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SUMMARY

The one-dimensional unsteady expansion of a mixture of gases is analyzed for conditions at which the deexcitation of molecular vibrational energies is the predominant rate process. Methods of calculation are formulated for treating the expansion as either an equilibrium or a nonequilibrium process. In the nonequilibrium analysis the method of characteristics is applied in a Lagrangian frame of reference, and the simultaneous vibrational deexcitation of a number of molecules can be handled.

Calculated results for equilibrium and nonequilibrium expansions are presented for a range of initial temperatures from 2000° K to 4000° K. The velocity, thermodynamic-property, and vibrational-energy variations are presented along specific particle paths designated by the scaling parameter. The general trends seen in the results agree well with trends expected from physical reasoning and are very similar to those exhibited by vibrationally relaxing flow in a hypersonic nozzle. Curves are presented to permit practical applications of the calculated results.

INTRODUCTION

The centered one-dimensional unsteady expansion has recently assumed new importance as a process for producing high-enthalpy flow for rate measurement experiments and reentry simulation. The expansion tube proposed in reference 1 is a prime example of the potential use of such an expansion to generate high-velocity flow without subjecting the gas to extreme stagnation temperatures and pressures.

The rapid expansion from elevated temperatures experienced by a gas mixture in an unsteady expansion necessitates an analysis which includes the effects of the nonequilibrium processes which exist in the flow. The present investigation is intended to present such an analysis for a limited range of conditions. For the temperatures and pressures considered, the nonequilibrium processes considered can be restricted to those governing the relaxation of the vibrational energies of the molecular species in the gas mixture. A constant-composition gas mixture in which the vibrational energies are rate controlled is used in the analysis.

The structure of a centered unsteady expansion in a vibrationally relaxing gas is first analyzed in reference 2. In reference 3 a more realistic vibrational rate equation is used to treat the same problem.

The purpose of the present work is to extend the existing knowledge of vibrationally relaxing unsteady expansions by treating a mixture of gases and the associated rate equations. The method of characteristics is used and calculations are performed in a Lagrangian coordinate system. Results are presented for a nitrogen-oxygen mixture over a range of conditions in which vibrational relaxation is the principal nonequilibrium process. The results given should prove valuable in the design and analysis of facilities operating in the range considered.

SYMBOLS

A_i,B_i,C_i	constants used in vibrational-relaxation-time expressions
a	speed of sound
b	Lagrangian coordinate denoting a fixed mass element
c_p	heat capacity at constant pressure
f_i	factor used to provide exclusion and inclusion of rotational energy of monatomic and diatomic molecules, respectively ($f_i = 0$ for monatomic molecule; $f_i = 1$ for diatomic molecule)
h	enthalpy per unit mass
i	species identification
l	distance from center of expansion
n	total number of species
p	pressure
R	universal gas constant

s	specific entropy
T	temperature
t	time
U	piston velocity
u	velocity
x	position coordinate of fluid particle
x_i	mass fraction of ith species
y	Lagrangian coordinate divided by t
γ	specific heat ratio
θ_i	characteristic vibrational temperature of ith species
μ	molecular weight
μ_i	molecular weight of ith species
ρ	density
σ_i	vibrational energy of ith species (σ_{N_2} and σ_{O_2} represent the vibrational energies of N_2 and O_2, respectively)
τ_i	vibrational relaxation time of ith species

Subscripts:

A,B,D,P	points in figure 2
AP,BP,DP	denote average of values at two points in figure 2
c	required for complete expansion

eq	equilibrium conditions
f	results for frozen flow
n	evaluated at intermediate condition
o	initial conditions of undisturbed gas
p	evaluated with pressure held constant
s	evaluated with specific entropy held constant
ρ	evaluated with density held constant
σ_i	evaluated with vibrational energy of ith species held constant
+,-,0	denote the three characteristic directions

A bar over a symbol denotes a nondimensional quantity.

THEORY

Physical Model of the Expansion

A physical picture is necessary in order to understand the unsteady one-dimensional expansion and its related boundary conditions. The model used in the present work is illustrated in figure 1.

A semi-infinite reservoir of constant cross-sectional area containing a gas mixture in a state of thermodynamic equilibrium is considered. At time zero, the piston is suddenly withdrawn with a constant velocity. A rarefaction wave which propagates into the undisturbed gas in the reservoir is produced. The first infinitesimal pressure pulse propagates into the undisturbed gas with the velocity of the speed of sound of that gas ($-a_o$). This pulse is followed by an infinite number of such pulses traveling at the speed of sound of the gas into which they are progressing ($u_n - a_n$). These infinitesimal pulses continue until the properties at a point in question are identical with those at the piston face. Figure 1 graphically depicts the structure of the expansion in distance-time coordinates. For a perfect gas, the centered rays of the expansion are straight lines along which the flow properties are constant. Typical particle paths are indicated on the x - t diagram by dashed lines.

The temperature and pressure of the undisturbed gas are assumed to be high and the vibrational energies of the molecular species of that gas are initially in an excited state. The temperature and pressure decrease as the molecules are processed by the expansion, and vibrational deexcitation must occur if thermodynamic equilibrium is to be maintained. However, the changes in vibrational energies are rate controlled and therefore rate processes must be included in the analysis of the expansion.

An indication of the effects of rate processes can be seen by considering the various particle paths shown in figure 1. Path I represents a particle which was very near the piston face initially. This particle has very little residence time in the expansion fan and thus the vibrational energies have insufficient time for adjustment to equilibrium. If very little adjustment occurs, the particle essentially experiences a frozen expansion and the vibrational energy is not converted to the translational and rotational energy modes. Particle III, on the other hand, has a relatively long residence time in the expansion and the rate processes are permitted adequate time for the flow to relax to equilibrium. Such a particle undergoes an equilibrium expansion. The energy contained in the excited vibrational states returns to the translational and rotational modes. Between the two limiting cases of frozen and equilibrium flow is the nonequilibrium case, illustrated by particle path II. The residence time is of a magnitude that allows some relaxation of the rate-controlled vibrational energies toward equilibrium. Only a portion of the vibrational energies is returned to the flow. The principal portion of this investigation concerns the nonequilibrium region. Solutions for equilibrium and frozen flows are also presented for comparison purposes.

Governing Equations

Flow equations.- The analysis is formulated in a Lagrangian frame of reference to facilitate the establishment of particle paths along which the rate equation can be applied. In Lagrangian coordinates, attention is given to what happens to an individual fluid particle in the course of time. Each individual fluid particle must therefore be labeled. In the present work, this labeling is accomplished by designating each particle according to its position coordinate x in the $x - t$ plane at some reference time $t = t_o$. This value is called b, the Lagrangian coordinate specifying the particle being considered. Independent variables in the Lagrangian coordinate system are therefore b and t. The governing equations for a one-dimensional flow in such a system are presented in reference 4. These equations, expressing the conservation of mass, momentum, and energy in a Lagrangian frame of reference, can be written as

$$\frac{\partial u}{\partial b} + \frac{\rho_o}{\rho^2}\frac{\partial \rho}{\partial t} = 0 \qquad (1)$$

$$\rho_o \frac{\partial u}{\partial t} + \frac{\partial p}{\partial b} = 0 \tag{2}$$

and

$$\frac{\partial h}{\partial t} - \frac{1}{\rho}\frac{\partial p}{\partial t} = 0 \tag{3}$$

provided body forces, viscous forces, diffusion, and heat conduction are neglected.

State equations.- If dissociation, ionization, and electronic excitation are neglected, the caloric equation of state can be expressed in the form

$$h = \sum_{i=1}^{n} \frac{x_i}{\mu_i}\left[\left(\frac{5}{2} + f_i\right) RT + \sigma_i\right] \tag{4}$$

The exclusion and inclusion of rotational energy of monatomic and diatomic molecules, respectively, is provided by use of f_i. For odd values of i, $f_i = 0$; for even values of i, $f_i = 1$. In the present application, the mass fractions of the various constituents of the gas mixture are assumed to remain constant throughout the expansion.

For the nonequilibrium analysis, the vibrational energies are rate controlled and are thus dependent upon the process which the gas has undergone. Equilibrium vibrational energies are calculated from the expression

$$\left(\sigma_{i,eq}\right) = \frac{R\theta_i}{\exp\left(\frac{\theta_i}{T}\right) - 1} \qquad (i = 2,4,. . .,n) \tag{5}$$

which can be derived from quantum mechanical considerations by using the simple harmonic oscillator model for diatomic molecules.

The gas is assumed to be a mixture of perfect gases. It therefore obeys the thermal equation of state

$$p = \frac{\rho RT}{\mu} \tag{6}$$

where

$$\mu = \left(\sum_{i=1}^{n} \frac{x_i}{\mu_i}\right)^{-1}$$

and is constant for a given gas composition.

Rate equations.- When the residence time in the expansion is not adequate for the vibrational energy of a molecule to relax to its equilibrium value, a rate equation must be used to describe the relaxation process. A form of the vibrational rate equation which indicates that a whole assembly of simple harmonic oscillators in various vibrational energy levels acts in such a way that a single relaxation time exists for the total vibrational energy was first established in reference 5. Such a form of the vibrational rate equation written in Lagrangian coordinates is

$$\frac{\partial \sigma_i}{\partial t} = \frac{\sigma_{i,eq} - \sigma_i}{\tau_i} \tag{7}$$

The vibrational relaxation time τ_i is taken to be of the form

$$\tau_i = \frac{A_i T^{B_i}}{p} \frac{\exp\left(C_i T^{-1/3}\right)}{1 - \exp\left(- \frac{\theta_i}{T}\right)} \tag{8}$$

The expression describes quite accurately experimentally measured values of vibrational relaxation times and is essentially the form predicted by the theoretical work in reference 6. The constants used for the various gases in this investigation are discussed subsequently when actual calculations are considered.

Nonequilibrium Solution

Characteristic equations.- The governing equations of a nonequilibrium one-dimensional unsteady expansion – equations (1), (2), (3), and (7) – constitute a system of quasi-linear partial differential equations which is hyperbolic in nature. Since real valued characteristics exist for such a system, the method of characteristics is used for obtaining a solution. The characteristics are lines across which the derivatives of the dependent variables may be discontinuous, and the slopes are found by equating the matrix of coefficients of the set of governing equations to zero and evaluating the resulting expression.

In the Lagrangian frame of reference the + and - characteristic directions are found to be

$$\left.\begin{aligned} \left(\frac{db}{dt}\right)_+ &= \frac{\rho a_f}{\rho_o} \\ \left(\frac{db}{dt}\right)_- &= - \frac{\rho a_f}{\rho_o} \end{aligned}\right\} \tag{9}$$

Along these characteristic lines, the respective compatibility relations

$$\left.\begin{aligned} \frac{dp}{dt} + \rho a_f \frac{du}{dt} - a_f^2 \frac{\sum_{i=1}^{n} \left(\frac{\partial h}{\partial \sigma_i}\right)_{p,\rho} \frac{\partial \sigma_i}{\partial t}}{\left(\frac{\partial h}{\partial \rho}\right)_{p,\sigma_i}} = 0 \\ \frac{dp}{dt} - \rho a_f \frac{du}{dt} - a_f^2 \frac{\sum_{i=1}^{n} \left(\frac{\partial h}{\partial \sigma_i}\right)_{p,\rho} \frac{\partial \sigma_i}{\partial t}}{\left(\frac{\partial h}{\partial \rho}\right)_{p,\sigma_i}} = 0 \end{aligned}\right\} \tag{10}$$

exist. It should be noted that a_f refers to the local frozen speed of sound which is defined as

$$a_f = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_{s,\sigma_i}} \tag{11}$$

for the gas model used herein.

The third characteristic direction is identical with a particle path and is written as

$$\left(\frac{db}{dt}\right)_0 = 0 \tag{12}$$

Along this line, both the energy equation

$$\frac{dh}{dt} - \frac{1}{\rho}\frac{dp}{dt} = 0 \tag{13}$$

and the rate equation

$$\frac{d\sigma_i}{dt} = \frac{\sigma_{i,eq} - \sigma_i}{\tau_i} \tag{14}$$

must be satisfied.

Modified Lagrangian coordinates.- In order to simplify the application of the boundary conditions to the problem, one further modification of the independent coordinates is necessary. This modification is made by dividing the Lagrangian particle coordinate b by the time variable t to define a new variable y. The independent variables then become y and t, where y is defined by the relation

$$y = \frac{b}{t} \tag{15}$$

The transformation maps the corner of the expansion fan into a straight line and readily permits application of the boundary conditions for $t \rightarrow 0$. In addition, the grid network becomes more nearly rectangular in the y - t plane.

In the modified coordinates, the equations which prescribe the characteristic curves, equations (9) and (12), become

$$\left.\begin{aligned} \left(\frac{dyt}{dt}\right)_+ &= \frac{\rho a_f}{\rho_o} \\ \left(\frac{dyt}{dt}\right)_- &= -\frac{\rho a_f}{\rho_o} \end{aligned}\right\} \tag{16}$$

and

$$\left(\frac{dyt}{dt}\right)_0 = 0 \tag{17}$$

respectively. The compatibility relations remain unchanged.

<u>Nondimensionalization of the characteristic equations.</u>- The following dimensionless quantities are defined:

$$\left.\begin{aligned} \bar{a}_f &= \frac{a_f}{a_{f,o}} & \bar{p} &= \frac{p}{p_o} & \bar{h} &= \frac{h}{h_o} \\ \bar{\rho} &= \frac{\rho}{\rho_o} & \bar{a}_{eq} &= \frac{a_{eq}}{a_{eq,o}} & \bar{u} &= \frac{u}{U_c} \\ \bar{b} &= \frac{b}{b_o} & \bar{t} &= \frac{a_{f,o}t}{b_o} & \bar{y} &= \frac{y}{a_{f,o}} \end{aligned}\right\} \tag{18}$$

The subscript o refers to the value of the quantity in the undisturbed gas before the piston is withdrawn. The velocity U_c is that required for a complete frozen expansion to $p = 0$. It can be readily shown that $U_c = \frac{p_o}{\rho_o a_{f,o}} \frac{2\gamma_o}{\gamma_o - 1}$. The reference length b_o is the initial x position of some reference particle.

The substitution of these expressions into the previously developed equations yields the dimensionless characteristic equations for the modified Lagrangian coordinate system. Along the + and - characteristic curves

$$\left.\begin{aligned}\left(\frac{d\overline{yt}}{d\bar{t}}\right)_+ &= \bar{\rho}\bar{a}_f \\ \left(\frac{d\overline{yt}}{d\bar{t}}\right)_- &= -\bar{\rho}\bar{a}_f\end{aligned}\right\} \tag{19}$$

the ordinary differential equations

$$\left.\begin{aligned}\frac{d\bar{u}}{d\bar{t}} + \frac{\gamma_o - 1}{2\gamma_o}\frac{1}{\bar{\rho}\bar{a}_f}\frac{d\bar{p}}{d\bar{t}} - \frac{b_o}{U_c}\frac{\bar{a}_f}{\bar{\rho}\dfrac{\partial\bar{h}}{\partial\bar{\rho}}}\sum_{i=1}^{n}\frac{\partial\bar{h}}{\partial\sigma_i}\frac{\partial\sigma_i}{\partial t} &= 0 \\ \frac{d\bar{u}}{d\bar{t}} - \frac{\gamma_o - 1}{2\gamma_o}\frac{1}{\bar{\rho}\bar{a}_f}\frac{d\bar{p}}{d\bar{t}} + \frac{b_o}{U_c}\frac{\bar{a}_f}{\bar{\rho}\dfrac{\partial\bar{h}}{\partial\bar{\rho}}}\sum_{i=1}^{n}\frac{\partial\bar{h}}{\partial\sigma_i}\frac{\partial\sigma_i}{\partial t} &= 0\end{aligned}\right\} \tag{20}$$

must be satisfied; along the particle path

$$\left(\frac{d\overline{yt}}{d\bar{t}}\right)_0 = 0 \tag{21}$$

the energy and rate expressions become

$$\frac{d\bar{h}}{d\bar{t}} - \frac{p_o}{h_o\rho_o}\frac{1}{\bar{\rho}}\frac{d\bar{p}}{d\bar{t}} = 0 \tag{22}$$

and

$$\frac{d\sigma_i}{d\bar{t}} = \frac{b_o}{a_{f,o}}\frac{\sigma_{i,eq} - \sigma_i}{\tau_i} \tag{23}$$

Scaling law.- For a fixed initial composition, the factor $\dfrac{\gamma_o - 1}{2\gamma_o}$ is constant and $1/U_c$ and $p_o/h_o\rho_o$ are functions of T_o. Equations (20) and (23) reveal that, for a fixed value of the product $p_o b_o$ and a given value of T_o, the rate equation remains the same. Thus, for fixed values of T_o and the scaling parameter $p_o b_o$, the set of characteristic equations is invariant and generates identical flow fields. Since for a given T_o, t_o (the time the reference particle enters the expansion fan) is directly proportional to b_o, the product $p_o t_o$ can also be used as the scaling parameter.

Evaluation of enthalpy derivatives.- In order to apply the characteristic equations, it is necessary to obtain expressions for $\left(\frac{\partial h}{\partial \sigma_i}\right)_{p,\rho}$, $\left(\frac{\partial h}{\partial \rho}\right)_{p,\sigma_i}$, and a_f in terms of p, ρ, and σ_i. By utilizing equations (4) and (6) and remembering that x_i is constant, it becomes apparent that

$$\left(\frac{\partial h}{\partial \sigma_i}\right)_{p,\rho} = \sum_{i=1}^{n} \frac{x_i}{\mu_i} \tag{24}$$

and

$$\left(\frac{\partial h}{\partial \rho}\right)_{p,\sigma_i} = -\frac{p\mu}{\rho^2} \sum_{i=1}^{n} \frac{x_i}{\mu_i}\left(\frac{5}{2} + f_i\right) \tag{25}$$

Similarly, the frozen sound speed can be shown to be

$$a_f = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{5}{2} + f_i\right)\frac{x_i}{\mu_i}}{\sum_{i=1}^{n}\left(\frac{3}{2} + f_i\right)\frac{x_i}{\mu_i}} \frac{p}{\rho}} \tag{26}$$

Boundary conditions.- Two basic boundary conditions are prescribed for the expansion region. First, the undisturbed gas in the reservoir is assumed to be in a state of thermodynamic equilibrium - that is, at $t = 0$ before the piston is withdrawn, the equilibrium properties of the gas mixture are known. This condition may be written for the $\bar{y},\bar{t}$ coordinate system as

$$\left.\begin{aligned} \bar{p}(1,\bar{t}) &= \bar{p}_o & \bar{\rho}(1,\bar{t}) &= \bar{\rho}_o \\ \bar{u}(1,\bar{t}) &= \bar{u}_o & \sigma_i(1,\bar{t}) &= \sigma_{i,o} \end{aligned}\right\} \tag{27}$$

The second boundary condition is obtained by considering the unsteady expansion as $\bar{t} \to 0$. A particle processed by the expansion for this second condition has a residence time in the expansion which approaches zero. The particle adjacent to the piston face experiences such an expansion but, because of the short residence time, no relaxation of the rate-controlled vibrational energies toward equilibrium occurs. It can be verified mathematically that, as $\bar{t} \to 0$, the properties throughout the expansion are those of a frozen expansion and the vibrational energies remain at their initial values. This boundary condition can be written as

$$\left.\begin{aligned}
\bar{p}(\bar{y},0) &= \bar{p}_f(\bar{y}) = \bar{y}^{\frac{2\gamma_o}{\gamma_o+1}} \\
\bar{\rho}(\bar{y},0) &= \bar{\rho}_f(\bar{y}) = \bar{y}^{\frac{2}{\gamma_o+1}} \\
\bar{u}(\bar{y},0) &= \bar{u}_f(\bar{y}) = 1 - \bar{y}^{\frac{\gamma_o-1}{\gamma_o+1}} + \bar{u}_o \\
\sigma_i(\bar{y},0) &= \sigma_{i,o}
\end{aligned}\right\} \tag{28}$$

These two boundary conditions are sufficient to allow calculation of the expansion region by the method of characteristics.

Solution Procedure

Finite-difference equations.- In order to establish a method for obtaining a numerical solution, the characteristic and compatibility equations must be written in finite-difference form. By using the general grid nomenclature established in figure 2 and the finite-difference approximations, equations (19) and (20) may be written as equations (29) to (32). Along

$$\bar{y}_P\bar{t}_P - \bar{y}_A\bar{t}_A = \left(\bar{\rho}\bar{a}_f\right)_{AP}\left(\bar{t}_P - \bar{t}_A\right) \tag{29}$$

the relation

$$\bar{u}_P - \bar{u}_A + \frac{\gamma_o - 1}{2\gamma_o}\left(\frac{1}{\bar{\rho}\bar{a}_f}\right)_{AP}\left(\bar{p}_P - p_A\right) - \frac{b_o}{U_c}\left(\frac{\bar{a}_f}{\bar{\rho}\,\dfrac{\partial\bar{h}}{\partial\bar{\rho}}}\sum_{i=1}^{n}\frac{\partial h}{\partial\sigma_i}\frac{\partial\sigma_i}{\partial t}\right)_{AP}\left(\bar{t}_P - \bar{t}_A\right) = 0 \tag{30}$$

applies. Along

$$\bar{y}_P\bar{t}_P - \bar{y}_B\bar{t}_B = -\left(\bar{\rho}\bar{a}_f\right)_{BP}\left(\bar{t}_P - \bar{t}_B\right) \tag{31}$$

the compatibility equation

$$\bar{u}_P - \bar{u}_B - \frac{\gamma_o - 1}{2\gamma_o}\left(\frac{1}{\bar{\rho}\bar{a}_f}\right)_{BP}\left(\bar{p}_P - \bar{p}_B\right) + \frac{b_o}{U_c}\left(\frac{\bar{a}_f}{\bar{\rho}\,\frac{\partial\bar{h}}{\partial\bar{\rho}}}\sum_{i=1}^{n}\frac{\partial h}{\partial\sigma_i}\frac{\partial\sigma_i}{\partial t}\right)\left(\bar{t}_P - \bar{t}_B\right) = 0 \tag{32}$$

holds. The particle path is described by

$$\bar{y}_P\bar{t}_P = \bar{y}_D\bar{t}_D \tag{33}$$

and, along this path, the energy and rate equations

$$\bar{h}_P - \bar{h}_D = \frac{p_o}{h_o\rho_o}\left(\frac{1}{\bar{\rho}}\right)_{DP}\left(\bar{p}_P - \bar{p}_D\right) \tag{34}$$

and

$$\sigma_{i,P} - \sigma_{i,D} = \frac{b_o}{a_{f,o}}\left(\frac{d\sigma_i}{dt}\right)_{DP}\left(\bar{t}_P - \bar{t}_D\right) \tag{35}$$

must be satisfied. These finite-difference equations can be used to prescribe a solution procedure.

Calculation outline.- The grid network generated by the flow field calculation is represented in figure 3. The equilibrium boundary condition prescribes properties along the line $\bar{y} = 1.0$, and along the line $\bar{t} = 0$ the frozen boundary condition applies. Therefore, the calculation begins in the lower right-hand corner of the grid network. A marching process is used to carry the calculation point by point through the desired flow field.

The key operation in computing the flow field is the calculation of values at any unknown point by using the known values at three adjacent points and the finite-difference characteristic equations. This operation can be performed by an iterative process, the steps of which are outlined herein. The nomenclature used is that defined in figure 2. The objective is the determination of the coordinates, properties, vibrational energies, and velocity at point P. Those quantities are known at points A, B, and C from the boundary conditions or preceding calculations.

As the first assumption, the values of the properties at point P are assumed to be identical with those at point A. For equilibrium flow the expansion is a simple wave region and properties along a characteristic line similar to line AP are constant. Changes in properties along line AP in the present study are due only to nonequilibrium effects and are generally smaller than those along line BP which are basically due to the expansion process. Equating property values at point P to those at point A should therefore provide more rapid iteration convergence than equating them to the average of values at points A and B. Equations (29) and (31) are solved simultaneously to give the coordinates of point P. The compatibility relations along lines AP and BP, equations (30) and (32), are applied to obtain improved values of velocity and pressure at point P. By using equation (33) the particle path through point P is extended backward and its point of intersection, point D, with line CA or CB is obtained. Properties at point D are determined by using a linear interpolation between points C and A or C and B. Vibrational rate equations of the form given in equation (35) are applied along the particle path (line DP) to obtain the vibrational energy value at point P. The energy equation, equation (34), is also used along the particle path to get an improved value of enthalpy. The caloric and thermal equations of state yield new values of temperature and density at point P. Thus, an entirely new set of quantities is calculated for the point. These improved values at point P are then used in a second-order approximation scheme for the next iteration. When two consecutive iterations produce temperature values within an acceptable accuracy, the calculation is performed at the next point. The process is repeated until values have been calculated at all desired points.

Computer program.- A program, written in FORTRAN IV language for the IBM 7094 electronic data processing system, was developed to perform the required calculations. This program may be used to treat a number of chemical species and their associated vibrational rate equations. Numerical accuracy of the program is good provided that the pressure drop throughout the expansion does not exceed two orders of magnitude. In the present application, this limitation is not serious inasmuch as the vibrational energies have either essentially frozen or become insignificant by the time the gas has experienced that degree of expansion.

Calculated results may be printed out in two ways. The properties, velocities, and vibrational energies can be printed out either at each point in the flow field for the coordinates of that point or at various points along specified particle paths. A numerical integration routine is included in the program to calculate the distance traveled by the specific particles.

Equilibrium Solution

When the residence time of a gas particle in the expansion is adequate to allow adjustment of the vibrational energies to their equilibrium values, the expansion is isentropic. The analysis of an equilibrium expansion is presented herein. The composition of the gas mixture is assumed to remain constant throughout the expansion.

Since the process is isentropic, the expression

$$ds = \frac{c_p\, dT}{T} - \frac{R}{\mu}\frac{dp}{p} = 0 \tag{36}$$

applies and can be integrated to give

$$\bar{p} = \frac{p}{p_o} = \exp\left[\mu \sum_{i=1}^{n} \frac{x_i}{\mu_i}\left(\frac{5}{2} + f_i\right) ln \frac{T}{T_o}\right] \exp\left(\sum_{i=2,4,6,\ldots}^{n} \mu \frac{\theta_i x_i}{\mu_i}\left\{\frac{1}{T\left[1 - \exp\left(-\frac{\theta_i}{T}\right)\right]} - \frac{1}{T_o\left[1 - \exp\left(-\frac{\theta_i}{T_o}\right)\right]} + \frac{ln \dfrac{\exp\left(\frac{\theta_i}{T_o}\right) - 1}{\exp\left(\frac{\theta_i}{T}\right) - 1}}{\theta_i}\right\}\right) \tag{37}$$

The differential equation describing the flow through an isentropic unsteady expansion

$$du = \left(\frac{dh}{a_{eq}}\right)_s \tag{38}$$

is numerically integrated to obtain the velocity throughout the expansion. The equilibrium sound speed a_{eq} can be shown to be

$$a_{eq} = \left\{ \frac{\displaystyle\sum_{i=1}^{n}\left(\frac{5}{2} + f_i\right)\frac{x_i}{\mu_i} + \frac{1}{T^2}\sum_{i=2,4,6,\ldots}^{n}\frac{x_i\theta_i^2 \exp\left(\frac{\theta_i}{T}\right)}{\left[\exp\left(\frac{\theta_i}{T}\right) - 1\right]^2}}{\displaystyle\sum_{i=1}^{n}\left(\frac{3}{2} + f_i\right)\frac{x_i}{\mu_i} + \frac{1}{T^2}\sum_{i=2,4,6,\ldots}^{n}\frac{x_i\theta_i^2 \exp\left(\frac{\theta_i}{T}\right)}{\left[\exp\left(\frac{\theta_i}{T}\right) - 1\right]^2}} \frac{p}{\rho} \right\}^{1/2} \tag{39}$$

for the gas model in the present study.

Values of T/T_o are chosen in small increments from 1.0 to zero. For each value of T/T_o, the pressure is calculated by using equation (37) and the density is found by using the thermal equation of state. The value of the coordinate $\bar{y}$ is found for each value of T/T_o from the expression

$$\bar{y} = \bar{\rho}\bar{a}_{eq} \tag{40}$$

Equation (38) is numerically integrated over the expansion to obtain values of velocity.

Description of Gas Model

A gas mixture of 21 percent O_2 and 79 percent N_2 was used to approximate air for calculation purposes. Conditions at which vibrational deexcitation is the dominant rate process were chosen. Dissociation of molecular species is assumed to be negligible. This assumption is made valid by the prescribing of minimum pressures for each initial temperature. The presence of nitric oxide NO is ignored, as it becomes appreciable only at the higher temperatures considered and, at those temperatures, produces very small changes in the thermodynamic properties.

The constants used in computing the vibrational relaxation times of O_2 and N_2 were obtained by curve fitting the values of reference 7 and are listed in the following table:

Physical constant	Value for –	
	O_2	N_2
θ_i, °K	2270	3390
A_i, atm-sec	0.1424	560.61
B_i	0.3718	-0.0995
C_i	179.33	163.63

Experiments described in reference 8 indicate that N_2 vibrational relaxation times in expanding flows are approximately 15 times as fast as those measured in compressive-flow experiments such as that of reference 7. These findings are substantiated in reference 9 for the expansion of both pure N_2 and air. The present calculations were made by using data from reference 7 as a base. By changing the scaling parameter $p_o t_o$ for a particular expansion, the results can readily be adjusted so that the faster deexcitation rates of references 8 and 9 may be used. The procedure for making this change is described subsequently.

It is further assumed that the N_2 and O_2 vibrational relaxation processes are independent and therefore no exchange of vibrational energy between the separate species occurs during collisions. The effect of an exchange in a compressive-flow situation is discussed in reference 10 where it was concluded that the vibrational relaxation rate of the N_2 molecule is increased by a vibrational energy exchange with the more rapidly relaxing O_2 molecule. No experimental evidence of a similar exchange in expanding flows is available, and vibrational energy exchange between excited molecules of the separate species is therefore neglected in the present analysis.

RESULTS AND DISCUSSION

The structure of a centered one-dimensional unsteady expansion in an N_2 and O_2 mixture closely approximating air was calculated for a number of flows. Results are presented along particle paths through the expansion. The correlating parameter $p_o t_o$, the product of initial pressure and the time the particle entered the expansion, designates the various particle paths. Numerical results are presented in figures 4 to 7 for initial temperatures from 2000° K to 4000° K in 500° increments. The pressure limitations within which the results are valid are stated in the figures. These limits are defined as the pressures at which the vibrational energy is one order of magnitude larger than the energies involved in dissociation. Vibrational energies, thermodynamic properties, and velocities are displayed as functions of the reduced time coordinate t/t_o, where t is the actual particle time and t_0 is the time at which the particle entered the expansion fan.

As already mentioned, recent experiments have indicated that vibrational relaxation rates in expanding N_2 and air are about 15 times as fast as the values measured behind shock waves. In the present calculations, the shock data of reference 7 are used as a base. In order to adjust the calculations to allow for the assumption of the more rapid rates, the scaling parameter $p_0 t_0$ appearing in figures 4 to 9 must be multiplied by 1/15.

The trends exhibited in the unsteady expansion of a vibrationally relaxing gas are found to be quite similar to those found in the quasi-one-dimensional nonequilibrium expansion in a hypersonic nozzle. These similarities are pointed out in the ensuing discussion.

Figure 4 depicts the variation of the vibrational energies of particles processed by an unsteady expansion. The equilibrium and frozen curves represent two limiting cases. The intermediate curves indicate the amount of vibrational nonequilibrium which exists along various particle paths.

Several observations can be made. First, the total amount of vibrational energy converted back to translational and rotational energy modes is highly dependent upon the pressure and the residence time of the particle, as characterized by the product $p_0 t_0$. An increase in initial pressure or residence time results in increased adjustment of the vibrational energies toward their equilibrium values.

In some near-equilibrium flows, the O_2 vibrational energy is less than the value which would be obtained in an equilibrium expansion. This phenomenon can be seen in figure 4(b). The vibrational energy of the O_2 molecules approaches equilibrium much more rapidly than the vibrational energy of the N_2 molecules. The O_2 molecules attain values of vibrational energy which are in equilibrium with the local translational temperature. However, since the N_2 vibrational energy is still in a nonequilibrium state higher than the equilibrium value, the translational temperature remains below that of an equilibrium expansion. The vibrational energy of the O_2 molecules adjusts to the equilibrium value for this temperature and therefore undershoots the value which would be attained in an expansion where both the N_2 and the O_2 vibrational energies remain in equilibrium throughout.

Another observation of significance is that the vibrational energies relax rapidly during the initial portion of the expansion and then the rate of adjustment quickly diminishes and the vibrational energies approach constant values as further expansion occurs. This freezing phenomenon can be attributed to the fact that the relaxation times are strongly dependent upon both temperature and pressure, as is evident from equation (8). As the gas is processed by the expansion, the temperature and pressure decrease rapidly and the relaxation times thus increase until the change of vibrational energy becomes negligible. Calculations made by carrying the expansions to pressures lower than those presented indicate that any further vibrational relaxation is negligible. This freezing of vibrational energy along a particle path in an unsteady expansion is very similar to the freezing which occurs in hypersonic nozzles. A comparison can readily be made between the results presented herein and the results presented in reference 11 for the hypersonic nozzle.

Thermodynamic properties of the expansion also reflect the degree of nonequilibrium which exists in the flow. Static temperature, defined for this work as the translational and rotational temperature of the gas, proves to be the property most affected by the relaxation process. Vibrational relaxation toward equilibrium returns energy to the translational and rotational modes. This energy manifests itself as an increase in the temperature and velocity of the gas. If vibrational equilibrium exists, the maximum temperature exists throughout the expansion. As $p_o t_o$ increases, the energy returned to the translational and rotational modes from the excited vibrational state increases, and so the temperatures increase. This behavior is demonstrated in figure 5. The dependence of pressure and density upon the degree of nonequilibrium is indicated in figure 6.

The effect of the rate processes on the flow velocity is shown in figure 7. As the parameter $p_o t_o$ is increased, vibrational relaxation increases, more energy appears in the translational mode, and higher velocities are attained. Maximum flow velocity exists for equilibrium flow.

Figures 8 and 9 are presented to permit practical applications of the results. If T_o and the product $p_o t_o$ are known, the effects of nonequilibrium on the thermodynamic properties and on flow variables can be obtained by using figures 3 to 7. When a desired velocity u is reached in the expansion at a distance l from the center of the expansion and when the undisturbed equilibrium temperature and pressure are known, figures 8 and 9 may be used to obtain the value of t_o. The procedure for obtaining this value is outlined in the next paragraph.

The values of p_o, T_o, and l are known, and the reference velocity U_c is given by $U_c = 2\sqrt{\frac{\gamma_o RT}{\mu}\frac{1}{\gamma - 1}}$. A value of slightly less than the desired u is assumed, and the curve for frozen flow in figure 8 is used to get $l/U_c t_o$ and thus an initial approximation for t_o. If this value of t_o is used to obtain the parameters $p_o t_o$ and $l/U_c t_o$ and if T_o is known, the ratio of nonequilibrium velocity to frozen velocity u/u_f can be determined from figure 9. Since the velocity value used in figure 8 is actually u_f, u is now determined. If this u is not the desired velocity, a new value of t_o is assumed and the procedure is repeated. This iterative scheme is continued until the desired velocity is obtained. The corresponding t_o is then the correct one for the nonequilibrium expansion and is used to form the parameter $p_o t_o$ for use in evaluating a given expansion from figures 3 to 7.

Values of $l/U_c t_o$ greater than those presented in figure 9 represent expansion beyond the point at which the flow becomes essentially frozen. For such an expansion, accurate approximations of t_o can be obtained by using the curve in figure 9 for $\frac{l}{U_c t_o} = 40$ in determining u/u_f. Also, curves are presented in figure 8 for determining t_o for equilibrium expansions from various initial temperatures.

CONCLUDING REMARKS

Methods are presented for the calculation of the one-dimensional unsteady expansion of a mixture of gases in which the vibrational energies may be either in equilibrium or rate controlled. The method of characteristics, formulated in a Lagrangian frame of reference, is used in the nonequilibrium analysis. Calculated results, obtained by using the IBM 7094 electronic data processing system, are presented over a range of initial temperatures from 2000° K to 4000° K. These results, given in terms of flow properties and vibrational energies along specific particle paths, agree well with the trends expected from physical reasoning. Curves are included to permit practical applications of the calculated results.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., September 2, 1966,
129-01-08-16-23.

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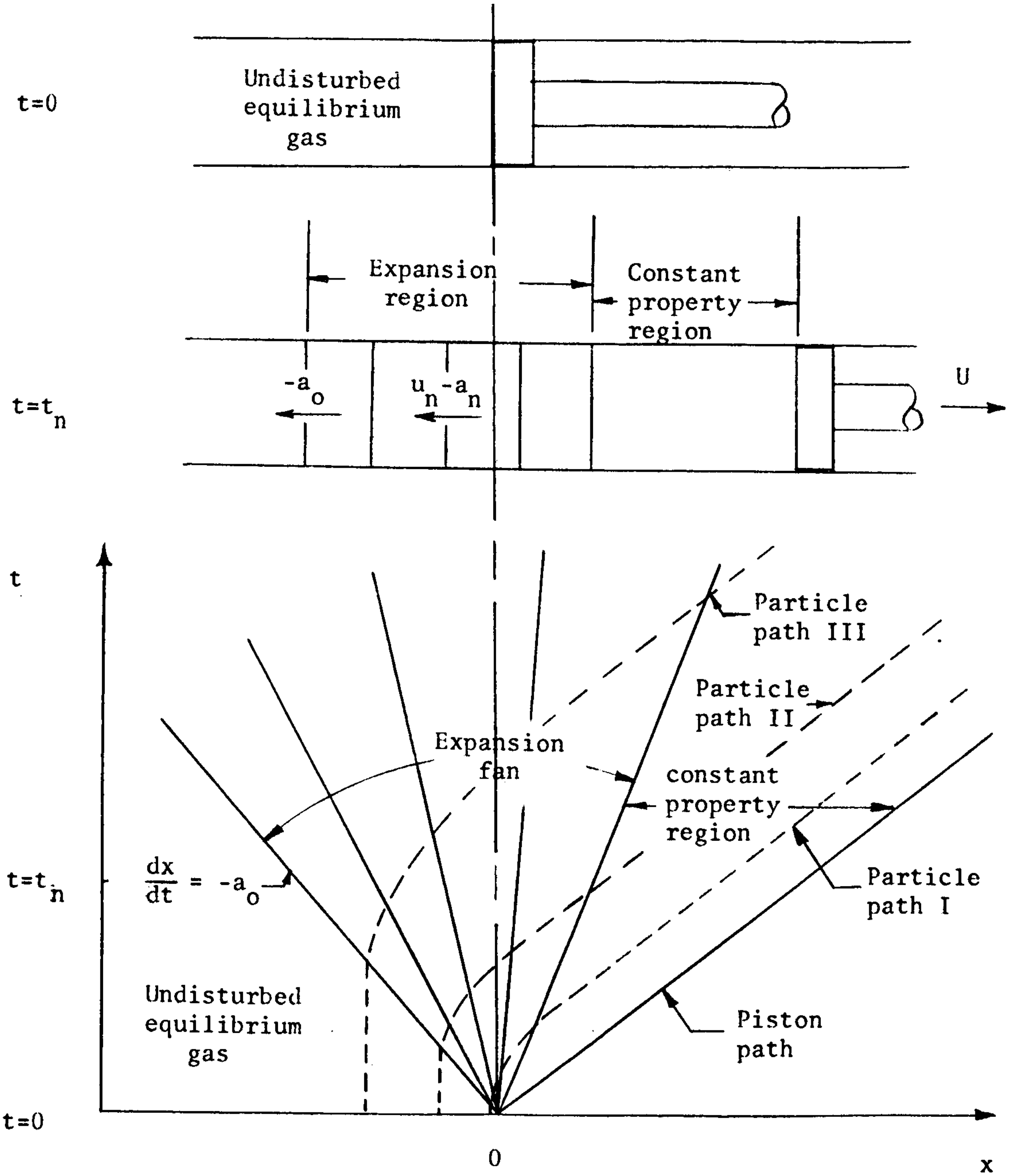


Figure 1.- Distance-time diagram of an unsteady expansion.

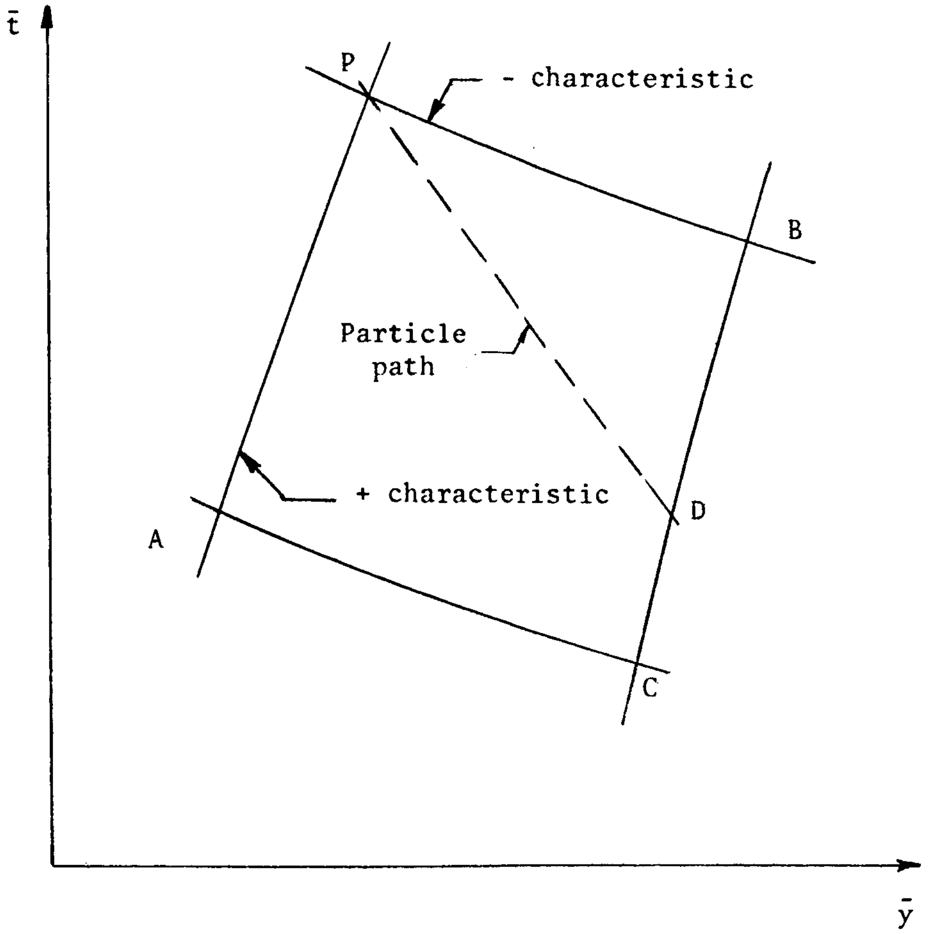


Figure 2.- General grid nomenclature.

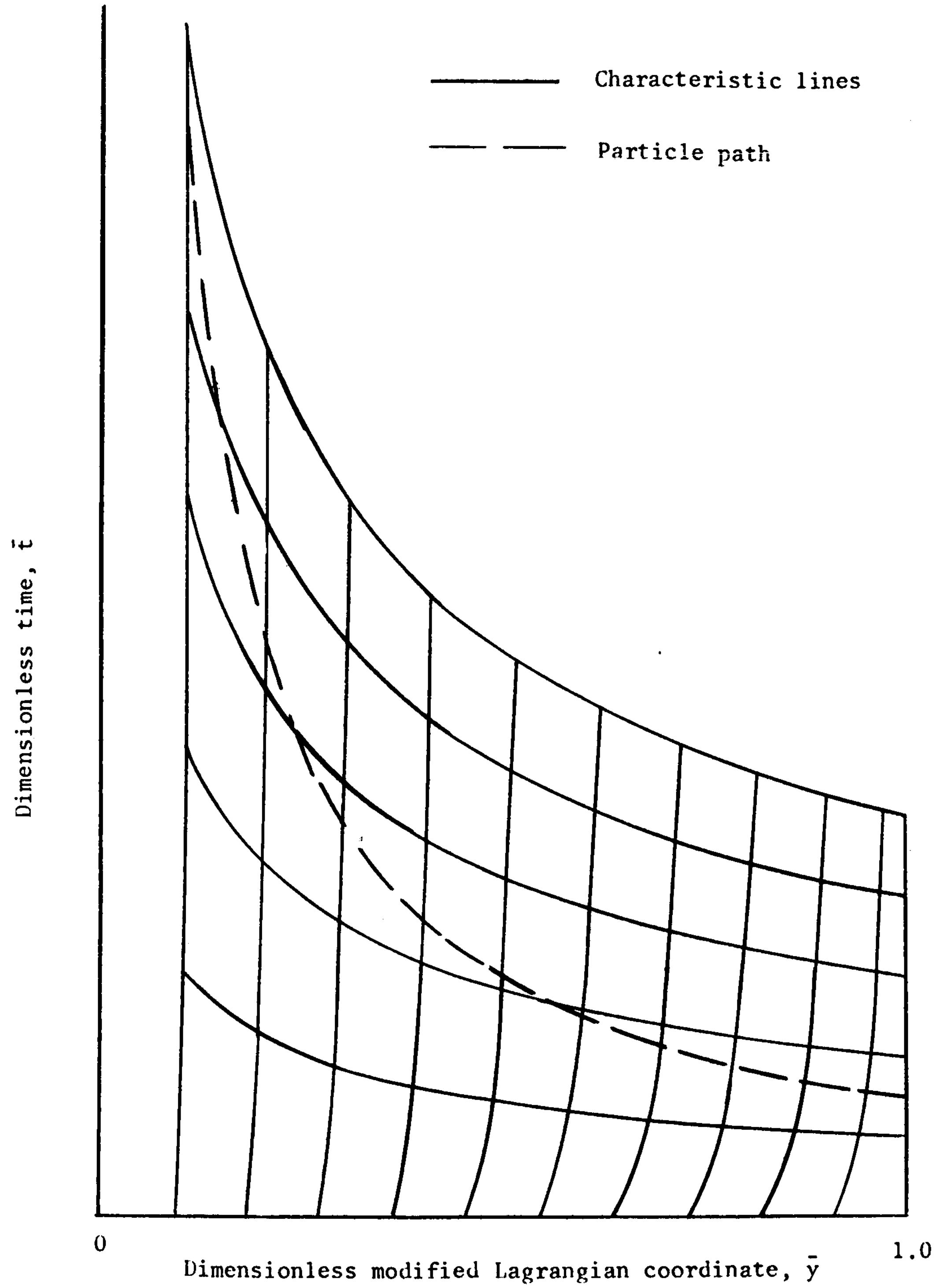
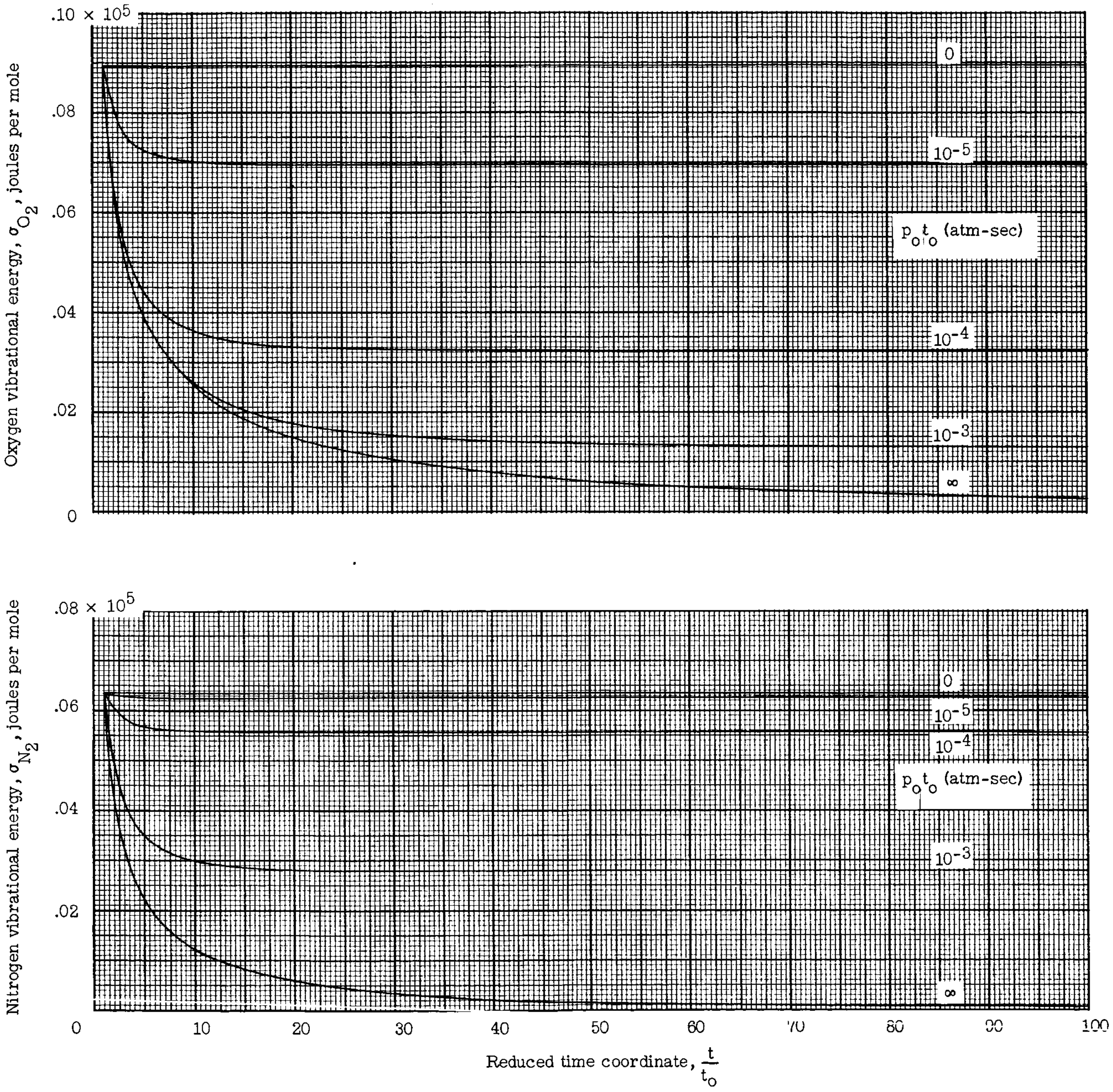
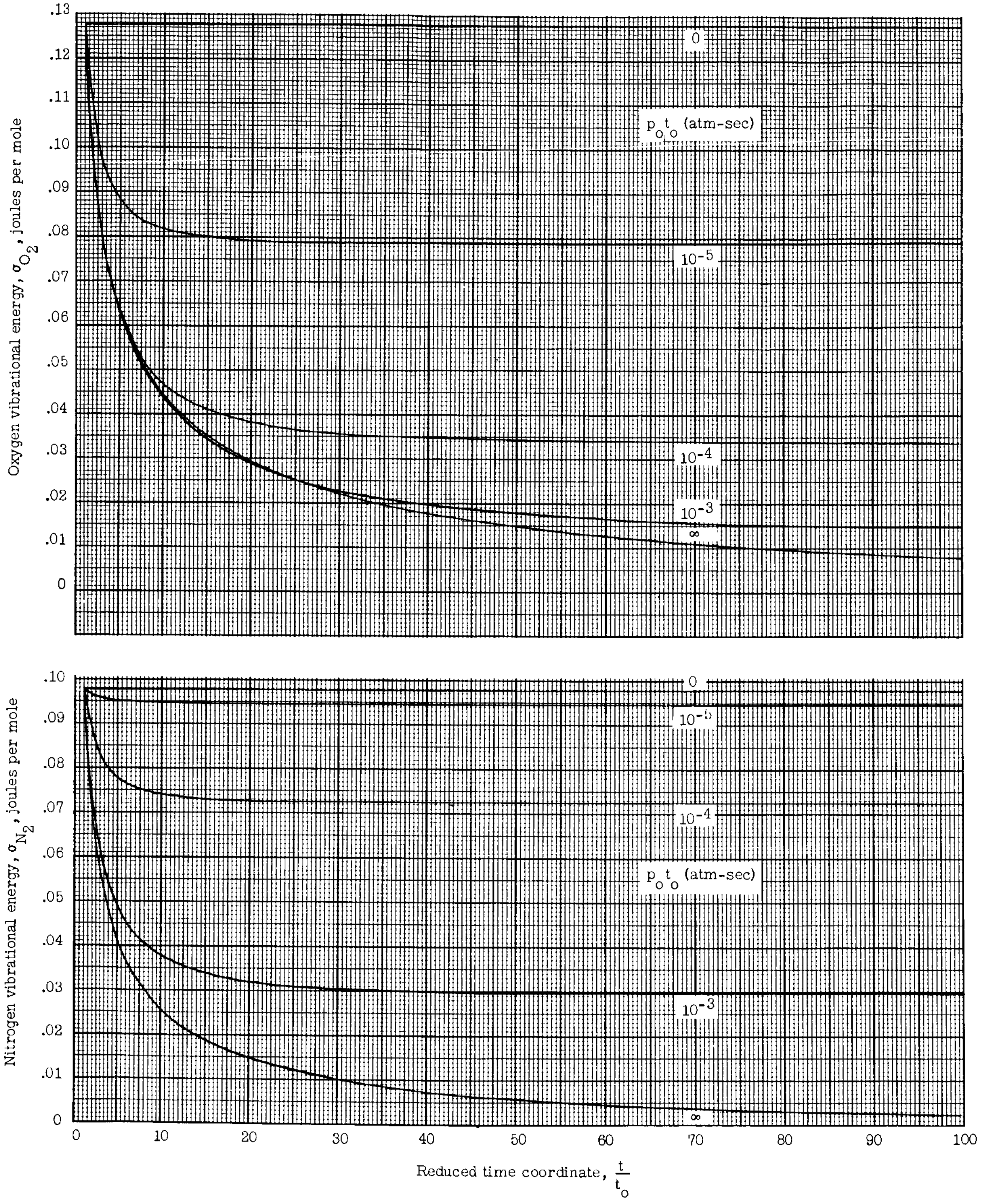


Figure 3.- Complete grid network.



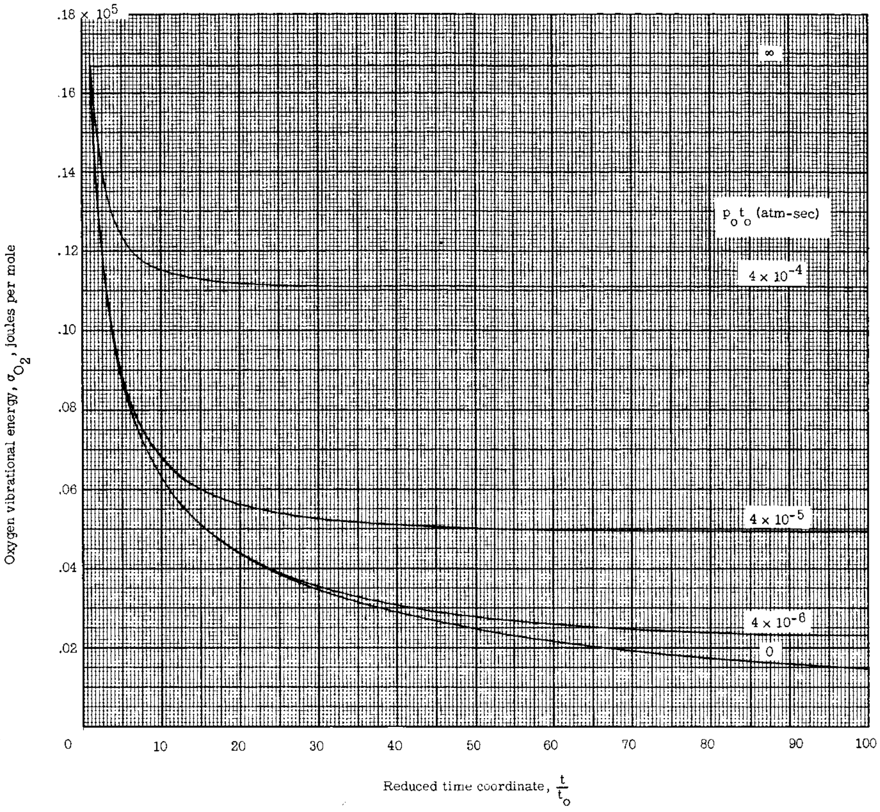
(a) $T_0 = 2000^0$ K; $p_0 > 0.015$ atm.

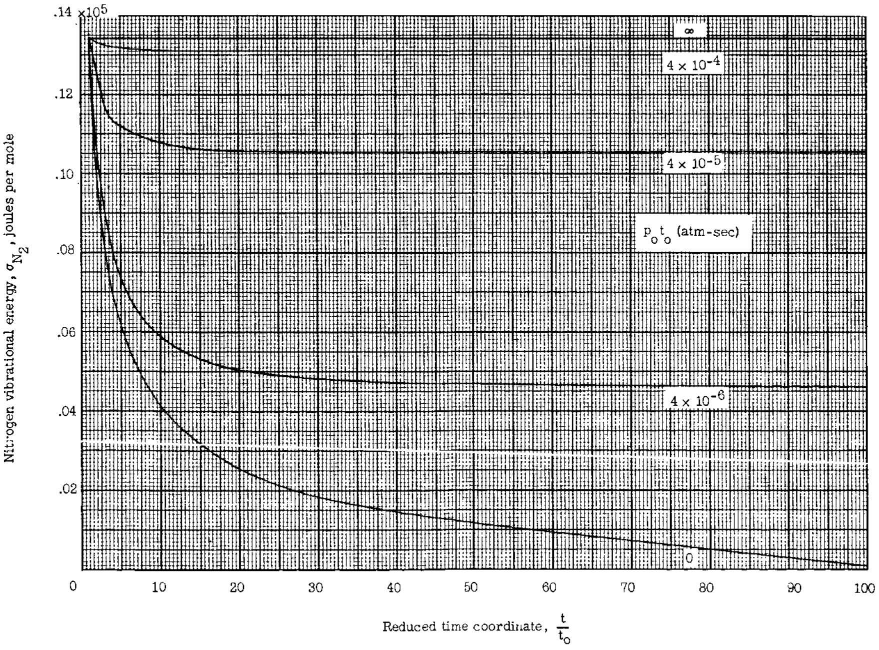
Figure 4.- Variation of oxygen and nitrogen vibrational energies in a nonequilibrium unsteady expansion.



(b) $T_0 = 2500^0$ K; $p_0 > 2.9$ atm.

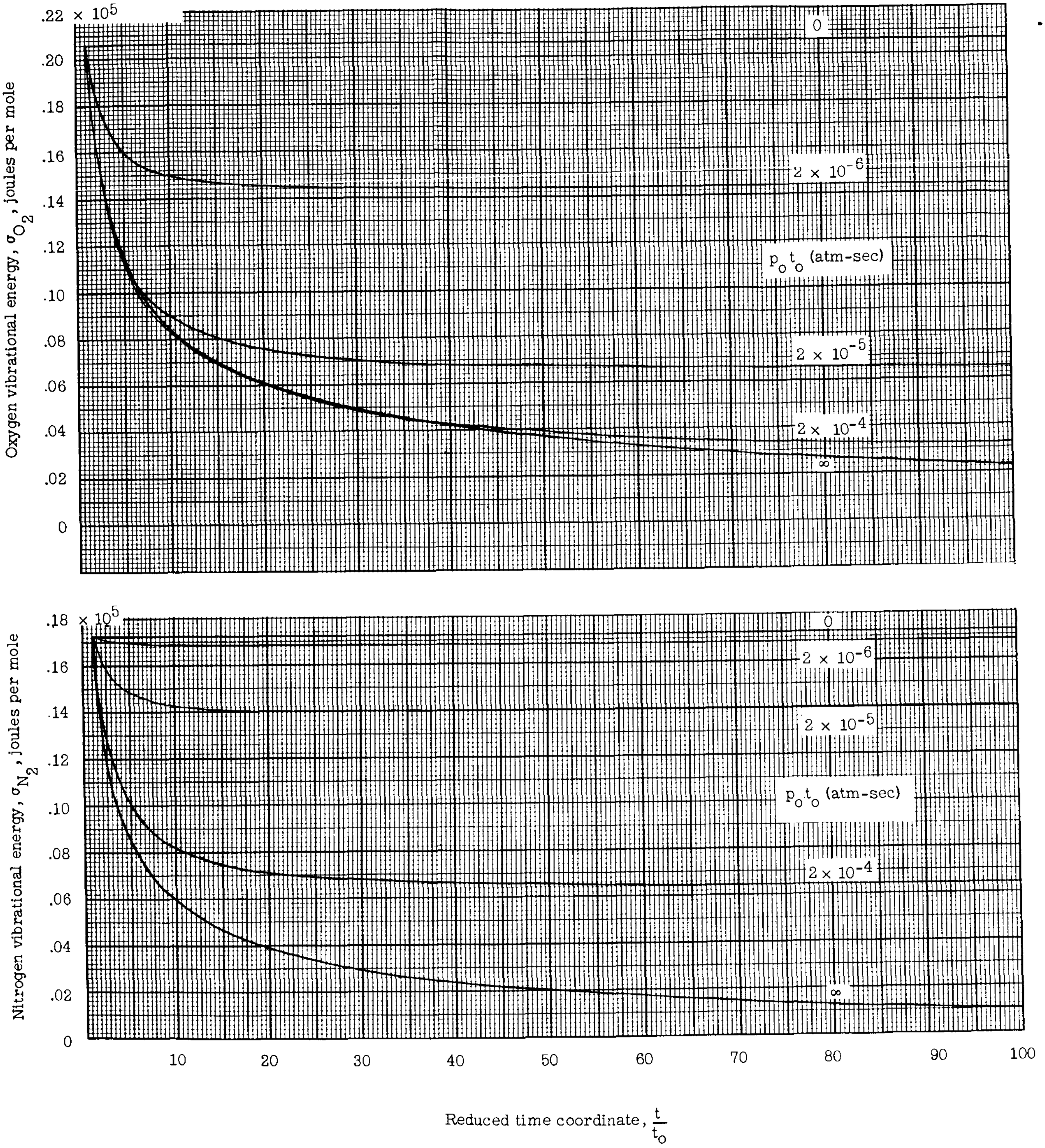
Figure 4.- Continued.





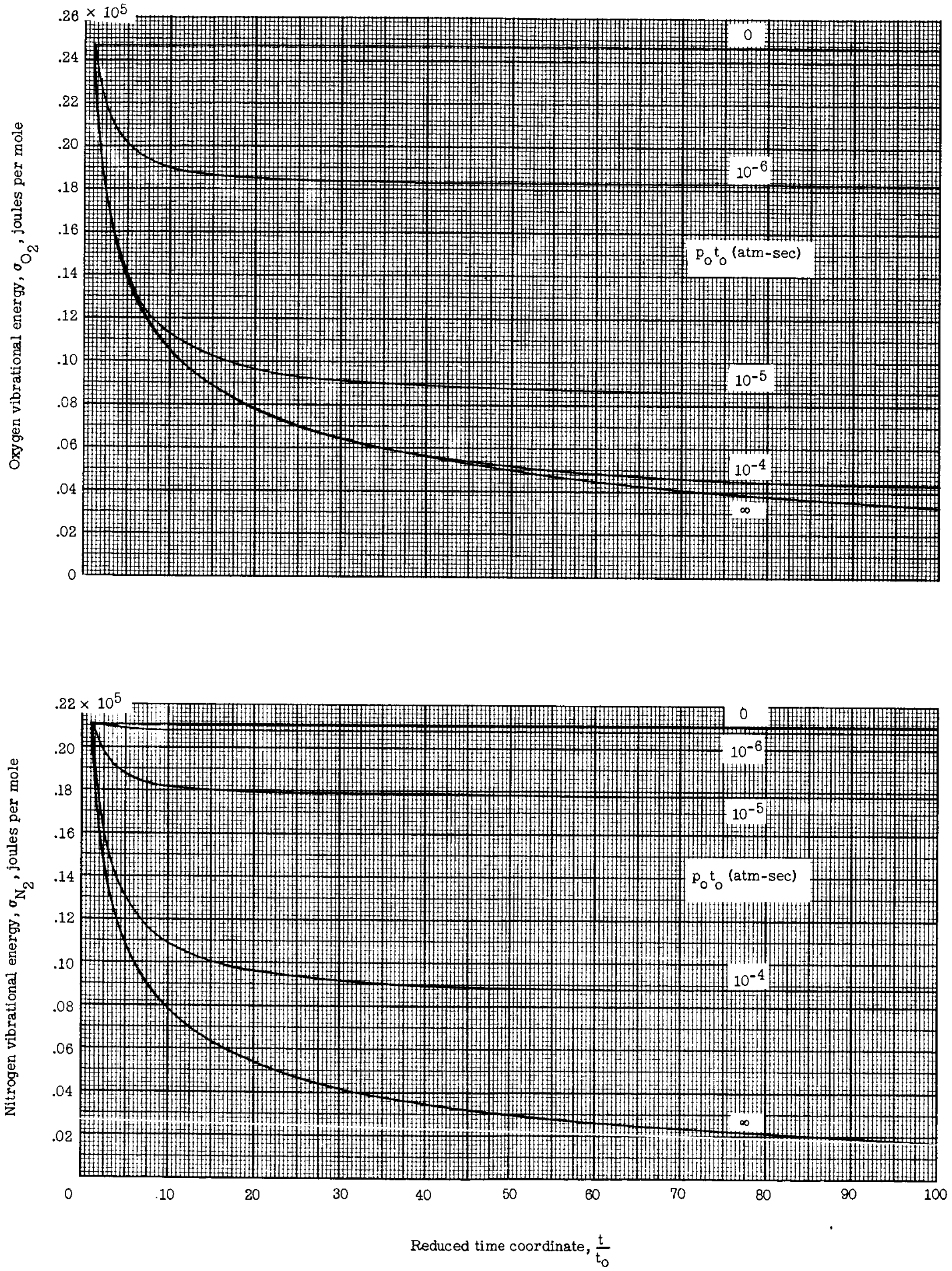
(c) $T_0 = 3000^0$ K; $p_0 > 90$ atm.

Figure 4.- Continued.



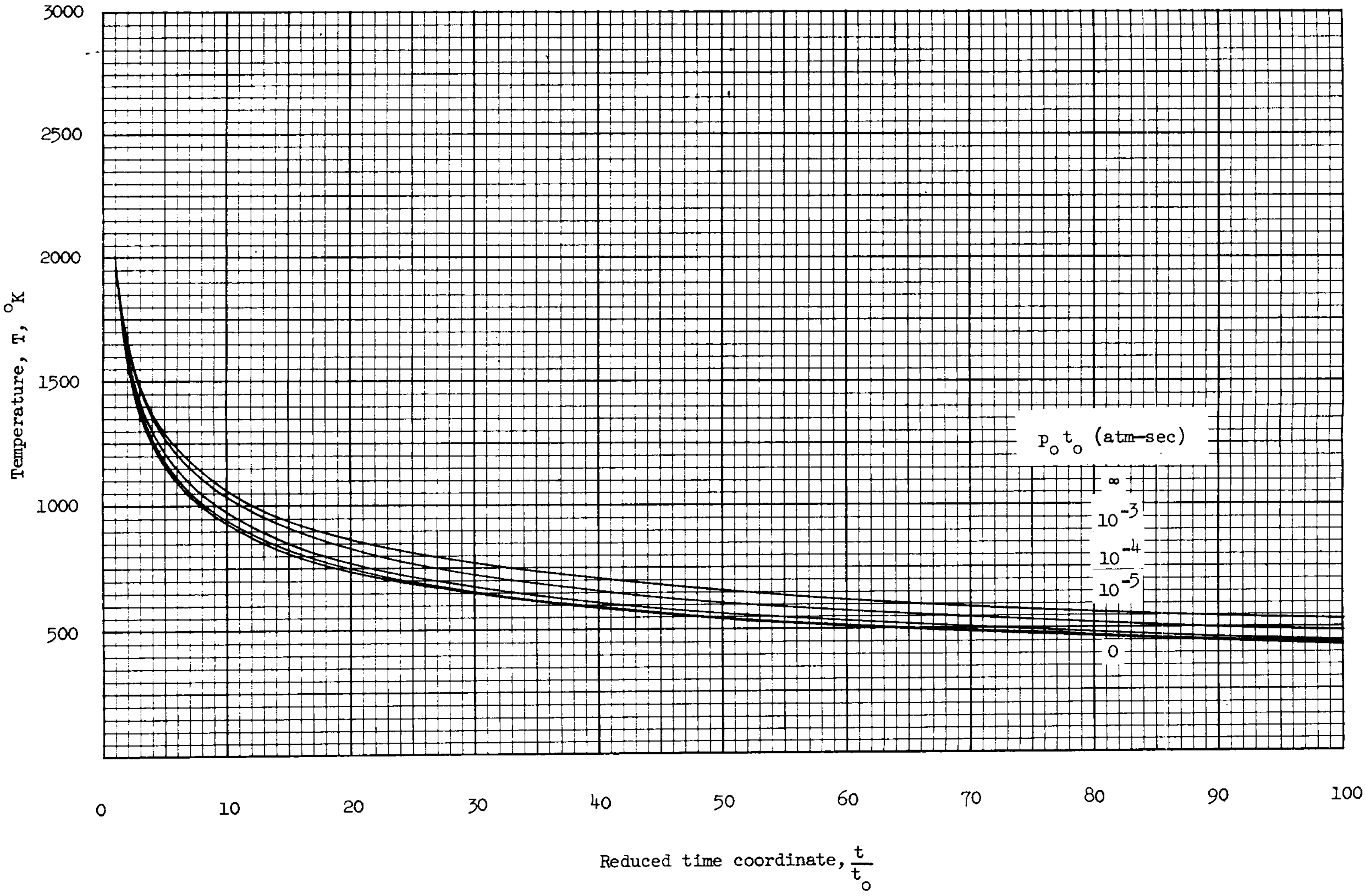
(d) $T_0 = 3500^0$ K; $p_0 > 1000$ atm.

Figure 4.- Continued.



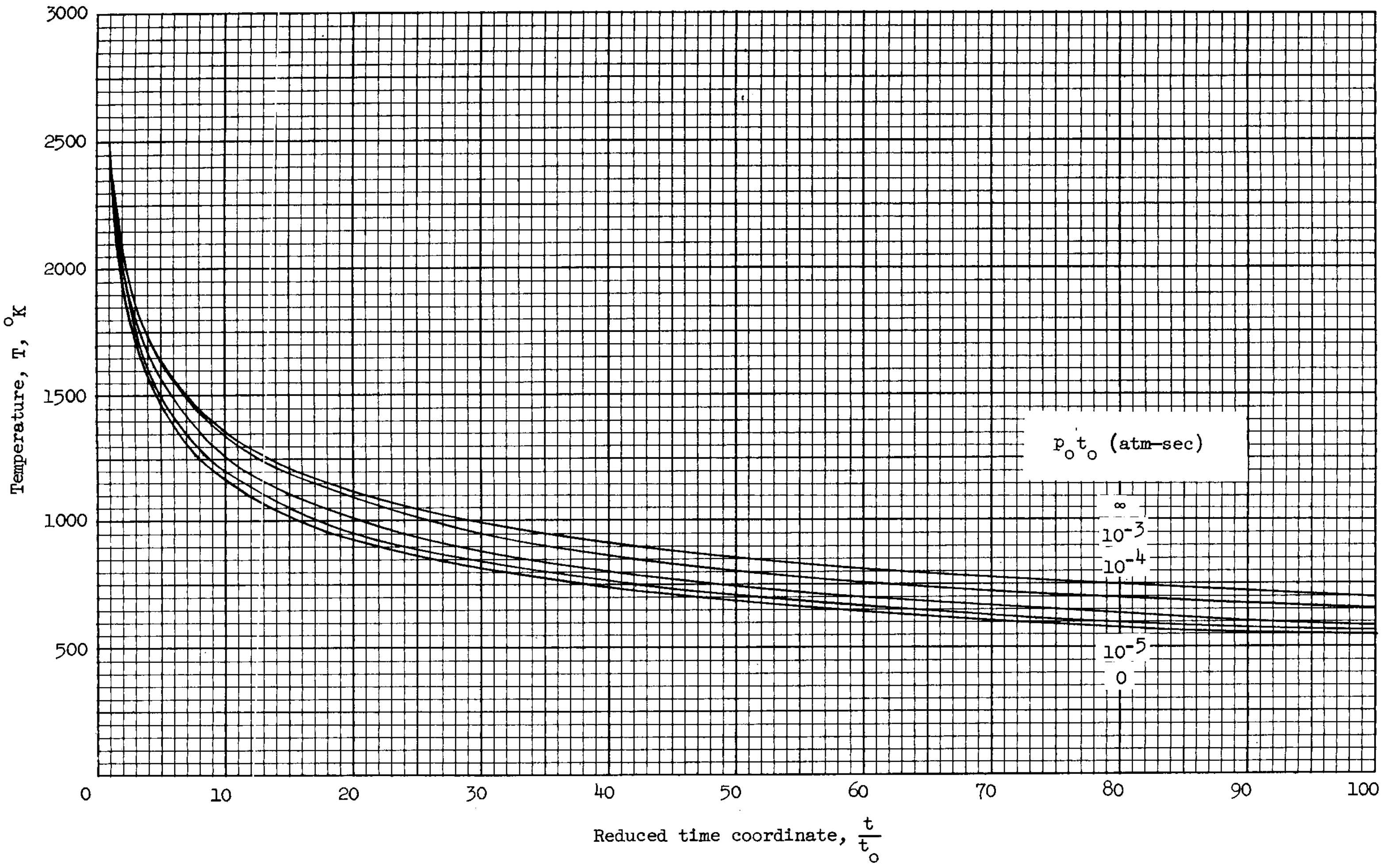
(e) $T_0 = 4000^\circ$ K; $p_0 > 6000$ atm.

Figure 4.- Concluded.



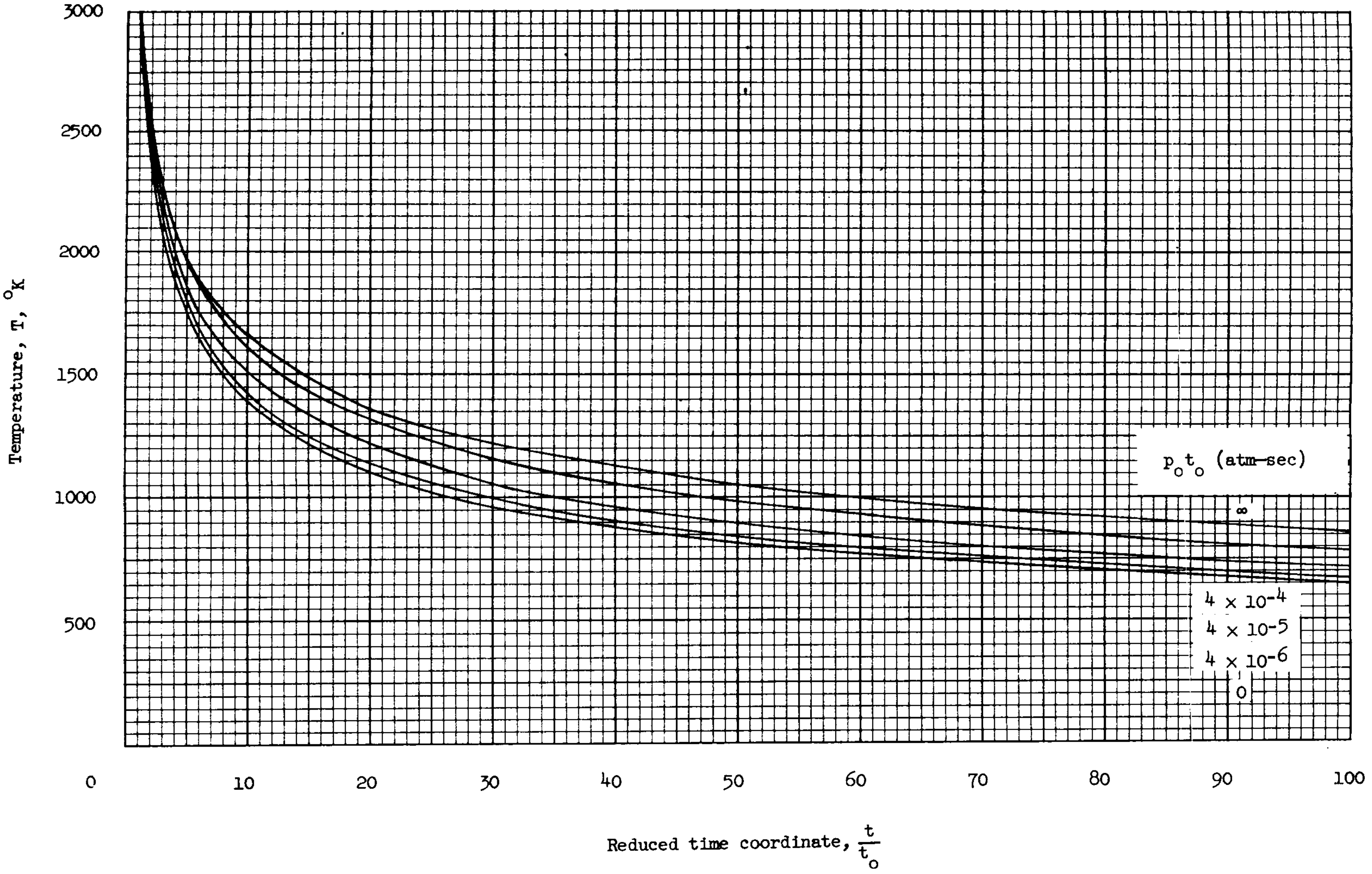
(a) $T_0 = 2000^0$ K; $p_0 > 0.015$ atm.

Figure 5.- Temperature variation in a nonequilibrium unsteady expansion.



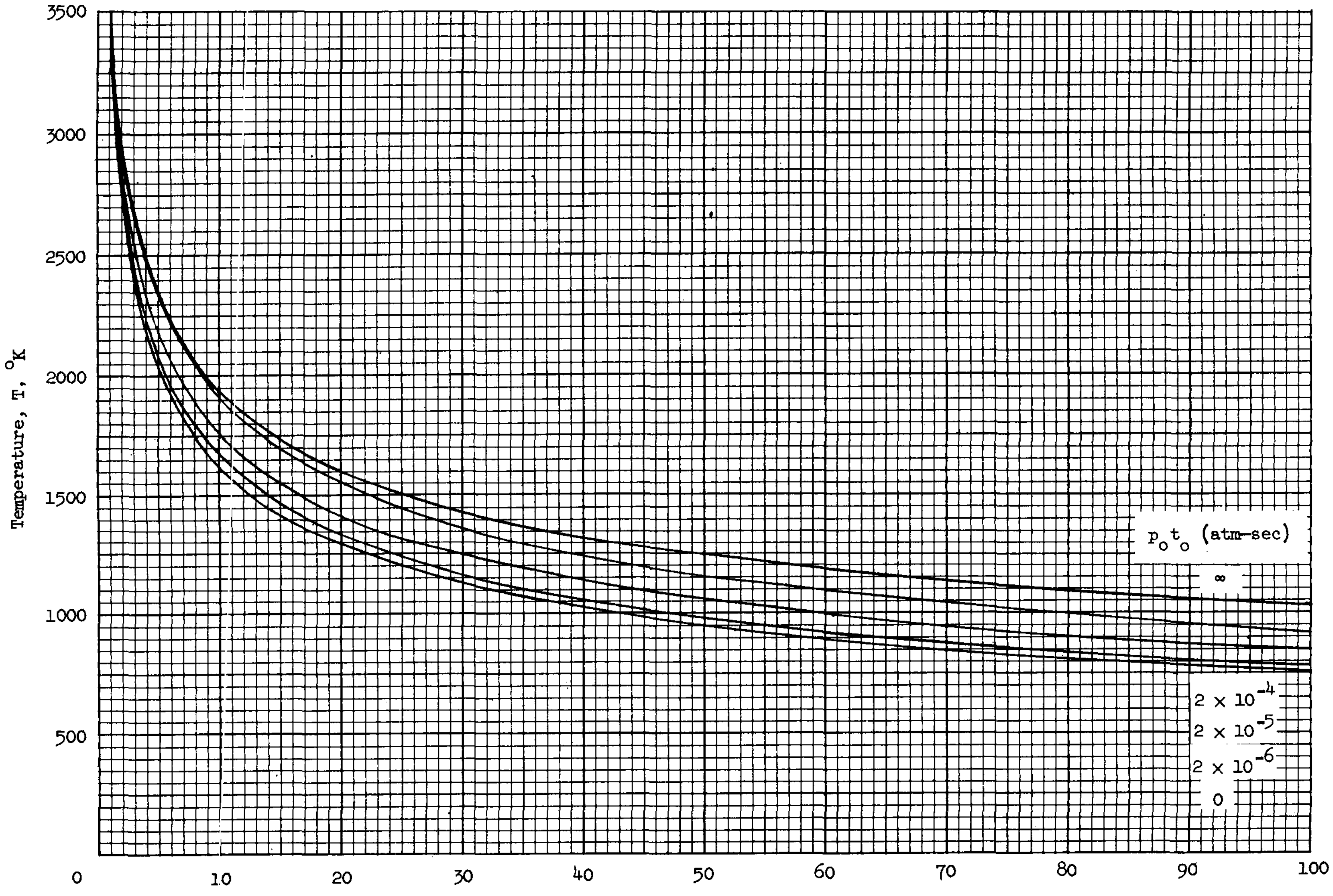
(b) $T_0 = 2500^0$ K; $p_0 > 2.9$ atm.

Figure 5.- Continued.



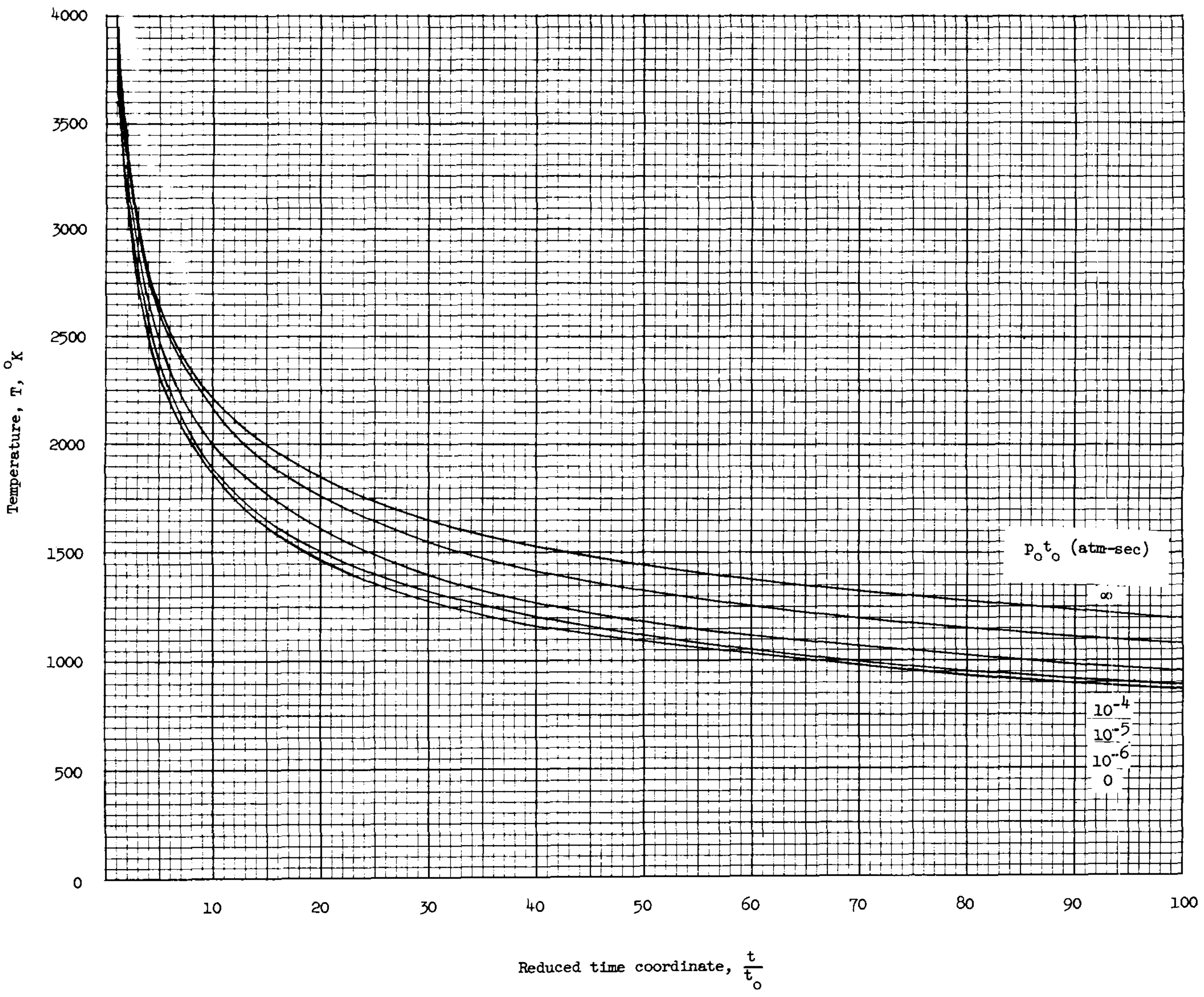
(c) $T_0 = 3000^0$ K; $p_0 > 90$ atm.

Figure 5.- Continued.



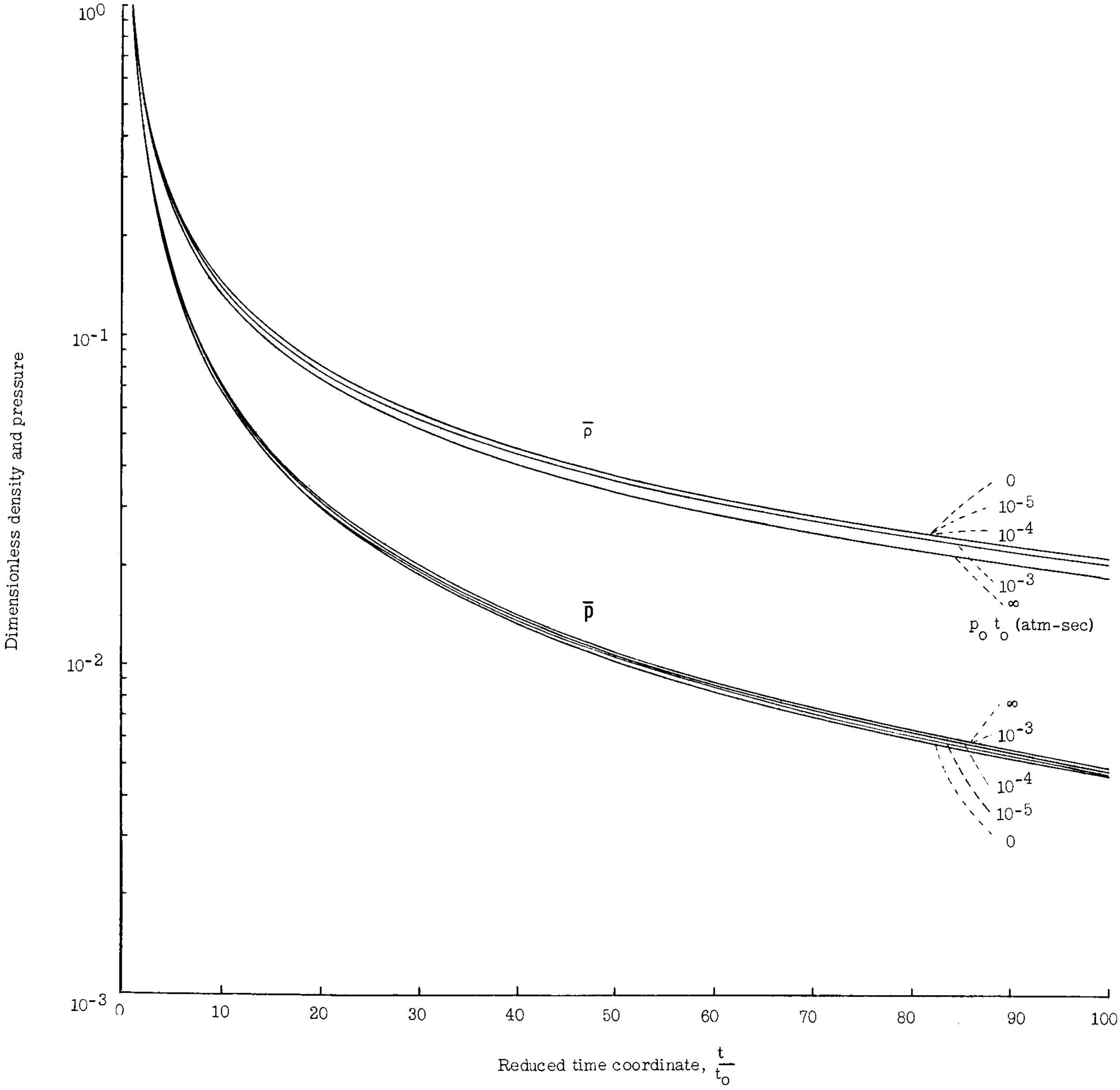
(d) $T_0 = 3500^0$ K; $p_0 > 1000$ atm.

Figure 5.- Continued.



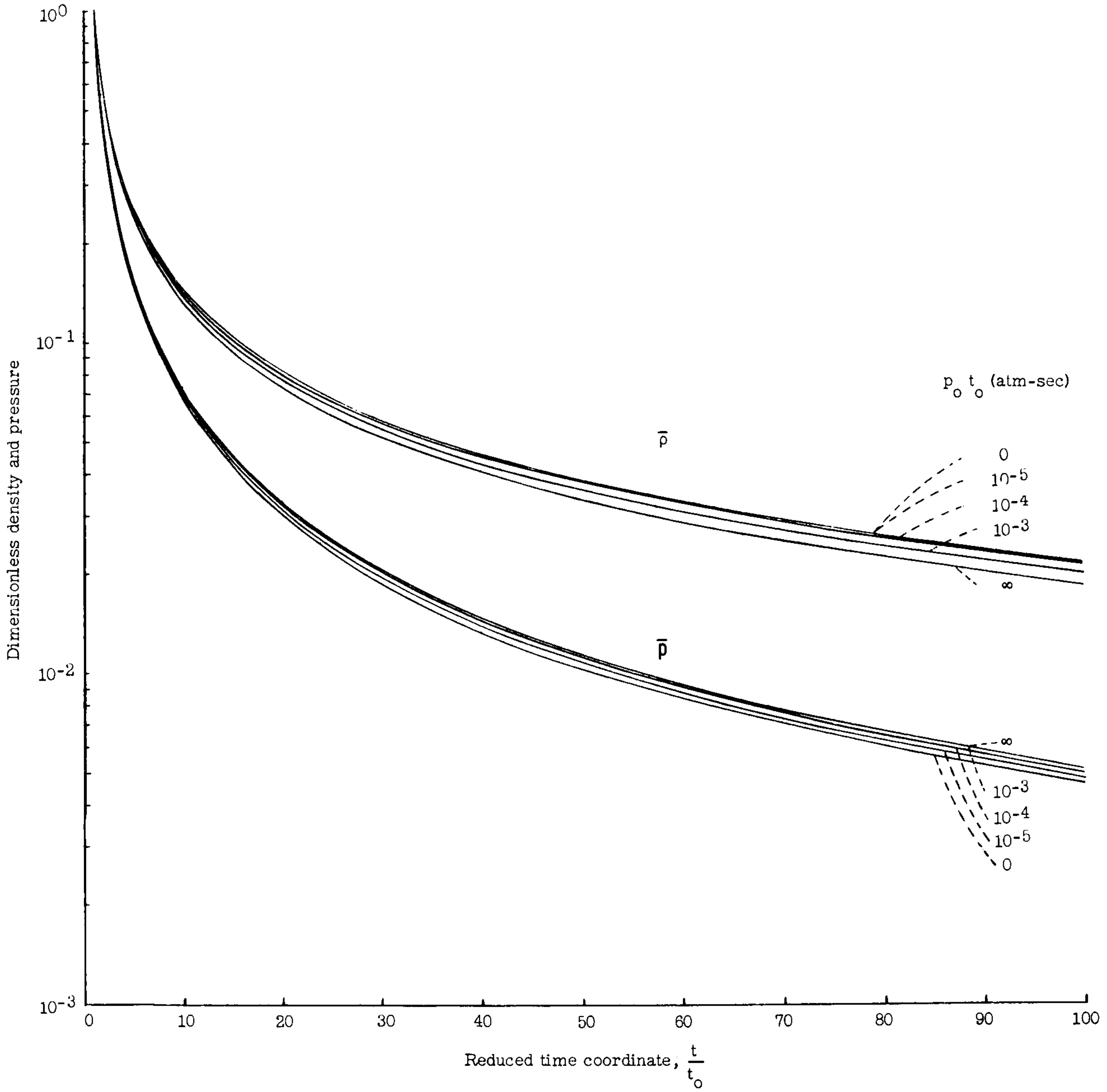
(e) $T_0 = 4000^0$ K; $p_0 > 6000$ atm.

Figure 5.- Concluded.



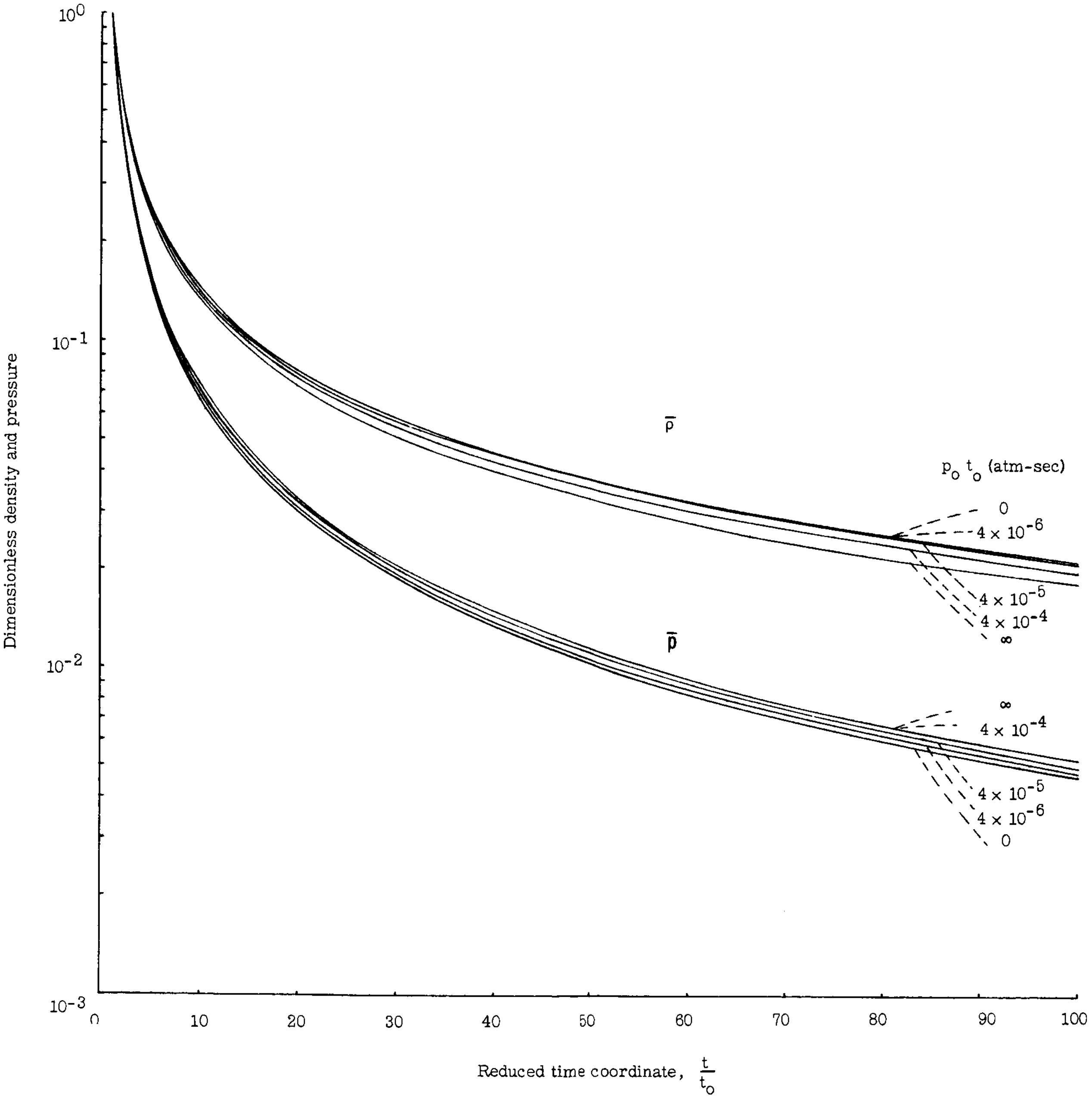
(a) $T_0 = 2000^0$ K; $p_0 > 0.015$ atm.

Figure 6.- Density and pressure variation in a nonequilibrium unsteady expansion.



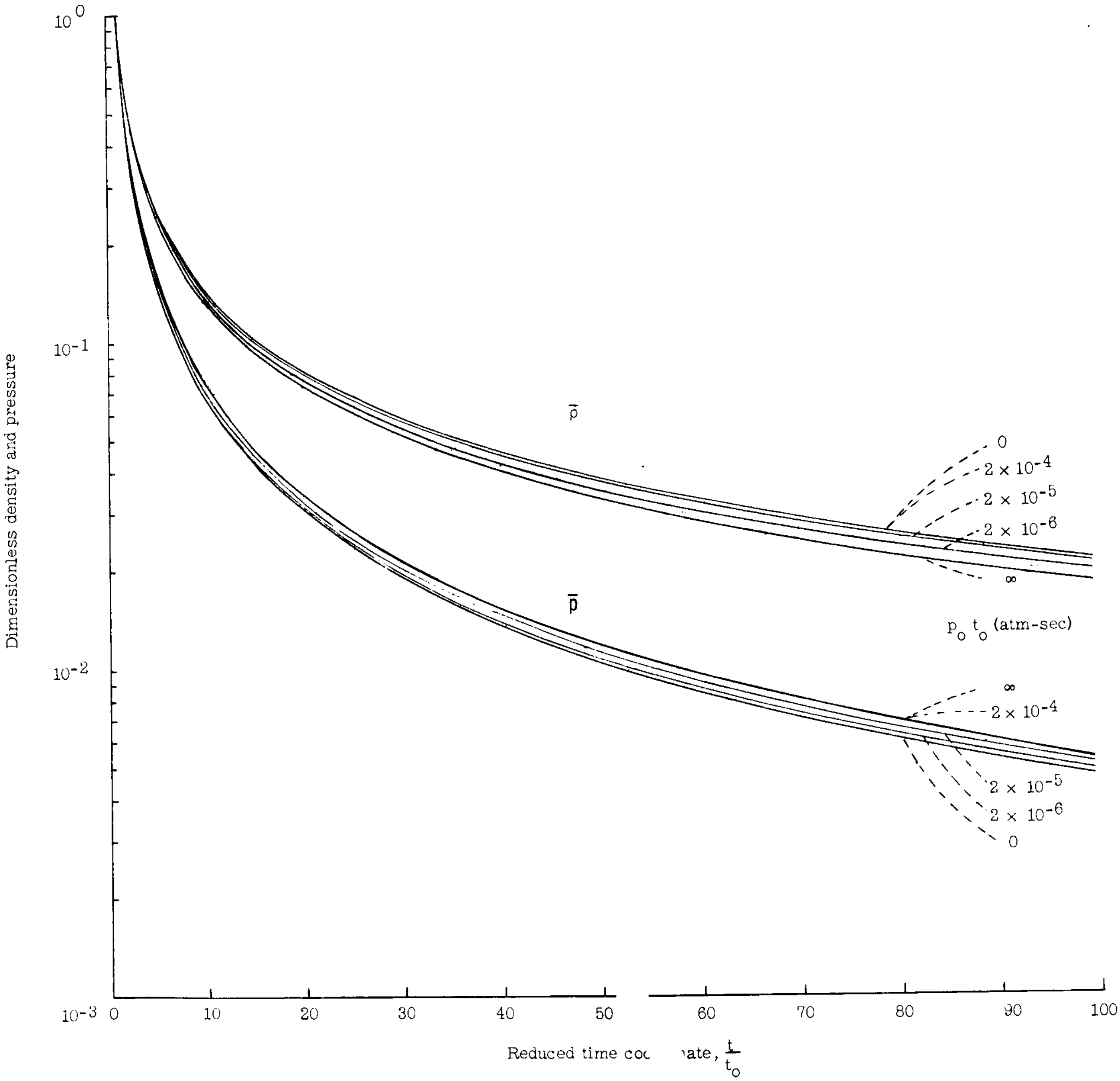
(b) $T_0 = 2500^0$ K; $p_0 > 2.9$ atm.

Figure 6.- Continued.



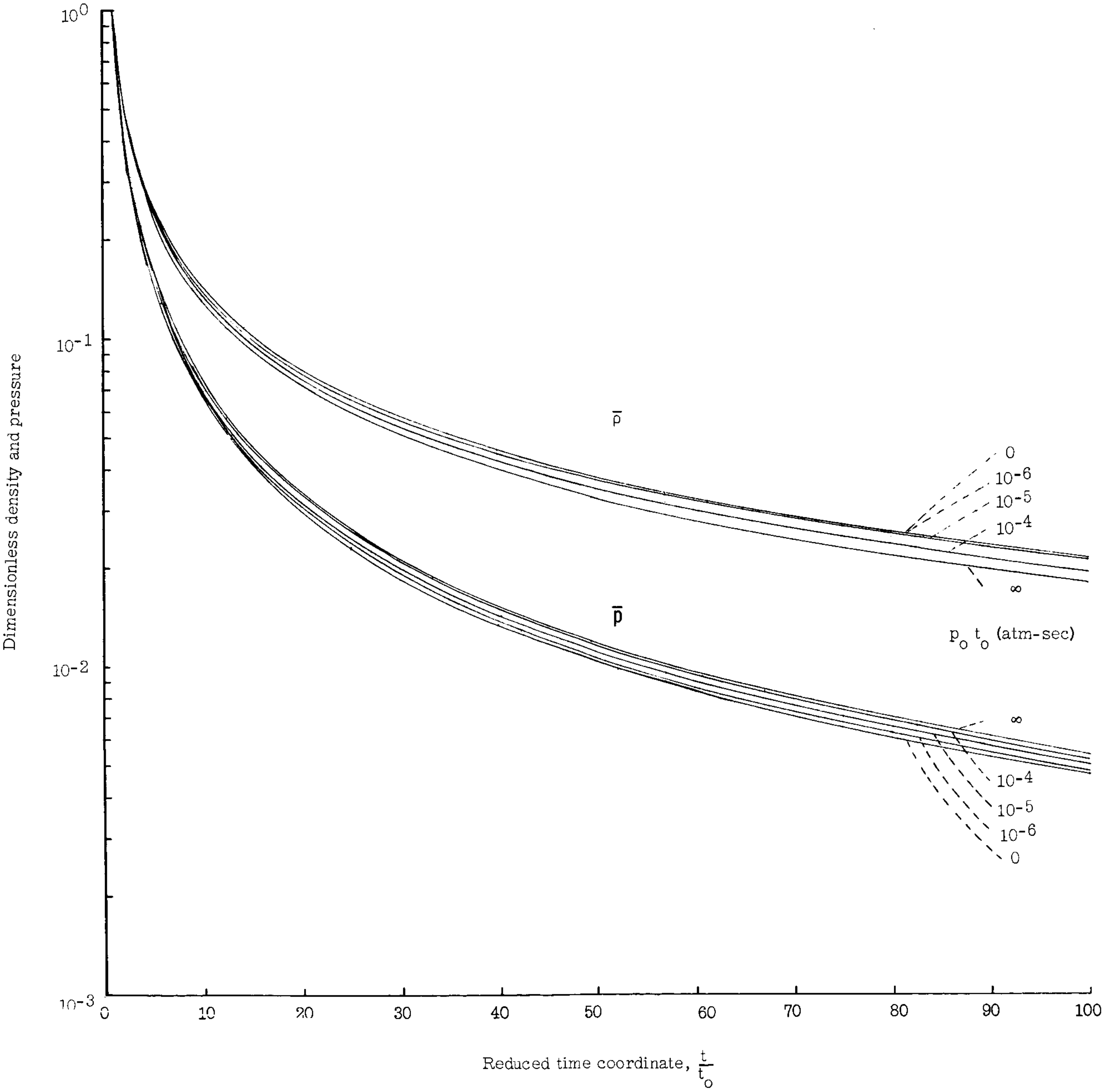
(c) $T_0 = 3000^0$ K; $p_0 > 90$ atm.

Figure 6.- Continued.



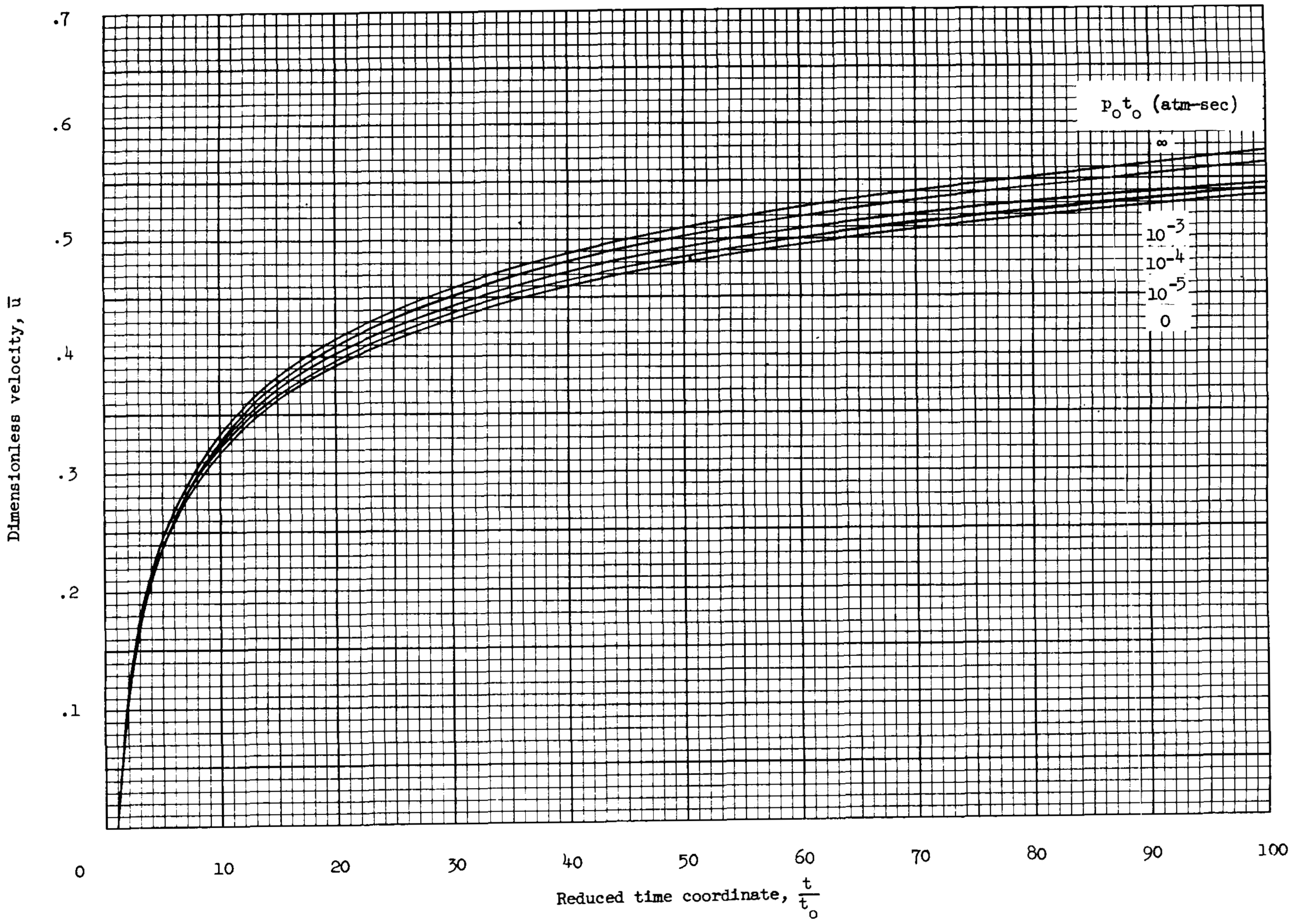
(d) $T_0 = 3500^0$ K; $p_0 >$ [illegible] atm.

Figure 6.- Continued.



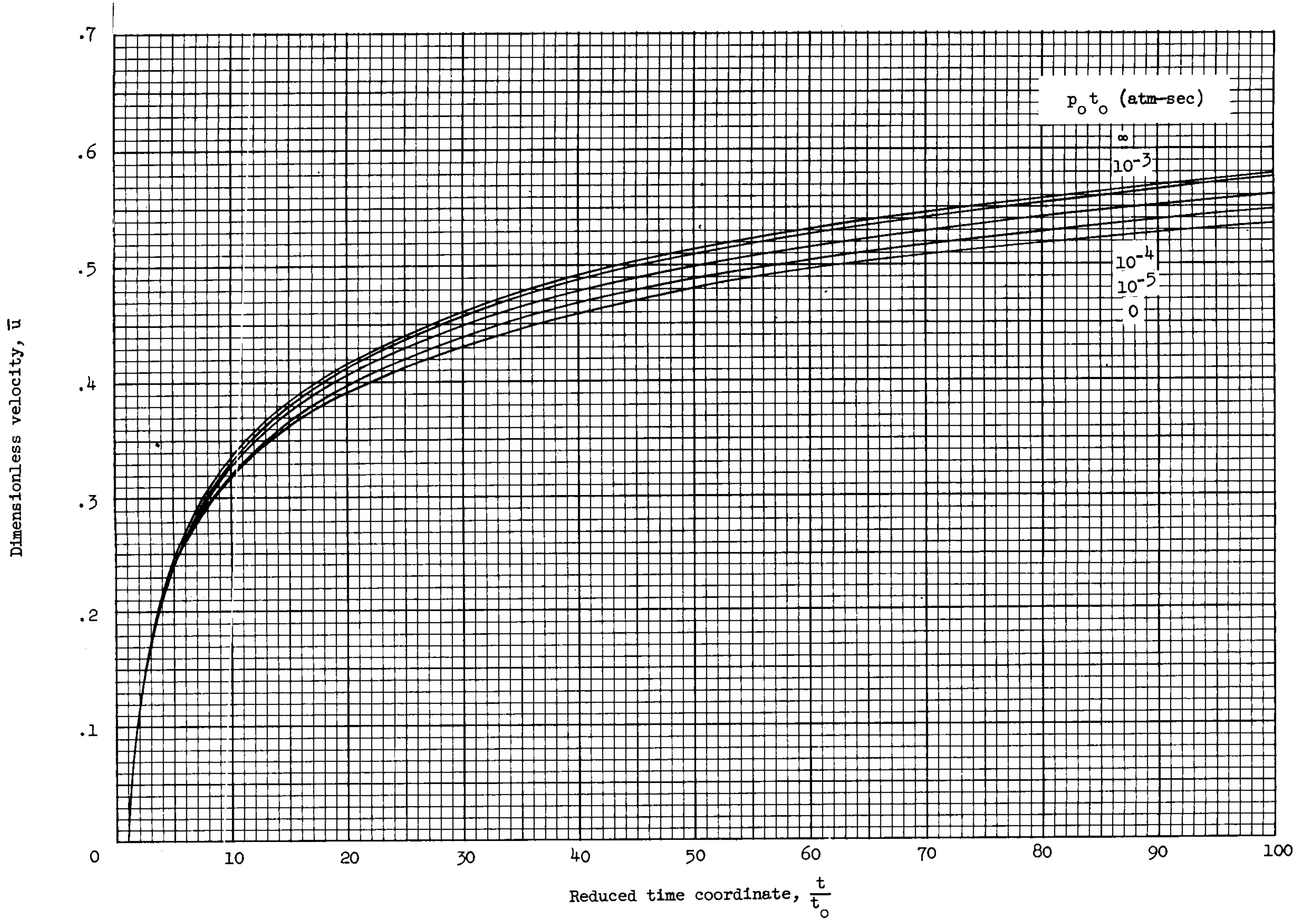
(e) $T_0 = 4000^0$ K; $p_0 > 6000$ atm.

Figure 6.- Concluded.



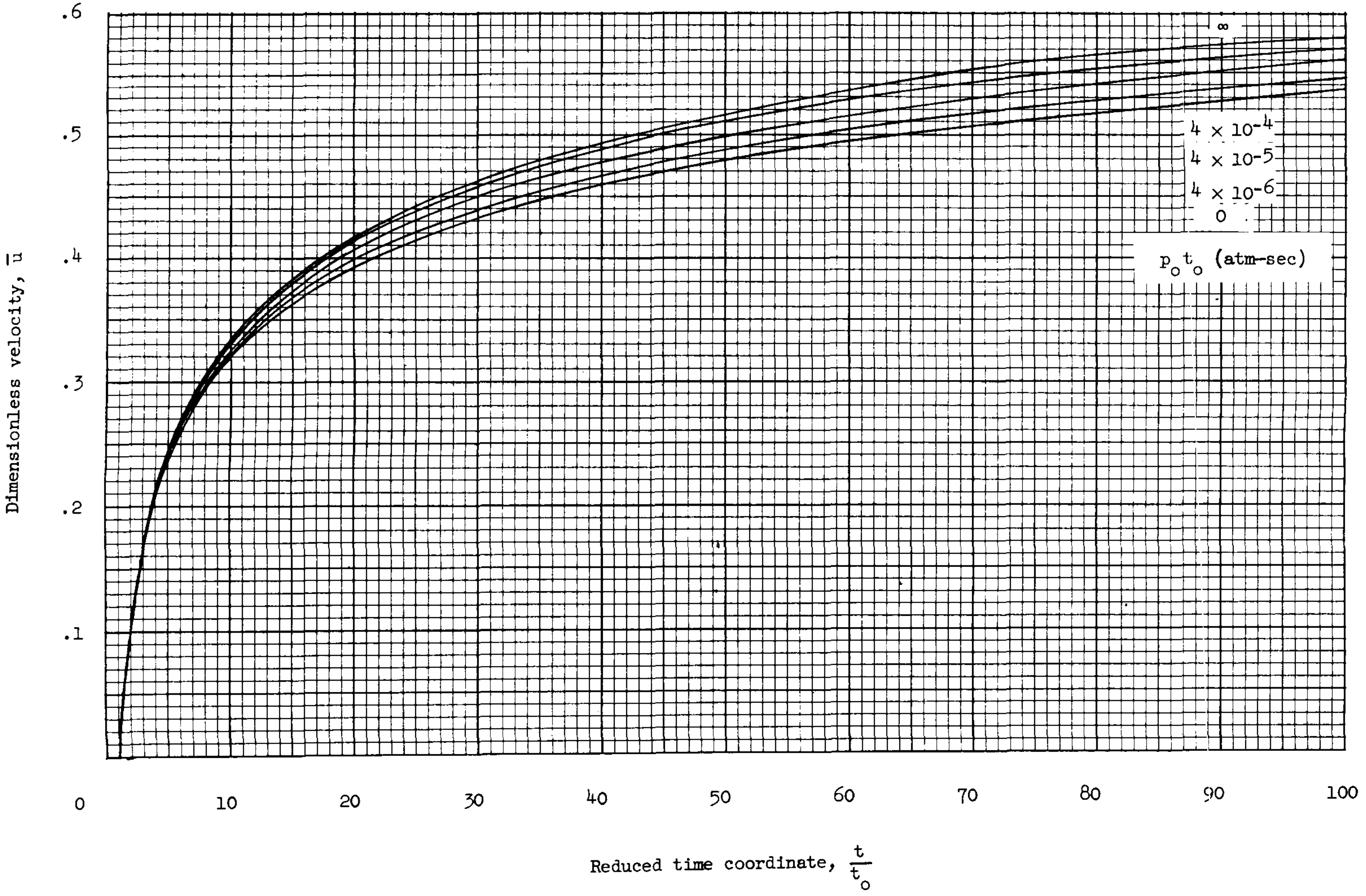
(a) $T_0 = 2000^0$ K; $p_0 > 0.015$ atm.

Figure 7.- Velocity variation in a nonequilibrium unsteady expansion.



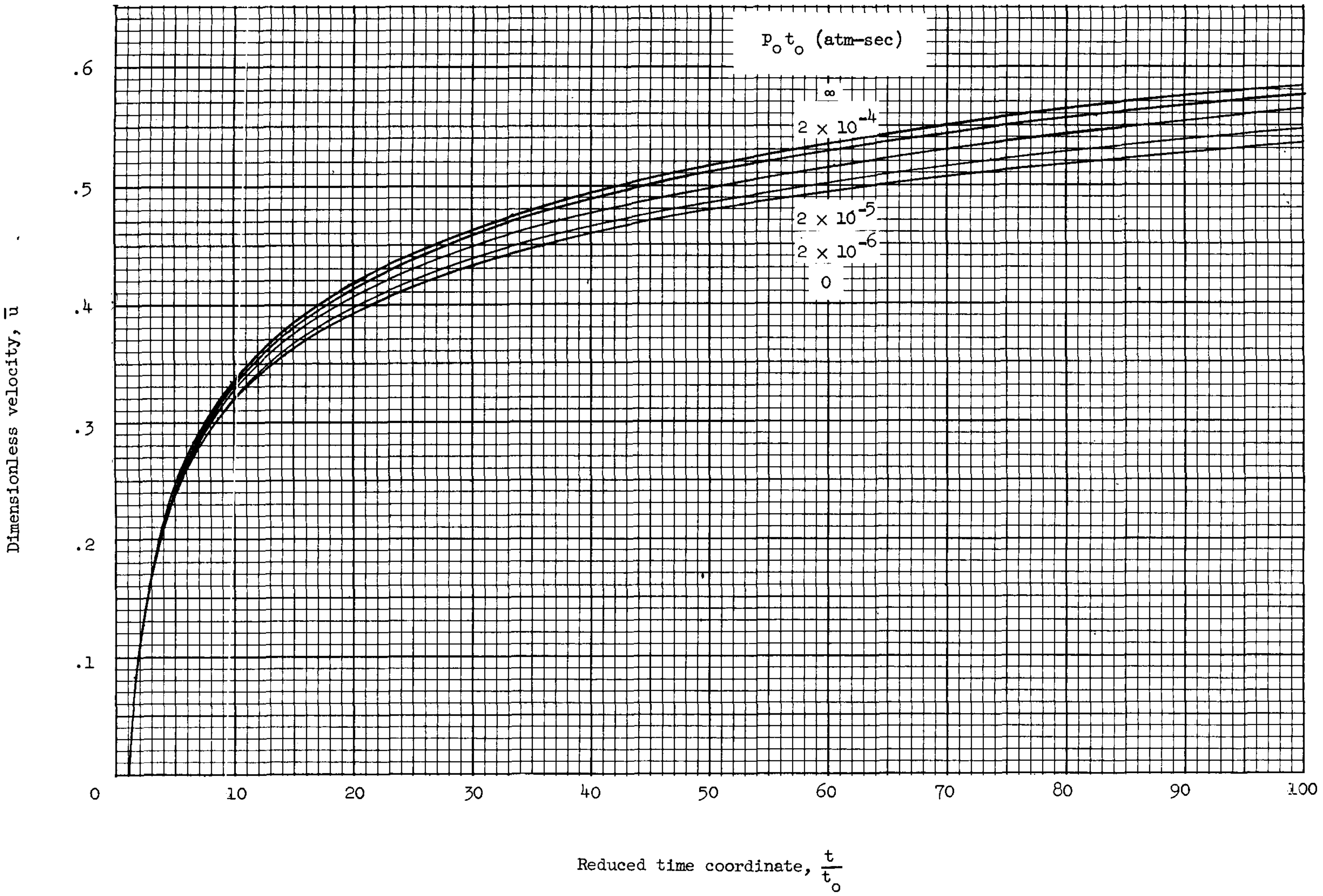
(b) $T_0 = 2500^0$ K; $p_0 > 2.9$ atm.

Figure 7.- Continued.



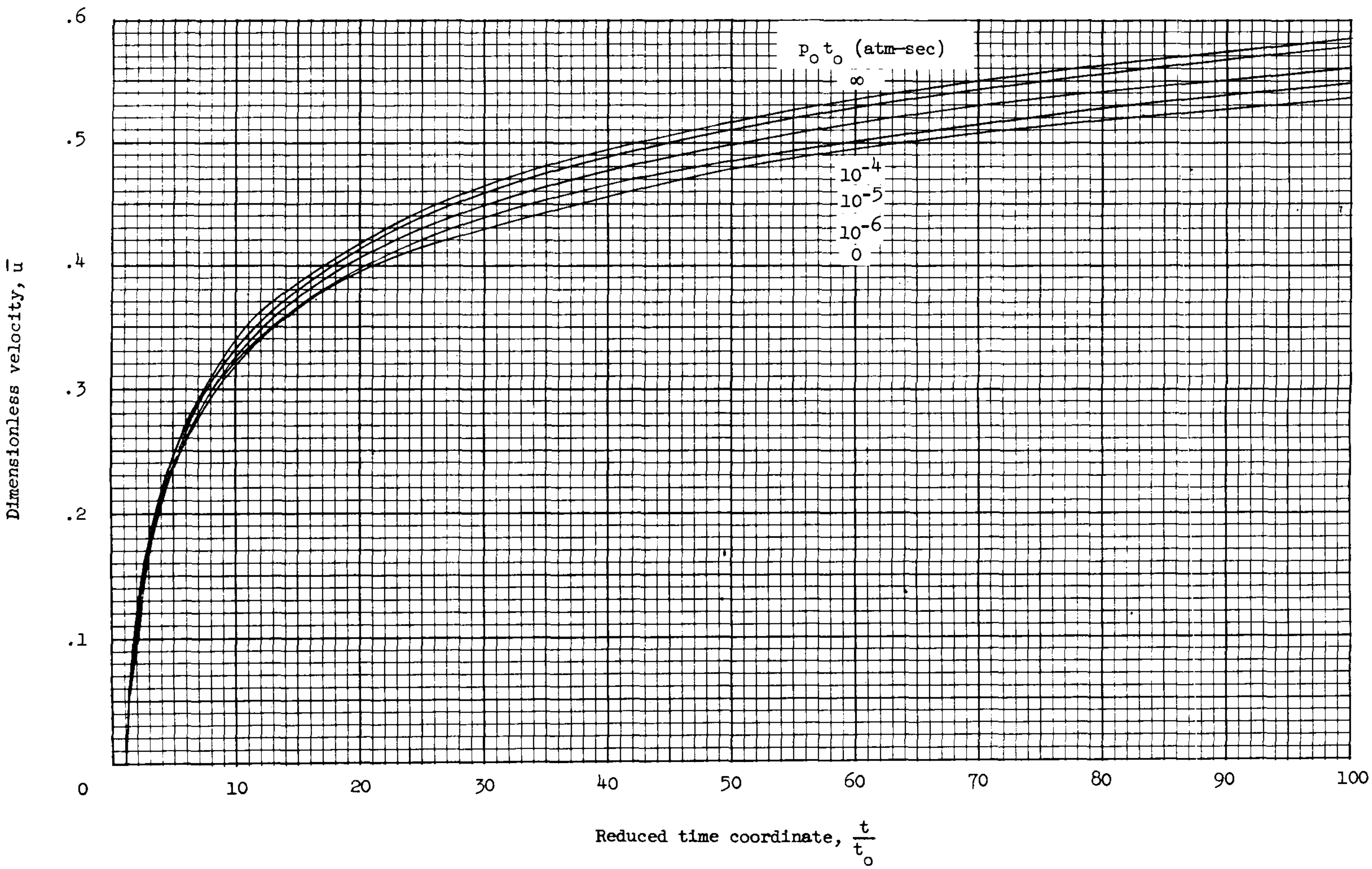
(c) $T_0 = 3000^0$ K; $p_0 > 90$ atm.

Figure 7.- Continued.



(d) $T_0 = 3500^0$ K; $p_0 > 1000$ atm.

Figure 7.- Continued.



(e) $T_0 = 4000^0$ K; $p_0 > 6000$ atm.

Figure 7.- Concluded.

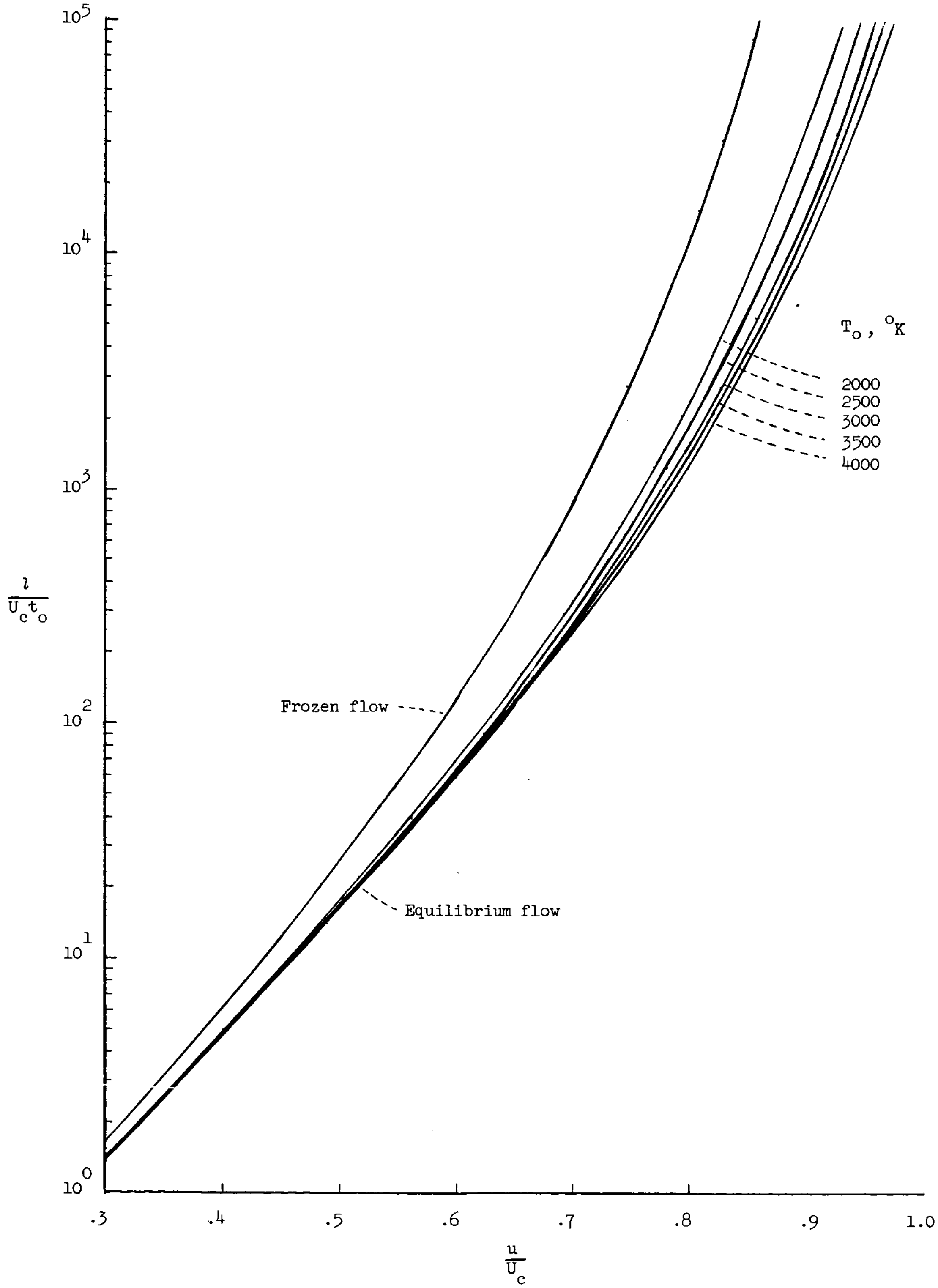


Figure 8.- Distance parameter as a function of dimensionless velocity for frozen and equilibrium flows.

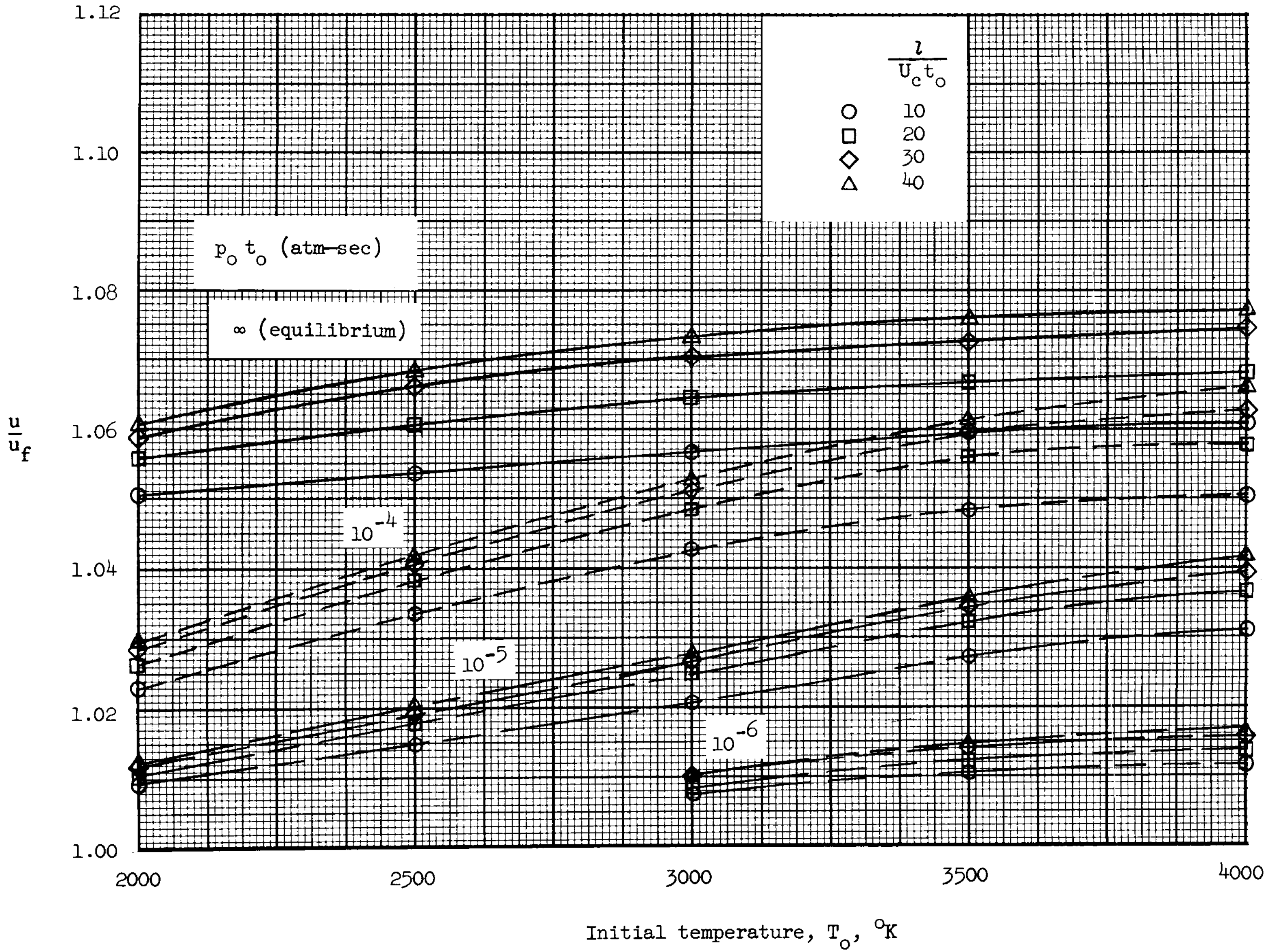


Figure 9.- Nonequilibrium-velocity correction as a function of T_o, $p_o t_o$, and $\frac{l}{U_c t_o}$.

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>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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