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RESEARCH MEMORANDUM

NOTE ON THE IMPORTANCE OF IMPERFECT-GAS EFFECTS AND VARIATION OF HEAT CAPACITIES ON THE ISENTROPIC FLOW OF GASES

By

Coleman duP. Donaldson

Langley Aeronautical Laboratory
Langley Field, Va.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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NOTE ON THE IMPORTANCE OF IMPERFECT-GAS EFFECTS AND VARIATION OF HEAT CAPACITIES ON THE ISENTROPIC FLOW OF GASES

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SUMMARY

The errors involved in using the perfect-gas law $pv = RT$ and the assumption of constant heat capacities are evaluated. The basic equations of gas flows taking into account these phenomena separately and at the same time are presented.

INTRODUCTION

The conventional method of obtaining high Mach numbers for aerodynamic tests is to accelerate the air by means of a pressure difference so that the random kinetic energy of the molecules of air at rest is converted into kinetic energy in the test section. For very high Mach numbers this may occasion high stagnation temperatures and pressures which introduce effects due to the vibrational heat capacity and molecular forces and size such that the perfect-gas law $pv = RT$ and the assumption of constant heat capacities may be no longer sufficiently accurate to evaluate gas flows.

It is the purpose of this paper to present formulas which are suitable for handling such problems and to point out the magnitude of the errors that may be involved in using the perfect-gas law and the assumption of constant heat capacities.

Tsien (reference 1) has published a theoretical discussion of this problem in which certain approximations were introduced in order to obtain solutions that were in a very neat form when the imperfect-gas effects were moderate. A comparison of Tsien's results with this work is presented to show the magnitude of these approximations.

In England Goldstein has previously investigated this problem at moderate temperatures and pressures in order to prove the small magnitude of imperfect-gas and vibrational-heat-capacity effects in most supersonic wind tunnels. This report indicates, in general, the range in which these effects are small but does not present formulas for handling problems in gas dynamics when these effects are large.

The present paper is arranged in the following three parts: temperature effects on perfect-gas flows due to variation of heat capacities; imperfect-gas effects on gases without variation of heat capacities; and gas flows in which both effects are present. This is done since the formulas in the first part may prove useful to those dealing with the flow of hot exhaust gases and since it may bring out more clearly the differences between the two effects.

SYMBOLS

a	term in Van der Waals' equation correcting for the effect of molecular forces
b	term in Van der Waals' equation correcting for the effect of molecular size
c	speed of sound, feet per second
C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume
E	energy, foot-pounds
M	Mach number (w/c)
p	pressure, pounds per square foot
R	gas constant
T	absolute temperature, degrees Fahrenheit
v	specific volume, cubic feet per slug
w	velocity, feet per second
γ	ratio of heat capacities (C_p/C_v)
ρ	density, slugs per cubic foot
θ	characteristic temperature of molecular vibration

Subscripts:

o	stagnation conditions
c	critical conditions

Errors Involved in Assuming Constant Specific Heats in the Presence of High Temperatures in a Perfect Gas

For a perfect gas with constant heat capacities the equation for conservation of energy of a steady isentropic process may be written as

$$C_pT + \frac{1}{2}w^2 = C_pT_o$$

If this equation is combined with the equation for the isentropic speed of sound $c^2 = \gamma RT$ the resulting equation is

$$M^2 = \frac{2}{\gamma - 1}\left(\frac{T_o}{T} - 1\right) \tag{1}$$

If the expansion is isentropic, the pressure and density ratios corresponding to the Mach number are

$$\left.\begin{aligned} \frac{p_o}{p} &= \left(\frac{T_o}{T}\right)^{C_p/R} \\ &\text{and} \\ \frac{\rho_o}{\rho} &= \left(\frac{T_o}{T}\right)^{C_v/R} \end{aligned}\right\} \tag{2}$$

However, if the temperature of the gas is high enough the heat capacities may not be assumed constant because the vibrational degrees of freedom of polyatomic molecules are excited. The variation of the equilibrium value of the heat capacity at constant volume of a perfect diatomic gas is found from quantum mechanical considerations to be of the form

$$\frac{C_v}{R} = \frac{5}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} \tag{3}$$

where θ is a constant depending on the gas. The formula may be used for the mixture air if the value of θ is placed equal to 5526 when absolute temperature is measured in degrees Fahrenheit. (See the appendix.) The value of the heat capacity at constant pressure for a perfect gas is then

$$\frac{C_p}{R} = \frac{7}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} \tag{4}$$

Figure 1 is a plot of equation (4) and shows that the heat capacity may not be considered constant above 600° F absolute.

When the heat capacity at constant pressure varies according to equation (4) the energy equation must be written

$$R\int_{T_o}^{T} \frac{C_p}{R}\, dT + \frac{1}{2}w^2 = 0 \tag{5}$$

Substituting equation (4) into equation (5) and integrating yields

$$7RT + \frac{2R\theta}{e^{\theta/T} - 1} + w^2 = 7RT_o + \frac{2R\theta}{e^{\theta/T_o} - 1} \tag{6}$$

The Mach number is obtained from equation (6) by dividing through by $\gamma RT = c^2$, which gives

$$M^2 = \frac{7}{\gamma}\left(\frac{T_o}{T} - 1\right) + \frac{2\theta}{\gamma T}\left(\frac{1}{e^{\theta/T_o} - 1} - \frac{1}{e^{\theta/T} - 1}\right) \tag{7}$$

where

$$\gamma = \frac{C_p/R}{C_v/R} = \frac{7\left(e^{\theta/T} - 1\right)^2 + 2\left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{5\left(e^{\theta/T} - 1\right)^2 + 2\left(\frac{\theta}{T}\right)^2 e^{\theta/T}} \tag{8}$$

The pressure ratio corresponding to this Mach number is obtained from the isentropic equation

$$\log \frac{p}{p_o} = \int_{T_o}^{T} \frac{C_p}{R} \frac{dT}{T} \tag{9}$$

by substituting equation (4) into equation (9) and integrating to give

$$\frac{p}{p_o} = \left(\frac{T}{T_o}\right)^{7/2} \frac{1 - e^{\theta/T_o}}{1 - e^{\theta/T}} e^{\left(\frac{\theta}{T} \frac{e^{\theta/T}}{e^{\theta/T}-1} - \frac{\theta}{T_o} \frac{e^{\theta/T_o}}{e^{\theta/T_o}-1}\right)} \tag{10}$$

Similarly, the density ratio is found to be

$$\frac{\rho}{\rho_o} = \left(\frac{T}{T_o}\right)^{5/2} \frac{1 - e^{\theta/T_o}}{1 - e^{\theta/T}} e^{\left(\frac{\theta}{T} \frac{e^{\theta/T}}{e^{\theta/T}-1} - \frac{\theta}{T_o} \frac{e^{\theta/T_o}}{e^{\theta/T_o}-1}\right)} \tag{11}$$

The differences involved in the use of equations (1) and (2) to predict the temperature, density, and pressure ratios corresponding to a given Mach number are given in figures 2(a) and 2(b), in terms of the percentage differences from the value given by equations (7), (10), and (11) for stagnation temperatures of 1000° and 2000° F absolute.

It is seen that the assumption of constant heat capacity leads to appreciable differences in applying the isentropic law for a perfect gas if stagnation temperatures above 1000° F absolute are involved.

Errors Involved in the Assumption of the Perfect-Gas Law $pv = RT$ for a Gas with Constant Heat Capacities

In order to evaluate flows in which imperfect-gas effects are present, an equation of state that takes into account these effects must be chosen. For the purposes of this paper an equation which takes into account the effects of molecular forces and size should be sufficient.

A suitable equation is that of Van der Waals

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{12}$$

where b is a term correcting for the volume occupied by the molecules and a is a term correcting for the effect of molecular forces.

Figure 3 is a graph of Van der Waals' equation in which the quantities p, v, and T have been made nondimensional by dividing by the values of these quantities at the critical point p_c, v_c, and T_c, thus making the graph suitable for any gas. (See reference 2.) The graph may be used for air if an empirical critical point ($p_c = 37.2$ atm, $T_c = 238.5^{\circ}$ F abs., $v_c = 0.6438$ slugs/ft^3) is assigned to that mixture of oxygen and nitrogen. To give this critical point the values of a, b, and R for air when the pressure is measured in pounds per square foot, the specific volume in cubic feet per slug and the absolute temperature in degrees Fahrenheit are $a = 8.78 \times 10^5$, $b = 0.654$, and $R = 1716$.

The proper equation for an isentropic expansion of a real gas is (see reference 3)

$$dE = C_v\, dT + \left[T\left(\frac{\partial p}{\partial T}\right)_{v=\text{Constant}}\right] dv = 0 \tag{13}$$

which for Van der Waals' equation becomes

$$dE = C_v\, dT + p\, dv + \frac{a}{v^2}\, dv = 0 \tag{14}$$

Equation (14) may be written as

$$dE = C_v\, dT + d(pv) - v\, dp + \frac{a}{v^2}\, dv = 0$$

and since $-v\, dp = w\, dw$

$$dE = C_v\, dT + d(pv) + \frac{a}{v^2}\, dv + w\, dw = 0 \tag{15}$$

Assuming constant heat capacity at constant volume and integrating equation (15) gives

$$E = C_vT + v\left(p - \frac{a}{v^2}\right) + \frac{w^2}{2} = \text{Constant} = E_o \tag{16}$$

This is then the energy equation for a Van der Waals gas. Dividing through by the isentropic speed of sound

$$c^2 = \frac{dp}{d\rho} = \left(1 + \frac{R}{C_v}\right)\frac{v^2RT}{(v-b)^2} - \frac{2a}{v} \tag{17}$$

and since

$$p - \frac{a}{v^2} = \frac{RT}{v-b} - \frac{2a}{v^2}$$

then

$$M^2 = \frac{2C_vT_o + 2v_o\left(\frac{RT_o}{v_o - b} - \frac{2a}{v_o{}^2}\right) - 2C_vT - 2v\left(\frac{RT}{v-b} - \frac{2a}{v^2}\right)}{\left(1 + \frac{R}{C_v}\right)\frac{v^2RT}{(v-b)^2} - \frac{2a}{v}} \tag{18}$$

The value of v for an isentropic expansion to be placed in equation (18) can be formed from equation (14) as follows:

$$C_v\ dT + p\ dv + \frac{a}{v^2}\ dv = C_v\ dT + \frac{RT}{v-b}\ dv = 0$$

then

$$\frac{C_v\ dT}{T} = -\frac{dv}{v-b} \tag{19}$$

and if C_v is constant

$$v = (v_o - b)\left(\frac{T_o}{T}\right)^{C_v/R} + b \tag{20}$$

From equations (18) and (20), knowing the stagnation conditions for an expansion from T_o to T, the Mach number may be calculated. The pressure ratio is then found to be

$$\frac{p}{p_o} = \frac{\dfrac{RT}{v - b} - \dfrac{a}{v^2}}{\dfrac{RT_o}{v_o - b} - \dfrac{a}{v_o^2}} \tag{21}$$

and substituting the value of v from equation (20) we obtain

$$\frac{p}{p_o} = \frac{\dfrac{RT}{(v_o - b)\left(\dfrac{T_o}{T}\right)^{C_v/R}} - \dfrac{a}{\left[(v_o - b)\left(\dfrac{T_o}{T}\right)^{C_v/R} + b\right]^2}}{\dfrac{RT_o}{v_o - b} - \dfrac{a}{v_o^2}} \tag{22}$$

Figure 4 shows the conventional pressure ratio and area ratio $\rho w/(\rho w)_{M=1}$ plotted against Mach number for air starting from stagnation conditions of 520° F absolute and various pressures compared with the value obtained using constant ratio of heat capacities and the perfect-gas law.

Also shown in figure 4 are the values of $\rho w/(\rho w)_{M=1}$ computed by Tsien's method. It is seen that as the imperfect-gas effects become large it is no longer possible to simplify the analysis by neglecting terms containing the squares of $\frac{b}{v}$ and $\frac{a}{pv^2}$, although Tsien's results are in good agreement at 50 atmospheres when the Van der Waals effect is moderate.

It is interesting to note that the speed of sound in a Van der Waals gas

$$c^2 = \frac{dp}{d\rho} = \left(1 + \frac{R}{C_v}\right)\frac{v^2RT}{(v - b)^2} - \frac{2a}{v} \tag{17}$$

is not equal to γRT. The expression for the ratio of specific heats in a Van der Waals gas is

$$\gamma = 1 + \frac{R}{C_v}\left(\frac{pv^2 + a}{pv^2 - a + \dfrac{2ab}{v}}\right) \tag{23}$$

The value of the heat-capacity ratio γ is plotted in figure 5 as a function of the pressure for air at room temperature (520° F abs.).

It must be remembered that these values of γ are important for calculating the relationship between physical quantities in gas flows but that these large changes in γ have only a small effect on the forces measured on a body in a wind tunnel, the important parameter in the case of forces being the Mach number in the test section.

Formulas for the Flow of an Imperfect Gas with Variable Heat Capacities

From equation (15) substituting the value of C_v from equation (3) gives

$$R\left[\frac{5}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}\right] dT + d(pv) + \frac{a}{v^2}\,dv + w\,dw = 0 \tag{24}$$

and the energy equation becomes

$$5RT + \frac{2R\theta}{e^{\theta/T} - 1} + 2v\left(p - \frac{a}{v^2}\right) + w^2 = \text{Constant} \tag{25}$$

thus

$$M^2 = \frac{5R(T_o - T) + \dfrac{2R\theta}{e^{\theta/T_o} - 1} - \dfrac{2R\theta}{e^{\theta/T} - 1} + 2v_o\left(\dfrac{RT_o}{v_o - b} - \dfrac{2a}{{v_o}^2}\right) - 2v\left(\dfrac{RT}{v - b} - \dfrac{2a}{v^2}\right)}{\left[1 + \dfrac{1}{\dfrac{5}{2} + \left(\dfrac{\theta}{T}\right)^2 \dfrac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}}\right]\dfrac{v^2RT}{(v - b)^2} - \dfrac{2a}{v}} \tag{26}$$

The value of v to be used in this equation may be found from equation (19)

$$\log \frac{v-b}{v_o-b} = \int_T^{T_o} \frac{C_v}{R} \frac{dT}{T} \tag{27}$$

Substituting the value of $\frac{C_v}{R}$ from equation (3) into equation (27) and integrating yields

$$\log \frac{v-b}{v_o-b} = \frac{5}{2} \log \frac{T_o}{T} + \log \frac{1-e^{\theta/T}}{1-e^{\theta/T_o}} + \frac{\theta}{T_o} \frac{e^{\theta/T_o}}{e^{\theta/T_o}-1} - \frac{\theta}{T} \frac{e^{\theta/T}}{e^{\theta/T}-1}$$

or

$$v = b + (v_o - b)\left(\frac{T_o}{T}\right)^{5/2} \frac{1-e^{\theta/T}}{1-e^{\theta/T_o}} e^{\left(\frac{\theta}{T_o} \frac{e^{\theta/T_o}}{e^{\theta/T_o}-1} - \frac{\theta}{T} \frac{e^{\theta/T}}{e^{\theta/T}-1}\right)} \tag{28}$$

The pressure ratio corresponding to this expansion is again found from

$$\frac{p}{p_o} = \frac{\dfrac{RT}{v-b} - \dfrac{a}{v^2}}{\dfrac{RT_o}{v_o-b} - \dfrac{a}{v_o^2}} \tag{21}$$

The value of the ratio of heat capacities γ in this case is

$$\gamma = \frac{\frac{5}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} + \frac{pv^2 + a}{pv^2 - a + \frac{2ab}{v}}}{\frac{5}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}} \tag{29}$$

but the speed of sound is found from equation (17) by substituting the value of C_v/R from equation (3) to be

$$c^2 = \left[1 + \frac{1}{\frac{5}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}}\right] \frac{v^2RT}{(v - b)^2} - \frac{2a}{v}$$

Figure 6 shows the conventional pressure ratio and area ratio plotted against Mach number for air starting from stagnation conditions of 2000° F absolute and various pressures compared with the value obtained using constant ratio of heat capacities and the perfect-gas law.

DISCUSSION

The foregoing analyses show that the effects of variation of heat capacities with temperature do not become important in isentropic expansions of air until stagnation temperatures of the order of 1000° F absolute are encountered. Above 1000° F absolute, however, for accurate analysis this variation must be taken into account. In general, it may be stated that for diatomic gases these effects are important when $\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$ becomes appreciable compared to the number 2.5.

The effects of Van der Waals' forces become important when either the temperature is extremely low for near atmospheric pressures or the pressure very high for moderate temperatures. These forces must be taken into account when the value of a/v^2 becomes appreciable compared to the pressure p, or b becomes appreciable compared to v. For air these effects are unimportant until stagnation pressures of the order of 50 atmospheres at stagnation temperature of 520° F absolute are encountered.

Tsien's method agrees well with the results of this investigation up to 50 atmospheres in this case, but it appears that it is not possible to neglect the squared terms of $\frac{b}{v}$ and $\frac{a}{v^2p}$ when the effects of Van der Waals' forces become appreciable.

CONCLUSIONS

In many cases found in very high Mach number wind tunnels and in flows of high stagnation temperature or pressure, imperfect-gas effects and the effects of variation of heat capacities may be present.

For diatomic gases the effect of variation of heat capacities becomes important when $\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$ becomes appreciable compared to 5/2. For air these effects become appreciable when stagnation conditions of 1000° F absolute or larger are encountered.

Imperfect-gas effects become important in gas dynamics when a/v^2 becomes appreciable compared to the pressure p or b becomes appreciable compared to v. When air is expanded from a stagnation temperature of 520° F absolute these effects become important if the stagnation pressures are of the order of 50 atmospheres or greater.

Formulas are presented for handling isentropic expansions taking into account these phenomena both separately and at the same time. Tsien's method is found to be applicable for small departures from a perfect gas but is not accurate when the effects of Van der Waals' forces become appreciable.

Langley Aeronautical Laboratory
National Advisory Committee for Aeronautics
Langley Field, Va.

APPENDIX

DERIVATION OF THE VIBRATIONAL HEAT CAPACITY OF A DIATOMIC GAS

To arrive at the vibrational heat capacity of a diatomic gas, the individual molecules are treated as linear harmonic oscillators of a fundamental frequency and Shrödinger's equation is solved for the allowable energy states of such an oscillator. These allowable states are then substituted into the equation for the canonical energy distribution and the average energy per particle as a function of the absolute temperature is found. This may be differentiated to obtain the contribution of the vibrational degrees of freedom of the molecule to the heat capacity of the gas at any temperature.

The average vibrational energy per particle found in this way is (see references 4 and 5)

$$\overline{E} = \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}$$

where

h Planck's constant

ν characteristic frequency of molecular vibration

T absolute temperature

Differentiating to obtain the contribution to the heat capacity of this energy yields

$$\frac{C_{vib}}{R} = \frac{1}{k}\frac{\partial \overline{E}}{\partial T} = \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2}$$

For a particular gas $\frac{h\nu}{k} = \theta$ is a constant and may be determined from spectroscopic data. The heat capacity at constant pressure is then

$$\frac{C_p}{R} = \frac{7}{2} + \frac{C_{vib}}{R} = \frac{7}{2} + \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$$

The value of θ for oxygen is 4010.4 and for nitrogen is 6044.4 for absolute temperatures measured in degrees Fahrenheit. The value 5526 may be used for air.

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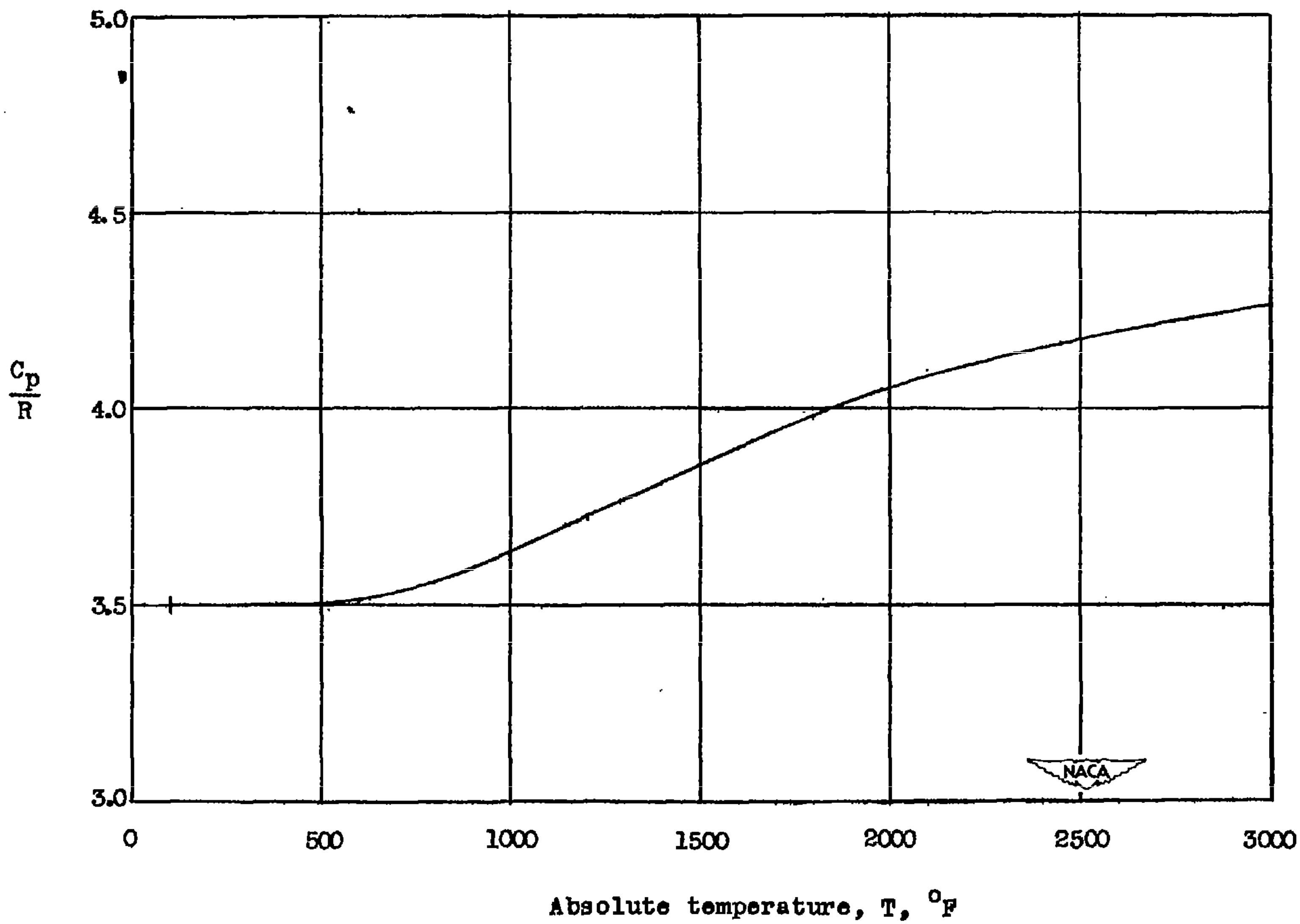
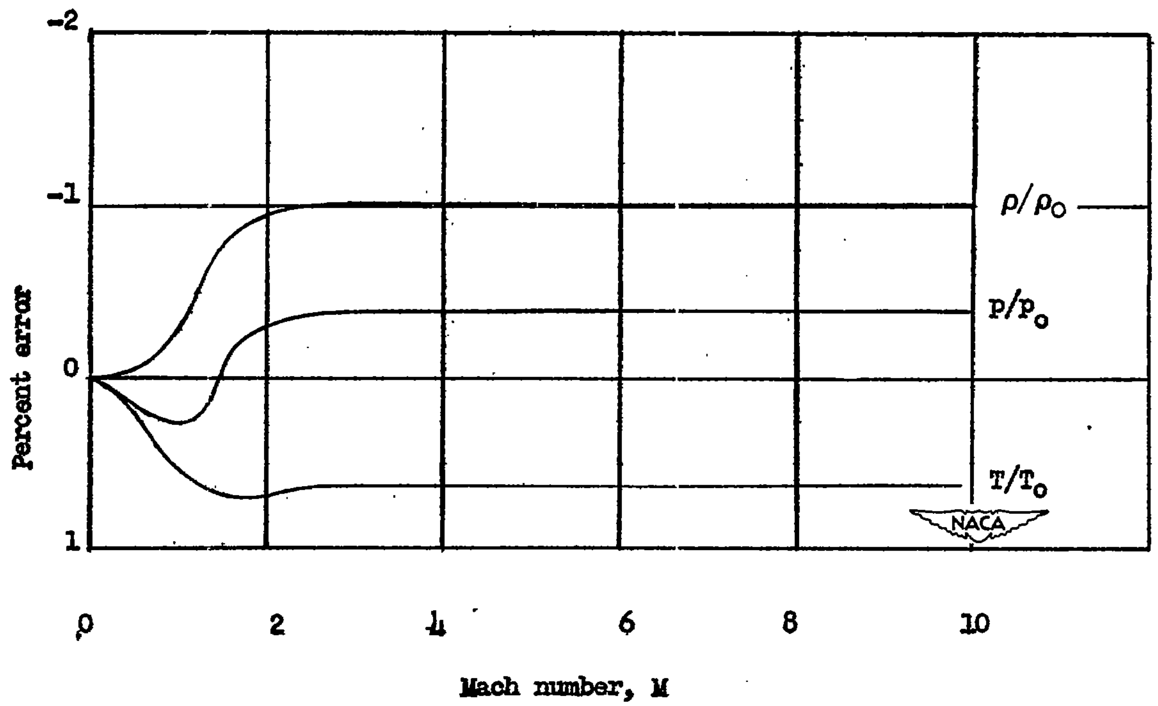
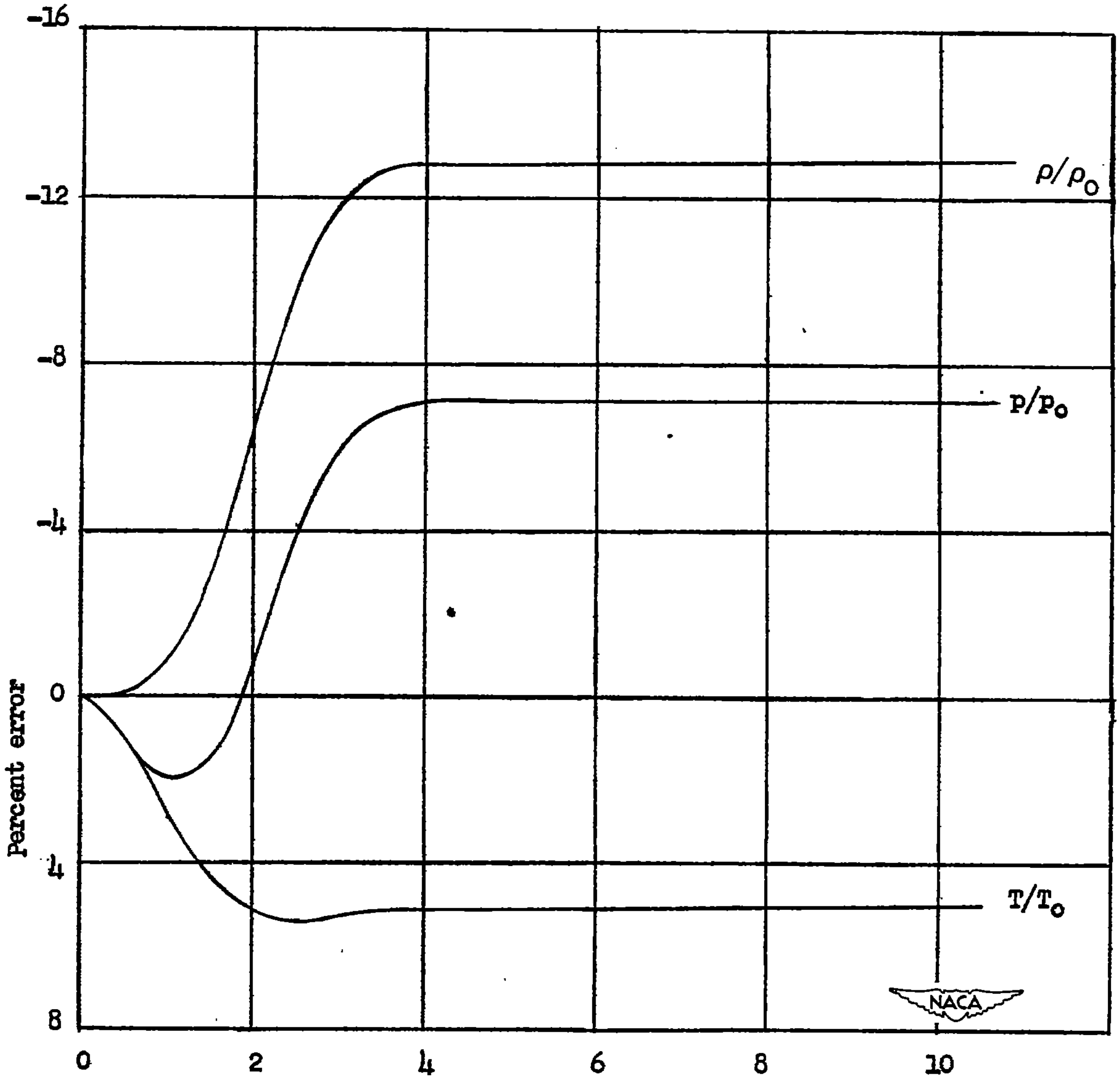


Figure 1.- Variation of heat capacity at constant pressure with temperature as given by equation (4).



(a) $T_o = 1000^\circ$ F abs.

Figure 2.- Percent error involved in the use of constant-heat-capacity formulas to obtain T/T_o, ρ/ρ_o, and p/p_o for air.



(b) T_o = 2000° F abs.

Figure 2.- Concluded.

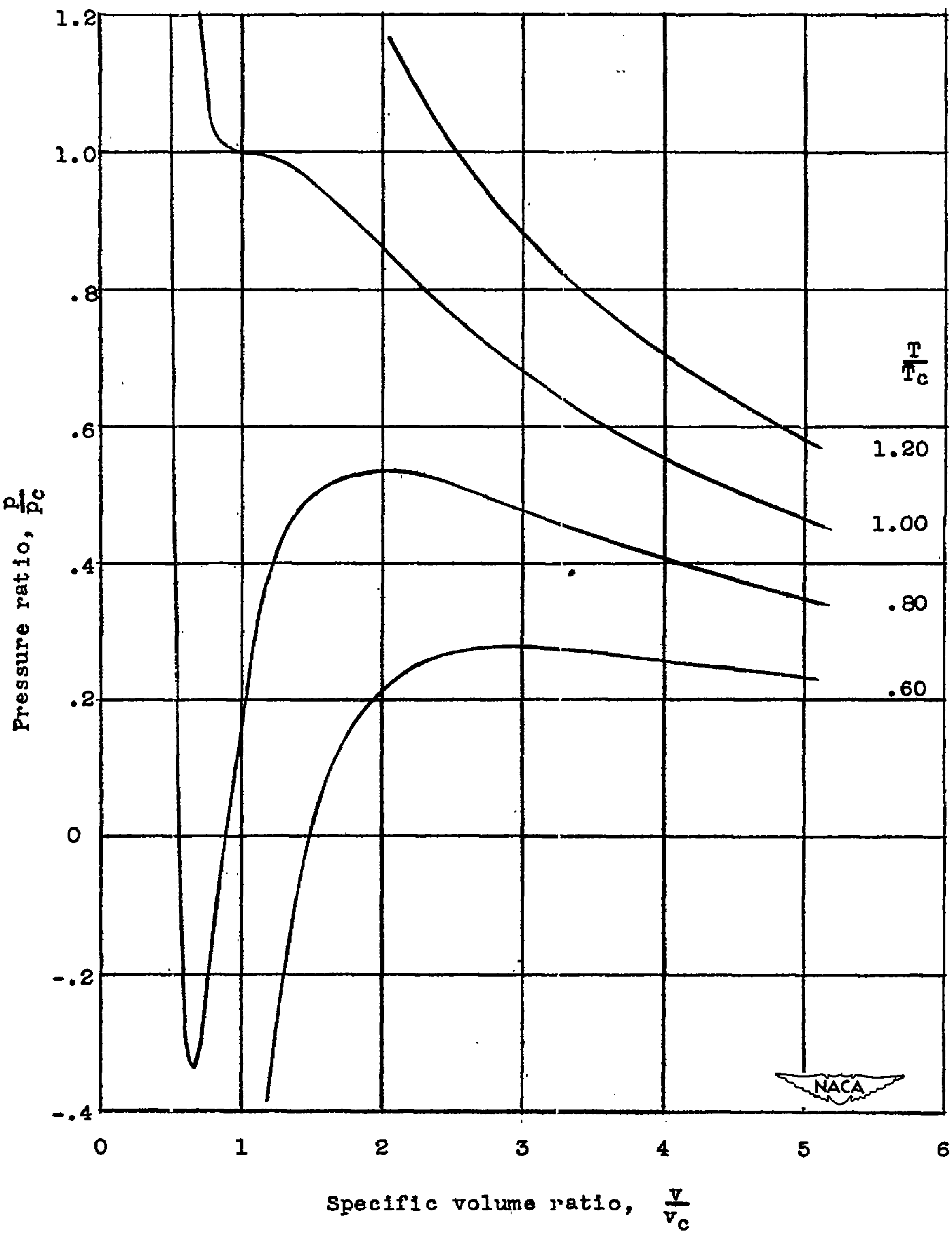


Figure 3.- Van der Waals' equation in nondimensional form.

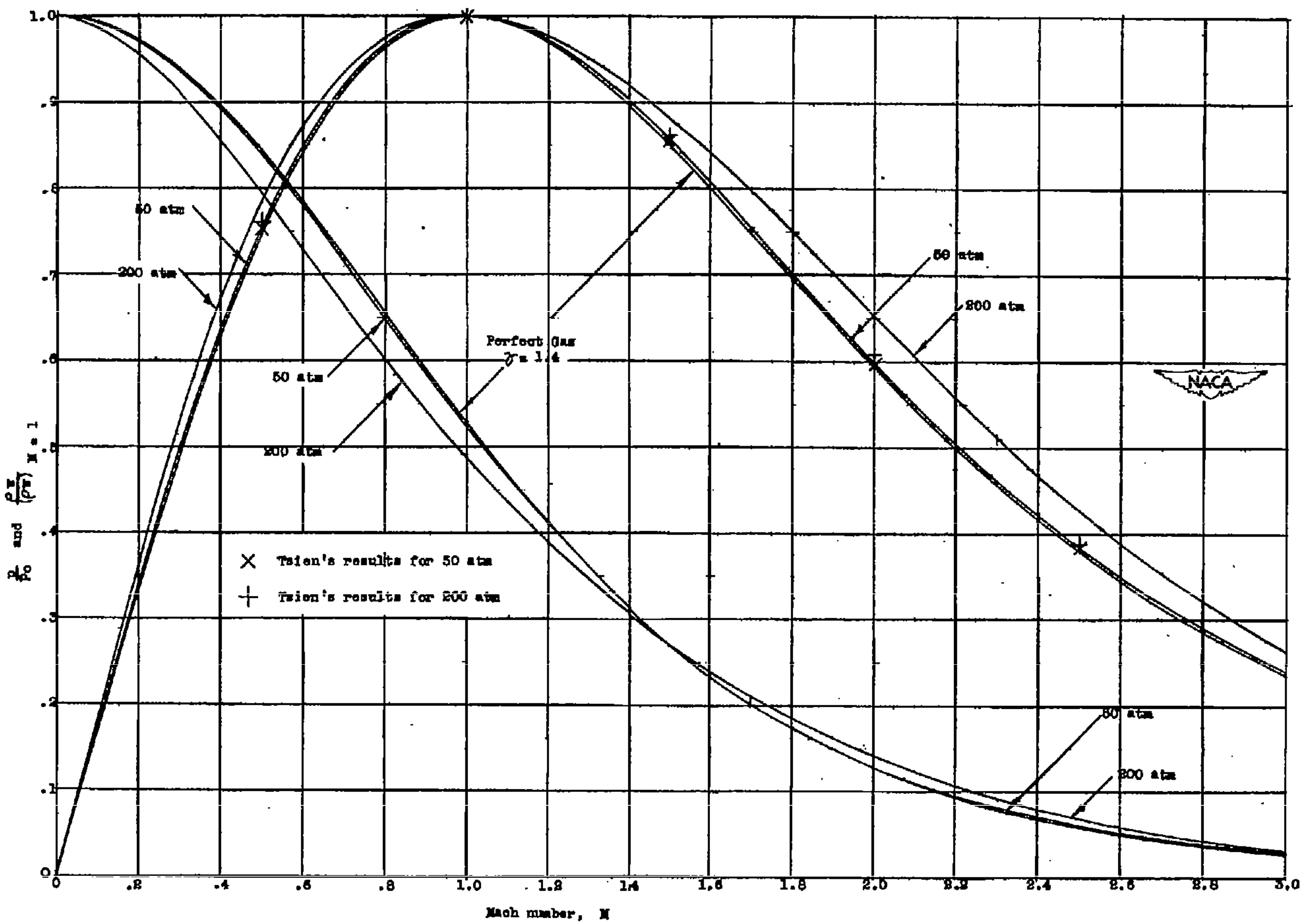


Figure 4.- Pressure ratio and area ratio plotted against Mach number for air as a Van der Waals gas. $T_o = 520^\circ$ F abs.

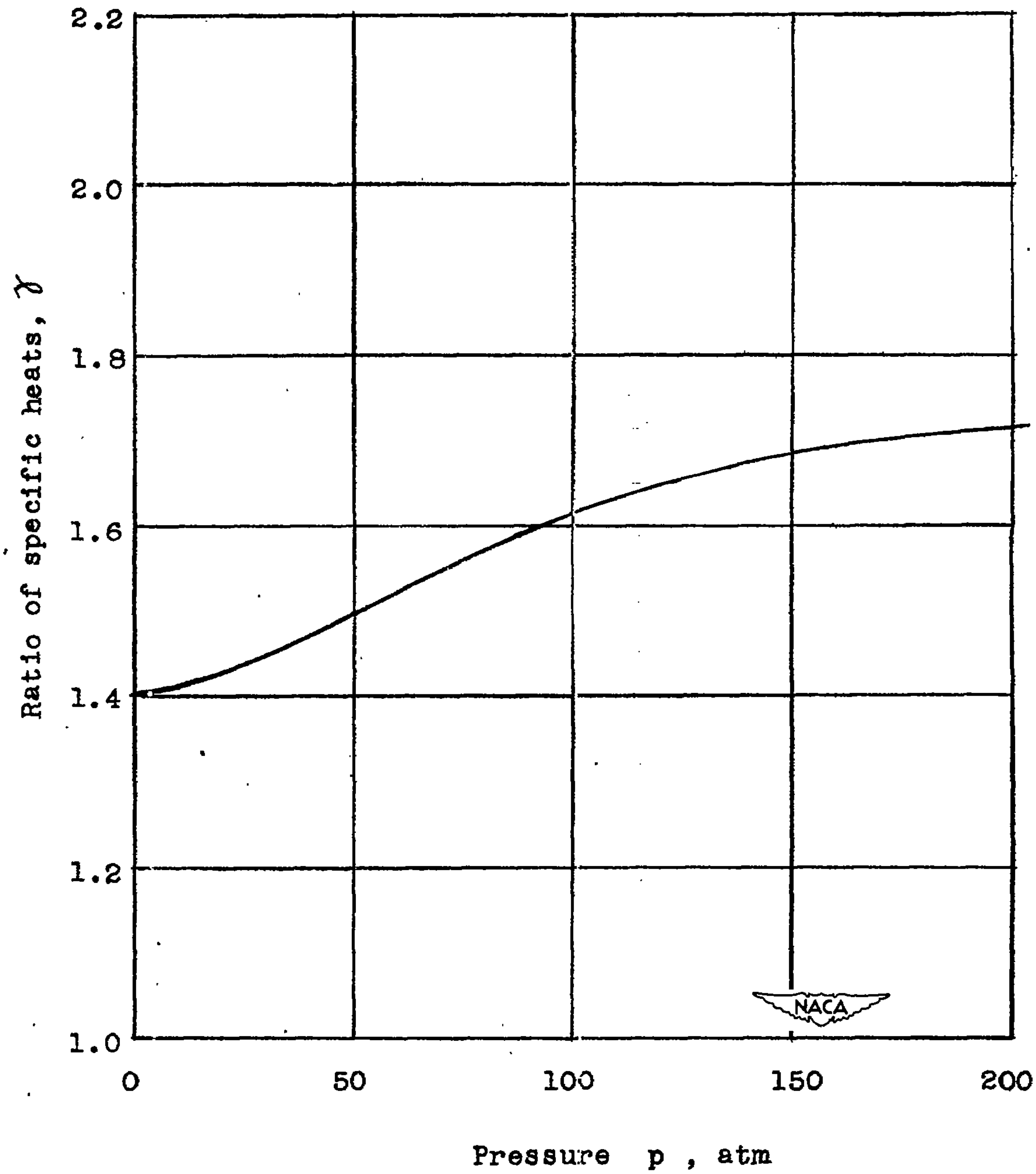


Figure 5.- Variation of the ratio of specific heats , γ for a Van der Waals gas. $T_o = 520^{\circ}$ F abs.

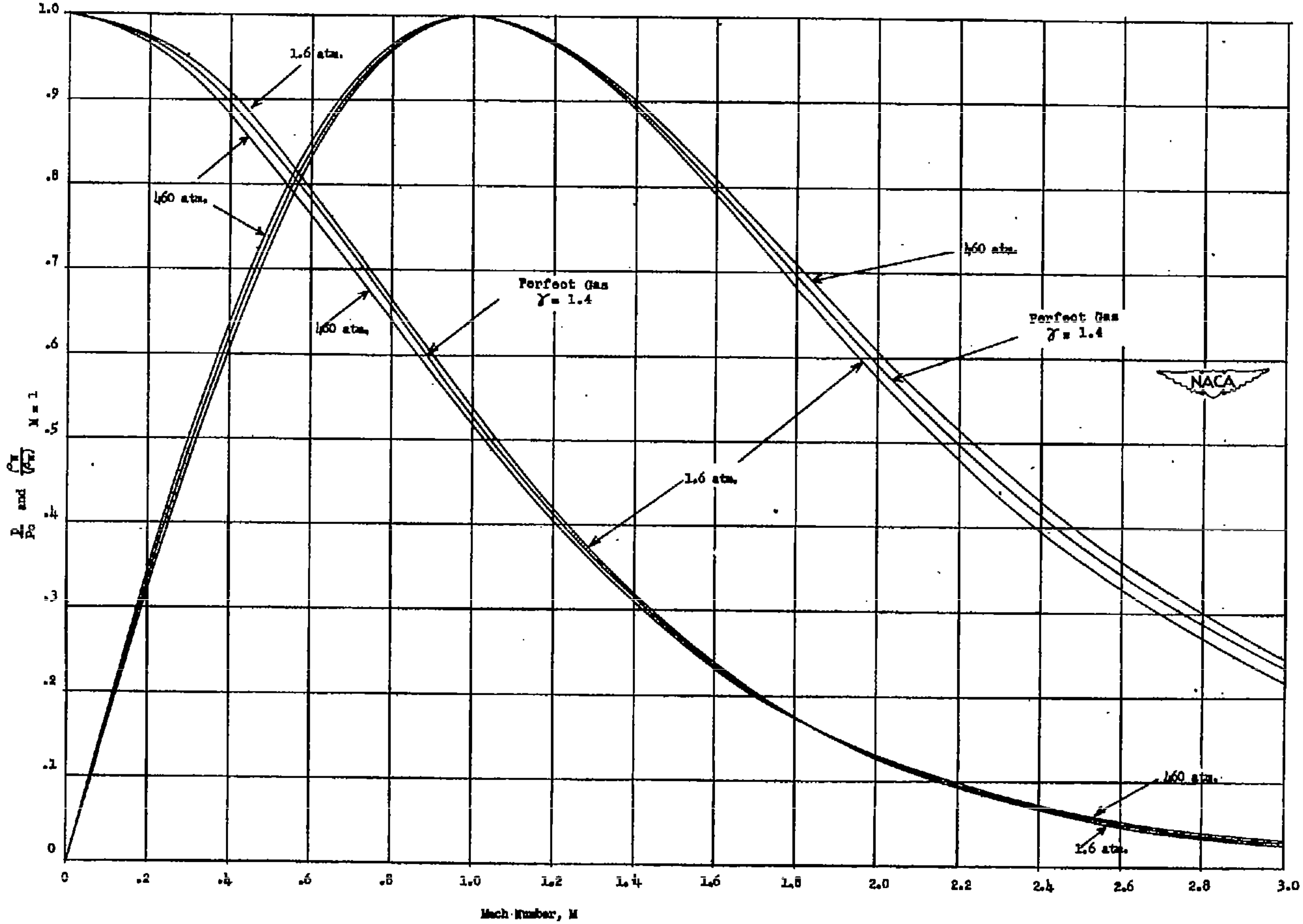


Figure 6.- Pressure ratio and area ratio plotted against Mach number for air (heat capacity and imperfect-gas effects considered). $T_0 = 2000^\circ$ F abs.