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REPORT 1259

SOME POSSIBILITIES OF USING GAS MIXTURES OTHER THAN AIR IN AERODYNAMIC RESEARCH

By DEAN R. CHAPMAN

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ERRATA

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Page 6, $\bar{R}$ should be $\overline{Re}$ in equation (17a).

Page 18, $\frac{Dp}{Dt}$ should be $\frac{D\rho}{Dt}$ in equation (C8).

NACA - Langley Field, Va.

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REPORT 1259

SOME POSSIBILITIES OF USING GAS MIXTURES OTHER THAN AIR IN AERODYNAMIC RESEARCH[1]

By DEAN R. CHAPMAN

SUMMARY

A study is made of the advantages that can be realized in compressible-flow research by employing a substitute heavy gas in place of air. Most heavy gases considered in previous investigations are either toxic, chemically active, or (as in the case of the Freons) have a ratio of specific heats greatly different from air. The present report is based on the idea that by properly mixing a heavy monatomic gas with a suitable heavy polyatomic gas, it is possible to obtain a heavy gas mixture which has the correct ratio of specific heats and which is nontoxic, nonflammable, thermally stable, chemically inert, and comprised of commercially available components.

Calculations were made of wind-tunnel characteristics for 63 gas pairs comprising 21 different polyatomic gases properly mixed with each of three monatomic gases (argon, krypton, and xenon). For a given Mach number, Reynolds number, and tunnel pressure, a gas-mixture wind tunnel having the same specific-heat ratio as air would be appreciably smaller and would require much less power than a corresponding air wind tunnel. Analogous though different advantages can be realized in compressor research and in firing-range research.

The most significant applications, perhaps, arise through selecting and proportioning a gas mixture so as to have at ordinary wind-tunnel temperatures certain dimensionless characteristics which air at flight temperatures possesses but which air at ordinary wind-tunnel temperatures does not possess. Characteristics which involve the relaxation time (or bulk viscosity), the variation of viscosity with temperature, and the variation of specific heat with temperature fall within this category. Other applications arise in heat-transfer research since certain gas mixtures can be concocted to have any Prandtl number in the range at least between 0.2 and 0.8.

INTRODUCTION

The reasons for considering gases other than air as possible test media for compressible-flow research stem primarily from the relatively low speed of sound in certain gases. In general, the heavier the gas, the lower the speed of sound at a fixed temperature. Hence, experiments conducted at a given Mach number in a heavy gas will be conducted at lower velocity than the corresponding experiment in air. Some significant advantages of conducting wind-tunnel, firing-range, and compressor experiments at a reduced velocity have been noted previously in the work of Theodorsen and Regier (ref. 1), Smelt (ref. 2), Kantrowitz (ref. 3), Huber (ref. 4), Buell (ref. 5), Donaldson (ref. 6), and von Doenhoff and Braslow (ref. 7). Some uses of gases other than air in shock tube research are discussed by Duff in reference 8. These investigations show that the substitution of a heavy gas for air offers the possibility of: (1) extending the range of existing research apparatus; (2) achieving greater economy of construction and operation of large high-speed wind tunnels; and (3) providing greater facility in obtaining data for special types of research. These advantages will be discussed briefly in the order listed.

The possibility of extending the range of existing apparatus was clearly demonstrated by the experiments of Theodorsen and Regier, which appear to be the first compressible-flow experiments in which supersonic aerodynamic data were obtained in a gas other than air. By rotating propellers in Freon 113 (CCl_2FCClF_2, having a speed of sound 0.39 times that of air, and a density 6.5 times as great) they were able to achieve tip Mach numbers of 2.7; whereas the highest tip Mach number achieved with the same apparatus using air was 1.0. Also, much higher Reynolds numbers were obtained. In a similar fashion, Buell employed the Freons, and Donaldson employed xenon as the test medium through which projectiles were fired in order to obtain Mach numbers much higher than could be obtained with the same apparatus by firing through air. An extended range of operation of a wind tunnel has been demonstrated by von Doenhoff and Braslow who report that the maximum attainable test-section Mach number of the Langley low-turbulence pressure tunnel was increased from 0.4 to 1.2 by replacing air with Freon 12.

A possibility of achieving greater economy by employing a substitute heavy gas in a wind tunnel arises because the test-section dimensions are smaller and the horsepower required is only a fraction of that required for an air wind tunnel operating at the same Mach number, Reynolds number, and pressure. Smelt has made a general study pointing out this possibility for various inert gases that have, unfortunately, a specific-heat ratio different from air. The importance of reduced power requirements, if accomplished without sacrifice in ratio of specific heats, needs no elaboration in view of the power of modern wind tunnels.

The third advantage mentioned, namely, facilitating certain types of aerodynamic research, arises in two separate

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[1] Supersedes NACA TN 3226 by Dean R. Chapman, 1954, to which various additions have been made in the present report.

ways. First, for a given Mach and Reynolds number, the use of a heavy gas with its low velocity of sound enables experiments to be conducted at lower velocity and lower pressure than if air were employed; this results, for example, in lower stresses in wind-tunnel models as well as in models launched from a gun. Similarly, the reduced velocity enables experiments on the release of objects from supersonic vehicles to be conducted at smaller scale while simulating the required value of the Froude number (U_∞^2/gl). Second, and more important, the use of certain gas mixtures other than air enables some of the dimensionless parameters pertinent to hypersonic flight through air to be simulated at the usual wind-tunnel temperatures which cannot be simulated by use of air at these wind-tunnel temperatures. Several of such possibilities are discussed later in this report.

As regards the various disadvantages involved by using substitute heavy gases in aerodynamic research, the main ones are: (1) The ratio of specific heats (γ) differs from that of air for the heavy gases proposed thus far; (2) the use of any gas other than air results in more severe practical problems of operating a research facility.[2] A general appraisement of the various advantages relative to disadvantages cannot be made since this would depend on each particular case. The purposes of this report are to study various heavy gas mixtures which appear satisfactory for aerodynamic testing and to evaluate the magnitude of the advantages such gases offer. Knowledge of these advantages will enable a comparison with the disadvantages to be made in a given case.

The present research was begun upon conception of the following simple idea:[3] The proper ratio of specific heats ($\gamma=1.4$) can be achieved with a heavy gas by suitably mixing a heavy monatomic gas ($\gamma>1.4$) with a heavy polyatomic gas ($\gamma<1.4$). Exploitation of this simple idea turned out to be unexpectedly arduous because of difficulties involved in obtaining adequate chemical, physical, pharmacological, and thermodynamic data on the many polyatomic gases known to modern chemistry. Primarily as a result of recent developments in the field of fluorochemicals, it was possible to find among the known polyatomic gases over 30 which were indicated by available data to be sufficiently nontoxic, nonflammable, chemically inert, and thermally stable to justify consideration. Evaluation of the relative advantages of each polyatomic gas for aerodynamic testing requires calculating the thermodynamic properties from spectroscopic data, determining the proper proportions for mixing from thermodynamic properties, and then computing the density and viscosity that would result when mixed with each of three monatomic gases considered (argon, krypton, and xenon).

NOTATION

a	speed of sound
c	speed of light
c_p	specific heat per unit mass
C_p	specific heat per mole
CR	wind-tunnel compression ratio
g	acceleration of gravity
h	Planck's constant
H	molar enthalpy
HP	horsepower
k	Boltzman's constant
l	characteristic length of model
L	characteristic dimension of wind-tunnel test section
m	molecular weight (29 grams per mole for air)
M	Mach number
n	number of atoms per molecule
p	pressure
q	dynamic pressure, $\frac{1}{2}\rho u^2$
R	universal gas constant per mole (1.987 cal. mole^{-1} °K^{-1})
Re	Reynolds number
T	temperature
u	velocity
V	volume of gas
w	mass-flow rate, (ρu) times (cross-section area)
x	mole fraction, equal to ratio of partial pressure to mixture static pressure and equal to fraction by volume
τ	relaxation time
γ	ratio of specific heats
κ	bulk viscosity coefficient
ρ	mass density
μ	viscosity coefficient
ω	wave number (cm^{-1}, from spectroscopic data)

SUBSCRIPTS

∞	free-steam conditions in test section
c	critical conditions for gaseous phase of a compound
t	total conditions for gas brought isentropically to rest (wind-tunnel reservoir conditions)
o	0° centigrade
1	monatomic gas
2	polyatomic gas

SUPERSCRIPTS

$-$	quantity divided by corresponding quantity for air

METHODS OF SELECTING GASES AND COMPUTING CHARACTERISTICS OF VARIOUS GAS MIXTURES

SELECTION OF GASES

The selection of monatomic gases for consideration is simple, since only four such gases are known—argon, krypton, xenon, and radon—that have a molecular weight greater than air. Radon, the heavist of all, unfortunately must be excluded because of its radioactivity. The remaining three gases are completely inert. Some of their properties

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[2] A possible disadvantage sometimes expressed (e. g., ref. 9) is that the relaxation time for molecular vibrations in certain polyatomic gases would invalidate data obtained at supersonic velocities. However, for most gases considered here, this is believed not to be the case. Reasons for this are discussed later.

[3] After completion of the main body of calculations, a short unpublished note by E. F. Relf, in England, became available in which the possibility of obtaining the proper ratio of specific heats through mixing gases also was pointed out. Relf made a rough estimation for a mixture of sulfur hexafluoride and xenon, which is one of the mixtures considered in the present research.

pertinent to the present analysis are listed in table I. Although argon is the only one now commercially available in large quantities, both krypton and xenon will be considered since they might be of use for special research in small apparatus, and since their availability undoubtedly will increase in the future.[4]

The selection of polyatomic gases for consideration was rather tedious. Of the approximately 13,000 polyatomic compounds listed in the 1952 Handbook of Chemistry and Physics (ref. 12), 103 were found to be gases at 0° C. Compounds that are not gaseous at 0° C were not considered. Most of the gases were not considered further because they possessed some intolerable characteristic such as being highly poisonous (e. g., $COCl_2$, S_2F_{10}, C_2N_2, SO_2), toxic (e. g., CH_3F, CF_2Br_2, CH_3CH_2F), combustible (e. g., COS, all hydrocarbon gases), unstable (e. g., CHCCl, ClN_3, PSF_3), or generally active chemically (e. g., BF_3, F_2O, CF_3SF_3, CF_3OF). Still others were eliminated for less obvious reasons, such as reacting with water vapor to yield corrosive products (e. g., SiF_4, PF_3, COF_2, TeF_6), or having a tendency to polymerize under pressure (e. g., $CClFCF_2$, CH_2CF_2, CF_2CF_2), or being active when in the presence of mercury (F_3CNNCF_3), or imparting, upon inhalation, an offensive odor to the breath which persists long after inhalation (TeF_6). This elimination process left 16 polyatomic gases for further consideration. It was noticed that all but two (CO_2 and N_2O, the lightest two on the list) contained at least two atoms of fluorine per molecule. Because fluorine appeared to be the key to the problem, recent technical publications on fluorine chemistry were scanned (especially refs. 13, 14, and 15) for further information. From this search 15 additional polyatomic gases were found which met the required conditions of being nontoxic, noncombustible, chemically inactive, and thermally stable. Among these 15 recently synthesized gases were several (e. g., $CBrF_3$) which turned out to be the most efficient for wind-tunnel use. Undoubtedly, additional new polyatomic gases will continue to be synthesized in the future inasmuch as a large industrial effort is being expended on fluorine chemistry. Quite a few apparently satisfactory gases (e. g., C_3ClF_7 and C_2HF_5) are known to be omitted from the list. Consequently, the present report which primarily indicates current possibilities of gas mixtures in reducing wind-tunnel power is by no means exhaustive and might considerably underestimate possibilities existing in the future.

It is pertinent to focus attention here on the extreme properties of fluorochemicals. Their chemistry often is totally unlike that of analogous halide compounds. Fluorochemicals include some of the most toxic compounds known, yet also include the most inactive and nontoxic compounds known. Their thermal stability and resistance to electric breakdown are unusually high. Most of these extreme properties can be illustrated by a few examples. First consider the following two gases: chloroform, $CHCl_3$, and fluoroform, CHF_3. The toxicity of chloroform is well known. Fluoroform, however, is indicated to be completely inert physiologically (ref. 16). Guinea pigs can live in an atmosphere of 80 percent fluoroform and 20 percent oxygen without being affected either during the test or afterward. Sulfur hexafluoride, SF_6, also is indicated to be physiologically inert on the basis of similar tests with small animals (ref. 17). On the other hand, the deceptively similar sulfur pentafluoride, $(SF_5)_2$, is extremely poisonous, since, for concentrations as low as one part per million—in which concentration phosgene is harmless—sulfur pentafluoride is lethal (ref. 18). Further illustration of the extreme properties of fluorochemicals is provided by carbon tetrafluoride, CF_4. The thermal decomposition temperature of CF_4 has not yet accurately been determined since it is so high as to be in the vicinity of the carbon arc temperature (ref. 19). Carbon tetrafluoride has been heated in the presence of many metals up to the temperature at which glass softens without any reaction occurring. (See ref. 14, p. 433.) Sulfur hexafluoride is equally remarkable in its chemical inactivity at all temperatures below the softening point of glass.

The chemical symbol, molecular weight, chemical name, and trade name of 31 polyatomic gases considered as possible components for aerodynamic test media are listed in the first four columns of table II. A symbol designating the general classification of each gas is listed in the fifth column. The meaning of each symbol is explained in the footnote of the table. Listed in table III are certain data, to be utilized later, regarding the boiling point, critical constants, viscosity coefficient, and spectroscopic frequencies of the various polyatomic gases. The sources of data for each gas are indicated by reference numbers in the last three columns of table II. These data were compiled from references 13 to 16 and 18 to 56.

COMPUTATION OF THERMODYNAMIC PROPERTIES

The first step in evaluating aerodynamic qualities of any gas is to determine its thermodynamic properties such as specific heat and enthalpy. When two gases are mixed, the resulting thermodynamic properties can be calculated from the thermodynamic properties of the individual components. Using subscript 1 to denote the monatomic component, and subscript 2 to denote the polyatomic component, the following equations apply for binary mixtures of thermally perfect gases:

molecular weight
$$m=x_1m_1+x_2m_2 \tag{1}$$

equation of state
$$p=\rho RT/m \tag{2}$$

specific heat
$$C_v+R=C_p=x_1C_{p_1}+x_2C_{p_2} \tag{3}$$

ratio of specific heats
$$\gamma=\frac{x_1C_{p_1}+x_2C_{p_2}}{x_1(C_{p_1}-R)+x_2(C_{p_2}-R)} \tag{4}$$

enthalpy
$$H=x_1H_1+x_2H_2 \tag{5}$$

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[4] See references 10 and 11 for information on the possible future availability of the monatomic gases.

where R is the universal gas constant (1.987 cal. $°K^{-1}$ mole^{-1}), and x denotes the mole fraction of a component (equal to the fraction by volume, or the fractional partial pressure of the component) and is subject to the relation $x_1+x_2=1$. For all monatomic gases,

$$C_{p_1}=\frac{H_1}{T}=\frac{5}{2}R=4.97 \text{ cal. } °K^{-1} \text{ mole}^{-1}$$

Hence, from equation (4), it follows that for $\gamma=7/5$,

$$1-x_1=x_2=\left(\frac{C_{p_2}}{R}-\frac{5}{2}\right)^{-1} \tag{6}$$

The thermodynamic properties of a polyatomic gas can be accurately computed from infrared and/or Raman spectroscopic data, using equations developed by methods of statistical mechanics (see ref. 57, for example). For linear molecules (e. g., CO_2 and N_2O), wherein the atoms are arranged in a straight line,

$$\frac{C_{p_2}}{R}=\frac{7}{2}+\sum_{1}^{3n-5}\frac{\left(\frac{hc\omega_i}{2kT}\right)^2}{\sinh^2\left(\frac{hc\omega_i}{2kT}\right)} \tag{7}$$

$$\frac{H_2}{RT}=\frac{7}{2}+\sum_{1}^{3n-5}\frac{\left(\frac{hc\omega_i}{kT}\right)}{\exp\left(\frac{hc\omega_i}{kT}\right)-1} \tag{8}$$

The various wave numbers ω_i determined from spectroscopic data for each gas are listed in table III. The constant hc/k is equal to 1.4385 °K cm. For nonlinear molecules not subject to internal rotation (e. g., CF_4, CHF_3, SF_6, etc.)

$$\frac{C_{p_2}}{R}=4+\sum_{1}^{3n-6}\frac{\left(\frac{hc\omega_i}{2kT}\right)^2}{\sinh^2\left(\frac{hc\omega_i}{2kT}\right)} \tag{9}$$

$$\frac{H_2}{RT}=4+\sum_{1}^{3n-6}\frac{\frac{hc\omega_i}{kT}}{\exp\left(\frac{hc\omega_i}{kT}\right)-1} \tag{10}$$

For nonlinear molecules subject to a torsional mode of oscillation (e. g., CF_3CF_3, CHF_2CClF_2, and all other ethane-like molecules) the above summations were employed only for the $3n$–5 normal modes, and the torsional contribution was computed from the Pitzer-Gwinn tables (reproduced in ref. 58) using values for the potential barrier estimated from spectroscopic data. Computations were greatly facilitated through use of the tables of reference 58. Typical curves showing the molar specific heat as a function of temperature for several of the various gases considered are presented in figure 1. Curves of this type, together with equation (4), were used for each gas to determine the mixture proportions necessary to obtain a value of 1.4 for γ. Similar data for the enthalpy were used to compute Mach number, pressure ratio, etc., for the different flow conditions considered.

It is noted that the thermodynamic properties calculated from spectroscopic data agree well with direct calorimetric measurements. This is illustrated in the following table:

Gas	T, °C	Calculated C_p (from spectroscopic data of table III)	Experimental C_p (from direct calorimetric measurements)	
CO_2	−75	7.71	7.78	ref. 57
	20	8.82	8.80	
	220	10.62	10.63	
CCl_2F_2	−30	15.6	15.7	ref. 51
	0	16.6	16.7	
	45	17.8	18.0	
	90	18.9	19.1	
CF_3CF_3	−50	21.1	21.0	ref. 22
	10	24.7	24.4	
	90	28.7	28.2	

COMPUTATIONS OF VISCOSITY

It will be seen subsequently that for a given Reynolds number and Mach number, the power required by a wind tunnel is directly dependent on the gas viscosity coefficient. The viscosity of a mixture of two gases can be approximately calculated from the equation (see ref. 59):

$$\mu=\frac{\mu_1}{1+\frac{\frac{x_2}{x_1}\left[1+\sqrt{\frac{\mu_1}{\mu_2}}\left(\frac{m_2}{m_1}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left(1+\frac{m_1}{m_2}\right)^{1/2}}}+\frac{\mu_2}{1+\frac{\frac{x_1}{x_2}\left[1+\sqrt{\frac{\mu_2}{\mu_1}}\left(\frac{m_1}{m_2}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left(1+\frac{m_2}{m_1}\right)^{1/2}}} \tag{11}$$

It is noted that a simple linear interpolation between the values of μ for each component is not an adequate method of estimating the viscosity of the mixture. This is illustrated by several examples in figure 2. Curves of this type were constructed for all gas mixtures considered.

Experimental data are available for the viscosity μ_1 of the three monatomic gases, but very little data are available for the various polyatomic gases. Fortunately, the coefficient of viscosity can be estimated quite satisfactorily from knowledge of the critical temperature T_c, critical volume V_c, and molecular weight by the equation

$$\mu=\frac{\sqrt{mT_c}}{(V_c)^{2/3}}F\left(\frac{T}{T_c}\right) \tag{12}$$

This equation may be deduced from the general equations for gases having intermolecular forces dependent only on powers of the distance between molecules. (See refs. 59 and 60). Rather than to use the elaborate theoretical evaluation of the function $F(T/T_c)$, the more simple empirical evaluation of reference 61 is used:

$$F\left(\frac{T}{T_c}\right)=\left\{\begin{array}{ll}27.1\,T/T_c & \text{for} \quad T<1.6T_c \\ \dfrac{27.1\,T/T_c}{1+0.0952\left(\frac{T}{T_c}-1.6\right)} & \text{for} \quad T>1.6T_c\end{array}\right\} \tag{12a}$$

where T is in °K, m is in gm./mole, V_c is in cc/gm. mole, and μ is in micropoise. A comparison of the calculated and experimental viscosity coefficients of all gases considered for

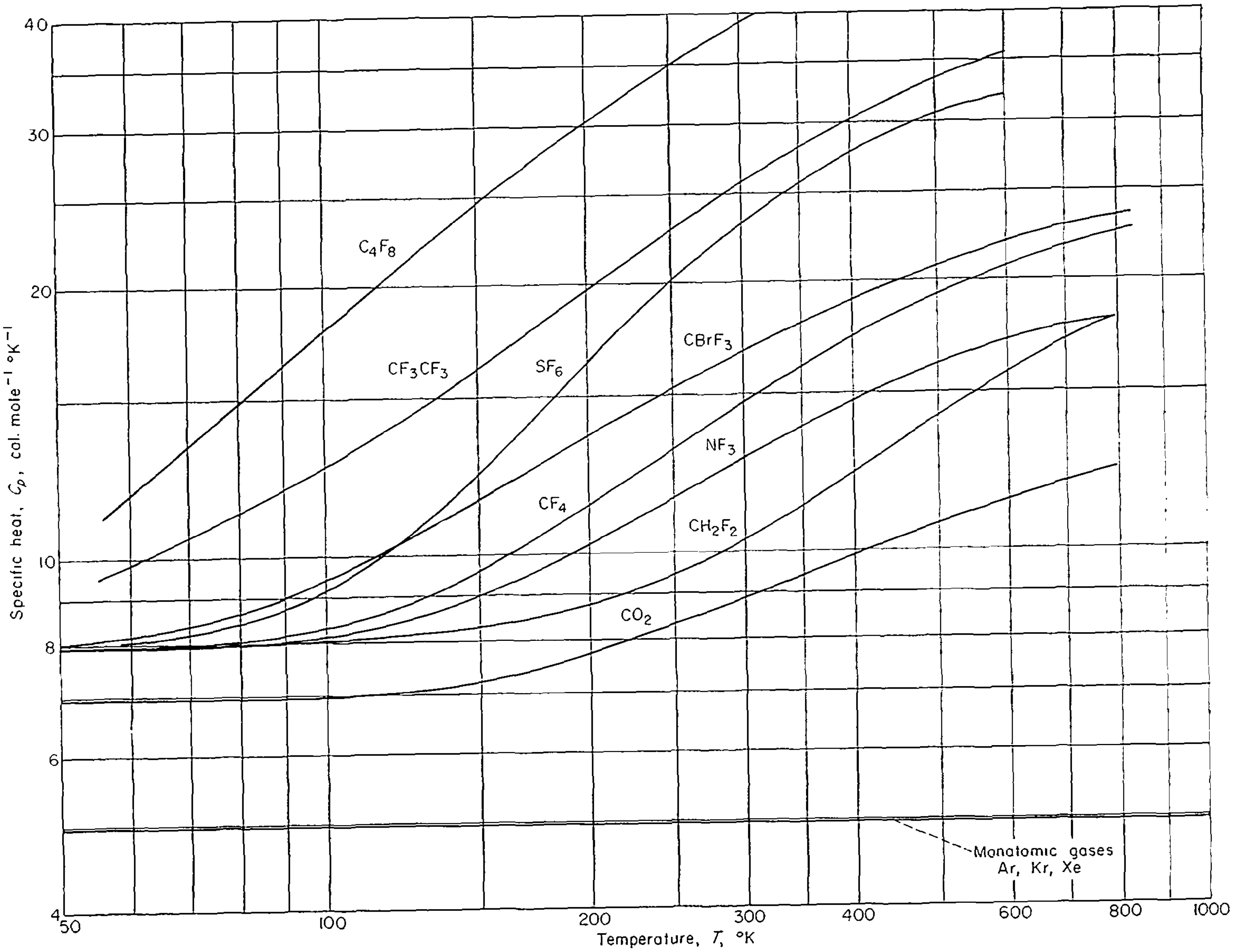


FIGURE 1.—Some typical examples of specific heat computed from spectroscopic data.

which experimental data could be found is given in the following table:

Gas	Viscosity at 0° C in micropoises	
	Calculated	Experimental
Ar	210	210
Kr	229	230
Xe	211	210
SF_6	146	142
CCl_2F_2	114	118
$CHClF_2$	119	120
CO_2	134	137
N_2O	132	135
Air	170	172

This agreement is satisfactory. Consequently, in the calculations of wind-tunnel power requirements, experimental values of μ are employed for the 9 gases listed above, but values computed from equation (12) are employed for the remaining gases for which experimental data are not available. Since molecules of the above 9 gases are either simple or approximately spherical in structure, the accuracy of calculations from equation (12) is expected to be less for greatly different molecular structures, such as that of C_4F_{10}, but probably is sufficient for present purposes.

WIND-TUNNEL POWER AND SIZE

The general equation for compressor power required to maintain a steady rate of mass flow w of a perfect gas through a compression ratio CR starting with an initial temperature T_t is given by the equation

$$HP=J\frac{wc_pT_t}{\eta}[(CR)^{(\gamma-1)/\gamma}-1] \tag{13}$$

where J is a numerical constant depending only on the units employed, η is the combined adiabatic and mechanical efficiency (assumed to be independent of the gas), and c_p is the specific heat per unit mass. It is noted that c_p in equation (13) is related to the molar specific heat C_p and the molar universal gas constant R through the equation

$$mc_p=C_p=\frac{\gamma}{\gamma-1}R \tag{14}$$

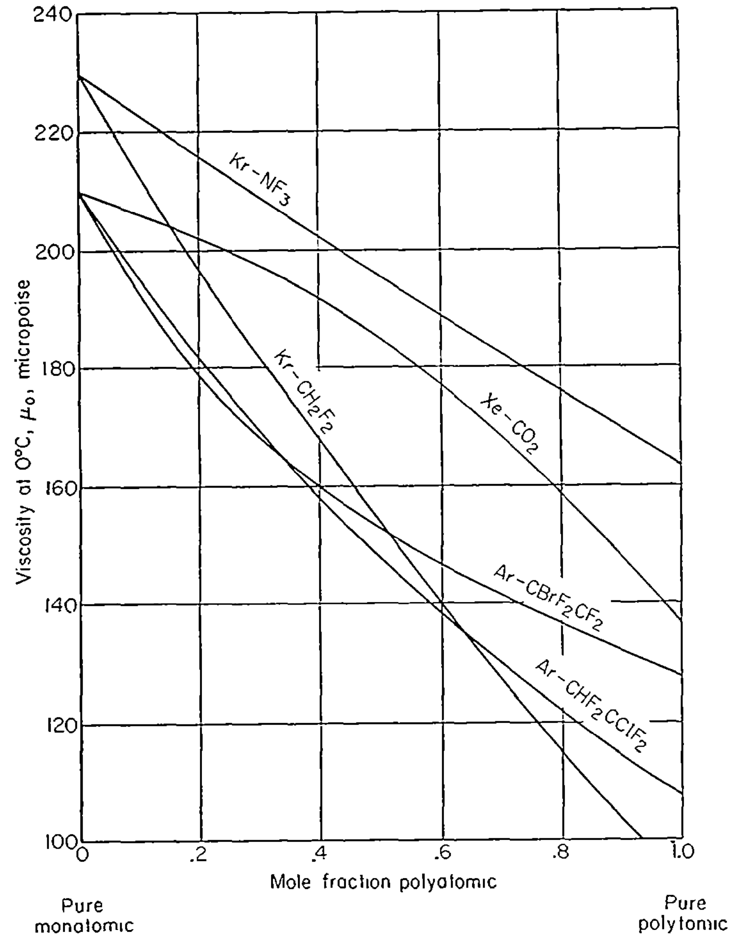


FIGURE 2.—Some typical examples of viscosity coefficient for gas mixtures.

By using a bar to denote a quantity divided by the corresponding quantity for air (e. g., $\overline{m}\equiv m/(m)_{\text{air}}$, $\overline{w}\equiv w/(w)_{\text{air}}$, $\overline{HP}\equiv HP/(HP)_{\text{air}}$, etc.), there results

$$\overline{HP}=\frac{\overline{w}}{\overline{m}}\,\overline{T}_t\overline{Y}(\gamma,CR)=\frac{\overline{\rho}_\infty\overline{u}_\infty\overline{L}^2}{\overline{m}}\,\overline{T}_t\overline{Y}(\gamma,CR) \tag{15}$$

where $Y(\gamma,CR)\equiv\frac{\gamma}{\gamma-1}\,[(CR)^{(\gamma-1)/\gamma}-1]$, and L is a characteristic dimension of the test section. A more convenient equation is obtained by introducing the Reynolds number

$$\overline{HP}=\frac{\overline{Re\mu L}}{\overline{m}}\,\overline{T}_t\overline{Y}(\gamma,CR) \tag{16}$$

from which it is apparent that, as Smelt (ref. 2) has pointed out, power economy can be achieved by employing a gas with low viscosity and high molecular weight, or by testing at the lowest temperature possible, or by testing in the smallest facility (highest operating pressure) that will yield the given Reynolds number. The quantities $\overline{Re}$ and $\overline{L}$ are related to the relative operating tunnel pressure $\overline{p}_t$

$$\overline{Re}=\frac{\overline{\rho}_\infty\overline{u}_\infty\overline{L}}{\overline{\mu}}=\left[\overline{\left(\frac{\rho_\infty}{\rho_t}\right)}\frac{\overline{p}_t\overline{m}}{\overline{T}_t}\right]\left[\overline{\left(\frac{u_\infty}{a_t}\right)}\sqrt{\frac{\overline{\gamma}\,\overline{T}_t}{\overline{m}}}\right]\frac{\overline{L}}{\overline{\mu}}$$

$$=\overline{p}_t\sqrt{\frac{\overline{m}}{\overline{T}_t}}\,\frac{\overline{L}}{\overline{\mu}}\overline{\left(\frac{\sqrt{\gamma}\rho_\infty u_\infty}{\rho_t a_t}\right)}$$

or, finally,

$$\overline{L}=\frac{\overline{Re}\,\overline{\mu}\sqrt{\overline{T}_t}}{\overline{p}_t\sqrt{\overline{m}}\,\overline{f}(\gamma,M_\infty)} \tag{17}$$

where

$$\overline{f}(\gamma,M_\infty)\equiv\overline{\left(\frac{\sqrt{\gamma}\rho_\infty u_\infty}{\rho_t a_t}\right)}$$

Equation (17) shows that by increasing the molecular weight, or decreasing the viscosity, the size of wind tunnel required to obtain a given Reynolds number can be reduced. Hence, an alternate equation for relative wind-tunnel power is

$$\overline{HP}=\frac{(\overline{Re})^2\,\mu^2\,(\overline{T}_t)^{3/2}}{\overline{p}_t(\overline{m})^{3/2}}\,\frac{\overline{Y}(\gamma,CR)}{\overline{f}(\gamma,M_\infty)} \tag{18}$$

Equations (16), (17), and (18) are a generalization of similar equations developed by Smelt.

For subsequent computations, the above equations can be simplified. It will be assumed that CR depends only on M_∞. (To achieve this in an air tunnel, the compressor speed would have to be reduced for a heavy gas.) For the case of transonic wind tunnels CR is the order of 1.3 or less, and direct numerical calculations show that $0.97<\overline{Y}(\gamma,1.3)<1$ for any γ between 1.1 and 1.4. Hence, $\overline{Y}=1$ is a good approximation for transonic wind tunnels irrespective of γ. For the case of supersonic wind tunnels, only gas mixtures having $\gamma\approx1.4$ are considered, for which $\overline{Y}(1.4,CR)=1$. Consequently, in all cases of concern here, $\overline{Y}=1$ is an adequate approximation. A similar argument shows that the ratio $\overline{Y}(\gamma,CR)/\overline{f}(\gamma,M_\infty)$ is approximately unity for the range of γ and M_∞ considered here. Inasmuch as all calculations will be made on the basis that $\overline{T}_t=1$, the above equations simplify to

$$\overline{HP}=\frac{\overline{Re}\,\overline{\mu}\,\overline{L}}{\overline{m}} \tag{16a}$$

$$\overline{L}=\frac{\overline{R}\;\overline{\mu}}{\overline{p}_t\sqrt{\overline{m}}} \tag{17a}$$

$$\overline{HP}=\frac{(\overline{Re})^2(\overline{\mu})^2}{\overline{p}_t(\overline{m})^{3/2}} \tag{18a}$$

Four illustrative cases will be considered: (1) given M_∞, Re, and L; (2) given M_∞, L, and p_t; (3) given M_∞, L, and HP; and (4) given M_∞, Re, and p_t. Since for all cases $\overline{T}_t=\overline{M}_\infty=1$, the reduction in velocity is always $\overline{u}_\infty=(\overline{m})^{-1/2}$.

Case (1): Given M_∞, Re, and L.—This case corresponds to operating a given wind tunnel ($\overline{L}=1$) with a gas other than air at the same values of M_∞ and Re as for air. The horsepower required for the gas mixture relative to that for air is $\overline{HP}=\overline{\mu}/\overline{m}$. However, from equation (17a), it is seen that $\overline{p}_t=\overline{\mu}/\sqrt{\overline{m}}$ for given values of Re and L. Hence, in order to achieve the same Re with a heavy gas as with air, the given tunnel would be operated at a lower pressure, resulting in model loads that are proportionately lower, since $\overline{q}=\overline{p}_t=\overline{\mu}/\sqrt{\overline{m}}$.

Case (2): Given M_∞, L, and p_t.—This case corresponds to substituting a gas other than air in a given wind tunnel and operating at the same pressure and Mach number as for air. From equation (17a) it follows that $\overline{Re}=\sqrt{\overline{m}}/\overline{\mu}$. This indicates that higher Reynolds numbers would be achieved with a heavy gas than with air, while (according to eq. (16a)) simultaneously drawing less power by the ratio $\overline{HP}=(\overline{m})^{-1/2}$ Since $\overline{p}_t=1$, model stresses are unchanged for this case.

Case (3): Given M_∞, L, and HP.—This case corresponds to replacing air in a given tunnel by a gas mixture and drawing the same power for a fixed Mach number. The Reynolds number, from equation (16a), would be increased by the factor $\overline{Re}=\overline{m}/\overline{\mu}$. In order to draw the same power as with air, the pressure and, hence, model loads would have to be increased by the factor $\overline{p}_t=\sqrt{\overline{m}}$.

Case (4): Given M_∞, Re, and p_t.—This case corresponds to conditions that might be prescribed in the initial design of a new wind tunnel whose size is to be determined by the required values of M_∞ and Re, by the selected value of p_t, and by the gas employed. From equation (18a) it is evident that in this case, the horsepower required for a heavy gas mixture is less than for air by the factor

$$\overline{HP}=\frac{(\overline{\mu})^2}{(\overline{m})^{3/2}} \tag{19}$$

This represents a greater power reduction than in the cases above because the gas-mixture wind tunnel, according to equation (17b), would be smaller than the corresponding air tunnel by the factor

$$\overline{L}=\overline{\mu}/\sqrt{\overline{m}} \tag{20}$$

The gas-mixture wind tunnel would produce the same aerodynamic data as the larger air tunnel with the same model stresses. Computations based on these latter two equations are presented later.

MACH NUMBER LIMIT FOR CONDENSATION

Although any of the polyatomic gases would be usable in apparatus where low temperatures are not involved, such as in a subsonic wind tunnel, a firing range, or a compressor research apparatus, only a limited number would be useful in a supersonic wind tunnel where the static temperatures encountered are low and can result in condensation. An essential step in evaluating various polyatomic gases, therefore, is to determine the approximate useful Mach number range for each gas. The method of determining this was to draw the isentropic expansion curve for the partial pressure of each polyatomic gas on log-log paper together with the curve for saturation vapor pressure of that gas. As indicated in figure 3, the intersection point yields T_{min}, from which the maximum Mach number can be calculated from the relation

$$M^2=\frac{2}{\gamma}\left(\frac{H_t}{RT}-\frac{H}{RT}\right)$$

where γ and H/T are determined from spectroscopic data by equations (4) through (10). Graphical solutions of this type were made for operating conditions of approximately 40° C (100° F) total temperature and several atmospheres total pressure. These solutions enabled the appropriate polyatomic gases to be selected for each of several design Mach numbers considered in the evaluation. It is emphasized that the graphical method included consideration of the variation of specific heat with temperature. As will be seen subsequently, such variation is of dominant importance in determining the limiting Mach number to which certain gases can be expanded without reaching saturation. Simplified criteria, such as boiling temperature, are quite inadequate for determining the saturation limit.

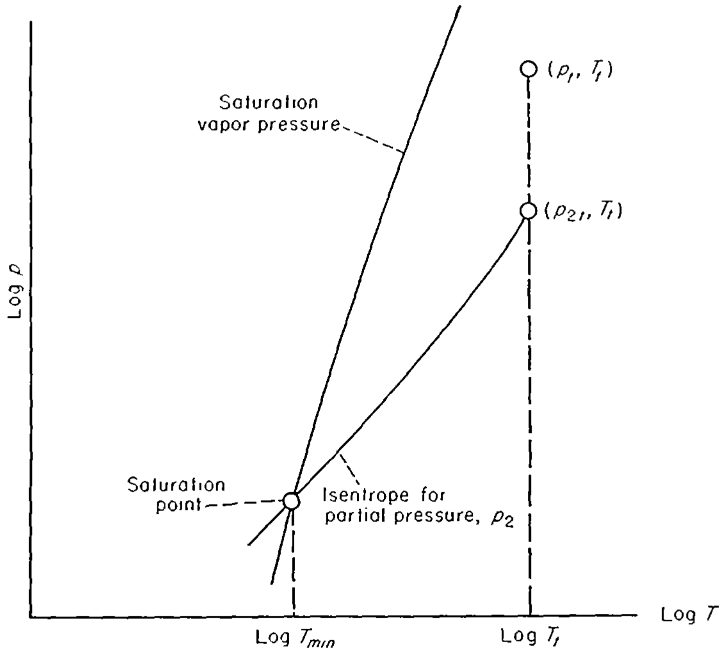


FIGURE 3.—Method of determining saturation limit.

RESULTS AND DISCUSSION

WIND-TUNNEL POWER AND SIZE

Complete computations could not be made for 10 of the 31 polyatomic gases listed in table II, since the necessary spectroscopic data and critical constants were not available for these 10 gases. Calculations have been made, however, of the relative wind-tunnel power requirements for 63 gas pairs comprising mixtures of the 21 polyatomic gases for which data are available with each of the 3 monatomic gases. Mixture proportions were determined from equation (6) by substituting a value of 1.4 for γ_∞. The calculations were made for three design Mach numbers, 1.3, 2.5, and 3.5. Results are tabulated in tables IV (a), IV (b), and IV (c), respectively. It should be noted that all 21 polyatomic gases are included in table IV (a), since all are free from condensation at $M_\infty=1.3$. Only 7 gases for $M_\infty=2.5$ (table IV (b)) and 2 gases for $M_\infty=3.5$ (table IV (c)) have sufficiently low boiling points to avoid saturation for the assumed condition of 40° C total temperature. Operation at Mach numbers above about 3.5 would require total temperatures higher than the value of 40° C arbitrarily assumed.

The values of relative horsepower $\overline{HP}$ given in table IV represent case (4) mentioned previously. This case corresponds to a comparison with an air wind tunnel for the same M_∞, Re, and p_t. If desired, any of the other three cases mentioned, or any of the individual relative quantities such as $\overline{u}_\infty$ or $\overline{\rho}_\infty$, can be readily calculated from the values of $\overline{m}$ and $\overline{\mu}$ listed in the tables and from the appropriate equations developed earlier.

The tabulated results show that there is no single polyatomic gas which is best for all Mach numbers or for use with all monatomic gases. For each monatomic gas, though, there are several polyatomic gases which appear roughly equal in their ability to require low wind-tunnel power. Of the gases that currently are commercially available and not classified questionable in table II, the most efficient ones for use with argon are: CH_2F_2, $CBrF_3$, and CCl_2F_2 for $M_\infty=1.3$; $CBrF_3$ and SF_6 for $M_\infty=2.5$; and CF_4 for $M_\infty=3.5$. In general, the horsepower and size of gas-mixture wind tunnels relative to equivalent air wind tunnels are very approximately as follows:

	Mixtures		
	Argon	Krypton	Xenon
Power relative to air, $\overline{HP}$	0.3	0.2	0.1
Test-section dimension relative to air, $\overline{L}$	0.7	0.6	0.5

These figures indicate significant advantages of gas mixtures as wind-tunnel test media.

It is interesting to note that the heaviest polyatomic gas—C_4F_{10}, having $\overline{m}_2=8.2$—does not result in either the heaviest mixture or the best mixture This is due to the high molar specific heat of C_4F_{10} which requires that only a small amount (6.5 percent) be mixed with a monatomic gas in order to obtain $\gamma=1.4$. However, for applications to low-speed subsonic research where the value of γ does not matter and, hence, a mixture is not needed, the heaviest gas is the best. For example, pure C_4F_{10}, having $\gamma=1.06$, would require only 1.8 percent of the power, and an apparatus one-fourth the size of that required by air for a given M_∞, Re, and p_t In this respect pure C_4F_{10} is several times more efficient than pure Freon 12. (See table III where corresponding values are given for all pure polyatomic gases considered.) It is evident that pure polyatomic gases having $\gamma\approx1.1$ are more efficient in reducing wind-tunnel power requirements than are gas mixtures having $\gamma=1.4$.

A possibility that should not be overlooked is that a value of γ close to 1.4 may not be necessary for transonic wind tunnels or other transonic research apparatus. In view of the surprisingly small differences observed at transonic speeds by von Doenhoff and Braslow (ref. 7) between uncorrected results in Freon 12 ($\gamma=1.13$) and in air ($\gamma=1.4$), it would appear that a reduced value of γ, perhaps between 1.3 and 1.2, might yield transonic data directly applicable to air for practical purposes. If a considerably reduced value of γ is satisfactory in transonic wind tunnels (such is not anticipated in supersonic wind tunnels), then the possible advantages of gas mixtures for transonic speeds are greater than the above calculations for $\gamma=1.4$ would indicate. The following table for $CBrF_3$–Ar mixtures at $M_\infty=1.3$ illustrates this:

	Case (4): given Re, p_t, and M_∞		Case (3): given HP, M_∞, and L	
γ	$\overline{HP}$	$\overline{L}$	$\overline{Re}$	
1.4	0.37	0.74	2.0	(from table IV(a))
1.35	.30	.69	2.3	
1.3	.22	.62	2.8	
1.25	.16	.53	3.4	
1.2	.10	.44	4.5	
1.15	.06	.37	6.2	(pure $CBrF_3$)

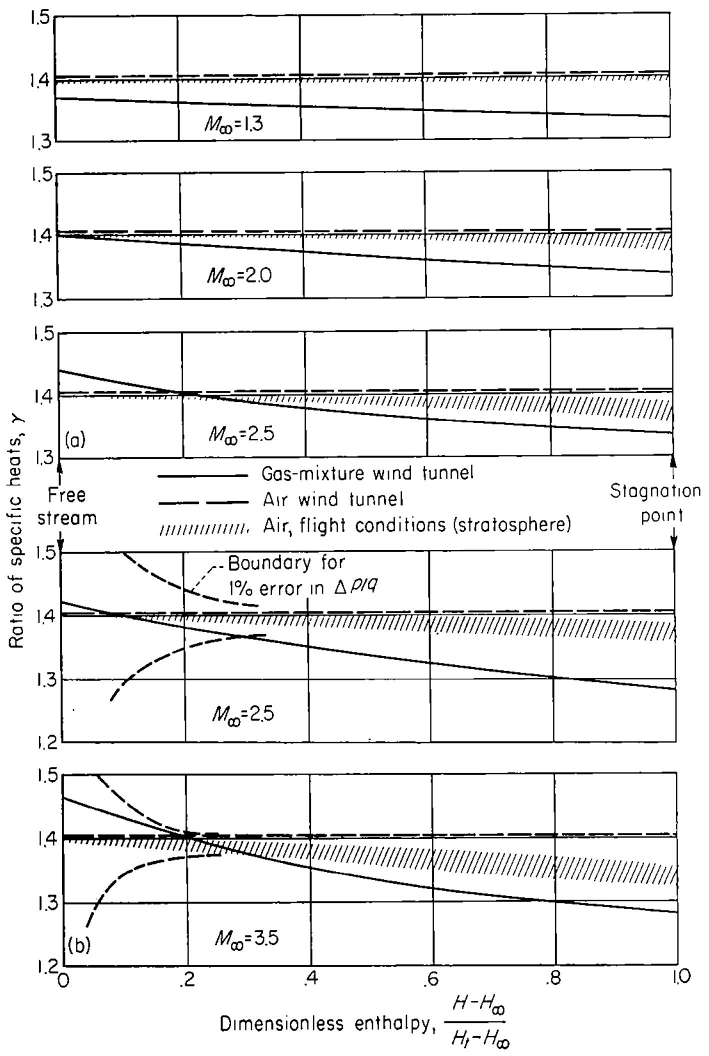
These figures, which are typical of many of the argon mixtures, show that by reducing γ to about 1.28, the power requirement for an argon gas mixture at transonic speeds would be about one-half that for the same type mixture proportioned to yield a γ of 1.4. This corresponds to one-fifth the power of an equivalent air wind tunnel operating at the same Reynolds number, total pressure, and Mach number (case (4)). Also, the Reynolds number of an existing transonic wind tunnel having a fixed horsepower (case (3)) would be about tripled if air were replaced by an argon gas mixture having $\gamma=1.28$, but only doubled by a mixture having $\gamma=1.4$. The advantages of reducing γ to the lowest practical value are apparent from the table. For xenon mixtures, however, there is less to gain by reducing γ below 1.4. It would be desirable to conduct some experiments varying the proportions of a gas mixture in order to determine to what limit γ can be reduced in a transonic flow and still yield data directly applicable to air for practical purposes.

DEVIATIONS FROM THERMAL AND CALORIC PERFECTION

Under wind-tunnel conditions air generally is considered as being both thermally perfect ($pm=\rho RT$) and calorically perfect (γ=constant). Most other gases can not be so considered. Calculations of the degree of deviation from thermal perfection for the various argon gas mixtures are presented in Appendix A. It will suffice here to state that such deviations are indicated to be unimportant for normal operating conditions of wind tunnels. The smallness of these deviations is due in part to the monatomic (argon) component, which by itself is almost thermally perfect, and, in part, to the fact that the polyatomic component is a fluorochemical. The unusually low intermolecular forces in fluorochemical gases result in small deviations from thermal perfection.

Deviations from caloric perfection, on the other hand, are not small and represent an important technical consideration. The specific heat of polyatomic gases varies widely, as figure 1 clearly indicates. Thus, a gas mixture proportioned to yield $\gamma=1.4$ for one Mach number will not yield the same value of γ at other Mach numbers. This may limit the Mach number range over which a single gas mixture could be used satisfactorily. Also, at a fixed Mach number, γ will vary with temperature. Under wind-tunnel conditions, γ for air is quite constant, but varies under flight conditions where higher temperatures are encountered.

To aid in evaluating the importance of caloric imperfections, the variation of γ with temperature has been computed for various gas mixtures and for air under both wind-tunnel and flight conditions. In these computations the spectroscopic frequencies listed in table III were employed to determine γ for the gas mixtures, whereas the tables of reference 62 were employed for air. Instead of showing the computed variation as a function of some temperature parameter, an enthalpy parameter $(H-H_\infty)/(H_t-H_\infty)$ is employed which always is zero for free-stream conditions and always is unity for reservoir conditions, regardless of the nature of the gas. Some of the results are shown in figure 4. Air under flight conditions at a given M_∞ is represented by a cross-sectioned band because ambient temperatures in the atmosphere vary considerably with altitude. Gases



(a) Gas mixture of 0.25 $CBrF_3$ with 0.75 monatomic.
(b) Gas mixture of 0.4 CF_4 with 0.6 monatomic.

FIGURE 4.—Variation of specific-heat ratio between free-stream and stagnation conditions for various gas mixtures.

under wind-tunnel conditions are represented by a single curve since a fixed reservoir temperature (about 40° C≈100° F) has been assumed. A single mixture of 25-percent $CBrF_3$ with 75-percent monatomic gas is considered in figure 4 (a). These proportions are about right for $M_\infty=2.0$. At $M_\infty=2.5$, γ_∞ is 1.44 and γ_t is 1.34. This variation does not seem excessive. At $M_\infty=1.3$, γ is uniformly less than 1.4, varying between 1.37 and 1.34. In view of previous comments about the apparent insensitivity of transonic flows to much larger variations in γ, as well as the complete insensitivity of subsonic flows to variations in γ, it would appear that a single mixture could be used satisfactorily from low subsonic speeds to at least $M_\infty=2.5$.

The situation is more complicated within the Mach number range between 2.5 and 3.5, as figure 4 (b) illustrates for the case of a single mixture of 40-percent CF_4 with 60-percent monatomic gas. It is to be noted that a variation of γ is not important at conditions close to free-stream conditions. For example, γ does not appear within the body of linearized subsonic or supersonic theory, but first appears in second-order terms. Hence, Busemann's second-order theory for two-dimensional flow has been used to estimate the range within which γ must be maintained in order to introduce less than 1-percent error in $\Delta p/q$. The boundaries of this range, indicated by dotted lines in figure 4 (b), shrink together as $M_\infty \rightarrow 1$ and as $M_\infty \rightarrow \infty$. For the moderate Mach numbers under consideration, it is seen that only the region of abscissa between about 0.2 and 1.0 is important when assessing the variations in specific-heat ratio. Consequently, it is deduced that the gas mixture of figure 4 (b) approximates flight conditions at $M_\infty=3.5$ about as well as does air in a wind tunnel. Such is not the case, though, at $M_\infty=2.5$ (top portion of fig. 4 (b)), and it is not known whether moderate γ variations near the stagnation region of the magnitude shown are important.

If moderate variations in γ are important, then the flow in an air wind tunnel will also show important differences from the flow in flight through air at Mach numbers of about 4 or greater. Throughout this report the operating temperature of a wind tunnel is assumed to be, as is current practice, either room temperature or that temperature which is sufficient to avoid condensation. Figure 5 compares the values of γ in an air wind tunnel (long dashed curves) with the corresponding values of γ in flight (cross-sectioned region). The observed γ differences between air in flight and in wind tunnels are considerably greater than any of figure 4 (b) between flight and gas-mixture wind tunnels. It

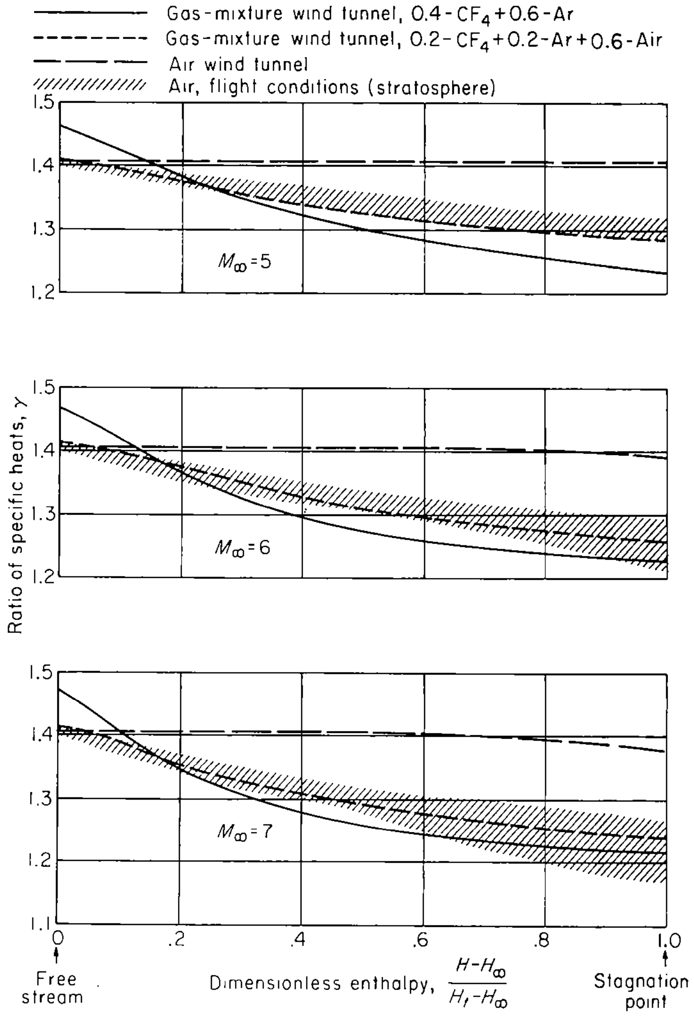


FIGURE 5.—Variation of specific-heat ratio between free-stream and stagnation conditions at hypersonic speeds.

is also evident from figure 5 that the temperature dependence of γ for polyatomic gases may actually represent a real virtue, particularly in hypersonic research. For polyatomic gases under wind-tunnel conditions, as well as for air under flight conditions, these caloric imperfections arise from a common physical phenomenon, namely, temperature dependent energy of vibration between atoms within a molecule. Under flight conditions at Mach numbers of about 6 or greater, additional energy can be transferred through dissociation, which is responsible for values of γ less than 1.28 in flight. Clearly, the ratio of specific heats is one dimensionless parameter pertinent to hypersonic flight through air—which is not simulated by air at wind-tunnel temperatures—but which is simulated by certain gas mixtures at wind-tunnel temperatures.

MACH NUMBER LIMIT FOR CONDENSATION

In order to achieve hypersonic Mach numbers in a wind tunnel without supersaturating the test medium, it is necessary, of course, to heat the medium. The approximate reservoir temperatures (estimated to nearest 25° K) corresponding to the particular gas mixtures considered in figure 4, are as follows:

Gas	Reservoir temperature °K to prevent saturation; $p_t=100$ psia		
	$M_\infty=5$	$M_\infty=6$	$M_\infty=7$
Air	350	450	550
$0.4-CF_4+0.6-Ar$	475	600	675
$0.2-CF_4+0.2-Ar+0.6$ air	500	625	750

As might be expected, the gas mixtures require higher operating temperatures than does air.

It is important to note that the trend of the results tabulated above can be reversed by not requiring that the γ variation of the gas mixtures in a wind tunnel duplicate that of flight through air. Certain pure polyatomic gases require less heating to achieve hypersonic flow without saturation than does air, as the following table illustrates:

Gas	T_b, °C	γ_∞	γ_t	Reservoir temperature °K to prevent saturation at $p_t=100$ psia; $M_\infty=7$
Air	−180	1.40	1.38	550
CF_4	−128	1.33	1.12	450
SF_6	−64	1.27	1.07	450
CF_3CF_3	−78	1.19	1.07	375

For the three gases, air, CF_4, and CF_3CF_3, the above trend is opposite to what would be expected from consideration solely of the respective boiling points (−180° C for air, −128° C for CF_4, and −78° C for CF_3CF_3) because of the dominating effect of the reduced values of γ. Reducing γ will reduce the rate at which temperature varies with pressure in an expansion process, since $T \sim p^{(\gamma-1)/\gamma}$. This results in producing lower pressures, and hence higher Mach numbers, before the temperature is reduced to a point where saturation occurs. From a physical viewpoint, this phenomenon can be traced to the conversion of internal vibrational energy of a molecule into directed kinetic energy during expansion of a polyatomic gas. To achieve a given ratio of directed to random energy (given Mach number), the polyatomic gas with large vibrational energy does not have to be expanded to as low a temperature as does a gas without vibrational energy.

DEVIATIONS FROM THERMAL EQUILIBRIUM (HEAT CAPACITY LAG)

When a polyatomic molecule passes through a region of rapid change in temperature, the energy stored in vibration between atoms within the molecules does not always adjust to its environment with sufficient rapidity to maintain thermodynamic equilibrium. This leads to a time lag in the heat capacity determined by the relaxation time τ. Measurements show that τ increases if either pressure or temperature decreases. An excessively long relaxation time could significantly affect a high-speed flow, especially in a wind tunnel where the pressures and temperatures encountered are low.

Detailed computations are presented in Appendix B which provide an estimate of relaxation-time effects for various gases. These estimates are based on a relation between relaxation time and bulk viscosity. The derivation of this relation, and a discussion of its range of validity are presented in Appendix C. Here, only end results are discussed. The relaxation time (τ_a) at atmosphere conditions is known for some of the fluorochemical gases, and generally is the order of 10^{-7} second. For others, τ_a is not known from direct measurements, but can be estimated from related measurements by using certain empirical relationships between relaxation time and molecular structure. Thus, τ_a for $CBrF_3$ is estimated to be in the range 10^{-8} to 10^{-7} second, and that for CF_3CF_3 to be in the range 10^{-9} to 10^{-8} second.

Relaxation time is not the only important quantity which must be considered. The basic parameters which measure effects of heat-capacity lag on a gas flow involve the product τC_i, where C_i is the heat capacity of internal vibrations within the molecules. From the estimates in Appendix B, heat-capacity lag appears of more importance in altering boundary-layer flow than in altering pressure distribution, and is of greatest importance at low Reynolds numbers. For air under wind-tunnel conditions, τ is so long that the small internal vibrational energy effectively is "frozen," thereby rendering relaxation effects negligible even at low Reynolds numbers. For most of the gas mixtures under wind-tunnel conditions, the estimated relaxation effects are negligible at Reynolds numbers of the order of 10^5 or greater. They can be significant, however, at low Reynolds numbers (the order of 10^4 or less). It should be remembered that for air under flight conditions, C_i is not negligible as it is in a wind tunnel. Thus, relaxation effects can be significant in flight, although the estimates of Appendix B suggest this may be the case only at high altitudes (low Reynolds numbers) and at high flight speeds. In broad terms, heat-capacity lag is estimated to be significant at Reynolds numbers below about 10^4 for moderate supersonic speeds, and below about 10^6 for hypersonic speeds. Although relaxation-time effects in flight would not be simulated in an air wind tunnel, it is possible to simulate them approximately in a gas-mixture wind tunnel by employing two polyatomic gases in the mixture—one having τC_i greater than for flight through air, and the other having τC_i less than for flight through air This possibility appears to be of interest in low-density, high Mach number research, and provides another example of an effect pertinent to hypersonic flight through air which cannot be studied in an air wind tunnel but can be studied in a gas-mixture wind tunnel.

It should be mentioned that the idea of employing more than one polyatomic gas in a mixture might be utilized profitably in other ways. For example, various pairs of some polyatomic gases when mixed in special proportions form an azeotropic mixture; that is, a mixture for which the boiling temperature is not intermediate between the boiling temperatures of the two constituent gases, as ordinarily is the case, but is lower than the boiling temperature of either constituent. A mixture of 32-percent C_3F_8 with 68-percent CH_2F_2, for example, boils at −58° C, whereas the respective individual gases boil at −38° C and −52° C (ref. 63). Thus, although neither C_3F_8 nor CH_2F_2 could individually be used at $M_\infty=2.5$ under normal wind-tunnel operating conditions without danger of condensation (and, hence, have not been included in table IV (b)), their azeotropic mixture would be usable under such conditions. Other gas pairs known to form azeotropic mixtures are CHF_3 with C_2F_6, CF_2Cl_2 with CF_2CFCF_3, $CHClF_2$ with CF_2CFCF_3, and CF_2Cl_2 with CH_3CHF_2 (see refs. 48 and 63). A related point worth mentioning is that certain polyatomic gases which would not be usable singly because of flammability characteristics may be usable when mixed with other gases. An extreme example illustrating this point is the obviously flammable butane (C_4H_{10}) which, when mixed with CF_2Cl_2 in portions up to about 30 percent, is no longer flammable (ref. 64).

VISCOSITY VARIATION WITH TEMPERATURE AND PRANDTL NUMBER FOR VARIOUS GASES

Thus far, mention has been made of two effects associated with hypersonic flight through air which are not simulated in an air wind tunnel operating at conventional temperatures but which can be simulated in a gas mixture wind tunnel. These effects pertain to specific-heat variation with temperature and to relaxation-time phenomena (or bulk-viscosity phenomena). To this can be added a third effect; namely, that pertaining to variation of viscosity with temperature. It is to be remembered, though, that not all of the three effects are significant simultaneously in a given research problem; likewise, not all can be simulated simultaneously by a single gas mixture. One gas which—in a wind tunnel—approximates the temperature-viscosity relationship of flight conditions is pure helium, as illustrated in figure 6. A different gas which approximates the corresponding relationship of air in a wind tunnel is pure argon, as also illustrated in figure 6. The various curves representing wind-tunnel conditions in this figure correspond to reservoir temperatures which will avoid saturation at $M=5$. Helium and argon have the same value of γ, and very nearly the same value of Pr; they differ in aerodynamic behavior only in their viscosity-temperature relationship. Separate measurements with these two gases, therefore, would single out any effect of viscosity-temperature relationship on a given phenomenon. This possibility would appear to be useful in boundary-layer research.

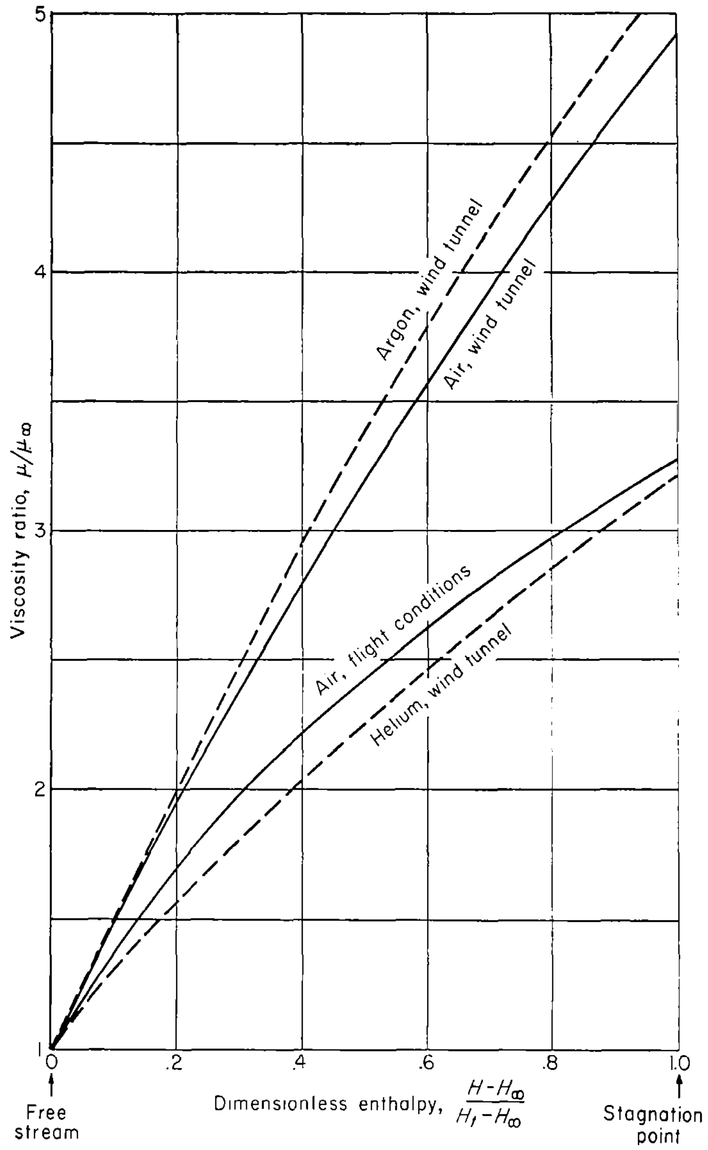


FIGURE 6.—Dimensionless viscosity variation for various gases at $M_\infty=5$.

When gases are mixed in arbitrary proportions, the Prandtl number can vary markedly. A rather extreme example of this is afforded by He and SF_6 mixtures. At 0° C the Prandtl number of He is the same as that of SF_6, namely, 0.69. Mixture of these two gases, however, can result in values of Pr as low as 0.21, according to the calculated curve shown in figure 7. Similarly, Pr for argon is 0.67, but mixtures with helium can result in values as low as 0.41. These mixtures provide values of Pr less than that of air (0.7 at room temperature), but other mixtures can provide values greater than air. For example, mixtures of CCl_2F_2 and He (results not shown) cover the Pr range between 0.82 and 0.22. As a test of the calculation method, which indicates such large variations in Pr, some experiments are available for the case of He-A mixtures (ref. 65 for viscosity, ref. 66 for conductivity). Calculation and measurement agree well for this case as is evident from figure 7. The particular equations employed in the calculations [5] are the rigorous mixture equations of kinetic theory developed by Hirschfelder, et al. (ref. 67). It is noted that the large reductions in *Pr* can be attributed primarily to the mixing of light with heavy molecules ($m_2/m_1=37$ for SF_6-He, $m_2/m_1=10$ for A-He). If gases of more comparable molecular weight were mixed, say A and CF_4 ($m_2/m_1=2.2$), the corresponding reduction in *Pr* would not be large. Large variations in *Pr* afforded by special mixtures of gases would appear to be a significant tool for conducting supersonic heat-transfer research, since the Prandtl number is an important parameter in such phenomena.

CONCLUDING REMARKS

By employing in place of air a test medium consisting of a heavy monatomic gas mixed with a heavy polyatomic gas in proportions that yield the desired value of 1.4 for the ratio of specific heats, it appears possible in conducting aerodynamic research to realize certain significant advantages. The existence of some of these advantages has been demonstrated by previous investigations concerned with pure heavy, polyatomic gases, especially the Freons. Because pure polyatomic gases have a specific-heat ratio much lower than that of air, they cannot be employed to yield aerodynamic data directly applicable to air for flows involving extensive supersonic regions. Aerodynamic data obtained with the gas mixtures considered herein would directly apply to air.

Perhaps the most significant result of this study is the observation that a gas mixture can be concocted which behaves—under low-temperature wind-tunnel conditions—dynamically similar in several respects to air under high-temperature flight conditions, whereas air under low-temperature wind-tunnel conditions behaves dissimilarly. This situation arises because the flow of two gases can be made dynamically similar on a macroscopic scale, even though they differ in microscopic structure, provided all the pertinent, *dimensionless*, macroscopic parameters (such as involve, for example, relaxation-time phenomena, temperature variation of specific heat, and temperature variation of viscosity), are duplicated between the two gases. In achieving dynamic similarity, the *dimensional* quantities, such as temperature, are not duplicated.

Many of the fluorochemical gases studied in the present research are more inert than Freon 12. This extreme inertness is highly desirable, especially since some of these gases when mixed with the necessary small amount of oxygen can be breathed even in large quantities without observable effect by animals, and presumably also by man. Likewise, because of their inertness they could be used without undesirable effect on machinery.

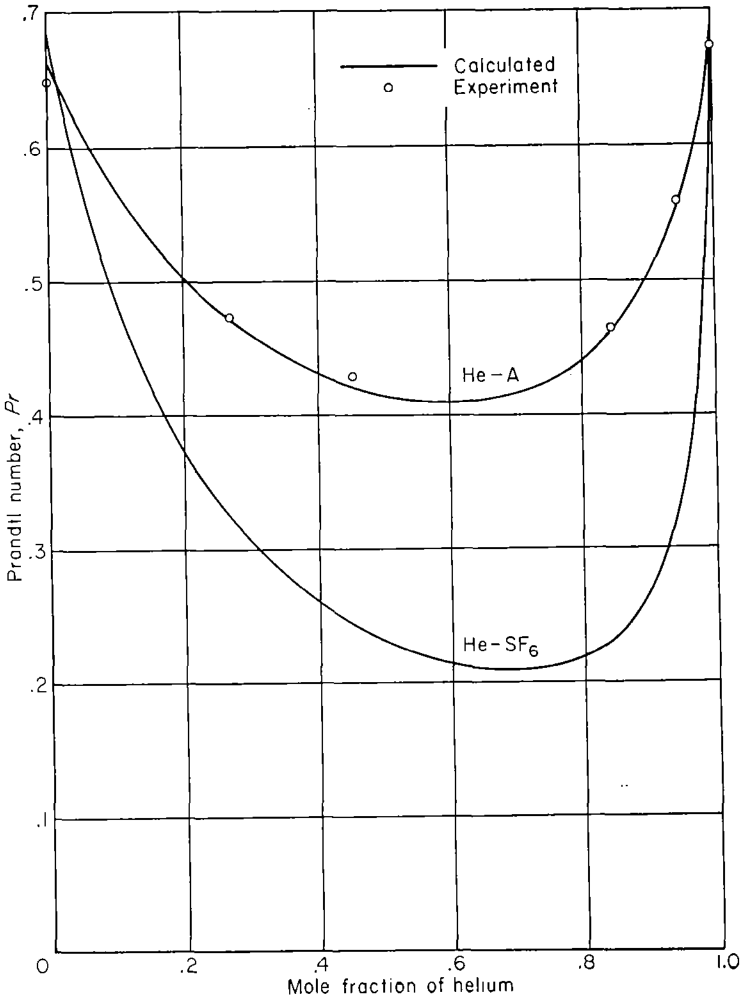


FIGURE 7.—Prandtl number variation for two gas mixtures containing helium; $T=0°$ C.

Since the magnitude of the advantages that can be realized through use of gas mixtures has been shown to be large, they may outweigh the evident operational disadvantages which result from use of any gas other than air. Whether or not the advantages surmount the disadvantages can only be ascertained by detailed study of individual cases. Clearly, though, the possible use of gas mixtures warrants consideration in the design of new research facilities. In view of the magnitude of the advantages, it appears that some experimental work with gas mixtures is in order.

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MOFFETT FIELD, CALIF., *Mar. 12, 1954*

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[5] These calculations were made by Mr. Donald Doran. Intermolecular forces were represented, in the nomenclature of reference 67, by a Lennard-Jones potential for He-SF_6 and a modified Buckingham potential (with $\alpha=12.4$) for He-A. Force constants ϵ/K were 9.16° K for He, 239° K for SF_6, and 123.2° K for A. Molecular dimensions were selected to yield the proper values of each transport property of the pure gas component.

APPENDIX A

ESTIMATE OF DEVIATIONS FROM THERMAL PERFECTION

By definition, a thermally perfect gas obeys the equation of state $pm=\rho RT$ given previously as equation (2). Real gases closely follow this equation if the density is low, or if the temperature is near the Boyle temperature (about 2.6 T_c), but deviate from it under other conditions. A more exact state equation is

$$\frac{pm}{\rho RT}=1+\frac{p}{RT}B(T) \tag{A1}$$

where $B(T)$ is the second virial coefficient having dimensions of volume. According to the law of corresponding states, $B(T)$ is proportional to the critical volume V_c.

From the results of reference 67, the second virial coefficient for a pure gas is approximately $0.75V_cB^*(T^*)$, where $T^*\equiv 1.3T/T_c$ and where $B^*(T^*)$ is a fixed dimensionless function tabulated in reference 67. For a mixture of two gases the appropriate relations are:

$$B(T)=x_1^2B_1(T)+2x_1x_2B_{12}(T)+x_2^2B_2(T) \tag{A2}$$

where

$$\left.\begin{aligned} B_1&=0.75V_{c1}B^*(1.3T/T_{c1})\\ B_2&=0.75V_{c2}B^*(1.3T/T_{c2})\\ B_{12}&=0.75\left(\frac{V_{c1}{}^{1/3}+V_{c2}{}^{1/3}}{2}\right)^3B^*(1.3T/\sqrt{T_{c1}T_{c2}})\end{aligned}\right\} \tag{A3}$$

By use of these equations, the term $pB(T)/RT$ of equation (A1)—which represents the fractional deviation from thermal perfection—has been calculated for the gas mixtures listed in table IV. Computations were made both for reservoir conditions (p_t,T_t) and test-section conditions (p_∞,T_∞) at Mach numbers of 1.3, 2.5, and 3.5. For $M_\infty=1.3$ the values of $p_tB(T_t)/RT_t$ and $p_\infty B(T_\infty)/RT_\infty$ were about the same. The average value of $|pB(T)/RT|$ per atmosphere of reservoir pressure varied from about 0.0014 (C_4F_8, C_3F_8, CF_3CF_3, CF_4, and NF_3 mixtures) to about 0.004 (CH_2F_2 mixture). Inasmuch as transonic research apparatus commonly are limited to reservoir pressures of several atmospheres (often because of critical model loads), the resulting deviations from thermal perfection would be within about 1 percent and can be neglected. For $M_\infty=2.5$ and $M_\infty=3.5$, the values of $|p_\infty B(T_\infty)/RT_\infty|$ are substantially lower than $|p_tB(T_t)/RT_t|$. Both are tabulated as follows:

Gas	$M_\infty=2.5$		$M_\infty=3.5$	
	$\frac{\lvert p_\infty B(T_\infty)\rvert}{RT_\infty}$	$\frac{\lvert p_tB(T_t)\rvert}{RT_t}$	$\frac{\lvert p_\infty B(T_\infty)\rvert}{RT_\infty}$	$\frac{\lvert p_tB(T_t)\rvert}{RT_t}$
$CBrF_3$	0.0017	0.0033	----------	----------
SF_6	.0013	.0027	----------	----------
CF_3CF_3	.0010	.0018	----------	----------
$CClF_3$	.0016	.0030	----------	----------
CF_4	.0012	.0019	0.0007	0.0023
NF_3	.0012	.0019	.0007	.0022
CHF_3	.0017	.0034	----------	----------
Air	.0005	.0002	.0002	.0002

It may be deduced that gas mixtures at test-section conditions (p_∞,T_∞) would deviate 1 percent from thermal perfection at reservoir pressures between about 6 and 10 atmospheres for $M_\infty=2.5$, and at about 14 atmospheres for $M_\infty=3.5$. Since practical operation pressures of wind tunnels are within these limits, the flow of these gas mixtures over a typical model can be regarded as closely approximating that of a thermally perfect gas. Deviations from thermal perfection at reservoir conditions (p_t, T_t) are two to three times as large as at test-section conditions. Hence, when computing test-section Mach number or dynamic pressure from measured values of p_t and T_t, the deviations near reservoir conditions may have to be considered for reservoir pressures of the order of 5 to 10 atmospheres or greater.

APPENDIX B

RELAXATION-TIME DATA AND ESTIMATE OF EFFECT FOR VARIOUS GAS MIXTURES

Results of measurements of relaxation time at atmospheric pressure (τ_a) for some of the polyatomic gases considered in this report are as follows:

Gas	Temperature, °K	τ_a microseconds	Reference
CCl_2F_2	293	0.09	68, 4
CF_4	373	.66	69
SF_6	293	.59	70
CHF_3	373	.42	69
$CHClF_2$	293	.10	68
CH_2F_2	373	.055	69
CO_2	293	7.0	68
N_2O	293	1.1	68

Although measurements of τ_a could be found only for those gases listed, certain known characteristics of relaxation time enable a rough estimate to be made for some of the remaining gases; for example, molecules with freedom of internal rotation invariably have very short relaxation times, generally less than 10^{-8} second (see ref. 71, for example). Also the smaller the lowest fundamental vibration frequency, the shorter the relaxation time (see refs. 68 and 69). These general characteristics indicate that fluorocarbon molecules with internal rotation (e. g., CF_3CBrF_2, CF_3CClF_2, CF_3CF_3, CH_3CClF_2 CH_3CHF_2, C_3F_8, and C_4F_{10}, but not C_4F_8) would have relaxation times (τ_a) in the range 10^{-8} to 10^{-9} second, and that the methane-like gases $CBrF_3$ and $CBrClF_2$ would have a relaxation time in the range of 10^{-7} to 10^{-8} second. It is to be noted that relaxation times listed are for pure gases, and that the presence of certain impurities can reduce τ_a for those gases having relatively long relaxation times.

Inasmuch as the relaxation time depends on temperature and pressure, some method of estimating τ for the particular conditions encountered in wind tunnels must be employed. The analysis of Bethe and Teller (ref. 72) yields for the relaxation time τ_ν of the lowest frequency (ν) mode

$$\tau_\nu=\frac{Z_{10}}{Z(1-e^{-h\nu/kT})} \tag{B1}$$

where Z is the total number of collisions one molecule experiences per second, and Z_{10} is the average number of collisions required to deactivate the lowest mode from the first quantum state to the zero state. Subsequent calculations are based on the additional equations

$$Z=1.3\frac{p}{\mu} \tag{B2}$$

which is a result from the rigorous kinetic theory of gases (ref. 73),

$$\tau\approx\frac{C_i\tau_\nu}{C_\nu} \tag{B3}$$

which is a result of the assumption (ref. 74) that once the lowest frequency mode (specific heat C_ν) is excited, energy is then rapidly transferred internally to all other modes (total internal specific heat C_i), and

$$Z_{10}\approx 25\left(\frac{b}{T^{1/3}}\right)^{-3/2} e^{b/T^{1/3}} \tag{B4}$$

which is an approximate result of Bethe and Teller (ref. 72). In this last equation, b is a constant to be evaluated for each gas from measurements of τ_a at the temperatures listed in the above table. These equations were developed for pure polyatomic gases. They will be used also for gas mixtures since the basic theory (especially eq. (B4)) is highly approximate, and since the effectiveness of an argon molecule in exciting vibration generally is roughly the same as that of an inert polyatomic molecule. (See the summary table in ref. 75 and the specific data for $CHClF_2$-Ar mixtures in ref. 76.)

Relaxation times τ_∞ corresponding to free-stream conditions (T_∞, p_∞) in a wind tunnel have been calculated for assumed reservoir conditions of one atmosphere total pressure and 40° C total temperature. The results, together with the "relaxation distance" $d\equiv\tau_\infty u_\infty$ for the gas mixture were computed to two significant figures and are tabulated to one significant figure as follows: [6]

Polyatomic component	$M_\infty=1.3$, $T_\infty=230°$ K, $p_\infty=0.36$ atm		$M_\infty=2.5$, $T_\infty=140°$ K, $p_\infty=0.059$ atm		$M_\infty=3.5$, $T_\infty=105°$ K, $p_\infty=0.013$ atm	
	τ_∞, sec	d, in.	τ_∞, sec	d, in.	τ_∞, sec	d, in.
CCl_2F_2	2×10^{-7}	0.002	------	------	------	------
CF_4	2×10^{-6}	.02	2×10^{-5}	0.3	1×10^{-4}	3
SF_6	1×10^{-6}	.01	9×10^{-6}	.15	------	------
CHF_3	2×10^{-6}	.02	1×10^{-5}	.2	------	------
$CHClF_2$	2×10^{-7}	.002	------	------	------	------
CH_2F_2	9×10^{-8}	.001	5×10^{-7}	.008	------	------
CO_2	3×10^{-5}	.4	------	------	------	------
N_2O	4×10^{-6}	.05	------	------	------	------

It is to be remembered that under wind-tunnel conditions, air has a much longer relaxation time than any of the gases tabulated above. At room temperature, for example, τ for air is the order of 10^{-3} second (ref. 77), which is 10^2 to 10^4 times as long as for the polyatomic gases. This does not mean, however, that relaxation effects are important for air in a wind tunnel because the amount of internal vibration heat capacity (C_i) that lags is very small. The effect of heat-capacity lag on flow conditions is influenced by both C_i and τ.

To determine the dimensionless parameters which form a pertinent measure of relaxation effects, use is made of the theoretical equivalence between relaxation phenomena and

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[6] Some of these values differ from corresponding values tabulated in the original publication of this research (TN 3226). Such differences are not large and are due to the use of a different definition of relaxation time (τ) in equation (B1). The relaxation time originally used is not consistent with the definition of Bethe and Teller, whereas that used above is (see Appendix C).

volume-viscosity (κ) phenomena. This equivalence is derived and discussed in Appendix C where the fundamental relation $\kappa = p\tau(\gamma-1)C_i/C_v$ is shown to be valid under conditions where the relaxation time is small compared to the characteristic time (l/u_∞ for aerodynamic problems). For purposes of estimation, then, the complete, first-order stress tensor, including the volume viscosity, is used as the basis of computation.

$$p_{ij} = (p_{ij})_{\substack{\text{Navier}\\ \text{Stokes}}} + \kappa \frac{\partial u_\alpha}{\partial x_\alpha} \delta_{ij} \qquad \text{(B5)}$$

In this equation κ is the coefficient of volume viscosity, $\partial u_\alpha/\partial x_\alpha$ is (using summation convention) the divergence of the velocity vector, and δ_{ij} is unity if i is equal to j, but is zero otherwise. The above equation, together with the equation relating κ to τ, will be employed to estimate effects of heat-capacity lag both for inviscid flow and viscous flow.

For inviscid flow the Navier-Stokes portion of the stress tensor is simply the static pressure p. The pertinent similarity parameter involving relaxation time is $\kappa u_\infty/(pl) = \gamma(\gamma-1)(\tau u_\infty/l)C_i/C_p$. Since the equation of steady motion involves $\rho u_j \partial u_i/\partial x_j$ and $\partial p_{ij}/\partial x_j$, the ratio of the relaxation term to the other stress term is, in order of magnitude,

$$\frac{\dfrac{\partial}{\partial x}\left(\kappa \dfrac{\partial u_\alpha}{\partial x_\alpha}\right)}{\dfrac{\partial}{\partial x}(p)} \sim \frac{\kappa u_\infty}{pl} \qquad \text{(B6)}$$

which is seen to be the same as the similarity parameter.[7] Hence, $\kappa u_\infty/pl$ is interpreted as a measure of the fractional effect of relaxation phenomena on pressure distribution. In a gas mixture, $C_i = x_2 C'_{i2}$. Computations of the resulting parameter $\kappa u_\infty/p_\infty l = \gamma(\gamma-1)(\tau_\infty u_\infty/l)C_i/(C_p)$ for wind-tunnel flow conditions over a 1-inch model yield the following results: [8]

Polyatomic component	$\gamma(\gamma-1)\dfrac{x_2 C_{i2}}{C_p}\dfrac{\tau_\infty u_\infty}{l} = \dfrac{\kappa u_\infty}{pl}$ for $l=1$ in. and $p_t=1$ atm		
	$M_\infty=1.3$	$M_\infty=2.5$	$M_\infty=3.5$
CCl_2F_2	0.0002	----------	----------
CF_4	.002	0.01	0.04
SF_6	.002	.013	----------
CHF_4	.001	.006	----------
$CHClF_2$	.002	----------	----------
CH_2F_2	.00005	.00008	----------
CO_2	.02	----------	----------
N_2O	.003	----------	----------

For transonic wind tunnels it is seen that only CO_2 mixtures would exhibit appreciable relaxation effects on pressure distribution. On the other hand, for $M_\infty = 3.5$, mixtures involving CF_4 would be affected roughly by 4 percent for the assumed conditions of $p_t = 1$ atmosphere and $l = 1$ inch. To maintain these effects below about 1 percent would require the product $p_t l$ to be greater than 4 atmosphere-inches (e. g., a 1-inch model in a 4-atmosphere tunnel). Such restrictions are believed not to represent significant limitations on the usefulness of gas mixtures, especially since the favorable effect of certain impurities in reducing τ has not been included in the analysis. It is concluded, then, that insofar as pressure distribution in inviscid flow is concerned, relaxation effects need not be considered for the usual wind-tunnel operation conditions at Mach numbers near 3.5 or below.

For viscous flow within a laminar boundary layer, the Navier-Stokes portion of the stress tensor customarily is approximated by $\mu \dfrac{\partial u}{\partial y}$. The ratio of the relaxation term to the ordinary term in the equation of motion is

$$\frac{\dfrac{\partial}{\partial x}\left(\kappa \dfrac{\partial u_k}{\partial x_k}\right)}{\dfrac{\partial}{\partial y}\left(\mu \dfrac{\partial u}{\partial y}\right)} \sim \frac{\dfrac{1}{l}\left(\kappa \dfrac{\partial u_\alpha}{\partial x_\alpha}\right)}{\dfrac{1}{\delta}\left(\mu \dfrac{\partial u}{\partial y}\right)} \sim \left(\frac{\delta}{l}\right)\frac{\kappa}{\mu}\frac{\dfrac{\partial u_\alpha}{\partial x_\alpha}}{\dfrac{\partial u}{\partial y}}$$

Examination of the solution to boundary-layer equations for flow over a flat plate (e. g., ref. 78) indicates the average value of $(\partial u_k/\partial x_k)/(\partial u/\partial y)$ to be of the order of $(\gamma-1)M_\infty^2/10\sqrt{Re}$, and δ/l to be of the order of $[6+(\gamma-1)M_\infty^2]/\sqrt{Re}$. Hence,

$$\frac{\dfrac{\partial}{\partial x}\left(\kappa \dfrac{\partial u_\alpha}{\partial x_\alpha}\right)}{\dfrac{\partial}{\partial y}\left(\mu \dfrac{\partial u}{\partial y}\right)} \sim \frac{\kappa}{\mu}\left[\frac{(\gamma-1)M_\infty^2}{10Re}\right][6+(\gamma-1)M_\infty^2] \qquad \text{(B7)}$$

This ratio, which is interpreted as a measure of the fractional effect of relaxation phenomena on boundary-layer flow, is important primarily at low Reynolds numbers and high Mach numbers, just as is the effect of relaxation phenomena on inviscid flow.

From the equation $\kappa u_\infty/pl = (\kappa/\mu)(\gamma M_\infty^2/Re)$ and from the preceding table, the ration κ/μ corresponding to free-stream conditions can be computed for the various gas mixtures. The results are as follows:

Polyatomic component	Calculated values of $(\kappa/\mu)_\infty$		
	$M_\infty=1.3$	$M_\infty=2.5$	$M_\infty=3.5$
CCl_2F_2	37	--------	--------
CF_4	350	410	370
SF_6	300	380	--------
CHF_3	230	170	--------
$CHClF_2$	37	--------	--------
CH_2F_2	8	2	--------
CO_2	3700	--------	--------
N_2O	530	--------	--------

At stagnation conditions κ/μ would be the same order as that tabulated for $M_\infty = 1.3$; hence, broadly speaking, the various fluorochemical gas mixtures cover a range in values of κ/μ between about 2 and about 400. For the gases of most interest, namely, CF_4 and SF_6, the corresponding value of κ/μ is seen to be about 400. Consequently, the value $\kappa/\mu = 400$ can be substituted into equation (B7) to obtain an estimate of relaxation-time effects on boundary-layer flow. The result is that the heat-capacity lag is found not to be significant except at low Reynolds numbers. In particular, at a Mach number of 3.5, it is indicated that only below or

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[7] A more precise calculation of this ratio of stress terms can be made using the continuity equation to eliminate $\partial u_\alpha/\partial x_\alpha$. This procedure ultimately yields a value $(\kappa u_\infty/pl)[M^2\partial(u/u_\infty)/\partial(x/l)]$, from which it can be deduced that, the simple parameter $(\kappa u_\infty/pl)$ will underestimate relaxation effects for bluff obstacles like the sphere, but will overestimate them for slender obstacles like an airfoil.

[8] The contribution of rotational energy to κ is disregarded since this is small compared to the contribution of vibrational energy.

near Reynolds numbers of about 2,000 would the effects of heat-capacity lag be significant. Even at a Mach number of 7 they would be significant only near or below Reynolds numbers of about 20,000.

Turning now to the case of air, a distinction must be made between wind-tunnel conditions and the conditions of flight. In a wind tunnel, the relaxation time for vibration is so long that the essential assumption inherent in the $\kappa-\tau$ relationship is not a valid assumption, since the vibration energy can lag far behind the translational energy. The energy in vibration for air at wind-tunnel temperatures, however, is negligible so that there are no appreciable effects of heat-capacity lag under such conditions. In flight, the situation is different, since the higher temperatures encountered reduce the relaxation time to values which are low enough to enable the vibrational energy almost to follow the translational energy. At a temperature of 1500° K, for example, the experiments of Blackman (ref. 77) show the relaxation time for air to be the order of 10^{-5} second. At 3000° K it is the order of 10^{-6} second. These times are short enough to apply equation (C9) at the temperatures of flight. The result is that the ratio κ/μ is calculated to be the order 1,000 at 1500° K and the order of 50 at 3000° K. Even if the higher value ($\kappa/\mu=1000$) is used and substituted into equation (B7), the effects of heat-capacity lag in flight are found to be small, except under the combined conditions of a high Mach number and simultaneously a low Reynolds number. Under such conditions, the heat-capacity lag could be significant. In order to simulate in a low-density gas-mixture wind tunnel the heat-capacity lag that would exist in the boundary layer during flight, the ratio κ/μ would have to be simulated. It is possible to simulate approximately this ratio in a gas-mixture wind tunnel inasmuch as the range of values of κ/μ covered by the various polyatomic gases bracket the corresponding values for flight conditions in air.

APPENDIX C

RELATION BETWEEN BULK VISCOSITY AND RELAXATION TIME

The calculations of Appendix B are based on a relation between relaxation time τ and bulk viscosity coefficient κ. This relation can be derived from the general equations of motion for a viscous compressible gas by considering the definition of relaxation time and one of the fundamental properties of entropy. The method of derivation presented here is rather general and leads to a simple result which is compared later with results of other analyses of the problem.

The general equations of motion involve the viscous stress tensor

$$\begin{aligned} p_{ij}&=\mu\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}+\frac{2}{3}\,\delta_{ij}\,\frac{\partial u_\alpha}{\partial x_\alpha}\right)+\kappa\,\frac{\partial u_\alpha}{\partial x_\alpha}\,\delta_{ij} \\ &=\left(p_{ij}\right)_{\substack{\text{Navier}\\ \text{Stokes}}}+\kappa\,\frac{\partial u_\alpha}{\partial x_\alpha}\,\delta_{ij} \end{aligned} \tag{C1}$$

and the energy dissipation function

$$\begin{aligned} \varphi&\equiv\frac{p_{ij}}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right) \\ &=\varphi_{\substack{\text{Navier}\\ \text{Stokes}}}+\kappa\left(\frac{\partial u_\alpha}{\partial x_\alpha}\right)^2 \\ &=\varphi_{\substack{\text{Navier}\\ \text{Stokes}}}+\kappa\left(\frac{D\rho}{\rho Dt}\right)^2 \end{aligned} \tag{C2}$$

where the operator D represents the substantial differential, and the Navier-Stokes portion of φ involves only the ordinary coefficient of viscosity. The bulk viscosity κ—just like the ordinary viscosity μ—is regarded as a state property and, therefore, can be evaluated as a function of temperature and pressure from any pertinent experiment. For example, suppose an experiment with Couette-type flow were selected wherein the effects of bulk viscosity are negligible and the effects of ordinary viscosity are large (as would be the case at low speed under which condition $\partial u_\alpha/\partial x_\alpha=-D\rho/\rho Dt$ is negligible). The viscous stress tensor would reduce to $p_{xy}=\mu\partial u/\partial y$, so that measurement of the shear and the velocity gradient would enable the state property μ to be determined. On the other hand, suppose an experiment were selected wherein the effects of ordinary viscosity are negligible and the effects of bulk viscosity are large (as would be the case for the rapid compression in front of a small pitot tube or for the velocity dispersion of ultrasonic waves, under which conditions the time rate of change of density is the dominant term). In this case, the dissipation function (eq. (C2)) simplifies to the single term $\kappa(D\rho/\rho Dt)^2$, so that measurements of the energy dissipation (total pressure loss) and the rate of density variation would enable the state property κ to be determined.

By analysis of a flow wherein $D\rho/Dt$ is unusually large and, hence, wherein the bulk viscosity term dominates all other terms in the stress tensor, a relationship can be established between κ and τ. For this type of flow, the energy equation can be written

$$\rho T\frac{DS}{Dt}=\varphi=\frac{\kappa}{\rho^2}\left(\frac{D\rho}{Dt}\right)^2 \tag{C3}$$

where S is the *irreversible* entropy increase. The definition of relaxation time τ is

$$\frac{DE_i}{Dt}=\frac{E_i(T)-E_i}{\tau} \tag{C4}$$

where T is the temperature corresponding to the translational degrees of freedom, $E_i(T)$ is the equilibrium value of internal energy corresponding to the temperature T, and E_i is the actual internal energy (corresponding to equilibrium at a different temperature T_i). From thermodynamic theory a third equation is obtained which completes the building blocks of the analysis; it provides an equation for the change of entropy when an amount of energy E_i flows from one source (translational energy at temperature T) to another source (vibration energy at temperature T_i).

$$DS=\frac{DE_i}{T_i}-\frac{DE_i}{T} \tag{C5}$$

The above three basic equations can be combined to yield the desired relation between bulk viscosity and relaxation time.

It is emphasized that no assumption is made about the variation of specific heat with temperature, nor is any assumption made either about the magnitude of the internal energy or about the form which that internal energy takes. For example, the internal energy could be in rotation of the molecules, or in vibration between the atoms of molecules, or in electronic excitation. The essential assumption made is that the internal energy E_i does not lag far behind the equilibrium internal energy corresponding to the temperature T. In other words, it is assumed that the relaxation-time effects are small, so that a first-order theory is applicable. The various quantities are illustrated in figure 8. Since a first-order theory is being considered, the internal specific heat C_i can be regarded as constant over the small temperature range $T-T_i$, and the following approximation can be made:

$$DS=DE_i\,\frac{(T-T_i)}{T^2}=DE_i\,\frac{E_i(T)-E_i}{C_iT^2} \tag{C6}$$

By combining this entropy equation with the equation defining relaxation time, there results

$$\frac{DS}{Dt}=\frac{[E_i(T)-E_i]^2}{\tau T^2C_i} \tag{C7}$$

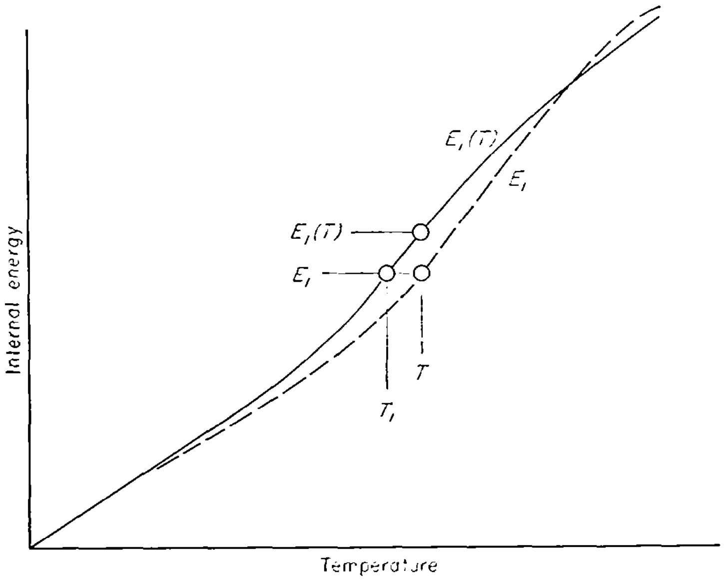

FIGURE 8.—Sketch of quantities related to internal energy lag.

Because the special experiment selected for consideration is an isentropic one except for first-order irreversible processes associated with κ, the following additional equations result from equation (C3):

$$\frac{\rho T}{\kappa}\frac{DS}{Dt}=\frac{1}{\rho^2}\left(\frac{Dp}{Dt}\right)^2=\frac{1}{(\gamma-1)^2T^2}\left(\frac{DT}{Dt}\right)^2$$

$$=\frac{1}{(\gamma-1)^2}C_i^2T^2\left(\frac{DE_i}{Dt}\right)^2=\left[\frac{E_i(T)-E_i}{(\gamma-1)C_iT\tau}\right]^2 \qquad \text{(C8)}$$

The final relation between bulk viscosity and relaxation time is obtained by combining equations (C8) and (C7) (and noting that $p=\rho RT=\rho(\gamma-1)C_vT$)

$$\kappa=p\tau(\gamma-1)\frac{C_i}{C_v} \qquad \text{(C9)}$$

Inasmuch as C_i can represent either rotational energy or vibrational energy, several comparisons can be made with other analyses. In reference 79, Tisza compared the approximate equations for the dispersion of ultrasonic waves with corresponding equations from the Navier-Stokes relations and obtained exactly equation (C9). However, in comparing with the approximate equations from ultrasonic theory, Tisza assumed in effect that the amount of energy in internal motion E_i is small compared to the total energy, that is, he assumed that C_i is small compared to C_v. The above analysis shows that the relation obtained by Tisza actually applies to the case where the internal energy is a large portion of the total energy. Tisza assumed, of course, that the departures from equilibrium are small enough to be represented by a first-order theory (this assumption is made in all of the analyses discussed).

A different approach to the problem is taken by Kohler, reference 73, who employed the equations of kinetic theory involving the Maxwell-Boltzmann equation. Kohler considered two cases—first, that of rotational internal energy, and second, that of vibrational internal energy. The definition of relaxation time for rotation (τ_r) employed by Kohler, however, is not the same as that employed above. The two are related by the equation

$$\frac{C_t+C_r}{C_t}\,\tau_r=\tau$$

where $C_t=3R/2$ is the specific heat due to translational degrees of freedom. Letting f_r be the number of rotational degrees of freedom, then $C_r=f_rR/2$, and $R/(\gamma-1)=C_v=(3+f_r)R/2$, so that equation (C9) becomes

$$\kappa=\frac{2}{3}\frac{f_r}{3+f_r}\,p\tau_r$$

which is identical to an equation developed by Kohler. When Kohler considered vibrational energy, he used the same definition of relaxation time as that used herein, but he assumed that the internal energy in vibration (E_{vib}) is small even compared to the rotational internal energy. With this approximation Kohler could write $C_r+C_{vib}\approx C_r$, and thus obtained the equation

$$\kappa=(\gamma-1)p\tau\frac{C_{vib}}{C_v-C_{vib}}$$

Since $C_v-C_{vib}\approx C_v$ within the approximation made by Kohler, his result for vibrational internal energy is consistent with the basic equation (C9) of this appendix.

In reference 80 Meixner considers the problem from an entirely different viewpoint, namely, that of the theory of irreversible thermodynamics. Meixner assumes in effect, as did Kohler, that the internal energy is small compared to the translational energy. The equation Meixner obtained can be reduced to

$$\kappa=p\tau(\gamma-1)\frac{C_i}{C_v-C_i}$$

Just as in the case of Kohler's analysis, this result is seen to be consistent with that of equation (C9), provided it is remembered that the assumption of small internal energy enables C_v-C_i to be approximated by C_v within the framework of Meixner's analysis.

In reference 81 Wang-Chang and Uhlenbeck considered the problem from the viewpoint of kinetic theory, only they did not assume as Kohler did that the internal energy was small. They did assume, however, that the internal energy did not vary significantly with temperature; that is, they assumed that the internal specific heat was constant, as this simplified their equations. Their final result can be written in the form

$$\kappa=p\tau(\gamma-1)\frac{C_i}{C_v}$$

which is identical to equation (C9) above. Thus, we see that the end result of the analysis of Wang-Chang and Uhlenbeck, just as the analysis of Kohler for rotational internal energy, actually applies to more general conditions than they assumed. Consequently, the derivation given above is seen to be rather general and to be confirmed by four separate analyses employing methods from several different fields of science.

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TABLE I.—PROPERTIES OF HEAVY MONATOMIC GASES AND AIR CONSTITUENTS

Symbol	Gas	$m, \frac{\text{gm.}}{\text{mole}}$	Boiling temp., ° C	Critical constants			Viscosity at 0° C μ_0, micropoise
				T_c, ° K	p_c, atm.	V_c, cc/gm. mole	
Ar	argon	40	−186	151	48	75.3	210
Kr	krypton	84	−153	210	54	92.1	230
Xe	xenon	131	−107	290	58.2	114	210
N_2	nitrogen	28	−196	126	33.5	90.0	166
O_2	oxygen	32	−183	154	49.7	74.4	189
	air	29	------	132	37.2	83	172

TABLE II.—GENERAL CHARACTERISTICS OF POLYATOMIC GASES

Formula	m_2, gm./mole	Chemical name	Common or trade name	General classification (1)	Remarks	References		
						Spectroscopic data	Toxicity data	Physical data
C_4F_{10}	238	n-perfluorobutane		S		------	14	14, 19, 15
C_3F_9N	221	perfluorotertiaryamine		S?	Reported "as nontoxic as fluorocarbons." Chemistry resembles NF_3. Stable to at least 400° C.	------	56	14, 56, 44, 46, 23
C_4F_8	200	perfluorocyclobutane	Freon C318	S		45	------	48, 15, 26
CF_3CBrF_2	199	bromoethforane		S?	Toxicity unknown	------	------	14, 56, 24
CF_3SF_5	196	trifluoromethylsulfurpentafluoride		S?	Toxicity, liquid density unknown	------	------	20
SeF_6	193	selenium hexafluoride		S?	Toxicity unknown	50	------	14, 25, 42
C_3F_8	188	perfluoropropane		S		------	14	14, 56, 19
C_2F_6NF	171	perfluorodimethylamine		S?	Musty odor. Toxicity, liquid density unknown.	------	------	44, 47
$CBrClF_2$	165	bromochlorodifluoromethane	Freon 12B1	Q	Toxicity probably excessive. More toxic than $CHClF_2$.	49	21	26
CF_3CClF_2	155	chloroethforane	Freon 115	S		33	------	14, 26
CF_3OCF_3	154	perfluoroether		S?	Reported "as nontoxic as fluorocarbons." Liquid density unknown. Stable to at least 400° C.	------	56	14, 56, 44, 23
$CBrF_3$	149	bromotrifluoromethane	Freon 13B1 Kulene 131.	S	Excellent fire extinguisher	35	21, 56	14, 26, 56
SF_6	146	sulfurhexafluoride		S, I	Excellent high-voltage gaseous insulator. Extremely inert chemically. Thermally stable to about 500° C.	29	17	14, 56, 25, 27, 52, 53
CF_3CF_3	138	ethforane		S	Thermally stable to about 700° C	34	------	14, 56, 19, 39, 22
$CClF_2CHF_2$	137	1-chloro-2-hydroethforane	Freon 124a	S?	Toxicity unknown	------	------	14, 26
CCl_2F_2	121	dichlorodifluoromethane	Freon 12	S		30, 51	18, 38, 63	14, 26, 63
CF_3NF_2	121	perfluoromethylamine		S?	Musty odor. Toxicity, liquid density unknown.	------	------	14, 56, 44
$CClF_3$	105	chlorotrifluoromethane	Freon 13	S		28, 30	------	14, 26
SO_2F_2	102	sulfuryl fluoride		S?	Toxicity, liquid density unknown. Chemistry resembles SF_6.	55	------	14
CHF_2CHF_2	102	1-hydro-2-hydroethforane		S?	Toxicity, liquid density unknown	------	------	14
CH_3CClF_2	101	1-chloro-1, 1-difluoroethane	Genetron 101	Q	Slightly flammable, toxicity marginal. (See remarks for Genetron 100.)	37	18	14, 26
$FCONF_2$	99	carbonylnitrogentrifluoride		S?	Toxicity, liquid density unknown. Reported as very inert.	------	------	14
CF_4	88	carbontetrafluoride	Freon 14	S	Extreme thermal stability and chemical inertness.	28, 30	21	14, 56, 19
$CHClF_2$	87	chlorodifluoromethane	Freon 22	Q	Toxicity marginal (classified U. A. L. group 5A)	30	38	14
CH_3CF_3	84	1,1,1-trifluoroethane		S?	Toxicity and flammability unknown	31, 32	------	14
NF_3	71	nitrogentrifluoride		S?	Toxicity uncertain since early tests (Ruff, ref. 43) are questionable.	54	43, 25	14, 43
CHF_3	70	fluoroform	Freon 23	S, I	Thermally stable to at least 1100° C	28, 30	16	14
CH_3CHF_2	66	1,1-difluoroethane	Genetron 100	Q	Slightly flammable, but forms nonflammable azeotropic mixture with Freon 12. Azeotropic mixture called "Carrene 7," has $m=100$, $T_b=-33$ ° C.	36	18, 25	14
CH_2F_2	52	difluoromethane	Freon 32	S?	Flammability unknown	30	25	14
CO_2	44	carbon dioxide		Q	Toxic for prolonged exposure at concentrations above about 3 per cent.	41	25	40, 13
N_2O	44	nitrous oxide		Q	Nonflammable but acts as oxidant at high temperature. Toxic at high concentrations.	41	25	40, 13

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[1] S *satisfactory*, in that sufficient information is available to regard the gas as nontoxic, noncorrosive, nonflammable, thermally stable to at least about 200° C, and inert chemically.

S? *may be satisfactory*, but available information is insufficient to judge it so. (See remarks for each gas thus classified.)

Q *questionable* because of possessing at least one undesirable characteristic (see remarks) which, however, may not be totally disqualifying.

I *inert physiologically*, as determined by tests with small animals living in atmosphere of 20-percent oxygen, 80-percent gas in question, and showing no observable effects either during the duration of tests (usually several hours) or afterwards.

TABLE III.—PHYSICAL CHARACTERISTICS OF POLYATOMIC GASES

Formula	m_2, $\frac{\text{gm}}{\text{mole}}$	Boiling temp., T_b° C (1)	Critical constants (2)			Viscosity at 0° C μ_2, micropoise	$\frac{\overline{m}_2}{\overline{\mu}_2}$	$\frac{(\overline{\mu}_2)^2}{(\overline{m}_2)^{3/2}}$	Spectroscopic data fundamental wave numbers, ω_i, cm^{-1} (3)
			T_c, °K	p_c, atm.	V_c cc/gm. mole				
C_4F_{10}	238	−2	387	23	378	111	12.7	0.018	
C_3F_9N	221	−11							
C_4F_8	200	−6	390e		331e	111	10.7	.023	1431, 1385, 1340, 1285, 1239 (2), 1220, 1008 (2), 963, 745 (2), 699, 660 (2), 613, 569, 439, 359, 338 (2), 285, 273, 258, 250 (2), 192 (2), 173, 86
CF_3CBrF_2	199	−22	386e	32e	268e	128	9.2	.031	
CF_3SF_5	196	−20							
SeF_6	193	−47 sub.	340e		219e	154	7.4	.047	787 (3), 708, 662 (2), 461 (3), 405 (3), 245 (3)
C_3F_8	188	−38	344e	26e	298e	122	9.1	.030	
C_2F_6NF	171	−37							
$CBrClF_2$	165	−4	427	41.2	232	121	8.1	.036	1150, 1102, 872, 648, 440, 400, 380, 300, 200
CF_3CClF_2	155	−38	353	30.8	260	119	7.7	.039	1350, 1241, 1236, 1186, 1132, 982, 763, 648, 595, 561, 454, 441, 366, 331, 315, torsion, 186 (2)
CF_3OCF_3	154	−59							
$CBrF_3$	149	−60	341		199	143	6.2	.059	1207 (2), 1087, 762, 548 (2), 348, 297 (2)
SF_6	146	−64 sub.	319	36.8	201	142	6.1	.060	940 (3), 775, 644 (2), 615 (3), 524 (3), 363 (3)
CF_3CF_3	138	−78	293	29.9	220	139	5.9	.063	1420, 1250 (2), 1235 (2), 1120, 810, 715, 620 (2), 520 (2), 380 (2), 350, 214 (2), torsion
$CClF_2CHF_2$	137	−10	400	36.7	251	108	7.5	.038	
CCl_2F_2	121	−30	385	39.6	218	118	6.1	.055	1159, 1101, 906, 667, 473, 455, 437, 318, 261
CF_3NF_2	121	−78							
$CClF_3$	105	−80	302	39	180	136	4.6	.091	1210 (2), 1102, 783, 560 (2), 478, 356 (2)
SO_2F_2	102	−55	340e						1502, 1269, 885, 848, 553, 544, 539, 385, 300
CHF_2CHF_2	102	−23							
CH_3CClF_2	101	−9	411	40.7	232	97	6.2	.049	3035, 2965, 1447, 1395, 1231, 1202, 1127, 1103, 967, 904, 683, 544, 526, 435, 429, 334, 305, torsion
$FCONF_2$	99	−82							
CF_4	88	−128	228	36.8	139	171	3.1	.19	1265 (3), 904, 630 (3), 437 (2)
$CHClF_2$	87	−41	370	48.5	165	120	4.3	.094	3023, 1347, 1311, 1178, 1116, 809, 595, 422, 365
CH_3CF_3	84	−47							3034 (2), 2975, 1409, 1442 (2), 1281, 1234 (2), 970 (2), 830, 606 (2), 541, 368 (2), 238, torsion
NF_3	71	−129	230e		125e	164	2.6	.24	1032, 647, 905 (2), 493 (2)
CHF_3	70	−84	306	47	136	134	3.1	.16	1376 (2), 1160 (2), 1117, 697, 508 (2), 3062
CH_3CHF_2	66	−25	387	44.3	181	96	4.1	.091	3018, 3001, 2979, 2963, 1460, 1452, 1414, 1372, 1360, 1171, 1145, 1120, 925, 868, 570, 472, 392, torsion
CH_2F_2	52	−52	351		170	93	3.3	.12	3012, 2949, 1508, 1435, 1262, 1176, 1116, 1090, 529
CO_2	44	−79 sub.	304	72.9	96	137	1.9	.34	2349, 1340, 667 (2)
N_2O	44	−88	310	71.7	98	135	1.9	.33	2237, 1288, 588 (2)

[1] sub. sublimes at atmospheric pressure.

[2] e estimated from similar gases, or from liquid density and reduced orthobaric density of similar gases.

[3] number in parentheses denotes degree of degeneracy of wave number it follows.

TABLE IV.—CHARACTERISTICS OF GAS-MIXTURE WIND TUNNELS

Polyatomic gas			Mixture proportions		Mixture molecular weight relative to air			Mixture viscosity at 0° C relative to air			Size of gas-mixture wind tunnel relative to air wind tunnel for same M_∞, Re, & p_t			Horsepower of gas-mixture wind tunnel relative to air tunnel for same M_∞, Re, & p_t		
Formula	m_2, $\frac{\text{gm.}}{\text{mole}}$	C_{p_2}, $\frac{\text{cal.}}{\text{mole °K}}$ (1)	x_2	x_1	argon $\overline{m}$	krypton $\overline{m}$	xenon $\overline{m}$	argon $\overline{\mu}$	krypton $\overline{\mu}$	xenon $\overline{\mu}$	argon $\overline{L}$	krypton $\overline{L}$	xenon $\overline{L}$	argon $\overline{HP}$	krypton $\overline{HP}$	xenon $\overline{HP}$
(a) Design Mach number 1.3 T_∞=230° K																
C_4F_{10}	238	35.8e	0.07	0.93	1.82	3.23	4.76	1.13	1.24	1.16	0.84	0.69	0.53	0.52	0.27	0.13
C_4F_8	200	33.5	.07	.93	1.77	3.17	4.69	1.12	1.23	1.15	.84	.69	.53	.53	.27	.13
$CF_3CB_7F_2$	199	24.4e	.10	.90	1.93	3.29	4.79	1.12	1.22	1.15	.80	.67	.53	.46	.25	.13
SeF_6	193	22.5	.11	.89	1.98	3.31	4.79	1.17	1.25	1.17	.83	.69	.53	.49	.27	.13
C_3F_8	188	29.5e	.08	.92	1.80	3.18	4.69	1.13	1.24	1.16	.84	.69	.53	.53	.27	.13
$CBrClF_2$	165	15.8	.19	.81	2.18	3.41	4.76	1.03	1.13	1.08	.70	.61	.50	.34	.20	.11
CF_3CClF_2	155	23.0	.11	.89	1.82	3.16	4.62	1.10	1.20	1.13	.81	.68	.53	.49	.26	.13
$CBrF_3$	149	14.7	.21	.79	2.15	3.35	4.65	1.09	1.17	1.12	.74	.64	.52	.37	.22	.13
SF_6	146	18.9	.14	.86	1.91	3.19	4.59	1.12	1.22	1.15	.81	.68	.53	.48	.26	.13
CF_3CF_3	138	21.8	.12	.88	1.78	3.11	4.55	1.13	1.23	1.16	.85	.70	.54	.54	.28	.14
CCl_2F_2	121	15.2	.20	.80	1.93	3.14	4.45	1.02	1.13	1.09	.74	.64	.52	.39	.23	.13
$CClF_3$	105	13.8	.23	.77	1.89	3.05	4.35	1.06	1.16	1.12	.77	.67	.54	.44	.26	.14
CH_3CClF_2	101	16.8	.17	.83	1.74	2.99	4.35	.99	1.12	1.08	.75	.65	.52	.43	.24	.13
CF_4	88	12.5	.27	.73	1.82	2.93	4.14	1.15	1.23	1.17	.85	.72	.57	.53	.30	.16
$CHClF_2$	87	12.0	.29	.71	1.84	2.92	4.10	.98	1.09	1.06	.73	.63	.53	.39	.24	.14
NF_3	71	11.1	.33	.67	1.73	2.74	3.86	1.11	1.20	1.16	.85	.73	.59	.54	.32	.18
CHF_3	70	10.7	.35	.65	1.74	2.72	3.79	1.01	1.11	1.08	.76	.67	.56	.44	.28	.16
CH_3CHF_2	66	13.5	.24	.76	1.59	2.74	4.00	.95	1.09	1.06	.76	.66	.53	.45	.26	.14
CH_2F_2	52	9.22	.47	.53	1.57	2.37	3.24	.78	.91	.93	.63	.59	.52	.31	.23	.15
CO_2	44	8.11	.63	.37	1.47	2.03	2.63	.92	1.02	1.02	.76	.72	.63	.48	.36	.25
N_2O	44	8.45	.57	.43	1.46	2.11	2.81	.94	1.04	1.04	.78	.72	.62	.50	.35	.23
(b) Design Mach number 2.5; T_∞=140° K																
$CBrF_3$	149	11.0	.33	.67	2.62	3.62	4.73	1.03	1.10	1.06	.64	.58	.49	.25	.17	.11
SF_6	146	11.5	.30	.70	2.49	3.54	4.69	1.04	1.12	1.07	.66	.59	.50	.28	.19	.11
CF_3CF_3	138	15.3	.19	.81	2.03	3.25	4.57	1.09	1.17	1.12	.76	.65	.52	.41	.24	.13
$CClF_3$	105	10.2	.39	.61	2.24	3.17	4.19	.98	1.07	1.05	.66	.60	.51	.29	.20	.13
CF_4	88	9.31	.46	.54	2.14	2.95	3.90	1.10	1.16	1.13	.75	.68	.57	.39	.27	.17
NF_3	71	8.74	.53	.47	1.94	2.65	3.43	1.05	1.13	1.10	.76	.69	.60	.41	.29	.19
CHF_3	70	8.60	.55	.45	1.95	2.63	3.38	.92	1.00	1.00	.66	.62	.54	.31	.23	.16
(c) Design Mach number 3.5; T_∞=105° K																
CF_4	88	8.40	.58	.42	2.34	2.97	3.66	1.07	1.12	1.10	.70	.65	.58	.32	.25	.17
NF_3	71	8.19	.62	.38	2.04	2.62	3.24	1.03	1.09	1.07	.72	.67	.60	.36	.28	.20

[1] e estimated from similar gases and from average bond frequencies of ref. 58.

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