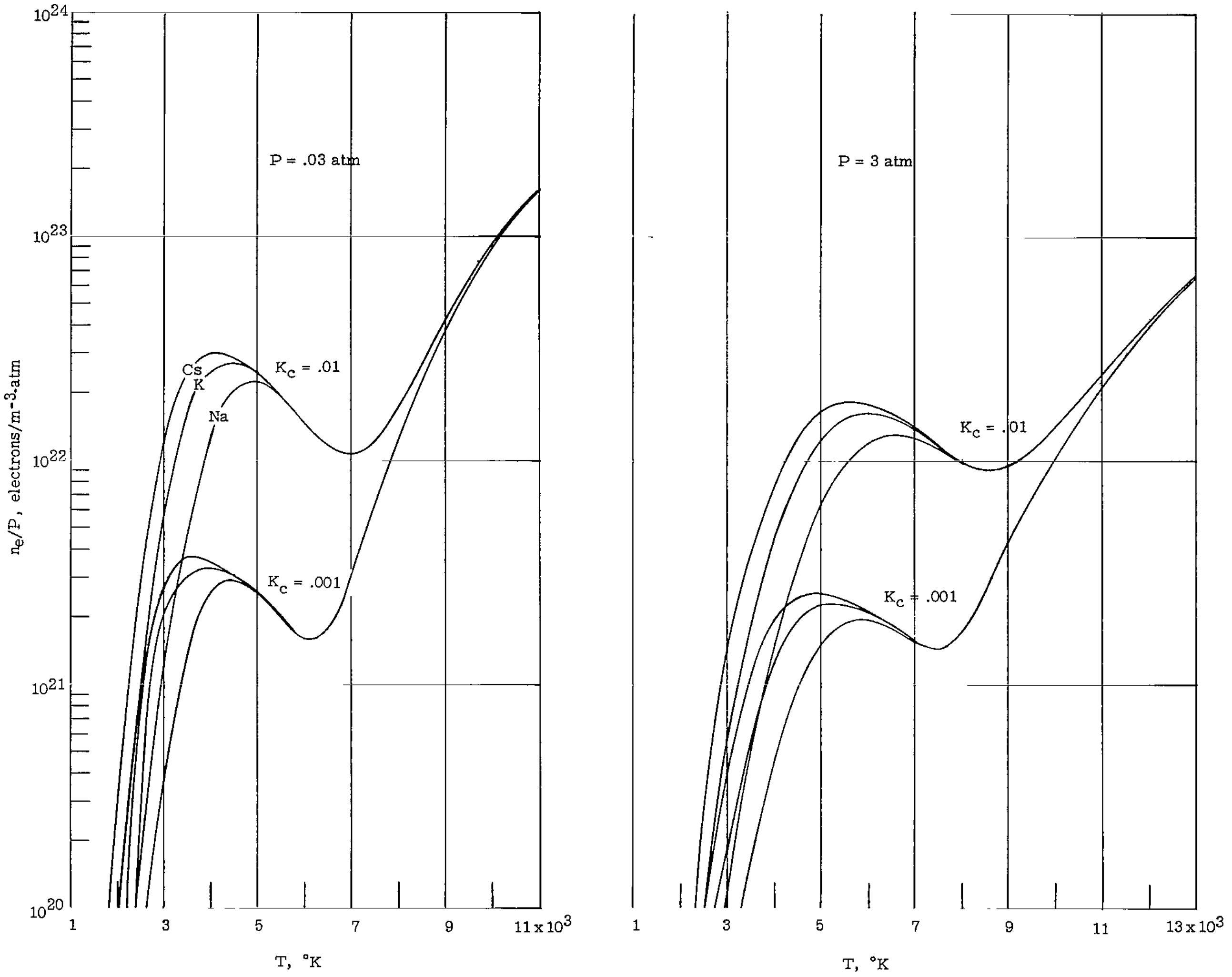

Figure 14.- The electron density for various seed materials.

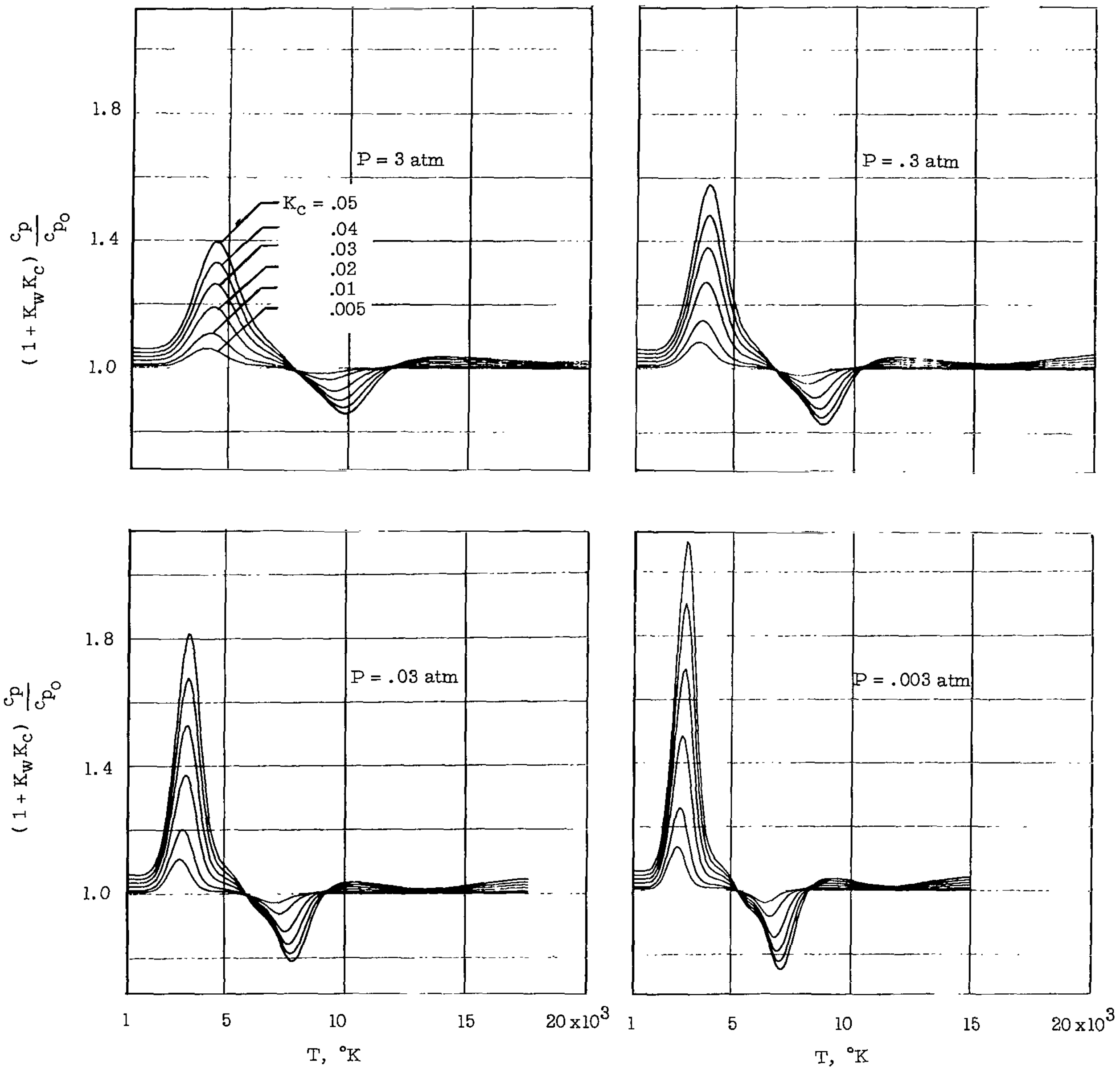

Figure 15.- The ratio of seeded to unseeded c_p/R for various degrees of seeding.

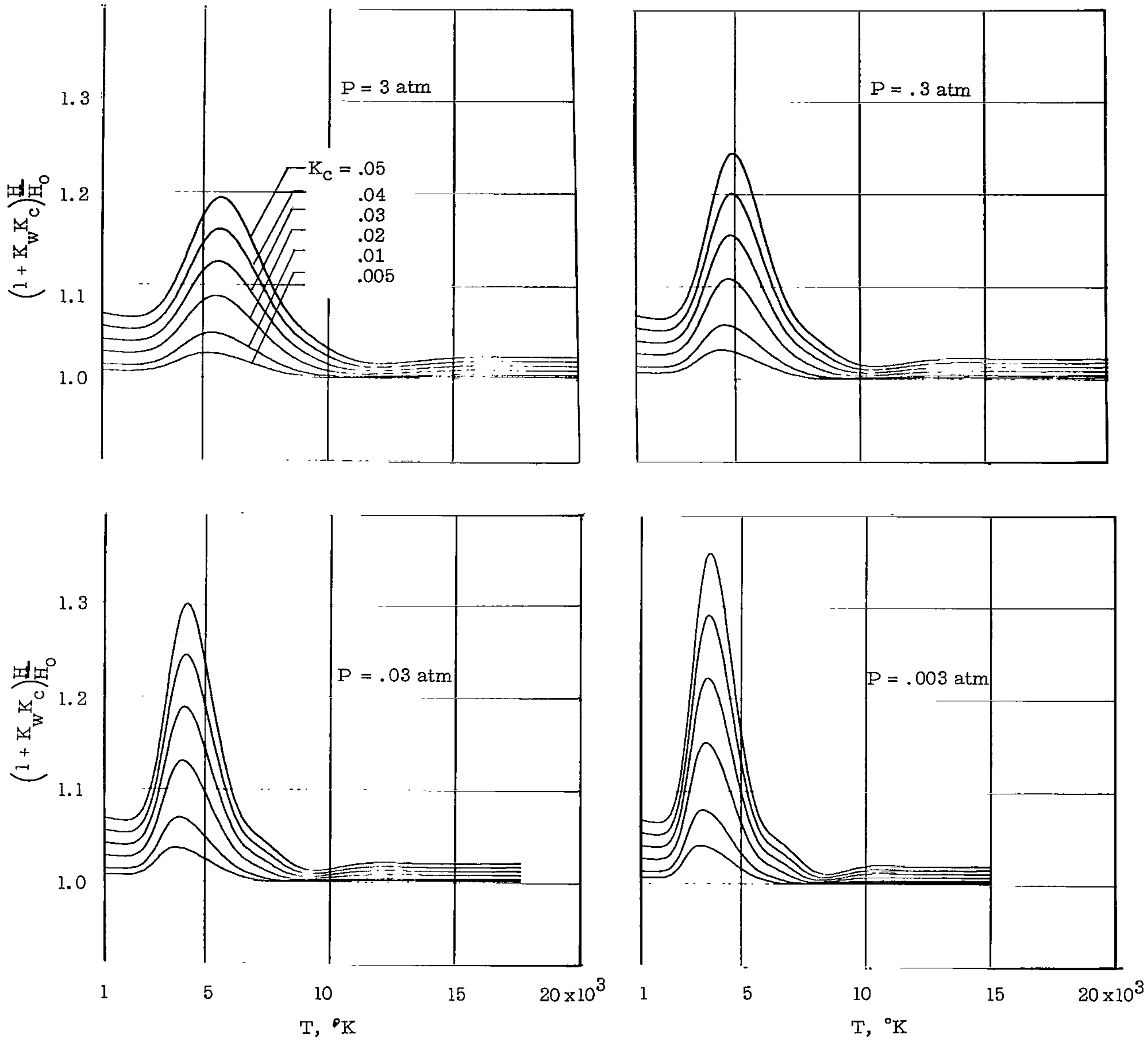

Figure 16.- The ratio of seeded to unseeded H/R for various degrees of seeding.

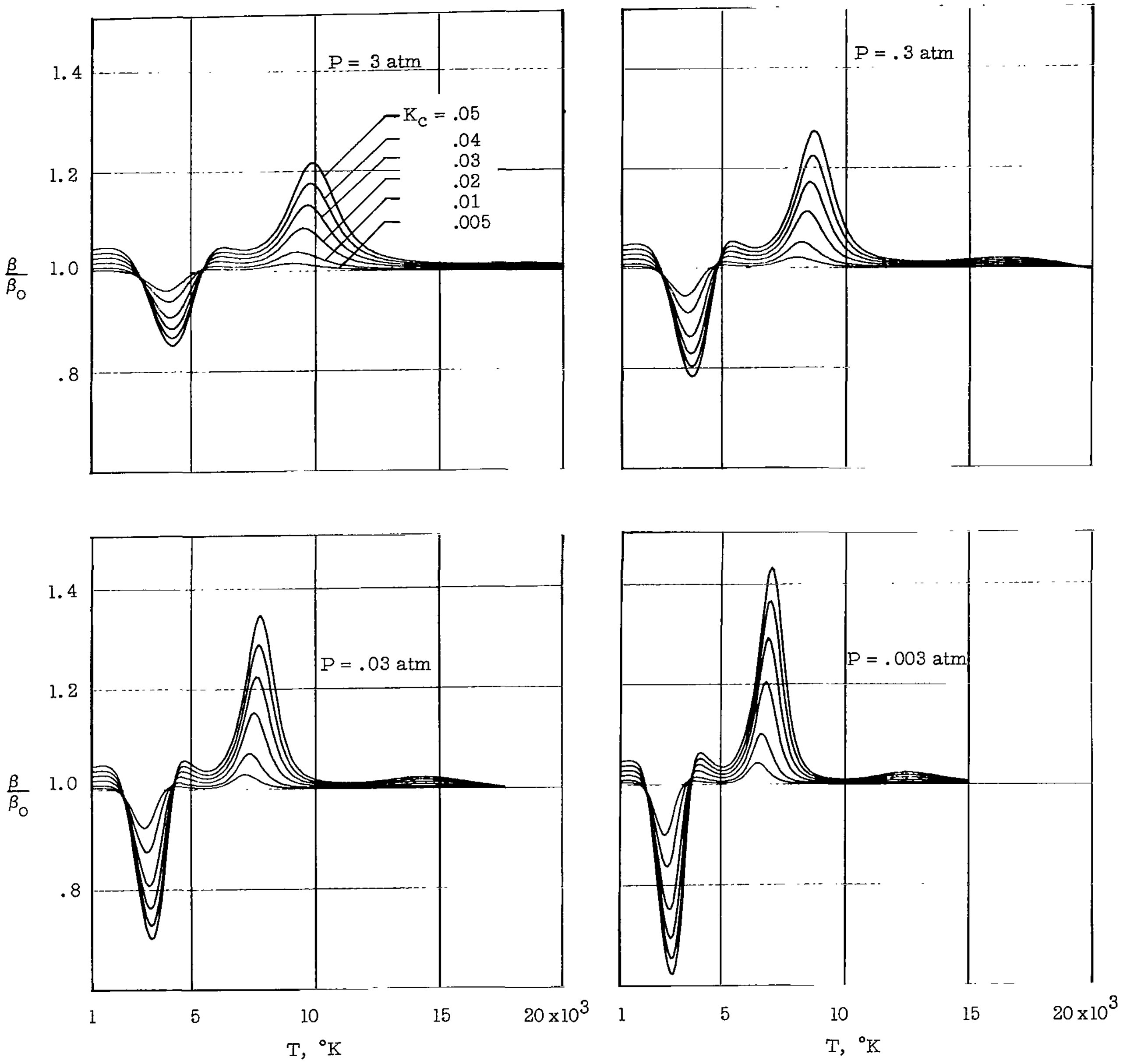

Figure 17.- The ratio of seeded to unseeded β for various degrees of seeding.

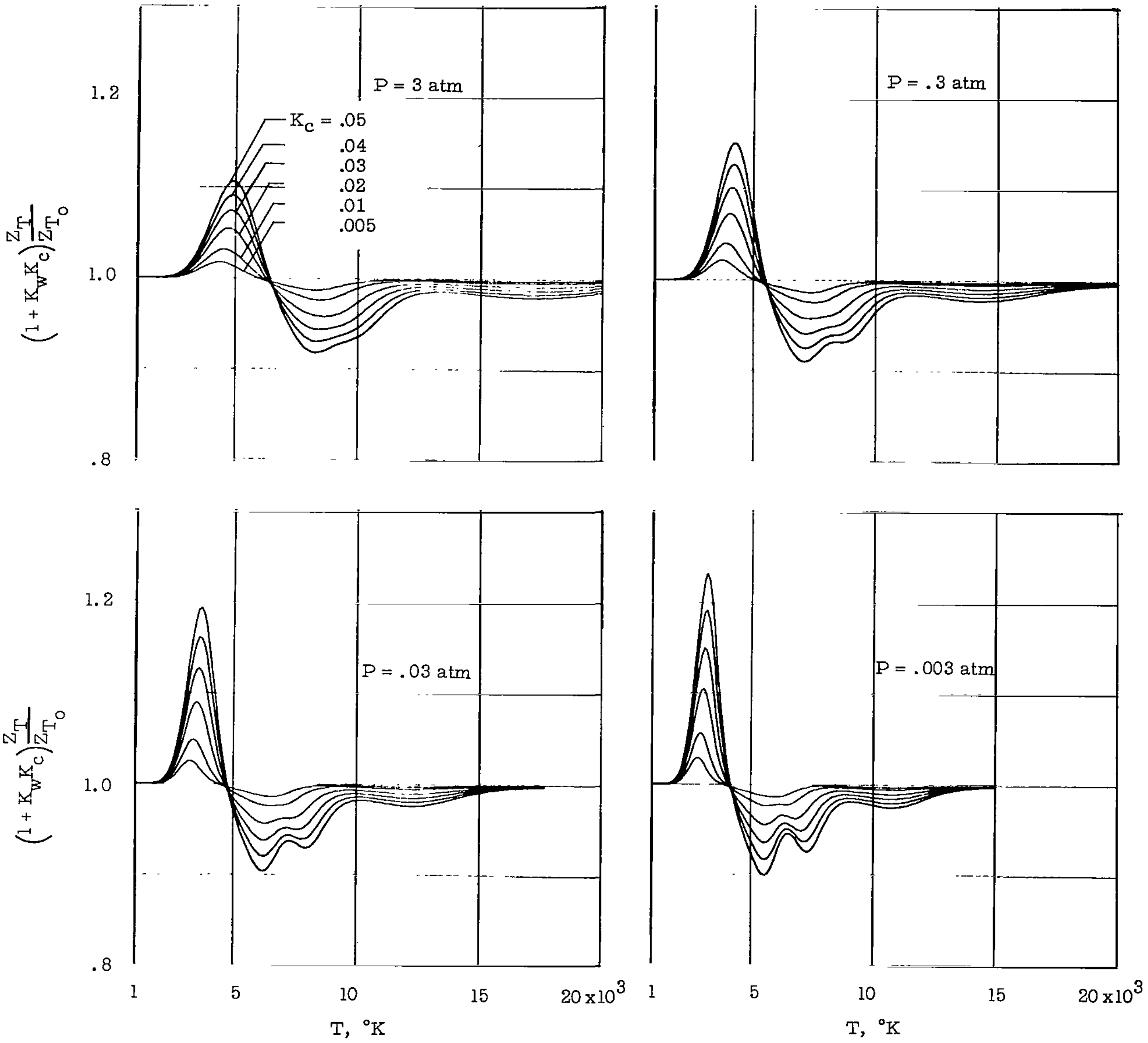

Figure 18.- The ratio of seeded to unseeded Z_T/R for various degrees of seeding.

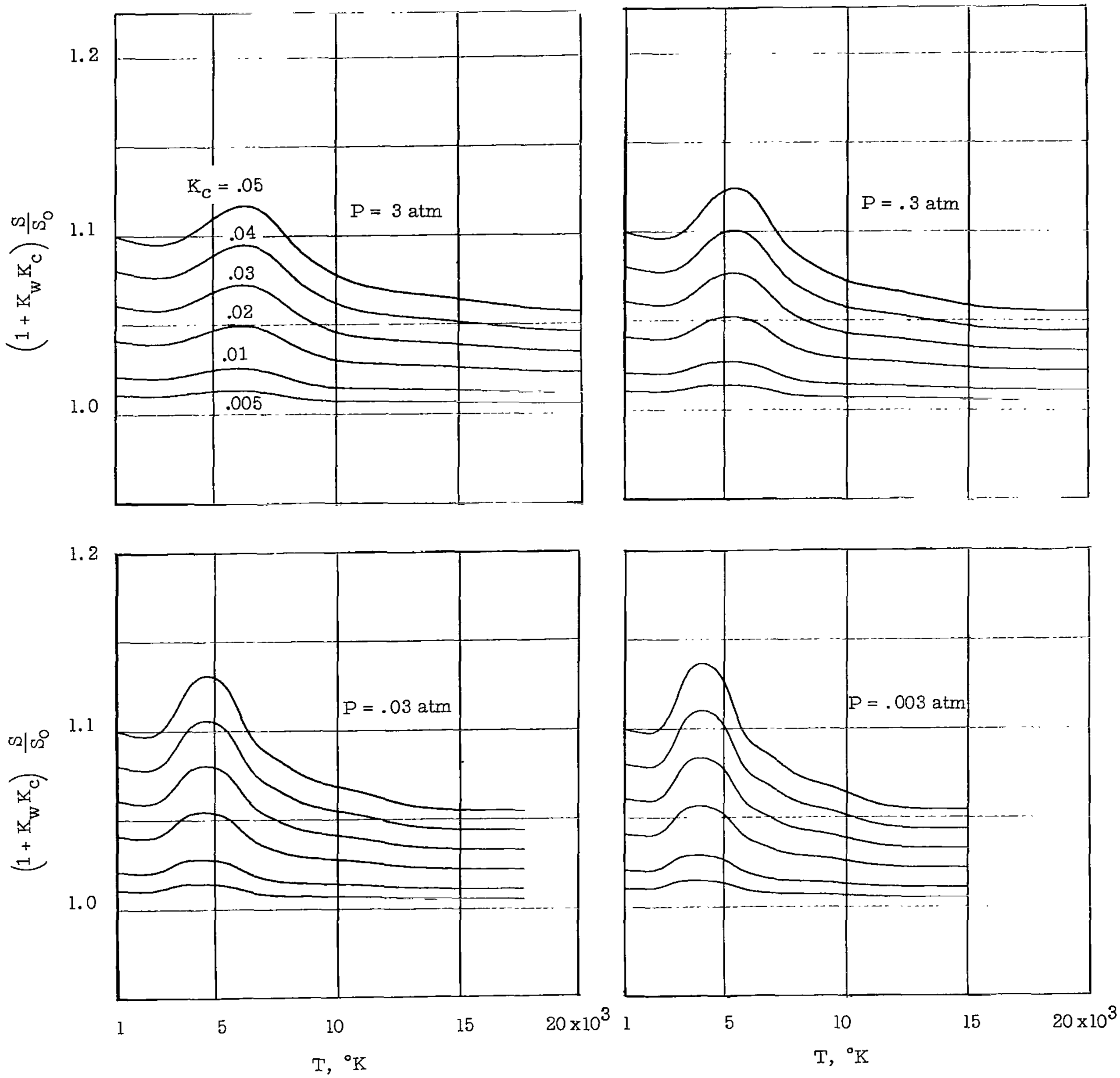

Figure 19.- The ratio of seeded to unseeded S/R for various degrees of seeding.

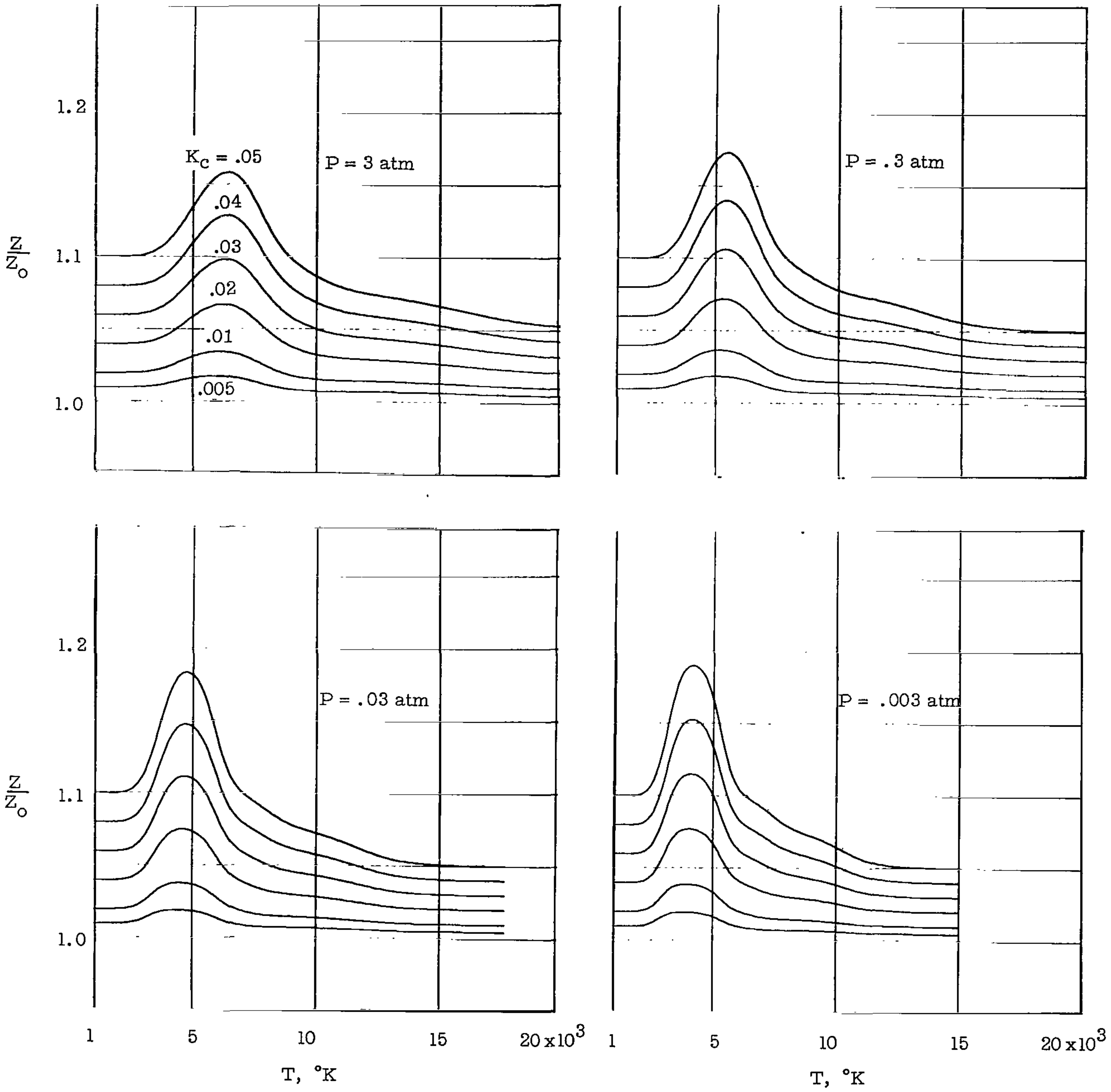

Figure 20.- The ratio of seeded to unseeded Z for various degrees of seeding.

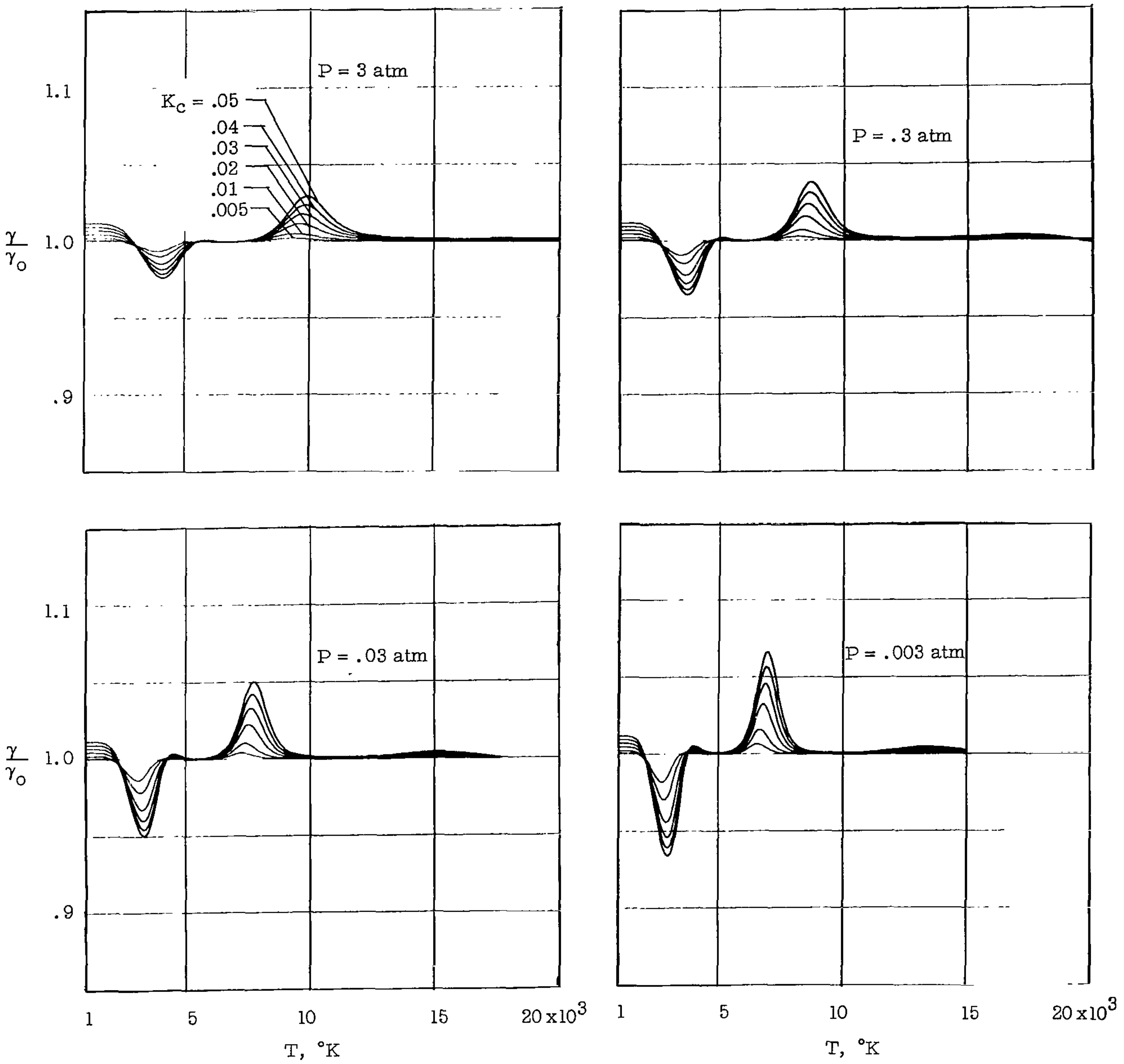

Figure 21.- The ratio of seeded to unseeded γ for various degrees of seeding.

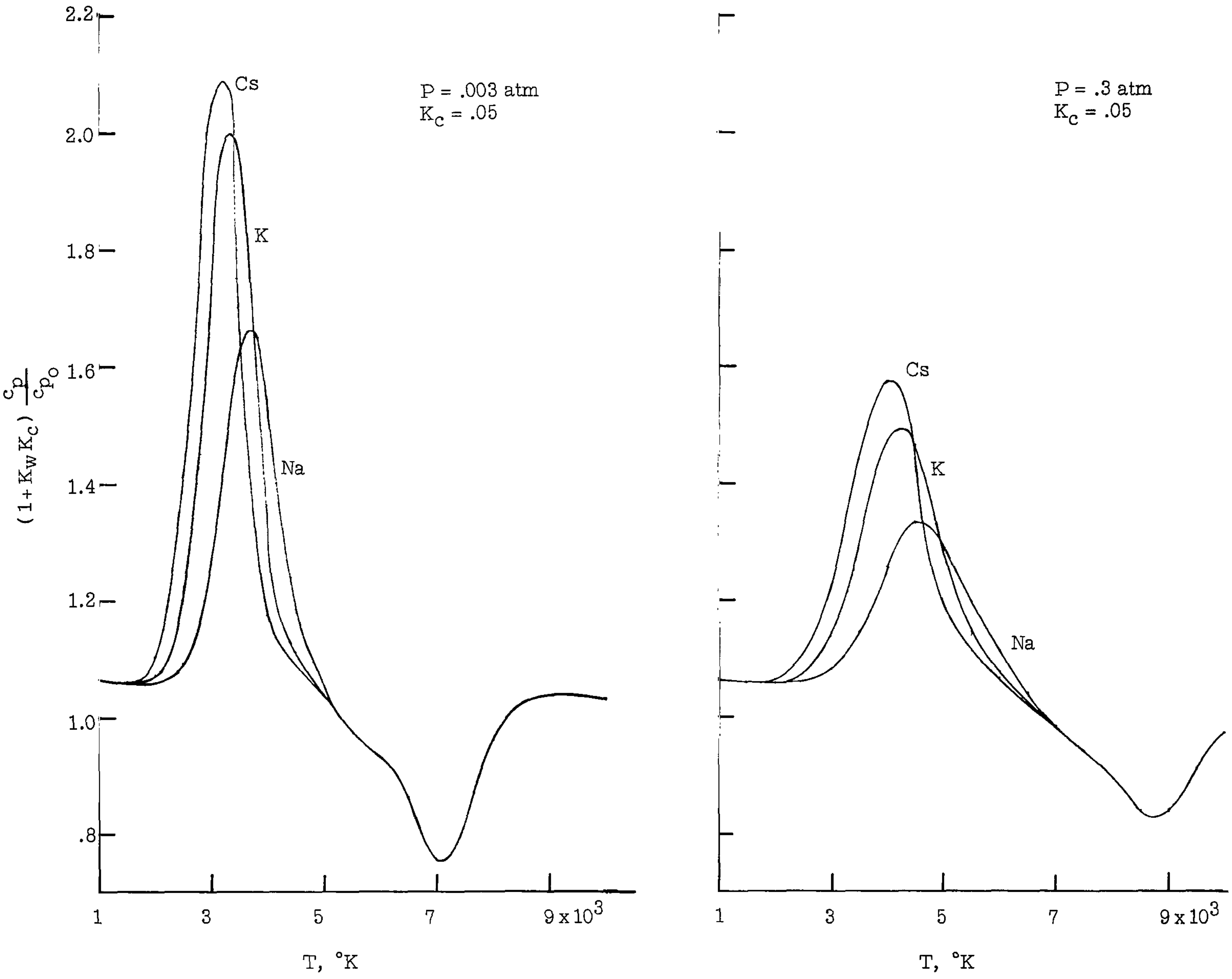

Figure 22.- The ratio of seeded to unseeded c_p/R for various seed materials.

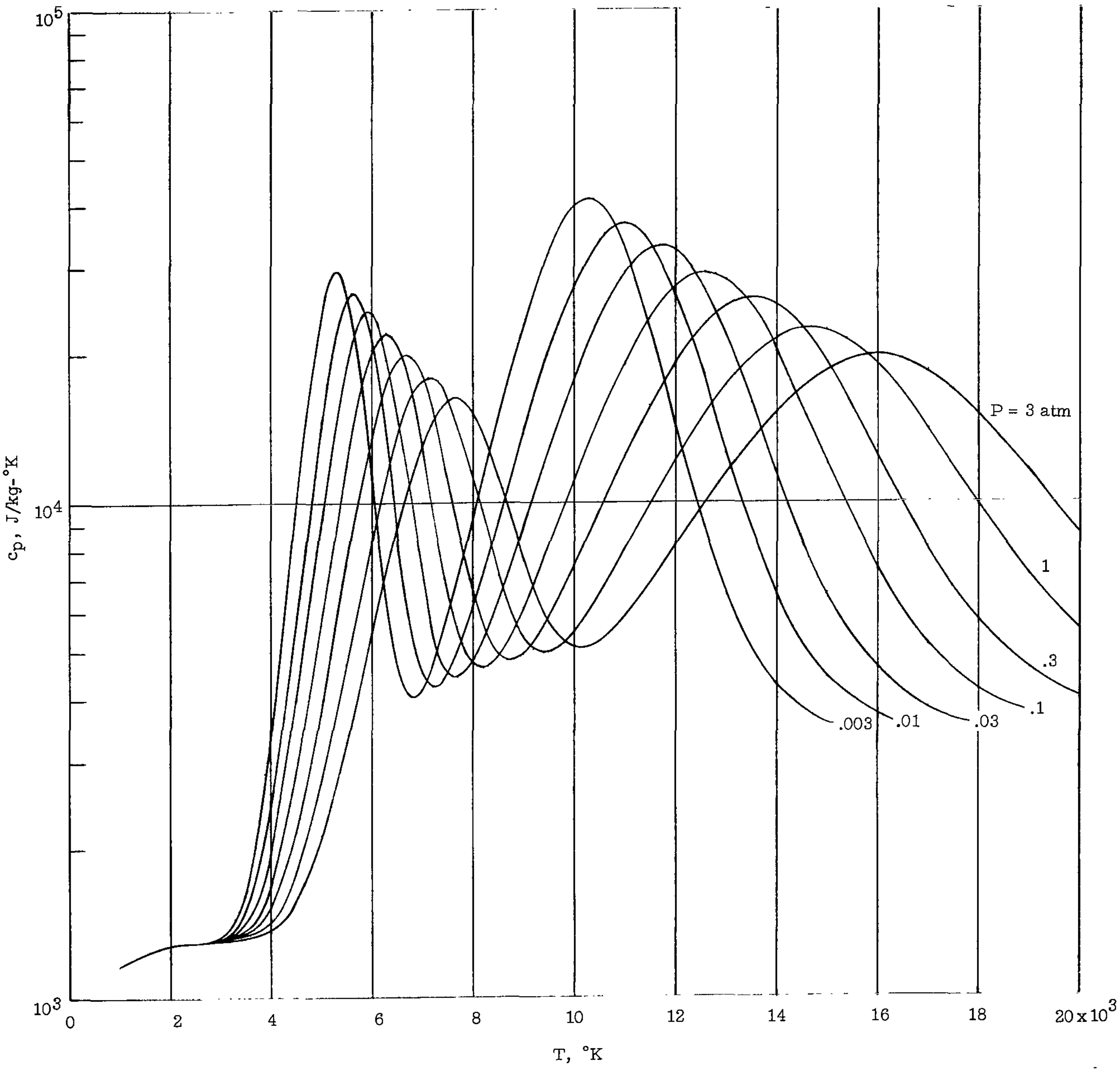

Figure 23.- The specific heat c_p of unseeded nitrogen.

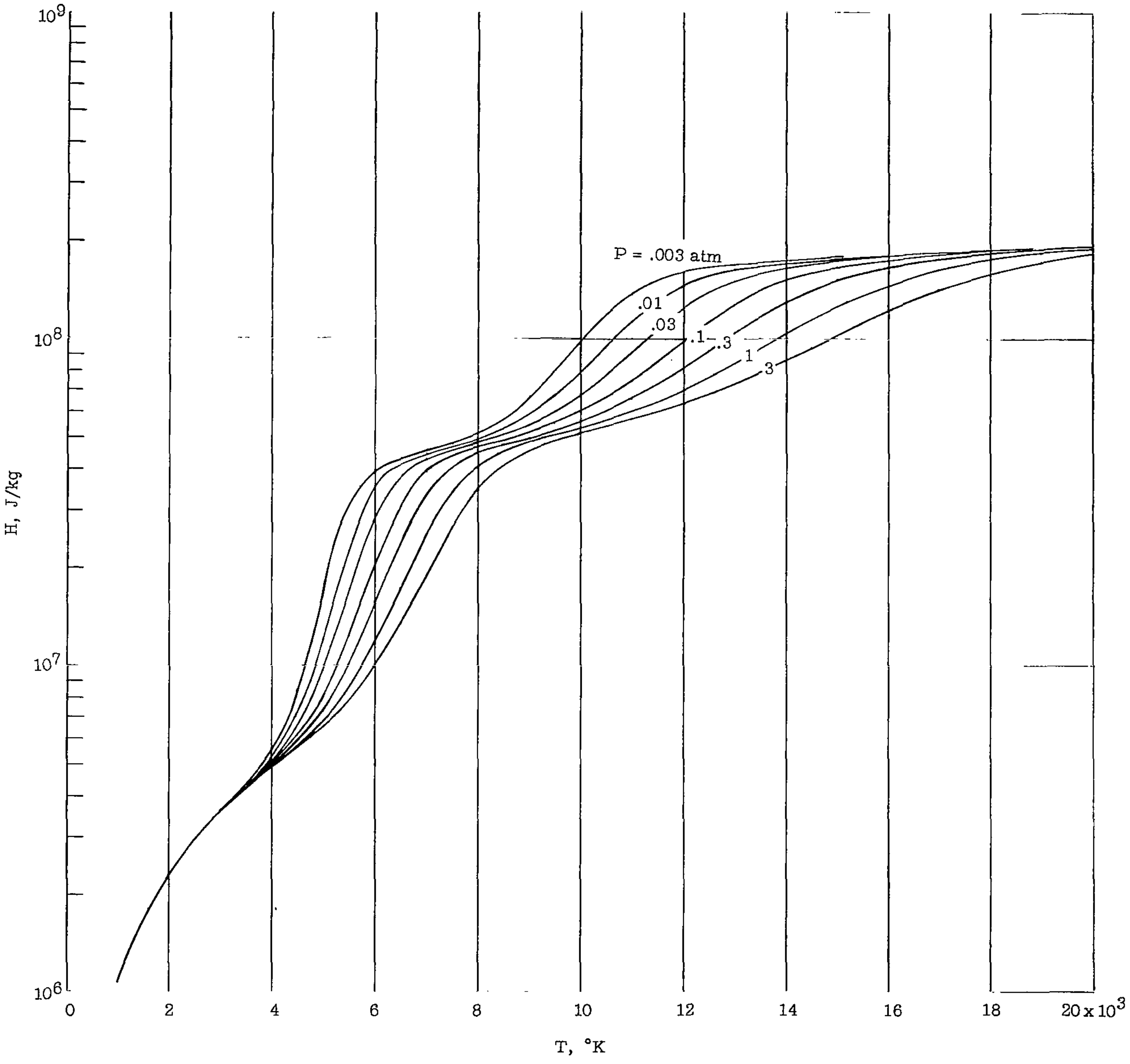

Figure 24.- The enthalpy H of unseeded nitrogen.

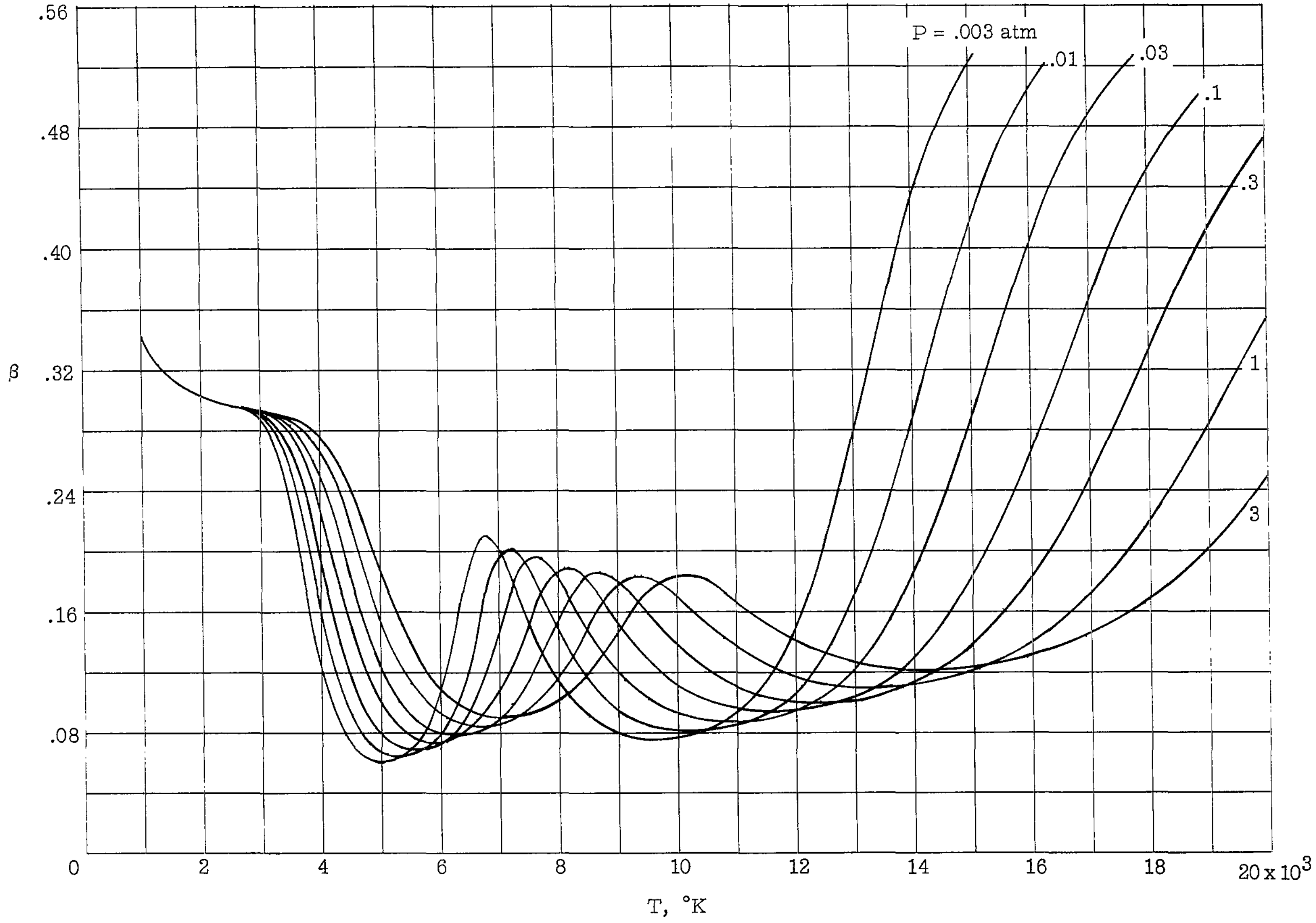

Figure 25.- The variation in β for unseeded nitrogen.

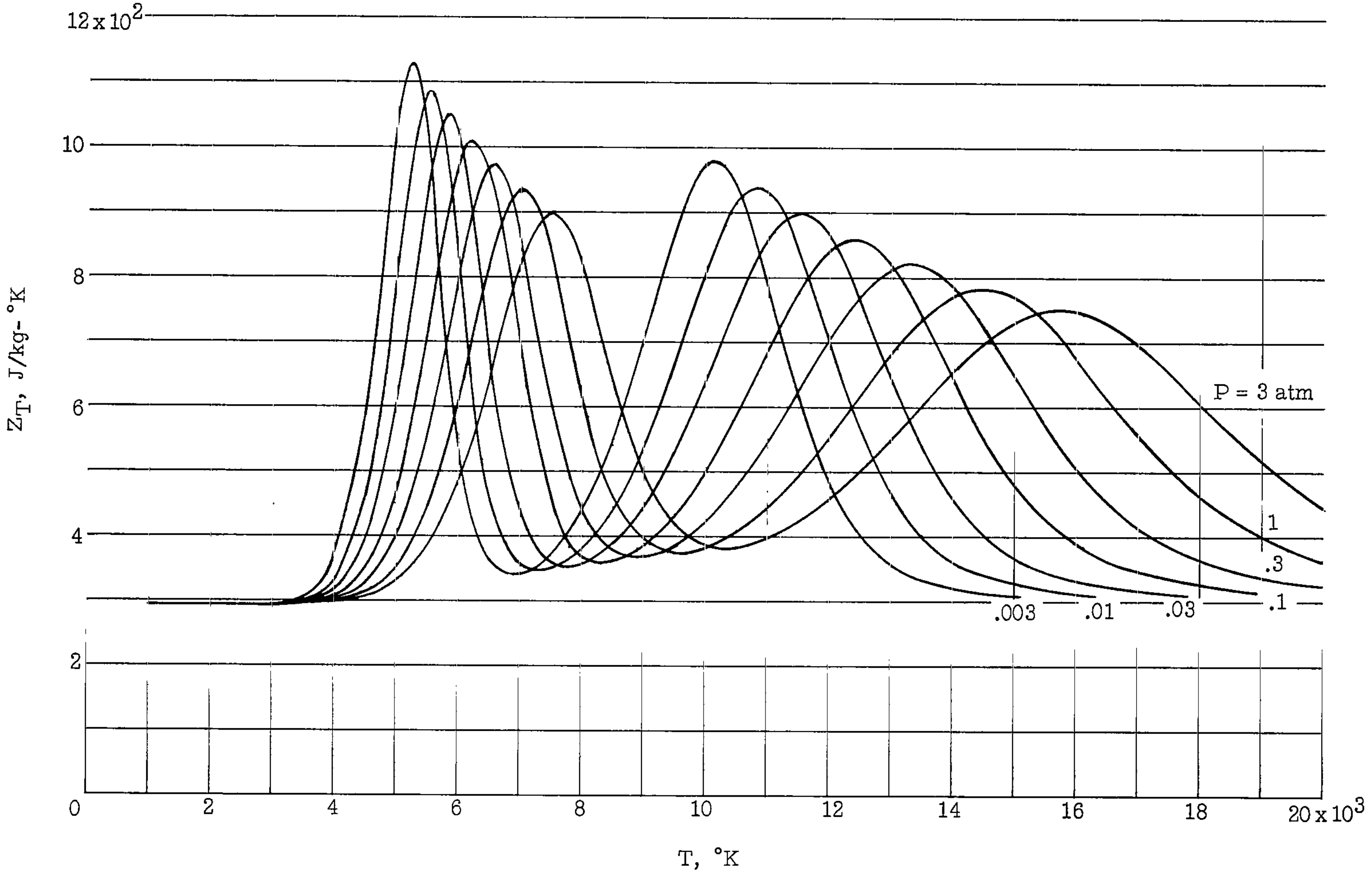

Figure 26.- The variation in Z_T for unseeded nitrogen.

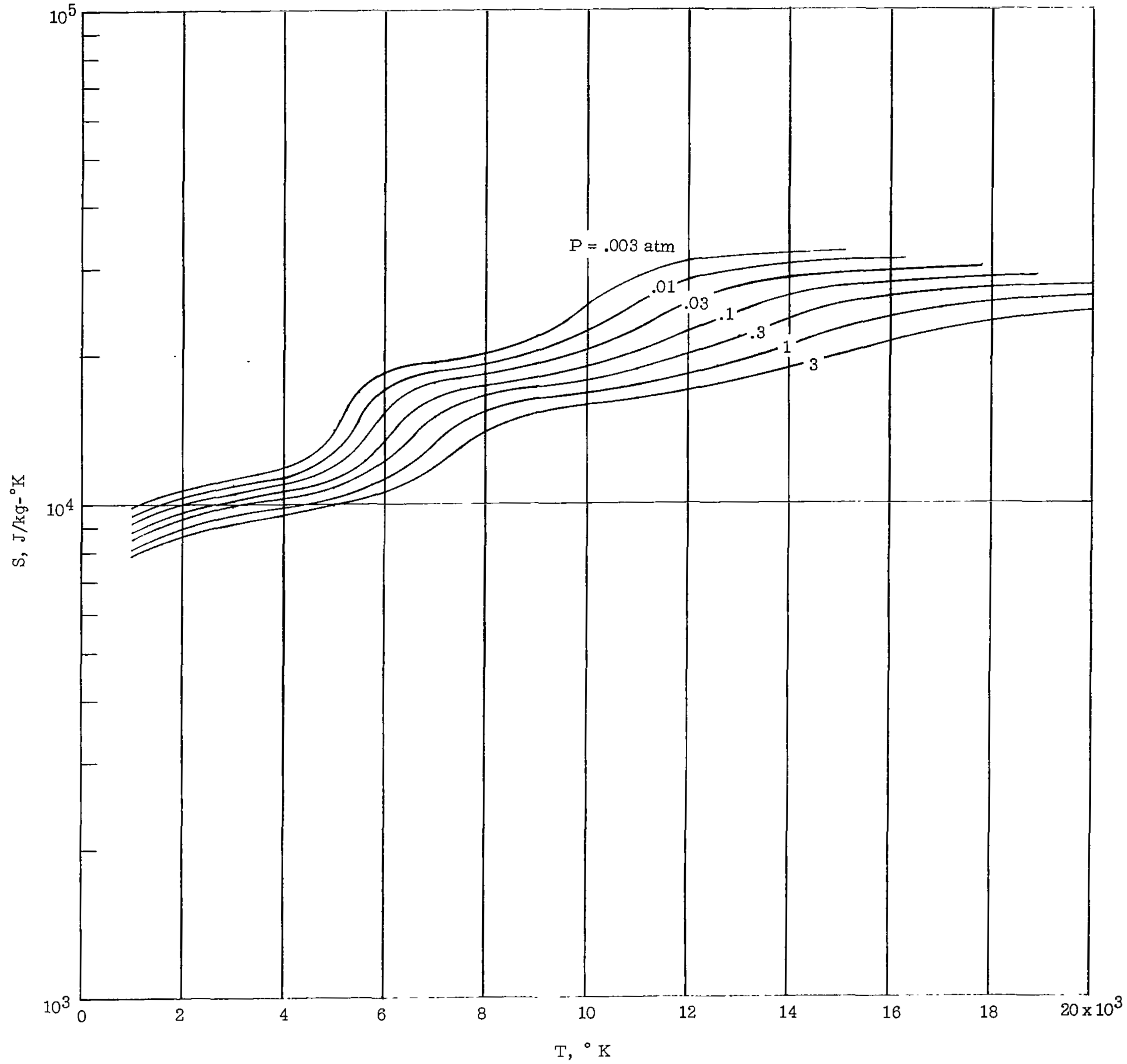

Figure 27.- The entropy S of unseeded nitrogen.

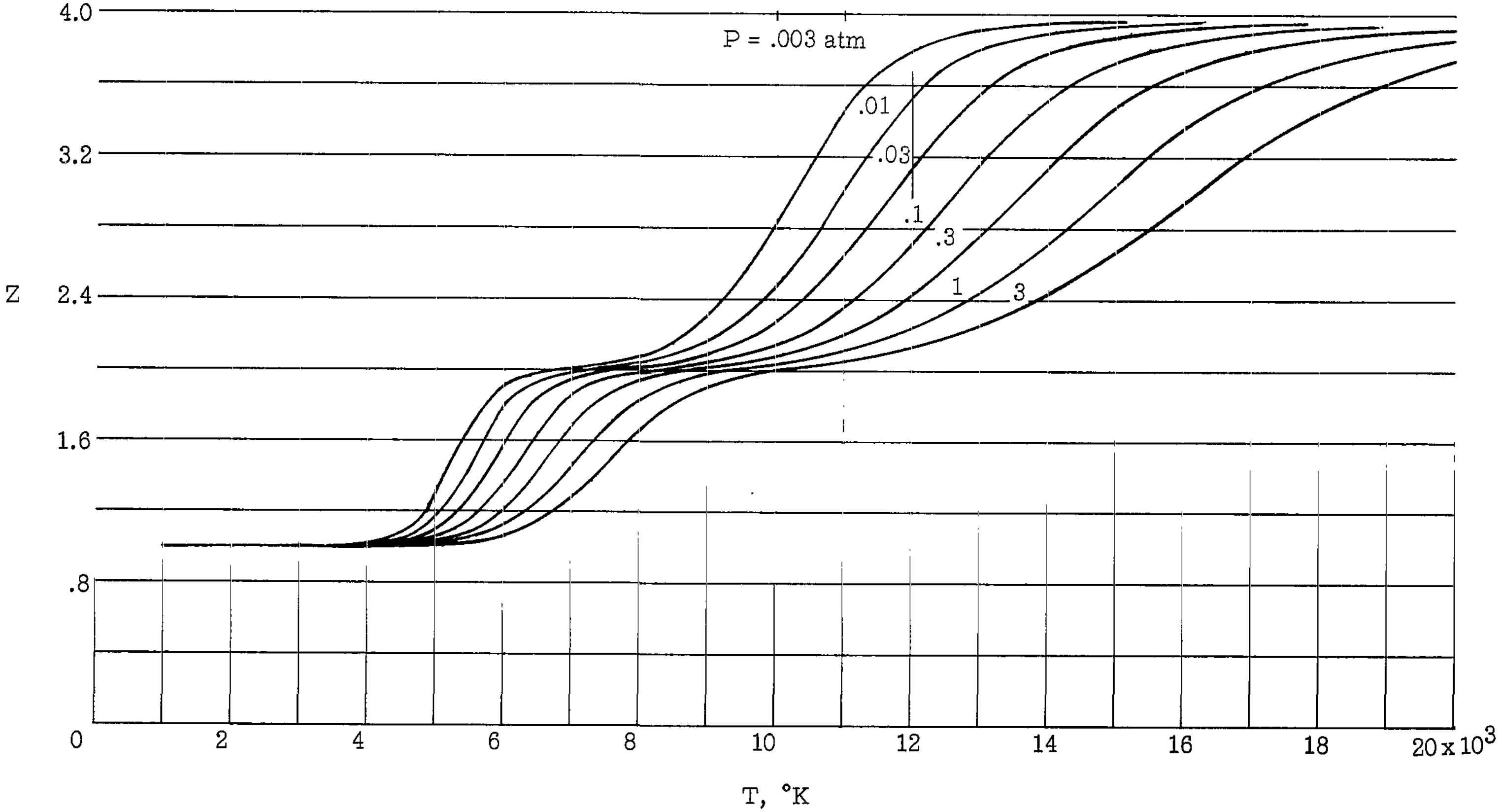

Figure 28.- The variation in Z for unseeded nitrogen.

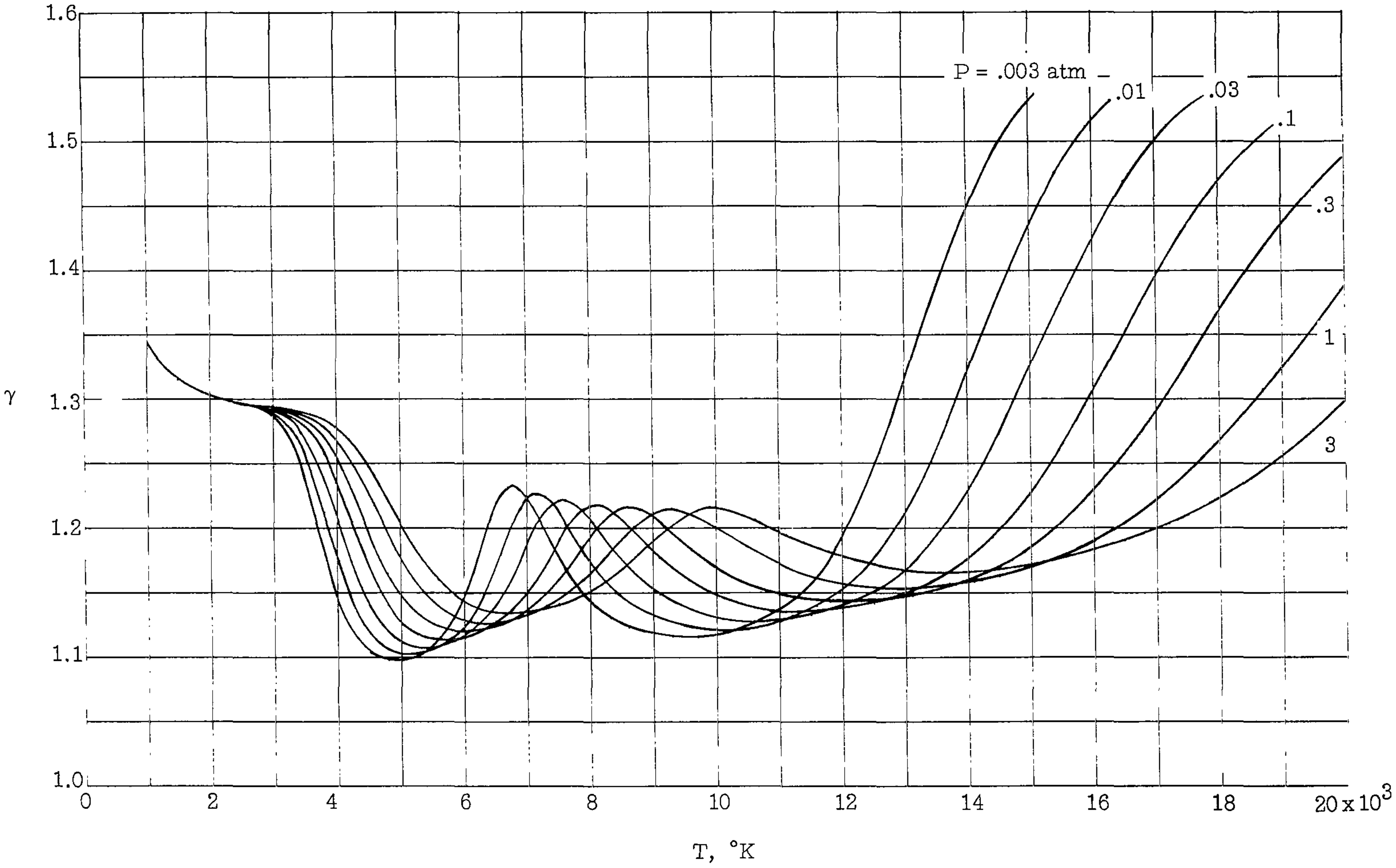

Figure 29.- The variation in γ for unseeded nitrogen.

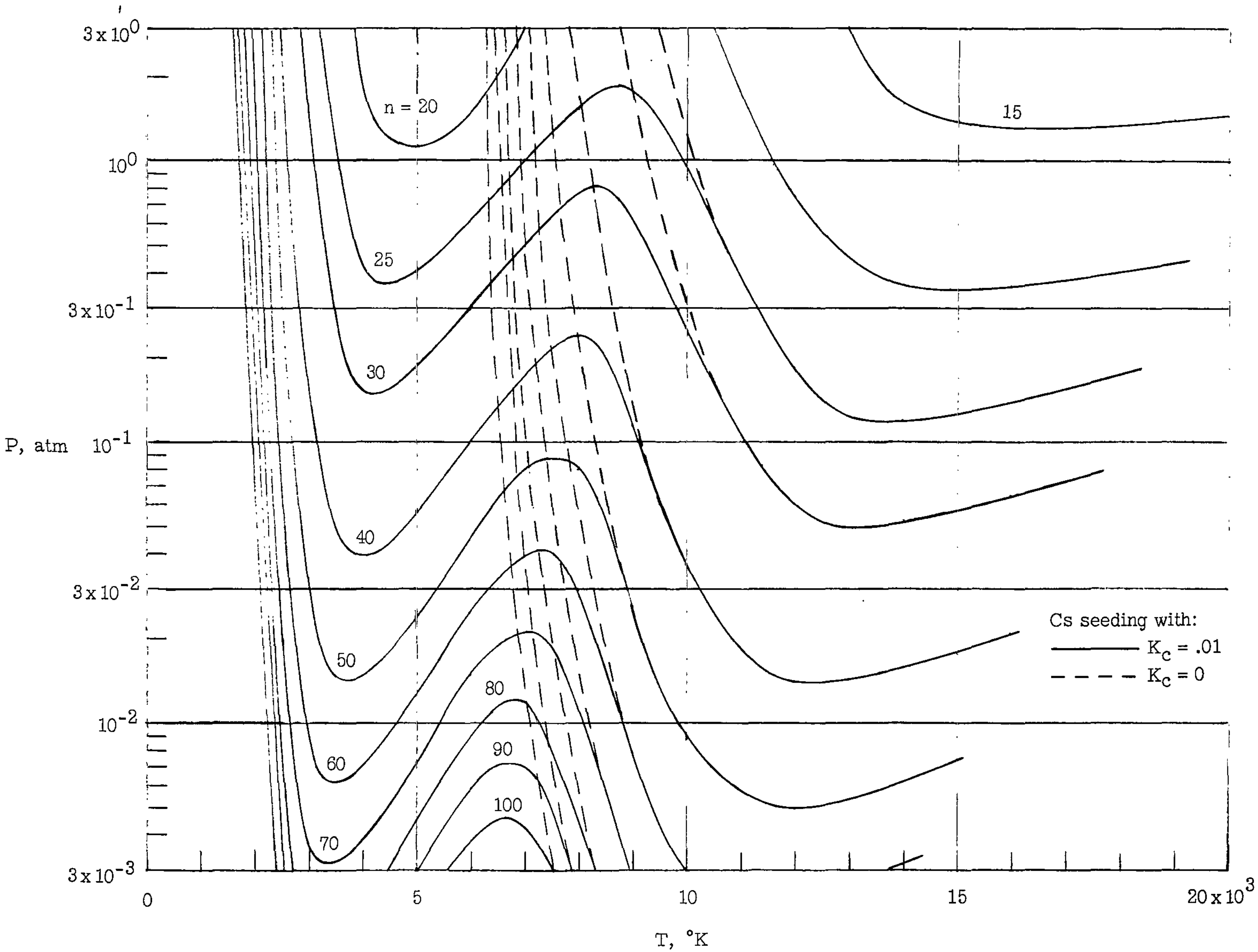

Figure 30.- The principal quantum number cutoff n for cesium-seeded (1 percent) and unseeded nitrogen.

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