

REAL GASES

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Preface

This small monograph was prepared to serve as an introduction to the physics of real gases. In the context of this volume, a real gas is defined as one which is found at the high thermal energy levels commonly associated with aerospace type situations.

It should be mentioned that this volume is based on material covered in a number of research reports which were prepared by the authors in 1960, to evaluate the state of the art. The demand for these reports exceeded the supply and we were asked to consolidate them into one volume for the convenience of a wider audience. In doing so, major additions and revisions were made so as to include all pertinent information available through the middle of 1962.

We do not claim original contributions to the physics of real gases because the foundations have been laid previously elsewhere. However, we have attempted to interpret and evaluate how the theoretical foundations may be applied in the development of engineering devices. In essence then, our objective in preparing this volume was to review the art and the science underlying the behavior of real gas. We hope that in doing so, this monograph will serve as a bridge between equilibrium and nonequilibrium thermodynamics on the one side and high speed gas dynamics on the other side.

Although we have presented briefly the equations which govern the dynamics of real gases, we have excluded all detailed treatment of high speed gas dynamics because this may be found in several existing treatises.

As a rule the dissociated and ionized gases encountered in the aerospace technology are at relatively low pressures. Accordingly, the treatment presented in this volume is primarily applicable to high temperatures and low pressures. However, for the convenience of the reader we did include a very brief chapter on high pressure effects, because these may be found in some propulsive devices and laboratory research facilities.

The choice of a consistent set of symbols to designate the various parameters posed serious problems since this study covers

aspects of gas dynamics, physics, thermodynamics, fluid mechanics, chemical kinetics, and aerodynamics. Although each discipline has a conventional nomenclature, they are not necessarily consistent with each other. In general, the symbols used in any section are those normally used in the field under discussion. For this reason, a separate List of Symbols has been compiled for each individual chapter and is located at the end of the chapter.

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Chapter 1

Introduction to Real Gas Effects

1.1 Introduction

It is a well-known fact that when a vehicle travels at very high speeds, the air in its immediate vicinity is raised in temperature, and "real gas effects" come into play. Similar aerothermochemical phenomena must be considered in connection with the internal flow in propulsive devices. Because the behavior of real gases is appreciably different from that of a "perfect gas," engineering devices operating in the domain of real gases must be carefully designed. In this chapter some of the characteristics of real gases are discussed, as well as their behavior in engineering applications.

1.2 The Concept of a Real Gas

A gas may be characterized as being perfect or ideal according to different criteria. To the aeronautical engineer two considerations are of primary importance. Thus, one may speak of a gas which is perfect in a thermodynamic sense, or in turn one may speak of an ideal gas in a fluid mechanic sense. Qualitative descriptions of a gas in either category may be made. This will not be done in this monograph because excellent published treatises exist already (see for example refs. 1 and 2).

Here, a gas which is thermodynamically perfect is defined categorically by the thermal equation of state

$$p = \rho RT. \quad (1-1)$$

A gas is fluid mechanically ideal if it has no viscosity. Thus,

$$\mu = 0. \quad (1-2)$$

This monograph will concern itself particularly with the behavior of gases where Eq. (1-1) is not valid.

A real gas is defined simply as one for which

$$p \neq \rho RT.$$

One may then write for a real gas

$$p = Z\rho RT \quad (1-3)$$

where Z is the departure (departure from perfect gas behavior) coefficient. Depending on the existing conditions, $Z \gtrsim 1$.

In a gas, real gas effects may be brought about primarily in any of three ways, namely, (1) by exposing the gas to very high temperatures, (2) by exposing the gas to very high pressures, or (3) by exposing the gas to high energy radiation.

The aeronautical engineer may encounter all of the above three modes. However, he will probably be most concerned with the effects brought about by high temperatures.

It should be noted parenthetically that at very low pressures a gas must be analyzed specially (see for example ref. 3). However, the regime of rarefied gas dynamics is outside the scope of this study.

A gas may assume a variety of degrees of freedom and with each there is associated an energy. Consider air at relatively low temperatures, say at considerably less than 1000 °K or corresponding to Mach numbers of $M < 2$ based on sea level conditions. One may represent a diatomic gas by a "dumbbell" or "rigid rotator" as depicted in Fig. 1-1.

At extremely low temperatures, namely, in the neighborhood of absolute zero, there will be three translational degrees of freedom, namely, in the x -, y -, and z -directions. At temperatures in the neighborhood of 10 °K, the rotational degrees of freedom are excited, although the molecular bond remains quite stiff. As the

temperature is raised further, the vibrational degree of freedom comes into play. This generally occurs around 1000 °K. When the molecular bond is stretched to the breaking point, dissociation results. At atmospheric pressure, oxygen starts to dissociate at about 3000 °K, whereas nitrogen starts to dissociate at about 4500 °K.

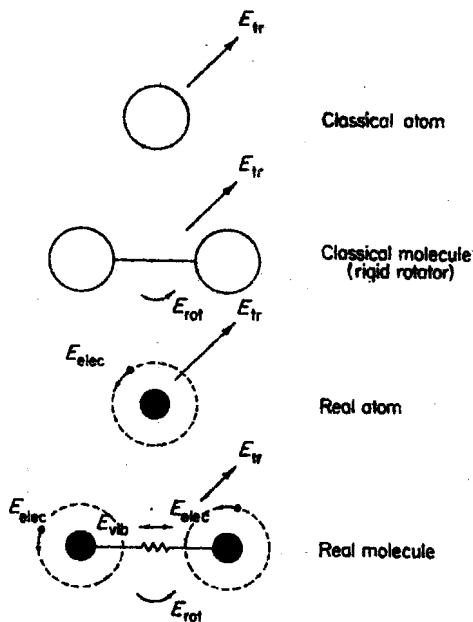
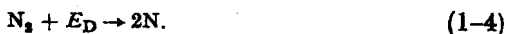


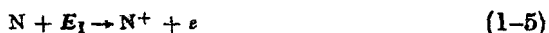
FIG. 1-1. Real gas models.

For example, for nitrogen dissociation we may write



The energy of dissociation E_D is commonly given in electron volts per molecule. The dissociation energy of nitrogen is 9.76 ev per molecule. At still higher temperatures, the electrons in the orbits around the atomic nucleus become excited to quantum states

above the ground state. This excitation too contributes to the total energy, but the effect is negligible up to about 5000 °K. Finally, at still higher temperatures, electrons leave their orbits and the gas becomes ionized. For example, at about 10,000 °K (at atmospheric pressure) the ionization of the oxygen and the nitrogen in the air becomes sufficiently significant to be considered in engineering applications. For the single ionization of a nitrogen atom, one writes



where E_1 is the ionization energy given in electron volts per electron.

If the number of free electrons and the number of positive ions are equal, the term plasma is also used, whenever the gas is ionized or electrically conducting. It should be noted that in the purest sense a plasma is electrically neutral, although electrically conducting. Because plasmas due to their electrical properties exhibit some markedly different characteristics, they have been called the "fourth state of matter," the other states being solid, liquid, and gas.

Both dissociation and ionization depend on pressure and temperature. Thus, a gas may be dissociated or ionized at a lower temperature if the pressure is reduced. For example, at atmospheric density the ionization of oxygen and nitrogen is significant at 10,000 °K, but ionization is significant at 6000 °K if the density is reduced to 10^{-6} times that at sea level.

In the preceding discussion the various levels of excitation were explained in a consecutive order. Actually this is not necessary, and in an actual application different levels of excitation occur not only in the aforementioned sequence but also concurrently. This is so because, during collisions, particles having higher energy (atoms, ions, and electrons) will impart their energy to the slower particles (such as molecules) exciting them, so to speak, prematurely.

The discussion so far made another simplification, namely, that one deals with a single component diatomic gas per se, such as

oxygen alone or nitrogen alone. In the case of air, which is of course a mechanical mixture of many components, at least one other set of chemical reactions must be considered. This is the formation of nitric oxide (NO) as well as its subsequent dissociation and ionization. Thus, at atmosphere pressure and at about 1500 °K the formation of nitric oxide must be taken into consideration. In turn, at about 4000 °K the dissociation of nitric oxide becomes important at sea level pressures. At sea level the ionization of nitric oxide becomes appreciable at about 9000 °K (ref. 4). At low pressures nitric oxide dissociation and ionization become significant at considerably lower temperatures. Furthermore, it is believed that all charged particles which occur at temperatures below which nitrogen and oxygen ionize are due to the ionization of NO. Although the percentage of these particles is very small at these lower temperatures, their effect on some of the properties of air (such as the electrical conductivity) may be quite significant.

1.3 Real Gas Effects in Gas Dynamics

In Section 1.2 the behavior of gas particles in the real gas regime was outlined briefly. Indeed, it is necessary to understand the particle theory of gases if the properties of gases are to be described rigorously. On the other hand, the engineer charged with the design of propulsive devices and hypersonic vehicles must be familiar with the gross effects which may occur when a gas no longer behaves as a perfect gas. In this section an attempt is made to summarize the important aspects of real gas dynamics.

In chemically reacting media one must consider three major aspects of the problem. These are (1) thermodynamic aspects, (2) transport phenomena, and (3) fluid dynamics. Subjectively one might suggest that the thermodynamics and the transport properties associated with the flowing medium influence its fluid dynamics.

1.3.1 Thermodynamic Aspects

In Chapter 3 the thermodynamic considerations are treated in some detail. However, for the convenience of the reader, the following important thermodynamic differences between a real and a perfect gas should be mentioned.

As the temperature of a gas is increased, its specific heat rises markedly at first, but later may fluctuate. For example, at a moderately high temperature of 7000 °K, the isobaric specific heat of air is about 12 times that at sea level temperature.

The molecular weight decreases as the temperature increases. The acoustic velocity is markedly influenced by real gas effects.

1.3.2 Transport Phenomena

The most important transport properties are thermal conductivity, diffusivity, and viscosity. In the ionized gas regime one must consider also the electrical conductivity.

In accounting for changes in the transport properties, one must recognize two flow regimes, namely, laminar flow and turbulent flow. It should be recalled that the transport properties are usually defined for the laminar conditions. However, most engineering applications are far from being laminar, and hence the convective and the eddy contributions must be included. This complicates the solution of problems because the eddy contributions depend on the flow and are not properties per se of the fluid. Thus, in establishing similarity (such as is commonly done by setting $Pr = Sc = 1$) one must proceed with caution.

If the dynamics of plasmas (with or without applied electromagnetic fields) is under consideration, one must recall that two regimes must be recognized further. These are where the short-range forces predominate (slight ionization) and where the long-range forces predominate (high ionization).

The case of short-range forces can be treated most adequately by kinetic theory and classical Boltzmann statistics. Although

experimental data is lacking (due to difficulties in designing the necessary high temperature apparatus), the analytical aspects are well known. However, the case of long-range forces is not well understood analytically or experimentally. Here, one must consider multibody collisions, and the associated statistics become quite complex, requiring quantum mechanical techniques. It would not be an understatement to suggest that much work remains to be done in establishing an adequate theory for the transport phenomena in highly ionized plasmas.

The application of magnetic fields to ionized gases for propulsive as well as for flight control has been suggested, and much concentrated research is in progress. Here it must be pointed out that in magnetohydrodynamics the transport properties are no longer scalar quantities but become tensors. This too is an area which requires very extensive research before reasonable generalizations may be made.

1.3.3 Fluid Dynamics

The numerous aspects of real gas dynamics have been treated by Hayes and Probstein (ref. 5) and by Truitt (ref. 6). However, for the convenience of the reader a brief qualitative summary of real gas effects in aerodynamics is presented here. The treatment will seek to differentiate between a flow phenomena in perfect gases (see for example ref. 7) (constant specific heats and chemical composition) and in real gases (dissociated, excited, ionized). For details of each phenomena the reader should consult references given at the end of this chapter.

1.3.3.1 *Isentropic Expansion*

Where the initial conditions and final pressure are given, the effect of real gases on an isentropic expansion is to increase the final temperature and, thereby, the speed of sound and the velocity,

and to decrease the final density. Because the effect on the speed of sound is greater than on the velocity, the Mach number is less for a real gas. The static temperature for a real gas is greater because the energy in the internal degrees of freedom[†] (which a perfect gas does not possess) is converted into translational energy during the expansion. There is consequently a pronounced real gas effect on area ratio, the real gas requiring a far greater area ratio to reach a given Mach number (ref. 8).

1.3.3.2 Prandtl-Meyer Expansion

For given initial conditions and the same expansion angle, the effect of real gases is to increase the final pressure, temperature, and velocity, but to decrease the final Mach number (refs. 8 and 9).

1.3.3.3 Normal Shock Wave

For a given shock velocity and free stream conditions, the effect of real gases is to increase the density ratio and the pressure ratio across the shock, while decreasing the temperature ratio (refs. 8 and 10).

1.3.3.4 Oblique Shock Wave

For given initial conditions and wedge angle, the shock deflection angle is less for real gases than for perfect gases. Further, at any given Mach number, the limiting wedge angle (before a shock wave becomes detached) is greater for a real gas (ref. 1).

1.3.3.5 Shock Tube Performance

For a given pressure ratio across the shock tube diaphragm, the effect of real gases is to decrease slightly the shock Mach number. However, if the shock Mach number is maintained the

[†] Translation is classified as an external degree of freedom, whereas rotation and vibration are internal degrees of freedom.

same, the stagnation temperature and the Reynolds number per foot are reduced for a real gas, while the flow Mach number behind the shock and the stagnation pressure are increased. The effect on the stagnation pressure is particularly large (refs. 1, 11, 12, and 13).

1.3.3.6 *Boundary Layer Flow*

Real gases generally affect boundary layer flow in the following ways: the temperature in the boundary layer is decreased; the skin friction (except at high angles of attack) is decreased; the displacement thickness is decreased; the boundary layer induced pressure is decreased (ref. 14).

1.3.3.7 *Magnetoaerodynamic Effects*

Where a magnetic field is applied to an ionized gas, the associated gas dynamics assumes many peculiarities which must be treated specially. This subject is outside the scope of this monograph and hence will not be treated here (ref. 15).

1.3.3.8 *Heat Transfer*

In accounting for the heat transfer phenomena, one must differentiate between real gases without chemical reactions, real gas flow with chemical reactions, and magnetohydrodynamic heat transfer. When there is no chemical reaction, the heat transfer to the wall is less with real gases than with a perfect gas. This is explained by the fact that the peak temperature in the boundary layer and thus the temperature gradient at the wall is less with real gases. However, if chemical phenomena such as the recombination of dissociated gases occur, then appreciable energy is imparted to the wall, and hence heat transfer becomes a serious problem. The heat transfer in the stagnation regime of a blunt body may be reduced by magnetoaerodynamic arrangements (refs. 5, 6, 16, and 17).

1.4 Availability and Validity of Property Tables

In solving high temperature, gas dynamic problems, it is convenient to use tabulated properties. Fortunately there exists a variety of tables for equilibrium gas properties. Some of the most important of these tables will be discussed in this section.

In developing accurate tables for the equilibrium thermodynamic properties of air, two uncertainties were (a) the correct dissociation energy of molecular nitrogen and (b) the formation of NO. The complications with the nitrogen dissociation energy arose because the available spectroscopic data were consistent with two different models for nitrogen dissociation, one leading to a dissociation energy of 7.37 eV per molecule and the other to 9.76 eV per molecule. At first, the lower value was widely accepted as the correct one. In recent years, a number of experiments were performed which confirmed the higher value as the correct one. Most tables of thermodynamic properties prepared before 1955 use the incorrect dissociation energy of nitrogen, and consequently may be used only at temperatures below that for which nitrogen dissociation begins.

Over the years a large number of tables of the thermodynamic properties of air have been prepared. The report by Bethe (ref. 18) was one of the earliest. However, this report does not include the effects of NO formation and the calculation is based on a value of 7.37 eV for the dissociation energy of nitrogen. The widely used tables by Hirschfelder and Curtiss (ref. 19) and Krieger and White (ref. 20) were also based on the lower value of 7.37 eV, and were carried out for a rather limited range of pressure and density.

Hilsenrath *et al.* (ref. 21) computed the thermal properties of air, argon, carbon dioxide, carbon monoxide, hydrogen, nitrogen, oxygen, and steam for temperatures up to 3000 °K and for density ratios (ρ/ρ_0) from 100 to 10^{-2} . These tables are based on the correct value of the dissociation energy for nitrogen, but because of the